APPLICATION OF FLAME AND FLAMELESS ATOMIC ABSORPTION METHODS TO THE "FINGERPRINTING" OF SPILLS ON WATER MEDIA OF NON-DISTILLATE PETROLEUM OILS

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ABSTRACT

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Four (4) samples of crude oil of varying origins and six (6) samples of non-distillate (bunker type) oils are analysed by flame and flameless atomic absorption techniques, using the ASTM 3327-74T preparatory approach for all samples. The trace metals nickel, vanadium, chromium, cobalt, iron, manganese, molybdenum, copper and zinc are determined using both the calibration standards and multiple spiking approaches. The various samples are then artificially weathered over synthetic seawater, and the entire analytical program repeated.

The various possible trace metal content ratios are examined, and it is found that only ratios involving vanadium, nickel, chromium, cobalt and iron are of real value in the "fingerprinting" of original against weathered oils. Using a plus point system for either positive matching or mismatching, single ratio and

ratio combinations are tested. A 90 ± 5 percent probability of correct fingerprinting is observed for the single ratios. Using multiple ratios (i.e. V/Ni, Ni/Co and V/Co), a probability of correct fingerprinting of 99 percent is achieved.

ACKNOWLEDGEMENTS

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1 INTRODUCTION

1.1 Oil Spills and Their Environmental Ecological and Economic Impacts

Since the early 1960's, increasing attention has been paid by government, industry, the public and the media to the environmental, ecological and economic impacts of spills of petroleum oils and, in particular, to such spills as they occur on water bodies.

The developing energy crisis has, relative to the petroleum industry, resulted in general increases in oil production, substantial increases in offshore exploration, drilling and production, significant increases in the quantities of petroleum oil and its products transported and the very significant increases in the capacities of bulk carriers such as oil tankers. This growth in activity has resulted in a world-wide upturn in the annual incidences of oil spills and of the quantities of oil spilled. The increases in the size of oil tankers to supertanker dimensions and capacities has increased the potential of truly disatrous spills at or near continental shores in particular, and on water bodies in general. The increase in offshore oil exploration, drilling and production has served to augment this potential (e.g. the recent offshore spill in the Gulf of Mexico). Where such offshore and/or onshore drilling operations involve the far north, the extent of the possible environmental and ecological impacts can be only guessed at.

A statistical study of spills of petroleum oils and petroleum-based products has been carried out for the Canadian Department of the Environment by Dick (1). This study outlined the various sources, causes and reasons for such spills and, as one of its significant conclusions, indicated that the major reason underlying oil spills was personnel failure or human error. On this basis, increased oil production and transport activity can be expected to lead eventually to a spill of monumental proportions.

The findings of the study reported following this introduction will have application essentially to oil spills on water, and the effects of such spills should be indicated.

Oil spills on waters involving oceans, seas, lakes and rivers carry with them always the possibilities of shore and bottom pollution. Such pollution can and does result in loss of marine life and associated loss of earnings for those engaged in the fishing industry, loss of shore life such as birds, loss of use of and revenue from beaches and shore real estate, loss of oil spilled, contamination of water supplies, contamination of harbours, fire hazards, cost of prosecution, insurance loss etc. The cost of cleanup for such spills, and the replacement of marine life are tremendous. The United States Environmental Protection Agency has estimated the cost of oil spill cleanup alone, by averaging out costs of cleanup for different spill locations and conditions, at appromately $7.50/U.S. gallon (2). In connection with this figure it should be noted that the Dick study showed a total of some 10 million Imperial gallons of oil was spilled on water in Canada over the period from 1974 to 1977. The cost for the replacement of marine life destroyed as the result of Santa Barbara offshore oil spill of 1969-70 has been estimated at a low of 10.5 million dollars and a high of 53.5 million dollars (3). The magnitude of these costs which, it must be remembered, cover cleanup and marine life replacement cost only, are indicative of the seriousness of the situation.

Where spills on water are concerned, the responsibility for associated costs can not be assigned except where the source of the spill can be pinpointed. Such pinpointing is not always simple, since in many instance multiple possible sources may exist. As an example, one may consider the situation where a crude oil offshore spill occurs at a time when at least four vessels were in the general vicinity of the spill. To assign responsibility to one of these vessels for the spill involved requires a comparison of the properties of the samples from the oil spill with those of samples obtained from the suspected source vessels. In any such comparison, the possibility of weathering of the spill oil before sampling must be considered, as must be its effect on the comparison methodologies.

