immediately adaptable to automation, as well as with the selection and application of methods not previously included as part of the established methodology. A third phase of the investigation, carried out simultaneously with the other two phases, deals with the automation of the pretitration sample preparation process involving the addition of reagents, silution dilution, solution heating, etc.

The results of the investigation indicate that automation of the analytical processes for commercial electroplating bath analysis is feasible, provides for results at least as precise and accurate as the corresponding technique in the established methodology, allows for a much improved time-to-obtain results, permits staff reductions for a stable workload or allows existing staff to significantly increase the workload handled, yields reductions in the space occupied and the cost per determination, and generally increases the overall efficiency. In addition, the time-to-complete is such as to permit a considerable increase in bath analysis frequency, with corresponding better control and improvement in plating quality and efficiency.

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MY PARENTS

HANA and JAIS ELCABETZ

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1. INTRODUCTION

1.1 The Electroplating Industry

The industrial and commercial electroplating industry embraces many different forms of operation. These range from relatively small organizations specializing in simple, decorative copper, nickel, brass, chromium, etc., plating operations to large free or captive installations where the plating procedures range from decorative to engineering speciality operations involving hard-chromium, hard-nickel, corrosion-resistant-coating plating, etc.

A common requirement for all commercial electroplating installations is the need to control the composition of the electroplating bath solutions within reasonably well-defined limits. This necessitates fairly frequent sampling and chemical analysis of the baths in order to establish the composition relative to the key components and the accumulating impurities, and to determine what corrective procedures need to be applied. The more frequent or prolonged the use of any electroplating bath, the greater the need for analytical control and, indeed, for increasing the frequency of sampling and analysis.

Over recent years the electroplating industry has experienced an increasing trend to the use of mechanized and highly-automated equipment for the handling of parts subject to plating. In addition, emphasis has been placed on high-speed deposition or plating processes. These innovative areas have had as their justification improvements in

plating efficiency and quality and, of even more subtle importance, reduction in the unitized cost of production. Such more efficient manufacturing procedures obliquely demand, of course, that the frequency of bath analysis be stepped up, and that the speed of carrying out and reporting the analytical processes be enhanced.

Although the industry has experienced considerable in the way of advances with respect to production mechanization, automation and improvement in the plating process, the methods of control by chemical analysis have not, except in certain isolated circumstances, been radically altered. The methods applied in the laboratory for the processes of chemical analysis have remained basically unchanged over many years, with only relatively minor modifications being introduced. These analytical techniques are largely manual titrimetric methods, many of them of types so long established as to be of almost historical significance in the field of analytical chemistry. Automated analytical techniques, and their application to automated bath control, have been the subject of much research, but application of the direct or implied results to the industry in general has been slow to materialize.

The research work described herein is based on a specific problem within the electroplating industry, although the areas of exploration imply application to the industry at large.

The suppliers of equipment and chemicals to the electroplating industry in general are very frequently required to act as centres for the chemical analysis of electroplating baths for their clients. An

operation of this nature is carried out largely as a customer service, and requires the treatment daily of large quantities of samples representing an extensive variety of commercial electroplating process baths. Each sample must be analyzed for at least all those components where the content range has a critical effect on electroplating quality.

Because of the large number of samples submitted, the need to provide a comparatively rapid output of results and the inherent demands with respect to staff size and laboratory space, such an operation should be as efficient as possible. The repetitive nature of the analytical processes, and the obvious connection between efficiency and economy of operation, indicates an area where any successful attempt at automation would be highly advantageous. Automation of such analytical processes should result in staff reduction for repetitive work loads, more consistent analytical procedures and results, less dependence on staff turnover and a more rapid treatment of incoming samples. All of this is desirable from the points of view of better client service, greater efficiency and improved economics. These are important factors in the type of client service operation involved.

The larger electroplating industries, where electroplating bath analysis is often carried out by their own laboratories, could also benefit from such an application of automated analytical procedures. Their use would permit, without staff or space enlargement, improved bath composition control through the ability to provide for more frequent sampling and a more rapid return of results.

An industrial research grant was provided by Canadian Industries Limited and Canadian Hanson Limited, the latter organization being one of the principal suppliers in Canada of electroplating equipment and chemicals. The purpose of the grant was to support research to explore the possibilities of automating the analytical processes applied in the electroplating industry in general, and in the laboratories of Canadian Hanson in particular. In general these analytical techniques were of the long-established manual titrimetric type discussed in the foregoing. While the research proposal did not preclude analytical method modification or substitution, the essential purpose was to adapt these techniques, insofar as possible, to a process of automation. Several specific factors dictate this wish to avoid radical modification or substitution relative to the established methodology. Two of these might be mentioned. The established methodology does, in many instances, provide for techniques capable of handling the analysis of the rather specialized compositions typical of electroplating baths. Again the established methodology, while it may yield results less accurate than those provided by more sophisticated methods, yields results of established patterns systematically interpreted by electroplaters in their subsequent composition control adjustments. The introduction of techniques of analysis permitting more accurate but significantly different results might, over the long run and without a very carefully-planned educative process of introduction, cause serious problems devolving from required control adjustments and those actually applied on the established basis of interpretation.

A survey of literature data, and of commercially available equipment, was carried out from the point of view of method automation. Although this survey was to a certain extent limited by consideration of the fact that, in the main, the potentiometric titration approach would be the one most suitable with respect to automation of the methods involved, a specific attempt was made to use equipment in the experimental work capable of simple adaptation from the potentiometric preset dead-stop endpoint titration technique to preset deadstop endpoint methods where absorptiometric, coulometric and amperometric titration principles were involved. The introductory discussions to follow will, however, largely surround the potentiometric form of automated determination.

1.2 Potentiometric Electrode Systems

A volumetric titration involves a solution containing an unknown quantity of a reactant species to which is added a measured and stoichiometrically equivalent volume of a known-concentration titrant solution. The detection of the equivalence point of the titration (and the associated equivalence point volume of the titrant solution) is the critical area of the titration. Where the detection system is such that the equivalence point volume and the volume at the detection endpoint are identical, they are said to coincide and no titration error situation exists. In many instances, however, the detection system may provide for some lack of agreement between the endpoint and equivalence point volumes. Depending upon the magnitude of this difference, volume corrections or blanks applied to the endpoint volume

may be required in order to avoid erroneous results.

There are many techniques of endpoint detection in titrimetry, and the method frequently varies according to the basic nature of the titration. For oxidation-reduction or redox titrations, and for all other titration types where an electrode can be found which responds directly or indirectly to critical solution component concentration changes associated with the titration reaction, the changing electrode potential can be correlated with the volume addition of the titrant. Significant changes in the concentration of the critical component in the neighbourhood of the equivalence point are reflected in similarly significant changes in the indicating or working electrode potential.

Where such indicating electrodes are used, in conjunction with an appropriate reference electrode, the changing potential of the electrode couple can be detected by a potentiometric device. As indicated in the foregoing, the changes in the electrode couple potential per unit addition of titrant are most pronounced in the neighbourhood of the equivalence point. A properly-recorded or tabulated plot of potential versus volume of titrant can be used to locate, in one way or another, the titration equivalence point volume.

For example, a glass indicating electrode may be used to follow the changing activity of hydrogen ion (or changing hydrogen ion concentration) during an acid-base neutralization titration. In a similar manner a platinum indicating electrode may be applied in the measurement of the changing potential of a redox system under titration, while

a silver indicating electrode may be used to detect silver ion concentration changes during titrations involving silver ion.

In general, a titration plot of potential versus titrant volume shows significant changes in the rate of change of potential per unit of titrant volume addition in the neighbourhood of the equivalence point, and attains its maximum at this point. These changes in $\Delta E/\Delta V$ result in the typical "S-shaped" titration curve. Location of the point of inflection of the curve in the equivalence point zone of $\Delta E/\Delta V$ change locates the titration equivalence point volume. Manual plots, recorder plots or data transalations yielding E versus V, $\Delta E/\Delta V$ versus V or $\Delta^2 E/\Delta V^2$ versus V can all be used as means of locating the equivalence point volume.

While platinum electrode systems (and certain others) respond in general to potential changes for redox systems under titration, other electrode systems are more specific or selective in their response. The standard glass electrode, for example, is selective with respect to response to changing pH, while the silver electrode is in general specific in its response to changing solution pAg.

A system of electrodes selective in their response to ion concentrations for different ions in solution involves what is known as ion-selective electrodes. Such electrodes have a general basis in the use of fixed-and-mobile-site ion-exchanging materials. These materials may be homogeneous solids, such as glass, polymeric membranes with ion-exchanging functionality, inorganic crystal membranes or membranes of

natural mineral substances. They may involve membrane-enclosed liquid ion-exchanging arrangements. Ion-exchanging materials of a heterogeneous nature are also used in the construction of ion-selective electrodes.

No ion-selective electrode is selective exclusively with respect to the ion specified. The presence of other ions can seriously impair electrode performance. Such interfering actions may take several forms, depending on the nature of the membrane and/or ion-exchange material, and can be based on interfering ion activity and/or type.

Ion-selective electrode behaviour under interfering conditions can be represented by an expression first used by Nicolsky (1) for a glass electrode. In the application involved, the glass electrode showed a mixed response with respect to hydrogen and sodium ions. The expression is sometimes referred to as a simplified Eisenmann equation (2).

$$E = \text{constant} \pm 0.059 \log(C_i + K_{ij}C_j) \qquad (1)$$

where:-

E = electrode potential

C_i = concentration of single-charge ion to which the electrode is primarily responsive (e.g. H^+)

C_j = concentration of single-charge ion providing the interfering response (e.g. Na^+)

K_{ij} = the selectivity coefficient

In order that the electrode should be predominantly responsive to the concentration C_i, the factor K_{ij} must be small.

Where ion-selective electrodes responsive primarily to double-charge ions are concerned, and for interference by single-charge ions, equation (1) modifies to:-

$$E = \text{constant} \pm \frac{0.059}{2}\log(C_i + K_{ij}C_j^2) \qquad (2)$$

where:-

E = the electrode potential

C_i = concentration of double-charge ion to which electrode is primarily responsive (e.g. Ca^{2+})

C_j = concentration of single-charge ion providing the interfering response (e.g. Na^+)

K_{ij} = the selectivity coefficient

For the calcium (II) ion-selective electrode, the selectivity coefficient with respect to interference by sodium (I) ion is about 10^{-3}, indicating that the electrode is very approximately 1000 times more responsive to Ca(II) ion than to Na(I) ion.

As the value of the ratio of C_j/C_i is increased, the electrode eventually displays no significant response to changes in the concentration of the primary ion, and a plot of E vs $\log C_i$ becomes approximately parallel to the $\log C_i$ axis. In the absence of any significant concentration of the interfering ion, the plot of E vs $\log C_i$ has a slope of $\pm 0.059/Z$, where Z is the primary ion charge.

Theories relative to the establishment of potentials across membranes have been reviewed by Eisenmann (3), and more recently by Simon

et al (4). The basic approach consists of combining interfacial potential terms (Donnan potentials) with interdiffusional terms arising out of the different mobilities of the ions associated with the membrane.

While liquid membrane ion-selective electrodes were known for many years, it was probably the introduction of the calcium ion-selective electrode by Ross (5) which stimulated the intensive developmental research which resulted in the present commercial availability of ion-selective electrodes for a significant number of cations and anions.

A general theory of the operation of liquid membrane electrodes based on ion-exchange properties has been given by Sandblom (6). The potentiometric response to a given ion depends not only on the activity of the ion in the solution and in the membrane, but also on the equilibrium constant for the ion-exchange process and on the mobility of the ion in the membrane. In general, ionic migration has been determined to be the only process responsible for the transport of charge through the membrane. This gives the effect of treating the membrane as a pure resistance. Although ionic migration has been determined as the sole transport process, the mechanism of ion transport through membranes and across membrane-solution interfaces is not yet fully understood. It is thought, however, that the ion-exchange reaction is not the sole rate-determining factor.

Among the more significant advances in potentiometry in recent

years has been the development of ion-selective electrodes employing inorganic crystalline materials as membranes. The properties of such solid membrane electrodes are analytically attractive. Their sensitivity to the primary ion is limited to dilute solutions which do not contain other ions capable of forming with the membrane materials salts of solubility product constant lower than those of the membrane compounds.

The mechanisms of response of these solid membrane electrodes are not as well understood as those of the glass membrane electrode. A theory has been put forward by Buck (7) in this connection in which rapid reversible ion exchange at the membrane interfaces with the solutions and mobile defects within the membrane crystals are assumed. Pungor (8) used radiochemical methods to investigate the exchange of iodide ions in a membrane consisting of silver iodide crystals dispersed in a silicone rubber matrix, and reported that the exchange rate was very fast. The ion-exchange reaction depends on ion adsorption at the membrane/solution interface, a process which may be the primary step in the ion-exchange mechanism.

The possibilities of interference relative to the potentiometric response for a solid membrane electrode through the mechanism of mixed crystal formation and simple adsorption have been recognized by Buck (9). Brand (10) made an attempt to correlate the solid membrane electrode selectivity coefficient for interfering ions with the solubility products of their corresponding silver or sulphide salts with those for the mixed silver sulphide membrane materials.

Many ion-selective electrodes which respond to different cations or anions have become commercially available over recent years. Such electrodes have demonstrated Nernstian response over an extended range of activity/concentration. They have also shown, in many instances, under prolonged use and in time, a gradual loss of selectivity and a general deterioration of response. Because of these degenerative factors it is necessary to evaluate the selectivity coefficients periodically and systematically. This can be accomplished quite simply. The potential of an ion-selective electrode in a solution containing only the single-charge cation to which it is primarily responsive is:-

$$E_i = \text{constant} + 0.059 \log \alpha_i \qquad (3)$$

where:- α_i = activity of primary single-charge ion

If the solution does not contain the cation to which the electrode is primarily responsive, but contains any other single-charge cation with a selectivity coefficient of K_{ij}, the potential of the electrode in such a solution is given by:-

$$E_j = \text{constant} + 0.059 \log K_{ij}\alpha_j \qquad (4)$$

where:- α_j = activity of nonprimary single-charge cation

Where the values of α_i and α_j are equal we have:-

$$\log K_{ij} = -(E_i - E_j)/0.059 \qquad (5)$$

The changing value of the selectivity coefficient for a given nonprimary single-charge ion can thus be determined by measuring periodically the difference in potential for the electrode in two solutions of equal activity for the primary and nonprimary ions.

Ion-selective electrodes can be used to monitor the solution activity of a large number of ion species. The response for a given electrode will be linear relative to the logarithm of the ion activity within the permissible activity range, providing interfering ion species are each either absent or present at some constant value of activity lower than that value significant with respect to the ability of the electrode to respond to the primary ion. Where ion-selective electrodes are used to record the changing activity of a species during a titration, the presence of an interfering species at less than such significant activity levels presents little difficulty.

In all instances, of course, ion-selective electrodes measure ion activity values and changes therein. Associated concentration values and changes approximate those for activity, providing the solutions are highly dilute -- a situation normal to most quantitative analytical titrimetric procedures.

1.3 The Potentiometric Titration Method

Electrode systems may be used in a direct potentiometric estimation of ion activity or concentration. The use of the glass electrode to

measure solution pH (hydrogen ion activity or concentration) is an example in point. The direct potentiometric technique has, according to Dick (11), the following significant limitations:-

(a) Yields at best the activity or concentration of a specific ion species in the solution tested.

(b) Where the substance to be determined exists in the solution tested to a significant extent in a form other than the ionic, the amount of that form will not be determinable from direct potentiometric data.

(c) In direct potentiometry, an accurate and precise measurement of E_{cell} must be made, and accurate values or compensations for the appropriate electrode junction potentials and the reference electrode potential must be known.

(d) The electrode responses will be seriously affected by variable ionic strength or background of the solutions investigated.

On the other hand, electrode systems may be used to measure the changing value of ion concentrations during a titration process. This potentiometric titration process, as it is called, provides certain well-defined advantages over direct potentiometric measurement. According to the same reference these include:-

(a) The technique is generally unaffected by the state (ionic, undissociated, complexed) of the electrode-responsive substance in the solution to be titrated.

(b) Since only the <u>changes</u> in electrode response during the titration are significant, accurate data concerning E_{cell}, $E_{reference}$ and $E_{junctions}$ are not required.

(c) Again, since the electrode response <u>changes</u> only are significant during the titration, the background ionic strength is relatively unimportant, providing

interfering ion species are held to within limiting concentrations relative to electrode response to the primary substance.

(d) Difficulties attendant upon the use of colour-change indicator substances to detect the titration endpoint are eliminated.

(e) The electrochemical interpretation of the titration equivalence point location renders the potentiometric titration technique highly adaptable to automation.

In potentiometric titration systems, the electrode couple (indicating and reference electrodes) provides a changing measure of the solution potential during titration, as based on the changing potential of the indicating electrode. Regardless of the nature of the indicating electrode (platinum, glass, ion-selective, etc.) the general response of the couple is given by:-

$$E_{cell} = E_{ind} - E_{ref} \qquad (6)$$

Where, for example, the indicating electrode is a silver-sensitive massive silver electrode, we have:-

$$E_{ind} = E_{Ag^+/Ag} = E^o_{Ag^+/Ag} + 0.059\log[Ag^+] \qquad (7)$$

$$= E^o_{Ag^+/Ag} - 0.059pAg \qquad (8)$$

For a titration involving silver ion titrated with a standard solution of sodium chloride, the concentration of Ag^+ will decrease during the titration so as to produce, for a plot of pAg versus volume of NaCl solution, a typical S-shaped titration curve. Obviously the plot of E_{ind} or E_{cell} versus volume NaCl solution will duplicate, in its

general form, the same S-shaped curve. Location of the point of inflection of this curve locates the titration equivalence point volume.

The potentiometric titration technique can be applied wherever an indicating electrode is available with a response relative to, directly or indirectly, the substance under titration. It can, subject to these limitations, be applied to neutralization, precipitation, complexation, redox and nonaqueous solvent titrations.

The application of the technique can range through the following:-

(a) Simple manual titration systems involving a burette, an electrode couple system and a potentiometer. Under these conditions the titration volume and the associated potential data are logged, and the titration equivalence point volume is located by curve plotting and graphic analysis or by data tabulation and analysis of $\Delta E/\Delta V$ vs V or $\Delta^2E/\Delta V^2$ vs V.

(b) Instrumental titration systems involving an automatic burette drive linked to a recorder to which is also linked the electrode couple potential output. Where some rate of continuous volume addition of titrant is selected the recorder provides a plot of electrode couple potential versus volume of titrant. A complete plot of potential versus volume is obtained and subsequently graphically analyzed for the equivalence point volume. Such systems can frequently be arranged to provide a plot of $\Delta E/\Delta V$ versus volume of titrant as a first-derivative titration curve from which the equivalence point volume can be located.

(c) Titration systems similar to (b), but where the addition of titrant can be stopped automatically when a preset potential representative of the equivalence point of the titration is attained. The preset potential is determined previously from a full titration plot of potential versus titration volume, or from logged potential/volume data, for a standard run. Such relatively simple dead-stop titrators, as they are called, operate generally on

the basis of an appropriate volume rate of titrant addition selected prior to the start of titration.

(d) Systems somewhat similar to (c), but where a sensing device anticipates the onset of the equivalence point zone (increasing rate of change of $\Delta E/\Delta V$ near the equivalence point), and adjusts the rate of addition of titrant (by pulsing the volume addition, amount per pulse and pulse frequency) to ensure titration dead-stop at the exact equivalence point. Such systems can be adapted to the carrying out automatically of multiple sequential titrations.

(e) Systems similar to (d), but embodying a variety of approaches to the control of the rate of volume addition of titrant in the neighbourhood of the equivalence point.

Note that all of the systems from (c) on could be described as automated titration techniques, since the final volume read at the dead-stop titration point is the equivalence point volume and since, once started, the titration or sequential multiple titrations are carried out under automatic control completely.

1.4 Automatic Potentiometric Titrations and Titrators

When it is necessary to analyze large numbers of routine samples daily on a titrimetric basis, manual titration techniques become tedious and time-consuming. In order to avoid analytical result delays a large laboratory staff is required, and this provides for poor operational economy as to both salaries and space occupied. Automatic titration systems have been applied in the solution of these problems, and many such systems are in use today in industry and elsewhere. These systems, as indicated in the previous section, range from simple-operator con-

controlled titrant delivery devices with potentiometers or potentiometric recorders, to complex assemblies capable of handling titrant delivery rate variation, titration curve characteristic sensing, dead-stop endpoint, digital and printer readout of each titration equivalence or endpoint value, sample changing, addition of pretitration reagents, etc. Although techniques other than the potentiometric can be used to provide automated titration procedures, early efforts to automate centered very largely around the potentiometric technique and it is today the most widely applied. To a considerable extent this is due to the high sensitivity of the potentiometric measuring method, and its adaptability to a wide range of reactant concentration and titrimetric reaction types.

Indeed, according to Lingane (12), the characteristics of a good automatic titrator should include adaptability to all types of reactions, ability to handle all types of electrode combinations, precision and accuracy as good at least as in the corresponding manual method, ability to record a full titration curve or to dead-stop the titration at a preset equivalence point potential, performance of successive titrations of two or more substances in a single sample solution, and the addition of successively smaller increments of titrant near the equivalence point or endpoint, as controlled by the changing potential in this zone, in order to avoid over-titrating in normal and slow reaction rate titrations.

Most modern automatic titrators use one of two general approaches. In one case, a gradual approach to the preset endpoint pH or potential is achieved by means of pulses of titrant delivered with diminishing

frequency and/or volume. Such variation in the pulse frequency and/or volume is obtained through sensing devices responding to the rate of change of $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ as the titration progresses. In the second case, the titrant is added continuously but with the rate of flow reducing as the preset endpoint pH or E value is approached. Rate of flow reduction is achieved by a similar sensing arrangement. The two types of automatic titrator action are sometimes called "on-off" and "on-reduced-off" respectively.

While the foregoing describes the preset dead-stop endpoint automatic titration method, automatic titrators may also involve the generation of the full titration curve by recorder to beyond the equivalence point. This curve, whether a standard curve of potential or pH versus titrant volume, or a first-derivative curve, may then be analyzed to obtain the equivalence point volume of titrant.

The preset dead-stop endpoint technique is more convenient and practical where the purpose of the titration is to obtain rapid analytical results on multiple routine samples, and where the titration characteristics are such as to lend themselves readily to this approach. A full recorded titration curve is frequently an advantage where the titration characteristics are such as to provide for very slight $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ changes around the equivalence point, where reaction rates or electrode responses are significantly slow or where recorded data must be retained. In any case, recorded curves of a full titration for each

titration type must be part of the preliminary approach to the preset dead-stop endpoint titration process, this in order to locate the dead-stop endpoint pH or potential to be preset.

In the automatic titrators described by Robinson (13) and by Lingane (14), it is indicated that the system must be arranged to satisfy two fundamental conditions. Recorder chart length must be proportional to the volume of titrant delivered, and the rate of addition of titrant must be controlled according to the changes in $\Delta pH/\Delta V$ or $\Delta E/\Delta V$, particularly those associated with the onset of the endpoint.

In the titrators described by Irving (15) and Glass (16), the mechanisms for adding the titrant and for driving the recorder are operated by a single servomotor, while in that described by Kelly (17) titrant addition and chart drive are carried out by two separate servomotors. Robinson (13) suggested that the burette-driving motor and the chart motor could be controlled by "on-off" circuits which, in turn, were controlled by potential changes detected by the electrode couple during the titration. The automatic titrator described by Kelly (17) has an intermittent balance circuit, a slow pen-balance servomotor in the recorder and a "thinking" velocity servomotor mechanism which controls the rate of continuous addition of the titrant automatically and proportionately.

Miyake (18) used the general systems of Robinson and Kelly to construct an automatic titrator of the recording type. The instrument consisted of a controlled burette and recorder system. Many commercial

titrators presently available employ a system which consists of a recording potentiometer linked mechanically to a syringe burette adding the titrant at a continuous but variable rate of flow. The total volume of titrant is thus given by the length of the recorder chart.

Even where the recorder and syringe burette motors are synchronized, or are one, a time-lag due to mixing and reaction time can result in a systematic error situation between the actaul volume of titrant delivered and the electrode couple response registered by the recorder. There are several ways of minimizing this time-lag, but it would not obviously be easy or expedient to periodically stop the syringe burette and recorder in order to attain a steady potentiometric readout, and this time-lag problem is a source of difficulty relative to continuous titrant flow titrators.

Jagner (19) describes a semiautomatic titrator capable of carrying out simultaneously several titrations. Each of these simultaneous titrations is carried out using individual motordriven syringe burettes which have been previously calibrated by obtaining the weight of titrant delivered per volume unit. A direct readout system on a teletype-operated punch tape and keyboard is employed during the titrations to provide data which, when fed to a properly-programmed computer, locates each titration equivalence point volume and weight of titrant. This titrator is suitable for titrations demanding a high degree of precision, since it involves the registration of a considerable number of titration

points around the equivalence point.

When the burettes for this system are triggered, they deliver different amounts of titrants to the respective titration vessels. The motor drives for the burettes are coupled to helipotentiometers which yield voltages proportional to the volumes of titrants added. It is thus possible to use a digital voltmeter to register accurate burette readings. The voltage signals from the burettes enter a ninety-channel input scanner. Since each titration system involves two signals, that for volume and that for electrode couple response, it is possible to handle signals from forty-five separate titration vessels. Scanning speed in channels/second can be varied and set to compensate for any time-lag associated with the attainment of equilibrium after addition of titrant. An additional ten channels are provided in order to permit short-circuiting pulses to a timer which, in combination with individual burette speed, governs the size of the increments of titrant. Thus the number of pulses for each titration increases in quantity but decreases in size in the neighbourhood of the equivalence point. The titration data thus obtained is tape-punched by teletype, fed to the computer and the critical titration point for each titration calculated.

Johansson (20) describes a method of titration which is particularly suitable to computerized data handling, and which gives good results for certain titrations that are not carried out too satisfactorily by the continuous titrant flow or the Jagner techniques. This method is of general applicability, although so far it has been described only in

reference to its application to the titration of acids by strong bases. Since the technique is not a dead-stop method, the equivalence point volume must be calculated. This is a disadvantage, but in many instances the method has compensating advantages such as speed, precision, accuracy and adaptability to automatic titration.

Johansson and Pehrsson (21) have described a fully-automatic titrator based on the system described by Johansson (20). The titrator carries out the transfer of the sample by pipette, the dilution and titration operations, and the post-titration rinsing of the electrodes, titration vessel, etc. These operations are carried out at different positions in the instrumental arrangement, thus facilitating high rates of analysis. Titrations are performed by adding the titrant stepwise in equal volume increments to the sample, with potential being recorded after each addition. Each titration is carried out until post-equivalence point potentials are attained. The titrator has a loading capacity of two hundred samples and consists of three main units; solution handling, potential measurement and operational control. The solution handling unit consists of five automatic solution handling pipettes and two sampling pipettes. All pipettes are of the plunger type and are driven by compressed air. They incorporate magnetically-operated valve systems. The control system governs the volume-increment pulse frequency and prints out a potential value after each volume addition. Since a set volume is delivered at each pulse, the number of pulses provides volume data which, when associated with the corresponding potential data, allows

calculation of the titration equivalence point volume. Computer linkage to the titration data outputs can permit automatic calculation of the critical titration point or points.

Hieftje and Mandorano (22) describe a microtitration system based on a novel concept involving the introduction of the titrant in the form of uniform submicroliter droplets which can be sent into a titration vessel at a rate controlled by a digital pulse train. Because of droplet uniformity, the titrant delivery rate is proportional to and determined by the pulse frequency, while the total delivered titrant volume is related to the cumulative pulse count. This system permits extremely precise volumes of titrant to be delivered in increments of less than one microliter. The instrument can be used in conjunction with most endpoint detection systems, with the latter being the precision-limiting component in most instances.

An advantage of the above system is the minimization of moving parts. All of the components are electronic, so that longer service, less maintenance and greater convenience can be anticipated. Routine titrations can be made more rapidly since the system eliminates much of the time-consuming burette refilling operation required by other titrant delivery systems. The electronic circuitry used to control and measure the droplet titrant delivery provides for electrode potential measurement after each droplet deflection into the titration vessel. The change in electrode potential depends on the duration and time of appli-

cation of the droplet pulse. In the circuit design there is provision for endpoint potential anticipation and subsequent reduction of the titrant delivery rate to minimize endpoint overshoot.

Hunter et al (23) compared two titration configurations using a titrant delivery system similar to that used by Hieftje and Mandarane (22), one operated by digital hardware and the other under computer control. Both the hardware-controlled system and the computer-controlled system showed improved performance over the technique described by Hieftje and Mandarane. Computer control resulted, however, in higher precision and enhanced versatility over hardware control.

In the hardware-controlled titrator the control section consists of a decision unit and a timing unit. The decision unit uses information relative to the progress of the titration with respect to potential change and, based on the rate of change, selects the required rate of titrant delivery. The timing unit, receiving data from the decision unit, transalates this into controlled pulses for the titrant delivery system. Logic level pulses are simultaneously sent to a counter which accumulates a number equal to the total number of droplets delivered to the titration vessel. The control section also senses the onset of the preset dead-stop endpoint for titration arrest. As the titration approaches the dead-stop endpoint, the rate of titrant addition is reduced by the control section. This rate reduction compensates for slow reaction and/or electrode response time-lag and serves to minimize endpoint overshoot. The total volume required to reach the dead-stop end-

point is expressed on the counter as total pulses.

In the computer-controlled titrator the decision unit, timing unit and counter are all embodied as computer software. The operator supplies the initial rate and rate reduction factors, as well as the dead-stop endpoint data, as programmed information. Once the programme has been initiated on operator command the computer decides the titrant pulse requirements based on electrode couple information.

2. EXPERIMENTAL

2.1 Introduction

Plating baths in the commercial electroplating industry can be classified under three general headings, these being acid, neutral and alkaline solution types. Baths containing simple salts of those metals commonly plated must be acidic, since most of the cations involved are hydrolyzable to insoluble hydroxides, hydrous oxides or basic salts at pH values exceeding about 5.5. Baths containing the desired metals in a complex ion form are usually, with some exceptions, neutral or alkaline. An important factor in this connection surrounds the fact that the discharge potential for hydrogen is appreciably less negative in acidic bath solutions, thus restricting applied potential ranges.

The halides are not anodically oxidized in acidic electroplating baths where their metallic salts are used. since the anodes of such baths generally comprise the same metal as that under deposition at the cathode. Metallic chloride, bromide and iodide salts can thus be used where hailde salts are the metal-incorporating compounds added to the bath. The electroplating of nickel from nonalkaline solutions usually involves the use of nickel chloride and/or nickel sulphate salts. In general the metallic chlorides show improved solubility over the sulphates, permitting higher bath concentrations with associated ability to apply higher current densities and to achieve lower deposition times. Chloride baths are, however, generally quite corrosive with respect to bath equipment and parts to be plated, thus allowing more rapid bath contamina-

tion. In a number of instances, even where the sulphate salts are used, for example in acid nickel baths, the chloride salt is often also added to promote easier dissolution of the anode by preventing or minimizing anodic passivation. With certain chloride salt plating solutions, the deposition of the metal at the cathode arises out of the cathodic discharge of a complex cation involving the metal and the chloride. The sulphate ion has less tendency to form stable complex ions with the various metals, and deposition from sulphate salt baths is apparently achieved by cathodic discharge of simple hydrated metal ions.

Fluoborates have some use where high deposit rates are required from plating baths, since such solutions permit high salt concentrations. Excess boric acid is often added to fluoborate baths to suppress hydrolysis to hydrofluoric acid, since this latter substance would permit the formation of slightly-soluble metal fluorides.

In general, the effect of the salt anion is manifested through its contribution to salt solubility and, therefore, the bath concentration of the metal ion. It is also manifested through its ability, if any, to coordinate with the metal ion in the formation of complexes capable of influencing the efficiency of the deposition process.

The single most important complexing agent in the electroplating of copper, silver and zinc metals is the cyanide ion. Since most cyanocomplexes are decomposed by acids with the evolution of poisonous hydrogen cyanide, baths involving such complexes are invariably alkaline. For

certain metal types, where hydroxide substances such as sodium or potassium hydroxide are not added to render the solution alkaline, the baths are made alkaline by the normal hydrolysis of an excess of free cyanide ion. Cyanide baths usually contain several complexes of the metal involved. The copper bath, for example, contains the di-, tri- and tetracyanocuprate (I) ions. Calculation of the cyanometal complex is, however, normally based on the use of the so-called "free cyanide" value, and is based on the assumption that, in the presence of significant excess of cyanide ion, only the highest complex ion will exist in appreciable concentrations.

Because the cyanide complex baths are alkaline, they tend to absorb carbon dioxide from the air. The resulting carbonate ion in solution has little effect on the deposition process until its concentration becomes high enough to permit precipitation as a carbonate salt of one or more of the metal cations in the bath. When this occurs, the precipitated crystals may become occluded in the metallic deposit, resulting in gross surface roughness. The higher solubility of potassium carbonate compared to sodium carbonate tends to defer this difficulty, and is one of the reasons for the preference relative to the use of potassium cyanide rather than sodium cyanide as a cyanide additive to the bath. In copper and silver cyanide baths, the presence of carbonate ion reduces anodic polarization. This can influence the nature of the metal complex ions formed as the result of anode dissolution. A low content of free cyanide can introduce the possibility in cyanide copper baths of the formation on the anode of an insoluble film of CuCN, resulting in a cessation of

current flow. When an alkali metal hydroxide is added to cyanide baths it prevents the formation of hydrogen cyanide, and the consequent loss of free cyanide ion, by reacting with carbon dioxide entering the bath from the atmosphere. In the zinc cyanide bath, some of the metal ion is converted to the zincate ion by the addition of alkali hydroxide. This is a tetrahydroxy complex, and the deposition of zinc occurs more readily from this complex ion than from the cyano-complex zinc ion, even in consideration of the fact that the latter still controls the physical nature of the deposit. Alkali carbonates are occasionally added to cyanide copper and silver baths in order to increase the conductivity function, as buffering substances and to prevent the formation on the anode of slightly-soluble films such as CuCN films.

The composition ranges for the various commercial electroplating baths, and the importance of the chemical substances required to be present or absent in order to provide good plating characteristics, emphasizes the importance of the chemical analysis procedures applied to maintain bath composition.

In the particular commercial electroplating supply organization studied in this investigation, the bath samples analyzed daily, and on a routine basis, include predominantly five different electroplating bath types. These are copper, zinc and silver cyanide baths, nickel acid baths and chromium acid baths. The determination of the metal under deposition for each bath is common to all samples. The components determined in addition vary with the bath type, and include free cyanide,

total cyanide, carbonate and total alkali in cyanide baths, chloride and boric acid in nickel baths and sulphate in chromium baths. In addition to these regularily-determined components, the determination of adulterating compounds is carried out where circumstances so dictate.

The composition of a controlled electroplating bath is reasonably constant, with changes occurring gradually with use in the plating process. For different electroplating plants, the operating conditions for the plating process may be slightly different, a situation which can give rise to different general compositions being found for the same type of bath. The samples analyzed by the supply establishment involved in this investigation originate from many client electroplating plants, so that considerable variation in composition may be found for any given bath type. For example, copper concentrations may vary from 1 to 5 oz/gal, silver concentrations from 0.2 to 5.5 oz/gal and free cyanide from 6 to 14 oz/gal. Such variations in bath composition reflect both usage effects and the application of different operating parameters.

2.2 Equipment Used in the Analytical Investigations

The investigations reported in Subsections (1.3) and (1.4) of Section (1.0) INTRODUCTION, and the general requirements covering the necessity of automating the existing manual techniques common in the electroplating industry, indicated that the potentiometric titration technique should be applied in the experimental approach to automation.

After an extensive review of commercially-available basic electrochemical titration instrumentation, certain units were selected as being the most suitable building blocks out of which the investigation data and subsequent method automation instrumentation would arise. These units are manufactured by Metrohm A.G. of Switzerland, and were supplied by the Canadian representatives of this organization, Brinkmann Instruments Canada Limited. The units, their operation and purpose, and the arrangements for automation are discussed in the details following shortly. Although the experimental work centered on the use of the finally-automated mode as a potentiometric titrator, modification of the final assembly by the incorporation of other available units could permit the application of analytical methods involving spectrophotometric, coulometric and amperometric titrations.

A very general description of the units assembled for the automatic titration system and their sequential programming, and a general schematic of the layout, is given in Tables 1 and 2, and in Figure 1 respectively. In addition to the equipment listed in these tables and figure, a Metrohm E436A recording potentiograph was used to prepare the full titration curves required to determine initially, for each analytical technique adapted to automation, the dead-stop endpoint potential required for presetting, and the general characteristics of the titration with respect to $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ changes in the neighbourhood of the equivalence point or endpoint. Data from titrations carried out on this unit were also used to monitor the automated and manual titrations carried out for each of the methods explored.

TABLE 1.

AUTOMATIC TITRATOR - UNIT FUNCTION

UNIT	FUNCTION
E503/1	AUTOMATIC SAMPLE CHANGER -- Transport and lifting pneumatics for beaker operation, dispensing valve controls for pretitration solution additions, 44 beaker capacity in 11 racks of 4 beakers each, titration head with accomodations for titration solution tip, electrodes, stirring and rinsing.
E543	INTERFACING UNIT -- Automatic sample changer controls, time and sequential controls for pretitration solution additions, stirring, titration and rinsing. Manual over-ride for beaker movement and other controls.
E526	DEAD-STOP ENDPOINT TITRATOR -- Speed and impulsing controls for titrant solution addition to preset potential or pH dead-stop endpoint. Interlocking circuitry to interface unit (E543) and Dosimat titration stand (E535/3).
E535/3	DOSIMAT TITRATION STAND -- Automatic control of burette refilling and delivery positions through interlocking circuitry with dead-stop titrator (E526), control of titrant volume pulse time and duration, digital readout of titration volume.
E552	INTERCHANGEABLE PLUG-IN GLASSWARE -- Titrant solution reservoir, automatic stopcock burette, 50ml, 20ml, etc., burette capacities.
E533	DOSIPRINT -- Interlocking circuitry to dead-stop endpoint titrator (E526), printout of sample number and endpoint volume of titrant for each titration.

TABLE 2

AUTOMATIC TITRATOR - SEQUENTIAL PROGRAM

1. Required plating solution sample volume added to each beaker, with or without minimal dilution. Beakers racked and program started.

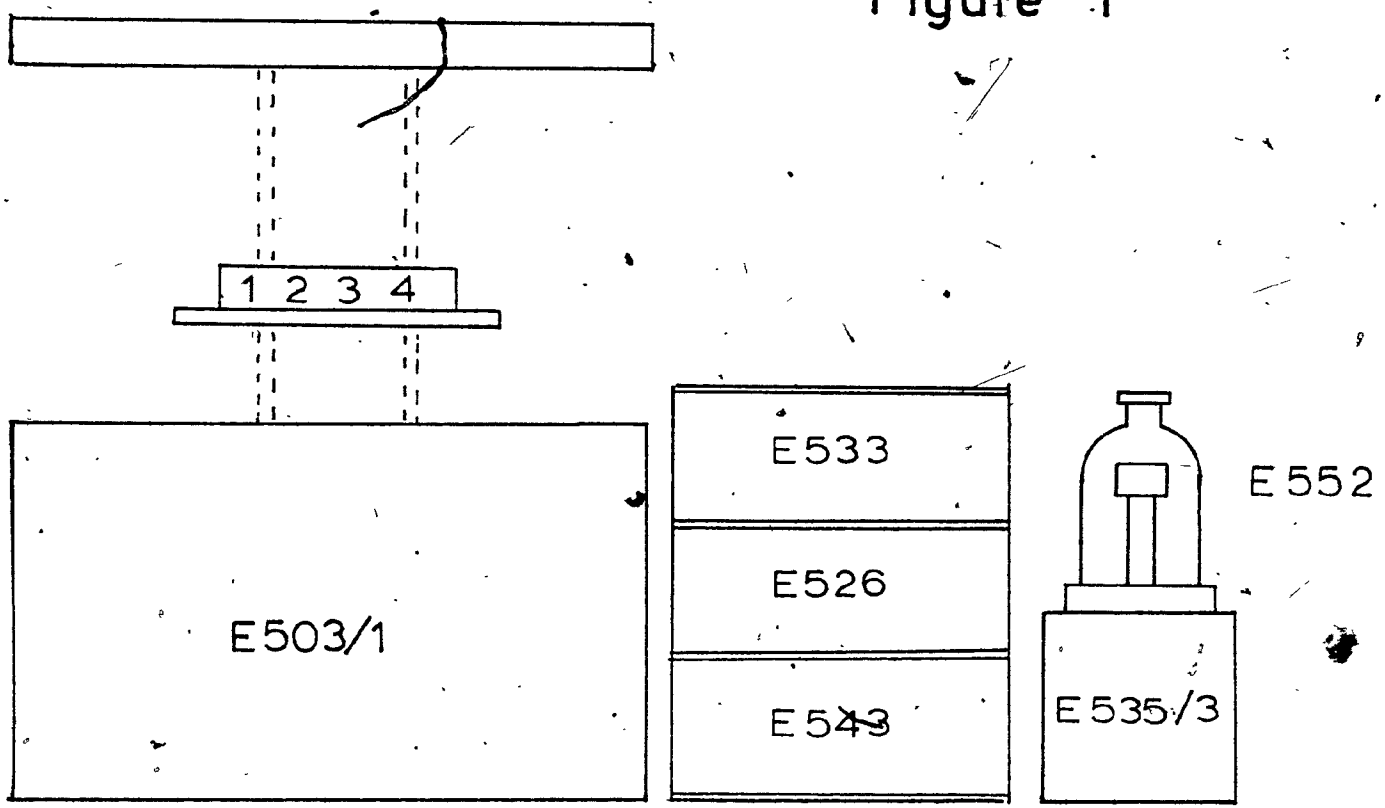
2. Beakers moved, elevated, depressed and stirred sequentially and automatically through pretitration solution addition positions and titration position.

3. In titrating position, beaker contents stirred and titrated to preset potential or pH dead-stop endpoint. Printout of sample number and endpoint titrant volume.

4. Titrated beaker lowered and titration head components rinsed while Dosimat burette automatically refilled and zeroed.

5. Up to 44 sample beakers titrated automatically and sequentially after program started. Depending on the nature of the titration, 44 titrations require 1.5 to 2 hours.

Figure 1



Schematic of Metrohm Automated Dead-Stop Titrator

The E436A recording potentiograph has a syringe burette system mechanically linked to the recorder chart drive through a single servomotor. This motor can be infinitely varied as to drive speed from zero to its maximum capacity, thus permitting variable rates of constant continuous delivery of titrant. Alternatively, the titrant delivery rate can be varied automatically as the titration curve becomes steeper in the neighbourhood of the equivalence point zone, thus preventing titration endpoint overshoot. In this mode, the titration is started at some desirable continuous speed which is then automatically decreased with increasing titration curve steepness. The control system here involves a second potentiometer, linked to the precision potentiometer of the compensating circuit, which gives a signal voltage proportional to the measured voltage of the electrode couple. This signal is differentiated so as to be proportional to the rate of change of the measured potential with titrant volume addition, and is applied, after a time delay of 3 seconds, as a countervoltage to the drive motor potentiometer. With this unit, recorder chart length represents titrant volume. The instrument has the capacity to provide first-derivative titration plots, as well as standard plots, and in addition can be applied in the preset dead-stop endpoint potential mode. The general parameters are:-

Syringe burette capacities	5, 10, 20, 50 ml
pH ranges, full-scale deflection	1, 5, 10, 14
Potential ranges, full-scale deflection	50, 100, 250, 500, 750 mV and 1, 1.5, 2 V
Calibrated compensation potential	+ and - 12 steps 100 mV each and 12 steps 1 pH each

pH calibration	shift range ± 1 pH unit
Temperature compensation for pH measurement	0-100°C in 2°C units
Automatic dead-stop	1% reproducibility for any constant setting

The E526 preset dead-stop endpoint titrator is operated in conjunction with the E535 electronic syringe burette. In combination these units provide for automatic adjustment of the titrant delivery rate as the rate of $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ increases in the neighbourhood of the endpoint, as well as for the onset of pulse feeding of the titrant at this point, with decreases in the pulse feed width with increasing proximity of the preset dead-stop pH or potential. A cut-off delay for sluggish reactions or electrode couple responses can be varied from 10 to 60 seconds. The difference between the preset point value and the actual titration value is continuously displayed during the course of the titration, and attainment of the preset potential and the titration endpoint is signaled by a "stop" light.

The control panel of the E526 incorporates a digital preset point adjustment on a four-figure selector, allowing selection of the dead-stop pH within ± 0.01 pH or potential within ± 1 mV. A calibration position and control, and two working positions are provided. The working positions cover ± pH or ± E changes during the titration and allow selection to cover titrations with either large or small $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ changes near the endpoint. A control to set pH mode, or negative/positive polarity of the indicator versus reference electrode at the titration start, is also included. Temperature compensation for the pH mode is supplied.

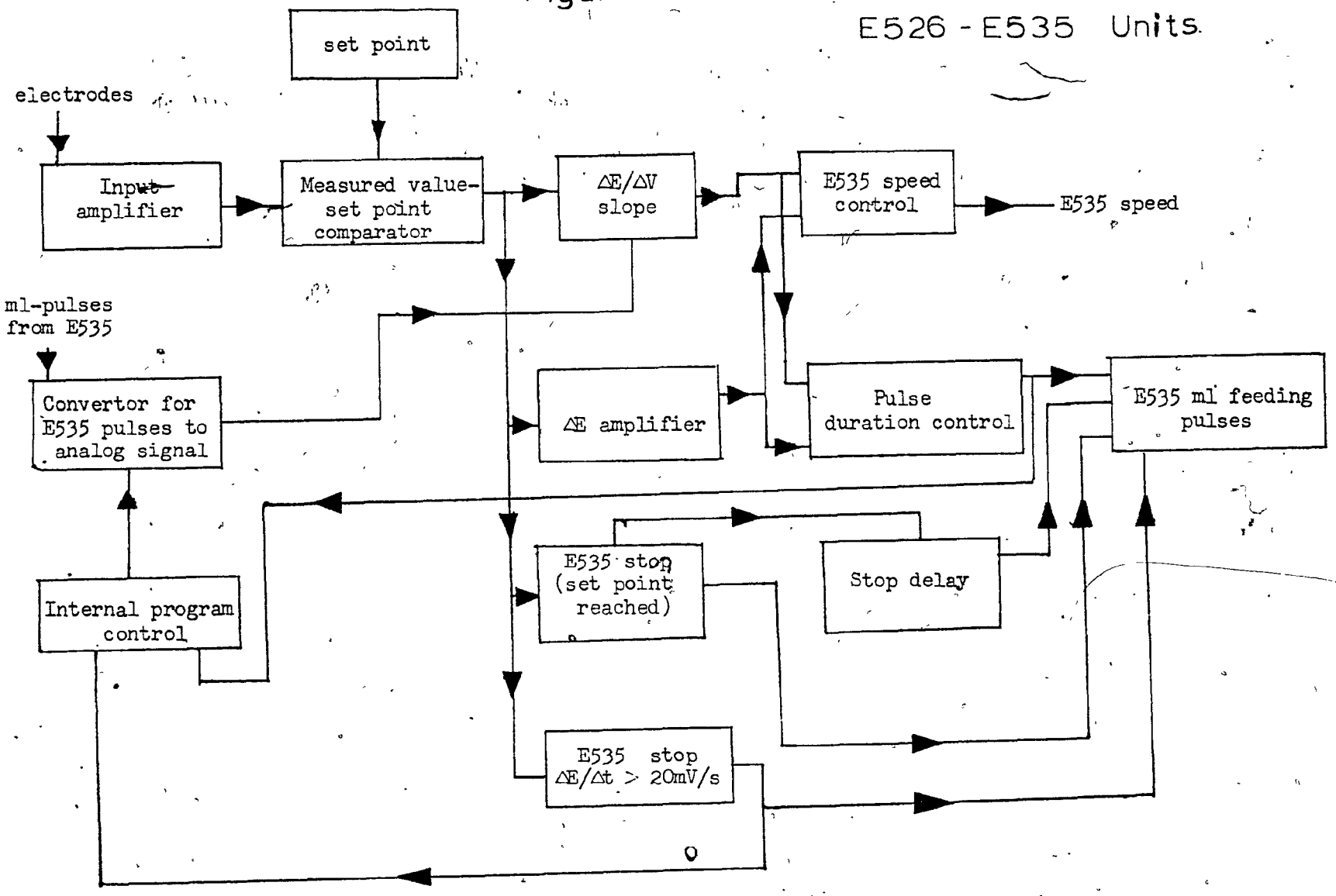
The E535 syringe burette unit or "Dosimat" carries the automatic feed pulse generator, automatic counter changeover when the syringe burette capacity is changed, digital volume readout and manual and/or automatic refilling and zeroing capablities. The general control schematic for these two units is shown as Figure 2.

The E503 unit provides the capacity to carry out large numbers of routine titrations automatically and sequentially. This sample handling unit has eleven sample magazines, each with a capacity of four 250 ml beakers of glass-reinforced plastic. An attached pretitration addition and titration stand carries four positions for raising and lowering the beakers under these positions. In addition to the titration operation, these positions can be arranged to carry out such functions as addition of pretitration reagent solutions, dilution with hot or cold water, etc. Automatic valves govern the volumes of such pretitration additions. Stirring of the solution after pretitration additions, and during the titration, starts and stops automatically at preset variable times, and rinsing of the burette tip, electrodes and stirrer is carried out automatically at the close of each titration. The sample magazines are moved horizontally and laterally, and the beakers raised and lowered, by pneumatic piston systems operated through a programming unit.

The E533 printout unit prints out both titrant endpoint volume and sample number for each sequential titration. Equipment is available which converts the endpoint volume value to an operating value (e.g. the sample oz/gal, percent of substance, etc.).

Figure 2

Interlinking of E526 - E535 Units



The control and programming unit which links the E503, E533, E526 and E535 units is the E543. This unit includes selection positions which permit manual operation (one beaker at a time) or 1 to 11 magazine operation. Selection positions permitting manual over-ride of magazine lateral and horizontal movement are also provided. Where both manual and automatic operations are concerned, a "start" control initiates the program selected. In its ultimate operation, 44 separate samples can be sequentially titrated automatically after initiation of the program start. In the various investigations reported in this project, manual operation was applied initially to determine the applicability of the selected preset dead-stop endpoint value, with adjustments being carried out as required. Establishment of a preset value providing accurate titration endpoint volume data then permitted automatic operation to be initiated for subsequent samples.

Initiation of the program "start" activates the E543 unit to move the first magazine, and its first sample beaker, up to the initial pre-titration and titration stand position, and to move the other magazines laterally and horizontally, as required, towards this position. It also activates the filling and zeroing of the E535 burette unit. The various pretitration operations, where required, are carried out sequentially until the first beaker reaches the titration position. Elevation of this beaker activates the stirring mechanism and allows the E526 unit to read the electrode couple potential for the solution. After stirring for a preset delay period, titration starts at a titrant delivery speed representing the result of the initial and preset dead-stop potential com-

parison. Approach to the endpoint automatically results in titrant delivery speed reduction, onset of titrant pulsing and pulse frequency and width adjustment. The completion of the titration activates the printout unit, refills and zeros the burette, stops the stirring action, lowers the beaker, rinses the titration components and initiates magazine and beaker movement for the next titration.

In order to provide the best accuracy, the calibration, and the selection of the preset dead-stop endpoint pH or potential, must be carefully carried out, as must be the selection of the titration curve characteristic setting. Full titration curves obtained from the E436 unit are used to provide endpoint pH or potential data, and to establish the general titration characteristics relative to the endpoint or equivalence point zone changes of $\Delta pH/\Delta V$ or $\Delta E/\Delta V$. Application of these data as E526 settings is followed by experimental evaluation of the titration endpoint volume value obtained for solutions of known endpoint volume as determined from manual and/or E436 titrations. Adjustment of this initial preset dead-stop value is frequently required on the basis of differences in the response system and other factors. The final preset value applied reflects the initial value modified as the result of such experimental evaluations.

2.3 General Experimental Procedures

It is possible to outline the experimental steps followed generally in the investigation of the process of automating each method of analysis. Exceptions occur with respect to such a generalized outline, but these

are treated as they occur relative to the method investigation involved.

The first approach to the problem of the use and automation of a specific method of analysis standard in the industry was to consider its adaptability to the projected potentiometric titration automated process. Considering that portion of the research directive associated with the adaptation of the standard methods insofar as possible, this step resulted in certain problems relative to adaptability. The criteria used in considering this factor were minimum pretitration treatment, reasonable $\Delta pH/\Delta V$ or $\Delta E/\Delta V$ change around the equivalence point and availability of a responsive electrode couple. Obviously such method techniques which require the destruction of cyanide-metal complexes by acid digestion prior to determination are not directly adaptable to simple automation, but need extensive pretreatment prior to and outside the automated titration system. These include the determination of zinc, silver and copper in their alkaline cyanide bath solutions. With techniques of analysis such as these, pretreatment prior to automated titration was essential and unavoidable. Again, in consideration of the need for a reasonable rate of change of $\Delta E/\Delta V$ around the equivalence point, those standard methods involving the determination of nickel and zinc by EDTA titration using metal-organic indicators represented problems. In such instances method modification was essential, and a very considerable amount of experimental work was required in order to ensure that the operating parameters for the modified and automated techniques yielded results comparable to those which could be obtained by the appropriate standard technique. In certain cases, such as the determination of sulphate in chromium solution baths, the lack

of an adequately sensitive and reproducible electrode couple created an insurmountable difficulty in adapting such a determination directly to the automated technique.

The essential steps in the investigation procedures were:-

(1) The necessary standard titrant solution was prepared in bulk. This solution was standardized initially, and in time, in not less than triplicate by (a) manual titration following where applicable the method of standardization recommended by the electroplating industry, (b) by E436A potentiographic titration and (c) by the E526 titration assembly complex. As indicated previously, the control parameters for the automated titration assembly were derived from the E436A titration curves as-is or modified as required.

(2) Synthetic solutions containing known amounts of the reactant of interest and/or synthetic solutions duplicating in general the associated bath composition were frequently prepared and analyzed by multiple determination by the techniques listed as (a), (b) and (c) in (1) of the foregoing.

(3) Samples of plating solutions actually and actively used by various different electroplating organizations were supplied by the granting agency. These had been previously analyzed routinely by the granting agency laboratories. Such solutions were analyzed by multiple determination by methods (a), (b) and (c) as outlined in (1) of the foregoing. In all such cases

of analysis by technique (c), previously-analyzed synthetic solutions were interspersed between the commercial bath samples to provide a check on the reproducibility and/or possible operational parameter drift factors. Where technique (c) was concerned all analyses were carried out on all of the related samples sequentially and automatically.

All data was statistically analyzed for each technique category and, for comparison purposes relative to techniques and results, analyzed as a total set of values.

Although the order of tackling the analytical problems involved, first, application to all methods where adaptation to automation was simple and straightforward, second, consideration of all methods where only minor modification was needed and, third, all situations where methods entirely different from the industry standards were required, the presentation of the experimental data is on the basis of bath type rather than by separation as to analytical approach.

2.4 The Analysis of Acid Nickel Plating Solutions

2.4.1 General

Nickel plating is applied for two purposes; to protect metallic parts from corrosion and to provide a decorative finish. The metallic parts involved are generally steel, brass, bronze or zinc-base alloys. Nickel coatings are usually applied after a preliminary electroplated coating of copper.

Nickel plating baths may of a complex ammoniacal pyrophosphate-citrate type specially designed to the plating of zinc and its alloys. The most common bath type is, however, the Watts bath. This is the basis of most modern electroplating baths and is used primarily to apply bright and semi-bright nickel deposits. It is also used to produce nickel deposits for engineering purposes. The original composition was approximately 32 oz/gal of nickel sulphate, 3 oz/gal of nickel chloride and 3 oz/gal of boric acid. At the present time, based on modern production techniques, the chloride content is about tripled, while the boric acid content is approximately doubled. Through the addition of other ionic substances, and by control of the plating conditions, nickel deposits can be obtained in various degrees of hardness, tensile strength and ductility to meet special mechanical requirements. Considerable interest exists with respect to all-chloride baths on the basis of their very high conductivity and superlative plating efficiency. The properly-buffered half-chloride, half sulphate bath has most of the advantages of the Watts bath and the all-chloride bath, and has been found to be particularly suitable for high speed plating production.

The types of nickel plating baths most commonly used today are the bright and semi-bright baths. Both are modified Watts baths which contain ordinarily 10-12 oz/gal of nickel with certain added agents. The bright nickel bath contains nickel chloride and sulphate, boric acid and brightener substances. These brighteners can be organic compounds such as naphthalene sulphonic acids or inorganic metal compounds of cadmium or mercury.

