INTERELEMENT ABSORPTION AND ENHANCEMENT EFFECTS IN AQUEOUS MATRIX AND CHEMICAL ANALYSIS OF MULTIELEMENT AQUEOUS SOLUTIONS BY X-RAY FLUORESCENCE SPECTROMETRY

Anh Duy Nguyen

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Dedicated to my family

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Anh Duy Nguyen

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ABSTRACT

Empirical mathematical approaches to the correction of the interelement absorption and enhancement effects, as based on simplifications of x-ray fluorescence theory, present several limitations relative to their application in the chemical analysis of multielement systems.

This thesis details the use of an experimental technique to compensate for some of these limitations. Aqueous solution systems were employed, at levels of component concentrations such that the absorption and/or enhancement effects were appreciable, in order to obtain reasonably accurate estimations of the correction coefficients.

The first portion of the investigation involved the determination and verification of the reliability of Lachance and Traill

correction coefficients as associated with those elements of interest relative to copper-base and ferrous-base alloy compositions. These correction coefficients were determined on the basis of the investigation of aqueous solution systems involving appropriate paired combinations of the elements of interest.

The second phase of the investigation concerned itself with testing the validity of the correction coefficients determined in the first phase. The testing procedures involved the application of the determined coefficients in the chemical analysis of high-solid-content synthetic solutions of known composition, as well as in the chemical analysis of solutions obtained by dissolving copper-base and ferrous-base alloy standards of established composition.

The results obtained with respect to both phases yielded several significant conclusions. It was shown that the investigation of aqueous solution systems provides a means for the determination of correction coefficients comparable as to precision and accuracy to those determined through the investigation of solid specimens of known composition, and without the perturbing influences associated with the particle-size, surface-finish and heterogeneity effects frequently encountered with respect to the use of solid specimens. In general, the determined coefficients are related in a sensible manner to the associated mass absorption coefficients. Again, the experimental results affirm, in general, the validity of the Lachance and Traill correction equation technique. The application of the derived correction coefficients in the chemical analysis of multicomponent systems displaying wide ranges of composition provides for relatively precise and accurate analytical results. The technique provides a new approach to the chemical analysis of high-concentration aqueous solutions and, in its application to the solutions of alloys, one that is largely independent of sample size and acid concentration.

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1. INTRODUCTION

1.1 The Absorption-Enhancement Effect

Absorption-enhancement effects which result in a nonlinear correlation between emitted radiation intensity and concentration of the emitting element constitute one of the major problems encountered in those methods of chemical analysis based on the x-ray fluorescence (XRF) technique.

The absorption effect occurs when fluorescent radiation for a given analyte is absorbed by associated elements in the matrix, and by the analyte itself. The effect may be positive or negative and, for each of such associated elements, depends on the magnitude of the mass absorption coefficient relative to that of the analyte.

For example, Birks(1) has investigated the measurement of NiKα radiation in binary alloys. Molybdenum, with a mass absorption coefficient of 220, and chromium with a value of 300, both relative to NiKα radiation and in comparison to the nickel self-absorption coefficient of 72, absorb NiKα radiation strongly, decrease the emitted intensity for NiKα and provide for positive absorption situations. Aluminum has almost the same mass absorption coefficient as nickel itself, but displays a negative absorption effect.

This is due to the fact that aluminum also has a low absorption coefficient for the primary radiation used, thereby permitting a higher NiKα radiation than would have been emitted in the presence of a similar concentration of a more absorbing element. Carbon has a very low absorption coefficient for NiKα radiation, and the calibration curve shows a negative absorption situation. Table 1 shows the mass absorption coefficients for the elements involved in the various binary combinations investigated, with Figure 1 showing the associated calibration curves. Typically, those curves representing positive absorption effects are convex to the analyte concentration axis; those representing negative absorption effects are concave to this axis.

The foregoing definition of positive and negative absorption effects is consistent with the trend of the mass absorption coefficients for matrix elements, and is convenient to use with respect to the discussion to follow. It is, however, in opposition to the definition proposed by Liebhafsky <u>et al</u>.(45)

Under certain circumstances there is another effect, called the enhancement effect, which may occur with the absorption effect. The enhancement effect is encountered where the characteristic radiation for an associated element lies on the short wavelength side, but close to the absorption edge of the analyte. This effect further complicates the nonlinearity problem with respect to the XRF

TABLE 1

MASS ABSORPTION COEFFICIENTS RELATIVE TO NiKα RADIATION *

Element	μ for NiKα
Molybdenum	220
Chromium	300
Aluminum	74
Nickel	72
Carbon	7

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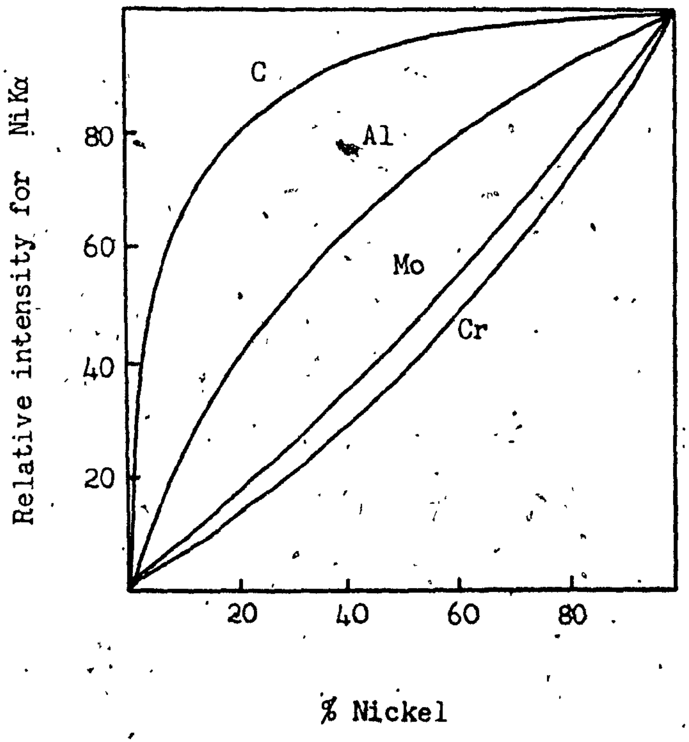
* Birks, L.S., X-Ray Spectrochemical Analysis, Interscience, 1969, p74.

FIGURE 1

CALIBRATION CURVES FOR NICKEL - NiKα RADIATION*



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* Birks, L.S., X-Ray Spectrochemical Analysis, Interscience, 1969, p74.

technique as applied in chemical analysis.

Mitchell,(2) working with binary oxide systems, clarified the nature of the absorption-enhancement effects. She found the variation in the fluorescent intensity, in general, inversely proportional to the mass absorption coefficient of the associated element. Exceptions were noted, however, for those matrix elements showing characteristic radiation close to the absorption edge of the measured element. Associated elements of this type, with characteristic radiation just on the short wavelength side of the absorption edge of the measured element, enhance its intensity. In the case of SnKα radiation, for example, the highest emitted intensity was not shown for the matrix element of lowest absorption coefficient, silver (atomic number 47), but for xenon (atomic number 54), several atomic numbers higher. Again, for FeKα radiation, the highest emitted intensity occurred for the matrix element nickel (atomic number 28), instead of manganese (atomic number 25) with the lowest absorption coefficient. Although binary oxide mixtures do not truly represent binary systems, because of the presence of oxygen, the work of Mitchell did show clearly that the absorption coefficient can be used to predict the absorption effect, even in cases of proximity to the absorption edge, and that the enhancement effect is entirely different in nature to the absorption effect.

1.2 Theoretical Studies of the Absorption-Enhancement Effect

Theoretical studies of the absorption-enhancement effect have been carried out by a number of investigators, notably by Gillam and Heal,(3) Sherman,(4) Müller,(5) Shiraiwa and Fujino,(6) and Criss and Birks.(7) Such studies generally involve the derivation of the primary fluorescent intensity due to excitation by the incident primary radiation, and the secondary fluorescent intensity due to excitation by the characteristic radiation of the associated element(s). Shiraiwa and Fujino carried out, in their work, the derivation of the tertiary fluorescent intensity due to excitation by the secondary fluorescent radiation.

The intensity equations derived by the authors mentioned in the foregoing are very similar. They generally differ only on a notational basis, and on the basis of the values for the associated constants.(6) In the discussion to follow, the intensity equations for the primary fluorescent and secondary fluorescent intensities were taken from Müller(5) with some modifications.

In a multicomponent mixture, the primary fluorescent intensity at radiation α for element A can be written as shown in Equation (1). The secondary fluorescent intensity at radiation α for element A, due to excitation by the characteristic radiation β for element B, can be written as shown in Equation (2). The total

EQUATION 1

$$I_A(1) = \frac{q}{\sin\varphi} E_A C_A \int_{\lambda_o}^{\lambda_{edge}} \frac{\mu_A(\lambda) I_o(\lambda)}{C_A\overline{\mu}_A(\alpha) + C_B\overline{\mu}_B(\alpha) + C_C\overline{\mu}_C(\alpha) + \cdots} \, d\lambda$$

where:-

$I_A(1)$ = the primary fluorescent intensity, radiation α for A

q = the fraction of fluorescent intensity passing through the collimator towards the crystal

E_A = a factor dependent upon the atomic number of A, with the value:-

$$E_A = \frac{S_K - 1}{S_K} W_K p_\alpha$$

where:-

S_K = the absorption jump ratio for Kα radiation

W_K = the fluorescent yield for the K series

p_α = the fraction of the fluorescent yield related to α radiation

$I_o(\lambda)$ = the incident intensity at wavelength λ

$C_A, C_B,$ = the weight fractions of the elements A, B, ...

$\overline{\mu}_A(\alpha) = \left[\frac{\mu(\lambda)}{\sin\varphi} + \frac{\mu(\alpha)}{\sin\psi}\right]_A$ = the average absorption coefficient of A at the incident radiation λ and the fluorescent radiation α

φ = the incident angle

ψ = the emergent angle

λ_o = the minimum wavelength of the primary spectrum

λ_{edge} = the wavelength at the absorption edge for A

EQUATION 2

$$I_A(2) = \frac{q}{2\sin\psi} E_A C_A \mu_A(\beta) \int_{\lambda_o}^{\lambda_{edge}} \frac{E_B C_B \mu_B(\lambda) I_o(\lambda)}{\left[\mu(\lambda)/\sin\psi + \mu(\alpha)/\sin\psi\right]_B} d\lambda \, L$$

where:-

$$L = \left[\frac{\ln\left(1 + \frac{\mu(\alpha)}{\mu(\beta)\sin\psi}\right)}{\mu(\alpha)/\sin\psi} + \frac{\ln\left(1 + \frac{\mu(\alpha)}{\mu(\beta)\sin\psi}\right)}{\mu(\lambda)/\sin\psi} \right]$$

$I_A(2)$ = the secondary fluorescent intensity, radiation α for A

and the remaining terms have definitions similar to those given for Equation (1) fluorescent intensity emitted by the specimen, at radiation α for element A, is given by the sum of the primary and secondary fluorescent intensities given by Equations (1) and (2).

The parameter E_A is a factor representing the relationship between the absorption jump ratio S_K for $K\alpha$ radiation, the fluorescent yield W_K for the K series and p'_α, the fraction of the fluorescent yield representing $K\alpha$ radiation.

The absorption jump ratio S_K is defined as the ratio of the absorption coefficients at the critical absorption wavelength, and is defined by the expression:-

$$S_K = \frac{\mu_K + \mu_{LI} + \mu_{LII} + \mu_{LIII} + \cdots}{\mu_{LI} + \mu_{LII} + \mu_{LIII} + \cdots}$$

The value of S_K is always greater than unity, and decreases as the atomic number increases. The accuracy for S_K is dependent on the resolving power of the spectrometer. In the literature, different values for the absorption jump ratio for a given element are frequently reported from different sources.$^{(8)}$

The fluorescent yield W_K represents the probability that the excited state will result in the emission of fluorescent radiation of the K series. It is defined as the ratio of the number of excited atoms emitting K series radiation to the total number of atoms to be excited. The fluorescent yield values for a number of elements have been reported in the literature, and the agreement is usually very poor.(8,9)

The principal source of difficulty relative to fluorescent intensity equations lies in the polychromatic nature of the incident primary radiation. The excitation efficiency for each element in the specimen under examination is a function of the primary wavelength, as shown by Birks(10) for fourteen elements ranging from titanium to silver. The mathematical deduction that the polychromatic primary beam can be considered as equivalent to a monochromatic wavelength, called the effective wavelength, lying between λ_{minimum} and λ_{edge} is theoretically correct.(11) Shiraiwa and Fujino(6) have shown, however, that the effective wavelength also varies with the element to be excited. Their calculations were based on the usual intensity distribution equation for continuous x-rays as emitted from a massive target. Criss and Birks(7) employed the measured primary spectral distribution for a given target and operating voltage to replace the integral by the summation of its values at different primary wavelengths. Müller,(5) and later Bäckerud,(12) used a similar method relative to intensity calculations. Only Sherman(4) applied the effective wavelength deduction in order to simplify the fluorescent intensity calculations.

The accuracy for the fluorescent yield, and for the absorption jump ratio, are each poorer than that for the mass absorption coefficient. In the calculation of the primary fluorescent intensity according to Equation (1), the result is usually expressed in the form of an intensity ratio, so that the yield and jump ratio parameters are eliminated. The secondary fluorescent intensity calculation depends explicitly, however, on the fluorescent yield and the absorption jump ratio values. The accuracy for these factors then directly affects the accuracy for the calculated intensity.

The results of theoretical calculations of fluorescent intensity generally show good agreement with the experimental values. Sherman(4) performed the calculations for binary mixtures of zinc and iron, and ternary and quaternary mixtures of zinc, nickel, iron and chromium. By assuming that the polychromatic incident beam was equivalent to an incident wavelength of 1.0 to 1.2 Å, the computed intensity ratios were found to agree well with the measured values. Shiraiwa and Fujino(6) calculated the intensity ratios for nickel-iron, iron-chromium and nickel-iron-chromium alloys. The theoretical results showed agreement within 1 percent of the experimental values.

1.3 Estimation of the Enhancement Effect

It will be observed that, for the secondary intensity equation,

Equation (2), the secondary fluorescent intensity is quantitatively dependent on the concentration and on the absorption coefficient of the enhancing element. Sherman$^{(4)}$ indicated that the limiting values for the ratio of the secondary fluorescent intensity to the primary fluorescent intensity may approach a value of 3.5 in some instances. Shiraiwa and Fujino$^{(6)}$ showed that the ratio of secondary to primary fluorescent intensity for CrKα in iron-chromium binary alloys was 55 percent at 2 percent chromium, and 12 percent at 60 percent chromium. These authors also indicated that the ternary fluorescent intensity was usually very low. For CrKα, for example, in a chromium-iron-nickel alloy system, the ternary fluorescent intensity was always less than 2.4 percent of the total fluorescent intensity. It is therefore of little importance, and can generally be neglected.

Müller$^{(5)}$ calculated the fluorescent intensity for several binary mixtures as a function of the concentration of the excited element, without taking into consideration the secondary excitation situation. He then compared the calculated intensities with the measured intensities in order to estimate the magnitude of the enhancement effect. It was found that the interelement excitation effect depends on the characteristic radiation of the associated elements in relationship to the absorption edge of the element to be excited. The enhancement effect is negligible when the characteristic radiation is far removed from the absorption edge. Where the characteristic radiation is close to the absorption edge, however, the associated element may cause an increase in the fluorescent intensity for the excited element of as much as 10 to 30 percent. This latter situation was shown by Müller relative to copper in tantalum.

Gillam and Heal(3) estimated that, in the case of a mixture of 80 percent iron and 20 percent nickel, the fluorescent intensity for nickel enhances the fluorescent intensity for iron by a factor of 10 percent.

The theoretical study of interelement excitation has proven that the secondary fluorescent intensity is of significance, and can not be neglected. Its magnitude is dependent on the proximity of the characteristic radiations for the associated elements to the absorption edge of the analyte, as well as on the concentrations of the associated elements and the analyte.

The experimental study of interelement excitation is not feasible, since the enhancing element also contributes in the absorption of the analyte radiation and of the primary incident beam. The substitution of the enhancing element by a comparable concentration of another element, with equivalent absorption coefficient relative to the characteristic radiation of the analyte, will result in two different systems. For example, nickel and aluminum have almost the same mass absorption coefficient for FeKα radiation

(μ_{Ni} = 94, μ_{Al} = 92), with nickel being an enhancing element and aluminum being one without enhancing effect with respect to iron. In two binary mixtures containing the same concentration of nickel and aluminum, the intensity of FeKα may be higher in the iron-aluminum mixture than in the iron-nickel mixture, although FeKα is enhanced by NiKα in the iron-nickel mixture. This is on account of the fact that aluminum absorbs the primary incident radiation to a much lesser extent than nickel, so that iron in the iron-aluminum mixture is excited by the primary beam to a greater degree than in the comparable iron-nickel mixture. This additional primary beam excitation exceeds the enhancement effect of nickel.

The only appropriate technique applicable to the study of the enhancement effect on an experimental basis would be the method mentioned in the foregoing, as used by Müller. The primary fluorescent intensity can be evaluated quite accurately from Equation (1). Its comparison subsequently with the measured intensity yields an estimation of the magnitude of the enhancement effect. In this way the inaccuracies introduced by the experimentally determined parameters S_K and W_K in Equation (2) are avoided. Work of an intensive nature in this area has not, however, been done.

1.4 Mathematical Corrections for the Absorption-Enhancement Effect

In the application of the XRF technique in chemical analysis, the purpose is to relate the measured fluorescent intensities to the chemical composition. Theoretically, this can be done by solving the intensity equations given as Equations (1) and (2), providing that all of the parameter constants are known in advance. The calculations are complicated, and would only be successful with a few component mixtures. The accuracy, in any case, would not be comparable to that associated with wet chemical analysis, because of the lack of sufficiently accurate data with respect to the intensity distribution for the primary beam and relative to the excitation probabilities for different elements. Analysts must therefore uncover other approaches to the solution of the problems introduced by absorption-enhancement effects.

A number of such methods have been investigated and the results published over the last twenty years. They all bear the same general characteristics, that is, further simplifications are made from theory, and the method becomes more restrictive in application as the degree of simplification increases. This characteristic can be used as a general criterion in the discussion to follow with respect to such methods of chemical analysis by XRF.

1.4.1 Methods derived directly from theory

The method most closely approaching fluorescent theory was published in 1968 by Criss and Birks,(7) and was referred to as the

"Fundamental Parameter Method". The only assumption made is that the specimen is homogeneous, thick and has a flat surface. This is also the sole assumptive situation in the derivation of the fluorescent intensity equations. Instead of making use of a mathematical expression for the continuous primary spectrum, Criss and Birks used the measured spectral distribution for a given target and operating voltage. Spectral distribution measurement had been described in an earlier publication by Birks and Gilfrich.(13) The incident beam is divided into a number of wavelength intervals $\Delta\lambda$, with the corresponding intensity $I(\lambda)$. The integrals in the intensity equations, Equations (1) and (2), were replaced by their summation from $\lambda_{minimum}$ to λ_{edge}. In order to eliminate the inaccuracies introduced by the parameter constants, the authors made use of the relative fluorescent intensity, which is the ratio of the intensity for the unknown specimen to that for a standard specimen of known composition. The concentration for each element of interest was then found by an iteration procedure which involved making successively better estimations of the concentration until the corresponding calculated intensity agreed with the measured intensity.

In this method of approach, the absorption-enhancement effect enters explicitly with respect to each sample. From the mathematical point of view, the technique should be applicable to any matrix and in any range of composition. Its application is not, however, very successful, primarily on account of the present ranges of uncertainty with respect to the values of the mass absorption coefficients and the fluorescent yield parameters. The use of the relative intensity does not, where Equation (2) is concerned, eliminate the influence of the fluorescent yield factor. Criss and Birks found that the accuracy associated with the determination of chromium, nickel, iron and manganese in steel alloys was frequently of a lower order than that for more simplified methods of calculation.

In 1968, Shiraiwa and Fujino(14) obtained linear correction factors directly from derivatives of the intensity equations. From the observation that, with certain types of alloys, the range of composition for the components of interest is limited, the authors found the increment in intensity associated with the exchange of weight between components from the first derivative of the intensity equations. From the second derivative, they found that range of composition where linear approximation is permissible. Correction factors were then computed directly from theory for each element to be determined.

Shiraiwa and Fujino applied their method of correction to the chemical analysis for nickel, copper and manganese in steel alloys. They obtained relative errors of approximately 1 to 2 percent, these being of the same order of magnitude as those for the theoretical values.

Both of the methods of approach outlined in the foregoing require an accurate knowledge of the primary intensity distribution, as well as of the fluorescent yields and mass absorption coefficients, insofar as accuracy in these directions can be achieved. The calculations are complicated, and the need for a computer approach is obvious. Their application to chemical analysis situations often provides for results which are no better than those obtainable by the application of other simple techniques. They have demonstrated, however, a new and unique approach to the absorption-enhancement effect in XRF methods of chemical analysis.

1.4.2 Empirical correction methods

The enhancement effect results in an increase in the fluorescent intensity for the analyte due to the additional excitation provided by the enhancing element. Physically, this effect is identical to the absorption effect of a less absorbing element. The enhancement effect could therefore be treated in the same manner as an absorption effect simply by replacing the absorption coefficient for the enhancing element by a hypothetical absorption coefficient which is lower than that for the analyte. This concept is usually referred to as "negative absorption", a term originated by Noakes(15) in 1954 and later used by Birks(16)

If the enhancement effect can be considered as a negative absorption, the effect of each of the associated elements on the fluorescent intensity of a given analyte is simply that of an absorption effect. The intensity equation may thus be dramatically simplified, since the secondary fluorescent intensity situation may now be dropped from consideration.

If a further approximation is made, to the effect that the polychromatic primary radiation behaves exactly like a single monochromatic wavelength, $\lambda_{\text{effective}}$ or λ_{eff}, the fluorescent intensity for a component A in a multicomponent mixture may be written as shown in Equation (3).

$$I_A = \frac{q}{\sin\psi} E_A C_A \frac{\mu_A(\lambda_{\text{eff}}) I_o(\lambda_{\text{eff}}) \lambda_{\text{eff}}}{C_A\overline{\mu}_A(\alpha) + C_B\overline{\mu}_B(\alpha) + C_C\overline{\mu}_C(\alpha) + \cdots} \qquad (3)$$

where:-

$$\overline{\mu}_A(\alpha) = \left[\frac{\mu(\lambda\,\text{eff})}{\sin\varphi} + \frac{\mu(\alpha)}{\sin\psi}\right]_A$$

and the remaining terms have definitions similar to those given for Equation (1).

In the expression above, in the case of enhancement, μ is a hypothetical absorption coefficient.

If the intensity ratio is used, the parameter constants, with the exception of the mass absorption coefficients, are eliminated, and Equation (3) is reduced to Equation (4):-

$$R_A = \frac{I_A}{I_A^o} = \frac{\bar{\mu}_A C_A}{C_A\bar{\mu}_A + C_B\bar{\mu}_B + C_C\bar{\mu}_C + \cdots} \qquad (4)$$

where I_A^o is the fluorescent intensity for pure element A. The terms in the denominator account for the interaction of the associated elements. The effect is proportional to the concentrations of the associated elements and the interaction coefficient $\bar{\mu}_j/\bar{\mu}_i$.

Equation (4) has been adopted by a number of investigators as the basis for the derivation of correction equations relative to the absorption-enhancement effect.

In 1966, Lachance and Traill$^{(22)}$ obtained a linear relationship between the relative intensity and the concentration, for a given element in a multicomponent system, directly from Equation (4). They replaced C_A in the denominator by $(1 - C_B - C_C - \cdots - C_N)$, and rearranged terms to obtain Equation (5):-

$$R_A = \frac{C_A}{1 + C_B\left(\frac{\bar{\mu}_B}{\bar{\mu}_A} - 1\right) + C_C\left(\frac{\bar{\mu}_C}{\bar{\mu}_A} - 1\right) + \cdots + C_N\left(\frac{\bar{\mu}_N}{\bar{\mu}_A} - 1\right)} \qquad (5)$$

The authors equated the value of $\frac{\bar{\mu}_B}{\bar{\mu}_A} - 1$ to α_{AB}, letting the latter term represent the effect of the element B on A, and so on to obtain the relationship for the concentration C_A in the form of Equation (6):-

$$C_A = R_A(1 + \alpha_{AB}C_B + \alpha_{AC}C_C + \cdots + \alpha_{AN}C_N) \qquad (6)$$

Analogous relationships for the other elements in the multicomponent mixture are obtained in a similar manner.

The relative intensity R for each element is measured experimentally. The α -correction coefficients are determined, also experimentally, from binary standards or, preferably, from multicomponent standards. The chemical compositions for specimens of unknown composition can then be obtained from the measured intensities by solving a system of simultaneous linear equations.

Lachance and Traill(23) applied their correction equations quite successfully in the analysis of 9 components in steel alloys. The average relative errors were 8 percent at the 0.5 percent concentration level, 3.7 percent at the 5.5 percent concentration level, and 0.96 percent at the 55 percent level.

A system of correction equations was proposed by Sherman.(18) This can be shown as follows:-

$$(a_{1,1} - t_1)c_1 + a_{2,1}c_2 + a_{3,1}c_3 = 0$$

$$a_{1,2}c_1 + (a_{2,2} - t_2)c_2 + a_{3,2}c_3 = 0 \qquad (7)$$

$$a_{1,3}c_1 + a_{2,3}c_2 + (a_{3,3} - t_3)c_3 = 0$$

where:-

c_1, c_2, c_3 = the concentrations of the components

t_1, t_2, t_3 = the counting times required to accumulate a predetermined number of counts

$a_{i,j}$ = the correction factor for the interaction effect of j on i

If we let N be the predetermined number of counts, I_1 and I_1^o are then respectively the measured intensity of component 1 in the specimen and in the pure standard. The first equation in the Sherman correction system may be rewritten:-

$$- t_1c_1 + a_{1,1}c_1 + a_{2,1}c_2 + a_{3,1}c_3 = 0 \qquad (8)$$

or:-

$$\frac{1}{t_1} = \frac{c_1}{a_{1,1}c_1 + a_{2,1}c_2 + a_{3,1}c_3} \qquad (9)$$

The value of t_1 is given by N/I_1, and we have:-

$$\frac{I_1}{N} = \frac{c_1}{a_{1,1}c_1 + a_{2,1}c_2 + a_{3,1}c_3} \qquad (10)$$

Multiplication of both sides of this expression by N/I_1^o then yields:-

$$\frac{I_1}{I_1^o} = \frac{c_1}{I_1^o/N(a_{1,1}c_1 + a_{2,1}c_2 + a_{3,1}c_3)} \qquad (11)$$

Since $I_1^o/N \neq 0$ and $a_{1,1} \neq 0$, the value of $I_1^o a_{1,1}/N$ can be set at unity ($I_1^o a_{1,1}/N = 1$), and we have:-

$$\frac{I_1}{I_1^o} = \frac{c_1}{c_1 + \frac{a_{2,1}}{a_{1,1}} \cdot c_2 + \frac{a_{3,1}}{a_{1,1}} \cdot c_3} \qquad (12)$$

which is of the basic form of Equation (4). The Sherman correction factors are then:-

$$a_{1,1} = \frac{N}{I_1^o} \quad ; \quad \frac{a_{2,1}}{a_{1,1}} = \frac{\bar{\mu}_2}{\bar{\mu}_1} \quad ; \quad \frac{a_{3,1}}{a_{1,1}} = \frac{\bar{\mu}_3}{\bar{\mu}_1}$$

Burnham(21) applied the Sherman correction equations to the determination of chromium, iron and nickel in steel alloys. The standard deviations obtained were 0.44 percent for chromium (range 4.3 to

20 percent), 0.50 percent for iron (range 69 to 95 percent) and 0.47 percent for nickel (range 0 to 11 percent).

A system of correction equations was proposed by Beattie and Brissey(17) in 1954. The general equations were:-

$$\begin{aligned} -(R_a - 1)W_a + A_{ab}W_b + A_{ac}W_c + \cdots &= 0 \\ A_{ba}W_a - (R_b - 1)W_b + A_{bc}W_c + \cdots &= 0 \\ A_{ca}W_a + A_{cb}W_b - (R_c - 1)W_c + \cdots &= 0 \end{aligned} \qquad (13)$$

where:-

A = the absorption parameter determined experimentally from binary standards of known composition

R_a = the intensity ratio for the intensity of pure standard to that for the specimen, and is given by I_a^o/I_a

W = the weight fraction of the individual components in the mixture

a, b, c = the individual components in the mixture

If we replace the notation W for the weight fraction with the notation C, the first expression for the Beattie and Brissey system can be written as:-

$$-(R_a - 1)C_a + A_{ab}C_b + A_{ac}C_c + \cdots = 0 \qquad (14)$$

Since R_a is given by I_a^o/I_a, this expression then becomes:-

$$\frac{I_a}{I_a^o} = \frac{C_a}{C_a + A_{ab}C_b + A_{ac}C_c + \cdots} \qquad (15)$$

Equation (15) is of the basic form of Equation (4). The Beattie and Brissey absorption parameters are identical to:-

$$A_{ab} = \frac{\bar{\mu}_b}{\bar{\mu}_a} \quad ; \qquad A_{ac} = \frac{\bar{\mu}_c}{\bar{\mu}_a}$$

The authors applied their correction system in the determination of chromium, iron, nickel and molybdenum in steel alloys. The calculated values agreed in all cases, to within ± 5 percent relative error, with the values determined by other analytical techniques.

Marti,(19,20) in 1960, suggested a system of correction equations indicated by the following:-

$$\begin{aligned} I_{Cr} &= i_{Cr}(\alpha_{Cr}C_{Cr} + \alpha_{Ni}C_{Ni} + \alpha_{Mo}C_{Mo} + \alpha_{Fe}C_{Fe} + \cdots) \\ I_{Ni} &= i_{Ni}(\beta_{Cr}C_{Cr} + \beta_{Ni}C_{Ni} + \beta_{Mo}C_{Mo} + \beta_{Fe}C_{Fe} + \cdots) \qquad (16) \\ I_{Mo} &= i_{Mo}(\gamma_{Cr}C_{Cr} + \gamma_{Ni}C_{Ni} + \gamma_{Mo}C_{Mo} + \gamma_{Fe}C_{Fe} + \cdots) \end{aligned}$$

where:-

I = the corrected intensity

i = the measured intensity

α, β, γ = the interaction coefficients for the associated elements relative to the particular fluorescent intensity involved

The corrected intensity is equal to $I^{o}_{Cr}C_{Cr}$ and, if i_{Cr} is replaced by the notation I_{Cr}, the first equation becomes:-

$$I^{o}_{Cr}C_{Cr} = I_{Cr}(\alpha_{Cr}C_{Cr} + \alpha_{Ni}C_{Ni} + \alpha_{Mo}C_{Mo} + \alpha_{Fe}C_{Fe} + \ldots) \tag{17}$$

or:-

$$\frac{I_{Cr}}{I^{o}_{Cr}} = \frac{C_{Cr}}{\alpha_{Cr}C_{Cr} + \alpha_{Ni}C_{Ni} + \alpha_{Mo}C_{Mo} + \alpha_{Fe}C_{Fe} + \ldots} \tag{18}$$

and this is again of the same basic form as Equation (4). In this case we have:-

$$\alpha_{Cr} = 1 \quad ; \quad \alpha_{Ni} = \frac{\bar{\mu}_{Ni}}{\bar{\mu}_{Cr}} \quad ; \quad \alpha_{Mo} = \frac{\bar{\mu}_{Mo}}{\bar{\mu}_{Cr}} \quad ; \quad \text{etc.}$$

Using the same approach, analogous expressions can be obtained for the β and γ interaction coefficients.

Marti applied this system of correction equations in the analysis of steels, where none of the coefficients was equal to unity. The author, in addition, made the assumption that the effect of iron on such elements as chromium, manganese, cobalt, nickel, copper and molybdenum was equatable to unity. This assumption introduced some unpredictable and significant uncertainties into the analytical results.

The formulations of Criss and Birks(7), were published in 1968, and can be shown as follows:-

$$\frac{C_{A(1)}}{R_{A(1)}} = \alpha_{AA}C_{A(1)} + \alpha_{AB}C_{B(1)} + \alpha_{AC}C_{C(1)} + \cdots$$

$$\frac{C_{A(2)}}{R_{A(2)}} = \alpha_{AA}C_{A(2)} + \alpha_{AB}C_{B(2)} + \alpha_{AC}C_{C(2)} + \cdots \qquad (19)$$

$$\frac{C_{A(3)}}{R_{A(3)}} = \alpha_{AA}C_{A(3)} + \alpha_{AB}C_{B(3)} + \alpha_{AC}C_{C(3)} + \cdots$$

where:-

C_A, C_B, C_C = the weight fractions of the individual components A, B, C in the particular mixture.

R_A, R_B, R_C = the ratio of the intensities for the components A, B, C in the specimen to those for pure standards

$\alpha_{i,j}$ = the correction factor for the effect of j on i

1, 2, 3 = the various specimens under examination

Rearrangement of the first equation yields the familiar form of Equation (4):-

$$R_{A(1)} = \frac{C_{A(1)}}{\alpha_{AA}C_{A(1)} + \alpha_{AB}C_{B(1)} + \alpha_{AC}C_{C(1)} + \cdots} \qquad (20)$$

and we have:-

$$\alpha_{AA} = 1 \quad ; \quad \alpha_{AB} = \frac{\bar{\mu}_B}{\bar{\mu}_A} \quad ; \quad \alpha_{AC} = \frac{\bar{\mu}_C}{\bar{\mu}_A}$$

Criss and Birks applied their correction system in the determination of chromium, iron, cobalt, nickel and molybdenum in steel alloys. The relative errors varied from 0.1 to 3.8 percent.

In essence, all of the systems outlined in the foregoing are identical. The Lachance and Traill (L-T) correction equation system is, however, perhaps the better known, basically because it is much more conveniently and practically applicable in chemical analysis. The concentrations can be easily computed, and the omission of minor concentration elements from consideration in the analytical scheme does not significantly affect the results. The α-correction coefficients, carrying positive sign for absorption effects, and negative sign for negative absorption and enhancement effects, are interpretable in a satisfactory manner from the physical point of view.

The L-T method has been used by Hughes$^{(26)}$ in the determination of iron in low-grade iron ores, using specimens obtained by the fusion method. This author introduced a constant to correct for the presence of oxygen in the oxide standards. The α-correction coefficients were determined for several elements of frequent occurrence in the ores involved, as well as for the lithium tetraborate compound used as the basis of the fusion technique.

Zimmerman and Ingles(27) modified the L-T equation system for application in the solution technique by the introduction of a concentration-intensity factor Z_A, and by the elimination of the I_A^o factor for the pure standard. This modification resulted in the general equation type:-

$$C_A = Z_A I_A (1 + k_{AB}C_B + k_{AC}C_C + \cdots + k_{AN}C_N + k_{AA}C_A) \tag{21}$$

According to the authors, k_{AA} represented the absorption correction factor for the difference between the solvent absorption and the self-absorption for element A.

The terms Z_A and k_{AA} are not derived directly from the fluorescent intensity equation. They are empirical factors which, in their own right, introduce additional uncertainties. The range of solution concentration investigated by Zimmerman and Ingles was very low, ranging from 2 to 15 g per liter, or approximately 0.2 to 1.5 percent by weight. The absorption-enhancement effects were, on this basis, quite minimal, and a correction method was therefore not necessarily required.

1.5 Higher-Order Correction Terms

In an effort to improve the accuracy of the L-T correction coefficients, Claisse and Quintin(25) modified the L-T equation to take into consideration the polychromaticity of the primary radiation beam. By considering the total fluorescent intensity as the sum of the intensities for each wavelength, they obtained a summation for the L-T equation. Their general equation is similar to the L-T equation, except for the inclusion of higher-order terms. In this system, the single correction coefficient α_{AB} of the L-T system for a binary mixture is given by:-

$$\alpha_{AB} = \alpha_{B} + \alpha_{BB}C_{B}^{2} + \alpha_{BBB}C_{B}^{3} + \cdots + \alpha_{nn}C_{B}^{(n-1)} \qquad (22)$$

Claisse and Quintin also conducted experimental investigations aimed at proving the existence of these higher-order terms, and estimating their magnitude in binary mixtures involving the oxides of iron, nickel and chromium. They found that only the second-order term is significant, and that it is particularly significant where enhancement effects are involved.

In 1970, Lachance(24) applied the calculation method proposed by Criss and Birks(7) to demonstrate the existence of the second-order term. He also showed, however, that its contribution to the attainment of improved accuracy in the chemical analysis application is negligible. The error to be anticipated where only the single correction coefficient α_{AB} of the L-T system is applied with respect to binary systems, was generally appreciably less in significance than that representing the normal precision and accuracy of the XRF analysis method.

If the second-order term α_{BB} is considered as being intended to correct only for the polychromaticity of the primary beam, then it is difficult to explain the satisfactory nature of the data obtained by Claisse and Quintin(25) and by Lachance.(24)

The experimental data outlined by Claisse and Quintin revealed that, in the case of enhancement effects, the deviation from linearity of the plot of $(C_A/R_A) - 1$ versus C_B, for binary systems, is more significant than it is in the case of absorption effects, and thus indicates the need for a larger second-order correction coefficient α_{BB}.

The calculated data of Lachance showed a considerable range of change for the α_{AB} coefficient with varying composition of the binary mixture, and in cases where enhancement effects were involved (e.g. the effect of nickel on iron). A lesser range of variation occurred in cases where absorption effects were encountered (e.g. the effect of oxygen on iron).

Since the enhancement effect can only occur subsequent to the general process of excitation by the primary beam, absorbing and enhancing elements behave similarily relative to the primary beam. The second-order correction term for primary beam polychromaticity would, from this aspect, be of the same order of magnitude in each case.

In addition to this situation, the assumption of an equivalent effective wavelength for the primary beam does not necessarily result in a larger error in the case of enhancement effects. This was demonstrated by Sherman.(4)

The second-order term α_{BB} is determined experimentally, and thus any error resulting from the assumption that the enhancement effect can be treated as negative absorption will be included. It is evident, therefore, that only a minor portion of the second-order correction term corrects for the polychromaticity of the primary beam, and that the major portion actually corrects for the enhancement effect.

In ternary, and more complex systems, an additional correction term has been proposed in order to take into account the effect of a third element on the second. This involves the product $C_B C_C$ in the Claisse and Quintin equation:-

$$C_A = R_A(1 + \alpha_B C_B + \alpha_C C_C + \cdots + \alpha_{BB} C_B^2 + \alpha_{CC} C_C^2 + \cdots + \alpha_{BC} C_B C_C + \cdots) \qquad (23)$$

Lachance(24) showed, on a theoretical basis, that α_{BC} can be calculated in all cases, and that it is not constant. However, the results obtained by assuming α_{BC} constant show errors that are, in general, less significant than the precision and accuracy of the XRF and chemical analysis data.

1.6 The Validity of the Lachance-Traill Correction Equation

The validity of the L-T equation system depends on the constancy of the α-correction coefficients. Since the equation itself is derived on the basis of considerations which are, to a degree, physically incorrect, the correction coefficients are not constant for all circumstances. In XRF analysis, however, physical correctness is not the primary concern of the analyst. He concerns himself mainly with the extent to which the equation system can be applied to provide accurate analytical data. In the discussion to follow, those factors influencing the values of the L-T α-correction coefficients will be outlined.

The first of the factors which enter explicitly relative to the L-T α-correction coefficients involve the angles of the incident and emergent beams, φ and ψ respectively. Spectrometers may have different values for these angles. Lachance(24) calculated the α-correction coefficients associated with three instrumental geometries that were different, and showed that the effect of instrumental geometry is minimal.

The second factor arises out of the assumption that the specimen surface is homogeneous, smooth and flat. These experimental prerequisites are fulfilled on a consistent basis only by liquid specimens; since powder, fused and metallic specimens frequently display particle-size, surface-finish and heterogeneity conditions.

The effects of particle-size and grain composition on the correction coefficients have been studied theoretically by Claisse.(28) In addition to the variation of the matrix effect with particle size, the grain composition, particularly where a disturbing element is present in the compound to be analyzed, may permit very significant variations. The application of correction coefficients in such instances may lead to serious errors with respect to the analytical results.

Surface smoothness, with respect to massive samples of a metallic nature, can be obtained by the application of careful polishing techniques. A theoretical study of the effect of polishing or finishing groove size has been done by Müller.(29) He showed that, where large absorption coefficients are involved, surface irregularities have a more pronounced effect on the fluorescent intensity than is the case where small absorption coefficients are involved. This is also related to the wavelength of the emitted radiation, surface irregularites being of more pronounced effect with the longer emitted wavelengths. The decrease in fluorescent intensity for aluminum, for example, is as high as 17 percent with a groove size of 35 µ in depth, while it is only 1 percent for copper relative to the same groove depth. The decrease in intensity increases, in general, with increasing groove depth. Since the reliability of the matrix effect correction method depends on the accuracy of the measured intensities, relatively rough surfaces may yield inaccurate results, particularly where the lower atomic number elements are involved.

A third factor which influences matrix correction coefficient values is the concentration of the analyte, and those of the associated matrix elements. Lachance(24) calculated, on a theoretical basis, the correction coefficients for iron and molybdenum ranging from 1 to 99 percent in various binary systems. He found that correction coefficients vary in value relative to the analyte concentration, and that the variation is very pronounced where the effect is one of enhancement. For ternary, and more complex, systems, the introduction of higher-order terms to account for interelement effects within the matrix is necessary. The L-T equation system thus becomes more complicated, and its application more difficult.

Criss and Birks(7) also demonstrated conclusively the dependency of correction ceofficients on analyte and associated matrix element concentrations. They indicated that a specific set of coefficients may be applied with real success only in association with unknowns of a matrix similar in composition to that involved in the determination of the coefficients. The use of correction coefficients from dissimilar sources relative to matrix composition can result in serious errors in the derived analytical data.

1.7 Purposes and Approaches to the Investigation

The purposes of the investigation were threefold. The first aim was the application of the L-T correction equation system in a general analytical approach. The second objective was to evolve an improved experimental technique for the determination of L-T α-correction coefficients, under conditions which would eliminate the influences of perturbing factors such as particle-size, grain-composition, surface-finish and heterogeneity effects. The third objective was to establish a technique of applying these α-correction coefficients in the general chemical analysis of multicomponent specimen systems, using an approach which would eliminate those perturbing factors just outlined, and which would, in addition, provide for extreme elasticity relative to the amount of the sample available, its physical nature and its general lack of homogeneity.

From the theoretical calculations of Lachance(24) three basic assumptions may be stated. These are:-

(a) The α-correction coefficients for the absorption effect of low atomic number elements, such as oxygen, silicon, etc., on high atomic number elements, such as iron, molybdenum, etc., can be considered as constant, regardless of concentration variation.

(b) The correction coefficients for the interelement effects of high atomic number elements are approximately constant where the concentration levels are below 10 to 20 percent.

(c) Second-order correction terms involving the product C_BC_C are not significant where concentration levels are below 10 percent.

The experimental technique to be evolved necessarily had to be aimed at taking advantage of these assumptions, and at compensating for the restrictive conditions frequently associated with the use of L-T α-correction coefficients.

There is only one experimental technique that can be considered as suitable, and this is the dilution technique, involving either dilution by fusion or dilution by aqueous solution. The fusion technique at high concentration levels is both difficult and time-consuming.(46) Dilution by the aqueous solution method was therefore chosen as the basis of the investigation.

In aqueous solution, any lack of reliability due to heterogeneity, particle-size, grain-composition and surface-finish effects does not exist. The solid content of the solution seldom exceeds 10 percent, so that the α-correction coefficients for the L-T system are quite constant. The interelement effects are greatly reduced by dilution, so that correction for the polychromatic nature of the primary beam, as well as for the third element effect, is not necessary. The aqueous matrix, which generally contains elements below oxygen in atomic number, constitutes more than 90 percent of the total specimen weight. Its correction relative to a given high atomic number element is accurately obtained through the use of a single α-correction coefficient.

For these experimental conditions, the L-T correction equation system remains simple, with only the first-order correction coefficients being required. The aqueous matrix also provides for a similar matrix for the various types of unknowns. The correction coefficients determined would be general, and could be applied in any analytical approach and, very likely, in association with any instrumental geometry.

1.8 Theoretical Background for Absorption-Enhancement Effect Correction in Aqueous Solutions

The theoretical derivation of the correction equations for the aqueous solution matrix is based on the following assumptions:-

(a) The incident radiation, or primary beam, is monochromatic, or is equivalent to monochromatic radiation

(b) The enhancement effect can be treated as negative absorption.

(c) The correction coefficients, for example α_{AB} as representing the effect of the element B on the element A in a binary system, can be considered constant, disregarding the effects of the other elements present in the specimen.

(d) The aqueous matrix, containing water and nitric acid, and sometimes carbon and hydrofluoric acid, is considered as a single effect relative to the higher atomic number elements, and can therefore be corrected for through the use of a single appropriate α - correction coefficient for each of these elements.

Where the aqueous matrix also involves hydrochloric or perchloric acid, the chlorine is considered separately as an element in the matrix.

The assumption that the specimen is homogeneous, flat and thick is provided for under the experimental conditions surrounding aqueous solution systems. The uncertainties introduced by assumptions (a), (b) and (c) are much less in magnitude in aqueous media than would be the case with solid specimens.

The correction equations associated with the foregoing assumptions is identical to the L-T equations, which latter could also include the aqueous matrix as one of the components. The correction equation for the fluorescent intensity of element A in a multicomponent system of an aqueous solution nature can be written as follows:-

$$\frac{I_A}{I_A^o} = \frac{C_A}{1 + \alpha_{AM}C_M + \alpha_{AB}C_B + \alpha_{AC}C_C + \cdots\cdots} \qquad (24)$$

where:-

I_A = the measured intensity for element A in the specimen

I_A^o = the intensity for pure element A

$C_A, C_B,$ = the weight fractions for the components A, B, etc.

C_M = the weight fraction for the aqueous matrix containing hydrogen, nitrogen, oxygen, and sometimes carbon and/or fluorine. Also given by the expression $(1 - C_A - C_B - \cdots)$

α_{AM}, α_{AB} = the correction coefficients for the effects of the aqueous matrix M, the element B, etc., on the element A.

Identical equations can be written for each of the other components in the solution system, with the exception of the aqueous matrix component. The measurement of the fluorescent intensity of the aqueous matrix component is, of course, not possible. There are therefore only $(n - 1)$ equations for the n components of the aqueous solution specimen. As indicated in the foregoing, the value of C_M is given by the expression $(1 - C_A - C_B - \cdots)$.

1.9 Determination of α-Correction Coefficients from Aqueous Solution Systems

The determination of α-correction coefficients for aqueous solution systems through the use of multicomponent standard solutions is not feasible, since the fluorescent intensity of the aqueous matrix portion is not measurable. The α-correction coefficients for the aqueous matrix effect must therefore be determined in advance through the use of simple binary systems involving each element of interest in an aqueous solution matrix. Subsequently, α-correction coefficients for the various interelement effects may be obtained, either from multicomponent standard solutions, or from separate solutions involving pair combinations of the elements of interest. The use of multicomponent standard solutions will result in α-correction coefficients incorporating large uncertainty factors, since the interelement effects are reduced significantly by the dilution effect in solution. The use of separate element-pair solutions was therefore chosen as the approach for this investigation.

When all of the required α-correction coefficients have been determined for the elements of interest, a single standard solution is needed to evaluate the I^o values. Subsequent to this, the chemical composition of solutions involving materials of unknown composition may be evaluated by solving a system of linear equations of the following form:-

$$C_A = R_A(1 + \alpha_{AM}C_M + \alpha_{AB}C_B + \alpha_{AC}C_C + \dots)$$

$$C_B = R_B(1 + \alpha_{BM}C_M + \alpha_{BA}C_A + \alpha_{BC}C_C + \dots) \qquad (25)$$

$$C_C = R_C(1 + \alpha_{CM}C_M + \alpha_{CA}C_A + \alpha_{CB}C_B + \dots)$$

etc., etc.,

with:-

$$(C_M + C_A + C_B + C_C + \dots) = 1$$

where:-

α values = the correction coefficients as determined in advance

R_A = the ratio of the measured intensity for the element A in the specimen solution to the intensity for pure A as obtained from a standard solution specimen. The ratio is given by I_A/I^o_A.

A,B,C, = the components of the solution specimen relative to elements

M = the aqueous matrix component

$C_M, C_A, C_B,$ = the weight fractions of the various components of the aqueous solution system

2. α-CORRECTION COEFFICIENTS - EXPERIMENTAL TECHNIQUES - RESULTS AND DISCUSSIONS

2.1 Determination of α-Correction Coefficients for the Effects of an Aqueous Solution Matrix

2.1.1 Introduction to techniques

The effect of an aqueous, or more generally, a liquid matrix on fluorescent intensity was investigated some time ago by Hower,(30) Gunn,(31) Dwiggins and Dunning,(32) Müller,(33) and others. If the specimen is dissolved in a liquid matrix, or is in the liquid form itself, the matrix M may be taken as constituting an extra element. The intensity equation, Equation (1), may in such cases be written as:-

$$I_A = \frac{q}{\sin\psi} E_A \epsilon_A \int_{\lambda_o}^{\lambda_{edge}} \frac{\mu_A(\lambda) I_o(\lambda)}{C_A\bar{\mu}_A + C_M\bar{\mu}_M + C_B\bar{\mu}_B + C_C\bar{\mu}_C} \, d\lambda \qquad (26)$$

where C_M is the concentration of the liquid matrix and $\bar{\mu}_M$ is its average absorption coefficient relative to the fluorescent radiation for element A.

Where the degree of dilution is high, the term $C_A\bar{\mu}_A$ in the denominator is small and negligible. The fluorescent intensity I_A is then in the practical sense dependent on the concentration of A and on the gross absorption of the liquid matrix. We have then:-

$$I_A = k \frac{C_A}{\bar{\mu}} \qquad (27)$$

where:-

k = a constant

$\bar{\mu}$ = the gross average absorption coefficient of the liquid matrix and given by:-

$$\bar{\mu} = \bar{\mu}_M C_M + \bar{\mu}_B C_B + \bar{\mu}_C C_C$$

For a given matrix, the gross absorption coefficient $\bar{\mu}$ is constant. Müller(33) has shown that, for the range of concentration of A between 0.0001 to 0.1 percent, the fluorescent intensity I_A is quite proportional to the concentration. However, where the gross absorption coefficient varies, either from a change in the liquid matrix or from changes in the concentrations of the associated elements, its effect is inversely proportional to the fluorescent intensity within the concentration range of 0.0001 to 0.1 percent. The author applied this correction method successfully in the analysis of trace elements in pharmaceutical products.

The variation in the gross absorption coefficient for the liquid matrix is particularly important in the analysis of minerals and in the analysis to determine trace elements in petroleum oils.

Hower(30) has proven that the cause of the variation of the aqueous matrix in geological samples is due to the wide ranges of composition. A correction was needed in the analysis for elements with atomic number higher then 28 (nickel). Later, Gunn(34) applied a similar method of absorption correction for all components in the analysis of minerals.

In petroleum oils, the gross absorption of the matrix is, to a very large extent, dependent on the sulphur content. Dwiggins and Dunning(32) corrected for the variation of the liquid matrix absorption in an analysis to determine trace elements, such as vanadium, iron and nickel. A similar investigation was conducted by Kang, Keel and Salomon.(35) In this latter instance, the results obtained were within ± 5 percent relative error, with respect to ranges in the neighbourhood of 20 ppm.

An important aspect of the aqueous, or generally, liquid matrix is its absorption effect relative to a large range of analyte concentration. This effect was observed by Gunn(31) and by Waterbury and Hakkila.(36)

Gunn(31) found that a linear relationship between intensity and concentration was obtained below 2000 ppm (0.2 percent) for zinc and 5000 ppm (0.5 percent) for vanadium in a homogeneous oil matrix with approximately 85.5 percent carbon and 14.5 percent hydrogen. The measured intensity for zinc at 8000 ppm (0.8 percent) was only 23 percent, however, of that predicted by linear extrapolation. The authors Waterbury and Hakkila(36) observed that the effect of the aqueous matrix absorption on iron, chromium and nickel became appreciable where the concentration was higher than 205 mg/10.00 ml or about 2 percent by weight. They called this effect a self-absorption effect.

The term "self-absorption effect" may not truly represent the nature of the aqueous absorption effect. The fluorescent intensity in a low-absorption aqueous matrix is greatly enhanced. As the concentration of the analyte is increased, the aqueous matrix is being replaced by the analyte, which is a heavier or stronger absorbant, resulting in a decrease in the fluorescent intensity. The loss of intensity, therefore, may be considered as a result of a decrease in the negative absorption due to the aqueous matrix.

No attempt has ever really been made to correct for the effect of the aqueous matrix on analyte intensity. The solution technique has been limited to the use of analyte concentrations within the range where a linear relationship between intensity and concentration is obtained.(37,38,39)

2.1.2 Purpose and experimental approach

One of the purposes of this present study was to investigate the absorption effect of the aqueous matrix on a given analyte. In this connection Lachance and Traill α-correction coefficients for the effect of the aqueous matrix were determined relative to each element of interest in steel, ferrous-base and copper-base alloys.

The aqueous matrix in this work consists most frequently of water and nitric acid. It has been recognized that the variation of nitric acid concentration does not influence significantly the fluorescent intensity of the higher atomic number elements.(40,41) It is possible, therefore, to assume that the water-nitric acid matrix is identical from one sample to another, for a given total matrix concentration, and can be designated as M in this investigation.

A solution containing the element A is actually a binary mixture, with M as the second component. The correction coefficient for the effect of M on A can be evaluated from two standard solutions using a relationship derived directly from the basic L-T equation. This is given as Equation (28):-

$$\alpha_{AM} = \frac{I_{A(2)}C_{A(1)}C_{M(2)} - I_{A(1)}C_{A(2)}C_{M(1)}}{I_{A(1)}C_{A(2)} - I_{A(2)}C_{A(1)}} \qquad (28)$$

The subscripts 1 and 2 indicate the standard solutions 1 and 2.

If the concentration of A for the two standard solutions is sufficiently well-separated, the difference in the aqueous matrix effect is large enough to permit accurate estimation of the correction coefficient α_{AM}.

In this investigation, a series of several solutions for each element of interest were prepared. These solutions, in each case, showed considerable variation in the concentration of the element of interest. The concentration range was generally from 1 to 10 percent by weight. The effect of the aqueous matrix on chlorine was also determined, since hydrochloric acid and/or perchloric acid were often required for the dissolution of the metals or alloys involved In this case, solutions of the analyte chlorine, using different concentrations of hydrochloric acid, were employed. The chloride from the hydrochloric acid was determined, by potentiometric titration with silver nitrate solution. The range of chlorine involved was from 3 to 20 percent by weight. The element tin was not soluble in nitric acid, so that hydrofluoric acid was sometimes required to be used. The water-hydrofluoric acid matrix employed in such cases was assumed to be similar in effect to a water-nitric acid matrix.

Each series of solutions was prepared from stock solutions, involving reagent grade chemicals, with concentrations of 0.1 g or 0.2 g per ml. The final weight of each prepared solution specimen was generally 100 g. The solution composition was expressed on a weight fraction basis.

Throughout the entire investigation, a Picker Nuclear spectrodiffractometer, ultrastable generator and radiation analyzer was used. The fluorescence spectrometer had 45° incident and emergent angles.

A chromium target x-ray tube, operating at 50 kV, with a PET analyzing crystal and a proportional flow counter, was used in the ClKα intensity measuring process. A tungsten target x-ray tube, operating at either 40 or 50 kV, with an LiF analyzing crystal and a scintillation counter, was used for the intensity measurements associated with the characteristic radiations of the other elements of interest.

The solutions subjected to XRF analysis were contained in Spex liquid cells, 1 inch in diameter and 1.25 inches in depth. Such cells hold approximately 10 ml of solution. The cell was covered with a Mylar film 0.00025 inches in thickness. Considerable effort and care was taken to avoid the inclusion of air bubbles, and to maintain a flat exposed surface.

All pertinent data associated with standard solution preparation, analysis and composition, x-ray operating parameters, etc., for each standard solution series may be found in Section 5.

2.1.3 Results and discussion

As an example of the general process of accumulating and treating experimental data, the determination of the effect of the aqueous matrix on copper, Series LA, Section 5.1.7, will be presented.

Seven (7) copper solutions, ranging from 1 to 11.7 percent copper by weight, were prepared by dilution of a copper stock solution which contained 0.200000 ± 0.000004 g of copper per ml. The measurement of the CuKα radiation was made at peak intensity, with the spectrometer operating at 40 kV and 20 mA. The average of 5 counting periods, with corrections for background and deadtime where required, is shown in Table 2, together with solution compositional data.

The results obtained were then explored by Equation (28) in order to determine the value of α_{CuM}, the correction coefficient for the effect of the aqueous matrix (water-nitric acid) on copper. The solution combinations chosen were such as to yield maximum differences in numerator and denominator values, this so as to obtain the best possible accuracy in the determination of the derived α-correction coefficient value.

Table 3 shows the solution combinations chosen and the corresponding α_{CuM} values obtained. The average value and the standard deviation were:-

$$\begin{aligned} \alpha_{CuM} &= -0.925^{9} \pm 0.004^{6} \\ &= -0.926 \pm 0.005 \end{aligned}$$

A Lachance and Traill equation, Equation (29), was then used to determine the value of the corrected intensity for each solution. The equation follows:-

$$I_{Cu(corr)} = I_{Cu(meas)}(1 + \alpha_{CuM}C_M) \qquad (29)$$

The corrected intensities determined are shown in Table 4, and

TABLE 2

DETERMINATION OF α_{CuM}

Standard Solution Composition and Intensity Measurement *

Solution	C_{Cu} weight fraction	C_M weight fraction	$I_{CuK\alpha}$ (cps) **
LA-1	0.0100	0.9900	30 532
LA-2	0.0200	0.9800	54 204
LA-3	0.0300	0.9700	74 618
LA-4	0.0500	0.9500	104 548
LA-5	0.0700	0.9300	127 026
LA-6	0.1000	0.9000	152 826
LA-7	0.1170	0.8830	163 825

* See Section 5.0.1 for uncertainty values

** Corrected for background, and for deadtime where required. Average of 5 counting periods.

TABLE 3

DETERMINATION OF α_{CuM}

Calculation of the α_{CuM} Correction Coefficient

Solution Combination	α_{CuM}
LA-1/LA-7	-0.9338
LA-1/LA-6	-0.9258
LA-2/LA-7	-0.9228
LA-2/LA-6	-0.9230
LA-3/LA-7	-0.9242
Average α_{CuM}	-0.9259
Standard deviation	± 0.0046

$$\alpha_{CuM} = -0.925^{9} \pm 0.004^{6}$$

$$= -0.926 \pm 0.005$$

TABLE 4

DETERMINATION OF α_{CuM}

Correction of I_{Cu}(meas) for the Effect of M*

Solution	I_{Cu}(meas) (cps)	I_{Cu}(corr) (cps)	I^{o}_{Cu}(calc) (cps)
LA-1	30 532	2 545	254 500
LA-2	54 204	5 020	251 000
LA-3	74 618	[illegible] 602	253 400
LA-4	104 548	12 587	251 740
LA-5	127 026	17 647	252 086
LA-6	152 826	25 475	254 750
LA-7	163 825	29 887	255 444

---

* See Section 5.0.1 for uncertainty values

shown with them are the values for I^{o}_{Cu} as calculated individually from Equation (24). Figure 2 shows the plots of measured intensity and corrected intensity versus the weight fraction of copper.

The corrected intensity, in each case, is well below the measured intensity. This corresponds to the negative absorption effect of the aqueous matrix. The corrected intensity for copper represents the intensity of copper in a hypothetical matrix with an absorption coefficient equal in magnitude to that of copper at CuKα radiation. The corrected intensity should, therefore, be linearly proportional to the concentration. This is verified by Figure 2, within the range of concentration studied. Beyond this range, verification was not conducted. However, for 100 percent copper (pure copper), the intensity value obtained by exprapolation of the corrected intensity versus concentration plot shows an acceptable agreement with the measured intensity for pure copper, as corrected for background and deadtime. These values are 2.53×10^5 cps as the plot value for I^{o}_{Cu} and 2.46×10^5 cps for the measured value.

Finally, a back-calculation of the copper concentration in each standard solution was conducted by solving the equations:-

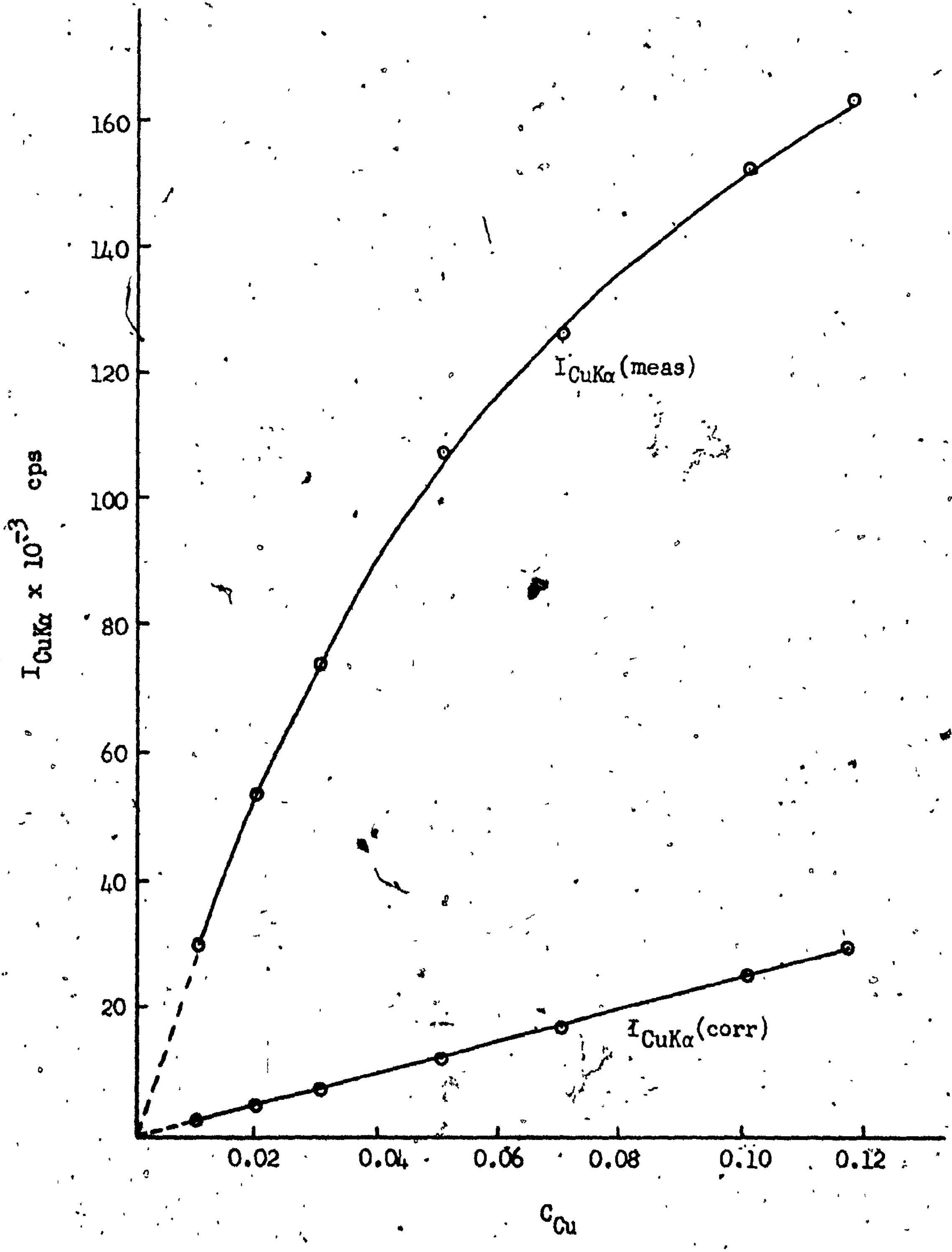
$$\frac{I_{Cu(meas)}}{I^{o}_{Cu(calc)}} = \frac{C_{Cu}}{1 - 0.925^{9} C_M}$$

(30)

$$C_M + C_{Cu} = 1$$

FIGURE 2

$I_{CuK\alpha}$ VERSUS C_{Cu} – IN AQUEOUS MATRIX M



The value of I^{o}_{Cu} used was the average calculated value derived from Table 4 data.

The results of these calculations are presented in Table 5, along with the associated absolute deviations.

The α-correction coefficients for the aqueous matrix effect on the other elements of interest were determined in a generally similar manner. The complete data and detailed calculations are given in Sections 5.1.1 to 5.1.11. The accumulated α-correction coefficients for the aqueous matrix effect are shown in Table 6.

All of these correction coefficients show negative signs, indicating the negative absorption effect for the aqueous matrix in each case. The negative absorption effect is more pronounced for the higher atomic number elements. It accounts for the major portion of the measured intensity.

The Lachance and Traill equation system can be employed to determine the limit of concentration below which the variation in the aqueous matrix is of negligible effect, and a linear approximation of measured intensity and concentration is allowed. For the binary system A-M, the L-T equation can be written as:-

$$I_{A(meas)} = \frac{I^{o}_{A}C_{A}}{1 + \alpha_{AM}C_{M}} \qquad (31)$$

TABLE 5

DETERMINATION OF α_{CuM}

Back-Calculation of Solution Composition *

Solution	C_{Cu} (actual)	C_{Cu} (calc)	Absolute deviation
LA-1	0.0100	0.0100	0.0000
LA-2	0.0200	0.0198	0.0002
LA-3	0.0300	0.0300	0.0000
LA-4	0.0500	0.0495	0.0005
LA-5	0.0700	0.0694	0.0006
LA-6	0.1000	0.1013	0.0013
LA-7	0.1170	0.1195	0.0025

---

* See Section 5.0.1 for uncertainty values

TABLE 6

α-CORRECTION COEFFICIENTS FOR THE AQUEOUS MATRIX EFFECT

Analyte element	α-Correction coefficient*
Chlorine	-0.33^{6}
Chromium	-0.847^{1}
Manganese	-0.863^{7}
Iron	-0.896^{7}
Cobalt	-0.922^{3}
Nickel	-0.917^{1}
Copper	0.925^{9}
Zinc	-0.942^{9}
Cadmium	-0.965^{6}
Tin	-0.954^{0}
Lead	-0.969^{9}

* Kα radiation in each case, except in the case of Lα radiation for Lead.

Since $C_A + C_M = 1$, we have:-

$$I_{A(meas)} = \frac{I_A^o C_A}{1 + \alpha_{AM} - \alpha_{AM}C_A} \tag{32}$$

The first derivative of Equation (32) is:-

$$I'_{A(meas)} = \frac{I_A^o(1 + \alpha_{AM})}{(1 + \alpha_{AM} - \alpha_{AM}C_A)^2} \tag{33}$$

Where $C_A \rightarrow 0$, $I'_{A(meas)}$ becomes:-

$$I'_{A(meas)} = \frac{I_A^o}{1 + \alpha_{AM}} \tag{34}$$

which is the slope of the plot of $I_{A(meas)}$ versus C_A at very low concentrations of A. The calibration curve of the dilution technique is given by the equation:-

$$I'_{A(meas)} = \frac{I_A^o C_A}{1 + \alpha_{AM}} \tag{35}$$

Let k be the fraction of deviation from linearity, and we have:-

$$k = \frac{I'_A - I_{A(meas)}}{I'_A} \tag{36}$$

The substitution of $I_A^\dagger$ and $I_{A(meas)}$ in Equation (36) by the values for $I_{A(meas)}^\dagger$ and $I_{A(meas)}$ from Equations (35) and (32) respectively, followed by a rearrangement of terms, leads to:-

$$k = \frac{\alpha_{AM} C_A}{\alpha_{AM} C_A - (1 + \alpha_{AM})} \qquad (37)$$

so that:-

$$C_A = \frac{1 + \alpha_{AM}}{\alpha_{AM}} \cdot \frac{k}{k - 1} \qquad (38)$$

α_{AM} being the experimentally determined value.

It is generally accepted that, when the deviation is less than 1 percent ($k < 0.01$), the linear relationship between the measured intensity and the concentration yields accurate analytical results. Equation (38) can be used to estimate the limit of concentration for each element. Since the solution technique applied by previous investigators generally involved a range of up to 1 percent concentration, Equation (37) permits the estimation of the expected deviation from the linear approximation for each element.

The calculated data are presented in Table 7. Additional data for a 5 percent deviation ($k = 0.05$) were also included.

From the calculated data a few observations may be made. The linear approximation is satisfactory for a much higher range of con-

TABLE 7

LIMIT OF CONCENTRATION FOR THE LINEAR APPROXIMATION

Element	Estimation of the percent deviation for a 1 percent concentration level	Limit of Concentration (%) k = 0.01	Limit of Concentration (%) k = 0.05
Chlorine	0.50	2.00	10.40
Chromium	5.25	0.18	0.95
Manganese	5.96	0.16	0.83
Iron	7.99	0.12	0.61
Cobalt	8.42	0.08	0.44
Nickel	9.96	0.09	0.48
Copper	11.1	0.08	0.42
Zinc	14.1	0.06	0.32
Cadmium	21.9	0.04	0.18
Tin	17.2	0.05	0.25
Lead	24.4	0.03	0.16

for chlorine than for the higher atomic number elements. This is explained by the fact that the components of the aqueous matrix, oxygen, nitrogen and hydrogen and sometimes carbon and/or fluorine, have larger absorption coefficients for ClKα than for characteristic radiation of the higher atomic number elements. This results in a lower negative absorption effect.

It is also expected that, for elements below chlorine in atomic number, the effect of the aqueous matrix is quite insignificant and, very likely, negligible. A linear relationship could be approximated within practical ranges of concentration.

For elements with an atomic number higher than 24 (chromium), and for concentration levels below 0.2 percent, the fluorescent intensity is practically proportional to the concentration, and independent of the variation of the aqueous matrix effect due to changes in its concentration. This agrees well with the observations by Müller which were noted previously.

At the 1 percent concentration level, the deviation of the measured intensity from the linear approximation situation is noted to be appreciable. Its magnitude is larger for the higher atomic number elements. This situation is not often encountered in the customary applications of the solution technique, however, since sample weights remain relatively constant and concentrations remain at a low level. The variation in the aqueous matrix effect is not important under these conditions, since the concentration of the matrix is quite constant.

2.2 Determination of α-Correction Coefficients for the Effects of Chlorine

2.2.1 Introduction to techniques

Investigations previously reported(36,38) indicated that the acid concentration should be closely controlled in order to obtain worthwhile accuracy in the XRF analysis of solution specimens. Diluted nitric acid was preferred(36,40,41) because of the low absorption coefficients of oxygen, nitrogen and hydrogen.

In the dissolving of metals and alloys, different acids are required. A most tedious process must be followed in order to keep the acid concentration constant from one specimen to another. Mitchell(42) recognized that a small change of 1 percent in the perchloric acid concentration (or about a 0.5 ml change in 100 ml of solution), could cause an error of greater than 1 percent in the analytical results. A similar observation was made by Waterbury and Hakkila.(36) They noted that a small variation of 0.4 ml for hydrochloric acid per 100 ml of solution resulted in a difference in the intensity for chromium, iron and nickel of as much as 1 percent.

To correct for the acid effect, Mitchell(42) used a control element which was added to the solution and which was affected by acid variation in the same way as the analyte. The ratio of the intensity of the analyte to that of the control element was shown to be independent of the acid concentration. Similar techniques had been developed earlier. Use of the ratio of the intensities of analyte/control elements, the ratio of the intensities of analyte/background(43) or that of analyte/coherent scattering ($WL_{\beta 1}$)(44) has each been shown to be effective in the correction of the acid effect.

2.2.2 Purposes and experimental approach

A mathematical investigation of the acid effect has not been done before, simply on account of the fact that the acid is not normally a component of interest. In this investigation, an attempt is made to correct for the effect of chlorine as introduced by the use of hydrochloric and/or perchloric acids, the attempt being made on a mathematical basis using the Lachance and Traill correction equation system. The purpose was to determine the effect of chlorine on the various elements of interest and, thereby, to permit the use of variable amounts of hydrochloric and/or perchloric acids in the dissolving and solution preparation of sample materials.

The investigation was carried out in solutions containing a constant weight fraction of the given analyte (0.01 or 0.02), and a variable weight fraction of the chlorine-bearing acid. Hydrochloric acid was used in all instances, except that where lead was involved as the analyte. Perchloric acid was employed in the preparation of the lead solutions, since lead (II) is only sparingly soluble in the presence of hydrochloric acid.

The chloride concentration in those solutions involving hydrochloric acid was determined accurately by potentiometric titration using standard silver nitrate solution. The chlorine concentration in those solutions involving perchloric acid was determined from the concentration of the acid as determined by titration with a standard solution of sodium hydroxide, proper corrections being made for the presence of lead and nitric acid as solution components.

The solutions to be investigated by XRF were actually ternary mixtures containing the analyte, chlorine and the residual aqueous matrix M of hydrogen, nitrogen and oxygen. The α-correction coefficients for the effects of the residual matrix had been determined previously, as outlined in Section 2.1. The α-correction coefficients for the interfering effects of chlorine on the various analytes of interest were determined from the relationship:-

$$\alpha_{ACl} = \frac{(I_{A(2)} - I_{A(1)}) + \alpha_{AM}(I_{A(2)}C_{M(2)} - I_{A(1)}C_{M(1)})}{I_{A(1)}C_{Cl(1)} - I_{A(2)}C_{Cl(2)}} \qquad (39)$$

where the subscripts (1) and (2) designate standard solutions (1) and (2)

2.2.3 Results and discussion

Following the approach taken in Section 2.1.3, the determination of the effect of chlorine on copper will be presented as an example of the general technique for this line of investigation. The data supporting this presentation can be found as Series LB in Section 5.2.6.

Six solutions, each containing 1 percent by weight of copper, were prepared from the stock solution of copper at 0.200000 ± 0.000004 g of copper per ml. Concentrated hydrochloric acid was added where required, and the chloride concentration was determined accurately by potentiometric titration with silver nitrate. The measurement of CuKα radiation was conducted using a tungsten target x-ray tube at 40kV and 20 mA, an LiF analyzing crystal and a scintillation counter. The average of 5 counting periods, with corrections for background and deadtime where required, is shown in Table 8, along with solution compositional data.

Appropriate pairs of solutions were selected, and the associated data explored by Equation (39) to determine the value of α_{CuCl}, the α-correction coefficient for the effect of chlorine on copper. The results obtained are shown in Table 9. The average value and the standard deviation were:-

$$\alpha_{CuCl} = -0.25^0 \pm 0.02^1$$
$$= -0.25 \pm 0.02$$

TABLE 8

DETERMINATION OF α_{CuCl}

Standard Solution Composition and Intensity Measurement *

Solution	C_{Cu} weight fraction	C_{Cl} weight fraction	C_M weight fraction	$I_{CuK\alpha}$ (cps) **
LB-1	0.01000	0.0000	0.9900	30 579
LB-2	0.01000	0.0396	0.9504	23 098
LB-3	0.01000	0.0793	0.9107	18 326
LB-4	0.01000	0.1207	0.8693	15 244
LB-5	0.01000	0.159^5	0.830^5	13 176
LB-6	0.01000	0.205^2	0.784^8	11 613

* See Section 5.0.1 for uncertainty values

** Corrected for background, and for deadtime where required. Average of 5 counting periods.

TABLE 9

DETERMINATION OF α_{CuCl}

Calculation of the α_{CuCl} Correction Coefficient

Solution Combination	α_{CuCl}
LB-1/LB-6	- 0.2624····
LB-1/LB-5	- 0.2356····
LB-2/LB-6	- 0.2738····
LB-2/LB-5	- 0.2291····

Average α_{CuCl}	- 0.2503····
Standard deviation	± 0.0213····

$\alpha_{CuCl} = -0.25^{0} \pm 0.02^{1}$

[illegible] $= -0.25 \pm 0.02$

The relatively high error, or uncertainty, in the value for this α-coefficient reflects the comparatively minimal differences between the chlorine effects for the various standard solutions.

Subsequently, the corrected intensities for CuKα were calculated from the L-T equation:-

$$I_{Cu}(corr) = I_{Cu}(meas)\left(1 + \alpha_{CuM}C_M + \alpha_{CuCl}C_{Cl}\right) \qquad (40)$$

The values of intensity for CuKα, corrected for the aqueous matrix effect alone, and for the effects of both the aqueous matrix and chlorine, are shown in Table 10. The plots of I_{Cu}(meas), I_{Cu}(meas) corrected for the aqueous matrix effect only and I_{Cu}(meas) corrected for both the aqueous matrix and chlorine effects, all versus chlorine and aqueous matrix concentrations as weight fractions, are given in Figure 3.

As shown by the calculated corrected intensities given in Table 10, and by the plots for Figure 3, the most important source of the variation in intensity for CuKα is the replacement of the aqueous matrix resulting from increasing the chlorine concentration. The latter substance is, of course, a stronger absorber. The effect of the negative absorption of the aqueous matrix decreases sharply with increasing chlorine concentration. The data of Table 10, and the plots for Figure 3, also show the intrinsic correctness of the L-T equations applied.

TABLE 10

DETERMINATION OF α_{CuCl}

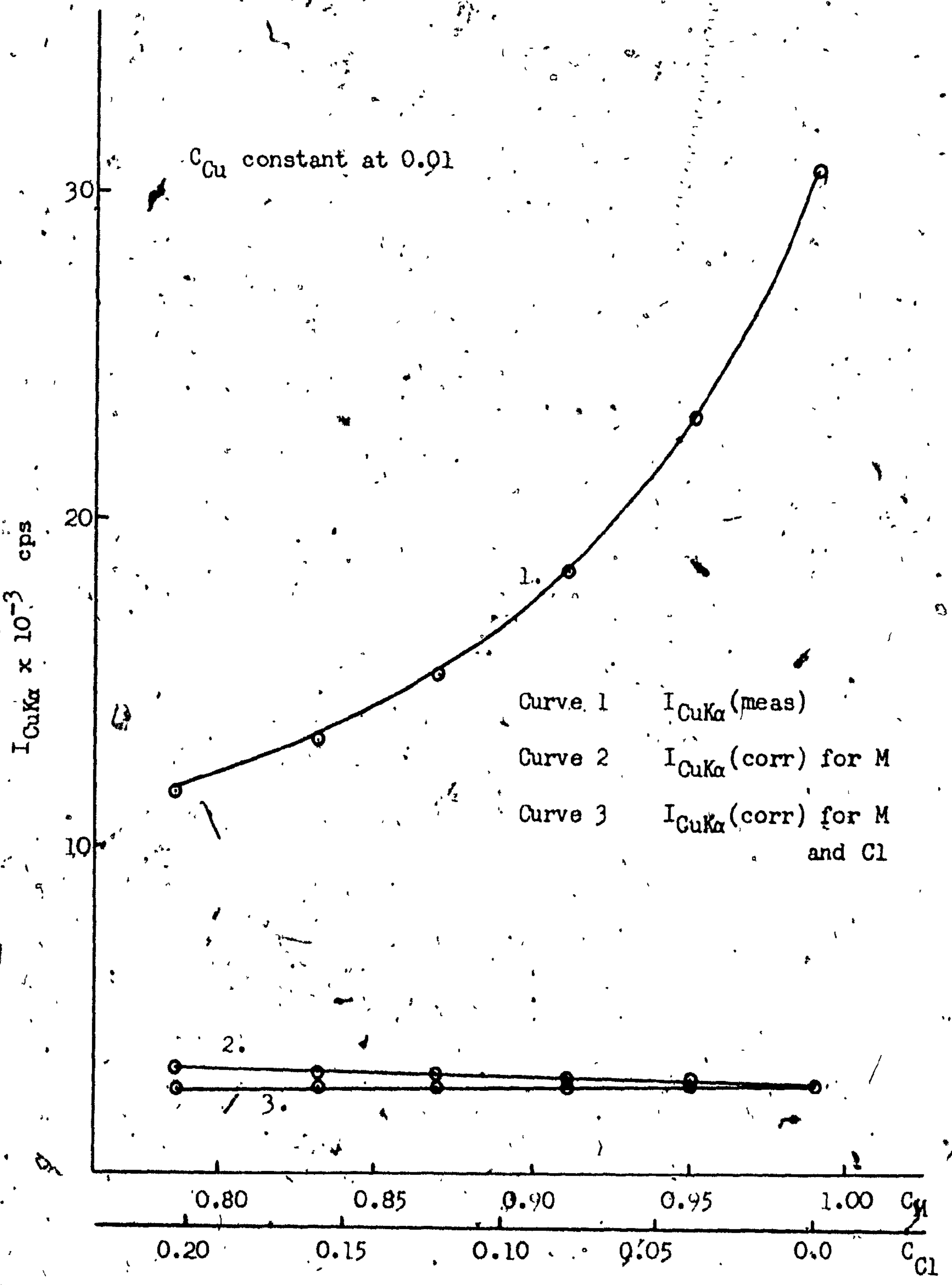
Correction of I_{Cu}(meas) for the Effects of M and Cl*

Solution	I_{Cu}(meas) (cps)	I_{Cu}(corr) for M (cps)	I_{Cu}(corr) for M and Cl (cps)	I^{o}_{Cu}(calc) (cps)
LB-1	30 579	2 549	2 549	254 900
LB-2	23 098	2 772	2 543	254 300
LB-3	18 326	2 874	2 510	251 000
LB-4	15 244	2 974	2 514	251 400
LB-5	13 176	3 044	2 519	251 900
LB-6	11 613	3 174	2 578	257 800

* See Section 5.0.1 for uncertainty values

FIGURE 3

$I_{CuK\alpha}$ VERSUS C_M AND C_{Cl}



It is worthy of note that the average I^{o}_{Cu}(calc) from Tables 4 and 10 show excellent agreement at, respectively, (2.53 ± 0.02) x 10^5 cps and (2.54 ± 0.03) x 10^5 cps. The uncertainties shown are the standard deviation values.

The α-correction coefficients for the effect of chlorine on the other elements of interest were determined in a similar manner. The complete data and calculations are given in Sections 5.2.1 to 5.2.10. The accumulated α-correction coefficients are shown in Table 11.

From Table 11 data several observations may be made. The first three elements of interest show α-coefficients that are positive in nature, and these are the three elements of lowest atomic number in the series. The effect here for chlorine is one of absorption. The remaining elements show negative coefficients, and the effect here is one of negative absorption. The values in brackets which follow after the α-correction coefficients represent the mass absorption coefficients for chlorine relative to the characteristic radiation involved. This listing indicates that the α-correction coefficients determined agree in general with the associated mass absorption coefficients.

2.3 Determination of α-Correction Coefficients for Interelement Effects

2.3.1 Introduction to techniques

The interelement absorption-enhancement effect may be greatly

TABLE 11

α-Correction Coefficients for the Effect of Chlorine

Analyte element	α-Correction coefficient*	
Chromium	0.46^6	(300)
Manganese	0.29^2	(220)
Iron	0.04^7	(188)
Cobalt	-0.172^6	(152)
Nickel	-0.16^2	(120)
Copper	-0.25^0	(100)
Zinc	-0.32^7	(81)
Cadmium	-0.857^6	(5)
Tin	-0.846^9	(4)
Lead	-0.695^6	(40)

---

* Kα radiation in each case, except in the case of Lα radiation for Lead.

reduced or virtually eliminated where the solution has a high degree of dilution. Where a residual absorption-enhancement effect persists, a variety of experimental techniques is available to deal with the situation.(62). The empirical/mathematical method has been explored by Waterbury and Hakkila.(36) A modified form of the Lachance and Traill equation system has been used by Zimmerman and Ingles.(27) The direct application of the Lachance and Traill equation system has, however, not been attempted prior to this investigation on account of the unavoidable presence of the aqueous matrix and the very significant reduction in the interelement effect with highly diluted solutions. The effect of the aqueous matrix can be corrected for if the necessary correction coefficients have been determined in advance. The minimal interference of the interelement effect in solution, which may permit a high degree of uncertainty for the correction coefficients obtained, can be overcome by using high concentration solutions under the proper conditions.

Throughout the literature, the solid content in solution techniques seldom exceeds about 2 percent by weight. Even at this level, interelement effects exist and their effects require correction. Waterbury and Hakkila(36) found that, at a level of about 2 percent concentration by weight, the absorption-enhancement effect in binary mixtures of iron, chromium and nickel was large enough to allow the determination of correction factors. This level of concentration is well below the limit of solubility for each of these elements. A survey of the relevant physical data indicates that the limit of solubility is commonly higher than 15 percent by weight. It is, therefore, possible to make use of high-solid-content solutions, for which the interelement effects are more pronounced, to determine α-correction coefficients applicable to such effects.

2.3.2 Purposes and experimental approach

The purpose of this portion of the investigation was to determine the Lachance and Traill α-correction coefficients for the interelement effects in aqueous solution of a variety of elements of interest. These elements represented, in the main, the major components in steel, ferrous-base and copper-base alloys of commercial and industrial importance. In general, binary combinations of the elements in question were used in the exploratory work although, in consideration of the aqueous matrix and, frequently, the presence of chlorine, the systems were often ternary or quaternary. It was anticipated that the interelement α-correction coefficients determined, together with the coefficients for the aqueous matrix and chlorine effects, would form a basis for the XRF technique of chemical analysis to be investigated subsequently.

A system of two elements A and B in solution actually consists of at least three components, these being A, B and the aqueous matrix M. Under certain circumstances, hydrochloric acid and/or perchloric acid may be used in the solution process and, in such instances, chlorine constitutes a fourth component. The equations required to determine the Lachance and Traill α-correction coefficients in the two cases involved are given respectively as Equations (41) and (42).

In this investigation, the solutions prepared as standards contained a constant weight fraction for the element affected, and variable weight fractions for the interfering element. Under these circumstances, Equations (41) and (42) simplify respectively to the forms shown as Equations (43) and (44).

2.3.3 Results and discussion

In accordance with the form of reporting adopted in Sections 2.1.3 and 2.2.3, the program carried out to determine the effect of chromium on copper, Series MAL, Section 5.3.6, is given as an example of the general approach.

Seven solutions were prepared, each with a constant weight fraction of copper (0.02) and a variable weight fraction for chromium (0.00 to 0.10). These were prepared from stock solutions of copper and chromium, each having a concentration value of 0.200000 ± 0.000004 g per ml. The CuKα and CrKα characteristic radiations were measured at peak values using a tungsten target x-ray tube operating at 50 kV, EQUATIONS (41), (42), (43) and (44)

$$\alpha_{AB} = \frac{I_{A(2)}C_{A(1)}\left(1 + \alpha_{AM}C_{M(2)}\right) - I_{A(1)}C_{A(2)}\left(1 + \alpha_{AM}C_{M(1)}\right)}{I_{A(1)}C_{A(2)}C_{B(1)} - I_{A(2)}C_{A(1)}C_{B(2)}} \qquad (41)$$

$$\alpha_{AB} = \frac{I_{A(2)}C_{A(1)}\left(1 + \alpha_{AM}C_{M(2)} + \alpha_{ACl}C_{Cl(2)}\right) - I_{A(1)}C_{A(2)}\left(1 + \alpha_{AM}C_{M(1)} + \alpha_{ACl}C_{Cl(1)}\right)}{I_{A(1)}C_{A(2)}C_{B(1)} - I_{A(2)}C_{A(1)}C_{B(2)}} \qquad (42)$$

$$\alpha_{AB} = \frac{I_{A(2)}\left(1 + \alpha_{AM}C_{M(2)}\right) - I_{A(1)}\left(1 + \alpha_{AM}C_{M(1)}\right)}{I_{A(1)}C_{B(1)} - I_{A(2)}C_{B(2)}} \qquad (43)$$

$$\alpha_{AB} = \frac{I_{A(2)}\left(1 + \alpha_{AM}C_{M(2)} + \alpha_{ACl}C_{Cl(2)}\right) - I_{A(1)}\left(1 + \alpha_{AM}C_{M(1)} + \alpha_{ACl}C_{Cl(1)}\right)}{I_{A(1)}C_{B(1)} - I_{A(2)}C_{B(2)}} \qquad (44)$$

an LiF analyzing crystal and a scintillation counter. The average of 3 counting periods, with corrections for background and deadtime, where required, are shown in Table 12, together with solution compositional data.

The effect of chromium on copper in solution media is relatively minor, and combinations of standard solutions were chosen permitting maximization of the effect. The several combinations selected to calculate α_{CuCr} are given in Table 13. The average value for α_{CuCr} and the standard deviation were:-

$$\alpha_{CuCr} = 0.89^{4} \pm 0.05^{7}$$
$$= 0.89 \pm 0.06$$

It will be noted that this α-coefficient is positive in nature, reflecting the absorption effect of chromium on CuKα radiation.

When α_{CuCr} had been determined, the corrected intensities for CuKα, relative to the aqueous matrix and chromium effects, were calculated using Equation (45):-

$$I_{Cu}(corr) = I_{Cu}(meas)\left(1 + \alpha_{CuM}C_M + \alpha_{CuCr}C_{Cr}\right) \quad (45)$$

The results are expressed in Table 14, and show only minor variations for the value of I_{Cu} corrected for both the effect of M and the effect of Cr. Plots of the measured intensity, the intensity

TABLE 12

DETERMINATION OF α_{CuCr}

Standard Solution Composition and Intensity Measurement*

Solution	Weight fractions			Intensities (cps)	
	C_{Cu}	C_{Cr}	C_M	$I_{CuK\alpha}$ (meas)**	$I_{CrK\alpha}$ (meas)**
MAL-1	0.02000	0.00	0.9800	114 416	-
MAL-2	0.02000	0.01000	0.9700	93 756	6 820
MAL-3	0.02000	0.02000	0.9600	81 823	13 321
MAL-4	0.02000	0.04000	0.9400	65 603	24 791
MAL-5	0.02000	0.06000	0.9200	52 530	33 939
MAL-6	0.02000	0.08000	0.9000	44 509	42 274
MAL-7	0.02000	0.10000	0.8800	38 267	47 770

* See Section 5.0.1 for uncertainty values

** Corrected for background, and for deadtime where required. Average of 3 counting periods.

TABLE 13

DETERMINATION OF α_{CuCr}

Calculation of the α_{CuCr} Correction Coefficient

Solution Combination	α_{CuCr}
MAL-1/MAL-7	0.9175·····
MAL-1/MAL-6	0.8924·····
MAL-1/MAL-5	0.9927·····
MAL-2/MAL-7	0.8534·····
MAL-2/MAL-6	0.8129·····
MAL-3/MAL-7	0.9166·····
MAL-3/MAL-6	0.8701·····
Average α_{CuCr}	0.894·····
Standard deviation	± 0.057·····

$$\alpha_{CuCr} = 0.89^{4} \pm 0.05^{7}$$

$$= 0.89 \pm 0.06$$

TABLE 14

DETERMINATION OF α_{CuCr}

Correction of I_{Cu}(meas) for the Effects of M and Cr*

Solution	I_{Cu}(meas) (cps)	I_{Cu}(corr) for M (cps)	I_{Cu}(corr) for M and Cr (cps)	I^{o}_{Cu}(calc) (cps)**
MAL-1	114 416	10 597	10 597	529 850
MAL-2	93 756	9 552	10 390	519 500
MAL-3	81 823	9 093	10 556	527 800
MAL-4	65 603	8 506	10 851	542 550
MAL-5	52 530	7 783	10 601	530 050
MAL-6	44 509	7 419	10 602	530 100
MAL-7	38 262	7 086	10 507	525 350

---

* See Section 5.0.1 for uncertainty values

** Higher than comparable values for Tables 4 and 10 on account of higher kV and mA operating parameters.

corrected for the aqueous matrix affect and intensity corrected for the aqueous matrix and chromium effects, all versus the appropriate concentrations of copper, chromium and aqueous matrix, are shown in Figure 4.

It will be observed from Figure 4 that the corrections for the aqueous matrix effect lower the intensity values, and in a significant manner. Those for the chromium effect increase the intensity values to, however, a relatively insignificant extent.

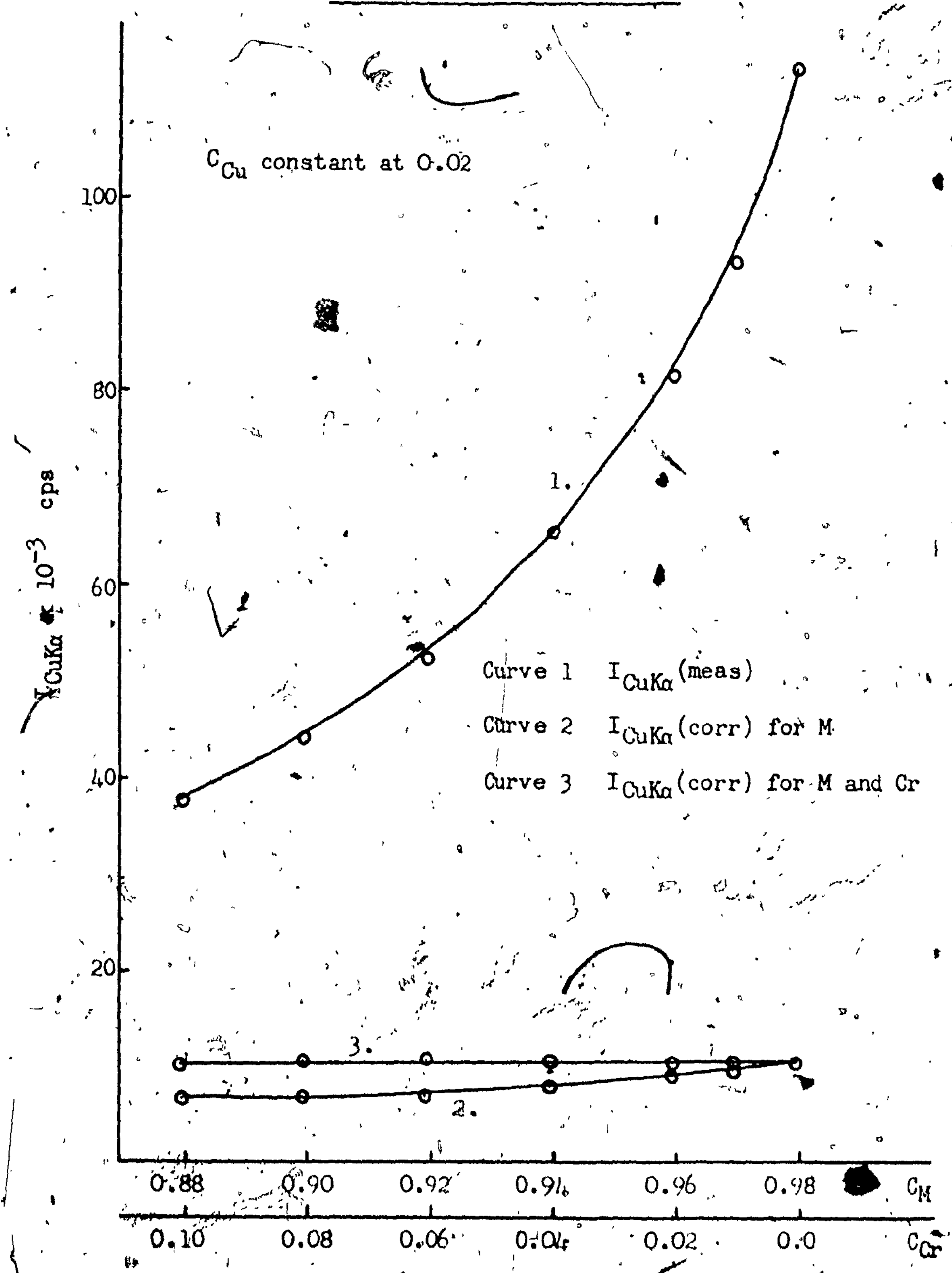
The effect of chromium on the characteristic radiation for the elements chlorine, manganese, iron, cobalt, nickel and zinc were determined in a similar manner. The data involved will be found in Sections 5.3.1 to 5.3.7.

In a generally similar manner, the interelement effects for all of the elements of interest were determined. All of the experimental data associated with these determinations may be found in the following Sections:-

Element causing effect	Section
Chromium	5.3.1 to 5.3.7
Manganese	5.4.1 to 5.4.7
Iron	5.5.1 to 5.5.8
Cobalt	5.6.1 to 5.6.7
Nickel	5.7.1 to 5.7.7
Copper	5.8.1 to 5.8.9
Zinc	5.9.1 to 5.9.9
Cadmium	5.10.1 to 5.10.2
Tin	5.11.1 to 5.11.5
Lead	5.12.1 to 5.12.3

FIGURE 4

$I_{CuK\alpha}$ VERSUS C_{Cr} AND C_M



The experimental data for the effects of the aqueous matrix and chlorine are given, as pointed out elsewhere, in Sections 5.1.1 to 5.1.11 and 5.2.1 to 5.2.10 respectively. Note that the Section 5 divisions correspond to the order of the increasing atomic number of the interfering element as main sections (5.1, 5.2, etc.), and in the same order as to the element affected relative to each set of sub-sections (5.1.1, 5.1.2, etc.).

In all, 85 α-correction coefficients were determined with respect to the entire series of elements of interest. Table 15 indicates, in chart form, the accumulated results of the entire survey relative to the determination from aqueous solution of the α-correction coefficients required for the subsequent analytical portion of the investigation. The horizontal headings list the elements affected. The vertical headings list the elements providing the interfering effect. Among these latter headings, the heading "M" indicates the residual aqueous combination of hydrogen, nitrogen, oxygen and, under certain circumstances, fluorine and carbon.

When all of the α-correction coefficients had been determined, correction of the intensities for the interfering elements, according to the appropriate I-T equations, was carried out for most of the experimental data obtained. The back-calculation of solution composition was carried out for almost all of the solutions investigated, wherever sufficient data on the various intensities were

TABLE 15

α-CORRECTION COEFFICIENTS DETERMINED FROM AQUEOUS MEDIA

α	Cl_{17}	Cr_{24}	Mn_{25}	Fe_{26}	Co_{27}	Ni_{28}	Cu_{29}	Zn_{30}	Cd_{48}	Sn_{50}	Pb_{82}
M	-0.33^{6}	-0.847^{1}	-0.863^{7}	-0.896^{7}	-0.922^{3}	-0.917^{1}	-0.925^{9}	-0.942^{9}	-0.965^{6}	-0.954^{0}	-0.969^{9}
Cl_{17}		0.46^{6}	0.29^{2}	0.04^{7}	-0.172^{6}	-0.16^{2}	-0.25^{0}	-0.32^{7}	-0.857^{6}	-0.846^{9}	-0.695^{6}
Cr_{24}	0.39^{6}		0.8^{2}	1.47^{9}	1.05^{3}	1.00^{5}	0.89^{4}	0.54^{0}			
Mn_{25}	0.66^{7}	-0.30^{1}		-0.31^{9}	1.24^{3}	1.21^{5}	1.0^{4}	0.63^{1}			
Fe_{26}	1.12^{7}	-0.49^{3}	-0.28^{1}		-0.22^{4}	1.32^{5}	1.25^{3}	0.6^{5}	-0.47^{6}		
Co_{27}	1.24^{2}	-0.55^{1}	-0.67^{4}	-0.23^{4}		-0.17^{5}	1.5^{1}	0.9^{4}			
Ni_{28}	1.26^{1}	-0.38^{9}	-0.39^{1}	-0.63^{3}	-0.37^{4}		-0.07^{4}	1.1^{6}			
Cu_{29}	1.40^{0}	-0.51^{0}	-0.50^{9}	-0.62^{1}	-0.66^{5}	-0.3^{5}		-0.26^{0}		-0.25^{2}	0.19^{7}
Zn_{30}	1.8^{3}	-0.38^{8}	-0.46^{0}	-0.61^{5}	-0.61^{0}	-0.52^{3}	-0.207^{2}			-0.23^{5}	0.35^{7}
Cd_{48}	1.31^{3}			1.12^{8}							
Sn_{50}	1.79^{6}			1.48^{6}			0.68^{4}	0.37^{9}			-0.26^{4}
Pb_{82}							0.51^{5}	0.26^{8}		1.03^{5}	

available. This provided one method of verifying the reliability of the α-correction coefficients obtained. Such back-calculation data will be found in the appropriate portions of Section 5.

The investigation described in the foregoing sections has shown that the Lachance and Traill equation system can be used to determine α-correction coefficients relating analyte fluorescent intensity to the concentration of the constituents in an aqueous solution. The α-coefficient values obtained are generally related to the mass absorption coefficients, and show good correspondence with the physical nature of the interelement effect.

With respect to those elements with absorption edge and characteristic radiation in close proximity, the specific absorption effect generally provides for quite positive α-coefficients. The enhancement effect is less obvious, however, in part because of the overlapping situation relative to the negative absorption effect of the aqueous matrix.

The α-correction coefficient values for analytes one atomic number higher or lower than that of the interfering element are, in general, small and negative. As an example, the α-coefficients to correct for the effects of iron (atomic number 26) on manganese (atomic number 25) and cobalt (atomic number 27) are respectively - 0.28[1] and - 0.22[4].

The aqueous matrix M is a very light matrix, giving an α_{CrM} value of -0.847^1, and approaching the minimum value of -1.0 for a hypothetical matrix with zero absorption as the atomic number of the affected element increases. For chlorine, however, seven atomic numbers lower than chromium, the aqueous matrix becomes a relatively heavy absorber, yielding an α_{ClM} value of -0.33^6. It is expected, therefore, that for elements below chlorine in atomic number the aqueous matrix effect will be still further reduced, rendering the determination of the α-correction coefficient by this method less accurate and sometimes, perhaps, not practical.

It is not generally considered good practice to compare the α-coefficients, determined by one laboratory using a specific method and a specific set of standards, with those determined by using a different method and standards. However, from the literature, the α-coefficients determined using other than the solution technique show, quite frequently, remarkably good agreement with those found as the result of applying the solution technique. This comparison, as presented in Table 16, serves to point out that, even where the interelement effects are greatly reduced by dilution, the aqueous solution method is still adequate to the determination of α-correction coefficients with values comparable to those derived through the application of methods involving solid standards of one type or another.

As noted by Marti,(20) the principal difficulty in obtaining

TABLE 16

COMPARISON OF α-COEFFICIENTS - DIFFERENT EXPERIMENTAL METHODS

α-Coefficient	Aqueous solution method	Literature values Other methods of approach	Reference number
$\alpha_{Fe(Li_2B_4O_7)}$	$-0.897(\alpha_{FeM})$	-0.86	26
α_{CrNi}	-0.39	-0.37	24
α_{FeCr}	1.48	1.47	24
α_{NiFe}	1.32	1.32	24
α_{FeNi}	-0.63	-0.60 *	23
α_{MnCo}	-0.67	-0.61	23
α_{CrCo}	-0.55	-0.54	23

* Theoretical, calculated value.

reliable and accurate correction coefficients lies in the availability of accurate and reliable standards. In addition, verification of the applicability of the derived coefficients was carried out relative to similar sets of unknowns. Therefore, as shown by Birks,(7) all of the shortcomings of the correction method are included in the determined coefficients. Such coefficients do not have analytical applicability in the general sense of being adaptable to the analysis of samples showing a wide variation as to composition. This difficulty is minimized to a considerable extent by the method of approach employed in the present investigation. Accurate standards are easy to prepare, and the reliability and applicability of the derived α-correction coefficients can be verified by the analysis of simple systems, before they are tested in the analysis of multicomponent independent systems. These are some of the main advantages devolving from the determination of α-correction coefficients in aqueous solution media.

3. APPLICATION OF THE DETERMINED α-CORRECTION COEFFICIENTS TO CHEMICAL ANALYSIS BY X-RAY FLUORESCENCE

3.1 Review of Techniques

The absorption and enhancement effects in ferrous-base and other-base alloys, such as nickel-base, cobalt-base, etc., provide for a particularly complicated problem in XRF analysis. The major elemental components in such materials are often relatively similar as to atomic number, ranging from chromium at atomic number 24 to copper at atomic number 29, for example. Table 17 and Figure 5 illustrate respectively the proximities of the emitted radiations and absorption edges for such components.

An example of the complexity of the absorption and enhancement effects occurring with the major components in ferrous-base alloys can be obtained from the discussions to follow. These discussions are related to the influence of the matrix on the fluorescent intensity for iron in different binary and ternary alloys involving this element.

In binary alloys of iron and chromium, the FeKα radiation (1.94Å) lies on the short wavelength side of the chromium Kedge (2.07Å), and is thus heavily absorbed. The mass absorption coefficient of chromium for FeKα radiation is 460, compared to a value

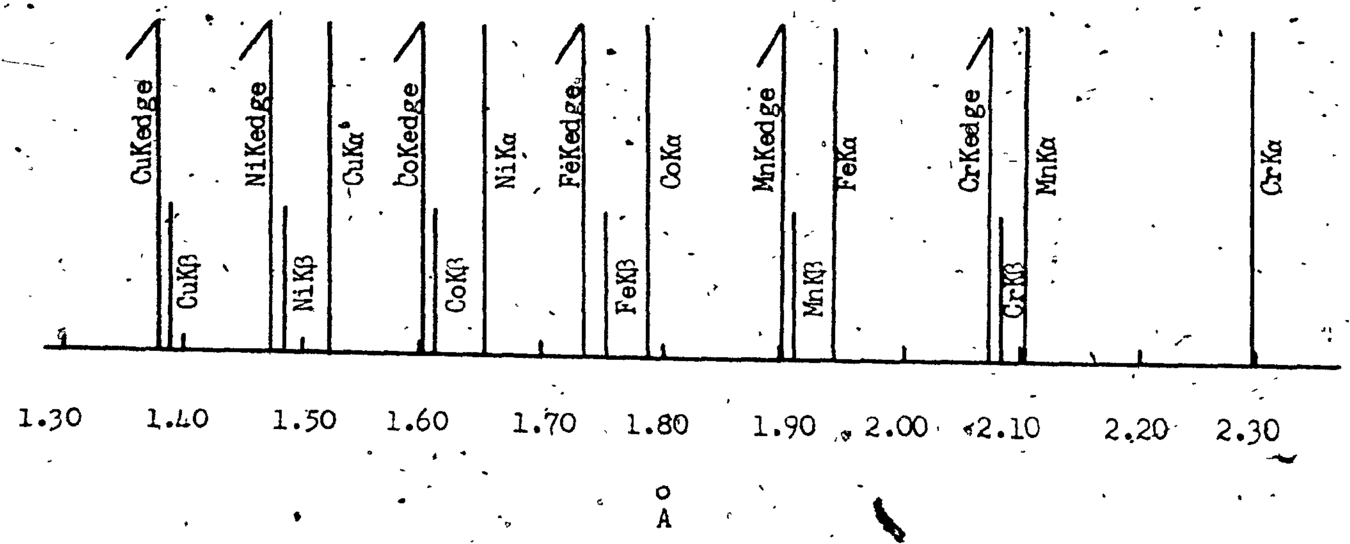
TABLE 17

ABSORPTION EDGE AND EMITTED RADIATION
MAJOR COMPONENTS IN FERROUS-BASE ALLOYS

Atomic number	Element	Kedge (Å)	Kα (Å)	Kβ (Å)
24	Chromium	2.07	2.29	2.08
25	Manganese	1.90	2.10	1.91
26	Iron	1.74	1.94	1.76
27	Cobalt	1.61	1.79	1.62
28	Nickel	1.49	1.66	1.50
29	Copper	1.38	1.54	1.39

FIGURE 5

ABSORPTION EDGE AND EMITTED RADIATION - MAJOR COMPONENTS IN FERROUS-BASE ALLOYS



of 76 for iron itself. It is expected that the Kα fluorescent intensity for iron will be lower in the presence of chromium than that predicted by the relationship $I_{FeK\alpha} = I^{o}_{FeK\alpha} \cdot C_{Fe}$.