It is apparent that the task of "fingerprinting" oil spills and suspected sources must fall to the analytical chemist, who must then apply techniques of chemical analysis and "fingerprinting" capable of rapidly providing data sufficiently reliable to provide positive matching and mismatching of spill and source oil samples. Such techniques must obviously be capable of standing in any subsequent legal action which may ensue.

1.2 Characterization and Identification of Oil Spills

Public concern with respect to environmental pollution has facilitated the development and adaptation of analytical techniques applicable to the characterization and identification of oil spills.

These techniques can be classified as follows:-

(a) Physical testing methods such as boiling point determination/simulated distillation (4)(5), specific gravity methods using improved density meters (6), viscosity measurement (7), etc.

(b) Spectroscopic techniques such as infrared spectroscopy (8), fluorescence spectroscopy (9), nuclear magnetic resonance spectroscopy (10), ultraviolet spectroscopy (11), mass spectroscopy (12), laser Raman spectroscopy (13), etc.

(c) Separation techniques such as gas-liquid chromatography (14), high-performance liquid chromatography (15), gas chromatography/mass spectrometry (16), thin-layer chromatography (17), etc.

(d) Elemental analysis methods such as X-ray fluorescence spectrometry (18)(19), neutron activation analysis (20)(21), emission spectrometry (22)(23), atomic absorption spectrometry (24)(25)(26), etc.

Complete reviews of recent techniques for oil spill identification can be found in the excellent monographs by Bentz (27) and Frazer (28).

With most of the spectroscopic and separation methods, the principle of identification is what is called "fingerprinting" matching. The spectra or the chromatograms of the spill sample are compared with those of the suspected source oils. In the case where an oil spill has been on the water for extended periods, or where the spill is of a very light petroleum distillate, losses due to evaporation, dissolution and oxidation may alter the spectra and the chromatograms sufficiently to render matching difficult. In such cases the suspected source oils can be weathered and then compared.

Perhaps the most comprehensive explorations into "fingerprinting" identification have been made by the United States Coast Guard. In their publication "Oil Spill Identification System" (Report No. CG-D52-77 Task No. 42432) (30), they reviewed and listed in detail the sampling and sample handling techniques, and gave detailed descriptions and examples of four analytical approaches used by the Coast Guard operational laboratory. These are:- gas chromatography, fluorescence spectroscopy, infrared spectroscopy and thin-layer chromatography. In addition, the Coast Guard included back-up techniques involving low temperature luminescence and high performance liquid chromatography. The need of using multi-method approach was also explained. In a given case any one of the methods might be adequate, but each may be sensitive to certain interferences from impurities picked up by the oil slick. Hence, for a positive identification, the analyst will be more confident where two or more methods of identification are applied.

There are cases when the results of two or more methods disagree as to the source of an oil spill. Fortunately in most of such cases, the reason for the disagreement is apparent from the results (i.e. the experienced analyst can detect interference sources in one or more of the methods). He can either discount the affected method, or attempt to remove the interfering substance without altering the oil composition. Inevitably there are instances where two suspected sources are nearly identical, or where the results from different techniques disagree for no apparent reason. Such instances may then require the application of additional analytical procedures. If such efforts fail to resolve the issue, the conclusion must then be that the source is indeterminate. The suspected/accused party is then given the benefit of doubt.

The advancement of computer technology in recent years has faciliated the development of computerized "fingerprinting" matchings. These techniques usually involve digitizing of data. For examples, with IR spectra, transmission at corresponding wavelengths serve as data inputs (31)(32) and with chromatograms the peak area versus retention times are used (15)(33). Comparison can be carried out in digital format against a data bank of references using prescribed statistical criteria. More complicated manipulations of data such as grouping and ratioing of spectroscopic transmission values or chromatographic peaks can be carried out simultaneously by the computer, providing fast and more reliable identification. The major drawbacks of the computer-assisted "fingerprinting" methods are the high cost of the sophisticated equipment and associated technicians and, in addition, the lack of system uniformity. Each individual research group has developed its own system of identification algorithm and statistical criteria, more cooperation and communication are required to facilitate advances in this field.