The components requiring the application of routine analytical control are nickel, chloride and boric acid. As indicated in Subsection (2.1) and elsewhere, variation in composition for each component is fairly extensive from bath to bath or for a given bath in time, such variations arising out of operational practices or usage time factors.

2.4.2 The determination of boric acid

Boric acid serves as a buffering substance in nickel plating solutions. Its primary purpose is the control of the pH at the cathode/solution interface. In the absence of a proper buffering substance, nickel deposits at normal temperatures tend to be hard and cracked. A secondary effect of such buffering situations is that of maintaining the proper operating pH range for a specific bath. There are special-purpose commercial baths which utilize buffering agents other than boric acid, but the latter substance is generally preferred since it is obtainable in a pure form, is inexpensive, relatively nonvolatile and stable, produces "whiter" deposits and minimizes deposit cracking.

The method of analysis applied by the industry for the determination of boric acid is essentially an acid-base titration using standard sodium hydroxide solution. The actual analytical process involves the prior warming of the sample bath solution to ensure solubilization of any sedimented salts. Since such solutions are normally operated at some temperature higher than room temperature, cooling of the bath to ambient temperature can result, for the higher boric acid solutions, in some separation of this component. Subsequent to warming the analytical steps

are:-

(1) Pipette 2.00 ml into the titration vessel.

(2) Add 50 ml of dilution water and 10 ml of saturated potassium ferrocyanide solution. Add 8-10 drops of 0.1% aqueous bromocresol purple.

(3) If the result of (2) is green, 0.1N NaOH is added drop-wise to a blue colour. If the result of (2) is a pronounced blue-purple, 0.1N HCl added to a distinct green colour, with backtitration with 0.1N NaOH to a blue solution colour.

(4) Add 5 g of d-mannitol powder and 15 drops of 0.1% alcoholic phenolphthalein.

(5) Titrate with 0.1N NaOH to a pink colour.

The purpose of the addition of $K_4Fe(CN)_6$ is to complex certain impurities, particularly iron.

The purpose of the bromocresol purple addition and the subsequent titration with NaOH or HCl-NaOH is to provide an approximate value of 7 pH for the titration start. In all of the commercial solutions which were eventually analyzed, very little adjustment was found to be required.

The use of d-mannitol centers around the fact that boric acid itself is a very weak acid with a K_1 value of about 10^{-10}. Free boric acid is thus difficult to titrate in a standard neutralization titration, since the poor rate of change of $\Delta pH/\Delta V$ around the equivalence point renders this point with considerable inaccuracy. Boric acid, however, forms complexes with organic polyhydroxy compounds such as glycerol and d-mannitol. Such complexes provide stronger acid substances than boric acid itself. The complex formed, for example, with d-mannitol has a

dissociation constant of about 10^{-4}, and can be readily titrated with strong base to a sharp endpoint. Dubou (24) titrated boric acid solutions containing variable amounts of d-mannitol, and noted that the calculated values for the pK_a varied from about 4.4 to 6.5. With such a variation in the pK_a the titration endpoint pH also varies, indicating the need to ensure some consistency in the amount of d-mannitol added prior to the start of the titration. The use of 5 g of d-mannitol prior to titration start, as demanded by the method outlined, guarantees complete reaction with the available boric acid with a substantial, almost constant, excess of d-mannitol. For the purposes of this investigation, and in order to organize the pretitration additions situation, the d-mannitol substance was added in the form of 50 ml of a 10 percent solution.

In point of fact, the official instructions for the standard analysis technique state "5.0 g of d-mannitol (approximately 1 1/2 to 2 level teaspoonfuls". This latter instruction as to the method of measuring the d-mannitol addition is by no means sufficiently accurate. Experimental work based on:-

(A) Adding 1 1/2 level teaspoonfuls

(B) Adding 50 ml of a 10 percent d-mannitol solution

yielded the results shown in Table 3. The appreciably higher inconsistencies in the volume values for the equivalence point for method (A) as compared to method (B) are apparent.

TABLE 3

COMPARISON OF METHODS (A) AND (B) FOR THE ADDITION OF d-MANNITOL PRIOR TO BORIC ACID TITRATION

Sample No.*	Equiv. pt. vol. NaOH (ml) Method (A)	Method (B)	Equiv. pt. pH value Method (A)	Method (B)
1.	16.07	15.86	8.2	8.4
	15.48	15.76	8.3	8.4
2.	17.91	17.81	8.2	8.4
	17.63	17.83	8.4	8.4
3.	15.47	15.17	8.9	8.4
	15.32	15.15	8.7	8.4
4.	18.10	17.95	8.3	8.4
	18.30	17.85	8.3	8.4

* Samples from different commercial electroplating baths

Details relative to the experimental work carried out with respect to the determination of boric acid are included in Appendix A. Tables and figures referred to with the suffix "-A" are contained in this Appendix.

A standard solution of NaOH was prepared so as to yield an approximate molarity of 0.1, and this solution was standardized by manual titration using potassium acid phthalate. The standardization details are given in Table 1-A. The average molarity for the NaOH solution was found to be, together with the standard deviation:-

$$0.1017^6 \pm 0.0003^5$$

A standard solution of boric acid was now prepared so as to provide a value of:-

$$1 \text{ ml} = 0.025000 \pm 0.000008 \text{ g } H_3BO_3$$

3 ml portions of the boric acid solution were pipetted and titrated with the standard NaOH solution. The details of these titrations are reported in Table 2-A, and the method followed was identical to the technique recommended as standard by the electroplating industry. The theoretical amount of boric acid titrated was:-

$$0.0750 \pm 0.0002 \text{ g}$$

The average and standard deviation for the H_3BO_3 values obtained by the manual titration process was:-

$$0.0750^8 \pm 0.0002^6 \text{ g}$$

representing a relative error of + 1.3 ppt.

Triplicate manual titrations were now carried out on the commercial acid nickel plating solutions provided by Canadian Hanson. These samples were warmed slightly to dissolve any soluble residue prior to pipetting the portion for analysis. The method details are outlined in Table 3-A, and were essentially identical to those of the industry standard.

Table 4 shows the values and standard deviations for boric acid, as well as the values reported by Canadian Hanson as the result of their routine laboratory analysis operations. It will be noted that, while the experimental values agree well with each other, the average values differ radically, in most instances, from the corresponding values as reported by Canadian Hanson. This situation will be discussed in some detail in the Conclusions section of the thesis.

The same general procedure was now followed with respect to the application of the E436A potentiograph titrator to the determination of boric acid. The previously-prepared standard NaOH solution was restandardized against KHP, this time using the E436A titrator to obtain full titration curves. The details as to this standardization process, and the experimental and theoretical titration characteristics are given in Table 4-A. The NaOH solution was found to have an average molarity and standard deviation of:-

$$0.1011^{9} \pm 0.0003^{8}$$

The $\pm \Delta pH$ change for $\pm$ 0.5 ml around the endpoint volume was determined from the titration curve as $\pm$ 1.89 units, while the equivalence or endpoint pH was located at an average pH value of 8.55 $\pm$ 0.02. These values

TABLE 4

MANUAL TITRATION DETERMINATION OF BORIC ACID IN COMMERCIAL ACID NICKEL PLATING SOLUTIONS

Sample No.	Boric acid (oz/gal) Project work	Boric acid (oz/gal) Canadian Hanson
1.	7.14 ± 0.04	6.4
2.	7.75 ± 0.02	6.2
3.	8.21 ± 0.04	6.2
4.	8.03 ± 0.02	4.9
5.	7.32 ± 0.01	5.5
6.	6.81 ± 0.03	6.3
7.	5.95 ± 0.03	6.4
8.	6.16 ± 0.02	5.2
9.	9.90 ± 0.04	7.4
10.	6.52 ± 0.03	5.5

compare very favourably with the theoretical calculated values of ± 1.9 pH units and 8.7 pH respectively.

The H_3BO_3 solution prepared for the manual titration work was now tested by titrating various solution volumes with standard NaOH solution standardized by the E436A titrator method. The volume of H_3BO_3 solution was varied in order to determine concentration range effects, if any, on the titration characteristics. The general details are outlined in Table 5-A. The theoretical weights of $H3BO_3$ titrated, and the obtained averages and standard deviations are shown in Table 5.

The low relative errors achieved indicate no significant change in the titration characteristics with variation in the amount of H_3BO_3 under titration. The average ± ΔpH for ± 0.5 ml around the endpoint, as determined from the individual values obtained from the titration curves, was 1.7 ± 0.1, while the average pH at the endpoint was similarly determined as 8.1 ± 0.2. These values agree well with the theoretical calculated values of ± 2.5 and 8.2 respectively and, as indicated at the close of Table 5-A, the difference in the experimental and theoretical ΔpH values around the endpoint are likely due to a combination of circumstances not the least of which is the errors introduced as the result of the calibration of the electrode couple with a 9.00 pH buffer.

The application of the E436A titrator method to the determination of boric acid in the commercial nickel plating solutions was now investigated. Solution preparation prior to titration was essentially similar to that

TABLE 5

TITRATION OF SYNTHETIC BORIC ACID SOLUTIONS WITH STANDARD NaOH AND THE E436A TITRATOR

H_3BO_3 vol. (ml)	Theor. weight H_3BO_3 (g)	Actual weight H_3BO_3 as determined (g)
2.000 ± 0.006	0.0500 ± 0.0001	0.0502 ± 0.0001 (s)
3.00 ± 0.01	0.0750 ± 0.0002	0.0749 ± 0.0004 (s)
4.00 ± 0.01	0.1000 ± 0.0002	0.0999 ± 0.0002 (s)

H_3BO_3 vol. (ml)	Relative error (ppt)
2.000	+ 4.6
3.00	− 1.3
4.00	− 1.0

which pertained in the manual method application, with the exception of the omission of the addition of phenolphthalein indicator. The parameters set and the operational factors for the E436A unit were similar to those applied in the E436A titration of synthetic boric acid solutions. The relevant details associated with this area of experimentation are covered in Table 6-A.

Table 6 shows the average values and standard deviations obtained with respect to the boric acid contents of the commercial solutions, and these are compared with the data reported by Canadian Hanson. Again the discrepancies between the experimental values and the Canadian Hanson values will be noted, as will be the general agreement between the E436A titrator values and the manual values reported in Table 4.

Table 6-A shows the accumulated data with respect to the pH value at the endpoint of each titration, and the $\pm \Delta pH$ for $\pm$ 0.5 ml around the endpoint. The allover average and standard deviation for the endpoint pH was found to be 8.4 $\pm$ 0.1, with minimum and maximum values of 8.3 and 8.6 pH. Some tendency for the endpoint pH to increase with increasing boric acid content titrated was noted, an expected characteristic as indicated by the theoretical calculations of Table 5-A and by the general endpoint pH increases for the variable boric acid solutions titrated in the experimental work reported in the same Table. All in all, the average endpoint pH values show good agreement with the theoretical values and with those obtained during the E436A titrations of synthetic boric acid solutions.

Again, from Table 6-A data, the $\pm \Delta pH$ for $\pm$ 0.5 ml around the end-

TABLE 6

TITRATION OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS WITH STANDARD NaOH AND THE E436A TITRATOR

Sample No.	Boric acid (oz/gal) ave ± s Experimental	Boric acid (oz/gal) Canadian Hanson
1.	7.05 ± 0.03	6.4
2.	7.53 ± 0.09	6.2
3.	8.19 ± 0.04	6.2
4.	7.91 ± 0.03	4.9
5.	$7.2^{0} \pm 0.1^{2}$	5.5
6.	6.69 ± 0.02	6.3
7.	$5.7^{7} \pm 0.1^{0}$	6.4
8.	6.12 ± 0.02	5.2
9.	9.69 ± 0.04	7.4
10.	6.46 ± 0.03	5.5

point averages out at 1.2 ± 0.1. This ± ΔpH range is appreciably lower than that found for the synthetic boric acid solution titrations. This is due largely to the higher onset pH values 0.5 ml before the endpoint and this, in turn, is due to the higher concentrations of boric acid in the starting solutions for the commercial sample solution titrations (about 0.025M compared to about 0.013M in the synthetic solution titrations). This higher starting concentration implies a pH value 0.5 ml before the endpoint about 0.4 units higher then the lowest of the synthetic boric acid solution titrations (see the closing paragraph of Table 6-A), and a corresponding reduction in the ± ΔpH around the endpoint for the commercial solution titrations.

It will be noted, however, that this average ± ΔpH of 1.2 ± 0.1 implies a range of 2.4 pH units for ± 0.5 ml around the endpoint volume and, while not overly extensive, should permit location of the endpoint volume in a preset dead-stop titration within ± 0.2 ml. This uncertainty in locating the endpoint volume would lead to an uncertainty in the determined oz/gal of boric acid of:-

$$\pm 0.2 \text{ ml} \times 0.1012\text{M NaOH} \times 4.12^{7} = \pm 0.08 \text{ oz/gal}$$

a satisfactory uncertainty in view of the standard deviations shown in Tables 4 and 6.

The experimental work was now arranged so as to carry out, on the E526 assembly, automatic titration of the various titration situations previously conducted manually and by the E436A tirator.

The operating parameters for those titrations involving the standar-

dization of the NaOH titrant solution were extracted from the details of Table 4-A. A titration endpoint of 8.5 was indicated therein, with a ΔpH range for $\pm$ 0.5 ml around the endpoint of 3.8 units. These data were secured by averaging the values obtained from the E436A full titration curves for the standardization process. The information indicates a titration characteristic of a reasonably gradual slope to the endpoint volume, so that the changes in $\Delta pH/\Delta V$ in this zone demand a reasonably coarse approach to the endpoint. The details of the operating settings placed on the E526 unit are given in Table 7-A, as are the data associated with the titrations. Four solutions involving potassium acid phthalate were titrated, these were placed in one magazine and were titrated sequentially and automatically. The average NaOH molarity and standard deviation were:-

$$M\ NaOH = 0.1024^{3} \pm 0.0001^{4}$$

Thus the various standardization techniques yielded NaOH molarity values of:-

Manual method	$0.1017^{6} \pm 0.0003^{5}$ M
E436A method	$0.1011^{9} \pm 0.0003^{8}$ M
E526 assembly method	$0.1024^{3} \pm 0.0001^{4}$ M

yielding an overall average and standard deviation of $0.1018^{6} \pm 0.0006^{0}$ M. Variance ratio tests indicated that the standard deviations for each of the methods are not significantly different, while null hypothesis tests indicated that there is just barely a significant difference between the averages for the E436A and E526 assemby methods only. This difference may be due to the preset dead-stop endpoint pH setting of 8.50 on the

E526 being just slightly under the value of 8.55 pH found as an average for the E436A titrations (Table 4-A). It was not felt that the minor difference indicated warranted additional testing in this connection.

The E526 assembly was now applied in the titration of synthetic boric acid solutions. The previous work conducted had indicated that, subsequent to the addition of saturated $K_4Fe(CN)_6$ solution and bromocresol purple indicator, no preliminary adjustments of pH involving NaOH or HCl-NaOH titration were required. For all of these titrations, therefore, arrangements were made to have the pretitration additions of 10 ml of saturated $K_4Fe(CN)_6$ solution and 50 ml of 10 percent d-mannitol solution made by the automatic injection valves as part of the pretitration addition sequence of the E526 assembly. Automatic stirring followed each of these additions. The pretitration and titration sequences were thus:- position 2, 10 ml saturated $K_4Fe(CN)_6$ and stir; position 3, 50 ml 10% d-mannitol and stir; position 4, stir and titrate.

The operating parameters for the E526 unit were generally extracted from the E436A titration data of Table 5-A. Since the endpoint pH tends to increase with increasing amount of boric acid under titration, and since Table 5-A data shows endpoint pH values from 8.0 to 8.3, a series of titrations involving dead-stop pH settings of 8.2, 8.3, 8.4 and 8.5, and variable volumes of standard boric acid solution under titration, were carried out. Table 8-A shows the general E526 operating parameters and titration details. Table 7 lists the average values for all titrations in terms of ml standard boric acid solution added, dead-stop pH setting,

TABLE 7

TITRATION OF VARIABLE CONCENTRATIONS OF BORIC ACID AT VARIABLE DEAD-STOP pH SETTINGS ON THE E526 ASSEMBLY

Vol. H_3BO_3	Vol. NaOH Soln. required Ave. ± std. dev.	Calculated vol. NaOH required for vol. of H_3BO_3 added	Dead-stop pH setting
2.00	7.63 ± 0.03	7.89	8.20
3.00	11.14 ± 0.00	11.84	8.20
2.00	7.66 ± 0.01	7.89	8.30
3.00	11.53 ± 0.06	11.84	8.30
2.00	7.86 ± 0.01	7.89	8.40
3.00	11.86 ± 0.05	11.84	8.40
4.00	15.68 ± 0.02	15.79	8.40
2.00	7.97 ± 0.02	7.89	8.50

actual NaOH solution volumes obtained and calculated NaOH solution volumes expected. It will be noted that the dead-stop pH setting of 8.40 provided the most suitable value.

Subsequent to this investigation four 3.00 ± 0.01 ml volumes of the standard boric acid solution were prepared, and the titrations carried out sequentially and automatically. Table 8-A carries the details in this connection. The theoretical weight of boric acid titrated was:-

$$0.0750 \pm 0.0002 \text{ g}$$

The average and standard deviation for the H_3BO_3 values obtained by automatic titration were:-

$$0.0744^7 \pm 0.0003^1 \text{ g}$$

representing a relative error of - 7.1 ppt.

The commercial nickel plating solutions were now analyzed on the E526 assembly. Again, since previous work had indicated that no adjustments were required subsequent to the $K_4Fe(CN)_6$ and bromocresol purple additions, automatic pretitration additions for the saturated $K_4Fe(CN)_6$ and 10 percent d-mannitol solutions were arranged, so that the general pretitration and titration sequences duplicated those for the synthetic boric acid solution titrations. The operating parameters for the E526 unit are given in Table 9-A, as are the titration details. Four samples for each plating solution were analyzed and, in addition, four samples involving 3.00 ± 0.01 ml of standard boric acid solution were interspersed between the 40 commercial samples. The purpose of these standard samples

was to provide a check on the possibility of drift of the E526 settings and electrode couple response in time.

This totaled 44 samples carried in 11 magazines, the full capacity of the E526 assembly sample-handling device. All titrations were sequentially and automatically titrated upon initiating the program start. The total elapsed time for the entire run was about 1.5 hours. Table 8 shows the average values in oz/gal(US) for boric acid in the commercial samples and the individual values of weight boric acid titrated, both actual and determined, for the synthetic control samples. A comparison with the results obtained by Canadian Hanson is also shown.

The permanency of the E526 operating parameters, and the lack of drift for the electrode couple, is indicated by the reproducibility of the standard solution values. The ability of the E526 to locate the end-point volume within the anticipated ± 0.2 ml or ± 0.08 oz/gal is also indicated.

Table 9 shows a comparison of the manual, E436A and E526 assembly values for the analysis of commercial acid nickel plating solutions. The Canadian Hanson values are included for comparison purposes.

It will be noted, first of all, that the manual, E436A and E526 values agree well with each other, and within each respective titration category. This is indicated by the standard deviations and the deviations from the overall averages. The single significant exception surrounds the data relative to the E526 titrations for Sample No. 3. Some

TABLE 8

TITRATION OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS WITH STANDARD NaOH AND THE E526 ASSEMBLY

Sample No.	Boric acid (oz/gal) Ave. ± Experimental	Boric acid (oz/gal) Canadian Hanson	Weight boric acid (g) deter.	theor.
1.	$7.1^{8} \pm 0.1^{1}$	6.4		
2.	$7.7^{4} \pm 0.1^{5}$	6.2		
Std.			0.0738	0.0750
3.	$7.7^{6} \pm 0.2^{2}$	6.2		
4.	8.00 ± 0.04	4.9		
Std.			0.0741	0.0750
5.	7.21 ± 0.06	5.5		
6.	6.91 ± 0.08	6.3		
Std.			0.0741	0.0750
7.	5.96 ± 0.03	6.4		
8.	6.21 ± 0.06	5.2		
Std.			0.0742	0.0750
9.	$9.6^{9} \pm 0.1^{1}$	7.4		
10.	6.56 ± 0.05	5.5		

TABLE 9

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS IN THE DETERMINATION OF BORIC ACID

All values expressed in oz/gal(US)

Sample No.	Can. Han. value	Manual (1)	E436A (2)	E526 (3)	Overall Ave.	Dev. from overall Ave. (1)	(2)	(3)
1.	6.4	7.14 ± 0.04	7.05 ± 0.03	$7.1^{8} \pm 0.1^{1}$	7.12	+ 0.02	- 0.07	+ 0.06
2.	6.2	7.75 ± 0.02	7.53 ± 0.09	$7.7^{4} \pm 0.1^{5}$	7.67	+ 0.08	- 0.14	+ 0.07
3.	6.2	8.21 ± 0.04	8.19 ± 0.04	$7.7^{6} \pm 0.2^{2}$	8.05	+ 0.16	+ 0.14	- 0.29
4.	4.9	8.03 ± 0.02	7.91 ± 0.03	8.00 ± 0.04	7.98	+ 0.05	- 0.07	+ 0.02
5.	5.5	7.32 ± 0.01	$7.2^{0} \pm 0.1^{2}$	7.21 ± 0.06	7.24	+ 0.08	- 0.04	- 0.03
6.	6.3	6.81 ± 0.03	6.69 ± 0.02	6.91 ± 0.08	6.80	+ 0.01	- 0.11	+ 0.11
7.	6.4	5.95 ± 0.03	$5.7^{7} \pm 0.1^{0}$	5.96 ± 0.03	5.89	+ 0.06	- 0.12	+ 0.07
8.	5.2	6.16 ± 0.02	6.12 ± 0.02	6.21 ± 0.06	6.16	± 0.00	- 0.04	+ 0.05
9.	7.4	9.90 ± 0.04	9.69 ± 0.04	$9.6^{9} \pm 0.1^{1}$	9.76	+ 0.14	- 0.17	- 0.07
10.	5.5	6.52 ± 0.03	6.46 ± 0.03	6.56 ± 0.05	6.51	+ 0.01	- 0.05	+ 0.05

OFFSET FROM CANADIAN HANSON VALUES

No.	Hanson value	Overall average	% devn. from Can. Han.
1.	6.4	7.12	+ 11.2
2.	6.2	7.67	+ 23.7
3.	6.2	8.05	+ 29.8
4.	4.9	7.98	+ 62.8
5.	5.5	7.24	+ 31.6
6.	6.3	6.80	+ 7.8
7.	6.4	5.89	- 8.0
8.	5.2	6.16	+ 18.5
9.	7.4	9.76	+ 31.9
10.	5.5	6.51	+ 18.4

considerable deviation is noted, both within the E526 values themselves and in the comparison of the average for these values with the overall average for this sample. It was assumed that some operational or solution preparation difficulty existed here.

The E436A titrator technique appears to yield consistently lower results than either the manual or the E526 assembly techniques. The significance here is in the direction of the deviation from the overall average rather than in its magnitude. Speculation tended to favour the idea that some minor response lag between the chart and burette drives permits readings of titrant volume from the chart to be somewhat lower than that actually added by the burette. Tests were conducted involving operating the chart and the burette for the full volume span. Examination of these charts indicated minor discrepancies in coordinated response. This was found to be based on slippage between the chart paper and the chart driving wheels. Since this instrument does not operate or drive the chart paper by a sprocketed drive wheel/perforated chart paper arrangement, but employs rather a friction principle, such minor slippages can be anticipated.

With the exception of Sample No. 7, all of the experimental values for boric acid, and their associated overall averages, showed persistently and significantly higher boric acid contents than those reported by Canadian Hanson. No speculation can be made as to the accuracy of the granting organization values, since this situation is both unknown

and incapable of verification. The E436A titration results were, however, based on the analysis of full titration curves, and the location of the endpoint volume is not therefore debatable. Speculation that the repeated warming of the commercial solutions prior to sampling for analysis may have resulted ultimately in solution concentration effects was not fruitful, since subsequent determinations of chloride and nickel on the same solutions showed general agreement with the Canadian Hanson values and, therefore, no indication of concentration effects.

The commercial plating solutions analyzed for H_3BO_3 were such that NaOH or HCl-NaOH adjustment titrations were not required in any instance, thereby permitting the addition of the saturated $K_4Fe(CN)_6$ and d-mannitol solutions to be made automatically as part of the analysis sequence. Such a situation could not be considered as general, however, and it is likely that, in an E526 automated technique, only the d-mannitol solution would be added automatically. The addition of saturated $K_4Fe(CN)_6$ and bromocresol purple indicator, and the subsequent examination and, where indicated, titration with NaOH or HCl-NaOH, would be carried out external to the system and before loading the sample beakers in the automatic unit magazines.

2.4.3 The determination of chloride

The primary function of chloride is to improve anode dissolution by reducing polarization. It also increases the conductivity of the bath, and has certain marked effects at the cathode. It increases throwing power in deposition as a result of increased cathode efficiency and elec-

trolyte conductivity. These effects are at their respective maxima in nickel baths containing nickel as the chloride only.

On the other hand, an excess of chloride in the bath carries certain disadvantages not the least of which are the more corrosive property of the electrolyte, preventing the use of lead metal tank linings and coils, and the tendency to cause a more rapid change of pH during bath use. A reduction in the chloride concentration can cause a profound alteration in the nature of the cathodic film and an associated effect in increasing the precipitation of colloidal matter. Such precipitated colloidal matter can become incorporated in the deposit with subsequent reduction in deposit quality. All of the se factors emphasize the importance of the analytical procedure for the determination of chloride. Frequent analysis for chloride can prevent situations such as the onset of an advanced degree of corrosiveness which can, on occasion, oblige the plater to change the entire bath.

The method of analysis applied as the standard technique by the industry involves its determination by the Mohr method. This method is itself one of the oldest volumetric procedures and requires titration of the sample by standard silver nitrate solution, using internally-added chromate ion as the indicator substance. Again, warming of the bath solution sample to ensure solubilization of any sedimented salts is essential. The analytical steps for the standard technique are:-

(1) Pipette 2 ml into the titration vessel.

(2) Add 100 ml of dilution water.

(3) Add 1 ml of 2% sodium chromate solution.

(4) Titrate with 0.1M silver nitrate solution until a first faint reddish-brown colour, persistent after vigourous shaking, is achieved.

Two factors are important in this titration, and these are the $[CrO_4^{2-}]$ at the endpoint and the pH of the solution under titration. The addition of Na_2CrO_4 required by the standard method involves a number of moles of CrO_4^{2-} given by:-

$$1 \text{ ml} \times \frac{2g}{161.97g/mol \times 100 \text{ ml}} = 0.000123 \text{ moles}$$

In consideration of an endpoint volume of about 110 ml average, this yields a $[CrO_4^{2-}]$ at the endpoint of:-

$$\frac{0.000123}{110} \times 1000 = 0.00112 \text{ M}$$

This concentration of CrO_4^{2-} will require, for equilibrium, an $[Ag^+]$ given by:-

$$[Ag^+] = \sqrt{\frac{Ksp(Ag_2CrO_4)}{[CrO_4^{2-}]}} = \sqrt{\frac{9.0 \times 10^{-12}}{1.12 \times 10^{-3}}} = 8.9 \times 10^{-5}\text{M}$$

This represents a volume of 0.1M $AgNO_3$ in excess of the equivalence point volume given simply and approximately by:-

$$\frac{\left(8.9 \times 10^{-5} - \sqrt{Ksp(AgCl)}\right) \times 110}{0.1}$$

$$= \frac{(8.9 \times 10^{-5} - \sqrt{1.56 \times 10^{-10}}) \times 110}{0.1} = 0.08 \text{ ml}$$

To this volume must now be added the volume of 0.1M $AgNO_3$ solution required to yield sufficient Ag_2CrO_4 to permit a detectable endpoint colour, this being about 0.08 ml according to Dick (25). Thus, a total excess volume of 0.1M $AgNO_3$, over the equivalence point volume, of some 0.16 ml is required to achieve the endpoint indication at the standard required addition of 1 ml of 2 percent sodium chromate solution. The standard technique as applied by the electroplating industry does not take this blank volume into consideration, assuming that, since the standardization volume and the actual field titration endpoint volumes will be approximately the same, ignoring the indicator blank in the routine determinations will be offset by nonapplication of the blank in the standardization process.

The second of the two important titration factors is that involving the pH of the titrated solution, and this derives its importance from the fact that the $[CrO_4^{2-}]$ available for the indication reaction decreases with decreasing solution pH according to:-

$$2CrO_4^{2-} + 2H_3O^+ \leftrightharpoons 2HCrO_4^- + 2H_2O \leftrightharpoons Cr_2O_7^{2-} + 3H_2O$$

According to Dick (26), a solution pH of about 7 is normally considered the minimum for efficient use of the available CrO_4^{2-}. Nickel bath solutions very frequently show pH values of about 4 so that, on this account, higher blank values of 0.1M $AgNO_3$ can be anticipated.

Details relative to the experimental work associated with the determination of chloride are included in Appendix B. Tables and figures carrying the suffix "-B" are found in this appendix.

A standard $AgNO_3$ solution was prepared so as to yield an approximate molarity of 0.1, and this solution was standardized against sodium chloride solution by manual titration using Fajan's method as outlined in Table 1-B. Fajan's method was applied, rather than the Mohr technique, in order to eliminate the use of a blank correction, since the ensuing potentiometric titrations would not require indicator blank corrections. The average molarity found for the $AgNO_3$ solution, together with the standard deviation, was:-

$$0.1054^1 \pm 0.0001^2$$

This titrant was now applied in the manual titration, using the industry standard technique, of the commercial nickel bath solutions provided by the granting agency, Canadian Hanson. These acid nickel bath solutions were warmed before sampling, and triplicate determinations were carried out. Table 2-B indicates the methodic details, while Table 10 provides the average values and standard deviations obtained, together with the chloride values reported by Canadian Hanson.

It will be noted that the experimental values agree well with each other for each solution analyzed. The average values tend to be somewhat higher than the granting agency values, and this discrepancy appears, in general, to increase with increasing chloride content under determination.

TABLE 10

MANUAL TITRATION DETERMINATION OF CHLORIDE IN COMMERCIAL ACID NICKEL PLATING SOLUTIONS

Sample No.	Chloride (oz/gal) Project work	Chloride (oz/gal) Canadian Hanson
1.	1.23 ± 0.01	1.2
2.	1.73 ± 0.02	1.7
3.	2.15 ± 0.01	2.0
4.	2.27 ± 0.01	2.1
5.	2.50 ± 0.01	2.3
6.	2.59 ± 0.01	2.4
7.	3.26 ± 0.01	2.9
8.	3.34 ± 0.01	3.1
9.	3.87 ± 0.01	3.4
10.	3.57 ± 0.01	3.4

this situation will be discussed in some detail later in this section, and in the Conclusions section.

The procedure used for the manual standardization was now applied with respect to the E436A titrator. The prepared $AgNO_3$ solution was re-standardized against the NaCl solution, this time using the E436A unit to obtain full titration curves. The standardization process details are given in Table 3-B. The $AgNO_3$ solution showed a molarity and standard deviation of:-

$$0.1056^7 \pm 0.0008^4$$

a value which agrees, within the limits of error, with that obtained by the manual titration technique.

The theoretical calculations to determine E_{cell} at the titration equivalence point, and the values for $\pm \Delta E$ at $\pm$ 0.5 ml around the equivalence point volume, are outlined in Table 3-B. The average equivalence point potential found by titration curve analysis, together with its standard deviation, is 298 $\pm$ 2 mV, and this agrees quite well with the theoretical value of 311 mV. The $\pm \Delta E$ for $\pm$ 0.5 ml around the equivalence point volume was found to have an average and standard deviation of 88 $\pm$ 1 mV and, again, this agrees quite well with the theoretical value of $\pm$ 100 mV. Discrepancies between actual and calculated values in this area are found to be relatively insignificant, and can usually be assumed to be due to such factors as uncompensated junction potentials, the use of concentrations rather than activities, uncertainties in mV measurement, effects of solution ionic strength, other than 25°C temperature, etc.

The E436A titrator was now applied in the titration of the commercial acid nickel plating solutions. The methodic details and experimental results are outlined in Table 4-B, while Table 11 shows the averages and standard deviations for the values obtained. Table 11 also provides a comparison between the experimental values and the results reported by the granting agency.

It will be noted that, when Table 11 results are compared with those for Table 10, the E436A values are, first, generally lower than the manual titration system values and, second, are generally in closer agreement with the granting agency values. It can be assumed, subject to confirmation relative to the E526 assembly results, that the use of the manual titration technique tends, in inexperienced hands, to yield higher values because of doubts as to the final endpoint colour. In addition to this, the manual method does inherently provide values somewhat higher than the real values on the basis of the nonapplication of blank corrections.

The average equivalence point value of E_{cell} from all of the commercial titrations on the E436A was 290 mV, with a standard deviation of ± 5 mV. This agrees reasonably well with the theoretical calculated value of 311 mV and the standardization sequence average value of 298 ± 2 mV. The larger standard deviation for the commercial plating solutions and the greater discrepancy between E_{cell} actual and calculated can be attributed to the factors mentioned earlier, in conjunction with the much greater solution composition variation for the commercial solutions.

TABLE 11

TITRATION OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS WITH 0.1M $AgNO_3$ IN THE DETERMINATION OF CHLORIDE BY E436A UNIT

Sample No.	Chloride (oz/gal) Project work	Chloride (oz/gal) Canadian Hanson
1.	1.14 ± 0.02	1.2
2.	1.63 ± 0.05	1.7
3.	1.94 ± 0.06	2.0
4.	2.06 ± 0.02	2.1
5.	2.38 ± 0.04	2.3
6.	2.54 ± 0.10	2.4
7.	3.04 ± 0.01	2.9
8.	3.22 ± 0.08	3.1
9.	3.60 ± 0.06	3.4
10.	3.40 ± 0.07	3.4

The average and standard deviation for the $\pm \Delta E$ ($\pm$ 0.5 ml around the equivalence point volume) was found, for all titrations, to work out to 77 $\pm$ 5 mV. This agrees reasonably well with the $\pm \Delta E$ value of 88 $\pm$ 1 mV found for the standardization sequence. It does show some significance in its difference from the theoretical calculated value of $\pm$ 100 mV. Again, it is felt that this difference may be due largely to the factors mentioned previously, plus the influence of the variation in the plating solution compositions compared to the constant solution composition matrix for the standardization solutions.

It should be pointed out that the $\pm \Delta E$ of 77 $\pm$ 5 mV implies a range of 154 mV for $\pm$ 0.5 ml around the equivalence point volume. This is quite reasonable, and should allow location of the equivalence point volume in a preset dead-stop endpoint titration within $\pm$ 0.1 to $\pm$ 0.2 ml of the real value. This uncertainty in locating the equivalence point volume would lead to an uncertainty in the determination of chloride of:-

$$(\pm 0.1 - \pm 0.2 \text{ ml}) \times 0.1057\text{M } AgNO_3 \times 2.3669 = \pm 0.02 - \pm 0.05 \text{ oz/gal}$$

a satisfactory uncertainty in view of the standard deviations for Tables 10 and 11.

The complete sequence of experimental approaches was now carried out in association with the E526 automatic titration assembly. The operating parameters for the process of standardization of the $AgNO_3$ titrant were taken from Table 3-B data covering the standardization of this solution using the E436A titrator. These data had indicated an average equivalence

point potential of + 298 ± 2 mV, and an average ΔE range for ± 0.5 ml around the equivalence point volume of 176 ± 2 mV. The ΔE range indicates a titration characteristic of a fairly sharp approach to the equivalence point, so that the extensive changes in $\Delta E/\Delta V$ in this zone demand a reasonably careful approach to the endpoint. The details of these preliminary and final operating parameters are shown in Table 5-B.

The initial titrations showed that, at the preset dead-stop potential of + 298 mV, the E526 system had a tendency to under-titrate to the extent of some 0.1 - 0.2 ml. This was demonstrated, in these preliminary titrations, by using the normal addition of dichlorfluorescein indicator and, when the dead-stop endpoint was obtained, over-riding the automatic controls and continuing the titration manually until the indicator achieved its colour change.

Further experimental work was carried out, with gradual increases in the value for the preset potential for dead-stop. A correspondence between the two endpoint values was finally attained with a preset potential of + 320 mV. Once this value had been established, four (4) final titrations were carried out without indicator addition, and by the sequential and automatic technique using one magazine programming. The average $AgNO_3$ molarity, with standard deviation, was found to be:-

$$M\ AgNO_3 = 0.1056^2 \pm 0.0004^6$$

The fact that the final dead-stop potential required was + 320 mV instead of the anticipated value of + 298 mV can be assumed to be due

to the differences in the titration conditions and/or the instrumental response systems for the E436A and E526 units. The approach to the equivalence point is of a different nature for the two instrumental systems, and differences in approach may require differences with respect to the settings for the E526 unit. This discrepancy, in this case, is some + 22 mV and, in view of the total ΔE range for ± 0.5 ml around the equivalence point of about 176 mV, is hardly of significance.

The various standardization techniques yielded $AgNO_3$ molarity values of:-

Manual method	$0.1054^1 \pm 0.0001^2$ M
E436A method	$0.1056^7 \pm 0.0008^4$ M
E526 assembly method	$0.1056^2 \pm 0.0004^6$ M

yielding an overall average and standard deviation of $0.1055^6 \pm 0.0001^3$ M. Variance ratio tests (0.95) indicated that the standard deviation for the molarity determined by the E436A technique differed significantly from that associated with the manual method. The individual average values were in good agreement, however, and it was not felt that the discrepancies observed were large enough to warrant further investigation by continued testing.

The E526 assembly was now applied in the determination of the content of chloride in the commercial acid nickel plating solutions. No pretitration additions were required, since all samples were prepared ready for titration. The pretitration burette stop stations were therefore

bypassed automatically by programming arrangement.

The operating parameters for the E526 unit were generally as indicated in Table 5-B for the final standardization titrations for the $AgNO_3$ titrant. Thus a preset dead-stop potential of + 320 mV was selected, this despite the fact that Table 4-B data had indicated that a value of + 290 mV might be required. This selection of + 320 mV was based on the final experimental findings for Table 5-B procedures.

The general operating parameters for the E526 unit are given in Table 6-B. Three samples were analyzed for each plating solution and, in addition, six samples involving 10.00 ± 0.01 ml of standard NaCl solution at $0.10000^0 \pm 0.00001^8$ M were interspersed between the commercial plating samples. Again, the purpose of these standards was to provide data concerning any possible drift in time of the E526 settings and silver/silver-silver chloride (3M KCl) electrode couple response.

The total of 36 samples was distributed in 9 magazines. All titrations were sequential and automatic upon initiation of the program start. The total elapsed time was approximately 1.25 hours. Table 12 shows the average values in oz/gal(US) of chloride and, for the standard solutions, the calculated molarity of $AgNO_3$ titrant versus the molarity determined from the standardization sequence. Included in this table are the results obtained by the granting agency.

The permanency of the E526 operating settings, and the stability of the electrode couple, is indicated by the reproducibility of the

TABLE 12

TITRATION OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS WITH 0.1M $AgNO_3$ IN THE DETERMINATION OF CHLORIDE BY E526

Sample No.	Chloride (oz/gal) Project work	Chloride (oz/gal) Can. Hans.
1.	1.12 ± 0.01	1.2
2.	1.60 ± 0.05	1.7
3.	1.96 ± 0.06	2.0
4.	2.07 ± 0.06	2.1
5.	2.42 ± 0.07	2.3
6.	2.56 ± 0.01	2.4
7.	3.13 ± 0.04	2.9
8.	3.08 ± 0.01	3.1
9.	3.76 ± 0.04	3.4
10.	3.41 ± 0.05	3.4

point we have:-

$$Cm = \frac{(110\ ml \times 0.0115M) - (12.55 \times 0.1M)}{122.55\ ml} = 8.1^5 \times 10^{-5}M$$

and from ~~equation (9) this~~ yields:-

$$[Ni^{2+}]\ (0.1\ ml\ before) = 8.9^6 \times 10^{-13}M$$

At the titration equivalence point $Cm = C_y$, and we have:-

$$[Ni(Y)^{2-}] = \frac{110\ ml \times 0.0115M}{122.65\ ml} - Cm$$

$$= 0.01031M - < 8.9^6 \times 10^{-13}M$$

$$= 1.0^3 \times 10^{-2}M$$

and since $Cm \ll [Ni(Y)^{2-}]$, equation (15) yields:-

$$\frac{1.0^3 \times 10^{-2}M}{(Cm)^2} = \frac{Kstab. \times \beta_o}{\alpha} = \frac{3.6 \times 10^{18} \times 1.1^0 \times 10^{-8}}{1.1^8}$$

so that Cm is given as $5.5^4 \times 10^{-7}M$, and we have:-

$$[Ni^{2+}]\ (equiv.\ pt.) = \beta_o Cm = 6.0^9 \times 10^{-15}M$$

At the titration point 0.1 ml after the equivalence point:-

$$[EDTA] = C_y = \frac{(12.75\ ml \times 0.1M) - (110\ ml \times 0.0115M)}{122.75\ ml}$$

$$= 8.1^4 \times 10^{-5}M$$

and:-

$$[Ni(Y)^{2-}] = (110\ ml \times 0.0115M)/122.75\ ml = 1.0^3 \times 10^{-2}M$$

from which equations (9) and (11) yield:-

$$Cm = 3.4^8 \times 10^{-9} M$$

and we have:-

$$[Ni^{2+}] \text{ (0.1 ml after)} = \beta_o Cm = 3.8^2 \times 10^{-17} M$$

Thus the value of $[Ni^{2+}]$ changes during the standardization titration as follows:-

$$[Ni^{2+}] \text{ (0.1 ml before equiv. pt.)} = 9.0 \times 10^{-13} M$$

$$[Ni^{2+}] \text{ (at equiv. pt.)} = 5.8 \times 10^{-15} M$$

$$[Ni^{2+}] \text{ (0.1 ml after equiv. pt.)} = 3.8 \times 10^{-17} M$$

The reaction of the murexide indicator to this situation can be calculated on the basis suggested by Reilley and Schmid (28) and Dick (29). The dissociation of murexide (H_3In) proceeds in three stages yielding H_3In, H_2In^-, HIn^{2-} and In^{3-}. At the solution pH of 11.3 for the standardization titration, the indicator is largely in the HIn^{2-} state. The metal-indicator reaction is:-

$$Ni^{2+} + HIn^{2-} + H_2O \leftrightharpoons NiIn^- + H_3O^+$$

and we have:-

$$\frac{[NiIn^-][H_3O^+]}{[Ni^{2+}][HIn^{2-}]} = K \qquad (16)$$

The third stage dissociation constant, K_3, for murexide is given by:-

$$\frac{[H_3O^+][In^{3-}]}{[HIn^{2-}]} = K_3 = 3.2 \times 10^{-11} \qquad (17)$$

and we have, from equations (16) and (17):-

$$\frac{[NiIn^-]}{[Ni^{2+}][In^{3-}]} = K/K_3 = \text{Kstab. (metal-indicator)}$$
$$= 2.0 \times 10^{-11}$$

so that the value of K for equation (16) is found to be 6.4.

From equation (16) we have:-

$$\frac{[NiIn^-]}{[Ni^{2+}][HIn^{2-}]} = \frac{K}{[H_3O^+]}$$

and:-

$$\frac{[NiIn^-]}{[HIn^{2-}]} = \frac{K.[Ni^{2+}]}{[H_3O^+]} \qquad (18)$$

The colour change range will occur over interval of:-

$$\frac{[NiIn^-]}{[HIn^{2-}]} = \frac{1}{10} \text{ to } 10$$

as the generally accepted range of change for colour shift detection by the human eye, and we have, from equation (18):-

$$pNi = 11.8 \pm 1$$

for a solution pH of 11.0. Note that:-

at 0.1 ml before equiv. pt.	pNi	= 12.0
at the equiv. pt.	pNi	= 14.2
at 0.1 ml after equiv. pt.	pNi	= 16.4

as calculated previously. The indicator therefore changes colour during the standardization titration at about the titration point 0.1 ml before the theoretical equivalence point volume.

Where the titration of commercial acid nickel plating solutions are concerned, the situation will be somewhat different but not radically so. Here we have amounts of nickel varying from about 5 to 15 oz/US gal. The amounts of free NH_3 and ammonium borate, $(NH_4)_3BO_3$, existing in each solution under titration will depend upon the amount of boric acid which was present in the original electroplating solution sample. For example, if electroplating solution contents of 8 oz/US gal are considered for boric acid and nickel (II), these would yield about 1M solution concentrations for each substance. The use of a 2 ml sample for titration then contributes 0.002 moles each of boric acid and nickel (II). If 10 ml of concentrated NH_3 and 90 ml of water is added this yields 0.148 moles of NH_3 and a total volume of 112 ml. Assuming all nickel converted to $Ni(NH_3)_4^{2+}$ and all H_3BO_3 converted to $(NH_4)_3BO_3$, this would then yield a pretitration solution containing:-

$[Ni(NH_3)_4^{2+}]$	=	0.0178M
$[(NH_4)_3BO_3]$	=	0.0178M
$[NH_3]$	=	1.19^6M
pH	=	10.6

so that, insofar as the manual titration situation is concerned, this and other electroplating solution titrations for nickel will show slightly lower endpoint volumes than the standardization procedure, these being about 0.3 ml lower rather than 0.1 ml lower. This difference amounts to a discrepancy of about -0.1oz/gal relative to the actual amount present.

The need to add ammonia prior to titration with EDTA is to permit the titration to be carried out at a solution pH compatible with the colour change requirements of the indicator, while avoiding precipitation of nickel by hydrolysis action. The quantitative titration of Ni(II) with EDTA can be carried out without the addition of NH_3 if the solution pH is not allowed to become less than about 3.2. Under such conditions, however, no simple indicator substance is available for endpoint detection.

If a nickel ion-selective electrode were available, this latter titration could be carried out, since such an electrode in conjunction with a suitable reference electrode could yield changes in Ecell, during the titration of Ni(II) with EDTA at pH values >3.5 and <5.5, large enough for easy equivalence point detection. Unfortunately, such an ion-selective electrode of a reliable nature is not commercially available, and consideration must be given to an alternate approach.

It is possible to apply a particular metal ion-selective electrode in potentiometric titrations involving cations forming soluble complexes with chelating agents such as EDTA, where the reacting or titrated cation

complex is much less stable than that for the metal ion representing the ion-selective electrode. Reilley and Schmid (30) developed a system of this nature, using a mercury electrode - reference electrode combination, a pretitration addition of a set concentration of Hg (II) - EDTA complex to a solution containing the metal ion reactive with EDTA to form a chelate appreciably less stable than the mercury-EDTA chelate, and the subsequent titration with standard EDTA solution. Such titrations show excellent ΔE shifts around the equivalence point, the magnitude of these shifts being influenced favourably by the larger degree of separation of the two stability constants. Difficulties associated with the Hg electrode occur, however, and in addition such an open-cup electrode for mercury would be poorly adaptable to an automated beaker-handling technique.

Titrations of this general type can be carried out using other ion-selective electrodes, and under conditions where the stability constants for the cations titrated may be higher or lower than that for the metal associated with the particular ion-selective electrode chosen. Baumann and Wallace (31) described the use of a copper(II) ion-selective electrode in the titration by EDTA of a number of metal cations. For those with metal-EDTA stability constants greater than that for the Cu(II)-EDTA complex, a small set addition of Cu(II)-EDTA complex was made prior to titration; for those with stability constants lower than that for Cu(II)-EDTA a larger set addition of Cu(II)-EDTA complex was made. These titrations were carried out at pH 5 for hydrolyzable metal cations tested, and at pH 5 and pH 10 for those which were nonhydrolyzable.

Ross and Frant (32) described the use of the copper(II) ion-selective electrode in the titration of various metal cations by TEPA (tetraethylenepentamine) and by EDTA. Such titrations were carried out at a variety of pH values, using ammonia-ammonium salt buffer solutions as additions for high pH titrations involving hydrolyzable cations. In general, additions of a copper(II) indicating solution preceded these titrations; the indicating solution consisting of a volume of 0.1M $Cu(NO_3)_2$ solution previously titrated to 90-99% completion with the appropriate chelating titrant. This indicator was added in a predetermined set total copper concentration varying from 1-10% of the approximate concentration of the metal cation to be titrated.

It was decided to investigate this latter technique in connection with the automated analysis of acid nickel electroplating solutions for nickel. Since the technique involves the possibility of both EDTA and TEPA titrations, the investigation was planned so as to apply EDTA titrant according to Baumann and Wallace (31), and TEPA.5HCl and TEPA generally according to Ross and Frant (32). Appendix C covers all of the experimental work conducted in these connections.

The first series of tests was carried with EDTA as the titrant. The titrant was prepared as an approximate 0.1M solution. For standardization purposes a copper(II) solution of 0.10000 ± 0.00005M and a nickel(II) solution of 0.09996 ± 0.00004M were prepared. The preparation of these solutions is described in Table 1-C of Appendix C.

Standardization of the EDTA titrant solution was now carried out

using an Orion 94-29 Cu(II) ion-selective electrode, an Orion 90-02 double-junction reference electrode (10% KNO_3), and the E436A recording titrator. Samples of standard Cu(II) solution were taken, a suitable solution pH was obtained by the pretitration addition of 0.5M NH_3/0.1M NH_4Cl buffer solution, and the final solution was tested for pH prior to titration. Table 2-C indicates the standardization details. The EDTA solution was found to have an average molarity and a standard deviation of:-

$$0.0901^3 \pm 0.0001^9$$

The average ΔE change for $\pm$ 0.5 ml around the equivalence point volume for these titrations (starting pH at 9.8 average) was $\pm$ 53 mV, or a spread of 106 mV.

A copper(II) indicating solution was now prepared by titrating a sample of standard Cu(II) solution to approximately 95% completion with standard EDTA solution. The 95% extent of titration completion was as generally recommended by Ross and Frant (32). The preparation of this solution is described in Table 3-C. The final solution contained Cu(II) on the basis of:-

$$1 \text{ ml} = 0.001270 \pm 0.000003 \text{ g.Cu}$$

The titration of nickel solutions was now carried out using 20.00 $\pm$ 0.02 ml of 0.09996 $\pm$ 0.00004M Ni(II) solution, 20 ml of distilled water and volumes of 0.5M NH_3/0.1M NH_4Cl buffer solution varied to provide starting solution pH values of 9 to 10. To each solution, prior to titration, 5.00 $\pm$ 0.01 ml of Cu(II)-EDTA indicating solution was

added. This addition represented 5 percent of the nickel (0.117 g approximately) present in the solutions to be titrated, and was in accordance with the Ross and Frant (32) recommendation of a total copper of 1-10% of the total nickel to be titrated. Table 4-C indicates the titration data involved, with Table 14 showing the pretitration solution pH values, the calculated nickel values and the average ΔE values for $\pm$ 0.5 ml around each equivalence point volume.

Several factors were noted relative to these titrations. First of all, the calculated nickel values in all instances are significantly lower than the actual value, with the titrations involving the lowest starting solution pH at 8.9 showing the greatest discrepancies. Second, the average $\pm \Delta E$ values for $\pm$ 0.5 ml around the equivalence point volume are significantly less than those noted for the standardization titrations against Cu(II) solution and, again, the 8.9 pH solutions show the least $\pm \Delta E$ spreads. Third, and a disturbing situation, was the erratic nature noted for the Ecell values at the equivalence points, varying as they did from - 338 mV to - 435 mV. Considering the $\pm \Delta E$ values at an average of approximately $\pm$ 28 mV, it is apparent that this relatively low $\pm \Delta E$ together with the erratic equivalence point Ecell would render titrations of nickel almost impossible to carry out by a preset dead-stop endpoint potential technique.

Examination of the titration curves for the standardization titrations had shown reasonably well-defined equivalence point changes. The curves for the nickel titrations showed, however rather poorly-defined

TABLE 14

DETERMINATION OF NICKEL - SYNTHETIC NICKEL SOLUTIONS IN TITRATION WITH STANDARD EDTA SOLUTION USING Cu(II)-EDTA INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE AND THE E436A RECORDING TITRATOR

Variable pH 9-10 at titration start

Actual amount of nickel(II) under titration = 0.1174 ± 0.0003 g

pH at start	Ecell equiv. pt. (mV)	Calculated value Ni (g ± 0.0003)	Ave. ± ΔE for ± 0.5 ml around eq. pt. (mV)
8.9	- 338	0.1032	18
8.9	- 340	0.1032	18
9.0	- 340	0.1133	27
9.0	- 360	0.1144	29
9.0	- 360	0.1111	28
9.3	- 382	0.1138	27
9.3	- 365	0.1143	27
9.3	- 390	0.1138	21
9.5	- 360	0.1130	28
9.5	- 377	0.1132	29
9.5	- 380	0.1124	27
10.0	- 433	0.1138	30
10.0	- 435	0.1148	31

changes around the equivalence point. Figure 3 indicates a general curve for a standardization titration, while Figure 4 indicates a general curve for a nickel solution titration. The curve characteristics will be duly noted.

In order to explore these difficulties as they would affect the determination of nickel in acid nickel bath plating solutions, several of these latter were titrated and the values obtained for nickel in oz/gal (US) were compared with the relevant Canadian Hanson analytical data. A new EDTA standard solution was prepared and standardized against Cu(II) as shown in Table 5-C. The average molarity and the standard deviation for this solution was found to be:-

$$0.1033^2 \pm 0.0005^1$$

Table 6-C shows the experimental set-up and data for the titration of acid nickel bath plating solutions, with Table 15 showing the essential data in terms of starting solution pH, calculated and Canadian Hanson nickel contents, Ecell at the equivalence point and the average ΔE for $\pm$ 0.5 ml around the equivalence point volume.