Similar absorption effects occur in the measurement of the characteristic radiation for cobalt in the presence of manganese, nickel in the presence of iron and copper in the presence of cobalt.

In an iron-manganese binary combination, iron and manganese have similar absorption coefficients for FeKα radiation, being respectively 74 and 76. FeKα radiation lies, in addition, on the long wavelength side of the manganese Kedge. As the iron concentration is increased, the overall matrix absorption does not vary significantly, so that the FeKα intensity would show an almost linear relationship with the iron concentration over the range of zero to 100 percent. Experimental data(42,47) have, however, shown a negative absorption effect. This is obviously not caused by any additional excitation of iron by manganese, but rather by the overlapping of MnKβ radiation (1.91Å) on FeKα radiation (1.94Å). Satisfactory approximate results for iron analyses in such cases can be obtained by using the second order line for FeKα.(47) This method is, however, not appropriate in the solution technique on account of low FeKα intensity. A ratio intensity method was used by Mitchell(42) to correct for this interfering situation.

Similar influences relative to matrix element Kβ radiation can be expected for MnKα by CrKβ, CoKα by FeKβ, NiKα by CoKβ, and CuKα by NiKβ.

Cobalt Kα radiation (1.79Å) is on the long wavelength side of the iron Kedge (1.74Å). There is thus no enhancement effect of iron by CoKα. However, CoKβ radiation (1.62Å), with an approximate intensity of 25 percent of CoKα, provides for additional excitation of iron in binary alloys of iron and cobalt. This enhancement effect is quite appreciable if the cobalt concentration is high relative to that of iron.

A simultaneous and opposing effect is created by the overall absorption of the matrix. Cobalt, with an absorption coefficient of 84, slightly higher than that of iron, would reduce the intensity of FeKα. The net effect of cobalt on iron is, however, one of enhancement, as shown by the data for Section 5.6.4 of this investigation. A similar observation has been made by Mitchell(42) with respect to the enhancement of manganese by FeKβ radiation.

An enhancement effect resulting from excitation by Kβ radiation can also be expected in the case of chromium by MnKβ, cobalt by NiKβ, and nickel by CuKβ. The experimental data for this investigation (Sections 5.4.2, 5.5.3, 5.7.5 and 5.8.6 respectively) showed good agreement with these observations.

Iron in a binary alloy of iron and nickel is known to be enhanced by NiKα radiation (1.66Å). The larger absorption coefficient of nickel for FeKα, at a value of 94 compared to iron itself at 76, results in the opposite effect on the FeKα intensity. The net effect of nickel on iron is nevertheless one of enhancement, with the FeKα intensity being higher than that expected from the relationship, $I_{FeK\alpha} = I^{o}_{FeK\alpha} \cdot C_{Fe}$.

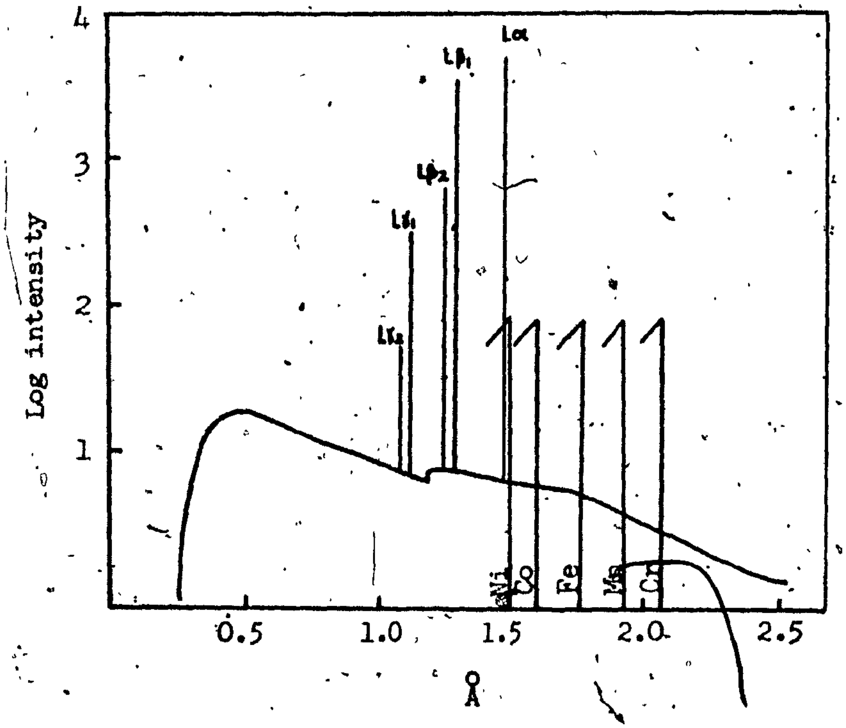
Similar enhancement effects occur with the combinations of ferrous-base components; chromium and iron, manganese and cobalt, and cobalt and copper.

In the previously-reported portion of this investigation, only interelement effects and overall matrix effects were considered. The study would not be complete if the effect of the primary spectrum was not taken into account. As an example, the spectrum for the tungsten target x-ray tube operated at 50 kV will be used in the discussion to follow, which is in itself related to the fluorescent intensity for iron in various binary combinations.

The primary spectrum consists of the characteristic tungsten radiation for this voltage, superimposed on the continuous x-ray spectrum. Fluorescence is only produced by that portion of the radiation which is shorter in wavelength than the absorption edge of the element to be excited. As illustrated in Figure 6, the absorption Kedges for chromium, manganese, iron, nickel and cobalt are on the long wavelength side of the tungsten characteristic radiations for

FIGURE 6

$L\alpha$, $L\beta$, LY RADIATION AND CONTINUOUS SPECTRUM FOR TUNGSTEN K-EDGES FOR CHROMIUM, MANGANESE, IRON, NICKEL AND COBALT



Lα, Lβ and Lγ. Excitation is therefore induced, for these elements, by the characteristic tungsten radiation and the continuous spectrum.

Binary mixtures of iron can be divided into two categories; those with absorption edges higher than that of FeKα radiation, as is the case with manganese and chromium, and those with lower absorption edges, as is the case with nickel and cobalt.

In the first category, primary radiation with sufficient energy for FeKα excitation is heavily absorbed by chromium or manganese. At a wavelength of 1.66Å, for instance, the absorption coefficients of chromium, manganese and iron are respectively 319, 348 and 397. Primary photons at this wavelength are thus distributed according to the concentration of iron and these associated elements. The FeKα fluorescent intensity is therefore strongly influenced by the presence of manganese or chromium. This situation is further complicated by the unknown nature of the continuous spectrum, and by the non-linear variation of the absorption coefficients with wavelength.

In the second category, primary radiation with wavelength values longer than that of the nickel or cobalt absorption edge are available quite generally for FeKα excitation. The absorption coefficients of cobalt and nickel at 1.66Å, for example, are much lower than that of iron (54 and 61 respectively compared to 397 for iron). Radiation shorter in wavelength than the absorption edge of cobalt or nickel is almost equally absorbed by iron. At a wavelength of 1.60Å, for example, below the cobalt absorption edge, the absorption coefficient of iron is 348 as compared to a value of 416 for cobalt. Radiation shorter than the cobalt or nickel edges is generally not as effective in FeKα excitation as is that situated between FeKα radiation and the cobalt or nickel edges.(10)

From these observations, one might expect the influence of the primary radiation on the excitation of iron to be of considerable importance in the first category of binary mixtures, but of lesser importance in the second category.

It would be appropriate to provide here some discussion relative to the physical meaning of the second-order term $\alpha_{BB}C_B^2$ intended to correct for the polychromaticity of the primary beam in the Lachance and Traill correction equation system.(24,25)

Consider two binary systems involving iron, the first iron and chromium, and the second iron and nickel. The first binary system involves an absorption effect on FeKα fluorescent intensity by chromium. The second involves an enhancement effect on FeKα by nickel. From the foregoing discussion, it is apparent that the primary radiation has much greater influence on the FeKα intensity in the iron-chromium system than in the iron-nickel system. Claisse and Quintin(25) and Lachance(24) indicated larger second-order correction terms for the iron-nickel system than for the iron-chromium system. This is in opposition to the assumed physical nature of the effects involved. A second fact supporting the idea that the second-order term $\alpha_{BB}C_B^2$ may not correct for the polychromaticity of the primary beam only is that a single theoretically-calculated α-coefficient of Lachance(24) includes the excitation efficiency at each increment of wavelength of the primary spectrum from λ_o to λ_{edge}.

The presence of a third element further complicates the absorption and enhancement effects. Iron in a ternary alloy of iron, nickel and cobalt, for instance, is enhanced by NiKα and CoKβ radiation. The enhancement effect of CoKβ radiation is stronger than it would be in a comparable binary alloy of iron and cobalt, since cobalt is, in turn, enhanced by NiKα radiation.

FeKα radiation in a ternary alloy of iron, cobalt and manganese is enhanced as a result of additional excitation by CoKβ radiation and by the overlapping of MnKβ radiation. CoKβ radiation simultaneously enhances manganese to produce a stronger MnKβ radiation than would be obtained in a comparable binary system of manganese and iron. Thus, the influence of MnKβ radiation on FeKα is different in the ternary system than in the comparable binary system.

The absorption effect due to the proximity of absorption edges and emitted radiations is subject to less in the way of interference by the presence of a third element. For example, FeKα radiation in iron - chromium - manganese alloys is absorbed by chromium and is independent of MnKα radiation.

These examples explain quite adequately why multicomponent systems can not be treated as combinations of binary systems without some regard for the components present. They also provide some physical basis of explanation for the need to include second-order terms, such as $\alpha_{Bc}C_BC_C$, to correct for the third element effect in applying the Lachance and Traill correction equation system, particularly where enhancement effects are involved.

Copper-base alloys, with the four major components copper, tin, zinc and lead, present situations where the proximity of absorption edges and emitted radiations is of a lesser order of importance and the absorption by the specimen of the primary radiation and radiation from the analytes are of greater importance. Table 18 shows the values of absorption edges and emitted radiations for copper, tin, zinc and lead.

Examination of the absorption edge and emitted radiation relationships show only some minor enhancement effects due to ZnKβ radiation (1.30Å) on CuKα (49) (copper Kedge 1.38Å), and due to the overlapping of CuKβ (1.39Å) on ZnKα (1.44Å).

The importance of the difference in the absorption of the primary beam for such alloys can best be illustrated by reference to binary alloys of lead and tin.(50) The calibration curve for PbLα in the

TABLE 18

ABSORPTION EDGE AND EMITTED RADIATION MAJOR COMPONENTS IN COPPER-BASE ALLOYS

Atomic number	Element	Kedge Å	L_{111}edge Å	Kα Å	Lα Å	Kβ Å
29	Copper	1.38	13.29	1.54	--	1.39
30	Zinc	1.28	12.13	1.44	--	1.30
50	Tin	0.42	3.16	0.49	3.60	0.43
82	Lead	0.14	0.95	0.17	1.17	0.15

range of zero to 100 percent shows a negative absorption effect. The reason for this could result from the differences in either absorption or enhancement. In this case, SnKα (0.49Å) can scarcely excite lead with an absorption edge located at 0.95Å, so that enhancement effects do not underly the negative absorption found. The effect must be explained in terms of differences in absorption. The absorption coefficient for PbLα is, however, very similar relative to lead and tin, being respectively 128 and 134. This small difference in the absorption coefficients would only be expected to yield a small positive absorption effect. This leaves the differences in absorption of the primary beam as the cause of the negative deviation from linearity for PbLα intensity versus concentration of lead. Indeed, the absorption coefficient for primary radiation shorter than the L_{111} edge of lead (0.95Å) is very much larger for lead than for tin. For instance, for primary radiation of 0.75Å, the approximate absorption coefficient values are 40 for tin and 160 for lead. This means that the efficiency of each primary wavelength in this area, relative to lead excitation, is higher with low lead concentrations. The measurement of PbLα radiation will thus show a negative absorption effect.

The measurement of SnKα over a range of zero to 100 percent tin in tin-lead binary alloys shows a positive absorption effect. At the SnKα wavelength (0.49Å) the absorption coefficient of lead is higher than that for tin (53 compared to 13 for tin), so that SnKα radiation is absorbed more in the presence of lead. For primary radiation shorter than the absorption edge of tin (0.42Å), the absorption coefficients for tin are somewhat larger than those for lead. This means that tin is more efficiently excited in the presence of high lead concentrations. This results in a small countereffect on the tin intensity. The net effect is positive absorption, as shown by the experimental data.(50)

The absorption and enhancement effects in ferrous-base and copper-base alloys become more complicated where all of the major components are present over large concentration ranges. They are often used to test for the validity of XRF methods of analysis. Emperical-mathematical have been applied successfully with respect to a relatively small range of concentration.(7,17,21,22) This was discussed in Section 1 of this presentation. In the interests of providing additional data, the purely empirical-mathematical approaches proposed by Mitchell and Hooper(51) and Lucas-Tooth(52,53) might be worthy of mention.

According to Mitchell and Hooper,(51) when plotted intensity-concentration data obviously lie on a straight line, the concentration C, may be predicted by a linear equation ~~of the form:-~~

$$C = a_o + a_1 I \qquad (46)$$

where:-

$a_o, a_1,$ = constants

I = measured fluorescent intensity

Where the plotted data do not yield a linear relationship, higher-order terms may be required, in the form:-

$$C = a_o + a_1 I + a_2 I^2 + \cdots \qquad (47)$$

In the majority of instances of analytical application, the authors found that XRF data might be fitted to a general equation of the form:-

$$C_1 = a_o + a_1 I_1 + a_2 I_2 + a_3 I_3 + a_4 I_1^2 + a_5 I_2^2 + a_6 I_3^2 + a_7 I_1 I_2 + a_8 I_1 I_3 + a_9 I_2 I_3 \qquad (48)$$

where:-

1,2,3, = component 1,2,3,

a_i = constants estimated by the least squares method.

In an application to the analysis of 31 samples of ferro-manganese the authors obtained average absolute errors of 0.33 percent for manganese in the range of 78.20 - 88.90 percent, and 0.11 percent in the range of 4.02 - 13.20 percent for iron.

A mathematical method proposed by Lucas-Tooth(52,53) is based on the assumption that absorption of the characteristic radiation for element A by element B is linearly proportional to the percentage concentration of B. The departure of the fluorescent intensity of A from linearity, as given by the relationship $I_A = I_A^o \cdot C_A$, is then proportional to the product $I_A C_B$. In a multicomponent system, the mathematical expression for the percentage concentration also included terms intended to correct for the effects of the other elements on I_A. The final expression is written in the general form:-

$$C_A = \alpha_A + \beta_A I_A (1 + \sum_i \gamma_{Ai} C_i) \qquad (49)$$

where:-

α, β, γ = constants determined from standards
C_A = percentage concentration of A
I_A = measured fluorescent intensity for A

The authors further simplified Equation (49) by replacing the product $\beta_A \gamma_{Ai}$ by a single constant b_{Ai} to obtain the final and basic correction expression in the form:-

$$C_A = \alpha_A + I_A (1 + \sum_i b_{Ai} C_i) \qquad (50)$$

where:-

α_A, b_{Ai} = experimentally determined coefficients
C_i = percentage concentration for component i in the system

Lucas-Tooth and Price$^{(52)}$ applied Equation (50) successfully in the analysis for copper in brass, bronze and gunmetal alloys. The root mean square difference from the known composition was 0.13 percent. Later, Lucas-Tooth and Pyne$^{(53)}$ extended this method to the analysis for chromium in a more complicated matrix with equal success.

Gillieson et al(54) employed the Lucas-Tooth method with somewhat less success in the analysis for both major and minor components in high-temperature alloys. The agreement with the known composition was found in the range of 5 to 10 percent relative absolute error for the major components, while minor components deviated as much as 30 percent relative absolute error from the known values.

Another equally important source of error in the practice of chemical analysis by the XRF technique which requires mention is that related to the physical nature of the specimen. Particle size, surface condition and heterogeneity effects are not associated with the use of liquid specimens, but may introduce, in powder and solid specimens, systematic errors as high as the errors introduced by absorption and enhancement effects.(55) This is, of course, one of the primary advantages associated with the use of liquid specimens.

Gunn(56) showed that there is no advantage for powder dilution over aqueous solution dilution in terms of fluorescent intensity. Powder specimens, however, require careful preparation. With ferrous alloys, for example, the standards and samples must be ground to the same particle size, and even to the same particle size distribution.

Surface finishing is of comparable importance where solid specimens are employed. The limiting values for the maximum groove depth for the finished surface of ferrous-base and copper-base alloy specimens can be found in various texts.(57) Special problems with respect to surface smearing may arise in the preparation of certain types of alloys and, in particular, where an alloy contains a matrix constituent appreciably softer than the others. The surface smearing effect of lead during the surface finishing process, and its ability to alter the fluorescent intensity for tin and/or lead is an example of this situation.(58,59) This effect may be minimized either by the use of the shorter characteristic wavelengths, if this is possible, since these are less affected by surface roughness,(58) or by a very careful polishing technique aimed at providing for a groove depth less than the critical maximum value for the most sensitive radiation from the matrix.

The aqueous dilution technique is generally unaffected by such physical sources of interference. The method also permits minimization of the absorption and enhancement effects. Its effectiveness in this direction depends on the degree of dilution and on the concentration ranges for the matrix components. As noted by Mitchell,(42) where the concentration range is extremely extensive (0.1 - 99.9 percent), even at a 1 percent total solids concentration in solution and with the intensity corrected by the ratio technique, the calibration curves for ferrous-base alloy components still show departures from linearity. This provides evidence of significant residual absorption and enhancement effects.

3.2 Purposes of the XRF Analytical Investigations

As outlined in Section 3.1, ferrous-base and copper-base alloys present complicated situations relative to the physical nature of the absorption and enhancement effects. Such alloy types present difficult situations with respect to the XRF method of analysis.

The XRF technique of analysis for such alloys was carried out in this investigation in order to test the validity of the Lachance and Traill equation system when applied to aqueous media solution specimens of the alloys in question.

A second important purpose here was to apply the α-correction coefficients, derived in the first portion of the investigation with respect to independent simple solution systems, in the analysis of multicomponent solution mixtures. This is rather in opposition to the generally-accepted procedure of applying empirical-mathematical correction methods to analytical situations. The approach, in the case of this investigation, was to determine both the validity of the derived α-coefficients and their ability to yield satisfactory results when applied in the analysis of such multicomponent systems.

A third purpose was to develop a high-concentration solution specimen, the preparation of which would be relatively independent of sample size available, heterogeneity of the original sample, and the acid concentration required in specimen solution preparation.

With these purposes in view, synthetic solutions of typical components with respect to the general compositions of ferrous-base and copper-base alloys were prepared in extended concentration ranges for these components, with variable total-solid content and variable acid concentration. In order to conform to the situation where XRF would be used in the actual analysis of such alloys, synthetic solutions were also prepared with component ranges typical of those to be encountered relative to actual solutions of industrial alloys of these types. Finally, analyses of actual ferrous-base alloys (NBS standards) and copper-base alloys (analyzed standards) were carried on solution specimens.

3.3 Examination of Aqueous Solutions Appropriate to the Chemical Analysis by XRF of Ferrous-Base, Nickel-Base, etc., Alloys

3.3.1 Ferrous-base, etc., synthetic solutions, preparation and examination

A group of stock solutions was prepared; each one involving one of the analytes of interest with respect to ferrous-type alloy analysis; iron, manganese, chromium, cobalt, nickel and copper. Each solution was of exactly-known composition. Two series of synthetic solutions of variable composition relative to the range of concentration for the total analytes were prepared from these stock solutions. These were Series SF and Series SG solutions, the main difference being that the first showed extended ranges of concentration for each analyte, for chlorine and for the residual aqueous matrix, while the second showed concentration ranges for these variables.

For those synthetic solutions where chlorine from hydrochloric and/or perchloric acids was a constituent, the chloride concentration was determined exactly by potentiometric titration with silver nitrate solution, although this determination was really necessary only for that solution which was to serve as the standard. The prospective alternation of standards provided the basis for these multiple determinations.

Each solution was eventually subjected to examination by the XRF method, this examination involving the measurement of the emitted characteristic radiation intensities for each analyte, as well as for chlorine. In every case, an average intensity was obtained, and this represented the average of 3 or 5 counting periods at the associated emission peak. For each series, one of the synthetic solutions was selected as a standard in order to determine the compositions of the other solutions in the series. Composition was determined by solving a system of linear equations of the general type shown as Equation (25) in Section 1.9. The pertinent data for the experimental program involving solution series SF and SG can be found in Sections 6.1.1 and 6.1.2.

Tables 19 and 20 show the compositions for Series SF and SG synthetic solutions. Each analyte concentration is shown in two forms of expression. The heading "solution percent" provides these values

TABLE 19

SYNTHETIC SOLUTIONS SIMULATING FERROUS-BASE ALLOYS - SERIES SF *

Solution No.	Chromium A	Chromium B	Manganese A	Manganese B	Iron A	Iron B	Cobalt A	Cobalt B	Nickel A	Nickel B	Copper A	Copper B
SF-1	0.10	1.39	0.20	2.78	0.50	6.94	5.00	69.40	0.40	5.56	1.00	13.89
SF-2	0.50	7.46	0.50	7.46	0.20	2.98	0.50	7.46	4.00	59.70	1.00	14.92
SF-3	0.10	0.94	0.10	0.94	0.10	0.94	2.00	18.87	0.30	2.83	8.00	75.47
SF-4	0.25	2.62	0.40	4.19	0.30	3.14	0.10	1.05	0.50	5.23	8.00	83.77
SF-5	0.75	12.60	0.50	8.40	4.00	67.23	0.20	3.36	0.10	1.68	0.40	6.72
SF-6	0.15	5.66	0.50	18.87	0.50	18.87	0.30	11.32	0.20	7.55	1.00	37.74
SF-7	1.00	22.22	2.00	44.44	0.20	4.44	1.00	22.22	0.10	2.22	0.20	4.44
SF-8	2.50	48.08	0.10	1.92	1.00	19.23	0.50	9.61	0.50	9.61	0.60	11.54
SF-9	0.25	3.82	1.00	15.27	2.00	30.53	1.50	22.90	1.00	15.27	0.80	12.21
SF-10	0.50	7.58	0.50	7.58	3.00	45.45	0.30	4.54	0.30	4.54	2.00	30.30
SF-11	0.25	3.22	0.30	3.87	0.70	9.03	0.50	6.45	2.00	25.81	4.00	51.61
SF-12	1.50	27.27	1.50	27.27	0.20	3.64	0.10	1.82	0.80	14.54	1.40	25.45
SF-13	0.05	0.53	0.10	1.07	0.10	1.07	0.10	1.07	3.00	32.09	6.00	64.17
SF-14	0.35	6.42	0.70	12.84	0.40	7.34	3.00	55.05	0.60	11.01	0.40	7.34
SF-15	0.10	16.67	0.10	16.67	0.10	16.67	0.10	16.67	0.10	16.67	0.10	16.67
SF-16	2.50	55.56	0.00	0.0	1.00	22.22	0.00	0.0	1.00	22.22	0.00	0.0
SF-17	0.50	8.20	0.00	0.0	5.00	81.97	0.00	0.0	0.60	9.84	0.00	0.0
SF-18	0.25	5.26	0.00	0.0	0.50	10.53	0.00	0.0	4.00	84.21	0.00	0.0

Column A elemental concentration in "solution percent"

Column B elemental concentration in "projected alloy percent"

All concentrations expressed to two decimal places, regardless of individual uncertainties

* The term "ferrous-base alloys" is obviously one of convenience. The alloys simulated are of iron-base, nickel-base, etc.

TABLE 20

SYNTHETIC SOLUTIONS SIMULATING IRON-BASE ALLOYS - SERIES SG

Solution No.	Chromium A	Chromium B	Manganese A	Manganese B	Iron A	Iron B	Cobalt A	Cobalt B	Nickel A	Nickel B	Copper A	Copper B
SG-1	0.50	10.00	0.50	10.00	3.55	71.00	0.05	1.00	0.25	5.00	0.15	3.00
SG-2	0.50	10.00	0.20	4.00	3.25	65.00	0.25	5.00	0.75	15.00	0.05	1.00
SG-3	1.00	20.00	0.10	2.00	3.15	63.00	0.10	2.00	0.50	10.00	0.15	3.00
SG-4	1.25	27.78	0.05	1.11	3.05	67.80	0.05	1.11	0.05	1.11	0.05	1.11
SG-5	0.60	12.00	0.15	3.00	3.65	73.00	0.15	3.00	0.35	7.00	0.10	2.00
SG-6	0.70	14.00	0.25	5.00	3.45	69.00	0.10	2.00	0.40	8.00	0.10	2.00
SG-7	0.75	15.00	0.25	5.00	3.30	66.00	0.05	1.00	0.60	12.00	0.05	1.00
SG-8	0.85	17.00	0.10	2.00	3.05	61.00	0.25	5.00	0.65	13.00	0.10	2.00
SG-9	1.10	22.00	0.05	1.00	3.00	60.00	0.20	4.00	0.50	10.00	0.15	3.00
SG-10	0.50	10.00	0.05	1.00	4.10	82.00	0.05	1.00	0.25	5.00	0.05	1.00

Column A elemental concentration in "solution percent"
Column B elemental concentration in "projected alloy percent"
All concentrations expressed to two decimal places, regardless of individual uncertainties

in the form of concentration as percent by weight in the solution. The heading "projected alloy percent" represents the percent value on the basis of the total weight of the analytes present, excluding of course the aqueous matrix and chlorine. It is important to realize at this point that, although the synthetic solutions were in general made up to a total weight of about 100 g, and so involved approximately 1 to 15 g of total analytes weight, a solution total weight of about 10 g would have sufficed for examination purposes, with a corresponding total analytes weight, or available sample weight, requirement of only 0.1 to 1.5 g.

Table 21 shows the analytical results obtained by applying the α-correction coefficient technique and the standard ratio technique to the Series SF synthetic solutions. For each technique, specimen solution SF-10 was used as the standard solution. Table 22 shows the results of both techniques as applied to the Series SG solutions. Here specimen solution SG-10 was used, in each case, as the standard. For both series, variation of the solution selected as the standard did not appreciably affect the results as expressed by the average absolute error.

The following observations are in order:-

SF Series

1. The α-correction coefficient technique showed, in general, a far more accurate analytical picture than did the ratio method.

TABLE 21

COMPARISON OF RESULTS - α-CORRECTION COEFFICIENT AND RATIO TECHNIQUES - SERIES SF

Solution	Chromium				Manganese				Iron			
No.	A	B	C	D	A	B	C	D	A	B	C	D
SF-1	1.39	0.00	2.01	0.62	2.68	0.10	4.08	1.30	6.81	0.13	9.51	2.57
SF-2	7.46	0.00	10.15	2.69	7.66	0.20	10.46	3.00	3.01	0.03	4.45	1.47
SF-3	0.91	0.03	1.33	0.39	0.89	0.05	1.33	0.39	0.90	0.04	1.40	0.46
SF-4	2.54	0.08	3.48	0.86	4.13	0.06	5.71	1.52	3.13	0.01	4.71	1.57
SF-5	12.50	0.10	11.16	1.44	8.30	0.10	7.36	1.04	65.88	1.35	57.31	9.92
SF-6	5.73	0.07	8.72	3.06	19.36	0.49	30.19	11.32	19.06	0.19	32.00	13.13
SF-7	21.04	1.18	26.89	4.76	45.56	1.12	57.11	12.67	4.58	0.14	5.84	1.40
SF-8	45.96	2.12	44.81	3.72	2.15	0.23	2.04	0.12	18.90	0.33	17.02	2.21
SF-9	3.76	0.06	4.30	0.48	14.76	0.49	17.10	1.83	29.46	1.07	34.35	3.82
* SF-10	7.58	--	7.58	--	7.58	--	7.58	--	45.45	--	45.45	--
SF-11	3.21	0.01	4.32	1.10	3.87	0.00	5.29	1.42	8.73	0.30	12.77	3.74
SF-12	26.36	0.91	30.91	3.64	27.64	0.37	31.45	4.18	3.69	0.05	4.27	0.63
SF-13	0.58	0.05	0.83	0.30	1.07	0.00	1.60	0.53	1.11	0.04	1.87	0.80
SF-14	6.24	0.18	8.86	2.44	12.11	0.73	17.74	4.90	6.92	0.42	9.93	2.59
SF-15	17.50	0.83	30.17	13.50	17.00	0.33	30.50	13.83	17.50	0.83	34.67	18.00
SF-16	54.44	1.12	53.11	2.45	--	--	--	--	22.67	0.45	20.51	1.71
SF-17	8.34	0.14	7.06	1.14	--	--	--	--	81.47	0.50	67.54	14.43
SF-18	5.39	0.13	7.73	2.47	--	--	--	--	10.53	0.00	17.05	6.52
Av. abs. error		0.41		2.65		0.30		4.15		0.34		5.00

Column A Results by α-correction coefficient technique - projected alloy percent
Column B Absolute error - α-correction coefficient technique
Column C Results by ratio technique - projected alloy percent
Column D Absolute error - ratio technique

All results expressed to two decimal places, regardless of individual uncertainties

* Solution used as the standard.

TABLE 21 cont'd

Solution No.	Cobalt A	Cobalt B	Cobalt C	Cobalt D	Nickel A	Nickel B	Nickel C	Nickel D	Copper A	Copper B	Copper C	Copper D
SF-1	70.14	0.74	87.92	18.52	5.31	0.27	8.29	2.73	13.54	0.35	13.75	0.14
SF-2	6.93	0.53	9.13	1.67	57.46	2.24	84.92	25.22	14.82	0.10	21.70	6.78
SF-3	17.45	1.42	26.13	7.26	2.74	0.09	4.41	1.58	71.98	3.49	85.38	9.91
SF-4	1.05	0.00	1.54	0.49	5.18	0.05	7.80	2.57	82.83	0.94	108.9	25.13
SF-5	3.44	0.08	3.02	0.34	1.71	0.03	1.50	0.18	6.99	0.27	6.35	0.37
SF-6	11.06	0.26	18.19	6.87	7.58	0.03	14.34	6.79	37.66	0.08	70.94	33.20
SF-7	21.31	0.91	22.44	0.22	2.33	0.11	3.11	0.89	4.53	0.09	5.87	1.43
SF-8	9.23	0.38	8.50	1.11	9.40	0.21	10.23	0.62	11.60	0.06	12.79	1.25
SF-9	21.98	0.92	23.36	0.46	14.64	0.63	16.79	1.52	12.09	0.12	12.87	0.66
* SF-10	4.54	--	4.54	--	4.54	--	4.54	--	30.30	--	30.30	--
SF-11	6.09	0.56	8.52	2.07	23.23	2.58	34.19	8.38	48.26	3.35	65.93	14.32
SF-12	1.84	0.02	1.89	0.07	14.02	0.52	17.53	2.99	25.27	0.18	32.54	7.09
SF-13	1.07	0.00	1.72	0.65	30.27	0.18	49.09	17.00	61.71	2.46	90.91	26.74
SF-14	52.66	2.39	67.52	12.47	10.51	0.50	16.66	5.65	7.06	0.28	8.77	1.43
SF-15	16.83	0.16	35.50	18.83	17.50	0.83	46.67	30.00	17.50	0.83	47.50	30.83
SF-16	--	--	--	--	21.89	0.33	24.00	1.78	--	--	--	--
SF-17	--	--	--	--	9.57	0.27	7.87	1.97	--	--	--	--
SF-18	--	--	--	--	87.58	3.37	144.4	60.24	--	--	--	--
Av. abs error		0.58		5.07		0.72		10.01		0.90		11.38

Column A Results by α-correction coefficient technique - projected alloy percent
Column B Absolute error - α-correction coefficient technique
Column C Results by ratio technique - projected alloy percent
Column D Absolute error - ratio technique

All results are expressed to two decimal places, regardless of individual uncertainties. Space requirements curtailed SF-4, Copper "C" and SF-18, Nickel "C" expression.

* Solution used as the standard

TABLE 22

COMPARISON OF RESULTS - α-CORRECTION COEFFICIENT AND RATIO TECHNIQUES - SERIES SG

Solution No.	Chromium				Manganese				Iron			
	A	B	C	D	A	B	C	D	A	B	C	D
SG-1	9.8	0.2	10.2	0.2	9.2	0.8	9.6	0.4	72.8	1.8	76.2	5.2
SG-2	9.8	0.2	10.4	0.4	3.6	0.4	4.00	0.00	64.6	0.4	70.2	5.2
SG-3	19.2	0.8	19.8	0.2	1.90	0.10	1.94	0.06	64.0	1.0	64.8	1.8
SG-4	25.1	2.7	25.8	2.0	1.11	0.00	1.13	0.02	67.5	0.2	67.8	0.0
SG-5	11.8	0.2	12.0	0.0	2.84	0.16	2.90	0.10	73.0	0.0	74.6	1.6
SG-6	13.6	0.4	14.0	0.0	4.80	0.20	4.90	0.10	69.2	0.2	71.0	2.0
SG-7	15.0	0.0	15.2	0.2	4.80	0.20	4.90	0.10	67.0	1.0	68.6	2.6
SG-8	16.6	0.4	17.2	0.2	1.94	0.06	2.00	0.00	61.6	0.6	63.4	2.4
SG-9	22.0	0.0	22.0	0.0	1.06	0.06	1.06	0.06	61.6	1.6	60.8	0.8
* SG-10	10.0	-	10.0	-	1.00	--	1.00	--	82.0	-	82.0	-
Av. abs error		0.5^4		0.3^6		0.2^2		0.0^9		0.2^6		2.4^0

Column A Results by α-correction coefficient technique - projected alloy percent
Column B Absolute error - α-correction coefficient technique
Column C Results by ratio technique - projected alloy percent
Column D Absolute error - ratio technique

All results expressed to one or two decimal places, depending on individual uncertainties

* Solution used as the standard

TABLE 22 cont'd

Solution No.	Cobalt A	Cobalt B	Cobalt C	Cobalt D	Nickel A	Nickel B	Nickel C	Nickel D	Copper A	Copper B	Copper C	Copper D
SG-1	1.00	0.00	1.00	0.00	5.03	0.08	5.24	0.24	2.86	0.14	2.94	0.06
SG-2	4.90	0.10	5.18	0.18	14.4	0.6	15.8	0.8	0.94	0.06	1.00	0.00
SG-3	1.90	0.10	1.90	0.10	9.9	0.1	10.4	0.5	2.84	0.16	2.98	0.02
SG-4	1.07	0.04	1.07	0.04	1.18	0.07	1.27	0.16	1.11	0.00	1.20	0.09
SG-5	3.00	0.00	3.02	0.02	7.00	0.00	7.26	0.26	1.92	0.08	1.98	0.02
SG-6	1.92	0.08	1.94	0.06	7.92	0.08	8.24	0.24	1.90	0.10	1.98	0.02
SG-7	0.98	0.02	0.98	0.02	11.6	0.4	12.2	0.1	0.96	0.04	1.00	0.00
SG-8	4.96	0.04	5.02	0.02	12.8	0.2	13.7	0.7	1.86	0.14	1.96	0.04
SG-9	3.92	0.08	3.82	0.18	10.1	0.1	10.5	0.5	2.84	0.16	2.94	0.06
* SG-10	1.00	--	1.00	--	5.00	-	5.00	-	1.00	--	1.00	--
Av. abs. error		0.05^1		0.06^9		0.1^8		0.3^9		0.1^0		0.0^3

Column A Results by α-correction coefficient technique - projected alloy percent
Column B Absolute error - α-correction coefficient technique
Column C Results by ratio technique - projected alloy percent
Column D Absolute error - ratio technique

All results expressed to one or two decimal places, depending on individual uncertainties

* Solution used as the standard

2. The total analyte concentration is high in this series, and the range of concentration for each analyte is extensive. In addition to this, the chlorine concentration is high, and with considerable variation. The residual matrix shows significant variation in concentration.

3. All of the above factors tend to test the α-correction coefficient technique under quite rigorous conditions but, even under such circumstances, a reasonable approach to the theoretical composition was obtained in the majority of instances.

SG Series

1. The α-correction coefficient technique shows a somewhat better accuracy than the ratio technique in the determination of iron, cobalt and nickel, with the ratio technique shading the correction method somewhat relative to the manganese, copper and chromium determinations.

2. The total analyte concentration is low in this series, and the range of concentration for each analyte quite restricted. Iron alone is of high concentration, but is relatively constant from specimen to specimen. The chloride concentration is low, and less than 0.06 percent by weight in all of the solutions. The residual matrix maintains a reasonably constant concentration.

3. The above factors tend to render less important the errors anticipated for the ratio technique, and to provide a lesser requirement for the use of α-coefficients.

3.3.2 Analysis of ferrous-base NBS standards

A large group of, for the most part, ferrous-base NBS standard alloys was made available, each in somewhat limited quantity. Samples of these alloys of from 2 g to 10 g were accurately weighed out and dissolved in a mixture of hydrochloric and nitric acids, with the assistance in some instances of added hydrogen peroxide. Where the carbon and/or silicon contents were high enough to create subsequent difficulty, these were filtered off prior to dilution to a total weight basis of about 100 g. Chloride was determined by potentiometric titration as before. These chloride concentrations were relatively high, varying from 2 to 20 percent by weight in the solution. The pertinent experimental data can be found in Section 6.2.1.

Table 23 shows the composition values for the NBS standards, with respect to the analytes of interest, under the "A" column heading for each analyte. Residual concentrations of other elements, such as vanadium, molybdenum, titanium, etc., were also present, but were not considered as separate from the aqueous matrix because of their very low concentration levels. Table 23 also shows the results of the XRF analysis on the basis of both the α-correction and ratio techniques and, in addition, the absolute error for each element. The treatment of the XRF data by the α-correction technique was identical to that already described in connection with the analysis of synthetic solutions. Cobalt was not determined, since it was present in only two samples, although its presence was compensated for in the calculation of the other components of interest.

The α-correction coefficient technique shows a significantly

TABLE 23

COMPOSITION OF NBS STEEL STANDARDS AND RESULTS OF XRF EXAMINATION

Alloy	Chromium					Manganese					Iron				
No.	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
36a	2.41	2.43	0.02	2.15	0.26	0.432	0.401	0.031	0.359	0.073	95.37	95.71	0.34	88.53	6.84
64	67.9	62.35	5.55	56.30	11.60	0.225	0.437	0.212	0.402	0.177	24.05	23.78	0.27	22.83	1.22
66a	-	-	-	-	-	19.77	19.62	0.15	21.53	1.76	73.58	73.77	0.19	86.82	13.34
68a	-	-	-	-	-	80.07	81.41	1.34	129.8	49.7	11.98	11.72	0.26	21.12	9.14
72e	0.950	1.02	0.07	0.885	0.065	0.538	0.59	0.052	0.51	0.028	97.28	97.90	0.62	88.46	8.82
72c	0.967	1.04	0.073	0.919	0.048	0.539	0.54	0.001	0.48	0.059	97.63	99.23	1.60	90.87	6.76
73a	14.09	13.14	0.95	12.00	2.09	0.249	0.29	0.041	0.27	0.021	84.49	82.77	1.72	75.75	8.74
73b	12.82	12.56	0.26	9.37	3.45	0.36	0.41	0.05	0.31	0.05	85.63	84.95	0.68	65.21	20.42
101d	18.68	18.17	0.51	19.27	0.59	0.739	0.83	0.091	0.87	0.131	70.53	70.52	0.01	75.35	4.82
106a	1.15	1.21	0.06	1.02	0.13	0.546	0.53	0.016	0.47	0.076	95.93	95.97	0.04	84.07	11.86
111b	0.070	0.147	0.077	0.119	0.049	0.706	0.67	0.036	0.55	0.156	96.56	93.14	3.42	77.09	19.47
115	2.17	2.35	0.18	0.317	1.853	1.01	0.99	0.02	1.40	0.39	70.21	71.34	1.13	106.4	36.19
* 121c	17.58	17.58	-	17.58	-	1.31	1.31	-	1.31	-	69.12	69.12	-	69.12	-
133a	12.89	12.66	0.23	9.84	3.05	1.03	1.02	0.01	0.81	0.22	84.48	83.40	1.08	66.45	18.03
156	0.429	0.51	0.081	0.439	0.010	1.40	1.39	0.01	1.19	0.21	96.71	98.65	1.94	85.06	11.05
159	1.00	1.09	0.09	0.667	0.333	0.807	0.77	0.037	0.64	0.167	96.47	97.67	1.20	82.49	13.48
16Ca	18.74	17.44	1.30	11.95	6.79	0.605	1.42	0.815	0.963	0.358	61.62	57.42	4.20	37.67	23.95
168	20.33	18.68	1.65	17.91	2.42	1.50	1.16	0.34	1.16	0.34	3.43	3.47	0.04	3.79	0.36
Av. abs. error			0.74		2.18			0.19		3.17			1.10		12.62

Column A	NBS values
Column B	values by α-correction coefficient technique
Column C	absolute error - α-correction coefficient technique
Column D	values by ratio technique
Column E	absolute error - ratio technique

All results expressed to two or three decimal places, regardless of individual uncertainties

* Alloy used as the standard

TABLE 23 cont'd

Alloy No.	Cobalt[a]					Nickel					Copper				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
36a	-	-	-	-	-	0.243	0.268	0.025	0.241	0.002	0.114	0.133	0.019	0.120	0.006
64	-	-	-	-	-	0.33	0.36	0.03	0.43	0.10	0.025	0.176	0.151	0.216	0.191
66a	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
68a	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
72e	-	-	-	-	-	0.241	0.269	0.028	0.234	0.007	0.105	0.159	0.054	0.138	0.033
72c	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
73a	-	-	-	-	-	0.159	0.178	0.019	0.161	0.002	0.080	0.127	0.047	0.114	0.034
73b	-	-	-	-	-	0.197	0.221	0.024	0.173	0.024	0.126	0.145	0.019	0.116	0.010
101d	0.058	-	-	-	-	9.05	8.96	0.09	9.74	0.69	0.184	0.165	0.019	0.179	0.005
106a	-	-	-	-	-	0.277	0.30	0.023	0.25	0.027	0.156	0.149	0.007	0.125	0.031
111b	-	-	-	-	-	1.81	1.74	0.07	1.37	0.44	0.028	0.082	0.054	0.005	0.023
115	-	-	-	-	-	15.89	15.67	0.22	24 58	8.69	6.44	6.01	0.43	4.74	1.70
* 121c	-	-	-	-	-	10.51	10.51	-	10.51	-	0.14	0.14	-	0.14	-
133a	-	-	-	-	-	0.241	0.262	0.021	0.213	0.028	0.118	0.136	0.018	0.110	0.008
156	-	-	-	-	-	0.475	0.509	0.034	0.404	0.071	0.053	1.018	0.965	0.082	0.029
159	-	-	-	-	-	0.137	0.165	0.028	0.147	0.010	0.181	0.189	0.008	0.168	0.013
160a	-	-	-	-	-	14.13	12.72	1.41	8.07	6.06	0.174	0.125	0.049	0.079	0.095
168	41.20	-	-	-	-	20.25	18.85	1.40	25.96	5.71	0.035	0.187	0.152	0.264	0.229
Av. abs. error								0.24		1.56			0.14		0.17

Column A	NBS values
Column B	values by α-correction coefficient technique
Column C	absolute error - α-correction coefficient technique
Column D	values by ratio technique
Column E	absolute error - ratio technique

[a] cobalt not determined - lack of standard values

* Alloy used as the standard

higher accuracy than the ratio method, although the general accuracy is not quite adequate to the requirements of a rigorous scheme of analysis. This is particularly the case where very high and very low concentrations are involved. In some instances of very low concentration poor relative accuracy is noted. For example, the low concentrations generally for copper provide for low intensity of emission with respect to background intensity, thus permitting a high relative error situation.

3.4 Examination of Aqueous Solutions Appropriate to the Chemical Analysis by XRF of Copper-Base Alloys

3.4.1 Copper-base synthetic solutions, preparation and examination

A series of synthetic solutions was prepared involving copper, lead and zinc in a manner analogous to that used in the preparation of the ferrous-base synthetic solutions. These solutions comprised Series SD, and Table 24 outlines the general compositions on a basis identical to that adopted previously. In general, total concentrations were high, and concentration ranges were extended, for this series. A second series of solutions was prepared involving copper, tin, lead and zinc. This was Series SB, and the compositions are shown in Table 25. For this series, both the total concentration and the ranges of concentration were, in general, appreciably lower and less extended. The pertinent experimental data can be found in

TABLE 24

SYNTHETIC SOLUTIONS SIMULATING COPPER-BASE ALLOYS - SERIES SD

Solution No.	Copper		Lead		Zinc	
	A	B	A	B	A	B
SD-1	1.00	47.62	0.10	4.76	1.00	47.62
SD-2	0.97	9.09	4.84	45.45	4.84	45.45
SD-3	10.00	90.09	0.10	0.90	1.00	9.01
SD-4	2.00	15.38	1.00	7.69	10.00	76.92
SD-5	0.50	25.00	1.00	50.00	0.50	25.00
SD-6	4.00	50.00	2.00	25.00	2.00	25.00
SD-7	6.00	63.16	0.50	5.26	3.00	31.58
SD-8	1.60	25.81	3.00	48.39	1.60	25.81
SD-9	0.40	10.00	3.40	85.00	0.20	5.00
SD-10	0.20	33.33	0.20	33.33	0.20	33.33

Column A elemental concentration in "solution percent"
Column B elemental concentration in "projected alloy percent"

All values expressed to two decimal places, regardless of individual uncertainties

TABLE 25

SYNTHETIC SOLUTIONS SIMULATING COPPER-BASE ALLOYS - SERIES SB

Solution No.	Copper		Tin		Lead		Zinc	
	A	B	A	B	A	B	A	B
SB-1	3.720	89.44	0.168	4.05	0.174	4.19	0.097	2.33
SB-2	3.093	84.11	0.291	7.91	0.162	4.42	0.131	3.55
SB-3	2.339	84.56	0.137	4.95	0.197	7.13	0.093	3.35
SB-4	2.786	85.15	0.065	1.97	0.190	5.80	0.231	7.08
SB-5	2.202	78.92	0.084	2.99	0.245	8.79	0.259	9.29
SB-6	6.729	92.29	0.380	5.21	0.100	1.38	0.082	1.12
SB-7	6.665	90.58	0.440	5.98	0.105	1.43	0.149	2.02

Column A	elemental concentration in "solution percent"
Column B	elemental concentration in "projected alloy percent"

All values for "solution percent" expressed to three decimal places, regardless of individual uncertainties

All values for "projected alloy percent" expressed to two decimal places, regardless of individual uncertainties

Sections 7.1.1 and 7.1.2.

The approach with respect to XRF examination and data treatment was identical to that described previously. The results obtained relative to the α-correction and ratio techniques, together with the absolute errors and the average absolute error for each element are shown in Tables 26 and 27. Although both sets of analytical data show accuracy situations strongly in favour of the [illegible]orrection technique, the general picture relative to the SD series is much more favourable in this respect than that for the SB series. This is , to a considerable extent, and as found for the ferrous-base synthetic solutions, due to the more extended concentration ranges and total concentrations of the SD series.

3.4.2 Analysis of copper-base alloy standards

A series of chemically analyzed solid specimens of various copper-base alloys, suitable for direct examination under XRF, were examined by both the α-correction and ratio techniques, using both prepared aqueous solution and solid specimen conditions. The application of α-correction coefficients derived from aqueous media to the analysis by XRF of solid specimens of copper-base alloys was for the purposes of experimental comparison only. No consideration that α-coefficients from aqueous solution media are identical to those derivable from other types of specimen media is to be implied. The experimental data

TABLE 26

COMPARISON OF RESULTS FROM α-CORRECTION COEFFICIENT AND RATIO TECHNIQUES - SERIES SD

Solution No.	Copper				Lead				Zinc			
	A	B	C	D	A	B	C	D	A	B	C	D
* SD-1	47.62	-	47.62	-	4.76	-	4.76	-	47.62	-	47.62	-
SD-2	8.58	0.51	4.26	4.83	44.42	1.03	16.53	28.92	44.98	0.47	20.28	25.17
SD-3	87.93	2.16	46.85	41.24	0.88	0.02	0.31	0.59	8.56	0.45	4.77	4.24
SD-4	14.69	0.69	7.61	7.71	7.69	0.00	2.23	5.46	76.07	0.85	32.31	44.61
SD-5	26.50	1.50	24.50	0.50	53.50	3.50	56.00	6.00	26.50	1.50	25.00	0.00
SD-6	47.75	2.25	28.87	21.13	24.62	0.38	11.50	13.50	24.37	0.63	14.50	10.50
SD-7	61.47	1.69	36.21	26.95	5.16	0.10	2.00	3.26	30.53	1.05	17.47	14.11
SD-8	25.00	0.81	16.13	9.68	47.90	0.49	27.42	20.97	25.81	0.00	16.13	9.68
SD-9	10.50	0.50	7.25	2.75	87.50	2.50	68.25	16.75	5.25	0.25	3.75	1.25
SD-10	36.67	3.34	41.67	8.34	35.00	1.67	53.33	20.00	35.00	1.67	40.00	6.67
Av. abs. error		1.49		13.68		1.07		12.82		0.76		12.91

Column A values by α-correction coefficient technique

Column B absolute error - α-correction coefficient technique

Column C values by ratio technique

Column D absolute error - ratio technique

All values expressed to two decimal places, regardless of individual uncertainties

*Solution used as the standard

TABLE 27

COMPARISON OF RESULTS FOR α-CORRECTION COEFFICIENT AND RATIO TECHNIQUES - SERIES SB

Solution No.	Copper				Tin				Lead				Zinc			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
SB-1	86.04	3.40	123.2	33.74	4.35	0.30	5.82	1.77	3.97	0.22	6.25	2.16	2.38	0.05	3.46	1.13
SB-2	84.20	0.09	120.3	36.20	8.21	0.30	11.23	3.32	4.54	0.12	7.42	3.00	3.75	0.20	5.41	1.86
SB-3	84.56	0.00	135.7	51.11	5.49	0.54	8.35	3.40	6.29	0.84	12.15	5.02	3.51	0.16	5.71	2.36
SB-4	85.49	0.34	129.1	43.93	2.20	0.23	3.15	1.18	5.56	0.24	9.60	3.80	7.46	0.38	11.28	4.20
SB-5	81.00	2.08	132.0	53.12	3.40	0.41	5.09	2.10	8.21	0.58	15.66	6.87	10.04	0.75	16.49	7.20
SB-6	92.00	0.29	91.57	0.72	5.22	0.01	5.25	0.04	1.33	0.05	1.33	0.05	1.08	0.04	1.07	0.05
* SB-7	90.58	-	90.58	-	5.98	-	5.98	-	1.43	-	1.43	-	2.02	-	2.02	-
Av. abs. error		1.03		36.47		0.30		1.97		0.34		3.48		0.26		2.80

Column A	values by α-correction coefficient technique
Column B	absolute error - α-correction coefficient technique
Column C	values by ratio technique
Column D	absolute error - ratio technique

All values expressed to two decimal places, regardless of individual uncertainties

* Solution used as the standard

related to these surveys are presented in Sections 7.2.1 and 7.2.2. Tables 28, 29 and 30 provide comparative data relative to these investigations. For the solution technique, the α-correction method shows a higher accuracy than the ratio method. In the solid specimen approach, the relative constancy of the general matrix permits the use of the ratio method without the introduction of undue inaccuracy.

3.5 Discussion

The XRF method of analysis is generally adopted on the basis of its inherent rapidity, this as compared to the more time-consuming and classical wet techniques. No analytical data obtainable by the XRF method can be more accurate than the values for the calibration standards used. The result errors for the XRF technique are usually within ± 1 to ± 4 percent relative.(61) The fairly extensive tests conducted with respect to this new approach, as outlined in this report, have provided strong evidence for the belief that this approach may be satisfactory for consideration with respect to chemical analysis. Table 31 shows the accumulated relative errors for the chemical analysis portion of the investigation. The observation should be made that the high average percent relative error in some cases arose out of a few very poor results within the associated series. The prior rejection of those values from the series would have improved the average percent relative error appreciably.

TABLE 28

COMPOSITION OF COPPER-BASE ALLOY STANDARDS

Alloy No.	Copper	Tin	Lead	Zinc
2-1	89.05	4.22	4.01	2.40
2-2	86.94	4.84	3.95	3.92
2-3	84.96	6.05	3.96	4.65
2-4	84.95	5.97	4.37	4.30
2-5	84.28	6.00	4.87	4.34
2-6	84.30	6.00	5.46	3.84
2-7	83.77	6.03	5.90	3.76
2-8	86.19	4.93	5.57	2.82
2-9	85.97	4.80	6.16	2.58
2-10	85.39	4.94	6.25	2.86
4-1	85.28	2.11	5.64	6.96
4-10	82.14	2.86	8.36	6.39
8-1	93.03	4.83	0.60	1.49
8-3	88.43	6.76	0.55	4.11
8-8	90.19	5.63	1.81	2.27
8-13	87.59	6.61	2.78	2.88

TABLE 29

COMPOSITION OF COPPER-BASE ALLOY STANDARDS AND RESULTS OF XRF EXAMINATION - SOLUTION TECHNIQUE

Alloy No.	Copper				Tin				Lead				Zinc			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
* 2-1	89.05	-	89.05	-	4.22	-	4.22	-	4.01	-	4.01	-	2.40	-	2.40	-
2-2	87.42	0.48	112.8	25.9	5.68	0.84	6.25	1.41	4.08	0.13	5.01	1.06	3.67	0.25	4.87	0.95
2-3	85.46	0.50	110.2	25.2	6.90	0.85	7.48	1.43	3.95	0.01	4.76	0.80	4.29	0.36	5.68	1.03
2-4	87.90	2.95	117.8	32.8	7.56	1.59	8.46	2.49	4.59	0.22	5.94	1.57	4.37	0.07	6.03	1.73
2-5	84.27	0.01	105.8	21.5	7.50	1.50	8.14	2.14	5.14	0.27	6.32	1.45	4.09	0.25	5.26	0.92
2-6	86.43	2.13	118.8	34.5	8.22	2.22	9.72	3.72	6.27	0.81	8.66	3.20	4.20	0.36	5.64	1.80
2-7	86.63	0.24	113.2	29.4	6.75	0.72	7.73	1.70	6.40	0.50	8.51	2.61	3.88	0.12	5.20	1.44
2-8	87.65	1.46	117.5	31.3	5.34	0.41	6.25	1.32	5.56	0.01	7.61	2.04	2.79	0.03	3.84	1.02
2-9	88.89	2.92	124.7	38.7	5.41	0.61	6.68	1.88	6.35	0.19	9.59	3.43	2.85	0.27	4.10	1.52
2-10	87.31	1.92	116.2	30.8	5.10	0.16	6.15	1.21	6.54	0.29	9.36	3.11	2.79	0.07	3.79	0.93
4-1	83.33	1.95	116.0	30.7	2.29	0.18	2.73	0.62	6.09	0.45	8.53	2.89	7.09	0.13	10.12	3.16
4-10	84.02	1.88	114.1	31.7	3.16	0.30	3.85	0.99	8.32	0.04	12.02	3.66	6.70	0.31	9.25	2.86
8-1	92.98	0.05	91.54	1.49	5.71	0.88	4.65	0.18	0.62	0.02	0.48	0.12	1.72	0.23	1.76	0.27
8-3	86.59	1.84	84.86	3.57	7.84	1.08	6.12	0.64	0.65	0.10	0.47	0.08	3.62	0.49	3.68	0.43
8-8	92.51	2.32	[illegible]2.33	17.86	6.54	0.91	5.23	0.40	1.83	0.02	2.11	0.30	2.19	0.18	2.32	0.05
8-13	90.57	2.98	109.5	21.9	7.80	1.19	7.92	1.31	2.93	0.15	3.20	0.42	2.82	0.06	3.52	0.64
Av. abs. error		1.57		25.1		0.90		1.43		0.21		1.78		0.21		1.25

Column A	values by α-correction coefficient technique
Column B	absolute error - α-correction coefficient technique
Column C	values by ratio technique
Column D	absolute error - ratio technique

All values expressed to two decimal places, regardless of individual uncertainties

* Alloy used as the standard

TABLE 30

COMPOSITION OF COPPER-BASE ALLOY STANDARDS AND RESULTS OF XRF EXAMINATION - SOLID SPECIMENS

Alloy No	Copper				Tin				Lead				Zinc			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
* 2-1	89.05	-	89.05	-	4.22	-	4.22	-	4.01	-	4.01	-	2.40	-	2.40	-
2-2	87.98	1.04	87.68	0.74	5.20	0.36	5.20	0.36	3.94	0.01	3.94	0.01	3.70	0.22	3.67	0.25
2-3	84.26	0.70	83.58	1.38	6.13	0.08	6.08	0.03	3.94	0.02	3.94	0.02	4.40	0.25	4.29	0.36
2-4	84.34	0.61	83.52	1.43	6.03	0.06	5.95	0.02	4.40	0.05	4.42	0.05	4.45	0.15	4.34	0.04
2-5	84.98	0.70	84.18	0.10	6.02	0.02	5.96	0.04	4.28	0.57	4.30	0.57	4.21	0.13	4.12	0.22
2-6	83.22	1.08	82.04	2.26	5.91	0.09	5.73	0.27	5.40	0.02	5.44	0.02	4.19	0.35	4.06	0.22
2-7	81.98	1.79	85.35	1.56	6.07	0.04	5.82	0.21	6.09	0.09	5.99	0.09	3.98	0.22	3.83	0.07
2-8	86.69	0.50	85.73	0.46	4.94	0.01	4.82	0.11	5.53	0.02	5.55	0.02	2.88	0.06	2.83	0.01
2-9	86.05	0.08	84.67	1.30	4.96	0.16	4.80	0.00	6.01	0.11	6.05	0.11	2.79	0.21	2.73	0.15
2-10	85.37	0.02	84.04	4.84	4.94	0.00	4.74	0.20	6.36	0.16	6.41	0.16	2.68	0.18	2.62	0.24
4-1	84.37	0.91	80.44	1.25	2.56	0.45	2.50	0.39	5.90	0.20	5.84	0.20	7.28	0.32	7.18	0.22
4-10	81.11	1.03	80.89	1.57	2.94	0.08	2.77	0.09	8.12	0.20	8.08	0.20	6.96	0.57	6.73	0.34
8-1	90.50	2.53	91.46	1.57	5.00	0.17	5.24	0.51	0.59	0.01	0.59	0.01	1.73	0.24	1.75	0.26
8-3	84.92	3.51	85.09	3.34	6.99	0.23	7.25	0.49	0.55	0.01	0.56	0.01	3.98	0.13	3.92	0.19
8-8	88.19	2.00	88.23	1.96	5.80	0.17	5.95	0.32	1.77	0.04	1.77	0.04	2.30	0.03	2.29	0.02
8-13	85.05	2.54	84.52	3.07	6.72	0.11	6.80	0.19	2.22	0.53	2.25	0.53	3.01	0.13	2.96	0.08
Av. abs. error		1.27		1.77		0.14		0.21		0.27		0.14		0.21		0.18

Column A	values by α-correction coefficient technique
Column B	absolute error - α-correction coefficient technique
Column C	values by ratio technique
Column D	absolute error - ratio technique

All values expressed to two decimal places, regardless of individual uncertainties

* **Alloy used as the standard**

TABLE 31

ACCUMULATED AVERAGE PERCENT RELATIVE ERRORS

Series	SF	SG	NBS	SD	SB	Copper alloys
Cr	3.14	3.43	6.74			
Mn	2.55	6.34	2.89			
Fe	1.93	1.13	1.51			
Co	3.39	1.94				
Ni	3.81	2.04	5.66			
Cu	3.03	4.83	22.63 *	4.22	1.21	1.80
Sn				—	6.20	14.62 **
Pb				3.16	6.86	4.63
Zn				2.48	5.60	5.57

* High due to very low copper values

** Some difficulty with high background at SnKα and the totality of sample solution relative to Sn.

Errors may arise from several source areas. One of these involves the low intensities for the minor components in solution, with respect to the relevant background intensities. The following examples were taken from the data for the analysis of NBS ferrous-base alloy standards, as given in Section 6.2.1.

Alloy	Element	Solution percent Chemical	Solution percent XRF	Net intensity (cps)	Background (cps)
111b	Chromium	0.00420	0.0088	38	107
159	Chromium	0.0370	0.0410	175	118
64	Manganese	0.00450	0.0087	82	216
73a	Manganese	0.0131	0.0154	144	190

This problem is often encountered in the analysis for minor components, as shown by data provided by Gillieson _et_ _al_ (54) for the analysis to determine tungsten and zirconium in high-temperature alloys.

The results of the analytical process can be improved slightly where pulse height analysis can be applied to suppress a high and inclined background in the measurement of the intensity for a minor component. It would not, however, be expected to yield by itself the accurate results required for a rigorous scheme of analysis, since the data on the compositions for the minor components also inherit the error contributions provided by the α-coefficients, the uncertainties in the intensity measurements and the compositional uncertainties relative to the major components. It might be more suitable, therefore, to determine the minor components by other rapid and independent techniques.

A second possible source of experimental error arises out of the dissolution technique. Within the limits of this investigation, the use of hydrochloric and/or perchloric acids only was permitted. In some instances, these acids, with or without the use of nitric and/or hydrofluoric acids, are not the most efficient in the dissolution of certain alloy types. Some of the high-chromium alloys of the NBS standards group, such as alloy numbers 64, 73a, 160a and 168, were indeed difficult to dissolve, even where both hydrochloric and nitric acids were used. Where complete solution is in doubt, low results may be obtained.

The validity of this new approach to the aqueous solution technique of XRF analysis can best be illustrated graphically, using the data for the copper, lead and zinc determinations in the synthetic solutions of Series SD. The calculated intensities, according to the L-T correction equation, and the known compositions of the solutions, are used to plot corrected intensity versus concentration as solution percent. These plots show excellent linear relationships, as indicated by Figures 7, 8 and 9. The scattered nature of the data for the associated measured intensities is also shown.

FIGURE 7

$I_{CuK\alpha}$ VERSUS COPPER IN SOLUTION PERCENT

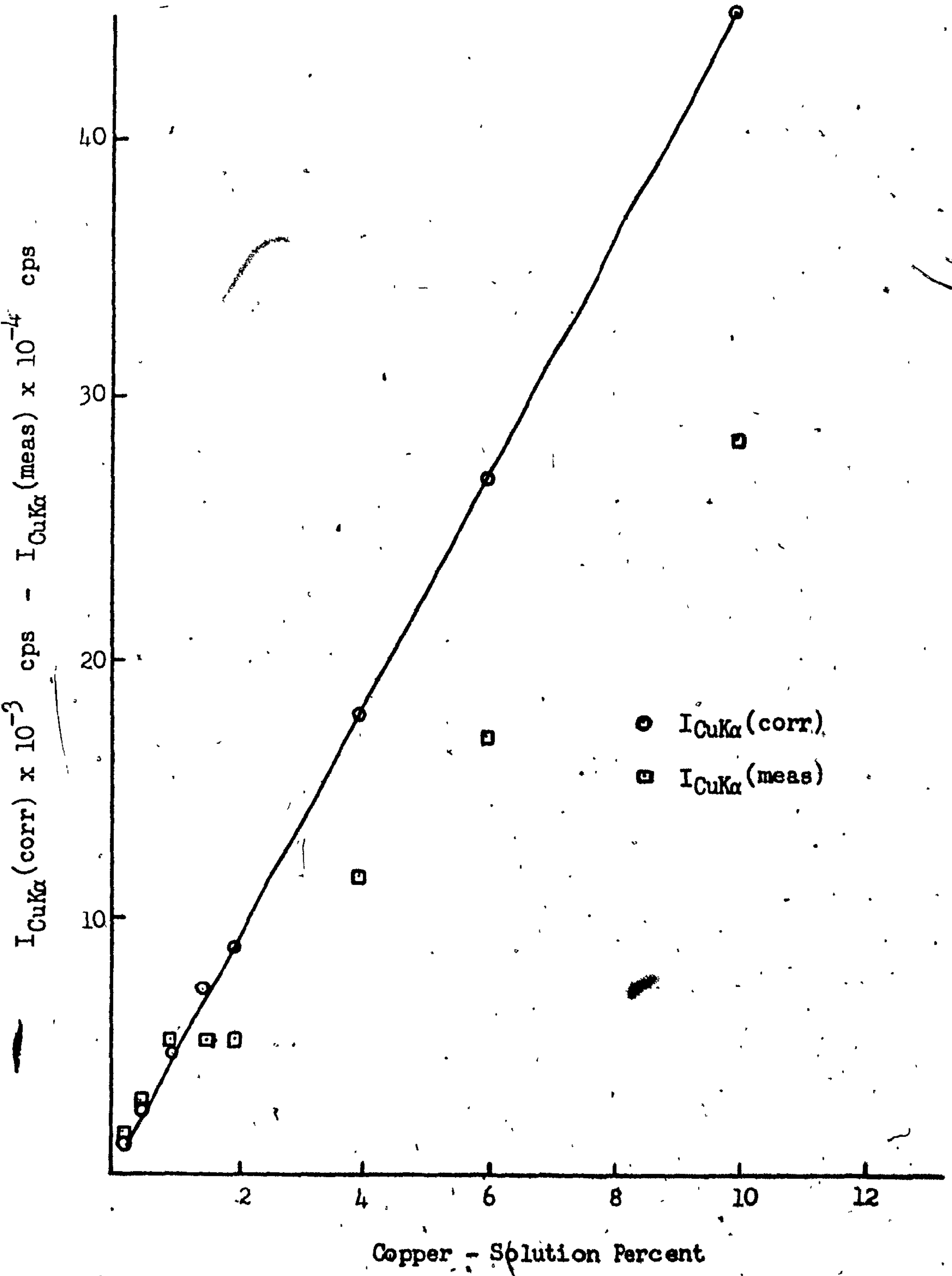


FIGURE 8

$I_{PbL\alpha}$ VERSUS LEAD IN SOLUTION PERCENT

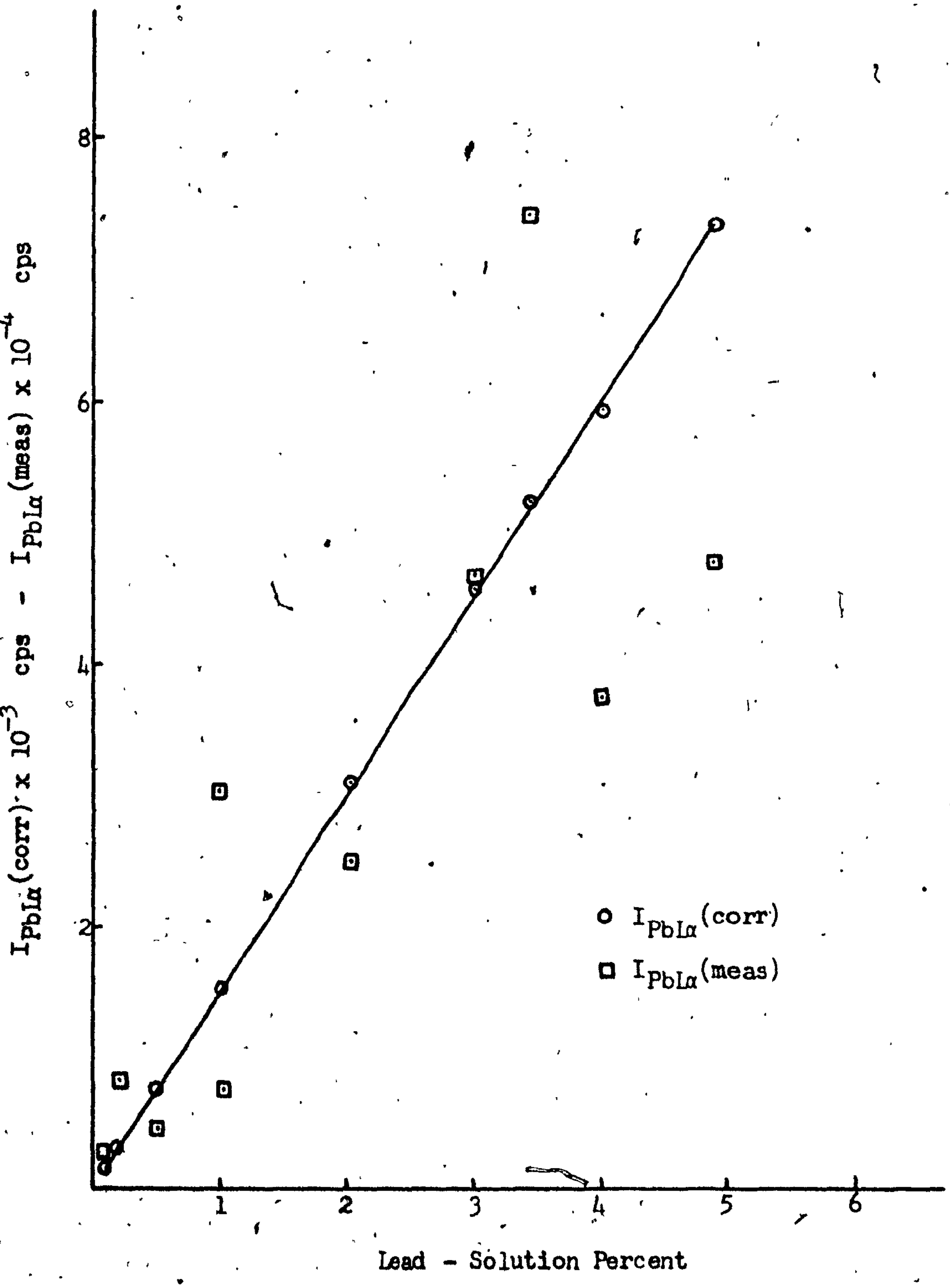
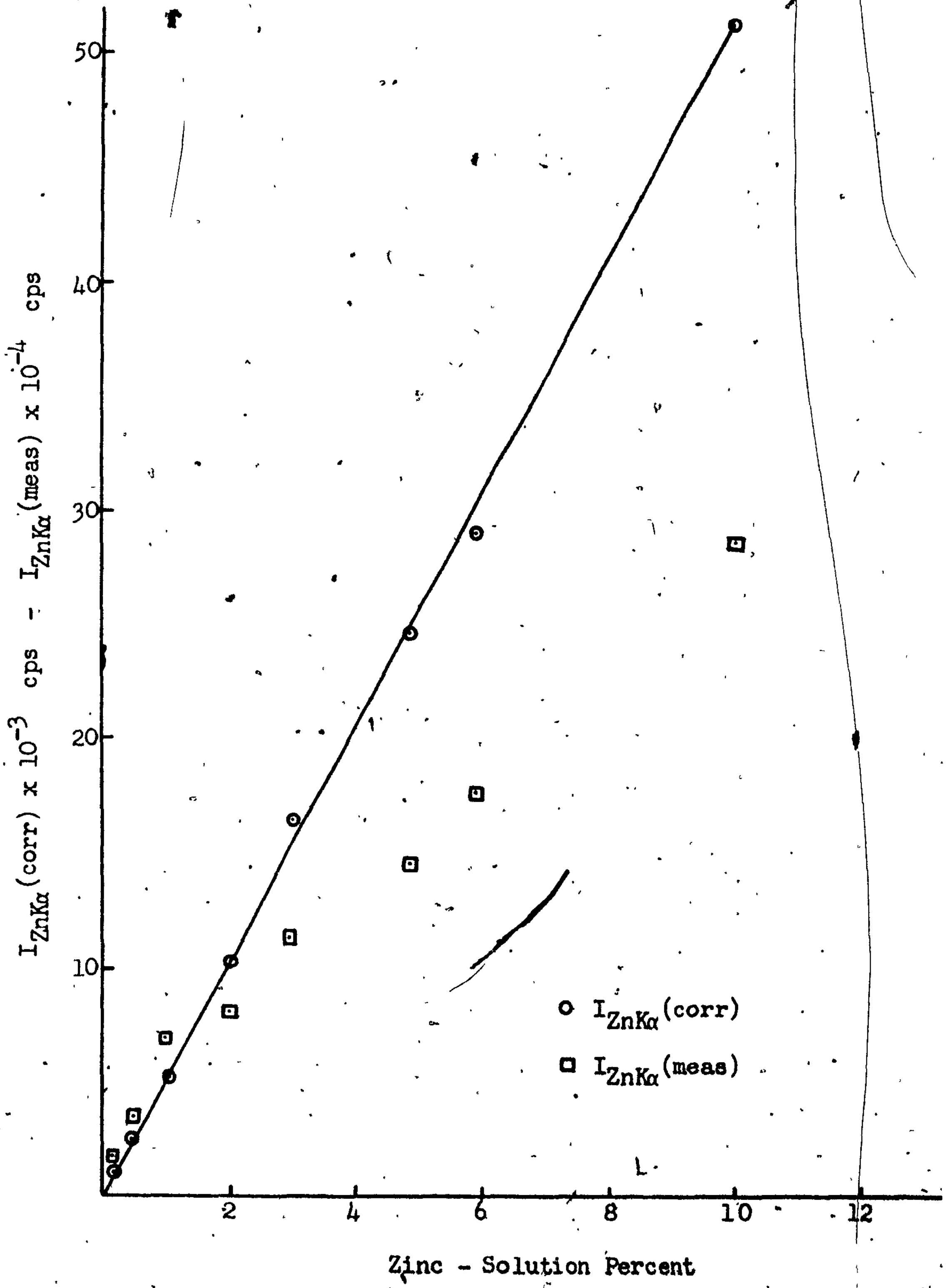


FIGURE 9

$I_{ZnK\alpha}$ VERSUS ZINC IN SOLUTION PERCENT



The comparable accuracies for those series of solutions involving extended ranges of concentration (the SF and SD series), and those with limited ranges of variation (the SG and SB series), indicate that errors which might have originated from the absorption and enhancement effects are properly corrected by the approach.

The merit of an analytical method can not be judged solely on the basis of its ability to yield accuracte results. It can also be evaluated on the basis of its convenience. From this point of view, the approach investigated here provides several obvious advantages over the empirical-mathematical approaches and the commonly-applied solution dilution technique. These are summarized in the discussion to follow.

1. α-correction coefficients derived from simple aqueous solution mixtures can be applied successfully in the analysis of multicomponent solutions with significantly different matrices.
2. Only one standard is required in the computation of the chemical compositions of solutions of unknown compositions.
3. The solution simultaneously of a series of linear equations yields the values for all of the elements of interest in one operation.
4. The omission of the minor components from the analytical scheme does not introduce appreciable errors, since their effects on the analytes can be included with that of the aqueous matrix.
5. Solution total-solids concentration, and acid concentration, are not limited as they are in the standard dilution technique.

6. An inherent advantage of the approach is that it is free from interferences arising out of the physical nature of the specimen.

7. There are no limitations imposed by the availability of standards, since these are prepared as required in the form of either synthetic solutions or solutions of alloy standards.

8. The approach provides a simple analytical technique for alloy samples regardless of available sample size, the physical nature of the sample (sawings, drillings, etc.), or the degree of heterogeneity of the sample material (a gross sample may be taken, dissolved and an appropriate aliquot used for the XRF analytical procedure). On this latter point, the approach provides a means of obtaining more representative samples in the sampling of heterogeneous collections of sample material such as mixed drillings, turnings, etc.

9. Its application is most suitable where rapidity and flexibility are equally as important as accuracy.

3.6 Recommended Practices

One or two comments with respect to recommended practices for the approach covered in this investigation may be provided.

In Section 2.1.3, the discussion revealed that the aqueous matrix effect on an analyte is not appreciable in the following two cases:-

1. Where elements of atomic number higher than 24 (chromium) are present at concentration levels in solution below 0.2 percent.

2. Where elements of atomic number lower than 17 (chlorine) are present at concentration levels in solution below 2 percent, or possibly below a somewhat higher level.

It is recommended that the analysis for minor components with atomic numbers equal to or higher than 24, present at less than a 0.2 percent level in the final solution, should be carried out by the calibration technique. Calibration curves are established by making use of the intensities corrected for the effects of the major components, as evaluated by the L-T correction equation system with the omission of the correction term $\alpha_{AM}C_M$ for the aqueous matrix effect. The equation involved would be:-

$$I_A(\text{corr}) = I_A(\text{meas})\left(1 + \alpha_{AB}C_B + \alpha_{AC}C_C + \cdots\right) \quad (51)$$

where:-

$C_B, C_C,$ = the concentrations of the major components B, C,

$\alpha_{AB}, \alpha_{AC},$ = the α-correction coefficients for the effects of the major components B, C, on the minor component A

In this way, the errors introduced by the α-coefficients, concentrations, and measured intensities for the major components are reduced in magnitude.

Higher optimum operating parameters for the x-ray tubes, as well as the application of pulse height analysis, might be employed in order to minimize errors due to a low fluorescent intensity relative to a high background intensity. This situation is often characteristic of liquid specimen systems.

In the analysis to determine low atomic number elements (atomic number < 17), the effect of the aqueous matrix could generally be ignored within many of the lower ranges of elemental concentration. Interelement effects, however, could be very significant on the basis of an estimation from appropriate absorption coefficient data. For AlKα radiation, for instance, the absorption coefficients for nitrogen, oxygen, fluorine, silicon, chromium, manganese and iron are respectively 1050, 1550, 1950, 440, 2700, 2950 and 3200. The significant differences in the values for nitrogen, oxygen and fluorine should be noted. The indication here is that variability of the composition of the aqueous matrix relative to oxygen, nitrogen, fluorine, carbon, etc., where analytes of atomic number less than 17 are concerned, may obviate the possibility of considering the effect of the aqueous matrix as a single effect. Additional investigations should, therefore, be carried out in order to locate the limit of analyte atomic number at which the assumption of a single effect for the aqueous matrix is no longer valid. The approach described in the investigation reported here might then be employed directly in the determination of elements of atomic number less than this limiting value, with the omission of the correction term for the aqueous matrix effect and the substitution of terms giving proper consideration to the elemental effects of the aqueous matrix. Of course, in this area of application, experimental error due to the low intensities for the lower atomic number elements should be minimized by the use of high-concentration solutions and optimum excitation conditions for the XRF approach.

4. CONCLUSIONS

This study of the determination of α-correction coefficients for aqueous solution media, and that of the interelement effects as associated with high-concentration multicomponent aqueous solutions, has disclosed several rather significant points.

1. An aqueous matrix consisting of nitric acid, water and, on occasion, hydrofluoric acid, can be assumed to be homogeneous in its effect relative to analytes of atomic number equal to or higher than 17.
2. The aqueous matrix effect for such elements is always one of negative absorption where the characteristic Kα radiation is involved, with the Lα radiation for lead being also included in this effect. The negative absorption effect accounts for a large portion of the total intensities for such analytes, and its correction relative to any variation in sample size, in high-concentration level solutions, is obviously required.
3. The effect of chlorine, due to the presence of hydrochloric and/or perchloric acids in the aqueous matrix, requires separate consideration. This effect has been properly corrected for by the application of the appropriate Lachance and Traill correction equation system.
4. The interelement effects occurring in high-solid-content solutions can be used to determine the required Lachance and Traill α-correction coefficients, and with an accuracy at least equal to that obtained relative to the use of specimens other than solution specimens. The reliability of these solution-derived α-coefficients is, however, often much greater, because of the availability of accurate synthetic standards.
5. The absorption and enhancement effects occurring with high-concentration multicomponent solutions can be properly corrected for by use of the Lachance and Traill

correction equation system, with the required α-correction coefficients being derived independently from simple aqueous solution matrices.

6. The validity of the approach has been verified quite successfully on the basis of the analysis of synthetic solutions, as well as on the basis of the analysis of solutions obtained by dissolving known-composition ferrous-base and copper-base alloys. The applicability of the approach over a wide range of total analytes concentration, and concentration for each analyte, has been demonstrated.

7. This approach to the analysis of aqueous media solutions permits a high degree of flexibility relative to available sample size, physical nature and heterogeneity of the sample material, solution acid concentration, etc., and indeed far more than is permitted by the standard dilution technique.

8. The high-concentration solution technique minimizes to a considerable extent difficulties relative to the low measured intensities often occurring with the dilution method.

9. A general approach to a compensation for some of the limitations of the Lachance and Traill correction equation system in its experimental application has been achieved in this investigation. It has been suggested that higher accuracy might be obtainable through some improvement in the technique of dissolving the samples and in the operational system relative to the measurement of emitted intensity.

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5.0 PRESENTATION OF DATA

It is not possible, with the very extensive data accumulated in the course of this investigation, to calculate the uncertainty parameters for each experimental or calculated value. With in excess of 20,000 values involved, the time required would be prohibitive. In addition, there would be little of a practical nature to be gained, since the number of variables involved in many of the equations used indicate an extremely low probability that such calculated relative uncertainties would be achieved. For example, the calculated concentration, obtained during the back-calculation of composition operation, involves the equation:-

$$C_A = \frac{I_A}{I_A^o}\left(1 + \alpha_{AM}C_M + \alpha_{AB}C_B + \alpha_{AC}C_C + \ldots\ldots\ldots\ldots\ldots\ldots\right)$$

The maximum relative uncertainty for this derived value would be given by:-

$$\frac{\Delta C_A}{C_A} = \frac{\Delta I_A}{I_A} \pm \frac{\Delta I_A^o}{I_A^o} \pm \frac{\left(\frac{\Delta\alpha_{AM}}{\alpha_{AM}} + \frac{\Delta C_M}{C_M}\right)\alpha_{AM}C_M \pm \left(\ldots\ldots\right)}{1 + \alpha_{AM}C_M + \alpha_{AB}C_B + \ldots\ldots}$$

with $\Delta I_A^o/I_A^o$ being determined from a similar expression and subject to the same type of relative uncertainty. Several worked-out values for such relative uncertainties, using the various Δ values involved, yielded ranges far beyond the actual uncertainties which were achived.

For these reasons, the basis indicated in the following was used with respect to data expression.

Tables Involving "Experimental Parameters"

For each series, the concentrations for each of the elements involved were expressed on the basis of a significant figure level set by the value of greatest uncertainty. For example, in tabulating seven concentrations for manganese, the significant figure level for all such values was set by the value of greatest uncertainty. In all cases, the matrix concentration, C_M, carries a significant figure decimal place expression dictated by the contributing value, for the elemental components, of the least number of decimal places. This situation is required on the basis that C_M is always given by the expression $1 - (C_A + C_B + \cdots)$.

The measurement of intensity is expressed as the average of the number of counts taken, with each average intensity being expressed to the full read-out capacity of the equipment. The uncertainty for any such intensity measurement is given by the associated sigma counting error in percent.

Tables Involving "Calculation of α"

Here the uncertainty in any average α-correction coefficient value calculated is given by the standard deviation for the series of individual calculations involved.

Tables Involving "Calculation of I_A(corr) and I_A^o"

All calculated intensity values are expressed on the same full read-out basis as the measured intensities. No attempt was made to determine the uncertainty contributions from each of the variables involved in the calculation equation, for the reasons given previously. The values of I_A^o as calculated represent average values, however, and accordingly carry the associated standard deviation.

Tables Involving "Back-calculation of Solution Composition"

All back-calculated composition values were carried out to the same significant figure level as the corresponding solution concentration value shown in the associated Experimental Parameters table.

Figures Involving "I_A versus C_B, C_M, etc."

The circles surrounding each experimentally determined locus on a curve are for identification of the locus only; they do not reflect the uncertainty parameters around the locus. This method was chosen reluctantly, but calculation of such exact uncertainty parameters would have involved a complicated and prolonged procedure.

Tables Involving the Analytical Application Process

All such tables expressed composition values, as determined by either of the XRF techniques employed, to the same significant figure level as the associated values as known from the synthetic solution preparation or from the analyzed standard basis.

5.1 Effects of Aqueous Matrix M

5.1.1 Effect of M on Cl

TABLE A Experimental Parameters (ClKα Radiation)

Solutions: Prepared by dilution of approximately 12N HCl with H_2O, and exact final weight of solution determined. Chloride determined by potentiometric titration with standard $AgNO_3$ solution. Least precise value of chloride series involved 1:300 uncertainty, and sets significant figure level of 1:150 to 1:1500 for all values.

Intensity: Cr-target, 50kV, 36mA, coarse collimation, PET crystal, PF counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 3 counts. Sigma counting error in percent is shown as s.

Solution	C_{Cl}	C_M	$I_{ClK\alpha}$ (cps)	s (%)
LZD-2	0.0381	0.9619	10 845	0.22
LZD-3	0.0758	0.9242	21 497	0.15
LZD-4	0.1152	0.8848	31 680	0.13
LZD-5	0.152^3	0.847^7	41 940	0.11
LZD-6	0.197^2	0.802^8	51 215	0.10

TABLE B Calculation of α_{ClM}

$$\alpha_{ClM} = \frac{I_{Cl(1)}C_{Cl(2)} - I_{Cl(2)}C_{Cl(1)}}{I_{Cl(2)}C_{Cl(1)}C_{M(2)} - I_{Cl(1)}C_{Cl(2)}C_{M(1)}}$$

Solutions	α_{ClM}
LZD-2/LZD-6	- 0.38182·····
LZD-2/LZD-5	- 0.22962·····
LZD-3/LZD-6	- 0.44565·····
LZD-3/LZD-5	- 0.28688·····

α_{ClM} average = - 0.33599····
std. devn. = ± 0.09632····

$$\alpha_{ClM} = -0.33^6 \pm 0.09^6$$
$$= -0.34 \pm 0.10$$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

$$I_{ClK\alpha}(\mathrm{corr}) = \underset{(A)}{I_{ClK\alpha}(\mathrm{meas})} - 0.33^{6}\underset{(B)}{I_{ClK\alpha}(\mathrm{meas})C_M}$$

$$I^{o}_{ClK\alpha} = I_{ClK\alpha}(\mathrm{corr})/C_{Cl}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{ClK\alpha}$(cps)
LZD-2	10 845	3 505	7 340	192 649
LZD-3	21 497	6 675	14 821	195 534
LZD-4	31 680	9 418	22 262	193 244
LZD-5	41 940	11 946	29 994	196 942
LZD-6	51 215	13 815	37 400	189 656

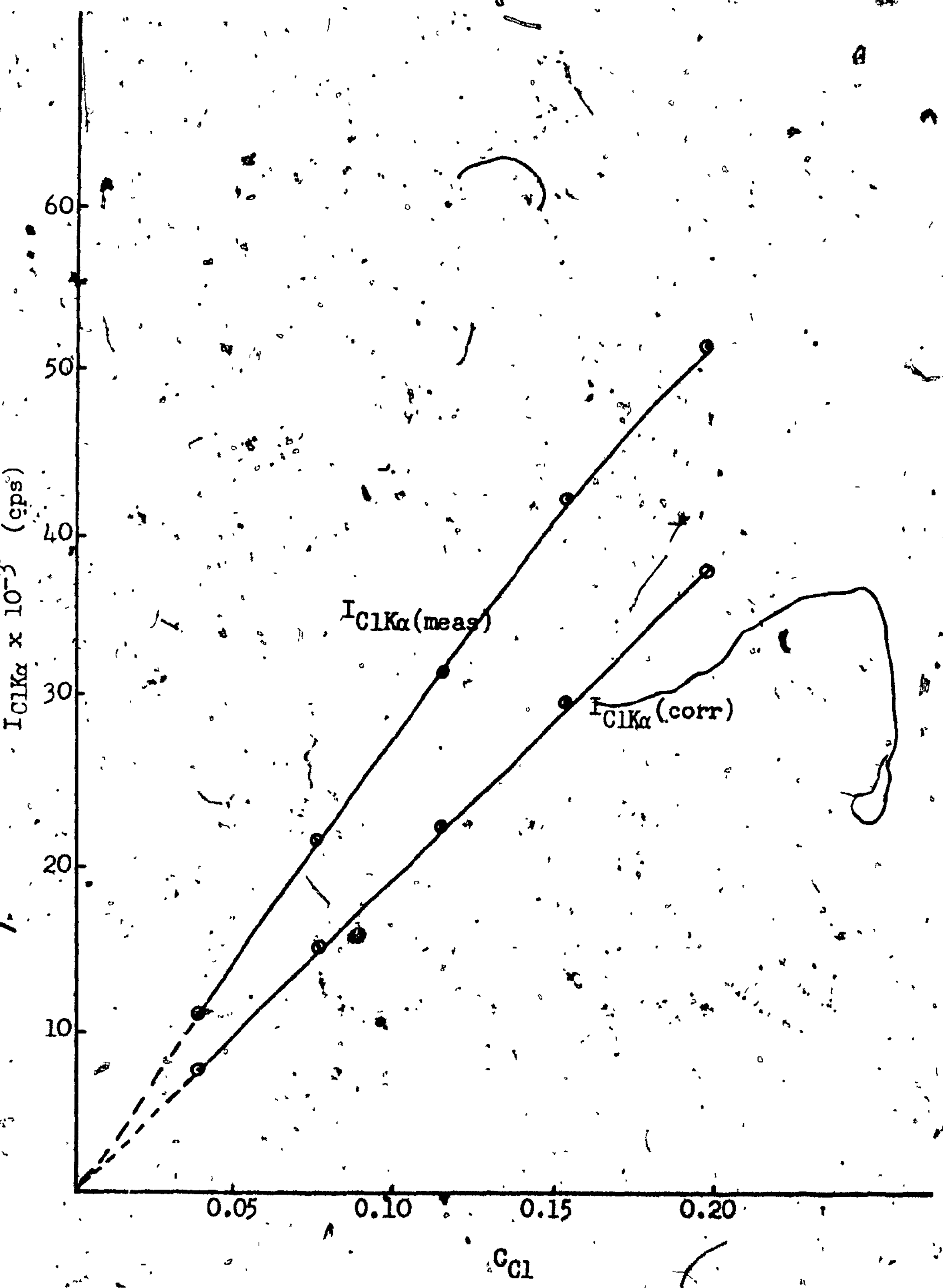
$I^{o}_{ClK\alpha}$ average = 193 605 cps
std. devn. = ± 2 806 cps

$$I^{o}_{ClK\alpha} = (1.93^{6} \pm 0.02^{8}) \times 10^{5}\ \mathrm{cps}$$
$$= (1.94 \pm 0.03) \times 10^{5}\ \mathrm{cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Cl}(theor)	C_{Cl}(calc)	Abs. error	Rel. error (%)
LZD-2	0.0381	0.0379	0.0002	0.52
LZD-3	0.0758	0.0766	0.0008	1.05
LZD-4	0.1152	0.1150	0.0002	0.17
LZD-5	0.152^{3}	0.155^{1}	0.002^{8}	1.84
LZD-6	0.197^{2}	0.192^{8}	0.004^{4}	2.22

FIGURE D $I_{ClK\alpha}$ versus C_{Cl}



5.1.2 Effect of M on Cr

TABLE A Experimental Parameters (CrKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.200000 ± 0.000004 g Cr) with H_2O. Exact final weight of the solution determined. Least precise value for Cr involved 1:580 uncertainty, and sets significant figure level of 1:290 to 1:2900 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, Scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent is shown as s.

Solution	C_{Cr}	C_M	$I_{CrK\alpha}$ (cps)	s (%)
KC-1	0.01000	0.99000	2 816	0.43
KC-2	0.1000	0.9000	18 998	0.17
KC-3	0.2000	0.8000	28 134	0.13

TABLE B Calculation of α_{CrM}

$$\alpha_{CrM} = \frac{I_{Cr(1)}C_{Cr(2)} - I_{Cr(2)}C_{Cr(1)}}{I_{Cr(2)}C_{Cr(1)}C_{M(2)} - I_{Cr(1)}C_{Cr(2)}C_{M(1)}}$$

Solutions	α_{CrM}
KC-1/KC-2	- 0.84989·····
KC-1/KC-3	- 0.84770·····
KC-2/KC-3	- 0.84368·····

α_{CrM} average = - 0.84709···

std. devn. = ± 0.0032····

$$\alpha_{CrM} = -0.847^{1} \pm 0.003^{2}$$

$$= -0.847 \pm 0.003$$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

$$I_{CrK\alpha}(\mathrm{corr}) = \underset{(A)}{I_{CrK\alpha}(\mathrm{meas})} - \underset{(B)}{0.847^{1} I_{CrK\alpha}(\mathrm{meas}) C_{M}}$$

$$I^{o}_{CrK\alpha} = I_{CrK\alpha}(\mathrm{corr})/C_{Cr}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{CrK\alpha}$ (cps)
KC-1	2 816	2 362	454	45 400
KC-2	18 998	14 484	4 514	45 140
KC-3	28 134	19 066	9 068	45 340

$I^{o}_{CrK\alpha}$ average = 45 293 cps

std. devn. = ± 136 cps

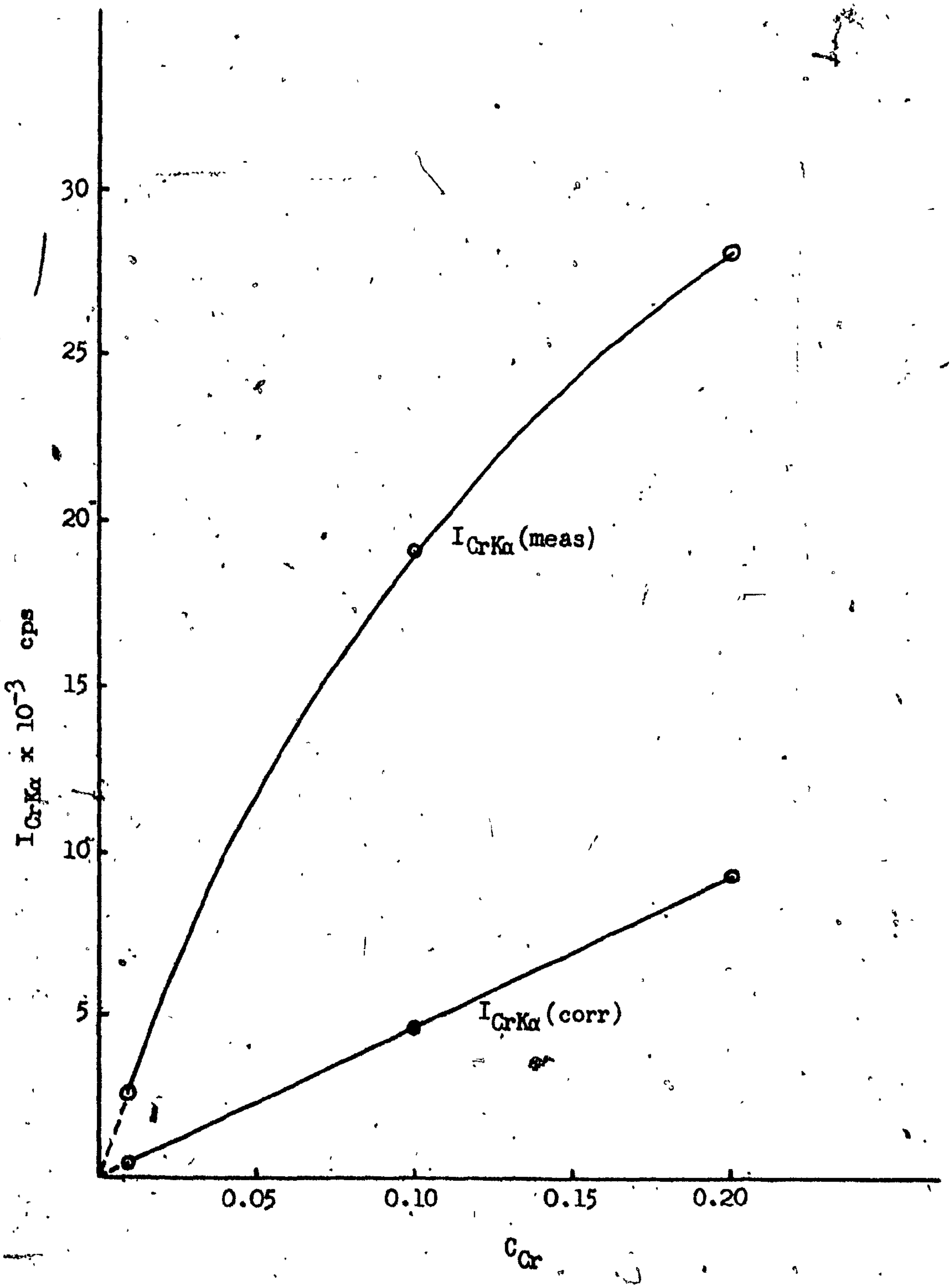
$$I^{o}_{CrK\alpha} = (4.52^{9} \pm 0.01^{3}) \times 10^{4} \text{ cps}$$

$$= (4.53 \pm 0.01) \times 10^{4} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Cr}(theor)	C_{Cr}(calc)	Abs. error	Rel. error (%)
KC-1	0.01000	0.01000	0.00000	0.00
KC-2	0.1000	0.0995	0.0005	0.50
KC-3	0.2000	0.2000	0.0000	0.00

FIGURE D $I_{CrK\alpha}$ versus C_{Cr}



5.1.3 Effect of M on Mn

TABLE A Experimental Parameters (MnKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.200000 ± 0.000004 g Mn) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Mn given by 1:400 uncertainty, and sets significant figure level of 1:200 to 1:2000 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent is shown as s.

Solution	C_{Mn}	C_M	$I_{MnK\alpha}$ (cps)	s (%)
LGG-1	0.01000	0.99000	6 427	0.29
LGG-2	0.01980	0.98020	12 024	0.20
LGG-3	0.0400^0	0.9600^0	21 527	0.15
LGG-4	0.0600^0	0.9400^0	29 558	0.13
LGG-5	0.0800^0	0.9200^0	36 175	0.12
LGG-6	0.1000	0.9000	41 832	0.11

TABLE B Calculation of α_{MnM}

$$\alpha_{MnM} = \frac{I_{Mn(1)}C_{Mn(2)} - I_{Mn(2)}C_{Mn(1)}}{I_{Mn(2)}C_{Mn(1)}C_{M(2)} - I_{Mn(1)}C_{Mn(2)}C_{M(1)}}$$

Solutions	α_{MnM}
LGG-1/LGG-6	- 0.8637••••••
LGG-1/LGG-5	- 0.8649••••••
LGG-2/LGG-6	- 0.8637••••••
LGG-2/LGG-5	- 0.8637••••••

α_{MnM} average = - 0.8637••••
std. devn. = ± 0.0000••••

$$\alpha_{MnM} = -0.863^7 \pm 0.000^0$$
$$= -0.864 \pm 0.000$$

TABLE C Calculation of $I_{MnK\alpha}$(corr) and $\overset{o}{I}_{MnK\alpha}$

$$\underset{(A)}{I_{MnK\alpha}(\text{corr}) = I_{MnK\alpha}(\text{meas})} - \underset{(B)}{0.863^{7} I_{MnK\alpha}(\text{meas}) C_{M}}$$

$$\overset{o}{I}_{MnK\alpha} = I_{MnK\alpha}(\text{corr})/C_{Mn}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$\overset{o}{I}_{MnK\alpha}$ (cps)
LGG-1	6 427	5 495	932	93 200
LGG-2	12 024	10 180	1 844	93 131
LGG-3	21 527	17 849	3 678	91 950
LGG-4	29 558	23 997	5 561	92 683
LGG-5	36 175	28 745	7 430	92 875
LGG-6	41 832	32 517	9 315	93 150

$\overset{o}{I}_{MnK\alpha}$ average = 92 832 cps

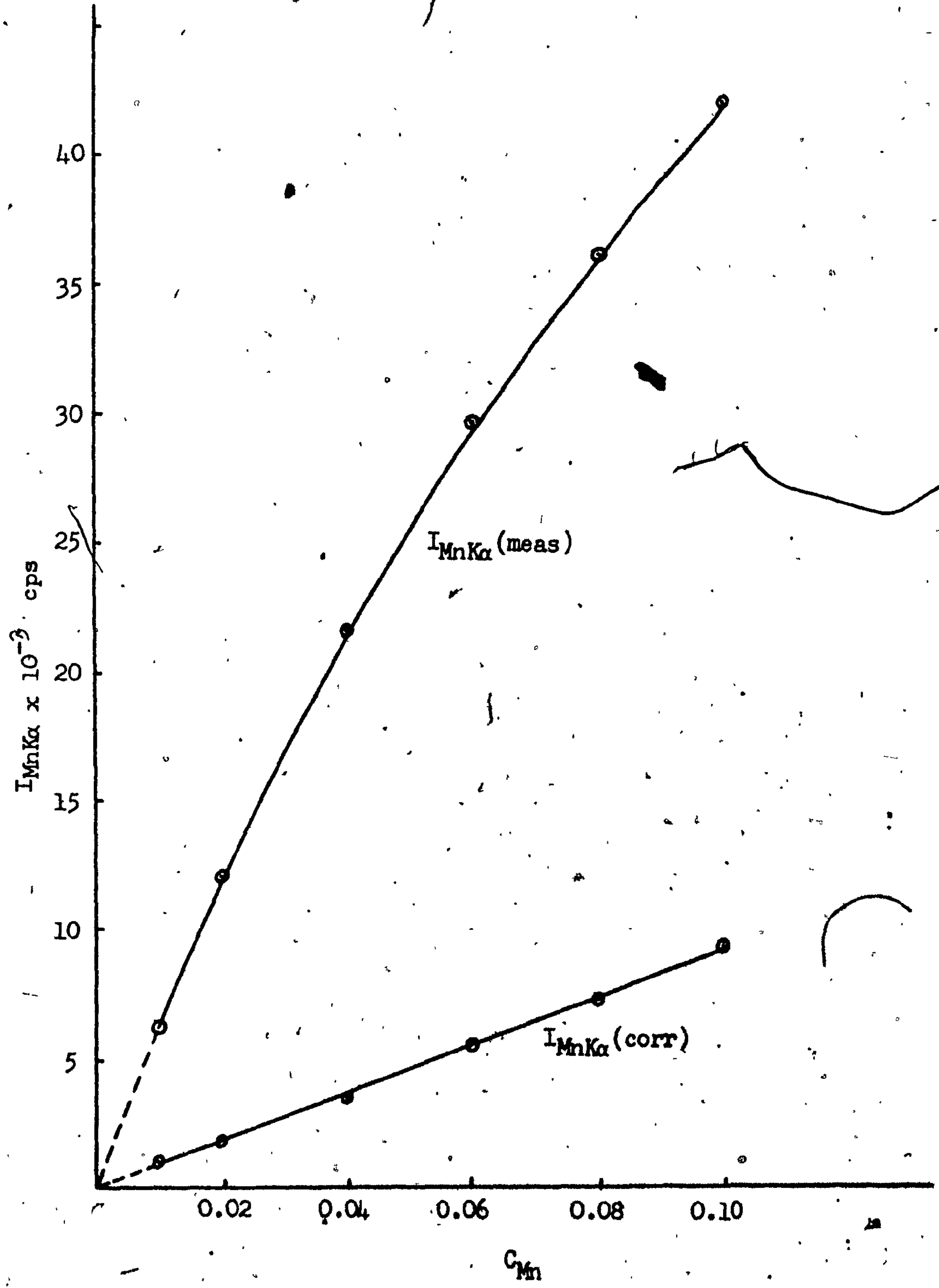
std. devn = ± 527 cps

$$\overset{o}{I}_{MnK\alpha} = (9.28^{3} \pm 0.05^{2}) \times 10^{4} \text{ cps}$$
$$= (9.28 \pm 0.05) \times 10^{4} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Mn}(theor)	C_{Mn}(calc)	Abs. error	Rel. error (%)
LGG-1	0.01000	0.01000	0.00000	0.00
LGG-2	0.01980	0.02020	0.00040	2.00
LGG-3	0.0400	0.0395	0.0005	1.25
LGG-4	0.0600	0.0599	0.0001	0.16
LGG-5	0.0800	0.0801	0.0001	0.12
LGG-6	0.1000	0.1006	0.0006	0.60

FIGURE D $I_{MnK\alpha}$ versus C_{Mn}



5.1.4 Effect of M on Fe

TABLE A. Experimental Parameters (FeKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.200000 ± 0.000004 g Fe) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Fe given by 1:600 uncertainty, and sets significant figure level of 1:300 to 1:3000 for all values

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent is shown as s.