Elemental analysis of metallic contents serve a variety of purposes in the petroleum industry, such as the fundamental understanding of the nature of petroleum, classification of crudes for suitability as cracking stocks, process studies, evaluation of catalysts and product quality studies (34).

Recently, elemental analysis has been employed in the characterization and identification of oil spills (18-26). Of all of the metallic elements, vanadium and nickel are the ones which have been most thoroughly studied. The reason for their importance is that these elements occur, in part, as nitrogen complexes (prophyrin) closely related to chlorophyll and haemoglobin, and thus appear to be associated with the genesis of crude oils. Many correlations based on the vanadium and nickel contents of petroleum oils have been made for identification purposes (35)(36). The analytical methods most commonly used are X-ray fluorescence and atomic absorption spectrometry; more recently emission spectroscopy and neutron activation analysis have also been employed.

The purpose of this project is to investigate the possibility of extending elemental analysis by atomic absorption through the determination of elements other than vanadium and nickel, such as cobalt, chromium, iron, manganese, molydenum, zinc and copper. Correlations between the elemental metallic contents will be established for the original oil samples and for the artificially-weathered oil samples. Attempts will be made to construct identification patterns for "fingerprinting" matching based upon the metal content correlations (i.e. the ratio of one element content to that of another)

The purpose of this study is not only to determine the individual contents of various metals in the oils examined, but to explore, using statistical criteria, which ratios of metal contents remain reasonably unchanged regardless of the weathering action to which oil spills are exposed. Such consistently-maintained ratios can then serve as a basis for oil spill/source "fingerprinting" and identification.

Since metallic contents are largely lost where distillates are involved, the present study involves only crude oils and crude oil residues, such as bunker oils. Ten such samples are explored, these having been provided by Shell Canada Limited.

2. INSTRUMENTATIONS

2.1 Atomic Absorption Spectroscopy as Applied by the Petroleum Industry

Since the early 1960's atomic absorption has been a versatile tool for trace analysis, in the ppm and ppb ranges, for some seventy elements in aqueous and organic solutions and, sometimes, directly on solids. However it was not until the early 1970's that any significant number of analytical applications to petroleum and petroleum products was published. A possible reason for this was the difficulties encountered in one of the earliest and most obvious applications-the determination of lead in gasoline (37)(38)(39).

Recently methods have proliferated, and in order to obtain some unification of atomic absorption test procedures, both the Institute of Petroleum, Atomic Absorption Sub-Panel (ST-G-4E) and a similar American Society for Testing and Materials Sub-Committee have published standard methodologies for the atomic absorption analysis of petroleum materials (40)(41)(42).

Most petroleum products are generally soluble in organic solvents such as methylisobutylketone (MIBK), xylene and white spirit. However the standard direct analysis of organic petroleum solutions often yields non-reproducible results, particularly with the graphite furnace method. The reasons are:- the inherent difficulties of carbon rod furnace with organic solvents and, more important, differences in the sensitivity for different organometallic matrices (37)(38)(39) (i.e. ligands in the organometallic calibration standards versus the ligands in the petroleum products to which the metallic elements are bonded). To overcome such matrix interferences, the indirect method/standard additions method (39) can be used. This is, however, tedious and time-consuming. As a alternative, a dry-ashing, acid take-up procedure (42) can be applied. This provides for simplicity and is relatively free from matrix interferences. In this study, the ASTM 3327-74T dry-ashing and acid take-up procedure was applied.

2.2 Atomic Absorption Spectroscopy-General

The basic features of an atomic absorption spectrophotometer are shown in the block diagram of figure 2-1.

The radiation source is usually a hollow cathode lamp, or an electrodeless discharge lamp. The source beam, being a line spectrum, will be attenuated by the atom reservoir. The monochromator is used to select the particular spectral line at which measurements are taken, while the detector measures the intensity of radiation at this wavelength.