The calculated nickels in oz/US gal showed, except for the 9 pH solution titrations, reasonable precision within each group and quite good agreement with the appropriate Canadian Hanson data. The 9 pH solution (14.1 oz nickel/US gal) group showed poor precision and poor agreement with the granting agency value. The $\pm \Delta E$ values showed a very low range for $\pm$ 0.5 ml around the equivalence point volume, the average value being only $\pm$ 14 mV. This low value, coupled with an

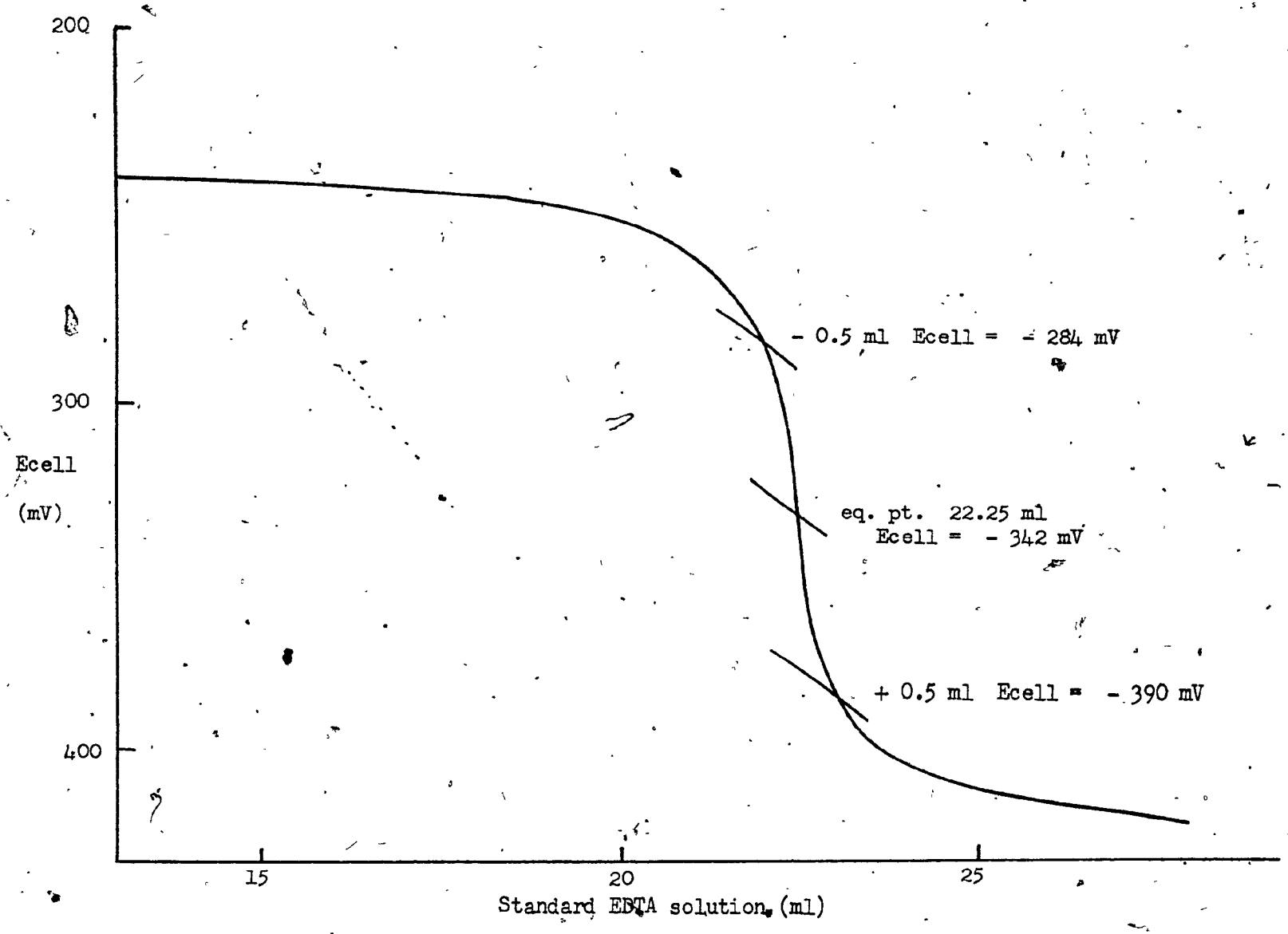


FIGURE 3 GENERAL TITRATION CURVE - STANDARDIZATION OF EDTA AGAINST Cu(II) SOLUTION

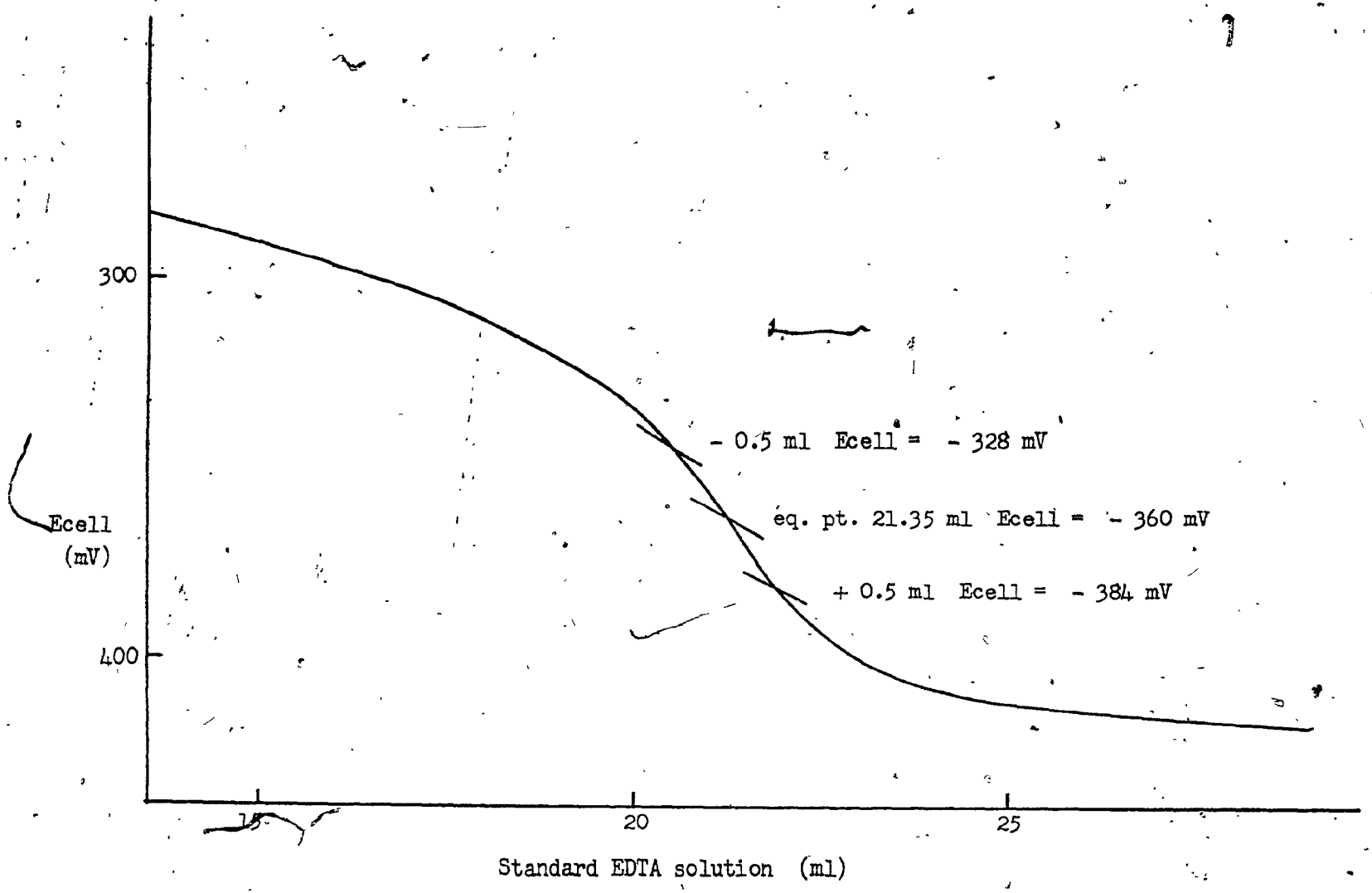


FIGURE 4 GENERAL TITRATION CURVE - TITRATION OF Ni(II) SOLUTION BY STANDARD EDTA.

TABLE 15

DETERMINATION OF NICKEL IN ACID NICKEL PLATING SOLUTIONS - TITRATION WITH STANDARD EDTA SOLUTION USING Cu(II)-EDTA INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE AND THE E436A TITRATOR

Variable pH at titration start

pH at start	Calc. Ni (oz/US gal)	Canadian Hanson Ni (oz/US gal)	Ecell at eq. pt. (mV)	Ave. $\Delta E \pm 0.5$ ml around the eq. pt. (mV)
9.0	14.68±0.09	14.1	- 326	± 10
9.0	15.99±0.09		- 316	± 9
9.0	14.98±0.09		- 400	± 16
9.0	14.90±0.09		- 400	± 13
9.0	14.27±0.08		- 396	± 16
9.3	11.64±0.08	11.6	- 382	± 15
9.2	11.94±0.08		- 368	± 15
9.2	11.66±0.08		- 376	± 14
9.3	10.47±0.07	10.6	- 386	± 16
9.3	10.41±0.07		- 388	± 14
9.3	10.43±0.07		- 376	± 16
9.5	4.76±0.04	5.1	- 400	± 16
9.5	4.72±0.04		- 400	± 13
9.6	4.86±0.04		- 396	± 16
9.6	5.02±0.04		- 416	± 16

equivalence point Ecell value varying from - 316 mV to - 416 mV as extremes and - 376 mV to - 400 mV generally, would create insurmountable problems if a preset dead-stop endpoint technique were to be applied to this titration system.

It was felt that the relatively minor difference in the EDTA stability constants for copper (6.2×10^{18}) and nickel (3.6×10^{18}) were, together with the high concentrations of nickel(II) involved, responsible for the small ΔE values around the equivalence point and the associated difficulty in interpreting the titration curves. Figure 5 shows a typical titration curve for the Table 6-C experimental work, and the poor curve characteristics in the neighbourhood of the equivalence point can be noted.

It was decided to explore the use of TEPA as a titrant. Here the much greater difference in the stability constants (6.3×10^{22} for copper and 2.7×10^{17} for nickel) would provide, even with high nickel concentrations, good curve characteristics and larger ΔE values for critical points around the equivalence point volume. Ross and Frant (32) had prepared their TEPA for titrant purposes by purifying the available technical grade to a TEPA.5HCl salt. This salt would appear to present the possibility of problems in that such a highly acid titrant would, in order to avoid serious pH changes during titration, require that the solution titrated be very strongly ammoniacal at the start. Such strongly ammoniacal solutions could provide for difficulties with respect to competition between the ammonia complexes and TEPA complexes for the copper and nickel cations in solution.

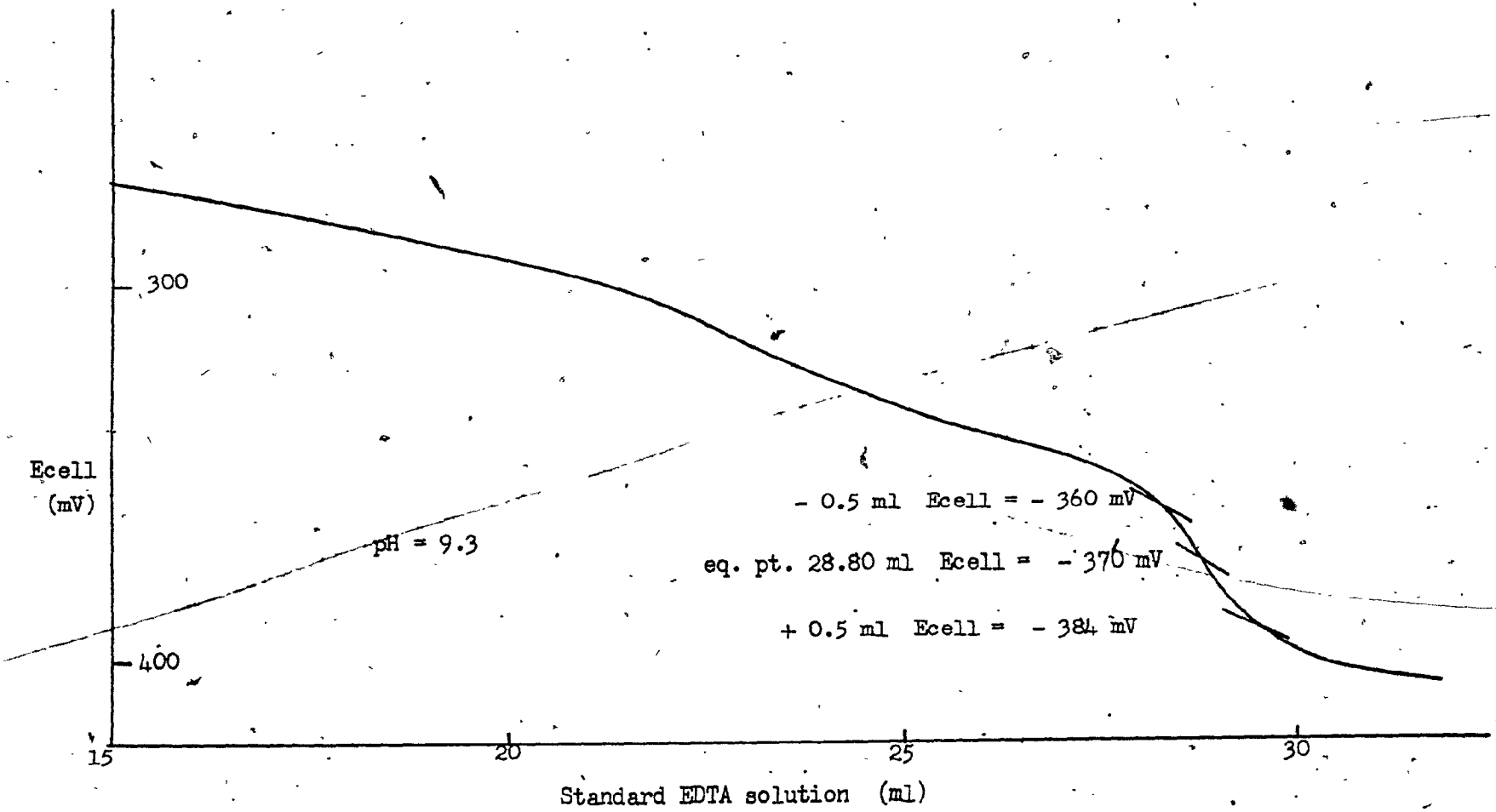


FIGURE 5 GENERAL TITRATION CURVE - TITRATION OF ACID NICKEL PLATING SOLUTION BY EDTA

It was therefore decided to carry out a very brief investigation using technical grade TEPA as the titrant, this in order to obtain some picture of the possibilities relative to ΔE changes around the equivalence point. An approximate 0.1M technical grade solution of TEPA was prepared, and this solution was used to titrate samples of 0.1M Cu(II) solution. Table 7-C shows the preparation and titration data involved. It was noted that the lower amounts of copper provided titration curves with large ΔE values ($\pm$ 80 mV to $\pm$ 50 mV for $\pm$ 0.5 ml around the equivalence point volume), while larger amounts of copper resulted in ΔE reduction to the point ($\pm$ 15 mV) where the value was comparable to that obtained with EDTA in the titration of acid nickel bath samples. It was felt that this might have been due to the starting solutions containing insufficient NH_3 to properly cover the acidity of the copper(II) solution added. The Ecell value at the titration equivalence points was, however, reasonably reproducible for all titrations, and the titrant volume at the equivalence point for each titration amount of copper(II) was consistent.

In order to determine whether or not an increase in titrant concentration would permit the larger amounts of copper to be titrated with improved ΔE values a stronger (0.2M approximately) titrant was prepared and, in addition, the pretitration solution was adjusted to 9.5 pH with NH_3. Table 8-C shows the preparation and titration data. A considerable improvement in the ΔE value ($\pm$ 30 mV) was noted, with continued precision relative to the equivalence point volume and Ecell values. It was felt that this improvement was due more to the controlled solution pH at 9.5 than to the increased titrant strength.

A brief series of tests was now conducted to determine the ability of the technical grade TEPA titrant to titrate synthetic nickel(II) solutions. No intention was implied here that these titrations would yield quantitative data; only that the titration curve characteristics and $\pm \Delta E$ data might be loosely determined. Accordingly, the stronger TEPA titrant prepared (Table 8-C) was used to prepare a Cu(II)-TEPA indicating solution by titrating a sample of standard Cu(II) solution to an approximate 95 percent extent. The preparation of this solution is outlined in Table 9-C, and the final solution contained total copper on the basis of:-

$$1 \text{ ml} = 0.000847 \pm 0.000003 \text{ g}$$

The synthetic nickel solutions to be titrated involved the proper addition of Cu(II)-TEPA indicating solution and amounts of NH_3 aimed at yielding a pretitration solution pH of about 9.5. The preparation and titration data are presented in Table 10-C. Reproducibility of the equivalence point potential and volume values will be noted. A slightly improved ΔE for $\pm$ 0.5 ml around the equivalence point volume ($\pm$ 30 mV) was also noted. Titration curve characteristics were improved, but still not quite suitable for automation.

It was decided now to apply the TEPA.5HCl titrant described by Ross and Frant (32), in the investigation series, despite the fact that the high acidity of this titrant could be expected to present problems with respect to maintaining a reasonable solution pH during high titrant volume titrations. Accordingly, purified TEPA and TEPA.5HCl were prepared by the technique described by these authors and outlined in Table 11-C.

This purified TEPA.5HCl was now used to prepare an approximate 0.2M solution. Table 12-C outlines the solution preparation, the preparation of Cu(II)-TEPA.5HCl indicating solution and the standardization of the titrant against standard Ni(II) solutions. The final average molarity and the standard deviation were:-

$$0.1780^4 \pm 0.0009^1$$

The tested pH of the titrant was 2.2. Table 12-C data shows good precision for both the equivalence point Ecell and volume values. The ΔE value of $\pm$ 30 mV for $\pm$ 0.5 ml around the equivalence point volume is still a little short of what might be felt to be ideal for automation purposes.

This titrant was now used to explore the titration of acid nickel plating solutions, where the volumes of TEPA.5HCl titrant required would be much higher than that used in the standardization process, and where the influence of titrant acidity might become important. The values obtained in these titrations of commercial solutions were compared with the Canadian Hanson values. Table 13-C gives the experimental details involved, while Table 16 shows essential data in terms of calculated and Canadian Hanson values, Ecell at equivalence point and ΔE for $\pm$ 0.5 ml around the equivalence point volume.

These titrations indicate reproducibility of the titrant volume for each analytical group. There is a tendency for Ecell at the equivalence point to drift to higher negative values with increasing volume of titrant used, and there is a tendency for the calculated results to

TABLE 16

DETERMINATION OF NICKEL IN ACID NICKEL PLATING SOLUTIONS - BY TITRATION WITH STANDARD TEPA.5HCl SOLUTION USING Cu(II)-TEPA. 5HCl INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE, THE E436A TITRATOR. INFLUENCED BY TITRANT VOLUME ACID ADDITIONS

Calc. Ni (oz/US gal)	Candn. Hanson Ni (oz/US gal)	Ecell at the eq. pt. (mV)	± ΔE for ± 0.5 ml around eq. pt.(mV)
10.73 ± 0.08	9.0	- 256	27
10.66 ± 0.08		- 252	25
10.66 ± 0.08		- 252	24
11.30 ± 0.08	8.7	- 252	23
11.29 ± 0.08		- 256	22
11.22 ± 0.08		- 252	23
14.10 ± 0.09	8.3	- 250	22
14.02 ± 0.09		- 247	24
14.06 ± 0.09		- 247	22
20.6 ± 0.1	12.9	- 272	14
20.7 ± 0.1		- 276	14
21.0 ± 0.1		- 260	15
11.54 ± 0.08	9.7	- 254	24
11.28 ± 0.08		- 252	26
11.29 ± 0.08		- 252	24

become increasingly higher than the granting agency values as the titrant volume consumed becomes greater. The generally high results and the drifting tendencies noted with respect to increasing titrant volume consumed were thought to be due to the acidity of the titrant relative to the fixed starting pH for the titrated solutions. The ΔE values were much better than those for the corresponding EDTA titrations (Table 15), although the titrations involving the highest volume of titrant showed much lower ΔE values.

In order to explore the effect of changing solution pH during a titration, as caused by titrant acidity, a series of acid nickel bath solutions was prepared under conditions where the pretitration solution would contain an amount of ammonia and ammonia/ammonium chloride buffer adequate to the control of the acid contributions from the titrant volumes consumed. Based on the possible addition of 40 ml approximately of TEPA.5HCl titrant at a pH of 2.2 in titrating 2 ml of an acid nickel bath solution containing 14.1 oz nickel/US gal, the use of a pretitration addition of 8 ml of 2:1 NH_3 and 25 ml of 0.5M NH_3/0.3M NH_4Cl buffer would more than adequately cover the situation and, indeed, any situation involving lower nickel content samples.

Table 14-C provides the preparation and titration details for the treatment of acid nickel bath solutions under the above conditions, with Table 17 showing relevant details including the calculated and granting agency nickel values, the starting and finishing values for solution pH, the Ecell values and the average ΔE for $\pm$ 0.5 ml around the equivalence point volumes.

TABLE 17

DETERMINATION OF NICKEL IN ACID NICKEL PLATING SOLUTIONS - BY TITRATION WITH STANDARD TEPA.5HCl SOLUTION USING Cu(II)-TEPA.5HCl INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE, THE E436A TITRATOR. UNINFLUENCED BY TITRANT VOLUME ACID ADDITIONS

pH at start	pH at finish	oz/US gal Ni calc.	Candn. Han.	Ecell at the eq. pt. (mV)	± ΔE for ± 0.5 ml around eq. pt. (mV)
10.2	9.5	13.86±0.08	14.1	- 230	23
10.2	9.5	13.78±0.08		- 230	24
10.2	9.5	13.41±0.08		- 230	24
10.2	9.6	11.42±0.07	11.6	- 234	26
10.2	9.6	11.34±0.07		- 225	25
10.2	9.8	4.83±0.04	5.1	- 260	31
10.2	9.8	4.73±0.04		- 266	29
10.2	9.8	4.70±0.04		- 256	30
10.2	9.6	9.78±0.06	9.7	- 240	27
10.4	9.8	9.87±0.06		- 240	24
10.4	9.8	9.87±0.06		- 242	26

Several important features, attributable to the adequate buffering of the solutions in order to accept the acid titrant additions, can be noted. First of all, the solution pH is reasonably stable from start to finish of each titration, with each titration ending up between 9.5 and 9.8 pH. Secondly, the equivalence point volumes and potentials are reasonably reproducible for each titration group. Thirdly, the calculated and actual values for nickel agree quite well and without radical variation with increasing nickel determined. Fourthly, the ΔE values around the equivalence point volume, while not high, are consistent and, finally, the Ecell values at the equivalence point are generally similar for all titrations.

The general difficulty with this type of titration centers largely around the relatively small ΔE shift around the equivalence point. This small spread, relative to what might be expected from the stability constant differences for copper and nickel, could originate with the large concentrations of NH_3 required to guarantee a solution pH of about 9.5 regardless of the titrant volume consumed, and the competition between TEPA and NH_3 in copper and nickel complex formation. This problem could possibly be minimized by the use of purified TEPA rather than TEPA.5HCl as the titrant, thus removing the need for large pre-titration additions of NH_3 and/or NH_3/NH_4Cl buffer solutions. This general position was indicated during the prior experimental work involving impure TEPA as the titrant substance.

In order to carry out a complete series of tests in this apparently

promising direction, a standard TEPA solution was prepared from the distilled impure TEPA obtained as described in Table 11-C. The preparation of this solution is outlined in Table 15-C, along with the standardization of the TEPA solution against copper(II) solution, the preparation of the Cu(II)-TEPA indicating solution and the standardization of the TEPA solution against nickel(II) solution. The Cu(II)-TEPA indicating solution contained a total copper given by:-

$$1 \text{ ml} = 0.001270 \pm 0.000003 \text{ g}$$

The standardization of the TEPA solution against standard Cu(II) solution yielded an average molarity and standard deviation of:-

$$0.0680^5 \pm 0.0002^3$$

while its standardization against standard Ni(II) solution yielded an average molarity and a standard deviation of:-

$$0.0660^0 \pm 0.0005^7$$

The reproducibility of the equivalence point volumes and potentials was found to be excellent for both copper and nickel standardization processes. The ΔE values for $\pm$ 0.5 ml around the equivalence point volume were excellent for the copper standardization process ($\pm$68 mV average), and reasonable ($\pm$ 40 mV average) for that involving nickel. The solution pH for both standardization groups remained at approximately 9.5 from start to finish.

Commercial acid nickel plating solutions were now analyzed using

the same TEPA titrant at its nickel standardization molarity of $0.0660^{0} \pm 0.0005^{7}$. The procedure applied is outlined in Table 16-C, as is the test data. Table 18 shows relevant data for these tests. It will be noted that the equivalence point potentials and volumes are reproducible for each solution group tested, and that the Ecell for the equivalence points of all titrations varies very little. Agreement of these Ecell values with that obtained during the Ni(II) standardization process (- 190 mV approximately) was very good. The ΔE values for ± 0.5 ml around the equivalence point volume averaged out at about ± 33 mV, comparing favourably with the ΔE for the Ni(II) standardization process (± 40 mV) and giving a spread for ± 0.5 ml of 66 mV. This spread should be high enough to permit adaptation of the technique to the automated preset dead-stop endpoint method, and this is paricularly the case when the reproducibility of Ecell at the equivalence point is also considered. In all titrations the start to finish solution pH did not vary appreciably from a value of 9.5.

At this point it was decided to carry out a series of tests to determine the applicability of the purified TEPA titrant to the E526 preset dead-stop automated titration arrangement.

A solution of purified TEPA titrant was prepared. The preparation, standardization against Cu(II) solution and standardization against Ni(II) solution are outlined in Table 17-C. The standardization against Cu(II) solution yielded an average molarity and standard deviation of:-

$$0.0777^{2} \pm 0.0007^{5}$$

TABLE 18

DETERMINATION OF NICKEL IN ACID NICKEL PLATING SOLUTIONS BY TITRATION WITH STANDARD TEPA SOLUTION, USING Cu(II)-TEPA INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE, CONSTANT ADDITION OF 0.5M NH_3/0.3M NH_4Cl BUFFER AND THE E436A TITRATOR

pH value start to finish - all titrations = 9.5

(oz/US gal) Calculated Ni	Canadian Hanson Ni	Ave. ± ΔE for ± 0.5 ml around eq. pt. (mV)
14.2 ± 0.2	14.1	33
14.2 ± 0.2		30
11.9 ± 0.1	11.6	33
11.8 ± 0.1		34
12.0 ± 0.1		34
10.5 ± 0.1	10.6	31
10.4 ± 0.1		36
10.4 ± 0.1		36
4.99 ± 0.05	5.1	32
4.97 ± 0.05		32
4.94 ± 0.05		34
8.81 ± 0.09	9.0	30
8.85 ± 0.09		36
8.74 ± 0.09		34
8.80 ± 0.09	8.7	34
8.70 ± 0.09		33
8.71 ± 0.09		33
8.49 ± 0.09	8.3	30
8.52 ± 0.09		34
8.44 ± 0.09		30
12.6 ± 0.1	12.9	34
12.6 ± 0.1		31
12.6 ± 0.1		30
9.5 ± 0.1	9.7	30
9.5 ± 0.1		32
9.5 ± 0.1		34

while that against Ni(II) solution provided an average molarity and a standard deviation of:-

$$0.0752^{8} \pm 0.0001^{6}$$

For both the Cu(II) and Ni(II) standardization titration sequences, the solution pH values at start and finish remained around 9.5. The Cu(II) titrations showed an average equivalence point Ecell value of - 260 ± 0 mV, with the Ni(II) titrations showing an average equivalence point Ecell of - 222 ± 2 mV. The ΔE values (± 0.5 ml around the equivalence point volume) were ± 54 mV for the Cu(II) titrations and ± 45 mV for the Ni(II) titrations. Both sets of ΔE values showed very good precision.

These standardization processes were now repeated using the E526-automatic titrator system. Preset dead-stop endpoint potentials were applied as indicated by the equivalence point potentials from the prior E436A titrator applications. These were subsequently modified as indicated by exploratory tests. These tests showed optimum preset dead-stop endpoint potentials of - 240 mV for the Cu(II) system and - 220 mV (unchanged) for the Ni(II) systems. Table 18-C provides the experimental set-ups and data for these standardizations. The average molarity and the standard deviation for the E526 Cu(II) standardization was:-

$$0.0771^{4} \pm 0.0003^{9}$$

and agrees, within the respective standard deviation limits, with the value obtained for the Cu(II) standardization procedure involving the E436A titrator. The average molarity and the standard deviation for

the E526 Ni(II) standardization was:-

$$0.0760^{1} \pm 0.0008^{4}$$

and this also agrees, within the respective standard deviation limits, with the value obtained relative to Ni(II) standardization using the E436A titrator.

The E526-automatic unit was now used in connection with the analysis of commercial acid nickel plating solutions. Table 19-C indicates the experimental data, with Table 19 showing the comparison between the calculated values of nickel and those obtained by the granting agency laboratories. Samples were analyzed in triplicate for each plating solution and, in addition, six samples involving 10.00 ± 0.01 ml of 0.09996 ± 0.00004M Ni(II) solution were interspersed between the plating solution samples. The purpose of these standard solutions was to provide data relative to the precision of the method, any possible drift of the E526 settings in time and any instability of the Cu(II) ion-selective/double-junction electrode couple.

The total of 33 samples was distributed in 9 magazines. All of the titrations were carried out sequentially and automatically upon program "start" initiation. The total elapsed time was about 1.5 hours.

The stability of the E526 operating parameters, and the stability of the electrode couple, are indicated by the reproducibility of the standard Ni(II) solution values as given in Table 19-C. The average TEPA molarity and standard deviation for the six standard solutions

TABLE 19

DETERMINATION OF NICKEL IN ACID NICKEL PLATING SOLUTIONS BY TITRATION WITH STANDARD TEPA SOLUTION, USING Cu(II)-TEPA INDICATING SOLUTION, Cu(II) ION-SELECTIVE ELECTRODE, CONSTANT ADDITION OF 0.5M NH_3/0.3M NH_4Cl BUFFER AND THE E526 ASSEMBLY

Calculated Ni (oz/US gal)	Canadian Hanson Ni (oz/US gal)
14.2 ± 0.3	14.1
14.4 ± 0.3	
14.1 ± 0.3	
11.6 ± 0.2	11.6
11.7 ± 0.2	
11.6 ± 0.2	
10.8 ± 0.2	10.6
10.6 ± 0.2	
10.6 ± 0.2	
4.85 ± 0.09	5.1
4.95 ± 0.09	
4.98 ± 0.09	
8.9 ± 0.2	9.0
9.1 ± 0.2	
9.0 ± 0.2	
8.8 ± 0.2	8.7
8.8 ± 0.2	
8.7 ± 0.2	
8.4 ± 0.2	8.3
8.5 ± 0.2	
8.5 ± 0.2	
12.7 ± 0.2	12.9
12.6 ± 0.2	
12.8 ± 0.2	
9.8 ± 0.2	9.7
9.6 ± 0.2	
9.6 ± 0.2	

was 0.0763 ± 0.0004, agreeing well with the Table 17-C values of $0.0752^{8} \pm 0.0001^{6}$M and the Table 18-C values of $0.0760^{1} \pm 0.0008^{4}$M, with these being respectively the Ni(II) solution standardization values for the E436A and the E526-automatic methods.

It will be noted that, for each acid nickel solution tested, the endpoint volumes show good agreement, and the calculated values for nickel in oz/US gal agree well with the respective Canadian Hanson values. The rather large uncertainties in the calculated results derives from the large uncertainties in the sample volume taken (1:100) and in the titrant molarity (8:760). These uncertainty values in the calculated results might be lowered by more accurate sample volume measurement (1.000 ± 0.005 ml) and by a larger number of standardization titrations reducing the molarity standard deviation.

Table 20 shows a comparison of the E436A, E526 and granting agency values. It will be noted that, in general, the E436A and E526 results show very good agreement, both with each other and within each titration group, and this is based on a consideration of the standard deviations for each titration group and the deviations from the overall averages. The overall average values show no serious departures from the granting agency results, neither in magnitude nor in direction.

2.5 The Analysis of Cyanide Silver Plating Solutions

2.5.1 General

Silver plating is applied for both decorative and engineering purposes. The ability to resist oxidation and corrosion is an important

TABLE 20

COMPARISON OF E436A, E526 ASSEMBLY AND CANADIAN HANSON TITRATIONS OF COMMERCIAL ACID NICKEL PLATING SOLUTIONS IN THE DETERMINATION OF NICKEL

all values expressed in oz/US gal

Sample No.	Can. Han. value	E436A (1)	E526 (2)	Ave. Overall	Devn. from overall ave. (1)	(2)
1.	5.1	4.97 ± 0.02	4.92 ± 0.06	4.94 ± 0.05	+ 0.03	- 0.02
2.	8.3	8.48 ± 0.04	8.4^{6} ± 0.0^{5}	8.4^{7} ± 0.0^{4}	+ 0.0^{1}	- 0.0^{1}
3.	8.7	8.74 ± 0.06	8.7^{6} ± 0.0^{5}	8.7^{5} ± 0.0^{5}	- 0.0^{1}	+ 0.0^{1}
4.	9.0	8.80 ± 0.06	9.0^{0} ± 0.1^{0}	8.9^{0} ± 0.1^{3}	- 0.1^{0}	+ 0.1^{0}
5.	9.7	9.5 ± 0.0	9.6^{6} ± 0.1^{1}	9.5^{8} ± 0.1^{1}	- 0.1^{1}	+ 0.0^{8}
6.	10.6	10.4^{3} ± 0.0^{5}	10.6^{6} ± 0.1^{4}	10.5^{5} ± 0.1^{5}	- 0.1^{3}	+ 0.1^{1}
7.	11.6	11.9 ± 0.1	11.6^{3} ± 0.0^{5}	11.7^{6} ± 0.1^{6}	+ 0.1^{4}	- 0.1^{3}
8.	12.9	12.6 ± 0.0	12.7 ± 0.1	12.6^{5} ± 0.0^{8}	- 0.0^{5}	+ 0.0^{5}
9.	14.1	14.2 ± 0.0	14.2^{3} ± 0.1^{5}	14.2^{1} ± 0.0^{9}	- 0.0^{1}	+ 0.0^{2}

OFFSET FROM CANADIAN HANSON VALUES

No.	Hanson value	Overall average	% devn. from Candn. Han.
1.	5.1	4.94	- 3.1
2.	8.3	8.4^{7}	+ 2.0
3.	8.7	8.7^{5}	+ 0.5
4.	9.0	8.9^{0}	- 1.1
5.	9.7	9.5^{8}	- 1.2
6.	10.6	10.5^{5}	- 0.4
7.	11.6	11.7^{6}	+ 1.3
8.	12.9	12.6^{5}	- 1.9
9.	14.1	14.2^{1}	+ 0.7

commercial property, as is the high electrical conductivity of the metal. Silver does, however, tarnish readily in the presence of sulphide atmospheres or sulphide-bearing substances.

A number of soluble silver salts are available, and silver has been deposited from many solutions containing these salts individually or in combination. Despite considerable research into other silver plating bath types, practically all commercial silver plating involves cyanide silver bath solutions. These latter are easy to prepare, relatively stable, have high anodic and cathodic efficiencies and good throwing power. Their chief drawback is the toxicity of the cyanide ion, although this is less serious than with other cyanide plating baths used in much more extensive operations and at higher bath temperatures.

The composition of cyanide silver plating baths varies according to the nature of the silver plating required. Decorative silver is usually plated from baths with a lower silver content than those used for engineering applications, where thicker deposits are normally required. The higher silver concentrations allow the use of higher current densities and therefore more economical plating speeds.

Silver cyanide is the most important source of silver in cyanide silver plating solutions. Insoluble silver cyanide can be dissolved in, for example, potassium cyanide solutions to form the soluble silver cyanide complex:-

$$AgCN + KCN \leftrightharpoons Ag(CN)_2^- + K^+$$

The dicyanoargentate(I) potassium salt is available as a convenient

source of silver. Cyanide silver baths are, however, commonly prepared from silver cyanide dissolved in a solution of potassium cyanide. A very low concentration of silver ions is provided by the ionization of the dicyanoargentate(I) complex. Excess cyanide, usually as potassium cyanide, is essential to the proper operation of the plating bath. This excess, which represents the amount over and above that required to dissolve the added silver cyanide, is known as "free cyanide". Its presence extends the plating range, increases the limiting current density, increases conductivity and enhances anodic dissolution. Salts such as carbonate and nitrate increase the bath conductivity and also broaden the plating range.

Baths prepared with potassium salts perform more efficiently then those prepared with sodium salts. Potassium salt baths can be operated at higher current densities, produce smoother deposits and respond better to the action of addition agents. Sodium salts are cheaper than potassium salts, and some savings can be realized without appreciable loss of productivity by the use of mixtures of sodium and potassium salts.

Experimental studies have indicated that chloride, formate, acetate, hydroxide, phosphate, borate and sulphate ions all have a tendency to increase the hardness of the silver deposit, with borate and chloride ions having the greatest influence.

The maintainance and control of cyanide silver baths are based primarily on chemical analysis taken daily on a routine basis, and on

the physical appearance of the deposit. The chemical analysis includes the determination of "free cyanide", carbonate, total silver and metallic impurities. For the purposes of this investigation these determinations will involve "free cyanide" as potassium cyanide, carbonate as potassium carbonate and total silver.

2.5.2 Determination of "free cyanide" as potassium cyanide

The determination of "free cyanide" is an essential aspect in the control of cyanide silver, cyanide copper and cyanide zinc plating baths. The method of analysis applied in the electroplating industry involves, for cyanide silver plating solutions:-

(1) Pipette 5.00 ml of plating bath solution into titration vessel.

(2) Add 100 ml of distilled water and 5.00 ml of 10% potassium iodide solution.

(3) Titrate with 0.1M $AgNO_3$ solution until a permanent turbidity is attained.

This is a modified Liebig titration, although not quite a Liebig-Denigés titration since this latter requires reasonably controlled additions of NH_3 prior to the titration start.

In the Liebig titration the titration reaction is:-

$$2CN^- + Ag^+ \leftrightharpoons Ag(CN)_2^-$$

resulting in the formation of the highly soluble complex dicyanoargentate(I) ion, $Ag(CN)_2^-$. Almost coinciding with the stoichiometric equivalence point of the titration, Ag^+ from the $AgNO_3$ titrant reacts

with $Ag(CN)_2^-$ to form the white slightly soluble salt silver dicyanoargentate, $Ag.Ag(CN)_2$, according to the reaction:-

$$Ag(CN)_2^- + Ag^+ \leftrightarrows Ag.Ag(CN)_2\ (s)$$

The resulting first permanent solution turbidity imparted to the solution signals the endpoint. This first indication of the endpoint occurs just slightly before the equivalence point but, since some further addition of $AgNO_3$ titrant is required to yield a truly visible turbidity, the final endpoint and equivalence point coincide to an excellent degree. There is some tendency for $Ag.Ag(CN)_2$ to form just before the true endpoint due to localized high concentrations of Ag^+, and this premature precipitate is slow to dissolve, thus extending the titration time by necessitating the slow addition of titrant near the endpoint. In order to permit a clearer endpoint and a faster titration, potassium iodide can be added to the solution prior to titration with $AgNO_3$. Since silver iodide is appreciably less soluble than silver dicyanoargentate, the presence of AgI as a precipitate occurs prior to the precipitation of $Ag.Ag(CN)_2$, and the turbidity given to the solution by AgI signals the endpoint. The following development indicates the general equilibria for both the Liebig and modified Liebig titrations.

For the Liebig titration, a typical cyanide silver bath "free cyanide" content of 10 oz KCN/US gal can be considered, so that the 5 ml sample volume taken in the manual method would represent 0.375 g of KCN. Since the solution volume at the start is 105 ml this repre-

sents a starting $[CN^-]$ of $5.48^6 \times 10^{-2}M$. This would require 28.80 ml of 0.1M $AgNO_3$ to attain the equivalence point. The $[Ag(CN)_2^-]$ at the equivalence point would therefore be:-

$$[Ag(CN)_2^-] = \frac{105 \text{ ml} \times 0.0548^6 M}{2 \times 128.8 \text{ ml}}$$

$$= 2.23^4 \times 10^{-2}M$$

The value of $[CN^-]$ at which $Ag.Ag(CN)_2$ just begins to precipitate can be obtained from the relationships:-

$$[Ag^+] = \frac{Ksp(Ag.Ag(CN)_2)}{[Ag(CN)_2^-]} \quad \text{and} \quad [Ag^+] = \frac{[Ag(CN)_2^-]}{[CN^-]^2.Kstab} \qquad (19)$$

so that the critical $[CN^-]$ is:-

$$[CN^-] = \sqrt{\frac{[Ag(CN)_2^-]^2}{Ksp(Ag.Ag(CN)_2) \times Kstab}}$$

$$= \sqrt{\frac{(2.23^4 \times 10^{-2})^2}{2.0 \times 10^{-12} \times 7.1 \times 10^{19}}}$$

$$= 1.9 \times 10^{-6}M$$

At the equivalence point of this titration we have:-

$$[CN^-] = 2[Ag^+] \quad \text{and} \quad \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = Kstab \qquad (20)$$

so that:-

$$[CN^-] \text{ eq. pt.} = \sqrt[3]{\frac{2.23^4 \times 10^{-2}}{0.5 \times 7.1 \times 10^{19}}} = 8.6 \times 10^{-8}M$$

This latter value is never achieved, however, since the precipita-

tion of $Ag.Ag(CN)_2$ starts as soon as the $[CN^-]$ reaches a value of 1.9×10^{-6}M. The endpoint thus occurs very slightly before the equivalence point, but not to any significant degree, particularly since additional 0.1M $AgNO_3$ must be added to provide sufficient turbidity for easy visual detection.

Where the modified Liebig titration is concerned, using generally the same "free cyanide data for the sample, an addition of 5 ml of 10 percent KI solution is made before the titration starts. This yields an $[I^-]$ concentration at the titration equivalence point of about:-

$$[I^-] = \frac{5 \text{ ml} \times 0.1 \text{ g/ml} \times 1000}{166.0 \text{ g/mol} \times 128.8 \text{ ml}} = 0.0234\text{M}$$

We now have, at the point where AgI is just ready to precipitate:-

$$[Ag^+] = \frac{[Ag(CN)_2^-]}{[CN^-]^2 Kstab} \quad \text{and} \quad [Ag^+] = \frac{Ksp(AgI)}{[I^-]} \qquad (21)$$

so that the critical $[CN^-]$ is given by:-

$$[CN^-] = \sqrt{\frac{[Ag(CN)_2][I^-]}{Ksp(AgI) \times Kstab}} = \sqrt{\frac{2.23^4 \times 10^{-2} \times 2.34 \times 10^{-2}}{1.5 \times 10^{-16} \times 7.1 \times 10^{19}}}$$

$$= 2.2^2 \times 10^{-4}\text{M}$$

As noted in the previous calculations the equivalence point value of $[CN^-]$ should be 8.6×10^{-8}M. The volume of 0.1M $AgNO_3$ required in order to yield a point in titration where the $[CN^-]$ is $2.2^2 \times 10^{-4}$M would be given by:-

$$\frac{(105\ \text{ml} \times 0.0548^{6}\text{M}) - (2 \times 0.1\text{M} \times \text{V})}{105\ \text{ml} + \text{V}} = 2.2^{2} \times 10^{-4}\text{M}$$

$$\text{V} = 28.65\ \text{ml}$$

This would appear to imply a blank of + 0.15 ml, but approximately 0.1 ml would be required to yield a visual turbidity, so that the actual blank would be about + 0.05 ml. The electroplating industry manual method does not apply a blank to either the Liebig or modified Liebig titration processes.

In both titrations the $[Ag^{+}]$ and $[CN^{-}]$ do not vary significantly for reasonable excess volumes of 0.1M $AgNO_3$ after the equivalence point, since either $Ag.Ag(CN)_2$ or AgI continues to precipitate. Thus the titration curve beyond the equivalence point is very sharp, and almost parallel to the titrant volume axis.

Details relative to the experimental work associated with the determination of "free cyanide" are included in Appendix D. Tables and figures carrying the suffix "-D" are found in this appendix.

A standard solution of $AgNO_3$ was prepared so as to yield an approximate molarity of 0.1, and this solution was standardized against sodium chloride solution by manual titration using Fajan's method as outlined in Table 1-D. The average molarity and the standard deviation were:-

$$0.1322^{7} \pm 0.0003^{4}$$

This titrant was now applied in the manual titration, using the

industry standard method, of the commercial cyanide silver bath solutions provided by the granting agency, Canadian Hanson. Table 2-D indicates the details involved, while Table 21 provides the average values and standard deviations obtained, together with the analytical data for "free cyanide" as KCN provided by Canadian Hanson laboratories. All solutions were reserved after titration for the manual titration determination of potassium carbonate, a practice carried out in accordance with the electroplating industry procedures.

It will be noted that the experimental values agree well with the granting agency values, except in the cases of the sample numbers 2, 5 and 8. These discrepancies will be discussed in the Conclusions section.

The procedure used for the manual standardization of the $AgNO_3$ solution was now applied with respect to the E436A titrator. The standardization details are given in Table 3-D. The average molarity and the standard deviation were found to be:-

$$0.1326^2 \pm 0.0007^0$$

and this agrees well, within the respective standard deviation limits, with the value obtained by the manual titration method.

The theoretical calculations to determine the Ecell at the titration equivalence point, and the values for Ecell at ± 0.5 ml around the equivalence point volume, are outlined in Table 3-D. The following outlines the actual and theoretical Ecell values.

TABLE 21

MANUAL TITRATION DETERMINATION OF "FREE CYANIDE" AS KCN IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	Ave. KCN (oz/US gal) Project work	KCN (oz/US gal) Canadian Hanson
1.	6.51 ± 0.02	6.6
2.	10.19 ± 0.02	12.5
3.	7.52 ± 0.01	8.0
4.	10.22 ± 0.02	10.0
5.	10.16 ± 0.06	13.1
6.	6.11 ± 0.01	6.0
7.	6.89 ± 0.02	6.9
8.	9.95 ± 0.03	12.3
9.	9.42 ± 0.02	9.5
10.	8.94 ± 0.01	9.4

	Found(mV)	Theoretical(mV)
Ave. Ecell 0.5 ml before eq. pt.	199 ± 1	198
Ave. Ecell at eq. pt.	300 ± 0	311
Ave. Ecell 0.5 ml after eq. pt.	429 ± 0	422
ΔE for ± 0.5 ml around eq. pt.	228 ± 0	224

These values all agree well, and any minor discrepancies can be assumed due to such factors as uncompensated junction potentials, use of concentrations instead of activities, uncertainties in mV measurement, effects of solution ionic strength, temperature variations from 25°C, etc.

The E436A titrator was now applied in the titration of commercial cyanide silver plating solutions. The experimental details are given in Table 4-D, while Table 22 shows the averages and standard deviations, together with the granting agency values. All titrated residues were preserved for a subsequent E436A titration to determine potassium carbonate.

It will be noted that Table 22 values agree very well with those outlined in Table 21, although the same discrepancies in results exist relative to the granting agency values for sample numbers 2, 5 and 8. Table 4-D data indicates an average Ecell at the equivalence point of - 207 ± 3 mV, and this agrees reasonably well with the Table 4-D theoretical calculated value of - 238 mV. The value of Ecell for 0.5 ml before the equivalence point volume was found to be - 400 ± 1 mV, and this does not compare too well with the theoretical value of - 324 mV. Values of Ecell for 0.5 ml after the equivalence point are meaningless since, because of the continued precipitation of AgI, the equivalence point Ecell value is generally maintained. The discre-

TABLE 22

E436A TITRATION DETERMINATION OF "FREE CYANIDE" AS KCN IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	Ave. KCN (oz/US gal) Project work	KCN (oz/US Gal) Canadian Hanson
1.	6.53 ± 0.05	6.6
2.	10.01 ± 0.07	12.5
3.	7.48 ± 0.02	8.0
4.	10.00 ± 0.01	10.0
5.	10.05 ± 0.02	13.1
6.	6.07 ± 0.04	6.0
7.	6.82 ± 0.05	6.9
8.	9.78 ± 0.07	12.3
9.	9.39 ± 0.06	9.5
10.	8.92 ± 0.02	9.4

pancies may be considered to originate from the various influencing factors previously mentioned, particularly with respect to the solution ionic strength factor.

The average ΔE range for the project work was found from Table 4-D data to be 193 ± 3 mV, and this should permit location of the equivalence point volume in a preset dead-stop endpoint titration within ± 0.1 to ± 0.2 ml of the real value. This uncertainty in volume location would lead to an uncertainty in the determination of KCN of:-

$$(\pm 0.1 \text{ to } \pm 0.2 \text{ ml}) \times 0.1326\text{M } AgNO_3 \times 3.47^8 = \pm 0.05 \text{ to } \pm 0.1 \text{ oz/gal}$$

The complete sequence of experimental approaches was now conducted in association with the E526 automatic titrator assembly. The operating parameters for the standardization of the $AgNO_3$ titrant were taken from Table 3-D data covering the standardization of this titrant using the E436 titrator. These data had indicated an average equivalence or endpoint Ecell of 300 ± 0 mV, and an average ΔE range for ± 0.5 ml of 230 ± 0 mV. This ΔE range represents a sharp approach to the endpoint, so that extensive $\Delta E/\Delta V$ changes in this zone will demand a careful approach to the endpoint. The final operating parameters were somewhat different from the above data, since initial exploratory work indicated a tendency for the E526 to under-titrate at a dead-stop potential of 300 mV, and an optimum value of 316 mV was found to be most suitable.

Once this value had been established, four (4) final titrations were carried out, using one magazine, and sequential and automatic programming. Table 5-D indicates all experimental details involved.

The average molarity and standard deviation obtained were:-

$$0.1336^{0} \pm 0.0002^{3}$$

The various standardization techniques yielded $AgNO_3$ molarity and standard deviation values of:-

Manual method	$0.1322^{7} \pm 0.0003^{4}$
E436A method	$0.1326^{2} \pm 0.0007^{0}$
E526 method	$0.1336^{0} \pm 0.0002^{3}$

providing an allover average and standard deviation of $0.1329^{0} \pm 0.0007^{1}$M. Variance ratio tests indicated that there was no significant difference in the standard deviations. Null hypothesis (95%) tests carried out on each pair of averages indicated that there was a slight significant difference in the E526 average as compared to the other two values. It was not felt that these indications were sufficiently serious to warrant further investigation.

The E526 assembly was now applied in the determination of "free cyanide" as KCN in commercial cyanide silver plating solutions. The equipment was set up for the automatic pretitration additions of dilution water and 10 percent KI solution.

The operating parameters for the E526 unit were generally as dictated by Table 4-D data, although preliminary exploratory work indicated a preset dead-stop potential of - 240 mV as optimum, closer to the theoretical value of - 238 mV but considerably more negative than the - 207 mV value found in Table 4-D data. Table 6-D gives the various

experimental data involved for these operational parameters and for the titration results. The total of 33 samples was distributed in nine magazines, and all pretitration additions and titrations were carried out sequentially and automatically. The total elapsed time was about 1.25 hours. Table 23 shows the average KCN values in oz/US gal, together with the associated Canadian Hanson results. These values show good precision, although not generally as good as either the manual or E436A methods. Agreement with the granting agency values is again reasonable, except in the case of sample numbers 2, 5 and 8. Sample number 10, for the E526 data, also appears to indicate a value somewhat lower than the Canadian Hanson value to a significant extent, certainly by an amount greater than the differences found for the manual and E436A techniques.

Table 24 shows a comparison of the manual, E436A, E526 and Canadian Hanson values. It will be noted that, by titration type class, the the results agree quite well with each other, although the precision as measured by the standard deviation becomes progressively poorer in moving from the manual → E436A → E526 techniques. In all cases of semi-automatic and automatic titration, the values of the standard deviations are within the expected maximum uncertainty predicted of ± 0.1 oz/US gal.

Comparison of the results for the individual titration types with the corresponding overall averages shows that, very generally, the manual method tends to slightly high results, the E436A slightly low results and the E526 to rather unbiased results. In some cases, for all methods,

TABLE 23

E526 TITRATION DETERMINATION OF "FREE CYANIDE" AS KCN IN COMMERCIAL CYANIDE SILVER PLATING SOLUTIONS

Sample No.	Ave. KCN (oz/US gal) Project work	KCN (oz/US gal) Canadian Hanson
1.	6.63 ± 0.07	6.6
2.	10.20 ± 0.06	12.5
3.	7.84 ± 0.08	8.0
4.	9.83 ± 0.07	10.0
5.	10.17 ± 0.09	13.1
6.	6.09 ± 0.02	6.0
7.	6.87 ± 0.07	6.9
8.	9.84 ± 0.06	12.3
9.	9.28 ± 0.06	9.5
10.	8.63 ± 0.04	9.4

TABLE 24

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF COMMERCIAL CYANIDE SILVER PLATING SOLUTIONS IN THE DETERMINATION OF "FREE CYANIDE" AS KCN

All results expressed in oz/US gal

Sample No.	Can. Han. value	Manual (1)	E436A (2)	E526 (3)	Overall ave.	Devn. from overall ave. (1)	(2)	(3)
1.	6.6	6.51 ± 0.02	6.53 ± 0.05	6.63 ± 0.07	6.56	- 0.04	- 0.03	+ 0.07
2.	12.5	10.19 ± 0.02	10.01 ± 0.07	10.20 ± 0.06	10.1^3	+ 0.06	- 0.12	+ 0.07
3.	8.0	7.52 ± 0.01	7.48 ± 0.02	7.84 ± 0.08	7.6^1	- 0.09	- 0.13	+ 0.23
4.	10.0	10.22 ± 0.02	10.00 ± 0.01	9.83 ± 0.07	10.0^1	+ 0.19	- 0.01	- 0.18
5.	13.1	10.16 ± 0.06	10.05 ± 0.02	10.17 ± 0.09	10.12	+ 0.04	- 0.07	+ 0.05
6.	6.0	6.11 ± 0.01	6.07 ± 0.04	6.09 ± 0.02	6.09	+ 0.02	- 0.02	± 0.00
7.	6.9	6.89 ± 0.02	6.82 ± 0.05	6.87 ± 0.07	6.86	+ 0.03	- 0.04	+ 0.01
8.	12.3	9.95 ± 0.03	9.78 ± 0.07	9.84 ± 0.06	9.86	+ 0.09	- 0.08	- 0.02
9.	9.5	9.42 ± 0.02	9.39 ± 0.06	9.28 ± 0.06	9.36	+ 0.06	+ 0.03	- 0.08
10.	9.4	8.94 ± 0.01	8.92 ± 0.02	8.63 ± 0.04	8.8^2	+ 0.12	+ 0.10	- 0.19

OFFSET FROM CANADIAN HANSON VALUES

No.	Hanson value	Overall average	% devn. from Can. Han.
1.	6.6	6.56	- 0.6
2.	12.5	10.1^3	- 19.0
3.	8.0	7.6^1	- 4.8
4.	10.0	10.0^1	+ 0.1
5.	13.1	10.12	- 22.7
6.	6.0	6.09	+ 1.5
7.	6.9	6.86	- 0.5
8.	12.3	9.86	- 17.3
9.	9.5	9.36	- 1.4
10.	9.4	8.8^2	- 6.1

the deviation from the overall average exceeds the expected uncertainty of ± 0.1 oz/US gal. It was not felt, however, that any of the discrepancies noted were of worthwhile significance.

In comparing the obtained overall averages with the Canadian Hanson values serious discrepancies were noted with respect to sample numbers 2, 5 and 8. In each case the overall average value was very much lower than the Canadian Hanson value and, since each technique applied showed the same situation, it must be assumed that some fundamental difficulty exists. Since titration curves were obtained in the E436A method, and since these definitely indicate the existence of a proper endpoint, it can be assumed that the values obtained, despite their differences relative to the granting agency data, are real and represent what the method of analysis can determine and report as KCN. A further commentary and speculation will be made in the Conclusions section.

2.5.3 Determination of carbonate as potassium carbonate

Although carbonate ion in cyanide silver plating baths has an enhancing effect with respect to silver deposition, carbonates tend to accumulate in time by various means (e.g. action of CO_2 in air). From time to time adjustment of the carbonate content is required, so that its determination on a routine basis is essential. The method of analysis used in the electroplating industry involves a neutralization titration involving sulphuric acid as the titrant. Such titrations are normally carried out on the residue from the "free cyanide" titration determination.

This titration is carried to the first-stage equivalence point relative to K_2CO_3, so that the titration reaction is generally:-

$$H_2SO_4 + K_2CO_3 \leftrightharpoons KHSO_4 + KHCO_3$$

Normally, for example where HCl is used as the titrant, the first-stage equivalence point solution would contain $KHCO_3$ and KCl, and would yield a solution pH of about 8.3, as given by the value of $[H_3O^+] = \sqrt{K_1K_2}$ for carbonic acid. Where H_2SO_4 is the titrant, the assumption is made that this acid, in its first-stage dissociation, acts as a strong acid and yields, at the titration first-stage equivalence point, a similar solution pH. That this assumption is made is apparent where the industry method is concerned, since phenolphthalein at a colour change range of 10-8.3 pH is used as the indicator substance. Some argument could be devised relative to this assumption on the basis of the solution pH attributable to a solution of both $KHCO_3$ and $KHSO_4$, the two endpoint substances in the H_2SO_4 titration, but the complexity of the solution relative to its content of $Ag(CN)_2^-$ apparently allows the assumed endpoint pH of about 8.3 to be successfully applied.

The industrial technique consists of the following:-

(1) Take the residue from the "free cyanide" titration and add a few drops of phenolphthalein indicator solution.

(2) Titrate the solution with 0.1N H_2SO_4 to the disappearance of the pink colour.

The experimental work details for this sub-section are contained in Appendix E, as are all tables bearing the suffix "-E".

A standard solution of H_2SO_4 was now prepared and standardized against NaOH standard solution, using the manual method with phenolphthalein as the indicator substance. Table 1-E provides the details in this connection. The average molarity and the standard deviation were found to be:-

$$0.14475^3 \pm 0.00004^1$$

This titrant was now applied in the manual titration of the residues from the manual titration determination of "free cyanide" (table 2-D). The technique of analysis is indicated in Table 2-E and the essential details in terms of the oz/US gal content of K_2CO_3 are shown in Table 25 along with the values attained by the granting agency laboratories.

It will be noted that the individual values agree well amongst themselves, but the average values show significant differences with respect to the Canadian Hanson data. This latter situation is particulary apparent in association with sample numbers 1, 3, 5, 6, 8 and 9. These differences are not necessarily consistent, in that numbers 1, 3, 6 and 9 show lower values and numbers 5 and 8 higher values. It is of interest to report that, in all titrations where the results differ radically from the Canadian Hanson values, the indicator colour change was quite gradual, rendering it difficult to pinpoint the exact endpoint volume.