Solution	C_{Fe}	C_M	$I_{FeK\alpha}$ (cps)	s (%)
DD-1	0.00500	0.99500	4 838	0.32
DD-2	0.01000	0.99000	9 147	0.22
DD-3	0.01500	0.98500	13 469	0.20
DD-4	0.02000	0.98000	17 114	0.17
DD-5	0.03000	0.97000	23 808	0.14
DD-6	0.0400^{0}	0.9600^{0}	30 158	0.13
DD-7	0.0500^{0}	0.9500^{0}	34 540	0.12
DD-8	0.0600^{0}	0.9400^{0}	39 820	0.11
DD-9	0.0650^{0}	0.9350^{0}	41 951	0.11

TABLE B Calculation of α_{FeM}

$$\alpha_{FeM} = \frac{I_{Fe(1)}C_{Fe(2)} - I_{Fe(2)}C_{Fe(1)}}{I_{Fe(2)}C_{Fe(1)}C_{M(2)} - I_{Fe(1)}C_{Fe(2)}C_{M(1)}}$$

Solutions	α_{FeM}
DD-1/DD-9	- 0.89761····
DD-1/DD-8	- 0.89678····
DD-2/DD-9	- 0.89141····
DD-2/DD-8	- 0.89112····
DD-3/DD-7	- 0.90767·····

α_{FeM} average = - 0.89674····
std. devn. = ± 0.0067·····

$$\alpha_{FeM} = -0.896^{7} \pm 0.006^{7}$$
$$= -0.897 \pm 0.007$$

TABLE C Calculation of $I_{FeK\alpha}(\mathrm{corr})$ and $I^{o}_{FeK\alpha}$

$$I_{FeK\alpha}(\mathrm{corr}) = \underset{(A)}{I_{FeK\alpha}(\mathrm{meas})} - \underset{(B)}{0.896^{7} I_{FeK\alpha}(\mathrm{meas}) C_M}$$

$$I^{o}_{FeK\alpha} = I_{FeK\alpha}(\mathrm{corr})/C_{Fe}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{FeK\alpha}$ (cps)
DD-1	4 838	4 316	522	104 400
DD-2	9 147	8 120	1 027	102 700
DD-3	13 469	11 896	1 573	104 867
DD-4	17 114	15 039	2 075	103 750
DD-5	23 808	20 708	3 100	103 333
DD-6	30 158	25 961	4 197	104 925
DD-7	34 540	29 423	5 117	102 340
DD-8	39 820	33 564	6 256	104 267
DD-9	41 951	35 172	6 779	104 292

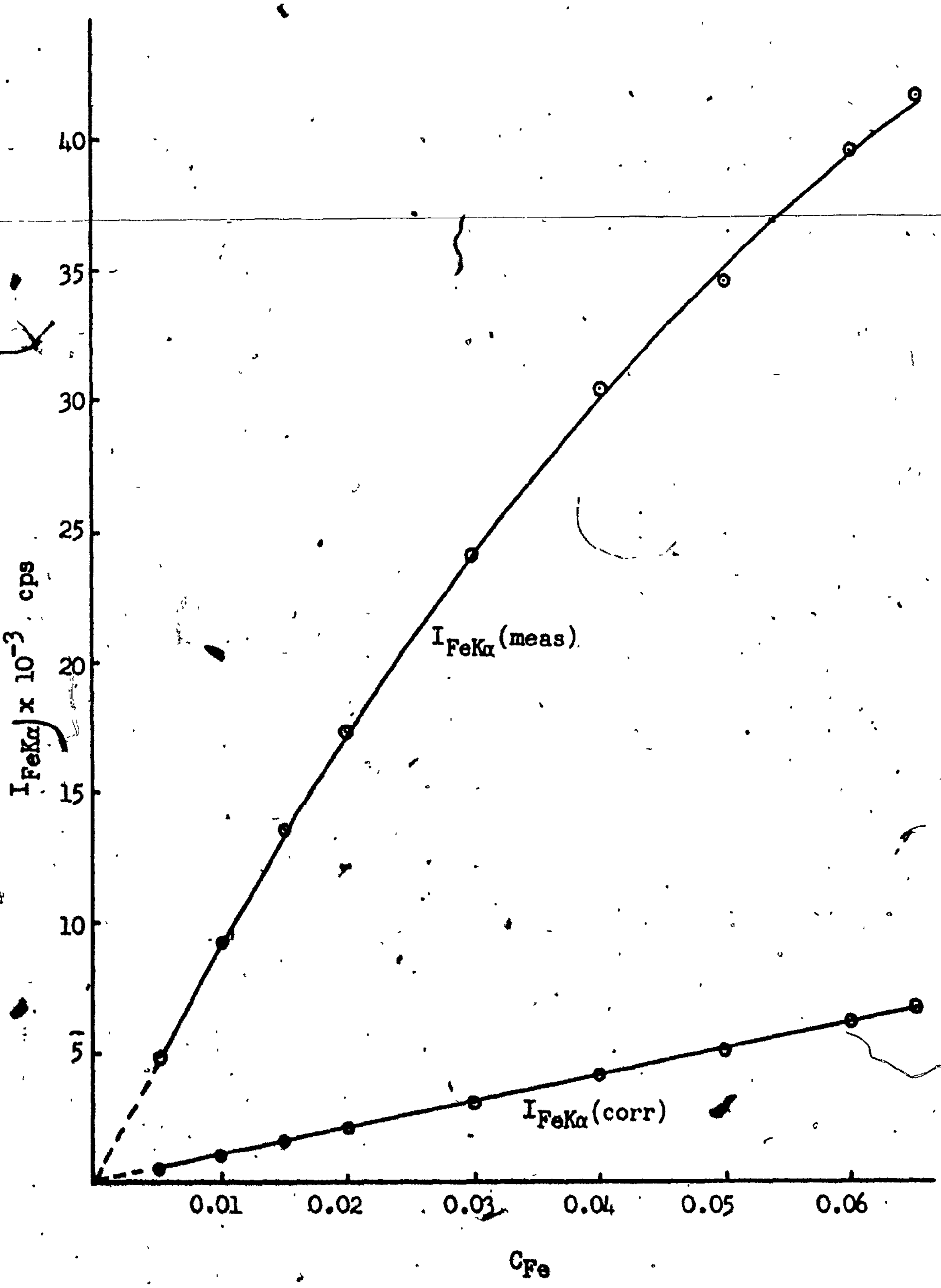
$I^{o}_{FeK\alpha}$ average = 103 875 cps
std. devn. = ± 917 cps

$$I^{o}_{FeK\alpha} = (1.038^{7} \pm 0.009^{1}) \times 10^{5} \text{ cps}$$
$$= (1.039 \pm 0.009) \times 10^{5} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Fe}(theor)	C_{Fe}(calc)	Abs. error	Rel. error (%)
DD-1	0.00500	0.00500	0.00000	0.00
DD-2	0.01000	0.00990	0.00010	1.00
DD-3	0.01500	0.01520	0.00020	1.33
DD-4	0.02000	0.02000	0.00000	0.00
DD-5	0.03000	0.02980	0.00020	0.67
DD-6	0.0400^{0}	0.0405	0.0005	1.25
DD-7	0.0500^{0}	0.0489	0.0011	2.20
DD-8	0.0600^{0}	0.0603	0.0003	0.50
DD-9	0.0650^{0}	0.0654	[illegible]0004	0.61

FIGURE D $I_{FeK\alpha}$ versus C_{Fe}



5.1.5 Effect of M on Co

TABLE A Experimental Parameters (CoKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.100000 ± 0.000028) by H_2O-HNO_3. Exact final weight of the solution determined. Least precise value for Co involved 1:560 uncertainty, and sets significant figure level for all values at 1:280 to 1:2800.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Co}	C_M	$I_{CoK\alpha}$ (cps)	s (%)
LI-1	0.01000	0.99000	22 080	0.15
LI-2	0.02000	0.98000	39 882	0.11
LI-3	0.0300^{0}	0.9700^{0}	54 567	0.10
LI-4	0.0400^{0}	0.9600^{0}	66 696	0.09
LI-5	0.0600^{0}	0.9400^{0}	87 131	0.08
LI-6	0.0700^{0}	0.9300^{0}	94 812	0.07
LI-7	0.0727^{0}	0.9273^{0}	95 845	0.07

TABLE B Calculation of α_{CoM}

$$\alpha_{CoM} = \frac{I_{Co(1)}C_{Co(2)} - I_{Co(2)}C_{Co(1)}}{I_{Co(2)}C_{Co(1)}C_{M(2)} - I_{Co(1)}C_{Co(2)}C_{M(1)}}$$

Solutions	α_{CoM}
LI-1/LI-7	− 0.92343·····
LI-1/LI-6	− 0.92148·····
LI-1/LI-5	− 0.92075·····
LI-2/LI-7	− 0.92352·····
LI-2/LI-6	− 0.92091·····
LI-3/LI-7	− 0.92382·····

α_{CoM} average = − 0.92232·····
std. devn. = ± 0.0014······

α_{CoM} = $-0.922^{3} \pm 0.001^{4}$
= − 0.922 ± 0.001

5

TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

$$I_{CoK\alpha}(\mathrm{corr}) = \underset{(A)}{I_{CoK\alpha}(\mathrm{meas})} - \underset{(B)}{0.922^{3} I_{CoK\alpha}(\mathrm{meas}) C_M}$$

$$I^{o}_{CoK\alpha} = I_{CoK\alpha}(\mathrm{corr})/C_{Co}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{CoK\beta}$(cps)
LI-1	22 080	20 161	1 919	191 900
LI-2	39 822	36 048	3 834	191 700
LI-3	54 567	48 817	5 750	191 667
LI-4	66 896	59 230	7 666	191 650
LI-5	87 131	75 539	11 592	193 200
LI-6	94 812	81 324	13 488	192 686
LI-7	95 845	81 971	13 874	190 839

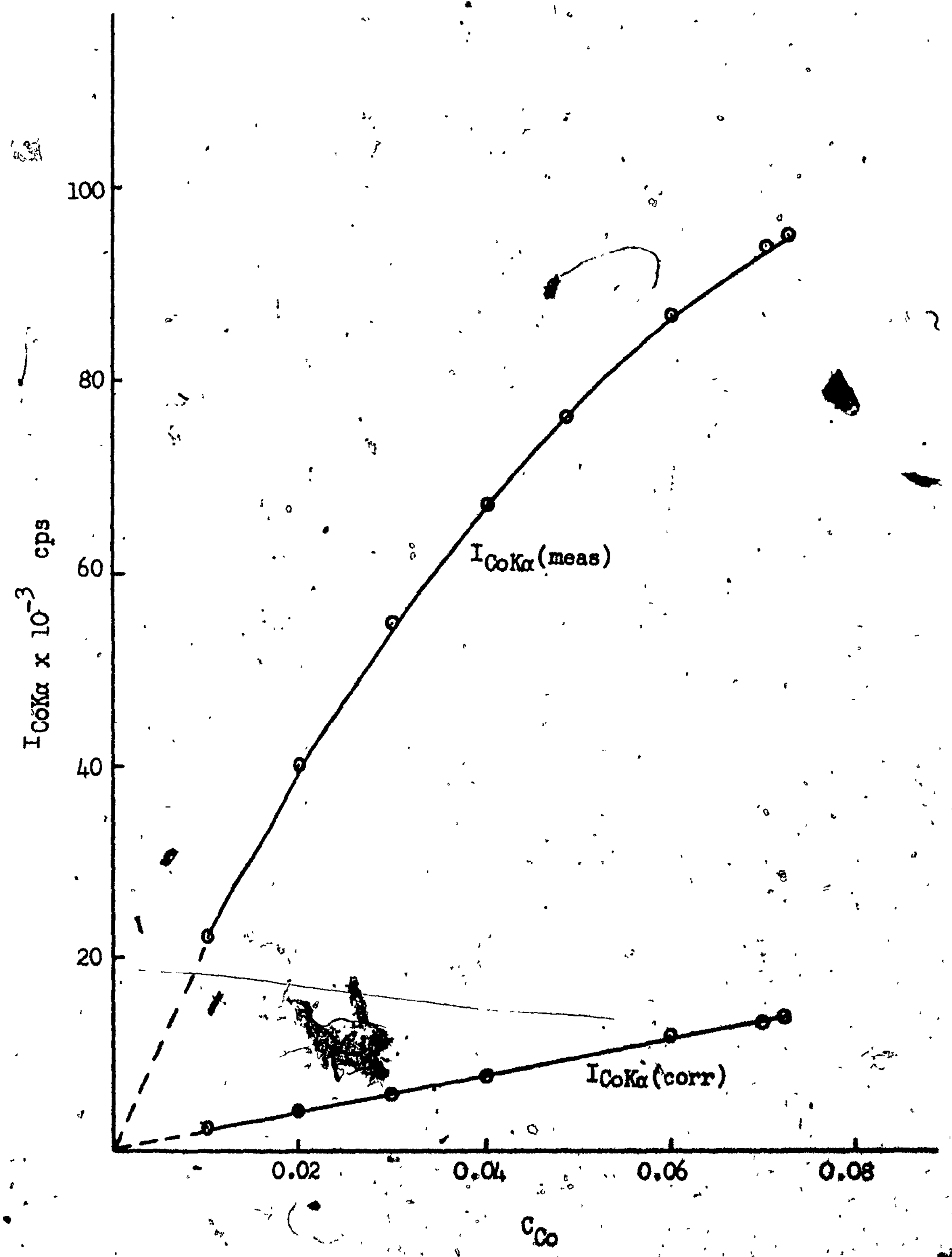
$I^{o}_{CoK\alpha}$ average = 191 949 cps
std. devn. = ± 770 cps

$$I^{o}_{CoK\alpha} = (1.919^{4} \pm 0.007^{7}) \times 10^{5}\ \mathrm{cps}$$
$$\doteq (1.919 \pm 0.008) \times 10^{5}\ \mathrm{cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Co}(theor)	C_{Co}(calc)	Abs. error	Rel. error (%)
LI-1	0.01000	0.01000	0.00000	0.00
LI-2	0.02000	0.02000	0.00000	0.00
LI-3	0.0300^{0}	0.0299	0.0001	0.33
LI-4	0.0400^{0}	0.0399	0.0001	0.25
LI-5	0.0600^{0}	0.0607	0.0007	1.16
LI-6	0.0700^{0}	0.0705	0.0005	0.71
LI-7	0.0727^{0}	0.0719	0.0008	1.10

FIGURE D $I_{CoK\alpha}$ versus C_{Co}



5.1.6 Effect of M on Ni

TABLE A Experimental Parameters (NiKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml. ≐ 0.20000 ± 0.00002 g Ni) by H_2O. Exact final weight of the solution determined. Least precise value for Ni given as 1:430 uncertainty, and sets significant figure level at 1:215 to 1:2150 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Ni}	C_M	$I_{NiK\alpha}$ (cps)	s (%)
LZE-1	0.01000	0.99000	32 191	0.12
LZE-2	0.02000	0.98000	57 839	0.10
LZE-3	0.0300^0	0.9700^0	81 188	0.08
LZE-4	0.0500^0	0.9500^0	114 684	0.07
LZE-5	0.0700^0	0.9300^0	140 608	0.07
LZE-6	0.1000^0	0.9000^0	169 246	0.06

TABLE B Calculation of α_{NiM}

$$\alpha_{NiM} = \frac{I_{Ni(1)}C_{Ni(2)} - I_{Ni(2)}C_{Ni(1)}}{I_{Ni(2)}C_{Ni(1)}C_{M(2)} - I_{Ni(1)}C_{Ni(2)}C_{M(1)}}$$

Solutions	α_{NiM}
LZE-1/LZE-6	- 0.9176·····
LZE-1/LZE-5	- 0.9178·····
LZE-1/LZE-4	- 0.9181·····
LZE-2/LZE-6	- 0.9150·····
LZE-2/LZE-5	- 0.9143·····
LZE-3/LZE-6	- 0.9201·····

α_{NiM} average = - 0.9171·····
std. devn. = ± 0.0021·····

α_{NiM} = $- 0.917^1 \pm 0.002^1$
= - 0.917 ± 0.002

TABLE C Calculation of $I_{NiK\alpha}(corr)$ and $I^{o}_{NiK\alpha}$

$$I_{NiK\alpha}(corr) = \underset{(A)}{I_{NiK\alpha}(meas)} - 0.917^{1}\underset{(B)}{I_{NiK\alpha}(meas)}C_{M}$$

$$I^{o}_{NiK\alpha} = I_{NiK\alpha}(corr)/C_{Ni}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{NiK\alpha}$ (cps)
LZE-1	32 191	29 227	2 964	296 386
LZE-2	57 839	51 983	5 856	292 787
LZE-3	81 188	72 224	8 964	298 807
LZE-4	114 684	99 918	14 766	295 323
LZE-5	140 608	119 925	20 683	295 472
LZE-6	169 246	139 694	29 552	295 520

$I^{o}_{NiK\alpha}$ average = 295 716 cps

std. devn. = ± 1 941 cps

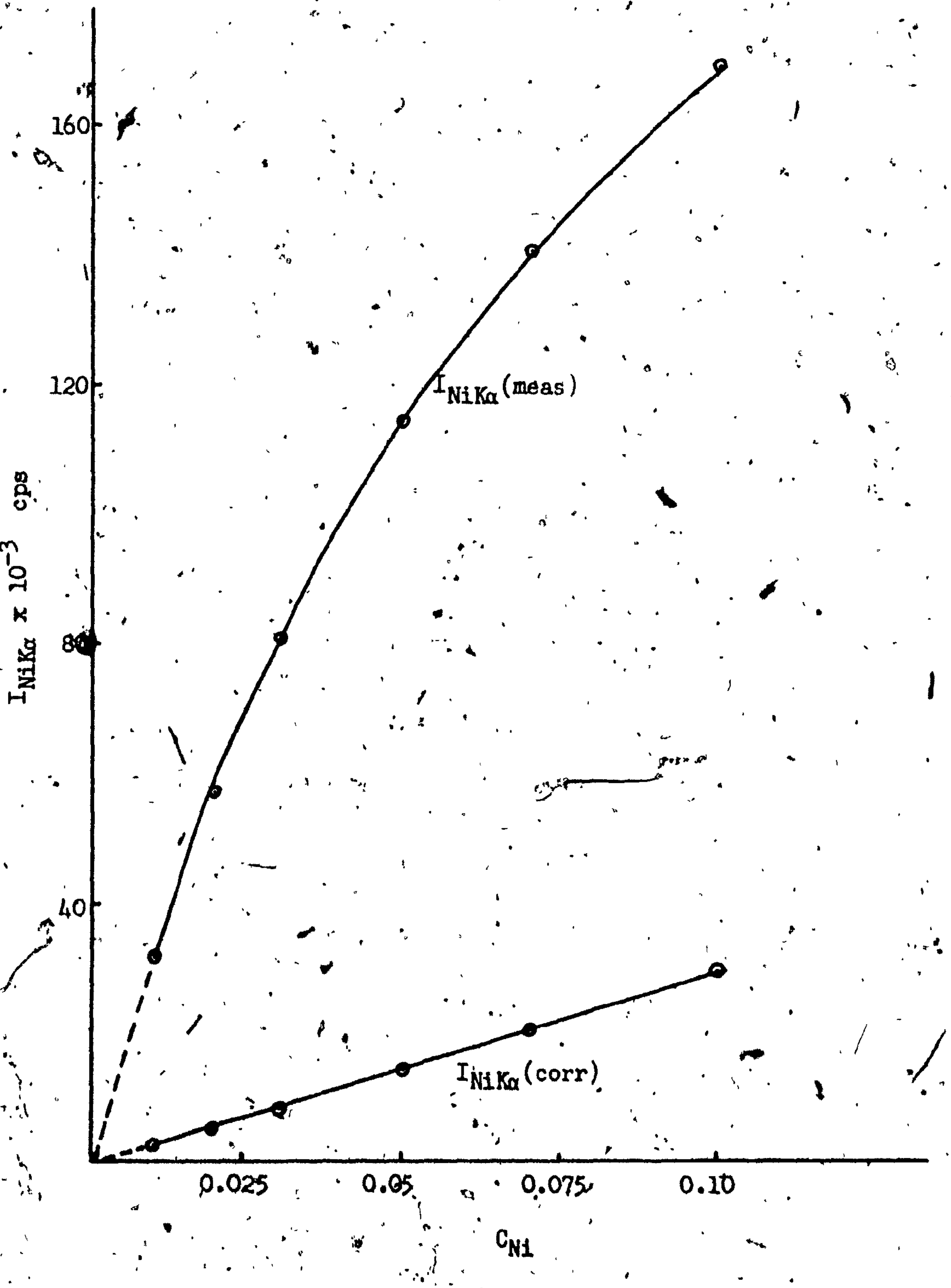
$$I^{o}_{NiK\alpha} = (2.95^{7} \pm 0.01^{9}) \times 10^{5} \text{ cps}$$

$$= (2.96 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Ni}(theor)	C_{Ni}(calc)	Abs. error	Rel. error (%)
LZE-1	0.01000_{0}	0.01000	0.00000	0.00
LZE-2	0.02000	0.01980	0.00020	1.00
LZE-3	0.0300^{0}	0.0304	0.0004	1.33
LZE-4	0.0500^{0}	0.0499	0.0001	0.20
LZE-5	0.0700^{0}	0.0699	0.0001	0.17
LZE-6	0.1000^{0}	0.0999	0.0001	0.10

FIGURE D $I_{NiK\alpha}$ versus C_{Ni}



5.1.7 Effect of M on Cu

TABLE A Experimental Parameters (CuKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.200000 ± 0.000004 g Cu) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Cu given by 1:580 uncertainty, and sets significant figure level at 1:290 to 1:2900 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Cu}	C_M	$I_{CuK\alpha}$ (cps)	s (%)
LA-1	0.01000	0.99000	30 532	0.13
LA-2	0.02000	0.98000	54 204	0.10
LA-3	0.0300^0	0.9700^0	74 618	0.08
LA-4	0.0500^0	0.9500^0	104 548	0.07
LA-5	0.0700^0	0.9300^0	127 026	0.06
LA-6	0.1000^0	0.9000^0	152 826	0.06
LA-7	0.1170^0	0.8830^0	163 825	0.05

TABLE B Calculation of α_{CuM}

$$\alpha_{CuM} = \frac{I_{Cu(1)}C_{Cu(2)} - I_{Cu(2)}C_{Cu(1)}}{I_{Cu(2)}C_{Cu(1)}C_{M(2)} - I_{Cu(1)}C_{Cu(2)}C_{M(1)}}$$

Solutions	α_{CuM}
LA-1/LA-7	- 0.9338·····
LA-1/LA-6	- 0.9258·····
LA-2/LA-7	- 0.9228·····
LA-2/LA-6	- 0.9230·····
LA-3/LA-7	- 0.9242·····

α_{CuM} average = - 0.9259····

std. devn. = ± 0.0045····

α_{CuM} = $-0.925^9 \pm 0.004^6$

= - 0.926 ± 0.005

TABLE C Calculation of $I_{CuK\alpha}(corr)$ and $I^{o}_{CuK\alpha}$

$$I_{CuK\alpha}(corr) = \underset{(A)}{I_{CuK\alpha}(meas)} - \underset{(B)}{0.925^{9} I_{CuK\alpha}(meas) C_M}$$

$$I^{o}_{CuK\alpha} = I_{CuK\alpha}(corr)/C_{Cu}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{CuK\alpha}$ (cps)
LA-1	30 532	27 987	2 545	254 500
LA-2	54 204	49 184	5 020	251 000
LA-3	74 618	67 016	7 602	253 400
LA-4	104 548	91 961	12 587	251 740
LA-5	127 026	109 380	17 647	252 086
LA-6	152 826	127 351	25 475	254 750
LA-7	163 825	133 938	29 887	255 444

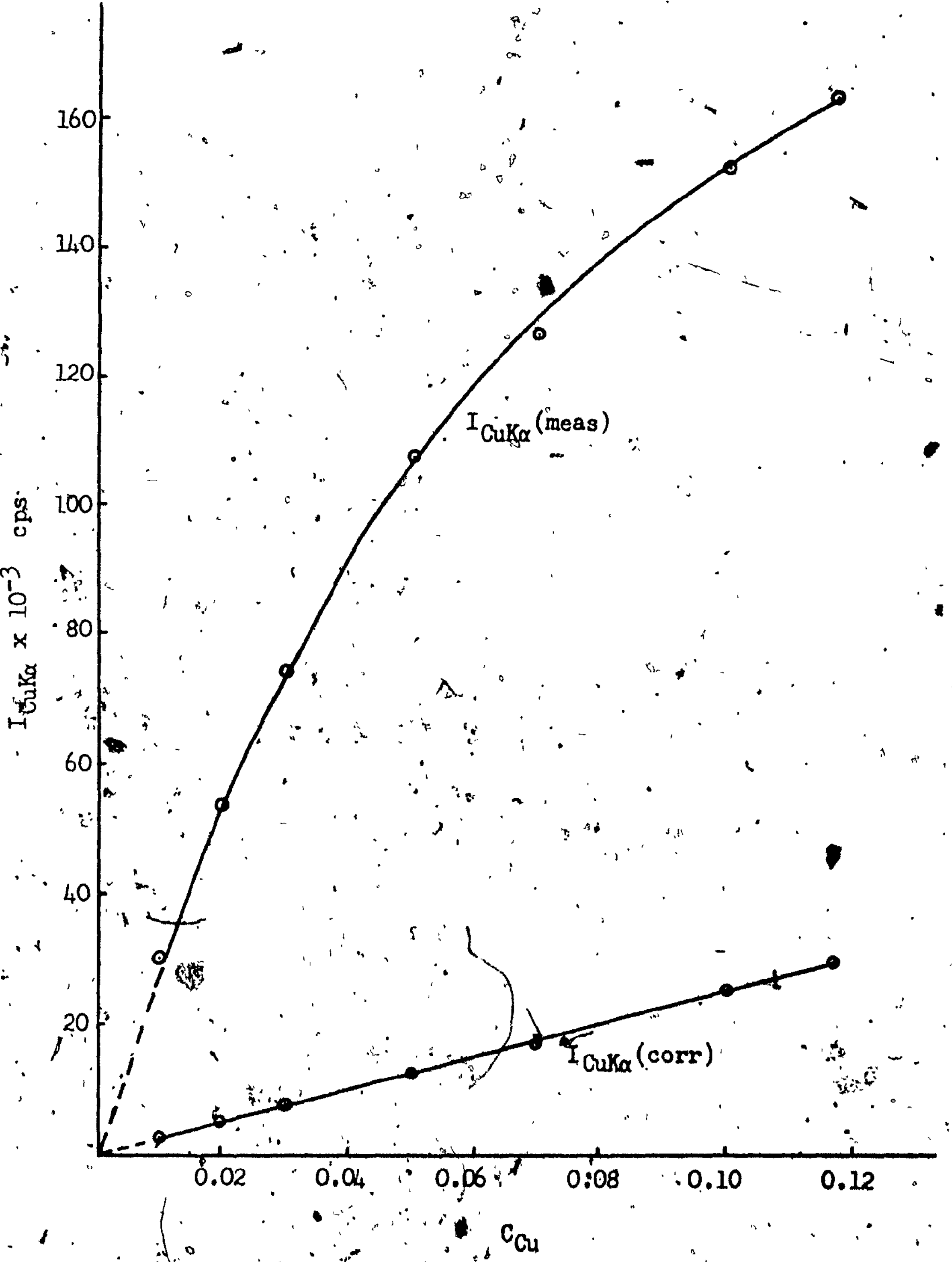
$I^{o}_{CuK\alpha}$ average = 253 274 cps
std. devn. = ± 1 722 cps

$$I^{o}_{CuK\alpha} = (2.53^{2} \pm 0.01^{7}) \times 10^{5} \text{ cps}$$
$$= (2.53 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Cu}(theor)	C_{Cu}(calc)	Abs. error	Rel. error (%)
LA-1	0.01000	0.01000	0.00000	0.00
LA-2	0.02000	0.01980	0.00020	1.00
LA-3	0.0300^{0}	0.0300	0.0000	0.00
LA-4	0.0500^{0}	0.0495	0.0005	1.00
LA-5	0.0700^{0}	0.0694	0.0006	0.85
LA-6	0.1000^{0}	0.1013	0.0013	1.30
LA-7	0.1170^{0}	0.1195	0.0025	2.10

FIGURE D $I_{CuK\alpha}$ versus C_{Cu}



5.1.8 Effect of M on Zn

TABLE A Experimental Parameters (ZnKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.20000 ± 0.00005 g Zn) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Zn given by 1:600 uncertainty, and sets significant figure level at 1:300 to 1:3000 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Zn}	C_M	$I_{ZnK\alpha}$ (cps)	s (%)
LC-1	0.01000	0.99000	46 663	0.11
LC-2	0.02000	0.98000	77 645	0.09
LC-3	0.03000	0.97000	103 824	0.07
LC-4	0.0500^{0}	0.9500^{0}	142 060	0.07
LC-5	0.0700^{0}	0.9300^{0}	169 033	0.06
LC-6	0.1000^{0}	0.9000^{0}	197 136	0.06
LC-7	0.1273^{0}	0.8727^{0}	219 332	0.05

TABLE B Calculation of α_{ZnM}

$$\alpha_{ZnM} = \frac{I_{Zn(1)}C_{Zn(2)} - I_{Zn(2)}C_{Zn(1)}}{I_{Zn(2)}C_{Zn(1)}C_{M(2)} - I_{Zn(1)}C_{Zn(2)}C_{M(1)}}$$

Solutions	α_{ZnM}
LC-1/LC-7	− 0.9446····
LC-1/LC-6	− 0.9471····
LC-2/LC-7	− 0.9384····
LC-2/LC-6	− 0.9411····
LC-3/LC-7	− 0.9376····
LC-1/LC-5	− 0.9484····

α_{ZnM} average = − 0.9429····

std. devn. = ± 0.0045····

$\alpha_{ZnM} = -0.942^{9} \pm 0.004^{5}$

$= -0.943 \pm 0.004$

TABLE C $\underline{\text{Calculation of } I_{ZnK\alpha}(\text{corr}) \text{ and } I^{o}_{ZnK\alpha}}$

$$I_{ZnK\alpha}(\text{corr}) = \underset{(A)}{I_{ZnK\alpha}(\text{meas})} - 0.942^{9}\underset{(B)}{I_{ZnK\alpha}(\text{meas})C_M}$$

$$I^{o}_{ZnK\alpha} = I_{ZnK\alpha}(\text{corr})/C_{Zn}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{ZnK\alpha}$(cps)
LC-1	46 663	43 558	3 104	310 400
LC-2	77 645	71 747	5 898	294 900
LC-3	103 824	94 959	8 865	295 500
LC-4	142 060	127 251	14 809	296 180
LC-5	169 033	148 224	20 808	297 257
LC-6	197 136	167 292	29 844	298 440
LC-7	219 332	180 481	38 850	305 185

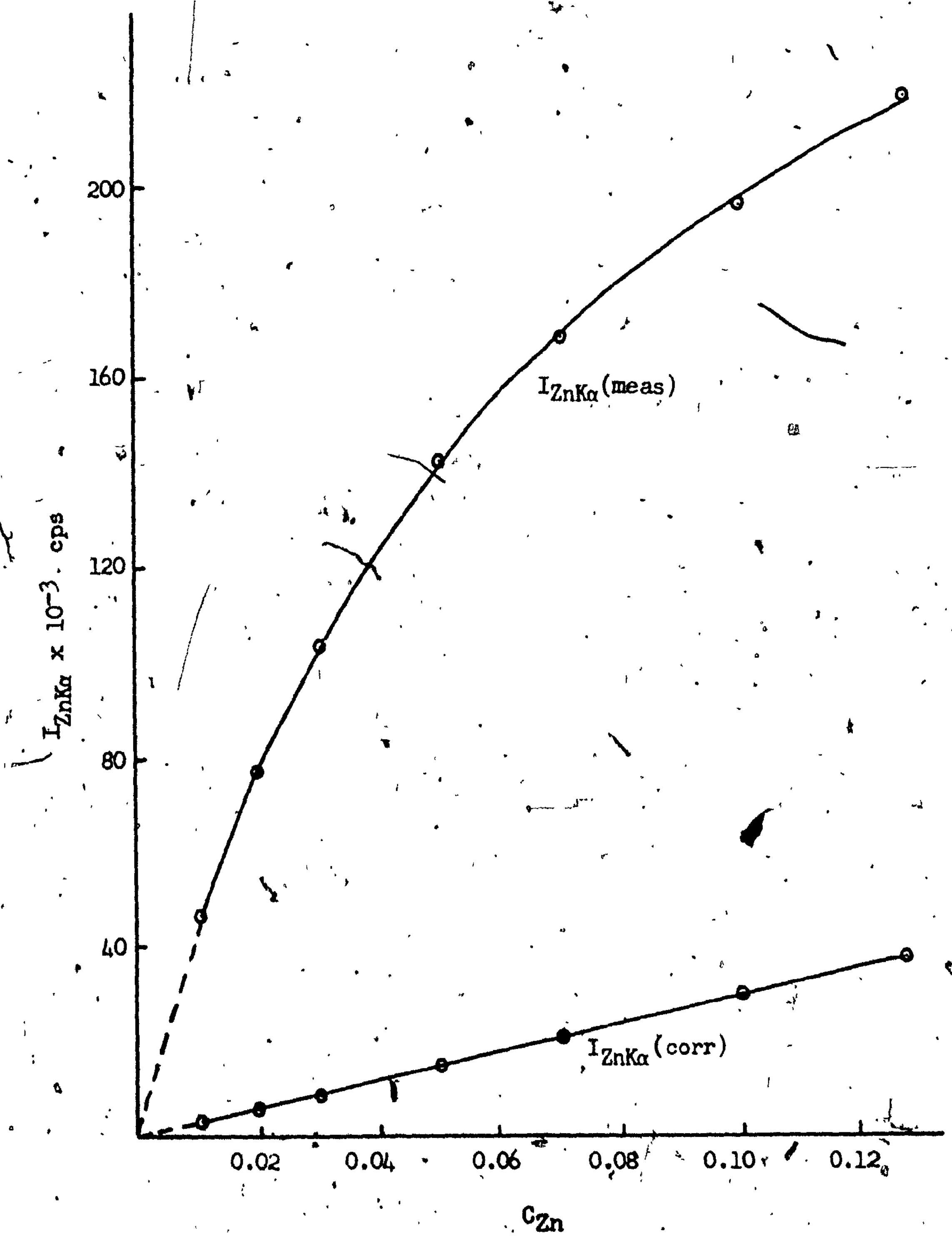
$I^{o}_{ZnK\alpha}$ average = 299 695 cps
std. devn. = ± 5 840 cps

$$I^{o}_{ZnK\alpha} = (2.99^{6} \pm 0.05^{8}) \times 10^{5} \text{ cps}$$
$$= (3.00 \pm 0.06) \times 10^{5} \text{ cps}$$

TABLE D Back-calculation of solution composition

Solution	C_{Zn}(theor)	C_{Zn}(calc)	Abs. error	Rel. error (%)
LC-1	0.01000	0.01040	0.00040	4.00
LC-2	0.02000	0.01960	0.00040	2.00
LC-3	0.03000	0.02940	0.00060	2.00
LC-4	0.0500^{0}	0.0489	0.0011	2.20
LC-5	0.0700^{0}	0.0688	0.0012	1.71
LC-6	0.1000^{0}	0.0989	0.0011	1.10
LC-7	0.1273^{0}	0.1348	0.0075	5.89

FIGURE D $I_{ZnK\alpha}$ versus C_{Zn}



5.1.9 Effect of M on Cd

TABLE A Experimental Parameters (CdKα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.200000 ± 0.000004 g Cd) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Cd given by 1:600 uncertainty, and sets significant figure level of 1:300 to 1:3000 for all values.

Intensity: W-target, 40kV, 20mA, fine collimation, LiF crystal, scin. counter, 10 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Cd}	C_M	$I_{CdK\alpha}$ (cps)	s (%)
C-1	0.00477^5	0.99522^5	5 625	0.41
C-2	0.00951^9	0.99048^1	10 194	0.32
C-3	0.01417^2	0.98582^8	13 528	0.26
C-4	0.01885^3	0.98114^7	16 708	0.26
C-5	0.02805^8	0.97194^2	21 109	0.22
C-6	0.0371^2	0.9628^8	24 589	0.20
C-7	0.0458^4	0.9541^6	26 881	0.20
C-8	0.0540^6	0.9459^4	28 714	0.18
C-9	0.0700^4	0.9299^6	31 856	0.18
C-10	0.0859^6	0.9140^4	33 778	0.17

TABLE B Calculation of α_{CdM}

$$\alpha_{CdM} = \frac{I_{Cd(1)}C_{Cd(2)} - I_{Cd(2)}C_{Cd(1)}}{I_{Cd(2)}C_{Cd(1)}C_{M(2)} - I_{Cd(1)}C_{Cd(2)}C_{M(1)}}$$

Solutions	α_{CdM}
C-1/C-10	- 0.96542···
C-1/C-9	- 0.96504···
C-1/C-8	- 0.96558···
C-2/C-10	- 0.96638···
C-2/C-9	- 0.96604···
C-2/C-8	- 0.96683···
C-3/C-10	- 0.96519···
C-3/C-9	- 0.96462···
C-3/C-8	- 0.96537···

α_{CdM} average = - 0.96561···
std. devn. = ± 0.00069···
α_{CdM} = $- 0.965^6 \pm 0.000^7$
- 0.966 ± 0.001

TABLE C **Calculation of $I_{CdK\alpha}(\text{corr})$ and $I^{o}_{CdK\alpha}$**

$$I_{CdK\alpha}(\text{corr}) = \underset{(A)}{I_{CdK\alpha}(\text{meas})} - \underset{(B)}{0.965^{6} I_{CdK\alpha}(\text{meas}) C_M}$$

$$I^{o}_{CdK\alpha} = I_{CdK\alpha}(\text{corr})/C_{Cd}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{CdK\alpha}$ (cps)
C-1	5 625	5 405	220	46 073
C-2	10 194	9 750	444	46 643
C-3	13 528	12 878	650	45 865
C-4	16 708	15 829	879	46 624
C-5	21 109	19 811	1 298	46 261
C-6	24 589	22 862	1 727	46 528
C-7	26 881	24 766	2 115	46 144
C-8	28 714	26 227	2 487	46 005
C-9	31 856	28 606	3 250	46 402
C-10	33 778	29 812	3 966	46 139

$I^{o}_{CdK\alpha}$ average = 46 268 cps

std. devn. = ± 270 cps

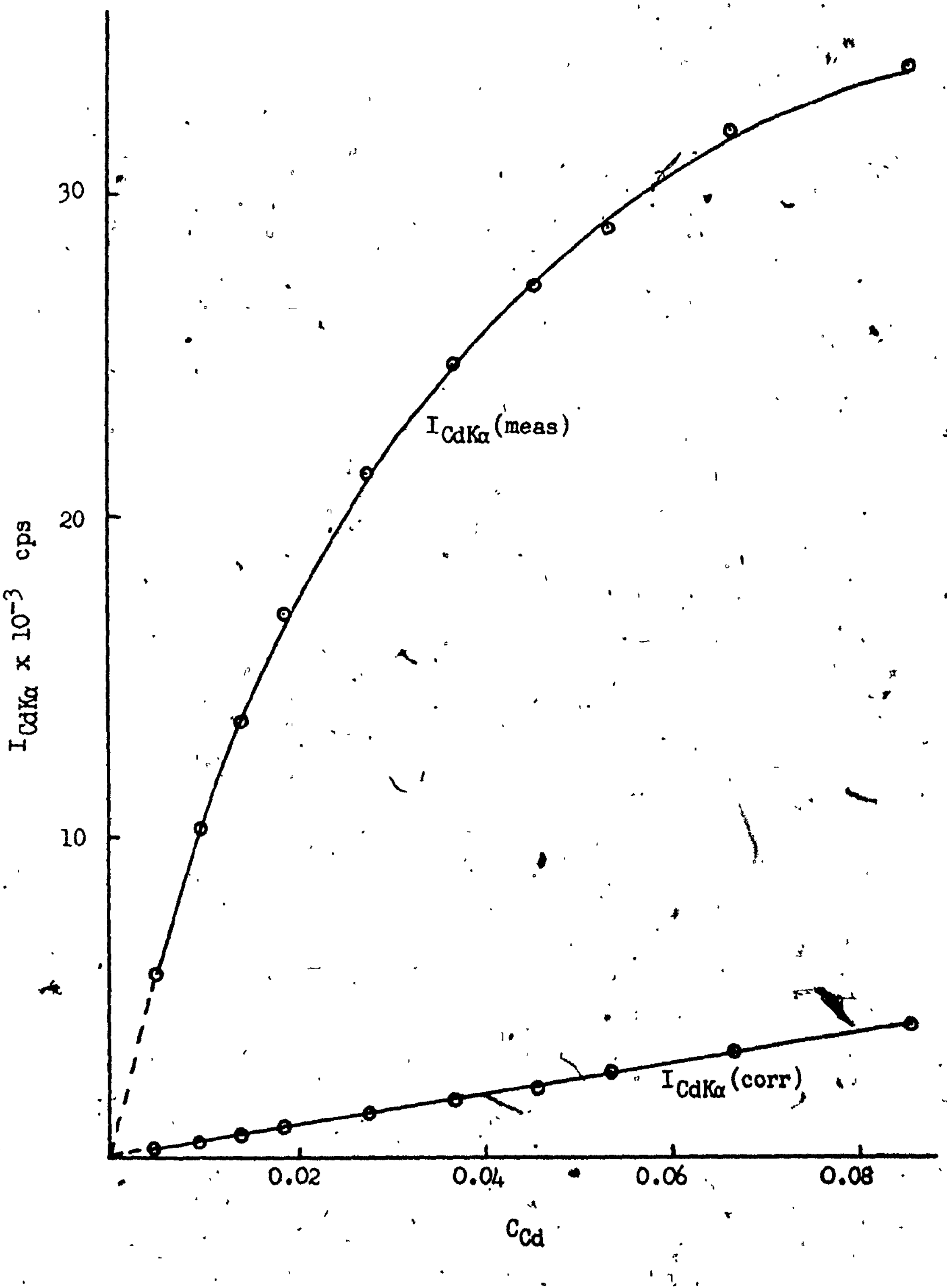
$$I^{o}_{CdK\alpha} = (4.62^{6} \pm 0.02^{7}) \times 10^{4} \text{ cps}$$

$$= (4.63 \pm 0.03) \times 10^{4} \text{ cps}$$

TABLE D **Back-calculation of solution composition**

Solution	C_{Cd}(theor)	C_{Cd}(calc)	Abs. error	Rel. error (%)
C-1	0.00477^{5}	0.00474	0.00003^{5}	0.73
C-2	0.00951^{9}	0.00963	0.00011^{9}	1.25
C-3	0.01417^{2}	0.01402	0.00014^{6}	1.03
C-4	0.01885^{3}	0.01908	0.00022^{7}	1.20
C-5	0.02805^{8}	0.02806	0.00000^{2}	0.01
C-6	0.0371^{2}	0.0376	0.0004^{8}	1.29
C-7	0.0458^{4}	0.0455	0.0003^{4}	0.74
C-8	0.0540^{6}	0.0533	0.0007^{6}	1.40
C-9	0.0700^{4}	0.0707	0.0006^{6}	0.94
C-10	0.0859^{6}	0.0851	0.0008^{6}	1.00

FIGURE D $I_{CdK\alpha}$ versus C_{Cd}



5.1.10 Effect of M on Sn

TABLE A Experimental Parameters (SnKα Radiation)

Solutions: Prepared by dilution of stock solution in HF (1 ml = 0.10000 ± 0.00004 g Sn) with H_2O. Exact final weight of solution determined. Least precise value for Sn given by 1:400 uncertainty, and sets significant figure level of 1:200 to 1:2000 for all values.

Intensity: W-target, 50kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Sn}	C_M	$I_{SnK\alpha}$ (cps)	s (%)
LZF-1	0.01000	0.99000	20 326	0.16
LZF-2	0.02000	0.98000	34 356	0.12
LZF-3	0.0300^0	0.9700^0	44 552	0.11
LZF-4	0.0500^0	0.9500^0	59 761	0.10
LZF-5	0.0700^0	0.9300^0	70 895	0.09
LZF-6	0.0833^0	0.9167^0	73 410	0.09

TABLE B Calculation of α_{SnM}

$$\alpha_{SnM} = \frac{I_{Sn(1)}C_{Sn(2)} - I_{Sn(2)}C_{Sn(1)}}{I_{Sn(2)}C_{Sn(1)}C_{M(2)} - I_{Sn(1)}C_{Sn(2)}C_{M(1)}}$$

Solutions	α_{SnM}
LZF-1/LZF-6	- 0.95592···
LZF-1/LZF-5	- 0.95276···
LZF-1/LZF-4	- 0.95502···
LZF-2/LZF-6	- 0.95540···
LZF-2/LZF-5	- 0.95073···
LZF-3/LZF-6	- 0.95438···

α_{SnM} average = - 0.95403···

std. devn. = ± 0.00195···

$$\alpha_{SnM} = -0.954^0 \pm 0.001^9$$
$$= -0.954 \pm 0.002$$

TABLE C Calculation of $I_{SnK\alpha}(\text{corr})$ and $I^{o}_{SnK\alpha}$

$$I_{SnK\alpha}(\text{corr}) = \underset{(A)}{I_{SnK\alpha}(\text{meas})} - 0.954^{0}\underset{(B)}{I_{SnK\alpha}(\text{meas})}C_M$$

$$I^{o}_{SnK\alpha} = I_{SnK\alpha}(\text{corr})/C_{Sn}$$

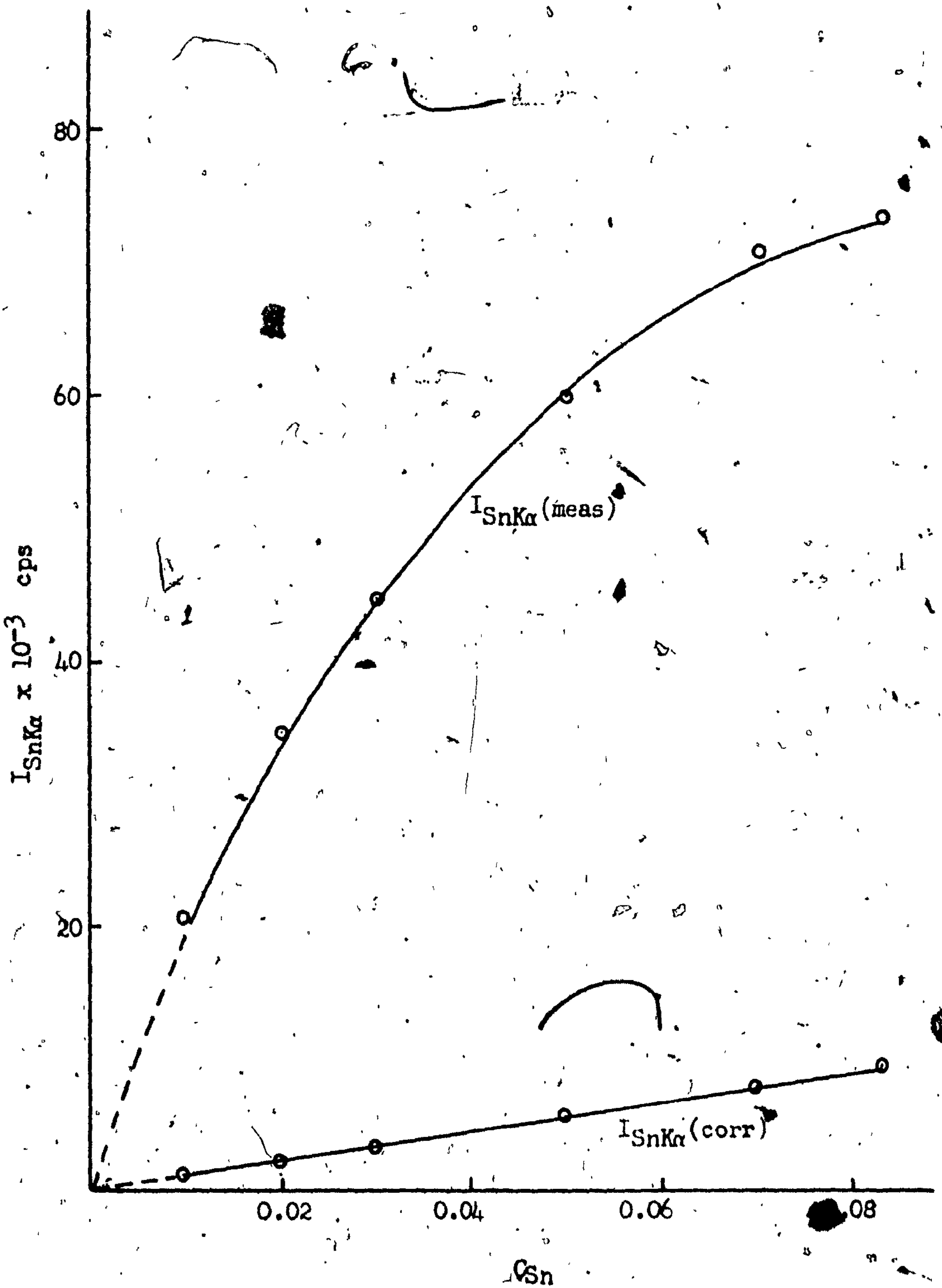
Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{SnK\alpha}$ (cps)
LZF-1	20 326	19 197	1 129	112 891
LZF-2	34 356	32 120	2 236	111 794
LZF-3	44 552	41 227	3 324	110 816
LZF-4	59 761	54 161	5 599	111 992
LZF-5	70 895	62 899	7 995	114 222
LZF-6	73 410	64 199	9 211	110 572

$I^{o}_{SnK\alpha}$ average = 112 048 cps
std. devn. = ± 1 356 cps
$I^{o}_{SnK\alpha} = (1.12^{0} \pm 0.01^{3}) \times 10^{5}$ cps
$= (1.12 \pm 0.01) \times 10^{5}$ cps

TABLE D Back-calculation of solution composition

Solution	C_{Sn}(theor)	C_{Sn}(calc)	Abs. error	Rel. error (%)
LZF-1	0.01000	0.01010	0.00010	1.00
LZF-2	0.02000	0.01990	0.00010	0.50
LZF-3	0.0300^{0}	0.0295	0.0005	1.67
LZF-4	0.0500^{0}	0.0499	0.0001	0.20
LZF-5	0.0700^{0}	0.0734	0.0034	4.86
LZF-6	0.0833^{0}	0.0804	0.0029	3.48

FIGURE D $I_{SnK\alpha}$ versus C_{Sn}



5.1.11 Effect of M on Pb

TABLE A Experimental Parameters (PbLα Radiation)

Solutions: Prepared by dilution of stock solution (1 ml = 0.20000 ± 0.00005 g Pb) with H_2O-HNO_3. Exact final weight of solution determined. Least precise value for Pb given by 1:700 uncertainty, and sets significant figure level of 1:350 to 1:3500 for all values.

Intensity: W-target, 50kV, 20mA, fine collimation, LiF crystal, scin. counter, 20 second counting. All counts corrected for background, and for deadtime where required. Averaging of 5 counts. Sigma counting error in percent shown as s.

Solution	C_{Pb}	C_M	$I_{PbL\alpha}$ (cps)	s (%)
LN-1	0.01000	0.99000	13 971	0.18
LN-2	0.02000	0.98000	22 129	0.15
LN-3	0.0500^{0}	0.9500^{0}	34 970	0.12
LN-4	0.0800^{0}	0.9200^{0}	40 684	0.11
LN-5	0.1000^{0}	0.9000^{0}	43 468	0.10
LN-6	0.1200^{0}	0.8800^{0}	45 104	0.10

TABLE B Calculation of α_{PbM}

$$\alpha_{PbM} = \frac{I_{Pb(1)}C_{Pb(2)} - I_{Pb(2)}C_{Pb(1)}}{I_{Pb(2)}C_{Pb(1)}C_{M(2)} - I_{Pb(1)}C_{Pb(2)}C_{M(1)}}$$

Solutions	α_{PbM}
LN-1/LN-6	- 0.9704·····
LN-1/LN-5	- 0.9702·····
LN-1/LN-4	- 0.9708·····
LN-2/LN-6	- 0.9695·····
LN-2/LN-5	- 0.9692·····
LN-3/LN-6	- 0.9696·····

α_{PbM} average = - 0.9699····

std. devn. = ± 0.0006····

α_{PbM} = - 0.9699 ± 0.0006

TABLE C Calculation of $I_{PbL\alpha}(\text{corr})$ and $I^{o}_{PbL\alpha}$

$$I_{PbL\alpha}(\text{corr}) = \underset{(A)}{I_{PbL\alpha}(\text{meas})} - 0.9699\underset{(B)}{I_{PbL\alpha}(\text{meas})C_M}$$

$$I^{o}_{PbL\alpha} = I_{PbL\alpha}(\text{corr})/C_{Pb}$$

Solution	A (cps)	B (cps)	(A)-(B) (cps)	$I^{o}_{PbL\alpha}$ (cps)
LN-1	13 971	13 415	556	55 603
LN-2	22 129	21 034	1 095	54 767
LN-3	34 970	32 221	2 748	54 969
LN-4	40 684	36 303	4 381	54 767
LN-5	43 468	37 944	5 524	55 243
LN-6	45 104	38 497	6 607	55 060

$I^{o}_{PbL\alpha}$ average = 55 068 cps

std. devn. = ± 319 cps

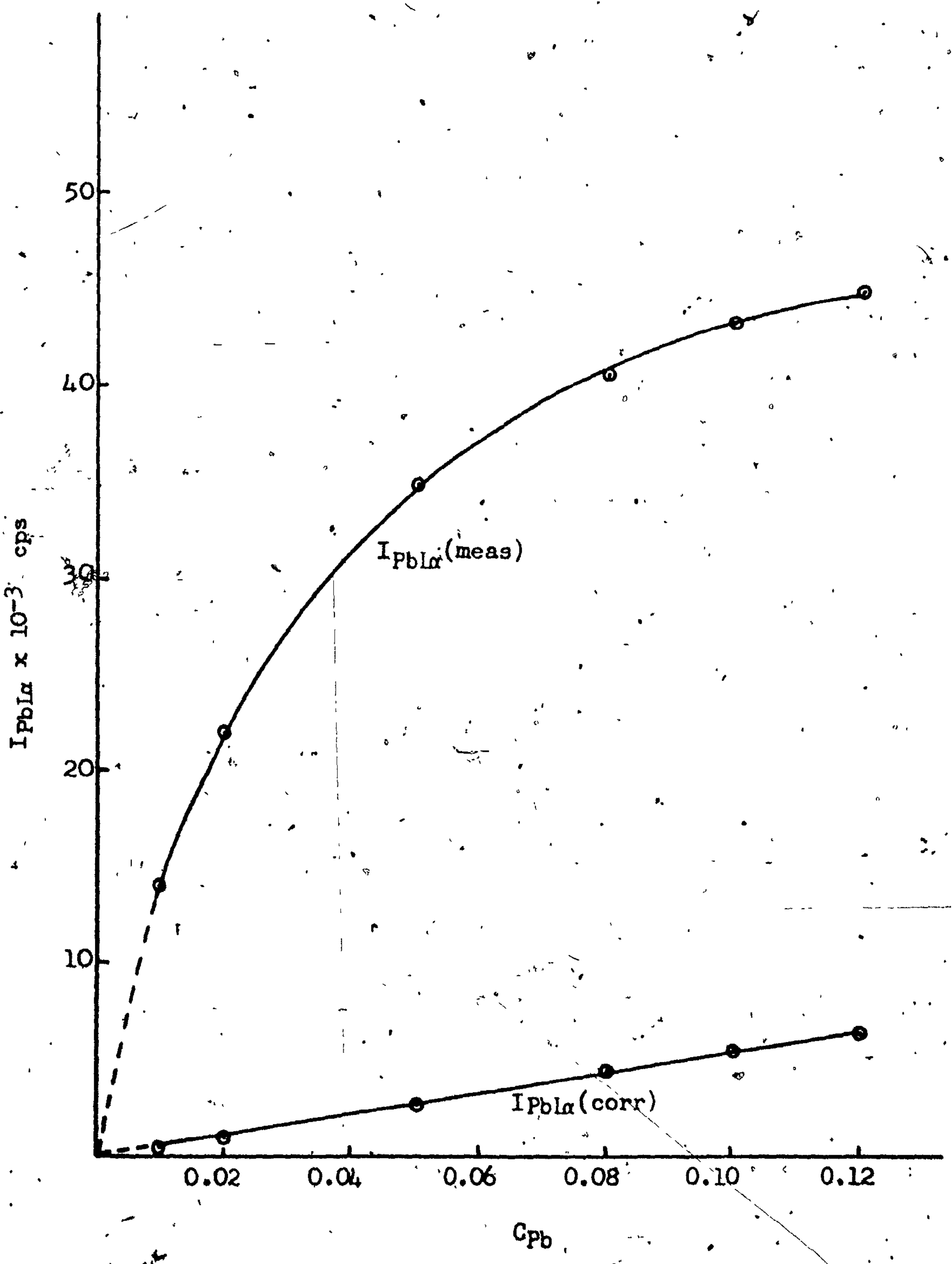
$I^{o}_{PbL\alpha}$ = $(5.50^{6} \pm 0.03^{1}) \times 10^{4}$ cps

= $(5.51 \pm 0.03) \times 10^{4}$ cps

TABLE D Back-calculation of solution composition

Solution	C_{Pb}(theor)	C_{Pb}(calc)	Abs. error	Rel. error (%)
LN-1	0.01000	0.01010	0.00010	1.00
LN-2	0.02000	0.01980	0.00020	1.00
LN-3	0.0500^{0}	0.0498	0.0002	0.40
LN-4	0.0800^{0}	0.0784	0.0016	2.00
LN-5	0.1000^{0}	0.1014	0.0014	1.40
LN-6	0.1200^{0}	0.1199	0.0001	0.08

FIGURE D. $I_{PbL\alpha}$ versus C_{Pb}



5.2 Effects of Chlorine

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Chromium 1 ml = 0.10000 ± 0.00005 g (dil. HNO_3)
Manganese 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Iron 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Cobalt 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Nickel 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Copper 1 ml = 0.200000 ± 0.000004 g (dil. HNO_3)
Zinc 1 ml = 0.200000 ± 0.000005 g (dil. HNO_3)
Cadmium 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)
Tin 1 ml = 0.20000 ± 0.00005 g (dil. $HCl-HNO_3$)
Lead 1 ml = 0.10000 ± 0.00002 g (dil. HNO_3)

For all solution series, except that involving lead, the chlorine was added as approximately 12N HCl. Determination of chloride was obtained through potentiometric titration of the final solution with standard $AGNO_3$ solution. For the lead solution series, chlorine was added as approximately 70 percent $HClO_4$, and determined by titration with standard NaOH solution with corrections for the amounts of HNO_3 and Pb(II).

The exact final weight of each solution was determined.

The least precise value for Cl determination, in each case, set the significant figure level for all values in the series. These were:-

Metal	Series	Uncertainty in Cl	Sig. figure level
Cr	KE	1:270	1:135 to 1:1350
Mn	LG	1:320	1:160 to 1:1600
Fe	HH	1:320	1:160 to 1:1600
Co	LJ	1:240	1:120 to 1:1200
Ni	LH	1:200	1:100 to 1:1000
Cu	LB	1:340	1:170 to 1:1700
Zn	LD	1:340	1:170 to 1:1700
Cd	LE	1:340	1:170 to 1:1700
Sn	LM	1:260	1:130 to 1:1300
Pb	LZA	1:120	1:60 to 1:600

Intensities: The operating parameters for each solution series were as given below:-

Metal	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Sn	Pb
Target	W	W	W	W	W	W	W	W	W	W
kV	40	40	40	40	40	40	40	40	50	50
mA	20	20	20	20	20	20	20	20	20	20
Coll^n	fine	fine	fine	fine	fine	fine	fine	fine	fine	fine
Crystal	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20	20	20
Counts	5	5	5	5	5	5	5	5	5	5
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Lα

The tabulated counts for each series represented averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent..

Equations: Calculation of α_{ACl} Equation (39)

Calculation of $I_A(corr)$ Equation (40)

Calculation of I_A^o $I_A(corr)/C_A$

5.2.1 Effect of Cl on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Cl}	C_M	$I_{CrK\alpha}$ (cps)	s(%)
KE-1	0.01000	0.00	0.99000	3 383	0.39
KE-2	0.01000	0.01015	0.97985	3 106	0.40
KE-3	0.01000	0.0202^3	0.9697^7	2 915	0.41
KE-4	0.01000	0.0379^3	0.9520^7	2 485	0.45
KE-5	0.01000	0.0762^4	0.9137^6	2 059	0.50
KE-6	0.01000	0.1170^0	0.8730^0	1 732	0.54
KE-7	0.01000	0.1512^1	0.8387^9	1 504	0.56
KE-8	0.01000	0.189^5	0.800^5	1 342	0.63

TABLE B Calculation of α_{CrCl}

Solutions	α_{CrCl}
KE-1/KE-8	0.4480..
KE-1/KE-7	0.4863..
KE-2/KE-8	0.4315..
KE-2/KE-7	0.4736..
KE-3/KE-8	0.4529..
KE-3/KE-7	0.5056..

α_{CrCl} average = 0.4663...

std. devn. = ± 0.027....

$$\alpha_{CrCl} = 0.46^6 \pm 0.02^7$$

$$= 0.47 \pm 0.03$$

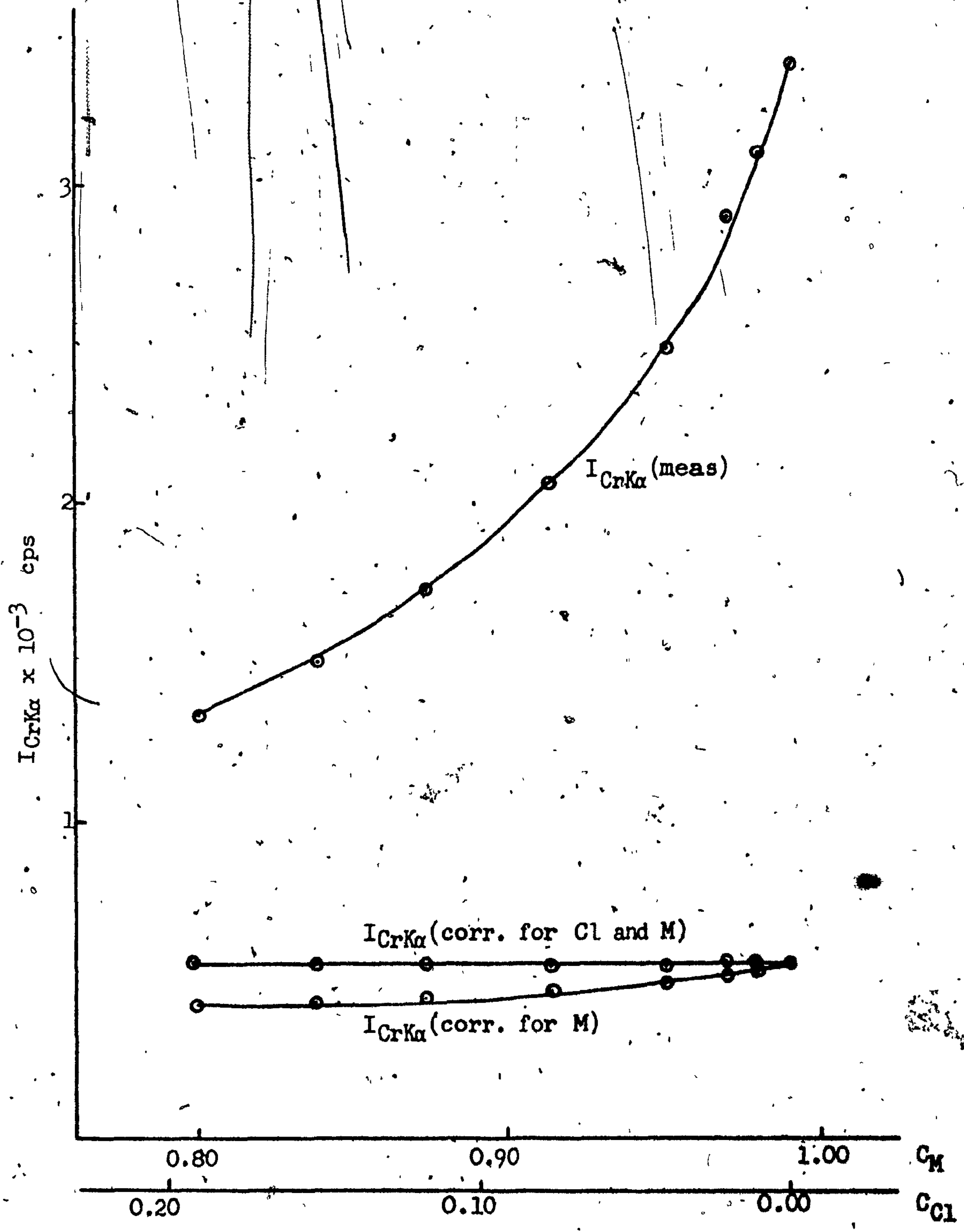
TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^o_{CrK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{CrK\alpha}$(corr) (cps)
KE-1	3 383	- 2 837	--	546
KE-2	3 106	- 2 578	+ 15	543
KE-3	2 915	- 2 395	+ 27	547
KE-4	2 485	- 2 004	+ 44	525
KE-5	2 059	- 1 594	+ 73	538
KE-6	1 732	- 1 281	+ 94	545
KE-7	1 504	- 1 069	+ 106	541
KE-8	1 342	- 910	+ 118	550

$I^{o}_{CrK\alpha}$ average = 54 200 cps
std. devn. = ± 791 cps

$$I^{o}_{CrK\alpha} = (5.42^{0} \pm 0.07^{9}) \times 10^{4}\ \text{cps}$$
$$= (5.42 \pm 0.08) \times 10^{4}\ \text{cps}$$

FIGURE D $I_{CrK\alpha}$ versus C_{Cl} and C_M



5.2.2 Effect of Cl on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Cl}	C_M	$I_{MnK\alpha}$ (cps)	s (%)
LG-1	0.01000	0.00	0.99000	6 663	0.26
LG-2	0.01000	0.0390	0.9510	4 996	0.32
LG-3	0.01000	0.0787	0.9113	3 998	0.35
LG-4	0.01000	0.1216	0.8684	3 346	0.40
LG-5	0.01000	0.163^0	0.827^0	2 882	0.43
LG-6	0.01000	0.198^1	0.791^9	2 529	0.45

TABLE B Calculation of α_{MnCl}

Solutions	α_{MnCl}
LG-1/LG-6	0.3301····
LG-1/LG-5	0.3002····
LG-2/LG-6	0.3025····
LG-2/LG-5	0.2482····
LG-3/LG-6	0.2777····

α_{MnCl} average = 0.2917····
std. devn. = ± 0.0306····

$\alpha_{MnCl} = 0.29^2 \pm 0.03^0$
$= 0.29 \pm 0.03$

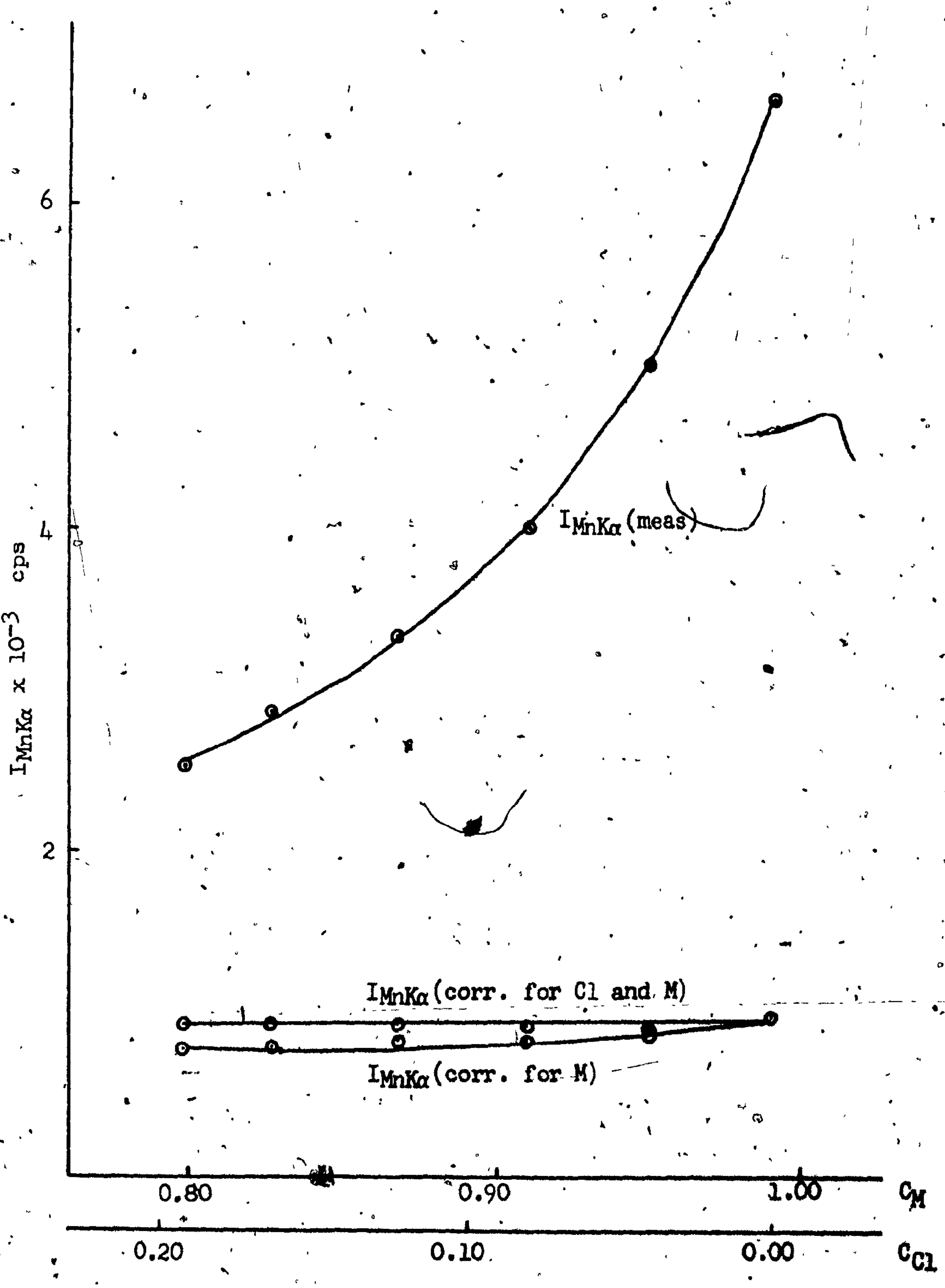
TABLE C Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{MnK\alpha}$(corr) (cps)
LG-1	6 663	- 5 697	--	966
LG-2	4 996	- 4 104	+ 57	949
LG-3	3 998	- 3 147	+ 92	943
LG-4	3 346	- 2 510	+ 119	955
LG-5	2 882	- 2 058	+ 137	960
LG-6	2 529	- 1 730	+ 146	945

$I^{o}_{MnK\alpha}$ average = 95 300 cps
std. devn. = ± 897 cps

$I^{o}_{MnK\alpha} = (9.53^0 \pm 0.08^9) \times 10^4$ cps
$= (9.53 \pm 0.09) \times 10^4$ cps

FIGURE D $I_{MnK\alpha}$ versus C_{Cl} and C_M



5.2.3 Effect of Cl on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s (%)
HH-1	0.01000	0.00	0.99000	11 456	0.20
HH-2	0.01000	0.0199	0.9701	9 824	0.22
HH-3	0.01000	0.0397	0.9503	8 643	0.22
HH-4	0.01000	0.0790	0.9110	6 878	0.26
HH-5	0.01000	0.1198	0.8702	5 716	0.32
HH-6	0.01000	0.1620	0.8280	4 858	0.32
HH-7	0.01000	0.2000	0.7900	4 307	0.33
HH-8	0.01000	0.2390	0.7510	3 803	0.35

TABLE B Calculation of α_{FeCl}

Solutions	α_{FeCl}
HH-1/HH-8	0.04857··
HH-1/HH-7	0.03504··
HH-1/HH-6	0.04452··
HH-2/HH-8	0.05203··
HH-2/HH-7	0.03475··
HH-3/HH-8	0.06779··
HH-3/HH-7	0.04704··

α_{FeCl} average = 0.04710···
std. devn. = ± 0.01125···
α_{FeCl} = 0.047 ± 0.01^1
= 0.05 ± 0.01

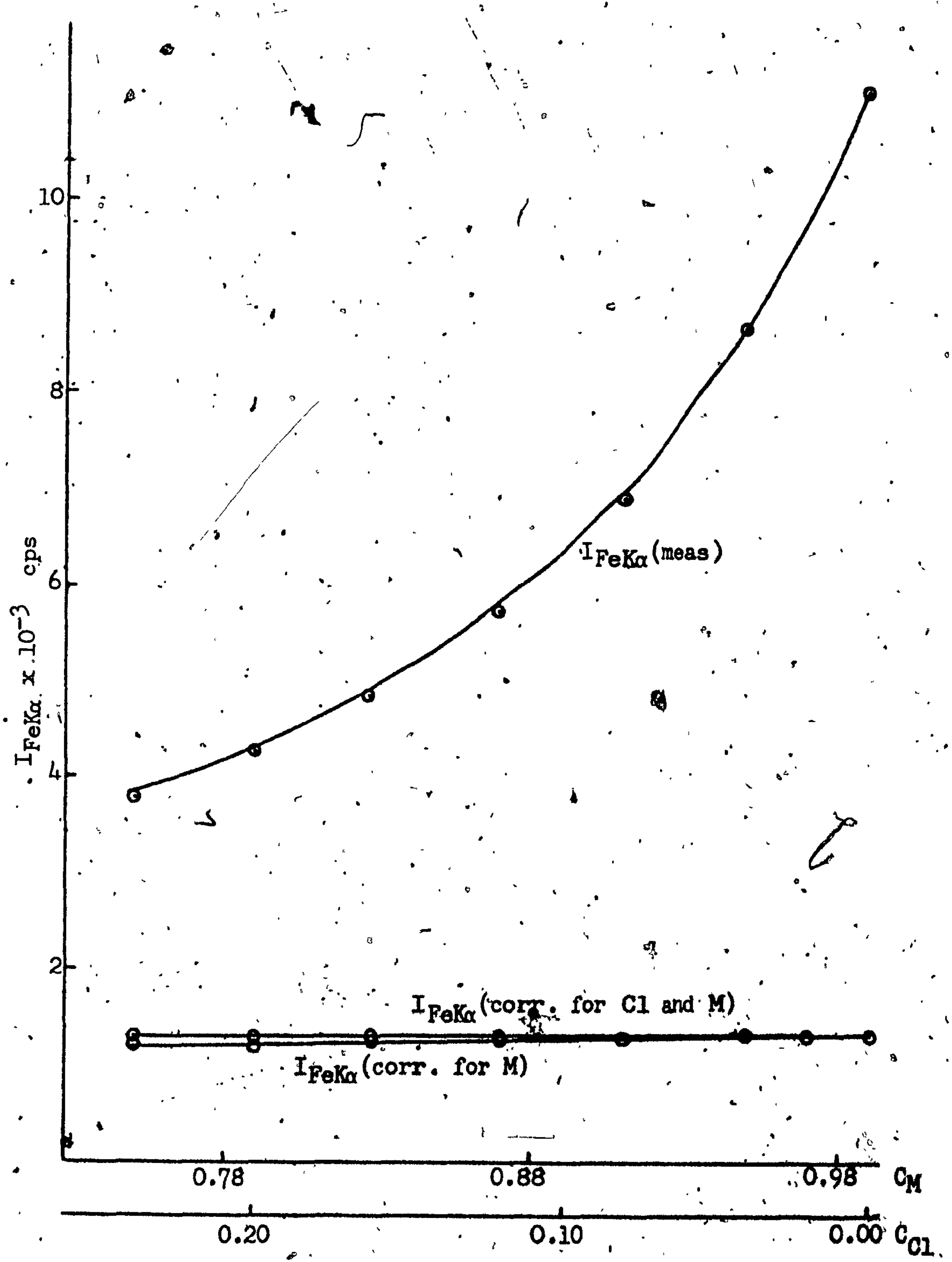
TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^o_{FeK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{FeK\alpha}$(corr) (cps)
HH-1	11 456	- 10 170	--	1 286
HH-2	9 824	- 8 545	+ 9	1 286
HH-3	8 643	- 7 363	+ 16	1 296
HH-4	6 878	- 5 618	+ 21	1 280
HH-5	5 716	- 4 459	+ 32	1 289
HH-6	4 858	- 3 607	+ 37	1 288
HH-7	4 307	- 3 051	+ 40	1 296
HH-8	3 803	- 2 561	+ 43	1 285

$I^o_{FeK\alpha}$ average = 128 825 cps
std. devn. = ± 547 cps

$I^o_{FeK\alpha}$ = (1.288 ± 0.005) x 10^5 cps

FIGURE D $I_{FeK\alpha}$ versus C_{Cl} and C_M



5.2.4 Effect of Cl on Co

TABLE A Experimental Parameters

Solution	C_{Co}	C_{Cl}	C_M	$I_{CoK\alpha}$ (cps)	s (%)
LJ-1	0.01000	0.00	0.99000	22 080	0.15
LJ-2	0.01000	0.0407	0.9493	16 301	0.18
LJ-3	0.01000	0.0815	0.9085	12 711	0.20
LJ-4	0.01000	0.122^4	0.867^6	10 811	0.22
LJ-5	0.01000	0.160^0	0.830^0	9 289	0.24
LJ-6	0.01000	0.198^1	0.791^9	8 097	0.25

TABLE B Calculation of α_{CoCl}

Solutions	α_{CoCl}
LJ-1/LJ-6	- 0.1647...
LJ-1/LJ-5	- 0.1732...
LJ-1/LJ-4	- 0.1822...
LJ-2/LJ-6	- 0.1642...
LJ-2/LJ-5	- 0.1796...

α_{CoCl} average = - 0.1726...
std. devn. = ± 0.0083...

$$\alpha_{CoCl} = -0.172^6 \pm 0.008^3$$
$$= -0.173 \pm 0.008$$

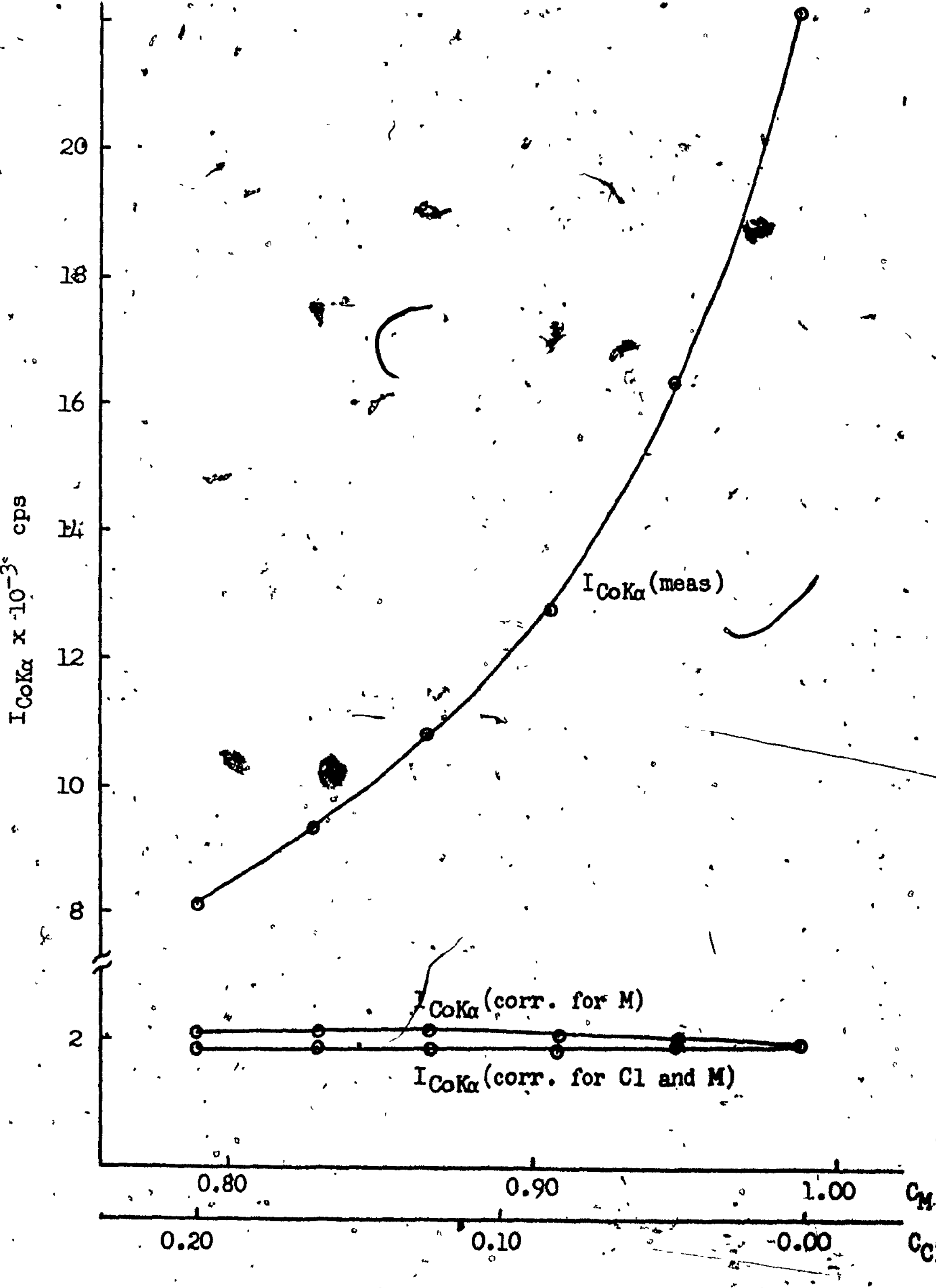
TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^o_{CoK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{CoK\alpha}$(corr) (cps)
LJ-1	22 080	- 20 161	--	1 919
LJ-2	16 301	- 14 272	- 115	1 914
LJ-3	12 711	- 10 651	- 179	1 881
LJ-4	10 811	- 8 651	- 229	1 931
LJ-5	9 289	- 7 112	- 257	1 920
LJ-6	8 097	- 5 914	- 277	1 906

$I^o_{CoK\alpha}$ average = 191 183 cps
std. devn. = ± 1 718 cps

$$I^o_{CoK\alpha} = (1.91^1 \pm 0.01^7) \times 10^5 \text{ cps}$$
$$= (1.91 \pm 0.02) \times 10^5 \text{ cps}$$

FIGURE D. $I_{CoK\alpha}$ versus C_{Cl} and C_M



5.2.5 Effect of Cl on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Cl}	C_M	$I_{NiK\alpha}$ (cps)	s (%)
LH-1	0.01000	0.00344	0.98656	33 690	0.13
LH-2	0.01000	0.0448	0.9452	25 226	0.14
LH-3	0.01000	0.0858	0.9042	20 870	0.16
LH-4	0.01000	0.126^{8}	0.863^{2}	17 065	0.17
LH-5	0.01000	0.168^{5}	0.821^{5}	14 568	0.18
LH-6	0.01000	0.208^{3}	0.781^{7}	12 664	0.20

TABLE B Calculation of α_{NiCl}

Solutions	α_{NiCl}
LH-1/LH-6	- 0.1495····
LH-1/LH-5	- 0.1643····
LH-1/LH-4	- 0.1697····
LH-2/LH-6	- 0.1500····
LH-2/LH-5	- 0.1763····

α_{NiCl} average = - 0.16196···
std. devn. = ± 0.0119····

α_{NiCl} = $-0.16^{2} \pm 0.01^{2}$
= -0.16 ± 0.01

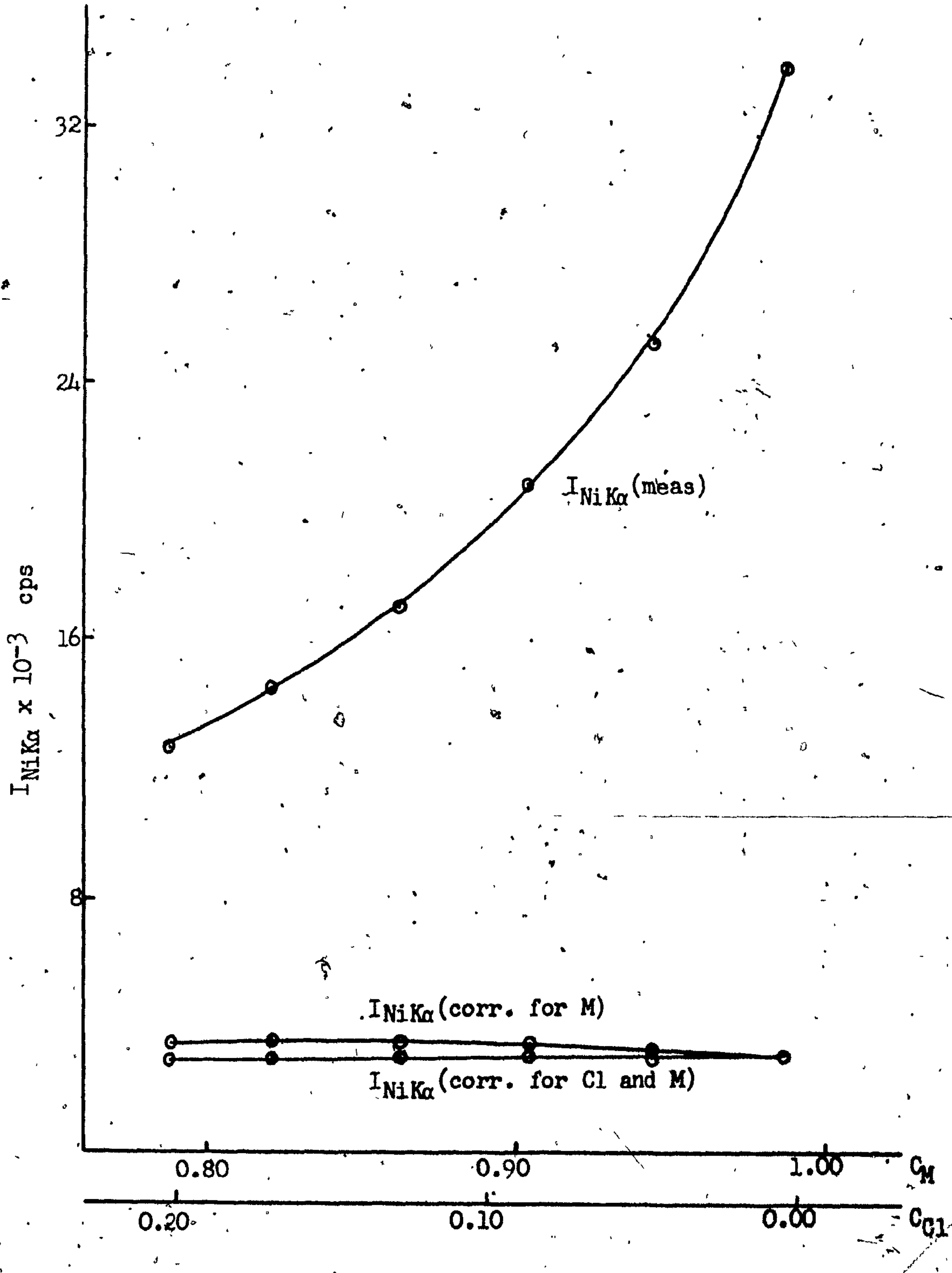
TABLE C Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{NiK\alpha}$(corr) (cps)
LH-1	33 690	- 30 842	-18	3 190
LH-2	25 226	- 21 867	- 183	3 176
LH-3	20 870	- 17 306	- 290	3 274
LH-4	17 065	- 13 509	- 350	3 205
LH-5	14 568	- 10 975	- 398	3 194
LH-6	12 664	- 9 079	- 427	3 158

$I^{o}_{NiK\alpha}$ average = 319 950 cps
std. devn. = ± 3 990 cps

$I^{o}_{NiK\alpha}$ = $(3.19^{9} \pm 0.03^{9}) \times 10^{5}$ cps
= $(3.20 \pm 0.04) \times 10^{5}$ cps

FIGURE D $I_{NiK\alpha}$ versus C_{Cl} and C_M



5.2.6 Effect of Cl on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Cl}	C_M	$I_{CuK\alpha}$ (cps)	s (%)
LB-1	0.01000	0.00	0.99000	30 579	0.13
LB-2	0.01000	0.0396	0.9504	23 098	0.15
LB-3	0.01000	0.0793	0.9107	18 326	0.17
LB-4	0.01000	0.1207	0.8693	15 244	0.18
LB-5	0.01000	0.1595	0.8305	13 176	0.20
LB-6	0.01000	0.205^2	0.784^8	11 613	0.21

TABLE B Calculation of α_{CuCl}

Solutions	α_{CuCl}
LB-1/LB-6	- 0.26245···
LB-1/LB-5	- 0.23564···
LB-2/LB-6	- 0.27385···
LB-2/LB-5	- 0.22908···

α_{CuCl} average = - 0.25026···
std. devn. = ± 0.0213···

$\alpha_{CuCl} = -0.25^0 \pm 0.02^1$
$= -0.25 \pm 0.02$

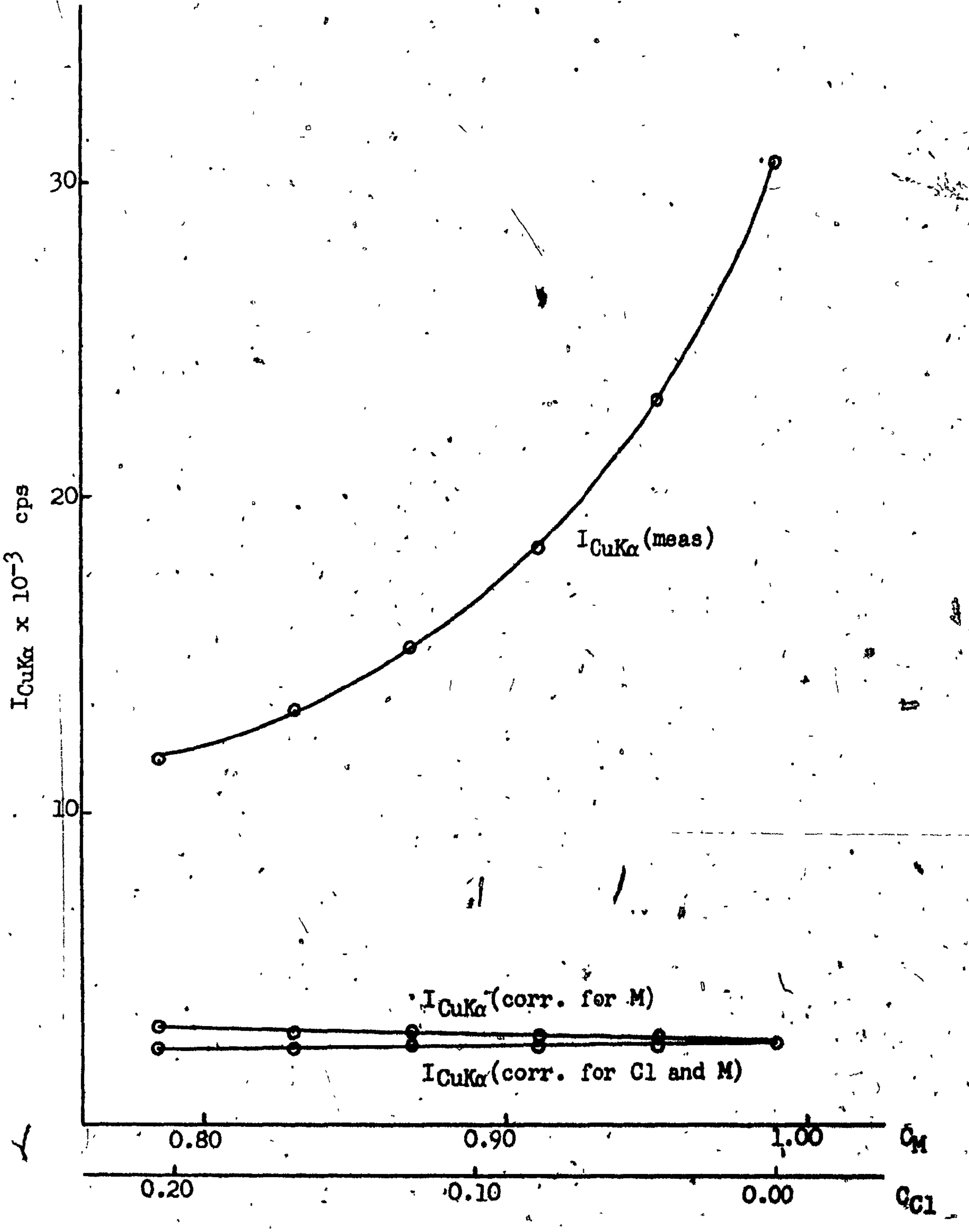
TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{CuK\alpha}$(corr) (cps)
LB-1	30 579	- 28 030	--	2 549
LB-2	23 098	- 20 326	- 229	2 543
LB-3	18 326	- 15 453	- 363	2 510
LB-4	15 244	- 12 270	- 460	2 514
LB-5	13 176	- 10 132	- 525	2 519
LB-6	11 613	- 8 438	- 596	2 578

$I^o_{CuK\alpha}$ average = 253 550 cps
std. devn. = ± 2 619 cps

$I^o_{CuK\alpha} = (2.53^5 \pm 0.02^6) \times 10^5$ cps
$= (2.54 \pm 0.03) \times 10^5$ cps

FIGURE D $I_{CuK\alpha}$ versus C_{Cl} and C_M



5.2.7 Effect of Cl on Zn

TABLE A **Experimental Parameters**

Solution	C_{Zn}	C_{Cl}	C_M	$I_{ZnK\alpha}$ (cps)	s (%)
LD-1	0.01000	0.00	0.99000	45 297	0.11
LD-2	0.01000	0.0397	0.9503	33 911	0.12
LD-3	0.01000	0.0743	0.9157	26 217	0.14
LD-4	0.01000	0.1115	0.8785	21 629	0.15
LD-5	0.01000	0.1587	0.8313	18 452	0.16
LD-6	0.01000	0.201^{6}	0.788^{4}	16 466	0.18

TABLE B **Calculation of α_{ZnCl}**

Solutions	α_{ZnCl}
LD-1/LD-6	- 0.3651···
LD-1/LD-5	- 0.3330···
LD-1/LD-4	- 0.2900···
LD-2/LD-6	- 0.3547···
LD-2/LD-5	- 0.2929···

α_{ZnCl} average = - 0.3271···
std. devn. = ± 0.0346···

$\alpha_{ZnCl} = -0.32^{7} \pm 0.03^{4}$
$= -0.33 \pm 0.03$

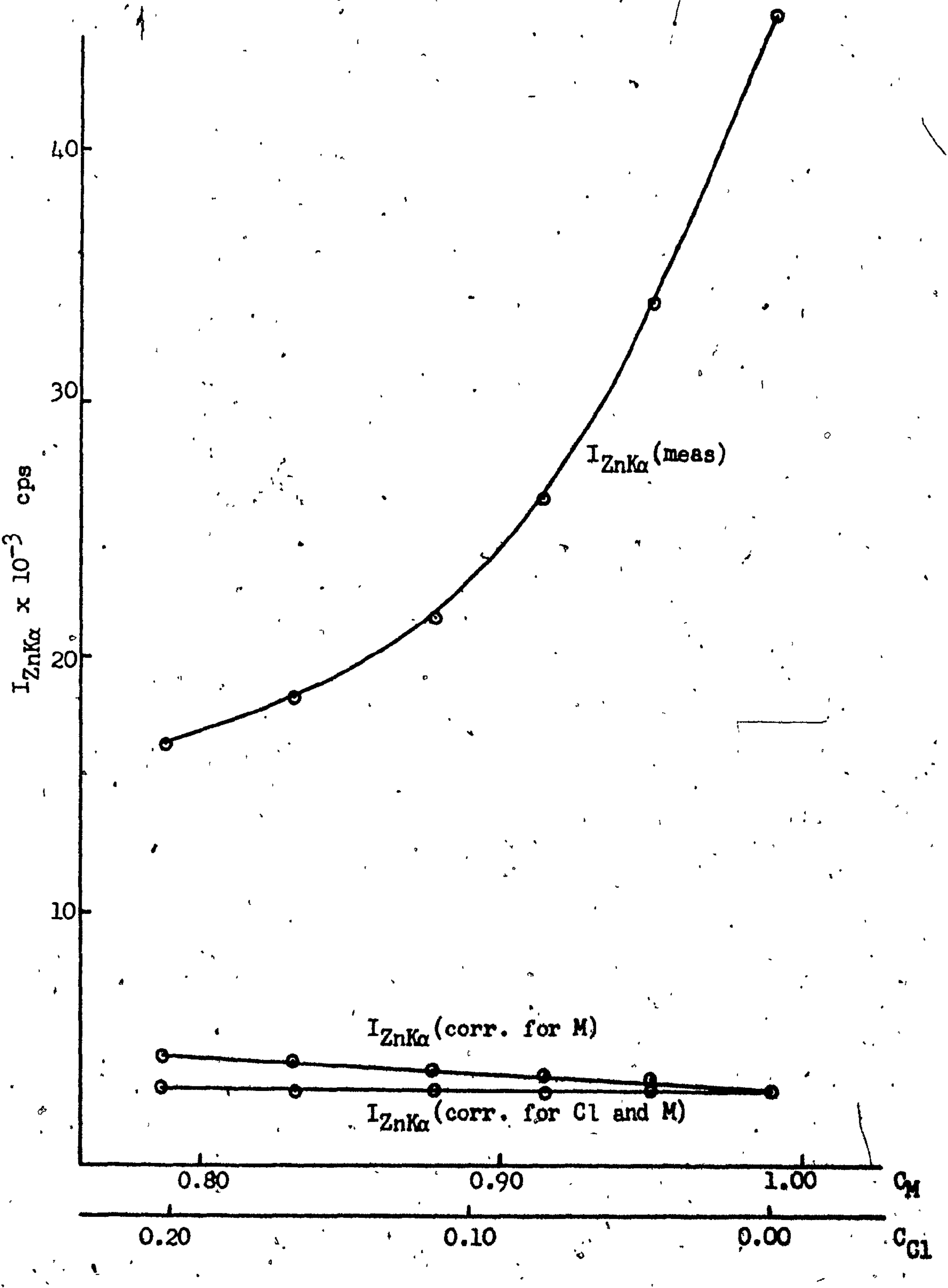
TABLE C **Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$**

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{ZnK\alpha}$(corr) (cps)
LD-1	45 297	- 42 283	--	3 014
LD-2	33 911	- 30 386	- 440	3 085
LD-3	26 217	- 22 636	- 637	2 944
LD-4	21 629	- 17 916	- 789	2 924
LD-5	18 452	- 14 463	- 958	3 031
LD-6	16 466	- 12 240	- 1 085	3 140

$I^{o}_{ZnK\alpha}$ average = 302 300 cps
std. devn. = ± 8 025 cps

$I^{o}_{ZnK\alpha} = (3.02^{3} \pm 0.08^{0}) \times 10^{5}$ cps
$= (3.02 \pm 0.08) \times 10^{5}$ cps.

FIGURE D $I_{ZnK\alpha}$ versus C_{Cl} and C_M



5.2.8 Effect of Cl on Cd

TABLE A Experimental Parameters

Solution	C_{Cd}	C_{Cl}	C_M	$I_{CdK\alpha}$ (cps)	s (%)
LE-1	0.01000	0.0	0.99000	15 472	0.18
LE-2	0.01000	0.0408	0.9492	13 963	0.19
LE-3	0.01000	0.0794	0.9106	12 772	0.20
LE-4	0.01000	0.1269	0.8631	11 929	0.21
LE-5	0.01000	0.1638	0.8262	11 004	0.22
LE-6	0.01000	0.210^3	0.779^7	10 114	0.22

TABLE B Calculation of α_{CdCl}

Solutions	α_{CdCl}
LE-1/LE-6	- 0.8546···
LE-1/LE-5	- 0.8564···
LE-2/LE-6	- 0.8567···
LE-2/LE-5	- 0.8598···
LE-3/LE-6	- 0.8604···

α_{CdCl} average = - 0.8576...

std. devn. = ± 0.0024···

$\alpha_{CdCl} = - 0.857^6 \pm 0.002^4$

$= - 0.858 \pm 0.002$

TABLE C Calculation of $I_{CdK\alpha}$(corr) and $I^o_{CdK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{CdK\alpha}$(corr) (cps)
LE-1	15 472	- 14 790	--	682
LE-2	13 963	- 12 798	- 488	677
LE-3	12 772	- 11 230	- 870	672
LE-4	11 929	- 9 942	- 1 298	689
LE-5	11 004	- 8 779	- 1 546	679
LE-6	10 114	- 7 615	- 1 824	675

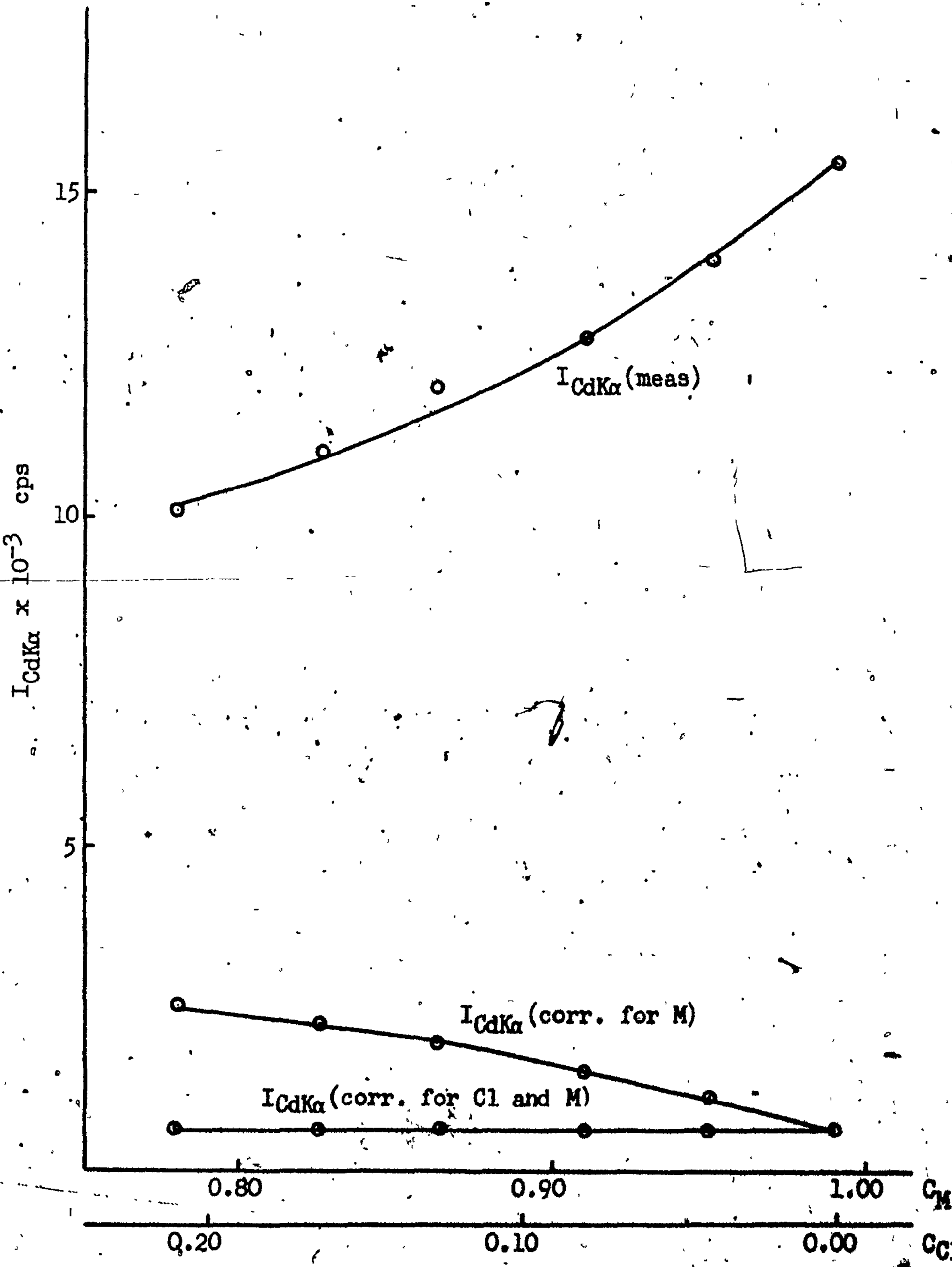
$I^o_{CdK\alpha}$ average = 67 900 cps

std. devn. = ± 590 cps

$I^o_{CdK\alpha} = (6.79^0 \pm 0.05^9) \times 10^4$ cps

$= (6.79 \pm 0.06) \times 10^4$ cps

FIGURE D $I_{CdK\alpha}$ versus C_{Cl} and C_M



5.2.9 Effect of Cl on Sn

TABLE A Experimental Parameters

Solution	C_{Sn}	C_{Cl}	C_M	$I_{SnK\alpha}$ (cps)	s (%)
LM-1	0.01000	0.0448	0.9452	17 983	0.17
LM-2	0.01000	0.079_2	0.9108	16 774	0.17
LM-3	0.01000	0.114_1	0.875_9	15 935	0.18
LM-4	0.01000	0.149^0	0.841^0	15 160	0.18
LM-5	0.01000	0.200^5	0.789^5	13 445	0.19

TABLE B Calculation of α_{SnCl}

Solutions	α_{SnCl}
LM-1/LM-5	- 0.8451···
LM-1/LM-4	- 0.8461···
LM-1/LM-3	- 0.8416···
LM-2/LM-5	- 0.8525···
LM-3/LM-5	- 0.8490···

α_{SnCl} average = - 0.84686···

std. devn. = ± 0.00411···

α_{SnCl} = $-0.846^9 \pm 0.004^1$

= -0.847 ± 0.004

TABLE C Calculation of $I_{SnK\alpha}$(corr) and $I^o_{SnK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{SnK\alpha}$(corr) (cps)
LM-1	17 983	- 16 215	- 682	1 085
LM-2	16 774	- 14 575	- 1 125	1 074
LM-3	15 935	- 13 315	- 1 540	1 080
LM-4	15 160	- 12 163	- 1 913	1 084
LM-5	13 445	- 10 080	- 2 283	1 081

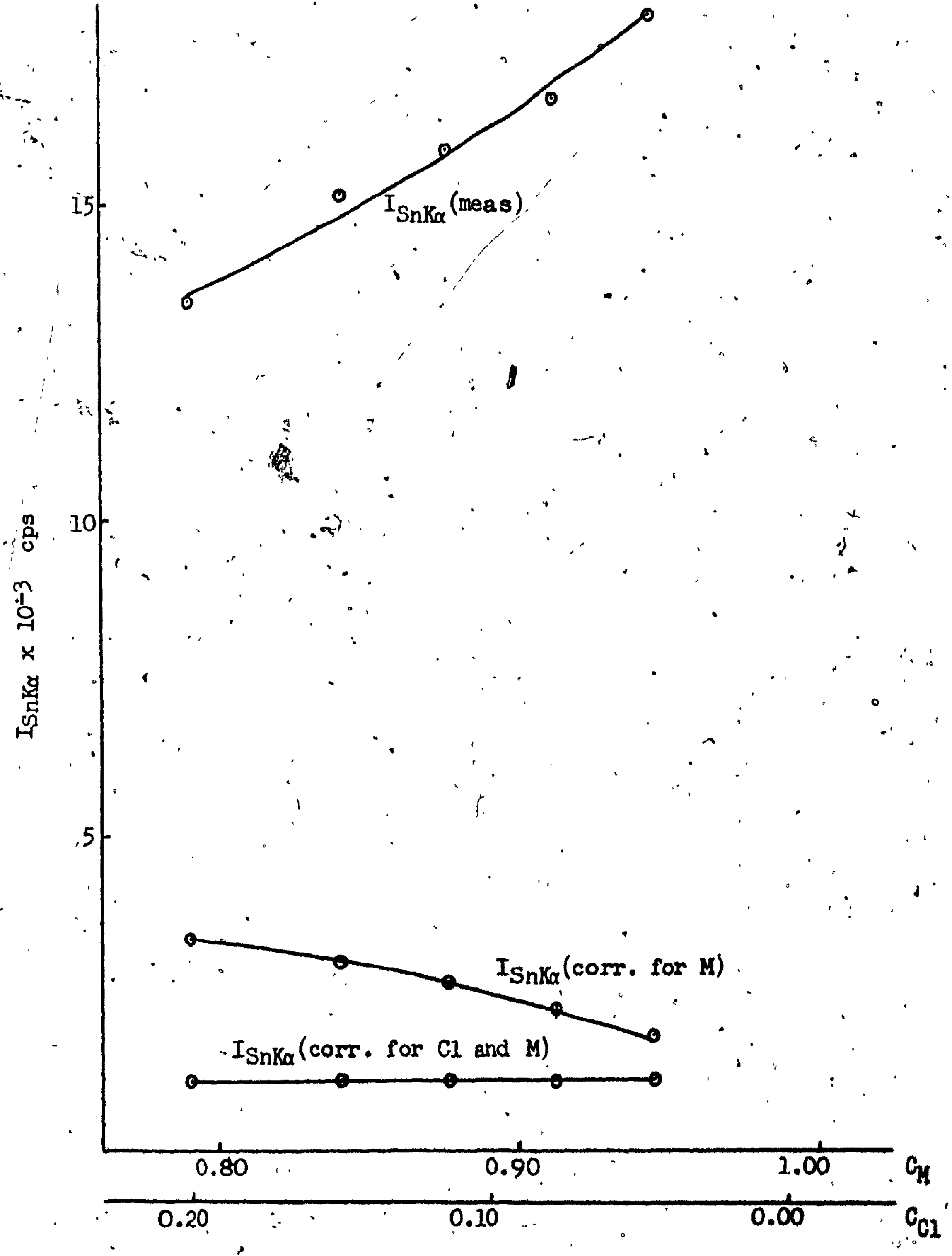
$I^o_{SnK\alpha}$ average = 108 080 cps

std. devn. = ± 432 cps

$I^o_{SnK\alpha}$ = $(1.080^8 \pm 0.004^3) \times 10^5$ cps

= $(1.081 \pm 0.004) \times 10^5$ cps

FIGURE D $I_{SnK\alpha}$ versus C_{Cl} and C_M



5.2.10 Effect of Cl on Pb

TABLE A Experimental Parameters

Solution	C_{Pb}	C_{Cl}	C_M	$I_{PbL\alpha}$ (cps)	s (%)
LZA-1	0.01000	0.00	0.99000	13 097	0.20
LZA-2	0.00990	0.0216^4	0.9684^6	11 241	0.21
LZA-3	0.01000	0.0400^8	0.9499^2	10 183	0.22
LZA-4	0 01000	0.087^7	0.902^3	8 107	0.25
LZA-5	0.01000	0.124^1	0.865^9	7 003	0.27

TABLE B Calculation of α_{PbCl}

Solutions	α_{PbCl}
LZA-1/LZA-5	- 0.6906···
LZA-1/LZA-4	- 0.6906···
LZA-2/LZA-5	- 0.6942···
LZA-2/LZA-4	- 0.7067···

α_{PbCl} average = - 0.6955···

std. devn. = ± 0.0076···

$\alpha_{PbCl} = - 0.695^5 \pm 0.007^6$

$= - 0.696 \pm 0.008$

TABLE C Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{PbL\alpha}$(corr) (cps)
LZA-1	13 097	- 12 575	--	521
LZA-2	11 241	- 10 559	- 169	513
LZA-3	10 183	- 9 382	- 284	517
LZA-4	8 107	- 7 095	- 494	518
LZA-5	7 003	- 5 881	- 605	517

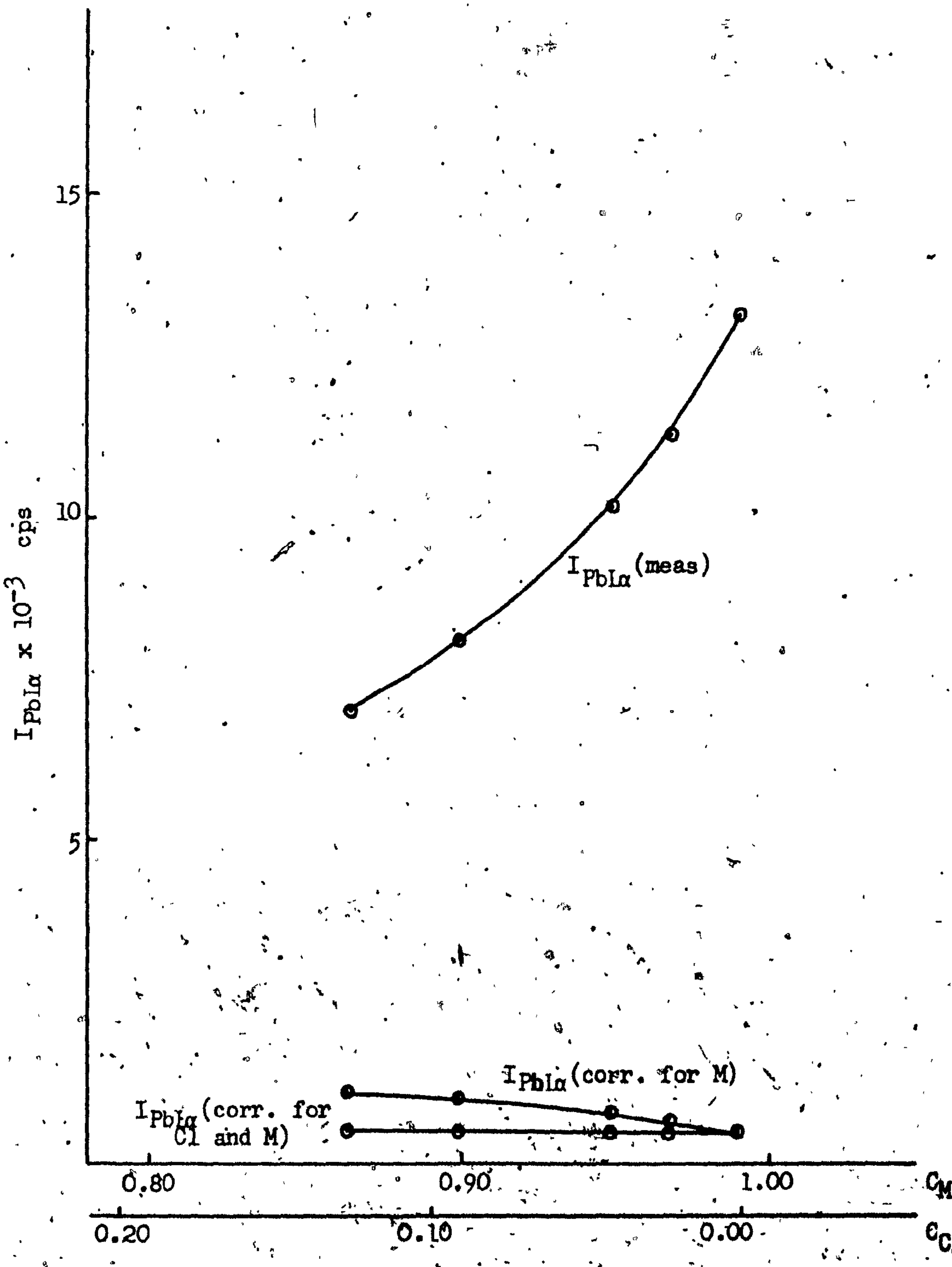
$I^{o}_{PbL\alpha}$ average = 51 720 cps

std. devn. = ± 348 cps

$I^{o}_{PbL\alpha} = (5.17^{2} \pm 0.03^{4}) \times 10^{4}$ cps

$= (5.17 \pm 0.03) \times 10^{4}$ cps

FIGURE D $I_{PbL\alpha}$ versus C_{Cl} and C_M



5.3 Effects of Chromium

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Chromium 1 ml = 0.2000 ± 0.0001 g (dil. HNO_3)
Manganese 1 ml = 0.10000 ± 0.00002 g (dil. HNO_3)
Iron 1 ml = 0.050000 ± 0.000008 g (dil. $HCl-HNO_3$)
Cobalt 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)
Nickel 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)
Copper 1 ml = 0.20000 ± 0.00008 g (dil. HNO_3)
Zinc 1 ml = 0.20000 ± 0.00008 g (dil. HNO_3)

Chlorine, where added as 1:2 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure leval for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBR	1:200 Cl	1:100 to 1:1000
Mn	LZN	1:380	1:190 to 1:1900
Fe	KA	1:150 Cl	1:75 to 1:750
Co	MAA	1:440	1:220 to 1:2200
Ni	MAM	1:500	1:250 to 1:2500
Cu	MAL	1:440	1:220 to 1:2200
Zn	MAK	1:440	1:220 to 1:2200

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn
Target	Cr	W	W	W	W	W	W	W
kV	50	*	50	40	50	40	50	50
mA	36	*	40	20	40	30	30	30
Coll^n	coarse	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LIf	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required.