The most common atom reservoirs are the flame cell and the graphite furnace systems. Atomization energy is supplied by the flame cell as thermal energy, and by the graphite furnace in the form of thermal energy provided by electrical resistance heating. The main difference between the two modes is that the flame is more stable but less sensitive due to large loss of analyte in the nebulization step, while the furnace, in confining the atomized vapour to a restricted area, provides much higher sensitivity but with poorer precision due to factors such as temperature gradients, atomization efficiency, etc.

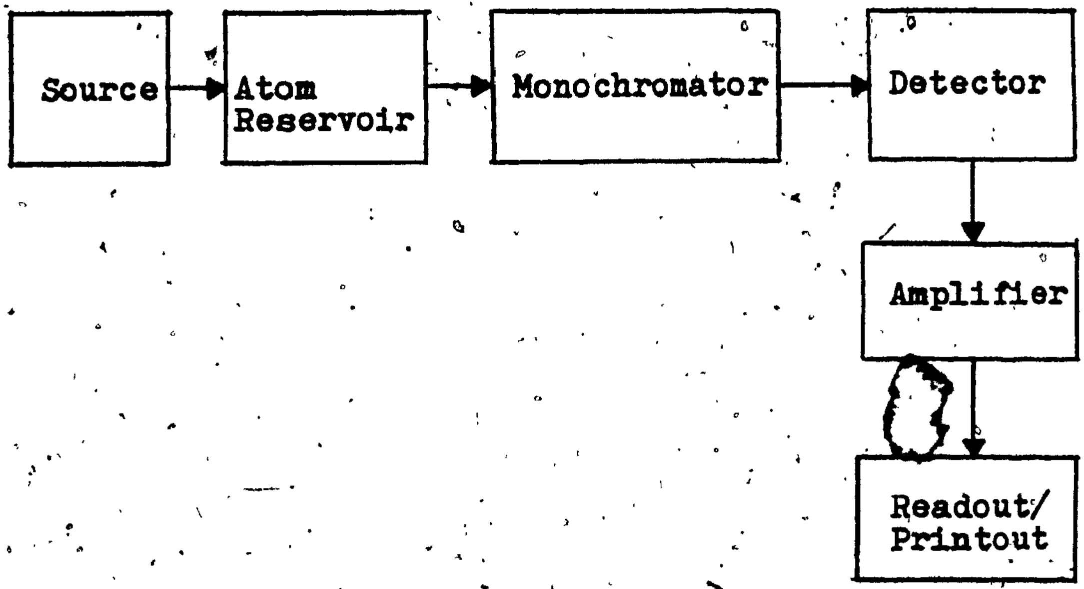


FIGURE 2-1 BLOCK DIAGRAM OF AN ATOMIC ABSORPTION SPECTROPHOTOMETER

As mentioned earlier, the atomic absorption technique operates on the basic principle of the attenuation of the source line emission spectrum by analyte atoms. The method is highly sensitive and selective and relatively free from spectral interferences when compared to other forms of optical spectrometry such as IR and UV when a monochromated continuous spectrum source is involved.

Technical refinements for the atomic absorption spectrophotometer include double-beam configuration, deuterium or hydrogen background correctors, time integration of signal, sample automation, etc. Details of atomic absorption theory and instrumentations can be found in numerous text books on the subject (43)(44)(45).

Atomic absorption, as with most of the analytical optical techniques, is an indirect method requiring the use of calibration standards. As with all of the methodologies of optical spectroscopy, there will be a loss of linearity at higher concentrations. For any element regardless of whether the graphite furnace or the flame method is involved, the calibration characteristics such as linear limit and sensitivity must be established for each element and each technique.

For samples involving complicated matrices, the matrix differences between sample solutions and standard solutions often provide for erroneous results. These matrix differences can be compensated for by matching the matrix of the standard solutions to that of the sample solutions. This requires a knowledge of the sample compositions and such procedures are often too tedious for routine application.

Very often the standard additions (spiking) technique is used to compensate for matrix interferences. A series of known amounts of the sought-for element is added to the individual sample solution. A graphical representation of the standard additions (spiking) method is shown in Figure 2-2.