The E436A titrator was now applied in the standardization of the

TABLE 25

MANUAL TITRATION DETERMINATION OF K_2CO_3 IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	K_2CO_3 (oz/US gal) Project work	K_2CO_3 (oz/US gal) Canadian Hanson
1.	4.15 ± 0.01	5.8
2.	7.51 ± 0.05	7.2
3.	5.21 ± 0.01	6.2
4.	1.15 ± 0.02	1.1
5.	6.96 ± 0.03	5.3
6.	7.14 ± 0.01	8.7
7.	7.22 ± 0.06	7.9
8.	7.17 ± 0.16	6.3
9.	8.02 ± 0.02	9.2
10.	5.19 ± 0.01	5.3

H_2SO_4 titrant. Table 3-E provides the experimental data. The average molarity and the standard deviation were:-

$$0.1448^5 \pm 0.0001^5$$

and this agrees well with the value found for the manual titration method. Table 3-E also indicates that the titration values for the equivalence point pH, and the pH values for ± 0.5 ml around the equivalence point, agree well with the theoretical values. This situation is outlined below.

		Found	Theoretical
0.5 ml before eq. pt.	(pH)	10.76	11.0
Equivalence point	(pH)	6.81	7.0
0.5 ml after eq. pt.	(pH)	2.80	3.0

This titrant was now applied in the E436A titration determination of K_2CO_3 for the residues from the E436A titration to determine "free cyanide" (Table 4-D). The details of these titrations are given in Table 4-E, and Table 26 indicates the average values found in comparison to the Canadian Hanson analytical data. Also provided in Table 26 are the average equivalence point pH values and the average ±ΔpH for ± 0.5 ml around the equivalence or endpoint volumes.

It will be observed that the E436A results agree well with each other for each solution titrated, and that the average values for each solution are in very good agreement with those found using the manual titration method. The single exception here involves the two averages for sample number 4, and it can be taken as a fact that the very small volume for this titration yielded a titration curve form difficult to

TABLE 26

E436A TITRATION DETERMINATION OF
K_2CO_3 IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	K_2CO_3 (oz/US gal) Project work	K_2CO_3 (oz/US gal) Canadian Hanson	Ave. pH eq. pt	± ΔpH ± 0.5 ml
1.	4.10 ± 0.06	5.8	8.31	0.38
2.	7.37 ± 0.04	7.2	8.32	0.38
3.	5.24 ± 0.02	6.2	8.32	0.44
4.	0.73 ± 0.06	1.1	8.36	0.45
5.	7.13 ± 0.03	5.3	8.38	0.45
6.	7.06 ± 0.06	8.7	8.37	0.40
7.	7.36 ± 0.02	7.9	8.33	0.45
8.	7.19 ± 0.10	6.3	8.32	0.44
9.	8.01 ± 0.01	9.2	8.30	0.43
10.	5.07 ± 0.06	5.3	8.32	0.45

analyze where the E436A titration was concerned. The differences between the experimental results for the E436A titrations and the Canadian Hanson data, for sample numbers 1, 3, 5, 6, 8 and 9, correspond to those found for the manual titration application.

The theoretical values for the solution pH at the equivalence point, and at the points ± 0.5 ml around the equivalence point, are calculated and shown in Table 4-E. These agree quite well with the experimental averages, as shown below.

		Found	Theoretical
0.5 ml before eq. pt.	(pH)	8.8±0.1	9.0
Equivalence point	(pH)	8.4±0.1	8.3
0.5 ml after eq. pt.	(pH)	8.0±0.1	7.7

It will be noted that the ± ΔpH for ± 0.5 ml around the endpoint volume was found to be about ± 0.45, or a spread of 0.90. This is by no means an extended range, so that the need for a careful approach to the equivalence point in any potentiometric titration is obvious.

Standardization of the H_2SO_4 titrant was now carried out on the E526 assembly. The parameters applied to this unit were those extracted from Table 3-E data covering the E436A titrator standardization. The molarity and standard deviation were:-

$$0.14478^0 \pm 0.00002^4$$

The various standardization processes thus gave values of:-

Manual method	$0.14475^{3} \pm 0.00004^{1}$
E436A method	$0.1448^{5} \pm 0.0001^{5}$
E526 method	$0.14478^{0} \pm 0.00002^{4}$

It was appreciated that these molarity and standard deviation values were, because of the precision of the standardization titrations in each case, expressed to significant figures beyond those permitted by the measurement uncertainties related to associated volumes. Rightly, these uncertainties would permit for the values above and respectively $0.1447^{5} \pm 0.0002^{9}$M, $0.1448^{5} \pm 0.0002^{9}$ and $0.1447^{8} \pm 0.0002^{9}$M. The extended values and standard deviations initially shown were used, however, in all calculations. Variance ratio and null hypothesis tests were not applied, since all values agreed very well within the measurement uncertainty limits. The overall average and standard deviation, still on the original expression basis, was found to be $0.1448^{0} \pm 0.00001^{0}$.

The preset dead-stop pH value of 6.90 provided no difficulty with respect to either over- or under-titration, and this is not surprising in view of the very large ΔpH spread (7.96 pH) for $\pm$ 0.5 ml around the equivalence point volume.

The E526 unit was applied in the determination of K_2CO_3 in the residues from the E526 assemby determinations of "free cyanide" (Table 6-D). The operating parameters set on the unit were initially those provided by the data for Table 4-E, including the preset dead-stop of 8.33 pH. Initial exploratory work indicated a slight tendency to under-titration at this value, and an optimum dead-stop setting of

8.50 pH was found to perform satisfactorily. The complete experimental data for these titrations is given in Table 6-E, with Table 27 showing the comparable project averages and the Canadian Hanson values. A total of 37 samples in ten magazines were titrated sequentially and automatically. Since no pretitration additions were required, the pretitration stops were set for automatic bypass by programming. It will be noted, once again, that individual solution analyses show good precision. The E526 process analyses as average values compare well with those obtained from the E436A (Table 26) and manual (Table 25) titrations. It will also be noted that sample numbers 1, 3, 5, 6, 8 and 9 again show very considerable differences relative to the granting agency data. Despite the low spread value for ΔpH of about 0.90 for ± 0.5 ml around the equivalence point the E526 gave highly precise endpoint values of volume and oz/US gal K_2CO_3 (an average of ± 0.07 ml and an average of ± 0.04 oz/gal). This is an indication of the general stability of both the E526 dead-stop setting and the electrode couple.

Table 28 gives a comparison of the values obtained from all method applications. All techniques show good precision and good agreement between the averages for each method. There is a slight tendency for two potentiometric methods to give a somewhat poorer precision than the manual method, and this is not surprising in view of the small ΔpH spread. These differences are not of any worthwhile significance.

There does not appear to be any directional trend for any method, this as observed from a survey of the data in Table 28 headed "Devn. from the overall average". From a comparison of the overall averages

TABLE 27

E526 TITRATION DETERMINATION OF
K_2CO_3 IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	K_2CO_3 (oz/US gal) Project work	K_2CO_3 (oz/US gal) Canadian Hanson
1.	4.25 ± 0.01	5.8
2.	7.68 ± 0.06	7.2
3.	5.17 ± 0.07	6.2
4.	1.20 ± 0.08	1.1
5.	$6.9^0 \pm 0.1^1$	5.3
6.	7.13 ± 0.03	8.7
7.	7.31 ± 0.05	7.9
8.	6.82 ± 0.01	6.3
9.	7.96 ± 0.03	9.2
10.	5.14 ± 0.01	5.3

TABLE 28

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF COMMERCIAL CYANIDE SILVER SOLUTIONS IN THE DETERMINATION OF K_2CO_3

All values expressed in oz/US gal

Sample No.	Can. Han. value	Manual (1)	E436A (2)	E526 (3)	Ave. Overall	Devn from overall ave. (1)	(2)	(3)
1.	5.8	4.15 ± 0.0[illegible]	4.10 ± 0.06	4.25 ± 0.01	4.16	- 0.01	- 0.06	+ 0.09
2.	7.2	7.51 ± 0.05	7.37 ± 0.04	7.68 ± 0.06	7.5^2	- 0.01	- 0.15	+ 0.16
3.	6.2	5.21 ± 0.01	5.24 ± 0.02	5.17 ± 0.07	5.20	+ 0.01	+ 0.04	- 0.03
4.	1.1	1.15 ± 0.02	0.73 ± 0.06	1.20 ± 0.08	1.0^2	+ 0.13	- 0.29	+ 0.18
5.	5.3	6.96 ± 0.03	7.13 ± 0.03	$6.9^0 \pm 0.1^1$	6.9^9	- 0.03	+ 0.14	- 0.09
6.	8.7	7.14 ± 0.01	7.06 ± 0.06	7.13 ± 0.03	7.11	+ 0.03	- 0.05	+ 0.02
7.	7.9	7.22 ± 0.06	7.36 ± 0.02	7.31 ± 0.05	7.29	- 0.07	+ 0.07	+ 0.02
8.	6.3	$7.1^7 \pm 0.1^6$	$7.1^9 \pm 0.1^0$	6.82 ± 0.01	7.0^6	+ 0.11	+ 0.13	- 0.24
9.	9.2	8.02 ± 0.02	8.01 ± 0.01	7.96 ± 0.03	7.99	+ 0.03	+ 0.02	- 0.03
10.	5.3	5.19 ± 0.01	5.07 ± 0.06	5.14 ± 0.01	5.13	+ 0.06	- 0.06	+ 0.01

OFFSET FROM CANADIAN HANSON VALUES

Sample No.	Can. Hanson	Overall average	% devn. from Can. Han.
1.	5.8	4.16	- 28.3
2.	7.2	7.5^2	+ 4.4
3.	6.2	5.20	- 16.0
4.	1.1	1.0^2	- 7.2
5.	5.3	6.9^9	+ 31.8
6.	8.7	7.11	- 18.2
7.	7.9	7.29	- [illegible]7
8.	6.3	7.0^6	+ 12[illegible]0
9.	9.2	7.99	- 13[illegible]1
10.	5.3	5.13	- 3.2

with the Canadian Hanson values, very considerable differences were noted for sample numbers 1, 3, 5, 6, 8 and 9. Again, some attempt will be made to explore this situation in the Conclusions section.

2.5.4 Determination of silver

The method applied by the electroplating industry in the determination of silver in cyanide silver plating solutions is as follows:-

(1) Pipette 5 ml of plating solution into a 250 ml Erlenmeyer flask.

(2) In the fume hood, add 20 ml of concentrated H_2SO_4 and boil. Add a few drops of concentrated HNO_3 if the solution turns a dark colour.

(3) Evaporate to dense white SO_3 fumes. If the dark colour persists, cool and add again a few drops of HNO_3. Finally continue to heat at dense white fumes until all solids are dissolved.

(4) Cool and dilute to 150 ml with water. Warm if necessary to dissolve any solids separated during cooling.

(5) Cool to room temperature and add 3 ml of saturated ferric ammonium sulphate solution. $(NH_4)_2SO_4.Fe_2(SO_4)_3$

(6) Titrate with standard (0.1M) ammonium thiocyanate solution to the first pink colour.

There is no possibility, of course, of automating the sulphuric acid sequence for the destruction of cyanide compounds. Attention was therefore paid to the possible automation of the titration procedure. This latter is a Volhard titration process, with Fe(III) as the indicator substance. The titration reaction:-

$$Ag^+ + SCN^- \leftrightharpoons AgSCN\ (s)$$

results in the formation of the slightly soluble silver thiocyanate

salt, AgSCN. The indicator reaction is:-

$$Fe^{3+} + SCN^{-} \leftrightharpoons Fe(SCN)^{2+}$$

and results in the formation of the intensely red soluble complex ion, $Fe(SCN)^{2+}$. An excellent discussion of the Volhard titration is given by Dick (33). The sensitivity of the Fe(III) indicator is based on the fact that a visible colour will be imparted to the solution when the $[Fe(SCN)^{2+}]$ in solution attains a value of 6.5×10^{-6}M. At the stoichiometric equivalence point the value of $[SCN^{-}]$ is:-

$$[SCN^{-}] = \sqrt{Ksp(AgSCN)} = \sqrt{1.07 \times 10^{-12}} \qquad (22)$$
$$= 1.03 \times 10^{-6}M$$

For the industry titration, 3 ml of saturated ferric ammonium sulphate (44g/ml) in 150 ml of pretitration solution yields a starting $[Fe^{3+}]$ of about 3.3×10^{-2}M. Considering a titrant volume of 0.1M NH_4SCN of about 10 ml for a 3 oz silver/US gal plating solution with 5 ml taken for analysis, this yields an endpoint total solution volume of about 160 ml, and an $[Fe^{3+}]$ at this point of about 3.1×10^{-2}M. Thus, at the stoichiometric equivalence point, the $[Fe(SCN)^{2+}]$ will be given by:-

$$\frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^{-}]} = Kstab. = 1.38 \times 10^{2} \qquad (23)$$

and from equation (22) and the $[Fe^{3+}]$ of 3.1×10^{-2}M at this point,

$$[Fe(SCN)^{2+}] = (1.38 \times 10^{2})(3.1 \times 10^{2})(1.03 \times 10^{-6}) = 4.4 \times 10^{-6}M$$

and this is a concentration of $Fe(SCN)^{2+}$ somewhat lower than the sensitivity value of $6.5 \times 10^{-6}M$. The equivalence point occurs very slightly before the endpoint. At the endpoint, where the required $[Fe(SCN)^{2+}]$ of $6.5 \times 10^{-6}M$ is attained, we have:-

$$[SCN^-] = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}]\ Kstab.} = \frac{6.5 \times 10^{-6}M}{3.1 \times 10^{-2}M \times 1.38 \times 10^{2}}$$

$$= 1.2 \times 10^{-6}M$$

The additional concentration of NH_4SCN required after the equivalence point can be calculated from:-

$$[NH_4SCN] = \underset{\text{formed after eq. pt.}}{[Fe(SCN)^{2+}]} + [SCN^-] + \underset{\text{formed after eq. pt.}}{[AgSCN]} \qquad (24)$$

The first expression on the right can be taken as:-

$$6.5 \times 10^{-6}M - 4.4 \times 10^{-6}M = 2.1 \times 10^{-6}M$$

while the third expression on the right is given by:-

$$[Ag^+] \text{ at eq. pt.} - [Ag^+] \text{ at endpoint}$$

$$= 1.03 \times 10^{-6}M - Ksp(AgSCN)/[SCN^-]$$

$$= 1.03 \times 10^{-6}M - (1.07 \times 10^{-12})/1.2 \times 10^{-6}M$$

$$= 1.4 \times 10^{-7}M$$

We now have:-

$$[NH_4SCN] = 2.1 \times 10^{-6}M + 1.2 \times 10^{-6}M + 1.4 \times 10^{-7}M$$

$$= 3.44 \times 10^{-6}M$$

and this represents, for an approximate 160 ml total solution volume at the endpoint, a volume of 0.1M NH_4SCN solution of:-

$$\frac{V\ 0.1M\ NH_4SCN \times 0.1M}{160\ ml} = 3.4^4 \times 10^{-6}M$$

$$V\ 0.1M\ NH_4SCN = 0.005\ ml < 0.01\ ml$$

so that the indicator error in this titration is insignificant, and the coincidence of the equivalence point and the endpoint can be taken as exact.

There is a tendency for the AgSCN precipitate to adsorb Ag^+ ions from the solution and, therefore, for a first colour change to show prematurely. The titration should thus be continued, with vigorous agitation, until the colour change is permanent.

Because the $[Ag^+]$ changes continuously during this titration, adaptation of the method to automatic potentiometric titration, using a silver indicating electrode, should be quite feasible.

All experimental details for this portion of the project work will be found in Appendix F, as will tables and figures with the suffix "-F".

The standardization of a prepared ammonium thiocyanate titrant was carried out by the manual technique standard to the industry. The details involved are given in Table 1-F. An average molarity and standard deviation was found:-

$$0.1184^{6} \pm 0.0004^{2}$$

The commercial cyanide plating solutions were now analyzed using the manual method and the titrant standardized by this technique. All results were expressed in troy oz silver/US gal, this being the method of reporting silver normal to the industry. The experimental data is given in Table 2-F. Table 29 shows a comparison of the average results obtained with the respective granting agency values. Only sample number 4 shows any radical difference between the two values, and the importance of this difference is minimized by the effect of the extremely low silver content involved

It was found that sample numbers 2, 5 and 8 developed dark solution colours upon treatment with sulphuric acid, and thus required additions of HNO_3 to clarify. The presence of some organic compound, very possibly a brightener substance, was suspected.

The E436A titrator was applied in the standardization of the NH_4SCN titrant. The details involved are outlined in Table 3-F, and the titrant showed a molarity and standard deviation of:-

$$0.1182^{1} \pm 0.0003^{3}$$

which are in good agreement with the values reported with respect to the manual standardization process. Table 3-F also shows the calculations to determine the theoretical values for Ecell at 0.5 ml before the equivalence point, at the equivalence point and 0.5 ml after the equivalence point. These were found to be respectively + 399 mV,

TABLE 29

MANUAL TITRATION DETERMINATION OF SILVER IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	Silver (troy oz/US gal) Project work	Silver (troy oz/US gal) Canadian Hanson
1.	$3.2^{9} \pm 0.1^{0}$	3.3
2.	5.12 ± 0.03	5.4
3.	3.18 ± 0.05	3.1
4.	0.43 ± 0.01	0.28
5.	4.35 ± 0.02	4.7
6.	1.09 ± 0.04	0.9
7.	3.21 ± 0.01	3.3
8.	4.07 ± 0.00	4.5
9.	2.50 ± 0.01	2.7
10.	3.27 ± 0.02	3.5

+ 247 mV and + 96 mV. The experimental average values, which showed very good precision, were respectively + 400 mV, + 240 mV and + 100 mV. Agreement of these two sets of values was excellent.

The standardizaed titrant was now applied in the E436A determination of silver in commercial cyanide silver plating solutions. Table 4-F shows the experimental data secured, with Table 30 giving the comparison between the result averages and the granting agency data. The E436A values show good precision relative to titration groups and, in addition, show good agreement with the results obtained from the manual method determinations. Agreement of the average values with the granting agency data was good, again with the exception and explanation concerning sample number 4.

The theoretical values for Ecell at the various critical points were calculated on the basis of a specific presumed cyanide silver bath content of silver. These calculations are shown in Table 4-F, and a comparison between these values and the experimental averages is shown below.

		Found	Theoretical
0.5 ml before the eq. pt.	(mV)	+ 429	+ 397
At the eq. pt.	(mV)	+ 241	+ 247
0.5 ml after the eq. pt.	(mV)	+ 105	+ 96

It will be noted that the agreement between each pair of values is quite good. The experimental ΔE spread (± 0.5 ml) averaged 324 mV, and this is representative of very large ΔE/ΔV changes around the equivalence point.

TABLE 30

E436A TITRATION DETERMINATION OF SILVER IN COMMERCIAL CYANIDE SILVER SOLUTIONS

Sample No.	Silver (troy oz/US gal) Project work	Silver (troy oz/ US gal) Can. Han.	E (mV) eq. pt.	ΔE±0.5 ml (mV)
1.	3.45 ± 0.09	3.3	237	± 160
2.	5.34 ± 0.06	5.4	241	± 163
3.	3.20 ± 0.01	3.1	240	± 163
4.	0.45 ± 0.05	0.28	248	± 160
5.	4.36 ± 0.02	4.7	238	± 170
6.	0.94 ± 0.15	0.9	241	± 147
7.	3.28 ± 0.02	3.3	242	± 167
8.	4.22 ± 0.03	4.5	240	± 165
9.	2.56 ± 0.01	2.7	241	± 162
10.	3.29 ± 0.04	3.5	239	± 160

The NH_4SCN titrant was now standardized against standard $AgNO_3$ solution using the E526 automatic titration assembly. A dead-stop potential of + 240 mV was initially applied, this in accordance with the value indicated in Table 3-E. Exploratory work indicated that this preset value was a little too high, and optimum results on standard solutions were found to be obtained at a preset dead-stop potential of + 200 mV. Table 5-F covers the experimental details, and a molarity and standard deviation of:-

$$0.1176^9 \pm 0.0002^7$$

were obtained. The values for this titrant by all methods were:-

Manual method	$0.1184^6 \pm 0.0004^2$
E436A method	$0.1182^1 \pm 0.0003^3$
E526 method	$0.1176^9 \pm 0.0002^7$

The overall average and standard deviation was $0.1180^8 \pm 0.0004^5$M. Variance ratio tests and null hypothesis tests (95%) indicated no really significant differences in the standard deviations and averages.

Titration of the commercial cyanide silver plating solutions was now carried out on the E526 assembly. Table 4-F had indicated an equivalence point potential of + 241 mV for this titration, and this value was initially applied as a preset dead-stop potential. As anticipated from the standardization situation, exploratory work indicated that a + 200 mV setting gave optimum results. It can be assumed perhaps, in both instances, that titration condition differences and/or instrumental response differences for the E436A and E526 instruments were responsible for the Ecell preset potential value being lower. Some 31

plating solution samples were involved, with five 10 ml samples of standard $AgNO_3$ solution properly diluted. These latter samples were interspersed between the plating solution samples and were intended to provide checks as to the stability of the E526 preset potential and the electrode couple. Since no pretitration additions were required, the pretitration station stops were bypassed automatically. Titration was sequential and automatic, with a higher-than-normal stirring speed being applied to permit vigorous mixing. The total elapsed time approximated 1.5 hours. Table 6-F gives the experimental details, with Table 31 showing the comparison between the project work averages and the Canadian Hanson values.

Again the results from the E526 titrations showed, for each solution group, excellent precision. The average values demonstrated good agreement with those obtained from the E436A application and the manual method. Good agreement was also shown between the E526 averages and the granting agency values, the single exception being that noted for sample number 4. The stability of the E526 setting and the electrode couple is shown, from Table 6-F data, by the repetitive nature of the volume values for the five standard $AgNO_3$ samples, a standard deviation of only ± 0.02 ml being obtained.

Table 32 shows the comparison of all of the methods of analysis applied, together with the granting agency values. All methods, from standard deviation comparisons, show good precision, although there is a tendency for the precision of the potentiometric methods to be slightly lower than that for the manual method. The data for the

TABLE 31

E526 ASSEMBLY TITRATION DETERMINATION OF SILVER IN COMMERCIAL CYANIDE SILVER PLATING SOLUTIONS

Sample No.	Silver (troy oz/ US gal) Project work	Silver (troy oz/US gal) Canadian Hanson
1.	3.21 ± 0.01	3.3
2.	5.14 ± 0.08	5.4
3.	3.05 ± 0.02	3.1
4.	0.45 ± 0.03	0.28
5.	4.17 ± 0.02	4.7
6.	1.04 ± 0.04	0.9
7.	3.28 ± 0.03	3.3
8.	4.11 ± 0.09	4.5
9.	2.67 ± 0.08	2.7
10.	3.16 ± 0.03	3.5

TABLE 32.

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF ~~COMMERCIAL CYANIDE~~ SILVER PLATING SOLUTIONS IN THE DETERMINATION OF SILVER

All values expressed in troy oz/US gal

Sample No.	Can. Han. values	Manual (1)	E436A (2)	E526 (3)	Overall average	Devn. from overall average (1)	(2)	(3)
1.	3.3	$3.2^{9} \pm 0.1^{0}$	3.45 ± 0.09	3.21 ± 0.01	3.3^{2}	- 0.03	+ 0.13	- 0.11
2.	5.4	5.12 ± 0.03	5.34 ± 0.06	5.14 ± 0.08	5.2^{2}	- 0.10	+ 0.12	- 0.08
3.	3.1	3.18 ± 0.05	3.20 ± 0.01	3.05 ± 0.02	3.14	+ 0.04	+ 0.06	- 0.09
4.	0.28	0.43 ± 0.01	0.45 ± 0.05	0.45 ± 0.03	0.44	- 0.01	+ 0.01	+ 0.01
5.	4.7	4.35 ± 0.02	4.36 ± 0.02	4.17 ± 0.02	4.2^{7}	+ 0.08	+ 0.09	- 0.10
6.	0.9	1.09 ± 0.04	$0.9^{4} \pm 0.1^{5}$	1.04 ± 0.04	1.0^{2}	+ 0.07	- 0.08	+ 0.02
7.	3.3	3.21 ± 0.01	3.28 ± 0.02	3.28 ± 0.03	3.25	- 0.04	+ 0.03	+ 0.03
8.	4.5	4.07 ± 0.00	4.22 ± 0.03	4.11 ± 0.09	4.13	- 0.06	+ 0.09	- 0.02
9.	2.7	2.50 ± 0.01	2.56 ± 0.01	2.67 ± 0.08	2.58	- 0.08	- 0.02	+ 0.09
10.	3.5	3.27 ± 0.02	3.29 ± 0.04	3.16 ± 0.03	3.24	+ 0.03	+ 0.05	- 0.08

OFF-SET FROM CANADIAN HANSON VALUES

Sample No.	Can. Hanson	Overall average	% devn. from overall ave.
1.	3.3	3.3^{2}	+ 0.6
2.	5.4	5.2^{2}	- 3.3
3.	3.1	3.14	+ 1.3
4.	0.28	0.44	+ 57.1
5.	4.7	4.2^{7}	- 9.1
6.	0.9	1.0^{2}	+ 13.3
7.	3.3	3.25	- 1.5
8.	4.5	4.13	- 8.2
9.	2.7	2.58	- 4.4
10.	3.5	3.24	- 7.4

deviations from the overall averages show no real directional trends. The deviation percentages of the overall averages from the Canadian Hanson values show no serious situations. The larger values for sample numbers 4 and 6, 57.1% and 13.3%, appear quite high but can be discounted on the basis of the low contents of silver involved. The values for sample numbers 5, 8 and 10 also appear slightly high at - 9.1%, - 8.2% and - 7.4%, but the preponderance of data favours the overall averages involved as being closer to the respective true values.

2.6 The Analysis of Alkaline Zinc Plating Solutions

2.6.1 General

Zinc is an amphoteric substance. As a base, it forms salts such as zinc chloride or zinc sulphate. As an acid it combines with a strong base to for a zincate such as sodium zincate, Na_2ZnO_2, produced when zinc oxide reacts with sodium hydroxide.

Zinc is generally deposited commercially from electroplating solutions containing both alkali and cyanide. Such alkali cyanide zinc solutions are finding an increasingly wide field of application in commercial zinc plating because of an ability to yield deposits that can be almost mirror-bright. The alkaline cyanide bath is also versatile in producing deposits of widely-varying appearance, has generally an excellent throwing power and a high degree of current efficiency.

Cyanide electrolytes for zinc plating, and their chemistry, have

been discussed by a number of investigators, and it is generally agreed that zinc can be deposited satisfactorily from such electrolytes only if they contain a mixture of sodium zincate and sodium zinc cyanide complexes, with some excess of sodium cyanide and sodium hydroxide.

A comparison of solutions of sodium zincate and sodium hydroxide, with solutions of sodium zinc cyanide complexes (which must necessarily contain some sodium zincate) by carrying out plating tests shows that it is essential to have all three primary constituents present in order to produce consistently high-grade deposits at high cathodic efficiencies. From baths containing sodium zincate and sodium hydroxide alone, poor quality, spongy deposits may be obtained at high current efficiencies and at low current densities, while matte deposits are obtained from sodium zinc cyanide baths at low current efficiencies and high current densities. Only after the formation of sodium zinc cyanide complexes in the zincate bath, by the addition of sodium cyanide, are worthwhile deposits obtained at reasonable current efficiencies and densities. The function of sodium cyanide in the bath is to combine with zinc in the formation of soluble cyanozinc(II) complexes and to provide control relative to the appearance of the deposit.

Current efficiency is also quite dependent on the excess sodium cyanide content and the ratio of total cyanide as sodium cyanide to the zinc content. The exact ration of sodium zincate to sodium zinc cyanide is difficult to determine, but there are indications that 75 to 90 percent of the zinc metal is present in the bath as sodium zincate, with the balance being present as sodium zinc cyanide. The

equilibrium is affected by the relative concentrations of uncombined sodium cyanide and sodium hydroxide, and zinc ions are available in the solution by the dissociation of sodium zincate and sodium zinc cyanide substances. The following gives some indication of this situation.

$$Na_2Zn(CN)_4 = 2Na^+ + Zn(CN)_4^{2-}$$

$$Zn(CN)_4^{2-} = Zn^{2+} + 4CN^-$$

$$Na_2Zn(CN)_4 + 4NaOH = Na_2ZnO_2 + 4NaCN + 2H_2O$$

$$Na_2ZnO_2 = 2Na^+ + ZnO_2^{2-}$$

$$ZnO_2^{2-} + 2H_2O = Zn^{2+} + 4OH^-$$

These equations give some picture of the general complexity of alkaline cyanide plating solutions. The basic constituents requiring analytical control are zinc, total cyanide as sodium cyanide and total alkali as sodium hydroxide. These components are largely interdependent, and a most important relationship is that between total cyanide and zinc. Other substances may be determined, such as impurities, various additive agents, etc., but these are not of interest to this project. The total cyanide is actually the total of the free sodium cyanide and the sodium cyanide equivalent of the cyanide tied up with zinc as the complex tetracyanozinc(II) ion.

2.6.2 Determination of "total alkali" as sodium hydroxide

The sodium hydroxide excess functions in several ways; to aid in anodic corrosion, to promote higher plating speeds and to minimize the hydrolytic losses of cyanide from the bath. Increasing the free sodium hydroxide increases the availability of zinc(II) ions; lowering

it decreases this availability. Baths formulated primarily to provide high deposition rates contain higher concentrations of sodium hydroxide relative to the total cyanide and zinc concentrations. In decorative plating, where increased emphasis is placed on deposit appearance and ability to cover complex shapes, lower proportions of sodium hydroxide are used. Baths formulated to contain minimal cyanide concentrations have high sodium hydroxide contents, even higher than the high-speed formulations.

The determination of total alkali as sodium hydroxide is obtained in the industry by a neutralization titration using sulphuric acid as the titrant. The details follow.

(1) Pipette 10 ml of plating solution into the titration vessel.

(2) Add about 1 g of solid NaCN and swirl to dissolve.

(3) Add 8 drops of Lamotte or Fisher sulfo-orange indicator and titrate with 1N H_2SO_4 until the orange colour changes to yellow with a greenish tinge.

This titration with H_2SO_4 is carried out in the presence of a large excess of sodium cyanide. Thus, prior to the equivalence point, the pH of the solution will be given very generally by the decreasing concentration of sodium hydroxide. At the equivalence point, the solution pH will be given by the concentration of sodium cyanide, and will of course be quite high and in the neighbourhood of 11. After the equivalence point sodium cyanide is gradually converted to hydrogen cyanide by the added H_2SO_4 titrant, and the solution pH will be given by the buffer action of the NaCN-HCN mixture. All of this pH development will

be discussed on a theoretical basis in one of the tables of the appropriate appendix. It should be noted that the indicator colour change is not a particularly good one, in that it involves a colour change basically from orange to yellow. It should also be noted that it can be expected that the $\Delta pH/\Delta V$ changes around the equivalence point will be minimal, and that the reason for keeping the pretitration solution as undiluted as possible is to enhance to the greatest extent this small $\Delta pH/\Delta V$ change.

All details relative to the experimental work carried out with respect to the determination of total alkali as NaOH are contained in Appendix G.

A standard solution of about 0.5M H_2SO_4 was prepared and standardized against a standard NaOH solution. The manual method was applied, the experimental details are contained in Table 1-G and the average molarity and standard deviation were:-

$$0.565^1 \pm 0.000^0$$

Using the manual method, this titrant was now used to determine the total alkali, as NaOH, for the alkaline zinc cyanide plating solutions provided by the granting agency. The experimental details are outlined in Table 2-G, and Table 33 shows the values obtained in comparison with the Canadian Hanson analytical data. It will be noted that, for each solution analyzed, the project values show good precision, but that there is a definite tendency for the experimental averages to be consistently lower than the respective granting agency

TABLE 33

MANUAL METHOD TITRATION DETERMINATION OF TOTAL ALKALI AS NaOH IN COMMERCIAL ALKALI ZINC CYANIDE PLATING SOLUTIONS

Sample No.	NaOH (oz/US gal) project work	NaOH (oz/US gal) Canadian Hanson
1.	9.91 ± 0.01	10.5
2.	5.36 ± 0.03	6.4
3.	12.11 ± 0.03	12.5
4.	4.27 ± 0.04	5.4
5.	9.69 ± 0.03	10.4
6.	9.45 ± 0.03	10.9
7.	9.09 ± 0.04	9.8
8.	7.63 ± 0.03	8.1
9.	9.03 ± 0.03	9.6
10.	6.71 ± 0.06	7.3

values. The H_2SO_4 titrant was now applied in a standardization process using the E436A titrator. Table 3-G gives the experimental data for this method, and average molarity and a standard deviation as follows were obtained.

$$0.566^7 \pm 0.001^1$$

This agrees well with the manual method data shown previously. Table 3-G also provides the calculation of the theoretical pH values for the critical titration points. These agree well with the experimental values found as shown below:-

		Experimental	Theoretical
0.5 ml before eq. pt.	(pH)	ave. 1.80	2.1
Equivalence point	(pH)	ave. 6.94	7.0
0.5 ml after eq. pt.	(pH)	ave. 12.15	12.2
ΔpH (± 0.5 ml)	(pH)	ave. ± 5.15	± 5.0

The E436A-standardizaed H_2SO_4 was now applied in the determination of total alkali as NaOH in the alkaline zinc cyanide commercial plating solutions. Table 4-G gives the experimental details, while Table 34 shows the experimental averages in comparison with the Canadian Hanson values. It will again be noted that, for the plating solution samples tested, precision is excellent. The average values agree well with those reported for the manual method, and they show the same general tendency to be lower than the granting agency results. Table 4-G also shows the theoretical calculation of the pH values for the critical titration points. Considering the complexity of the solutions, and the relatively simple calculation methods used, agreement between these theoretical values and the experimental averages was quite good, as

TABLE 34

E436A TITRATION DETERMINATION OF TOTAL ALKALI IN COMMERCIAL ALKALI ZINC CYANIDE PLATING SOLUTIONS

Sample No.	NaOH (oz/US gal) Project work ave. ± s	NaOH (oz/US gal) Canadian Hanson	Ave. pH eq. pt.	± ΔpH ± 0.5 ml
1.	9.97 ± 0.06	10.5	11.24	0.60
2.	5.34 ± 0.05	6.4	11.27	0.66
3.	$12.1^{8} \pm 0.2^{2}$	12.5	11.18	0.72
4.	4.36 ± 0.06	5.4	11.31	0.66
5.	9.60 ± 0.03	10.4	11.20	0.67
6.	9.42 ± 0.02	10.9	11.31	0.58
7.	8.93 ± 0.04	9.8	11.31	0.62
8.	7.74 ± 0.02	8.1	11.31	0.64
9.	9.04 ± 0.06	9.6	11.31	0.57
10.	6.74 ± 0.02	7.3	11.31	0.50

shown below:-

			Experimental	Theoretical
0.5 ml before eq. pt.	(pH)	ave.	11.9	12.3
Equivalence point	(pH)	ave.	11.2	11.6
0.5 ml after eq. pt.	(pH)	ave.	10.7	10.8
ΔpH (± 0.5 ml)		ave.	± 0.6	± 0.8

The H_2SO_4 titrant was finally standardizaed using the E526 assembly. Table 5-G provides the details involved, and the average molarity and standard deviation were found to be:-

$$0.568^5 \pm 0.001^7$$

The values obtained in standardization by all three methods were thus:-

Manual method	$0.565^1 \pm 0.000^0$
E436A method	$0.566^7 \pm 0.001^1$
E526 method	$0.568^5 \pm 0.001^7$

These agree well, and the usual statistical tests showed no significant differences to exist between either the standard deviations or the average molarities. The E526 unit had been set on a dead-stop pH value of 7.00, in accordance with the data reported in Table 3-G, and this value was found to be optimum. Dilution of the solution prior to titration with 50 ml of water, as required to satisfy the volume demands for the E526 apparatus, obviously gave no difficulty.

The E526 method was now applied in the determination of total alkali as NaOH in the commercial plating solutions. Again, it was necessary to dilute the solution samples in order to meet the beaker volume

needs of the E526 unit. In this instance two requirements were served in the same step. Instead of adding 50 ml of dilution water and 1 g of solid NaCN prior to titration, a 2 percent by volume NaCN solution was prepared and 50 ml of this solution was added automatically by the pretitration addition system. The preset dead-stop endpoint pH was set initially at 11.2 and corresponded to the average value found from Table 4-G data. This preset value was found, by initial exploratory work, to be optimum. The final data was obtained from 30 samples racked on 8 magazines. Titration was sequential and automatic, as was the pretitration addition of 50 ml of 2 percent NaCN, and the total elapsed time was about 1.25 hours. Table 6-G outlines the experimental details, with Table 35 providing the comparison between the average values and the granting agency data. Again, precision within each group of solutions titrated was good. These results tend, on inspection, to be slightly higher than those for the other methods, although no differences of much significance were noted. In general, the differences between the method averages and the granting agency values repeated the pattern noted for the manual and E436A techniques, and were consistently lower.

Despite the small $\pm \Delta pH$ ($\pm$ 0.5 ml around the endpoint volume) of $\pm$ 0.69, and the need to dilute the solutions to accomodate the E526 beaker volume demands, the system provided precise titration volumes and results agreeing well with those representing the other two methods.

Table 36 shows the comparison between all methods applied. In general, the methods show average results agreeing well with each

TABLE 35

E526 TITRATION DETERMINATION OF TOTAL ALKALI
IN COMMERCIAL ALKALI ZINC CYANIDE PLATING SOLUTIONS

Sample No.	NaOH (oz/US gal) project work ave. ± s	NaOH (oz/US gal) Canadian Hanson
1.	9.91 ± 0.08	10.5
2.	5.56 ± 0.08	6.4
3.	12.16 ± 0.07	12.5
4.	4.53 ± 0.06	5.4
5.	9.79 ± 0.02	10.4
6.	9.56 ± 0.02	10.9
7.	9.15 ± 0.03	9.8
8.	7.82 ± 0.04	8.1
9.	9.12 ± 0.04	9.6
10.	6.86 ± 0.00	7.3

TABLE 36

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATION DETERMINATIONS OF TOTAL ALKALI IN COMMERCIAL ALKALI ZINC CYANIDE PLATING SOLUTIONS

All results expressed in oz/US gal

Sample No.	Can. Han. value	Manual (1)	E436A (2)	E526 (3)	Overall average	Devn. from overall ave. (1)	(2)	(3)
1.	10.5	9.97 ± 0.01	9.97 ± 0.06	9.91 ± 0.08	9.95	+ 0.02	+ 0.04	- 0.04
2.	6.4	5.36 ± 0.03	5.34 ± 0.05	5.56 ± 0.08	5.41	- 0.05	- 0.07	+ 0.15
3.	12.5	12.11 ± 0.03	12.1^8 ± 0.2^2	12.16 ± 0.07	12.1^5	- 0.04	+ 0.03	+ 0.01
4.	5.4	4.27 ± 0.04	4.36 ± 0.06	4.53 ± 0.06	4.3^8	- 0.11	- 0.02	+ 0.15
5.	10.4	9.69 ± 0.03	9.60 ± 0.03	9.79 ± 0.02	9.69	± 0.00	- 0.09	+ 0.10
6.	10.9	9.45 ± 0.03	9.42 ± 0.02	9.56 ± 0.02	9.46	- 0.01	- 0.04	+ 0.10
7.	9.8	9.09 ± 0.04	8.93 ± 0.04	9.15 ± 0.03	9.0^5	+ 0.04	- 0.12	+ 0.10
8.	8.1	7.63 ± 0.03	7.74 ± 0.02	7.82 ± 0.04	7.73	- 0.10	+ 0.01	+ 0.09
9.	9.6	9.03 ± 0.03	9.04 ± 0.06	9.12 ± 0.04	9.12	- 0.03	- 0.02	+ 0.06
10.	7.3	6.71 ± 0.06	6.74 ± 0.02	6.86 ± 0.00	6.75	- 0.04	- 0.01	+ 0.11

OFFSET FROM CANADIAN HANSON VALUES

Sample No.	Can. Hanson value	Overall ave.	% devn. from Can. Han.
1.	10.5	9.95	- 5.2
2.	6.4	5.41	- 15.5
3.	12.5	12.1^5	- 2.8
4.	5.4	4.3^8	- 18.9
5.	10.4	9.69	- 6.8
6.	10.9	9.46	- 13.1
7.	9.8	9.0^5	- 7.6
8.	8.1	7.73	- 4.6
9.	9.6	9.06	- 5.6
10.	7.3	6.75	- 7.5

other, as noted by the comparisons involving deviations from the overall average, although there is a definite tendency for the E526 unit to over-titrate by an average of about 0.1 to 0.2 ml. This represents about 0.06 to 0.12 oz/US gal of NaOH on the high side, and was not considered a large enough deviation to warrant further experimental work. The overall average values were consistently lower than the granting agency values, as will be noted from the "% devn. from Canadian Hanson" column.

2.6.3 Determination of total sodium cyanide

The determination of "total cyanide" as sodium cyanide is required as a control measure, and establishes, with the determined zinc content, the important ratio of total sodium cyanide to zinc. The industry method involves:-

(1) Pipette 2.00 ml of plating solution into a 300 ml Erlenmeyer flask and dilute with 100 ml of water.

(2) Add 5 ml of 20% NaOH solution and 1 ml of 10% KI solution.

(3) Titrate with 0.1M $AgNO_3$ solution to the first permanent turbidity.

(4) Add 1 ml of 20% NaOH solution and, if the turbidity disappears, continue the titration with 0.1M $AgNO_3$ until a permanent turbidity again appears.

(5) The total sodium cyanide is calculated from:-

$$\text{Total NaCN} = \frac{V\ AgNO_3 \times M\ AgNO_3 \times 2 \times 49.01 \times 3785.306}{1000 \times 2.00 \times 28.349}$$

where:-

3785.306 = ml/US gal
28.349 = g/oz
49.01 = GMW NaCN

Total NaCN = V $AgNO_3$ x M $AgNO_3$ x 6.53

The addition of NaOH solution results in the reaction:-

$$Zn(CN)_4^{2-} + 4NaOH \leftrightharpoons 4NaCN + ZnO_2^{2-} + 2H_2O$$

and the conversion of the CN^- content of the tetracyanozinc(II) complex to NaCN. This NaCN, added to the excess normally present, provides the total NaCN for titration by 0.1M $AgNO_3$. The subsequent addition of 1 ml of 20 percent NaOH solution merely serves to ensure that all of the $Zn(CN)_4^{2-}$ was reacted.

The titration itself, as carried out by 0.1M $AgNO_3$, is identical to the method of analysis applied in the determination of "free cyanide" as KCN in cyanide silver plating solutions. (Sub-section 2.5.2). Since this technique, and its excellent adaptability to automated analysis on the E526 assembly, has already been thoroughly covered by this sub-section, it was felt that, with ample justification, no further exploratory work was required in connection with the automation of the method for total cyanide determination in alkali cyanide zinc plating solutions. Some commentary with respect to indications that adaptability of the technique to the automated E526 analysis for total cyanide is satisfactory is given in the Conclusions section.

2.6.4 Determination of zinc

The chief function of the zinc cyanide and zincate complexes is to provide a reservoir from which zinc plated may be replaced. The size

of this reservoir can be caried several-fold with little effect, if appropriate changes are made in operating conditions and in the concentrations of other bath constituents. As the zinc content is reduced, however, the effects of small changes in the other variables is magnified, and fluctuations in performance may lead to increasing difficulties. To reach a suitable compromise, the desirability of easier control and more consistent performance must be balanced against increased chemical and waste-disposal problems and costs. In a well-operated bath, additions of zinc salts should not be required on any large scale. The anodes will normally provide more than sufficient zinc to replace that lost by plating and by dragout. Steel or other inert anodes are sometimes used to prevent the excessive zinc accumulations frequently arising with zinc anodes. Chemical analysis for zinc should be made frequently enough to obviate the need for major additions of zinc salts.

The method of analysis applied by the industry involves a compleximetric titration using EDTA as the titrant and Eriochrome black T as the indicator substance. The steps in this analytical technique are:-

(1) Pipette 2.00 ml of plating solution into a 300 ml Erlenmeyer flask and add 100 ml of water.

(2) Add 2 or 3 drops of 0.04% (aq.) thymol blue indicator and titrate dropwise with 1N H_2SO_4 to a pale yellow endpoint.

(3) Add 25 ml of buffer solution (50 g NH_4Cl and 400 ml of concentrated NH_3 per liter)

(4) Add 0.2 - 0.3 g of Eriochrome black T indicator (0.2 g of Eriochrome black T ground with 100 g reagent-grade NaCl)

(5) Add 10 ml of 5% formaldehyde solution and titrate immediately with 0.05M EDTA solution from a reddish-purple colour to a blue endpoint colour.

The purpose of the initial titration with 1N H_2SO_4 is to neutralize the contained alkali and to convert the NaCN and cyanide zinc complex insofar as possible to available zinc ion and HCN. The EDTA solution used as titrant is standardized against zinc contained in the solution largely in a cyanide complex form, so that the standardization process is basically an empirical one.

A thorough reporting of the equilibria, etc., for a somewhat similar compleximetric titration involving nickel was made in Sub-section 2.4.4. Despite that the situation here is further complicated by the presence during titration of cyanide as well as ammonia, it was not felt at all necessary to repeat any such development for the zinc-EDTA titration.

The experimental details relating to this portion of the project work will be found in Appendix H.

The first step in the experimental work involved the preparation and standardization of the EDTA solution. The details of this process are given in Table 1-H. Both the empirical method employed by industry and the normal method applied in general analytical work were used. The former provides a solution containing the zinc as zinc cyanide complexes; the latter yields a solution with the zinc as zinc(II) ion. The average molarities and standard deviations found were:-

	Average M	Standard Devn.
Industry method	0.0899^{6}	$\pm 0.0001^{1}$
General method	0.0898^{6}	$\pm 0.0001^{3}$

The values, to all intents and purposes, are identical. This titrant was now applied, using the industry method manual titration, to the determination of zinc in the commercial alkali zinc cyanide plating solutions provided by the granting agency. Table 2-H gives the experimental details, while Table 37 gives the values obtained relative to the granting agency values. It will be noted that the precision for each solution group is excellent, and that very good agreement with the Canadian Hanson values was attained.

The details with respect to applying such a titration in the potentiometric sense were now considered. A zinc(II) ion-selective electrode is not commercially available, so that this avenue of approach could not be considered. The details of Sub-section 2.4.4 describe the use of a Cu(II)-EDTA indicating solution and a Cu(II) ion-selective electrode/double-junction reference in an EDTA titration to determine nickel. This technique, generally described by Ross and Frant (32), was now applied in the determination of zinc using the E436A titrator. The standardization of the EDTA titrant against standard zinc solution was first attempted. The details involved are outlined in Table 3-H. An average molarity and standard deviation were found of:-

$$0.0915^{4} \pm 0.0005^{4}$$

This is not in particularly good agreement with the values found

TABLE 37

MANUAL METHOD (EDTA) TITRATIONS IN THE DETERMINATION OF ZINC IN ALKALI ZINC CYANIDE PLATING SOLUTIONS

Sample No.	Zinc (oz/US gal) project work	Zinc (oz/US gal) Canadian Hanson
1.	4.87 ± 0.03	4.9
2.	1.31 ± 0.01	1.3
3.	0.92 ± 0.02	0.9
4.	1.94 ± 0.01	1.9
5.	1.51 ± 0.01	1.5
6.	1.75 ± 0.01	1.8
7.	2.00 ± 0.02	2.0
8.	4.99 ± 0.02	5.1
9.	1.51 ± 0.00	1.5
10.	1.98 ± 0.00	2.0

with respect to the manual techniques, although the difference is not of great significance. The relatively low value of $\pm \Delta E$ for $\pm$ 0.5 ml around the equivalence point volume, $\pm$ 27 units, will be noted.

This titrant was now applied to determine zinc in the commercial plating solutions, the experimental details being given in Table 4-H. It will be noted that only the lowest zinc content solution at 0.9 oz/US gal gave any electrode response of a detectable nature and, in this instance, the equivalence point Ecell variation and the low $\pm \Delta E$ ($\pm$ 0.5 ml) of about $\pm$ 6 mV indicated no possibility of adaptation of the method to the automatic dead-stop titration technique.

It was felt that the high zinc and copper concentrations, the relative proximity of the stability constants (6.2×10^{18} for copper and 1.8×10^{16} for zinc) and the high concentrations of both cyanide and ammonia all make contributions to the low or nonexistent ΔE shifts noted. The Ross and Frant (32) technique is basically intended to be applied to very low concentration solutions (i.e $[Zn^{2+}]$ at 10^{-3}M), so that the high zinc concentration solutions attempted are unlikely to suit the methodology.

An extensive investigation was carried out using purified TEPA as the titrant substance, since this had given a successful method in the determination of nickel in acid nickel plating solutions. The associated data covering this investigation is not given since, even with this titrant, the method gave no electrode response situations stable enough or large enough to provide any hope for adaptation to an automated dead-stop titration technique.

It was now felt that a method of analysis requiring prior destruction of the cyanide content of the commercial plating solutions would have to be explored. The obvious method of destroying the cyanide is the H_2SO_4-HNO_3 evaporation treatment applied prior to the determination of silver in cyanide silver plating solutions (Sub-section 2.5.4)

The destruction of the cyanide content would provide solutions, which, once properly adjusted as required, would be available for the determination of zinc by a titration method easily adaptable to an automatic dead-stop potentiometric titration. It was decided, in view of the well-known characteristics of large ΔE shifts around the equivalence point and adaptability to Ecell detection using a platinum-reference electrode couple, to investigate the determination of zinc in cyanide-destroyed solutions by titration with standard potassium ferrocyanide solution.

Zinc can be titrated with potassium ferrocyanide in the reaction:-

$$3Zn^{2+} + 2K_4Fe(CN)_6 \leftrightharpoons K_2Zn_3[Fe(CN)_6]_2 + 6K^+$$

The product is a highly insoluble substance, and the equivalence point can be detected potentiometrically if a pretitration addition of potassium ferricyanide, $K_3Fe(CN)_6$, is made. On this basis, the solution potential during titration changes according to the system:-

$$E_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = E^o + 0.059 \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$$

A platinum electrode will respond to this changing potential which,

"free cyanide" will lower the cathodic efficiency, however, and this must be avoided since a decrease in cathode efficiency results in the production of deposits of inferior quality. Satisfactory deposits can be obtained where no "free cyanide" is present, but this results in poor anode corrosion rates. Potassium cyanide is normally used to yield the cyanide complexes and the "free cyanide" for alkaline copper cyanide plating solutions.

Carbonates tend to build up in the electrolyte during operation because of the absorption of carbon dioxide from the air. There are no appreciable harmful effects from alkali carbonates up to about 10 oz/US gal. Higher concentrations will lower the optimum current density range. The carbonate content must, therefore, be controlled by analysis on a routine basis.

The components requiring routine analytical control are "free cyanide" as KCN, total alkali as KOH, carbonate as K_2CO_3 and copper.

2.7.2 <u>Determination of total alkali as potassium hydroxide.</u>

The method applied in the industry is:-

(1) Pipette 10 ml of plating solution and add 10 ml of water

(2) Add 1 g of solid KCN, swirl to dissolve and add 5 drops of LaMotte or Fisher sulfo-orange indicator

(3) Titrate with 1N H_2SO_4 until the orange colour changes to yellow with a slight greenish tinge.

It will be observed that this technique is identical to that used in the determination of "total alkali" in alkaline zinc cyanide plating

solutions (Sub-section 2.6.2). Since this technique, and its excellent adaptability to automatic analysis on the E526 assembly, has already been covered thoroughly in this sub-section, it was felt that no further experimental work was required with respect to the present determination. Some commentary relative to the actual application of this technique automated on the E526 and applied in the present connection will be made in the Conclusions section.

2.7.3 Determination of "free cyanide" as KCN

The technique used by the electroplating industry is outlined in the following:-

(1) Pipette 10 ml of plating solution and dilute to about 100 ml with water.

(2) Add 5 ml of 10% KI solution.

(3) Titrate with 0.1M $AgNO_3$ solution until a first permanent turbidity is obtained.

(4) As a footnote When testing brass plating solutions, add 5 ml of 20% NaOH solution prior to titration.

The method as outlined above is identical in all critical aspects to that for the determination of "free cyanide" in cyanide silver plating solutions (Sub-section 2.5.2), or "total cyanide" as NaCN in alkali zinc cyanide plating solutions (Sub-section 2.6.3). It was therefore felt to be amply justified, in view of the work already done, to assume that the application of this technique to alkali copper cyanide plating solutions would show the same excellent adaptability to automation on the E526 assembly. No further exploratory work was

carried out, and a commentary on the suitability of the automated technique is provided in the Conclusions section.

2.7.4 Determination of carbonate as potassium carbonate

The industrial technique is:-

(1) Pipette 10 ml of plating solution into a 250 ml beaker.

(2) Add 100 ml of distilled water and warm.

(3) Add 25 ml of 10% barium chloride solution while stirring vigorously. Allow the precipitated barium carbonate to settle.

(4) Filter and wash with hot water.

(5) Transfer the filter and paper back to the original beaker and add 25 ml of water. Macerate and add a few drops of methyl purple indicator.

(6) Titrate with standard HCl solution until the colour change is permanent.

This is a straightforward titration of precipitated $BaCO_3$ with hydrochloric acid titrant. In view of the nature of the analytical process, only the last or titration step could be considered adaptable to automation. The value of the automated process, relative to the time required in the precipitation and filtration steps, would be decreased considerably, and it was the granting agency's feeling that this process and its automation should not be part of the directive.

Several tests were made, nevertheless, relative to E436A and E526 units as applied to a modified version of the final titration step. No difficulties were experienced in this modified version relative to ΔpH changes around the equivalence point, or in adapting these changes to the dead-stop pH endpoint technique. Since this work was not part

of the project directive, no detailed discussions are included. In point of fact, however, a technique was written up for the granting agency in this connection. This is outlined briefly below, and it was found to yield excellent data relative to both precision and accuracy.

(1) Carry out all steps of the industry method through to the end of step (4).

(2) Transfer the filter and paper back to the original E526 beaker in which the work was started. Add 50.00 ± 0.02 ml of 1.0M HCl and macerate.

(3) Rack the beaker on the E526 beaker changer

(4) Calibrate the E526 with a 7.00 buffer and then with a 5.00 pH buffer. Set the dead-stop pH at 5.10.

Use a glass-Ag/AgCl (3M KCl) combination electrode, set the titration direction control at increasing pH during the titration and set the large ΔpH increment mode in operation.

(5) Titrate automatically and sequentially with 1.0M NaOH solution

2.7.5 Determination of copper

The method applied by the industry is essentially the old-line determination of copper by sodium thiosulphate, $Na_2S_2O_3$, titration. The steps are:-

(1) Pipette 5 ml of plating solution into a 250 ml flask.

(2) Add 8 ml of concentrated sulphuric acid in the fume hood.

(3) Evaporate to dense white fumes of SO_3

(4) If the solution is dark, cool and add a few drops of concentrated nitric acid. Reevaporate to dense SO_3 fumes.

(5) Dilute to 100 ml and add concentrated NH_3 gradually until a deep blue colour is produced after swirling.

(6) Boil for 10 to 14 minutes and then add glacial acetic acid until the colour changes to a lighter blue. Add a 2 ml excess of acetc acid.

(7) Boil and then cool.

(8) Add about 4 g of KI and 2 g of NH_4HF_2, and titrate with 0.1M $Na_2S_2O_3$, using a freshly-prepared starch solution as indicator. (Do not add starch until the brown colour has almost disappeared). Allow to stand for 30 seconds, and if a bluish-grey colour does not reappear, call it the endpoint. The colour should be white.

Obviously, as was the case with the silver determination in cyanide silver solutions, the cyanide-destruction step can not be automated, so that the experimental work was directed to automation of the final titration step alone.

The preliminary and titration reactions are:-

$$2Cu^{2+} + 4I^- \leftrightharpoons 2CuI + I_2$$

$$I_2 + 2S_2O_3^{2-} \leftrightharpoons 2I^- + S_4O_6^{2-}$$

In order to avoid interference from Fe^{3+}, which is also reduced by sodium thiosulphate, ammonium bifluoride, NH_4HF_2, is added to convert the Fe^{3+} to the soluble but very slightly dissociated complex ion, FeF_6^{3-}. Theoretical calculations as associated with the Ecell values at critical titration points will be developed in one of the associated appendices. Experimental data for this portion of the project work will be found in Appendix J.