The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α_{ACr} (absence of Cl as fourth component)	Equation (43)
	Calculation of α_{ACr} (presence of Cl as fourth component)	Equation (44)
	Calculation of $I_A(corr)$	Equation (45) or a modification
	Calculation of I_A^o	$I_A(corr)/C_A$

5.3.1. Effect of Cr on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Cr}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
MBR-1	0.0208	0.00	0.9792	5 220	0.32	--	--
MBR-2	0.0208	0.01000	0.9692	5 238	0.32	6 731	0.28
MBR-3	0.0208	0.02000	0.9592	5 130	0.32	12 704	0.20
MBR-4	0.0208	0.03000	0.9492	4 974	0.32	18 377	0.17
MBR-5	0.0208	0.06000	0.9192	4 900	0.32	32 692	0.13
MBR-6	0.0208	0.08000	0.8992	4 688	0.33	39 388	0.11
MBR-7	0.0208	0.10000	0.8792	4 643	0.33	46 808	0.10
MBR-8	0.0208	0.1200	0.8592	4 661	0.33	53 921	0.10
MBR-9	0.0208	0.1400	0.8392	4 561	0.33	59 438	0.09

*50kV, 40mA

TABLE B Calculation of α_{ClCr}

Solutions	α_{ClCr}
MBR-1/MBR-9	0.3565···
MBR-1/MBR-8	0.3346···
MBR-1/MBR-7	0.4978···
MBR-2/MBR-9	0.4266···
MBR-2/MBR-8	0.4277···
MBR-3/MBR-9	0.3764···
MBR-3/MBR-8	0.3530···

α_{ClCr} average = 0.3961···
std. devn. = ± 0.0575···

$$\alpha_{ClCr} = 0.39^{6} \pm 0.05^{7}$$
$$= 0.40 \pm 0.06$$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chromium effect	$I_{ClK\alpha}$(corr) (cps)
MBR-1	5 220	- 1 717	--	3 503
MBR-2	5 238	- 1 706	+ 21	3 553
MBR-3	5 130	- 1 653	+ 41	3 517
MBR-4	4 974	- 1 586	+ 59	3 447
MBR-5	4 900	- 1 513	+ 116	3 503
MBR-6	4 688	- 1 416	+ 148	3 420
MBR-7	4 643	- 1 372	+ 184	3 455
MBR-8	4 661	- 1 346	+ 221	3 537
MBR-9	4 561	- 1 286	+ 253	3 528

$I^{o}_{ClK\alpha}$ average = 168 070 cps
std. devn. = ± 2 171 cps

$$I^{o}_{ClK\alpha} = (1.68^{0} \pm 0.02^{1}) \times 10^{5} \text{ cps}$$
$$= (1.68 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for matrix effect	Correction for chlorine effect	$I_{CrK\alpha}$(corr) (cps)
MBR-2	6 731	- 5 526	+ 65	1 270
MBR-3	12 704	- 10 322	+ 123	2 505
MBR-4	18 377	- 14 776	+ 178	3 779
MBR-5	32 692	- 25 456	+ 317	7 553
MBR-6	39 388	- 30 002	+ 382	9 767
MBR-7	46 808	- 34 861	+ 454	12 400
MBR-8	53 921	- 39 245	+ 523	15 198
MBR-9	59 438	- 42 254	+ 576	17 760

$I^{o}_{CrK\alpha}$ average = 125 461 cps
std. devn. = ± 1 678 cps

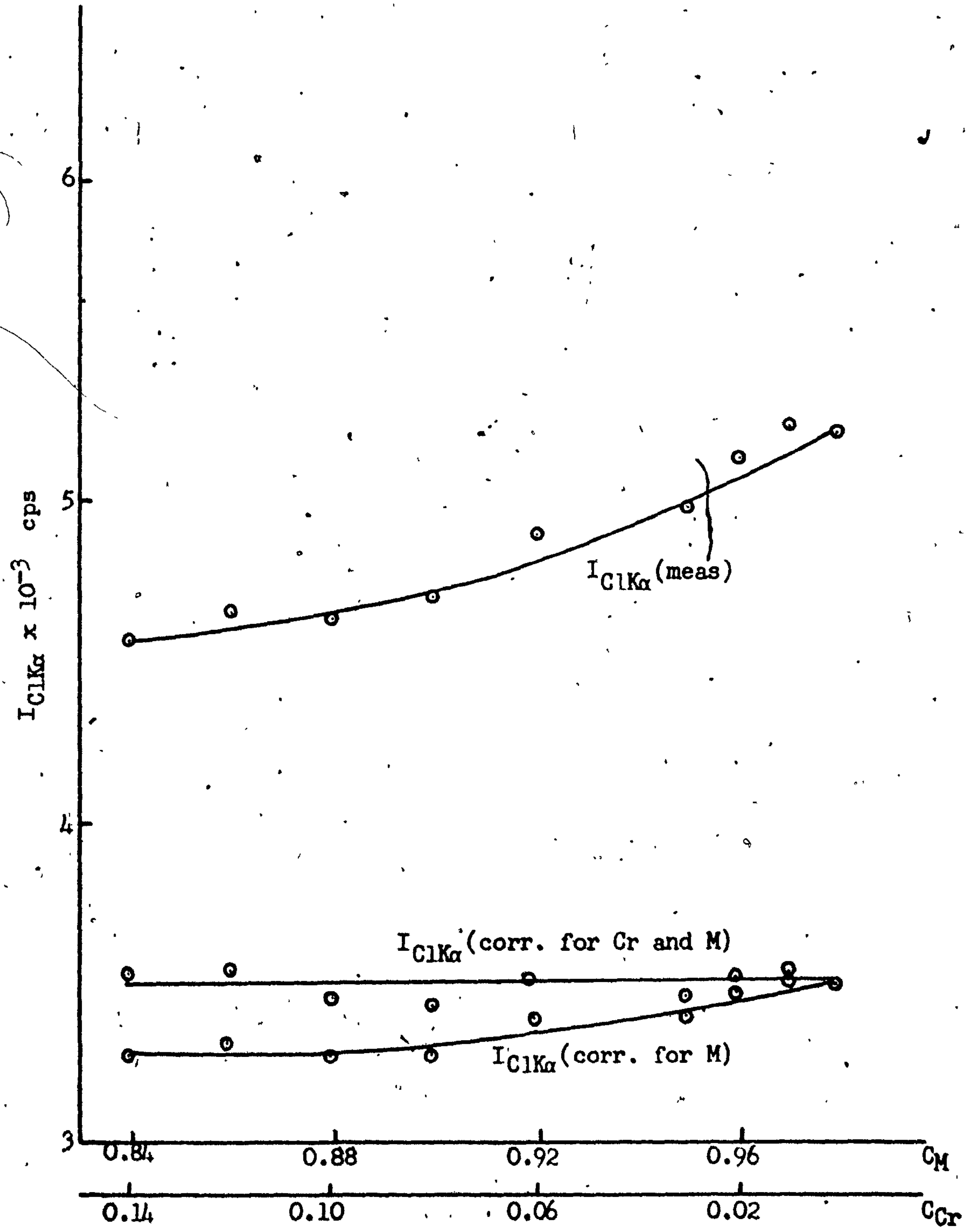
$$I^{o}_{CrK\alpha} = (1.25^{4} \pm 0.01^{6}) \times 10^{5} \text{ cps}$$
$$= (1.25 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution of systems of linear equations using calculated I^{o} values.

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Cr}(calc)	Abs. error	Error %
MBR-1	0.0208	0.0000	0.00	---	---	---
MBR-2	0.0211	0.0003	1.44	0.0101	0.0001	1.00
MBR-3	0.0209	0.0001	0.48	0.0200	0.0000	0.00
MBR-4	0.0205	0.0003	1.44	0.0301	0.0001	0.33
MBR-5	0.0208	0.0000	0.00	0.0603	0.0003	0.50
MBR-6	0.0203	0.0005	2.40	0.0768	0.0032	4.00
MBR-7	0.0205	0.0003	1.44	0.0981	0.0019	1.90
MBR-8	0.0211	0.0003	1.44	0.122^{0}	0.002^{0}	1.67
MBR-9	0.0210	0.0002	0.96	0.143^{1}	0.003^{1}	2.21

FIGURE D⁻ $I_{ClK\alpha}$ versus C_{Cr} and C_M



5.3.2 Effect of Cr on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Cr}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
LZN-1	0.01000	0.0	0.99000	18 000	0.17	--	—
LZN-2	0.01000	0.01000	0.98000	15 151	0.18	3 562	0.38
LZN-3	0.01000	0.0200	0.9700	14 475	0.18	5 961	0.30
LZN-4	0.01000	0.0400	0.9500	12 539	0.20	11 081	0.21
LZN-5	0.01000	0.0600	0.9300	10 981	0.22	15 047	0.18
LZN-6	0.01000	0.0800	0.9100	8 948	0.24	18 210	0.17
LZN-7	0.01000	0.1000	0.8900	8 187	0.26	21 523	0.16

*50kV,20mA

TABLE B Calculation of α_{MnCr}

Solutions	α_{MnCr}
LZN-1/LZN-7	0.8730···
LZN-1/LZN-6	0.9691···
LZN-1/LZN-5	0.6803···
LZN-2/LZN-7	0.6491···
LZN-2/LZN-6	0.7294···
LZN-3/LZN-7	0.8584···
LZN-3/LZN-6	0.9655···

α_{MnCr} average = 0.8178···

std. devn. = ± 0.132····

$\alpha_{MnCr} = 0.8^{2} \pm 0.1^{3}$

$= 0.8 \pm 0.1$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{CrK\alpha}$(corr) (cps)
LZN-2	3 562	- 2 957	- 11	594
LZN-3	5 961	- 4 898	- 18	1 045
LZN-4	11 081	- 8 917	- 33	2 121
LZN-5	15 047	- 11 854	- 45	3 148
LZN-6	18 210	- 14 037	- 55	4 118
LZN-7	21 523	- 16 227	- 65	5 231

$I^{o}_{CrK\alpha}$ average = 53 530 cps

std. devn. = ± 2 943 cps

$I^{o}_{CrK\alpha} = (5.35 \pm 0.2^{9}) \times 10^{4}$ cps

$= (5.4 \pm 0.3) \times 10^{4}$ cps

TABLE D Calculation of $I_{MnK\alpha}(corr)$ and $I^o_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{MnK\alpha}(corr)$ (cps)
LZN-1	18 000	- 15 391	--	2 609
LZN-2	15 151	- 12 824	+ 124	2 451
LZN-3	14 475	- 12 127	+ 237	2 585
LZN-4	12 539	- 10 288	+ 411	2 662
LZN-5	10 981	- 8 820	+ 540	2 700
LZN-6	8 948	- 7 033	+ 587	2 502
LZN-7	8 187	- 6 293	+ 671	2 565

$I^o_{MnK\alpha}$ average = 258 229 cps

std. devn. = ± 8 665 cps

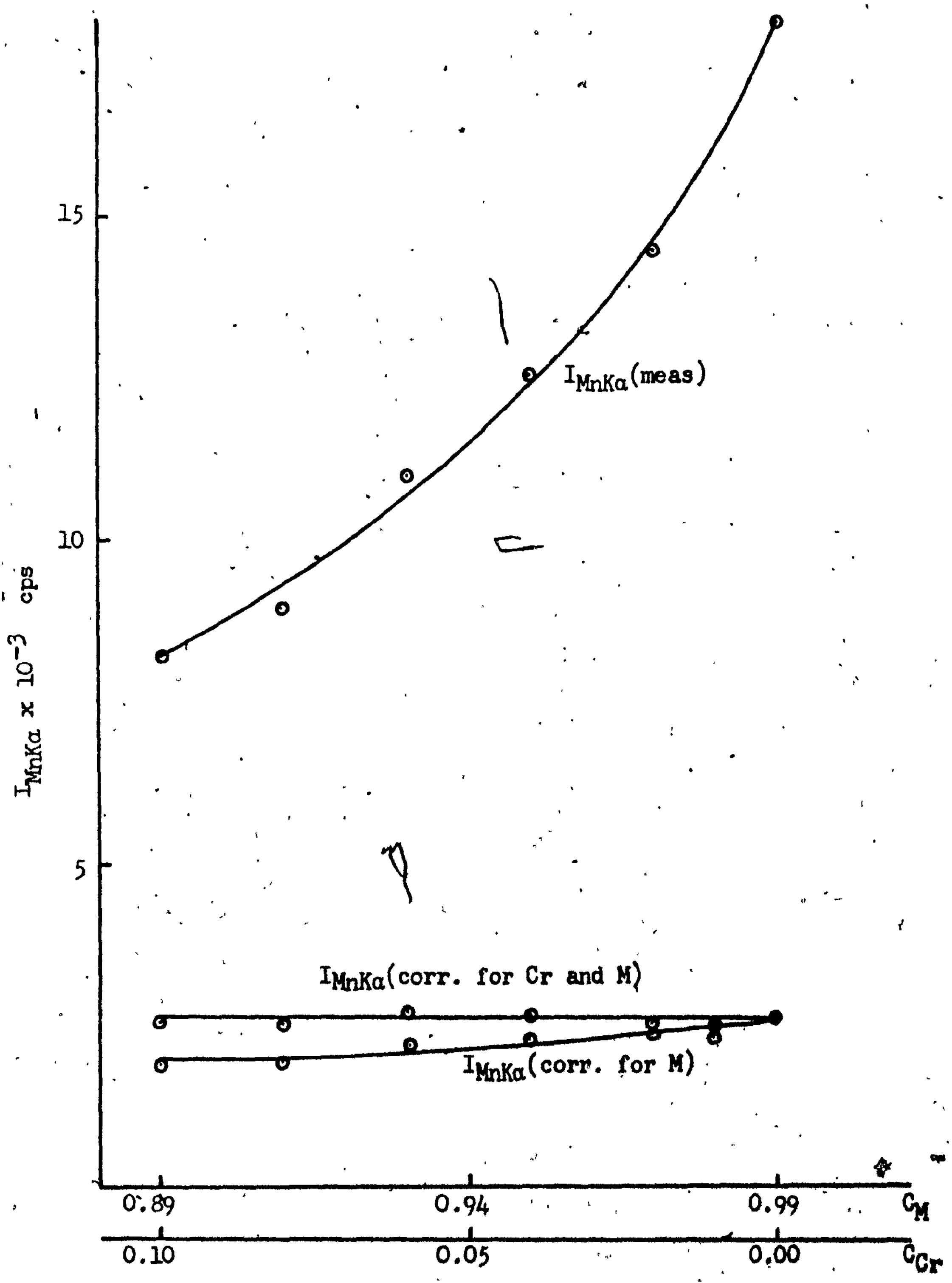
$$I^o_{MnK\alpha} = (2.58^2 \pm 0.08^6) \times 10^5 \text{ cps}$$

$$= (2.58 \pm 0.09) \times 10^5 \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	$C_{Mn}(calc)$	Abs. error	Error %	$C_{Cr}(calc)$	Abs. error	Error %
LZN-1	0.01010	0.00010	1.00	--	--	--
LZN-2	0.00960	0.00040	4.00	0.01110	0.00110	11.00
LZN-3	0.01000	0.00000	0.00	0.0195	0.0005	2.50
LZN-4	0.01030	0.00030	3.00	0.0398	0.0002	0.50
LZN-5	0.01040	0.00040	4.00	0.0585	0.0015	2.50
LZN-6	0.00940	0.00060	6.00	0.0755	0.0045	5.62
LZN-7	0.00970	0.00030	3.00	0.0965	0.0035	3.50

FIGURE D . $I_{MnK\alpha}$ versus C_{Cr} and C_M



5.3.3 Effect of Cr on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Cr}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
KA-1	0.01000	0.0	0.0149	0.9751	10 668	0.22	--	--
KA-2	0.01000	0.01000	0.0149	0.9651	8 900	0.24	2 551	0.45
KA-3	0.01000	0.02000	0.0149	0.9551	7 728	0.26	4 853	0.32
KA-4	0.01000	0.03000	0.0149	0.9451	6 824	0.28	7 006	0.27
KA-5	0.01000	0.04000	0.0149	0.9351	6 082	0.30	8 895	0.24
KA-6	0.01000	0.05000	0.0149	0.9251	5 472	0.31	10 717	0.22
KA-7	0.01000	0.06000	0.0149	0.9151	5 043	0.32	12 304	0.20
KA-8	0.01000	0.0800	0.0149	0.8951	4 113	0.35	15 086	0.18
KA-9	0.01000	0.0900	0.0149	0.8851	3 986	0.36	16 663	0.17

* 40kV, 20mA

TABLE B Calculation of α_{FeCr}

Solutions	α_{FeCr}
KA-1/KA-9	1.4563···
KA-1/KA-8	1.6200···
KA-1/KA-7	1.4518···
KA-2/KA-9	1.4047···
KA-2/KA-8	1.6226···
KA-2/KA-7	1.3846···
KA-3/KA-9	1.4185···

$$\alpha_{FeCr} \text{ average} = 1.4798\cdots$$

$$\text{std. devn.} = \pm\, 0.09987\cdots$$

$$\therefore \alpha_{FeCr} = 1.47^{9} \pm 0.09^{9}$$

$$= 1.48 \pm 0.10$$

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	chromium	$I_{FeK\alpha}$(corr) (cps)
KA-1	10 668	- 9 328	+ 7	--	1 347
KA-2	8 900	- 7 702	+ 6	+ 132	1 336
KA-3	7 728	- 6 618	+ 5	+ 228	1 343
KA-4	6 824	- 5 783	+ 5	+ 303	1 349
KA-5	6 082	- 5 100	+ 4	+ 360	1 346
KA-6	5 472	- 4 539	+ 4	+ 405	1 342
KA-7	5 043	- 4 138	+ 3	+ 447	1 355
KA-8	4 113	- 3 301	+ 3	+ 487	1 302
KA-9	3 986	- 3 163	+ 3	+ 530	1 356

$I^{o}_{FeK\alpha}$ average = 134 178 cps
std. devn. = ± 688 cps
$I^{o}_{FeK\alpha} = (1.341^{7} \pm 0.006^{8}) \times 10^{5}$ cps
$= (1.342 \pm 0.007) \times 10^{5}$ cps

TABLE D Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

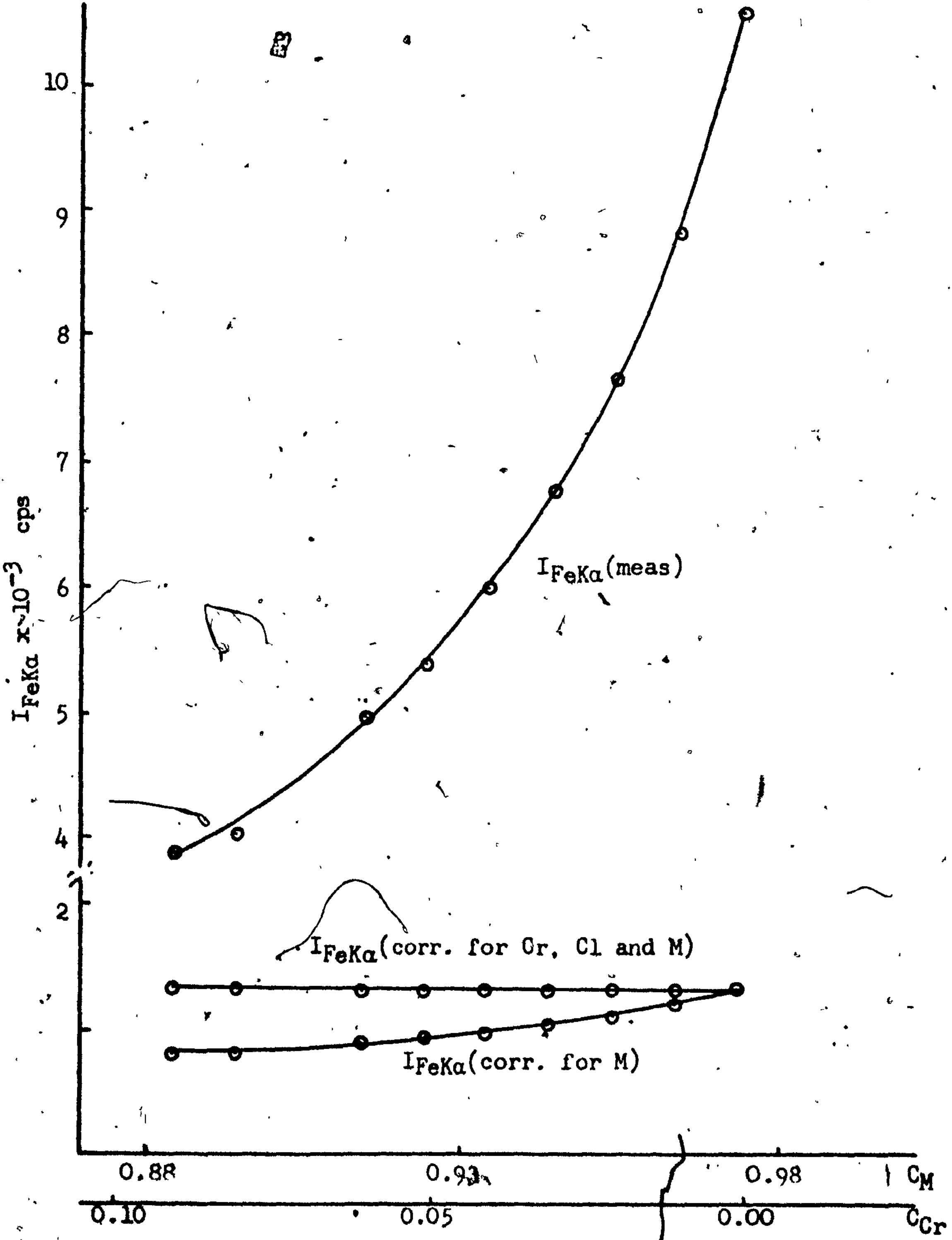
Solution	Measured	Correction for effect of matrix	Correction for effect of iron	Correction for effect of chlorine	$I_{CrK\alpha}$(corr) (cps)
KA-2	2 551	- 2 085	- 13	+ 18	471
KA-3	4 853	- 3 926	- 24	+ 34	937
KA-4	7 006	- 5 609	- 34	+ 49	1 412
KA-5	8 895	- 7 046	- 44	+ 62	1 867
KA-6	10 717	- 8 398	- 53	+ 74	2 340
KA-7	12 304	- 9 538	- 61	+ 85	2 790
KA-8	15 086	- 11 439	- 74	+ 105	3 678
KA-9	16 663	- 12 493	- 82	+ 116	4 204

$I^{o}_{CrK\alpha}$ average = 46 709 cps
std. devn. = ± 346 cps
$I^{o}_{CrK\alpha} = (4.67^{0} \pm 0.03^{4}) \times 10^{4}$ cps
$= (4.67 \pm 0.03) \times 10^{4}$ cps

TABLE E

Data not available, since ClKα not counted

FIGURE D $I_{FeK\alpha}$ versus C_{Cr} and C_M



5.3.4 Effect of Cr on Co

TABLE A **Experimental Parameters**

Solution	C_{Co}	C_{Cr}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
MAA-1	0.02000	0.00	0.98000	118 162	0.07	—	—
MAA-2	0.02000	0.01000	0.97000	95 916	0.07	8 378	0.17
MAA-3	0.02000	0.02000	0.96000	84 255	0.08	16 278	0.15
MAA-4	0.02000	0.0300	0.9500	72 266	0.09	23 070	0.15
MAA-5	0.02000	0.0600	0.9200	52 316	0.10	40 130	0.11
MAA-6	0.02000	0.0800	0.9000	44 785	0.11	49 842	0.10
MAA-7	0.02000	0.1000	0.8800	38 495	0.11	57 663	0.10

*50kV,40mA

TABLE B **Calculation of α_{CoCr}**

Solutions	α_{CoCr}
MAA-1/MAA-7	1.0675···
MAA-1/MAA-6	1.0468···
MAA-1/MAA-5	1.0955···
MAA-2/MAA-7	0.9878···
MAA-2/MAA-6	0.9514···
MAA-2/MAA-5	1.0001···
MAA-3/MAA-7	1.1104···
MAA-3/MAA-6	1.0774···
MAA-3/MAA-5	1.1899···
MAA-4/MAA-7	1.0050···

α_{CoCr} average = 1.0531···

std. devn. = ± 0.0701···

α_{CoCr} = $1.05^3 \pm 0.07^0$

= 1.05 ± 0.07

TABLE C **Calculation of $I_{CoK\alpha}(\text{corr})$ and $I^0_{CoK\alpha}$**

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{CoK\alpha}(\text{corr})$ (cps)
MAA-1	118 162	- 106 801	--	11 361
MAA-2	95 916	- 85 809	+ 1 010	11 117
MAA-3	84 255	- 74 600	+ 1 774	11 429
MAA-4	72 226	- 63 283	+ 2 282	11 225
MAA-5	52 316	- 44 391	+ 3 305	11 230
MAA-6	44 785	- 37 175	+ 3 773	11 383
MAA-7	38 495	- 31 243	+ 4 053	11 305

$I^{o}_{CoK\alpha}$ average = 564 643 cps
std. devn. = ± 5 449 cps
$I^{o}_{CoK\alpha}$ = $(5.64^{6} \pm 0.05^{4}) \times 10^{5}$
= $(5.65 \pm 0.05) \times 10^{5}$

TABLE D Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

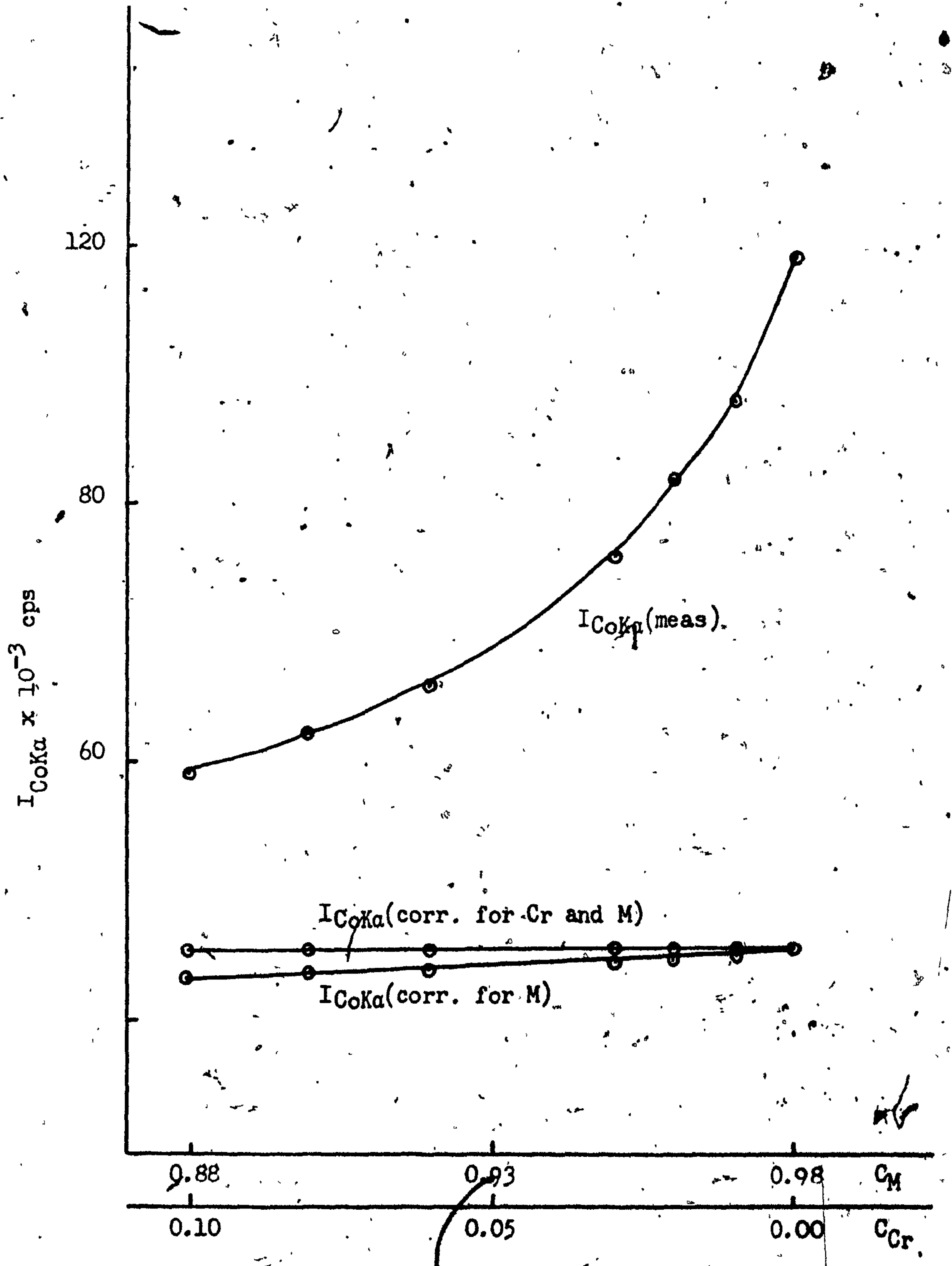
Solution	Measured	Correction for effect of		$I_{CrK\alpha}$(corr) (cps)
		matrix	cobalt	
MAA-2	8 378	- 6 891	- 92	1 395
MAA-3	16 278	- 13 237	- 179	2 862
MAA-4	23 070	- 18 565	- 254	4 251
MAA-5	40 130	- 31 274	- 442	8 414
MAA-6	49 842	- 37 999	- 549	11 294
MAA-7	57 663	- 42 985	- 635	14 043

$I^{o}_{CrK\alpha}$ average = 141 023 cps
std. devn. = ± 1 095 cps
$I^{o}_{CrK\alpha}$ = $(1.41^{0} \pm 0.01^{0}) \times 10^{5}$
= $(1.41 \pm 0.01) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Cr}(calc)	Abs. error	Error %
MAA-1	0.02010	0.00010	0.50	--	--	--
MAA-2	0.01960	0.00040	2.00	0.00990	0.00010	1.00
MAA-3	0.02040	0.00040	2.00	0.02030	0.00030	1.50
MAA-4	0.01990	0.00010	0.50	0.0301	0.0001	0.33
MAA-5	0.01980	0.00020	1.00	0.0595	0.0005	0.83
MAA-6	0.02020	0.00020	1.00	0.0800	0.0000	0.00
MAA-7	0.01990	0.00010	0.50	0.0992	0.0008	0.80

FIGURE D $I_{CoK\alpha}$ versus C_{Cr} and C_M



5.3.5 Effect of Cr on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Cr}	C_M	$I_{NiK\alpha}$	s(%)	$I_{CrK\alpha}^{*}$	s(%)
MAM-1	0.02000	0.0	0.98000	91 683	0.07		
MAM-2	0.02000	0.01000	0.97000	73 793	0.08	6 763	0.29
MAM-3	0.02000	0.02000	0.96000	65 596	0.09	13 271	0.20
MAM-4	0.02000	0.0400	0.9400	50 188	0.10	24 662	0.14
MAM-5	0.02000	0.0600	0.9200	41 491	0.11	33 526	0.12
MAM-6	0.02000	0.0800	0.9000	35 488	0.12	41 144	0.11
MAM-7	0.02000	0.1000	0.8800	31 300	0.13	48 710	0.10

* 50kV, 40mA.

TABLE B Calculation of α_{NiCr}

Solutions	α_{NiCr}
MAM-1/MAM-7	1.0360···
MAM-1/MAM-6	1.0516···
MAM-1/MAM-5	1.1241···
MAM-2/MAM-7	0.8814···
MAM-2/MAM-6	0.9286···
MAM-2/MAM-5	0.9500···
MAM-3/MAM-7	0.9927···
MAM-3/MAM-6	1.0789···

α_{NiCr} average = 1.0054···
std. devn. = ± 0.082····

α_{NiCr} = $1.00^5 \pm 0.08^2$
= 1.00 ± 0.08

TABLE C Calculation of $I_{NiK\alpha}(corr)$ and $I^o_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{NiK\alpha}(corr)$ (cps)
MAM-1	91 683	- 82 563	--	9 300
MAM-2	73 793	- 65 645	+ 742	8 890
MAM-3	65 596	- 57 752	+ 1 318	9 162
MAM-4	50 188	- 43 266	+ 2 017	8 939
MAM-5	41 491	- 35 007	+ 2 502	8 986
MAM-6	35 488	- 29 291	+ 2 853	9 050
MAM-7	31 300	- 25 261	+ 3 145	9 184

$I^o_{NiK\alpha}$ average = 453 650 cps
std. devn. = ± 7 415 cps

$I^o_{NiK\alpha}$ = $(4.53^6 \pm 0.07^4) \times 10^5$ cps.
= $(4.54 \pm 0.07) \times 10^5$ cps

TABLE D Calculation of $I_{CrK\alpha}(\text{corr})$ and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{CrK\alpha}(\text{corr})$ (cps)
MAM-2	6 763	- 5 557	- 53	1 153
MAM-3	13 271	- 10 792	- 103	2 376
MAM-4	24 662	- 19 638	- 192	4 832
MAM-5	33 526	- 26 128	- 261	7 137
MAM-6	41 144	- 31 368	- 320	9 456
MAM-7	48 710	- 36 311	- 379	12 020

$I^{o}_{CrK\alpha}$ average = 118 708 [illegible]

std. devn. = ± 1 917 cp[illegible]

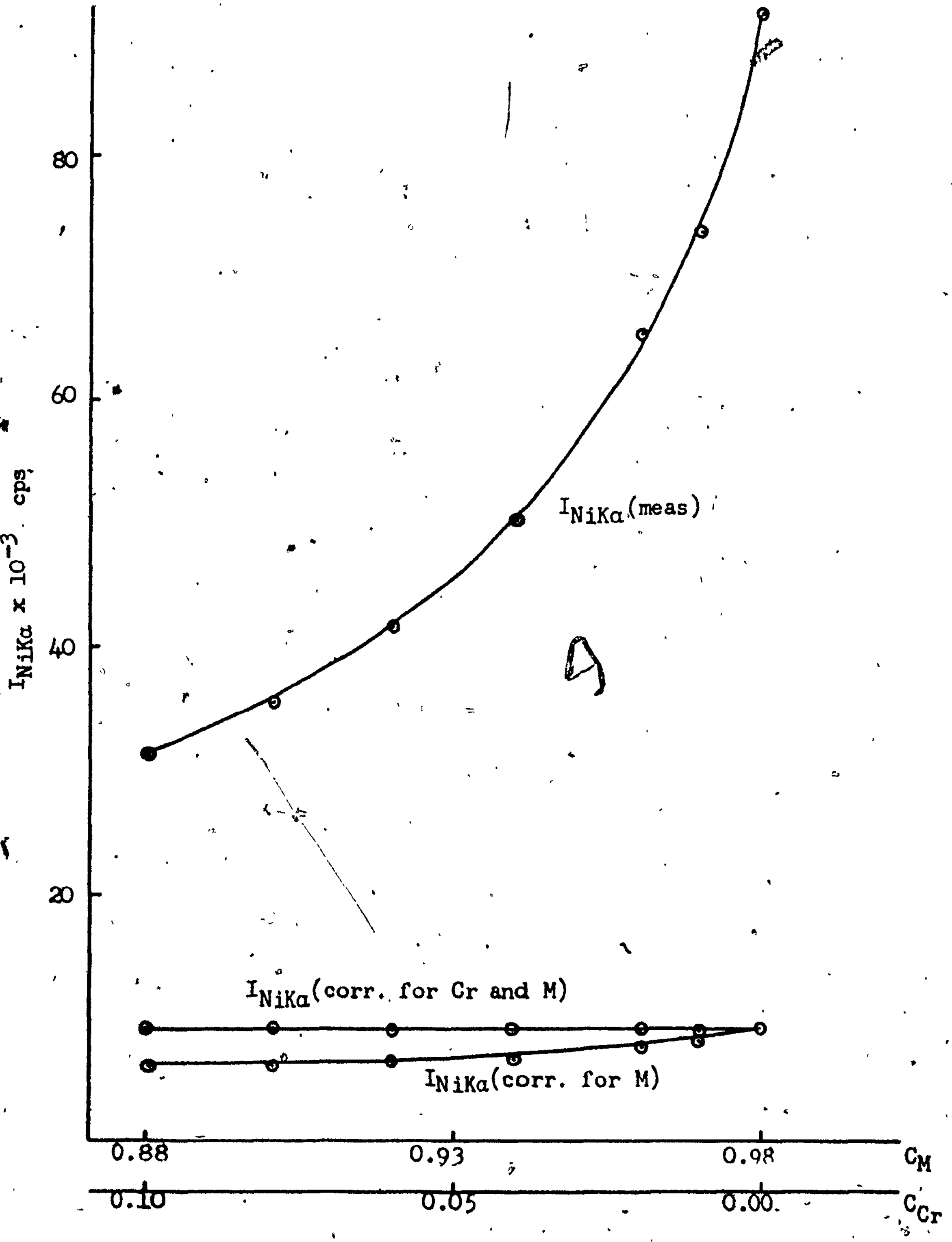
$I^{o}_{CrK\alpha}$ = $(1.18^{7} \pm 0.01^{9}) \times 10^{5}$ cps

= $(1.19 \pm 0.02) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

Solution	$C_{Ni}(\text{calc})$	Abs. error	Error %	$C_{Cr}(\text{calc})$	Abs. error	Error %
MAM-1	0.02060	0.00060	3.00	—	—	—
MAM-2	0.01940	0.00060	3.00	0.00970	0.00030	3.00
MAM-3	0.02020	0.00020	1.00	0.02020	0.00020	1.00
MAM-4	0.01990	0.00010	0.50	0.0408	0.0008	2.00
MAM-5	0.01980	0.00020	1.00	0.0601	0.0001	0.17
MAM-6	0.01990	0.00010	0.50	0.0795	0.0005	0.62
MAM-7	0.02060	0.00060	3.00	0.1021	0.0021	2.10

FIGURE D $I_{NiK\alpha}$ versus C_{Cr} and C_M



5.3.6 Effect of Cr on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Cr}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
MAL-1	0.02000	0.0	0.98000	114 416	0.07	--	--
MAL-2	0.02000	0.01000	0.97000	93 756	0.08	6 820	0.27
MAL-3	0.02000	0.02000	0.96000	81 823	0.08	13 321	0.20
MAL-4	0.02000	0.0400	0.9400	65 603	0.09	24 971	0.14
MAL-5	0.02000	0.0600	0.9200	52 530	0.10	33 939	0.12
MAL-6	0.02000	0.0800	0.9000	44 509	0.11	42 274	0.11
MAL-7	0.02000	0.1000	0.8800	38 262	0.12	47 770	0.10

*50kV.40mA

TABLE B Calculation of α_{CuCr}

Solutions	α_{CuCr}
MAL-1/MAL-7	0.9175···
MAL-1/MAL-6	0.8924···
MAL-1/MAL-5	0.9927···
MAL-2/MAL-7	0.8534···
MAL-2/MAL-6	0.8129···
MAL-3/MAL-7	0.9166···
MAL-3/MAL-6	0.8701···

α_{CuCr} average = 0.8936···

std. devn. = ± 0.0571···

$\alpha_{CuCr} = 0.89^4 \pm 0.05^7$

$= 0.89 \pm 0.06$

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{CuK\alpha}$(corr) (cps)
MAL-1	114 416	- 103 819	--	10 597
MAL-2	93 756	- 84 204	+ 838	10 390
MAL-3	81 823	- 72 729	+ 1 463	10 557
MAL-4	65 603	- 57 097	+ 2 346	10 852
MAL-5	52 530	- 44 746	+ 2 818	10 602
MAL-6	44 509	- 37 090	+ 3 183	10 602
MAL-7	38 262	- 31 176	+ 3 421	10 507

$I^o_{CuK\alpha}$ average = 529 336 cps

std. devn. = ± 6 976 cps

$I^o_{CuK\alpha} = (5.29^3 \pm 0.06^9) \times 10^5$ cps

$= (5.29 \pm 0.07) \times 10^5$ cps

TABLE D Calculation of $I_{CrK\alpha}(corr)$ and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of		$I_{CrK\alpha}(corr)$ (cps)
		matrix	copper	
MAL-2	6 820	- 5 604	- 70	1 146
MAL-3	13 321	- 10 833	- 136	2 352
MAL-4	24 971	- 19 884	- 255	4 832
MAL-5	33 939	- 26 450	- 346	7 143
MAL-6	42 274	- 32 229	- 431	9 614
MAL-7	47 770	- 35 610	- 487	11 673

$I^{o}_{CrK\alpha}$ average = 118 159 cps

std. dev. = ± 2 303 cps

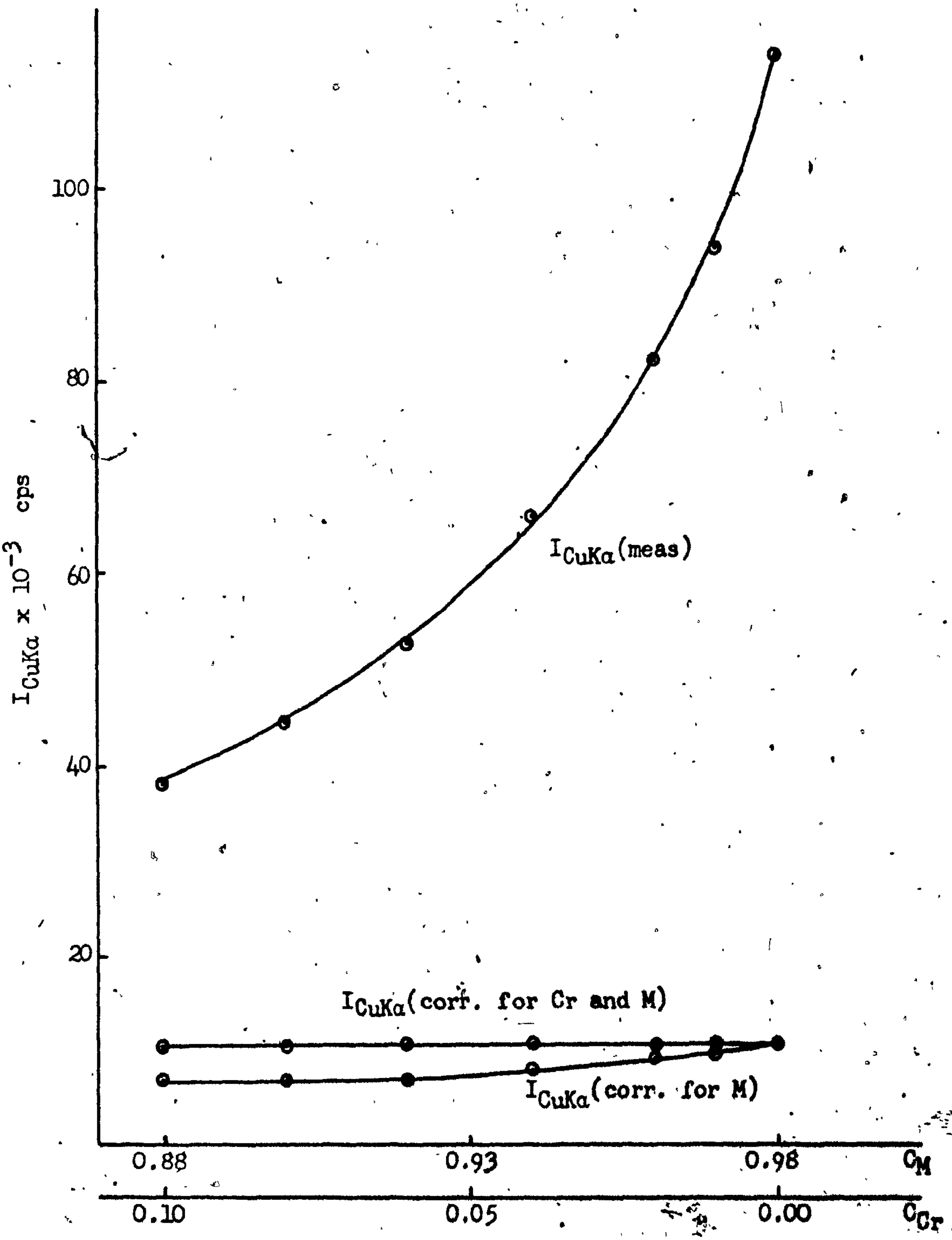
$$I^{o}_{CrK\alpha} = (1.18^{1} \pm 0.02^{3}) \times 10^{5} \text{ cps}$$

$$= (1.18 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Cr}(calc)	Abs. error	Error %
MAL-1	0.02000	0.00000	0.00	--	--	--
MAL-2	0.01940	0.00060	3.00	0.00970	0.00030	3.00
MAL-3	0.01990	0.00010	0.50	0.01990	0.00010	0.50
MAL-4	0.02090	0.00090	4.50	0.0412	0.0012	3.00
MAL-5	0.02010	0.00010	0.50	0.0606	0.0006	1.00
MAL-6	0.02040	0.00040	2.00	0.0820	0.0020	2.50
MAL-7	0.01960	0.00040	2.00	0.0980	0.0020	2.00

FIGURE D $I_{CuK\alpha}$ versus C_{Cr} and C_M



5.3.7 Effect of Cr on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Cr}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{CrK\alpha}$* (cps)	s(%)
MAK-1	0.02000	0.0	0.98000	169 870	0.06	--	--
MAK-2	0.02000	0.01000	0.97000	136 006	0.07	6 626	0.30
MAK-3	0.02000	0.02000	0.96000	121 926	0.07	13 553	0.19
MAK-4	0.02000	0.0400	0.9400	96 341	0.07	25 726	0.14
MAK-5	0.02000	0.0600	0.9200	78 759	0.08	33 327	0.12
MAK-6	0.02000	0.0800	0.9000	64 087	0.09	42 457	0.11
MAK-7	0.02000	0.1000	0.8800	56 878	0.10	50 275	0.10

* 50kV,40mA

TABLE B Calculation of α_{ZnCr}

Solutions	α_{ZnCr}
MAK-1/MAK-7	0.5660···
MAK-1/MAK-6	0.6243···
MAK-1/MAK-5	0.5216···
MAK-2/MAK-7	0.4459···
MAK-2/MAK-6	0.5073···
MAK-3/MAK-7	0.5777···

α_{ZnCr} average = 0.5405···

std. devn. = ± 0.0624···

$$\alpha_{ZnCr} = 0.54^{0} \pm 0.06^{2}$$

$$= 0.54 \pm 0.06$$

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{ZnK\alpha}$(corr) (cps)
MAK-1	169 870	- 156 967	--	12 903
MAK-2	136 006	- 124 393	+ 734	12 347
MAK-3	121 926	- 110 365	+ 1 317	12 878
MAK-4	96 341	- 85 389	+ 2 081	13 033
MAK-5	78 759	- 68 321	+ 2 552	12 990
MAK-6	64 087	- 54 385	+ 2 768	12 470
MAK-7	56 878	- 47 194	+ 3 071	12 755

$I^{o}_{ZnK\alpha}$ average = 638 400 cps

Std. devn. = ± 13 100 cps

$$I^{o}_{ZnK\alpha} = (6.3^{8} \pm 0.1^{3}) \times 10^{5} \text{ cps}$$

$$= (6.4 \pm 0.1) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CrK\alpha}(corr)$ and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of		$I_{CrK\alpha}(corr)$ (cps)
		matrix	zinc	
MAK-2	6 626	- 5 444	- 51	1 131
MAK-3	13 553	- 11 021	- 105	2 427
MAK-4	25 726	- 20 485	- 200	5 041
MAK-5	33 327	- 25 973	- 259	7 095
MAK-6	42 457	- 32 369	- 329	9 759
MAK-7	50 275	- 37 477	- 390	12 408

$I^{o}_{CrK\alpha}$ average = 120 799 cps

std. devn. = ± 4 600 cps

$I^{o}_{CrK\alpha}$ = $(1.20^{8} \pm 0.04^{6}) \times 10^{5}$ cps

= $(1.21 \pm 0.05) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Cr}(calc)	Abs. error	Error %
MAK-1	0.02030	0.00030	1.50	--	--	--
MAK-2	0.01890	0.00110	5.50	0.00930	0.00070	7.00
MAK-3	0.02020	0.00020	1.00	0.02010	0.00010	0.50
MAK-4	0.02110	0.00110	5.50	0.0422	0.0022	5.50
MAK-5	0.02010	0.00010	0.50	0.0584	0.0016	2.66
MAK-6	0.01970	0.00030	1.50	0.0811	0.0011	1.38
MAK-7	0.02060	0.00060	3.00	0.1044	0.0044	4.40

FIGURE D $I_{ZnK\alpha}$ versus C_{Cr} and C_M

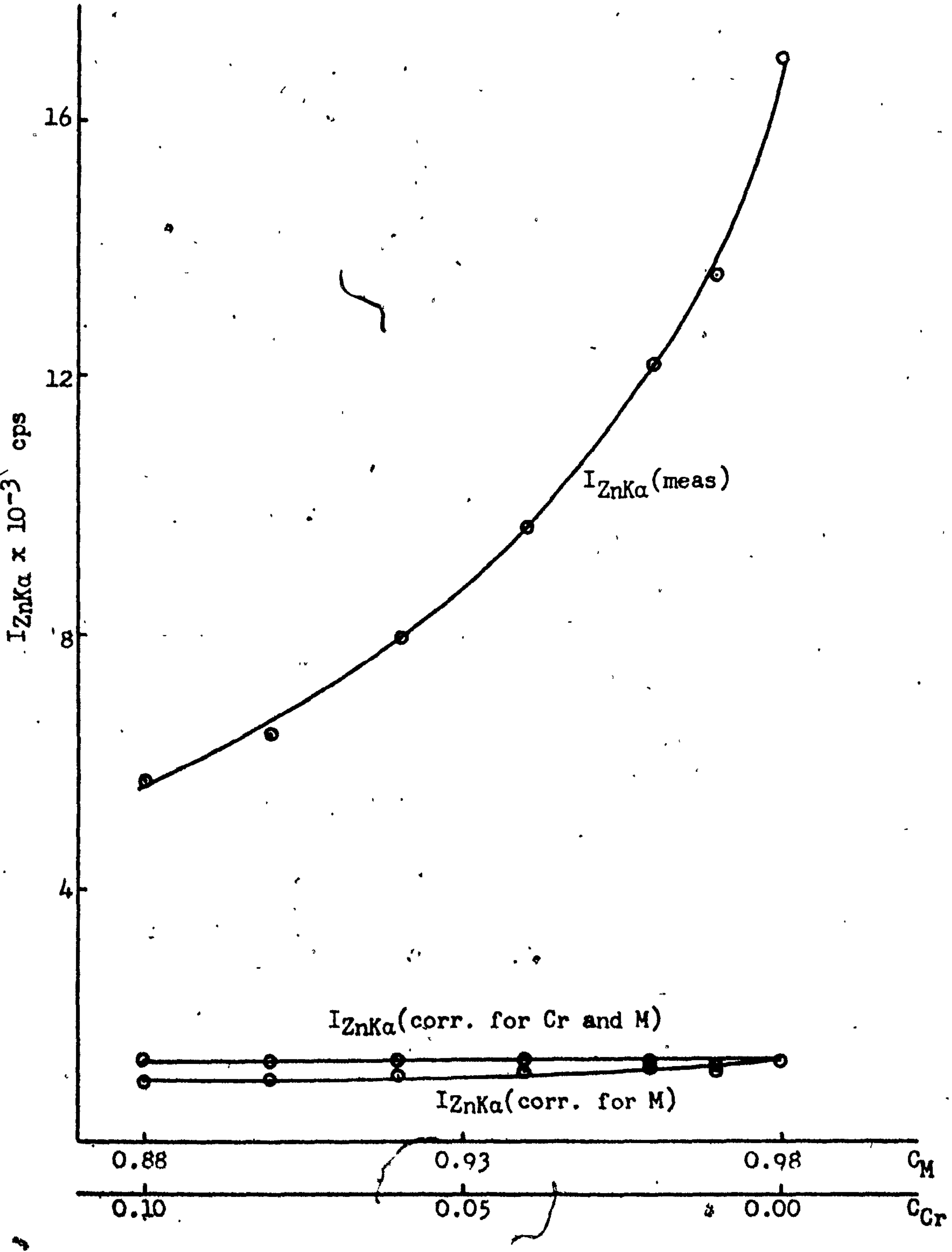
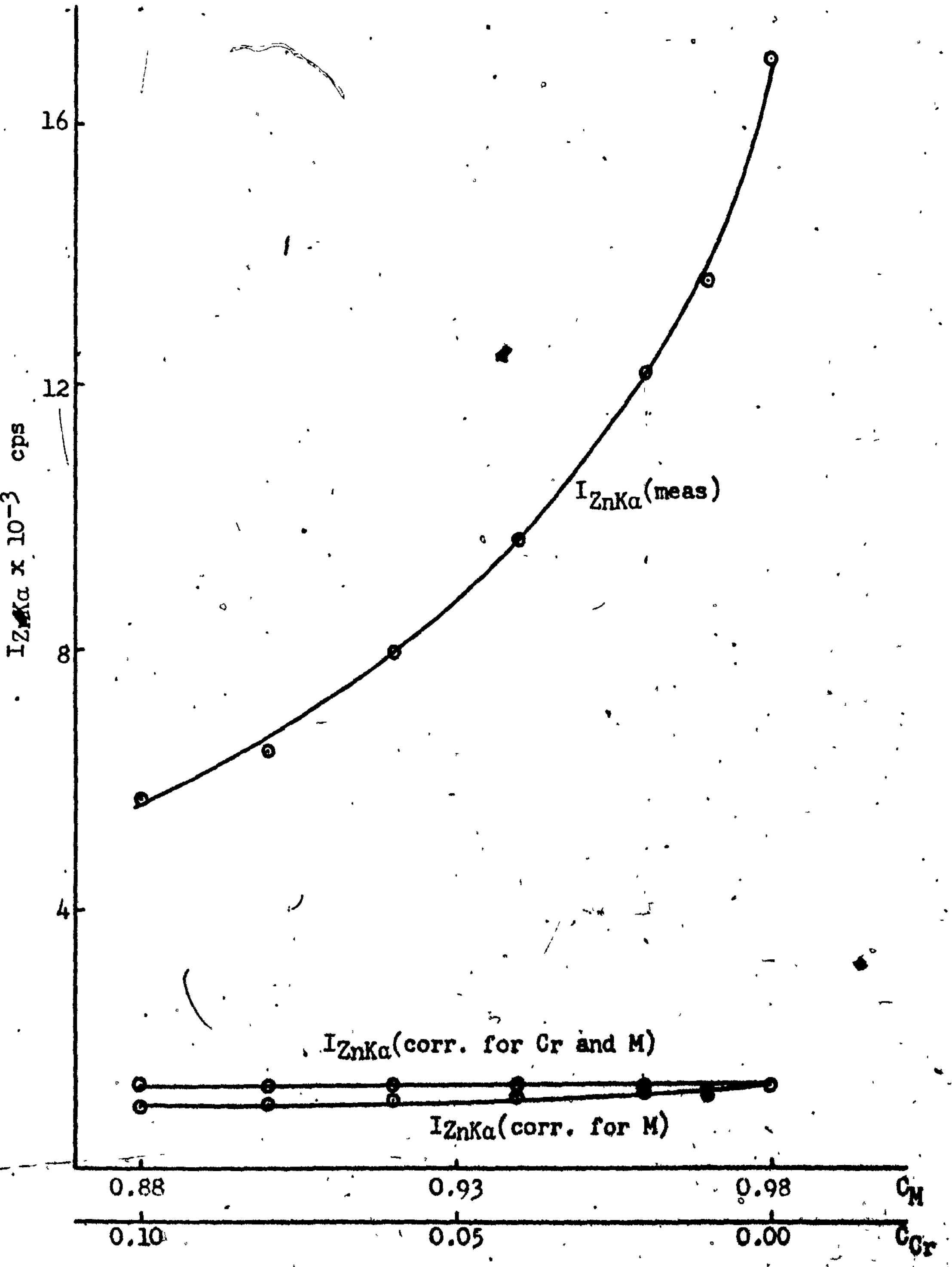


FIGURE D $I_{ZnK\alpha}$ versus C_{Cr} and C_M



The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α_{AM_n} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{AM_n} (presence of chlorine as fourth component)	Equation (44)
	Calculation of I_A(corr)	Equation (45) or a modification
	Calculation of I_A^o	$I_A(corr)/C_A$

5.4.1 Effect of Mn on Cl

TABLE A – Experimental Parameters

Solution	C_{Cl}	C_{Mn}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}^*$ (cps)	s(%)
LZJ-1	0.0196	0.0	0.9804	5 942	0.30	—	--
LZJ-2	0.0196	0.01000	0.9704	5 851	0.30	5 331	0.32
LZJ-3	0.0196	0.02000	0.9604	5 803	0.30	10 010	0.22
LZJ-4	0.0196	0.04000	0.9404	5 611	0.31	18 406	0.17
LZJ-5	0.0196	0.05000	0.9304	5 512	0.31	22 074	0.15
LZJ-6	0.0196	0.06000	0.9204	5 466	0.31	25 273	0.14

* 40kV, 20mA

TABLE B Calculation of α_{ClMn}

Solutions	α_{ClMn}
LZJ-1/LZJ-6	0.6373···
LZJ-1/LZJ-5	0.7103···
LZJ-1/LZJ-4	0.6530···
LZJ-2/LZJ-6	0.6222···
LZJ-2/LZJ-5	0.7111···

α_{ClMn} average = 0.6668···
std. devn. = ± 0.0318···
α_{ClMn} = $0.66^7 \pm 0.03^2$
= 0.67 ± 0.03

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{ClK\alpha}$(corr) (cps)
LZJ-1	5 942	- 1 957	—	3 985
LZJ-2	5 851	- 1 908	+ 39	3 982
LZJ-3	5 803	- 1 872	+ 77	4 008
LZJ-4	5 611	- 1 773	+ 150	3 988
LZJ-5	5 512	- 1 723	+ 184	3 973
LZJ-6	5 466	- 1 690	+ 219	3 995

$I^o_{ClK\alpha}$ average = 203 482 cps
std. devn. = ± 608 cps
$I^o_{ClK\alpha}$ = $(2.034^8 \pm 0.006^0) \times 10^5$ cps
= $(2.035 \pm 0.006) \times 10^5$ cps

TABLE D Calculation of $I_{MnK\alpha}(corr)$ and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	$I_{MnK\alpha}(corr)$ (cps)
LZJ-2	5 331	− 4 468	+ 30	893
LZJ-3	10 010	− 8 303	+ 57	1 764
LZJ-4	18 406	− 14 950	+ 105	3 561
LZJ-5	22 074	− 17 738	+ 126	4 462
LZJ-6	25 273	− 20 091	+ 145	5 327

$I^{o}_{MnK\alpha}$ average = 88 912 cps

srd. devn. = ± 455 cps

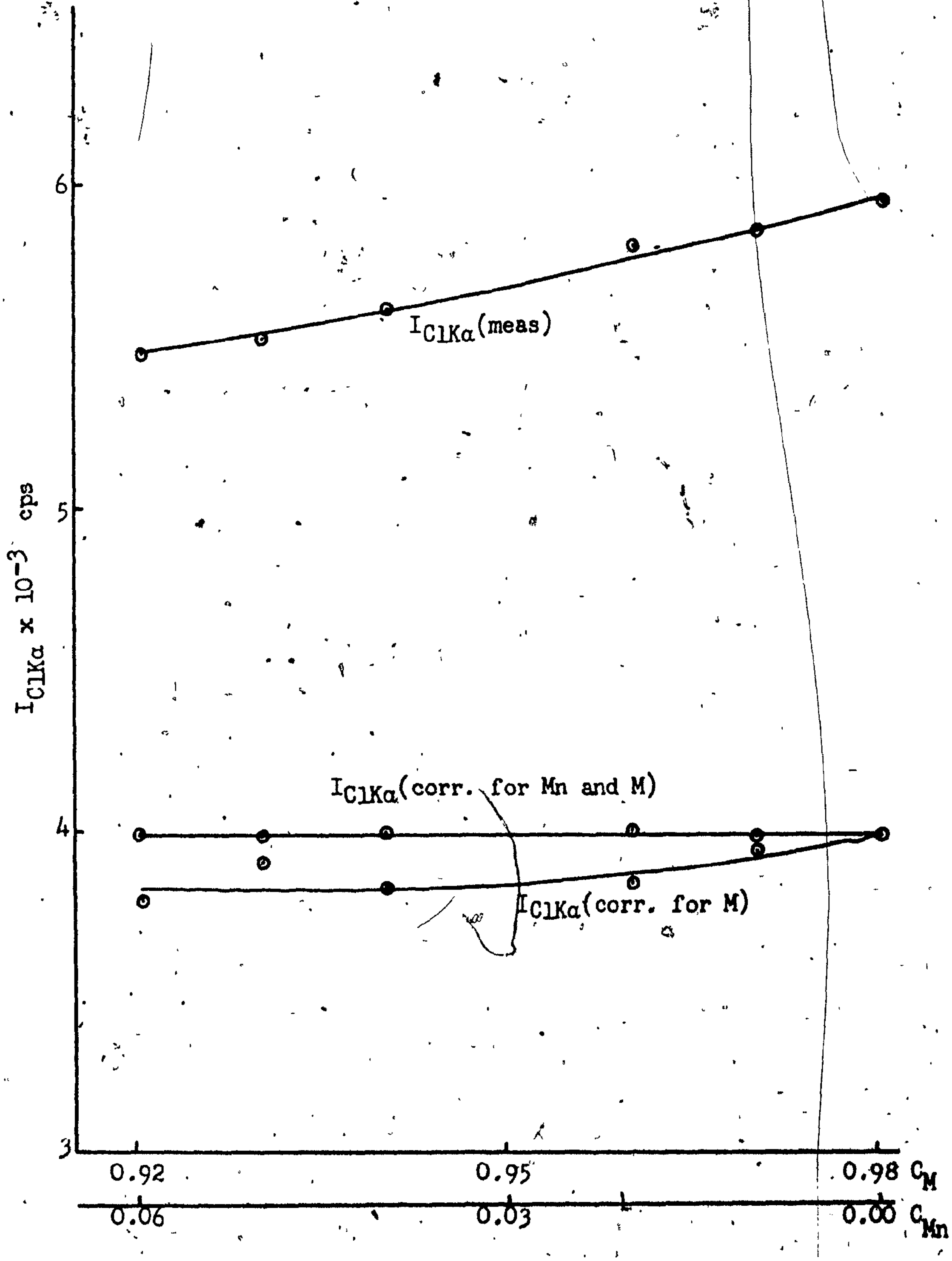
$I^{o}_{MnK\alpha}$ = $(8.89^{1} \pm 0.04^{5}) \times 10^{4}$ cps

= $(8.89 \pm 0.04) \times 10^{4}$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error %
LZJ-1	0.0196	0.0000	0.00	--	--	--
LZJ-2	0.0196	0.0000	0.00	0.0100	0.0000	0.00
LZJ-3	0.0197	0.0001	0.50	0.0198	0.0002	1.00
LZJ-4	0.0196	0.0000	0.00	0.0401	0.0001	0.25
LZJ-5	0.0195	0.0001	0.50	0.0502	0.0002	0.40
LZJ-6	0.0196	0.0000	0.00	0.0599	0.0001	0.17

FIGURE D $I_{ClK\alpha}$ versus C_{Mn} and C_M



5.4.2 Effect of Mn on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Mn}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{MnK\beta}$* (cps)	s(%)
MBG-1	0.02000	0.0	0.98000	12 247	0.20	—	—
MBG-2	0.02000	0.01000	0.97000	11 417	0.21	2 517	0.45
MBG-3	0.02000	0.02000	0.96000	11 135	0.21	4 615	0.33
MBG-4	0.02000	0.0400	0.9400	10 631	0.21	8 478	0.24
MBG-5	0.02000	0.0600	0.9200	10 110	0.22	11 433	0.21
MBG-6	0.02000	0.0800	0.9000	9 598	0.22	14 237	0.19
MBG-7	0.02000	0.1000	0.8800	8 771	0.24	16 849	0.17

*50kV, 40mA

TABLE B Calculation of α_{CrMn}

Solutions	α_{CrMn}
MBG-1/MBG-7	- 0.1740···
MBG-1/MBG-6	- 0.2612···
MBG-1/MBG-5	- 0.2488···
MBG-2/MBG-7	- 0.2580···
MBG-2/MBG-6	- 0.3745···
MBG-2/MBG-5	- 0.3963···
MBG-3/MBG-7	- 0.2336···
MBG-3/MBG-6	- 0.3682···
MBG-3/MBG-5	- 0.3936···

α_{CrMn} average = $-0.3009\cdots$

srd. devn. = $\pm 0.0824\cdots$

$$\alpha_{CrMn} = -0.30^1 \pm 0.08^2$$

$$= -0.30 \pm 0.08$$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^o_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{CrK\alpha}$(corr) (cps)
MBG-1	12 247	- 10 167	--	2 080
MBG-2	11 417	- 9 381	- 34	2 002
MBG-3	11 135	- 9 055	- 67	2 013
MBG-4	10 631	- 8 465	- 128	2 038
MBG-5	10 110	- 7 879	- 182	2 049
MBG-6	9 598	- 7 317	- 231	2 050
MBG-7	8 771	- 6 538	- 264	1 969

$I^{o}_{CrK\alpha}$ average = 101 436 cps
std. devn. = ± 1 858 cps
$I^{o}_{CrK\alpha}$ = $(1.01^{4} \pm 0.01^{8}) \times 10^{5}$ cps
= $(1.01 \pm 0.02) \times 10^{5}$ cps

TABLE D Calculation of $I_{MnK\beta}$(corr) and $I^{o}_{MnK\beta}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{MnK\beta}$(corr) (cps)
MBG-2	2 517	- 2 109	+ 41	449
MBG-3	4 615	- 3 826	+ 76	865
MBG-4	8 478	- 6 883	+ 139	1 734
MBG-5	11 433	- 9 085	+ 187	2 535
MBG-6	14 237	- 11 067	+ 233	3 403
MBG-7	16 849	- 12 806	+ 276	4 319

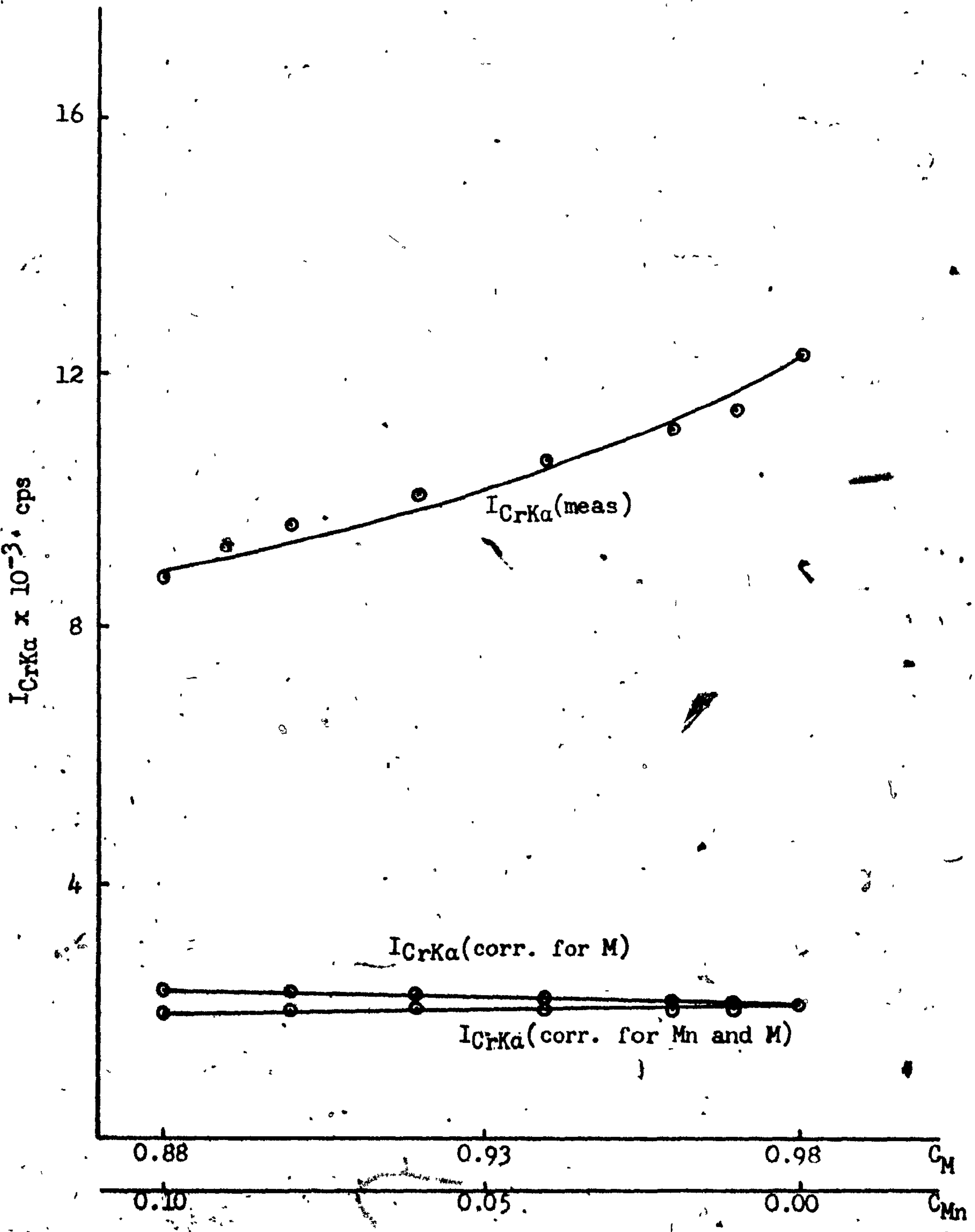
$I^{o}_{MnK\beta}$ average = 43 246 cps
std. devn. = ± 938 cps
$I^{o}_{MnK\beta}$ = $(4.32^{4} \pm 0.09^{3}) \times 10^{4}$ cps
= $(4.32 \pm 0.09) \times 10^{4}$ cps

MnKβ radiation measured for this series only because of proximity of MnKα and CrKβ lines. This proximity was really not close enough to create real problems except at very high concentrations of both elements

TABLE E Back-calculation of solution composition

Solution	C_{Cr} (calc)	Abs. error	Error %	C_{Mn} (calc)	Abs. error	Error %
MBG-1	0.02060	0.00060	3.00	--	--	--
MBG-2	0.01970	0.00030	1.50	0.01040	0.00040	4.00
MBG-3	0.01980	0.00020	1.00	0.01990	0.00010	0.50
MBG-4	0.02010	0.00010	0.50	0.0401	0.0001	0.25
MBG-5	0.02010	0.00010	0.50	0.0583	0.0017	2.83
MBG-6	0.02010	0.00010	0.50	0.0783	0.0017	2.12
MBG-7	0.01930	0.00070	3.50	0.0991	0.0009	0.90

FIGURE D $I_{CrK\alpha}$ versus C_{Mn} and C_M



5.4.3 Effect of Mn on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Mn}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MAT-1	0.01000	0.0	0.01611	0.97389	22 706	0.15	--	--	4 471	0.33
MAT-2	0.01000	0.01000	0.01611	0.96389	20 866	0.16	9 581	0.22	4 480	0.33
MAT-3	0.01000	0.02000	0.01611	0.95389	19 124	0.16	18 996	0.16	4 402	0.33
MAT-4	0.01000	0.0400	0.01611	0.9339	18 104	0.17	33 842	0.12	4 312	0.33
MAT-5	0.01000	0.0600	0.01611	0.9139	17 071	0.17	47 538	0.10	4 254	0.34
MAT-6	0.01000	0.0800	0.01611	0.8939	15 829	0.18	58 770	0.10	4 103	0.35
MAT-7	0.01000	0.1000	0.01611	0.8739	15 129	0.18	68 953	0.09	4 037	0.35

*50kV,40mA

TABLE. B Calculation of α_{FeMn}

Solutions	α_{FeMn}
MAT-1/MAT-7	- 0.2583···
MAT-1/MAT-6	- 0.2044···
MAT-1/MAT-5	- 0.1954···
MAT-2/MAT-7	- 0.3360···
MAT-2/MAT-6	- 0.2896···
MAT-2/MAT-5	- 0.3036···
MAT-3/MAT-7	- 0.4462···
MAT-3/MAT-6	- 0.4215···
MAT-4/MAT-7	- 0.4159···

α_{FeMn} average = - 0.3190···

std. devn. = ± 0.093····

α_{FeMn} = $-0.31^{9} \pm 0.09^{3}$

= - 0.32 ± 0.09

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of manganese	$I_{FeK\alpha}$(corr) (cps)
MAT-1	22 706	- 19 829	+ 17	--	2 894
MAT-2	20 866	- 18 035	+ 16	- 66	2 781
MAT-3	19 124	- 16 358	+ 14	- 122	2 658
MAT-4	18 104	- 15 160	+ 14	- 231	2 727
MAT-5	17 071	- 13 989	+ 13	- 327	2 768
MAT-6	15 829	- 12 688	+ 12	- 404	2 749
MAT-7	15 129	- 11 855	+ 11	- 483	2 802

$I^{o}_{FeK\alpha}$ average = 276 843 cps
std. devn. = ± 7 229 cps
$I^{o}_{FeK\alpha}$ = $(2.76^{8} \pm 0.07^{2}) \times 10^{5}$ cps
= $(2.77 \pm 0.07) \times 10^{5}$ cps

TABLE D Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of iron	$I_{MnK\alpha}$(corr) (cps)
MAT-2	9 581	- 7 976	+ 45	- 27	1 623
MAT-3	18 996	- 15 650	+ 89	- 53	3 382
MAT-4	33 842	- 27 297	+ 159	- 95	6 609
MAT-5	47 538	- 37 523	+ 224	- 133	10 106
MAT-6	58 776	- 45 373	+ 276	- 165	13 508
MAT-7	68 953	- 52 044	+ 324	- 194	17 039

$I^{o}_{MnK\alpha}$ average = 167 383 cps
std. devn. = ± 2 762 cps
$I^{o}_{MnK\alpha}$ = $(1.67^{3} \pm 0.02^{7}) \times 10^{5}$ cps
= $(1.67 \pm 0.03) \times 10^{5}$ cps

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of iron	Correction for effect of manganese	$I_{ClK\alpha}$(corr) (cps)
MAT-1	4 471	- 1 463	+ 50	--	3 058
MAT-2	4 480	- 1 451	+ 50	+ 30	3 109
MAT-3	4 402	- 1 411	+ 50	+ 59	3 100
MAT-4	4 312	- 1 353	+ 49	+ 115	3 123
MAT-5	4 254	- 1 306	+ 48	+ 170	3 166
MAT-6	4 103	- 1 232	+ 46	+ 219	3 136
MAT-7	4 037	- 1 185	+ 45	+ 269	3 166

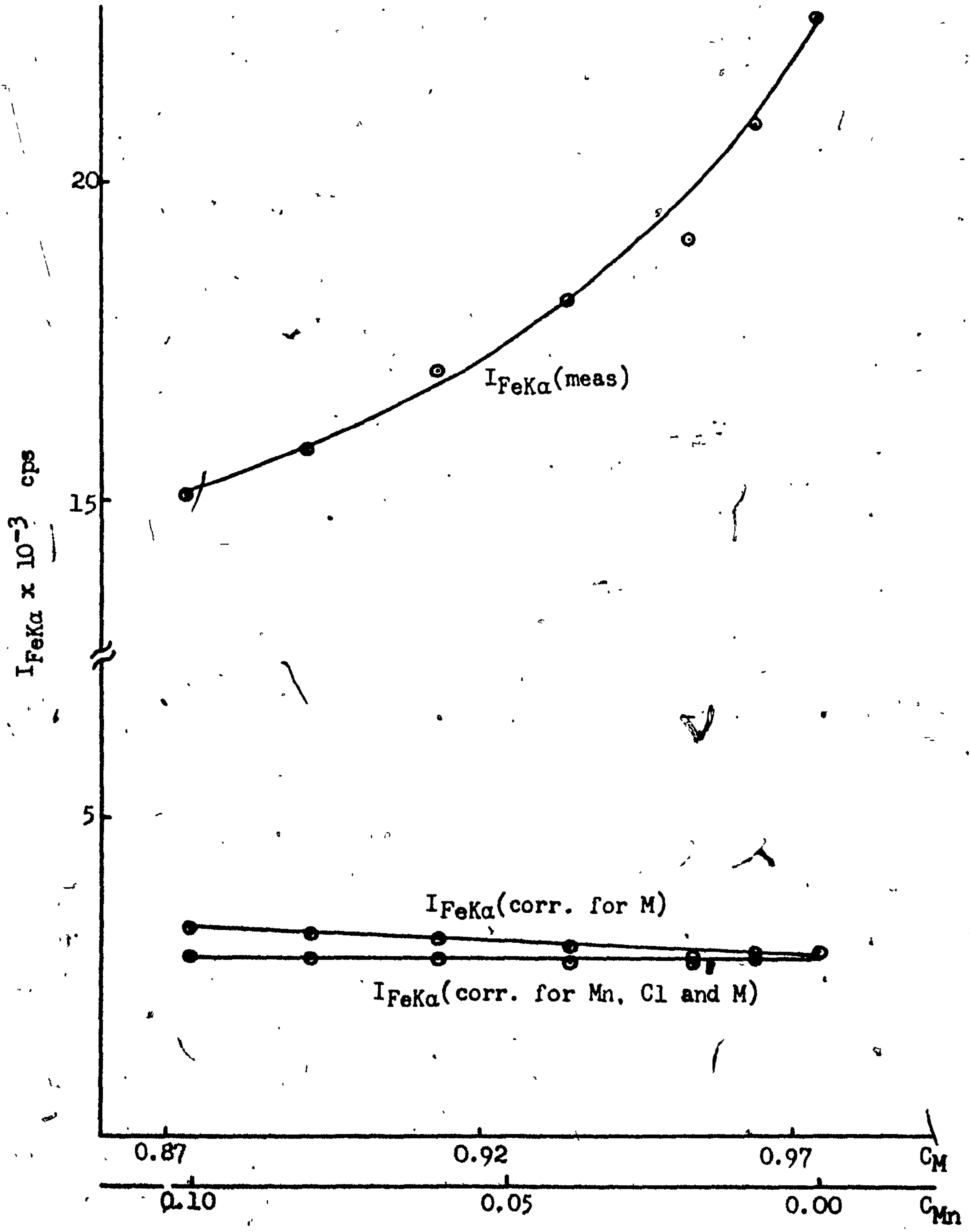
$I^{o}_{ClK\alpha}$ average = 193 828 cps
std, devn. = ± 2 378 cps
$I^{o}_{ClK\alpha}$ = $(1.93^{8} \pm 0.02^{4}) \times 10^{5}$ cps
= $(1.94 \pm 0.02) \times 10^{5}$ cps

TABLE F Back-calculation of solution composition

Solution	C_{Fe}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error %
MAT-1	0.01050	0.00050	5.00	--	--	--
MAT-2	0.01000	0.00000	0.00	0.00970	0.00030	3.00
MAT-3	0.00960	0.00040	4.00	0.02020	0.00020	1.00
MAT-4	0.00980	0.00020	2.00	0.0393	0.0007	1.80
MAT-5	0.01000	0.00000	0.00	0.0606	0.0006	1.00
MAT-6	0.01000	0.00000	0.00	0.0810	0.0010	1.30
MAT-7	0.01020	0.00020	2.00	0.1031	0.0031	3.10

Solution	C_{Cl}(calc)	Abs. error	Error %
MAT-1	0.01579	0.00032	1.99
MAT-2	0.01603	0.00008	0.50
MAT-3	0.01599	0.00012	0.74
MAT-4	0.01609	0.00002	0.12
MAT-5	0.01635	0.00024	1.49
MAT-6	0.01620	0.00009	0.56
MAT-7	0.01641	0.00030	1.86

FIGURE D $I_{FeK\alpha}$ versus C_{Mn} and C_M



5.4.4 Effect of Mn on Co

TABLE A Experimental Parameters

Solution	C_{Co}	C_{Mn}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}$* (cps)	s(%)
MBH-1	0.02000	0.00	0.98000	118 162	0.07	--	--
MBH-2	0.02000	0.01000	0.97000	97 606	0.07	18 493	0.17
MBH-3	0.02000	0.02000	0.96000	81 196	0.08	34 195	0.12
MBH-4	0.02000	0.0300	0.9500	71 701	0.09	49 117	0.10
MBH-5	0.02000	0.0600	0.9200	50 071	0.10	84 018	0.10
MBH-6	0.02000	0.0800	0.9000	42 587	0.11	104 248	0.07
MBH-7	0.02000	0.1000	0.8800	36 558	0.12	118 402	0.06

*50kV, 40mA

TABLE B Calculation of α_{CoMn}

Solutions	α_{CoMn}
MBH-1/MBH-7	1.2238···
MBH-1/MBH-6	1.2105···
MBH-1/MBH-5	1.2568···
MBH-2/MBH-7	1.2680···
MBH-2/MBH-6	1.2538···
MBH-2/MBH-5	1.3311···
MBH-3/MBH-7	1.1899···
MBH-3/MBH-6	1.1596···
MBH-4/MBH-7	1.3231···

α_{CoMn} average = 1.2429···

std. devn. = ± 0.0573···

$$\alpha_{CoMn} = 1.24^{3} \pm 0.05^{7}$$

$$= 1.24 \pm 0.06$$

TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of		$I_{CoK\alpha}$(corr) (cps)
		matrix	manganese	
MBH-1	118 162	- 106 801	--	11 361
MBH-2	97 606	- 87 321	+ 1 213	11 498
MBH-3	81 196	- 71 891	+ 2 018	11 323
MBH-4	71 701	- 62 823	+ 2 674	11 552
MBH-5	50 071	- 42 486	+ 3 734	11 319
MBH-6	42 587	- 35 350	+ 4 235	11 472
MBH-7	36 558	- 29 671	+ 4 544	11 431

$I^{o}_{CoK\alpha}$ average = 571 114 cps
std. devn. = ± 4 525 cps
$I^{o}_{CoK\alpha}$ = $(5.71^{1} \pm 0.04^{5}) \times 10^{5}$
= $(5.71 \pm 0.04) \times 10^{5}$

TABLE D Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

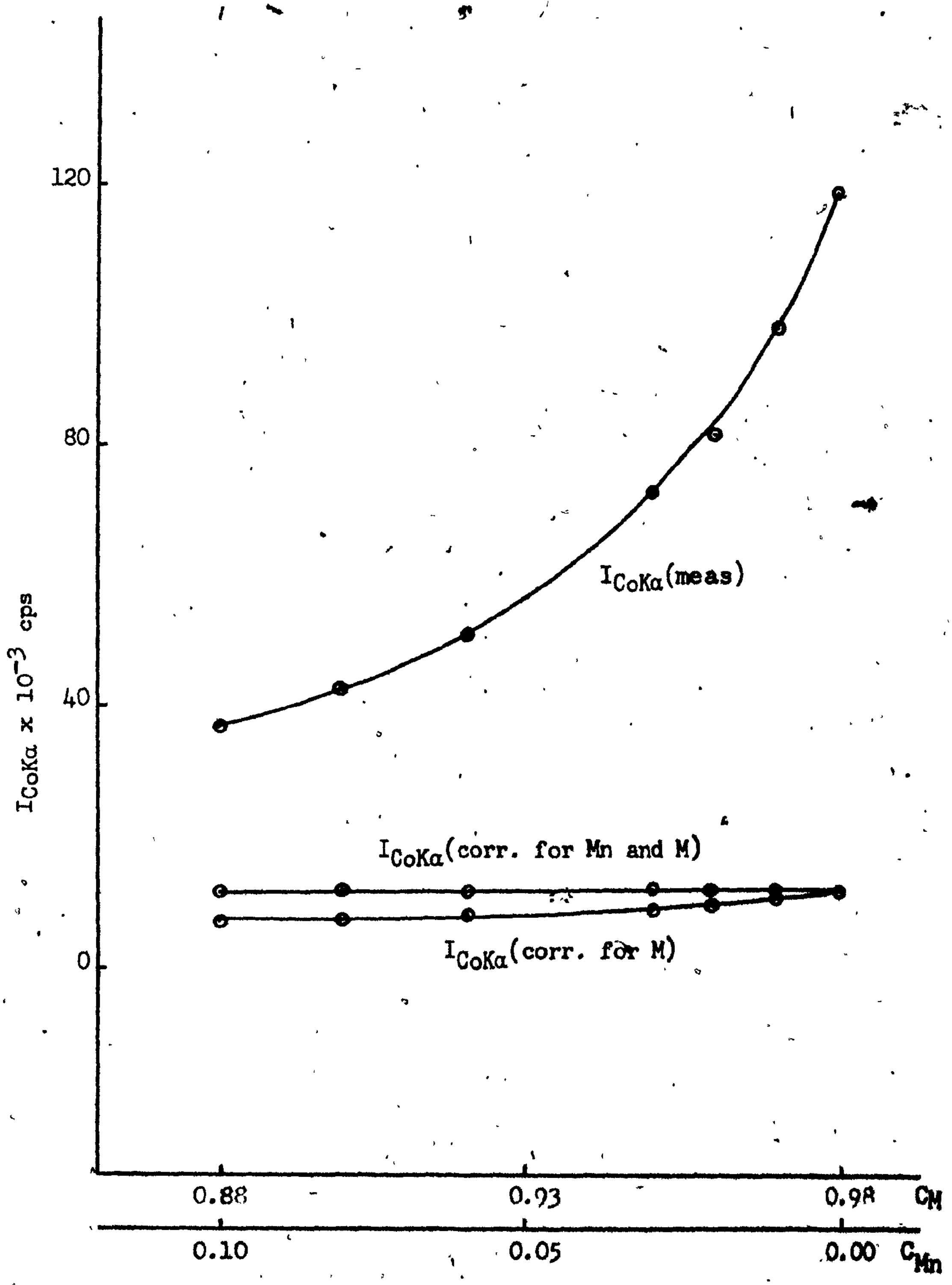
Solution	Measured	Correction for effect of		$I_{MnK\alpha}$(corr) (cps)
		matrix	cobalt	
MBH-2	18 493	- 15 493	- 249	2 751
MBH-3	34 195	- 28 353	- 461	5 381
MBH-4	49 117	- 40 301	- 662	8 154
MBH-5	84 018	- 66 761	- 1 133	16 124
MBH-6	104 248	- 81 305	- 1 405	21 808
MBH-7	118 402	- 89 992	- 1 596	26 814

$I^{o}_{MnK\alpha}$ average = 270 887 cps
std. devn. = ± 2 700 cps
$I^{o}_{MnK\alpha}$ = $(2.70^{8} \pm 0.02^{7}) \times 10^{5}$
= $(2.71 \pm 0.03) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error%
MBH-1	0.01990	0.00010	0.50	—	—	—
MBH-2	0.02020	0.00020	1.00	0.01020	0.00020	2.00
MBH-3	0.01970	0.00030	1.50	0.01980	0.00020	1.00
MBH-4	0.02030	0.00030	1.50	0.0301	0.0001	0.33
MBH-5	0.01970	0.00030	1.50	0.0593	0.0007	1.16
MBH-6	0.02020	0.00020	1.00	0.0808	0.0008	1.00
MBH-7	0.01980	0.00020	1.00	0.0983	0.0017	1.70

FIGURE D $I_{CoK\alpha}$ versus C_{Mn} and C_M



5.4.5 Effect of Mn on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Mn}	C_M	$I_{NiK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}$* (cps)	s(%)
MBI-1	0.02000	0.00	0.98000	119 096	0.06	--	--
MBI-2	0.02000	0.01000	0.97000	101 382	0.07	13 531	0.19
MBI-3	0.02000	0.02000	0.96000	86 239	0.08	26 519	0.14
MBI-4	0.02000	0.0400	0.9400	67 507	0.09	46 503	0.11
MBI-5	0.02000	0.0600	0.9200	53 928	0.10	65 047	0.10
MBI-6	0.02000	0.0800	0.9000	45 173	0.10	79 675	0.08
MBI-7	0.02000	0.1000	0.8800	41 242	0.11	91 862	0.07

*50kV, 40mA

TABLE B Calculation of α_{NiMn}

Solutions	α_{NiMn}
MBI-1/MBI-7	0.9941···
MBI-1 MBI-6	1.1538···
MBI-1/MBI-5	1.1219···
MBI-2/MBI-6	1.2716···
MBI-2/MBI-5	1.2452···
MBI-3/MBI-6	1.2838···

α_{NiMn} average = 1.2153···

std. devn. = ± 0.0729···

$\alpha_{NiMn} = 1.21^5 \pm 0.07^3$

$= 1.21 \pm 0.07$

TABLE C Calculation of $I_{NiK\alpha}$(corr) and $I^o_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{NiK\alpha}$(corr) (cps)
MBI-1	119 096	- 107 038	--	12 058
MBI-2	101 382	- 90 188	+ 1 232	12 426
MBI-3	86 239	- 75 926	+ 2 096	12 409
MBI-4	67 507	- 58 196	+ 3 280	12 591
MBI-5	53 928	- 45 501	+ 39931	12 358
MBI-6	41 242	- 33 284	+ 5 011	12 969

$I^o_{NiK\alpha}$ average = 622 071 cps

std. devn. = ± 10 115 cps

$I^0_{NiK\alpha} = (6.2^2 \pm 0.1^0) \times 10^5$

TABLE D Calculation of $I_{MnK\alpha}(corr)$ and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{MnK\alpha}(corr)$ (cps)
MBI-2	13 531	- 11 336	- 248	1 947
MBI-3	26 519	- 21 988	- 486	4 045
MBI-4	46 503	- 37 755	- 853	7 895
MBI-5	65 047	- 51 687	- 1 193	12 167
MBI-6	79 675	- 61 934	- 1 461	16 280
MBI-7	91 862	- 69 820	- 1 685	20 357

$I^{o}_{MnK\alpha}$ average = 200 696 cps

std. devn. = ± 3 802 cps

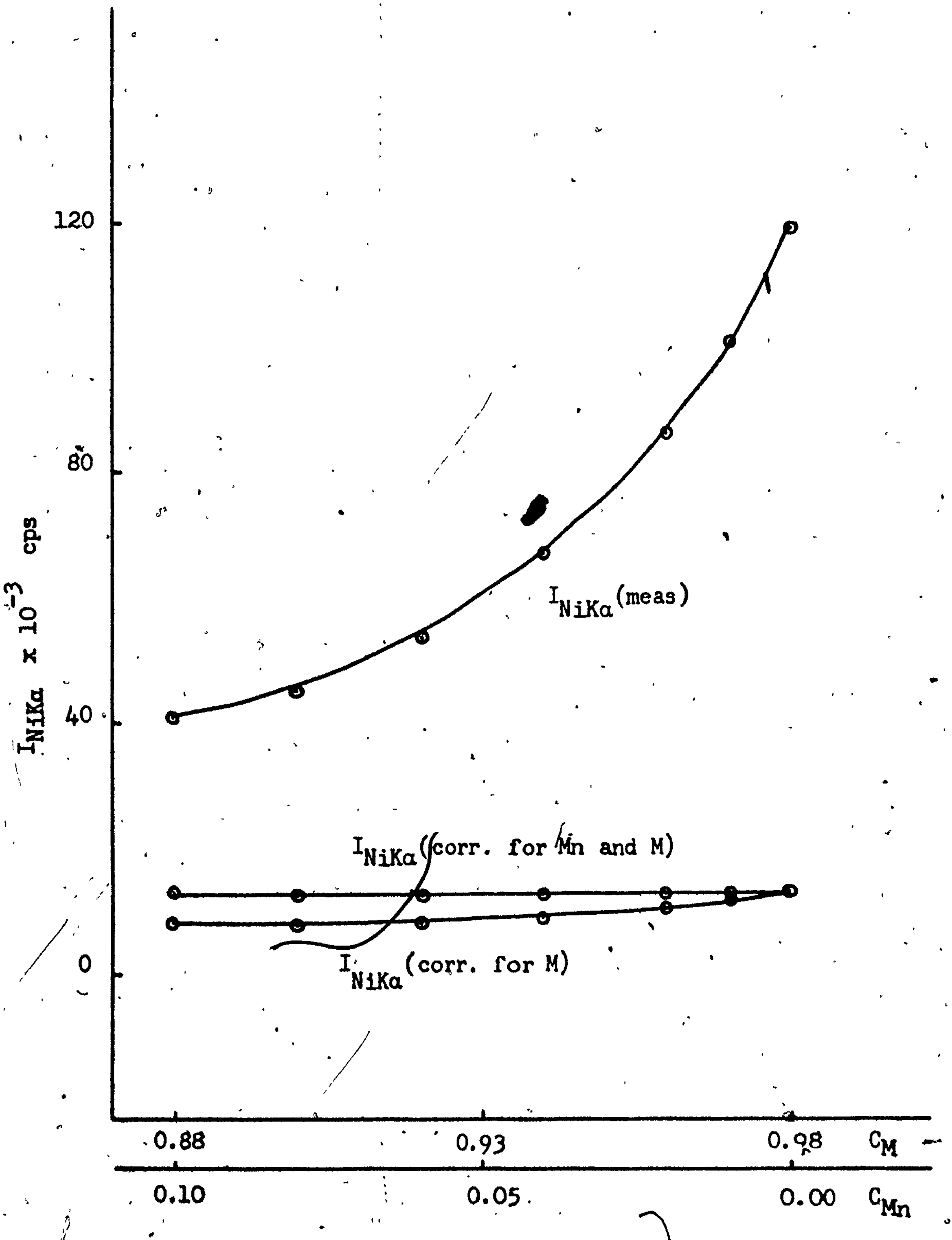
$$I^{o}_{MnK\alpha} = (2.00^{6} \pm 0.03^{8}) \times 10^{5}$$

$$\doteqdot (2.01 \pm 0.04) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	C_{Ni}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error %
MBI-1	0.01930	0.00070	3.50	—	—	—
MBI-2	0.02010	0.00010	0.50	0.01040	0.00040	4.00
MBI-3	0.02050	0.00050	2.50	0.02180	0.00180	9.00
MBI-4	0.02090	0.00090	4.50	0.0423	0.0023	5.75
MBI-5	0.02100	0.00100	5.00	0.0658	0.0058	9.66
MBI-6	0.02110	0.00110	5.50	0.0884	0.0084	15.00
MBI-7	0.02260	0.00260	13.00	0.1113	0.0113	11.30

FIGURE D $I_{NiK\alpha}$ versus C_{Mn} and C_M



5.4.6 Effect of Mn on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Mn}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}$* (cps)	s(%)
MBK-1	0.02000	0.00	0.98000	108 691	0.07	—	—
MBK-2	0.02000	0.01000	0.97000	90 120	0.07	14 208	0.19
MBK-3	0.02000	0.02000	0.96000	73 660	0.09	26 257	0.14
MBK-4	0.02000	0.0400	0.9400	57 598	0.10	45 933	0.11
MBK-5	0.02000	0.0600	0.9200	46 408	0.10	64 868	0.09
MBK-6	0.02000	0.0800	0.9000	40 656	0.11	79 525	0.08
MBK-7	0.02000	0.1000	0.8800	36 142	0.12	94 014	0.07

* 50kV., 40mA

TABLE B Calculation of α_{CuMn}

Solutions	α_{CuMn}
MBK-1/MBK-7	0.9332···
MBK-1/MBK-6	1.0115···
MBK-1/MBK-5	1.1458···
MBK-2/MBK-7	0.9168···
MBK-2/MBK-6	1.0225···
MBK-2/MBK-5	1.2238···

α_{CuMn} average = 1.0423···

std. devn. = ± 0.120···

$\alpha_{CuMn} \approx 1.0^{4} \pm 0.1^{2}$

$= 1.0 \pm 0.1$

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{CuK\alpha(corr)}$ (cps)
MBK-1	108 691	- 98 624	—	10 067
MBK-2	90 120	- 80 939	+ 937	10 118
MBK-3	73 660	- 65 474	+ 1 532	9 718
MBK-4	57 598	- 50 130	+ 2 396	9 864
MBK-5	46 408	- 39 532	+ 2 896	9 772
MBK-6	40 656	- 33 879	+ 3 382	10 159
MBK-7	36 142	- 29 448	+ 3 759	10 453

$I^{o}_{CuK\alpha}$ average = 501 079 cps

std. devn. = ± 11 972 cps

$I^{o}_{CuK\alpha} \simeq (5.0^{1} \pm 0.1^{1}) \times 10^{5}$

$= (5.0 \pm 0.1) \times 10^{5}$

TABLE D Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{MnK\alpha}$(corr) (cps)
MBK-2	14 208	- 11 903	- 145	2 160
MBK-3	26 257	- 21 771	- 267	4 219
MBK-4	45 933	- 37 292	- 467	8 174
MBK-5	64 868	- 51 544	- 660	12 664
MBK-6	79 525	- 61 817	- 809	16 899
MBK-7	94 014	- 71 456	- 957	21 601