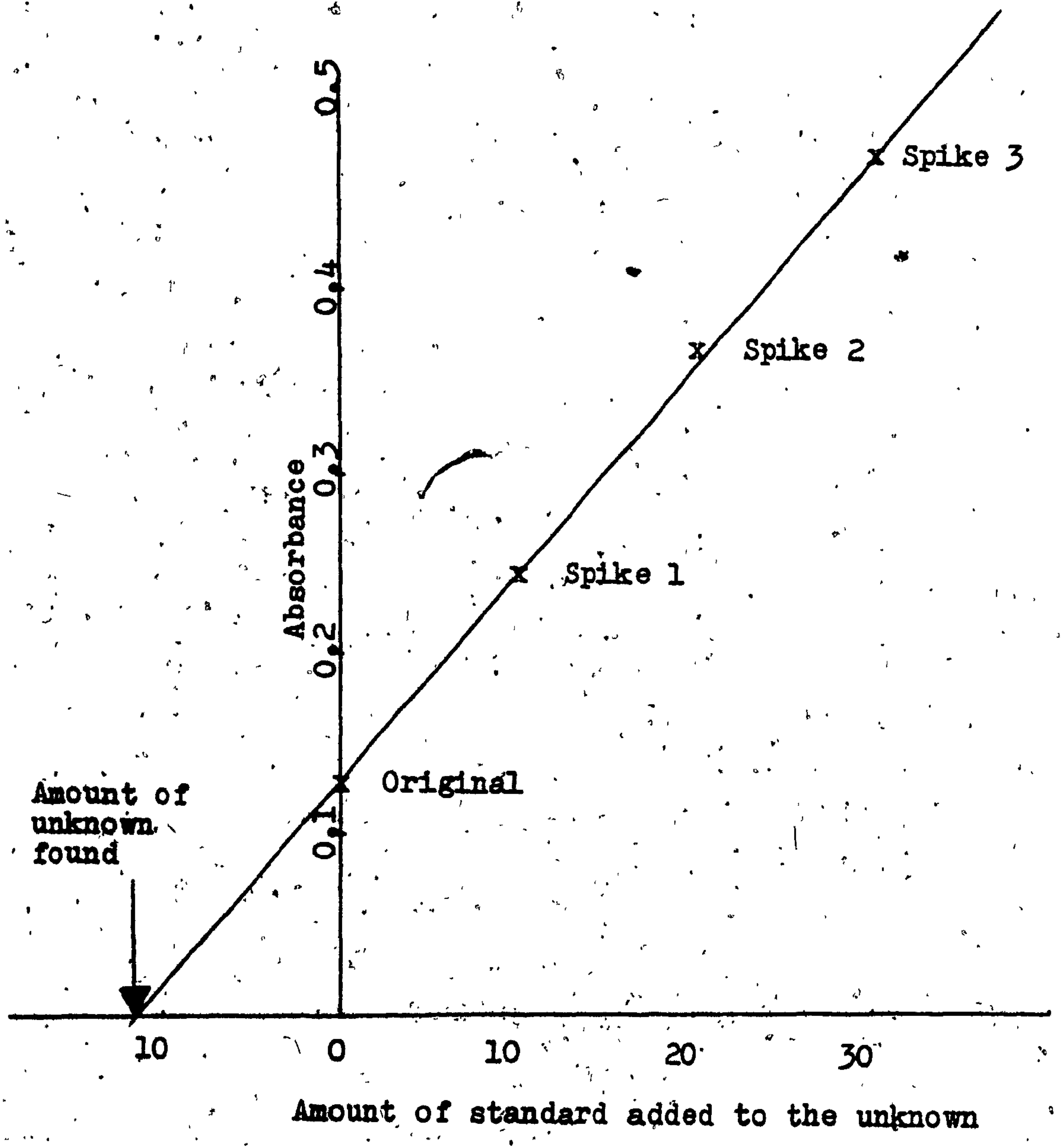


FIGURE 2-2 SPIKING TECHNIQUE

The intercept on the horizontal axis gives the amount of unknown in the original sample. Any interferent present will affect the atom population of the analyte either present originally or added as standard additions.

Some conditions to be observed with the standard additions technique are:-

(a) The concentration of the spike-solutions (original analyte plus amount of standard added) should not be higher than what is specified as the linear response limit.