An approximate 0.1M sodium thiosulphate solution was prepared and standardized against pure copper using the manual method. The details

of these procedures are given in Table 1-J. The average molarity and the standard deviation were found to be:-

$$0.1047^{8} \pm 0.0001^{1}$$

This solution was now applied in the industry-standard manual method for the determination of copper in commercial alkali copper cyanide plating solutions. The experimental details are given in Table 2-J, with Table 41 showing the average values obtained in comparison with the granting agency values. The values obtained were quite precise. In general, agreement with Canadian Hanson results was good; although there was a tendency for the experimental values to be somewhat on the high side. It was noted that it was essential, when darkly-coloured solutions were obtained with the sulphuric acid treatment, that these be clarified properly by nitric acid additions. A few exploratory tests indicated that, where such solutions were not properly clarified, significantly low copper values are obtained. The use of organic additives as brighteners explains the darkly-coloured solutions sometimes noted.

The E436A unit was now used to standardize the sodium thiosulphate solution. The standardization details are shown in Table 3-J. The average molarity and standard deviation values were:-

$$0.100^{6} \pm 0.001^{0}$$

While this value does not agree too closely with the value found by the manual method application, they can not really be compared, since

TABLE 41

MANUAL TITRATION DETERMINATION OF COPPER IN COMMERCIAL ALKALI COPPER CYANIDE PLATING SOLUTIONS

Sample No.	Copper (oz/US gal) project work	Copper (oz/US gal) Canadian Hanson
1.	3.92 ± 0.01	3.7
2.	3.41 ± 0.00	3.3
3.	5.14 ± 0.01	4.6
4.	6.85 ± 0.02	6.2
5.	2.27 ± 0.01	2.1
6.	4.06 ± 0.00	3.8
7.	6.89 ± 0.00	6.6
8.	4.44 ± 0.01	4.4
9.	1.89 ± 0.01	1.8
10.	4.81 ± 0.01	4.8

the time interval between these standardizations and the general instability of sodium thiosulphate solutions tend to provide for value variations.

The theoretical Ecell calculations for titration critical points are shown in Table 3-J. The comparison of these with the experimental values is shown below.

	(mV) Experimental	Theoretical
Ave. Ecell 0.5 ml before eq. pt.	320	275
Ave. Ecell at eq. pt.	213	220
Ave. Ecell 0.5 ml after eq. pt.	90	44
Ave. ± ΔE (± 0.5 ml)	+ 107 - 123	+ 55 - 176

The experimental values for Ecell at ± 0.5 ml around the equivalence point appear to be elevated for some undetermined reason. No attempt was made to investigate this situation, since the important factor, the ΔE (± 0.5 ml) was sufficiently high and in agreement with the theoretical value. The expected assymmetry did not materialize.

This titrant was now applied in the determination of copper in plating solutions using the E436A titrator. The experimental details can be found in Table 4-J, and Table 42 gives the usual comparison of results. It will be noted that these values are somewhat lower than those obtained with the manual method and are, indeed, somewhat closer to the granting agency values. The precision is good for each plating solution group. In general, the experimental average Ecell values agree with the theoretically calculated ones, although the Ecell value at 0.5 ml after the equivalence point (average 90 mV) shows a consi-

TABLE 42

E436A TITRATION DETERMINATION OF COPPER IN COMMERCIAL ALKALI COPPER CYANIDE PLATING SOLUTIONS

Sample No.	Copper (oz/US gal) project work	Copper (oz/US gal) Canadian Hanson
1.	3.74 ± 0.01	3.7
2.	3.28 ± 0.04	3.3
3.	4.69 ± 0.00	4.6
4.	6.57 ± 0.04	6.2
5.	2.11 ± 0.01	2.1
6.	3.90 ± 0.01	3.8
7.	6.62 ± 0.08	6.6
8.	4.10 ± 0.08	4.4
9.	1.71 ± 0.08	1.8
10.	4.63 ± 0.05	4.8

derable difference from the theoretical value of 44 mV.

The sodium thiosulphate titrant was now standardized using the E526 assembly. Table 5-J gives the experimental details. The average molarity and the standard deviation were:-

$$0.100^6 \pm 0.001^0$$

and these agree exactly with the data obtained from the E436A method. This coincidence of results, compared to the significant difference between the manual and E436A values, may be explained by the shorter time interval between the E436A and E526 standardization procedures, as well as on the fact that it is likely that, in time, the titrant solution had achieved a degree of stability. The optimum value of the dead-stop potential setting was found to be as originally applied and based on the E436A standardization details of Table 3-J. The value involved was + 220 mV.

The titrant was now used in the determination of copper in plating solutions using the E526 assembly. Experimental details in this connection are found in Table 6-J. Table 43 gives the usual comparison of results with the granting agency values. The optimum dead-stop potential setting was found to be + 230 mV, and this was located after minor exploratory work. Five standard copper solutions were interspersed between the plating samples as a check on instrument and electrode couple stability. Pretitration additions of KI and NH_4HF_2 were made in the form of solutions, and this was carried out automatically on the beaker changing unit. The KI was added as 10 ml of a 40 percent

TABLE 43

E526 TITRATION DETERMINATION OF COPPER IN COMMERCIAL ALKALI COPPER CYANIDE PLATING SOLUTIONS

Sample No.	Copper (oz/US gal) project work	Copper (oz/US gal) Canadian Hanson
1.	3.79 ± 0.00	3.7
2.	3.41 ± 0.06	3.3
3.	5.01 ± 0.02	4.6
4.	6.68 ± 0.00	6.2
5.	2.22 ± 0.01	2.1
6.	3.94 ± 0.01	3.8
7.	6.72 ± 0.04	6.6
8.	4.34 ± 0.00	4.4
9.	1.84 ± 0.02	1.8
10.	4.79 ± 0.01	4.8

solution, and the NH_4HF_2 as 10 ml of a 20 percent solution. The ammonium bifluoride solution was held in a plastic reservoir and dispensed through acid-resistant measuring valves and Teflon tubing. 35 beakers were involved, held in 9 magazines, and titration was sequential and automatic. Elapsed time was about 1.4 hours.

Table 43 shows that the results were precise and in good agreement, although slightly higher than the granting agency values. The interspersed standard solution samples showed excellent titration volume reproducibility, indicating dead-stop setting and electrode couple stability. Table 44 shows the allover comparison of results. The manual method tends to somewhat higher values, with the E436A showing slightly lower values. The E526 data shows little bias. All values for each of the three methods show good precision. Comparison of the overall averages with the granting agency values showed some tendency for the averages to be somewhat higher, although no really serious discrepancies were noted.

2.8 Analysis of Acid Chromium Plating Solutions

2.8.1 General

Chromium, molybdenum and tungsten are on the edges of that group of metals which can be deposited from aqueous solution. Although chromium can not be considered to be easily deposited, it can be laid down from many bath types. The cathode efficiency is always low, and not over 15 percent in the most common bath, the chromic acid bath.

Chromium can not be readily deposited from a solution which contains only chromic acid, CrO_3, and water. There must be present in the

TABLE 44

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF ALKALI COPPER CYANIDE PLATING SOLUTIONS IN THE DETERMINATION OF COPPER

All results are expressed in oz/US gal

Sample No.	Can. Han. values	Manual (1)	E436A (2)	E526 (3)	Overall average	Devn. from overall ave. (1)	(2)	(3)
1.	3.7	3.92 ± 0.00	3.74 ± 0.01	3.79 ± 0.00	3.82	+ 0.10	- 0.08	- 0.03
2.	3.3	3.41 ± 0.00	3.28 ± 0.04	3.41 ± 0.06	3.37	+ 0.04	- 0.09	+ 0.04
3.	4.6	5.13 ± 0.01	4.69 ± 0.00	5.01 ± 0.02	4.94	+ 0.19	- 0.25	+ 0.07
4.	6.2	6.84 ± 0.02	6.57 ± 0.04	6.68 ± 0.00	6.70	+ 0.14	- 0.13	- 0.02
5.	2.1	2.27 ± 0.01	2.11 ± 0.01	2.22 ± 0.01	2.20	+ 0.07	- 0.09	+ 0.02
6.	3.8	4.06 ± 0.00	3.90 ± 0.01	3.94 ± 0.01	3.97	+ 0.09	- 0.07	- 0.03
7.	6.6	6.88 ± 0.00	6.62 ± 0.08	6.72 ± 0.04	6.74	+ 0.14	- 0.12	- 0.02
8.	4.4	4.44 ± 0.01	4.10 ± 0.08	4.34 ± 0.00	4.29	+ 0.15	- 0.19	+ 0.05
9.	1.8	1.89 ± 0.01	1.71 ± 0.08	1.84 ± 0.02	1.81	+ 0.08	- 0.10	+ 0.03
10.	4.8	4.81 ± 0.01	4.63 ± 0.05	4.79 ± 0.01	4.74	+ 0.07	- 0.11	+ 0.05

OFFSET OF OVERALL AVERAGE FROM CANADIAN HANSON VALUES

Sample No.	Can. Han. values	Overall aveerage	% Devn. from overall ave.
1.	3.7	3.82	+ 3.2
2.	3.3	3.37	+ 2.1
3.	4.6	4.94	+ 7.4
4.	6.2	6.70	+ 8.1
5.	2.1	2.20	+ 4.7
6.	3.8	3.97	+ 4.4
7.	6.6	6.74	+ 2.1
8.	4.4	4.29	- 2.5
9.	1.8	1.81	+ 0.5
10.	4.8	4.74	- 1.2

bath, in addition, one or more acid radicals to act as promoters in bringing about proper cathodic deposition of chromium. Useful acid radicals include sulphate, fluoride, fluosilicate, etc., with the sulphate radical, added quite frquently as sulphuric acid, being the most popular. For continuous operation, the ratio of chromium by weight to the acid radical must be maintained within quite definite limits, centering around about 100:1 in the case of sulphate.

The current efficiency varies widely with bath temperature, concentration of chromic acid and proportion of promoting ion or ions added. A change in the proportion, or the use of a different anion, seriously affects the physical nature of the deposit and, since chromium is very frequently a decorative coating, can cause significant problems. It is thought that the formation of an adherent film of chromium chromate, $Cr(OH)CrO_4$, on the cathode inhibits the deposition of the metal from pure chromic acid solution baths, and that the acid anions modify favourably the composition and properties of this film. In addition, certain anions, such as sulphate, form complexes with Cr(III), thus reacting to combine with Cr(III) produced during cathode reaction and preventing the formation of basic salts to a considerable degree at the cathode.

2.8.2 Determination of chromic acid (CrO_3) and Cr(III)

There are only two essential components in the acid chromium plating bath. These are chromium, as Cr(VI) and as Cr(II), and the amount of the acid anion used. The essential criterion of bath composition in the chromic acid/sulphate ratio where sulphate is the radical applied.

This should be kept within the limits of 50:1 to 250:1, and preferably around 100:1. A bath prepared with chromic acid and sulphate does not retain its composition during operation. Some Cr(VI) is reduced to Cr(III). The plating bath sample is normally analyzed for its contained value of Cr(VI), this being reported as chromic acid. A sample is then fully oxidized to convert all chromium to Cr(VI) and this quantity is determined. The difference between the Cr(VI) in the second determination and that in the first represents the chromium present as Cr(III). The industry methods of analysis are:-

(1) Pipette 2 ml of solution into a 100 ml volumetric flask and dilute to the mark with distilled water.

(2) Pipette 10 ml of this diluted sample into each of two 300 ml Erlenmeyer flasks. Add 100 ml of distilled water to each flask.

Determination of Chromic Acid (Hexavalent Chromium)

(1A) Add 3 g of ammonium bifluoride, 10 ml of concentrated HCl and 10 ml of 10% KI solution to one of the above flasks and mix thoroughly.

(2A) Titrate with standard sodium thiosulphate solution until the brown colour changes to a straw yellow.

(3A) Add several drops of freshly-prepared 1% soluble starch solution, and continue titrating until the blue colour disappears.

Determination of Trivalent Chromium

(1B) To the other flask add approximately 0.2 g of sodium peroxide. Add several glass beads and boil for at least 20 minutes.

(2B) Allow to cool, then add 3 g of ammonium bifluoride, 10 ml of concentrated HCl and 10 ml of 10% KI solution.

(3B) Titrate with standard sodium thiosulphate solution until the brown colour changes to a straw yellow.

(4B) Add several drops of freshly-prepared 1% starch solution and titrate until the blue colour disappears.

The Cr(III) is, of course, calculated from the disparity between the first and second titration volumes. The preliminary and titration reactions are:-

$$2Cr^{6+} + 6I^- \leftrightharpoons 2Cr^{3+} + 3I_2$$

$$I_2 + 2S_2O_3^{2-} \leftrightharpoons 2I^- + S_4O_6^{2-}$$

Ammonium bifluoride is added to complex any plating solution Fe^{3+} as the FeF_6^{3-} complex, since Fe^{3+} alone interferes by reaction with $Na_2S_2O_3$. No attempt was made to investigate the processes of analysis for both chromic acid and Cr(III), since the titration steps are identical. The exploratory work centered around the determination of Cr(VI) as chromic acid, with the understanding that if this determination was capable of adaptation to automated titration, the associated Cr(III) determination determination capability obviously followed.

The sulphate determination in acid chromium baths is a gravimetric procedure in the industry analytical process. This could not be subject to study here, although several suggestions in this connection will be found in the Conclusions section.

The experimental details for the investigation of the Cr(VI) determination will be found in Appendix K.

A solution of sodium thiosulphate was prepared and standardized by the manual application of the industry method. The details in this connection are shown in Table 1-K. The average molarity and the standard

deviation were:-

$$0.0999^{9} \pm 0.0002^{1}$$

The details of the application of this titrant to the determination of chromium as chromic acid are given in Table 2-K, with the comparison of the result averages for this manual method determination with the granting agency values given in Table 45. The results were precise in respect to the volume measurements and chromic acid contents. A tendency to yield values so,ewhat higher than the granting agency values was noted. It will be important, when considering any of the values obtained by this general method, to note that $\pm$ 0.1 ml of titrant is capable of giving a value of $\pm 0.2^{2}$ oz/US gal of chromic acid, so that minor result differences and some lower precision is to be expected.

The E436A unit was now applied in the standardization of the $Na_2S_2O_3$ titrant. The experimental details are given in Table 3-K, and the values for the molarity and standard deviation were:-

$$0.1061^{5} \pm 0.0000^{0}$$

Since this titrant was freshly-prepared, comparison of the above value for molarity with the manual method value can not be made. The theoretical calculations for Ecell at titration critical points is mentioned in Table 3-K and, without actually indicating the development, were carried out in precisely the same manner as that shown in Table 3-J, since the titrations are identical in nature. The values obtained were:-

TABLE 45

MANUAL TITRATION DETERMINATION OF CHROMIC ACID IN COMMERCIAL ACID CHROMIUM PLATING SOLUTIONS

Sample No.	Chromic acid (oz/US gal) project work	Canadian Han.
1.	32.19 ± 0.16	31.9
2.	40.83 ± 0.05	41.3
3.	35.65 ± 0.02	31.0
4.	32.59 ± 0.03	33.2
5.	37.32 ± 0.12	38.9
6.	42.41 ± 0.07	44.1
7.	36.23 ± 0.06	37.1
8.	24.80	26.0
9.	34.24 ± 0.08	Not given
10.	30.42 ± 0.03	33.4

		Experimental	Theoretical
0.5 ml before eq. pt.	(mV)	390	367
At eq. pt.	(mV)	278	257
0.5 ml after eq. pt.	(mV)	80	40
± ΔE (± 0.5 ml)	(mV)	+ 112 - 198	+ 110 - 217

The expected assymmetry materialized, although the Ecell values found experimentally differ quite significantly from the theoretical data. It is important to note, however, the the ΔE (± 0.5 ml) value is large and easily adaptable to a dead-stop titration method.

This titrant was now used to determine chromic acid in the acid chromium plating solutions. Table 4-K gives the experimental details. The E436A titrator was applied in this series of analyses. Table 46 gives the usual comparison with the granting agency data. It will be noted that the volume and chromic acid values are reasonably precise, although the precision was not as good as that displayed by the manual method application. Reasonable agreement with the Canadian Hanson values was again noted. All of the above conclusions are drawn, and must be considered in the light of the sensitivity of the titrant with respect to the volume/oz/gal relationship, The Ecell values noted experimentally, in comparison with the theoretical values previously mentioned were:-

		Experimental	Theoretical
0.5 ml before eq. pt.	(mV)	360	365
Eq. pt	(mV)	291	271
0.5 ml after eq. pt.	(mV)	166	90
± ΔE (± 0.5 ml)	(mV)	+ 69 - 135	+ 94 - 181

These theoretical values were calculated for plating solution titration conditions by the method outlined in Table 3-J. The expected assymmetry will be noted, although the experimental Ecell for 0.5 ml after

TABLE 46

E436A TITRATION DETERMINATION OF CHROMIC ACID IN COMMERCIAL ACID CHROMIUM PLATING SOLUTIONS

Sample No.	Chromic acid (oz/US gal) project work	Canadian Han.
1.	$32.8^{2} \pm 0.1^{3}$	31.9
2.	$40.8^{2} \pm 0.1^{1}$	41.3
3.	$35.8^{0} \pm 0.3^{5}$	31.0
4.	$32.2^{2} \pm 0.1^{2}$	33.2
5.	$38.5^{2} \pm 0.2^{4}$	38.9
6.	$42.6^{8} \pm 0.1^{3}$	44.1
7.	$36.0^{2} \pm 0.3^{2}$	37.1
8.	$25.5^{6} \pm 0.1^{9}$	26.0
9.	$34.8^{3} \pm 0.5^{7}$	not given
10.	$31.3^{1} \pm 0.1^{9}$	33.4

the equivalence point differs radically from the theoretical value. In addition, the other experimental Ecell values show some differences, particularly the equivalence point Ecell value. The ΔE range, however, is more than adequate to cover adaptation to the dead-stop technique.

The E526 assembly was now applied in the standardization of the same titrant. The experimental details are given in Table 5-K.. The addition of KI was made automatically as a pretitration addition of 10 ml of a 10 percent solution. After exploratory test work, the optimum dead-stop potential setting was found to be + 290 mV, and this was appreciably higher than either the experimental or theoretical values found in Table 3-K. The molarity and the standard deviation were:-

$$0.1026^{7} \pm 0.0001^{8}$$

The lack of agreement with the E436A value obtained is not significant due to the expected deterioration of sodium thiosulphate solutions in time.

The E526 assembly was used for the determination of chromic acid in the acid chromium plating solution samples. The additions of KI and NH_4HF_2 required were made automatically as pretitration additions of 10 ml of 20 percent ammonium bifluoride and 10 ml of 10 percent potassium iodide. The dead-stop setting used for the standardization process, + 290 mV, was found to be satisfactory for these titrations. 30 beakers were racked in 8 magazines and the titrations were carried out sequentially and automatically in about 1.25 hours. Table 47 shows the com-

TABLE 47

E526 TITRATION DETERMINATION OF CHROMIC ACID IN COMMERCIAL ACID CHROMIUM PLATING SOLUTIONS

Sample No.	Chromic acid (oz/US gal) project work	Canadian Han.
1.	32.74 ± 0.08	31.9
2.	$40.5^{6} \pm 0.6^{0}$	41.3
3.	$35.2^{4} \pm 0.1^{3}$	31.0
4.	$31.9^{9} \pm 0.1^{7}$	33.2
5.	37.41 ± 0.07	38.9
6.	$41.6^{5} \pm 0.1^{4}$	44.1
7.	$35.0^{8} \pm 0.5^{2}$	37.1
8.	$25.0^{1} \pm 0.1^{7}$	26.0
9.	$33.7^{5} \pm 0.3^{3}$	not given
10.	$30.3^{2} \pm 0.2^{5}$	33.4

parison of the average values obtained with the granting agency data. Again, the results for the averages and standard deviations showed good precision relative to the titrant sensitivity. Reasonable agreement with the Canadian Hanson values was also noted on the same basis. Table 48 gives the allover comparison of the methods and the Canadian Hanson values. The standard deviations were noted to be higher, even for the manual method application, than were generally observed in the use and adaptation of the techniques of analysis investigated previously, and it was felt that the titrant sensitivity might have been largely responsible in this connection. The deviations from the overall average show that the E436A technique tends to higher results, while the E526 unit tends to lower values. Deviation from the granting agency values was not really significant in view of the sensitivity of the titrant.

TABLE 48

COMPARISON OF MANUAL, E436A AND E526 ASSEMBLY TITRATIONS OF COMMERCIAL ACID CHROMIUM PLATING SOLUTIONS IN THE DETERMINATION OF CHROMIC ACID

All results expressed in oz/US gal

Sample No.	Can. Han. values	Manual (1)	E436A (2)	E526 (3)	Overall average	Devn from overall ave. (1)	(2)	(3)
1.	31.9	$32.1^{9} \pm 0.1^{6}$	$32.8^{2} \pm 0.1^{3}$	$32.7^{4} \pm 0.0^{8}$	32.5^{8}	- 0.39	+ 0.24	+ 0.16
2.	41.3	40.83 ± 0.05	$40.8^{2} \pm 0.1^{1}$	$40.5^{6} \pm 0.6^{0}$	40.7^{4}	+ 0.09	+ 0.08	- 0.18
3.	31.0	35.65 ± 0.02	$35.8^{0} \pm 0.3^{5}$	$35.2^{4} \pm 0.1^{3}$	35.5^{6}	+ 0.09	+ 0.23	- 0.32
4.	33.2	32.59 ± 0.03	$32.2^{2} \pm 0.1^{2}$	$31.9^{9} \pm 0.1^{7}$	32.3^{6}	+ 0.33	- 0.04	- 0.27
5.	38.9	$37.3^{2} \pm 0.1^{2}$	$38.5^{2} \pm 0.2^{4}$	37.41 ± 0.07	37.7^{5}	- 0.43	+ 0.77	- 0.34
6.	44.1	42.41 ± 0.07	$42.6^{8} \pm 0.1^{3}$	$41.6^{5} \pm 0.1^{4}$	42.2^{5}	+ 0.16	+ 0.43	- 0.60
7.	37.1	36.23 ± 0.06	$36.0^{2} \pm 0.3^{2}$	$35.0^{8} \pm 0.5^{2}$	35.7^{8}	+ 0.45	+ 0.24	- 0.70
8.	26.0	24.80 ± 0.02	$25.5^{6} \pm 0.1^{9}$	$25.0^{1} \pm 0.1^{7}$	25.1^{2}	- 0.32	+ 0.44	- 0.11
9.	not given	34.24 ± 0.08	$34.8^{3} \pm 0.5^{2}$	$33.7^{5} \pm 0.3^{3}$	34.2^{7}	- 0.03	+ 0.56	- 0.52
10.	33.4	30.42 ± 0.03	$31.3^{1} \pm 0.1^{9}$	$30.3^{2} \pm 0.2^{5}$	30.5^{8}	- 0.25	+ 0.63	- 0.36

OFFSET OF OVERALL AVERAGE FROM CANADIAN HANSON VALUES

Sample No.	Hansón value	Overall average	% devn. from Can. Han.
1.	31.9	32.5^{8}	+ 2.1
2.	41.3	40.2^{4}	- 1.4
3.	31.0	35.5^{6}	+ 14.7
4.	33.2	32.2^{6}	- 2.8
5.	38.9	37.7^{5}	- 2.9
6.	44.1	42.2^{5}	- 4.2
7.	37.1	35.7^{8}	- 3.5
8.	26.0	25.1^{2}	- 3.3
9.	not given	34.2^{7}	—
10.	33.4	30.6^{8}	- 8.1

3. DISCUSSIONS AND CONCLUSIONS

3.1 General

The analytical methods applied by the electroplating industry may not, in many instances, be the best available or even the most modern applicable. Their use in this investigation was based on a portion of the project directive which, in itself, had a sound and reasonable basis.

The industry has used these analytical techniques for many years, and the plating bath control systems have centered on the results obtained from the application of these techniques. Suppose, for example, that a specific old-line method of electroplating solution analysis has a tendency to yield results that are appreciably high. Bath control judgments have been made on the basis of these results and on the associated alterations in composition required to provide acceptable deposits. The introduction of a more accurate method, with corresponding lower results, and the excercising of the original control systems against these results, could lead to problems with respect to satisfactory plating operations.

The potentiometric technique was chosen as the basis upon which this investigation into the automation of plating solution analysis would be carried out. This choice was dictated predominantly by the fact that this approach seemed the one most suited to the adaptation of the old-line methods to automation. In only a few instances,

notably those involving the compleximetric titrations for nickel and zinc by EDTA, was it found impossible to adapt the industry technique directly to the automated process.

Due to matrix complexities, it was not always simple to adapt the industry methods to the automated method. The whole situation would have been rendered much simpler if ion-selective electrodes had been available and adaptable to the conditions under which the analyses must be carried out. The determinations of cyanide and chloride, for example, could be carried out readily in synthetic solutions which contained individually these substances practically alone in the matrix, but the complexity of the electroplating solutions, and particularly the cyanide and alkali cyanide solutions, rendered the use of the appropriate ion-selective electrodes for such analyses extremely risky. For the nickel and zinc compleximetric titrations, some interesting and very likely fruitful exploratory work could have been carried on with respect to the use of the appropriate nickel(II) ion-selective and zinc(II) ion-selective electrodes. Unfortunately, reliable electrodes of these types were not available on a commercial basis. The necessity of adapting a copper(II) ion-selective electrode in the determination of nickel in acid nickel plating solutions is an interesting analytical feat, but it is an oblique approach with the usual disadvantages and precautionary measures typical of such approaches.

3.2 Precision and Accuracy

3.2.1 General

In order to consider the precision and accuracy of the automated

techniques of analysis, it is essential to give thought to the basis that can be used for comparison in each case. Where precision is concerned this is relatively simple; the experimental results should show good agreement in replicate analysis of the plating solution samples involved.

Where accuracy is concerned the situation is more difficult, since a judgment with respect to accuracy implies a knowledge of the true content for the substance under determination, or at least some value very closely approaching the true content. For the experimental work carried out in this investigation, there were two factors to consider. First of all it is apparent that, of the three methods of analysis applied, the E436A titrator technique might be considered as likely to provide the best picture of the real content of the solution for the substance involved. The main reason for drawing this conclusion is the fact that the E436A unit provides, with its full-scale titration curve, a visual record of the entire titration for careful analysis and examination. On the other hand, the experimental work in each area indicated that, properly applied, similar methods of analysis attacked by each of the three techniques yielded overall average values where no significant deviation existed for any of the techniques. On this basis, the use of the overall averages as approximations to the true values appeared most feasible.

The second factor involves the granting agency results, and these should carry some weight in evaluating the accuracy of the automated

technique. One would anticipate that, for a worthwhile adaptation to automation, the results obtained should not show undue departures from the granting agency analytical data. This criterion can not be applied too rigidly, however, since the granting agency laboratories carry out a very large number of analyses daily under conditions which can only be described as extremme high pressure. Under the conditions prevailing, its results can be expected to show, from time to time, departures from the real values involved.

For the purposes of the conclusions to be drawn with respect to precision, therefore, the criterion used was the reproducibility of the results determined for each method and for each technique. The accuracy levels were largely judged against the overall averages, with some consideration being given at all times to the appropriate granting agency values.

3.2.2 Precision and analytical characteristics adaptable to automated potentiometric analysis

The most important methodic characteristic for adaptation to automation under the potentiometric system is the magnitude of the ΔpH range or ΔE range for critical volume points around the equivalence point volume. It is difficult to make generalizations in this connection, since methodic and instrumental variations tend to set up specific limitations in each instance. It was apparent, however, that the E436A titrator and the E526 assembly were capable of providing very adequate equivalence point volume replications for titrations with $\pm \Delta E$ values of as low as $\pm$ 20 mV around the equivalence point Ecell value. The tables numbered 9, 13, 20, 24, 28, 32, 36, 40, 44

and 48 were analyzed in order to provide the following information.

(1) The substance determined and the titrant strength.

(2) The $\pm \Delta pH$ as $\pm \Delta E$, or the $\pm \Delta E$, for the points $\pm$ 0.5 ml around the equivalence point volume.

(3) The calculated deviation for $\pm$ 20 mV around the equivalence point, as based on the data in (2).

(4) The corresponding calculated deviation in the result expression form as oz/US gal.

(5) The actual deviation in oz/US gal for the E436A and E526 applications. These were found by averaging the standard deviations for the replicate determinations which were carried out on each plating solution sample in the group.

(6) The precision, based on the standard deviation, was obtained for the E436A and E526 applications. These were calculated, for each group, by determining the precision for the replicate analyses for each plating solution in the group and taking the overall average.

The massed data is shown in Table 49. It will be noted that, for both the E436A and E526 systems, the actual deviations in oz/US gal are in excellent agreement with those predicted by calculation. The more important picture is that associated with the E526 unit, since this automated equipment underlies the entire purpose of the project. The deviation values obtained may be compared with those associated with the manual method as obtained from the tables listed in the foregoing. They are of the same order of magnitude always, sometimes a little smaller and sometimes a little larger. The precision values may, for some methods appear to be somewhat on the high side, attaining as they do values as high as 18 ppt. It should be remembered, however, that

TABLE 49

COMPARISON OF EXPECTED AND ACTUAL DEVIATIONS AND PRECISIONS

Pltg. Soln.	Subst. deter.	Titrant	± ΔpH as ± ΔE and ± ΔE (mV)	Calc. devn. vol.	Calc. devn. oz/gal	Actual devn. oz/gal based on std. devn. E436A	Actual devn. oz/gal based on std. devn. E526	Precision as based on std. devn. (ppt) E436A	Precision as based on std. devn. (ppt) E526
Ni	H_3BO_3	0.1M	72	± 0.15	± 0.06	± 0.05	+ 0.09	± 10	± 12
	Cl	0.1M	75	± 0.15	± 0.04	± 0.05	± 0.04	± 21	± 18
	Ni	0.1M	35	± 0.3	± 0.2	± 0.04	± 0.09	± 4.0	± 8.8
Ag	KCN	0.1M	95	± 0.1	± 0.3	± 0.04	± 0.06	± 5.0	± 7.3
	K_2CO_3	0.05M	30	± 0.3	± 0.06	± 0.05	± 0.05	± 7.3	± 6.4
	Ag	0.1M	160	± 0.05	± 0.01	± 0.05	± 0.04	± 9.6	± 12
Zn	NaOH	0.5M	36	± 0.3	± 0.15	± 0.06	± 0.05	± 6.9	± 5.8
	Zn	0.1M	200	± 0.05	± 0.02	± 0.03	± 0.02	± 13	± 7.2
Cu	K_2CO_3	1M	240	± 0.05	± 0.04	± 0.05	± 0.04	N.A.	N.A. *
	Cu	0.1M	110	± 0.1	± 0.02	± 0.04	± 0.02	± 7.5	± 4.8
Cr	CrO_3	0.1M	110	± 0.1	± 0.22	± 0.23	± 0.25	± 6.7	± 5.8

* Not available from granting agency installation

the amounts of substances determined and expressed in oz/gal range from 1 to about 10, with many of them in the 1 - 5 oz/gal area. It is not surprising, with deviations on the order of ± 0.05 oz/gal, to find that such high precision values are reported.

It is important to note that the industry method of reporting does not normally involve more than the first decimal place for oz/gal in values which are mostly of two, sometimes three, significant figures. High precision is obviously not expected, required or attained.

It was concluded from this review that the experimental work had indicated that the E526 assembly provides an automated technique of good precision, certainly more than adequate for the requirements of the industry, and certainly comparable to that anticipated from the standard manual methods applied.

3.2.3 Accuracy of the E526 assembly automated analysis technique

The accuracy of the automated technique was judged primarily on the comparison of the E526 averages with the respective overall averages corresponding to the application of the manual, E436A and E526 techniques. It should be pointed out, first of all, that the deviations of the average results for each technique of approach from the respective overall average value was in no instance of a significant nature, although certain minor trends were from time to time observed. The E526 average result data were also compared with the granting agency data in order to explore this aspect of the situation.

In order to carry out these comparisons, the tables numbered as

indicated in the section on Precision were analyzed as follows:-

(1) For each group of solutions analyzed for a specific component, each E526 average was compared with the overall average on the basis:-

E526 average - Overall average

and the differences in oz/gal were separated into + ive and - ive errors. For each group the + ive and - ive errors were averaged separately, and also averaged together to give an average absolute error.

(2) The accuracy for each E526 average compared to the overall average for each sample in each group analyzed for a specific component was determined from:-

$$\frac{(\text{E526 average} - \text{Overall average})}{\text{Overall average}} \times 1000$$

and the data grouped into + ive and - ive accuracies. For each group the + ive and - ive accuracies were averaged separately, and also averaged together as an average absolute accuracy.

(3) All data for (1) and (2) are shown in Table 50, where the bracketed figures represent the number of units contributing to the average value indicated.

(4) For each group of samples analyzed for a specific component, each E526 average was compared with the appropriate granting agency value on the basis of:-

E526 average - granting agency value

and the differences in oz/gal were grouped into + ive and - ive differences. For each group, these + ive and - ive differences were averaged separately, and then averaged together to give an average absolute difference.

(5) The relative differences for each E526 average compared to the granting agency value were determined from:-

$$\frac{(\text{E526 average} - \text{granting agency value})}{\text{granting agency value}} \times 1000$$

and the data grouped as + ive and - ive values, with the averaging situation being as carried out in (4)

TABLE 50

ACCURACY OF E526 AVERAGES RELATIVE TO THE OVERALL AVERAGES

Pltg. soln.	Subst. deter.	Error in E526 averages vs the overall averages (oz/US gal) +	−	absolute	(ppt) +	−	absolute
Ni	H_3BO_3	0.06(7)	0.05(3)	0.06(10)	9.1(7)	16(3)	11(10)
	Cl	0.02(1)	0.05(7)	0.04(10)	5.3(1)	21(7)	15(10)
	Ni	0.06(6)	0.05(3)	0.06(9)	6.1(6)	5.4(3)	5.8(9)
Ag	KCN	0.09(5)	0.12(4)	0.10(10)	11(5)	12(4)	12(10)
	K_2CO_3	0.08(6)	0.10(4)	0.09(10)	10(6)	14(4)	12(10)
	Ag	0.04(4)	0.08(6)	0.06(10)	22(4)	22(6)	22(10)
Zn	NaOH	0.10(9)	0.04(1)	0.10(10)	14(9)	4(1)	13(10)
	Zn	0.02(4)	0.02(6)	0.02(10)	6.8(4)	10(6)	8.8(10)
Cu	K_2CO_3	SUFFICIENT DATA NOT AVAILABLE					
	Cu	0.04(6)	0.02(4)	0.04(10)	12(6)	5.4(4)	9.5(10)
Cr	CrO_3	0.16(1)	0.38(9)	0.36(10)	4.9(1)	11(9)	10(10)

Bracketed figures represent number of contributing values to average.

(6) All data for (4) and (5) are massed as Table 51, where the bracketed figures represent the number of units contributing to the average shown.

In considering Table 50 it was decided that any distribution of data within the limits of 6:4 or better for the (+ ive:- ive) distribution could be considered as indicative of accidental or non-trend differences. On this basis the following was noted:-

(1) The determination of H_3BO_3 by the E526 shows a slight tendency to high values, while the determination of NaOH (total alkali) on the same unit shows a tendency to high values.

(2) The determination of chloride and CrO_3 show a tendency in each case to low values relative to E526 unit determination.

Since, in no case, are the deviations involved of any worthwhile magnitude, these tendencies must be considered demonstrated but unimportant. It was concluded therefore that the automated technique has no bias relative to yielding high or low values in any of the analysis applications.

In order to explore the question of whether or not the accuracies shown represented accidental or determinate sources of departure from the overall averages, the average absolute accuracy in ppt was divided by the associated average precision in ppt. Where the quotient was 2.0 or less, the methodic accuracy involved and its associated error was considered accidental with a 95 percent probability of being correct in this assumption. An example of this approach is noted with respect

TABLE 51

RELATIVE DIFFERENCES BETWEEN E526 AVERAGES AND GRANTING AGENCY VALUES

Pltg. soln.	Subst. deter.	Difference in E526 averages vs granting agency values (oz/US gal) +	−	absolute	(ppt) +	−	absolute
Ni	H_3BO_3	1.51(9)	0.44(1)	1.4(10)	262(9)	69(1)	242(10)
	Cl	0.18(5)	0.05(5)	0.11(10)	61(5)	33(5)	47(10)
	Ni	0.09(5)	0.14(3)	0.09(9)	8.7(5)	18(3)	11(9)
Ag	KCN	0.06(2)	1.12(8)	0.90(10)	9.8(2)	93(8)	76(10)
	K_2CO_3	0.68(4)	1.02(6)	0.88(10)	135(4)	142(6)	140(10)
	Ag	---	0.21(8)	0.21(8)	---	50(8)	50(8)
Zn	NaOH	---	0.64(10)	0.64(10)	---	77(10)	77(10)
	Zn	0.26(10)	---	0.26(10)	140(10)	---	140(10)
Cu	K_2CO_3	SUFFICIENT DATA NOT AVAILABLE					
	Cu	0.19(8)	0.04(2)	0.16(10)	45(8)	7.8(2)	37(10)
Cr	CrO_3	2.54(2)	1.71(7)	1.89(9)	81(2)	48(7)	55(9)

Bracketed figures represent number of contributing values for average

to the determination of boric acid, H_3BO_3.

absolute accuracy/absolute precision = 11/12 < 2.0

Applying this criterion to all data indicated that only in the case of the NaOH (total alkali) determination on alkali cyanide zinc plating solutions did the E526 unit technique show any evidence of an error other than accidental. Even here the quotient at 2.2 did not indicate any serious discrepancy. It can be taken as a conclusion, therefore, that the E526 automated technique gives values that are accurate relative to the overall averages from the manual, E436A and E526 techniques.

The Table 51 comparisons with the granting agency values show an entirely different situation, however, and it will be best to analyze these method by method. It should be remembered that, in these comparisons, the E526 automated set-up has already been shown to give precise and accurate results with respect to the overall averages.

H_3BO_3

The E526 averages are almost consistently higher than the granting agency values. The average absolute relative difference is 242 ppt and this difference divided by the average precision for the E526 data gives a value of 242/12 = 20 >> 2.0, giving a 95 percent probability that the difference is not accidental but determinate in origin. The granting agency gives consistently low values. No dependable single explanation could be given for this situation. Since the application

of the same method manually gave averages for each plating solution instance in close agreement with the overall averages involved, the method itself can not be at fault. It was thought that inconsistent addition of d-mannitol (see Table 3 for the effect of this situation), improper pH adjustment prior to titration, incomplete re-solution of residues in the sample, etc., could all contribute in this connection, and these are all determinate error possibilities affected by pressure-to-produce situations.

Chloride

There are no real directional tendencies here, although the granting agency values show a slight trend to lower levels. The ratio value shows $47/18 = 2.6$, indicating that the differences are just barely other than accidental. Agreement here between E526 and granting agency values was reasonably good.

Nickel

No really significant directional tendencies were noted, although there is a slight trend towards lower values on the part of the granting agency. The ratio was calculated as $11/8.8 = 1.25 < 2.0$, so that the agreement here is excellent.

KCN

The E526 averages show a definite trend to lower values than the granting agency data. The ratio was given by $76/7.3 = 10 \gg 2.0$, so that the differences are strongly other than accidental. The determination of KCN involves the precipitation of AgI as a turbidity indication, and it may be possible that the endpoint is guaranteed in the granting agency laboratories by a slight over-titration. This can be

only part of a possible explanation, however, and an examination of Table 24 shows that the difference average is largely augmented by the large differences found for sample numbers 2, 5 and 8. It was noted that these three samples gave very darkly-coloured solutions upon treatment with H_2SO_4 in the silver determination, indicating the presence of organic substances, probably brighteners, used as additives. It was first thought that these substances were affecting the KCN determination by consuming in some way additional titrant and yielding high results, but the proper application of the same manual method as used by the granting agency gave results in complete agreement with the overall averages, and not with those from the granting agency. On this basis, it must be concluded that the differences lie in application rather than on some methodic problem.

K_2CO_3

No real bias tendencies were noted, and the E526 results appeared to be haphazardly different from the granting agency values. The ratio was noted to be $140/6.4 = 22 \gg 2.0$, and the differences are thus determined to be determinate in origin. Samples 2, 5 and 8 all show E526 values that are higher than those from the granting agency, but a pattern similar to that found with the KCN determination could not be assumed with any certainty. It is important to note that the project application of the manual method gave satisfactory results with respect to the overall averages, so that an applications rather than a methodic source of error is likely. It was noted, however, that where the manual method was applied to those samples which showed large dif-

ferences in the E526 vs granting agency comparisons, the colour shift for the phenolphthalein indicator was very gradual and the endpoint correspondingly difficult to pinpoint. There may be some agent in certain solutions which inhibits the indicator colour shift, thereby providing erratic endpoint and solution content situations.

Silver

There was a definite tendency for the E526 technique to give lower values than the granting agency data. The ratio is $50/12 \doteq 4 > 2.0$ and is, while indicative of a determinate error source, at least not representative of a serious discrepancy. There were no indications of any special situations with respect to samples 2, 5 and 8, although these samples did give darkly-coloured solutions upon treatment with sulphuric acid. The discrepancies noted are particularly of minor importance in view of the granting agency tendency to report the results to two significant figures only.

NaOH

There is a definite tendency for the E526 averages to be lower than the granting agency data. The ratio is given by $77/5.8 = 13 \gg 2.0$, indicating a non-accidental error source. Again, it is difficult to pinpoint any particular cause. The determination is straight-forward, although the indicator colour shift in the manual method is of poor detectability. However, a difference of about 1 ml of titrant would be required to compensate for the lower range of analytical differences found, and this seems an unlikely error relative to indicator colour shift problems alone. Possibly inaccuracies in the addition of NaCN prior to titration may be partially at fault. In any case, because of

the project manual method application giving results in agreement with the overall averages, application technique and not methodic error must be at the root of the difficulty.

Zinc

The E526 unit tends to give consistently higher values. The ratio is given by 140/7.2 = 19 >> 2.0, so that the differences are significant and not accidental in nature. It should be remembered that the methods applied are not similar, and that the manual method is an empirically-based compleximetric titration. Since there is some indication that the relative difference decreases with increasing amount of zinc determined, there might be justification in considering that some uncorrected blank (about + 0.5 ml) is not being covered in the manual titration method. That the situation might involve a general methodic error, and not an application problem, is indicated by the fact that the experimental manual titrations by the old-line method gives values in close agreement with the granting agency data. The standardization and solution titration methods are based on an empirical relationship established by the standardization process, and it is possible that the standardization process is subject to a blank, but one which varies according to the amount of zinc under determination. The differences noted, while real, are relatively unimportant in view of the result expression by the granting agency to two significant figures only.

Copper

The E526 averages tend to be higher than the granting agency values.

The ratio works out to $37/4.8 = 7.7 > 2.0$, so that the difference is not accidental. The discrepancies are relatively unimportant in view of the method content expression to two significant figures.

CrO_3

The E526 values tend to be lower than those for the granting agency. The ratio is $55/5.8 = 9.5 \gg 2.0$, and the differences are not of an accidental nature. This is again difficult to understand, since the oz/gal differences are based on an average value of 1.89, representing a difference in volume of about 0.85 ml of titrant. It is hard to picture a situation where over-titration could take place to this extent. The differences are not always important, however, since the results expressed by the granting agency are carried to three significant figures only.

The differences observed in the foregoing comparisons of the E526 averages with the granting agency data have been attributed mainly to errors of application of the techniques involved. There are other possibilities to consider, and the most important of these surrounds the possibility that, because of improper sampling, poor sealing of the sample containers, etc., at the granting agency laboratories, the plating solutions samples provided did not duplicate exactly their composition at the time of analysis by these laboratories. While this might explain some discrepancies, it can not explain them all, since discrepancy patterns are not repeated for all components analyzed for a given solution, and since it is unlikely that, where a given component is found to be consistently higher, that all of the samples

could have been affected by poor sampling, evaporation, etc. It must be concluded that the methodic applications by the granting agency frequently shows error situations on the basis of pressure-to-produce, inconsistent pretitration additions and/or treatment, etc.

It can be concluded that the automated pretitration and titration analysis of the E526 assembly is capable of yielding results having accuracies at least adequate to the requirements of the industry and superior to those presently achieved by the granting agency laboratories.

3.3 Advantages and Operational Set-Up of the E526 Assembly in Commercial Plating solution Analysis

3.3.1 Methodic advantages

The following methodic advantages have been proven and concluded with respect to the use of the E526 assembly for the automated analytical control of plating solutions. Much of the detail in this connection was established during the operation of the equipment for the experimental project, and an almost equal amount was obtained as the result of the installation and operation of the unit in the granting agency's laboratories subsequent to project completion.

(1) The use of the automated potentiometric technique eliminates the need to use indicator substances for endpoint detection, thus removing the human factor from this operation. The uncetainties attendant upon endpoint detection using certain indicator methods can be of quite significant magnitude.

(2) the stability of the electronics, the dead-stop setting and the electrode couples used guarantees repetitive endpoint volumes over an indefinite period.

(3) The use of solutions of set concentrations for the automatic addition of pretitration reagents provides a consistent solution concentration of these reagents prior to titration. Variable concentrations of some of the critical reagents can cause serious errors in the final results.

(4) The E526 unit can be adapted to other endpoint detection methods, such as absorptimetric, amperometric, etc., and can also be used in the coulometric titration mode. Versatility is an important feature for equipment of this type.

(5) The carrying-out of the pretitration additions, the titration steps, the printing out of the endpoint titrant volumes and the automatic refilling and zeroing of the titrant burette all tend to reduce significantly the human factor and associated error possibilities.

(6) In the case of the KCN titration, follwed normally by the K_2CO_3 titration determination in cyanide silver plating solutions, the beakers remain racked on the beaker-changer while the operating parameters and the electrode couple are changed. The new titration sequence then takes place with a minimum of lost time.

(7) The speed of titrant delivery away from and near the endpoint is always repetitive for a given titration type and amount, thus eliminating problems related to the human factor in producing too slow or too fast a titrant addition rate.

(8) The printout unit for titrant volume printout can be modified by the attachment of an accessory calculator which when properly programmed, will allow printout directly in oz/gal for each sample titrated.

3.3.2 Economic advantages

(1) The time to carry out 44 analyses for a given group of samples of the same type averages out at about 85 minutes. This time is available to the operator in the preparation of the next group of similar or different samples to be analyzed. The time to titrate does not vary too much from what manual titration would produce, although the installation of the oz/gal printout device probably reduces the overall time

for a complete series, from start to finish, on the manual titration basis. The important feature is the operator's time saved in titration, and the economic value of this time when used to prepare the next group of analyses.

(2) This time-saving process permits either increased analytical production with the same staff, thereby allowing additional control samples to be taken, with corresponding increased ability to maintain optimum bath conditions and optimum plating deposition. This results in an allover advantage economically. As an alternate consideration, the same number of daily analyses can be pursued with a substantial reduction in analytical staff, again resulting in a very favourable economic situation.

(3) The installation of the E526 unit requires comparitively little in the way of laboratory space (one bench about four feet wide and 16 feet long). This would provide more than adequate operational and storage space, with the normal additional space being required, dictated by the analytical traffic, for preparatory work. Space occupancy at minimal levels is an important feature in the economics of laboratory planning.

(4) The overall cost approximates some $25,000, and the automatic savings in operating personnel in a fairly busy laboratory will more than pay for the unit in the first year of operation.

3.3.3 Precautionary steps in commercial operation of the E526

(1) It is apparent that the initial setting-up of the unit requires the use of a recording potentiometric titrator to establish the proper operating parameters of Ecell or pH for the dead-stop value, E for the titration directional shift and the ΔE increment modes required. It is not always essential to purchase such equipment, since in many cases the supplier will put such equipment out on loan for a setting-up period.

(2) Regardless of the findings of the recording titrator, it is often essential to optimize the dead-stop settings by exploratory work using standard known-concentration plating solutions. This is required since the electrode couples used and/or response differences between the systems require, between one unit and the other, somewhat different settings.

(3) It is essential that bulk samples of each plating solution type to be analyzed be prepared and carefully analyzed for each component of interest. This should be carried out on the E526 at the time of its being set-up under optimum conditions. These solutions are then used as standards to put the equipment into operating condition each day, and as interspersed samples to assure continued dead-stop and electrode couple stability.

(4) The completion of the entire project was followed by the preparation for the granting agency of a laboratory manual providing complete details on the set-up and daily operation of the E526 assembly for the analysis of commercial plating solutions. Subsequent operations have shown that the techniques of analysis not covered in this project, because this would have duplicated work already carried out on similar techniques (e.g. total alkali and cyanide on copper solutions, total cyanide in zinc solutions and potassium carbonate in copper solutions), were performed without problems relative to precision or accuracy when adapted to the automated method.

3.4 Suggestions for Further Research

The following are suggested as areas of research in which results of considerable value relative to the automation of plating solution analysis might be obtained.

(1) An investigation of possible conditions under which ion-selective electrodes might be used for the determination in plating solutions of cyanide, chloride, sulphate, silver, copper and zinc.

(2) An investigation into the reasons underlying the discrepancies in the manual method results when applied by commercial plating organization laboratories.

(3) An investigation into the possible use of modern methods of analysis for plating solution components, under automated conditions.

(4) An investigation of the possibility of using the E526 unit

for determinations carried out on plating solutions automatically and involving other components, such as various metallic impurities, brightener substances, etc.

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APPENDIX A

TABLE 1-A

Standardization of NaOH solution with potassium acid phthalate (Manual method)

Preparation of potassium acid phthalate solution

5.3430 ± 0.0002 g of KHP weighed out, dissolved in distilled water and diluted to exactly 1 liter.

$$M\ KHP = 5.3430/204.228 = 0.026161^{9} \pm 0.000001^{0}$$

Standardization of NaOH solution (Manual method)

50.00 ± 0.02 ml KHP solution pipetted into 250 ml Erlenmeyer flask and diluted with 50 ml of distilled water. 5 drops of 0.1% alcoholic phenolphthalein indicator added. Titrated with standard NaOH solution. Triplicate determination.

Titration Volumes (ml)	M NaOH
12.81 ± 0.04	0.10211—
12.85 ± 0.04	0.10179—
12.90 ± 0.04	0.10140—

Average M NaOH = 0.10176—
Std. dev. = ± 0.00035—

$$M\ NaOH = 0.1017^{6} \pm 0.0003^{5}$$

TABLE 2-A

Preparation and titration of standard H_3BO_3 solution (Manual method)

Reagents 1. Standard H_3BO_3 solution - 25.0000 ± 0.0002 g H_3BO_3 dissolved in 500 ml of distilled H_2O and diluted to exactly 1 liter.

$$1\ ml\ H_3BO_3 = 0.025000 \pm 0.000008\ g\ H_3BO_3$$

2. Saturated $K_4Fe(CN)_6$ solution - 500 g $K_4FE(CN)_6.3H_2O$ in 500 ml hot distilled H_2O. Allow to cool and excess salt to crystallize out.

TABLE 2-A cont'd

3. 10% d-mannitol solution - 100g d-mannitol dissolved in 900 ml of distilled water.

Titration of H_3BO_3 solution with standard NaOH (Manual method)

Pipette 3.00 ± 0.01 ml of H_3BO_3 solution (0.0750 ± 0.0002 g H_3BO_3) into 25 ml of distilled H_2O in a 250 ml Erlenmeyer flask. Add 10 ml of saturated $K_4Fe(CN)_6$ solution. Add 9 drops of 0.1% aqueous bromocresol purple indicator. Examine for green or blue-purple colour. No instances here required titration with NaOH or HCl-NaOH to provide the proper starting pH level. Add 50 ml of 10% d-mannitol solution and 5 drops of 0.1% alcoholic phenolphthalein indicator. Titrate with standard NaOH to the first pink colour. Triplicate determination.

$$\text{weight } H_3BO_3 = \frac{\text{vol. NaOH} \times \text{M NaOH} \times 61.83}{1000}$$

Titration volumes (ml)	H_3BO_3 (g)
11.98 ± 0.04	0.075376--
11.90 ± 0.04	0.074872--
11.92 ± 0.04	0.074998--

Average weight H_3BO_3 = 0.075082-- g
Std. dev. = ± 0.000262-- g

Weight H_3BO_3 = $0.0750^8 \pm 0.0002^6$
Actual weight H_3BO_3 = 0.0750 ± 0.0002
Relative error = + 1.3 ppt

TABLE 3-A

Determination of boric acid in commercial acid nickel plating solutions (Manual method)

Reagents See Table 2-A

Titration of commercial acid nickel plating solutions (Manual method)

Warm the plating solution to dissolve any soluble residue. Pipette 2.000 ± 0.006 ml of plating solution into 25 ml of distilled H_2O in a 250 ml

Erlenmeyer flask. Add 10 ml of saturated $K_4Fe(CN)_6$ solution and 9 drops of 0.1% aqueous bromocresol purple indicator. Examine for need to neutralize using NaOH or HCl-NaOH titration. Carry out where indicated. Add 50 ml of 10% d-mannitol solution and 5 drops of 0.1% alcoholic phenolphthalein indicator. Titrate to the first pink colour with standard NaOH solution. Triplicate determination each solution sample.

$$\text{oz/gal(US) boric acid} = \frac{\text{VNaOH} \times \text{MNaOH} \times 3785.306 \times 61.83}{1000 \times 2.000 \times 28.349}$$

where:-

3785.306	=	ml/US gal
28.349	=	g/oz
61.83	=	GMW H_3BO_3

$$\text{oz/gal(US) boric acid} = \text{VNaOH} \times \text{MNaOH} \times 4.12^7$$

Sample No.	Vol. 0.1017[6]M NaOH (ml ± 0.04)	Boric acid (oz/gal)	Boric acid (oz/gal) Ave. ± s
1.	17.00	7.14	
	16.90	7.10	7.14 ± 0.04
	17.10	7.18	
2.	18.40	7.73	
	18.45	7.75	7.75 ± 0.02
	18.50	7.77	
3.	19.42	8.16	
	19.60	8.23	8.21 ± 0.04
	19.59	8.23	
4.	19.12	8.03	
	19.18	8.05	8.03 ± 0.02
	19.05	8.00	
5.	17.41	7.31	
	17.41	7.31	7.32 ± 0.01
	17.46	7.33	
6.	16.20	6.80	
	16.15	6.78	6.81 ± 0.03
	16.30	6.84	
7.	14.09	5.92	
	14.21	5.97	5.95 ± 0.03
	14.20	5.96	
8.	14.65	6.15	
	14.65	6.15	6.16 ± 0.02
	14.75	6.19	
9.	23.50	9.87	
	23.52	9.88	9.90 ± 0.04
	23.68	9.95	

10.	15.50	6.51	6.52 ± 0.03
	15.60	6.55	
	15.48	6.50	

TABLE 4-A

Standardization of NaOH solution with potassium acid phthalate (E436A method)

Preparation of potassium acid phthalate solution

See Table 1-A. M KHP = $0.026161^{9} \pm 0.000001^{0}$

Standardization of NaOH solution (E436A method)

The E436A was set in the pH mode with the full-scale deflection at 14 pH. A combination glass/Ag-AgCl (3M KCl) electrode system, calibrated with a 9.00 pH buffer solution was used. The titration was carried out in the variable titrant delivery mode, and a full titration curve to well beyond the equivalence point was obtained. Triplicate determination was carried out. Each curve was analyzed by the tangential method to locate the endpoint volume and the endpoint pH. The curve in each case was also analyzed to determine the pH values for the points ± 0.5 ml arounf the endpoint volume. For solution preparation see Table 1-A.

Titration vols (ml)	M NaOH	pH (0.5 ml before e.p.	Endpoint pH	pH (0.5 ml after e.p	ΔpH ± 0.5 ml
12.95 ± 0.02	0.10101..	6.64	8.54	10.40	1.88
12.87 ± 0.02	0.10164..	6.73	8.54	10.46	1.86
12.96 ± 0.02	0.10093..	6.68	8.57	10.55	1.94

Average M NaOH = 0.10119...
Std. devn. = ± 0.00038...

M NaOH = $0.1011^{9} \pm 0.0003^{8}$

Average pH endpoint = 8.55 ± 0.02
Average ±ΔpH (± 0.5 ml) = 1.89 ± 0.04

The theoretical calculated values for the endpoint pH, the pH 0.5 ml before the endpoint and 0.5 ml after the endpoint are given simply by:-

$$\text{Endpoint pH} = -\log\sqrt{(K_wK_2/C_{KNaP})} = -\log\sqrt{\frac{10^{-14} \times 3.9 \times 10^{-6}}{50 \times 0.026162/112.92 \text{ ml}}}$$

$$= 8.7$$

pH 0.5 ml before the endpoint

$$= -\log \frac{K_2 C_{KHP}}{C_{KNaP}} = -\log 3.9 \times 10^{-6} \cdot \frac{(50 \times 0.026162) - (12.52 \times 0.1012)}{12.52 \times 0.1012}$$

$$= 6.9$$

pH 0.5 ml after the endpoint

$$= -\log \frac{Kw}{[OH^-]} = -\log \frac{10^{-14}}{(0.5 \text{ ml} \times 0.1012)/113.52 \text{ ml}} = 10.6$$

Theoretical ΔpH (0.5 ml around endpoint) = ± 1.8

The generally close agreement between the theoretical and experimental values for the foregoing will be noted.