$I^{o}_{MnK\alpha}$ average = 211 602 cps

std. devn. = ± 4 303 cps

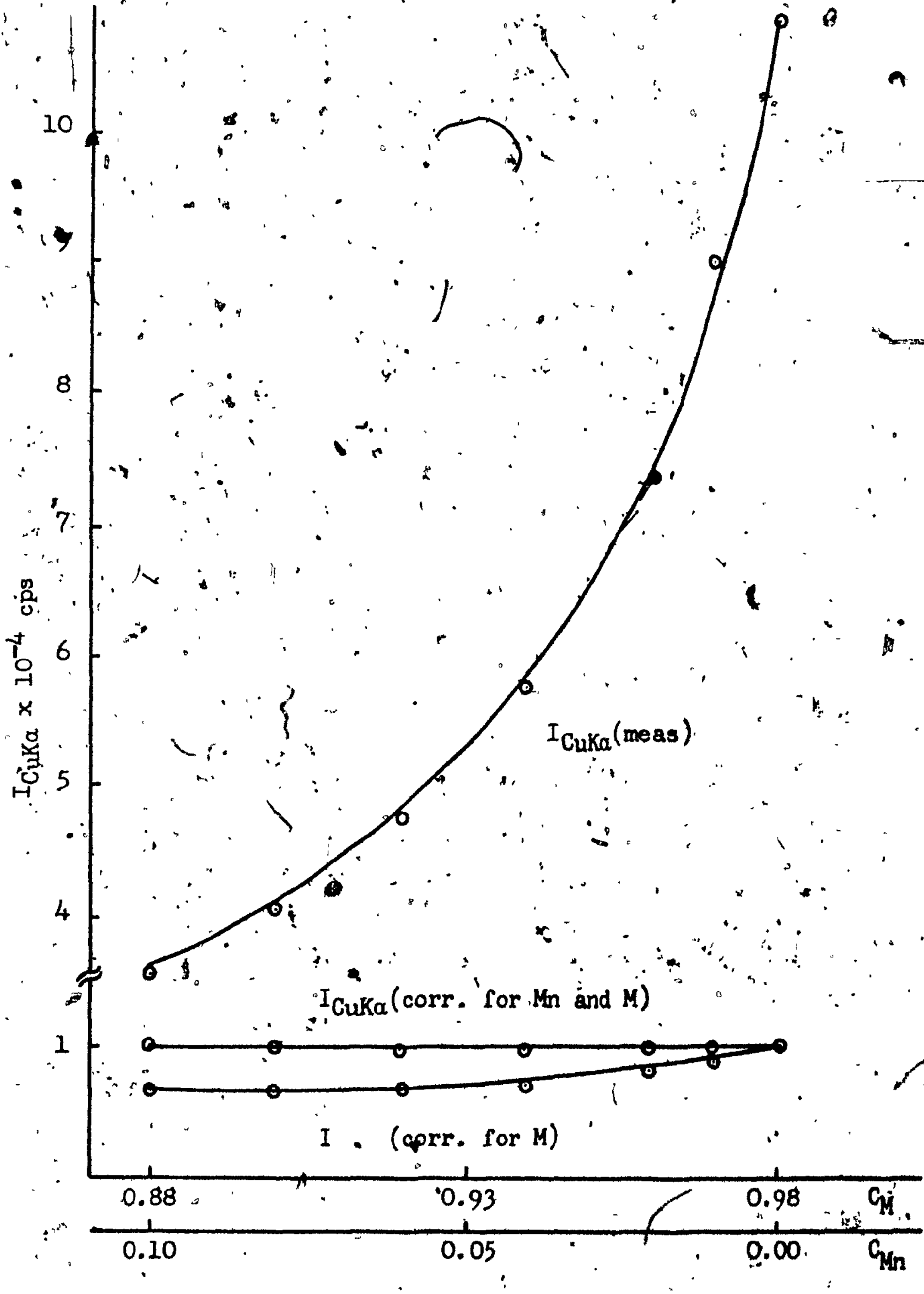
$I^{o}_{MnK\alpha} = (2.11^{6} \pm 0.04^{3}) \times 10^{5}$

$\simeq (2.12 \pm 0.04) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error %
MBK-1	0.02020	0.00020	1.00	—	—	—
MBK-2	0.02040	0.00040	2.00	0.01020	0.00020	2.00
MBK-3	0.01930	0.00070	3.50	0.01990	0.00010	1.00
MBK-4	0.01930	0.00070	3.50	0.0382	0.0018	4.50
MBK-5	0.01950	0.00050	2.50	0.0597	0.0003	0.50
MBK-6	0.02030	0.00030	1.50	0.0799	0.0001	0.10
MBK-7	0.02160	0.00160	8.00	0.1038	0.0038	3.80

FIGURE D $I_{CuK\alpha}$ versus C_{Mn} and C_M



5.4.7 Effect of Mn on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Mn}	C_{M}	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{MnK\alpha}^{*}$ (cps)	s(%)
MBL-1	0.02000	0.00	0.98000	159 768	0.07	--	--
MBL-2	0.02000	0.01000	0.97000	134 312	0.07	15 860	0.19
MBL-3	0.02000	0.02000	0.96000	112 103	0.07	25 701	0.14
MBL-4	0.02000	0.0400	0.9400	86 224	0.08	48 041	0.10
MBL-5	0.02000	0.0600	0.9200	72 582	0.09	62 628	0.09
MBL-6	0.02000	0.0800	0.9000	60 242	0.10	79 057	0.08
MBL-7	0.02000	0.1000	0.8800	51 522	0.10	92 643	0.07

* 50kV. 40mA

TABLE B Calculation of α_{ZnMn}

Solutions	α_{ZnMn}
MAL-1/MAL-7	0.6529···
MAL-1/MAL-6	0.6257···
MAL-1/MAL-5	0.5778···
MAL-2/MAL-7	0.7080···
MAL-2/MAL-6	0.6756···
MAL-2/MAL-5	0.6139···
MAL-3/MAL-7	0.6383···
MAL-3/MAL-6	0.5855···
MAL-4/MAL-7	0.6047···

α_{ZnMn} average = 0.6314···

std. devn. = ± 0.0424···

α_{ZnMn} = $0.63^{1} \pm 0.04^{2}$

= 0.63 ± 0.04

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{ZnK\alpha}$(corr) (cps)
MBL-1	159 768	- 147 632	--	12 136
MBL-2	134 312	- 122 84[illegible]	+ 847	12 316
MBL-3	112 103	- 101 474	+ 1 415	12 044
MBL-4	86 224	- 76 422	+ 2 176	11 987
MBL-5	72 582	- 62 692	+ 2 748	12 368
MBL-6	60 242	- 51 122	+ 3 041	12 161
MBL-7	51 522	- 42 750	+ 3 251	12 023

$I^{o}_{ZnK\alpha}$ average = 607 330 cps
std. devn. = ± 7 387 cps
$I^{o}_{ZnK\alpha}$ = $(6.07^{3} \pm 0.07^{3}) \times 10^{5}$
= $(6.07 \pm 0.07) \times 10^{5}$

TABLE D Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

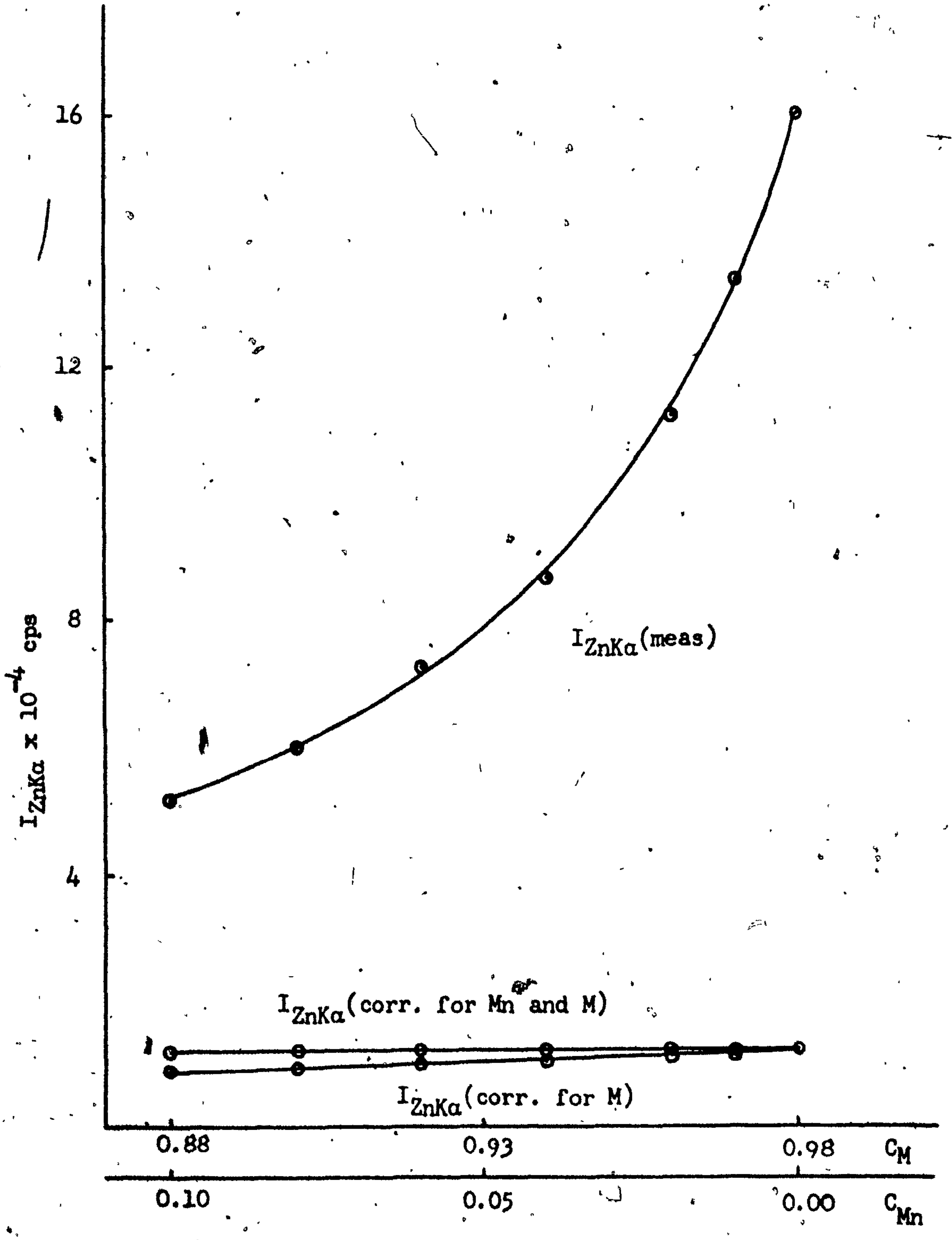
Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{MnK\alpha}$(corr) (cps)
MBL-2	13 860	– 11 612	– 127	2 121
MBL-3	25 701	– 21 310	– 236	4 155
MBL-4	48 041	– 39 003	– 442	8 596
MBL-5	62 628	– 49 764	– 576	12 288
MBL-6	79 057	– 61 453	– 727	16 877
MBL-7	92 643	– 70 414	– 852	21 377

$I^{o}_{MnK\alpha}$ average = 210 714 cps
std. devn. = ± 3 800 cps
$I^{o}_{MnK\alpha}$ = $(2.10^{7} \pm 0.03^{8}) \times 10^{5}$
= $(2.11 \pm 0.04) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Mn}(calc)	Abs. error	Error %
MBL-1	0.02000	0.00000	0.00	—	—	—
MBL-2	0.02040	0.00040	2.00	0.01010	0.00010	1.00
MBL-3	0.01970	0.00030	1.50	0.01970	0.00030	1.50
MBL-4	0.01990	0.00010	0.50	0.0410	0.0010	2.50
MBL-5	0.01990	0.00010	0.50	0.0577	0.0023	4.00
MBL-6	0.02010	0.00010	0.50	0.0802	0.0002	0.25
MBL-7	0.02010	0.00010	0.50	0.1024	0.0024	2.40

FIGURE D $I_{ZnK\alpha}$ versus C_{Mn} and C_M



5.5 Effects of Iron

Solutions: The metal concentration for each series were obtained by dilution of the following stock solutions:-

Chromium	1 ml =	0.10000	± 0.00005 g	(dil. HNO_3)
Manganese	1 ml =	0.10000	± 0.00002 g	(dil. HNO_3)
Iron	1 ml =	0.10000	± 0.00002 g	(dil. $HCl-HNO_3$)
Cobalt	1 ml =	0.10000	± 0.00006 g	(dil. HNO_3)
Nickel	1 ml =	0.10000	± 0.00006 g	(dil. HNO_3)
Copper	1 ml =	0.10000	± 0.00006 g	(dil. HNO_3)
Zinc	1 ml =	0.10000	± 0.00008 g	(dil. HNO_3)
Cadmium	1 ml =	0.2000	± 0.0001 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBS	1:126 Cl	1:63 to 1:630
Cr	KB	1:240	1:120 to 1:1200
Mn	MBB	1:500	1:250 to 1:2500
Co	MBE	1:500	1:250 to 1:2500
Ni	MBD	1:500	1:250 to 1:2500
Cu	MBC	1:500	1:250 to 1:2500
Zn	MBA	1:500	1:250 to 1:2500
Cd	FFF	1:250	1:125 to 1:1250

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd
Target	Cr	W	W	W	W	W	W	W	W
kV	50	40	50	*	50	50	50	50	40
mA	36	20	40	*	40	40	40	40	20
Coll^n	coarse	fine	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20	20
Counts	3	5	5	5	5	5	5	5	5
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα

* See each series

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α_{AFe} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{AFe} (presence of chlorine as fourth component)	Equation (44)
	Calculation of I_A(corr)	Equation (45) or a modification
	Calculation of I_A^o	I_A(corr)/C_A

5.5.1 Effect of Fe on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Fe}	C_M	$I_{ClK\alpha}$	s(%)	$I_{FeK\alpha}$*	s(%)
MBS-1	0.0129	0.01000	0.9771	3 833	0.36	15 915	0.18
MBS-2	0.0258	0.02000	0.9542	7 396	0.26	26 221	0.14
MBS-3	0.129^{0}	0.10000	0.771^{0}	30 427	0.13	63 677	0.10
MBS-4	0.155^{0}	0.1200	0.725^{0}	35 331	0.12	66 860	0.09
MBS-5	0.189^{6}	0.1470	0.663^{4}	40 528	0.11	71 306	0.09

* 50kV, 20mA

TABLE B Calculation of α_{ClFe}

Solutions	α_{ClFe}
MBS-1/MBS-5	1.1765···
MBS-1/MBS-4	1.1149···
MBS-1/MBS-3	1.2038···
MBS-2/MBS-5	1.1152···
MBS-2/MBS-4	1.0342···
MBS-2/MBS-3	1.1198···

α_{ClFe} average = 1.1274···

std. devn. = ± 0.0588···

$\alpha_{ClFe} = 1.12^{7} \pm 0.05^{9}$

$= 1.13 \pm 0.06$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of iron	$I_{ClK\alpha}$(corr) (cps)
MBS-1	3 833	- 1 258	+ 43	2 618
MBS-2	7 396	- 2 371	+ 167	5 192
MBS-3	30 427	- 7 882	+ 3 429	25 974
MBS-4	35 311	- 8 602	+ 4 775	31 484
MBS-5	40 528	- 9 034	+ 6 714	38 208

$I^{o}_{ClK\alpha}$ average = 202 029 cps

std. devn. = ± 921 cps

$I^{o}_{ClK\alpha} = (2.020^{2} \pm 0.009^{2}) \times 10^{5}$

$= (2.020 \pm 0.009) \times 10^{5}$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of		$I_{FeK\alpha}$(corr) (cps)
		matrix	chlorine	
MBS-1	15 915	- 13 944	+ 10	1 981
MBS-2	26 221	- 22 435	+ 32	3 818
MBS-3	63 677	- 44 023	+ 386	20 040
MBS-4	66 860	- 43 466	+ 487	23 481
MBS-5	71 306	- 42 418	+ 635	29 593

$I^{o}_{FeK\alpha}$ average = 197 831 cps

std. devn. = ± 4 049 cps

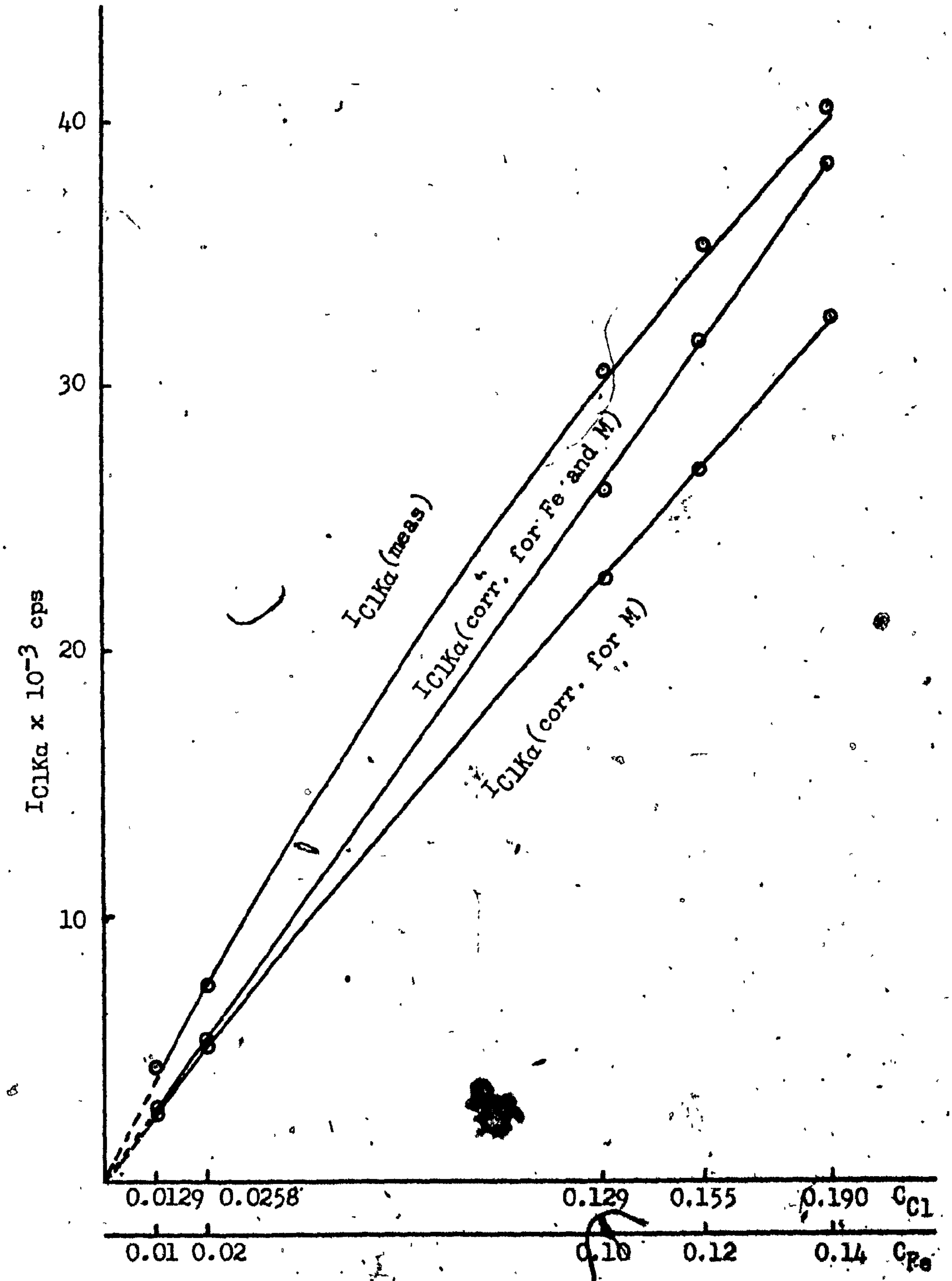
$I^{o}_{FeK\alpha}$ = $(1.97^{8} \pm 0.04^{0}) \times 10^{5}$

= $(1.98 \pm 0.04) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
MBS-1	0.0129	0.0000	0.00	0.0100	0.0000	0.00
MBS-2	0.0256	0.0002	0.78	0.0192	0.0008	4.00
MBS-3	0.129^{0}	0.000^{0}	0.00	0.1018	0.0018	1.80
MBS-4	0.156^{3}	0.001^{3}	0.84	0.1216	0.0016	1.33
MBS-5	0.190^{2}	0.000^{6}	0.32	0.1506	0.0036	2.45

FIGURE D $I_{ClK\alpha}$ versus C_{Cl} and C_{Fe}



5.5.2 Effect of Fe on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Fe}	C_{Cl}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}$* (cps)	s(%)
KB-1	0.01000	0.0	0.0	0.99000	2 816	0.43	--	--
KB-2	0.01000	0.01000	0.0220	0.9578	2 368	0.46	8 244	0.25
KB-3	0.01000	0.0200	0.0440	0.9260	1 998	0.50	13 912	0.19
KB-4	0.01000	0.0300	0.0668	0.8912	1 796	0.53	17 873	0.17
KB-5	0.01000	0.0400	0.0892	0.8608	1 597	0.55	21 016	0.15
KB-6	0.01000	0.0500	0.1038	0.8362	1 442	0.61	23 626	0.14
KB-7	0.01000	0.0600	0.124^{6}	0.805^{4}	1 317	0.63	25 797	0.14
KB-8	0.01000	0.0700	0.146^{3}	0.773^{7}	1 205	0.62	27 320	0.14

* 50kV, 20mA

TABLE B Calculation of α_{CrFe}

Solutions	α_{CrFe}
KB-1/KB-8	- 0.5095...
KB-1/KB-7	- 0.5128...
KB-1/KB-6	- 0.4980...
KB-2/KB-8	- 0.4325...
KB-2/KB-7	- 0.4279...
KB-3/KB-8	- 0.5797...

α_{CrFe} average = - 0.4934...

std. devn. = ± 0.057...

α_{CrFe} = $- 0.4^{o3} \pm 0.05^{7}$

= - 0.49 ± 0.06

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	 chlorine	 iron	$I_{CrK\alpha}$(corr) (cps)
KB-1	2 816	- 2 363	--	--	454
KB-2	2 368	- 1 921	+ 24	- 12	459
KB-3	1 998	- 1 567	+ 41	- 20	452
KB-4	1 796	- 1 356	+ 58	- 26	471
KB-5	1 597	- 1 164	+ 66	- 31	466
KB-6	1 442	- 1 021	+ 70	- 36	454
KB-7	1 317	- 898	+ 76	- 39	455
KB-8	1 205	- 790	+ 82	- 42	455

$I^{o}_{CrK\alpha}$ average = 45 825 cps

std. devn. = ± 676 cps

$I^{o}_{CrK\alpha} = (4.58^{2} \pm 0.06^{7}) \times 10^{5}$

$= (4.58 \pm 0.07) \times 10^{5}$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}$(corr) (cps)
		matrix	chromium	chlorine	
KB-2	8 244	- 7 080	+ 122	+ 9	1 295
KB-3	13 912	- 11 552	+ 206	+ 29	2 595
KB-4	17 873	- 14 283	+ 264	+ 59	3 913
KB-5	21 016	- 16 222	+ 311	+ 88	5 193
KB-6	23 626	- 17 715	+ 349	+ 115	6 375
KB-7	25 797	- 18 631	+ 381	+ 151	7 698
KB-8	27 320	- 18 954	+ 404	+ 188	8 958

$I^{o}_{FeK\alpha}$ average = 129 040 cps

std. devn. = ± 1 089 cps

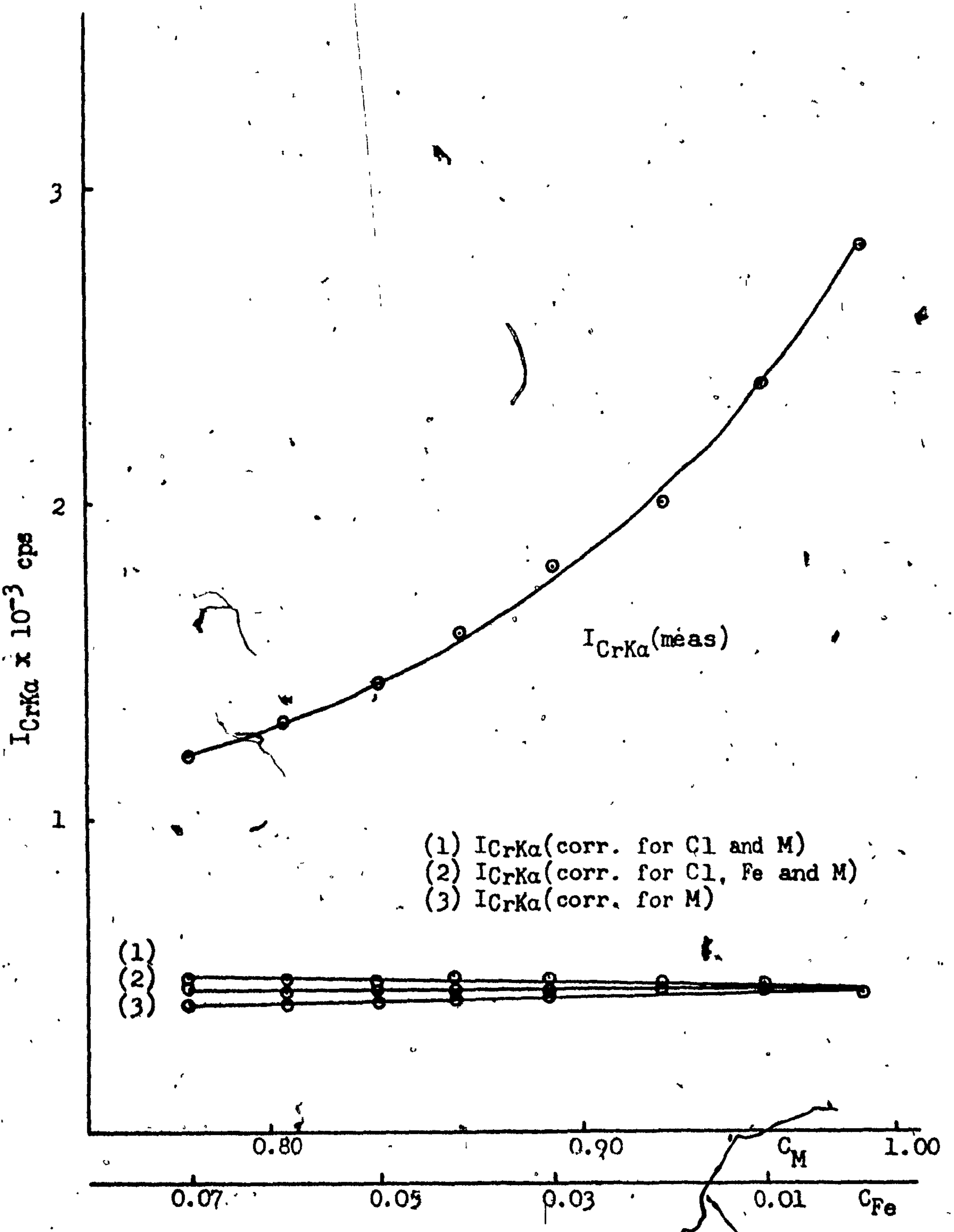
$I^{o}_{FeK\alpha} = (1.29^{0} \pm 0.01^{0}) \times 10^{5}$

$= (1.29 \pm 0.01) \times 10^{5}$

TABLE E Back-calculation of solution composition

Chlorine intensities were not measured

FIGURE D $I_{CrK\alpha}$ versus C_{Fe} and C_M



5.5.3 Effect of Fe on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Fe}	C_{Cl}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}$ (cps)	s(%)	$I_{ClK\alpha}$	s(%)
MBB-1	0.01000	--	--	0.99000	11 983	0.20	--	--	--	--
MBB-2	0.01000	0.01000	0.01611	0.96389	9 963	0.22	10 643	0.22	4 555	0.33
MBB-3	0.01000	0.02000	0.0322	0.9378	8 805	0.24	17 748	0.17	8 782	0.24
MBB-4	0.01000	0.0300	0.0483	0.9117	7 579	0.26	22 285	0.15	12 257	0.20
MBB-5	0.01000	0.0500	0.0805	0.8595	6 185	0.29	29 576	0.13	20 373	0.16
MBB-6	0.01000	0.0600	0.0966	0.8334	5 860	0.31	34 038	0.12	23 565	0.15
MBB-7	0.01000	0.0700	0.1127	0.8073	5 398	0.32	36 450	0.12	26 956	0.14

50kV, 20mA

TABLE B Calculation of α_{MnFe}

Solutions	α_{MnFe}
MBB-1/MBB-7	- 0.1997···
MBB-1/MBB-6	- 0.2015···
MBB-2/MBB-7	- 0.3475···
MBB-2/MBB-6	- 0.3654···
MBB-3/MBB-7	- 0.2780···
MBB-3/MBB-6	- 0.2934···

α_{MnFe} average = - 0.281···

[illegible] devn. = ± 0.070···

$\alpha_{MnFe} = -0.28^{1} \pm 0.07^{0}$

$= -0.28 \pm 0.07$

TABLE C Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of			$I_{MnK\alpha}$(corr) (cps)
		matrix	chlorine	iron	
MBB-1	11 983	- 10 246	--	--	1 737
MBB-2	9 963	- 8 294	+ 47	- 28	1 688
MBB-3	88805	- 7 [illegible]2	+ 83	- 50	1 706
MBB-4	7 579	- 5 968	+ 107	- 63	1 655
MBB-5	6 185	- 4 591	+ 145	- 87	1 652
MBB-6	5 860	- 4 217	+ 165	- 99	1 709
MBB-7	5 398	- 3 763	+ 178	- 106	1 707

$I^{o}_{MnK\alpha}$ average = 169 343 cps
std. devn. = ± 3 082 cps

$$I^{o}_{MnK\alpha} = (1.69^{3} \pm 0.03^{0}) \text{ x } 10^{5}$$
$$= (1.69 \pm 0.03) \text{ x } 10^{5}$$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}$(corr) (cps)
		matrix	chlorine	manganese	
MBB-2	10 643	- 9 199	+ 8	- 34	1 418
MBB-3	17 748	- 14 924	+ 27	- 57	2 794
MBB-4	22 285	- 18 218	+ 50	- 71	4 046
MBB-5	29 576	- 22 793	+ 112	- 94	6 801
MBB-6	34 038	- 25 435	+ 155	- 108	8 650
MBB-7	36 450	- 26 384	+ 193	- 116	10 143

$I^{o}_{FeK\alpha}$ average = 140 242 cps
std. devn. = ± 4 155 cps

$$I^{o}_{FeK\alpha} = (1.40^{2} \pm 0.04^{1}) \text{ x } 10^{5}$$
$$= (1.40 \pm 0.04) \text{ x } 10^{5}$$

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of			$I_{ClK\alpha}$(corr) (cps)
		matrix	iron	manganese	
MBB-2	4 555	- 1 475	+ 51	+ 30	3 161
MBB-3	8 782	- 2 767	+ 198	+ 59	6 272
MBB-4	12 257	- 3 755	+ 414	+ 82	8 998
MBB-5	20 373	- 5 883	+ 1 148	+ 136	15 774
MBB-6	23 565	- 6 598	+ 1 593	+ 157	18 717
MBB-7	26 956	- 7 311	+ 2 127	+ 180	21 952

$$I^{o}_{ClK\alpha}\text{, average} = 193\ 530 \text{ cps}$$

$$\text{std. devn.} = \pm 2\ 105 \text{ cps}$$

$$I^{o}_{ClK\alpha} = (1.93^{5} \pm 0.02^{1}) \times 10^{5}$$

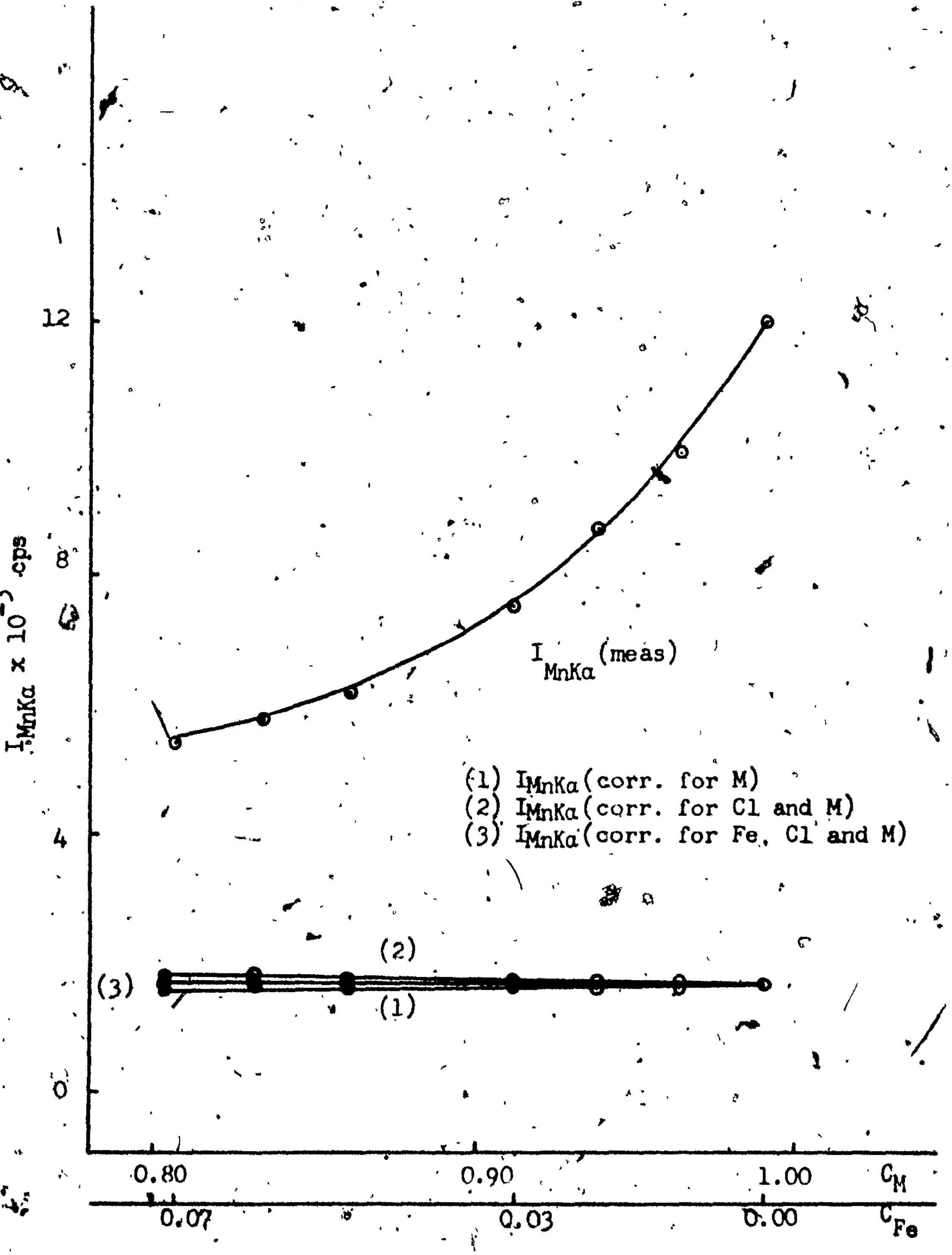
$$= (1.94 \pm 0.02) \times 10^{5}$$

TABLE F Back-calculation of solution composition

Solution	C_{Mn}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
MBB-1	0.01030	0.00030	3.00	—	—	—
MBB-2	0.01000	0.00000	0.00	0.01010	0.00010	1.00
MBB-3	0.01010	0.00010	1.00	0.01990	0.00010	0.50
MBB-4	0.00960	0.00040	4.00	0.0283	0.0017	5.66
MBB-5	0.00970	0.00030	3.00	0.0483	0.0017	3.40
MBB-6	0.01020	0.00020	2.00	0.0623	0.0023	3.83
MBB-7	0.01020	0.00020	2.00	0.0735	0.0035	5.00

C_{Cl}(calc)	Abs. error	Error %
—	—	—
0.01634	0.00023	1.43
0.0324	0.0002	0.62
0.0463	0.0020	4.14
0.0812	0.0007	0.87
0.0972	0.0006	0.62
0.1142	0.0015	1.33

FIGURE D $I_{MnK\alpha}$ versus C_{Fe} and C_M



5.5.4 Effect of Fe on Co

TABLE A Experimental Parameters

Solution	C_{Co}	C_{Fe}	C_{Cl}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}^{*}$ (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MBE-1	0.01000	0.00	0.00	0.99000	46 946	0.10	—	—	—	—
MBE-2	0.01000	0.01000	0.01611	0.96389	38 505	0.11	10 394	0.22	4 438	0.33
MBE-3	0.01000	0.02000	0.0322	0.9378	33 203	0.12	17 691	0.17	8 686	0.24
MBE-4	0.01000	0.0300	0.0483	0.9117	29 802	0.13	23 561	0.14	12 752	0.20
MBE-5	0.01000	0.0500	0.0806	0.8594	22 348	0.15	29 952	0.13	20 253	0.16
MBE-6	0.01000	0.0600	0.0967	0.8333	20 326	0.16	33 287	0.12	23 753	0.15
MBE-7	0.01000	0.0700	0.1128	0.8072	19 121	0.16	35 019	0.12	26 772	0.14

* 50kV, 20mA

TABLE B Calculation of α_{CoFe}

Solutions	α_{CoFe}
MBE-1/MBE-6	- 0.2327···
MBE-1/MBE-5	- 0.2166···
MBE-2/MBE-6	- 0.2365···
MBE-2/MBE-5	- 0.2124···

α_{CoFe} average = - 0.2245 ...

std. devn. = ± 0.0118 ...

$\alpha_{CoFe} = -0.22^{4} \pm 0.01^{2}$

$= -0.22 \pm 0.01$

TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of			$I_{CoK\alpha}$(corr) (cps)
		matrix	chlorine	iron	
MBE-1	46 946	- 42 865	—	--	4 081
MBE-2	38 505	- 34 231	- 107	- 86	4 081
MBE-3	33 203	- 28 718	- 185	- 148	4 152
MBE-4	29 802	- 25 508	- 248	- 200	4 296
MBE-5	22 348	- 17 715	- 311	- 251	4 071
MBE-6	20 326	- 15 622	- 339	- 273	4 092
MBE-7	19 121	- 14 236	- 372	- 300	4 213

$I^{o}_{CoK\alpha}$ average = 414 086 cps

std. devn. = ± 8 501 cps

$I^{o}_{CoK\alpha} = (4.14^{0} \pm 0.08^{5}) \times 10^{5}$

$= (4.14 \pm 0.08) \times 10^{5}$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}$(corr) (cps)
		matrix	chlorine	cobalt	
MBE-2	10 394	- 8 984	+ 8	- 24	1 394
MBE-3	17 691	- 14 876	+ 27	- 41	2 801
MBE-4	23 561	- 19 261	+ 53	- 55	4 298
MBE-5	29 952	- 23 083	+ 113	- 70	6 912
MBE-6	33 287	- 24 874	+ 151	- 78	8 486
MBE-7	35 019	- 25 348	+ 186	- 82	9 775

$I^{o}_{FeK\alpha}$ average = 140 340 cps

std. devn. = ± 1 777 cps

$I^{o}_{FeK\alpha} = (1.40^{3} \pm 0.1^{7}) \times 10^{5}$

$= (1.40 \pm 0.02) \times 10^{5}$

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of iron	Correction for effect of cobalt	$I_{ClK\alpha}$(corr) (cps)
MBE-2	4 438	- 1 437	+ 50	+ 55	3 106
MBE-3	8 686	- 2 737	+ 196	+ 108	6 253
MBE-4	12 752	- 3 906	+ 431	+ 158	9 435
MBE-5	20 253	- 5 849	+ 1 141	+ 251	15 796
MBE-6	23 737	- 6 646	+ 1 605	+ 295	18 991
MBE-7	26 772	- 7 261	+ 2 112	+ 332	21 955

$I^{o}_{ClK\alpha}$ average = 194 890 cps

std. devn. = ± 1 360 cps

$I^{o}_{ClK\alpha}$ = $(1.94^{8} \pm 0.01^{3}) \times 10^{5}$

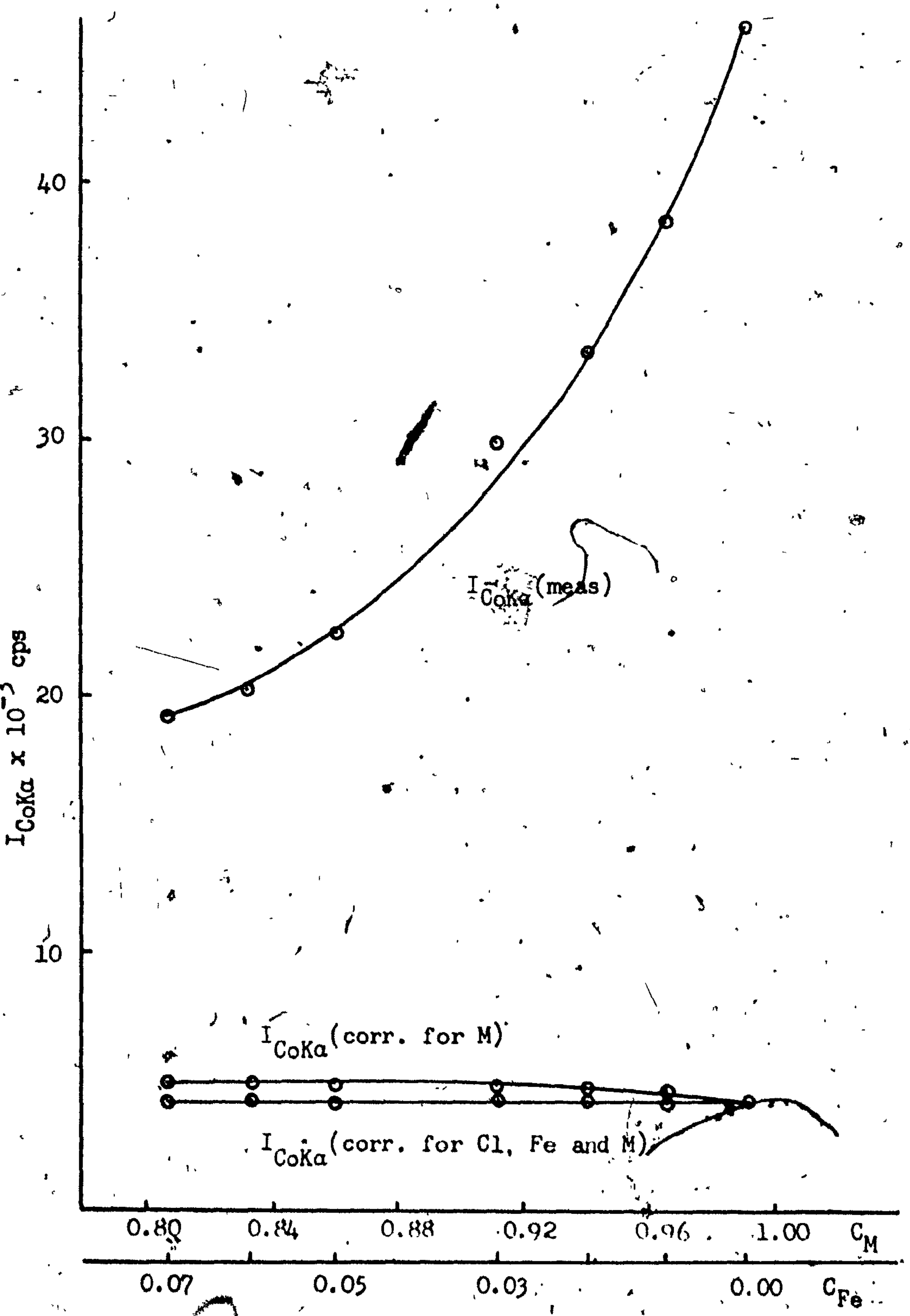
= $(1.95 \pm 0.01) \times 10^{5}$

TABLE F Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
MBE-1	0.00980	0.00020	2.00	—	—	—
MBE-2	0.00980	0.00020	2.00	0.00990	0.00010	1.00
MBE-3	0.01000	0.00000	0.00	0.01990	0.00010	0.50
MBE-4	0.01050	0.00050	5.00	0.0308	0.0008	2.66
MBE-5	0.00980	0.00020	2.00	0.0491	0.0009	1.80
MBE-6	0.00990	0.00010	1.00	0.0609	0.0009	1.50
MBE-7	0.01020	0.00020	2.00	0.0695	0.0005	0.72

C_{Cl}(calc)	Abs. error	Error %
—	—	—
0.01592	0.00019	1.19
0.0321	0.0001	0.31
0.0485	0.0002	0.41
0.0809	0.0003	0.37
0.0976	0.0009	0.93
0.1126	0.0002	0.18

FIGURE D I_{CoKa} versus C_{Fe} and C_M



5.5.5 Effect of Fe on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Fe}	C_{Cl}	C_M	$I_{NiK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MBD-1	0.01000	0.00	0.00	0.99	76 917	0.09	—	—	—	—
MBD-2	0.01000	0.01000	0.01611	0.96389	55 405	0.10	10 507	0.22	4 570	0.33
MBD-3	0.01000	0.02000	0.0322	0.9378	42 920	0.11	17 954	0.17	8 942	0.23
MBD-4	0.01000	0.0300	0.0483	0.9117	36 071	0.12	23 431	0.15	12 807	0.20
MBD-5	0.01000	0.0500	0.0806	0.8594	27 156	0.14	31 745	0.13	20 817	0.16
MBD-6	0.01000	0.0600	0.0967	0.8333	23 637	0.15	34 316	0.12	24 442	0.14
MBD-7	0.01000	0.0700	0.1128	0.8072	20 763	0.16	37 303	0.12	27 473	0.14

* 50kV, 40mA

TABLE B Calculation of α_{NiFe}

Solutions	α_{NiFe}
MBD-1/MBD-7	1.4237···
MBD-1/MBD-6	1.3252···
MBD-1/MBD-5	1.2407···
MBD-2/MBD-7	1.4129···
MBD-2/MBD-6	1.2508···
MBD-3/MBD-7	1.2952···

α_{NiFe} average = 1.325···

std. devn. = ± 0.0787···

$\alpha_{NiFe} = 1.32^5 \pm 0.07^9$

$= 1.32 \pm 0.08$

TABLE C Calculation of $I_{NiK\alpha}(corr)$ and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of			$I_{NiK\alpha}(corr)$ (cps)
		matrix	chlorine	iron	
MBD-1	76 917	- 69 835	--	--	7 082
MBD-2	55 405	- 48 977	- 144	+ 734	7 018
MBD-3	42 920	- 36 913	- 224	+ 1 137	6 920
MBD-4	36 071	- 30 159	- 282	+ 1 433	7 063
MBD-5	27 156	- 21 404	- 354	+ 1 799	7 197
MBD-6	23 637	- 18 064	- 370	+ 1 879	7 082
MBD-7	20 763	- 15 371	- 379	+ 1 926	6 934

$I^{o}_{NiK\alpha}$ average = 704 300 cps

std. devn. = ± 9 444 cps

$I^{o}_{NiK\alpha}$ = $(7.04^{3} \pm 0.09^{4}) \times 10^{5}$

= $(7.04 \pm 0.09) \times 10^{5}$

TABLE D Calculation of $I_{FeK\alpha}(corr)$ and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}(corr)$ (cps)
		matrix	chlorine	nickel	
MBD-2	10 507	- 9 081	+ 8	- 66	1 368
MBD-3	17 954	- 15 098	+ 27	- 144	2 769
MBD-4	23 431	- 19 155	+ 53	- 148	4 181
MBD-5	31 745	- 24 465	+ 120	- 201	7 199
MBD-6	34 316	- 25 643	+ 156	- 217	8 612
MBD-7	37 303	- 27 001	+ 198	- 236	10 264

$I^{o}_{FeK\alpha}$ average = 141 460 cps

std. devn. = ± 3 803 cps

$I^{o}_{FeK\alpha}$ = $(1.41^{4} \pm 0.03^{8}) \times 10^{5}$

= $(1.41 \pm 0.04) \times 10^{5}$

TABLE E Calculation of $I_{ClK\alpha}(corr)$ and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	iron	nickel	$I_{ClK\alpha}(corr)$ (cps)
MBD-2	4 570	- 1 080	+ 51	+ 58	3 199
MBD-3	8 942	- 2 818	+ 201	+ 113	6 438
MBD-4	12 807	- 3 923	+ 433	+ 161	9 487
MBD-5	20 817	- 6 011	+ 1 173	+ 262	16 241
MBD-6	24 443	- 6 844	+ 1 653	+ 308	19 559
MBD-7	27 473	- 7 451	+ 2 167	+ 346	22 535

$I^{o}_{ClK\alpha}$ average = 199 714 cps

std. devn. = ± 2 230 cps

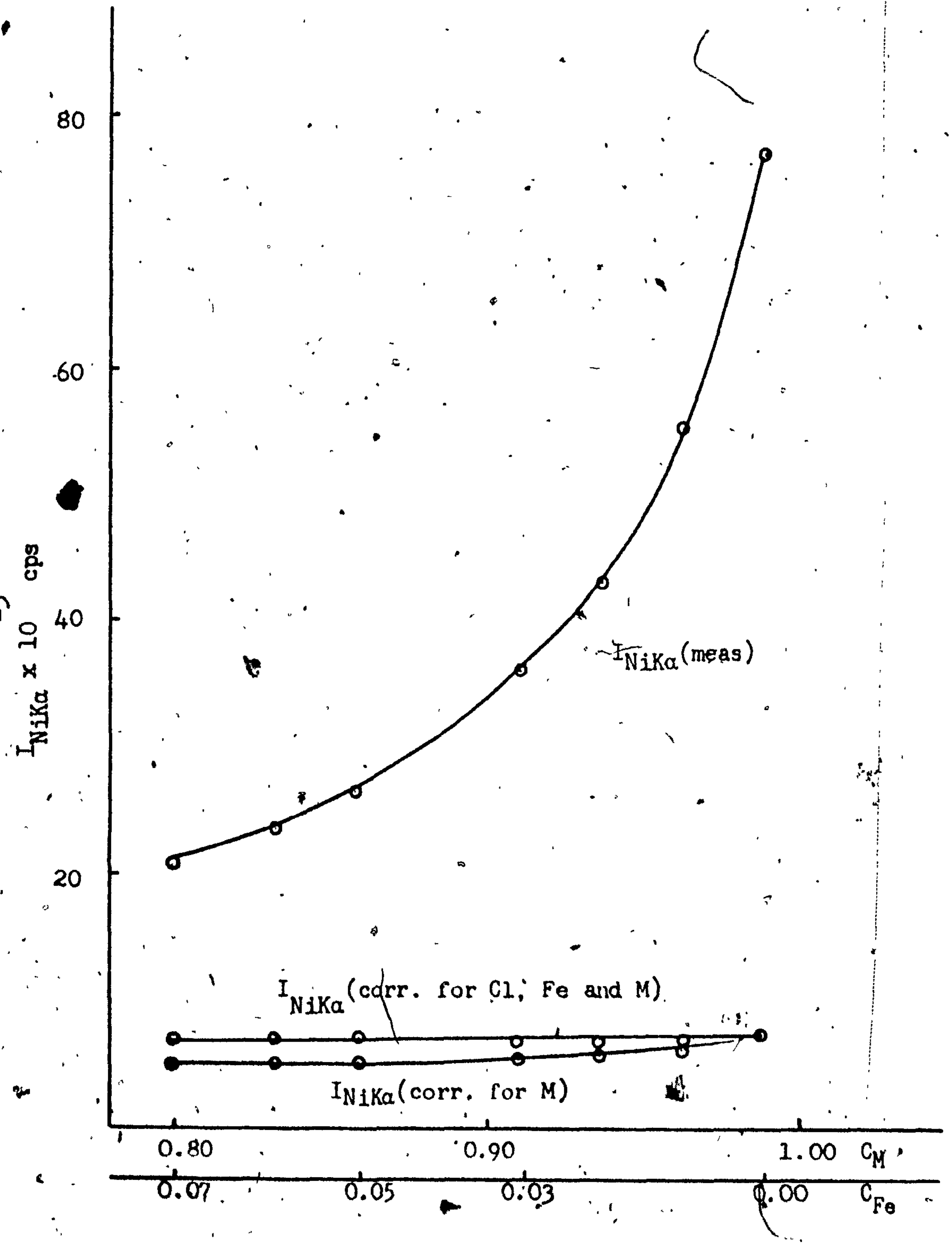
$$I^{o}_{ClK\alpha} = (1.99^{7} \pm 0.02^{2}) \times 10^{5}$$

$$= (2.00 \pm 0.02) \times 10^{5}$$

TABLE F Back-calculation of solution composition

Solution	C_{Ni}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %	C_{Cl}(calc)	Abs. error	Error %
MBD-1	0.01010	0.00010	1.00	--	--	--	--	--	--
MBD-2	0.00990	0.00010	1.00	0.00960	0.00040	4.00	0.01600	0.00011	0.68
MBD-3	0.00970	0.00030	3.00	0.01950	0.00050	2.50	0.0322	0.0000	0.00
MBD-4	0.00990	0.00010	1.00	0.0474	0.0007	2.33	0.0474	0.0009	1.86
MBD-5	0.01040	0.00040	4.00	0.0816	0.0015	3.00	0.0816	0.0010	1.24
MBD-6	0.01020	0.00020	2.00	0.0983	0.0016	2.66	0.0983	0.0016	1.65
MBD-7	0.01010	0.00010	1.00	0.1136	0.0037	5.30	0.1136	0.0008	0.71

FIGURE D $I_{NiK\alpha}$ versus C_{Fe} and C_M



5.5.6 Effect of Fe on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Fe}	C_{Cl}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MBC-1	0.01000	0.00	0.00	0.99	70 125	0.09	--	--	--	--
MBC-2	0.01000	0.01000	0.0161	0.96389	50 791	0.10	11 218	0.21	4 476	0.33
MBC-3	0.01000	0.02000	0.0322	0.9378	40 556	0.11	18 682	0.17	8 785	0.24
MBC-4	0.01000	0.0300	0.0483	0.9117	30 990	0.13	23 473	0.15	12 937	0.20
MBC-5	0.01000	0.0500	0.0806	0.8594	23 881	0.14	32 815	0.12	20 726	0.16
MBC-6	0.01000	0.0600	0.0967	0.8333	21 119	0.16	34 350	0.12	24 143	0.14
MBC-7	0.01000	0.0700	0.1128	0.8072	18 679	0.17	36 702	0.12	27 586	0.14

* 50kV, 20mA

TABLE B Calculation of α_{CuFe}

Solutions	α_{CuFe}
MBC-1/MBC-7	1.2651···
MBC-1/MBC-6	1.2091···
MBC-1/MBC-5	1.2136···
MBC-2/MBC-7	1.3328···
MBC-2/MBC-6	1.2430···
MBC-2/MBC-5	1.2545···

α_{CuFe} average = 1.2530···

std. devn. = ± 0.0449...

α_{CuFe} = $1.25^3 \pm 0.04^5$

= 1.25 ± 0.04

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for effect of			$I_{CuK\alpha(corr)}$ (cps)
		matrix	chlorine	iron	
MBC-1	70 125	- 64 279	--	--	5 846
MBC-2	50 791	- 45 329	- 204	+ 636	5 894
MBC-3	40 556	- 35 214	- 327	+ 1 016	6 031
MBC-4	30 990	- 26 159	- 374	+ 1 165	5 622
MBC-5	23 881	- 19 004	- 480	+ 1 496	5 893
MBC-6	21 119	- 16 295	- 510	+ 1 588	5 902
MBC-7	18 679	- 13 961	- 527	+ 1 638	5 829

$I^o_{CuK\alpha}$ average = 585 957 cps

std. devn. = ± 12 335 cps

$$I^o_{CuK\alpha} = (5.8^5 \pm 0.1^2) \times 10^5$$
$$= (5.8 \pm 0.1) \times 10^5$$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^o_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha(corr)}$ (cps)
		matrix	chlorine	copper	
MBC-2	11 282	- 9 696	+ 0	- 70	1 461
MBC-3	18 682	- 15 710	+ 28	- 116	2 884
MBC-4	23 473	- 19 189	+ 53	- 146	4 191
MBC-5	32 815	- 25 289	+ 124	- 204	7 446
MBC-6	34 350	- 25 668	+ 156	- 213	8 625
MBC-7	36 702	- 26 566	+ 194	- 228	10 102

$I^o_{FeK\alpha}$ average = 144 497 cps

std. devn. = ± 3 020 cps

$$I^o_{FeK\alpha} = (1.44^4 \pm 0.03^0) \times 10^5$$
$$= (1.44 \pm 0.03) \times 10^5$$

TABLE E Calculation of $I_{ClK\alpha}$(calc) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	iron	copper	$I_{ClK\alpha(corr)}$ (cps)
MBC-2	4 476	- 1 450	+ 50	+ 63	3 139
MBC-3	8 785	- 2 768	+ 198	+ 123	6 338
MBC-4	12 937	- 3 963	+ 437	+ 181	9 592
MBC-5	20 726	- 5 985	+ 1 168	+ 290	16 199
MBC-6	24 143	- 6 760	+ 1 632	+ 338	19 353
MBC-7	27 586	- 7 482	+ 2 176	+ 386	22 666

$I^{o}_{ClK\alpha}$ average = 198 720 cps

std. devn. = ± 2 529 cps

$$I^{o}_{ClK\alpha} = (1.98^{7} \pm 0.02^{5}) \times 10^{5}$$

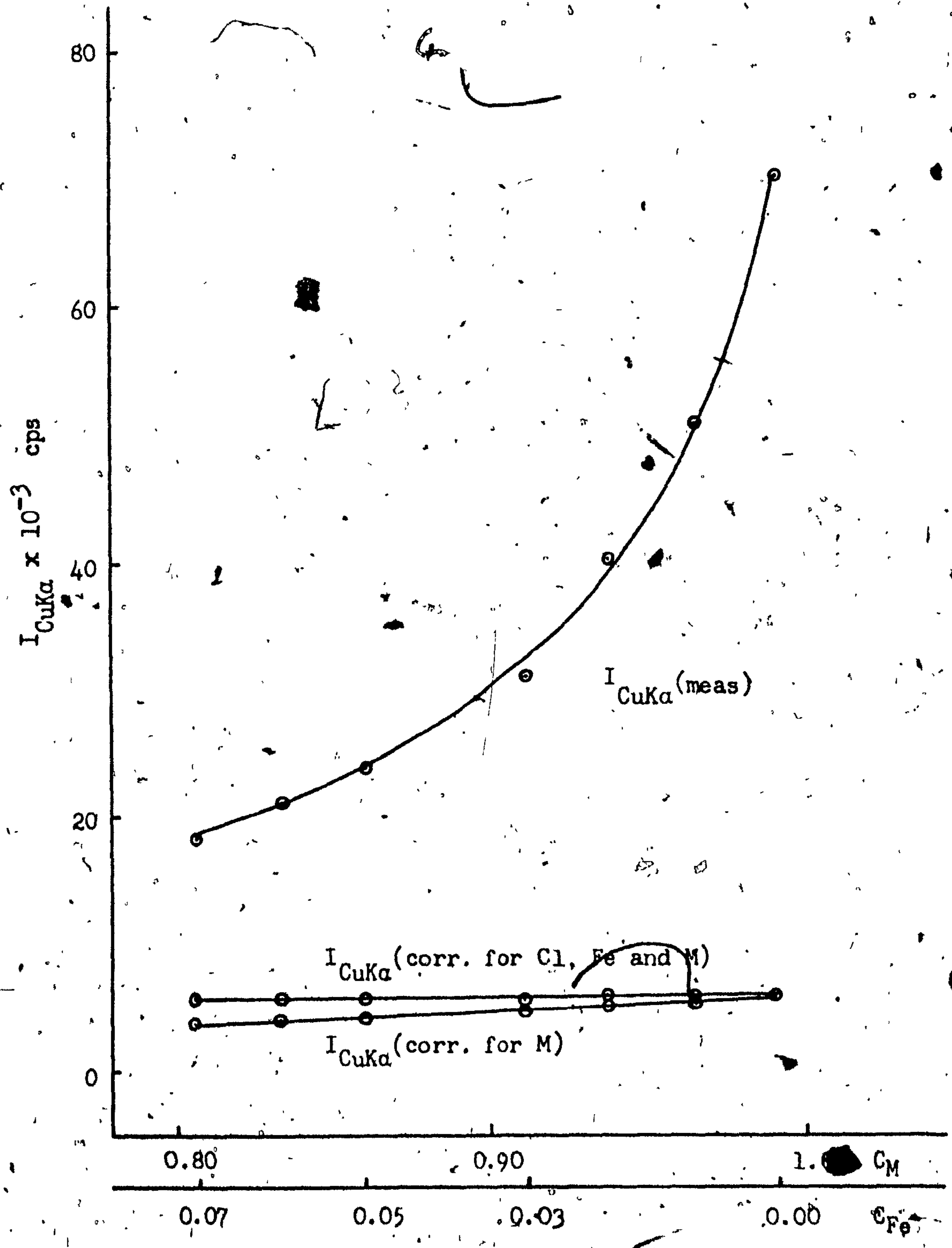
$$= (1.99 \pm 0.02) \times 10^{5}$$

TABLE F Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
MBC-1	0.01000	0.00000	0.00	--	--	--
MBC-2	0.01010	0.00010	1.00	0.01010	0.00010	1.00
MBC-3	0.01030	0.00030	3.00	0.01990	0.00010	0.50
MBC-4	0.00940	0.00060	6.00	0.0288	0.0012	4.00
MBC-5	0.01030	0.00030	3.00	0.0523	0.0023	4.60
MBC-6	0.01010	0.00010	1.00	0.0598	0.0002	0.33
MBC-7	0.01000	0.00000	0.00	0.0703	0.0003	0.43

C_{Cl}(calc)	Abs. error	Error %
--	--	--
0.01580	0.00031	1.92
0.0319	0.0003	0.93
0.0481	0.0002	0.41
0.0820	0.0014	1.73
0.0974	0.0007	0.72
0.1142	0.0014	1.24

FIGURE D $I_{CuK\alpha}$ versus C_{Fe} and C_M



5.5.7 Effect of Fe on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Fe}	C_{Cl}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MBA-1	0.01000	0.00	0.00	0.99	103 084	0.07	--	--	--	--
MBA-2	0.01000	0.01000	0.01611	0.96389	72 618	0.09	11 546	0.21	4 466	0.33
MBA-3	0.01000	0.02000	0.0322	0.9378	58 554	0.10	18 820	0.17	8 722	0.24
MBA-4	0.01000	0.0300	0.0483	0.9117	45 933	0.10	23 065	0.14	12 523	0.20
MBA-5	0.01000	0.0500	0.0806	0.8594	36 126	0.12	31 396	0.13	20 441	0.16
MBA-6	0.01000	0.0600	0.0967	0.8333	31 371	0.13	33 767	0.12	23 967	0.14
MBA-7	0.01000	0.0700	0.1128	0.8072	26 770	0.14	35 601	0.12	26 996	0.14

* 50kV, 20mA

TABLE B Calculation of α_{ZnFe}

Solutions	α_{ZnFe}
MBA-1/MBA-7	0.7742···
MBA-1/MBA-6	0.5996···
MBA-1/MBA-5	0.5311···
MBA-2/MBA-7	0.7225···
MBA-3/MBA-6	0.6078···

α_{ZnFe} average = 0.6470···
std. devn. = ± 0.0988···

$$\alpha_{ZnFe} = 0.64^{7} \pm 0.09^{9}$$
$$= 0.65 \pm 0.10$$

TABLE C Calculation of $I_{ZnK\alpha}(corr)$ and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of iron	$I_{ZnK\alpha(corr)}$ (cps)
MBA-1	103 084	- 96 226	--	--	6 858
MBA-2	72 618	- 65 999	- 382	+ 472	6 709
MBA-3	58 554	- 51 775	- 617	+ 761	6 923
MBA-4	45 933	- 39 485	- 726	+ 896	6 618
MBA-5	36 126	- 29 275	- 951	+ 1 174	7 074
MBA-6	31 371	- 24 650	- 992	+ 1 223	6 952
MBA-7	26 770	-20 376	- 987	+ 1 218	6 625

$I^{o}_{ZnK\alpha}$ average = 682 271 cps

std. devn. = ± 17 600 cps

$$I^{o}_{ZnK\alpha} = (6.8^{2} \pm 0.1^{7}) \times 10^{5}$$

$$= (6.8 \pm 0.2) \times 10^{5}$$

TABLE D Calculation of $I_{FeK\alpha}(corr)$ and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of zinc	$I_{FeK\alpha(corr)}$ (cps)
MBA-2	11 546	- 9 979	+ 9	- 71	1 505
MBA-3	18 820	- 15 826	+ 28	- 116	2 906
MBA-4	23 065	- 18 855	+ 52	- 142	4 120
MBA-5	31 396	- 24 196	+ 119	- 193	7 126
MBA-6	33 767	- 25 232	+ 153	- 204	8 480
MBA-7	35 601	- 25 769	+ 189	- 219	9 802

$I^{o}_{FeK\alpha}$ average = 142 835 cps

std. devn. = ± 4 560 cps

$$I^{o}_{FeK\alpha} = (1.42^{8} \pm 0.04^{5}) \times 10^{5}$$

$$= (1.43 \pm 0.04) \times 10^{5}$$

TABLE E . Calculation of $I'_{ClK\alpha}$(corr) and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of iron	Correction for effect of zinc	$I_{ClK\alpha}$(corr) (cps)
MBA-2	4 466	- 1 446	+ 50	+ 82	3 152
MBA-3	8 722	- 2 748	+ 197	+ 160	6 331
MBA-4	12 523	- 3 836	+ 423	+ 229	9 339
MBA-5	20 441	- 5 903	+ 1 152	+ 374	16 064
MBA-6	23 967	- 6 711	+ 1 621	+ 438	19 315
MBA-7	26 996	- 7 322	+ 2 130	+ 494	22 298

$I^o_{ClK\alpha}$ average = 197 058 cps

std. devn. = ± 2 477 cps

$I^o_{ClK\alpha}$ = $(1.97^0 \pm 0.02^4) \times 10^5$

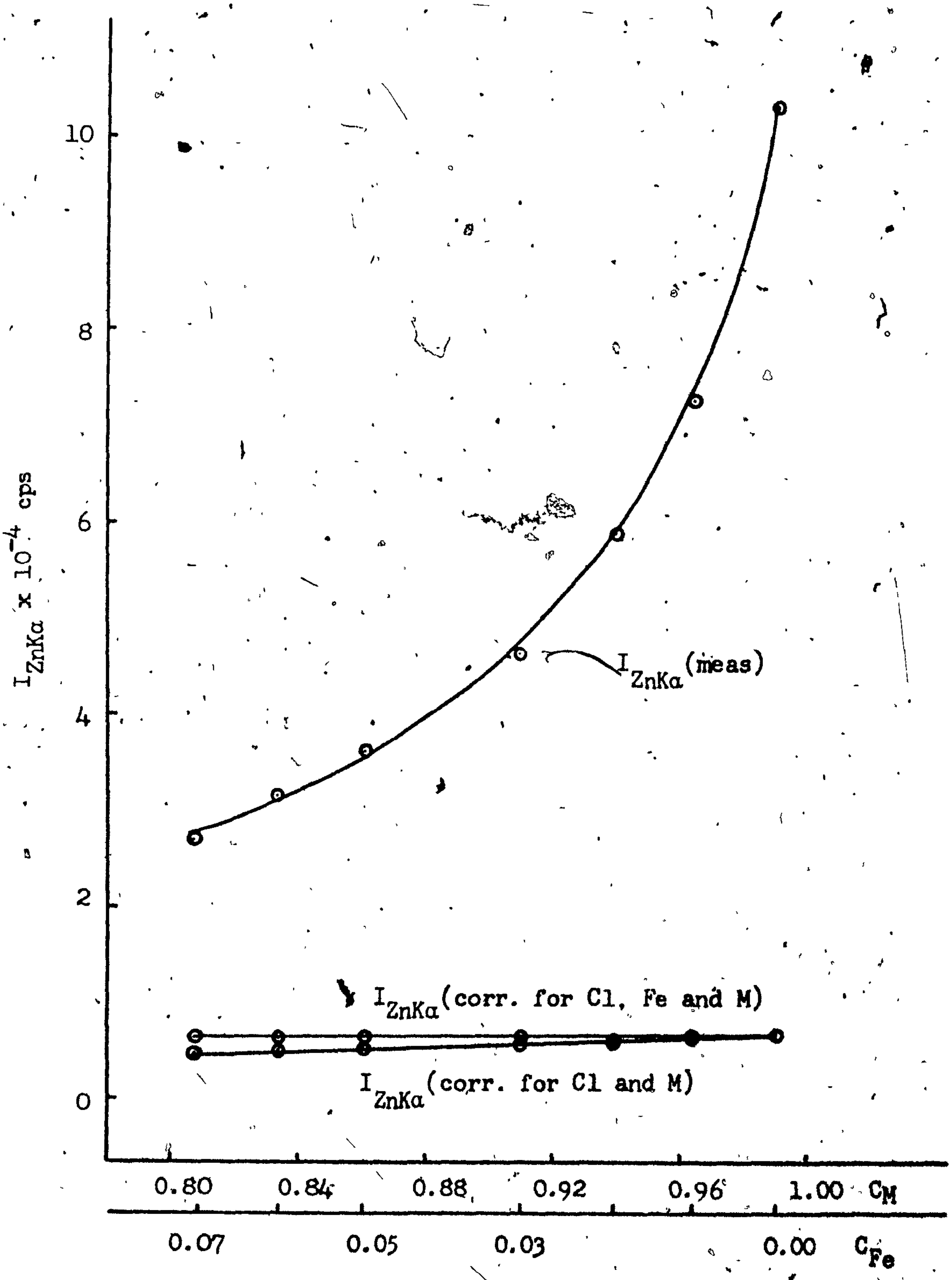
= $(1.97 \pm 0.02) \times 10^5$

TABLE F . Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
MBA-1	0.01010	0.00010	1.00	--	--	--
MBA-2	0.00990	0.00010	1.00	0.01060	0.00060	6.00
MBA-3	0.01020	0.00020	2.00	0.02040	0.00040	2.00
MBA-4	0.00950	0.00050	5.00	0.0284	0.0016	5.33
MBA-5	0.01050	0.00050	5.00	0.0502	0.0002	0.40
MBA-6	0.01020	0.00020	2.00	0.0596	0.0004	0.66
MBA-7	0.00960	0.00040	4.00	0.0682	0.0018	2.51

C_{Cl}(calc)	Abs. error	Error%
--	--	--
0.01601	0.00010	0.62
0.0322	0.0000	0.00
0.0471	0.0012	2.48
0.0817	0.0011	1.36
0.0981	0.0014	1.45
0.1127	0.0001	0.09

FIGURE D. $I_{ZnK\alpha}$ versus C_{Fe} and C_M



5.5.8 Effect of Fe on Cd

TABLE A Experimental Parameters

Solution	C_{Cd}	C_{Fe}	C_M	$I_{CdK\alpha}$ (cps)	s(%)	$I_{FeK\alpha}^{*}$ (cps)	s(%)
FFF-1	0.02000	0.00	0.98000	19 697	0.16	--	--
FFF-2	0.02000	0.01000	0.97000	18 625	0.16	6 642	0.30
FFF-3	0.02000	0.0200	0.9600	16 967	0.17	12 591	0.20
FFF-4	0.02000	0.0300	0.9500	16 009	0.18	17 654	0.17
FFF-5	0.02000	0.0400	0.9400	15 007	0.18	22 588	0.15
FFF-6	0.02000	0.0500	0.9300	13 983	0.19	26 911	0.14
FFF-7	0.02000	0.0600	0.9200	13 307	0.20	31 259	0.13
FFF-8	0.02000	0.0700	0.9100	11 917	0.20	31 765	0.13

* 40kV, 20mA

TABLE B Calculation of α_{CdFe}

Solutions	α_{CdFe}
FFF-1/FFF-8	- 0.4647...
FFF-1/FFF-7	- 0.5357...
FFF-1/FFF-6	- 0.5266...
FFF-2/FFF-8	- 0.4095...
FFF-2/FFF-7	- 0.4990...
FFF-2/FFF-6	- 0.4795...
FFF-3/FFF-8	- 0.4175...

α_{CdFe} average = - 0.4761 ...
std. devn. = ± 0.0494 ...

$$\alpha_{CdFe} = -0.47^{6} \pm 0.04^{9}$$
$$= -0.48 \pm 0.05$$

TABLE C Calculation of $I_{CdK\alpha}$(corr) and $I^{o}_{CdK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of iron	$I_{CdK\alpha}$(corr) (cps)
FFF-1	19 697	- 18 639	--	1 058
FFF-2	18 625	- 17 145	- 89	1 091
FFF-3	16 967	- 15 728	- 161	1 078
FFF-4	16 009	- 14 685	- 229	1 095
FFF-5	15 007	- 13 621	- 286	1 100
FFF-6	13 983	- 12 557	- 333	1 093
FFF-7	13 307	- 11 821	- 380	1 106
FFF-8	11 917	- 10 471	- 397	1 049

$I^{o}_{CdK\alpha}$ average = 54 188 cps

std. devn. = ± 1 228 cps

$I^{o}_{CdK\alpha} = (5.4^{1} \pm 0.1^{2}) \times 10^{5}$

$= (5.4 \pm 0.1) \times 10^{5}$

TABLE D Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cadmium	$I_{FeK\alpha}$(corr) (cps)
FFF-2	6 642	- 5 777	+ 150	1 015
FFF-3	12 591	- 10 839	+ 284	2 036
FFF-4	17 654	- 15 039	+ 398	3 013
FFF-5	22 588	- 19 039	+ 509	4 058
FFF-6	26 911	- 22 442	+ 607	5 076
FFF-7	31 259	- 25 787	+ 705	6 177
FFF-8	31 765	- 25 920	+ 717	6 562

$I^{o}_{FeK\alpha}$ average = 101 608 cps

std. devn. = ± 803 cps

$I^{o}_{FeK\alpha} = (1.016^{0} \pm 0.008^{0}) \times 10^{5}$

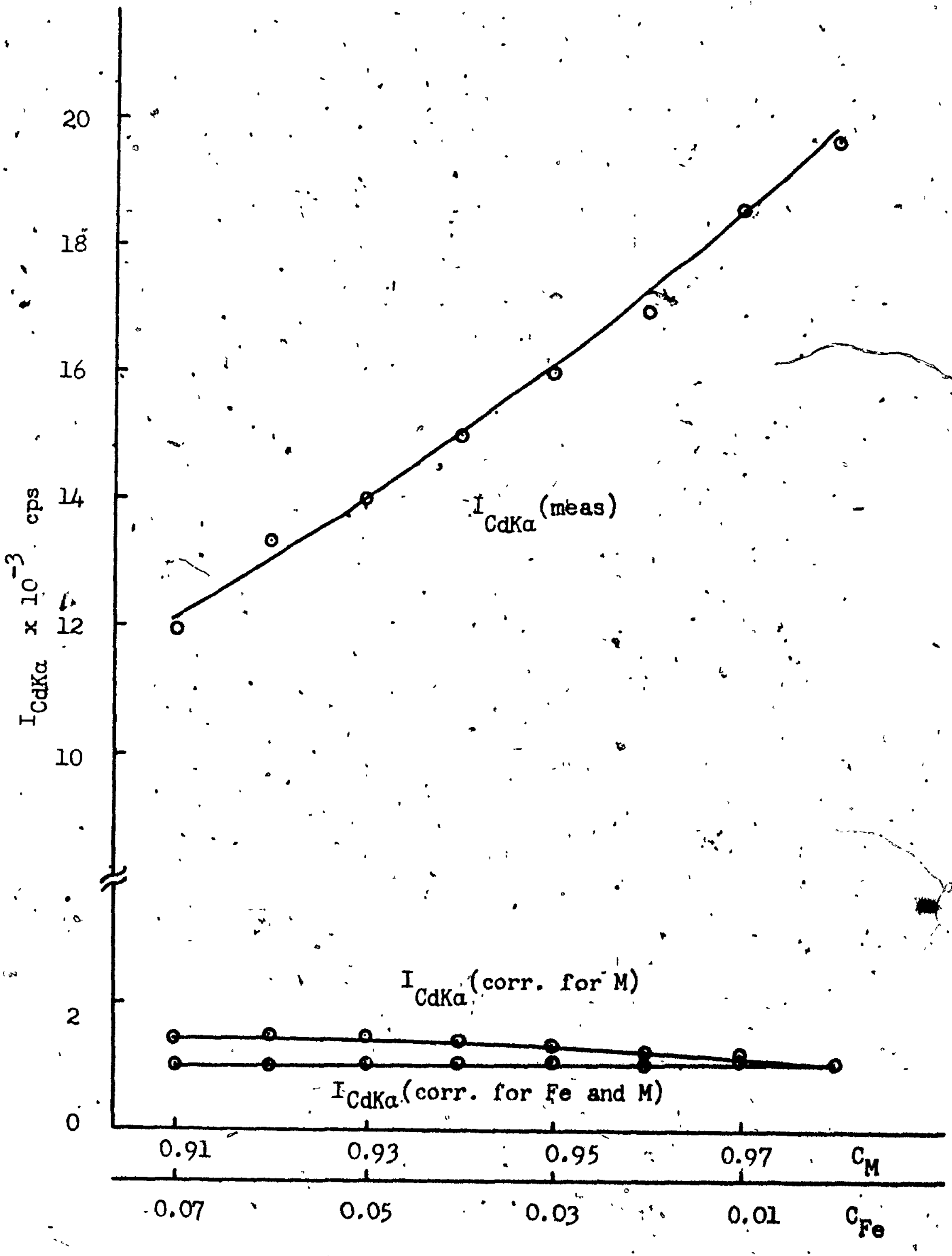
$= (1.016 \pm 0.008) \times 105$

TABLE E <u>Back-calculation of solution composition</u>

Solution	C_{Cd}(calc)	Abs. error	Error %	C_{Fe}(calc)	Abs. error	Error %
FFF-1	0,01930	0.00070	3.50			
FFF-2	0,02020	0.00020	1.00	0.01000	0.00000	0.00
FFF-3	0.01980	0.00020	1.00	0.0200	0.0000	0.00
FFF-4	0,02020	0.00020	1.00	0.0297	0.0003	1.00
FFF-5	0.02040	0.00040	2.00	0.0402	0.0002	0.50
FFF-6	0.02030	0.00030	1.50	0.0501	0.0001	0.20
FFF-7	0.02080	0.00080	4.00	0.0618	0.0018	3.00
FFF-8	0.01790	0.00210	10.50	0.0606	0.0094	13.43

Solution FFF-8 has apparently some source of built-in error.

FIGURE D $I_{CdK\alpha}$ versus C_{Fe} and C_M



5.6 Effects of Cobalt

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Chromium 1 ml = 0.2000 ± 0.0001 g (dil. HNO_3)
Manganese 1 ml = 0.10000 ± 0.00002 g (dil. HNO_3)
Iron 1 ml = 0.10000 ± 0.00002 g (dil. $HCl-HNO_3$)
Cobalt 1 ml = 0.10000 ± 0.00005 g (dil. HNO_3)
Nickel 1 ml = 0.2000 ± 0.0001 g (dil. HNO_3)
Copper 1 ml = 0.20000 ± 0.00008 g (dil. HNO_3)
Zinc 1 ml = 0.2000 ± 0.0001 g (dil. HNO_3)

Chlorine., where added as 1:3 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	LZL	1:400 Cl	1:200 to 1:2000
Cr	MAD	1:440	1:220 to 1:2200
Mn	LZO	1:400	1:200 to 1:2000
Fe	MAU	1:440	1:220 to 1:2200
Ni	MAF	1:400	1:200 to 1:2000
Cu	MAN	1:440	1:220 to 1:2200
Zn	MAJ	1:350	1:175 to 1:1750

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn
Target	Cr	W	W	W	W	W	W	W
kV	50	50	50	50	*	50	50	50
mA	36	40	40	30	*	30	30	30
Coll^n	coarse	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα

* See each series

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α_{ACo} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{ACo} (presence of chlorine as fourth component)	Equation (44)
	Calculation of I_A(corr)	Equation (45) or a modification
	Calculation of I_A^o	$I_A(\mathrm{corr})/C_A$

5.6.1 Effect of Co on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Co}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{CoK\alpha}$* (cps)	s(%)
LZL-2	0.01913	0.01000	0.97087	6 038	0.30	19 489	0.16
LZL-3	0.01913	0.02000	0.96087	5 923	0.30	34 199	0.12
LZL-4	0.01913	0.0400	0.9409	5 634	0.31	59 405	0.10
LZL-5	0.01913	0.0500	0.9309	5 548	0.31	71 203	0.09
LZL-6	0.01913	0.0600	0.9209	5 425	0.31	78 247	0.08

* 40kV, 20mA.

TABLE B Calculation α_{ClCo}

Solutions	α_{ClCo}
LZL-2/LZL-6	1.2141···
LZL-2/LZL-5	1.1777···
LZL-2/LZL-4	1.3057···
LZL-3/LZL-6	1.2766···
LZL-3/LZL-5	1.2380···

α_{ClCo} average = 1.2424···

std. devn. = ± 0.0504···

$\alpha_{ClCo} = 1.24^2 \pm 0.05^0$

$= 1.24 \pm 0.05$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	cobalt	$I_{ClK\alpha}$(corr) (cps)
LZL-2	6 038	- 1 970	+ 75	4 143
LZL-3	5 923	- 1 912	+ 147	4 158
LZL-4	5 634	- 1 781	+ 280	4 133
LZL-5	5 548	- 1 735	+ 344	4 157
LZL-6	5 425	- 1 679	+ 404	4 150

$I^o_{ClK\alpha}$ average = 216 842 cps

std. devn. = ± 550 cps

$I^o_{ClK\alpha} = (2.168^4 \pm 0.005^5) \times 10^5$ cps

$= (2.168 \pm 0.006) \times 10^5$ cps

Table D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of		$I_{CoK\alpha}$(corr) (cps)
		matrix	chlorine	
LZL-2	18 489	- 16 556	- 61	1 872
LZL-3	34 199	- 30 307	- 113	3 779
LZL-4	59 405	- 51 549	- 196	7 660
LZL-5	71 203	- 61 131	- 235	9 837
LZL-6	78 247	- 66 456	- 258	11 583

$I^{o}_{CoK\alpha}$ average = 191 321 cps

std. devn. = ± 3 629 cps

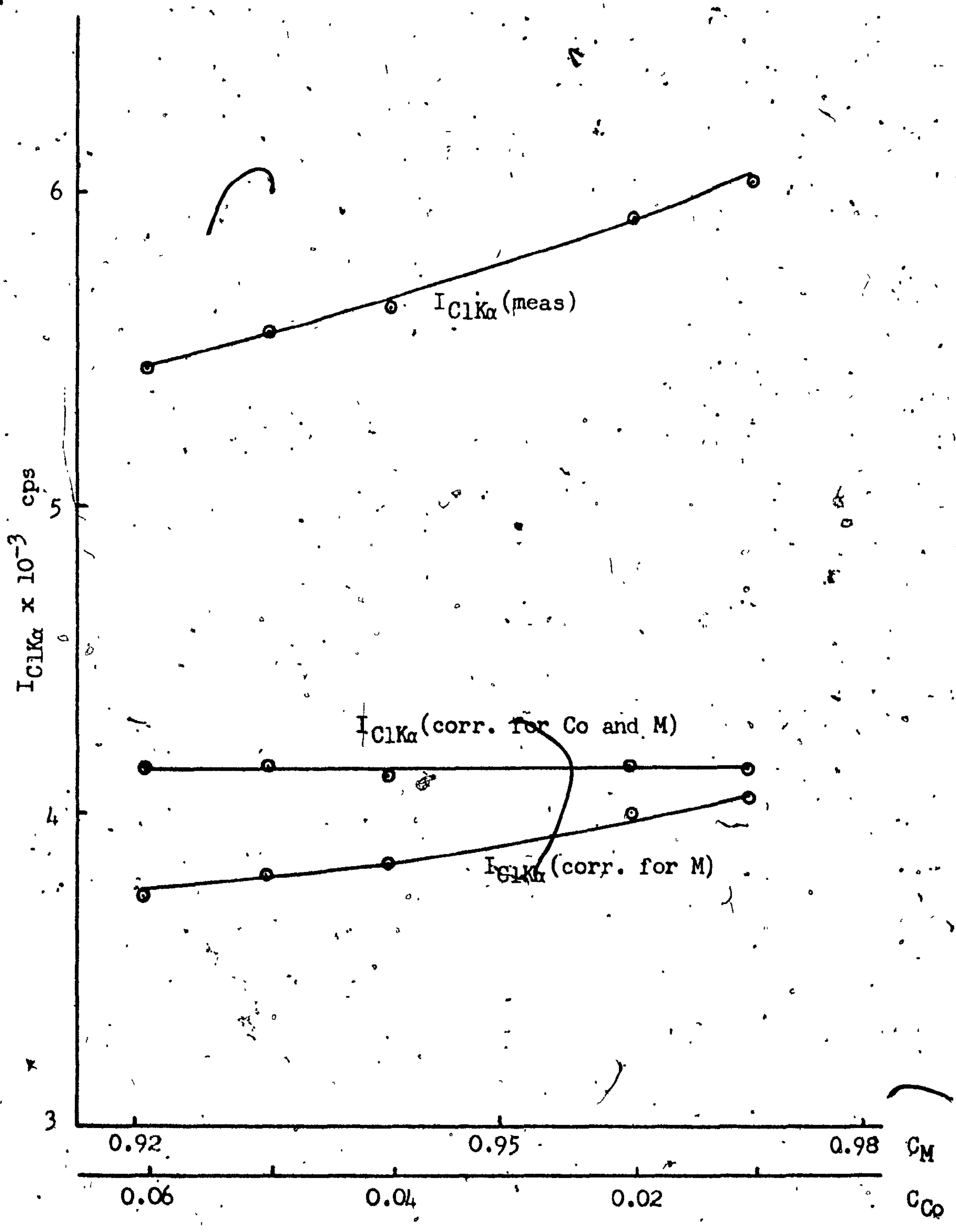
$$I^{o}_{CoK\alpha} = (1.91^{3} \pm 0.03^{6}) \times 10^{5} \text{ cps}$$

$$= (1.91 \pm 0.04) \times 10^{5} \text{ cps}$$

TABLE E. Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
LZL-2	0.01910	0.00003	0.16	0.01030	0.00030	3.00
LZL-3	0.01920	0.00007	0.36	0.01970	0.00030	1.50
LZL-4	0.01910	0.00003	0.16	0.0400	0.0000	0.00
LZL-5	0.01930	0.00017	0.89	0.0522	0.0022	4.40
LZL-6	0.01920	0.0000	0.36	0.0605	0.0005	0.83

FIGURE D $I_{ClK\alpha}$ versus C_{Co} and C_M



5.6.2 Effect of Co on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Co}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{CoK\alpha}$* (cps)	s(%)
MAO-1	0.02000	0.0	0.98000	12 523	0.20	--	--
MAO-2	0.02000	0.01000	0.97000	12 821	0.20	19 223	0.16
MAO-3	0.02000	0.02000	0.96000	12 389	0.20	33 614	0.12
MAO-4	0.02000	0.0400	0.9400	12 166	0.20	62 585	0.09
MAO-5	0.02000	0.0600	0.9200	11 433	0.21	85 845	0.08
MAO-6	0.02000	0.0800	0.9000	11 211	0.21	104 756	0.07
MAO-7	0.02000	0.1000	0.8800	10 964	0.21	126 976	0.07

*50kV, 20mA

TABLE B Calculation of α_{CrCo}

Solutions	α_{CrCo}
MAO-1/MAO-7	– 0.6056···
MAO-1/MAO-6	– 0.5986···
MAO-1/MAO-5	– 0.5772···
MAO-2/MAO-7	– 0.5213···
MAO-2/MAO-6	– 0.4913···
MAO-3/MAO-7	– 0.5619···
MAO-3/MAO-6	– 0.5388···
MAO-4/MAO-7	– 0.5123···

α_{CrCo} average = – 0.5509···

std. devn. = ± 0.0416···

$\alpha_{CrCo} = -0.55^1 \pm 0.04^2$

$= -0.55 \pm 0.04$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^o_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cobalt	$I_{CrK\alpha}$(corr) (cps)
MAO-1	12 523	– 10 396	--	2 127
MAO-2	12 821	– 10 535	– 71	2 215
MAO-3	12 389	– 10 075	– 136	2 178
MAO-4	12 166	– 9 687	– 268	2 211
MAO-5	11 433	– 8 910	– 378	2 145
MAO-6	11 211	– 8 547	– 494	2 170
MAO-7	10 964	– 8 173	– 604	2 187

$I^{o}_{CrK\alpha}$ average = 108 807 cps

std. devn. = ± 1 617 cps

$$I^{o}_{CrK\alpha} = (1.08^{8} \pm 0.01^{6}) \times 10^{5} \text{ cps}$$

$$\doteq (1.09 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$.

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{CoK\alpha}$(corr) (cps)
MAO-2	19 223	- 17 197	+ 307	2 333
MAO-3	33 614	- 29 762	+ 538	4 390
MAO-4	62 585	- 54 259	+ 1 001	9 327
MAO-5	85 845	- 72 841	+ 1 373	14 377
MAO-6	104 756	- 86 955	+ 1 576	19 477
MAO-7	126 976	- 103 057	+ 2 032	25 951

$I^{o}_{CoK\alpha}$ average = 238 094 cps

std. devn. = ± 13 284 cps

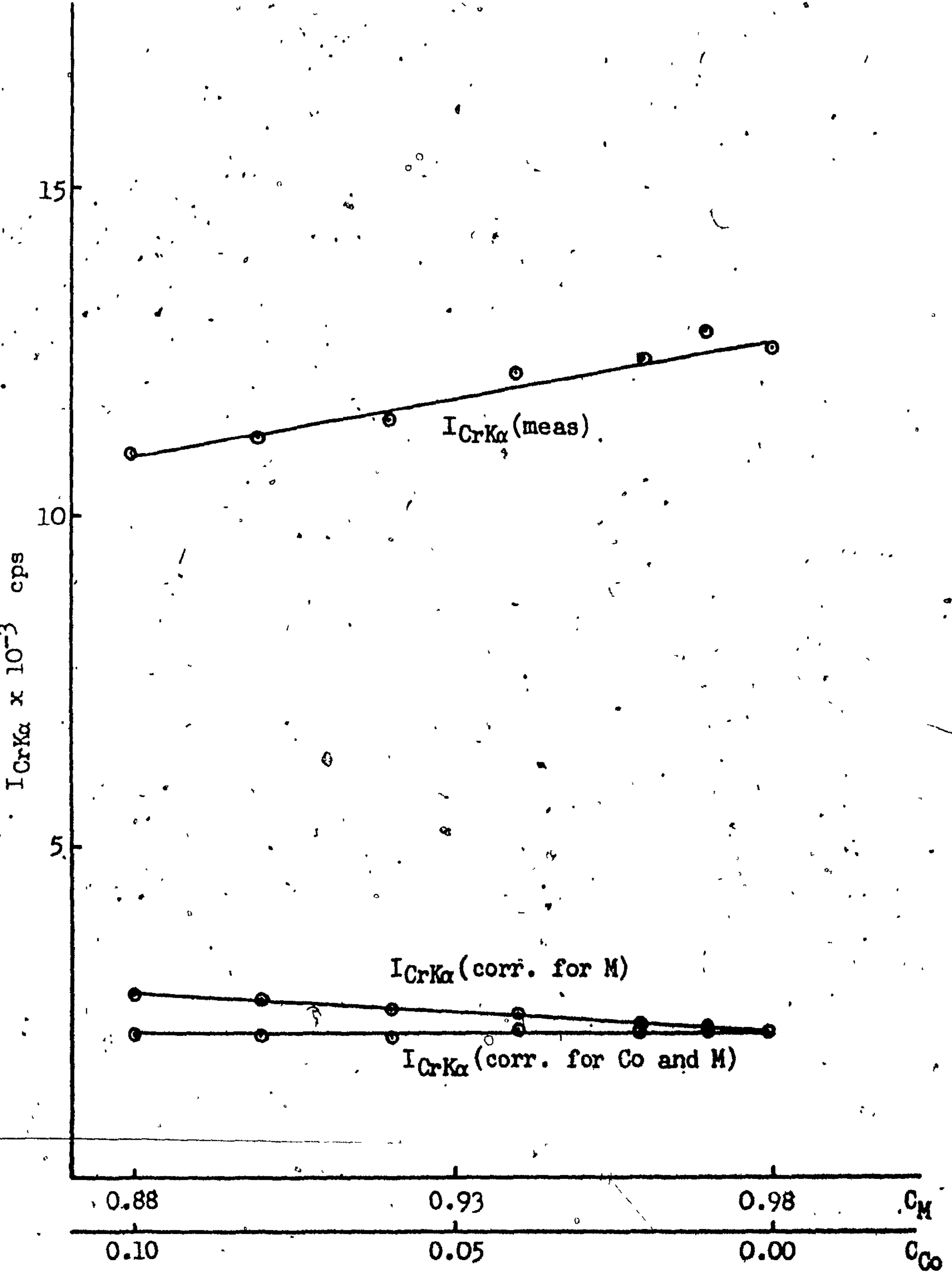
$$I^{o}_{CoK\alpha} = (2.3^{8} \pm 0.1^{3}) \times 10^{5} \text{ cps}$$

$$= (2.4 \pm 0.1) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cr}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
MAO-1	0.01950	0.00050	2.50	--	--	--
MAO-2	0.02040	0.00040	2.00	0.00984	0.00016	1.60
MAO-3	0.01990	0.00010	0.50	0.01820	0.00180	9.00
MAO-4	0.02030	0.00030	1.50	0.0391	0.0009	2.25
MAO-5	0.01970	0.00030	1.50	0.0603	0.0003	0.50
MAO-6	0.02000	0.00000	0.00	0.0831	0.0031	4.00
MAO-7	0.02070	0.00070	3.50	0.1190	0.0190	19.00

FIGURE D $I_{CrK\alpha}$ versus C_{Co} and C_M



5.6.3 Effect of Co on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Co}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{CoK\alpha}$* (cps)	s(%)
LZO-2	0.01000	0.01000	0.98000	15 909	0.18	15 132	0.18
LZO-3	0.01000	0.02000	0.97000	15 634	0.18	27 158	0.14
LZO-4	0.01000	0.0400	0.9500	15 290	0.18	47 859	0.10
LZO-5	0.01000	0.0500	0.9400	15 090	0.18	59 119	0.10
LZO-6	0.01000	0.0600	0.9300	14 681	0.18	66 344	0.10
LZO-7	0.01000	0.0700	0.9200	14 877	0.18	73 355	0.09

* 40kV, 20mA

TABLE B Calculation of α_{MnCo}

Solutions	α_{MnCo}
LZO-2/LZO-7	− 0.6942···
LZO-2/LZO-6	− 0.6171···
LZO-2/LZO-5	− 0.6643···
LZO-3/LZO-7	− 0.7131···
LZO-3/LZO-6	− 0.6206···
LZO-3/LZO-5	− 0.6852···
LZO-4/LZO-7	− 0.7244···

$$\alpha_{MnCo} \text{ average} = -0.6741\cdots$$

$$\text{std. devn.} = \pm 0.0424\cdots$$

$$\alpha_{MnCo} = -0.67^{4} \pm 0.04^{2}$$

$$= -0.67 \pm 0.04$$

TABLE C Calculation of $I_{MnK\alpha}$(corr) and $I^{0}_{MnK\alpha}$

Solution	Measured	Corrected for effect of		$I_{MnK\alpha}$(corr) (cps)
		matrix	cobalt	
LZO-2	15 909	− 13 466	− 107	2 336
LZO-3	15 634	− 13 098	− 211	2 325
LZO-4	15 290	− 12 546	− 412	2 332
LZO-5	15 090	− 12 251	− 508	2 331
LZO-6	14 681	− 11 792	− 594	2 295
LZO-7	14 877	− 11 821	− 702	2 354

$$I^{0}_{MnK\alpha} \text{ average} = 232\ 883 \text{ cps}$$

$$\text{std. devn.} = \pm 1\ 923 \text{ cps}$$

$$I^{0}_{MnK\alpha} = (2.32^{9} \pm 0.01^{9}) \times 10^{5} \text{ cps}$$

$$= (2.33 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of Matrix	Correction for effect of manganese	$I_{CoK\alpha}$(corr) (cps)
LZO-2	15 132	- 13 677	+ 188	1 643
LZO-3	27 158	- 24 296	+ 337	3 199
LZO-4	47 859	- 41 933	+ 595	6 521
LZO-5	59 119	- 51 254	+ 735	8 600
LZO-6	66 344	- 56 906	+ 824	10 262
LZO-7	73 355	- 62 243	+ 911	12 023

$I^{o}_{CoK\alpha}$ average = 167 010 cps

std. devn. = ± 5 222 cps

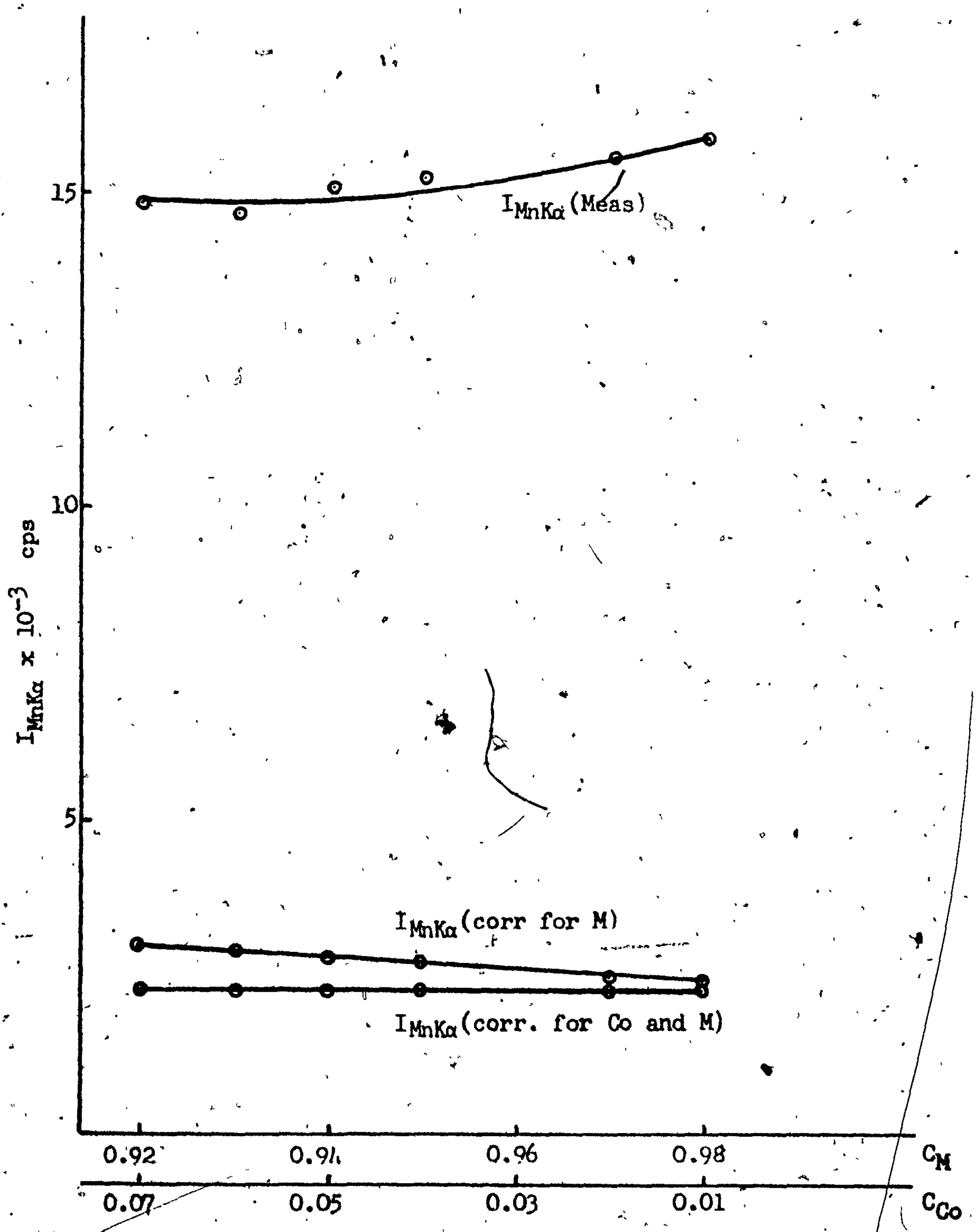
$$I^{o}_{CoK\alpha} = (1.67^{0} \pm 0.05^{2}) \times 10^{5} \text{ cps}$$

$$= (1.67 \pm 0.05) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Mn}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
LZO-2	0.01000	0.00000	0.00	0.00983	0.00007	2.00
LZO-3	0.00997	0.00003	0.30	0.01900	0.00100	5.00
LZO-4	0.01000	0.00000	0.00	0.0387	0.0013	3.25
LZO-5	0.01000	0.00000	0.00	0.0523	0.0023	4.60
LZO-6	0.00990	0.00010	1.00	0.0621	0.0021	3.50
LZO-7	0.01020	0.00020	2.00	0.0736	0.0036	5.15

FIGURE D $I_{MnK\alpha}$ versus C_{Co} and C_M



5.6.4 Effect of Co on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Co}	C_{Cl}	C_M	$I_{FeK\alpha}$(cps)	s(%)	$I_{CoK\alpha}^{*}$(cps)	s(%)	$I_{ClK\alpha}$(cps)	s(%)
MAU-1	0.01000	0.0	0.01611	0.97389	18 468	0.17	--	--	4 765	0.32
MAU-2	0.01000	0.01000	0.01611	0.96389	16 997	0.17	14 446	0.19	4 668	0.33
MAU-3	0.01000	0.02000	0.01611	0.95389	15 326	0.18	36 796	0.12	4 604	0.33
MAU-4	0.01000	0.0400	0.01611	0.9339	14 683	0.18	64 130	0.09	4 314	0.34
MAU-5	0.01000	0.0600	0.01611	0.9139	13 204	0.20	90 345	0.08	4 131	0.35
MAU-6	0.01000	0.0800	0.01611	0.8939	12 577	0.20	107 721	0.07	3 954	0.36
MAU-7	0.01000	0.1000	0.01611	0.8739	11 686	0.21	120 455	0.07	3 768	0.37

* 50kV,20mA

TABLE B Calculation of α_{FeCo}

Solutions	α_{FeCo}
MAU-2/MAU-7	- 0.2188...
MAU-2/MAU-6	- 0.2229...
MAU-4/MAU-7	- 0.2395...
MAU-4/MAU-6	- 0.2557...

α_{FeCo} average = - 0.2342...

std. devn. = ± 0.0168...