(b) The amount of standard added should be in the vicinity of the amount of original analyte so as to assure matrix interference will affect the analyte and the standard additions in a similar fashion.

(c) All unspiked and spiked solutions should be of equal volume to avoid tedious calculations.

(d) Since the standard added is often of small volume. accuracy in addition has to be strictly observed

(e) Since spiking often involves dilution of the original sample solution, the detection limit has to be observed in order to avoid loss of precision due to excessive dilution.

2.3 The Perkin Elmer Model 503 Atomic Absorption Spectrophotometer

The equipment used in this study was a Perkin Elmer Model 503 atomic absorption spectrophotometer. For graphite furnace work, additional equipment was required and will be discussed later in this section.

The Perkin Elmer 503 ultilizes a double beam optical system (46). Figure 2.3 shows a general flow diagram. For this work the radiation sources used were single element hollow cathode lamps.

Flame atomic absorption is a very simple approach, and ultilizes burner, mixing chamber and atomizer. The sample solution is aspirated into the mixing chamber and is followed by the formation of a sample aerosol and the atomization step. Attenuation of the radiation source by sample atom vapour is detected and displayed as absorbance.

Flame atomic absorption, simple as it is, suffers from the fact that the atomization efficiency is low owing to the loss of sample at the nebulization stage. For work where greater sensitivity is required, the graphite furnace flameless atomization technique should be used.

For graphite furnace flameless work, in addition to the Perkin Elmer 503, the equipment involved was a Perkin