TABLE 5-A

Titration of H_3BO_3 solution with standard NaOH (E436A method)

Reagents

See Table 2-A

Titration of H_3BO_3 solutions

The E436A titrator was set-up, and the titration curves analyzed, in the same manner as outlined in Table 4-A (standardization of NaOH solution, E436A method)

The solution preparation for the titration process was as outlined in Table 2-A (Titration of H_3BO_3 solution with NaOH, manual method), except that variable solution volumes of H_3BO_3 were pipetted in order to check on any variation in the titration characteristics with varying H_3BO_3 concentration.

$$\text{weight } H_3BO_3 \text{ (g)} = \frac{\text{vol. NaOH} \times \text{M NaOH} \times 61.83}{1000}$$

Vol. H_3BO_3 (ml)	Titr^n. vol. (ml)	H_3BO_3 (g)	pH 0.5 ml before ep	Endpoint pH	pH 0.5 ml after ep	±ΔpH ± 0.5 ml
2.000± 0.006	8.04 ± 0.02	0.05030	6.13	7.93	9.93	1.80
	8.02 ± 0.02	0.05017	6.14	7.94	9.74	1.80
3.00 ± 0.01	12.05 ± 0.02	0.07539	6.62	8.22	9.92	1.65
	11.96 ± 0.02	0.07482	6.38	8.01	9.65	1.69
	11.92 ± 0.02	0.07458	6.44	7.92	9.51	1.54

TABLE 5-A cont'd

4.00 ± 0.01	15.94 ± 0.02	0.09972	6.69	8.33	9.95	1.63
	15.98 ± 0.02	0.09998	6.69	8.33	9.98	1.65
	16.00 ± 0.02	0.10010	6.59	8.19	9.77	1.57

Average actual weights H_3BO_3	2.00 ml	0.0500 ± 0.0001 g
	3.00 ml	0.0750 ± 0.0002 g
	4.00 ml	0.1000 ± 0.0002 g
Average calculated weights H_3BO_3	2.00 ml	$0.0502^{3} \pm 0.0001^{0}$ g (s)
	3.00 ml	$0.0749^{3} \pm 0.0004^{1}$ g (s)
	4.00 ml	$0.0999^{3} \pm 0.0001^{9}$ g (s)
Relative error	2.00 ml	+ 4.6 ppt
	3.00 ml	- 1.3 ppt
	4.00 ml	- 1.0 ppt
Average endpoint pH	2.00 ml	7.93 ± 0.01 (s)
	3.00 ml	8.0 ± 0.1 (s)
	4.00 ml	8.28 ± 0.08 (s)
Average ± ΔpH (± 0.5 ml)	2.00 ml	2.25 ± 0.01 (s)
	3.00 ml	2.1 ± 0.1 (s)
	4.00 ml	2.07 ± 0.03 (s)

The theoretical calculated values for the endpoint pH, and for the pH for ± 0.5 ml around the endpoint volume, are found most simply from the equations following and by considering that the most probable pKa value for the d-mannitol/boric acid complex is about 4.4 (4×10^{-5}).

$$\text{pH 2.00 ml endpoint} = -\log\sqrt{\frac{KwKa}{Cs}} = -\log\sqrt{\frac{10^{-14} \times 4 \times 10^{-5}}{(0.05/61.83) \times 1/96 \times 1000}}$$

$$= 8.2$$

$$\text{pH 3.00 ml endpoint} = -\log\sqrt{\frac{10^{-14} \times 4 \times 10^{-5}}{(0.075/61.83) \times 1/100\text{ml} \times 1000}}$$

$$= 8.2$$

$$\text{Ph 4.00 ml endpoint} = -\log\sqrt{\frac{10^{-14} \times 4 \times 10^{-5}}{(0.1/61.83) \times 1/104\text{ml} \times 1000}}$$

$$= 8.3$$

pH 0.5 ml before the endpoint (2.00 ml) $= -\log \frac{K_a C_a}{C_s}$

$$= -\log 4 \times 10^{-5} \cdot \frac{[(0.05/61.83) \times 1000] - 7.5 \times 0.1012}{7.5 \times 0.1012}$$

$$= 5.6$$

pH 0.5 ml before the endpoint (3.00 ml)

$$= -\log 4 \times 10^{-5} \cdot \frac{[(0.075/61.83) \times 1000] - 11.5 \times 0.1012}{11.5 \times 0.1012}$$

$$= 5.8$$

pH 0.5 ml before the endpoint (4.00 ml)

$$= -\log 4 \times 10^{-5} \cdot \frac{[(0.1/61.83) \times 1000] - 15.5 \times 0.1012}{15.5 \times 0.1012}$$

$$= 5.9$$

pH 0.5 ml after the endpoint (2.00 ml) $= -\log \frac{10^{-14}}{(0.5 \text{ ml} \times 0.1012)/96 \text{ ml}}$

$$= 10.7$$

pH 0.05 ml after the endpoint (3.00 ml) $= -\log \frac{10^{-14}}{(0.5 \text{ ml} \times 0.1012)/100 \text{ ml}}$

$$= 10.7$$

pH 0.5 ml after the endpoint (4.00 ml) $= -\log \frac{10^{-14}}{(0.5 \text{ ml} \times 0.1012)/104 \text{ ml}}$

$$= 10.7$$

The general agreement between the theoretical and experimental values for the foregoing will be noted. Different onset and offset values of pH for the ± 0.5 ml points around the endpoint may be due to a combination of circumstances including the effect of the excess of d-mannitol and the calibration of the electrode couple with a 9.00 pH buffer. For example, the average pH at the start of the titrations listed was approximately 5.8. The calculated starting pH, based on the simple equation (pH = $-\log \sqrt{K_a C_a}$) is about 3.7, and the discrepancy can be generally assigned to the inability of the electrode couple to report accurately pH values in the zone of 4 pH when calibrated with a 9.00 pH buffer.

TABLE 6-A

Determination of boric acid in commercial acid nickel plating solutions (E436A method)

Reagents

See Table 2-A

Titration of commercial acid nickel plating solutions (E436A method)

The solution preparation prior to titration was carried out exactly as outlined in Table 3-A (Titration of commercial acid nickel plating solutions, manual method), except that the phenolphthalein indicator was not added. Triplicate determinations were carried out for each solution sample after some experimentation with initial samples.

The E436A titrator was set-up, and the titration curves analyzed, in the same manner as outlined in Table 4-A (Standardization of NaOH solution, E436A method).

The calculation of boric acid in oz/gal(US) was based on:-

$$\text{oz/gal(US) boric acid} = \text{V NaOH} \times \text{M NaOH} \times 4.12^{7}$$

as derived in Table 3-A.

Sample No.	Vol. NaOH (ml ± 0.02)	H_3BO_3 as det.	(oz/gal) Ave. ± s	pH at - 0.5ml	pH at eq. pt.	pH at + 0.5 ml	± ΔpH ± 0.5 ml
1.	16.95	7.08		7.1	8.4	9.6	1.2^{5}
	16.80	7.02	7.05±0.03	6.9	8.3	9.5	1.3
	17.13	7.16		7.2	8.4	9.5	1.1^{5}
2.	18.12	7.57		7.2	8.4	9.5	1.1^{5}
	18.18	7.60	7.53±0.09	7.1	8.4	9.5	1.2
	17.78	7.43		7.4	8.4	9.5	1.0^{5}
3.	19.50	8.15		7.0	8.4	9.7	1.4
	19.58	8.18	8.19±0.04	7.1	8.4	9.5	1.2
	19.71	8.24		7.1	8.4	9.5	1.2
4.	19.00	7.94		7.0	8.5	9.8	1.4
	18.88	7.89	7.91±0.03	7.2	8.5	9.7	1.2^{5}
	18.90	7.90		7.2	8.5	9.7	1.2^{5}
5.	17.45	7.29		7.2	8.5	9.8	1.3
	17.38	7.25	$7.2^{0}\pm0.1^{2}$	7.1	8.5	9.7	1.3
	16.90	7.06		7.3	8.5	9.6	1.1^{5}
6.	16.05	6.71		7.3	8.4	9.5	1.1
	15.95	6.67	6.69±0.02	7.3	8.4	9.5	1.1
	16.00	6.69		7.4	8.4	9.5	1.0^{5}

7.	14.10	5.89		7.1	8.3	9.3	1.1
	13.65	5.71	$5.7^{7}\pm0.1^{0}$	7.0	8.3	9.5	1.2^{5}
	13.70	5.73		7.1	8.3	9.3	1.1
8.	14.62	6.11		7.1	8.4	9.5	1.2
	14.68	6.14	6.12±0.02	7.1	8.4	9.7	1.3
	14.62	6.11		7.0	8.4	9.6	1.3
9.	23.18	9.69		7.3	8.5	9.5	1.1
	23.28	9.73	9.69±0.04	7.4	8.6	9.7	1.1^{5}
	23.10	9.65		7.4	8.6	9.7	1.1^{5}
10.	15.40	6.44		7.1	8.4	9.6	1.2^{5}
	15.50	6.49	6.46±0.03	7.0	8.4	9.7	1.3^{5}
	15.42	6.45		7.1	8.4	9.6	1.2^{5}

The average values for the endpoint pH relative to the above show in a very general manner increases with increasing concentration of boric acid titrated. This is as expected. The overall average endpoint pH value, with standard deviation, is 8.4 ± 0.1, and this is somewhat higher than the experimental average and standard deviation of 8.1 ± 0.2 for the synthetic boric acid solution titrations and the theoretical average and standard deviation for these titrations of 8.2 ± 0.1. This can be attributed to the higher boric acid concentrations titrated relative to the commercial plating solutions.

The average range and standard deviation for ± ΔpH (± 0.5 ml around the endpoint) is only 1.2 ± 0.1, compared to 1.7 ± 0.1 for the synthetic boric solution titrations and 5.5 ± 0.1 for the theoretical calculations associated with these titrations. Again, the higher H_3BO_3 solution concentrations in the nickel plating solutions can be assumed responsible. For example, in the titration of Sample 3 of the plating solutions, we have:-

Starting concentration of boric acid:-

$$\frac{8.2 \text{ oz/gal} \times 28.3 \text{ g/oz} \times 200 \text{ ml} \times 1000}{3785 \text{ ml/gal} \times 61.83 \times 88 \text{ ml start vol.}} = 0.0225\text{M}$$

pH at 0.5 ml before endpoint volume of 19.6 ml:-

$$= -\log 4 \times 10^{-5} \cdot \frac{88 \times 0.0225 - 19.1 \times 0.1012}{19.1 \times 0.1012}$$

$$= 6.0$$

Even here the onset value of pH ranges some 0.4 unit higher than that calculated for the lowest concentration of the synthetic boric acid solutions at pH 5.6, so that the reduction in ± ΔpH around the endpoint seems reasonable where the commercial plating solutions are concerned.

TABLE 7-A

Standardization of NaOH solution with potassium acid phthalate (E526-automatic method)

Preparation of potassium acid phthalate solution

See Table 1-A. M KHP = $0.026161^{9} \pm 0.0000001^{0}$

Standardization of NaOH solution (E526-automatic method)

The solution preparation prior to titration was carried out as outlined in Table 1-A (Standardization of NaOH, manual method), except that the phenolphthalein indicator was not added.

A combination glass/Ag-AgCl (3M KCl) electrode system was used. The E526 unit was calibrated first with a 7.00 pH buffer solution as required, and then calibrated for the endpoint titration pH zone using a 9.00 pH buffer solution. The dead-stop endpoint pH value was preset at 8.50, this in accordance with the findings of Table 4-A (Standardization of NaOH solution, E436A method). The titration directional control was set for increasing pH during the titration and, in accordance with the Table 4-A data relative to $\pm \Delta pH$ around the endpoint zone, in the small pH increment mode required for titrations displaying fairly low $\Delta pH/\Delta V$ changes in the neighbourhood of the endpoint.

All final titrations, after several initial exploratory titrations, were carried out at the above parameters. These final titrations, four in all, were conducted with the beakers in one magazine and the automatic programmer set for one magazine operation. The titrations were sequential and automatic.

Printout vols. (ml)	M NaOH
12.79	0.102274..
12.78	0.102354..
12.75	0.102595..
12.76	0.102515..

Average M NaOH = 0.10243...
Std. dev. = ± 0.00014...

M NaOH = $0.1024^{3} \pm 0.0001^{4}$

TABLE 8-A

Titration of H_3BO_3 solutions with standard NaOH (E526-automatic method)

Reagents

See Table 1-A

Titration of H_3BO_3 solutions (E526-automatic method)

The solution preparation prior to titration was essentially identical to that outlined in Table 2-A (Titration of H_3BO_3 solutions, manual method). Since previous work had indicated that no NaOH or HCl-NaOH adjustment titrations subsequent to the addition of saturated $K_4Fe(CN)_6$ and bromocresol purple, arrangements were made to add the 10 ml of saturated $K_4Fe(CN)_6$ and the 50 ml of 10% d-mannitol as part of the automatic pretitration addition sequence of the E526 assembly. The general procedure then involved:- position 2, 10 ml addition of saturated $K_4Fe(CN)_6$; position 3, 50 ml addition of 10% d-mannitol; position 4, titration. Automatic stirring followed each addition.

The operating parameters for the E526 unit involved calibration and buffering as outlined in Table 7-A (Standardization of NaOH solution, E526-automatic method). Since the endpoint pH, as indicated by Table 5-A data (Titration of H_3BO_3 solutions, E436A titrator method) varied from about 8.0 to 8.3, it was decided to run a series of preliminary titrations to establish the optimum dead-stop pH value for these titrations. In all of these titrations, with varying dead-stop values of 8.2, 8.3, 8.4 and 8.5 pH, the titration directional control was set at increasing pH and in the small pH increment mode for fairly low $\Delta pH/\Delta V$ changes in the neighbourhood of the endpoint. These titrations were carried out with manual operation of the beakers and the magazines in order to permit change-over of the preset dead-stop pH value.

Vol. std. boric acid soln. (ml)	Printout vol. NaOH obtained (ml)	Calculated vol. NaOH req. (ml)	Preset dead-stop (pH)
2.00	7.61	7.89	8.20
2.00	7.66		8.20
2.00	7.67		8.30
2.00	7.67		8.30
2.00	7.65		8.30
2.00	7.65		8.30
2.00	7.85		8.40
2.00	7.87		8.40
2.00	7.86		8.40
2.00	7.87		8.40
2.00	7.97		8.50
2.00	7.95		8.50
2.00	7.99		8.50
3.00	11.14	11.84	8.20
3.00	11.14		8.20
3.00	11.49		8.30
3.00	11.57		8.30
3.00	11.47		8.30

3.00	11.59	11.84	8.30
3.00	11.85		8.40
3.00	11.84		8.40
3.00	11.81		8.40
3.00	11.93		8.40
4.00	15.69	15.79	8.40
4.00	15.71		8.40
4.00	15.65		8.40
4.00	15.69		8.40

In consideration of the above, the preset dead-stop pH was set at 8.40 for the four final titrations involving 3.00 ± 0.01 ml of standard boric acid solution. These titrations were carried out, for pretitration additions and titration, sequentially and automatically using a one magazine program.

$$\text{weight } H_3BO_3 \text{ (g)} = \frac{\text{vol. NaOH x M NaOH x 61.83}}{1000}$$

Printout vols. (ml)	Weight H_3BO_3 (g)
11.75	0.074415....
11.75	0.074415....
11.71	0.074162....
11.83	0.074922....

Average weight H_3BO_3 = 0.074478... g
Std. devn. = ± 0.000318... g

Average weight H_3BO_3 = $0.0744^7 \pm 0.0003^1$ g

Actual weight H_3BO_3 = 0.0750 ± 0.0002 g

Relative error = −7.1 ppt

TABLE 9-A

Determination of boric acid in commercial acid nickel plating solutions (E526 - automatic method)

Reagents

See Table 2-A

Titration of commercial acid nickel plating solutions (E526 - automatic method)

The solution preparation prior to titration was generally as outlined in Table 3-A (Titration of commercial acid nickel plating solutions, manual method). Previous work on these solutions had indicated no need to add NaOH or HCl-NaOH subsequent to the addition of saturated $K_4Fe(CN)_6$ solution and bromocresol purple indicator. Arrangements were therefore made to add the saturated $K_4Fe(CN)_6$ solution and the 10% mannitol solution as part of the automatic pretitration sequence of the E526 assembly. The general solution arrangements then were identical to those outlined in Table 8-A (Titration of H_3BO_3 solutions, E526 - automatic method). Titration in quadruplicate for each plating solution sample was carried out, so that 40 samples were magazine racked in this connection.

Interspersed between the commercial plating solution samples were placed four standard boric acid solution samples involving each 3.00 ± 0.01 ml of the standard boric acid solution. Solution preparation here was identical to what is outlined in Table 8-A. These solutions were titrated in order to verify the E526 assembly precision and susceptibility to drift over the time of the total titration sequence (about 1.4 hours).

The operating parameters for the E526 assembly were similar in all respects to those adopted for the four final synthetic boric acid solution samples titrated under Table 8-A, and included a preset dead-stop endpoint pH of 8.40 as demanded by the exploratory investigation reported in the same Table. Programming involved 11 magazine units, and all titrations were carried out, pretitration additions and titrations, sequentially and automatically.

Sample No.	Vol. NaOH (ml)	H_3BO_3 (oz/gal) as det.	H_3BO_3 (oz/gal) ave. ± s	H_3BO_3 (oz/gal) Candn. Han.	Weight actual	H_3BO_3 (g) as det.
	17.19	7.25				
1.	16.64	7.02		6.4		
	17.21	7.26	$7.1^8 \pm 0.1^1$			
	17.05	7.19				
2.	18.66	7.87		6.2		
	18.49	7.80	$7.7^4 \pm 0.1^5$			
	18.39	7.76				
	17.83	7.52				
Std.	11.66				0.0750	0.0738
3.	19.17	8.09		6.2		
	18.18	7.67	$7.7^6 \pm 0.2^2$			
	18.28	7.71				
	17.98	7.57				
4.	19.06	8.04		4.9		
	18.88	7.96	8.00 ± 0.04			
	18.87	7.96				
	19.00	8.02				

Std.	11.70				0.0750	0.0741
5.	17.04	7.19		5.5		
	16.95	7.15	7.21±0.06			
	17.11	7.22				
	17.28	7.29				
6.	16.41	6.92		6.3		
	16.64	7.02	6.91±0.08			
	16.21	6.84				
	16.24	6.85				
Std.	11.70				0.0750	0.0741
7.	14.21	6.00		6.4		
	14.15	5.97	5.96±0.03			
	14.03	5.92				
	14.14	5.96				
8.	14.56	6.14		5.2		
	14.80	6.24	6.21±0.06			
	14.89	6.28				
	14.66	6.18				
Std.	11.71				0.0750	0.0742
9.	23.28	9.82		7.4		
	22.81	9.62	9.69±0.11			
	22.83	9.63				
10.	15.70	6.62		5.5		
	15.58	6.57	6.56±0.05			
	15.56	6.56				
	15.40	6.50				

It will be noted that, as predicted by the ΔpH range around the endpoint of 2.4 for ± 0.5 ml, the titrations above generally locate the endpoint within ± 0.2 ml.

The constancy of the titration values for the four standard boric acid solutions indicates minimal drift with respect to settings placed on the dead-stop system and minimal electrode couple drift over the 1.5 hour total elapsed titration time.

APPENDIX B

TABLE 1-B

Standardization of $AgNO_3$ solution with sodium chloride (Manual method)

Preparation of sodium chloride solution

5.8450 ± 0.0002 g of NaCl was weighed out from a mass of 10 g of reagent grade NaCl which had been dried overnight at 110°C. This weight was dissolved in distilled water and dilution to exactly 1 liter was carried out.

$$M\ NaCl = 5.8450/58.45 = 0.10000^{0} \pm 0.00001^{8}$$

Standardization of $AgNO_3$ solution (Fajan's method - manual technique)

Reagents

1. 0.1M acetic acid - 6.0 ml of glacial acetic acid diluted to 1 liter.
2. 0.1M sodium acetate solution - 13.6 g of $CH_3.COONa.3H_2O$ dissolved in distilled H_2O and diluted to 1 liter.
3. 10% dextrin solution - 100 g reagent grade dextrin dissolved in 900 ml of distilled water.
4. 0.1% dichlorfluorescein solution - 0.1 g dichlorfluorescein dissolved in 100 ml of 95% ethyl alcohol.

Method

10.00 ± 0.01 ml of 0.1M standard NaCl solution pipetted into a 250 ml Erlenmeyer flask. 1.0 ml each of 0.1M acetic acid and 0.1M sodium acetate solutions added. 10 ml of 10% dextrin solution and 50 ml of distilled H_2O now added, and the mixture mixed thoroughly. 10 drops of 0.1% dichlorfluorescein solution added and the solution titrated with standard $AgNO_3$ solution to the first permanent pink colour. Vigourous shaking of the flask was carried out during the titration.

9.50 ± 0.02 ml	0.105263...
9.48 ± 0.02 ml	0.105485...
9.48 ± 0.02 ml	0.105485...
Average M $AgNO_3$ =	0.105411...
Std. devn. =	± 0.000128...

$$M\ AgNO_3 = 0.1054^{1} \pm 0.0001^{2}$$

TABLE 2-B

Determination of chloride in commercial acid nickel plating solutions (Manual application of standard method)

Reagents 1. 2% sodium chromate solution - 2.0 g reagent grade Na_2CrO_4 dissolved in 98 ml of distilled H_2O.

Titration of commercial acid nickel plating solutions (Manual method)

Warm the plating solution sample to dissolve any soluble residue. Pipette 2.000 ± 0.006 ml of plating solution into 25 ml of distilled H_2O in a 250 ml Erlenmeyer flask. Add 75 ml of distilled H_2O and 1.0 ml of 2% Na_2CrO_4 solution. Titrate with standard $AgNO_3$ solution to the first faint reddish-brown colour that persists after vigourous shaking. Triplicate determination on each bath sample.

$$\text{oz/gal(US) chloride} = \frac{VAgNO_3 \times MAgNO_3 \times 35.453 \times 3785.306}{1000 \times 2.000 \times 28.349}$$

where:-

3785.306	=	ml/US gal
28.349	=	g/oz
35.453	=	GAW chlorine

$$\text{oz/gal(US)} = VAgNO_3 \times MAgNO_3 \times 2.366^9$$

Sample No.	Vol. 0.1054[1]M $AgNO_3$ (ml ± 0.02)	Chloride (oz/gal)	Chloride (oz/gal) Ave. ± s
1.	4.91	1.22	
	4.95	1.23	1.23 ± 0.01
	4.94	1.23	
2.	6.92	1.73	
	7.00	1.75	1.73 ± 0.02
	6.85	1.71	
3.	8.59	2.14	
	8.60	2.15	2.15 ± 0.01
	8.62	2.15	
4.	9.08	2.27	
	9.10	2.27	2.27 ± 0.01
	9.06	2.26	
5.	10.05	2.51	
	10.03	2.50	2.50 ± 0.01
	10.02	2.50	

TABLE 2-B'cont'd

6.	10.37	2.59	
	10.39	2.60	2.59 ± 0.01
	10.38	2.59	
7.	13.01	3.25	
	13.05	3.26	3.26 ± 0.01
	13.03	3.26	
8.	13.35	3.33	
	13.37	3.34	3.34 ± 0.01
	13.38	3.34	
9.	15.48	3.86	
	15.55	3.88	3.87 ± 0.01
	15.56	3.88	
10.	14.33	3.58	
	14.28	3.57	3.57 ± 0.01
	14.31	3.57	

TABLE 3-B

Standardization of $AgNO_3$ solution with sodium chloride (E436A method)

Preparation of sodium chloride solution

See Table 1-B. M NaCl = $0.10000^0 \pm 0.00001^8$

Standardization of $AgNO_3$ solution (E436A method)

Solution preparation was identical to that outlined in Table 1-B, except that no dichlorfluorescein indicator was added.

The E436A was set in the potential mode, with the full-scale deflection at 500 mV and the range at + 300 to - 200 mV. A combination silver indicator electrode - silver-silver chloride (s. KNO_3) reference electrode was used as the electrode couple system. The titration was carried out in the variable titrant delivery mode, and a full scale titration curve to well beyond the equivalence point volume was obtained. Triplicate determination was carried out. Each curve was analyzed by the tangential method to locate the equivalence point volume and the equivalence point electrode couple potential value. In addition, each curve was analyzed to determine the potential values at ± 0.5 ml around the equivalence point volume.

Vol. $AgNO_3$ (ml ± 0.02)	M $AgNO_3$	E (-0.5 ml) (mV)	Eq. pt. E (mV)	E (+0.5 ml) (mV)	± ΔE ± 0.5 ml
9.43	0.106044..	212	300	390	89
9.55	0.104712..	208	298	382	87
9.41	0.106269..	211	297	387	88

Average M $AgNO_3$ = 0.105675..
Std. devn. = ± 0.000841..

M $AgNO_3$ = $0.1056^7 \pm 0.0008^4$

Average E endpoint = 298 ± 2 mV

Average ± ΔE (± 0.5 ml) = 88 ± 1 (range 176 ± 2 mV)

The theoretical value of the equivalence point potential for the titration would be given by the following:-

Theoretical equivalence point $[Ag^+] = \sqrt{Ksp(AgCl)}$

$= \sqrt{1.56 \times 10^{-10}}$ (25°C)

$= 1.26 \times 10^{-5}$M

$$E_{Ag^+/Ag} = E^o_{Ag^+/Ag} + 0.059 \log [Ag^+]$$

$$= 0.800 + 0.059 \log 1.26 \times 10^{-5} = 0.511 \text{ V}$$

E_{cell} for the equivalence point would thus be given by:-

$$E_{Ag^+/Ag} - E_{reference} = 0.511 - 0.200 = 0.311 \text{ V}$$

where the value of 0.200 V represents the potential of the Ag/AgCl (3M KCl) reference.

Thus the calculated equivalence point potential for the system shows a value of 0.311 V or 311 mV. This agrees reasonably well with the found average value of 298 ± 2 mV. The discrepancy can be assumed to be due to such factors as uncompensated junction potentials, use of concentrations instead of activities, uncertainties in mV measurement, effect of solution ionic strength, temperature departure from 25°C, etc.

At the point 0.5 ml before the equivalence point volume the calculated potential value is given by:-

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log \frac{1.56 \times 10^{-10}}{(10 \text{ ml} \times 0.1\text{M} - 9 \text{ ml} \times 0.1057)/80 \text{ ml}}$$

$$= 0.411 \text{ V}$$

$$E_{cell} = 0.411 - 0.200 = 0.211 \text{ V}$$

$$= 211 \text{ mV}$$

This also agrees well with the average found value of 210 ± 2 mV

At the point 0.5 ml after the equivalence point volume the calculated potential value of the solution is given by:-

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log \frac{0.5 \text{ ml} \times 0.1057\text{M}}{80 \text{ ml}}$$

$$= 0.612 \text{ V}$$

$$E_{cell} = 0.612 - 0.200 = 0.412 \text{ V}$$

$$= 412 \text{ mV}$$

Again this agrees well with the average found value for the titration of 386 ± 4 mV.

It will be noted that, in the above calculations, a general value of 80 ml has been taken as the equivalence point total volume of the solution. This is, of course, obtained by adding the equivalence point volume of titrant (10 ml approximately) to the starting solution volume of 70 ml approximately.

TABLE 4-B

Determination of chloride in commercial acid nickel plating solutions (E436A method)

Reagents None required. (no addition of Na_2CrO_4 indicator)

TABLE 4-B cont'd

Titration of commercial acid nickel plating solutions (E436A method)

The solution preparation was as outlined in Table 2-B, except that no addition of 2% Na_2CrO_4 was made.

The E436A unit was set up exactly as outlined in Table 3-B. The method of titration curve analysis was similar to that outlined in the same table. Triplicate determinations were made on each plating solution sample analyzed.

Sample No.	Vol. 0.10567 M $AgNO_3$ (ml ± 0.02)	Chloride (oz/gal)	E (-0.5 ml) (mV)	E eq. pt. (mV)	E (+0.5 ml) (mV)	± ΔE ± 0.5 ml
1.	4.61	1.15	209	285	361	76
	4.66	1.16	212	286	362	75
	4.52	1.12	209	287	363	77
2.	6.49	1.66	208	286	364	79
	6.62	1.65	220	290	362	71
	6.30	1.57	208	288	368	80
3.	7.71	1.92	200	282	362	81
	7.60	1.90	210	292	372	81
	8.05	2.01	206	286	362	78
4.	8.17	2.04	211	295	375	82
	8.30	2.07	224	304	384	82
5.	9.70	2.42	205	293	379	87
	9.41	2.35	214	294	374	80
	9.45	2.36	216	294	370	77
6.	10.55	2.64	208	286	362	77
	10.25	2.56	206	286	366	80
	9.75	2.44	212	288	364	76
7.	12.20	3.05	211	290	362	76
	12.18	3.05	214	289	363	74
	12.10	3.03	219	291	363	72
8.	12.67	3.16	220	296	372	76
	12.70	3.18	220	296	373	76
	13.25	3.31	236	296	356	60
9.	14.50	3.63	212	288	363	75
	14.08	3.53	209	287	363	77
	14.52	3.63	210	286	360	75
10.	13.37	3.34	214	294	372	79
	13.50	3.38	220	292	364	72
	13.98	3.47	220	294	366	73

Average chloride (oz/gal) and std. devn.

Sample No.	
1.	1.14 ± 0.02
2.	1.63 ± 0.05
3.	1.94 ± 0.06
4.	2.06 ± 0.02

TABLE 4-B cont'd

Sample No. 5.	2.38 ± 0.04
6.	2.54 ± 0.10
7.	3.04 ± 0.01
8.	3.22 ± 0.08
9.	3.60 ± 0.06
10.	3.40 ± 0.07

Average E endpoint and std. devn. = 290 ± 5 mV

Average ± ΔE (±0.5 ml) and std. devn. = 77 ± 5 mV

The average E_{cell} at the equivalence point of 290 ± 5 mV agrees quite well with the 298 ± 2 mV value found for the standardization sequence, and reasonably well with the theoretical calculated value of 311 mV. The average ± ΔE (±0.5 ml around the equivalence point volume) of 77 ± 5 mV also agrees reasonably well with the 89 ± 1 mV value found for the standardization sequence, although there is a significant difference between this value and the theoretical calculated value of ± 100 mV. These differences between the theoretical and actual values of E_{cell} and ± ΔE can be attributed to the different and variable solution matrix composition for the acid nickel plating solutions compared to the consistent general composition for the standardization solutions. This, in conjunction with the factors outlined in Table 3-B, can be assumed to carry the responsibility for such operational differences in parameters.

TABLE 5-B

Standardization of $AgNO_3$ solution with sodium chloride (E526 - automatic method)

Preparation of sodium chloride solution

See Table 1-B. M NaCl = $0.10000^0 \pm 0.00001^8$

Standardization of $AgNO_3$ solution (E526 - automatic method)

The solution preparation was identical to that outlined in Table 1-B.

The E526 unit was set in the potential mode at "+ mV", and in the "calibration" position. The electrode connections were shorted with the EA854-2B/10 shorting cable. The digital readout was set at "0000" mV, and the

zero balance indicator needle was set at the exact central line position with the countervoltage control. The shorting cable was then removed.

A combination silver-Ag/AgCl (sat. KNO_3) reference electrode system was used as the electrode couple. The titration direction was set for increasing mV during the titration and at the " + mV" starting potential position. In accordance with the data obtained from Table 3-B, a preset dead-stop potential of + 298 mV was set. Again, in accordance with Table 3-B data, which showed a ΔE range of 176 mV for ± 0.5 ml around the equivalence point volume, the large ΔE increment for fairly high $\Delta E/\Delta V$ changes around the equivalence point was selected.

The initial titrations were carried out using additions of dichlorfluorescein indicator in order to determine the general agreement between the dead-stop and indicator colour change endpoints. These initial titrations showed a distinct tendency to under-titrate, the dead-stop endpoint being achieved before the indicator colour change. Over-riding the automatic controls each time, and continuing the titration to the indicator endpoint showed the titrations to be under-titrated to the extent of some 0.1 ml to 0.2 ml.

Subsequent exploratory tests finally achieved correspondence between the two endpoint volume values at a preset dead-stop potential of + 320 mV. It is felt that the difference between the E436A and E526 potential values can be attributed to differences in titration conditions and/or instrumental response systems .

The final titrations were carried out with a preset dead-stop potential of + 320 mV, and without the addition of indicator solution. These final titrations, four in all, were conducted with the beakers in one magazine and under sequential and automatic titration conditions.

Printout vols. (ml)	M $AgNO_3$
9.48	0.105485...
9.51	0.105152...
9.41	0.106269...
9.47	0.105596...

Average M $AgNO_3$ = 0.105625...
Std. devn. = ± 0.000468...

M $AgNO_3$ = $0.1056^2 \pm 0.0004^6$

TABLE 6-B

Determination of chloride in commercial acid nickel plating solutions (E526 assembly method)

Reagents None required for commercial solutions (no addition of Na_2CrO_4 indicator solution)

For sodium chloride standard solutions - see Table 1-B

Titration of commercial acid nickel plating solutions (E526 - automatic method

The solution preparation prior to titration was generally as outlined in Table 2-B, except that the 2.00 ml of warmed plating solution was, in each case, pipetted into a 100 ml portion of distilled water in the 250 ml E526 beaker. No Na_2CrO_4 indicator solution was added. Titration in triplicate was carried out.

Interspersed between the commercial plating solutions was placed six standard sodium chloride solution samples involving 10.00 ml of sodium chloride solution. These standards were prepared exactly as outlined in Table 1-B, but without indicator addition. These standards were intended to permit estination of the constancy of the E526 settings and electrode couple over the entire titration period (about 1.25 hours). Thus a total of 36 samples, racked in nine (9) magazines, were involved.

The operating parameters for the E526 unit were initially set as indicated for the final titrations listed in Table 5-B, despite the individual indications from Table 4-B that an equivalence point potential of + 290 mV might be anticipated. The use of the preset dead-stop potential of + 320 mV was found during the experimental work to be satisfactory, and again the difference between the indicated setting of + 290 mV and the practical setting of + 320 mV can be attributed to titration conditions and/or response system differences with respect to the E436A and E526 units. The pretitration burette stops were bypassed, since no pretitration additions were required. Programming involved 9 magazines, and all titrations were carried out sequentially and automatically.

$$\text{chloride (oz/gal US)} = \text{vol. } AgNO_3 \times 0.1056^2 \times 2.366^9$$

Sample No.	Vol. $AgNO_3$ (ml)	Cl (oz/gal) as det.	Cl (oz/gal) ave. ± s	Cl (oz/gal) Candn.	Cl (oz/gal) Han.	M $AgNO_3$ standards actual	M $AgNO_3$ standards as det.
1.	4.53	1.13		1.2			
	4.53	1.13	1.12±0.01				
	4.45	1.11					

TABLE 6-B cont'd

Std.	9.46				0.1056	0.1057
2.	6.64	1.66		1.7		
	6.29	1.57	1.60±0.05			
	6.29	1.57				
3.	8.06	2.02		2.0		
	7.55	1.89	1.96±0.06			
	7.84	1.96				
Std.	9.46				0.1056	0.1057
4.	8.53	2.13		2.1		
	8.11	2.03	2.07±0.06			
	8.14	2.04				
Std.	9.50				0.1056	0.1053
5.	9.54	2.39		2.3		
	9.48	2.37	2.42±0.07			
	10.01	2.50				
6.	10.22	2.56		2.4		
	10.21	2.56	2.56±0.01			
	10.20	2.55				
Std.	9.48				0.1056	0.1055
7.	12.40	3.10		2.9		
	12.70	3.18	3.13±0.04			
	12.45	3.12				
8.	12.39	3.10		3.1		
	12.30	3.08	3.08±0.01			
	12.30	3.08				
Std.	9.46				0.1056	0.1057
9.	15.19	3.80		3.4		
	15.07	3.77	3.76±0.04			
	14.86	3.72				
10.	13.54	3.39		3.4		
	13.50	3.38	3.41±0.05			
	13.85	3.47				
Std.	9.48				0.1056	0.1055

It will be noted that, as predicted by the ΔE range around the equivalence point of 154 mV for ± 0.5 ml as given by Table 4-B, the titrations generally locate the endpoint within ± 0.1 to ± 0.2 ml, or ± 0.02 to ± 0.05 oz/gal of chloride.

The constancy of the titration values for the six standard NaCl solution samples, and the general agreement of the associated molarity calculations with the standardization value of $0.1056^2 \pm 0.0004^6$ M, indicate minimal drift with respect to the preset potential for dead-stop and the response of the electrode couple.

APPENDIX C

TABLE 1-C

Preparation of EDTA solution, standard Cu(II) solution and standard Ni(II) solution. (EDTA titration investigation)

EDTA solution

50 g of reagent-grade disodium dihydrogen EDTA salt were dried for 1 hour at 75°-80°C. 37 g of the dried and cooled salt was weighed out and dissolved in 500 ml of previously boiled and cooled distilled water. To this solution a few drops of 0.1M NaOH were added for clarification purposes, and the solution was diluted to exactly 1 liter in a volumetric flask.

Cu(II) solution

Exactly 6.3540 ± 0.0002 g of pure copper were dissolved in 30 ml of concentrated HNO_3. The oxides of nitrogen were expelled by boiling. The solution was cooled and diluted to exactly 1 liter in a volumetric flask. A concentration value was assumed of:-

0.10000 ± 0.00005M Cu(II)

Ni(II) solution

Exactly 5.8690 ± 0.0002 g of pure nickel were dissolved in 30 ml of concentrated HNO_3. The oxides of nitrogen were expelled by boiling. The solution was cooled and diluted to exactly 1 liter in a volumetric flask. A concentration value was assumed of:-

0.09996 ± 0.00004M Ni(II)

TABLE 2-C

Standardization of EDTA solution with standard Cu(II) solution (E436A method)

Method

The initial solution preparation involved 20.00 ± 0.02 ml of 0.10000 ± 0.00005M Cu(II) solution pipetted into a 150 ml beaker. 20 ml of distilled water and 20.00 ± 0.02 ml of 0.5M NH_3/0.1M NH_4Cl buffer solution were added. The pH of each solution was obtained prior to titration with EDTA solution. Quadruplicate determination was carried out.

The E436A titrator was set in the potential mode, with a full-scale deflection of 500 mV, and a range of 0 to - 500 mV. An Orion 94-29 Cu(II) ion-selective electrode and an Orion 90-02 double-junction

calomel reference electrode (10% KNO_3) were attached to the E436A titrator by adaptor connections. Titration was carried out in the variable titrant delivery mode, and a full titration curve to well beyond the equivalence point was obtained in each case. Each curve was analyzed by the tangential method to locate the equivalence point potential and volume values. In addition, each curve was analyzed to determine the potential values at ± 0.5 ml around the equivalence point volume.

pH at start	Vol. EDTA (ml ± 0.02)	E (mV) − 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)	M EDTA
9.7	22.15	− 284	− 342	− 386	± 51	0.09029..
9.7	22.15	− 294	− 352	− 401	± 54	0.09029..
9.8	22.25	− 284	− 342	− 390	± 53	0.08988..
9.8	22.20	− 280	− 342	− 388	± 54	0.09009..

Average M EDTA = 0.09013....
Std. Devn. = ± 0.00019....

M EDTA = $0.0901^3 \pm 0.0001^9$

TABLE 3-C

Preparation of Cu(II)-EDTA indicating solution

20.00 ± 0.02 ml of 0.10000 ± 0.00005M Cu(II) solution was diluted with 20 ml of distilled water and 20.00 ± 0.02 ml of 0.5M NH_3/0.1M NH_4Cl buffer solution. 21.10 ± 0.02 ml of $0.0901^3 \pm 0.0001^9$M EDTA solution was now added (95% of theoretical equivalence point volume), and this solution was diluted to exactly 100 ml in a volumetric flask. The copper content of this solution was taken as:-

1 ml = 0.001270 ± 0.000003 g total Cu
= 0.001207 g (approx.) Cu(II)-EDTA
= 0.000063 g (approx.) Cu(II)

TABLE 4-C

Titration of Ni(II) solutions by standard EDTA using Cu(II)-EDTA indicating solution and Cu(II) ion-selective electrode (E436A method).

Method

For each titration 20.00 ± 0.02 ml of 0.09996 ± 0.00004M Ni(II) solution was taken. This represented 0.1174 g of nickel. 20 ml of distilled H_2O was added and 5.00 ± 0.01 ml of Cu(II)-EDTA indicating solution (Table 3-C). This latter addition represented a total Cu of approximately 5%

of the nickel present. Volumes of 0.5M NH_3/0.1M NH_4Cl buffer solution were now added so as to yield variable pretitration pH values of from 9 to 10 as tested prior to titration.

The set-up and operating arrangements for the E436A titrator were as outlined in Table 2-C.

pH at start	Vol. EDTA (ml ± 0.02)	Calc. Ni (g)	E (mV) − 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
8.9	19.50	0.1032	− 324	− 338	− 360	± 18
8.9	19.50	0.1032	− 326	− 340	− 362	± 18
9.0	21.42	0.1133	− 308	− 340	− 362	± 27
9.0	21.63	0.1144	− 324	− 360	− 382	± 29
9.0	21.00	0.1111	− 328	− 360	− 384	± 28
9.3	21.50	0.1138	− 350	− 382	− 404	± 27
9.3	21.60	0.1143	− 333	− 365	− 387	± 27
9.3	21.50	0.1138	− 370	− 390	− 412	± 21
9.5	21.35	0.1130	− 328	− 360	− 384	± 28
9.5	21.40	0.1132	− 343	− 377	− 401	± 29
9.5	21.25	0.1124	− 350	− 380	− 404	± 27
10.0	21.50	0.1138	− 397	− 433	− 457	± 30
10.0	21.70	0.1148	− 399	− 435	− 461	± 31

The actual value of nickel titrated was 0.1174 ± 0.0003 g

TABLE 5-C

Preparation of EDTA solution and standardization with standard Cu(II) solution (E436A method)

The EDTA solution was prepared as indicated in Table 1-C. The details of the standardization process were as outlined in Table 2-C

pH at start	Vol. EDTA (ml ± 0.02)	E (mV) − 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)	M EDTA
9.6	19.27	− 280	− 340	− 390	± 55	0.10332..
9.7	19.46	− 288	− 353	− 408	± 60	0.10277..
9.7	19.34	− 290	− 346	− 402	± 56	0.10341..

Average M EDTA = 0.10332...
Std. devn. = ± 0.00051...

M EDTA = $0.1033^2 \pm 0.0005^1$

TABLE 6-C

Determination of nickel in commercial acid nickel bath plating solutions by standard EDTA using Cu(II)-EDTA indicating solution (E436A method)

Method

The commercial acid nickel bath solutions were warmed to dissolve all residue. 2.00 ± 0.01 ml of each solution was pipetted into a 150 ml beaker containing 35 ml of distilled water. 5.00 ± 0.01 ml of Cu(II)-EDTA indicating solution was added, this solution being as prepared in Table 3-C. This represented 0.00635 g of total copper. Since the acid nickel solutions ranged from 5.1 to 14.1 oz/ US gal or, for the 2 ml of solution taken, a total nickel in solution varying from 0.076 to 0.211 g, this addition of Cu(II) indicating solution represented a total copper varying from about 3% to 8% of the nickel content, well within the prescribed limits of 1% to 10%. Varying volumes of 0.5M NH_3/0.1M NH_4Cl buffer solution were now added to yield pretitration tested solution pH values between 9 and 10.

The E436A titrator was set-up and operated in exactly the same manner as outlined in Table 2-C.

All nickel content calculations were based on:-

$$\text{oz/US gal nickel} = \frac{\text{V EDTA} \times \text{M EDTA} \times 58.71 \times 3785.306}{1000 \times 2.00 \times 28.349}$$

where:-

3785.306 = ml/US gal
28.349 = g/oz
58.71 = GAW nickel

$$\text{oz/US gal nickel} = \text{V EDTA} \times \text{M EDTA} \times 3.91^{9}$$

pH at start	Vol. EDTA (ml ± 0.05)	Calc. Ni oz/gal US	C.H. Ni oz/gal US	E (mV) - 0.5 ml	E (mV) eq.pt.	E (mV) + 0.5 ml	Ave. ΔE ±0.5 ml around the eq. pt. (mV)
9.0	36.50	14.7	14.1	- 316	- 326	- 336	± 10
9.0	39.50	16.0		- 307	- 316	- 325	± 9
9.0	37.00	15.0		- 388	- 400	- 420	± 16
9.0	36.80	14.9		- 380	- 400	- 406	± 13
9.0	35.25	14.3		- 380	- 396	- 412	± 16
9.3	28.75	11.6	11.6	- 366	- 382	- 396	± 15
9.2	29.50	11.9		- 354	- 368	- 384	± 15
9.2	28.80	11.7		- 360	- 376	- 388	± 14
9.3	25.85	10.5	10.6	- 370	- 386	- 402	± 16
9.3	25.72	10.4		- 374	- 388	- 402	± 14
9.3	25.75	10.4		- 360	- 376	- 391	± 16

9.5	11.75	4.8	5.1	- 388	- 400	- 420	± 16
9.5	11.65	4.7		- 380	- 400	- 406	± 13
9.6	12.00	4.9		- 380	- 396	- 412	± 16
9.6	12.40	5.0		- 400	- 416	- 432	± 16

TABLE 7-C

Preparation of technical grade TEPA as titrant and titration of solutions of Cu(II) (E436A method)

19 g of technical grade TEPA (Fisher Scientific) was dissolved in 250 ml of distilled water and the solution diluted to exactly 1 liter in a volumetric flask. Based on a MW of 189 for TEPA, this solution was assumed to be 0.1M subject to correction on the basis of the degree of purity of the technical grade material.

Method

The titration medium was prepared by taking 1.00 ± 0.01 ml, 2.00 ± 0.01 ml and 10.00 ± 0.02 ml of 0.10000 ± 0.00005M Cu(II) standard solution. These were diluted with 100 ml of distilled water. 2.00 ± 0.01 ml of concentrated NH_3 was added.

The E436A titrator was set-up and operated in the manner outlined in Table 2-C.

Vol. Cu(II) soln. (ml)	Vol. TEPA soln. (ml)	E (mV) - 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
1.00	1.47 ± 0.02	- 125	- 200	- 285	± 80
1.00	1.55 ± 0.02	- 120	- 200	- 284	± 82
1.00	1.50 ± 0.02	- 132	- 210	- 296	± 82
2.00	2.87 ± 0.02	- 143	- 198	- 259	± 58
2.00	2.87 ± 0.02	- 138	- 198	- 248	± 55
10.00	13.60 ± 0.02	- 188	- 200	- 216	± 14
10.00	13.47 ± 0.02	- 179	- 199	- 211	± 16

TABLE 8-C

Preparation of stronger technical grade TEPA solution and titration of solutions of Cu(II) (E436A method)

38 g of technical grade TEPA was dissolved in 300 ml of distilled H_2O and the solution diluted to exactly 1 liter in a volumetric flask. Based on MW 189 for TEPA, this solution was assumed to be 0.2M subject to correction for the purity of the technical grade material.

Method

The solution preparation prior to titration involved 10.00 ± 0.02 ml

of 0.10000 ± 0.00005M Cu(II) standard solution diluted with 100 ml of distilled water. Concentrated NH_3 was added until a tested pH of 9.5 was obtained. The TEPA titrant was pH tested and found to yield a value of about 10.4.

The E436A titrator was set-up and operated in the manner outlined in Table 2-C.

Vol. Cu(II) soln. (ml)	Vol. TEPA soln. (ml)	E (mV) − 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
10.00	7.55 ± 0.02	− 210	− 240	− 272	± 31
10.00	7.50 ± 0.02	− 209	− 238	− 276	± 34
10.00	7.56 ± 0.02	− 210	− 240	− 270	± 30

TABLE 9-C

Preparation of Cu(II)-TEPA indicating solution using technical grade TEPA solution.

20.00 ± 0.02 ml of 0.10000 ± 0.00005M Cu(II) solution was diluted with 100 ml of distilled water. Concentrated NH_3 was added carefully until the solution registered a tested pH of 9.5. Based on the data from Table 8-C (7.50 ml TEPA solution for the complete titration of 10 ml of Cu(II) solution), 14.25 ml of the stronger TEPA titrant was added to provide a 95% completion point. This solution was now diluted to exactly 150 ml. The copper content of this solution was:-

1 ml = 0.000847 ± 0.000003 g total Cu
= 0.000804 g (approx.) Cu(II)-TEPA
= 0.000043 g (approx.) Cu(II)

TABLE 10-C

Titration of Ni(II) solutions by impure TEPA using Cu(II)-TEPA indicating solution and Cu(II) ion-selective electrode (E436A method)

Method

For each titration 10.00 ± 0.01 ml of Ni(II) standard solution (0.09996 ± 0.00004M) was taken and diluted with 100 ml of distilled water. This represented 0.05868 g of nickel. 3.50 ± 0.01 ml of Cu(II)-TEPA indicating solution (Table 9-C) was added. This addition represented a total copper of approximately 5% of the nickel present. Concentrated NH_3 was now added dropwise to yield a pretitration solution pH as tested of about 9.5.

The set-up and operation of the E436A titrator were exactly as outlined in Table 2-C.

Vol. Ni(II) soln. (ml)	Vol. TEPA soln. (ml)	E (mV) - 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
10.00	7.70 ± 0.02	- 230	- 260	- 294	± 32
10.00	7.70 ± 0.02	- 236	- 256	- 292	± 28
10.00	7.70 ± 0.02	- 217	- 250	- 277	± 30

TABLE 11-C

Preparation of purified TEPA and TEPA.5HCl (Ross and Frant (32))

350 g of technical grade TEPA (Fisher Scientific) was distilled under a pressure of 49 mm Hg. The fraction between 199° - 201°C was collected. Some 301 g resulted, representing about 86% of the total impure TEPA treated.

100 g of purified TEPA was now added dropwise with vigourous stirring to 1200 ml of concentrated HCl contained in a 3000 ml Erlenmeyer flask imbedded in an ice bath. The resulting suspension was cooled further and mixed with an equal volume of methanol. Filtering by suction through a No. 1 Whatman paper was carried out using Buchner equipment. The filter was washed several times with minimal amounts of methanol. This process yielded about 660 g of damp precipitate.

The precipitate was dissolved in the minimum amount of hot water (70°C). 150 g of activated charcoal (Darco G-60) was added and mixed in well for 10 minutes. The charcoal was filtered off by suction through a No. 1 Whatman paper using Buchner equipment, and the filter was washed three times with a minimal amount of hot water. The filtrate was heated to 50°-55°C, and methanol added until a permanent suspension was obtained. Settling for 1.5 hours was followed by suction filtration through a No. 1 Whatman paper. This filtrate was heated to reduce volume and put through the same process. The subsequent filtrate was again treated similarly. All of the filters were combined, spread out and air-dried for 24 hours. The final air-dried mass weighed 107 g and represented TEPA.5HCl. The yield, from the 100 g purified TEPA treated, approximated 55%.

TABLE 12-C

Preparation of TEPA.5HCl titrant and standardization against Ni(II) standard solution using Cu(II)-TEPA.5HCl indicating solution and Cu(II) ion-selective electrode (E436A method)

37 g of purified TEPA.5HCl (Table 11-C) was dissolved in 100 ml of distilled water and diluted to exactly 1 liter in a volumetric flask. The pH of this titrant was tested at 2.2 approximately. Titration against standard Cu(II) solutions indicated a molarity of about 0.180,

and on this basis a Cu(II)-TEPA.5HCL indicating solution was prepared generally as indicated in Table 9-C.

Standardization against Ni(II) solution

10.00 ± 0.02 ml of 0.09996 ± 0.0004M Ni(II) solution was pipetted into a 250 ml beaker and diluted with 100 ml of distilled water. 3.50 ± 0.01 ml of Cu(II)-TEPA.5HCl indicating solution was added. Concentrated NH_3 was added dropwise to yield a pretitration solution pH as tested of 9.5.

The E436A titrator was set-up and operated as indicated in Table 2-C.

Vol. Ni(II) soln. (ml)	Vol. TEPA. 5HCl (ml)	M TEPA. 5HCl	E (mV) - 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave ΔE ± 0.5 ml
10.00	5.60 ± 0.02	0.17857..	- 218	- 248	- 278	± 30
10.00	5.65 ± 0.02	0.17699..	- 223	- 252	- 281	± 29
10.00	5.60 ± 0.02	0.17587..	- 226	- 256	- 286	± 30

Average M TEPA.5HCl = 0.17804..
Std. devn. = ± 0.00091..

M TEPA.5HCl = $0.1780^4 \pm 0.0009^1$

TABLE 13-C

Determination of nickel in commercial acid nickel plating solutions by standard TEPA.5HCl using Cu(II)-TEPA.5HCl indicating solution and Cu(II) ion-selective electrode (E436A method)

The commercial plating solutions were warmed to dissolve all residue. 1.00 ± 0.01 of each solution was pipetted into a 250 ml beaker which contained 100 ml of distilled water. 5.00 ± 0.01 ml of Cu(II)-TEPA.5HCl indicating solution was added and sufficient concentrated NH_3 to yield a tested pretitration solution pH of 9.6. The addition of 5 ml of the indicating solution represented a total copper content of 0.00423 g and, since the commercial solutions ranged from 8.3 to 12.9 oz nickel/US gal, this represented a copper:nickel ratio of 6.8% to 4.4% (within the required limits of 1% to 10%). These solutions were titrated with $0.1780^4 \pm 0.0009^1$M TEPA.5HCl (Table 12-C).

The E436A titrator was set-up and operated as indicated in Table 2-C.

All nickel contents were calculated from:-

$$\text{oz/US gal nickel} = \frac{\text{V TEPA} \times \text{M TEPA} \times 58.71 \times 3785.306}{1000 \times 1.00 \times 28.349}$$

$$= \text{V TEPA} \times \text{M TEPA} \times 7.83^8$$

where the values shown are as given in Table 6-C.

Vol. TEPA (ml ± 0.02)	Calc. Ni (oz/US gal)	C.H. Ni (oz/US gal)	E (mV) − 0.5 ml	eq. pt.	+ 0.5 ml	Ave. ΔE ± 0.5 ml
7.70	10.73 ± 0.08	9.0	− 230	− 256	− 285	± 27
7.65	10.66 ± 0.08		− 224	− 252	− 274	± 25
7.65	10.66 ± 0.08		− 224	− 252	− 272	± 24
8.11	11.30 ± 0.08	8.7	− 228	− 252	− 274	± 23
8.10	11.29 ± 0.08		− 232	− 256	− 276	± 22
8.05	11.22 ± 0.08		− 228	− 252	− 274	± 23
10.12	14.10 ± 0.09	8.3	− 227	− 250	− 272	± 22
10.06	14.02 ± 0.09		− 223	− 247	− 271	± 24
10.09	14.06 ± 0.09		− 224	− 247	− 269	± 22
14.80	20.6 ± 0.1	12.9	− 256	− 272	− 284	± 14
14.83	20.7 ± 0.1		− 260	− 276	− 289	± 14
15.04	21.0 ± 0.1		− 244	− 260	− 274	± 15
8.28	11.54 ± 0.08	9.7	− 228	− 254	− 275	± 24
8.09	11.28 ± 0.08		− 224	− 252	− 275	± 26
8.10	11.29 ± 0.08		− 226	− 252	− 273	± 24

TABLE 14-C

Determination of nickel in commercial acid nickel plating solutions by standard TEPA.5HCl using Cu(II)-TEPA.5HCl indicating solution, Cu(II) ion-selective electrode and controlled solution pH conditions (E436A)

The commercial plating solutions were warmed to dissolve all residue. 2.00 ± 0.01 ml of each solution was pipetted into a 250 ml beaker that contained 25 ml of distilled water. 8.00 ± 0.01 ml of Cu(II)-TEPA.5HCl indicating solution was added, followed by 8.0 ml of 2:1 NH_3 and 25.0 ml of 0.5M NH_3/0.3M NH_4Cl buffer solution. This addition of indicating solution represented a total copper content of 0.00679 g and, since the commercial solutions for this series varied from 5.1 to 14.1 oz nickel/US gal, a copper:nickel ratio of 8% to 3% was provided (within the 1% to 10% required limits). These solutions were pH tested before titration and after titration with 0.17804 ± 0.00091M TEPA.5HCl.

The E436A titrator was set-up and operated as indicated in Table 2-C.

All nickel calculations were made on the same basis as outlined in Table 6-C.