$\alpha_{FeCo} = -0.23^{4} \pm 0.01^{7}$

$= -0.23 \pm 0.02$

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of cobalt	$I_{FeK\alpha}$(corr) (cps)
MAU-1	18 468	- 16 128	+ 14	--	2 354
MAU-2	16 997	- 14 691	+ 13	- 40	2 279
MAU-3	15 326	- 13 109	+ 12	- 78	2 151
MAU-4	14 683	- 12 296	+ 11	- 137	2 261
MAU-5	13 204	- 10 820	+ 10	- 185	2 209
MAU-6	12 577	- 10 081	+ 10	- 235	2 271
MAU-7	11 783	- 9 233	+ 9	- 276	2 283

	C_{Cl}(calc)	Abs. error	Error %
MAU-1	0.01626	0.00015	0.93
MAU-2	0.01615	0.00004	0.25
MAU-3	0.01636	0.00025	1.55
MAU-4	0.01598	0.00013	0.81
MAU-5	0.01611	0.00000	0.00
MAU-6	0.01612	0.00001	0.06
MAU-7	0.01594	0.00017	1.06

FIGURE D $I_{FeK\alpha}$ versus C_{Co} and C_M

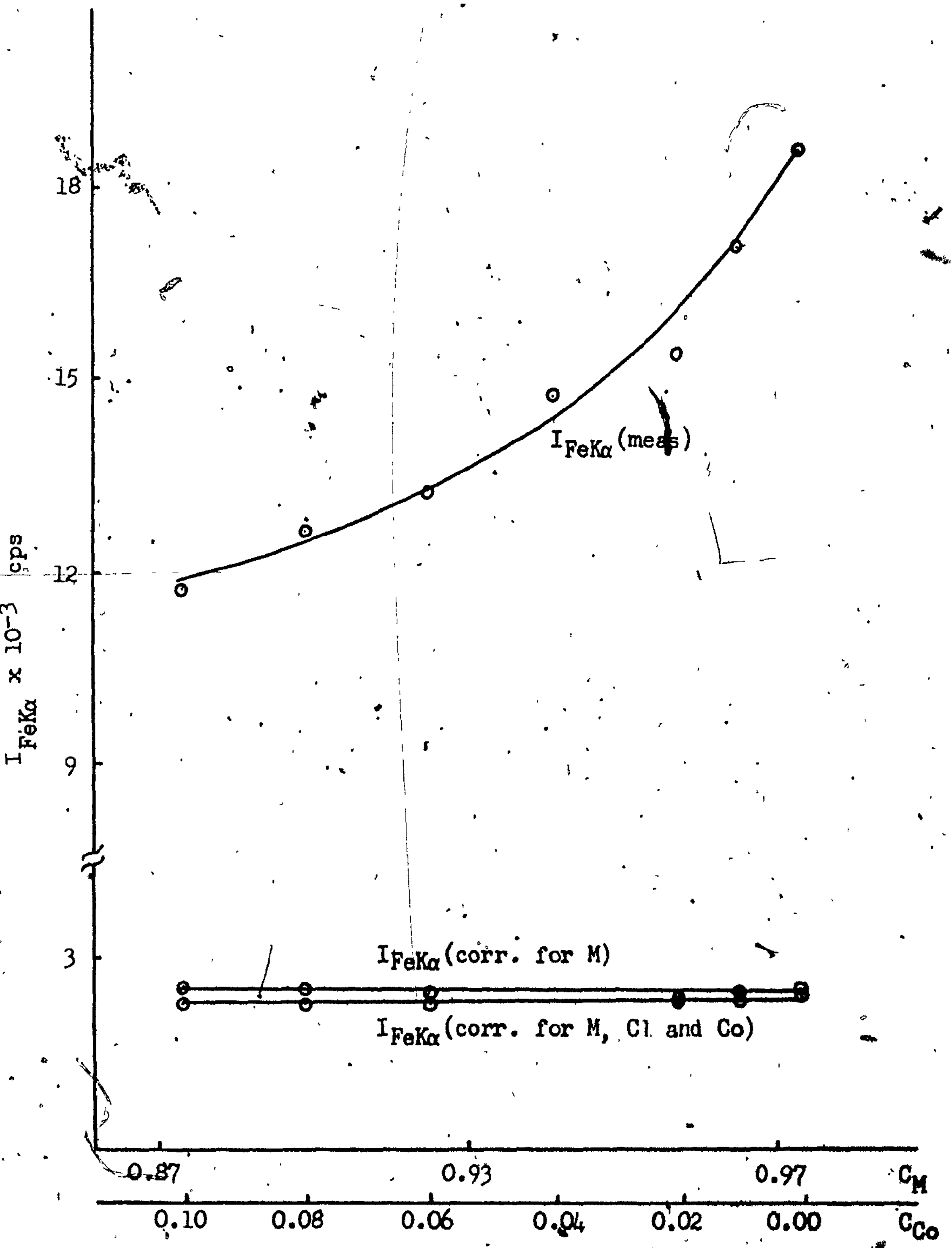


TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of			$I_{CoK\alpha}$(corr) (cps)
		matrix	chlorine	iron	
MAU-2	14 446	- 12 842	- 40	- 32	1 532
MAU-3	36 796	- 32 372	- 102	- 82	4 240
MAU-4	64 130	- 55 237	- 178	- 144	8 571
MAU-5	90 345	- 76 150	- 251	- 202	13 742
MAU-6	107 721	- 88 809	- 299	- 241	18 372
MAU-7	120 455	- 97 085	- 335	- 270	22 765

$I^{o}_{CoK\alpha}$ average = 222 522 cps

std. devn. = ± 8 642 cps

$$I^{o}_{CoK\alpha} = (2.22^{5} \pm 0.08^{6}) \times 10^{5} \text{ cps}$$

$$= (2.22 \pm 0.09) \times 10^{5} \text{ cps}$$

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of			$I_{ClK\alpha}$(corr) (cps)
		matrix	cobalt	iron	
MAU-1	4 765	- 1 559	--	+ 58	3 264
MAU-2	4 668	- 1 512	+ 60	+ 53	3 269
MAU-3	4 604	- 1 476	+ 114	+ 52	3 294
MAU-4	4 314	- 1 354	+ 214	+ 49	3 223
MAU-5	4 131	- 1 268	+ 308	+ 46	3 217
MAU-6	3 954	- 1 188	+ 393	+ 45	3 204
MAU-7	3 768	- 1 106	+ 468	+ 42	3 172

$I^{o}_{ClK\alpha}$ average = 200 789 cps

std. devn. = ± 2 597 cps

$$I^{o}_{ClK\alpha} = (2.00^{7} \pm 0.02^{6}) \times 10^{5} \text{ cps}$$

$$= (2.01 \pm 0.03) \times 10^{5} \text{ cps}$$

TABLE F Back-calculation of solution composition

Solution	C_{Fe}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
MAU-1	0.01050	0.00050	5.00	--	--	--
MAU-2	0.00990	0.00010	1.00	0.00670	0.00330	33.00
MAU-3	0.00950	0.00050	5.00	0.01880	0.00120	6.00
MAU-4	0.00990	0.00010	1.00	0.0379	0.0020	5.00
MAU-5	0.00990	0.00010	1.00	0.0627	0.0027	4.50
MAU-6	0.01020	0.00020	2.00	0.0848	0.0048	6.00
MAU-7	0.01020	0.00020	2.00	0.1046	0.0046	4.60

5.6.5 Effect of Co on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Co}	C_M	$I_{NiK\beta}$ (cps)	s(%)	$I_{CoK\alpha}$* (cps)	s(%)
MAF-1	0.01000	0.0	0.99000	65 634	0.09	--	--
MAF-2	0.01000	0.01000	0.98000	59 801	0.09	24 805	0.14
MAF-3	0.01000	0.02000	0.97000	55 402	0.10	47 934	0.10
MAF-4	0.01000	0.0400	0.9500	49 634	0.10	86 497	0.08
MAF-5	0.01000	0.0600	0.9300	43 625	0.10	108 745	0.07
MAF-6	0.01000	0.0700	0.9200	41 554	0.11	131 609	0.07

* 50kV,20mA

TABLE B Calculation of α_{NiCo}

Solutions	α_{NiCo}
MAF-1/MAF-6	- 0.1549···
MAF-1/MAF-5	- 0.1429···
MAF-1/MAF-4	- 0.1751···
MAF-2/MAF-6	- 0.1901···
MAF-2/MAF-5	- 0.1796···
MAF-3/MAF-6	- 0.2091···

α_{NiCo} average = - 0.1753···

std. devn. = ± 0.0238···

α_{NiCo} = $- 0.17^5 \pm 0.02^4$

= - 0.17 ± 0.02

TABLE C Calculation of $I_{NiK\alpha}$(corr) and $I^o_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cobalt	$I_{NiK\alpha}$(corr) (cps)
MAF-1	65 634	- 59 591	--	6 043
MAF-2	59 801	- 53 747	- 105	5 949
MAF-3	55 402	- 49 255	- 193	5 924
MAF-4	49 634	- 43 243	- 347	6 044
MAF-5	43 625	- 37 208	- 458	5 959
MAF-6	41 554	- 35 060	- 509	5 985

$I^o_{NiK\alpha}$ average = 598 400 cps

std. devn. = ± 4 995 cps

$I^o_{NiK\alpha}$ = $(5.98^4 \pm 0.04^9) \times 10^5$ cps

= $(5.98 \pm 0.05) \times 10^5$ cps

TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^0_{CoK\alpha}$

Solution	Measured	Correction for effect of		$I_{CoK\alpha}$(corr) (cps)
		matrix	nickel	
MAF-2	24 805	- 22 420	- 93	2 292
MAF-3	47 934	- 42 883	- 179	4 872
MAF-4	86 497	- 75 787	- 323	10 387
MAF-5	108 745	- 93 275	- 407	15 063
MAF-6	131 609	- 111 672	- 492	19 445

$I^0_{CoK\alpha}$ average = 252 262 cps

std. devn. = ± 19 355 cps

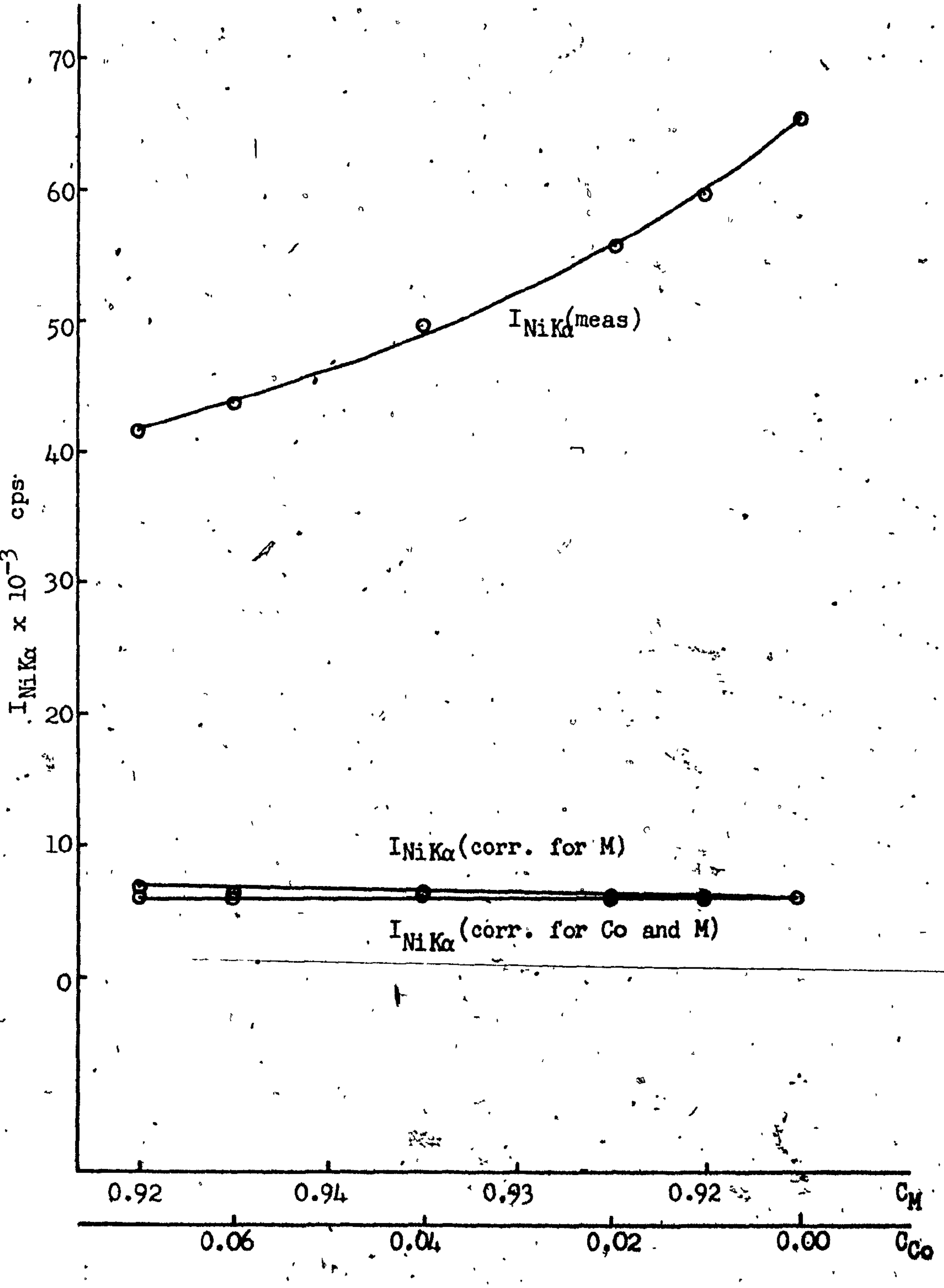
$I^0_{CoK\alpha}$ = $(2.5^2 \pm 0.1^9) \times 10^5$ cps

= $(2.5 \pm 0.2) \times 10^5$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Ni}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
MAF-1	0.01010	0.00010	1.00	--	--	--
MAF-2	0.00990	0.00010	1.00	0.00920	0.00080	8.00
MAF-3	0.00990	0.00010	1.00	0.01970	0.00030	1.50
MAF-4	0.01030	0.00030	3.00	0.0433	0.0033	8.25
MAF-5	0.01010	0.00010	1.00	0.0620	0.0020	3.33
MAF-6	0.01100	0.00100	10.00	0.0882	0.0082	10.25

FIGURE D $I_{NiK\alpha}$ versus C_{Co} and C_M



5.6.6 Effect of Co on Cu

TABLE A Experimental Parameters

Solutions	C_{Cu}	C_{Co}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{CoK\alpha}^{*}$ (cps)	s(%)
MAN-1	0.02000	0.0	0.98000	112 534	0.06	--	--
MAN-2	0.02000	0.01000	0.97000	90 626	0.08	25 306	0.14
MAN-3	0.02000	0.02000	0.96000	72 938	0.09	47 396	0.10
MAN-4	0.02000	0.0400	0.9400	55 717	0.10	86 139	0.07
MAN-5	0.02000	0.0600	0.9200	43 140	0.10	111 912	0.07
MAN-6	0.02000	0.0800	0.9000	36 570	0.12	136 220	0.07
MAN-7	0.02000	0.1000	0.8800	31 383	0.13	154 951	0.06

* 50kV, 20mA

TABLE B Calculation of α_{CuCo}

Solutions	α_{CuCo}
MAN-1/MAN-7	1.4690····
MAN-1/MAN-6	1.4798····
MAN-1/MAN-5	1.5571····
MAN-2/MAN-7	1.5324····
MAN-2/MAN-6	1.5534····
MAN-2/MAN-5	1.6886····
MAN-3/MAN-7	1.3656····
MAN-3/MAN-6	1.3704····
MAN-4/MAN-7	1.5518····

α_{CuCo} average = 1.5075···

std. devn. = ± 0.1007···

$\alpha_{CuCo} = 1.5^1 \pm 0.1^0$

$= 1.5 \pm 0.1$

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cobalt	$I_{CuK\alpha}$(corr) (cps)
MAN-1	112 534	- 102 111	--	10 423
MAN-2	90 626	- 90 626	+ 1 368	10 601
MAN-3	72 938	- 64 832	+ 2 203	10 309
MAN-4	55 717	- 48 493	+ 3 365	10 589
MAN-5	43 140	- 36 748	+ 3 908	10 300
MAN-6	36 570	- 30 474	+ 4 418	10 514
MAN-7	31 383	- 25 571	+ 4 739	10 551

$I^{o}_{CuK\alpha}$ average = 523 478 cps

std. devn. = ± 6 352 cps

$I^{o}_{CuK\alpha} = (5.23^{5} \pm 0.06^{3}) \times 10^{5}$ cps

$= (5.24 \pm 0.06) \times 10^{5}$ cps

TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{CoK\alpha}$(corr) (cps)
MAN-2	25 306	- 22 639	- 336	2 331
MAN-3	47 396	- 41 965	- 630	4 801
MAN-4	86 139	- 74 679	- 1 146	10 314
MAN-5	111 912	- 94 959	- 1 488	15 465
MAN-6	136 220	- 113 072	- 1 812	21 336
MAN-7	154 951	- 125 762	- 2 061	27 128

$I^{o}_{CoK\alpha}$ average = 254 455 cps

std. devn. = ± 15 000 cps

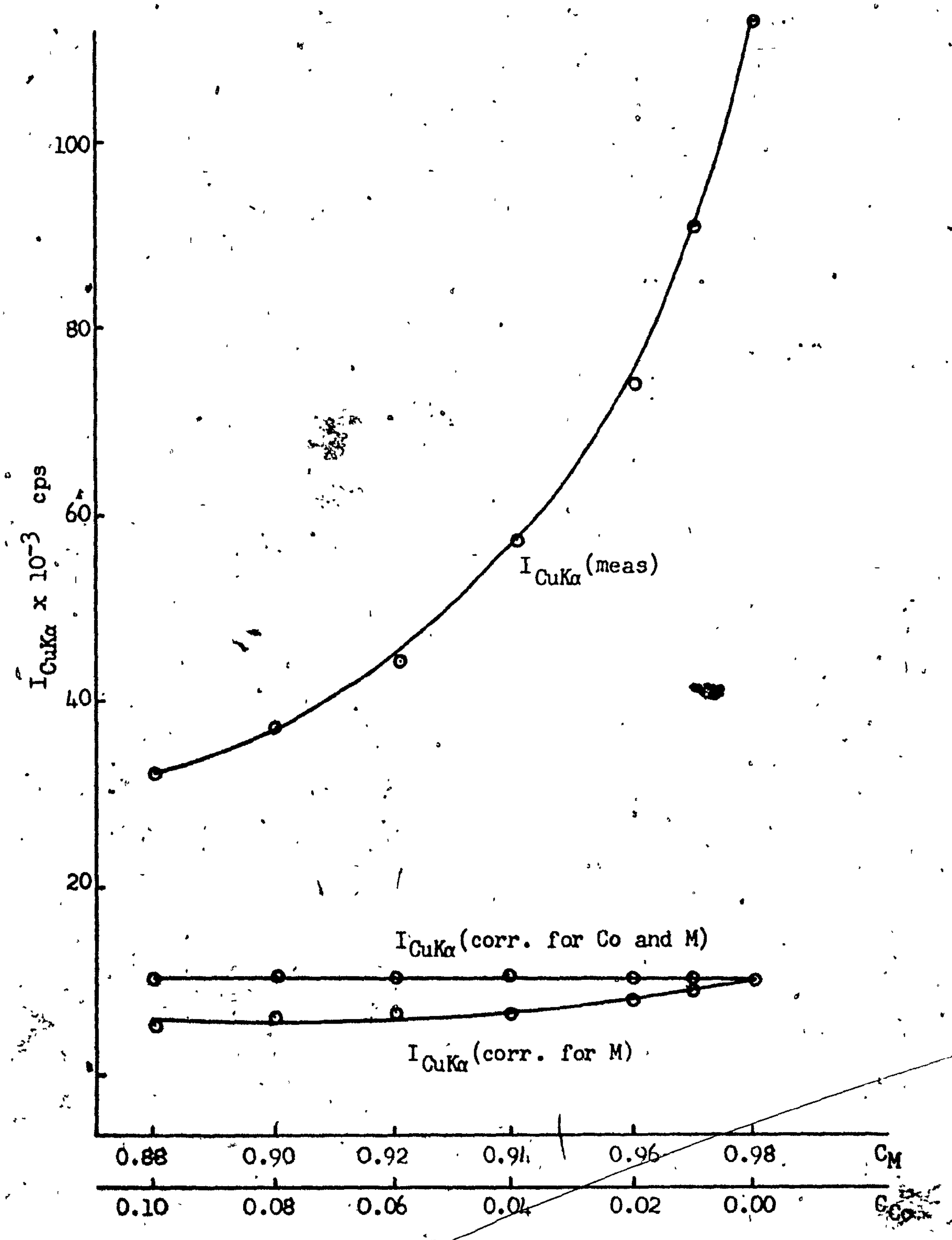
$I^{o}_{CoK\alpha} = (2.5^{4} \pm 0.1^{5}) \times 10^{5}$ cps

$= (2.5 \pm 0.2) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
MAN-1	0.01990	0.00010	0.50	--	--	--
MAN-2	0.01980	0.00020	1.00	0.00910	0.00090	9.00
MAN-3	0.01910	0.00090	4.50	0.01850	0.00150	7.50
MAN-4	0.02050	0.00050	2.50	0.0408	0.0008	2.00
MAN-5	0.01990	0.00010	0.50	0.0613	0.0013	2.16
MAN-6	0.02150	0.00150	7.50	0.0880	0.0080	10.00
MAN-7	0.02260	0.00260	13.00	0.1160	0.0160	16.00

FIGURE D $I_{CuK\alpha}$ versus C_{Co} and C_M



5.6.7 Effect of Co on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Co}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{CoK\alpha}$* (cps)	s(%)
MAJ-1	0.02000	0.0	0.98000	144 277	0.07	--	--
MAJ-2	0.02000	0.01000	0.97000	115 183	0.07	23 648	0.15
MAJ-3	0.02000	0.0200	0.9600	96 080	0.07	42 808	0.10
MAJ-4	0.02000	0.0400	0.9400	70 080	0.09	74 927	0.09
MAJ-5	0.02000	0.0600	0.9200	62 327	0.10	89 544	0.08
MAJ-6	0.02000	0.0800	0.9000	57 968	0.10	100 376	0.07
MAJ-7	0.02000	0.1000	0.8800	52 972	0.10	112 529	0.07

* 50kV, 20mA

TABLE B Calculation of α_{ZnCo}

Solutions	α_{ZnCo}
MAJ-1/MAJ-7	0.8546···
MAJ-1/MAJ-6	0.9420···
MAJ-1/MAJ-5	1.0545···
MAJ-1/MAJ-4	1.0676···
MAJ-2/MAJ-7	0.8230···
MAJ-2/MAJ-6	0.9253···
MAJ-2/MAJ-5	1.1007···
MAJ-3/MAJ-7	0.7737···

α_{ZnCo} average = 0.9427···

std. devn. = ± 0.122···

$\alpha_{ZnCo} = 0.9^{4} \pm 0.1^{2}$

$= 0.9 \pm 0.1$

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of Matrix	Correction for effect of cobalt	$I_{ZnK\alpha}$(corr) (cps)
MAJ-1	144 277	- 133 318	--	10 959
MAJ-2	115 183	- 105 348	+ 1 083	10 918
MAJ-3	96 080	- 86 970	+ 1 806	10 916
MAJ-4	70 080	- 62 114	+ 2 635	10 601
MAJ-5	62 327	- 54 654	+ 2 929	10 602
MAJ-6	57 968	- 50 285	+ 3 269	10 952
MAJ-7	52 972	- 45 452	+ 3 485	11 005

$I^{o}_{ZnK\alpha}$ average = 542 521 cps

std. devn. = ± 8 627 cps

$$I^{o}_{ZnK\alpha} = (5.42^{5} \pm 0.08^{6}) \times 10^{5} \text{ cps}$$

$$= (5.42 \pm 0.09) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of		$I_{CoK\alpha}$(corr) (cps)
		matrix	zinc	
MAJ-2	23 648	- 21 156	- 288	2 204
MAJ-3	42 808	- 37 902	- 522	4 384
MAJ-4	74 927	- 64 959	- 914	9 054
MAJ-5	89 544	- 76 805	- 1 092	11 647
MAJ-6	100 376	- 85 171	- 1 225	13 980
MAJ-7	112 529	- 94 445	- 1 372	16 712

$I^{o}_{CoK\alpha}$ average = 228 439 cps

std. devn. = ± 7 788 cps

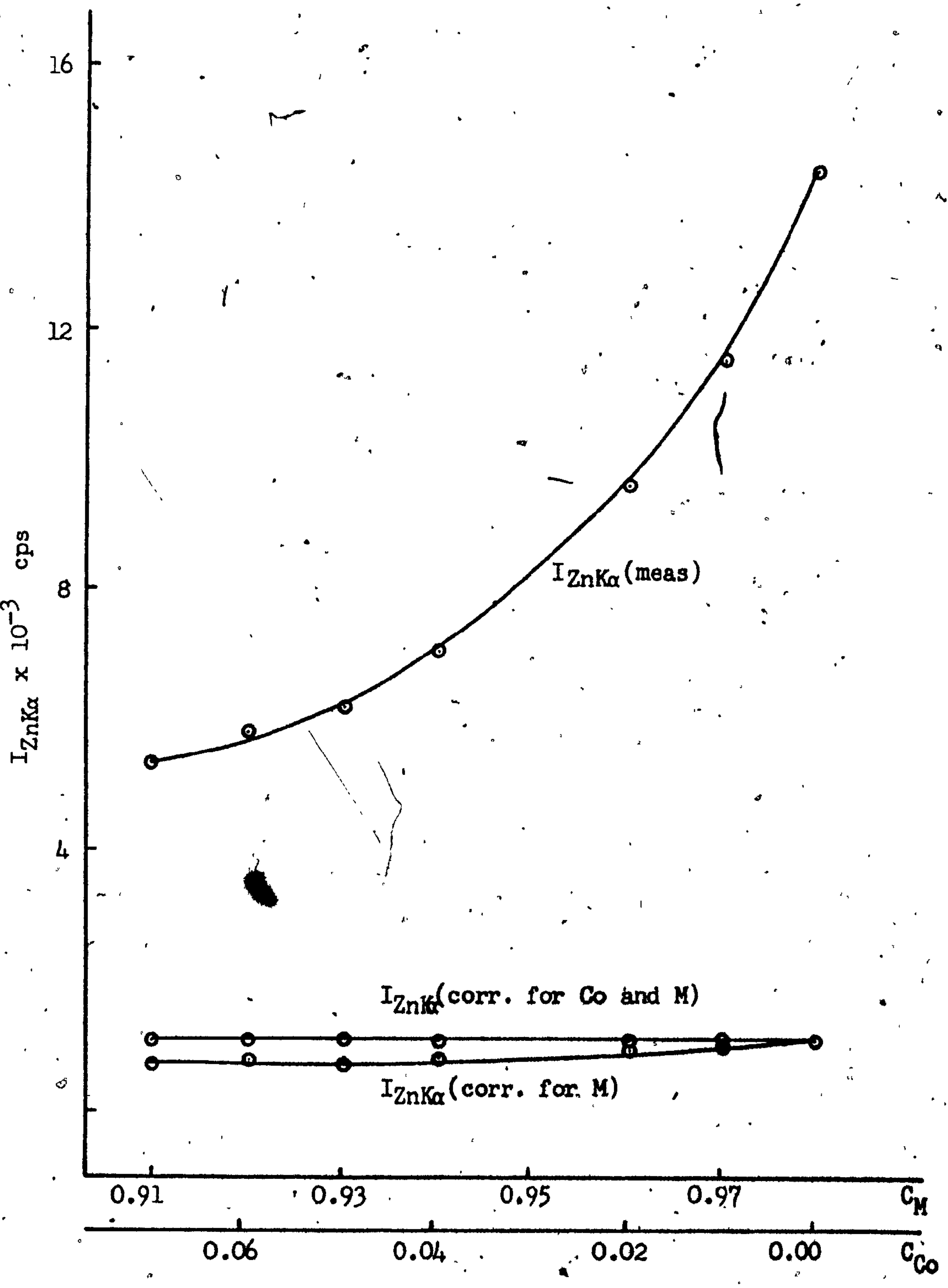
$$I^{o}_{CoK\alpha} = (2.28^{4} \pm 0.07^{8}) \times 10^{5} \text{ cps}$$

$$= (2.28 \pm 0.08) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Co}(calc)	Abs. error	Error %
MAJ-1	0.02030	0.00030	1.50	--	--	--
MAJ-2	0.02000	0.00000	0.00	0.00960	0.00040	4.00
MAJ-3	0.01970	0.00030	1.50	0.01900	0.00100	5.00
MAJ-4	0.01930	0.00070	3.50	0.0394	0.0006	1.50
MAJ-5	0.01980	0.00020	1.00	0.0515	0.0015	3.00
MAJ-6	0.02070	0.00070	3.50	0.0622	0.0022	3.67
MAJ-7	0.02160	0.00160	8.00	0.0762	0.0062	8.86

FIGURE D $I_{ZnK\alpha}$ versus C_{Co} and C_M



5.7 Effects of Nickel

Solutions: The metal concentration for each series were obtained by dilution of the following stock solutions:-

Chromium	1 ml = 0.2000	± 0.0001 g	(dil. HNO_3)
Manganese	1 ml = 0.10000	± 0.00002 g	(dil. HNO_3)
Iron	1 ml = 0.10000	± 0.00002 g	(dil. HCl-HNO_3)
Cobalt	1 ml = 0.10000	± 0.00005 g	(dil. HNO_3)
Nickel	1 ml = 0.10000	± 0.00002 g	(dil. HNO_3)
Copper	1 ml = 0.20000	± 0.00005 g	(dil. HNO_3)
Zinc	1 ml = 0.2000	± 0.0001 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBN	1:72 Cl	1:36 to 1:630
Cr	MAQ	1:440	1:220 to 1:2200
Mn	LZP	1:400	1:200 to 1:2000
Fe	MAV	1:440	1:220 to 1:2200
Co	MAC	1:400	1:200 to 1:2000
Cu	MAP	1:440	1:220 to 1:2200
Zn	MAI	1:440	1:220 to 1:2200

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn
Target	Cr	W	W	W	W	W	W	W
kV	50	50	50	50	50	*	50	50
mA	36	40	20	40	30	*	30	30
Coll^n	coarse	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα

* See each series

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:-	Calculation of α_{ANi} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{ANi} (presence of chlorine as fourth component)	Equation (44)
	Calculation of $I_A(corr)$	Equation (45) or a modification.
	Calculation of I_A^o -	$I_A(corr)/C_A$

5.7.1 Effect of Ni on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Ni}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}^{*}$ (cps)	s(%)
MBN-1	0.0214^5	0.00	0.9785^5	6 180	0.29	--	--
MBN-2	0.0214^5	0.01000	0.9685^5	6 079	0.30	40 470	0.11
MBN-3	0.0214^5	0.02000	0.9585^5	5 940	0.30	74 729	0.09
MBN-4	0.0214^5	0.0300	0.9485^5	5 776	0.31	104 362	0.07
MBN-5	0.0214^5	0.0500	0.9285^5	5 554	0.31	149 309	0.07
MBN-6	0.0214^5	0.0600	0.9185^5	5 433	0.32	169 630	0.06

* 50kV, 20mA

TABLE B Calculation of α_{ClNi}

Solutions	α_{ClNi}
MBN-1/MBN-6	1.2021...
MBN-1/MBN-5	1.1771...
MBN-2/MBN-6	1.2990...
MBN-2/MBN-5	1.2885...
MBN-3/MBN-6	1.3065...
MBN-3/MBN-5	1.2945...

α_{ClNi} average = 1.2613

std. devn. = ± 0.0564

$$\bar{\alpha}_{ClNi} = 1.26^1 \pm 0.05^6$$

$$= 1.26 \pm 0.06$$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of		$I_{ClK\alpha(corr)}$ (cps)
		matrix	nickel	
MBN-1	6 180	- 2 032	--	4 148
MBN-2	6 079	- 1 978	+ 77	4 178
MBN-3	5 940	- 1 913	+ 150	4 177
MBN-4	5 776	- 1 841	+ 218	4 153
MBN-5	5 554	- 1 732	+ 350	4 172
MBN-6	5 433	- 1 677	+ 411	4 167

$I^{o}_{ClK\alpha}$ average = 194 211 cps.
std. devn. = ± 570 cps
$I^{o}_{ClK\alpha}$ = $(1.942^{1} \pm 0.005^{7}) \times 10^{5}$
= $(1.942 \pm 0.006) \times 10^{5}$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

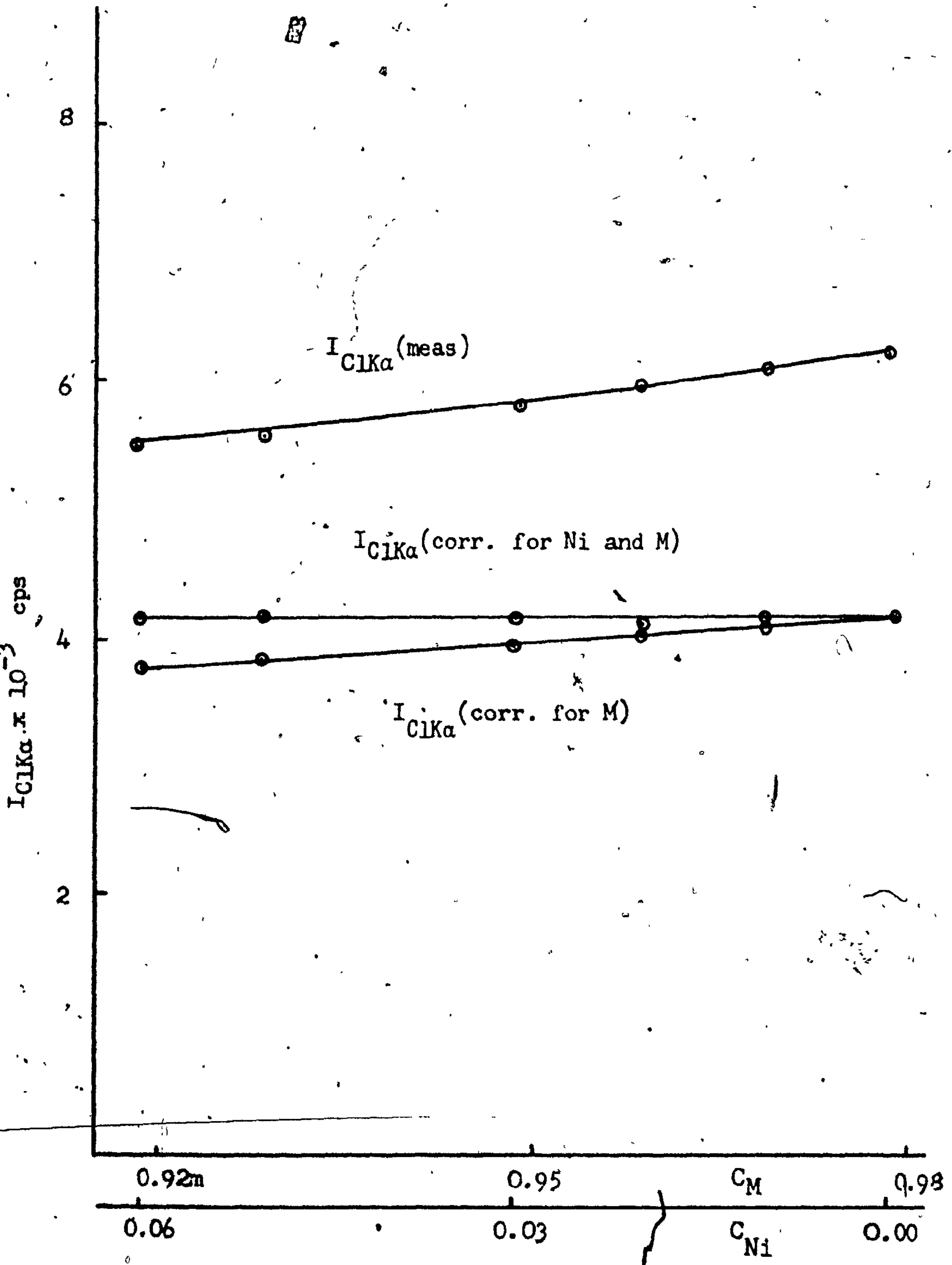
Solution	Measured	Correction for effect of		$I_{NiK\alpha}$(corr) (cps)
		matrix	chlorine	
MBN-2	40 470	- 35 948	- 141	4 381
MBN-3	74 729	- 65 693	- 260	8 776
MBN-4	104 362	- 90 786	- 363	13 213
MBN-5	149 309	- 127 147	- 519	21 643
MBN-6	169 630	- 142 897	- 589	26 144

$I^{o}_{NiK\alpha}$ average = 437 119 cps
std. devn. = ± 2 961 cps
$I^{o}_{NiK\alpha}$ = $(4.37^{1} \pm 0.02^{9}) \times 10^{5}$
= $(4.37 \pm 0.03) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs.error	Error %	C_{Ni}(calc)	Abs. error	Error %
MBN-1	0.0214	0.0000	0.00	—	—	—
MBN-2	0.0215	0.0001	0.30	0.01000	0.00000	0.00
MBN-3	0.0215	0.0001	0.30	0.02010	0.00010	0.50
MBN-4	0.0214	0.0000	0.00	0.0303	0.0003	1.00
MBN-5	0.0214	0.0000	0.00	0.0493	0.0007	1.40
MBN-6	0.0214	0.0000	0.00	0.0597	0.0003	0.50

FIGURE D $I_{ClK\alpha}$ versus C_{Ni} and C_M



5.7.2 Effect of Ni on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Ni}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}$* (cps)	s(%)
MAQ-1	0.02000	0.00	0.98000	14 104	0.19	—	—
MAQ-2	0.02000	0.01000	0.97000	14 049	0.19	25 529	0.13
MAQ-3	0.02000	0.02000	0.96000	13 630	0.19	54 443	0.10
MAQ-4	0.02000	0.0400	0.9400	13 107	0.20	96 498	0.07
MAQ-5	0.02000	0.0600	0.9200	12 182	0.20	125 105	0.07
MAQ-6	0.02000	0.0800	0.9000	11 688	0.21	149 214	0.07
MAQ-7	0.02000	0.1000	0.8800	11 385	0.21	177 313	0.06

* 50 kV, 20mA

TABLE B Calculation of α_{CrNi}

Solutions	α_{CrNi}
MAQ-1/MAQ-7	- 0.4415···
MAQ-1/MAQ-6	- 0.4082···
MAQ-1/MAQ-5	- 0.4005···
MAQ-2/MAQ-7	- 0.3937···
MAQ-2/MAQ-6	- 0.3424···
MAQ-3/MAQ-7	- 0.4067···
MAQ-3/MAQ-6	- 0.3492···
MAQ-4/MAQ-7	- 0.3709···

α_{CrNi} average = - 0.3891

std. devn. = ± 0.0331

$$\alpha_{CrNi} = -0.38^{9} \pm 0.03^{8}$$

$$= -0.39 \pm 0.04$$

TABLE C Calculation of $I_{CrK\alpha}(corr)$ and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{CrK\alpha}(corr)$ (cps)
MAQ-1	14 104	- 11 708	--	2 396
MAQ-2	14 049	- 11 543	- 55	2 450
MAQ-3	13 630	- 11 084	- 106	2 440
MAQ-4	13 107	- 10 437	- 204	2 466
MAQ-5	12 182	- 9 493	- 284	2 405
MAQ-6	11 688	- 8 910	- 364	2 414
MAQ-7	11 385	- 8 487	- 443	2 455

$I^{o}_{CrK\alpha}$ average = 121 621 cps

std. devn. = ± 1 383 cps

$$I^{o}_{CrK\alpha} = (1.21^{6} \pm 0.01^{4}) \times 10^{5}$$
$$= (1.22 \pm 0.01) \times 10^{5}$$

TABLE D Calculation of $I_{NiK\alpha}(corr)$ and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{NiK\alpha}(corr)$ (cps)
MAQ-2	29 529	- 26 269	+ 593	3 833
MAQ-3	54 443	- 47 932	+ 1 094	7 605
MAQ-4	96 498	- 83 188	+ 1 940	15 250
MAQ-5	125 015	- 125 015	+ 2 513	22 049
MAQ-6	149 214	- 123 160	+ 2 999	29 053
MAQ-7	177 313	- 143 100	+ 35564	37 777

$I^{o}_{NiK\alpha}$ average = 375.536 cps

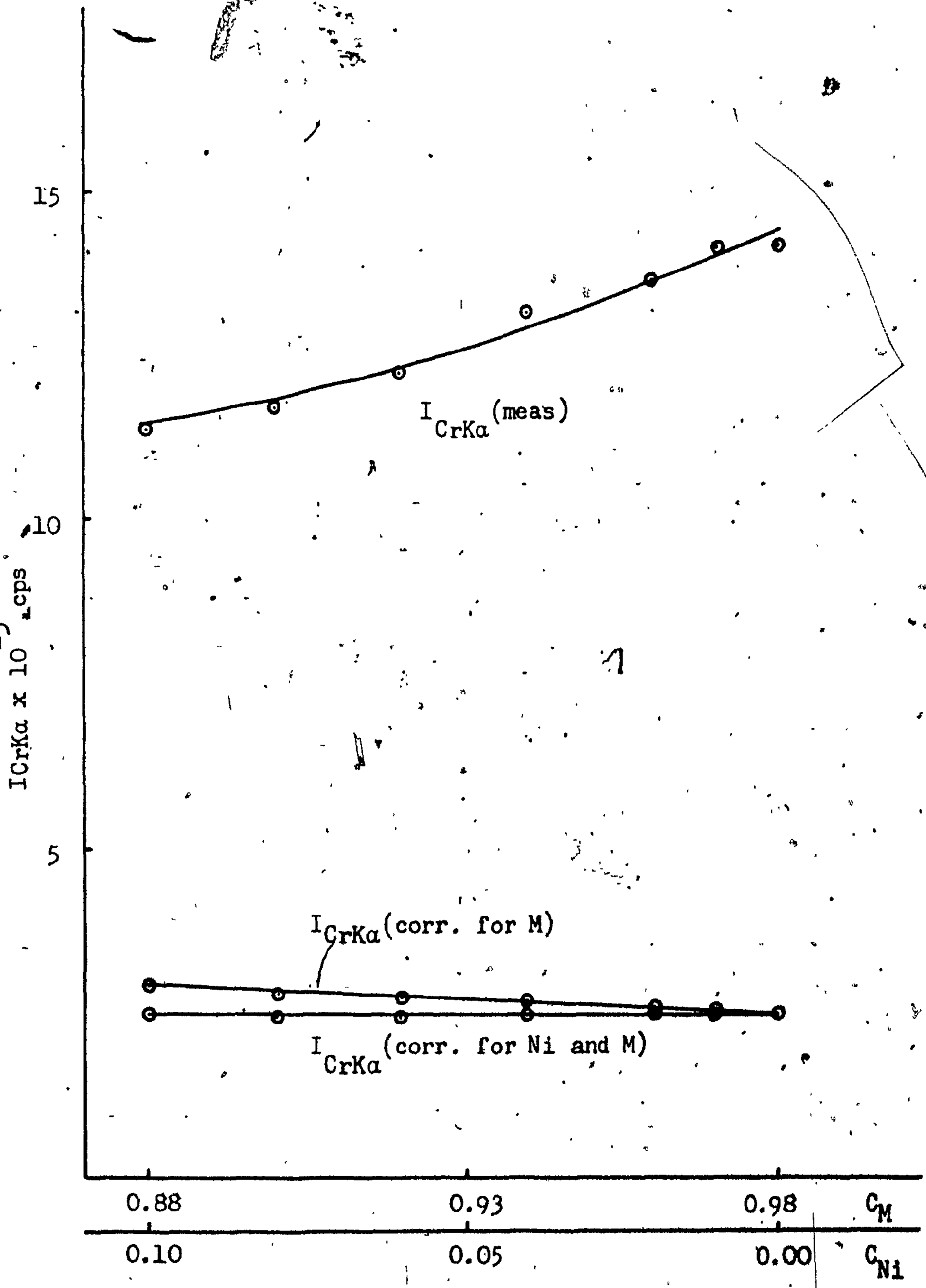
std. devn. = ± 8 630 cps

$$I^{o}_{NiK\alpha} = (3.75^{5} \pm 0.08^{6}) \times 10^{5}$$
$$= (3.76 \pm 0.09) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cr}(calc)	Abs. error	Error %	C_{Ni}(calc)	Abs. error	Error %
MAQ-1	0.01970	0.00030	1.50	--	--	--
MAQ-2	0.02020	0.00020	1.00	0.01030	0.00030	3.00
MAQ-3	0.02000	0.00000	0.00	0.02030	0.00030	1.50
MAQ-4	0.02030	0.00030	1.50	0.0409	0.0009	2.25
MAQ-5	0.01960	0.00040	2.00	0.0577	0.0023	4.00
MAQ-6	0.01950	0.00050	2.50	0.0752	0.0048	6.75
MAQ-7	0.02020	0.00020	1.00	0.1011	0.0011	1.10

FIGURE D $I_{CrK\alpha}$ versus C_{Ni} and C_M



5.7.3 Effect of Ni on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Ni}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}$* (cps)	s(%)
LZP-1	0.01000	0.00	0.99000	7 307	0.26	—	—
LZP-2	0.01000	0.01000	0.98000	7 062	0.27	24 161	0.14
LZP-3	0.01000	0.02000	0.97000	6 710	0.28	45 451	0.10
LZP-4	0.01000	0.0400	0.9500	6 372	0.29	80 410	0.08
LZP-5	0.01000	0.0600	0.9300	6 205	0.29	105 105	0.07
LZP-6	0.01000	0.0800	0.9100	5 857	0.31	126 336	0.07
LZP-7	0.01000	0.1000	0.8900	5 293	0.32	126 841	0.07

* 40 kV, 20 mA

TABLE B Calculation of α_{MnNi}

Solutions	α_{MnNi}
LZP-1/LZP-7	− 0.3122...
LZP-1/LZP-6	− 0.4152...
LZP-1/LZP-5	− 0.4347...
LZP-2/LZP-7	− 0.3047...
LZP-2/LZP-6	− 0.4248...
LZP-2/LZP-5	− 0.4520...

α_{MnNi} average = − 0.3906...
std. devn. = ± 0.065...

$$\alpha_{MnNi} = -0.39^{1} \pm 0.06^{5}$$
$$= -0.39 \pm 0.06$$

TABLE C Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{MnK\alpha}$(corr) (cps)
LZP-1	7 307	− 6 248	—	1 059
LZP-2	7 062	− 5 977	− 28	1 057
LZP-3	6 710	− 5 621	− 52	1 037
LZP-4	6 372	− 5 228	− 100	1 044
LZP-5	6 205	− 4 984	− 146	1 075
LZP-6	5 857	− 4 603	− 183	1 071
LZP-7	5 293	− 4 069	− 207	1 017

$I^{o}_{MnK\alpha}$ average = 105 143 cps
std. devn. = ± 2 043 cps

$$I^{o}_{MnK\alpha} = (1.05^{1} \pm 0.02^{0}) \times 10^{5}$$
$$\doteq (1.05 \pm 0.02) \times 10^{5}$$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{NiK\alpha(corr)}$ (cps)
LZP-2	24 161	- 21 715	+ 293	2 749
LZP-3	45 451	- 40 433	+ 552	5 570
LZP-4	80 410	- 70 057	+ 977	11 330
LZP-5	105 105	- 89 644	+ 1 277	16 738
LZP-6	126 336	- 105 435	+ 1 535	22 436
LZP-7	126 841	- 103 530	+ 1 844	24 852

$I^{o}_{NiK\alpha}$ average = 279 013 cps
std. devn. = ± 3 382 cps

$$I^{o}_{NiK\alpha} = (2.79^{0} \pm 0.03^{4}) \times 10^{5} \;{}^{*}$$
$$= (2.79 \pm 0.03) \times 10^{5}$$

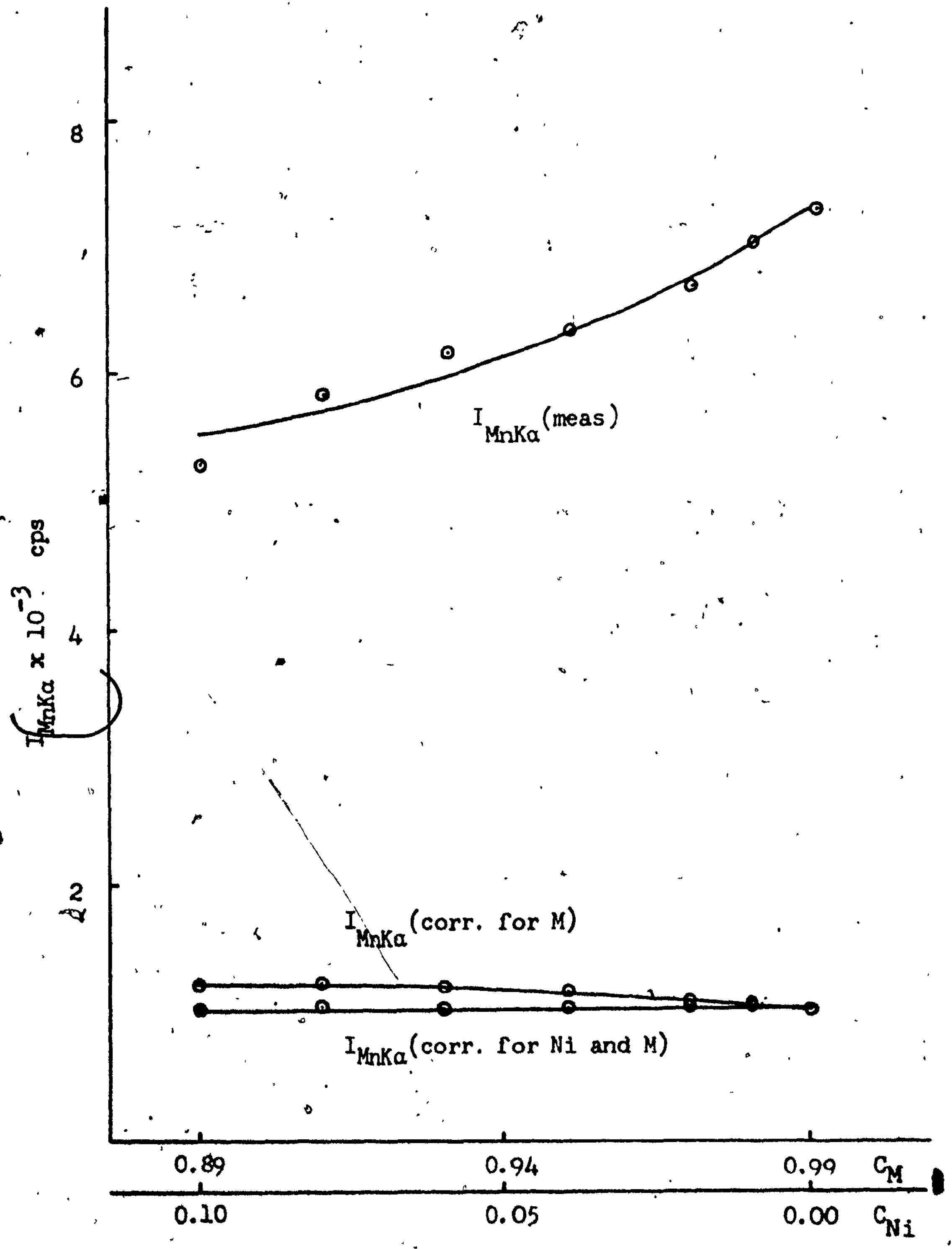
* Omit LZP-7

TABLE E Back-calculation of solution composition

Solution	C_{Mn}(calc)	Abs. error	Error%	C_{Ni}(calc)	Abs. error	Error %
LZP-1	0.01010	0.00010	1.00	--	--	--
LZP-2	0.01000	0.00000	0.00	0.00980	0.00020	2.00
LZP-3	0.00984	0.00016	2.00	0.01990	0.00010	0.50
LZP-4	0.01060	0.00060	6.00	0.0413	0.0013	3.25
LZP-5	0.01020	0.00020	2.00	0.0603	0.0003	0.50
LZP-6	0.01020	0.00020	2.00	0.0811	0.0011	1.37
LZP-7	0.00916	0.00084	8.40	0.0799	0.0201	20.1 *

* Doubtful value in series

FIGURE D $I_{MnK\alpha}$ versus C_{Ni} and C_M



5.7.4 Effect of Ni on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Ni}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MAV-1	0.01000	0.00	0.01611	0.97389	25 265	0.14	--	--	4 631	0.33
MAV-2	0.01000	0.01000	0.01611	0.96389	24 787	0.14	28 513	0.13	4 502	0.33
MAV-3	0.01000	0.02000	0.01611	0.95389	24 079	0.14	53 049	0.10	4 439	0.33
MAV-4	0.01000	0.0400	0.01611	0.9339	23 720	0.15	91 954	0.07	4 281	0.34
MAV-5	0.01000	0.0600	0.01611	0.9139	22 052	0.15	123 615	0.07	4 083	0.35
MAV-6	0.01000	0.0800	0.01611	0.8939	21 385	0.16	152 977	0.07	3 870	0.36
MAV-7	0.01000	0.1000	0.01611	0.8739	21 515	0.16	380 193	0.06	3 657	0.37

* 50 kV, 20 mA

TABLE B Calculation of α_{FeNi}

Solutions	α_{FeNi}
MAV-1/MAV-7	- 0.6745···
MAV-1/MAV-6	- 0.6076···
MAV-1/MAV-5	- 0.5872···
MAV-2/MAV-7	- 0.6776···
MAV-2/MAV-6	- 0.6003···
MAV-2/MAV-5	- 0.5725···
MAV-3/MAV-7	- 0.7010···
MAV-3/MAV-6	- 0.6173···
MAV-4/MAV-7	- 0.6630···

α_{FeNi} average = - 0.6334···

std. devn. = ± 0.0448···

α_{FeNi} = $- 0.63^3 \pm 0.04^5$

= - 0.63 ± 0.04

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of nickel	$I_{FeK\alpha}$(corr) (cps)
MAV-1	25 265	- 22 064	+ 19	--	3 220
MAV-2	24 787	- 21 424	+ 19	- 157	3 225
MAV-3	24 079	- 20 506	+ 18	- 305	3 196
MAV-4	23 720	- 19 864	+ 18	- 600	3 274
MAV-5	22 052	- 18 071	+ 17	- 837	3 161
MAV-6	21 385	- 17 141	+ 16	- 1 083	3 177
MAV-7	21 515	- 16 859	+ 16	- 1 362	3 310

$I^{o}_{FeK\alpha}$ average = 322 328 cps

std. devn. = ± 5 313 cps

$$I^{o}_{FeK\alpha} = (3.22^{3} \pm 0.05^{3}) \times 10^{5}$$

$$= (3.22 \pm 0.05) \times 10^{5}$$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of iron	$I_{NiK\alpha}$(corr) (cps)
MAV-2	28 513	- 25 205	- 74	+ 378	3 612
MAV-3	53 094	- 46 408	- 138	+ 703	7 206
MAV-4	91 954	- 78 756	- 240	+ 1 218	14 176
MAV-5	123 615	- 103 305	- 323	+ 1 638	21 325
MAV-6	1152 977	- 125 408	- 399	+ 2 027	29 197
MAV-7	171 491	- 137 440	- 447	+ 2 272	35 876

$I^{o}_{NiK\alpha}$ average = 359 173 cps

std. devn. = + 3 883 cps

$$I^{o}_{NiK\alpha} = (3.59^{2} \pm 0.03^{9}) \times 10^{5}$$

$$= (3.59 \pm 0.04) \times 10^{5}$$

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	Correction for effect of iron	$I_{ClK\alpha}$(corr) (cps)
MAV-1	4 631	- 1 515	--	+ 52	3 168
MAV-2	4 502	- 1 458	+ 57	+ 51	3 152
MAV-3	4 439	- 1 423	+ 112	+ 50	3 178
MAV-4	4 281	- 1 343	+ 216	+ 48	3 202
MAV-5	4 083	- 1 254	+ 309	+ 46	3 184
MAV-6	3 870	- 1 162	+ 390	+ 44	3 142
MAV-7	3 657	- 1 074	+ 461	+ 41	3 085

$$I^{o}_{ClK\alpha} \text{ average} = 196\ 072 \text{ cps}$$

$$\text{std. devn.} = \pm\ 2\ 359 \text{ cps}$$

$$I^{o}_{ClK\alpha} = (1.96^{1} \pm 0.02^{3}) \text{ x } 10^{5}$$

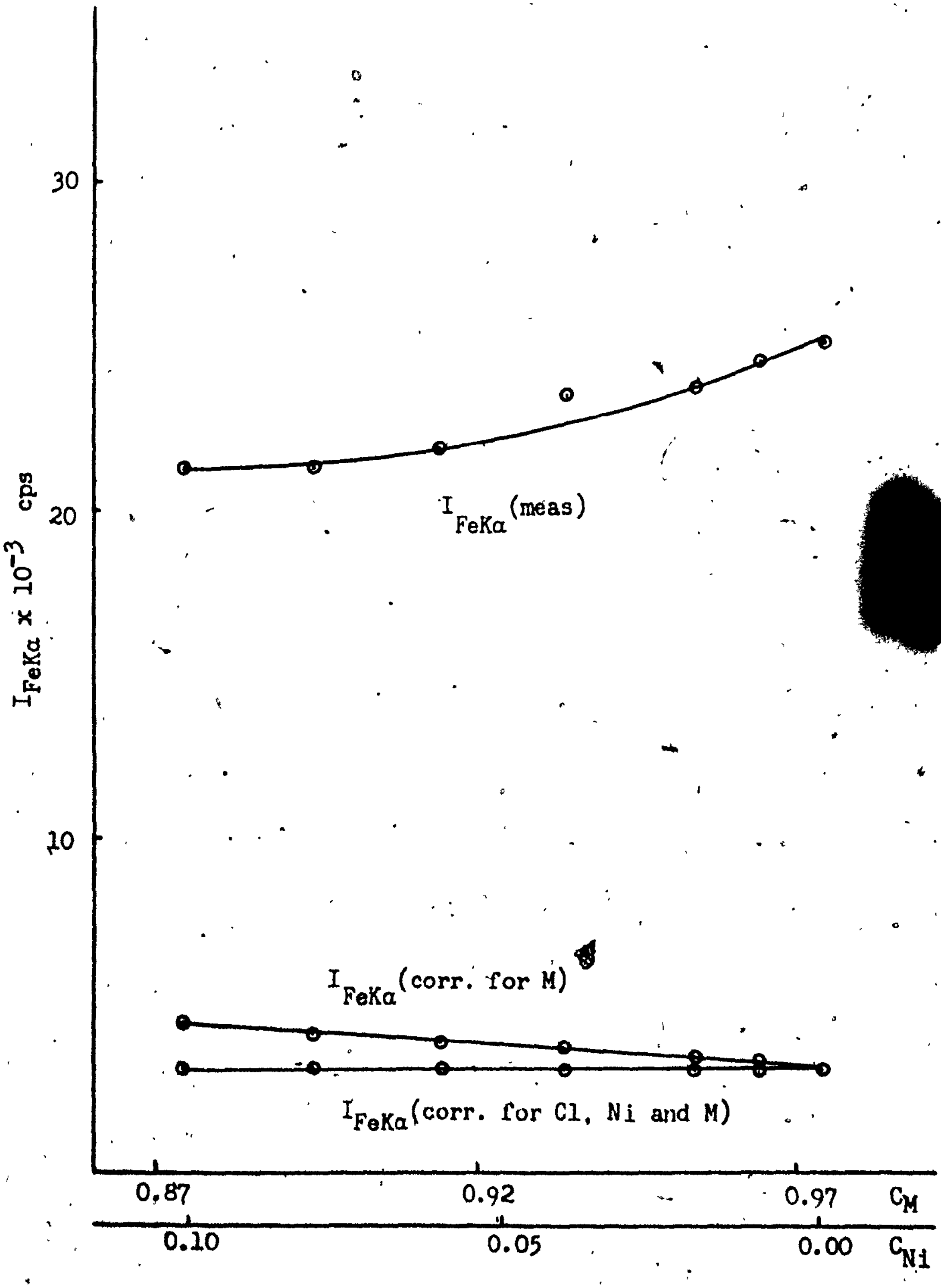
$$\doteq (1.96 \pm 0.02) \text{ x } 10^{5}$$

TABLE F <u>Back-calculation of solution composition</u>

Solution	C_{Fe}(calc)	Abs. error	Error %	C_{Ni}(calc)	Abs. error	Error %
MAV-1	0.01000	0.00000	0.00	—	—	—
MAV-2	0.01000	0.00000	0.00	0.01010	0.00010	1.00
MAV-3	0.00990	0.00010	1.00	0.02000	0.00000	0.00
MAV-4	0.01020	0.00020	2.00	0.0395	0.0005	1.67
MAV-5	0.00980	0.00020	2.00	0.0589	0.0011	1.83
MAV-6	0.00990	0.00010	1.00	0.0819	0.0019	2.37
MAV-7	0.01030	0.00030	3.00	0.1000	0.0000	0.00

C_{Cl}(calc)	Abs. error	Error %
0.01616	0.00005	0.31
0.01608	0.00003	0.19
0.01621	0.00010	0.62
0.01632	0.00021	1.30
0.01620	0.00009	0.56
0.01608	0.00003	0.19
0.01574	0.00037	2.31

FIGURE D $I_{FeK\alpha}$ versus C_{Ni} and C_M



5.7.5 Effect of Ni on Co

TABLE A Experimental Parameters

Solution	C_{Co}	C_{Ni}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}^{*}$ (cps)	s(%)
MAC-2	0.01000	0.01000	0.98000	38 199	0.11	62 806	0.09
MAC-3	0.01000	0.02000	0.97000	35 848	0.12	119 540	0.07
MAC-4	0.01000	0.0400	0.9500	31 291	0.13	199 888	0.06
MAC-5	0.01000	0.0600	0.9300	29 201	0.14	255 900	0.05
MAC-6	0.01000	0.0800	0.9100	27 128	0.14	305 424	0.05
MAC-7	0.01000	0.1000	0.8900	24 725	0.14	335 660	0.05

* 50 kV, 30 mA

TABLE B Calculation of α_{CoNi}

Solutions	α_{CoNi}
MAC-2/MAC-7	- 0.3620...
MAC-2/MAC-6	- 0.3842...
MAC-2/MAC-5	- 0.3514...
MAC-3/MAC-7	- 0.3716...
MAC-3/MAC-6	- 0.4000...

α_{CoNi} average = - 0.3738...

std. devn. = ± 0.0189...

$$\alpha_{CoNi} = -0.37^{4} \pm 0.01^{9}$$

$$= -0.37 \pm 0.02$$

TABLE C Calculation of $I_{CoK\alpha}$ (corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of		$I_{CoK\alpha}$(corr) (cps)
		matrix	nickel	
MAC-2	38 199	- 34 526	- 143	3 530
MAC-3	35 848	- 32 071	- 268	3 509
MAC-4	31 291	- 27 417	- 468	3 406
MAC-5	29 201	- 25 047	- 655	3 499
MAC-6	27 128	- 22 768	- 812	3 548
MAC-7	24 725	- 20 295	- 925	3 505

$I^{o}_{CoK\alpha}$ average = 349 950 cps

std. devn. = ± 4 920 cps

$I^{o}_{CoK\alpha} = (3.49^{9} + 0.04^{9}) \times 10^{5}$

$= (3.50 \pm 0.05) \times 10^{5}$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cobalt	$I_{NiK\alpha}$(corr) (cps)
MAC-2	62 806	- 56 447	- 110	6 249
MAC-3	119 540	- 106 341	- 209	12 990
MAC-4	199 888	- 174 151	- 350	25 387
MAC-5	255 900	- 218 258	- 448	37 194
MAC-6	305 424	- 254 895	- 534	49 995
MAC-7	335 600	- 273 923	- 587	61 090

$I^{o}_{NiK\alpha}$ average = 627 468 cps

std. devn. = ± 13 276 cps

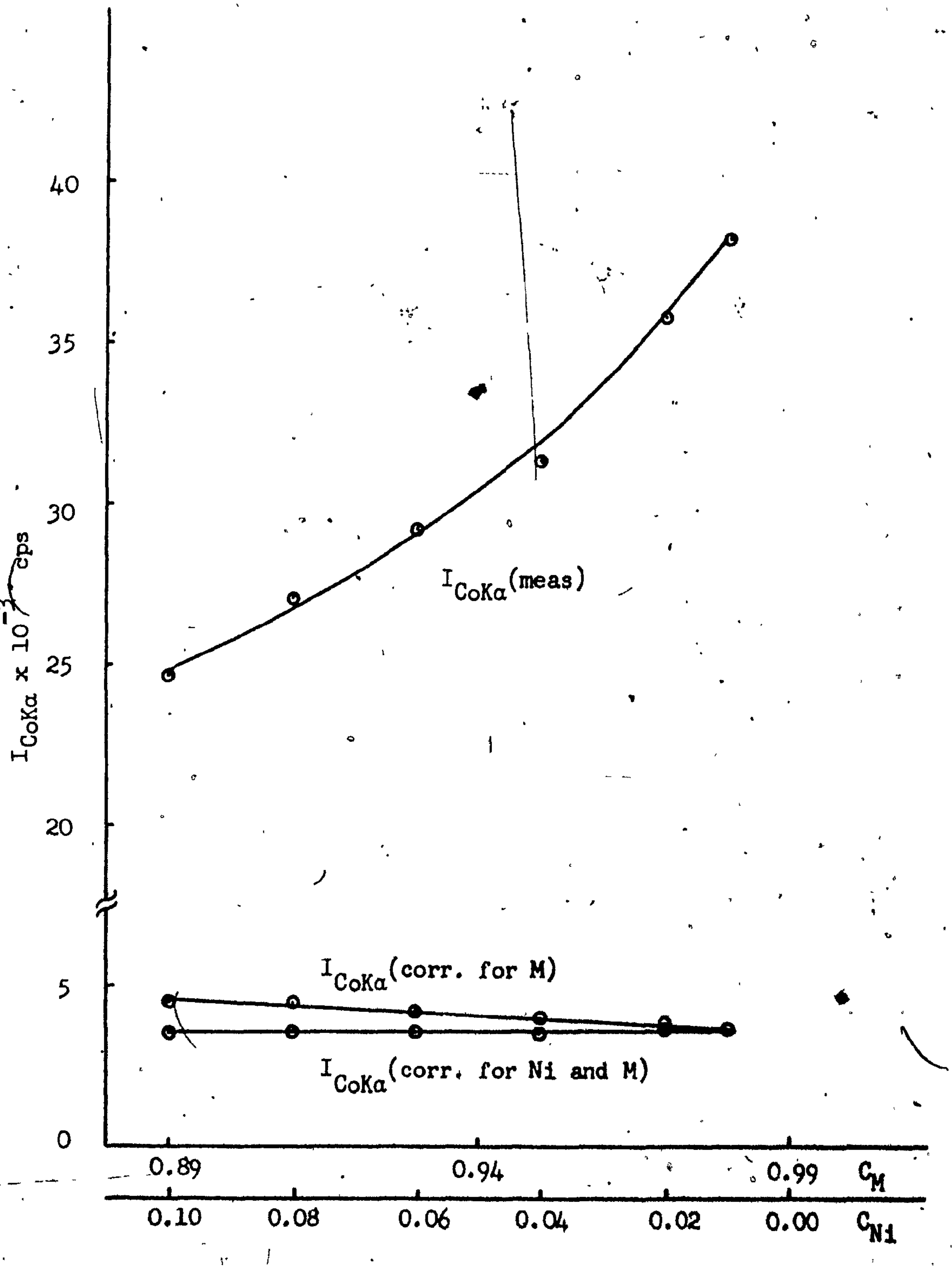
$I^{o}_{NiK\alpha} = (6.2^{7} \pm 0.1^{3}) \times 10^{5}$

$= (6.3 \pm 0.1) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Ni}(calc)	Abs. error	Error %
MAC-2	0.01010	0.00010	1.00	0.01000	0.00000	0.00
MAC-3	0.01010	0.00010	1.00	0.02000	0.00090	4.50
MAC-4	0.00970	0.00030	3.00	0.0406	0.0006	1.50
MAC-5	0.00990	0.00010	1.00	0.0588	0.0012	2.00
MAC-6	0.01010	0.00010	1.00	0.0795	0.0005	0.65
MAC-7	0.00980	0.00020	2.00	0.0947	0.0053	5.30

FIGURE D $I_{CoK\alpha}$ versus C_{Ni} and C_M



5.7.6 Effect of Ni on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Ni}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}$* (cps)	s(%)
MAP-1	0.02000	0.00	0.98000	116 452	0.07	--	--
MAP-2	0.02000	0.01000	0.97000	104 889	0.07	40 361	0.11
MAP-3	0.02000	0.02000	0.96000	97 334	0.07	75 368	0.08
MAP-4	0.02000	0.0400	0.9400	85 331	0.08	128 394	0.07
MAP-5	0.02000	0.0600	0.9200	74 215	0.08	168 690	0.06
MAP-6	0.02000	0.0800	0.9000	65 400	0.09	209 326	0.05
MAP-7	0.02000	0.1000	0.8800	61 316	0.10	230 936	0.03

* 50 kV, 20 mA

TABLE B Calculation of α_{CuNi}

Solutions	α_{CuNi}
MAP-1/MAP-7	- 0.0931···
MAP-1/MAP-6	- 0.0222···
MAP-1/MAP-5	- 0.0474···
MAP-2/MAP-7	- 0.1319···
MAP-2/MAP-6	- 0.0516···
MAP-2/MAP-5	- 0.0913···
MAP-3/MAP-7	- 0.1288···
MAP-3/MAP-6	- 0.0256···

α_{CuNi} average = - 0.0740 ...

std. devn. = ± 0.0435 ...

$$\alpha_{CuNi} = -0.07^{4} \pm 0.04^{3}$$

$$= -0.07 \pm 0.04$$

TABLE C Calculation of $I_{CuK\alpha}$ (corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{CuK\alpha}$(corr) (cps)
MAP-1	116 452	- 105 666	--	10 786
MAP-2	104 889	- 94 203	- 78	10 763
MAP-3	97 334	- 86 517	- 144	10 673
MAP-4	85 331	- 74 263	- 252	10 811
MAP-5	74 215	- 63 218	- 329	10 667
MAP-6	65 400	- 54 498	- 387	10 514
MAP-7	61 316	- 49 960	- 454	10 902

$I^{o}_{CuK\alpha}$ average = 536 543 cps

std. devn. = ± 6 264 cps

$I^{o}_{CuK\alpha} = (5.36^{5} \pm 0.06^{3}) \times 10^{5}$

$= (5.36 \pm 0.06) \times 10^{5}$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of		$I_{NiK\alpha}$(corr) (cps)
		matrix	copper	
MAP-2	40 361	- 35 905	- 282	4 174
MAP-3	75 368	- 66 355	- 527	8 486
MAP-4	128 394	- 110 685	- 899	16 810
MAP-5	168 890	- 142 329	- 1 181	25 180
MAP-6	209 326	- 172 776	- 1 465	35 085
MAP-7	230 936	- 186 376	- 1 616	42 944

$I^{o}_{NiK\alpha}$ average = 424 936 cps.

std. devn. = ± 7 921 cps

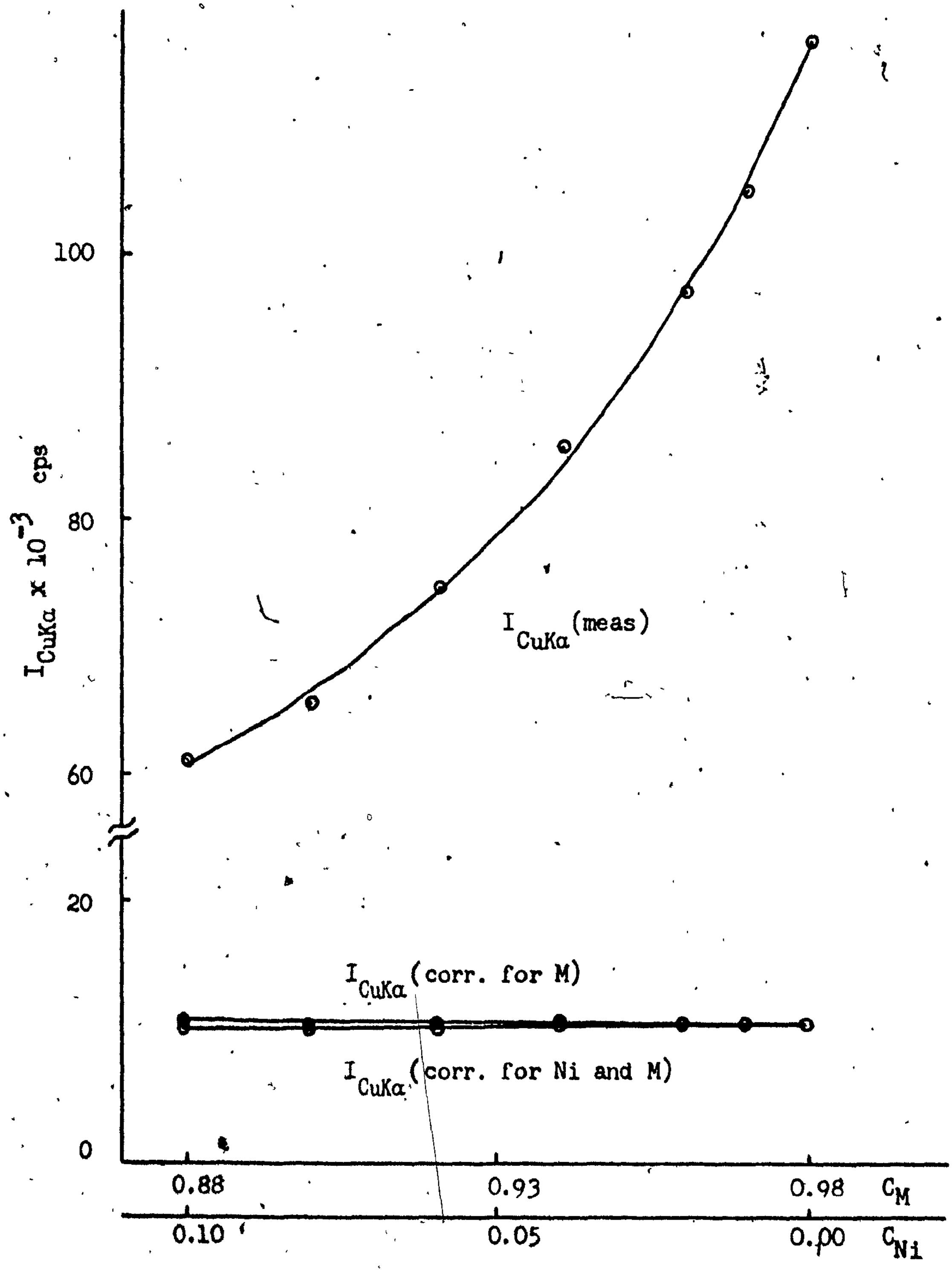
$I^{o}_{NiK\alpha} = (4.24^{9} \pm 0.07^{9}) \times 10^{5}$

$= (4.25 \pm 0.08) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Ni}(calc)	Abs. error	Error %
MAP-1	0.02010	0.00010	0.50	—	—	—
MAP-2	0.01970	0.00030	1.50	0.00979	0.00021	2.10
MAP-3	0.01990	0.00010	0.50	0.01990	0.00010	0.50
MAP-4	0.02010	0.00010	0.50	0.0394	0.0006	1.50
MAP-5	0.01970	0.00030	1.50	0.0587	0.0013	2.16
MAP-6	0.02010	0.00010	0.50	0.0847	0.0047	6.00
MAP-7	0.02060	0.00060	3.00	0.1025	0.0025	2.50

FIGURE D $\overset{o}{I}_{CuK\alpha}$ versus C_{Ni} and C_M



5.7.7 Effect of Ni on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Ni}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{NiK\alpha}$* (cps)	s(%)
MAI-1	0.02000	0.00	0.98000	144 277	0.07	—	—
MAI-2	0.02000	0.01000	0.97000	103 600	0.07	39 894	0.11
MAI-3	0.02000	0.02000	0.96000	88 229	0.08	74 324	0.09
MAI-4	0.02000	0.0400	0.9400	64 451	0.10	120 359	0.07
MAI-5	0.02000	0.0600	0.9200	55 569	0.10	155 144	0.07
MAI-6	0.02000	0.0800	0.9000	44 452	0.10	180 300	0.06
MAI-7	0.02000	0.1000	0.8800	36 239	0.10	211 944	0.05

* 50 kV, 20 mA

TABLE B Calculation of α_{ZnNi}

Solutions	α_{ZnNi}
MAI-1/MAI-7	1.3216···
MAI-1/MAI-6	1.1893···
MAI-1/MAI-5	1.0780...
MAI-2/MAI-7	1.0342...
MAI-3/MAI-7	1.1810...

α_{ZnNi} average = 1.1608···

std. devn. = ± 0.112···

$\alpha_{ZnNi} = 1.1^6 \pm 0.1^1$

$= 1.2 \pm 0.1$

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^o_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{ZnK\alpha}$(corr) (cps)
MAI-1	144 277	- 133 318	--	10 954
MAI-2	103 600	- 94 754	+ 1 202	10 048
MAI-3	88 229	- 79 863	+ 2 047	10 413
MAI-4	64 451	- 57 125	+ 2 990	10 316
MAI-5	55 569	- 48 204	+ 3 867	11 232
MAI-6	44 452	- 37 722	+ 4 125	10 855
MAI-7	36 239	- 30 069	+ 4 204	10 374

$I^{o}_{ZnK\alpha}$ average = 529 979 cps
std. devn. = ± 21 000 cps

$$I^{o}_{ZnK\alpha} = (5.3^{0} \pm 0.2^{1}) \times 10^{5}$$
$$= (5.3 \pm 0.2) \times 10^{5}$$

TABLE D Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{NiK\alpha}$(corr) (cps)
MAI-2	39 894	- 35 489	- 417	3 988
MAI-3	74 324	- 65 436	- 777	8 111
MAI-4	120 359	- 103 758	- 1 259	15 342
MAI-5	155 144	- 130 900	- 1 623	22 621
MAI-6	180 300	- 148 818	- 1 886	29 596
MAI-7	211 944	- 171 049	- 2 217	38 678

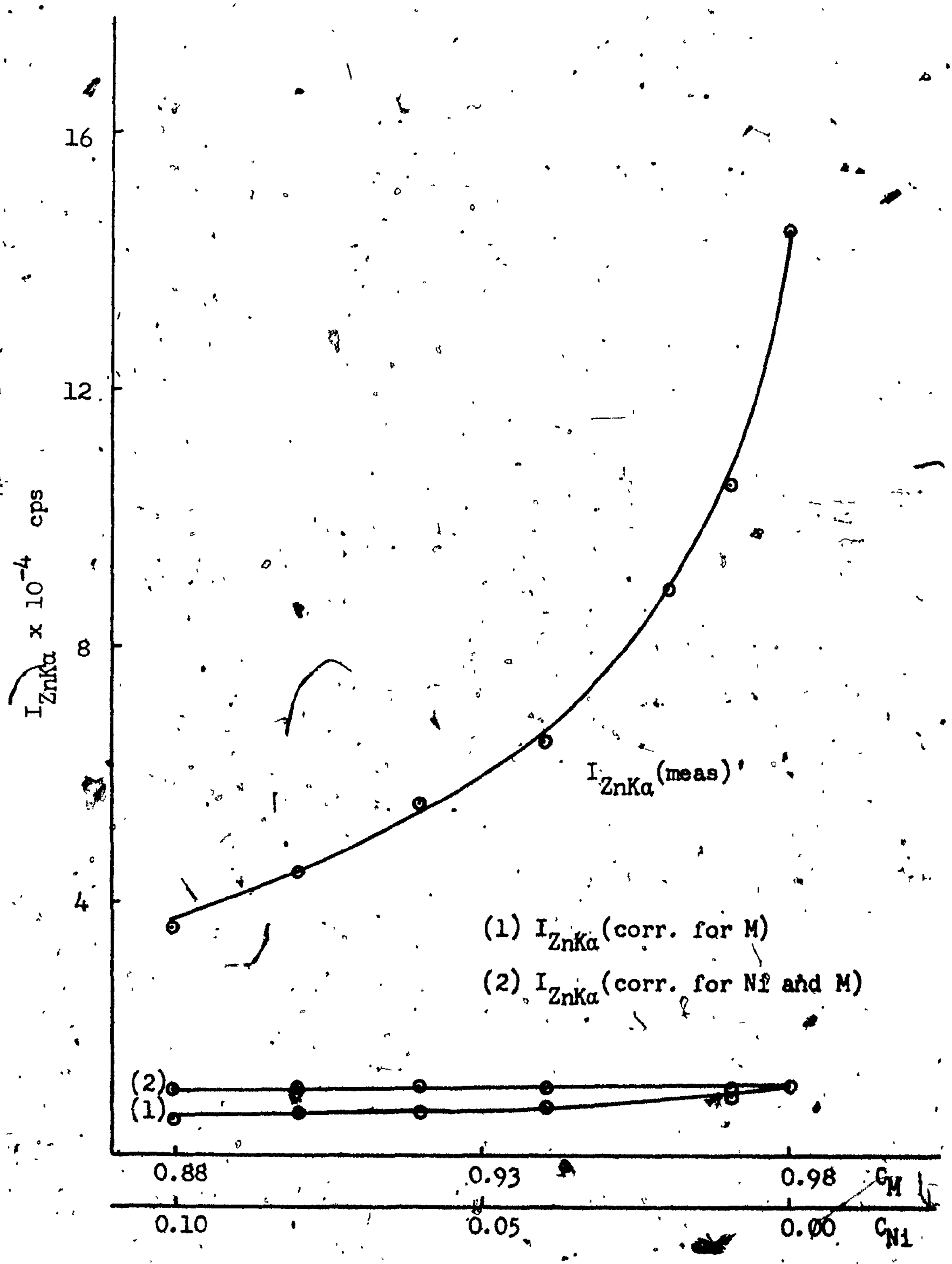
$I^{o}_{NiK\alpha}$ average = 386 941 cps
std. devn. = ± 13 293 cps

$$I^{o}_{NiK\alpha} = (3.8^{7} \pm 0.1^{3}) \times 10^{5}$$
$$= (3.9 \pm 0.1) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Ni}(calc)	Abs. error	Error %
MAI-1	0.02090	0.00090	4.50	—	—	—
MAI-2	0.01890	0.00110	5.50	0.01030	0.00030	3.00
MAI-3	0.02010	0.00010	0.50	0.02120	0.00120	6.00
MAI-4	0.01920	0.00080	4.00	0.0394	0.0006	1.50
MAI-5	0.02080	0.00080	4.00	0.0578	0.0022	3.70
MAI-6	0.01930	0.00070	3.50	0.0736	0.0064	8.00
MAI-7	0.01950	0.00050	2.50	0.0997	0.0003	0.30

FIGURE D $I_{ZnK\alpha}$ versus C_{Ni} and C_M



5.8 Effects of Copper

Solutions: The metal concentration for each series were obtained by dilution of the following stock solutions:-

Chromium	1 ml = 0.2000	± 0.0001 g	(dil. HNO_3)
Manganese	1 ml = 0.10000	± 0.00002 g	(dil. HNO_3)
Iron	1 ml = 0.10000	± 0.00002 g	(dil. HCl-HNO_3)
Cobalt	1 ml = 0.10000	± 0.00005 g	(dil. HNO_3)
Nickel	1 ml = 0.2000	± 0.0001 g	(dil. HNO_3)
Copper	1 ml = 0.20000	± 0.00005 g	(dil. HNO_3)
Zinc	1 ml = 0.20000	± 0.00008 g	(dil. HNO_3)
Tin	1 ml = 0.20000	± 0.00005 g	(dil. HCl-HNO_3)
Lead	1 ml = 0.20000	± 0.00005 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCl, or present from a stock solution , was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBO	1:72 Cl	1:36 to 1:360
Cr	MAR	1:440	1:220 to 1:2200
Mn	LZQ	1:400	1:200 to 1:2000
Fe	MAX	1:400	1:200 to 1:2000
Co	MAD	1:400	1:200 to 1:2000
Ni	MAG	1:400	1:200 to 1:2000
Zn	LO	1:450	1:225 to 1:2250
Sn	LS	1:180 Cl	1:90 to 1:900
Pb	LQ	1:800	1:400 to 1:4000

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sn	Pb
Target	Cr	W	W	W	W	W	W	W	W	W
kV	50	50	50	50	50	50	*	40	50	50
mA	36	40	20	40	30	30	*	20	20	20
Coll^{n}	coarse	fine	fine	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20	20	20
Counts	3	3	3	3	3	5	3-5	3	5	5
Rad^{n}	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Lα

* See each series

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as sigma counting error in percent.

Equations:-

Calculation of α_{ACu} (absence of chlorine as fourth component) Equation (43)

Calculation of α_{ACu} (presence of chlorine as fourth component) Equation (44)

Calculation of $I_A(corr)$ Equation (45) or a modification

Calculation of I_A^o $I_A(corr)/C_A$

5.8.1 Effect of Cu on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Cu}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}^{*}$ (cps)	s(%)
MBO-1	0.02145	0.00	0.97855	6 349	0.29	--	--
MBO-2	0.02145	0.01000	0.96855	6 266	0.29	36 921	0.12
MBO-3	0.02145	0.02000	0.95855	6 140	0.30	65 910	0.08
MBO-4	0.02145	0.0300	0.9486	5 934	0.30	93 913	0.07
MBO-5	0.02145	0.0600	0.9186	5 544	0.31	154 846	0.07
MBO-6	0.02145	0.0800	0.8986	5 323	0.32	181 804	0.06
MBO-7	0.02145	0.1000	0.8786	5 064	0.32	206 181	0.05

* 50 kV, 20 mA

TABLE B Calculation of α_{ClCu}

Solutions	α_{ClCu}
MBO-1/MBO-7	1.3672···
MBO-1/MBO-6	1.2812···
MBO-1/MBO-5	1.2883···
MBO-2/MBO-7	1.4822···
MBO-2/MBO-6	1.4068···
MBO-2/MBO-5	1.4596···
MBO-3/MBO-6	1.4736···
MBO-4/MBO-7	1.4423···

α_{ClCu} average = 1.4000···
std. devn. = ± 0.0793···

$$\alpha_{ClCu} = 1.40^{0} \pm 0.07^{9}$$
$$= 1.40 \pm 0.08$$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{ClK\alpha}$(corr) (cps)
MBO-1	6 349	- 2 087	--	4 261
MBO-2	6 266	- 2 039	+ 88	4 315
MBO-3	6 140	- 1 977	+ 172	4 334
MBO-4	5 934	- 1 891	+ 249	4 292
MBO-5	5 544	- 1 711	+ 466	4 299
MBO-6	5 323	- 1 607	+ 596	4 312
MBO-7	5 064	- 1 494	+ 709	4 278

$I^{o}_{ClK\alpha}$ average = 200 408 cps
std. devn. = ± 1 135 cps

$I^{o}_{ClK\alpha} = (2.00^{4} \pm 0.01^{1}) \times 10^{5}$
$= (2.00 \pm 0.01) \times 10^{5}$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	$I_{CuK\alpha}$(corr) (cps)
	36 921	- 33 110	- 198	3 613
MBO-3	65 910	- 58 496	- 353	7 060
MBO-4	93 913	- 82 480	- 504	10 926
MBO-5	154 846	- 131 694	- 830	22 321
MBO-6	181 804	- 151 255	- 975	29 574
MBO-7	206 181	- 167 718	- 1 106	37 357

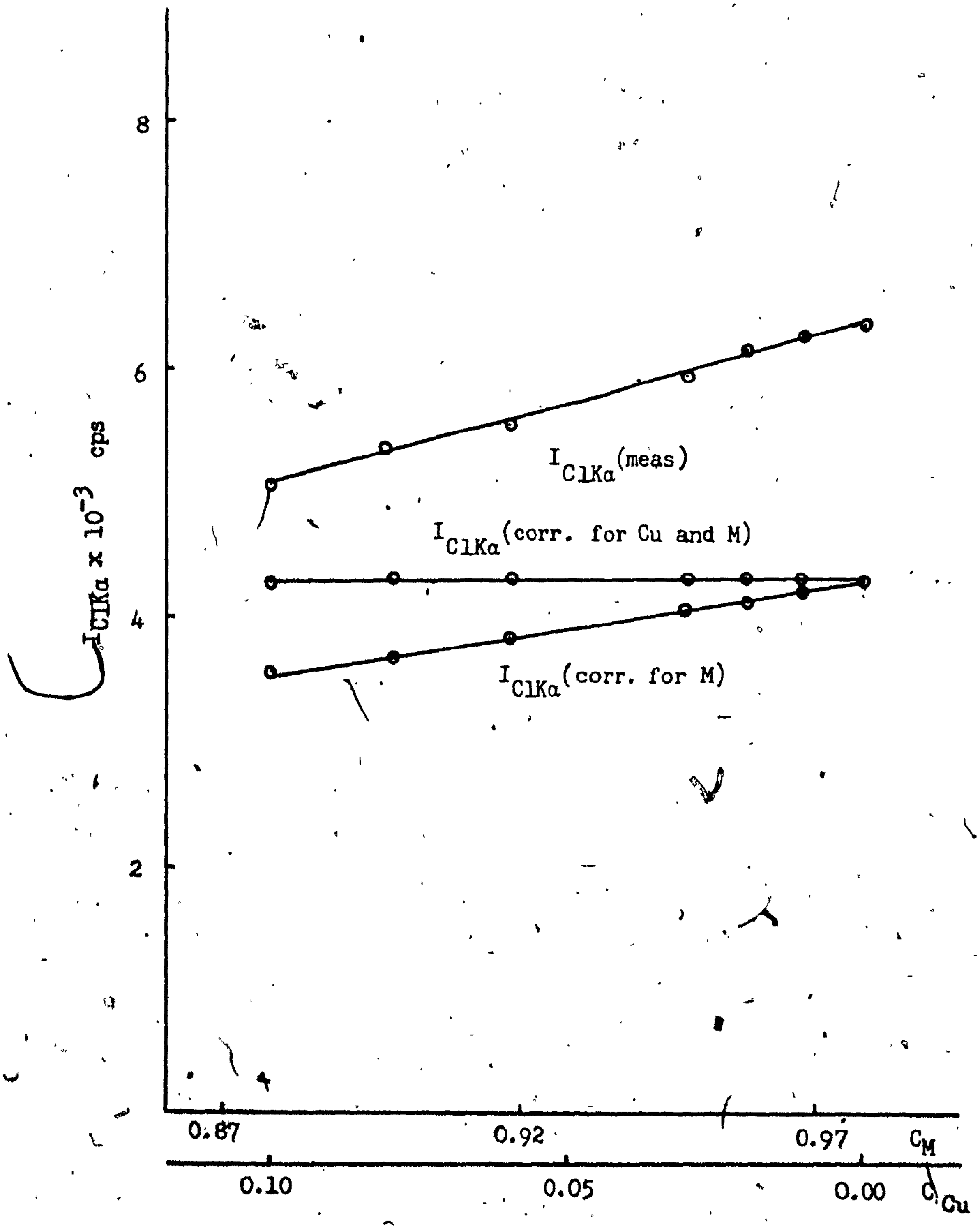
$I^{o}_{CuK\alpha}$ average = 365 646 cps
std. devn. = ± 7 751 cps

$I^{o}_{CuK\alpha} = (3.65^{6} \pm 0.07^{7}) \times 10^{5}$
$= (3.66 \pm 0.08) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
MBO-1	0.0213	0.0002	0.93	—	—	—
MBO-2	0.0216	0.0001	0.46	0.0099	0.0001	1.00
MBO-3	0.0216	0.0001	0.46	0.0192	0.0008	4.00
MBO-4	0.0214	0.0001	0.46	0.0298	0.0002	0.67
MBO-5	0.0215	0.0000	0.00	0.061^{8}	0.001^{8}	3.00
MBO-6	0.0216	0.0001	0.46	0.081^{7}	0.001^{7}	2.12
MBO-7	0.0215	0.0000	0.00	0.105	0.005	5.00

FIGURE D $I_{ClK\alpha}$ versus C_{Cu} and C_M



5.8.2 Effect of Cu on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Cu}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
MAR-1	0.02000	0.00	0.98000	9 297	0.23	—	—
MAR-2	0.02000	0.01000	0.97000	9 130	0.23	22 619	0.15
MAR-3	0.02000	0.02000	0.96000	8 952	0.23	41 417	0.11
MAR-4	0.02000	0.0400	0.9400	8 603	0.24	72 053	0.09
MAR-5	0.02000	0.0600	0.9200	8 338	0.25	94 823	0.07
MAR-6	0.02000	0.0800	0.9000	8 228	0.25	112 506	0.07
MAR-7	0.02000	0.1000	0.8800	7 523	0.26	137 184	0.07

* 50 kV, 20 mA

TABLE B Calculation of α_{CrCu}

Solutions	α_{CrCu}
MAR-1/MAR-7	- 0.4466···
MAR-1/MAR-6	- 0.5713···
MAR-1/MAR-5	- 0.5215···
MAR-2/MAR-7	- 0.4342···
MAR-2/MAR-6	- 0.5769···
MAR-2/MAR-5	- 0.5182···
MAR-3/MAR-7	- 0.4237···
MAR-3/MAR-6	- 0.5905···

α_{CrCu} average = $-0.5104\ldots$

std. devn. = $\pm 0.0677\ldots$

$\alpha_{CrCu} = -0.51^{0} \pm 0.06^{8}$

$= -0.51 \pm 0.07$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{CrK\alpha}$(corr) (cps)
MAR-1	9 297	- 7 718	—	1 579
MAR-2	9 130	- 7 502	- 47	1 581
MAR-3	8 952	- 7 280	- 91	1 581
MAR-4	8 603	- 6 850	- 175	1 577
MAR-5	8 338	- 6 498	- 255	1 585
MAR-6	8 228	- 6 273	- 356	1 619
MAR-7	7 523	- 5 608	- 384	1 531

$$I^{o}_{CrK\alpha} \text{ average} = 78\,956 \text{ cps}$$
$$\text{std. devn.} = \pm 1\,283 \text{ cps}$$
$$I^{o}_{CrK\alpha} = (7.9^{0} \pm 0.1^{3}) \times 10^{4}$$
$$= (7.9 \pm 0.1) \times 10^{4}$$

TABLE D Calculation of $I_{CuK\alpha}(\text{corr})$ and $I^{o}_{CuK\alpha}$

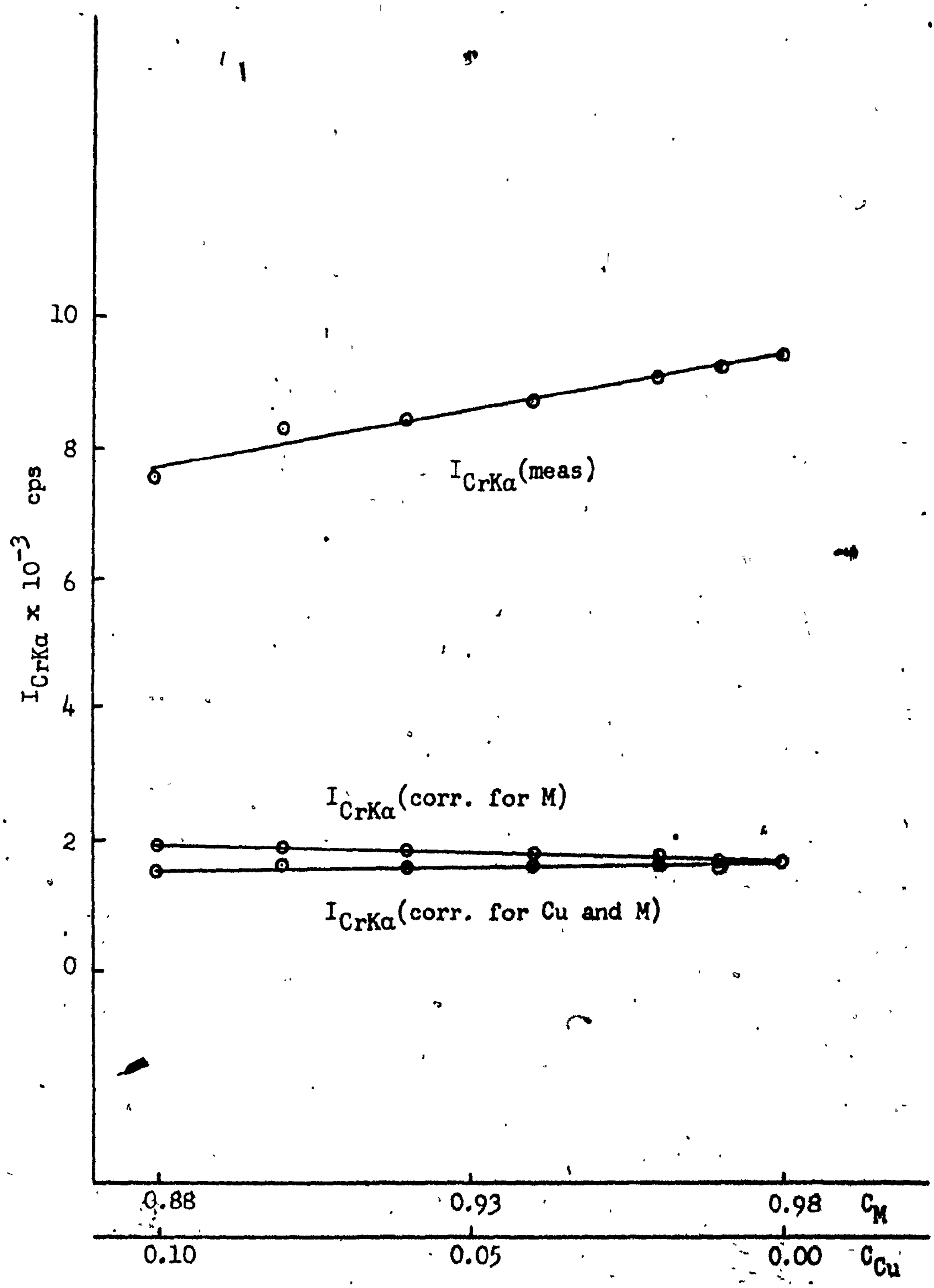
Solution	Measured	Correction for effect of		$I_{CuK\alpha}(\text{corr})$ (cps)
		matrix	chromium	
MAR-2	22 619	- 20 315	+ 404	2 709
MAR-3	41 117	- 36 547	+ 735	5 304
MAR-4	72 053	- 62 711	+ 1 288	10 630
MAR-5	94 823	- 80 773	+ 1 695	15 745
MAR-6	112 506	- 93 752	+ 2 012	20 765
MAR-7	137 184	- 111 776	+ 2 453	27 860

$$I^{o}_{CuK\alpha} \text{ average} = 267\,078 \text{ cps}$$
$$\text{std. devn.} = \pm 6\,780 \text{ cps}$$
$$I^{o}_{CuK\alpha} = (2.67^{1} \pm 0.06^{8}) \times 10^{5}$$
$$= (2.67 \pm 0.07) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	$C_{Cr}(\text{calc})$	Abs. error	Error %	$C_{Cu}(\text{calc})$	Abs. error	Error %
MAR-1	0.02000	0.00000	0.00	—	—	—
MAR-2	0.02000	0.00000	0.00	0.01020	0.00020	2.00
MAR-3	0.02000	0.00000	0.00	0.01980	0.00020	1.00
MAR-4	0.02000	0.00000	0.00	0.0397	0.0003	0.75
MAR-5	0.02000	0.00000	0.00	0.0585	0.0015	2.50
MAR-6	0.02040	0.00040	2.00	0.0769	0.0031	4.00
MAR-7	0.01960	0.00040	2.00	0.1075	0.0075	7.50

FIGURE D $I_{CrK\alpha}$ versus C_{Cu} and C_M



5.8.3 Effect of Cu on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Cu}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}^{*}$ (cps)	s(%)
LZQ-1	0.01000	0.00	0.99000	8 155	0.25	--	--
LZQ-2	0.01000	0.01000	0.98000	8 880	0.26	24 061	0.15
LZQ-3	0.01000	0.02000	0.97000	7 746	0.26	44 818	0.10
LZQ-4	0.01000	0.0400	0.9500	7 373	0.27	74 059	0.09
LZQ-5	0.01000	0.0600	0.9300	7 130	0.27	97 375	0.07
LZQ-6	0.01000	0.0800	0.9100	6 765	0.28	119 849	0.07
LZQ-7	0.01000	0.1000	0.8900	6 528	0.28	132 362	0.07

* 40 kV, 20 mA

TABLE B Calculation of α_{MnCu}

Solutions	α_{MnCu}
LZQ-1/LZQ-7	- 0.5025...
LZQ-1/LZQ-6	- 0.4914...
LZQ-1/LZQ-5	- 0.5164...
LZQ-2/LZQ-7	- 0.5223...
LZQ-2/LZQ-6	- 0.5142...
LZQ-3/LZQ-7	- 0.5091....