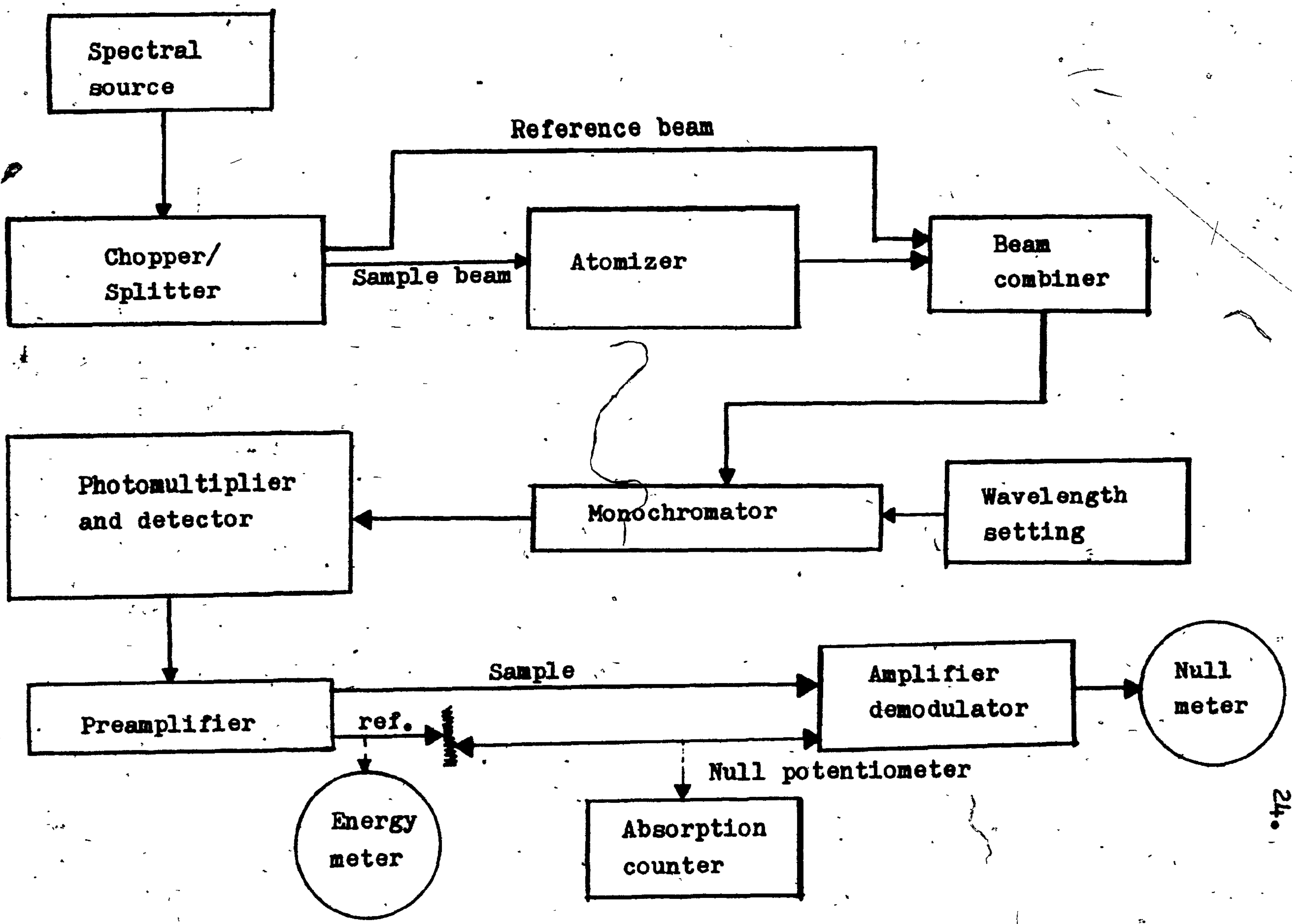


FIGURE 2.3 FLOW DIAGRAM OF THE COMPONENTS OF A PERKIN ELMER SPECTROPHOTOMETER

Elmer HGA 2100(47) graphite furnace attached with the control-programmer, a Perkin Elmer 56 servo-recorder, a Perkin Elmer deuterium arc background corrector (48) and a Perkin Elmer HGA ramp programmer (47)(49).

The atomization cycle involves a three stage heating program:-

(a) A low current/voltage to dry the sample.
(b) A intermediate current/voltage to char and ash the sample.
(c) A high current/voltage to heat the atomizer to incandescence and to atomize the sample.

Again as in the flame technique, the radiation source attenuation is detected and amplified. A Perkin Elmer Model 56 recorder was used for all determinations to record the peak heights, while the absorbance peak integration was obtained simultaneously from the digital readout of the spectrophotometer.

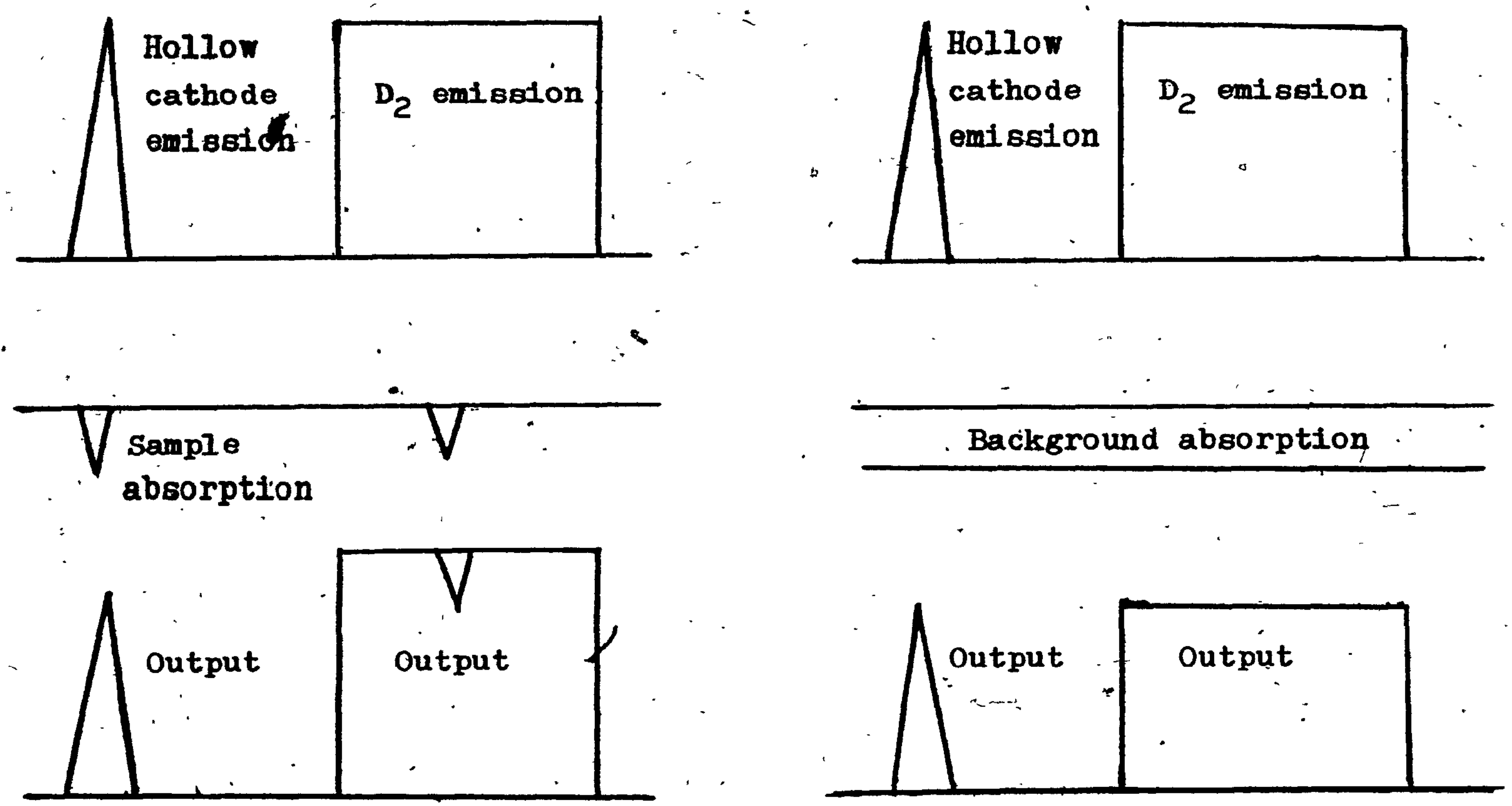
In the normal double beam configuration, the reference beam does not pass through the atomization cell, and hence will correct for the instrumental fluctuation only. Background absorption or scatterings within the atomization cell is not corrected for.