Titration number	pH at start	pH at finish	Vol. TEPA (ml ± 0.02)	Calc. Ni (oz/US gal)	C.H. Ni (oz/US gal)
1	10.2	9.5	19.87	13.86 ± 0.08	14.1
2	10.2	9.5	19.74	13.78 ± 0.08	
3	10.2	9.5	19.22	13.41 ± 0.08	

4	10.2	9.6	16.38	11.42 ± 0.07	11.6
5	10.2	9.6	16.25	11.34 ± 0.07	
6	10.2	9.8	6.92	4.83 ± 0.04	5.1
7	10.2	9.8	6.78	4.73 ± 0.04	
8	10.2	9.8	6.74	4.70 ± 0.04	
9	10.2	9.6	14.01	9.78 ± 0.06	9.7
10	10.4	9.8	14.14	9.87 ± 0.06	
11	10.4	9.8	14.14	9.87 ± 0.06	

Titration number	E (mV) - 0.5 ml	eq. pt.	+ 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
1	- 201	- 230	- 252	± 23
2	- 206	- 230	- 254	± 24
3	- 206	- 230	- 254	± 24
4	- 208	- 234	- 259	± 26
5	- 200	- 225	- 250	± 25
6	- 230	- 260	- 292	± 31
7	- 234	- 266	- 292	± 29
8	- 226	- 256	- 286	± 30
9	- 212	- 240	- 265	± 27
10	- 216	- 240	- 264	± 24
11	- 217	- 242	- 268	± 26

TABLE 15-C

Preparation of standard TEPA (purified) solution, standardization against Cu(II) solution, preparation of Cu(II)-TEPA indicating solution and standardization of TEPA solution against Ni(II) solution

Preparation of TEPA solution

18 g of distilled TEPA (Table 11-C) was dissolved in 300 ml of distilled water and diluted to exactly 1 liter in a volumetric flask.

Standardization of TEPA solution against Cu(II) solution

10.00 ± 0.01 ml of o.10000 ± 0.00005M Cu(II) solution was diluted with 50 ml of distilled water. 20.00 ± 0.02 ml of 0.5M NH_3/0.3M NH_4Cl buffer solution was added. Titration with prepared TEPA solution was conducted.

The E436A titrator was set-up and operated exactly as outlined in Table 2[illegible].

Vol. TEPA soln. (ml)	M TEPA	E (mV) - 0.5 ml	eq. pt.	+ 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
14.65	0.068259..	- 168	- 252	- 312	± 72
14.68	0.068119..	- 172	- 248	- 312	± 70
14.75	0.067796..	- 187	- 252	- 312	± 63

All TEPA volume values subject to ± 0.02 ml uncertainty. pH start and finish – 9.5.

Average M TEPA = 0.06805....
Std. devn. = ± 0.00023....

M TEPA = $0.0680^5 \pm 0.0002^3$

Preparation of Cu(II)-TEPA indicating solution

20.00 ± 0.02 ml of standard Cu(II) solution (0.10000 ± 0.00005M) was diluted with 25 ml of distilled water. 20.00 ± 0.02 ml of 0.5M NH_3/0.3M NH_4Cl buffer solution was added. Based on the data from the copper(II) standardization process (14.70 ml TEPA solution for 10 ml of Cu(II) solution), 27.90 ml of TEPA solution was added to provide a 95% completion point. This solution was then diluted to exactly 100 ml in a volumetric flask. The copper content of the solution was:-

1 ml = 0.001270 ± 0.000003 g total Cu
= 0.001207 g (approx.) Cu(II)-TEPA
= 0.000063 g (approx.) Cu(II)

Standardization of TEPA solution against nickel(II) solution

10.00 ± 0.01 ml of 0.09996 ± 0.00004M Ni(II) solution was diluted with 50 ml of distilled water. 3.50 ± 0.01 ml of Cu(II)-TEPA indicating solution was added, followed by 20.00 ± 0.02 ml of 0.5M NH_3/0.3M NH_4Cl buffer solution. The amount of nickel contained was 0.05868 g, and the 3.5 ml addition of indicating solution represented 0.00444 ± 0.00001 g of total copper, or about 7% of the nickel content. These solutions were titrated with TEPA titrant.

The E436A titrator was set-up and operated as outlined in Table 2-C.

pH start and finish, as tested, 9.5 approximately.

Vol. TEPA soln. (ml ± 0.02)	M TEPA	E (mV) – 0.5 ml	E (mV) eq. pt.	E (mV) + 0.5 ml	Ave. ΔE ± 0.5 ml around the eq. pt. (mV)
15.00	0.066666..	– 152	– 194	– 234	± 41
15.20	0.065789..	– 157	– 197	– 236	± 40
15.25	0.065573..	– 160	– 200	– 239	± 40

Average M TEPA = 0.066009...
Std. devn. = ± 0.00057....

M TEPA = $0.0660^0 \pm 0.0005^7$

TABLE 16-C

Determination of nickel in commercial acid nickel plating solutions by standard TEPA (Table 15-C) using Cu(II)-TEPA indication solution, Cu(II) ion-selective electrode, set buffer solution addition and E436A titrator

Method

The commercial nickel plating solutions were warmed to dissolve all residue. 1.00 ± 0.01 ml of each solution was pipetted into 50 ml of distilled water in a 150 ml beaker. 3.00 ± 0.01 ml of Cu(II)-TEPA indicating solution (Table 15-C) was added, followed by 20.00 ± 0.02 ml of 0.5M NH_3/0.3M NH_4Cl buffer solution. The addition of 3 ml of indicating solution represented a total copper of 0.00381 g and, since the nickel plating solutions varied from 5.1 to 14.1 oz nickel/US gal, this yielded a copper:nickel ratio of from 3.6% to 9.9% (within the limits of 1% to 10%). These solutions were pH tested before and after the titration with standard TEPA at $0.0660^0 \pm 0.00057$M.

The E436A titrator was set-up and operated as outlined in Table 2-C.

The nickel contents were calculated as shown by the formula in Table 13-C.

The solution pH remained unchenged at approximately 9.5 from start to finish of the titration.

Vol. TEPA (ml ± 0.02)	(oz/US gal) Calc. Ni	Can. Han. Ni	E (mV) − 0.5 ml	eq. pt.	+ 0.5 ml	Ave. ΔE ± 0.5 ml around the Eq. pt. (mV)
27.37	14.2 ± 0.2	14.1	− 152	− 186	− 218	± 33
27.35	14.2 ± 0.2		− 140	− 170	− 200	± 30
23.00	11.9 ± 0.1	11.6	− 156	− 190	− 222	± 33
22.75	11.8 ± 0.1		− 159	− 195	− 227	± 34
23.10	12.0 ± 0.1		− 156	− 190	− 224	± 34
20.25	10.5 ± 0.1	10.6	− 155	− 187	− 217	± 31
20.00	10.4 ± 0.1		− 140	− 180	− 212	± 36
20.20	10.4 ± 0.1		− 138	− 178	− 210	± 36
9.65	4.99 ± 0.05	5.1	− 162	− 196	− 226	± 32
9.60	4.97 ± 0.05		− 162	− 194	− 226	± 32
9.54	4.94 ± 0.05		− 160	− 196	− 228	± 34
17.04	8.81 ± 0.09	9.0	− 159	− 189	− 219	± 30
17.11	8.85 ± 0.09		− 154	− 190	− 225	± 36
16.89	8.74 ± 0.09		− 154	− 188	− 222	± 34
17.01	8.80 ± 0.09	8.7	− 157	− 187	− 225	± 34
16.82	8.70 ± 0.09		− 157	− 190	− 223	± 33
16.83	8.71 ± 0.09		− 154	− 186	− 220	± 33
16.42	8.49 ± 0.09	8.3	− 158	− 188	− 218	± 30
16.48	8.52 ± 0.09		− 148	− 188	− 216	± 34
16.31	8.44 ± 0.09		− 156	− 186	− 216	± 30
24.39	12.6 ± 0.1	12.9	− 150	− 190	− 219	± 34
24.30	12.6 ± 0.1		− 161	− 192	− 222	± 31
24.34	12.6 ± 0.1		− 162	− 192	− 222	± 30
18.36	9.5 ± 0.1	9.7	− 159	− 189	− 219	± 30
18.40	9.5 ± 0.1		− 154	− 188	− 216	± 32
18.30	9.5 ± 0.1		− 155	− 189	− 223	± 34

TABLE 3-D

Standardization of $AgNO_3$ solution with sodium chloride (E436A method)

Preparation of sodium chloride solution

See Table 1-D M NaCl = $0.10000^0 \pm 0.00001^8$

Standardization of $AgNO_3$ solution (E436A method)

Solution preparation was identical to that outlined in Table 1-D, except that no indicator was added.

The E436A titrator was set in the potential mode, with full-scale deflection at 500 mV and the range at 0 to + 500 mV. A combination silver indicating electrode - silver/silver chloride (s. KNO_3) reference electrode was used. The titrations were carried in the variable titrant delivery mode, and a full titration curve to well beyond the equivalence point was obtained in each case. Each curve was analyzed by the tangential method to locate the equivalence point potential and volume. In addition, each curve was analyzed to determine the potential values at ± 0.5 ml around the equivalence point.

Vol. $AgNO_3$ (ml ± 0.02)	M $AgNO_3$	E (mV) - 0.5 ml	eq. pt.	+ 0.5 ml	ΔE for ± 0.5 ml
7.54	0.132625..	198	300	429	± 115
7.58	0.131926..	200	301	429	± 114
7.50	0.133333..	200	300	429	± 114

Average M $AgNO_3$ = 0.132627...
Std. devn. = ± 0.000700...

M $AgNO_3$ = $0.1326^2 \pm 0.0007^0$

The theoretical value for the equivalence point potential, and the ± ΔE values for ± 0.5 ml around the equivalence point, can be obtained from the same form of calculation used in Table B-3, since the general standardization procedure is identical. Thus the Ecell at the equivalence point has a theoretical value of 311 mV. This agrees reasonably well with the average Ecell value found from the above titrations of 300 mV. Any discrepancy can be assumed due to factors such as uncompensated junction potentials, use of concentrations instead of activities, effect of solution ionic strength, etc.

At the point 0.5 ml before the equivalence point volume, the calculated potential is given by:-

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log \frac{1.56 \times 10^{-10}}{(10\ ml \times 0.1M) - (7\ ml \times 0.1326M)/70ml}$$

$$= 0.398\ V.$$

$$Ecell = 0.398 - 0.200\ (ref.) = 0.198\ V = 198\ mV$$

This agrees well with the average value found of 199 ± 1 mV

At the point 0.5 ml after the equivalence point the calculated value is

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log \frac{0.5\ ml \times 0.1326M}{70\ ml} = 0.622\ V$$

$$Ecell = 0.622 - 0.200\ (ref.) = 0.422\ V = 422\ mV$$

and this also agrees well with the average found value of 429 ± 0 mV

TABLE 4-D

Determination of "free cyanide" as KCN in commercial cyanide silver plating solutions (E436A method)

Reagents See Table 2-D

Method

See Table 2-D for pretitration solution preparation. All titrated solutions were reserved for the E436A determination of K_2CO_3.

The E436A titrator was set-up and operated generally as outlined in Table 3-D. The exceptions were that the the full-scale deflection was 500 mV at a range of 0 to - 500 mV, and that the titration curves were analyzed by the circle-fit method rather than the tangential method. This latter was required since the titration reaction involves 1 mole of Ag^+ to 2 moles of CN^-.

The molarity of the titrant was taken as the Table 3-D value of $0.1326^2 \pm 0.0007^0$, and the value of KCN in oz/US gal was calculated from the equation shown in Table 2-D.

Sample No.	Vol. $AgNO_3$ (ml ± 0.02)	KCN (oz/US gal) as det.	KCN (oz/US gal) ave. ± s	KCN (oz/US gal) Canadian Hanson	E and ΔE (mV) -0.5 ml	eq.pt.	ΔE
1.	14.28	6.59		6.6	-400	-209	191
	14.08	6.49	6.53 ± 0.05		-400	-209	191
	14.10	6.50			-400	-209	191
2.	21.88	10.09		12.5	-400	-208	192
	21.56	9.94	10.01 ± 0.07		-400	-208	192
	21.68	10.00			-400	-208	192

3.	16.26	7.50		8.0	-400	-201	191
	16.21	7.47	7.48 ± 0.02		-400	-201	191
	16.21	7.47			-400	-201	191
4.	21.65	9.99		10.0	-407	-209	198
	21.71	10.01	10.00 ± 0.01		-406	-209	197
	21.65	9.99			-407	-210	203
5.	21.78	10.05		13.1	-400	-208	192
	21.75	10.03	10.05 ± 0.02		-400	-206	194
	21.84	10.07			-400	-206	194
6.	13.06	6.02		6.0	-400	-208	192
	13.21	6.09	6.07 ± 0.04		-400	-208	192
	13.24	6.10			-400	-206	194
7.	14.73	6.79		6.9	-400	-212	188
	14.74	6.80	6.82 ± 0.05		-400	-210	190
	14.91	6.88			-400	-208	192
8.	21.03	9.70		12.3	-400	-206	194
	21.32	9.83	9.78 ± 0.07		-400	-206	194
	21.29	9.82			-400	-206	194
9.	20.46	9.44		9.5	-400	-208	192
	20.21	9.32	9.39 ± 0.06		-400	-208	192
	20.39	9.40			-400	-208	192
10.	19.40	8.95		9.4	-400	-208	192
	19.31	8.91	8.92 ± 0.02		-400	-204	196
	18.31	8.91			-400	-206	194

Because of the insignificant changes in $[Ag^+]$ at 0.5 ml after the equivalence point volume, the Ecell tends to remain at a constant value relative to the equivalence point potential. For this reason no measurements were made at 0.5 ml after the equivalence point, and the ΔE value represents the difference between the endpoint and 0.5 ml before the endpoint potential values.

The theoretical equivalence point Ecell is obtained from the following:-

$$[I^-]_{\text{at eq. pt.}} = \frac{5 \text{ ml} \times 0.1 \text{g/ml} \times 1000}{135 \text{ ml} \times 166.0 \text{ g/mole}} = 0.0223\text{M}$$

135 ml representing the approximate total volume for the 10 oz KCN/US gal bath solution. The $[Ag^+]$ at the theoretical equivalence point is then:-

$$[Ag^+] = \frac{Ksp(AgI)}{[I^-]} = \frac{1.5 \times 10^{-16}}{0.0223\text{M}} = 6.7 \times 10^{-15}\text{M}$$

so that:-

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 6.7 \times 10^{-15}\text{M} = -0.036 \text{ V}$$

$$\text{Ecell} = -0.038 - 0.200 \text{ (ref.)} = -0.238 \text{ V}$$

$$= -238 \text{ mV}$$

This is somewhat more negative than the average practical Ecell at the equivalence point of -207 ± 3 mV, and the difference can be assigned to the factors noted in Table 3-D, particularly the solution ionic strength value influence which is apt to be quite significant in the plating bath solutions.

The theoretical Ecell value for 0.5 ml before the equivalence or endpoint volume can be approximated only where simple calculations are made. The calculations below are based on a pretitration solution involving a cyanide silver bath of 10 oz KCN/US gal. Based on a starting solution volume of 110 ml, this solution will be about 0.0524M to KCN. At the - 0.5 ml point the $[CN^-]$ will be approximately:-

$$[CN^-] = \frac{(110 \text{ ml} \times 0.0524\text{M}) - (2 \times 21.15 \text{ ml} \times 0.1326\text{M})}{130 \text{ ml}}$$

$$= 0.0012\text{M}$$

and the $[Ag^+]$ at this point, discounting the $[Ag(CN)_2^-]$ from silver complex in the bath, will be:-

$$[Ag^+] = \frac{[Ag(CN)_2^-]}{[CN^-]^2 K_{stab}} = \frac{(21.15 \times 0.1326)/130}{(0.0012)^2 \times 7.1 \times 10^{19}}$$

$$= 2.1 \times 10^{-16}\text{M}$$

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 2.1 \times 10^{-16}\text{M}$$

$$= 0.800 - 0.925 = -0.125 \text{ V}$$

$$\text{Ecell} = -0.125 - 0.200 \text{ (ref,)} = -0.325 \text{ V}$$

$$= -325 \text{ mV}$$

This is appreciably less negative than the average practical value found of -400 ± 1 mV, and it is likely that the usual factors plus the very approximate nature of the above calculations underlies this difference.

TABLE 5-D

Standardization of $AgNO_3$ solution with sodium chloride (E526-automatic method)

Preparation of sodium chloride solution

See Table 1-D $\quad$ MNaCl $= 0.10000^0 \pm 0.00001^8$

Standardization of $AgNO_3$ solution (E526 assembly method)

The solution preparation was identical to that outlined in Table 1-D, except that no indicator was added to the final solutions.

The E526 unit was set in the potential mode at the " + mV" position, and in the "calibration" position. The electrode connections were shorted with the EA854-2B/10 shorting cable. The digital readout was set at "0000" mV, and the zero balance indicator needle was set at the exact center line position with the counter-voltage control. The shorting cable was then removed.

A combination silver-Ag/AgCl (sat. KNO_3) electrode couple was used as the electrode system. The titration direction was set for increasing mV during the titration and at the " + mV" starting potential position. In accordance with the data obtained from Table 3-D, a preset dead-stop potential of + 300 mV was set. Again, in accordance with Table 3-D data, which showed a ΔE range of 230 mV for ± 0.5 ml around the equivalence point volume, the large ΔE range increment for high $\Delta E/\Delta V$ changes around this point was selected.

The initial titrations were carried out using additions of dichlorfluorescein indicator in order to determine the general agreement between the dead-stop and indicator colour change endpoints. These initial titrations showed a tendency for under-titration, the dead-stop endpoint being achieved before the indicator changed colour. Over-riding the automatic controls each time, and continuing the titrations to the indicator endpoint, showed the titrations to be under-titrated to the extent of approximately 0.1 to 0.2 ml.

Subsequent exploratory work finally achieved a correspondence between both endpoints when the E526 was set at a dead-stop potential of + 316 mV. Comments have been made previously (Table 5-B) concerning the effects of titration conditions and/or instrumental response in this connection.

The final titrations, four in all, were carried out with a preset dead-stop endpoint potential of + 316 mV, and without the use of indicator solution. All of these titrations were carried out in one magazine, sequentially and automatically.

Printout Vols. (ml)	M $AgNO_3$
7.48	0.133589..
7.50	0.133333..
7.49	0.133511..
7.47	0.133868..

Average M $AgNO_3$ = 0.13360...
Std. devn. = ± 0.00023...

M $AgNO_3$ = $0.1336^0 \pm 0.0002^3$

TABLE 6-D

Determination of "free cyanide" as KCN in commercial cyanide silver plating solutions (E526-automatic method)

Reagents See "Reagents" in Table 2-D

Method

The solutions were prepared as in Table 2-D. Arrangements were made to add the dilution water and the 5 ml of 10% KI solution required as part of the automatic pretitration addition sequence of the E526 unit. The general procedure involved:- position 2, 100 ml addition of water; position 3, 5 ml addition of 10% KI solution; position 4, titration. Automatic stirring followed each addition. No attempt was made to intersperse standard solutions between the cyanide silver solution samples, since E526 and electrode stability had already been demonstrated and because simple preparations involving sodium chloride could not be titrated at the same dead-stop potential and operating parameters. All titrated solutions were reserved for the E526 titrations involving the determination of K_2CO_3.

The operating parameters of the E526 were initially set at the - 207 mV equivalence point potential indicated by Table 4-D, and in the " + mV" directional mode, the " - mV" starting potential position and the large ΔE increment mode. Experimental work of a preliminary nature indicated significant over-titration at the preset dead-stop value of - 207 mV, and an optimum value was located at - 240 mV, very close to the theoretical value of - 238 mV.

Programming involved 9 magazines (33 samples) and the titrations were carried out sequentially and automatically in about 1.25 hours.

The molarity of the $AgNO_3$ titrant was taken as the Table 5-D value of $0.1336^0 \pm 0.0002^3$, and the calculation of KCN in oz/US gal involved the equation outlined in Table 2-D.

Sample No.	Printout vols (ml)	KCN (oz/US gal) as det.	KCN (oz/US gal) ave. ± s	KCN (oz/US gal) Canadian Hanson
1.	14.32	6.65		6.6
	14.10	6.55	6.63 ± 0.07	
	14.41	6.70		
2.	22.00	10.23		12.5
	22.04	10.24	10.20 ± 0.06	
	21.80	10.13		
3.	16.72	7.76		8.0
	17.10	7.93	7.84 ± 0.08	
	16.90	7.84		
4.	21.25	9.88		10.0
	20.98	9.75	9.83 ± 0.07	
	21.21	9.85		

5.	21.73	10.10		13.1
	21.82	10.14	10.17 ± 0.09	
	22.09	10.27		
6.	13.09	6.08		6.0
	13.15	6.11	6.09 ± 0.02	
	13.11	6.09		
7.	14.66	6.80		6.9
	14.95	6.94	6.87 ± 0.07	
	14.83	6.88		
8.	21.04	9.78		12.3
	21.26	9.88	9.84 ± 0.06	
	21.24	9.87		
9.	20.09	9.34		9.5
	19.93	9.27	9.28 ± 0.06	
	19.83	9.22		
10.	18.46	8.58		9.4
	18.54	8.61	8.63 ± 0.04	
	18.66	8.67		

APPENDIX E

TABLE 1-E

Preparation and standardization of H_2SO_4 titrant (Manual method)

Preparation of KHP solution and NaOH solution and Standardization of NaOH solution

1. A potassium acid phthalate solution was prepared by dissolving 88.0172 ± 0.0002 g of standard grade KHP in distilled water and diluting to exactly 1 liter in a volumetric flask.

   Value:- 88.0172/204.228 = $0.43097^5 \pm 0.00006^4$M

2. An approximate 1M solution of NaOH was prepared by dissolving 40 g of reagent-grade NaOH in distilled water and diluting to exactly 1 liter with distilled water.

3. A 0.1% alcoholic solution of phenolphthalein was prepared.

4. 50.00 ± 0.02 ml of the KHP solution was taken and 5 drops of phenolphthalein indicator solution was added. This solution was titrated with prepared NaOH solution.

Vol. NaOH (ml ± 0.04)	M NaOH
21.40	1.00695..
21.40	1.00695..
21.40	1.00695..

Average M NaOH = 1.00695...
Std. dev. = ± 0.00000...
M NaOH = $1.0069^5 \pm 0.0000^0$

Preparation and standardization of H_2SO_4 solution

1. Approximately 17 ml of concentrated H_2SO_4 was dissolved in 500 ml of distilled water. The solution was cooled and diluted to exactly 2 liters in a volumetric flask.

2. 10.00 ± 0.01 ml of 1.0069^5 NaOH solution was diluted with 100 ml of ditilled water and 5 drops of phenolphthalein indicator added. The resulting solution was titrated manually with prepared H_2SO_4.

Vol. H_2SO_4 (ml ± 0.04)	M H_2SO_4
34.77	0.144794....
34.79	0.144711....
34.78	0.144753....

Average M H_2SO_4 = 0 144752....
Std. devn. = ± 0.000041...

M H_2SO_4 = $0.14475^2 \pm 0.00004^1$

TABLE 2-E

Determination of K_2CO_3 in commercial cyanide silver plating solutions (Manual method)

The solutions involved were the residues from the manual titration determination of "free cyanide" (Table 2-D). To these residues, 5 drops of 0.1% phenolphthalein indicator were added, and the titration carried out with $0.14475^2 \pm 0.00004^1$M H_2SO_4.

The value for K_2CO_3 in oz/US gal was calculated from:-

$$\text{Oz/US gal } K_2CO_3 = \frac{V\ H_2SO_4 \times M\ H_2SO_4 \times 138.21 \times 3785.306}{1000 \times 5.00 \times 28.349}$$

where:-

3785.306 = ml/US gal
28.349 = g/oz
138.21 = GMW K_2CO_3

$$\text{oz/US gal } K_2CO_3 = V\ H_2SO_4 \times M\ H_2SO_4 \times 3.69^0$$

Sample No.	Vol. H_2SO_4 (ml ± 0.04)	K_2CO_3 (oz/US gal) as det.	K_2CO_3 (oz/US gal) ave. ± s	K_2CO_3 (oz/US gal) Canadian Hanson
1.	7.81	4.17		5.8
	7.79	4.15	4.15 ± 0.01	
	7.78	4.14		
	7.80	4.15		
	7.80	4.15		
2.	14.00	7.46		7.2
	14.10	7.51	7.51 ± 0.05	
	14.20			
3.	9.78	5.20		6.2
	9.80	5.22	5.21 ± 0.01	
	9.79	5.21		
	9.80	5.22		

4.	2.15	1.14		1.1
	2.17	1.16	1.15 ± 0.02	
	2.20	1.17		
	2.10	1.12		
5.	13.10	6.98		5.3
	13.09	6.97	6.96 ± 0.03	
	13.09	6.97		
	13.00	6.92		
6.	13.40	7.14		8.7
	13.40	7.14	7.14 ± 0.01	
	13.42	7.15		
	13.40	7.14		
7.	13.62	7.25		7.9
	13.60	7.24	7.22 ± 0.06	
	13.65	7.27		
	13.41	7.14		
8.	13.85	7.06		6.3
	13.82	7.36	$7.1^7 \pm 0.1^6$	
	13.30	7.08		
9.	15.08	8.03		9.2
	15.10	8.04	8.02 ± 0.02	
	15.10	8.04		
	15.00	7.99		
10.	9.72	5.18		5.3
	9.74	5.19	5.19 ± 0.01	
	9.75	5.19		
	9.80	5.21		

TABLE 3-E

Standardization of H_2SO_4 solution with NaOH solution (E436A method)

Solution preparation for NaOH solution exactly as outlined in Table 1-E

The E436A titrator was set in the pH mode with a full-scale deflection at 14pH and the range at 0 to 14pH. A combination glass/Ag-AgCl (3M KCl) electrode was used, and the unit was calibrated against a 7.00 pH buffer. Each titration was carried to obtain a full titration curve to beyond the equivalence point. Each curve was analyzed by the tangential method to locate the equivalence point pH and volume. In addition, each curve was analyzed to obtain the pH values for ± 0.5 ml around the equivalence point volume.

Vol. H_2SO_4 (ml ± 0.02)	M H_2SO_4	pH − 0.5 ml	pH eq. pt.	pH + 0.5 ml	Δ pH for vol. ± 0.5 ml on eq. pt.
34.76	0.144836..	10.76	6.80	2.80	± 3.98
34.78	0.144752..	10.76	6.82	2.80	± 3.98
34.78	0.144752..	10.76	6.82	2.80	± 3.98
34.70	0.145086..	10.76	6.80	2.80	± 3.98

$$\text{Average M } H_2SO_4 = 0.14485\ldots$$
$$\text{Std. devn.} = \pm 0.00015\ldots$$

$$\text{M } H_2SO_4 = 0.1448^5 \pm 0.0001^5$$

Note that the equivalence point pH, which should be 7.00, is approximated very closely by the average titration value of 6.81. The pH value for 0.5 ml before the equivalence point is theoretically calculated from:-

$$[OH^-] = \frac{(10 \text{ ml} \times 1.0069\text{M}) - (34.26 \text{ ml} \times 2 \times 0.14485\text{M})}{144 \text{ ml}}$$

$$= 0.001 \text{ M} \qquad pH = 11.0$$

and this is closely approximated by the experimental value of 10.76 pH.

The pH value 0.5 ml after the equivalence point is found from:-

$$[H_3O^+] = \frac{(35.26 \text{ ml} \times 2 \times 0\ 14485) - (10 \text{ ml} \times 1.0069\text{M})}{145 \text{ ml}}$$

$$= 0.001 \text{ M} \qquad pH = 3.0$$

and this also very close to the experimental value of 2.80 pH.

TABLE 4-E

Determination of K_2CO_3 in commercial cyanide silver plating solutions (E436A method)

The solutions used were the residues from the E436A titration determination of "free cyanide" (Table 4-D). No indicator was added, and the solutions were titrated with $0.1448^5 \pm 0.0001^5$M H_2SO_4.

The E436A titrator was set-up and operated exactly as outlined in Table 3-E, except that calibration was carried out against a 9.00 pH buffer solution.

The content of K_2CO_3 was calculated from the equation shown in Table 2-E.

Sample No.	Vol. H_2SO_4 (ml ± 0.02)	K_2CO_3 values in oz/US gal as det.	ave. ± s.	Can. Han	-0.5	eq.pt	+0.5	ΔpH ±0.5 ml
1.	7.68	4.09		5.8	8.80	8.31	8.00	± 0.40
	7.80	4.16	4.10 ± 0.06		8.80	8.34	8.00	± 0.40
	7.52	4.04			8.70	8.28	8.00	± 0.35
2.	13.82	7.37		7.2	8.68	8.30	7.90	± 0.39

	13.75	7.33	7.37 ± 0.04		8.66	8.36	7.92	± 0.37
	13.90	7.41			8.70	8.30	7.90	± 0.40
3.	9.85	5.25		6.2	8.72	8.32	7.90	± 0.41
	9.80	5.22	5.24 ± 0.02		8.70	8.32	7.90	± 0.40
	9.85	5.25			8.90	8.32	7.90	± 0.50
4.	1.38	0.73		1.1	8.90	8.36	8.00	± 0.45
	1.50	0.80	0.73 ± 0.06		8.91	8.36	8.00	± 0.46
	1.25	0.69			8.90	8.36	8.00	± 0.45
5.	13.39	7.14		5.3	8.86	8.39	7.95	± 0.46
	13.45	7.17	7.13 ± 0.01		8.84	8.38	7.95	± 0.45
	13.43	7.16			8.84	8.38	7.95	± 0.45
6.	13.13	7.00		8.7	8.80	8.37	8.00	± 0.40
	13.24	7.06	7.06 ± 0.06		8.80	8.37	8.00	± 0.40
	13.34	7.11			8.80	8.37	8.00	± 0.40
7.	13.84	7.38		7.9	8.88	8.32	8.00	± 0.44
	13.77	7.34	7.36 ± 0.02		8.89	8.35	8.00	± 0.45
	13.81	7.36			8.89	8.33	8.00	± 0.45
8.	13.68	7.29		6.3	8.89	8.31	8.00	± 0.45
	13.32	7.10	7.19 ± 0.10		8.88	8.30	8.00	± 0.44
	13.47	7.18			8.88	8.34	8.00	± 0.44
9.	15.03	8.01		9.2	8.90	8.30	8.00	± 0.45
	15.06	8.03	8.01 ± 0.01		8.90	8.30	8.06	± 0.43
	15.01	8.00			8.90	8.30	8.10	± 0.40
10.	9.40	5.01		5.3	8.80	8.31	7.90	± 0.45
	9.61	5.12	5.07 ± 0.06		8.80	8.31	7.90	± 0.45
	9.51	5.07			8.80	8.34	7.90	± 0.45

Using the simplest possible calculations, we note that the theoretical equivalence point pH is estimated from:-

$$[H_3O^+] = \sqrt{K_1K_2(H_2CO_3)} = \sqrt{4.3 \times 10^{-7} \times 5.6 \times 10^{-11}}$$

$$= 4.9 \times 10^{-9}M \qquad pH = 8.3$$

For the point 0.5 ml before the equivalence point we have:-

Considering a 5.3 oz/US gal K_2CO_3, this gives a molarity of K_2CO_3 at the start of:-

$$\frac{5.3 \times 28 \times 5 \times 1000}{3785 \times 130 \text{ ml} \times 138} = 0.0109M$$

so that, at 0.5 ml before the equivalence point we have:-

$$[H_3O^+] = \frac{K_2[KHCO_3]}{[K_2CO_3]} = 5.6 \times 10^{-11} \times \frac{(9.3 \text{ ml} \times 0.1448M)}{(130\text{ml} \times 0.0109)-(9.3 \times 0.1448)}$$

$$= 1.1 \times 10^{-9}M \qquad pH = 9.0$$

For the point 0.5 ml after the equivalence point, and for the same cyanide silver bath content of 5.3 oz/US gal K_2CO_3, we have:-

$$[H_3O^+] = \frac{K_1[H_2CO_3]}{[KHCO_3]} = \frac{4.3 \times 10^{-7} \times 0.5 \text{ ml} \times 0.1448M}{9.8 \text{ ml} \times 0.1448M}$$

$$= 2.2 \times 10^{-8}M \qquad pH = 7.7$$

It will be noted that the experimental values, which as averages are 8.8 pH for - 0.5 ml, 8.4 pH for the endpoint and 8.0 pH for + 0.5 ml, agree well with the theoretical values calculated above.

TABLE 5-E

Standardization of H_2SO_4 titrant with NaOH solution (E526 method)

The solution preparation was exactly as outlined in Table 1-E

A combination glass-Ag/AgCl (3M KCl) electrode was used. The E526 unit was calibrated first, as required, with a 7.00 pH buffer solution, and then with the same buffer to set the endpoint pH. The dead-stop endpoint pH value was preset at 6.90, this in accordance with the data shown in Table 3-E. The titration direction control was set for decreasing pH during the titration and, according to Table 3-E data, in the large increment ΔpH mode required for large ΔpH/ΔV changes around the equivalence point. The final titrations were carried out in 4 beakers racked in 1 magazine, and under sequential and automatic programming. Since no pretitration additions were required, the pretitration addition stops were set to be bypassed automatically.

Printout vols. (ml)	M H_2SO_4
34.78	0.144752...
34.77	0.144794...
34.77	0.144794...

Average M H_2SO_4 = 0.144780...
Std. devn. = ± 0.000024...

M H_2SO_4 = $0.14478^0 \pm 0.00002^4$

TABLE 6-E

Determination of K_2CO_3 in commercial cyanide silver plating solutions (E526 assembly method)

The solutions titrated were the residues from the E526 titration deter

minations of "free cyanide" (Table 6-D). No indicator was added and the titrations were carried out with $0.14478^0 \pm 0.00002^4$M H_2SO_4

The E526 unit was calibrated first with a 7.00 buffer solution and then with a 9.00 buffer solution for the endpoint zone pH. The electrode couple used was glass-Ag/AgCl (3M KCl) combination. The dead-stop pH was, after some exploratory work, set at 8.50, which agrees generally with the E436A found value at the endpoint of 8.33 pH average and the theoretical value of 8.3 pH. The titration direction control was set at decreasing pH. In accordance with the small ΔpH expected for ± 0.5 ml around the endpoint (Table 4-E), the small ΔpH increment mode was selected. The programmer was set for 37 beakers in 10 magazines, and the pretitration addition stop positions were automatically bypassed. Titration was sequential and automatic, and required about 1.25 hours.

The value of K_2CO_3 in oz/US gal was calculated from the equation given in Table 2-E.

In order to permit thorough stirring to cover the small ΔpH/ΔV changes around the endpoint, the normal speed of the automatic stirring motor was increased.

Sample No.	Printout vol. (ml)	K_2CO_3 (oz/US gal) as det.	K_2CO_3 (oz/US gal) ave ± s	K_2CO_3 (oz/US gal) Canadian Hanson
1.	7.96	4.24		5.8
	7.99	4.26	4.25 ± 0.01	
	7.96	4.24		
2.	14.33	7.63		7.2
	14.42	7.68	7.68 ± 0.06	
	14.53	7.74		
3.	9.83	5.24		6.2
	9.57	5.10	5.17 ± 0.07	
	9.68	5.16		
4.	2.46	1.31		1.1
	2.22	1.18	1.20 ± 0.08	
	2.15	1.14		
	2.16	1.15		
5.	12.70	6.77		5.3
	12.82	6.83	$6.9^0 \pm 0.1^1$	
	13.18	7.02		
	13.07	6.96		
6.	13.35	7.11		8.7
	13.34	7.11	7.13 ± 0.03	
	13.43	7.16		
	13.42	7.15		
7.	13.84	7.37		7.9
	13.76	7.33	7.31 ± 0.05	
	13.67	7.28		
	13.65	7.27		

8.	12.81	6.82		6.3
	12.79	6.81	6.82 ± 0.01	
	12.81	6.82		
	12.82	6.83		
9.	14.85	7.91		9.2
	15.00	7.99	7.96 ± 0.03	
	14.94	7.96		
	14.96	7.97		
10.	9.65	5.14		5.3
	9.64	5.14	5.14 ± 0.01	
	9.67	5.15		
	9.67	5.15		

APPENDIX F

TABLE 1-F

Preparation and standardization of NH_4SCN titrant (Manual method)

Preparation and standardization of $AgNO_3$ Solution

This solution was prepared and standardizaed exactly as outlined in Table 1-B. The standard value was found to be:-

$$M\ AgNO_3 = 0.1329^1 \pm 0.0007^2$$

Preparation and standardization of NH_4SCN solution (manual method)

15.2240 ± 0.0002 g of reagent-grade NH_4SCN was dissolved in 500 ml of distilled water and diluted to exactly 2 liters in a volumetric flask.

200 g of $(NH_4)_2SO_4.Fe_2(SO_4)_3$ was added to 200 ml of distilled water containing 20 ml of concentrated sulphuric acid. The mixture was stirred to equilibrate. Undissolved salt was decanted and filtered off. This is a saturated solution of ferric ammonium sulphate.

10.00 ± 0.01 ml of $0.1329^1 \pm 0.0007^2$M $AgNO_3$ was pipetted and diluted to 120 ml with distilled water. 30.0 ml of 1:1 H_2SO_4 was added and then 3 ml of saturated ferric ammonium sulphate solution. The solution was cooled and titrated with the NH_4SCN titrant to the first permanent pink colour. Shaking was vigorous near the endpoint.

Vol. NH_4SCN (ml ± 0.02)	M NH_4SCN
11.22	0.118458....
11.18	0.118881....
11.26	0.118037....

Average M NH_4SCN = 0.118458....
Std. devn. = ± 0.000422....

M NH_4SCN = $0.1184^5 \pm 0.0004^2$

TABLE 2-F

Determination of silver in commercial cyanide silver plating solutions (Manual method)

5.00 ± 0.01 ml of eacg plating solution was pipetted into a 300 ml Erlenmeyer flask. 20.0 ± 0.1 ml of concentrated sulphuric acid was added and the solution was boiled. Solutions which turned a brown or black colour were treated with 1 ml of concentrated HNO_3 (sample numbers 2, 5 and 8). The solution was then evaporated to dense white

fumes of SO_3. If the dark colour persists, additional (1 ml) HNO_3 is added after cooling the solution somewhat, and the solution is re-evaporated. Evaporation was finally continued to copious SO_3 fumes and to the solution of any solids. The solution was cooled and diluted to 150 ml with distilled water, 3.0 ± 0.1 ml of saturated ferric ammonium sulphate solution was added and the titration with $0.1184^5 \pm 0.0004^2$M NH_4SCN carried out with vigorous shaking to the first permanent pink colour.

The value for silver was calculated from:-

$$\text{silver, troy oz/US gal} = \frac{V\ NH_4SCN \times M\ NH_4SCN \times 107.87 \times 3785.306}{1000 \times 5.00 \times 31.103}$$

where:-

3785.306 = ml/US gal
31.103 = g/oz
107.87 = GAW Ag

$$\text{silver, troy oz/US gal} = V\ NH_4SCN \times M\ NH_4SCN \times 2.62^5$$

Sample No.	Vol. NH_4SCN (ml ± 0.02)	Silver (troy oz/US gal) as det.	Ave. ± s	Silver, troy oz/US gal) Canadian Hanson
1.	10.95	3.41		3.3
	10.42	3.25	$3.2^9 \pm 0.1^0$	
	10.35	3.22		
2.	16.48	5.13		5.4
	16.52	5.15	5.12 ± 0.03	
	16.35	5.09		
3.	10.40	3.24		3.1
	10.12	3.15	3.18 ± 0.05	
	10.15	3.16		
4.	1.40	0.44		0.28
	1.35	0.42	0.43 ± 0.01	
	1.35	0.42		
5.	14.05	4.37		4.7
	13.95	4.35	4.35 ± 0.02	
	13.90	4.33		
6.	3.60	1.12		0.9
	3.55	1.11	1.09 ± 0.04	
	3.35	1.04		
7.	10.32	3.22		3.3
	10.28	3.20	3.21 ± 0.01	
	10.28	3.20		
8.	13.05	4.07		4.5
	13.05	4.07	4.07 ± 0.00	
	13.05	4.07		

9.	8.00	2.49		2.7
	8.05	2.51	2.50 ± 0.01	
	8.05	2.51		
10.	10.56	3.29		3.5
	10.48	3.26	3.27 ± 0.02	
	10.45			

TABLE 3-F

Standardization of NH_4SCN titrant (E436A method)

The solutions were prepared and titrated exactly as outlined in Table 1-F, except that no indicator was added. Stirring by magnetic stirrer was kept vigorous during each titration.

The E436A unit was set in the potential mode, with full-scale deflection at 500 mV. A combination silver - Ag/AgCl (sat. KNO_3) electrode was used and the scale range was set at 0 to + 500 mV. The unit was set in the variable titrant delivery mode and full titration curves, to well beyong the equivalence point, were obtained. Each curve was analyzed by the tangential method to locate the equivalence point or endpoint potential and volume. In addition, each curve was analyzed to determine the Ecell at ± 0.5 ml around the endpoint volume.

Vol. NH_4SCN (ml ± 0.02)	M NH_4SCN	E (mV) - 0.5	eq. pt.	+ 0.5	ΔE ± 0.5 (mV)
11.28	0.117828..	+ 400	+ 239	+ 100	± 150
11.23	0.118352..	+ 400	+ 241	+ 100	± 150
11.22	0.118458..	+ 400	+ 240	+ 100	± 150

Average M NH_4SCN = 0.118212...
Std. devn. = ± 0.000337...

M NH_4SCN = $0.1182^1 \pm 0.0003^3$

The theoretical value for Ecell 0.5 ml before the equivalence point is given by:-

$$[Ag^+] = \frac{(10\text{ ml} \times 0.1329\text{M}) - (10.7\text{ ml} \times 0.1182\text{M})}{160\text{ ml}}$$

$$= 3.9 \times 10^{-4}\text{M}$$

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 3.9 \times 10^{-4}\text{M}$$
$$= 0.800 - 0.201$$
$$= 0.599\text{ V}$$

$$\text{Ecell} = 0.599 - 0.200\text{ (ref,)} = 0.399\text{V} = 399\text{ mV}$$

At the equivalence point we have:-

$$[Ag^+] = \sqrt{Ksp(AgSCN)} = \sqrt{1.07 \times 10^{-12}} = 1.03 \times 10^{-6}M$$

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 1.03 \times 10^{-6}M$$
$$= 0.800 - 0.353$$
$$= 0.447 \text{ V}$$

$$Ecell = 0.447 - 0.200 \text{ (ref.)}$$
$$= 0.247 \text{ V} = 247 \text{ mV}$$

At the point 0.5 ml after the equivalence point we have:-

$$[Ag^+] = \frac{Ksp(AgSCN)}{[SCN^-]} = \frac{1.07 \times 10^{-12}}{(0.5 \text{ ml} \times 0.1182M)/161 \text{ ml}}$$

$$= 2.9 \times 10^{-9}M$$

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 2.9 \times 10^{-9}M$$
$$= 0.800 - 0.504$$
$$= 0.296 \text{ V}$$

$$Ecell = 0.296 - 0.200 \text{ (ref.)} = 0.096 \text{ V} = 96 \text{ mV}$$

All values are in good agreement with the experimental values found.

TABLE 4-F

Determination of silver in commercial cyanide silver plating solutions (E436A method)

The solution preparation was exactly as outlined in Table 2-F, except that no indicator was added prior to titration under vigorous stirring with $0.1182^1 \pm 0.00033M$ NH_4SCN.

The E436A titrator was set-up and operated exactly as outlined in Table 3-F.

The values for silver were calculated from the equation shown in Table 2-F.

Sample No.	Vol. NH_4SCN (ml ± 0.02)	Ag (troy oz/US gal) as det.	Ave. ± s	Han.	E (mV) − 0.5	eq. pt.	+ 0.5	ΔE for ± 0.5 ml
1.	11.25	3.50		3.3	+ 440	+ 244	+ 120	+ 160
	11.25	3.50	3.45 ± 0.09		+ 440	+ 238	+ 120	± 160
	10.78	3.35			+ 440	+ 238	+ 120	± 160
2.	17.25	5.36		5.4	+ 440	+ 242	+ 120	± 160
	16.95	5.27	5.34 ± 0.06		+ 450	+ 240	+ 110	± 170
	17.38	5.40			+ 440	+ 240	+ 120	± 160
	17.11	5.32			+ 440	+ 242	+ 120	± 160
3.	10.25	3.19		3.1	+ 450	+ 240	+ 120	± 165
	10.25	3.19	3.20 ± 0.01		+ 450	+ 240	+ 120	± 165

	10.32	3.21			+ 440	+ 240	+ 120	± 160
4.	1.24	0.39		0.28	+ 420	+ 250	+ 100	± 160
	1.54	0.48	0.45 ± 0.05		+ 420	+ 248	+ 100	± 160
	1.51	0.47			+ 420	+ 248	+ 100	± 160
5.	14.00	4.35		4.7	+ 440	+ 238	+ 100	± 170
	14.05	4.37	4.36 ± 0.02		+ 440	+ 238	+ 100	± 170
	14.12	4.39			+ 440	+ 238	+ 100	± 170
	14.00	4.35			+ 440	+ 238	+ 100	± 170
6.	3.62	1.12		0.9	+ 400	+ 242	+ 110	± 145
	2.75	0.85	0.94 ± 0.15		+ 400	+ 242	+ 100	± 150
	2.75	0.85			+ 400	+ 240	+ 110	± 145
7.	10.51	3.27		3.3	+ 440	+ 240	+ 105	± 167
	10.60	3.30	3.28 ± 0.02		+ 440	+ 242	+ 105	± 167
	10.50	3.26			+ 440	+ 244	+ 105	± 167
8.	13.50	4.20		4.5	+ 420	+ 240	+ 90	± 165
	13.67	4.25	4.22 ± 0.03		+ 420	+ 240	+ 90	± 165
	13.50	4.20			+ 420	+ 241	+ 90	± 165
9.	8.25	2.56		2.7	+ 420	+ 241	+ 95	± 162
	8.28	2.57	2.56 ± 0.01		+ 420	+ 242	+ 95	± 162
	8.25	2.56			+ 420	+ 240	+ 96	± 162
10.	10.42	3.24		3.5	+ 420	+ 239	+ 100	± 160
	10.67	3.32	3.29 ± 0.04		+ 420	+ 239	+ 98	± 161
	10.62	3.30			+ 420	+ 239	+ 100	± 160

Average Ecell (- 0.5 ml) = 429 mV
Average Ecell eq. pt. = 241 mV
Average Ecell (+ 0.5 ml) = 105 mV
Average ΔE (± 0.5 ml) = ±162 mV

The theoretical value for Ecell 0.5 ml before the equivalence point is given, for a pretitration solution involving 4.7 troy oz silver/US gal:-

4.7 troy oz/US gal and 5 ml of solution taken.

$$\frac{4.7 \times 31 \times 5}{3785 \times 107.87} = 0.00178 \text{ mol Ag}$$

This will require about 15.10 ml of 0.1182M NH_4SCN for equivalence. The starting volume is 150 ml and the starting molarity for Ag^+ is therefore 0.0119. At 0.5 ml before the equivalence point we have:-

$$[Ag^+] = \frac{(150 \text{ ml} \times 0.0119\text{M}) - (14.6 \text{ ml} \times 0.1182\text{M})}{164.6 \text{ ml}}$$

$$= 3.6 \times 10^{-4}\text{M}$$

$$E_{Ag^+/Ag} = 0.800 + 0.059 \log 3.6 \times 10^{-4}\text{M}$$
$$= 0.800 - 0.203$$
$$= 0.597 \text{ V}$$

$$E_{cell} = 0.597 - 0.200 \text{ (ref.)} = 0.397 \text{ V} = 397 \text{ mV}$$

At the equivalence point we have the same situation as calculated for this point in Table 3-F, and the theoretical equivalence point Ecell is given as 247 mV.

At the point 0.5 ml after the equivalence point we have, again, the same situation outlined for this point in Table 3-F, and the Ecell at this point is given as 96 mV.

Generally speaking, the experimental averages and the theoretical values are in good agreement.

TABLE 5-F

Standardization of NH_4SCN titrant (E526 assembly method)

The solution preparation was exactly as outlined in Table 1-F, except that no indicator was added. The automatic stirrer of the E526 was adjusted to a speed high enough to give vigorous stirring during the titration with NH_4SCN titrant.

The E526 unit was placed in the potential mode at "+ mV", and in the "calibration" position. The electrode connections were shorted with the EA854-2B/10 shorting cable. The digital readout was set at "0000" mV, and the zero balance indicator needle was set at the exact center line with the countervoltage control. The shorting cable was then removed.

A combination silver-Ag/AgCl (sat. KNO_3) electrode was used as the electrode couple. The titration direction was set for " + mV", for decreasing mV during the titration, and at the " + mV" starting Ecell position. In accordance with the data indicated in Table 3-F, a preset dead-stop potential of + 240 mV was set. Again, in accordance with Table 3-F data, which showed a ΔE range of 300 mV (± 150 mV), for ± 0.5 ml around the equivalence point volume, the large ΔE increment for high $\Delta E/\Delta V$ changes around this point was selected.

Initial titrations were carried out using additions of saturated ferric sulphate indicator, and it was noted that some minor tendency to under-titrate was obtained with the dead-stop potential set at + 240 mV. Over-riding the automatic controls until the indicator changed colour finally demonstrated that the optimum dead-stop potential setting was + 200 mV. Again it can be assumed that titration conditions and/or instrumental response situations, in association with the E436A and E526 units, underlie the difference between the + 240 and + 200 mV settings.

The final titrations were carried out at a preset dead-stop potential of ± 200 mV. These final titrations, four in all, involved 4 beakers

in one magazine, sequential and automatic titration and programmed bypassing of the pretitration additions stops.

Printout vol. (ml)	M NH_4SCN
11.29	0.117723...
11.33	0.117308...
11.27	0.117932...
11.28	0.117828...

Average M NH_4SCN = 0.11769...
Std. devn. = ± 0.00027...

M NH_4SCN = $0.1176^9 \pm 0.0002^7$

TABLE 6-F

Determination of silver in commercial cyanide silver plating solutions (E526 assembly method)

The solution preparation was exactly as outlined in Table 2-F, except that no indicator was added before titration with $0.1176^9 \pm 0.0002^7$M NH_4SCN. Vigorous stirring during titration was obtained by increasing the speed of the automatic stirrer.

The E526 unit was set-up and operated exactly as outlined in Table 5-F. As indicated in the data for this table, an optimum dead-stop potential of + 200 mV was found necessary, this as opposed to the indicated value of 241 mV. This situation was also found for the silver determination titrations.

Five 10.00 ml samples of standard $AgNO_3$ solution, properly diluted, were interspersed between the commercial bath samples, and it was expected that the volume values for these standards would indicate the stability of the E526 settings and the electrode couple used.

36 beakers were therefore racked in 9 magazines, and these were then titrated sequentially and automatically. Since no pretitration additions were required, the pretitration stops were bypassed by programming arrangement. Total elapsed time from program initiation approximated 1.5 hours. Calculations were by Table 2-F equation.

Sample No.	Printout vol. (ml)	Silver, (troy oz/US gal) as det.	Ave ± s	Silver (troy oz/US gal) Canadian Hanson
1.	10.34	3.20		3.3
	10.42	3.22	3.21 ± 0.01	
	10.42	3.22		

2.	16.42	5.08		5.4
	16.93	5.24	5.14 ± 0.08	
	16.50	5.11		
Std.	11.29			
3.	9.86	3.05		3.1
	9.96	3.08	3.05 ± 0.02	
	9.80	3.03		
4.	1.54	0.48		0.28
	1.37	0.42	0.45 ± 0.03	
	1.39	0.43		
	1.49	0.46		
Std.	11.30			
5.	13.40	4.15		4.7
	13.52	4.18	4.17 ± 0.02	
	13.46	4.17		
6.	3.29	1.02		0.9
	3.33	1.03	1.04 ± 0.04	
	3.45	1.07		
7.	10.72	3.32		3.3
	10.52	3.26	3.28 ± 0.03	
	10.53	3.26		
Std.	11.30			
8.	12.97	4.01		4.5
	13.40	4.15	4.11 ± 0.09	
	13.48	4.17		
Std.	11.27			
9.	8.46	2.62		2.7
	8.50	2.63	2.67 ± 0.08	
	8.96	2.77		
10.	10.16	3.14		3.5
	10.13	3.14	3.16 ± 0.03	
	10.31	3.19		
Std.	11.31			

APPENDIX G

TABLE 1-G

Preparation and standardization of H_2SO_4 titrant (Manual method)

Preparation and standardization of standard NaOH solution

The potassium acid phthalate solution prepared for Table 1-E was used in the standardization of the NaOH solution.

$$M\ KHP = 0.43097^5 \pm 0.00006^4$$

About 40 g of reagent-grade NaOH was dissolved in distilled water and diluted to exactly 1 liter in a volumetric flask.

50.00 ± 0.02 ml of KHP solution was pipetted into a 250 ml Erlenmeyer flask, and 5 drops of 0.1% phenolphthalein indicator solution were added. Titration with prepared NaOH solution was carried out to the first pink colour.

Vol. NaOH (ml ± 0.02)	M NaOH
21.40	1.00695.....
21.40	1.00695.....
21.40	1.00695.....

Average M NaOH = 1.00695...
Std. devn. = ± 0.00000...

$$M\ NaOH = 1.006^9 \pm 0.000^0$$

Preparation and standardization of H_2SO_4 titrant

About 65 ml of concentrated sulphuric acid was dissolved in 1000 ml of distilled water and diluted, after cooling, to exactly 2 liters in a volumetric flask.

20.00 ± 0.02 ml of this H_2SO_4 solution was pipetted into a 250 ml Erlenmeyer flask and diluted with 25 ml of distilled water. 5 drops of 0.1% bromothymol blue indicator (70% alcohol) were added, and titration with standard NaOH solution was carried out to the first blue colour shift from yellow.

Vol. NaOH (ml ± 0.04)	M H_2SO_4
22.45	0.56512...
22.45	0.56512...
22.45	0.56512...

Average M H_2SO_4 = 0.56512..
Std. devn. = ± 0.00000..

M H_2SO_4 = $0.565^1 \pm 0.000^0$

TABLE 2-G

Determination of total alkali as NaOH in commercial alkaline zinc cyanide plating solutions (Manual method)

10.00 ± 0.02 ml of agitated alkaline zinc cyanide plating solution was pipetted into the appropriate vessel. Agitation was applied to ensure the dissolving of any settled residue. 1 g of solid NaCN was added and the solution swirled to dissolve. 8 drops of Lamotte or Fisher sulfo-orange indicator were added, and the solution was titrated with 0.565^1M H_2SO_4 until the orange colour changed to a yellow with a greenish tinge.

$$\text{Total alkali as NaOH (oz/US gal)} = \frac{V\ H_2SO_4 \times M\ H_2SO_4 \times 2 \times 40.00 \times 3785.306}{1000 \times 10.00 \times 28.349}$$

where:-

3785.306 = ml/US gal
28.349 = g/oz
40.00 = GMW NaOH

$$\text{Total alkali as NaOH (oz/US gal)} = V\ H_2SO_4 \times M\ H_2SO_4 \times 1.06^8$$

Sample No.	Vol. H_2SO_4 (ml ± 0.04)	NaOH (oz/US gal) as det.	NaOH (oz/US gal) ave ± s	NaOH (oz/US gal) Canadian Hanson
1.	16.50	9.97		10.5
	16.47	9.95	9.97 ± 0.01	
	16.50	9.97		
2.	8.90	5.38		6.4
	8.80	5.32	5.36 ± 0.03	
	8.90	5.38		
3.	20.00	12.09		12.5
	20.10	12.15	12.11 ± 0.03	
	20.00	12.09		
4.	7.00	4.23		5.4
	7.10	4.29	4.27 ± 0.04	
	7.10	4.29		
5.	16.00	9.67		10.4
	16.00	9.67	9.69 ± 0.03	
	16.10	9.73		

6.	15.60	9.43		10.9
	15.70	9.49	9.45 ± 0.03	
	15.60	9.43		
7.	15.00	9.07		9.8
	15.10	9.13	9.09 ± 0.04	
	15.00	9.07		
8.	12.60	7.61		8.1
	12.70	7.67	7.63 ± 0.03	
	12.60	7.61		
9.	15.00	9.07		9.6
	14.90	9.01	9.03 ± 0.03	
	14.90	9.01		
10.	11.00	6.65		7.3
	11.20	6.77	6.71 ± 0.06	
	11.10	6.71		

TABLE 3-G

Standardization of H_2SO_4 titrant (E436A method)

The solution preparation was identical to that outlined in Table 1-G, but no indicator was added.