α_{MnCu} average = - 0.5093...

std. devn. = ± 0.011...

$$\alpha_{MnCu} = -0.50^{0} \pm 0.01^{1}$$

$$= -0.51 \pm 0.01$$

TABLE C Calculation of $I_{MnK\alpha}(corr)$ and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{MnK\alpha(corr)}$ (cps)
LZQ-1	8 155	- 6 973	--	1 182
LZQ-2	7 880	- 6 670	- 40	1 170
LZQ-3	7 746	- 6 489	- 79	1 177
LZQ-4	7 373	- 6 050	+ 150	1 173
LZQ-5	7 130	- 5 727	+ 218	1 185
LZQ-6	6 765	- 5 317	+ 275	1 172
LZQ-7	6 528	- 5 018	+ 332	1 177

$$I^{o}_{MnK\alpha} \text{ average} = 117\ 688 \text{ cps}$$

$$\text{std. devn.} = \pm\ 540 \text{ cps}$$

$$I^{o}_{MnK\alpha} = (1.176^{9} \pm 0.005^{4}) \times 10^{5}$$

$$= (1.177 \pm 0.005) \times 10^{5}$$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{CuK\alpha}$(corr) (cps)
LZQ-2	24 061	- 21 832	+ 250	2 489
LZQ-3	44 813	- 40 252	+ 466	5 032
LZQ-4	74 059	- 65 143	+ 770	9 686
LZQ-5	97 375	- 83 848	+ 1 013	14 539
LZQ-6	119 849	- 100 981	+ 1 246	20 114
LZQ-7	132 362	- 109 073	+ 1 376	24 665

$$I^{o}_{CuK\alpha} \text{ average} = 247\ 007 \text{ cps}$$

$$\text{std. devn.} = \pm\ 4\ 170 \text{ cps}$$

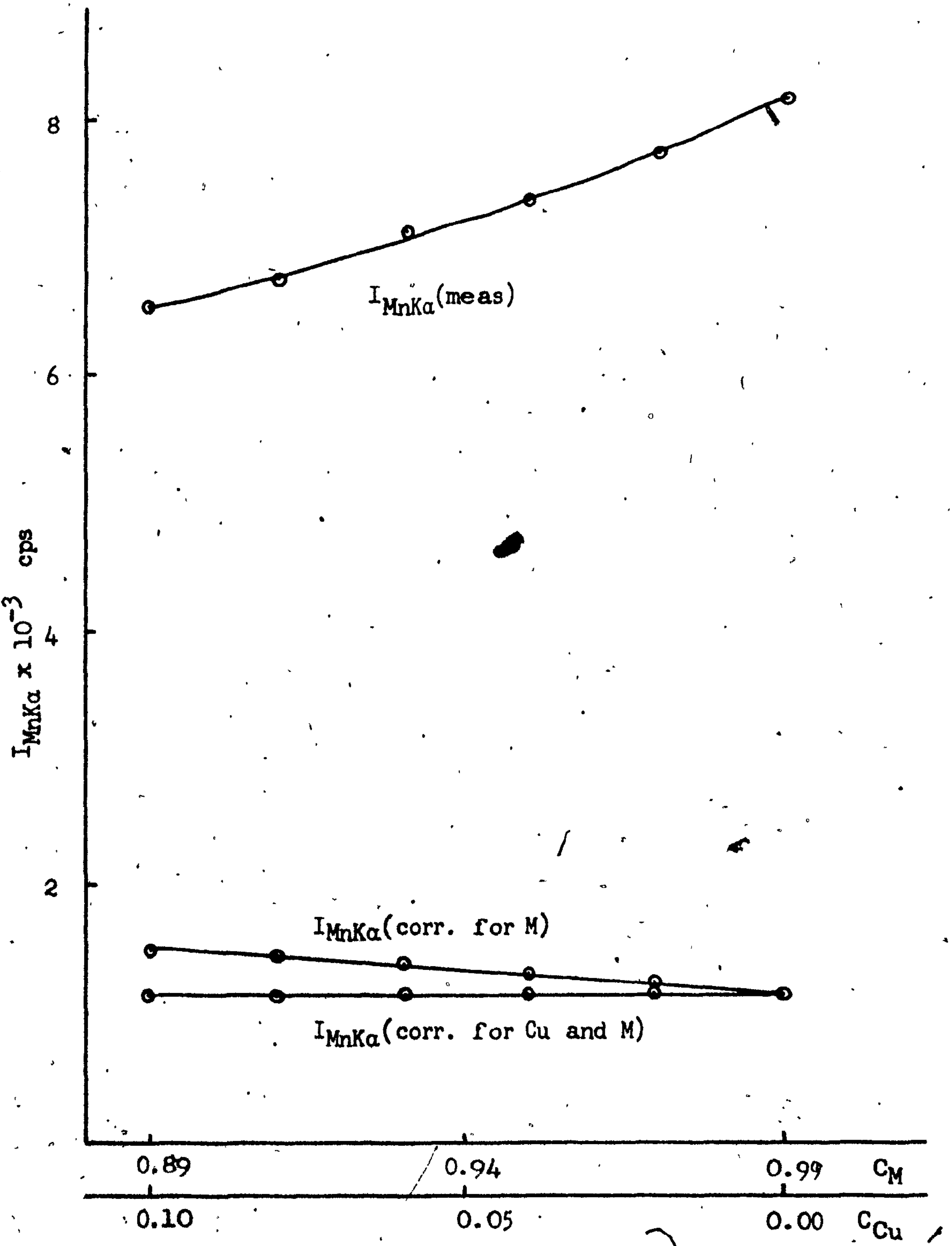
$$I^{o}_{CuK\alpha} = (2.47^{0} \pm 0.04^{2}) \times 10^{5}$$

$$= (2.47 \pm 0.04) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	C_{Mn}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
LZQ-1	0.01000	0.00000	0.00	—	—	—
LZQ-2	0.00990	0.00010	1.00	0.01000	0.00000	0.00
LZQ-3	0.01000	0.00000	0.00	0.02040	0.00040	2.00
LZQ-4	0.00990	0.00010	1.00	0.0389	0.0011	2.75
LZQ-5	0.01000	0.00000	0.00	0.0582	0.0018	3.00
LZQ-6	0.01000	0.00000	0.00	0.0826	0.0026	3.25
LZQ-7	0.01000	0.00000	0.00	0.0997	0.0003	0.30

FIGURE D $I_{MnK\alpha}$ versus C_{Cu} and C_M



5.8.4 Effect of Cu on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Cu}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
MAX-1	0.01000	0.00	0.01611	0.97389	20 952	0.16	--	--
MAX-2	0.01000	0.01000	0.01611	0.96389	21 021	0.16	23 719	0.15
MAX-3	0.01000	0.02000	0.01611	0.95389	20 973	0.16	42 878	0.11
MAX-4	0.01000	0.0400	0.01611	0.9339	20 454	0.16	76 065	0.10
MAX-5	0.01000	0.0600	0.01611	0.9139	18 598	0.17	99 741	0.07
MAX-6	0.01000	0.0800	0.01611	0.8939	18 [illegible]	0.17	120 614	0.07
MAX-7	0.01000	0.1000	0.01611	0.8739	17 667	0.17	137 391	0.07

* 50 kV, 20 mA

$I_{ClK\alpha}$ (cps)	s(%)
4 764	0.33
4 508	0.33
4 525	0.33
4 325	0.34
4 116	0.35
3 964	0.35
3 727	0.37

TABLE B Calculation of α_{FeCu}

Solutions	α_{FeCu}
MAX-1/MAX-7	- 0.6597···
MAX-1/MAX-6	- 0.6829···
MAX-1/MAX-5	- 0.6265···
MAX-2/MAX-7	- 0.6220···
MAX-2/MAX-6	- 0.6405···
MAX-2/MAX-5	- 0.5540···
MAX-3/MAX-7	- 0.5839···
MAX-3/MAX-6	- 0.5956···

α_{FeCu} average = - 0.6208...

std. devn. = ± 0.0418...

$$\alpha_{FeCu} = -0.62^1 \pm 0.04^2$$

$$= -0.62 \pm 0.04$$

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	 chlorine	 copper	$I_{FeK\alpha(corr)}$ (cps)
MAX-1	20 952	- 18 297	+ 16	--	2 671
MAX-2	21 021	- 18 169	+ 16	- 130	2 737
MAX-3	20 973	- 17 939	+ 16	- 260	2 789
MAX-4	20 454	- 17 128	+ 15	- 508	2 833
MAX-5	18 588	- 15 233	+ 14	- 692	2 676
MAX-6	18 437	- 14 407	+ 14	- 918	2 763
MAX-7	17 667	- 13 844	+ 13	- 1 097	2 739

$I^{o}_{FeK\alpha}$ average = 274 404 cps

std. devn. = + 5 800 cps

$I^{o}_{FeK\alpha} = (2.74^{4} \pm 0.05^{8}) \times 10^{5}$

$= (2.74 \pm 0.06) \times 10^{5}$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	 chlorine	 iron	$I_{CuK\alpha(corr)}$ (cps)
MAX-2	23 719	- 21 168	- 95	+ 297	2 752
MAX-3	42 878	- 37 870	- 172	+ 537	5 372
MAX-4	76 065	- 65 772	- 306	+ 953	10 939
MAX-5	99 741	- 84 398	- 402	+ 1 250	16 191
MAX-6	120 614	- 99 826	- 480	+ 1 511	21 813
MAX-7	137 391	- 111 167	- 553	+ 1 721	27 391

$I^{o}_{CuK\alpha}$ average = 272 293 cps

std. devn. = ± 2 538 cps

$I^{o}_{CuK\alpha} = (2.72^{3} \pm 0.02^{5}) \times 10^{5}$

$= (2.72 \pm 0.02) \times 10^{5}$

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	copper	iron	$I_{ClK\alpha}$(corr) (cps)
MAX-1	4 764	− 1 559	--	+ 54	3 259
MAX-2	4 508	− 1 460	+ 63	+ 51	3 162
MAX-3	4 525	− 1 450	+ 127	+ 51	3 252
MAX-4	4 325	− 1 357	+ 242	+ 49	3 259
MAX-5	4 116	− 1 264	+ 346	+ 46	3 244
MAX-6	3 964	− 1 911	+ 444	+ 45	3 262
MAX-7	3 727	− 1094	+ 522	+ 42	3 196

$I^{o}_{ClK\alpha}$ average = 200 715 cps

std. devn. = ± 2 413 cps

$$I^{o}_{ClK\alpha} = (2.00^{7} \pm 0.02^{4}) \times 10^{5}$$

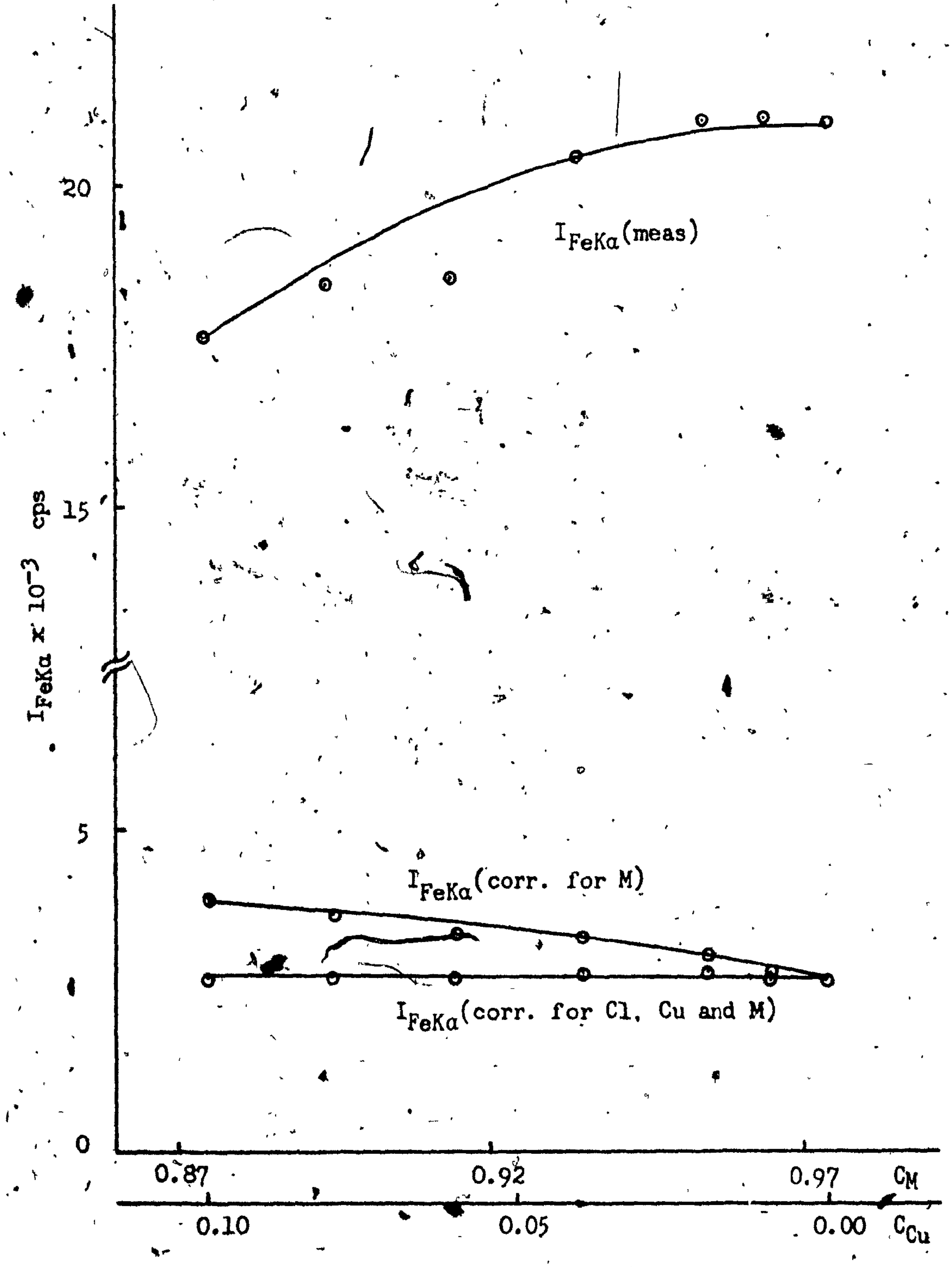
$$= (2.01 \pm 0.02) \times 10^{5}$$

TABLE F Back-calculation of solution composition

Solution	C_{Fe}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
MAX-1	0.00970	0.00030	3.00	--	--	--
MAX-2	0.00990	0.00010	1.00	0.01010	0.00010	1.00
MAX-3	0.01020	0.00020	2.00	0.01980	0.00020	2.00
MAX-4	0.01040	0.00040	4.00	0.0406	0.0006	1.50
MAX-5	0.00970	0.00030	3.00	0.0588	0.0012	2.00
MAX-6	0.01010	0.00010	1.00	0.0804	0.0004	0.50
MAX-7	0.01000	0.00000	0.00	0.1010	0.0010	1.00

C_{Cl}(calc)	Abs. error	Error %
0.01623	0.00012	0.75
0.01575	0.00036	2.23
0.01620	0.00009	0.56
0.01627	0.00016	0.99
0.01612	0.00001	0.06
0.01627	0.00016	0.90
0.01596	0.00015	0.93

FIGURE D $I_{FeK\alpha}$ versus C_{Cu} and C_M



5.8.5 Effect of Cu on Co

TABLE A Experimental Parameters

Solution	C_{Co}	C_{Cu}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}^{*}$ (cps)	s(%)
MAD-2	0.01000	0.01000	0.98000	42 183	0.11	30 879	0.13
MAD-3	0.01000	0.02000	0.97000	40 287	0.11	58 889	0.10
MAD-4	0.01000	0.0400	0.9500	38 632	0.11	102 861	0.07
MAD-5	0.01000	0.0600	0.9300	37 125	0.12	98 521	0.07
MAD-6	0.01000	0.0800	0.9100	34 919	0.12	161 538	0.07
MAD-7	0.01000	0.1000	0.8900	33 023	0.12	184 991	0.06

* 50 kV, 20 mA

TABLE B Calculation of α_{CoCu}

Solutions	α_{CoCu}
MAD-2/MAD-7	- 0.6459···
MAD-2/MAD-6	- 0.6561···
MAD-3/MAD-7	- 0.6694···
MAD-3/MAD-6	- 0.6876···

α_{CoCu} average = - 0.6647...
std. devn. = ± 0.018...
α_{CoCu} = $-0.66^{5} \pm 0.01^{8}$
= - 0.66 ± 0.02

TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of matrix	copper	$I_{CoK\alpha}$(corr) (cps)
MAD-2	42 183	- 38 127	- 280	3 775
MAD-3	40 287	- 36 038	- 536	3 709
MAD-4	38 632	- 33 894	- 1 028	3 756
MAD-5	37 125	- 31 844	- 1 481	3 800
MAD-6	34 919	- 29 307	- 1 858	3 754
MAD-7	33 023	- 27 107	- 2 196	3 720

$I^{o}_{CoK\alpha}$ average = 375 233 cps

std. devn. = ± 33392 cps

$I^{o}_{CoK\alpha} = (3.75^{2} \pm 0.03^{4}) \times 10^{5}$

$= (3.75 \pm 0.03) \times 10^{5}$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of		$I_{CuK\alpha(corr)}$ (cps)
		matrix	cobalt	
MAD-2	30 879	- 28 019	+ 466	3 326
MAD-3	58 889	- 52 889	+ 889	6 889
MAD-4	102 861	- 90 477	+ 1 553	13 937
MAD-5	98 521	- 84 835	+ 1 488	15 173
MAD-6	161 538	- 136 107	+ 2 439	27 870
MAD-7	184 991	- 152 442	+ 2 793	35 342

* $I^{o}_{CuK\alpha}$ average = 345 457 cps

std. devn. = ± 7 852 cps

$I^{o}_{CuK\alpha} = (3.45^{4} \pm 0.07^{8}) \times 10^{5}$

$= (3.45 \pm 0.08) \times 10^{5}$

* MAD-5 was omitted

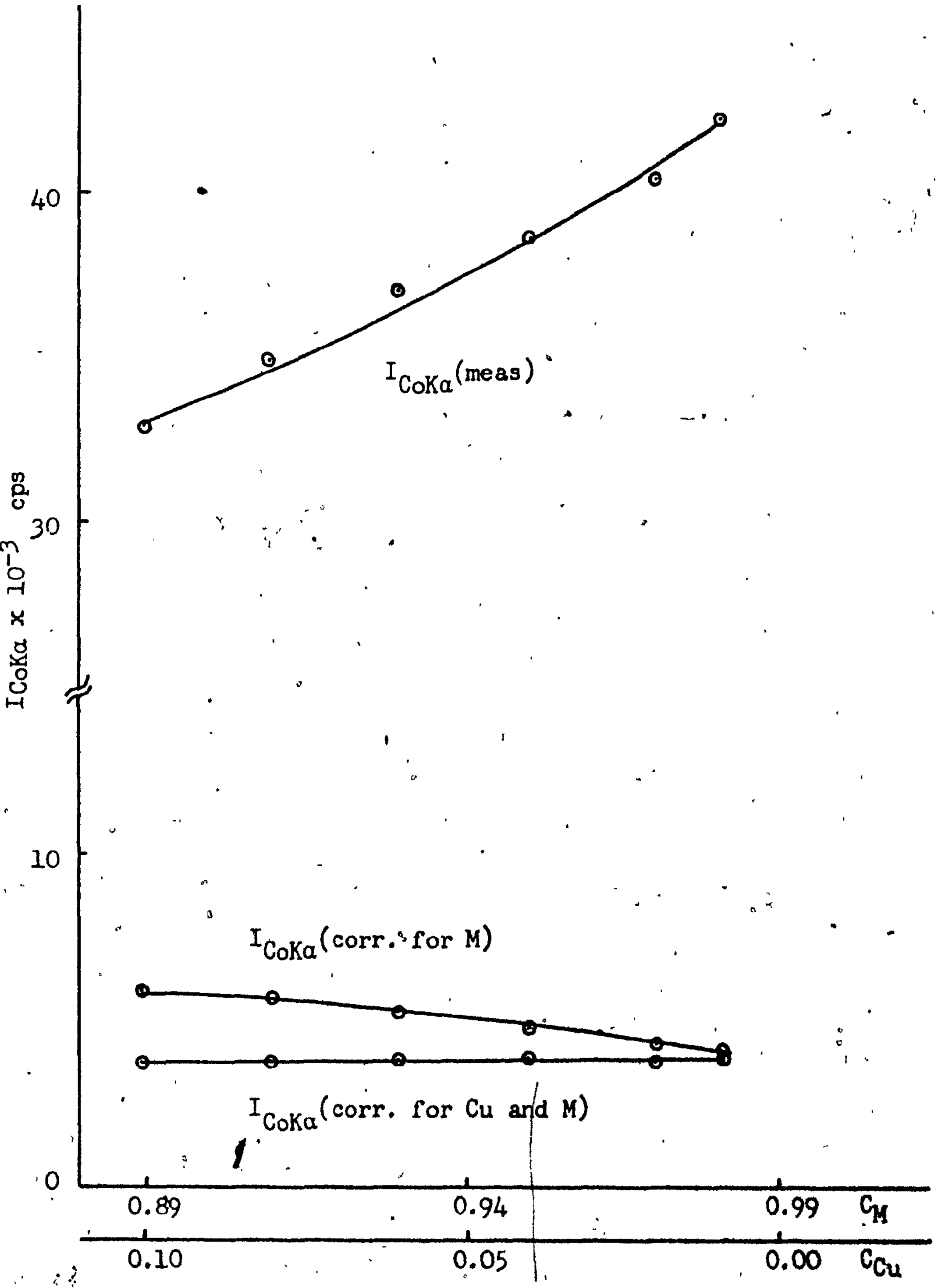
TABLE E Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
MAD-2	0.01000	0.00000	0.00	0.00960	0.00040	4.00
MAD-3	0.00990,	0.00010	1.00	0.01990	0.00010	0.50
MAD-4	0.01000	0.00000	0.00	0.0405	0.0005	1.25
MAD-5	0.00950	0.00050	5.00	0.0377	0.0223	5.75
MAD-6	0.01000	0.00000	0.00	0.0813	0.0013	1.62
MAD-7	0.01000	0.00000	0.00	0.1046	0.0046	4.60

*

MAD-5 Doubtful values

FIGURE D $I_{CoK\alpha}$ versus C_{Cu} and C_M



5.8.6 Effect of Cu on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Cu}	C_M	$I_{NiK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
MAG-1	0.01000	0.00	0.99000	65 876	0.09	--	--
MAG-2	0.01000	0.01000	0.98000	62 782	0.09	36 014	0.12
MAG-3	0.01000	0.02000	0.97000	57 648	0.10	66 520	0.09
MAG-4	0.01000	0.0400	0.9500	52 479	0.10	119 633	0.07
MAG-5	0.01000	0.0600	0.9300	47 944	0.10	150 948	0.07
MAG-6	0.01000	0.0800	0.9100	43 686	0.11	180 927	0.06
MAG-7	0.01000	0.1000	0.8900	41 943	0.11	202 250	0.05

* 50 kV, 20 mA

TABLE B Calculation of α_{NiCu}

Solutions	α_{NiCu}
MAG-1/MAG-7	- 0.3917...
MAG-1/MAG-6	- 0.3325...
MAG-1/MAG-5	- 0.3430...
MAG-2/MAG-7	- 0.3791...
MAG-2/MAG-6	- 0.3039...

α_{NiCu} average = - 0.3500...

std. devn. = ± 0.0356...

$$\alpha_{NiCu} = -0.35^{0} \pm 0.03^{6}$$

$$= -0.35 \pm 0.04$$

TABLE C Calculation of $I_{NiK\alpha}$(corr) and $I^{o}_{NiK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{NiK\alpha}$(corr) (cps)
MAG-1	65 876	- 59 811	--	6 065
MAG-2	62 782	- 56 426	- 220	6 136
MAG-3	57 648	- 51 283	- 403	5 961
MAG-4	52 479	- 45 722	- 735	6 022
MAG-5	47 944	- 40 891	- 1 007	6 045
MAG-6	43 686	- 36 459	- 1 223	6 004
MAG-7	41 943	- 34 235	- 1 468	6 240

$I^{o}_{NiK\alpha}$ average = 606 793 cps

std. devn. = ± 9 344 cps

$I^{o}_{NiK\alpha}$ = $(6.06^{8} \pm 0.09^{3}) \times 10^{5}$

= $(6.07 \pm 0.09) \times 10^{5}$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of		$I_{CuK\alpha}$(corr) (cps)
		matrix	nickel	
MAG-2	36 014	- 32 678	- 27	3 309
MAG-3	66 520	- 59 743	- 49	6 728
MAG-4	119 633	- 105 230	- 88	14 315
MAG-5	150 948	- 129 979	- 112	20 857
MAG-6	180 927	- 152 443	- 134	28 350
MAG-7	202 250	- 166 664	- 150	35 436

$I^{o}_{CuK\alpha}$ average = 346 914 cps

std. devn. = ± 10 947 cps

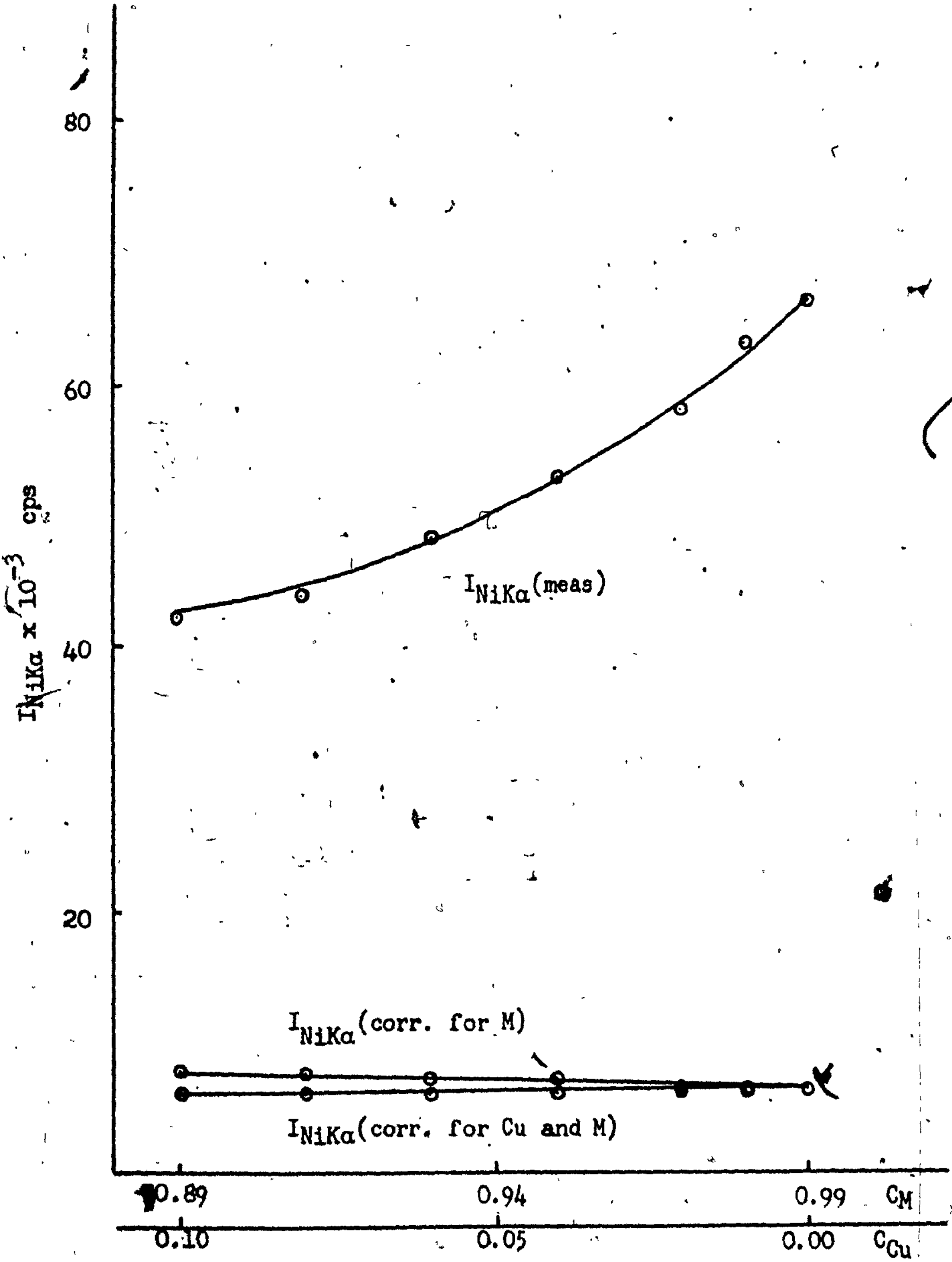
$I^{o}_{CuK\alpha}$ = $(3.4^{7} \pm 0.1^{1}) \times 10^{5}$

= $(3.5 \pm 0.1) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Ni}(calc)	Abs. error	Error%	C_{Cu}(calc)	Abs. error	Error%
MAG-1	0.01000	0.00000	0.00	—	—	—
MAG-2	0.01010	0.00010	1.00	0.00950	0.00050	5.00
MAG-3	0.00980	0.00020	2.00	0.01920	0.00080	4.00
MAG-4	0.01000	0.00000	0.00	0.0419	0.0019	4.75
MAG-5	0.01000	0.00000	0.00	0.0602	0.0002	0.66
MAG-6	0.01000	0.00000	0.00	0.0833	0.0033	4.15
MAG-7	0.01050	0.00050	5.00	0.1052	0.0052	5.20

FIGURE D $I_{NiK\alpha}$ versus C_{Cu} and C_M



5.8.7 Effect of Cu on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Cu}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
LO-1	0.01000	0.01000	0.98000	36 279	0.12	26 715	0.14
LO-2	0.01000	0.02000	0.97000	33 062	0.12	45 973	0.10
LO-3	0.01000	0.0400	0.9500	27 877	0.13	81 216	0.08
LO-4	0.01000	0.0800	0.9100	21 934	0.15	125 218	0.07
LO-5	0.01000	0.1000	0.8900	19 558	0.16	139 282	0.07

* 40 kV, 20 mA

TABLE B Calculation of α_{ZnCu}

Solutions	α_{ZnCu}
LO-1/LO-5	- 0.2446...
LO-1/LO-4	- 0.2573...
LO-2/LO-5	- 0.2489...
LO-2/LO-5	- 0.2659...
LO-3/LO-5	- 0.2846...

α_{ZnCu} average = - 0.2603...

std. devn. = ± 0.0159...

$\alpha_{ZnCu} = -0.26^0 \pm 0.01^6$

$= -0.26 \pm 0.02$

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^o_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{ZnK\alpha}$(corr) (cps)
LO-1	36 279	- 33 523	- 94	2 662
LO-2	33 062	- 30 239	- 172	2 651
LO-3	27 877	- 24 971	- 290	2 616
LO-4	21 934	- 18 820	- 456	2 658
LO-5	19 558	- 16 413	- 508	2 637

$I^{o}_{ZnK\alpha}$ average = 264 459 cps

std. devn. = ± 1 846 cps

$I^{o}_{ZnK\alpha}$ = $(2.64^{4} \pm 0.01^{8}) \times 10^{5}$

= $(2.64 \pm 0.02) \times 10^{5}$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{CuK\alpha}$(corr) (cps)
LO-1	26 715	- 24 241	- 55	2 419
LO-2	45 973	- 41 289	- 95	4 588
LO-3	81 216	- 71 438	- 168	9 610
LO-4	125 218	- 105 505	- 259	19 453
LO-5	139 282	- 114 775	- 288	24 218

$I^{o}_{CuK\alpha}$ average = 239 184 cps

std. devn. = ± 5 074 cps

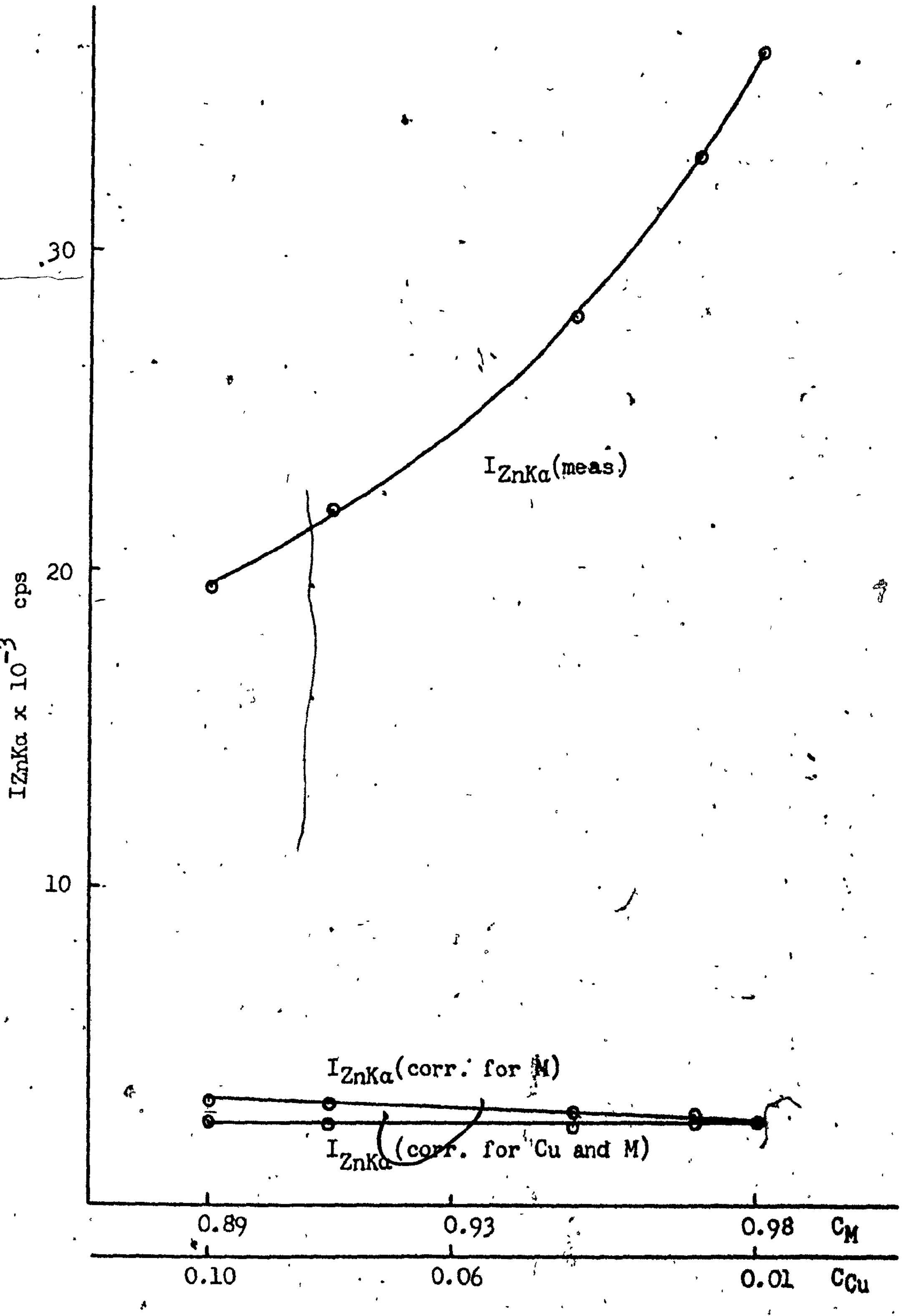
$I^{o}_{CuK\alpha}$ = $(2.39^{2} \pm 0.05^{1}) \times 10^{5}$

= $(2.39 \pm 0.05) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
LO-1	0.01010	0.00010	1.00	0.01010	0.00010	1.00
LO-2	0.00990	0.00010	1.00	0.01900	0.00100	5.00
LO-3	0.00990	0.00010	1.00	0.0402	0.0002	0.50
LO-4	0.01020	0.00020	2.00	0.0827	0.0027	3.50
LO-5	0.01010	0.00010	1.00	0.1028	0.0028	2.80

FIGURE D $I_{ZnK\alpha}$ versus C_{Cu} and C_M



5.8.8 Effect of Cu on Sn

TABLE A Experimental Parameters

Solution	C_{Sn}	C_{Cu}	C_{Cl}	C_M	$I_{SnK\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
LS-1	0.01000	0.00	0.0123	0.9777	19 871	0.16	--	--
LS-2	0.01000	0.01000	0.0430	0.9370	16 561	0.17	18 458	0.17
LS-3	0.01000	0.02000	0.0490	0.9210	15 495	0.18	34 234	0.12
LS-4	0.01000	0.0400	0.0892	0.8608	12 290	0.20	50 180	0.10
LS-5	0.01000	0.0600	0.1267	0.8033	10 142	0.22	61 809	0.09
LS-6	0.01000	0.0800	0.1211	0.7889	9 003	0.24	78 088	0.08
LS-7	0.01000	0.1000	0.1409	0.7491	7 872	0.26	86 288	0.07

* 40 kV, 20 mA

TABLE B Calculation of α_{SnCu}

Solutions	α_{SnCu}
LS-1/LS-7	- 0.2233···
LS-1/LS-6	- 0.2428···
LS-2/LS-7	- 0.2406···
LS-2/LS-6	- 0.2655···
LS-2/LS-5	- 0.2884···

α_{SnCu} average = - 0. 2521...

std. devn. = ± 0.0252···

$\alpha_{SnCu} = -0.25^2 \pm 0.02^5$

$= -0.25 \pm 0.02$

TABLE C Calculation of $I_{SnK\alpha}$(corr) and $I^o_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of copper	$I_{SnK\alpha}$(corr) (cps)
LS-1	19 871	- 18 534	- 207	--	1 130
LS-2	16 561	- 14 804	- 603	- 42	1 112
LS-3	15 495	- 13 614	- 643	- 78	1 160
LS-4	12 290	- 10 092	- 928	- 124	1 146
LS-5	10 142	- 7 772	- 1 088	- 153	1 129
LS-6	9 003	- 6 776	- 923	- 181	1 123
LS-7	7 872	- 5 625	- 939	- 198	1 110

$I^{o}_{SnK\alpha}$ average = 112 588 cps

std. devn. = ± 1 791 cps

$I^{o}_{SnK\alpha}$ = $(1.12^{5} \pm 0.01^{7}) \times 10^{5}$

= $(1.12 \pm 0.02) \times 10^{5}$

TABLE D <u>Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$</u>

Solution	Measured	Correction for effect of			$I_{CuK\alpha}$(corr) (cps)
		matrix	chlorine	tin	
LS-2	18 458	- 16 014	- 198	+ 126	2 372
LS-3	34 234	- 29 193	- 419	+ 234	4 856
LS-4	50 180	- 39 994	- 1 119	+ 343	9 410
LS-5	61 809	- 45 972	- 1 958	+ 423	14 302
LS-6	78 088	- 57 039	- 2 364	+ 534	19 219
LS-7	86 288	- 59 848	- 3 039	+ 590	2[illegible] 990

$I^{o}_{CuK\alpha}$ average = 238 960 cps

std. devn. = ± 2 617 cps

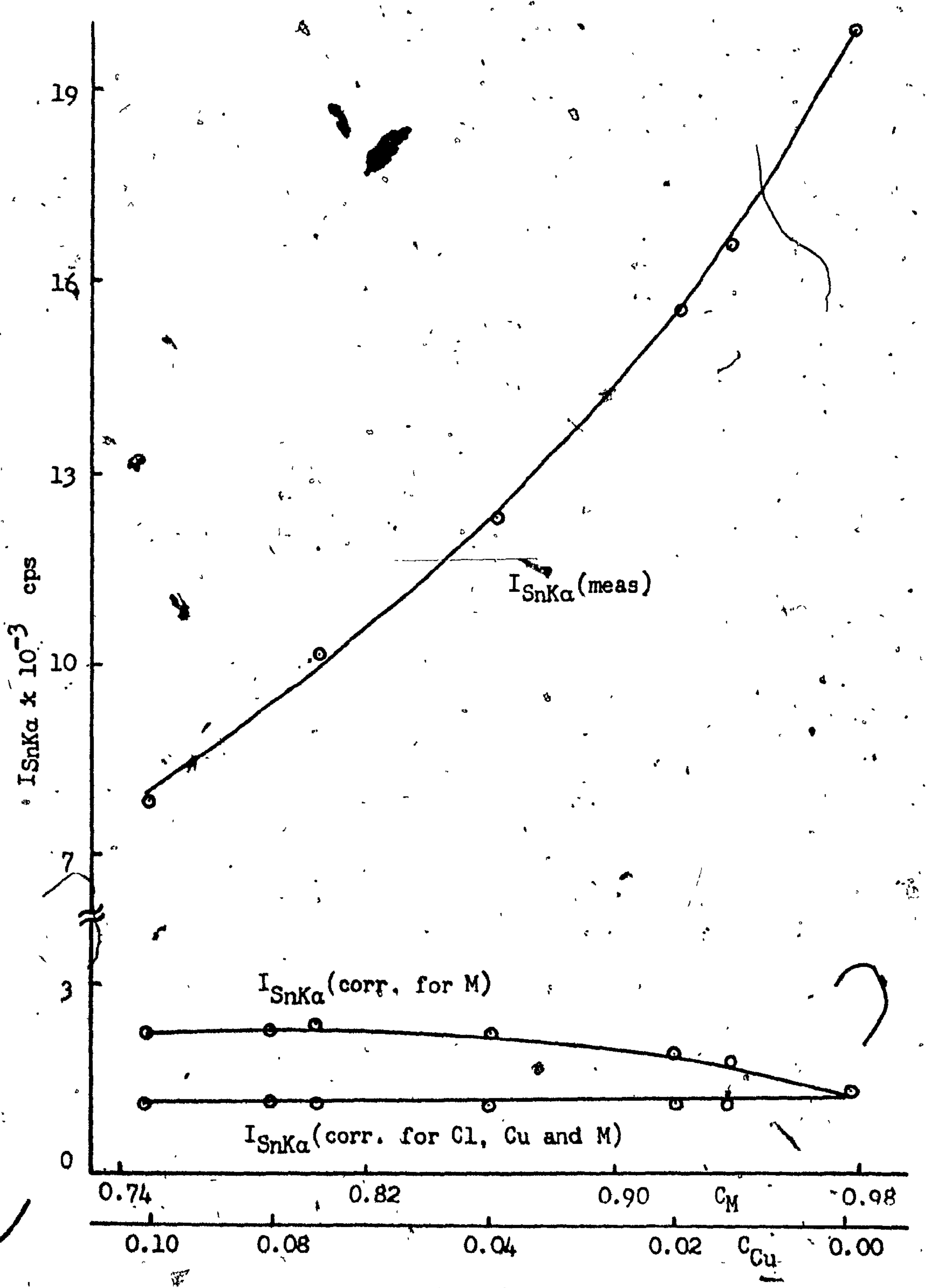
$I^{o}_{CuK\alpha}$ = $(2.38^{9} \pm 0.02^{6}) \times 10^{5}$

= $(2.39 \pm 0.03) \times 10^{5}$

TABLE E <u>Back-calculation of solution composition</u>

Chlorine intensity was not counted.

FIGURE D $I_{SnK\alpha}$ versus C_{Cu} and C_M



5.8.9 Effect of Cu on Pb

TABLE A Experimental Parameters

Solution	C_{Pb}	C_{Cu}	C_M	$I_{PbL\alpha}$ (cps)	s(%)	$I_{CuK\alpha}$* (cps)	s(%)
LQ-1	0.01000	0.01000	0.98000	10 665	0.22	25 015	0.14
LQ-2	0.01000	0.02000	0.97000	8 763	0.23	45 170	0.11
LQ-3	0.01000	0.04000	0.95000	6 361	0.29	76 286	0.08
LQ-4	0.01000	0.0600	0.9300	5 000	0.32	99 496	0.07
LQ-5	0.01000	0.0800	0.9100	4 170	0.34	110 330	0.07
LQ-6	0.01000	0.1000	0.8900	3 500	0.38	133 352	0.07

* 40 kV, 20 mA

TABLE B Calculation of α_{PbCu}

Solutions	α_{PbCu}
LQ-1/LQ-6	0.1990···
LQ-1/LQ-5	0.1661···
LQ-1/LQ-4	0.1932···
LQ-2/LQ-6	0.2257···
LQ-2/LQ-5	0.1816···
LQ-3/LQ-6	0.2186···

α_{PbCu} average = 0.1974···
std. devn. = ± 0.0224···

$$\alpha_{PbCu} = 0.19^7 \pm 0.02^2$$
$$= 0.20 \pm 0.02$$

TABLE C Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{PbL\alpha}$(corr) (cps)
LQ-1	10 665	- 10 137	+ 21	549
LQ-2	8 763	- 8 244	+ 34	553
LQ-3	6 361	- 5 861	+ 50	550
LQ-4	5 000	- 4 510	+ 59	549
LQ-5	4 170	- 3 680	+ 66	556
LQ-6	3 500	- 3 021	+ 69	548

$I^{o}_{PbL\alpha}$ average = 55 083 cps
std. devn. = ± 306 cps

$$I^{o}_{PbL\alpha} = (5.50^{8} \pm 0.03^{0}) \times 10^{4}$$
$$= (5.51 \pm 0.03) \times 10^{4}$$

TABLE D Calculation of $I_{CuK\alpha}$(corr) and $I^{o}_{CuK\alpha}$

Solution	Measured	Correction for effect of		$I_{CuK\alpha}$(corr) (cps)
		matrix	lead	
LQ-1	25 015	- 22 698	+ 129	2 446
LQ-2	45 170	- 40 568	+ 233	4 835
LQ-3	76 286	- 67 101	+ 393	9 578
LQ-4	99 496	- 85 675	+ 512	14 333
LQ-5	119 330	- 100 544	+ 614	19 400
LQ-6	133 352	- 109 889	+ 687	24 150

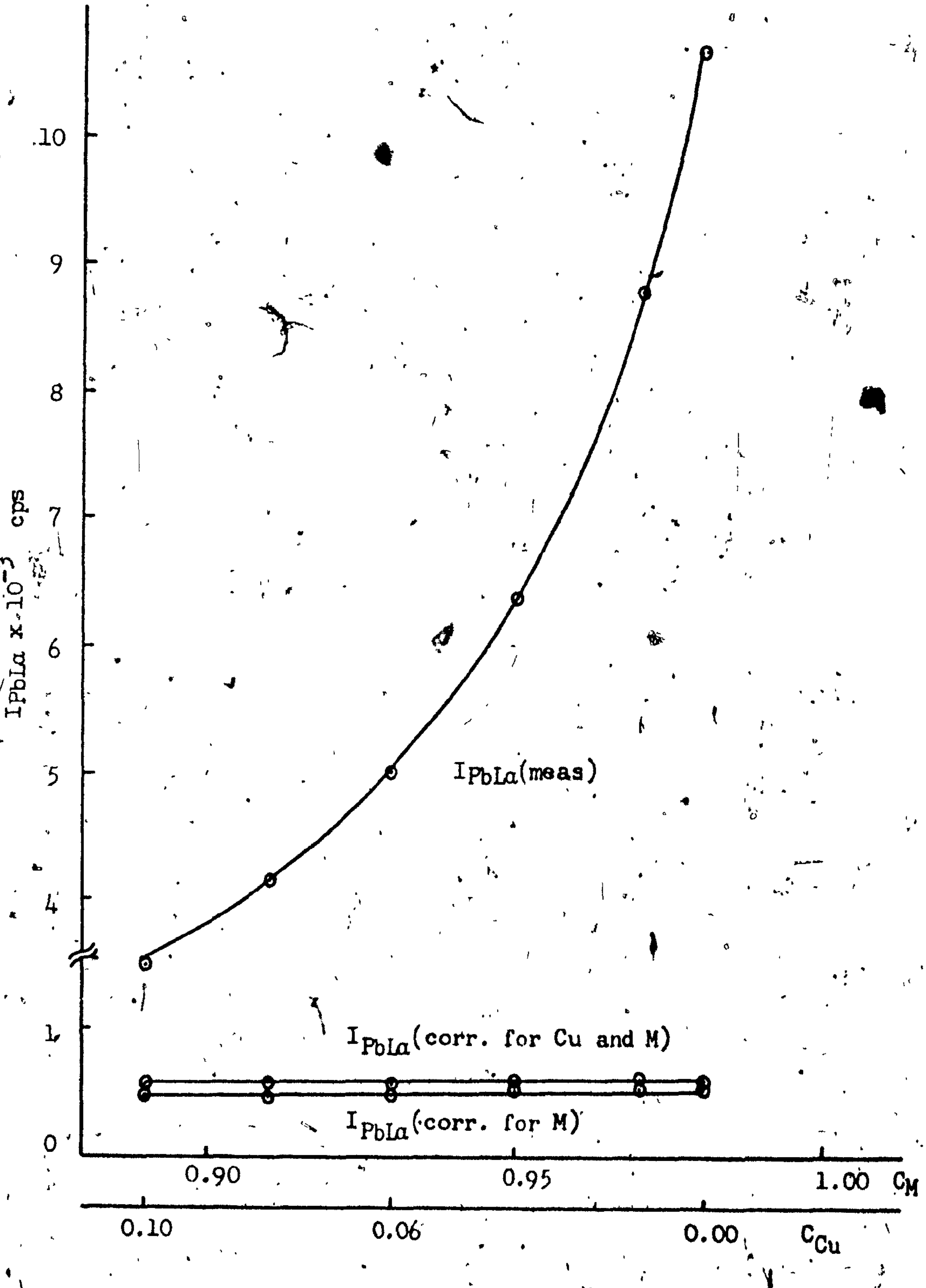
$I^{o}_{CuK\alpha}$ average = 241 447 cps
std. devn. = ± 2 074 cps

$$I^{o}_{CuK\alpha} = (2.41^{4} \pm 0.02^{0}) \times 10^{5}$$
$$= (2.41 \pm 0.02) \times 10^{5}$$

TABLE E Back-calculation of solution composition

Solution	C_{Pb}(calc)	Abs. error	Error %	C_{Cu}(calc)	Abs. error	Error %
LQ-1	0.01000	0.00000	0.00	0.01010	0.00010	1.00
LQ-2	0.01010	0.00010	1.00	0.02000	0.00000	0.00
LQ-3	0.00990	0.00010	1.00	0.03950	0.00050	1.25
LQ-4	0.00980	0.00020	2.00	0.0588	0.0012	2,00
LQ-5	0.01020	0.00020	2.00	0.0809	0.0009	1.12
LQ-6	0.00990	0.00010	1.00	0.0999	0.0001	0.10

FIGURE D $I_{PbL\alpha}$ versus C_{Cu} and C_M



5.9 Effects of Zinc

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Chromium	1 ml =	0.2000	± 0.0001 g	(dil. HNO_3)
Manganese	1 ml =	0.10000	± 0.00002 g	(dil. HNO_3)
Iron	1 ml =	0.10000	± 0.00002 g	(dil. HCl-HNO_3)
Cobalt	1 ml =	0.10000	± 0.00005 g	(dil. HNO_3)
Nickel	1 ml =	0.2000	± 0.0001 g	(dil. HNO_3)
Copper	1 ml =	0.20000	± 0.00005 g	(dil. HNO_3)
Zinc	1 ml =	0.20000	± 0.00005 g	(dil. HNO_3)
Tin	1 ml =	0.20000	± 0.00005 g	(dil. HNO_3-HCl)
Lead	1 ml =	0.20000	± 0.00005 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCL, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	LZH	1:440 Cl	1:220 to 1:2200
Cr	MAS	1:400	1:200 to 1:2000
Mn	LZR	1:400	1:200 to 1:2000
Fe	MAY	1:400	1:200 to 1:2000
Co	MAE	1:400	1:200 to 1:2000
Ni	MAH	1:400	1:200 to 1:2000
Cu	LP	1:400	1:200 to 1:2000
Sn	LX	1:250	1:125 to 1:1250
Pb	LU	1:400	1:200 to 1:2000

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cr	Mn	Fe	Co	Ni	Cu	Zn	Sn	Pb
Target	Cr	W	W	W	W	W	W	W	W	W
kV	50	50	50	50	50	50	40	*	50	50
mA	36	40	20	40	30	30	20	*	20	20
Coll^n	coarse	fine	fine	fine	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Lα

* See each series

The tabulated counts for each series represented the averages of the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α'_{AZn} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{AZn} (presence of chlorine as fourth component)	Equation (44)
	Calculation of I_A(corr)	Equation (45) or a modification
	Calculation of I_A^o	$I_A(\text{corr})/C_A$

5.9.1 Effect of Zn on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Zn}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
LZH-1	0.01899	0.0	0.98101	5 891	0.30	--	—
LZH-2	0.01899	0.01000	0.97101	5 777	0.31	33 986	0.12
LZH-3	0.01899	0.02000	0.96101	5 619	0.31	61 329	0.10
LZH-4	0.01899	0.0400	0.9410	5 278	0.32	102 351	0.07
LZH-5	0.01899	0.0600	0.9210	5 020	0.32	133 770	0.07
LZH-6	0.01899	0.0800	0.9010	4 702	0.33	155 244	0.06
LZH-7	0.01899	0.1000	0.8810	4 467	0.33	173 348	

*40kV, 20mA

TABLE B Calculation of α_{ClZn}

Solutions	α_{ClZn}
LZH-1/LZH-7	1.8010···
LZH-1/LZH-6	1.7830···
LZH-1/LZH-5	1.6025···
LZH-2/LZH-7	1.9220···
LZH-2/LZH-6	1.9274···
LZH-3/LZH-7	1.9379···

α_{ClZn} average = 1.8350···

std. devn. = ± 0.137····

$\alpha_{ClZn} = 1.8^{3} \pm 0.1^{4}$

$= 1.8 \pm 0.1$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{ClK\alpha}$(corr) (cps)
LZH-1	5 891	- 1 942	--	3 949
LZH-2	5 777	- 1 885	+ 106	3 998
LZH-3	5 619	- 1 814	+ 206	4 011
LZH-4	5 278	- 1 669	+ 386	3 995
LZH-5	5 020	- 1 553	+ 551	4 018
LZH-6	4 702	- 1 423	+ 688	3 967
LZH-7	4 467	- 1 322	+ 817	3 962

$I^{o}_{ClK\alpha}$ average = 209 885 cps

std. devn. = ± 1 379 cps

$I^{o}_{ClK\alpha} = (2.09^{8} \pm 0.01^{3}) \times 10^{5}$ cps

$= (2.10 \pm 0.01) \times 10^{5}$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of		$I_{ZnK\alpha}$(corr) (cps)
		matrix	chlorine	
LZH-2	33 986	- 31 116	- 211	2 659
LZH-3	61 329	- 55 572	- 381	5 376
LZH-4	102 351	- 90 814	- 636	10 901
LZH-5	133 770	- 116 168	- 831	16 771
LZH-6	155 244	- 131 889	- 964	22 391
LZH-7	173 348	- 144 001	- 1 076	28 271

$I^{o}_{ZnK\alpha}$ average = 274 884 cps

std. devn. = ± 6 808 cps

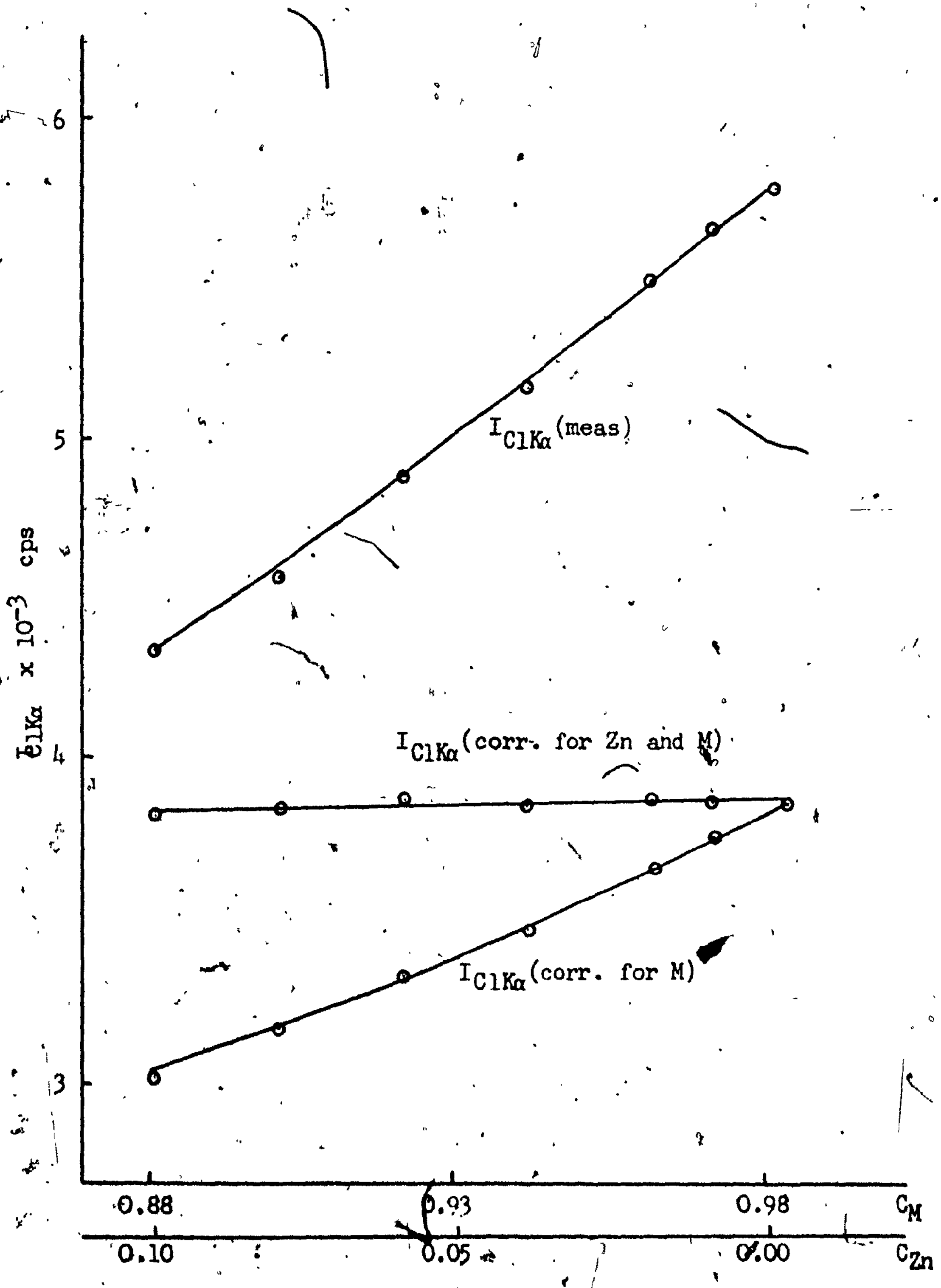
$I^{o}_{ZnK\alpha} = (2.74^{9} \pm 0.06^{8}) \times 10^{5}$ cps

$= (2.75 \pm 0.07) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
LZH-1	0.01881	0.00018	0.95	--	--	--
LZH-2	0.01903	0.00004	0.21	0.00960	0.00040	4.00
LZH-3	0.01908	0.00009	0.47	0.01940	0.00060	3.00
LZH-4	0.01901	0.00002	0.10	0.0395	0.0005	1.25
LZH-5	0.01925	0.00026	1.37	0.0620	0.0020	3.30
LZH-6	0.01905	0.00006	0.32	0.0832	0.0032	4.00
LZH-7	0.01921	0.00022	1.16	0.1072	0.0072	7.20

FIGURE D $I_{ClK\alpha}$ versus C_{Zn} and C_M



5.9.2 Effect of Zn on Cr

TABLE A Experimental Parameters

Solution	C_{Cr}	C_{Zn}	C_M	$I_{CrK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
MAS-1	0.01000	0.0	0.99000	4 979	0.32	--	--
MAS-2	0.01000	0.01000	0.98000	4 688	0.33	36 380	0.12
MAS-3	0.01000	0.02000	0.97000	4 644	0.33	66 004	0.09
MAS-4	0.01000	0.0400	0.9500	4 470	0.33	112 136	0.07
MAS-5	0.01000	0.0800	0.9100	4 021	0.35	168 291	0.06
MAS-6	0.01000	0.1000	0.8900	3 782	0.36	187 029	

*50kV.20mA

TABLE B Calculation of α_{CrZn}

Solutions	α_{CrZn}
MAS-1/MAS-7	- 0.3363···
MAS-1/MAS-6	- 0.3665···
MAS-2/MAS-7	- 0.4058···
MAS-2/MAS-6	- 0.4554···
MAS-3/MAS-7	- 0.3596···
MAS-3/MAS-6	- 0.4077···

α_{CrZn} average = - 0.3[illegible]85···

std. devn. = ± 0.043····

α_{CrZn} = $- 0.38^{8} \pm 0.04^{3}$

= $- 0.39 \pm 0.04$

TABLE C Calculation of $I_{CrK\alpha}$(corr) and $I^{o}_{CrK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{CrK\alpha}$(corr) (cps)
MAS-1	4 979	- 4 175	--	804
MAS-2	4 686	- 3 890	- 18	778
MAS-3	4 644	- 3 816	- 36	792
MAS-4	4 470	- 3 591	- 69	804
MAS-5	4 021	- 3 099	- 125	797
MAS-6	3 782	- 2 851	- 147	784

$I^{o}_{CrK\alpha}$ average = 79 317 cps

std. devn. = ± 2 368 cps

$I^{o}_{CrK\alpha}$ = $(7.9^{9} \pm 0.2^{3}) \times 10^{4}$ cps

= $(8.0 \pm 0.2) \times 10^{4}$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chromium	$I_{ZnK\alpha}$ (corr) (cps)
MAS-2	36 380	- 33 617	+ 196	2 960
MAS-3	66 004	- 60 368	+ 356	5 992
MAS-4	112 136	- 100 446	+ 605	12 295
MAS-5	168 291	- 144 400	+ 909	24 800
MAS-6	187 029	- 156 951	+ 1 010	31 088

$I^{o}_{ZnK\alpha}$ average = 304 771 cps

std. devn. = ± 6 659 cps

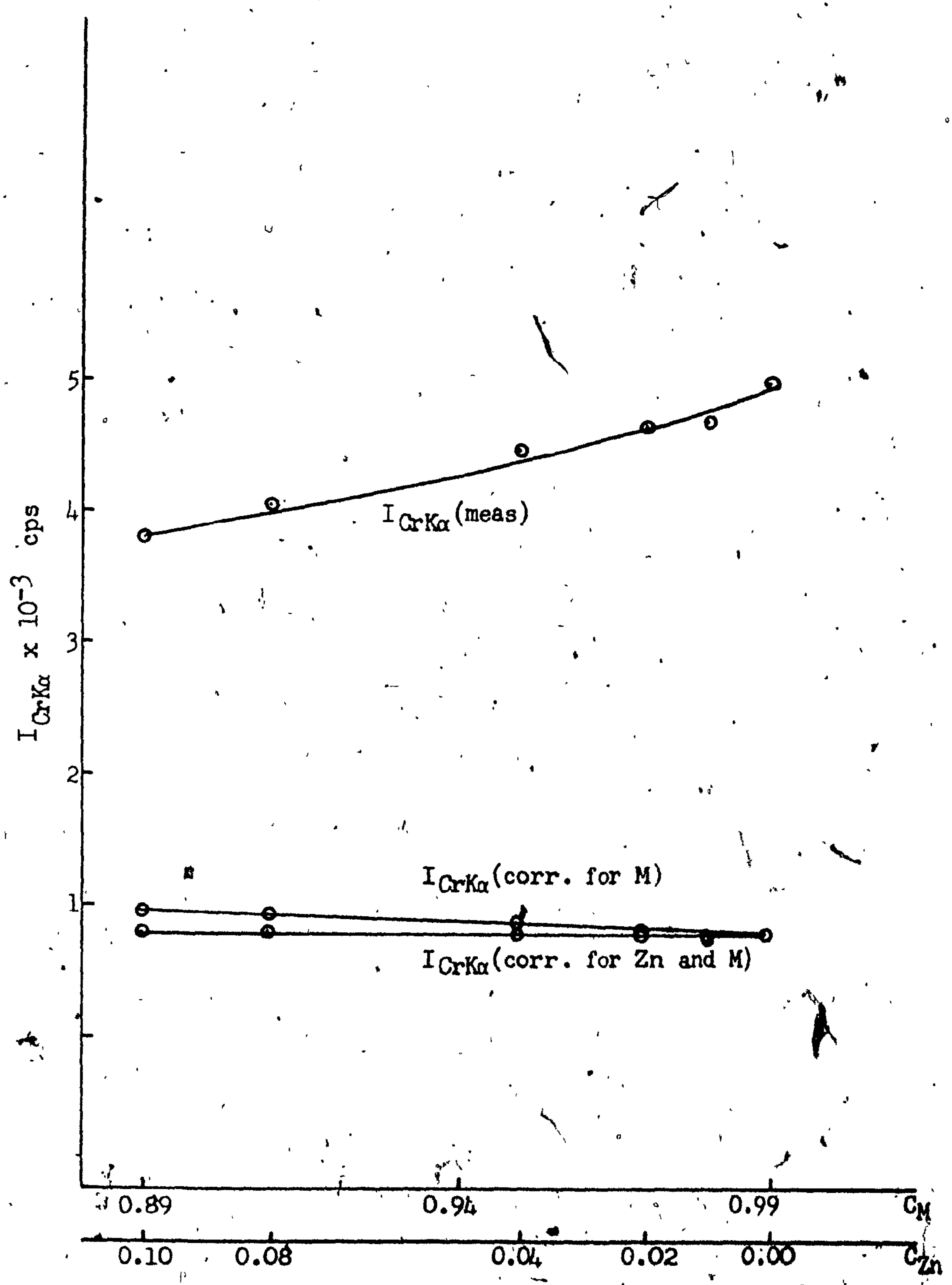
$I^{o}_{ZnK\alpha}$ = $(3.04^{7} \pm 0.06^{6}0 \times 10^{5}$ cps

= $(3.05 \pm 0.07) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

Solution	C_{Cr}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
MAS-1	0.01000	0.00000	0.00	--		---
MAS-2	0.00970	0.00030	3.00	0.01000	0.00000	0.00
MAS-3	0.00990	0.00010	1.00	0.0204	0.0004	2.00
MAS-4	0.01010	0.00010	1.00	0.0424	0.0024	6.00
MAS-5	0.01010	0.00010	1.00	0.0867	0.0067	8.37
MAS-6	0.01000	0.00000	0.00	0.1097	0.0097	9.70

FIGURE D $I_{CrK\alpha}$ versus C_{Zn} and C_M



5.9.3 Effect of Zn on Mn

TABLE A Experimental Parameters

Solution	C_{Mn}	C_{Zn}	C_M	$I_{MnK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
LZR-1	0.01000	0.0	0.99000	8 199	0.25	--	--
LZR-2	0.01000	0.01000	0.98000	7 853	0.26	33 928	0.12
LZR-3	0.01000	0.02000	0.97000	7 581	0.26	60 304	0.10
LZR-4	0.01000	0.0400	0.9500	7 316	0.27	101 262	0.07
LZR-5	0.01000	0.0600	0.9300	6 967	0.28	131 349	0.07
LZR-6	0.01000	0.0800	0.9100	6 607	0.29	155 752	0.06

* 40kV, 20mA

TABLE B Calculation of α_{MnZn}

Solutions	α_{MnZn}
LZR-1/LZR-6	- 0.4272···
LZR-1/LZR-5	- 0.4365···
LZR-2/LZR-6	- 0.4624···
LZR-2/LZR-5	- 0.4854···
LZR-3/LZR-6	- 0.4892···

α_{MnZn} average = $-0.4601\cdots$

std. devn. = $\pm 0.028\cdots$

$\alpha_{MnZn} = -0.46^{0} \pm 0.02^{8}$

$= -0.46 \pm 0.03$

TABLE C Calculation of $I_{MnK\alpha}$(corr) and $I^{o}_{MnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{MnK\alpha}$(corr) (cps)
LZR-1	8 199	- 7 011	--	1 188
LZR-2	7 853	- 6 647	- 36	1 170
LZR-3	7 581	- 6 351	- 70	1 160
LZR-4	7 316	- 6 003	- 135	1 178
LZR-5	6 967	- 5 596	- 192	1 179
LZR-6	6 607	- 5 193	- 243	1 171

$I^{o}_{MnK\alpha}$ average = 117 438 cps

std. devn. = ± 968 cps

$I^{o}_{MnK\alpha} = (1.17^{4} \pm 0.009^{7}) \times 10^{5}$ cps

$= (1.174 \pm 0.010) \times 10^{5}$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of manganese	$I_{ZnK\alpha}$(corr) (cps)
LZR-2	33 928	- 31 351	+ 214	2 791
LZR-3	60 304	- 44 155	+ 380	5 529
LZR-4	101 262	- 90 706	+ 639	11 195
LZR-5	131 349	- 115 179	+ 829	16 999
LZR-6	155 752	- 133 641	+ 983	23 094

$I^{o}_{ZnK\alpha}$ average = 281 483 cps

std. devn. = ± 4 693 cps

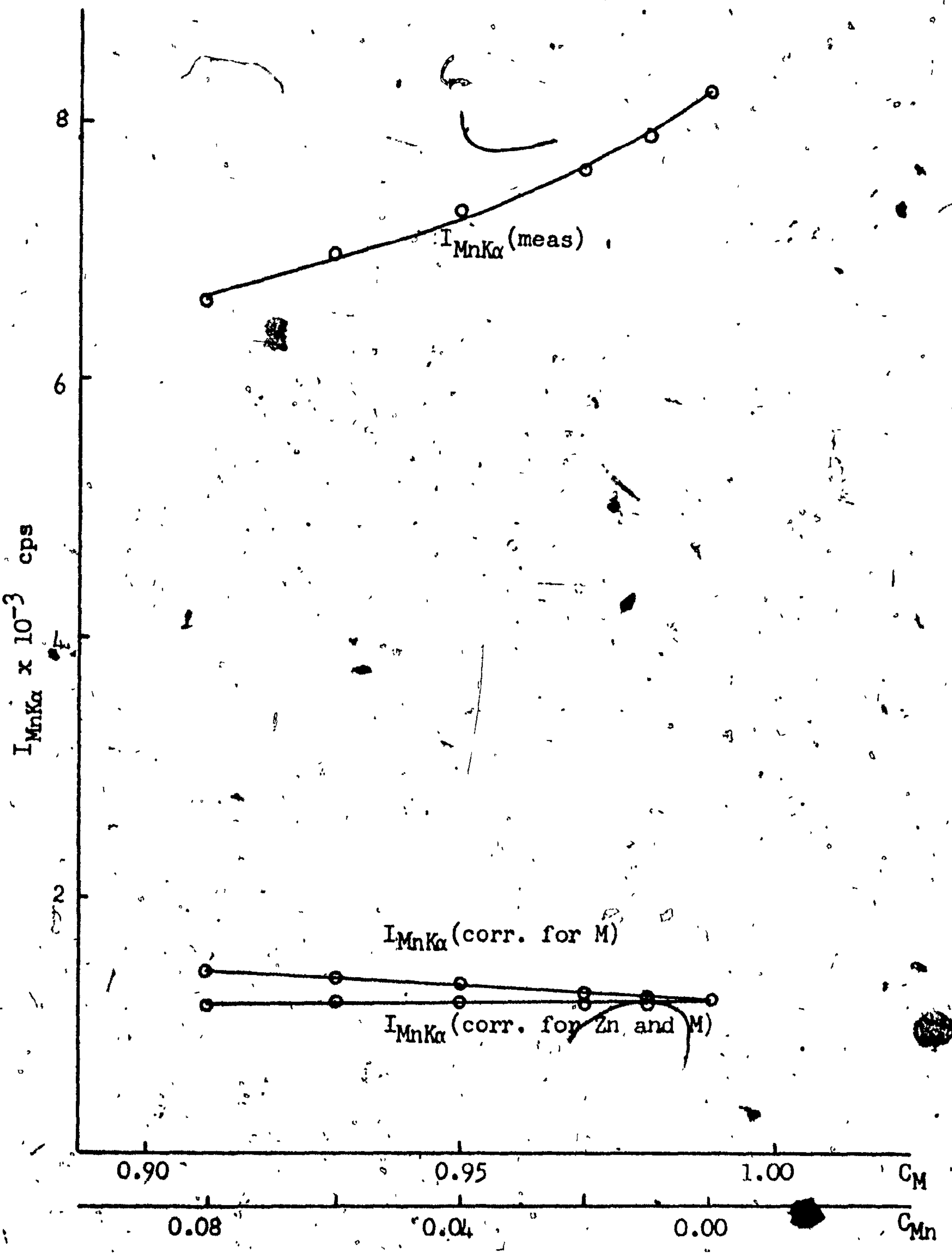
$$I^{o}_{ZnK\alpha} = (2.81^{4} \pm 0.04^{6}) \times 10^{5} \text{ cps}$$

$$= (2.81 \pm 0.05) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Mn}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
LZR-1	0.01010	0.00010	1.00	--	--	--
LZR-2	0.01000	0.00000	0.00	0.00990	0.00010	1.00
LZR-3	0.00990	0.00010	1.00	0.01950	0.00050	2.50
LZR-4	0.01000	0.00000	0.00	0.0397	0.0003	0.75
LZR-5	0.01010	0.00010	1.00	0.0608	0.0008	1.33
LZR-6	0.01010	0.00010	1.00	0.0844	0.0044	5.50

FIGURE D $I_{MnK\alpha}$ versus C_{Zn} and C_M



5.9.4 Effect of Zn on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Zn}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)	$I_{ClK\alpha}$ (cps)	s(%)
MAY-1	0.01000	0.0	0.01611	0.97389	21 094	0.16	--	--	4 706	0.33
MAY-2	0.01000	0.01000	0.01611	0.96389	20 312	0.16	33 379	0.12	4 603	0.33
MAY-3	0.01000	0.02000	0.01611	0.95389	20 424	0.16	60 287	0.10	4 406	0.33
MAY-4	0.01000	0.0400	0.01611	0.9339	19 337	0.16	104 281	0.07	4 129	0.34
MAY-5	0.01000	0.0600	0.01611	0.9139	18 592	0.17	138 939	0.07	3 905	0.35
MAY-6	0.01000	0.0800	0.01611	0.8939	17 648	0.17	169 210	0.06	3 681	0.37
MAY-7	0.01000	0.1000	0.01611	0.8739	17 235	0.17	191 506	0.06	3 481	0.39

* 50kV, 20mA

TABLE B. Calculation of α_{FeZn}

Solutions	α_{FeZn}
MAY-1/MAY-7	- 0.6113···
MAY-1/MAY-6	- 0.5856···
MAY-1/MAY-5	- 0.6108···
MAY-2/MAY-7	- 0.6387···
MAY-2/MAY-6	- 0.6158···
MAY-2/MAY-5	- 0.6564···
MAY-3/MAY-7	- 0.5876···

α_{FeZn} average = - 0.6152···

std. devn. = ± 0.0256···

$\alpha_{FeZn} = -0.61^5 \pm 0.02^6$

$= -0.61 \pm 0.03$

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^{o}_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}$(corr) (cps)
		matrix	chlorine	zinc	
MAY-1	21 094	- 18 421	+ 16	---	2 688
MAY-2	20 312	- 17 556	+ 15	- 125	2 646
MAY-3	20 424	- 17 470	+ 15	- 251	2 718
MAY-4	19 337	- 16 193	+ 15	- 476	2 683
MAY-5	18 592	- 15 236	+ 14	- 686	2 684
MAY-6	17 648	- 14 146	+ 13	- 868	2 647
MAY-7	17 235	- 13 506	+ 13	- 1 060	2 682

$I^{o}_{FeK\alpha}$ average = 267 828 cps

Std. devn. = ± 2 518 cps

$I^{o}_{FeK\alpha}$ = $(2.67^{8} \pm 0.02^{5}) \times 10^{5}$ cps

= $(2.68 \pm 0.02) \times 10^{5}$ cps

Table D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of			$I_{ZnK\alpha}$(corr) (cps)
		matrix	chlorine	iron	
MAY-2	33 379	- 30 336	- 176	+ 217	3 084
MAY-3	60 287	- 54 223	- 317	+ 392	6 139
MAY-4	104 281	- 91 826	- 549	+ 678	12 584
MAY-5	138 939	- 119 725	- 732	+ 903	19 385
MAY-6	169 210	- 142 618	- 891	+ 1 099	26 800
MAY-7	191 506	- 157 799	- 1 009	+ 1 245	33 943

$I^{o}_{ZnK\alpha}$ average = 321 247 cps

std. devn. = ± 13 906 cps

$I^{o}_{ZnK\alpha}$ = $(3.2^{1} \pm 0.1^{3}) \times 10^{5}$ cps

= $(3.2 \pm 0.1) \times 10^{5}$ cps

TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

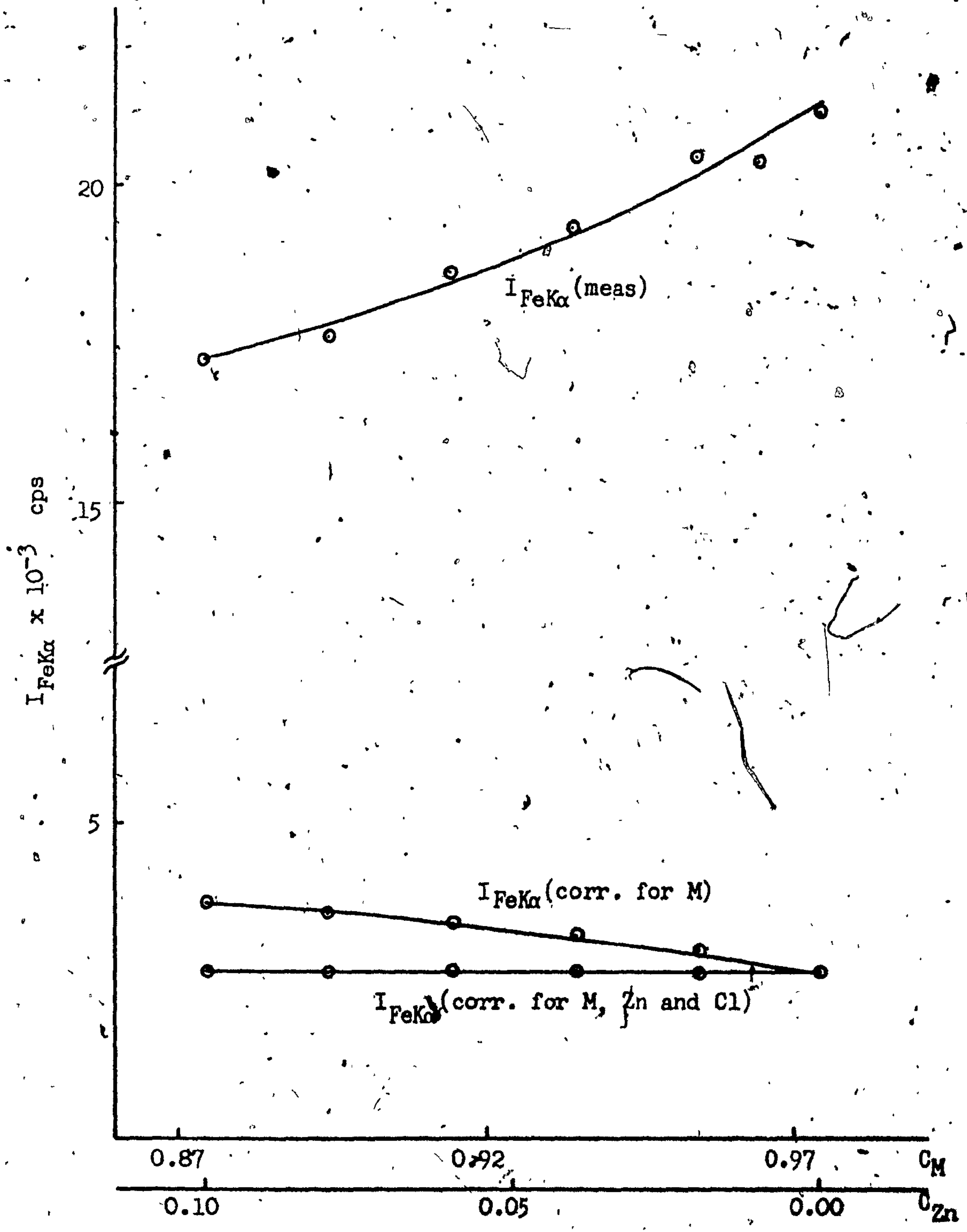
Solution	Measured	Correction for effect of			$I_{ClK\alpha}$(corr) (cps)
		matrix	zinc	iron	
MAY-1	4 706	- 1 540	---	+ 53	3 219
MAY-2	4 603	- 1 491	+ 84	+ 52	3 248
MAY-3	4 406	- 1 412	+ 161	+ 50	3 205
MAY-4	4 129	- 1 296	+ 302	+ 46	3 181
MAY-5	3 905	- 1 199	+ 429	+ 44	3 179
MAY-6	3 681	- 1 106	+ 539	+ 41	3 155
MAY-7	3 481	- 1 022	+ 637	+ 39	3 135

$$
\begin{aligned}
I^{o}_{ClK\alpha} \text{ average} &= 197\,960 \text{ cps} \\
\text{std. devn.} &= \pm\, 2\,382 \text{ cps} \\
I^{o}_{ClK\alpha} &= (1.97^{9} \pm 0.02^{4}) \times 10^{5} \text{ cps} \\
&= (1.98 \pm 0.02) \times 10^{5} \text{ cps}
\end{aligned}
$$

TABLE F Back-calculation of solution composition

Solution	C_{Fe}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %	C_{Cl}(calc)	Abs. error	Error %
MAY-1	0.01000	0.00000	0.00	--	--	--	0.01[illegible]	0.00013	0.80
MAY-2	0.00990	0.00010	1.00	0.00950	0.00050	5.00	0.01638	0.00017	1.05
MAY-3	0.01010	0.00010	1.00	0.01900	0.00100	5.00	0.01614	0.00003	0.18
MAY-4	0.01000	0.00000	0.00	0.0388	0.0012	3.00	0.01602	0.00009	0.55
MAY-5	0.01000	0.00000	0.00	0.0606	0.0006	1.00	0.01608	0.00003	0.18
MAY-6	0.01000	0.00000	0.00	0.0869	0.0069	8.50	0.01622	0.00011	0.68
MAY-7	0.01030	0.00030	3.00	0.1138	0.0138	13.80	0.01637	0.00026	1.61

FIGURE D $I_{FeK\alpha}$ versus C_{Zn} and C_M



5.9.5 Effect of Zn on Co

TABLE A. Experimental Parameters

Solution	C_{Co}	C_{Zn}	C_M	$I_{CoK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
MAE-2	0.01000	0.01000	0.98000	40 993	0.11	51 014	0.10
MAE-3	0.01000	0.02000	0.97000	40 342	0.11	79 905	0.08
MAE-4	0.01000	0.0400	0.9500	38 613	0.11	143 293	0.07
MAE-5	0.01000	0.0600	0.9300	36 280	0.12	183 803	0.06
MAE-6	0.01000	0.0800	0.9100	33 721	0.12	214 024	0.05
MAE-7	0.01000	0.1000	0.8900	31 293	0.13	250 201	0.05

* 50kV, 20mA

TABLE B. Calculation of α_{CoZn}

Solutions	α_{CoZn}
MAE-2/MAE-7	- 0.6122...
MAE-2/MAE-6	- 0.6460...
MAE-3/MAE-7	- 0.5836...
MAE-3/MAE-6	- 0.6179...

$$\alpha_{CoZn} \text{ average} = -0.6149\cdots$$

$$\text{std. devn.} = \pm 0.0256\cdots$$

$$\alpha_{CoZn} = -0.61^{5} \pm 0.02^{6}$$

$$= -0.61 \pm 0.03$$

TABLE C Calculation of $I_{CoK\alpha}$(corr) and $I^{o}_{CoK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{CoK\alpha}$(corr) (cps)
MAE-2	40 993	- 37 052	- 252	3 689
MAE-3	40 342	- 36 091	- 496	3 755
MAE-4	38 613	- 33 832	- 950	3 831
MAE-5	36 280	- 31 119	- 1 339	3 822
MAE-6	33 721	- 28 302	- 1 659	3 760
MAE-7	31 293	- 25 687	- 1 924	3 682

$$I^{o}_{CoK\alpha} \text{ average} = 375\,652 \text{ cps}$$

$$\text{std. devn.} = \pm 6\,331 \text{ cps}$$

$$I^{o}_{CoK\alpha} = (3.75^{6} \pm 0.06^{3}) \times 10^{5} \text{ cps}$$

$$= (3.76 \pm 0.06) \times 10^{5} \text{ cps}$$

TABLE D. Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cobalt	$I_{ZnK\alpha}$(corr) (cps)
MAE-2	51 014	- 47 139	+ 479	4 354
MAE-3	79 905	- 73 082	+ 751	7 574
MAE-4	143 293	- 128 355	+ 1 347	16 285
MAE-5	183 803	- 161 176	+ 1 728	24 355
MAE-6	214 024	- 183 641	+ 2 012	32 395
MAE-7	250 201	- 209 964	+ 2 352	42 589

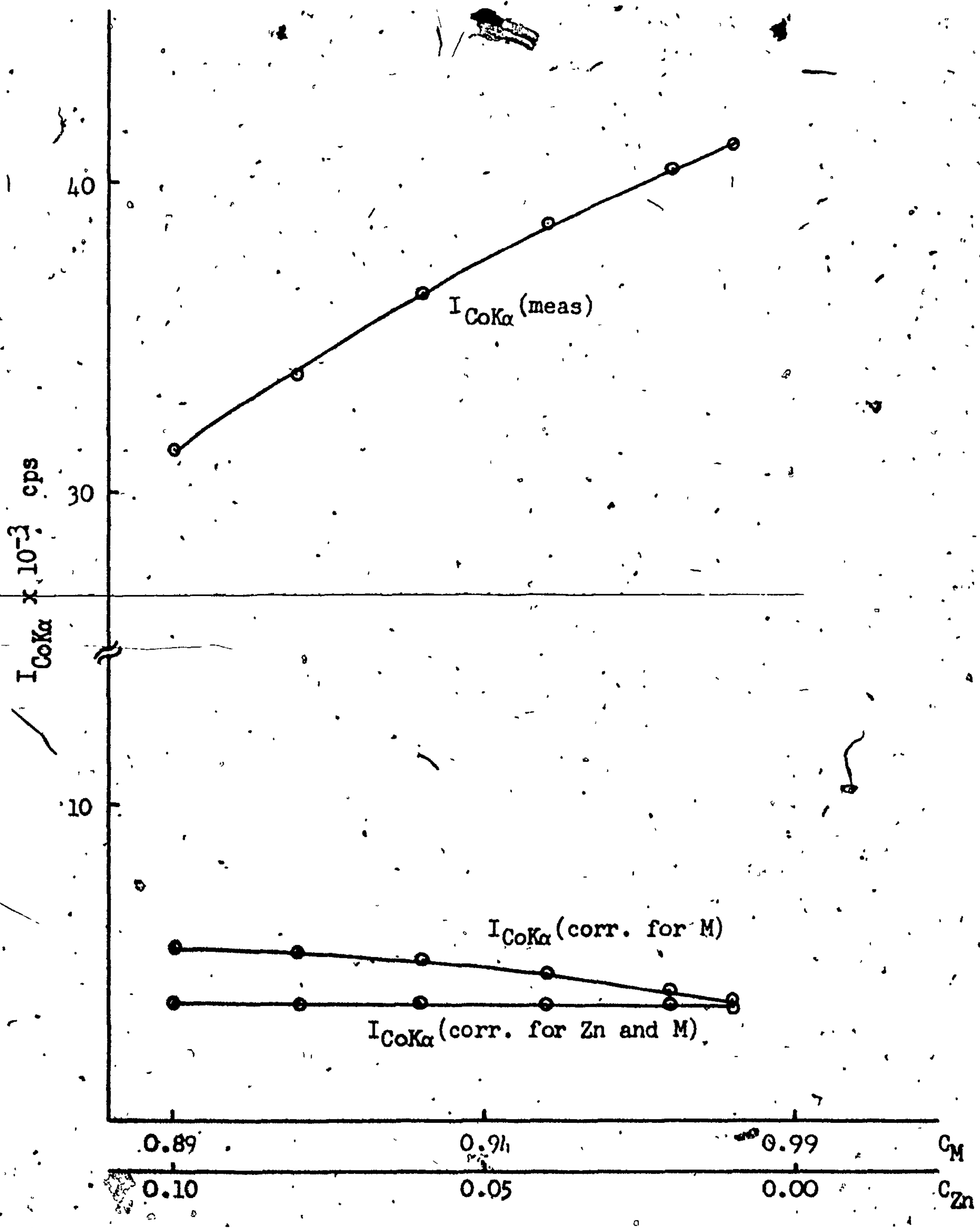
$I^{o}_{ZnK\alpha}$ average 415 258 cps.
std. devn. = ± 14 102 cps

$$I^{o}_{ZnK\alpha} = (4.1^{6} \pm 0.1^{4}) \times 10^{5} \text{ cps}$$
$$= (4.2 \pm 0.1) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Co}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
MAE-2	0.00980	0.00020	2.00	0.01050	0.00050	5.00
MAE-3	0.00990	0.00010	1.00	0.01780	0.00220	11.00
MAE-4	0.01020	0.00020	2.00	0.0389	0.0011	2.75
MAE-5	0.01010	0.00010	1.00	0.0577	0.0023	4.00
MAE-6	0.00990	0.00010	1.00	0.0758	0.0042	5.25
MAE-7	0.01000	0.00000	0.00	0.1055	0.0055	5.50

FIGURE D $I_{CoK\alpha}$ versus C_{Zn} and C_M



5.9.6 Effect of Zn on Ni

TABLE A Experimental Parameters

Solution	C_{Ni}	C_{Zn}	C_M	$I_{NiK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
MAH-1	0.01000	0.0	0.99000	69 747	0.08	--	--
MAH-2	0.01000	0.01000	0.98000	67 627	0.09	45 072	0.10
MAH-3	0.01000	0.02000	0.97000	64 840	0.09	76 386	0.08
MAH-4	0.01000	0.0400	0.9500	59 596	0.09	133 255	0.07
MAH-5	0.01000	0.0600	0.9300	54 846	0.10	174 000	0.06
MAH-6	0.01000	0.0800	0.9100	52 231	0.10	205 788	0.05
MAH-7	0.01000	0.1200	0.8900	49 250	0.10	244 630	0.05

* 50kV, 20mA

TABLE B Calculation of α_{NiZn}

Solutions	α_{NiZn}
MAH-1/MAF-7	- 0.5339...
MAH-1/MAH-6	- 0.5311...
MAH-1/MAH-5	- 0.5002...
MAH-2/MAH-7	- 0.5189...
MAH-2/MAH-6	- 0.5123...
MAH-3/MAH-7	- 0.5215...
MAH-4/MAH-7	- 0.5422...

α_{NiZn} average = - 0.5229...

std. devn. = ± 0.0138...

$$\alpha_{NiZn} = -0.52^3 \pm 0.01^4$$

$$= -0.52 \pm 0.01$$

TABLE C Calculation of $I_{NiK\alpha}$(corr) and $I^o_{NiK\alpha}$

Solution	Measured	Correction for effect of		$I_{NiK\alpha}$(corr) (cps)
		matrix	zinc	
MAH-1	69 747	- 63 325	--	6 422
MAH-2	67 627	- 60 780	- 354	6 493
MAH-3	64 840	- 57 681	- 678	6 481
MAH-4	59 596	- 51 923	- 1 247	6 426
MAH-5	54 846	- 46 778	- 1 721	6 347
MAH-6	52 231	- 43 590	- 2 185	6 456
MAH-7	49 250	- 39 295	- 3 091	6 864

$I^{o}_{NiK\alpha}$ average = 644 347 cps
std. devn. = ± 5 078 cps
$I^{o}_{NiK\alpha}$ = $(6.44^{3} \pm 0.05^{1}) \times 10^{5}$ cps
= $(6.44 \pm 0.05) \times 10^{5}$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

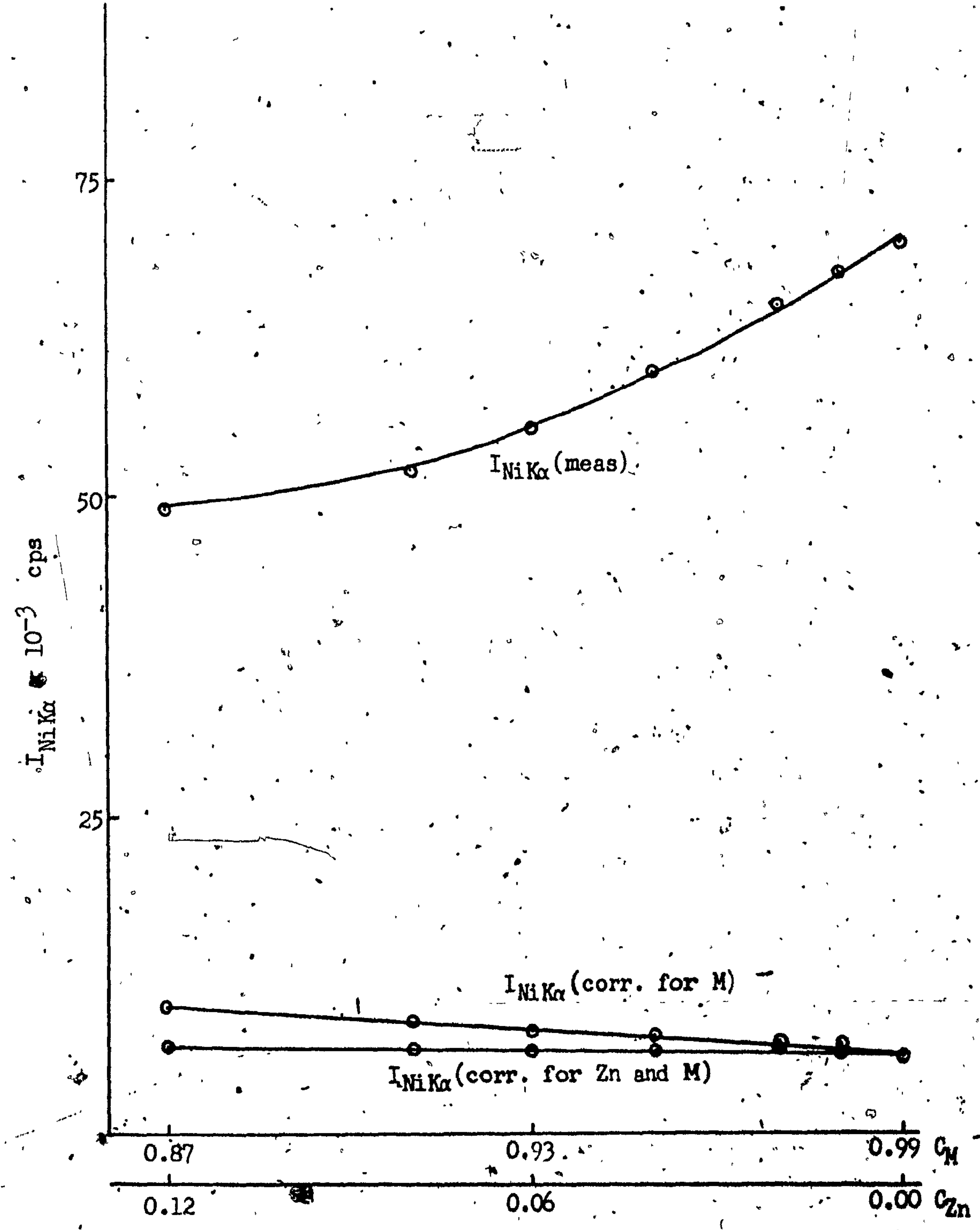
Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{ZnK\alpha}$(corr) (cps)
MAH-2	45 072	- 4 648	+ 523	3 947
MAH-3	76 386	- 69 864	+ 886	7 408
MAH-4	133 255	- 119 364	+ 1 546	15 437
MAH-5	174 000	- 152 580	+ 2 018	23 438
MAH-6	205 788	- 176 574	+ 2 387	31 601
MAH-7	244 630	- 206 676	+ 2 838	40 792

$I^{o}_{ZnK\alpha}$ average = 390 765 cps
std. devn. = ± 12 377 cps
$I^{o}_{ZnK\alpha}$ = $(3.9^{0} \pm 0.1^{2}) \times 10^{5}$ cps
= $(3.9 \pm 0.1) \times 10^{5}$ cps

TABLE C Back-calculation of solution composition

Solution	C_{Ni}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
MAH-1	0.01000	0.00000	0.00	--	--	--
MAH-2	0.01010	0.00010	1.00	0.01020	0.00020	2.00
MAH-3	0.01000	0.00000	0.00	0.01890	0.00110	5.50
MAH-4	0.01000	0.00000	0.00	0.0397	0.0003	0.75
MAH-5	0.00990	0.00010	1.00	0.0607	0.0007	1.16
MAH-6	0.01010	0.00010	1.00	0.0835	0.0035	4.37
MAH-7	0.01090	0.00090	9.00	0.1248	0.0048	4.00

FIGURE D $I_{NiK\alpha}$ versus C_{Zn} and C_M



5.9.7 Effect of Zn on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Zn}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
LP-1	0.01000	0.01000	0.98000	26 759	0.14	36 567	0.12
LP-2	0.01000	0.02000	0.97000	24 858	0.14	65 266	0.10
LP-3	0.01000	0.0400	0.9500	21 335	0.16	106 417	0.07
LP-4	0.01000	0.0600	0.9300	19 178	0.16	136 919	0.07
LP-5	0.01000	0.0800	0.9100	17 241	0.17	159 786	0.06
LP-6	0.01000	0.1000	0.8900	15 660	0.17	173 512	0.06

* 40kV,20mA

TABLE B Calculation of α_{CuZn}

Solutions	α_{CuZn}
LP-1/LP-6	- 0.2105···
LP-1/LP-5	- 0.2093···
LP-1/LP-4	- 0.2074···
LP-2/LP-6	- 0.2057···
LP-2/LP-5	- 0.2032···

α_{CuZn} average = - 0.2072···

std. devn. = ± 0.0029···

α_{CuZn} = $- 0.207^2 \pm 0.002^9$

= $- 0.207 \pm 0.003$

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for effect of		$I_{CuK\alpha}$(corr)
		matrix	zinc	(cps)
LP-1	26 759	- 24 723	- 55	2 431
LP-2	24 858	- 22 318	- 103	2 437
LP-3	21 335	- 18 760	- 177	2 398
LP-4	19 178	- 16 508	- 238	2 431
LP-5	17 241	- 14 522	- 286	2 433
LP-6	15 660	- 12 900	- 324	2 436

$I^o_{CuK\alpha}$ average = 242 171 cps

std. devn. = ± 2 075 cps

$I^o_{CuK\alpha}$ = $(2.42^1 \pm 0.02^0) \times 10^5$ cps

= $(2.42 \pm 0.02) \times 10^5$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of nickel	$I_{ZnK\alpha}$(corr) (cps)
LP-1	36 567	- 33 789	- 95	2 683
LP-2	65 266	- 59 693	- 170	5 403
LP-3	106 417	- 95 324	- 277	10 816
LP-4	136 919	- 120 064	- 356	16 499
LP-5	159 786	- 137 103	- 415	22 268
LP-6	173 512	- 145 608	- 451	27 453

$I^{o}_{ZnK\alpha}$ average = 272 782 cps

std. devn. = ± 3 793 cps

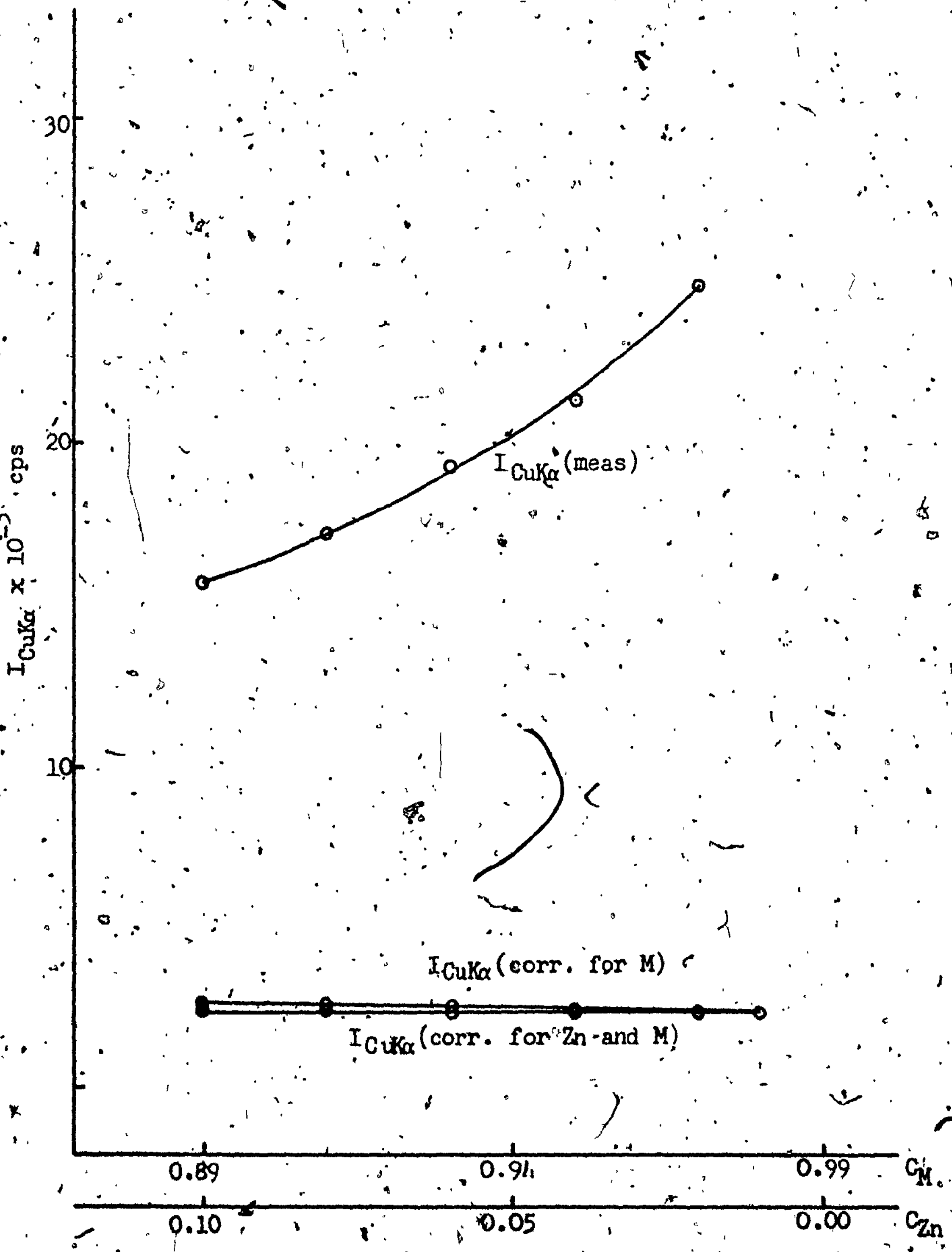
$$I^{o}_{ZnK\alpha} = (2.72^{7} \pm 0.03^{7}) \times 10^{5} \text{ cps}$$

$$= (2.73 \pm 0.04) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of soluti~~on composition~~

Solution	C_{Cu}(calc)	Abs. error	Error %	θ_{Zn}(calc)	Abs. error	ERror %
LP-1	0.01000	0.00000	0.00	0.00980	0.00020	2.00
LP-2	0.01000	0.00000	0.00	0.01980	0.00020	1.00
LP-3	0.00980	0.00020	2.00	0.0394	0.0006	1.50
LP-4	0.01010	0.00010	1.00	0.0610	0.0010	1.66
LP-5	0.01020	0.00020	2.00	0.0839	0.0039	4.87
LP-6	0.01010	0.00010	1.00	0.1017	0.0017	1.70

FIGURE D $I_{CuK\alpha}$ versus C_{Zn} and C_M



5.9.8 Effect of Zn on Sn

TABLE A Experimental Parameters.

Solution	C_{Sn}	C_{Zn}	C_{Cl}	C_M	$I_{SnK\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
LX-1	0.01000	0.0	0.0144	0.9756	20 366	0.16	--	--
LX-2	0.01000	0.01000	0.0144	0.9659	17 297	0.17	31 011	0.13
LX-3	0.01000	0.02000	0.0137	0.9563	16 095	0.18	56 624	0.10
LX-4	0.01000	0.0400	0.0139	0.9361	13 351	0.20	94 690	0.07
LX-5	0.01000	0.0600	0.0173	0.9127	11 386	0.21	120 409	0.07
LX-6	0.01000	0.0800	0.0141	0.8959	9 841	0.22	147 224	0.06
LX-7	0.01000	0.1000	0.0139	0.8761	8 910	0.23	164 052	0.06

* 40kV,20mA

TABLE B Calculation of α_{SnZn}

Solutions	α_{SnZn}
LX-1/LX-7	− 0.2174...
LX-1/LX-5	− 0.2073...
LX-2/LX-7	− 0.2855...
LX-2/LX-6	− 0.2597...
LX-2/LX-5	− 0.2997...
LX-3/LX-7	− 0.2327...
LX-1/LX-6	− 0.1883...
LX-3/LX-6	− 0.1869...

α_{SnZn} average = − 0.2347...

std. devn. = ± 0.0429...

$$\alpha_{SnZn} = -0.23^{5} \pm 0.04^{3}$$

$$= -0.23 \pm 0.04$$

TABLE C Calculation of $I_{SnK\alpha}$ corr) and $I^{o}_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	zinc	$I_{SnK\alpha}$(corr) (cps)
LX-1	20 366	− 18 955	− 248	--	1 163
LX-2	17 297	− 15 939	− 206	− 41	1 111
LX-3	16 095	− 14 684	− 187	− 76	1 148
LX-4	13 351	− 11 923	− 157	− 126	1 145
LX-5	11 386	− 9 914	− 167	− 160	1 145
LX-6	9 841	− 8 411	− 117	− 185	1 128
LX-7	8 910	− 7 447	− 105	− 209	1 149

$I^{o}_{SnK\alpha}$ average = 114 120 cps
std. devn. = ± 1 678 cps
$I^{o}_{SnK\alpha}$ = $(1.14^{1} \pm 0.01^{6}) \times 10^{5}$ cps
= $(1.14 \pm 0.02) \times 10^{5}$ cps

Table D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

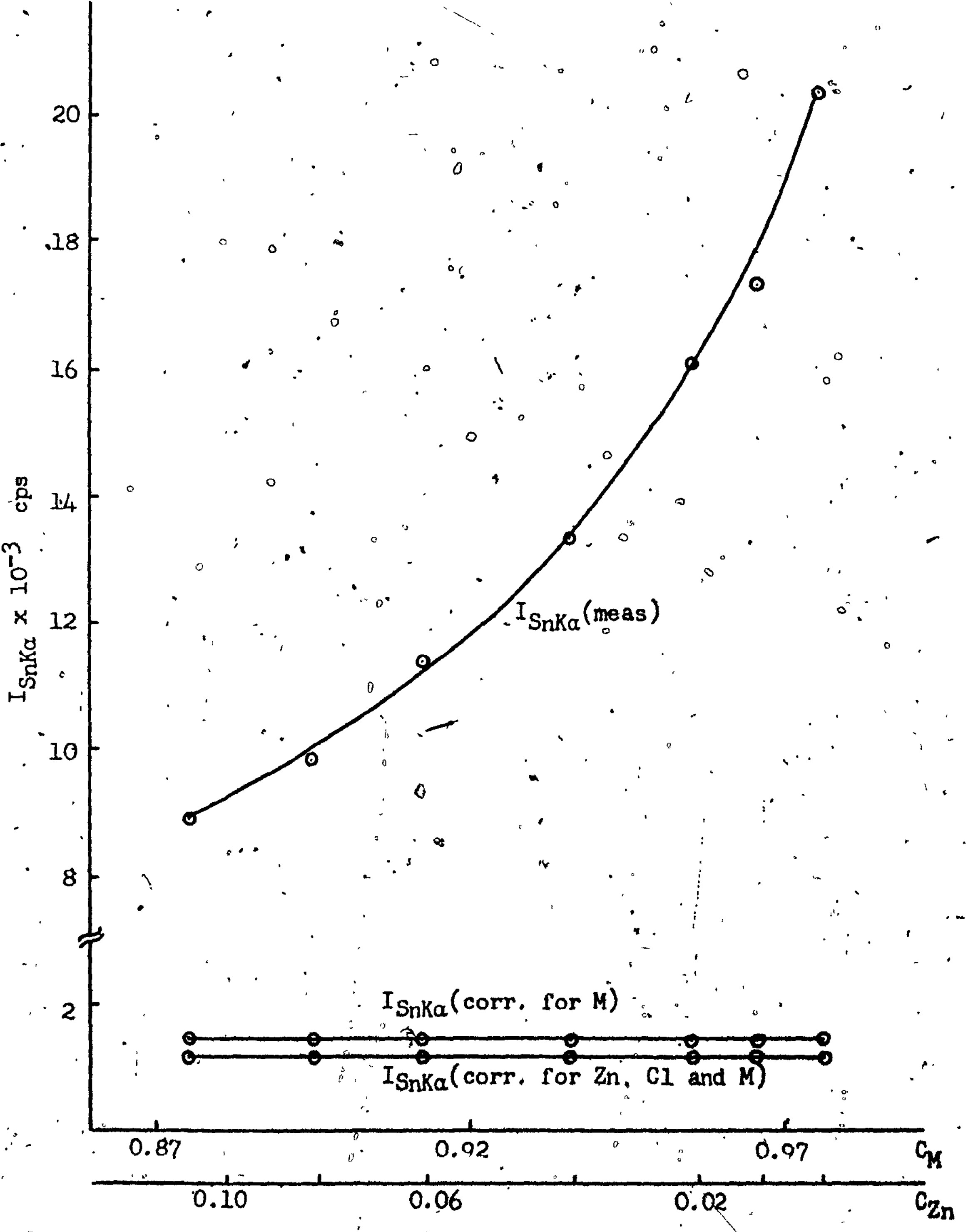
Solution	Measured	Correction for effect of			$I_{ZnK\alpha}$(corr) (cps)
		matrix	chlorine	tin	
LX-2	31 011	- 28 243	- 143	+ 117	2 743
LX-3	56 624	- 51 058	- 254	+ 215	5 527
LX-4	94 690	- 83 578	- 430	+ 359	11 041
LX-5	120 409	- 103 622	- 681	+ 456	16 562
LX-6	147 224	- 124 367	- 679	+ 558	22 736
LX-7	164 052	- 135 519	- 746	+ 622	28 409

$I^{o}_{ZnK\alpha}$ average = 278 608 cps
std. devn. = ± 4 070 cps
$I^{o}_{ZnK\alpha}$ = $(2.78^{6} \pm 0.04^{1}) \times 10^{5}$ cps
= $(2.79 \pm 0.04) \times 10^{5}$ cps

TABLE E Back-calculation of solution composition

ClKα intensity not taken, and back-calculation of solution composition not carried out.