The E436A titrator was set in the pH mode with a full-scale deflection at 14pH. A combination glass - Ag/AgCl (3M KCl) electrode couple was used, and calibration against a 7.00 pH buffer solution was carried out. The variable titrant delivery mode was applied and full titration curves to well beyond the equivalence point were obtained. These were analyzed by the circle fit method to locate the equivalence point volume and pH values. The curves were also analyzed to locate the values of pH for ± 0.5 ml around the equivalence point volume.

Vol. NaOH (ml ± 0.02)	M H_2SO_4	pH - 0.5	eq. pt.	+ 0.5	ΔpH ± 0.5 ml
22.46	0.56537...	1.80	6.94	12.08	± 5.14
22.54	0.56738...	1.80	6.94	12.06	± 5.13
22.54	0.56738...	1.80	6.94	12.16	± 5.18

Average M H_2SO_4 = 0.56671...
Std. devn. = ± 0.00113...

M H_2SO_4 = $0.566^7 \pm 0.001^1$

The theoretical pH values for the critical points in titration around

the equivalence point are calculated from:-

0.5 ml before the equivalence point:-

$$[H_3O^+] = \frac{(20\ ml \times 0.5667M) - (0.5 \times 22\ ml \times 1.0069M)}{32\ ml}$$

$$= 8 \times 10^{-3}M \qquad pH = 2.1$$

At the equivalence point:- pH = 7.0 (strong acid vs strong base)

0.5 ml after the equivalence point:-

$$[OH^-] = \frac{(23\ ml \times 1.0069M) - (2 \times 20\ ml \times 0.5667M)}{33\ ml}$$

$$= 1.5 \times 10^{-2} \qquad pH = 12.2$$

All experimental and theoretical pH values agree well.

TABLE 4-G

Determination of total alkali as NaOH in alkaline zinc cyanide plating solutions (E436A method)

The solution preparations were carried out exactly as outlined in Table 2-G except that no indicator was added. Titration involved the $0.566^7 \pm 0.001^1$M H_2SO_4 solution.

The E436A titrator was set-up and operated exactly as outlined in Table 3-G, with the exception that an 11.00 buffer solution was used for calibration purposes.

All calculations of total alkali as NaOH were made using the equation shown in Table 2-G.

Sample No.	Vol. H_2SO_4 (ml ± 0.02)	NaOH (oz/US gal) as det.	ave. ± s	pH − 0.5	eq. pt	+ 0.5	± ΔpH ± 0.5 ml
1.	16.42	9.94		11.80	11.20	10.80	0.50
	16.52	10.01	9.97±0.06	11.92	11.25	10.41	0.76
	16.55	10.03		11.72	11.25	10.60	0.56
2.	8.90	5.39		12.02	11.25	10.70	0.66
	8.73	5.29	5.34±0.05	12.02	11.30	10.70	0.66
	8.77	5.31		12.02	11.25	10.70	0.66
3.	19.80	12.00		11.90	11.10	10.40	0.75
	19.95	12.09	$12.1^8 \pm 0.2^2$	11.90	11.20	10.55	0.68
	20.50	12.43		11.92	11.25	10.45	0.74
4.	7.30	4.42		11.90	11.31	10.50	0.70
	7.15	4.33	4.36±0.06	11.75	11.31	10.50	0.63
	7.10	4.30		11.30	11.31	10.45	0.68

5.	15.80	9.57		12.00	11.20	10.60	0.70
	15.90	9.64	9.60±0.03	11.90	11.20	10.60	0.65
	15.80	9.57		11.90	11.20	10.60	0.65
6.	15.55	9.42		11.90	11.31	10.74	0.58
	15.55	9.42	9.42±0.02	11.90	11.31	10.75	0.57
	15.50	9.41		11.95	11.31	10.75	0.60
7.	14.80	8.97		11.84	11.31	10.78	0.58
	14.70	8.91	8.93±0.04	11.92	11.31	10.78	0.62
	14.70	8.91		12.00	11.31	10.80	0.67
8.	12.80	7.76		12.02	11.32	10.71	0.66
	12.75	7.73	7.74±0.02	12.00	11.31	10.75	0.66
	12.75	7.73		11.95	11.31	10.76	0.60
9.	15.00	9.09		11.89	11.31	10.78	0.56
	14.95	9.06	9.04±0.06	12.00	11.31	10.79	0.62
	14.80	8.97		11.90	11.31	10.70	0.53
10.	11.15	6.76		12.00	11.31	10.78	0.51
	11.10	6.73	6.74±0.02	11.96	11.31	10.76	0.48
	11.10	6.73		11.99	11.31	10.78	0.50

Ave. pH 0.5 ml before eq. pt. = 11.9 ± 0.1
Ave. Eq. pt. pH = 11.2 ± 0.1
Ave. pH 0.5 ml after eq. pt. = 10.7 ± 0.1
Ave. ± ΔpH (± 0.5 ml) = ± 0.6

A palting solution containing 10 oz NaOH/US gal is used as an example in calculating the theoretical pH values for the critical titration points. The starting volume is 10 ml, so that the starting molarity of NaOH is given by:-

$$\frac{10\text{ml} \times 28 \times 10\text{oz} \times 1000}{3785 \times 40 \times 10\text{ml}} = 1.849\text{M}$$

The amount of 0.5667M H_2SO_4 required to reach the equivalence point will then be:-

$$(10\text{ ml} \times 1.849\text{M})/(2 \times 0.5667\text{M}) = 16.3\text{ ml}$$

With the added 1 g of NaCN, omitting any other contribution, we have:-

at the start 2.0M NaCN at eq. pt. 0.775M NaCN

At 0.5 ml before the eq. pt.:-

$$[OH^-] = \frac{(10\text{ml} \times 1.849\text{M}) - (15.8\text{ml} \times 2 \times 0.5667\text{M})}{25.8\text{ ml}}$$

$$= 2.2 \times 10^{-2} \qquad pH = 12.3$$

At the equivalence point:-

$$[H_3O^+] = \sqrt{\frac{KwKa(HCN)}{C(NaCN)}} = \sqrt{\frac{10^{-14} \times 5 \times 10^{-10}}{(1/49) \times 1000/26.3\text{ml}}} = 2.5 \times 10^{-12}$$

$$pH = 11.6$$

At 0.5 ml after the equivalence point:-

$$[H_3O^+] = \frac{Ka(HCN) \times C(HCN)}{C(NaCN)} =$$

$$= \frac{5 \times 10^{-10} \times (0.5\ ml \times 2 \times 0.5667M)}{(26.3ml \times 0.775M) - (0.5ml \times 2 \times 0.5667M)}$$

$$= 1.4 \times 10^{-11} M$$

$$pH = 10.8$$

TABLE 5-G

Standardization of H_2SO_4 titrant (E526 assembly method)

Solution preparation was exactly as outlined in Table 1-G, except that no indicator was added and 50 ml of dilution water was added.

The E526 unit was set in the pH mode and was operated and calibrated exactly as outlined in Table 5-E.

Printout vol. (ml)	M H_2SO_4
22.57	0.568143..
22.57	0.568130..
22.68	0.570912..
22.52	0.566884..

Average M H_2SO_4 = 0.568520..
Std. devn. = ± 0.001701..

M H_2SO_4 = $0.568^5 \pm 0.001^7$

TABLE 6-G

Determination of total alkali as NaOH in commercial alkali zinc cyanide plating solutions (E526 assembly method)

The sample solutions were prepared exactly as outlined in Table 2-G, except that no indicator was added and, in place of the 1 g addition of solid NaCN, 50 ml of a 2% solution of NaCN was added. This extra volume was necessitated by the volume requirement for the E526 beakers.

The E526 was set-up and operated exactly as outlined in Table 5-E with the following exceptions. The final calibration was made against an 11.00 pH buffer solution, the preset dead-stop pH was set at 11.20 in accordance with the findings of Table 4-G and a pretitration addition stop was arranged for the addition of the 50 ml of 2% NaCN solution. The 30 beakers were arranged in 8 magazines and the titrations were

carried out, including the pretitration addition, sequentially and automatically in about 1.25 hours.

Sample No.	Printout vol. (ml)	NaOH (oz/US gal) as det.	NaOH (oz/US gal) ave. ± s	NaOH (oz/US gal) Canadian Hanson
1.	16.40	9.97	9.91 ± 0.08	10.5
	16.20	9.85		
	lost			
2.	9.28	5.64		6.4
	9.15	5.56	5.56 ± 0.08	
	9.00	5.47		
3.	20.06	12.20		12.5
	20.08	12.21	12.16 ± 0.07	
	19.86	12.08		
4.	7.56	4.59		5.4
	7.40	4.50	4.53 ± 0.06	
	7.39	4.49		
5.	16.10	9.79		10.4
	16.13	9.81	9.79 ± 0.02	
	16.08	9.78		
6.	15.76	9.58	9.56 ± 0.02	10.9
	15.71	9.55		
	lost			
7.	15.02	9.12		9.8
	15.04	9.14	9.15 ± 0.03	
	15.10	9.18		
8.	12.93	7.86		8.1
	12.36	7.82	7.82 ± 0.04	
	12.82	7.79		
9.	15.01	9.13		9.6
	14.93	9.08	9.12 ± 0.04	
	15.07	9.16		
10.	11.28	6.86		7.3
	11.28	6.86	6.86 ± 0.00	
	11.28	6.86		

APPENDIX H

TABLE 1-H

Preparation and standardization of EDTA solution (Manual method)

Industry method

40 g of reagent-grade NaCN was dissolved in 500 ml of distilled water. 28.0000 ± 0.0002 g of dried (120°C) reagent-grade ZnO was added and dissolved in this solution. Dilution to exactly 1 liter was carried out in a volumetric flask.

Value: 22.49 g Zn/liter
= 0.34410 ± 0.00005M Zn

37.2 g of disodium dihydrate EDTA was dissolved in 500 ml of distilled water and diluted to exactly 1 liter in a volumetric flask.

0.2 g of solid Eriochrome black T was ground with 100 g reagent-grade NaCl.

2.00 ± 0.01 ml of the standard zinc solution was pipetted and diluted with 100 ml of distilled water. The analytical steps outlined for the industrial method were then carried out. 3 drops of 0.04% (aq.) thymol blue indicator was added and the solution titrated dropwise with 0.5M H_2SO_4 until a yellow endpoint was obtained. 25.0 ml of a buffer solution (50 g NH_4Cl and 400 ml of concentrated NH_3 per liter) was added followed by 0.3 g of Eriochrome black T indicator. 10.0 ml of 5% formaldehyde was added and the solution was titrated with the prepared EDTA solution to a blue endpoint.

Vol. EDTA (ml ± 0.02)	M EDTA
7.66	0.089843...
7.64	0.090078...
7.65	0.089960...

Average M EDTA = 0.089960...
Std. devn. = ± 0.000117...

M EDTA = $0.0899^6 \pm 0.0001^1$

As a precautionary measure, the EDTA solution was also standardized in a more general technique.

A zinc solution was prepared by dissolving 6.5370 ± 0.0002 g of pure zinc in 30 ml of concentrated HNO_3. The oxides of nitrogen were expelled by boiling, and the solution was cooled and diluted to exactly 1 liter in a volumetric flask.

Value:- $0.10001^{5} \pm 0.00003^{0}$ M Zn

10.00 ± 0.02 ml of this solution was pipetted and diluted with 50 ml of distilled water. The pH value was tested at about 3.0. 25.0 ml of 0.5M NH_3/0.5M NH_4Cl buffer solution was added, and the resulting solution pH was about 10.0. 0.3 g of Eriochrome black T indicator was added, 10 ml of 5% formaldehyde was added and the solution was titrated with the EDTA solution.

Vol. EDTA (ml ± 0.02)	M EDTA
11.12	0.089942...
11.12	0.089942...
11.15	0.089700...

Average M EDTA = 0.089861...
Std. devn. = ± 0.00013....

M EDTA = $0.0898^{6} \pm 0.0001^{3}$

It will be noted that the two molarity values as averages agreed very closely.

TABLE 2-H

Determination of zinc in commercial alkali zinc cyanide plating solutions (Manual method)

The solution preparation was exactly as outlined in Table 1-H covering the industry technique, except that 10 ml of 2:1 NH_3 and 25 ml of 0.5M NH_3/0.5M NH_4Cl buffer solution was added, providing the same total NH_3 as the industry technique. The titrant applied was the EDTA solution at a molarity of $0.0898^{6} \pm 0.0001^{3}$.

The zinc contents were calculated from:-

$$\text{Zn oz/US gal} = \frac{\text{V EDTA} \times \text{M EDTA} \times 65.37 \times 3785.306}{1000 \times 2.00 \times 28.349}$$

$$= \text{V EDTA} \times \text{M EDTA} \times 4.36^{3}$$

Sample No.	Vol. EDTA (ml ± 0.02)	Zn (oz/US gal) as det.	Zn (oz/US gal) ave. ± s	Zn (oz/US gal) Canadian Han.
1.	12.40	4.86		4.9
	12.37	4.85	4.87 ± 0.03	
	12.50	4.90		
2.	3.31	1.30		1.3
	3.37	1.32	1.31 ± 0.01	
	3.36	1.32		

3.	2.30	0.90		0.9
	2.34	0.92	0.92 ± 0.02	
	2.37	0.93		
4.	4.95	1.94		1.9
	4.92	1.93	1.94 ± 0.01	
	4.95	1.94		
5.	3.84	1.50		1.5
	3.86	1.51	1.51 ± 0.01	
	3.85	1.51		
6.	4.49	1.76		1.8
	4.46	1.75	1.75 ± 0.01	
	4.46	1.75		
7.	5.05	1.98		2.0
	5.15	2.02	2.00 ± 0.02	
	5.10	2.00		
8.	12.70	4.98		5.1
	12.78	5.01	4.99 ± 0.02	
	12.73	4.99		
9.	3.86	1.51		1.5
	3.86	1.51	1.51 ± 0.00	
	3.86	1.51		
10.	5.05	1.98		2.0
	5.05	1.98	1.98 ± 0.00	
	5.06	1.98		

TABLE 3-H

Standardization of EDTA titrant (E436A method using Cu(II)-EDTA indicating solution and Cu(II) ion-selective electrode)

Preparation of Cu(II)-EDTA indicating solution

20.00 ± 0.02 ml of 0.10000 ± 0.00005M Cu(II) solution was diluted with 20 ml of distilled water and 20.00 ± 0.02 ml of 0.5M NH_3/0.5M NH_4Cl buffer solution was added. The solution was tested for pH and titrated with $0.0898^6 \pm 0.0001^3$M EDTA solution.

The E436A titrator was set-up and operated exactly as outlined in Table 2-C.

pH at start	Vol. EDTA (ml ± 0.02)	E (mV) − 0.5	E (mV) eq. pt.	E (mV) + 0.5	± ΔE mV ± 0.5 ml	calc. M EDTA
9.8	22.18	− 283	− 348	− 403	60	0.09017
9.7	22.20	− 294	− 356	− 412	59	0.09009
9.8	22.16	− 284	− 350	− 404	60	0.09025

The average volume of EDTA consumed was 22.18 ml.

10.00 ± 0.02 ml of the Cu(II) solution was now taken and diluted with 20 ml of distilled water. 20.00 ± 0.02 ml of 0.5M NH_3/0.5M NH_4Cl buffer

was added. 10.55 ± 0.02 ml of EDTA solution was now added (95% of the equivalence point volume average of 22.18 ml divided by 2), and this solution was diluted to exactly 100 ml in a volumetric flask. The total copper content was given by:-

1 ml = 0.000635 g toral Cu

Stabdardization of EDTA solution (E436A method using Cu(II) indicating solution and Cu(II) ion-selective electrode)

10.00 ± 0.02 ml of $0.10001^5 \pm 0.00003^0$M zinc solution was diluted to 60 ml with distilled water. 25.00 ± 0.04 ml of 0.5M NH_3/0.5M NH_4Cl buffer was added. This solution now contained 0.0653 g of zinc. 5.00 ± 0.01 ml of Cu(II)-EDTA indicating solution was now added; giving a total copper content of 0.00318 g, and a copper:zinc ratio of about 4.8% (limits 1% to 10%). The tested solution pH at this point was 9.9. Titration was carried out with EDTA solution.

The E436A titrator was set-up and operated as shown in Table 2-C.

Vol. EDTA (ml ± 0.02)	E (mV) - 0.5	eq. pt.	+ 0.5	± ΔE (mV) ± 0.05 ml	M EDTA
10.85	- 178	- 210	- 230	± 26	0.092179...
10.95	- 177	- 208	- 231	± 27	0.091337...
11.00	- 164	- 220	- 242	± 28	0.090922...
10.90	- 186	- 216	- 238	± 26	0.091756...

Average M EDTA = 0.09154...
Std. devn. = ± 0.00054...

M EDTA = $0.0915^4 \pm 0.0005^4$

TABLE 4-H

Determination of zinc in commercial alkali zinc cyanide plating solutions (E436A method using Cu(II)-EDTA indicating solution, etc.)

The preparation of the plating solutions was exactly as outlined in Table 2-H, but Cu(II) indicating solution was added instead of the normal indicator. The volume of Cu(II)-EDTA solution added was 2.00 ± 0.01 ml. This yielded a total copper content of 0.00127 g. Since the plating solutions varied in zinc from 0.9 to 5.1 oz/gal (0.0133 to 0.0754 g in the pretitration solution), this represnted ratios of copper:zinc of 9.5% to 1.7%.

The E436A unit was set-up and operated exactly as shown in Table 2-C.

Sample No.	Vol. EDTA (ml ± 0.02)	Zn (oz/US gal) as det.	Zn (oz/US gal) ave. ± s	Zn(oz/US gal) Candn. Han.	E (mV) - 0.5	E (mV) eq. pt.	E (mV) + 0.5
1.	No electrode response			4.9			
2.	No worthwhile electrode response			1.3			
3.	6.00	2.38		0.9	- 189	- 198	- 203
	5.90	2.36	2.40±0.04		- 180	- 190	- 196
	6.10	2.44					
4.	No worthwhile electrode response			1.9			
5.	" " " "			1.5			
6.	" " " "			1.8			
7.	" " " "			2.0			
8.	No electrode response			5.1			
9.	No worthwhile electrode response			1.5			
10.	" " " "						

TABLE 5-H

Preparation and standardization of $K_4Fe(CN)_6$ solution (E436A method)

Preparation of standard zinc solution

6.5370 ± 0.0002 g of pure zinc dissolved in the minimum amount of 1:1 HCl (about 50 ml). An additional 10 ml of 1:1 HCl was added and the solution was diluted to exactly 1 liter in a volumetric flask.

Value:- 0.10000 ± 0.00003M Zn

Preparation of $K_3Fe(CN)_6$ solution (1%)

1.00 ± 0.02 g of reagent-grade $K_3Fe(CN)_6$ was dissolved in 50 ml of distilled water and diluted to 100 ml. This solution was prepared freshly as required.

Preparation of 0.1M $K_4Fe(CN)_6$ solution

84.0 g of reagent-grade $K_4Fe(CN)_6.3H_2O$ was dissolved in 700 ml of distilled water and diluted to exactly 2 liters in a volumetric flask.

20.00 ± 0.02 ml of standard zinc solution was pipetted and diluted with 80 ml of distilled water. 10 drops of 1% $K_3Fe(CN)_6$ solution were added and the solution was further treated by the addition of 5 ml of concentrated HCl. Titration was carried out with $K_4Fe(CN)_6$ solution.

The E436A titrator was set in the potential mode. A combination platinum-Ag/AgCl (3M KCl) electrode couple was attached. The unit was set for a full-scale deflection of 500 mV in a range of + 500 mV to 1000 mV. The variable titrant delivery mode was applied, and full titration curves to well beyond the equivalence point were obtained.

These curves were analyzed by the circle-fit method since the reaction is 3 moles Zn/2 moles $K_4Fe(CN)_6$. The equivalence point volume and Ecell were thus located. Each curve was also analyzed to locate the Ecell values for ± 0.5 ml around the equivalence point.

Vol. $K_4Fe(CN)_6$ (ml ± 0.02)	M $K_4FE(CN)_6$	E (mV) − 0.5	E (mV) eq. pt.	E (mV) + 0.5	ΔE (mV) ± 0.5 ml
12.10	0.110192...	760	536	340	± 210
12.10	0.110192...	740	524	342	± 199
12.15	0.109739...	760	536	350	± 205

Average M $K_4Fe(CN)_6$ = 0.110041...
Std. devn. = ± 0.000244...

M $K_4Fe(CN)_6$ = 0.1100 ± 0.0002

Average Ecell 0.5 ml before eq. pt. = 753 mV
Average Ecell at eq, pt. = 532 mV
Average Ecell 0.5 ml after eq. pt. = 344 mV

The theoretical values for Ecell at the critical titration points are:-

The addition of 10 drops of 1% $K_3Fe(CN)_6$, and the 112 ml total volume at the equivalence point, yield an equivalence point $[Fe(CN)_6^{3-}]$ of:-

$$[Fe(CN)_6^{3-}] = \frac{0.5 \text{ ml} \times 0.01\text{g/ml} \times 1000}{112 \text{ ml} \times 329.3}$$

$$= 1.35 \times 10^{-4}\text{M}$$

The starting molarity of of $[Zn^{2+}]$ is given by:-

$$[Zn^{2+}] = (20 \text{ ml} \times 0.1\text{M})/100 \text{ ml}$$
$$= 0.020\text{M}$$

At the point 0.5 ml before the equivalence point:-

$$[Zn^{2+}] = \frac{(100\text{ml} \times 0.02\text{M}) - (1.5 \times 11.6\text{ml} \times 0.11\text{M})}{111.6 \text{ ml}}$$

$$= 7.7 \times 10^{-4}\text{M}$$

$$[Fe(CN)_6^{4-}] = \sqrt{\frac{Ksp(K_2Zn_3[Fe(CN)_6]_2}{[Zn^{2+}]^3}} = \sqrt{\frac{1.8 \times 10^{-25}}{(7.7 \times 10^{-4}\text{M})^3}}$$

$$= 2.2 \times 10^{-8}\text{M}$$

$$E_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = 0.690 + 0.059 \log \frac{[Fe(CN)_6^{3-}]}{[Fe(CN)_6^{4-}]}$$

$$= 0.690 + 0.059 \log \frac{1.35 \times 10^{-4}}{2.2 \times 10^{-8}}$$

$$= 0.690 + 0.226 = 0.916 \text{ V}$$

$$\text{Ecell} = 0.916 - 0.200 \text{ (ref.)}$$
$$= 0.716 = 716 \text{ mV}$$

At the equivalence point:-

$$[Fe(CN)_6^{4-}] = \sqrt[5]{\frac{Ksp \times 8}{27}} = \sqrt[5]{\frac{1.8 \times 10^{-25} \times 8}{27}}$$

$$= 8.8 \times 10^{-6} M$$

$$E_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = 0.690 + 0.059 \log \frac{1.35 \times 10^{-4}}{8.8 \times 10^{-6}}$$

$$= 0.690 + 0.070 = 0.760 \text{ V}$$

$$\text{Ecell} = 0.760 - 0.200 \text{ (ref.)}$$
$$= 0.560 = 560 \text{ mV}$$

At the point 0.5 ml after the equivalence point:-

$$[Fe(CN)_6^{4-}] = \frac{(12.6\text{ml} \times 0.11\text{M}) - (100\text{ml} \times 0.02\text{M})}{112.6 \text{ ml}}$$

$$= 1.28 \times 10^{-2} M$$

$$E_{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}} = 0.690 + 0.059 \log \frac{1.35 \times 10^{-4}}{1.28 \times 10^{-2}}$$
$$= 0.690 - 0.116$$
$$= 0.574 \text{ V}$$

$$\text{Ecell} = 0.574 - 0.200 \text{ (ref.)}$$

$$= 0.374 \text{ V} = 374 \text{ mV}$$

The experimental and theoretical values agreed quite well.

TABLE 6-H

Determination of zinc in commercial alkali zinc cyanide plating solutions by titration with $K_4Fe(CN)_6$ (E436A method)

5.00 ± 0.01 ml of each plating solution was pipetted into a 250 ml beaker. In the fume hood, 5 ml of concentrated H_2SO_4 and 3 ml of concentrated HNO_3 were added, and the solution evaporated to dense white fumes of SO_3. If the solution still maintained a dark colour, an additional 1 ml of HNO_3 was added, and evaporation to dense SO_3 fumes again carried out. The solution was cooled and diluted with 100 ml of distilled water. 10 drops of 1% potassium fericyanide solution were added, and the solution titrated with 0.1100 m $K_4Fe(CN)_6$. These titration results were identified as "A".

It was realized that the $K_4Fe(CN)_6$ titration would yield high results in the presence of Fe^{3+} ions from the plating solution. Although preliminary tests indicated that such contamination was minimal, a second set of samples was prepared using a modification permitting the removal prior to titration of any Fe^{3+} from the plating solution.

After the final evaporation to dense fumes of SO_3, the solutions were cooled and diluted with 25 ml of distilled water. 50 ml of concentrated NH_3 was carefully added and the solution allowed to stand on the hot plate for 20 minutes. The precipitated $Fe(OH)_3$ was filtered off and the filter washed three times with 5 ml volumes of hot distilled water. The solution was now made acid to litmus using 1:1 H_2SO_4. An excess of 10 ml of 1:1 H_2SO_4 was added. 10 drops of 1% potassium ferricyanide was added and the titration carried out with 0.1100 M $K_4Fe(CN)_6$. These results were identified as "B".

In each case the zinc content was calculated from:-

$$\text{Zn, oz/US gal} = \frac{V\ K_4Fe(CN)_6 \times M\ K_4Fe(CN)_6 \times 3 \times 65.37 \times 3785.306}{1000 \times 2 \times 5.00 \times 28.349}$$

$$= V\ K_4Fe(CN)_6 \times M\ K_4Fe(CN)_6 \times 2.62$$

Sample No.	Vol. $K_4Fe(CN)_6$ (ml ± 0.02)	Zn (oz/US gal) as det.	Zn (oz/US gal) ave ± s	Can. Han	E (mV) − 0.5	E (mV) eq. pt	E (mV) + 0.5	± ΔE ± 0.5
1A	18.31	5.28		4.9	760	544	360	200
	18.44	5.31	5.28 ± 0.03		740	534	340	200
	18.23	5.25			760	544	360	200
1B	18.40	5.30			760	538	350	205
	18.05	5.20	5.23 ± 0.06		780	526	360	210
	18.05	5.20			760	540	340	210
2A	5.12	1.47		1.3	760	540	360	200
	5.05	1.45	1.45 ± 0.02		740	540	340	200

	5.01	1.44			760	536	340	210
2B	5.15	1.48			760	536	340	210
	5.22	1.50	1.47 ± 0.03		760	529	350	205
	5.01	1.44			760	540	350	205
3A	3.75	1.08		0.9	750	530	340	205
	3.99	1.15	1.07 ± 0.08		750	536	340	205
	3.40	0.98			740	537	345	198
3B	3.91	1.13			760	538	345	208
	3.80	1.10	1.12 ± 0.02		740	538	350	190
	3.95	1.14			760	530	340	210
4A	7.23	2.08		1.9	760	544	360	200
	7.48	2.15	2.12 ± 0.04		750	536	340	205
	7.37	2.12			740	540	340	200
4B	7.34	2.11			750	540	330	210
	7.51	2.16	2.14 ± 0.02		740	520	350	195
	7.44	2.14			760	540	340	210
5A	6.30	1.81		1.5	750	540	350	200
	6.19	1.78	1.78 ± 0.03		760	540	340	210
	6.09	1.75			760	540	350	205
5B	6.43	1.85			760	536	360	200
	6.36	1.83	1.83 ± 0.02		760	538	360	200
	6.33	1.82			760	540	360	200
6A	7.27	2.09		1.8	740	520	340	200
	7.13	2.05	2.06 ± 0.02		750	525	340	205
	7.13	2.05			730	540	350	190
6B	7.30	2.10			740	530	360	190
	7.09	2.04	2.07 ± 0.03		740	530	340	200
	7.16	2.06			750	535	340	205
7A	7.82	2.25		2.0	750	540	350	200
	7.75	2.23	2.24 ± 0.01		760	540	350	205
	7.79	2.24			760	530	350	205
7B	7.65	2.20			760	540	360	200
	7.65	2.20	2.22 ± 0.03		760	530	360	200
	7.86	2.26			740	530	360	190
8A	18.78	5.41		5.1	740	540	340	200
	18.96	5.46	5.44 ± 0.03		750	540	340	205
	18.95	5.46			750	538	350	200
8B	18.78	5.41			750	536	350	200
	18.71	5.39	5.42 ± 0.03		760	530	340	210
	18.92	5.45			750	425	340	205
9A	6.64	1.91		1.5	760	520	350	205
	6.61	1.90	1.90 ± 0.01		760	530	360	200
	6.61	1.90			760	540	360	200
9B	6.43	1.85			760	530	360	200
	6.61	1.90	1.87 ± 0.03		760	530	360	200
	6.42	1.85			740	530	360	190
10A	7.61	2.19		2.0	730	540	340	195
	7.82	2.25	2.23 ± 0.03		740	540	340	200
	7.79	2.24			740	540	350	195
10B	7.64	2.20			740	540	350	195
	7.65	2.20	2.22 ± 0.03		750	530	350	200
	7.83	2.25			740	530	360	190

In general these Ecell values for the critical points, for both the "A" and "B" results, agree well with the theoretical values.

TABLE 7-H

Standardization of $K_4Fe(CN)_6$ solution (E526 assembly method)

The solutions of zinc were prepared exactly as outlined in Table 5-H.

The E526 unit was set-up in the potential mode and calibrated in the usual manner. A platinum-Ag/AgCl (3M KCl) electrode couple was used, and the instrument was set for a starting potential of " + mV", a titration direction control setting of " - mV" and in the large ΔE increment mode. The preset dead-stop potential was set initially at + 540 mV, but exploratory work indicated an optimum setting of + 570 mV. The standardizing solutions were racked in 1 magazine, the pre-titration addition stops were automatically bypassed and the titrations were carried out sequentially and automatically.

Printout vol. (ml)	M $K_4Fe(CN)_6$
12.00	0.111111..
12.10	0.110192..
12.08	0.110375..

Average M $K_4Fe(CN)_6$ = 0.110559..
Std. devn. = ± 0.000485..

M $K_4Fe(CN)_6$ = $0.1105^5 \pm 0.0004^8$

TABLE 8-H

Determination of zinc in commercial alkali zinc cyanide plating solutions (E526 assembly method)

The solutions were prepared exactly as outlined in Table 6-H, "B" method.

The E526 unit was set-up and operated exactly as outlined in Table 7-H, with the optimum dead]stop potential of + 570 mV

The 33 beakers were racked in 9 magazines, the pretitration addition stops were bypassed automatically and the titrations were carried out sequentially and automatically in about 1.25 hours.

Sample No.	Printout vol. (ml)	Zn (oz/US gal) as det.	Zn (oz/US gal) ave. ± s
1.	18.37	5.32	
	18.39	5.33	5.32 ± 0.01
	18.39	5.33	

2.	5.10	1.48	
	4.99	1.44	1.45 ± 0.02
	4.98	1.44	
3.	3.71	1.07	
	3.65	1.06	1.06 ± 0.01
	3.68	1.06	
4.	7.30	2.11	
	7.24	2.10	2.11 ± 0.01
	7.28	2.11	
5.	6.29	1.82	
	6.20	1.80	1.80 ± 0.02
	6.19	1.79	
6.	7.28	2.11	
	7.31	2.12	2.10 ± 0.02
	7.20	2.08	
7.	7.71	2.23	
	7.81	2.26	2.25 ± 0.02
	7.78	2.25	
8.	18.70	5.42	
	18.69	5.41	5.41 ± 0.01
	18.69	5.41	
9.	6.63	1.92	
	6.54	1.89	1.90 ± 0.02
	6.56	1.90	
10.	7.59	2.20	
	7.59	2.20	2.20 ± 0.00
	7.61	2.20	

APPENDIX J

TABLE 1-J

Standardization of $Na_2S_2O_3$ with standard copper solution (Manual method)

Preparation of standard copper solution

6.2296 ± 0.0002 g of pure copper was dissolved in 30 ml of concentrated nitric acid. The solution was boiled to expel the oxides of nitrogen and diluted to exactly 200 ml with distilled.

Value:- 6.2296/63.54 = $0.4902^1 \pm 0.0001^5$M Cu

Preparation of sodium thiosulphate solution.

40.0 g of reagent-grade $Na_2S_2O_3.5H_2O$ was dissolved in boiled distilled water to which 3 g of sodium carbonate had been added. This solution was diluted to exactly 2 liters in a volumetric flask. The solution was allowed to stand for 1 day before standardization.

10.00 ± 0.02 ml of standard copper solution was pipetted to a 250 ml Erlenmeyer flask and diluted to 100 ml with distilled water. 2:1 NH_3 was now added until the solution showed a clear deep blue colour due to the tetraaminocopper(II) complex (about 10 ml required). The solution was boiled for 10 minutes and cooled. Enough glacial acetic acid was now added to produce a light clear blue colour (about 7.0 ml). The solution was boiled briefly and cooled. 4 g of solid KI was added and 2 g of solid NH_4HF_2. The solution was allowed to stand for 2 minutes and was then titrated with sodium thiosulphate solution. Just before the yellow colour of the triiodide ion disappeared, 5 ml of a 1% solution of soluble starch (freshly prepared) was added, and the titration continued to the permanent disappearance of the blue colour due to the starch-triiodide complex.

Vol. $Na_2S_2O_3$ (ml ± 0.04)	M $Na_2S_2O_3$
46.79	0.104768..
46.78	0.104790..
46.78	0.104790..

Average M $Na_2S_2O_3$ = 0.10478...
Std. devn. = ± 0.00011....

M $Na_2S_2O_3$ = $0.1047^8 \pm 0.0001^1$

TABLE 2-J

Determination of copper in alkali copper cyanide plating solutions (Manual method)

Solution preparation involved 5.00 ± 0.01 ml of plating solution pipetted into a 300 ml Erlenmeyer flask. ' ml of concentrated H_2SO_4

was added and 3 ml of concentrated HNO_3. The solution was evaporated to strong fumes of SO_3. Solutions which persisted in showing a dark colour were treated with an additional 1 ml of HNO_3 after cooling, and again evaporated to dense SO_3 fumes. The solution was cooled and diluted with 100 ml of distilled water. Subsequent to this point the treatment was exactly as outlined in Table 1-J.

The copper content of the plating solution was calculated from:-

$$\text{Cu oz/US gal} = \frac{V\ Na_2S_2O_3 \times M\ Na_2S_2O_3 \times 63.54 \times 3785.306}{1000 \times 5.00 \times 28.349}$$

$$= V\ Na_2S_2O_3 \times M\ Na_2S_2O_3 \times 1.69^7$$

Sample No.	Vol. $Na_2S_2O_3$ (ml ± 0.04)	Cu (oz/US gal) as det.	Cu (oz/US gal) ave. ± s	Cu (oz/US gal) Canadian Hanson
1.	22.10	3.93		3.7
	22.05	3.92	3.92 ± 0.00	
	22.05	3.92		
2.	19.20	3.41		3.3
	19.22	3.41	3.41 ± 0.00	
	19.22	3.41		
3.	28.90	5.14		4.6
	28.95	5.15	5.14 ± 0.01	
	28.90	5.14		
4.	38.45	6.84		6.2
	38.45	6.84	6.85 ± 0.02	
	38.60	6.86		
5.	12.75	2.26		2.1
	12.77	2.27	2.27 ± 0.01	
	12.80	2.27		
6.	22.85	4.06		3.8
	22.86	4.06	4.06 ± 0.00	
	22.88	4.06		
7.	38.75	6.89		6.6
	38.73	6.89	6.88 ± 0.00	
	38.72	6.89		
8.	24.95	4.43		4.4
	24.98	4.44	4.44 ± 0.01	
	24.98	4.44		
9.	10.65	1.89		1.8
	10.63	1.89	1.89 ± 0.01	
	10.68	1.90		
10.	27.01	4.80		4.8
	27.06	4.81	4.81 ± 0.01	
	27.08	4.81		

TABLE 3-J

Standardization of sodium thiosulphate solution (E436A method)

A standard copper solution was prepared as outlined in Table 1-J, but at a lower strength.

Value:- $0.2518^2 \pm 0.0001^2$M Cu

The preparation of the solution of standard copper was exactly as outlined in Table 1-J. No starch solution was added.

The E436A unit was set in the potential mode at a fullscale deflection of 500 mV and a range of 0 to + 500 mV. A platinum - Ag/AgCl (3M KCl) electrode couple was used. The variable titrant delivery mode was put in operation. Complete titration curves to beyond the equivalence point were obtained and these were analyzed by the circle-fit method to locate the equivalence point volume and potential. In addition, each curve was analyzed to locate the Ecell values for ± 0.5 ml around the equivalence point volume.

Vol. $Na_2S_2O_3$ (ml ± 0.05)	M $Na_2S_2O_3$	E (mV) - 0.5	eq. pt.	+ 0.5	± ΔE (mV) ± 0.5 ml
25.20	0.099920.	320	210	90	115
24.72	0.101860.	320	212	90	115
25.18	0.099999.	320	216	90	115

Average M $Na_2S_2O_3$ = 0.100601...
Std. devn. = ± 0.001097...

M $Na_2S_2O_3$ = $0.100^6 \pm 0.001^0$

The theoretical calculations of Ecell for critical titration points:-

Volume at start = 128 ml Equivalence point volume $Na_2S_2O_3$ = 25.0 ml
KI added = 4 g/166 = 0.0241 moles
Amount copper = (10ml x 0.25182M)/1000 = 0.00252 moles
I_2 formed = 1/2 of copper moles = 0.00126 moles
I^- left = 0.0241 - 2 x copper moles = 0.01906 moles

At 0.5 ml before equivalence point:-

I^- returned = moles $Na_2S_2O_3$ added = 24.5ml x A.1006M/1000 = 0.00246 moles
Total I^- = 0.01906 + 0.00246 = 0.02150 moles
I_2 at this point = 0.00126 - (0.5 x 0.00246) = 0.00003 moles

$[I^-]$ = (0.0215/152.5) x 1000 = 0.141M
$[I_2]$ = (0.00003/152.5) x 10000 = 1.97×10^{-4}M

$$E_{I_2/I^-} = 0.534 + 0.059/2 \log \frac{[I_2]}{[I^-]^2}$$

$$= 0.534 + 0.059/2 \log \frac{1.97 \times 10^{-4}}{1.41 \times 10^{-1}}$$

$$= 0.534 - 0.059 = 0.475 \text{ V}$$

$$\text{Ecell} = 0.475 - 0.200 \text{ (ref.)} = 0.275 \text{ V} = 275 \text{ mV}$$

At the equivalence point:-

$$\frac{[I^-]^2[S_4O_6^{2-}]}{[I_2][S_2O_3^{2-}]^2} = \text{Keq.} = 14.5$$

$$[I^-] = (0.0241/153\text{ml}) \times 1000 = 1.575 \times 10^{-1}\text{M}$$

$$S_4O_6^{2-} = \text{moles of } I_2 \text{ originally formed} = 0.00126$$

$$[S_4O_6^{2-}] = (0.00126/153\text{ml}) \times 1000 = 8.23 \times 10^{-3}\text{M}$$

$$[S_2O_3^{2-}] = 2[I_2]$$

so that:-

$$\frac{(1.575 \times 10^{-1})^2 \times 8.23 \times 10^{-3}}{10^{14.5}} = 4[I_2]^3$$

$$[I_2] = 5.4 \times 10^{-7}\text{M}$$

$$E_{I_2/I^-} = 0.534 + 0.059/2 \log \frac{5.4 \times 10^{-7}}{(1.575 \times 10^{-1})^2}$$

$$= 0.420 \text{ V}$$

$$\text{Ecell} = 0.420 - 0.200 \text{ (ref.)} = 0.220 \text{ V} = 220 \text{ mV}$$

At 0.5 ml after the equivalence point:-

$$[S_4O_6^{2-}] = (0.00126/153.5\text{ml}) \times 1000 = 8.2 \times 10^{-3}\text{M}$$

$$[S_2O_3^{2-}] = (0.5\text{ml} \times 0.1006\text{M})/153.5\text{ml} = 3.3 \times 10^{-4}\text{M}$$

$$E_{S_4O_6^{2-}/S_2O_3^{2-}} = 0.100 + 0.059/2 \log \frac{8.2 \times 10^{-3}}{(3.3 \times 10^{-4})^2}$$

$$= 0.100 + 0.144 = 0.244 \text{ V}$$

$$\text{Ecell} = 0.244 - 0.200 \text{ (ref.)} = 0.044 \text{ V} = 44 \text{ mV}$$

The assymmetry expected on the + ΔE and - ΔE values was not obtained and, in addition, the terminal Ecell values deviated from the theoretical considerably, insofar as the experimental data were concerned.

TABLE 4-J

Determination of copper in commercial alkali copper cyanide plating solutions (E436A method)

The plating solutions were prepared exactly as outlined in Table 2-K, except that, as a preliminary test for E526 arrangements, the addition of KI was made as 10 ml of a 10% solution and the addition of NH_4HF_2 was made as 10 ml of a 20% solution. Titration was carried out with the $Na_2S_2O_3$ standardized in Table 3-K.

The E436A was set-up and operated exactly as outlined in Table 3-K.

Sample No.	Vol. $Na_2S_2O_3$ (ml ± 0.02)	Cu (oz/US gal) as det.	ave. ± s	E (mV) - 0.5	eq.pt.	+ 0.5	± ΔE mV ± 0.5
1.	21.88	3.73		286	234	90	98
	21.99	3.73	3.74 ± 0.01	284	236	90	96
	21.98	3.75		292	245	89	97
2.	19.00	3.24		280	232	91	95
	19.52	3.33	3.28 ± 0.04	281	232	90	95
	19.25	3.28		300	252	92	104
3.	27.49	4.69	4.69 ± 0.00	288	240	90	99
	27.50	4.69		288	246	90	99
	lost						
4.	38.25	6.52	6.52	292	240	90	101
	38.75	6.61	6.57 ± 0.04	280	250	90	95
	38,50	6.57		288	240	90	99
5.	12.27	2.09		288	246	92	98
	12.50	2.13	2.11 ± 0.01	292	256	92	100
	12.40	2.11		288	256	91	98
6.	22.90	3.91	3.90 ± 0.01	292	240	90	101
	22.88	3.90		292	240	90	101
	lost						
7.	38.25	6.52		288	234	90	95
	38.75	6.61	6.62 ± 0.08	292	236	90	101
	39.37	6.72		290	240	91	100
8.	23.37	3.99		288	239	90	99
	24.25	4.14	4.10 ± 0.08	288	240	90	99
	24.40	4.16		290	234	90	100
9.	9.68	1.65		288	236	89	100
	10.67	1.82	1.71 ± 0.08	292	240	90	101
	9.75	1.66		289	246	90	100
10.	26.90	4.60		292	242	90	101
	26.88	4.59	4.63 ± 0.05	288	244	90	99
	27.50	4.69		294	244	90	102

Average Ecell 0.5 ml before eq. pt.	288 ± 4 mV
Average Ecell eq. pt.	241 ± 6 mV
Average Ecell 0.5 ml after eq. pt.	90 ± 2 mV
Average ± ΔE (± 0.5 ml)	99 ± 2 mV

TABLE 5-J

Standardization of sodium thiosulphate titrant (E526 method)

The preparation of the standard copper soutions was identical to the outlined in Table 1-J, with the following exceptions. The additions of KI and NH_4HF_2 were made as automatic pretitration additions on the E526 equipment. The KI was added first as 10 ml of a 10% solution, the NH_4HF_2 being added second as 10 ml of a 20% solution. The latter solution, because of its highly corrosive properties, was kept in a plastic holding bottle, passed through an acid-resistant measuring valve system and handled by Teflon tubing.

The E526 assembly was set in the potential mode and calibrated in the usual manner. A combination platinum - Ag/AgCl (3M KCl) electrode couple was attached. The starting potential control was set at " + mV", the titration direction control at " - mV" and the ΔE control in the large increment mode. The preset dead-stop potential was set at a value of + 220 mV, generally in accordance with Table 3-J data. This value was found to yield optimum results. The titrations were carried out sequentially and automatically including the pretitration additions of KI and NH_4HF_2.

Printout vol. (ml)	M $Na_2S_2O_3$
24.78	0.101622...
25.01	0.100687...
25.29	0.099573...

Average M $Na_2S_2O_3$ = 0.10062...
Std. devn. = ± 0.00102...

M $Na_2S_2O_3$ = $0.100^6 \pm 0.001^0$

TABLE 6-J

Determination of copper in commercial alkali copper cyanide plating solutions (E526 assembly method)

The solution preparation was exactly as outlined in Table 2-J, except that the additions of KI and NH_4HF_2 were made automatically in the manner outlined in Table 5-J.

The E526 unit was set-up and operated exactly as outlined in Table 5-J, except that exploratory work indicated an optimum dead-stop potential

of + 230 mV. This was somewhat lower than the average experimental value found of + 241 mV.

The value of copper was calculated from the equation shown in Table 2-J.

Five solutions involving standard copper solution additions as indicated in Table 5-J were interspersed between the plating samples as a check on instrument setting and electrode couple stability.

Sample No.	Printout vol. (ml)	Cu (oz/US gal) as det.	Cu (oz/US gal) ave. ± s	Cu (oz/US gal) Canadian Han.
1.	22.22	3.79		3.7
	22.17	3.78	3.79 ± 0.00	
	lost			
2.	19.80	3.38		3.3
	19.77	3.37	3.41 ± 0.06	
	20.39	3.48		
Std.	24.90			
3.	29.35	5.01		4.6
	29.21	4.99	5.01 ± 0.02	
	29.44	5.03		
4.	39.09	6.68		6.2
	39.17	6.69	6.68 ± 0.00	
	39.13	6.68		
5.	13.09	2.23		2.1
	13.03	2.22	2.22 ± 0.01	
	12.97	2.21		
Std.	25.06			
6.	23.07	3.93		3.8
	23.17	3.95	3.94 ± 0.01	
	23.14	3.94		
7.	39.32	5.71		6.6
	39.13	6.68	6.72 ± 0.04	
	39.62	6.76		
Std.	25.05			
8.	25.43	4.34		4.4
	25.37	4.33	4.34 ± 0.00	
	25.44	4.34		
Std.	25.02	4.34		
9.	11.03	1.87		1.8
	10.67	1.82	1.84 ± 0.02	
	10.85	1.84		
10.	27.97	4.78		4.8
	28.06	4.79	4.79 ± 0.01	
	28.10	4.80		
Std.	24.96			

APPENDIX K

TABLE 1-K

Standardization of $Na_2S_2O_3$ titrant with standard potassium dichromate (Manual method)

Preparation of potassium dichromate solution

4.9035 ± 0.0002 g of reagent-grade potassium dichromate, $K_2Cr_2O_7$, dissolved in 200 ml of distilled water and diluted to exactly 1 liter in a volumetric flask.

Value:- 4.9035/294.22 = 0.016667 ± 0.000005M

Preparation of sodium thiosulphate solution

49 g of reagent-grade $Na_2S_2O_3.5H_2O$ was dissolved in 500 ml of boiled water and diluted to exactly 2 liters in a volumetric flask with the same water. Prior to dilution, 0.5 g of sodium carbonate, was added.

10.00 ± 0.02 ml of standard potassium dichromate solution waspipetted and diluted with 100 ml of distilled water. 10.0 ml of concentrated HCl was added, followed bu 10 ml of a 10% solution of KI. After the solution had stood for 2 minutes, titration was made using the prepared sodium thiosulphate solution. When the dark brown colour had changed to straw yellow, 5 ml of 1% soluble starch solution was added and the titration continued to the first disappearance of the blue colour.

Vol. $Na_2S_2O_3$ (ml ± 0.02)	M $Na_2S_2O_3$
10.02	0.0997802...
9.98	0.1002020...
10.00	0.1000021...

Average M $Na_2S_2O_3$ = 0.099994...
Std. devn. = ± 0.000211...

M $Na_2S_2O_3$ = $0.0999^9 \pm 0.0002^1$

TABLE 2-K

Determination of chromic acid in commercial acid chromium plating solutions (Manual method)

2.00 ± 0.01 ml of chromium plating solution was pipetted and diluted to exactly 100 ml in a volumetric flask. 10.00 ± 0.02 ml of this solution was pipetted and diluted with 100 ml of distilled water. 2 g of ammonium bifluoride, 10 ml of concentrated HCl and 10 ml of 10% KI solution were added. After 2 minutes the solution was titrated with standard sodium thiosulphate solution until the dark brown colour changed to a straw yellow. 5 ml of 1% soluble starch solution was added, and the titration continued until the blue colour had disappeared.

The chromic acid content was calculated from:-

$$\text{Chromic acid, (oz/US gal)} = \frac{V\ Na_2S_2O_3 \times M\ Na_2S_2O_3 \times 99.99 \times 3785.306}{1000 \times 3 \times 0.200 \times 28.349}$$

where:-

$$99.99 = \text{GMW } CrO_3$$

$$\text{Chromic acid, oz/US gal} = V\ Na_2S_2O_3 \times M\ Na_2S_2O_3 \times 22.2^5$$

Sample No.	Vol. $Na_2S_2O_3$ (ml ± 0.04)	Chromic acid (oz/US gal) as det.	ave. ± s	Candn. Han.
1.	14.37	31.99		31.9
	14.52	32.32	$32.1^9 \pm 0.1^6$	
	14.49	32.26		
2.	18.32	40.78		41.3
	18.34	40.83	40.83 ± 0.05	
	18.36	40.87		
3.	16.01	35.64		31.0
	16.03	35.68	35.65 ± 0.02	
	16.01	35.64		
4.	14.65	32.61		33.2
	14.62	32.55	32.59 ± 0.03	
	14.65	32.61		
5.	16.71	37.20		38.9
	16.82	37.44	$37.3^2 \pm 0.1^2$	
	16.76	37.31		
6.	19.05	42.41		44.1
	19.01	42.34	42.41 ± 0.07	
	19.08	42.47		
7.	16.28	36.24		37.1
	16.30	36.29	36.23 ± 0.06	
	16.25	36.17		
8.	11.13	24.77		26.0
	11.15	24.82	24.80 ± 0.02	
	11.14	24.80		
9.	15.42	34.33		noy given
	15.35	34.17	34.24 ± 0.08	
	15.37	34.22		
10.	13.65	30.39		33.4
	13.67	30.43	30.42 ± 0.03	
	13.68	30.45		

TABLE 3-K

Standardization of sodium thiosulphate titrant with standard potassium dichromate solution (E436A method)

The dichromate solution was prepared as indicated in Table 1-K and was used in this titration process as 0.016667 ± 0.000005M

The solution preparation was exactly as outlined in Table 1-K.

The E436A unit was set in the potential mode with the full-scale deflection at 750 mV and with a range of 0 to + 750 mV. The electrode system was a combination platinum - Ag/AgCl (3M KCl) electrode and the unit was used in the variable titrant delivery mode. Full titration curves were obtained to well-beyond the equivalence point, and these were analyzed by the circle-fir method to locate the equivalence point volume and potential. Each curve was also analyzed to locate the Ecell values for ± 0.5 ml around the equivalence point volume.

Vol. $Na_2S_2O_3$ (ml ± 0.02)	M $Na_2S_2O_3$	E (mV) - 0.5	eq. pt.	+ 0.5	± ΔE (mV) ± 0.5 ml
9.42	0.106159..	390	278	80	155
9.42	0.106159..	390	278	80	155
9.42	0.106159..	390	278	80	155

Average M $Na_2S_2O_3$ = 0.106159...
Std. devn. = ± 0.000000...

M $Na_2S_2O_3$ = $0.1061^5 \pm 0.0000^0$

The theoretical calculations are not shown here, since the method used was identical to that employed in Table 3-J. The values obtained were:-

0.5 ml before eq,pt.	=	367 mV
At eq. pt.	=	257 mV
0.5 ml after eq. pt.	=	40 mV

TABLE 4-K

Determination of chromic acid in commercial acid chromium plating solutions (E436A method)

The preparation of the plating solution samples was identical to that outlined in Table 2-K. No starch indicator solution was added.

The E436A unit was set-up and operated exactly as outlined in Table 3-K.

The chromic acid content was calculated using the equation shown in Table 2-K.

Sample No.	Vol. $Na_2S_2O_3$ (ml ± 0.02)	CrO_3 (oz/US gal) as det.	ave ± s	Can. Han.	− 0.5	eq. pt.	+ 0.5	± ΔE ± 0.5
1.	13.93	32.91		31.9	360	294	172	90
	13.85	32.73	32.82 ± 0.1^3		360	292	172	90
	lost							
2.	17.22	40.69		41.3	360	290	166	97
	17.30	40.8[illegible]	$0.8^2 \pm 0.1^1$		360	290	166	97
	17.30	40.88			360	290	166	97
3.	15.15	35.80		31.0	360	297	172	94
	15.00	35.44	$35.8^0 \pm 0.3^5$		360	297	178	94
	15.30	36.15			360	294	172	90
4.	13.60	32.14		33.2	360	288	160	100
	13.61	32.16	$32.2^2 \pm 0.1^2$		360	288	160	100
	13.69	32.35			360	288	160	100
5.	16.20	38.28		38.9	360	286	160	100
	16.40	38.75	$38.5^2 \pm 0.2^4$		360	294	160	100
	lost							
6.	18.10	42.77		44.1	360	302	160	100
	17.99	42.51	$42.6^8 \pm 0.1^3$		360	288	160	100
	18.10	42.77			360	288	160	100
7.	15.38	36.34		37.1	360	302	160	95
	15.25	36.03	$36.0^2 \pm 0.3^2$		360	288	170	95
	15.10	35.68			360	299	170	95
8.	10.77	25.45		26.0	360	290	170	95
	10.91	25.78	25.56 ± 0.1^9		360	291	170	95
	10.78	25.47			360	290	170	95
9.	14.88	35.16		N.G.	360	288	160	100
	14.88	35.16	$34.8^3 \pm 0.5^7$		360	288	160	100
	14.46	34.19			360	290	170	95
10.	13.30	31.43		33.4	360	294	172	94
	13.30	31.43	31.31 ± 0.1^9		360	291	172	94
	13.15	31.07			360	292	172	94

Average E cell 0.5 ml before 360 MV
Average Ecell at eq. pt. 291 mV
Average Ecell 0.5 ml after 166

± ΔE (± 0.5 ml) assymetric + 69 − 125 mV

The theoretical calculated values, using Table 3-J formulations, were:-

0.5 ml before	365 mV
Eq. pt.	271 mV
0.5 ml after	90 mV

TABLE 5-K

Standardization of sodium thiosulphate titrant with potassium dichromate standard solution (E526 assembly method)

The $K_2Cr_2O_7$ standard solution was that prepared and used in Table 1-K.

The solution preparation was exactly as described in Table 1-K, except that no indicator was added and the pretitration addition of the required volume if KI solution was carried out automatically.

The E526 unit was set in the potential mode and calibrated in the usual manner. A combination platinum - Ag/AgCl (=M KCl) electrode system was used. The instrument was set in the "+ mV" initial potential mode, in the decreasing "- mV" titration direction position and in the large ΔE increment mode. The optimum dead-stop potential was found, after some exploratory work, to be + 290 mV, slightly more posutive than the value found in Table 3-K. The samples were titrated, and the pretitration additions made, sequentially and automatically.

Printout vol. (ml)	M $Na_2S_2O_3$
9.75	0.102566...
19.72	0.102882...
9.75	0.102566...

Average M $Na_2S_2O_3$ = 0.10267...
Std. devn. = ± 0.00018...

M $Na_2S_2O_3$ = $0.1026^7 \pm 0.0001^8$

TABLE 6-K

Determination of chromic acid in acid chromium plating solutions (E526 assembly method)

Preparation of the plating solutions was exactly as outlined in Table 2-K, except that no indicator was added and the additions of 10 ml of 10% KI solution and 10 ml of 20% NH_4HF_2 solutions was carried out automatically in the pretitration additions position of the E526 unit.

The E526 unit was set-up and operated exactly as outlined in Table 5-K. The dead-stop potential was found to be + 290 mV, the same value as found experimentally in Table 4-K.

The chromic acid content was calculated from the equation shown in Table 2-K.

The 30 beakers were racked in 8 magazines and titrated sequentially and automatically in about 1.25 hours.

Sample No.	Printout vol. (ml)	CrO_3 (oz/US gal) as det.	CrO_3 (oz/US gal) ave. ± s	CrO_3 (oz/US gal) Canadian Hanson
1.	14.36	32.82		31.9
	14.29	32.66	32.74 ± 0.08	
	14.33	32.75		
2.	17.44	39.86		41.3
	17.88	40.86	$40.5^6 \pm 0.6^0$	
	17.93	40.95		