FIGURE D $I_{SnK\alpha}$ versus C_{Zn} and C_M



5.9.9 Effect of Zn on Pb

TABLE A Experimental Parameters

Solution	C_{Pb}	C_{Zn}	C_M	$I_{PbL\alpha}$ (cps)	s(%)	$I_{ZnK\alpha}$* (cps)	s(%)
LU-1	0.01000	0.0	0.99000	14 242	0.19	--	--
LU-2	0.01000	0.01000	0.98000	10 687	0.22	33 586	0.12
LU-3	0.01000	0.02000	0.97000	8 525	0.24	60 645	0.10
LU-4	0.01000	0.0400	0.9500	6 111	0.30	100 664	0.07
LU-5	0.01000	0.0600	0.9300	4 787	0.32	129 661	0.07
LU-6	0.01000	0.0800	0.9100	3 875	0.36	147 620	0.07
LU-7	0.01000	0.1000	0.8900	3 627	0.39	164 685	0.06
LU-8	0.05000	0.0500	0.9000	19 042	0.16	81 394	0.08

* 40kV, 20mA

TABLE B Calculation of α_{PbZn}

Solutions	α_{PbZn}
LU-1/LU-7	0.3637···
LU-1/LU-6	0.3576···
LU-2/LU-7	0.3700···
LU-2/LU-6	0.3613···
LU-2/LU-5	0.3287···
LU-3/LU-7	0.3664···

α_{PbZn} average = 0.3579···

std. devn. = ± 0.0149···

$\alpha_{PbZn} = 0.35^7 \pm 0.01^4$

$= 0.36 \pm 0.01$

TABLE C Calculation of $I_{PbL\alpha}$(corr) and $I^o_{PbL\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{PbL\alpha}$(corr) (cps)
LU-1	14 242	- 13 675	--	567
LU-2	10 687	- 10 158	+ 38	567
LU-3	8 525	- 8 020	+ 61	566
LU-4	6 111	- 5 631	+ 87	567
LU-5	4 787	- 4 318	+ 102	572
LU-6	3 875	- 3 420	+ 111	566
LU-7	3 267	- 2 820	+ 117	564
LU-8	19 042	- 16 622	+ 340	2 760

$I^{o}_{PbL\alpha}$ average = 56 700 cps

std. devn. = ± 212 cps

$I^{o}_{PbL\alpha}$ = $(5.67^{0} \pm 0.02^{1}0 \times 10^{4}$ cps

= $(5.67 \pm 0.02) \times 10^{4}$ cps

TABLE D Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of		$I_{ZnK\alpha}$(corr)
		matrix	lead	(cps)
LU-2	33 586	− 31 035	+ 90	2 641
LU-3	60 645	− 55 467	+ 162	5 340
LU-4	100 664	− 90 170	+ 270	10 764
LU-5	129 661	− 113 699	+ 347	16 309
LU-6	147 520	− 126 578	+ 395	21 337
LU-7	164 685	− 138 200	+ 441	26 926
LU-8	81 394	− 69 072	+ 1 091	13 413

$I^{o}_{ZnK\alpha}$ average = 268 042 cps

std. devn. = ± 2 417 cps

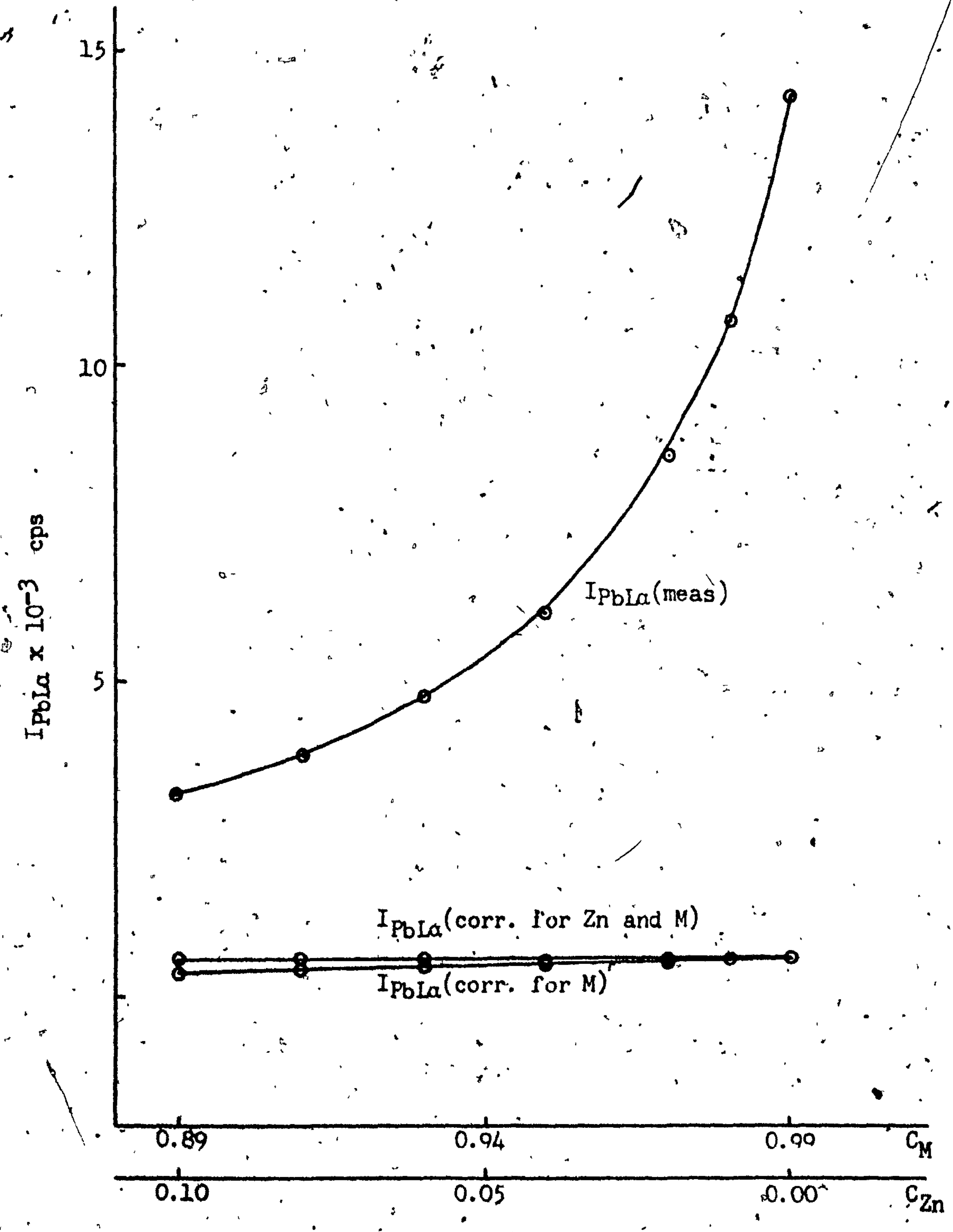
$I^{o}_{ZnK\alpha}$ = $(2.68^{0} \pm 0.02^{4}) \times 10^{5}$

= $(2.68 \pm 0.02) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Pb}(calc)	Abs. error	Error %	C_{Zn}(calc)	Abs. error	Error %
LU-1	0.01000	0.00000	0.00	--	--	--
LU-2	0.01000	0.00000	0.00	0.00980	0.00020	2.00
LU-3	0.01000	0.00000	0.00	0.0199	0.0001	0.50
LU-4	0.01010	0.00010	1.00	0.0403	0.0003	0.75
LU-5	0.01040	0.00040	4.00	0.0619	0.0019	3.30
LU-6	0.00990	0.00010	1.00	0.0791	0.0009	0.12
LU-7	0.01010	0.00010	1.00	0.1012	0.0012	1.20
LU-8	0.0475	0.0025	5.00	0.0487	0.0013	2.60

FIGURE D $I_{PbL\alpha}$ versus C_{Zn} and C_M



5.10 Effects of Cadmium

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Iron	1 ml = 0.0466 ± 0.0001 g	(dil. HNO_3)
Cadmium	1 ml = 0.2000 ± 0.0001 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for the metal or for chloride, set the significant figure for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	LZI	1:450 Cl	1:225 to 1:2250
Fe	F	1:200	1:100 to 1:1000

Intensities: The operating parameters for each solution series were:-

Element	Cl	Fe	Cd
Target	Cr	W	W
kV	50	40	*
mA	36	24	*
Coll^n	coarse	fine	fine
Crystal	PET	LiF	LiF
Counter	PF	Sc	Sc
Time (s)	20	20	20
Counts	3	5	3
Rad^n	Kα	Kα	Kα

* See each series

The tabulated counts for each series represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations: Calculation of α_{ACd} (absence of chlorine as fourth component) Equation (43)

Calculation of α_{ACd} (presence of chlorine as fourth component) Equation (44)

Calculation of $I_A(\text{corr})$	Equation (45) or a modification
Calculation of $I_{\underline{A}}^{o}$	$I_A(\text{corr})/C_A$

5.10.1 Effect of Cd on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Cd}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{CdK\alpha}$* (cps)	s(%)
LZI-1	0.01899	0.00	0.98101	5 947	0.29	--	--
LZI-2	0.01899	0.01000	0.97101	5 759	0.30	12 900	0.20
LZI-3	0.01899	0.02000	0.96101	5 651	0.30	21 785	0.16
LZI-4	0.01899	0.0400	0.9410	5 402	0.31	33 177	0.11
LZI-5	0.01899	0.0600	0.9210	5 152	0.32	39 688	0.11
LZI-6	0.01899	0.0800	0.9010	4 931	0.32	43 974	0.10
LZI-7	0.01899	0.1000	0.8810	4 780	0.32	47 928	0.10

* 40kV, 20mA

TABLE B Calculation of α_{ClCd}

Solutions	α_{ClCd}
LZI-1/LZI-7	1.3007···
LZI-1/LZI-6	1.3905···
LZI-1/LZI-5	1.3880···
LZI-2/LZI-7	1.2251···
LZI-2/LZI-6	1.3116···
LZI-3/LZI-7	1.2638···

α_{ClCd} average = 1.3133···

std. devn. = ± 0.0662···

$$\alpha_{ClCd} = 1.31^3 \pm 0.06^6$$

$$= 1.31 \pm 0.07$$

TABLE C Calculation of $I_{ClK\alpha}(corr)$ and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cadmium	$I_{ClK\alpha}$(corr) (cps)
LZI-1	5 947	- 1 960	--	3 987
LZI-2	5 759	- 1 879	+ 76	3 956
LZI-3	5 651	- 1 825	+ 148	3 974
LZI-4	5 402	- 1 708	+ 284	3 978
LZI-5	5 152	- 1 594	+ 406	3 964
LZI-6	4 931	- 1 493	+ 518	3 956
LZI-7	4 780	- 1 415	+ 628	3 993

$I^{o}_{ClK\alpha}$ average = 209 192 cps

std. devn. = ± 769 cps

$$I^{o}_{ClK\alpha} = (2.091^{9} \pm 0.007^{6}) \times 10^{5} \text{ cps}$$

$$= (2.092 \pm 0.008) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{CdK\alpha}$(corr) and $I^{o}_{CdK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	$I_{CdK\alpha}$(corr) (cps)
LZI-2	12 900	- 12 095	- 210	595
LZI-3	21 785	- 20 215	- 355	1 215
LZI-4	33 177	- 30 146	- 540	2 491
LZI-5	39 688	- 35 296	- 646	3 746
LZI-6	43 974	- 38 258	- 716	5 000
LZI-7	47 928	- 40 772	- 780	6 376

$I^{o}_{CdK\alpha}$ average = 61 865 cps

std. devn. = ± 1 503 cps

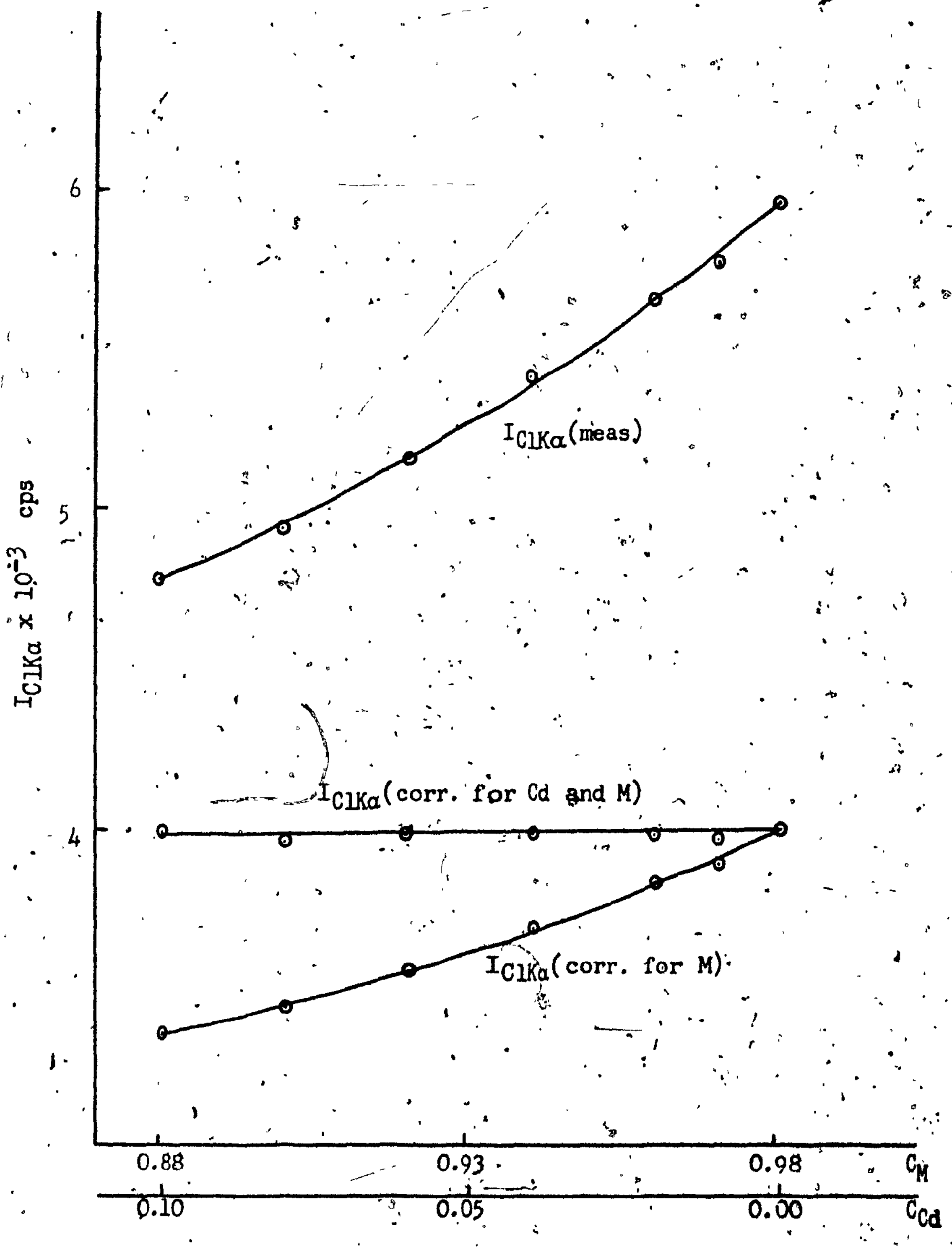
$$I^{o}_{CdK\alpha} = (6.1^{8} \pm 0.1^{5}) \times 10^{4} \text{ cps}$$

$$= (6.2 \pm 0.2) \times 10^{4} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Cd}(calc)	Abs. error	Error %
LZI-1	0.01906	0.00007	0.36	—	—	—
LZI-2	0.01889	0.00010	0.52	0.00950	0.00050	5.00
LZI-3	0.01898	0.00001	0.05	0.01940	0.00060	3.00
LZI-4	0.01904	0.00005	0.26	0.0405	0.0005	1.25
LZI-5	0.01901	0.00002	0.10	0.0615	0.0015	2.50
LZI-6	0.01901	0.00002	0.10	0.0826	0.0026	3.25
LZI-7	0.01955	0.00056	2.94	0.1123	0.0123	12.30

FIGURE D $I_{ClK\alpha}$ versus C_{Cd} and C_M



5.10.2 Effect of Cd on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Cd}	C_M	$I_{FeK\alpha}$ (cps)	s(%)	$I_{CdK\alpha}$* (cps)	s(%)
F-1	0.00930	0.0	0.99070	11 308	0.21	--	—
F-2	0.00930	0.01000	0.98070	9 520	0.23	12 245	0.20
F-3	0.00930	0.0200	0.9707	8 276	0.25	20 740	0.16
F-4	0.00930	0.0300	0.9607	7 326	0.26	26 115	0.14
F-5	0.00930	0.0400	0.9507	6 550	0.28	30 597	0.13
F-6	0.00930	0.0500	0.9407	5 852	0.30	34 710	0.12
F-7	0.00930	0.0600	0.9307	5 444	0.31	36 533	0.12
F-8	0.00930	0.0693	0.9200	4 973	0.32	39 698	0.11
F-9	0.00930	0.0800	0.9107	4 641	0.33	42 262	0.11
F-10	0.00930	0.0900	0.9007	4 237	0.34	44 375	0.10

* 40kV, 20mA

TABLE B Calculation of α_{FeCd}

Solutions	α_{FeCd}
F-1/F-10	1.1585···
F-1/F-9	1.0919···
F-2/F-10	1.1762···
F-2/F-9	1.1274···
F-2/F-8	1.0873···
F-3/F-9	1.0866···
F-3/F-8	1.1562···

α_{FeCd} average = 1.1277···

std. devn. = ± 0.0383···

$$\alpha_{FeCd} = 1.12^8 + 0.03^8$$

$$= 1.13 \pm 0.04$$

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^o_{FeK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of cadmium	$I_{FeK\alpha}$(corr) (cps)
F-1	11 308	- 10 049	--	1 259
F-2	9 520	- 8 366	+ 107	1 261
F-3	8 276	- 7 198	+ 187	1 265
F-4	7 326	- 6 306	+ 248	1 268
F-5	6 550	- 5 580	+ 295	1 265

F-6	5 852	- 4 933	+ 330	1 249
F-7	5 444	- 4 540	+ 368	1 272
F-8	4 973	- 4 102	+ 389	1 260
F-9	4 691	- 3 787	+ 419	1 273
F-10	4 237	- 3 419	+ 430	1 248

$I^{o}_{FeK\alpha}$ average = 135.699 cps

std. devn. = ± 916 cps

$I^{o}_{FeK\alpha}$ = $(1.356^{9} \pm 0.009^{1}) \times 10^{5}$ cps

= $(1.357 \pm 0.009) \times 10^{5}$ cps

TABLE D Calculation of $I_{CdK\alpha}$(corr) and $I^{o}_{CdK\alpha}$

Solution	Measured	Correction for effect of		$I_{CdK\alpha}$(corr) (cps)
		matrix	iron	
F-2	12 245	- 11 587	- 54	604
F-3	20 740	- 19 426	- 92	1 222
F-4	26 115	- 24 208	- 116	1 791
F-5	30 597	- 28 067	- 125	2 395
F-6	34 710	- 31 505	- 154	3 051
F-7	36 533	- 32 807	- 162	3 564
F-8	39 698	- 35 266	- 176	4 256
F-9	42 263	- 37 136	- 187	4 940
F-10	44 375	- 38 564	- 196	5 615

$I^{o}_{CdK\alpha}$ average = 60 783 cps

std. devn. = ± 1 008 cps

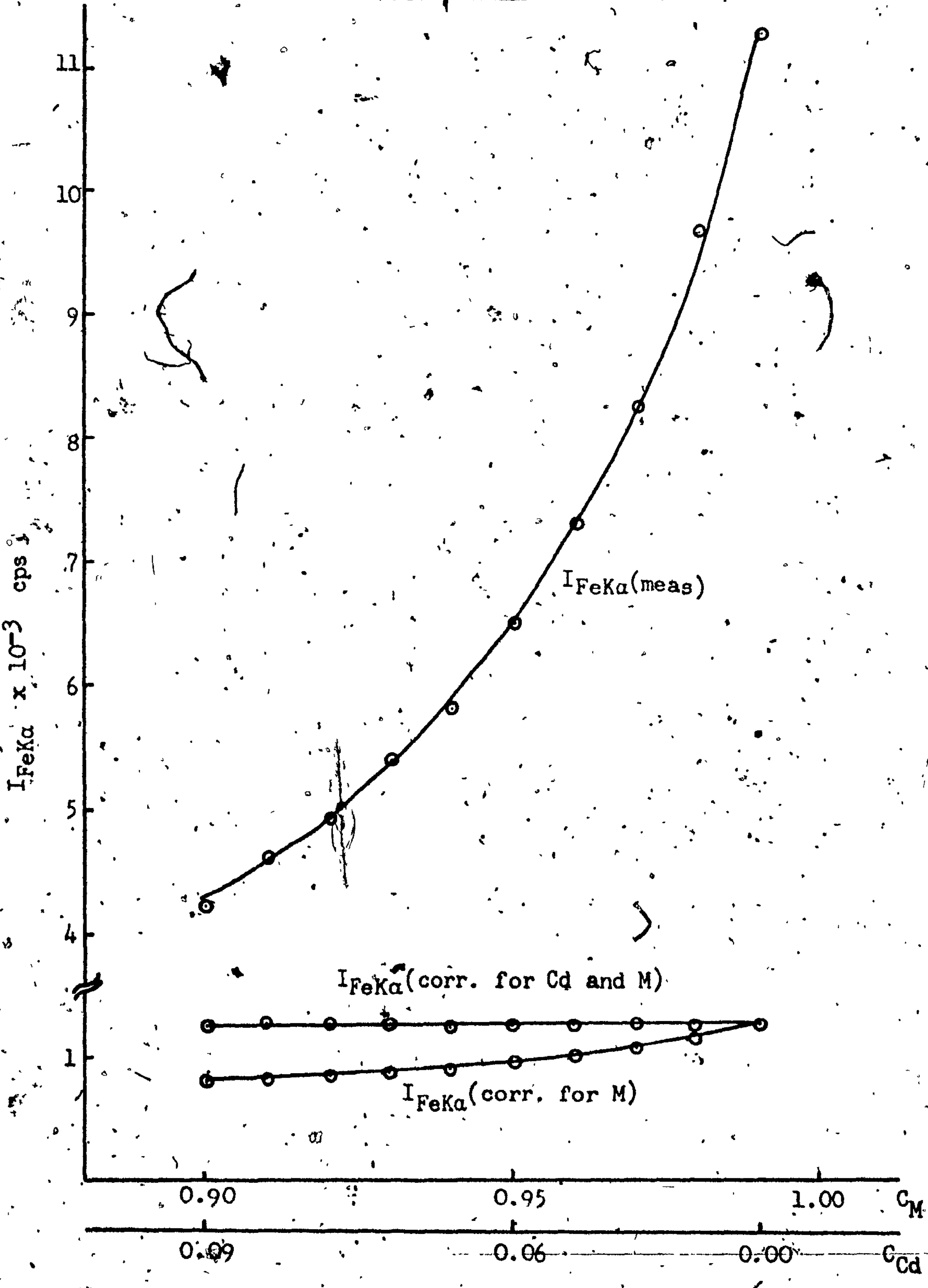
$I^{o}_{CdK\alpha}$ = $(6.0^{7} \pm 0.1^{0}) \times 10^{4}$ cps

= $(6.1 \pm 0.1) \times 10^{4}$ cps

TABLE E Back-calculation of solution composition

Omitted - not germane to analytical investigation

FIGURE D $I_{FeK\alpha}$ versus C_{Cd} and C_M



5.11 Effects of Tin

Solutions: The metal concentrations for each series were obtained by dilution of the following stock solutions:-

Iron	1 ml = 0.050000 ± 0.000008 g	(dil. $HCl-HNO_3$)
Copper	1 ml = 0.20000 ± 0.00005 g	(dil. HNO_3)
Zinc	1 ml = 0.20000 ± 0.00005 g	(dil. HNO_3)
Tin (Cl)	1 ml = 0.10000 ± 0.00002 g	(dil. HCl)
Tin (CuZn)	1 ml = 0.20000 ± 0.00004 g	(dil. $HCl-HNO_3$)
Tin (Pb)	1 ml = 0.10000 ± 0.00005 g	(dil. HF)
Lead	1 ml = 0.10000 ± 0.00005 g	(dil. HNO_3)

Chlorine, where added as 1:3 HCl, or present from a stock solution, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

The least precise value, for metal or for chloride, sets the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBG	1:420	1:210 to 1:2100
Fe	JC	1:100	1:50 to 1:500
Cu	LT	1:164	1:82 to 1:820
Zn	LY	1:300	1:150 to 1:1500
Pb	LZB	1:440	1:220 to 1:2200

Intensities: The operating parameters for each solution series were:-

Element	Cl	Fe	Cu	Zn	Sn	Pb
Target	Cr	W	W	W	W	W
kV	50	40	40	40	*	50
mA	36	20	20	20	*	20
Coll^n	coarse	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20
Counts	3	5	5	5	5	5
Rad^n	Ka	Ka	Ka	Ka	Ka	La

* See each series

The tabulated counts for each series represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as the sigma counting error in percent.

Equations:	Calculation of α_{ASn} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{ASn} (presence of chlorine as fourth component)	Equation (44)
	Calculation of I_A(corr)	Equation (45) or a modification
	Calculation of I_A^o	$I_A(corr)/C_A$

5.11.1 Effect of Sn on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Sn}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{SnK\alpha}$* (cps)	s(%)
MBG-1	0.00979	0.01000	0.98021	2 976	0.41	23 429	0.15
MBG-2	0.01958	0.02000	0.96042	5 717	0.31	39 270	0.13
MBG-3	0.0294	0.0300	0.9406	8 380	0.25	52 286	0.10
MBG-4	0.0490	0.0500	0.9010	13 062	0.20	65 886	0.10
MBG-5	0.0685	0.0700	0.8614	17 057	0.17	71 739	0.10
MBG-6	0.0783	0.0800	0.8417	19 065	0.16	78 579	0.10

* 50kV,20mA

TABLE B Calculation of α_{ClSn}

Solutions	α_{ClSn}
MBG-1/MBG-6	1.7818···
MBG-1/MBG-5	1.8780···
MBG-1/MBG-4	1.7271···
MBG-2/MBG-6	1.6997···
MBG-2/MBG-5	1.8047···
MBG-3/MBG-6	1.8842···

α_{ClSn} average = 1.7959···

std. devn. = ± 0.0759···

α_{ClSn} = $1.79^6 \pm 0.07^6$

= 1.80 ± 0.08

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^0_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of tin	$I_{ClK\alpha}$(corr) (cps)
MBG-1	2 976	- 980	+ 53	2 049
MBG-2	5 717	- 1 845	+ 205	4 077
MBG-3	8 380	- 2 648	+ 451	6 183
MBG-4	13 062	- 3 955	+ 1 173	10 281
MBG-5	17 057	- 4 937	+ 2 144	14 264
MBG-6	19 065	- 5 392	+ 2 739	16 412

$I^0_{ClK\alpha}$ average = 209 246 cps

std. devn. = ± 854 cps

$I^0_{ClK\alpha}$ = $(2.092^4 \pm 0.008^5) \times 10^5$ cps

= $(2.092 \pm 0.008) \times 10^5$ cps

TABLE D Calculation of $I_{SnK\alpha}(corr)$ and $I^{o}_{SnK\alpha}$

Solution	Measured	Correction for effect of		$I_{SnK\alpha}(corr)$ (cps)
		matrix	chlorine	
MBG-1	23 429	- 21 909	- 194	1 326
MBG-2	39 270	- 35 981	- 651	2 638
MBG-3	52 286	- 46 919	- 1 301	4 066
MBG-4	65 886	- 56 635	- 2 732	6 519
MBG-5	71 739	- 58 957	- 4 164	8 618
MBG-6	78 571	- 63 095	- 5 213	10 271

$I^{o}_{SnK\alpha}$ average = 130 319 cps

std. devn. = ± 4 255 cps

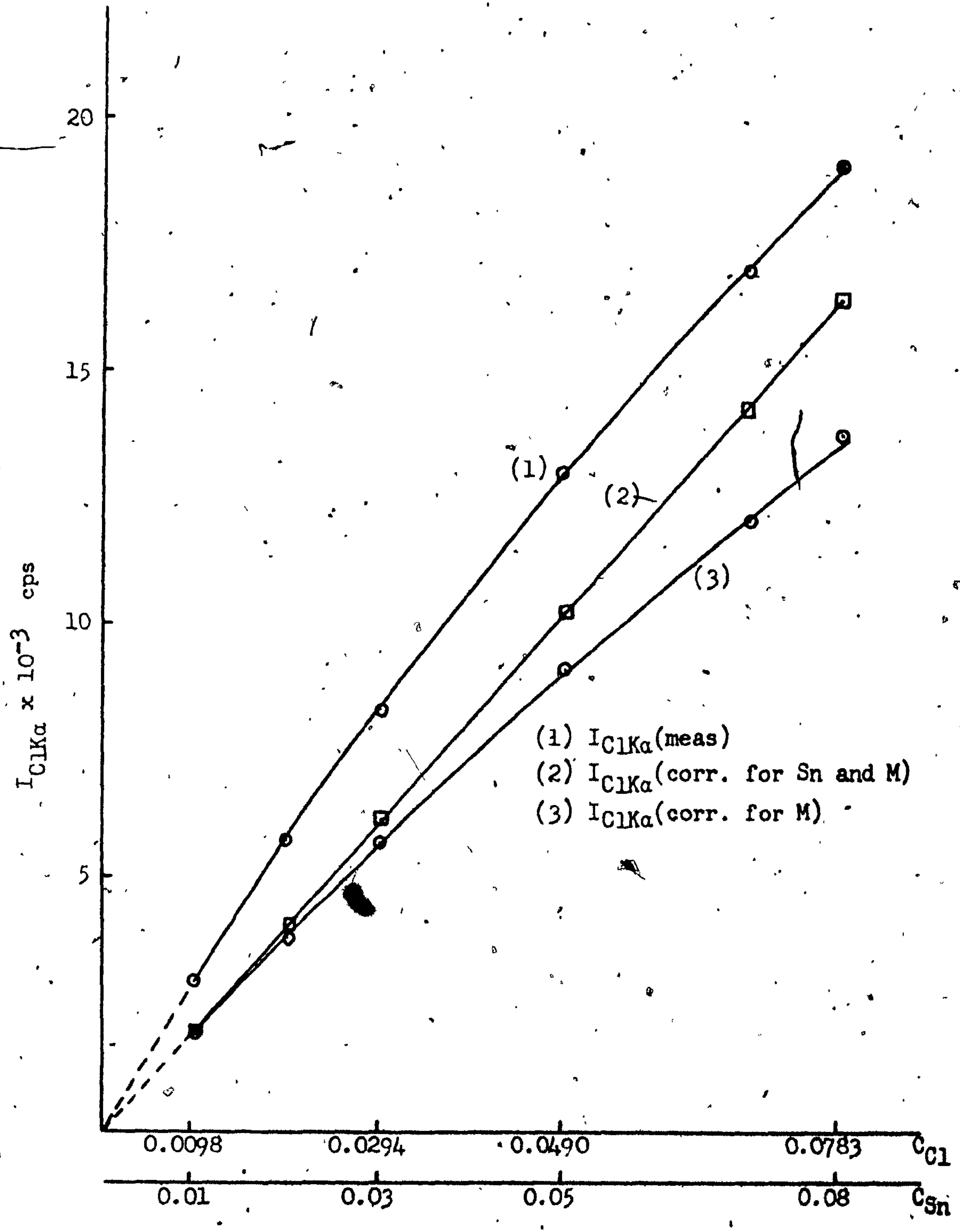
$$I^{o}_{SnK\alpha} = (1.30^{3} \pm 0.04^{2}) \times 10^{5} \text{ cps}$$

$$= (1.30 \pm 0.04) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Sn}(calc)	Abs error	Error %
MBG-1	0.00979	0.00000	0.00	0.01010	0.00010	1.00
MBG-2	0.01948	0.00010	0.51	0.02000	0.00000	0.00
MBG-3	0.0297	0.0003	1.00	0.0314	0.0014	4.66
MBG-4	0.0490	0.0000	0.00	0.0490	0.0010	2.00
MBG-5	0.0664	0.0021	3.06	0.0602	0.0098	14.00
MBG-6	0.0774	0.0009	1.15	0.0751	0.0049	6.12

FIGURE D $I_{ClK\alpha}$ versus C_{Sn} and C_{Cl}



5.11.2 Effect of Sn on Fe

TABLE A Experimental Parameters

Solution	C_{Fe}	C_{Sn}	C_{Cl}	C_M	$I_{FeK\alpha}$ (cps)	$\bar{s}$(%)
JC-1	0.01000	0.0	0.00655	0.98345	10 105	0.22
JC-2	0.01000	0.0100	0.02030	0.9597	7 704	0.27
JC-3	0.01000	0.0200	0.0336	0.9364	6 352	0.29
JC-4	0.01000	0.0300	0.0473	0.9127	5 328	0.31
JC-5	0.01000	0.0400	0.0601	0.8891	4 549	0.33
JC-6	0.01000	0.0500	0.0745	0.8655	4 034	0.35
JC-7	0.01000	0.0600	0.0879	0.8421	3 595	0.37
JC-8	0.01000	0.0700	0.100	0.819^1	3 230	0.40
JC-9	0.01000	0.0800	0.115	0.794^9	2 939	0.41
JC-10	0.01000	0.0900	0.128	0.771^3	2 724	0.43

TABLE B Calculation of α_{FeSn}

Solutions	α_{FeSn}
JC-1/JC-10	1.5130···
JC-1/JC-9	1.5669···
JC-1/JC-8	1.5699···
JC-2/JC-10	1.3221···
JC-2/JC-9	1.3901···
JC-2/JC-8	1.3839···
JC-3/JC-10	1.4689···
JC-3/JC-9	1.5820···
JC-3/JC-8	1.5901···
JC-4/JC-10	1.4142···

α_{FeSn} average = 1.4801···

std. devn. = ± 0.0977···

$\alpha_{FeSn} = 1.48^0 \pm 0.09^7$

= [illegible].48 ± 0.10

TABLE C Calculation of $I_{FeK\alpha}$(corr) and $I^o_{FeK\alpha}$

Solution	Measured	Correction for effect of			$I_{FeK\alpha}$(corr) (cps)
		matrix	chlorine	tin	
JC-1	10 105	- 8 912	+ 3	--	1 196
JC-2	7 704	- 6 630	+ 7	+ 114	1 195
JC-3	6 352	- 5 334	+ 10	+ 188	1 216
JC-4	5 328	- 4 362	+ 12	+ 236	1 214
JC-5	4 549	- 3 626	+ 13	+ 269	1 205

JC-6	4 034	- 3 129	+ 14	+ 298	1 217
JC-7	3 595	- 2 714	+ 15	+ 319	1 215
JC-8	3 230	- 2 372	+ 15	+ 335	1 208
JC-9	2 939	- 2 095	+ 16	+ 348	1 208
JC-10	2 724	- 1 883	+ 16	+ 363	1 220

$I^{o}_{FeK\alpha}$ average = 120 940 cps

std. devn. = ± 866 cps

$$I^{o}_{FeK\alpha} = (1.209^{4} \pm 0.008^{6}) \times 10^{5} \text{ cps}$$

$$= (1.209 \pm 0.009) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{SnK\alpha}$(corr) and $I^{o}_{SnK\alpha}$

SnKα counts not taken

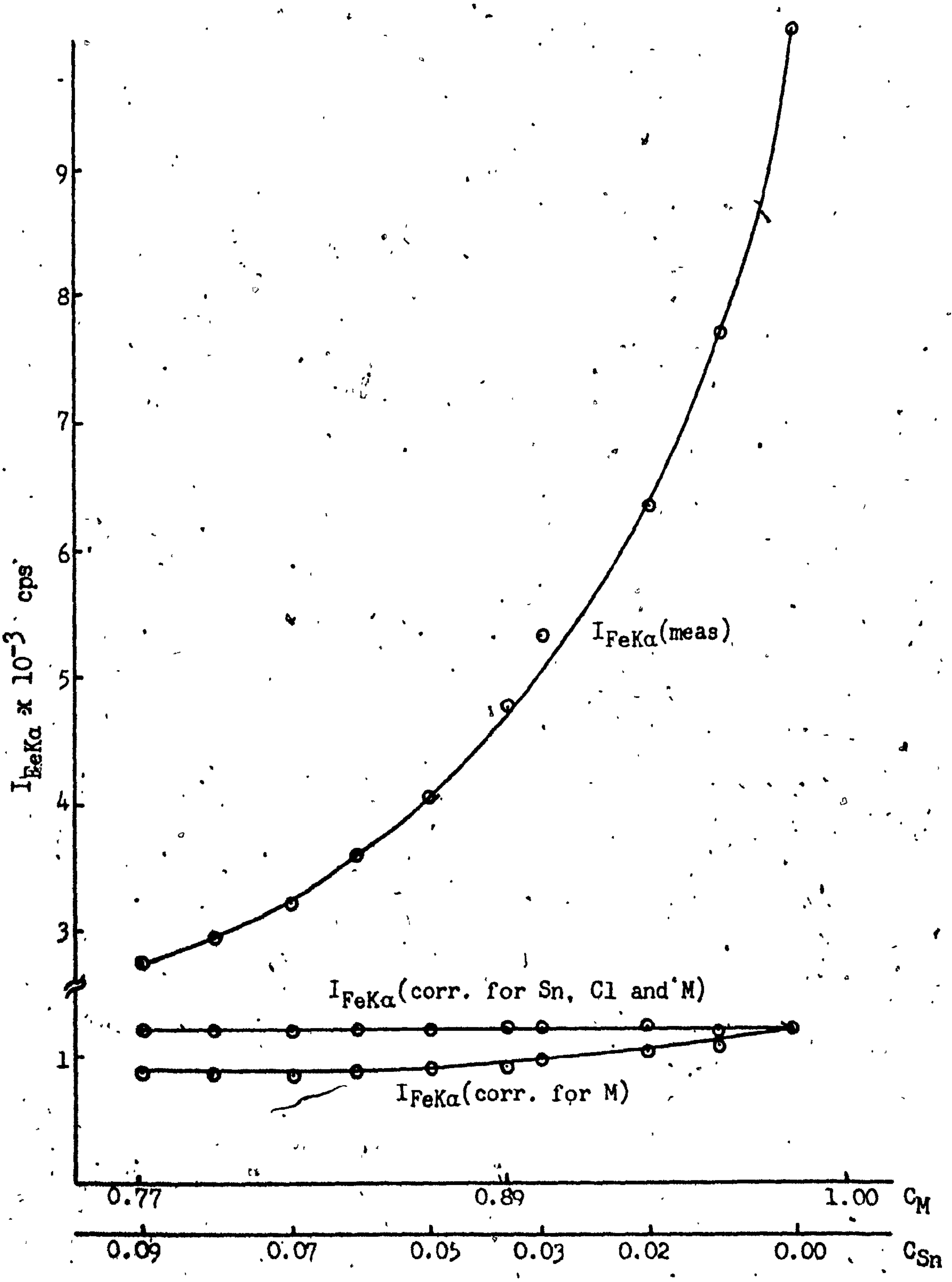
TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

ClKα counts not taken

TABLE F Back-calculation of solution composition

No back-calculation - SnKα and ClKα counts not taken

FIGURE D $I_{FeK\alpha}$ versus C_{Sn} and C_M



5.11.3 Effect of Sn on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Sn}	C_{Cl}	C_M	$I_{CuK\alpha}$ (cps)	s(%)
LT-1	0.01000	--	0.0092	0.9808	27 080	0.14
LT-2	0.01000	0.01000	0.0500	0.9300	18 221	0.17
LT-3	0.01000	0.02000	0.0652	0.9048	13 813	0.19
LT-4	0.01000	0.0400	0.090^9	0.859^1	11 356	0.21
LT-5	0.01000	0.0600	0.111^9	0.818^1	9 520	0.23
LT-6	0.01000	0.0800	0.124^8	0.785^2	8 029	0.25
LT-7	0.01000	0.1000	0.155^4	0.734^6	7 071	0.27

$I_{SnK\alpha}$* (cps)	s(%)
--	--
16 854	0.17
27 595	0.15
43 120	0.11
52 901	0.10
59 601	0.10
63 941	0.10

* 40kV, 20mA

TABLE B Calculation of α_{CuSn}

Solutions	α_{CuSn}
LT-1/LT-7	0.6207...
LT-1/LT-6	0.7542...
LT-1/LT-5	0.6710...
LT-2/LT-7	0.6030...
LT-2/LT-6	0.7870...
LT-2/LT-5	0.6707...

α_{CuSn} average = 0.6844...

std. devn. = ± 0.0727...

$$\alpha_{CuSn} = 0.68^4 \pm 0.07^3$$

$$= 0.68 \pm 0.07$$

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^o_{CuK\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	tin	$I_{CuK\alpha}$(corr) (cps)
LT-1	27 080	- 24 592	- 62	--	2 426
LT-2	18 221	- 15 690	- 228	+ 125	2 428

LT-3	13 813	- 11 572	- 225	+ 189	2 205
LT-4	11 356	- 9 033	- 258	+ 311	2 376
LT-5	9 520	- 7 211	- 266	+ 391	2 434
LT-6	8 029	- 5 837	- 250	+ 439	2 381
LT-7	7 071	- 4 809	- 275	+ 484	2 471

$I^{o}_{CuK\alpha}$ average = 238 871 cps

std. devn. = ± 8 729 cps

$I^{o}_{CuK\alpha}$ = $(2.38^{8} \pm 0.08^{7}) \times 10^{5}$ cps

= $(2.39 \pm 0.09) \times 10^{5}$ cps

TABLE D Calculation of $I_{SnK\alpha}$(corr) and $I^{o}_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	copper	$I_{SnK\alpha}$(corr) (cps)
LT-2	16 854	- 14 953	- 714	- 42	1 145
LT-3	27 595	- 23 819	- 1 524	- 69	2 183
LT-4	43 120	- 35 340	- 3 319	- 109	4 352
LT-5	52 901	- 41 287	- 5 013	- 133	6 468
LT-6	59 601	- 44 646	- 6 299	- 150	8 506
LT-7	63 941	- 44 810	- 8 415	- 161	10 555

$I^{o}_{SnK\alpha}$ average = 108 687 cps

std. devn. = ± 3 169 cps

$I^{o}_{SnK\alpha}$ = $(1.08^{7} \pm 0.03^{2}) \times 10^{5}$ cps

= $(1.09 \pm 0.03) \times 10^{5}$ cps

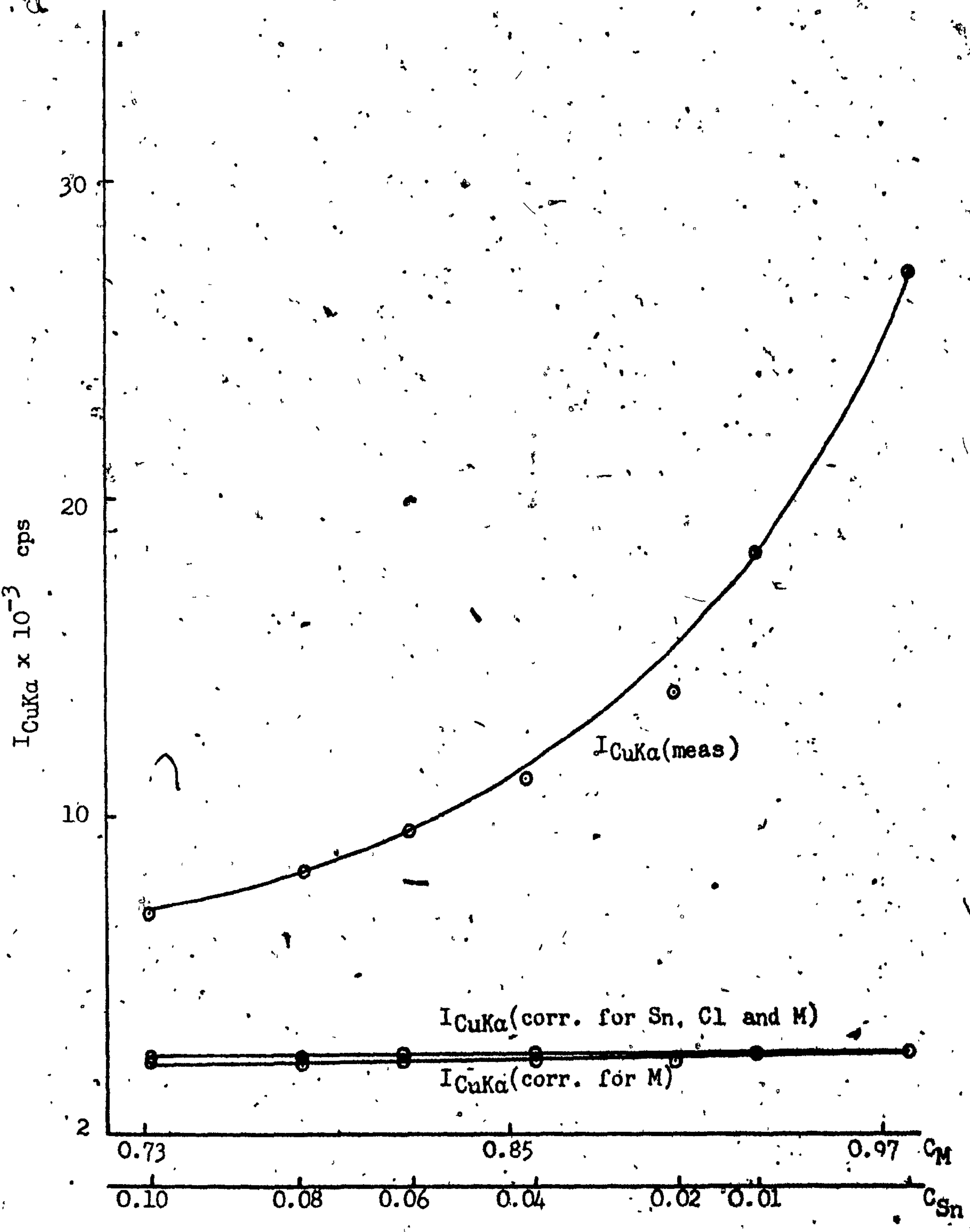
TABLE E Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

ClKα counts not taken

TABLE F ~~Back-calculation~~ Back-calculation of solution composition

No back-calculation - ClKα counts not taken

FIGURE D $I_{CuK\alpha}$ versus C_{Sn} and C_M



5.11.4 Effect of Sn on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Sn}	C_{Cl}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{SnK\alpha}$* (cps)	s(%)
LY-1	0.01000	--	--	0.99000	42 562	0.11	--	--
LY-2	0.01000	0.01000	0.0256	0.9544	29 437	0.13	17 746	0.17
LY-3	0.01000	0.02000	0.0467	0.9233	23 599	0.15	29 581	0.13
LY-4	0.01000	0.0400	0.0752	0.8748	16 970	0.17	44 622	0.11
LY-5	0.01000	0.0600	0.0937	0.8363	13 952	0.19	55 368	0.10
LY-6	0.01000	0.0800	0.1160	0.7940	11 607	0.21	61 065	0.10

* 50kV, 20mA

TABLE B Calculation of α_{ZnSn}

Solutions	α_{ZnSn}
LY-1/LY-6	0.3818···
LY-1/LY-5	0.3690···
LY-2/LY-6	0.3383···
LY-2/LY-5	0.3111···
LY-3/LY-6	0.4748···
LY-4/LY-6	0.3123···

α_{ZnSn} average = 0.3794···
std. devn. = ± 0.0683···

α_{ZnSn} = $0.37^9 \pm 0.06^8$
= 0.38 ± 0.07

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of chlorine	Correction for effect of tin	$I_{ZnK\alpha}$(corr) (cps)
LY-1	42 562	− 39 730	--	---	2 832
LY-2	29 347	− 26 409	− 246	+ 111	2 803
LY-3	23 599	− 20 545	− 360	+ 179	2 873
LY-4	16 970	− 13 998	− 417	+ 257	2 813
LY-5	13 952	− 11 002	− 427	+ 317	2 840
LY-6	11 607	− 8 690	− 440	+ 352	2 829

$I^{o}_{ZnK\alpha}$ average = 283 136 cps
std. devn. = ± 2 459 cps

$I^{o}_{ZnK\alpha}$ = $(2.83^{1} \pm 0.02^{1}) \times 10^{5}$
= $(2.83 \pm 0.02) \times 10^{5}$

TABLE D — Calculation of $I_{SnK\alpha}$(corr) and $I^{o}_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	zinc	$I_{SnK\alpha}$(corr) (cps)
LY-2	17 746	- 16 158	- 361	- 42	1 160
LY-3	29 581	- 26 056	- 1 174	- 69	2 282
LY-4	44 622	- 37 240	- 2 851	- 105	4 426
LY-5	55 368	- 44 174	- 4 394	- 130	6 670
LY-6	61 065	- 46 255	- 5 999	- 143	8 668

$I^{o}_{SnK\alpha}$ average = 112 160 cps
std. devn. = ± 2 722 cps

$I^{o}_{SnK\alpha}$ = $(1.12^{1} \pm 0.02^{7}) \times 10^{5}$
= $(1.12 \pm 0.03) \times 10^{5}$

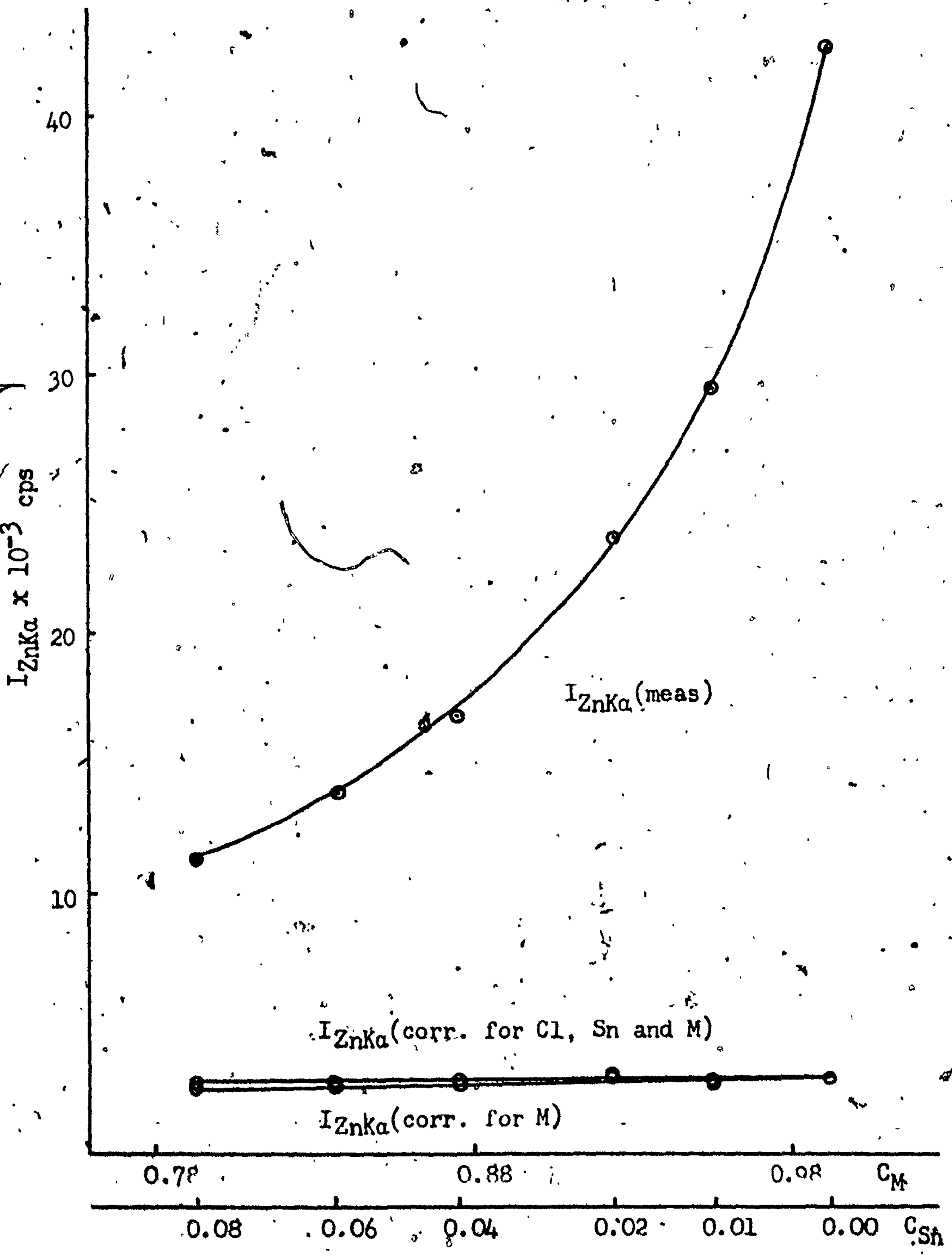
TABLE E — Calculation of $I_{ClK\alpha}$(corr) and $I^{o}_{ClK\alpha}$

ClKα counts not taken

TABLE F — Back-calculation of solution composition

No back-calculation–ClKα counts not taken

FIGURE D. $I_{ZnK\alpha}$ versus C_{Sn} and C_M



5.11.5 Effect of Sn on Pb

TABLE A Experimental Parameters

Solution	C_{Pb}	C_{Sn}	C_M	$I_{PbL\alpha}$ (cps)	s(%)	$I_{SnK\alpha}$* (cps)	s(%)
LZB-1	0.01000	---	0.99000	14 314	0.19	—	—
LZB-2	0.01000	0.01000	0.98000	11 996	0.20	14 992	0.18
LZB-3	0.01000	0.02000	0.97000	10 542	0.22	26 378	0.14
LZB-4	0.01000	0.0400	0.9500	8 363	0.25	43 830	0.11
LZB-5	0.01000	0.0500	0.9400	7 474	0.26	49 562	0.10
LZB-6	0.01000	0.0600	0.9300	6 846	0.28	54 710	0.10
LZB-7	0.01000	0.0700	0.9200	6 384	0.30	58 632	0.10

* 50kV, 20mA

TABLE B Calculation of α_{PbSn}

Solutions	α_{PbSn}
LZB-1/LZB-7	- 0.2655···
LZB-1/LZB-6	- 0.2482···
LZB-1/LZB-5	- 0.2433···
LZB-2/LZB-7	- 0.2885···
LZB-2/LZB-6	- 0.2669···
LZB-2/LZB-5	- 0.2625···
LZB-3/LZB-7	- 0.2707···

α_{PbZn} average = - 0.2637···
std. devn. = ± 0.0149···

$$\alpha_{PbZn} = -0.26^{4} \pm 0.01^{5}$$
$$= -0.26 \pm 0.01$$

TABLE C Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of tin	$I_{PbL\alpha}$(corr) (cps)
LZB-1	14 314	- 13 744	--	570
LZB-2	11 996	- 11 402	- 32	562
LZB-3	10 542	- 9 918	- 56	568
LZB-4	8 363	- 7 706	- 88	569
LZB-5	7 474	- 6 814	- 99	561
LZB-6	6 846	- 6 175	- 108	563
LZB-7	6 384	- 5 696	- 118	570

$I^{0}_{PbL\alpha}$ average = 56 614 cps

std. devn. = ± 398 cps

$I^{0}_{PbL\alpha}$ = $(5.66^{1} \pm 0.03^{9}) \times 10^{4}$

= $(5.66 \pm 0.04) \times 10^{4}$

TABLE D Calculation of $I_{SnK\alpha}$(corr) and $I^{0}_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of lead	$I_{SnK\alpha}$(corr) (cps)
LZB-2	14 992	- 14 016	+ 155	1 131
LZB-3	26 378	- 24 410	+ 273	2 241
LZB-4	43 830	- 39 723	+ 454	4 561
LZB-5	49 562	- 44 445	+ 513	5 630
LZB-6	54 710	- 48 540	+ 566	6 736
LZB-7	58 632	- 51 460	+ 607	7 779

$I^{0}_{SnK\alpha}$ average = 112 526 cps

std. devn. = ± 973 cps

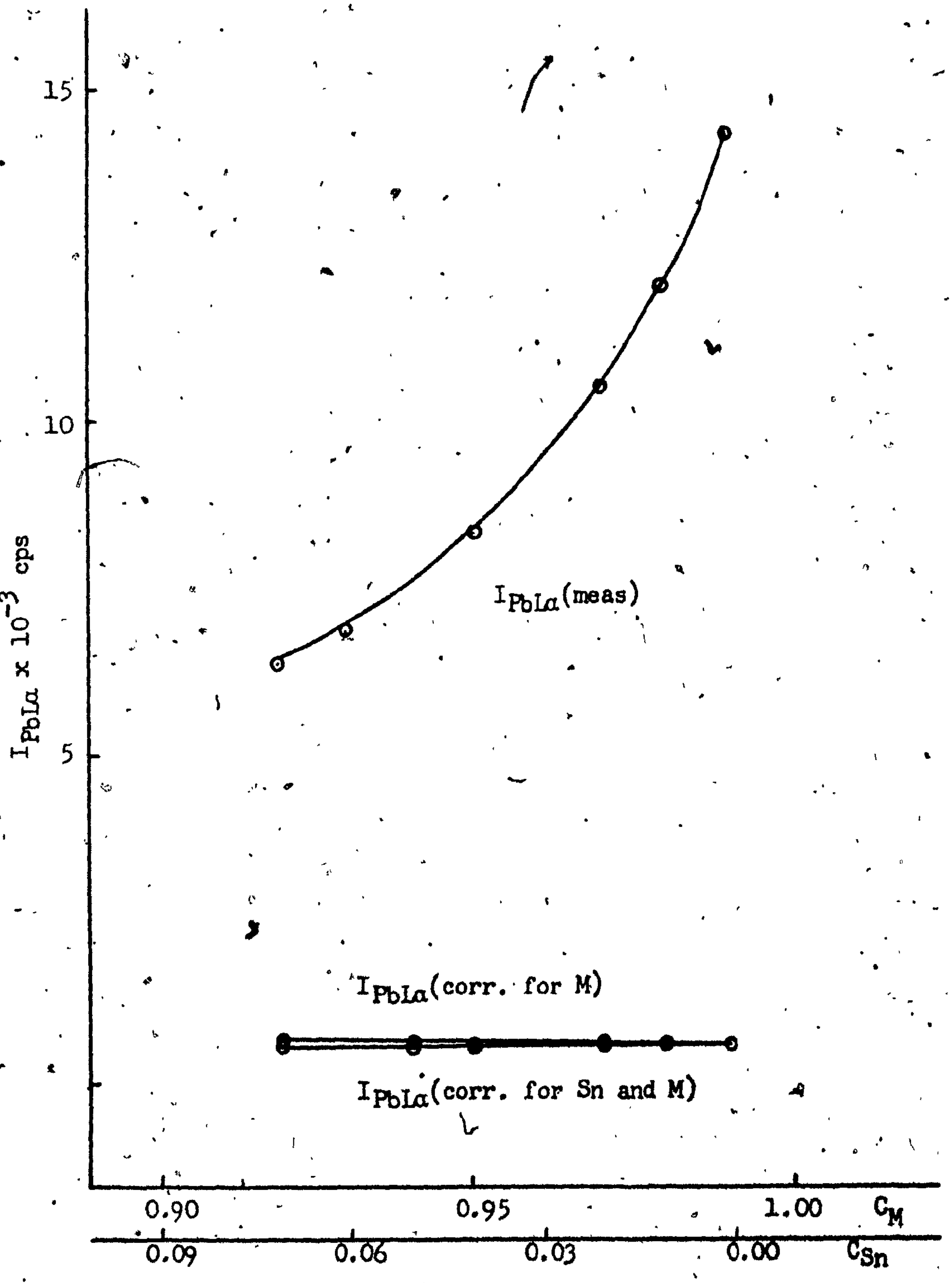
$I^{0}_{SnK\alpha}$ = $(1.125^{3} \pm 0.009^{7}) \times 10^{5}$

= $(1.125 \pm 0.010) \times 10^{5}$

TABLE E Back-calculation of solution composition

Solution	C_{Pb}(calc)	Abs. error	Error %	C_{Sn}(calc)	Abs. error	Error %
LZB-1	0.01010	0.00010	1.00	--	--	--
LZB-2	0.00990	0.00010	1.00	0.01000	0.00000	0.00
LZB-3	0.01000	0.00000	0.00	0.01990	0.00010	0.50
LZB-4	0.01020	0.00020	2.00	0.0411	0.0011	2.75
LZB-5	0.00990	0.00010	1.00	0.0499	0.0001	0.20
LZB-6	0.00990	0.00010	1.00	0.0595	0.0005	0.83
LZB-7	0.00990	0.00010	1.00	0.0680	0.0020	2.85

FIGURE D $I_{PbL\alpha}$ versus C_{Sn} and C_M



5.12 Effect of Lead

Solutions: The metal concentration for each series were obtained by dilution of the following stock solutions:-

Copper 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)
Zinc 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)
Tin 1 ml = 0.10000 ± 0.00005 g (dil. HF)
Lead (ClSn) 1 ml = 0.10000 ± 0.00002 g (dil. HNO_3)
Lead (CuZn) 1 ml = 0.20000 ± 0.00005 g (dil. HNO_3)

Chlorine was added as $HClO_4$, and determined by potentiometric titration with standard NaOH solution. Corrections were applied for HNO_3 and Pb(II).

The exact final weight of each solution was determined.

The least precise value, for metal or for chloride, set the significant figure level for all values of the type in the series. These were:-

Element	Series	Uncertainty	Significant figure level
Cl	MBT	1:216	1:116 to 1:1160
Cu	LR	1:620	1:310 to 1:3100
Zn	LV	1:440	1:220 to 1:2200
Sn	LZC	1:440	1:220 to 1:2200

Intensities: The operating parameters for each solution series were:-

Element	Cl	Cu	Zn	Sn	Pb
Target	Cr	W	W	W	W
kV	50	40	40	50	*
mA	36	20	20	20	*
Coll^n	coarse	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc
Time (s)	100	20	20	20	20
Counts	3	5	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Lα

* See each series

The tabulated counts for each series represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required. The tabulated values for each series show s as sigma counting error in percent.

Equations:	Calculation of α_{APb} (absence of chlorine as fourth component)	Equation (43)
	Calculation of α_{APb} (presence of chlorine as fourth component)	Equation (44)
	Calculation of $I_A(corr)$	Equation (45) or a modification.
	Calculation of I_A^o	$I_A(corr)/C_A$

5.12.1 Effect of Pb on Cl

TABLE A Experimental Parameters

Solution	C_{Cl}	C_{Pb}	C_M	$I_{ClK\alpha}$ (cps)	s(%)	$I_{PbL\alpha}^{*}$ (cps)	s(%)
MBT-1	0.0216^4	0.00	0.9783^6	5 688	0.31	--	--
MBT-2	0.0216^4	0.01000	0.9683^6	5 361	0.32	28 375	0.13
MBT-3	0.0216^4	0.02000	0.9583^6	5 042	0.32	48 664	0.10
MBT-4	0.0216^4	0.0300	0.9483^6	4 610	0.33	61 496	0.09
MBT-5	0.0216^4	0.0500	0.9283^6	4 219	0.34	79 161	0.08
MBT-6	0.0216^4	0.0600	0.9183^6	4 072	0.35	84 974	0.08
MBT-7	0.0216^4	0.0700	0.9083^6	3 740	0.37	87 855	0.07

*50kV, 40mA

TABLE B Calculation of α_{ClPb}

Solutions	α_{ClPb}
MBT-1/MBT-7	4.6588···
MBT-1/MBT-6	4.1040···
MBT-1/MBT-5	4.3386···
MBT-2/MBT-7	4.8906···
MBT-2/MBT-6	4.2011···
MBT-2/MBT-5	4.5362···
MBT-3/MBT-7	5.0939···
MBT-3/MBT-6	4.2021···

α_{ClPb} average = 4.5032···

std. devn. = ± 0.36···

$\alpha_{ClPb} = 4.5^0 \pm 0.3^6$

$= 4.5 \pm 0.4$

TABLE C Calculation of $I_{ClK\alpha}$(corr) and $I^o_{ClK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of lead	$I_{ClK\alpha}$(corr) (cps)
MBT-1	5 688	- 1 870	--	3 818
MBT-2	5 361	- 1 744	+ 241	3 858
MBT-3	5 042	- 1 623	+ 454	3 873

MBT-4	4 610	- 1 469	+ 622	3 763
MBT-5	4 219	- 1 316	+ 949	3 852
MBT-6	4 072	- 1 256	+ 1 099	3 915
MBT-7	3 740	- 1 141	+ 1 178	3 777

$I^{o}_{ClK\alpha}$ average = 177 287 cps

std. devn. = ± 2 489 cps

$$I^{o}_{ClK\alpha} = (1.77^{3} \pm 0.02^{5}) \times 10^{5} \text{ cps}$$

$$= (1.77 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE D Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

Solution	Measured	Correction for effect of matrix	chlorine	$I_{PbL\alpha}$(corr) (cps)
MBT-2	28 375	- 26 650	- 427	1 298
MBT-3	48 664	- 45 234	- 732	2 698
MBT-4	61 496	- 56 565	- 926	4 005
MBT-5	79 161	- 71 278	- 1 192	6 691
MBT-6	84 974	- 75 688	- 1 279	8 007
MBT-7	87 855	- 77 402	- 1 322	9 131

$I^{o}_{PbL\alpha}$ average = 132 648 cps

std. devn. = ± 2 046 cps

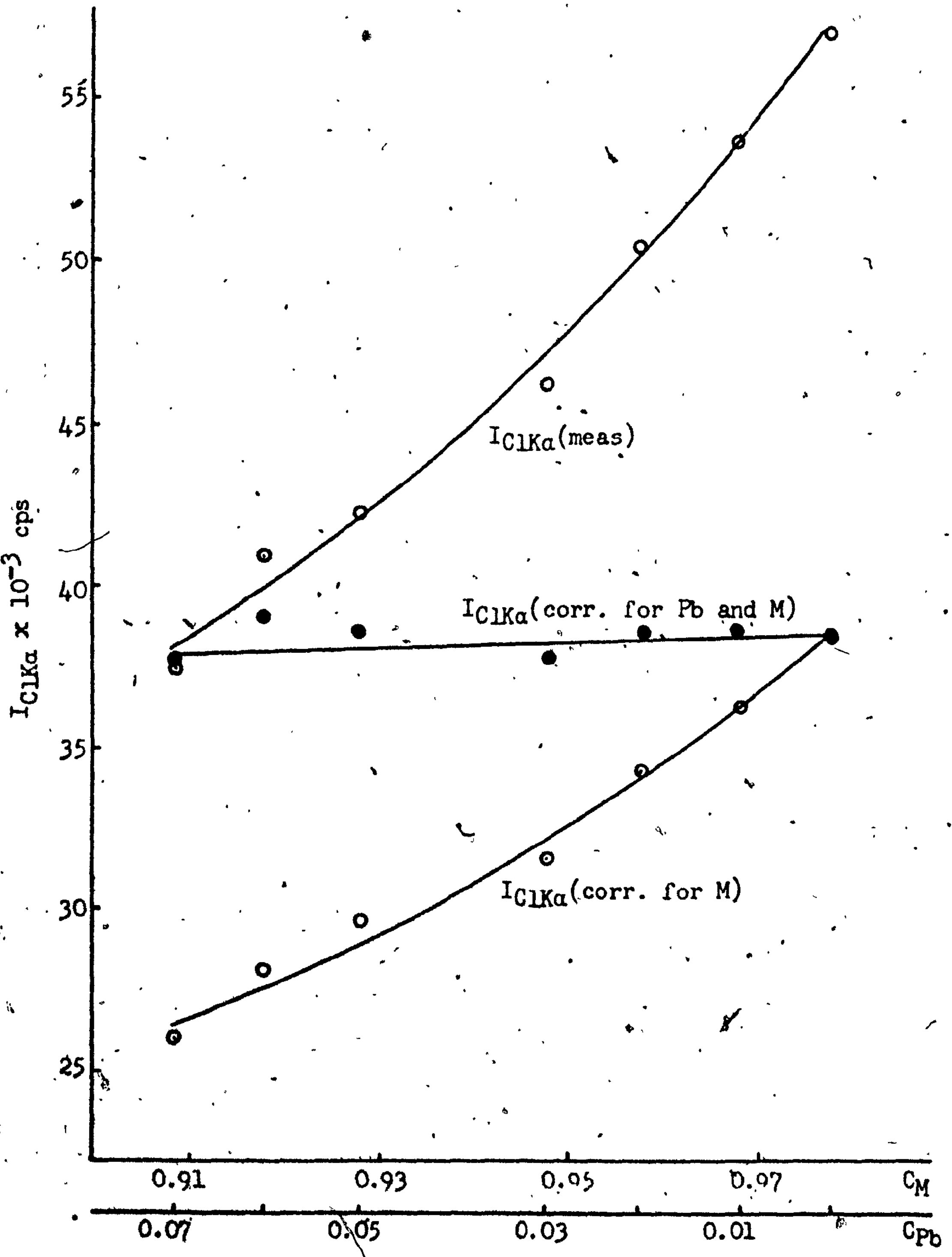
$$I^{o}_{PbL\alpha} = (1.32^{6} \pm 0.02^{0}) \times 10^{5} \text{ cps}$$

$$= (1.33 \pm 0.02) \times 10^{5} \text{ cps}$$

TABLE E Back-calculation of solution composition

Solution	C_{Cl}(calc)	Abs. error	Error %	C_{Pb}(calc)	Abs. error	Error %
MBT-1	0.0215	0.0001	0.46	--	--	--
MBT-2	0.0217	0.0001	0.46	0.00973	0.00027	2.70
MBT-3	0.0219	0.0003	1.39	0.0206	0.0006	3.00
MBT-4	0.0213	0.0003	1.39	0.0303	0.0002	0.66
MBT-5	0.0219	0.0003	1.39	0.0511	0.0011	2.20
MBT-6	0.0222	0.0006	2.78	0.0612	0.0012	2.00
MBT-7	0.0209	0.0003	1.39	0.0664	0.0036	5.14

FIGURE D $I_{ClK\alpha}$ versus C_{Pb} and C_M



5.12.2 Effect of Pb on Cu

TABLE A Experimental Parameters

Solution	C_{Cu}	C_{Pb}	C_M	$I_{CuK\alpha}$ (cps)	s(%)	$I_{PbK\alpha}^*$ (cps)	s(%)
LR-1	0.01000	0.00	0.99000	29 068	0.13	--	--
LR-2	0.01000	0.01000	0.98000	24 588	0.14	10 923	0.22
LR-3	0.01000	0.02000	0.97000	21 464	0.15	17 601	0.17
LR-4	0.01000	0.04000	0.95000	16 931	0.17	26 970	0.14
LR-5	0.01000	0.0600	0.9300	14 096	0.18	32 626	0.12
LR-6	0.01000	0.0800	0.9100	12 081	0.20	36 775	0.12
LR-7	0.01000	0.1000	0.8900	10 662	0.22	39 914	0.11

* 50kV, 20mA

TABLE B Calculation of α_{CuPb}

Solutions	α_{CuPb}
LR-1/LR-7	0.5186···
LR-1/LR-6	0.5447···
LR-2/LR-7	0.4946···
LR-2/LR-6	0.5264···
LR-3/LR-7	0.4932···

α_{CuPb} average = 0.5155···

std. devn. = ± 0.0218···

α_{CuPb} = $0.51^5 \pm 0.02^2$

= 0.51 ± 0.02

TABLE C Calculation of $I_{CuK\alpha}$(corr) and $I^0_{CuK\alpha}$

Solution	Measured	Correction for effect of		$I_{CuK\alpha}$(corr) (cps)
		matrix	lead	
LR-1	29 068	- 26 636	--	2 432
LR-2	24 588	- 22 303	+ 127	2 411
LR-3	21 464	- 19 271	+ 221	2 414
LR-4	16 931	- 14 888	+ 349	2 392
LR-5	14 096	- 12 134	+ 436	2 398
LR-6	12 081	- 10 176	+ 498	2 403
LR-7	10 662	- 8 783	+ 549	2 428

$I^{o}_{CuK\alpha}$ average = 241 114 cps

std. devn. = ± 1 500 cps

$I^{o}_{CuK\alpha} = (2.41^{1} \pm 0.01^{5}) \times 10^{5}$

$= (2.41 \pm 0.02) \times 10^{5}$

TABLE D Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of copper	$I_{PbL\alpha}$(corr) (cps)
LR-2	10 923	- 10 382	+ 21	562
LR-3	17 601	- 16 559	+ 35	1 077
LR-4	26 970	- 24 850	+ 53	2 173
LR-5	32 626	- 29 429	+ 64	3 261
LR-6	36 775	- 32 458	+ 72	4 389
LR-7	39 914	- 34 454	+ 79	5 539

$I^{o}_{PbL\alpha}$ average = 54 773 cps

std. devn. = ± 800 cps

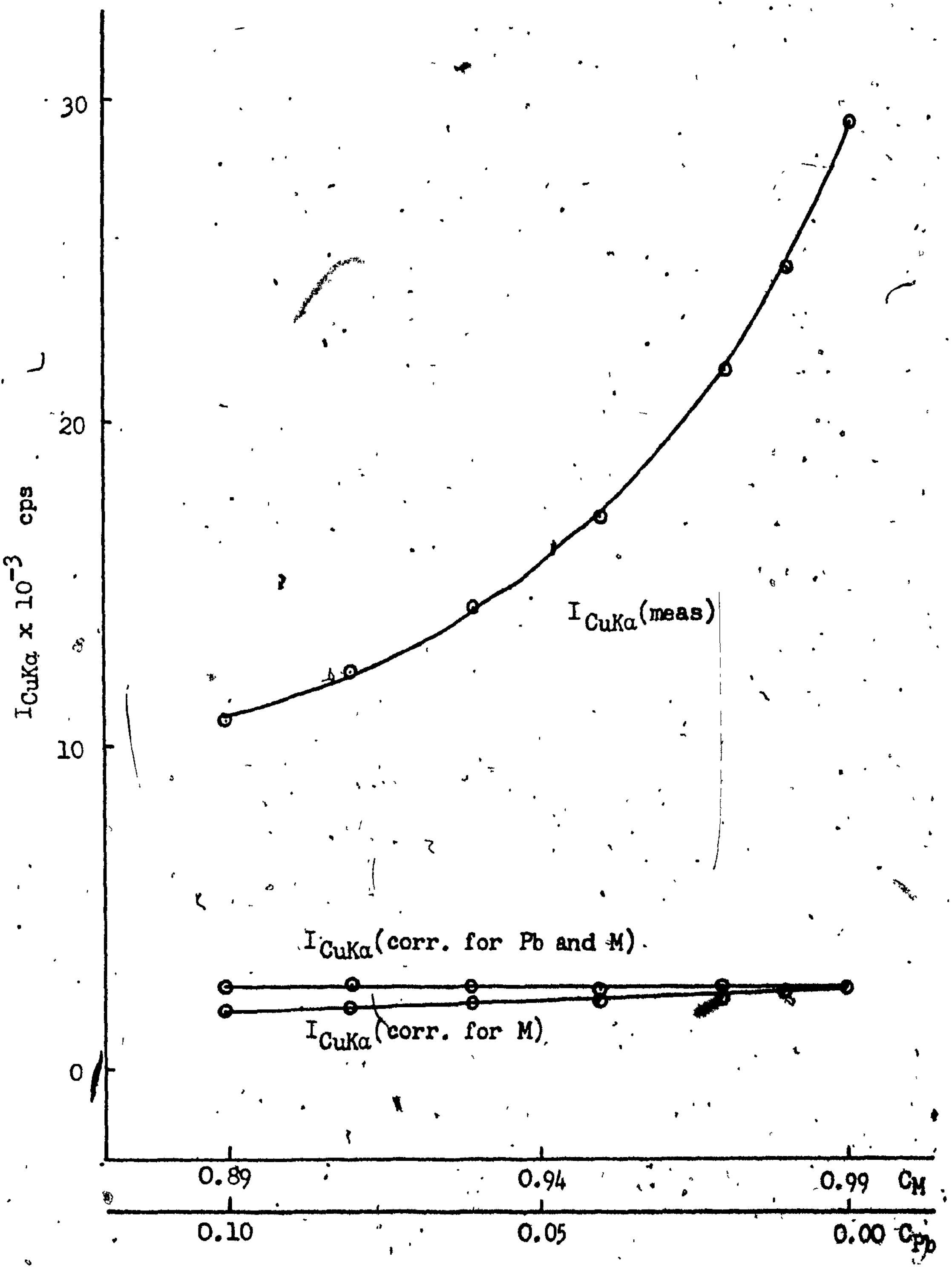
$I^{o}_{PbL\alpha} = (5.47^{7} \pm 0.08^{0}) \times 10^{4}$

$= (5.48 \pm 0.08) \times 10^{4}$

TABLE E Back-calculation of solution composition

Solution	C_{Cu}(calc)	Abs. error	Error %	C_{Pb}(calc)	Abs. error	Error %
LR-1	0.01010	0.00010	1.00	--	--	--
LR-2	0.01000	0.00000	0.00	0.01030	0.00030	3.00
LR-3	0.00990	0.00010	1.00	0.01940	0.00060	2.00
LR-4	0.00980	0.00020	2.00	0.0391	0.0009	2.25
LR-5	0.00980	0.00020	2.00	0.0586	0.0014	2.33
LR-6	0.01000	0.00000	0.00	0.0803	0.0003	0.42
LR-7	0.01040	0.00040	4.00	0.1049	0.0049	4.90

FIGURE D $I_{CuK\alpha}$ versus C_{Pb} and C_M



5.12.3 Effect of Pb on Zn

TABLE A Experimental Parameters

Solution	C_{Zn}	C_{Pb}	C_M	$I_{ZnK\alpha}$ (cps)	s(%)	$I_{PbL\alpha}$* (cps)	s(%)
LV-1	0.01000	0.00	0.99000	41 751	0.11	--	--
LV-2	0.01000	0.01000	0.98000	33 979	0.12	10 594	0.22
LV-3	0.01000	0.02000	0.97000	29 222	0.13	17 415	0.17
LV-4	0.01000	0.0400	0.9500	24 098	0.14	26 783	0.14
LV-5	0.01000	0.0600	0.9300	19 502	0.16	32 455	0.13
LV-6	0.01000	0.0800	0.9100	16 596	0.17	35 760	0.12
LV-7	0.01000	0.1000	0.8900	14 977	0.18	39 823	0.11

* 50kV, 20mA

TABLE B Calculation of α_{ZnPb}

Solutions	α_{ZnPb}
LV-1/LV-7	0.2464···
LV-1/LV-6	0.3176···
LV-1/LV-5	0.3221···
LV-1/LV-4	0.2755···
LV-2/LV-6	0.2277···
LV-2/LV-5	0.2171···

α_{ZnPb} average = 0.2677···

std. devn. = ± 0.0392···

$$\alpha_{ZnPb} = 0.26^{8} \pm 0.03^{9}$$

$$= 0.27 \pm 0.04$$

TABLE C Calculation of $I_{ZnK\alpha}$(corr) and $I^{o}_{ZnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of lead	$I_{ZnK\alpha}$(corr) (cps)
LV-1	41 751	- 38 973	--	2 778
LV-2	33 979	- 31 398	+ 91	2 672
LV-3	29 222	- 26 727	+ 157	2 652

LV-4	24 098	- 21 586	+ 258	2 770
LV-5	19 502	- 17 101	+ 313	2 714
LV-6	16 596	- 14 240	+ 356	2 712
LV-7	14 977	- 12 568	+ 401	2 810

$I^{o}_{ZnK\alpha}$ average = 272 972 cps

std. devn. = ± 5 289 cps

$$I^{o}_{ZnK\alpha} = (2.72^{9} \pm 0.05^{2}) \times 10^{5}$$
$$= (2.73 \pm 0.05) \times 10^{5}$$

TABLE D **Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$**

Solution	Measured	Correction for effect of matrix	Correction for effect of zinc	$I_{PbL\alpha}$(corr) (cps)
LV-2	10 594	- 10 070	+ 38	562
LV-3	17 415	- 16 384	+ 62	1 093
LV-4	26 783	- 24 678	+ 96	2 201
LV-5	32 455	- 29 275	+ 116	3 296
LV-6	35 760	- 34 376	+ 128	4 326
LV-7	39 823	- 34 376	+ 142	5 589

$I^{o}_{PbL\alpha}$ average = 55 132 cps

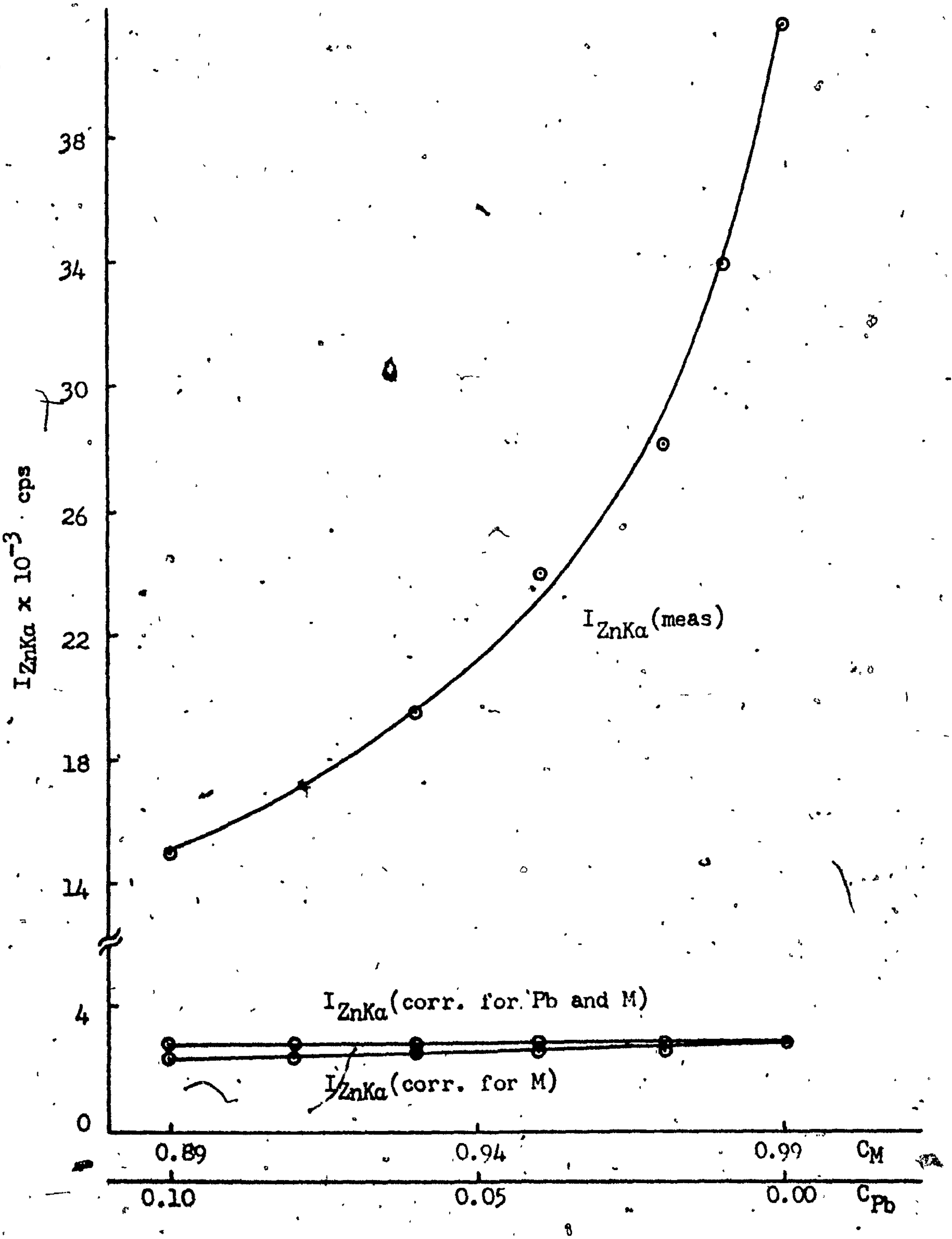
std. devn. = ± 797 cps

$$I^{o}_{PbL\alpha} = (5.51^{3} \pm 0.07^{9}) \times 10^{4}$$
$$= (5.51 \pm 0.08) \times 10^{4}$$

TABLE E **Back-calculation of solution composition**

Solution	C_{Zn}(calc)	Abs. error	Error %	C_{Pb}(calc)	Abs. error	Error %
LV-1	0.01020	0.00020	2.00	--	--	--
LV-2	0.00980	0.00020	2.00	0.01020	0.00020	2.00
LV-3	0.00960	0.00040	4.00	0.01950	0.00050	2.50
LV-4	0.01020	0.00020	2.00	0.0400	0.0000	0.00
LV-5	0.00990	0.00010	1.00	0.0593	0.0007	1.40
LV-6	0.00950	0.00050	5.00	0.0747	0.0053	6.50
LV-7	0.01080	0.00020	2.00	0.1072	0.0072	7.20

FIGURE D $I_{ZnK\alpha}$ versus C_{Pb} and C_M



5.12.4 Effect of Pb on Sn

TABLE A Experimental Parameters

Sloution	C_{Sn}	C_{Pb}	C_M	$I_{SnK\alpha}$ (cps)	s(%)	$I_{PbL\alpha}$* (cps)	s(%)
LZC-1	0.01000	0.00	0.99000	20 247	0.16	--	--
LZC-2	0.01000	0.01000	0.98000	15 336	0.18	12 128	0.20
LZC-3	0.01000	0.02000	0.97000	12 205	0.20	19 850	0.16
LZC-4	0.01000	0.0400	0.9500	8 668	0.24	29 750	0.13
LZC-5	0.01000	0.0500	0.9400	7 353	0.26	32 224	0.13
LZC-6	0.01000	0.0600	0.9300	6 548	0.29	35 487	0.12
LZC-7	0.01000	0.0700	0.9200	5 903	0.31	37 539	0.12

*
50kV, 20mA

TABLE B Calculation of α_{SnPb}

Solutions	α_{SnPb}
LZC-1/LZC-7	0.9740...
LZC-1/LZC-6	0.9826...
LZC-1/LZC-5	0.9938...
LZC-2/LZC-7	1.0622...
LZC-2/LZC-6	1.0838...
LZC-3/LZC-7	1.1157...

α_{SnPb} average = 1.0353···
std. devn. = ± 0.0597···

α_{SnPb} = $1.03^{5} \pm 0.06^{0}$
= 1.03 ± 0.06

TABLE C Calculation of $I_{SnK\alpha}$(corr) and $I^{o}_{SnK\alpha}$

Solution	Measured	Correction for effect of matrix	Correction for effect of lead	$I_{SnK\alpha}$(corr) (cps)
LZC-1	20 247	- 19 122	--	1 125
LZC-2	15 336	- 14 338	+ 159	1 157
LZC-3	12 205	- 11 294	+ 253	1 164
LZC-4	8 668	- 7 856	+ 359	1 171
LZC-5	7 353	- 6 594	+ 380	1 139
LZC-6	6 548	- 5 809	+ 407	1 146
LZC-7	5 903	- 5 181	+ 428	1 150

$I^{o}_{SnK\alpha}$ average = 115 002 cps
std. devn. = ± 1 555 cps
$I^{o}_{SnK\alpha}$ = $(1.15^{0} \pm 0.01^{5}) \times 10^{5}$
= $(1.15 \pm 0.02) \times 10^{5}$

TABLE D Calculation of $I_{PbL\alpha}$(corr) and $I^{o}_{PbL\alpha}$

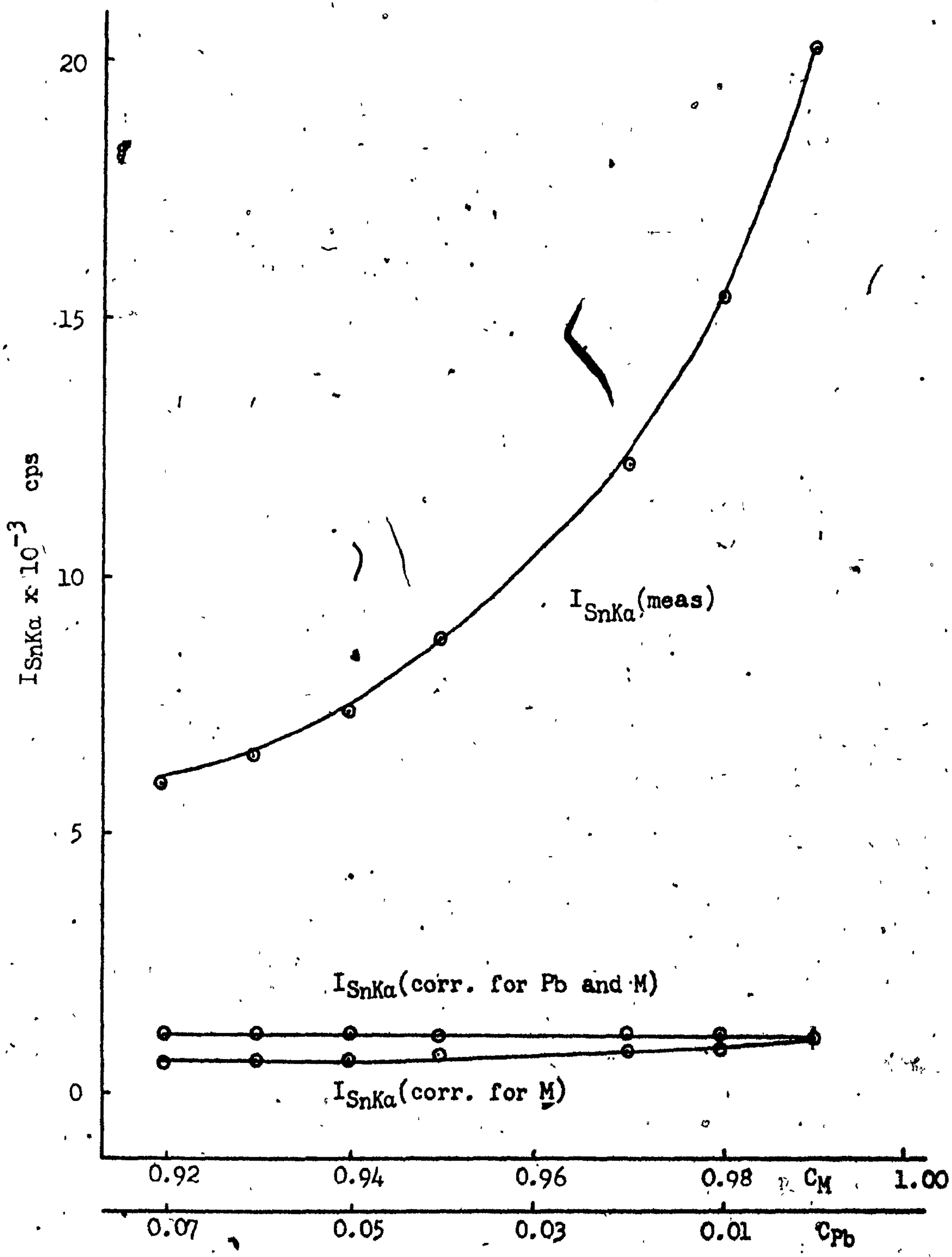
Solution	Measured	Correction for effect of		$I_{PbL\alpha}$(corr)
		matrix	tin	(cps)
LZC-2	12 128	- 11 528	- 32	568
LZC-3	19 850	- 18 675	- 52	1 123
LZC-4	29 750	- 27 412	- 78	2 260
LZC-5	32 224	- 29 379	- 85	2 760
LZC-6	35 487	- 32 009	- 94	3 384
LZC-7	37 539	- 33 496	- 99	3 944

$I^{o}_{PbL\alpha}$ average = 56 231 cps
std. devn. = ± 553 cps
$I^{o}_{PbL\alpha}$ = $(5.62^{3} \pm 0.05^{5}) \times 10^{4}$
= $(5.62 \pm 0.05) \times 10^{4}$

TABLE E Back-calculation of solution composition

Solution	C_{Sn}(calc)	Abs. error	Error %	C_{Pb}(calc)	Abs. error	Error %
LZC-1	0.00970	0.00030	3.00	—	—	—
LZC-2	0.01010	0.00010	1.00	0.01020	0.00020	2.00
LZC-3	0.01010	0.00010	1.00	0.02000	0.00000	0.00
LZC-4	0.01030	0.00030	3.00	0.0406	0.0006	1.50
LZC-5	0.00960	0.00040	4.00	0.0475	0.0025	5.00
LZC-6	0.01000	0.00000	0.00	0.0605	0.0005	0.83
LZC-7	0.01000	0.00000	0.00	0.0704	0.0004	0.57

FIGURE D $I_{SnK\alpha}$ versus C_{Pb} and C_M



6.0 ANALYSIS OF FERROUS-BASE AND OTHER BASE SOLUTIONS AND ALLOYS

6.1 Analysis of Ferrous-Base and Other Base Synthetic Solutions

6.1.1 Synthetic Solutions of Cr, Mn, Fe, Co, Ni and Cu with Large Range in Composition. Series SF

Solutions: The metal concentrations for each solution were obtained by dilution of the following stock solutions:-

Chromium 1 ml = 0.05000 ± 0.00001 g (dil. HCl)
Manganese 1 ml = 0.10000 ± 0.00006 g (dil. HNO_3)
Iron 1 ml = 0.10000 ± 0.00002 g (dil. $HCl-HNO_3$)
Cobalt 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Nickel 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Copper 1 ml = 0.20000 ± 0.00004 g (dil. HNO_3)

Chlorine, present in the solutions, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

Ranges of concentration in solutions and in projected alloys were:-

Element	Range in solution %	Range in projected alloy %
Chromium	0.10 - 2.50	0.94 - 55.56
Manganese	0.10 - 2.00	0.94 - 44.44
Iron	0.10 - 5.00	0.94 - 67.23
Cobalt	0.10 - 3.00	1.05 - 55.05
Nickel	0.10 - 4.00	1.68 - 59.70
Copper	0.10 - 8.00	4.44 - 83.77

The solution composition and the projected alloy composition for Series SF are given in Table 19 of the text.

Intensities: The operating parameters for Series SF were:-

Metal	Cl	Cr	Mn	Fe	Co	Ni	Cu
Target	Cr	W	W	W	W	W	W
kV	50	50	50	50	50	50	50
mA	36	40	40	40	20	20	20
Coll^n	coarse	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various components. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear equation of the type given as Equation (25). Calculated projected alloy compositions were obtained by multiplication using the dilution factor (solution weight versus total solid weight, excluding chlorine) for each solution.

The analytical results for the α-correction coefficient and ratio techniques, as applied to Series SF, are shown in Table 21 of the text.

TABLE A Intensity measurement

Solution	$I_{CrK\alpha}$ (cps)	$I_{MnK\alpha}$ (cps)	$I_{FeK\alpha}$ (cps)	$I_{CoK\alpha}$ (cps)	$I_{NiK\alpha}$ (cps)	$I_{CuK\alpha}$ (cps)	$I_{ClK\alpha}$ (cps)
SF-1	940	3 760	15 389	115 426	13 148	17 367	3 838
SF-2	4 419	8 966	6 693	11 175	125 346	25 507	5 071
SF-3	917	1 799	3 313	50 583	10 268	158 656	1 215
SF-4	2 162	6 965	10 093	2 678	16 407	182 505	3 439
SF-5	4 316	5 605	76 608	3 289	1 973	6 630	29 750
SF-6	1 505	10 234	19 028	8 801	8 363	33 044	4 857
SF-7	7 879	32 861	5 897	18 484	3 095	4 630	9 830
SF-8	15 185	1 354	19 862	8 069	11 723	11 669	23 708
SF-9	1 832	14 350	50 572	28 001	24 226	14 785	14 470
SF-10	3 251	6 394	67 349	5 474	6 608	35 077	21 807
SF-11	2 176	5 242	22 161	12 051	58 448	89 636	5 808
SF-12	11 067	22 107	5 283	1 903	21 229	31 404	12 730
SF-13	510	1 916	3 941	2 037	101 136	149 151	967
SF-14	3 140	12 361	12 139	67 089	20 005	8 378	5 382
SF-15	1 176	2 343	4 679	3 893	5 896	5 003	1 664
SF-16	15 526	---	20 727	---	23 801	---	24 426
SF-17	2 800	---	92 602	---	10 570	---	33 219
SF-18	2 385	---	18 196	---	151 006	---	4 475

6.1.2 Synthetic Solutions of Cr, Mn, Fe, Co, Ni and Cu with Small Range in Composition. Series SG

Solutions: The metal concentration for each solution was obtained by dilution of the following stock solutions:-

Chromium 1 ml = 0.10000 ± 0.00006 g (dil. HCl)
Manganese 1 ml = 0.10000 ± 0.00006 g (dil. HNO_3)
Iron 1 ml = 0.10000 ± 0.00006 g (dil. HCl-HNO_3)
Cobalt 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Nickel 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)
Copper 1 ml = 0.10000 ± 0.00003 g (dil. HNO_3)

Chlorine, present in the solutions, was determined by potentiometric titration with standard $AgNO_3$ solution.

The exact final weight of each solution was determined.

Ranges of concentration in solutions and in projected alloys were:-

Element	Range in solution %	Range in projected alloy %
Chromium	0.50 - 1.25	10.00 - 27.78
Manganese	0.10 - 0.25	1.00 - 10.00
Iron	3.05 - 4.10	60.00 - 82.00
Cobalt	0.05 - 0.25	1.00 - 5.00
Nickel	0.05 - 0.75	1.11 - 15.00
Copper	0.05 - 0.15	1.00 - 3.00

The solution composition and the projected alloy composition for Series SG are given in Table 20 of the text.

Intensities: The operating parameters for Series SG were:-

Metal	Cl	Cr	Mn	Fe	Co	Ni	Cu
Target	Cr	W	W	W	W	W	W
kV	50	50	50	50	50	50	50
mA	36	40	40	20	40	40	40
Coll^{n}	coarse	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3
Rad^{n}	Kα	Kα	Kα	Kα	Kα	Kα	Kα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various components. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear eqution of the type given as Equation (25). Calculated projected alloy compositions were obtained by multiplication using the dilution factor (solution weight versus total solid weight, excluding chlorine) for each solution.

The analytical results for the α-correction coefficient and ratio techniques, as applied to Series SG, are shown in Table 22 of the text.

TABLE A <u>Intensity measurement</u>

Solution	$I_{CrK\alpha}$ (cps)	$I_{MnK\alpha}$ (cps)	$I_{FeK\alpha}$ (cps)	$I_{CoK\alpha}$ (cps)	$I_{NiK\alpha}$ (cps)	$I_{CuK\alpha}$ (cps)	$I_{ClK\alpha}$ (cps)
SG-1	3 500	6 878	42 794	1 932	11 790	6 179	18 950
SG-2	3 569	2 846	39 437	9 918	35 514	2 114	17 380
SG-3	6 733	1 389	36 360	3 648	23 475	6 254	19 358
SG-4	7 918	730	34 288	1 854	2 572	2 254	20 084
SG-5	4 127	2 089	41 931	5 790	16 325	4 161	19 992
SG-6	4 779	3 519	39 824	3 694	18 544	4 136	19 665
SG-7	5 224	3 522	38 466	1 871	27 201	2 114	19 606
SG-8	5 899	1 439	35 637	9 582	30 811	4 129	19 013
SG-9	7 594	757	34 172	7 304	23 677	6 174	20 161
SG-10	3 413	718	46 017	1 912	11 239	2 094	21 571

6.2 Analysis of NBS Ferrous-Base Alloys

Solutions: NBS ferrous-base alloys were obtained in finely-divided form and covered a large range of composition for the major components. These are:-

Chromium	0.070 - 67.9 %
Manganese	0.36 - 80.07 %
Iron	3.43 - 97.63 %
Cobalt	0.058 - 41.20 %
Nickel	0.159 - 20.25 %
Copper	0.025 - 6.44 %

Various sample sizes from 2 to 10 g were dissolved in hydrochloric acid with some small added amounts of nitric acid and, occasionnally, hydrogen peroxide. Where the carbon content was high, solutions were filtered. Water was used to dilute the solutions up to approximately 100 g.

The chemical composition of the NBS alloys is shown in Table 23 of the text.

Intensities: The operating parameters for NBS Series were:-

Metal	Cl	Cr	Mn	Fe	Co	Ni	Cu
Target	Cr	W	W	W	W	W	W
kV	50	50	50	50	50	50	50
mA	36	40	40	20	40	40	40
Coll^n	coarse	fine	fine	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20	20	20
Counts	3	3	3	3	3	3	3
Rad^n	Kα	Kα	Kα	Kα	Kα	Kα	Kα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various components. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear equation of the type given as Equation (25). Calculated projected alloy compositions were obtained by multiplication using dilution factor (solution weight versus total solid weight, excluding chlorine) for each solution.

The analytical results for the α-correction coefficient and ratio techniques, as applied to Series of NBS standards, are shown in Table 23 of the text.

TABLE A <u>Intensity measurement</u>

Alloy	$I_{CrK\alpha}$ (cps)	$I_{MnK\alpha}$ (cps)	$I_{FeK\alpha}$ (cps)	$I_{NiK\alpha}$ (cps)	$I_{CuK\alpha}$ (cps)	$I_{ClK\alpha}$ (cps)	$I_{CoK\alpha}$ (cps)
36a	548	173	39 637	466	428	39 610	--
64	5 995	82	4 268	344	320	42 485	--
66A	--	4 374	16 363	--	--	32 284	--
68A	--	28 445	4 290	--	--	8 933	--
72E	242	270	42 526	483	524	40 439	--
72C	237	237	41 134	--	--	40 153	--
73A	3 388	144	37 747	345	453	36 913	--
73b	2 516	159	30 871	356	434	52 934	--
101d	4 493	391	31 036	17 056	585	27 769	258
106a	291	252	42 083	551	495	42 503	--
111b	38	336	43 647	3 336	291	45 908	--
115	412	344	24 342	24 249	8 635	16 704	--
121c	4 731	670	32 806	21 472	524	30 607	--
133a	2 674	421	31 884	441	422	49 444	--
156	133	692	46 080	949	350	41 746	--
159	175	241	29 417	233	470	50 090	--
160a	6 668	1 019	36 943	34 081	613	51 840	--
168	1 744	217	650	19 162	357	40 039	24 511

7.0 ANALYSIS OF COPPER-BASE SOLUTIONS AND ALLOYS

7.1 Analysis of Copper-Base Synthetic Solutions

7.1.1 Synthetic Solutions of Cu, Zn and Pb. Series SD

Solutions: The metal concentrations for each solution were obtained by dilution of the following stock solutions:-

Copper 1 ml = 0.20000 ± 0.00005 g (dil. HNO$_3$)
Zinc 1 ml = 0.20000 ± 0.00005 g (dil. HNO$_3$)
Lead 1 ml = 0.10000 ± 0.00002 g (dil. HNO$_3$)

The exact final weight of each solution was determined.

Ranges of concentration in solutions and in projected alloys were:-

Element	Range in solution %	Range in projected alloy %
Copper	0.20 - 10.00	9.09 - 90.09
Zinc	0.20 - 10.00	5.00 - 76.92
Lead	0.10 - 4.80	0.90 - 85.00

The solution compositions and the projected alloy compositions for SD Series are given in Table 24 of the text.

Intensities: The operating parameters for Series SD were:-

Element	Cu	Zn	Pb
Target	W	W	W
kV	50	50	50
mA	20	20	40
Coll^{n}	fine	fine	fine
Crystal	LiF	LiF	LiF
Counter	Sc	Sc	Sc
Time (s)	20	20	20
Counts	3	3	3
Rad^{n}	Kα	Kα	Lα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various components. Calculated concentration was then obtained by direct solution of a system of simultaneous linear equation of the type given as Equation (25). Calculated projected alloy composition was obtained by multiplication using dilution factor (solution weight versus total solid weight, excluding chlorine) for each solution.

The analytical results for the α-correction coefficient and ratio technique, as applied to Series SD are shown in Table 26 of the text.

TABLE A Intensity measurement

Solution	$I_{CuK\alpha}$ (cps)	$I_{ZnK\alpha}$ (cps)	$I_{PbK\alpha}$ (cps)
SD-1	48 759	68 701	2 714
SD-2	22 150	146 647	47 844
SD-3	253 394	36 055	946
SD-4	48 278	285 835	7 855
SD-5	24 157	34 269	30 282
SD-6	112 781	78 752	25 015
SD-7	167 887	112 896	5 243
SD-8	48 614	68 196	46 017
SD-9	14 391	10 409	74 137
SD-10	12 060	16 528	8 593
SD-11	23 512	175 027	37 445

7.1.2 Synthetic Solutions of Cu, Sn, Pb and Zn. Series SB

Solutions: The metal concentrations for each solution were obtained by dissolving synthetic solid mixtures of copper, tin, lead and zinc of chemical reagent grade in a mixture of hydrochloric acid and nitric acid.

The exact final weight of each solution was determined.

Ranges of concentration in solutions and in projected alloys were:-

Element	Range in solution %	Range in projected alloy %
Copper	2.20 - 6.73	84.11 - 92.29
Tin	0.06 - 0.44	1.97 - 5.98
Lead	0.10 - 0.25	1.38 - 8.79
Zinc	0.08 - 0.26	1.12 - 9.29

The solution compositions and the projected alloy compositions for Series SB are given in Table 25 of the text.

Intensities: The operating parameters for Series SB were:-

Element	Cl	Cu	Sn	Pb	Zn
Target	Cr	W	W	W	W
kV	50	50	50	50	50
mA	36	20	40	40	40
Coll^{n}	coarse	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20
Counts	3	3	3	3	3
Rad^{n}	Kα	Kα	Kα	Lα	Kα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various componenents. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear equation of the type given as Equation (25). Calculated projected alloy compositions were obtained by multiplication using dilution factor (solution weight versus total solid weight, excluding chlorine) for each solution.

The analytical results for the α-correction coefficient and ratio technique, as applied to Series SB are shown in Table 27 of the text.

TABLE A Intensity measurement

Solution	$I_{CuK\alpha}$ (cps)	$I_{SnK\alpha}$ (cps)	$I_{PbK\alpha}$ (cps)	$I_{ZnK\alpha}$ (cps)	$I_{ClK\alpha}$ (cps)
SB-1	101 734	6 580	2 501	7 649	7 005
SB-2	87 826	11 219	2 633	10 573	8 031
SB-3	74 515	6 268	3 233	8 385	6 292
SB-4	83 835	2 796	3 020	19 602	7 504
SB-5	73 135	3 844	4 213	24 418	5 330
SB-6	132 559	10 406	932	4 160	16 018
SB-7	132 327	11 940	1 011	7 915	15 245

7.2 Analysis of Copper-Base Alloy Standards

7.2.1 Analysis of Copper-Base Alloy Standards in Solution

Solutions: Copper-base alloy standards available were covered a relatively small range of composition for the major componenents. These are:-

Copper	82.14 - 93.03 %
Tin	2.11 - 6.76 %
Lead	0.60 - 6.25 %
Zinc	1.49 - 6.90 %

Various sample sizes from 1 to 2 g, depending on the lead content, were dissolved in nitric acid with some small amount of hydrochloric acid. Water was used to dilute solutions up to approximately 50 g.

The exact final weight of each solution was determined.

The chemical compositions of copper-base alloy standards are shown in Table 28 of the text.

Intensities: The operating parameters for copper-base alloy standard solutions were:-

Element	Cl	Cu	Sn	Pb	Zn
Target	Cr	W	W	W	W
kV	50	50	50	50	50
mA	36	20	40	40	40
Coll^n	coarse	fine	fine	fine	fine
Crystal	PET	LiF	LiF	LiF	LiF
Counter	PF	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20	20
Counts	3	3	3	3	3

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background and for deadtime where required, and are shown as Table A.

Calculations: One solution was selected as standard to calculate I^o values for various components. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear equation ofthe type given as Equation (25). Calculated alloy compositions were obtained by multiplication using dilution factor (solution weight versus total solid weight, excluding chlorine.) for each solution.

The analytical results for the α-correction coefficient and ratio technique, as applied to the Series are shown in the Table 29 of the text.

TABLE A Intensity measurement

Alloy	$I_{CuK\alpha}$ (cps)	$I_{SnK\alpha}$ (cps)	$I_{PbL\alpha}$ (cps)	$I_{ZnK\alpha}$ (cps)	$I_{ClK\alpha}$ (cps)
2-1	48 555	3 411	1 550	3 707	23 091
2-2	56 548	4 639	1 798	6 911	10 702
2-3	59 810	6 020	1 851	8 747	10 131
2-4	54 408	5 777	1 965	7 894	9 276
2-5	51 143	5 845	2 172	7 196	12 108
2-6	34 784	4 203	1 804	4 675	12 556
2-7	41 562	4 229	2 225	5 417	11 857
2-8	41 567	3 273	1 920	3 846	11 229
2-9	30 983	2 458	1 701	2 885	10 791
2-10	30 833	2 420	1 767	2 848	12 876
4-1	41 898	1 461	2 202	10 355	9 727
4-10	28 763	1 436	2 160	6 605	12 259
8-1	118 660	8 936	446	6 441	12 735
8-3	125 553	13 428	501	15 406	10 632
8-8	100 710	8 682	1 172	6 977	11 332
8-13	72 660	7 795	1 517	6 608	10 836

7.2.2 Analysis of Copper-Base Alloy Standards in Solid Form

Solid Specimen: Copper-base alloy standards were available in solid form appropriate for XRF study.

The chemical compositions of copper-base alloy standards are shown in Table 28 of the text.

Intensities: The operating parameters for copper-base alloy standards were:-

Element	Cu	Sn	Pb	Zn
Target	W	W	W	W
kV	40	40	50	40
mA	20	20	20	20
Coll^n	fine	fine	fine	fine
Crystal	LiF	LiF	LiF	LiF
Counter	Sc	Sc	Sc	Sc
Time (s)	20	20	20	20
Counts	3	3	3	3
Rad^n	Kα	Kα	Lα	Kα

The tabulated counts represented the averages for the number of counts shown. All counts were corrected for background, and for deadtime where required, and are shown as Table A.

Calculations: One sample was selected as standard to calculate I^o values for various components. Calculated concentrations were then obtained by direct solution of a system of simultaneous linear equation of the type given as Equation (25).

The analytical results for the α-correction coefficient and ratio technique, as applied to the Series, are shown in the Table 30 of the text.

TABLE A **Intensity measurement**

Alloy	$I_{CuK\alpha}$ (cps)	$I_{SnK\alpha}$ (cps)	$I_{ZnK\alpha}$ (cps)	$I_{PbL\alpha}$ (cps)
2-1	261 286	1 942	6 734	1 477
2-2	257 268	2 395	10 303	1 451
2-3	245 242	2 797	12 048	1 453
2-4	245 074	2 739	12 186	1 584
2-6	240 714	2 641	11 382	2 004
2-7	236 013	2 678	10 745	2 208
2-8	251 548	2 218	7 955	2 044
2-9	249 009	2 208	7 670	2 227
2-10	246 602	2 184	7 352	2 360
2-11	237 702	2 589	9 600	2 302
4-1	250 364	1 150	20 140	2 152
4-10	237 337	1 273	18 887	2 976
8-1	268 349	2 411	4 924	219
8-3	249 663	3 338	11 007	205
8-8	258 884	2 739	6 428	654
8-13	247 992	3 130	8 303	828

8.0 APPENDIX

Suggested Method of Data Treatment in the Determination of α-Correction Coefficient by G.R. Lachance

The suggested method is based on the assumption that the magnitude of the interfering effect is proportional to the concentration of the component(s) providing the effect and is divided into two cases: a/ binary solutions, b/ ternary and multicomponent solutions.

a/ Binary solutions: In a series of solutions containing components A and B, with A is the component being affected and B is the component providing the interfering effect; the determination of the α_{AB} correction coefficient is carried out according to the following steps:

1/ One solution is chosen as reference.

2/ The apparent concentration of A, $C_{A(app)}$, is calculated from the intensity ratio.

$$C_{A(app)} = C_{A(ref)} \frac{I_A}{I_{A(ref)}}$$

3/ The interfering effect Δ of B on A is given by the following relationship:

$$\Delta = \frac{C_A - C_{A(app)}}{C_{A(app)}}$$

4/ The corresponding concentration of B is given by:

$$\Delta C_B = C_B - C_{B(ref)}$$

5/ The ratio k of Δ to ΔC_B is computed, and rejection of doubtful data is carried out. The average value of k is determined. The ratio k can be obtained graphically by plotting of Δ versus ΔC_B.

6/ α_{AB} correction coefficient is calculated by the following expression:

$$\alpha_{AB} = \frac{k}{1 - kC_{B(ref)}}$$

b/ <u>Ternary and multicomponent solutions:</u> In a series of solutions containing components A, B and C, with A is the component being affected, B and C are components providing the effect and the correction coefficient α_{AB} determined in advance; the determination of α_{AC} correction coefficient is carried out in the following way:

1/ The total interfering effect of B and C on A is calculated according to the steps 1, 2 and 3 in Part a. The reference intensity is the corrected intensity of A for the effect of B.

$$I_{A(ref)} = I_{A(meas)} (1 + \alpha_{AB}C_B)$$

2/ The portion of the total interfering effect due to B is given by:

$$\delta = \alpha_{AB}C_B$$

3/ The effect of C on A is given by the difference of $\Delta - \delta$.

4/ The correction coefficient α_{AC} is calculated by the following expression:

$$\alpha_{AC} = \frac{\Delta - \delta}{C_C'}$$

5/ Rejection of doubtful data is carried out and the average value of α_{AC} is determined. This can be done graphically by plotting of $\Delta - \delta$ versus C_C.

For multicomponent solutions, similar treatment is employed.