In this study, a D_2 arc background corrector was used. This replaces the ordinary reference beam in the system, but passes through the atomization cell. A chopper is used to split the D_2 beam, so that for a half-cycle the atomized sample is irradiated by the hollow cathode beam, and for the other half-cycle, by the D_2 beam.

A variable attenuator for the D_2 beam serves to balance the reference beam energy against the hollow cathode beam energy in a manner such that the D_2 beam intensity is just slightly higher. Subsquently the two beams are balanced as to digital absorbance by an automatic electronic zeroing device.

Any background absorption and scattering is continuous, and will affect the D_2 and the hollow cathode beams equally. However absorption by analyte atom vapour is discrete absorption and, ~~while~~ affecting the hollow cathode beam, will have little effect on the continuum for the D_2 beam. The difference in attenuation represents the absorption caused by the analyte.

Figure 2.4 shows graphical representation of the functioning of the D_2 beam corrector.



Sample absorption, hollow cathode emission is absorbed proportional to concentration. Sample absorption of D_2 emission is negligible.

Background absorption is shown to be equal for both light sources (hollow cathode and D_2)

FIGURE 2.4 FUNCTIONING OF D_2 ARC BACKGROUND CORRECTOR

Another attachment to the PE 503 is the Perkin Elmer pyro-coating gas control accessory (47). This accessory provides for pyrolysis of the normal graphite furnace tube surface. These pyrolyzed tubes were originally introduced for determination of refractory metals (50) such as vanadium, molybdenum, etc, to prevent atom vapour penetration into the graphite wall. Thus their use decreases the memory effect for consecutive multiple determinations, a factor common with the use of conventional graphite tubes. Other advantages to the use of pyrolytic tubes (47)(51) are increased sensitivity for many metals, and particularly at higher atomization temperatures, extention of tube life.

The last accessory for the PE 503 in graphite furnace usage was the Perkin Elmer HGA ramp programmer.

Frequently for the analysis of complex samples, isothermal (stepwise) temperature programming is not sufficient, since the thermal treatment for any cycle in the program may not be complete. By using temperature ramping, each of the components in a multi-component sample may be subjected to a thermal treatment more closely related to the requirements for these components. Figure 2.5 indicates the temperature/time cycles for ramp programming.

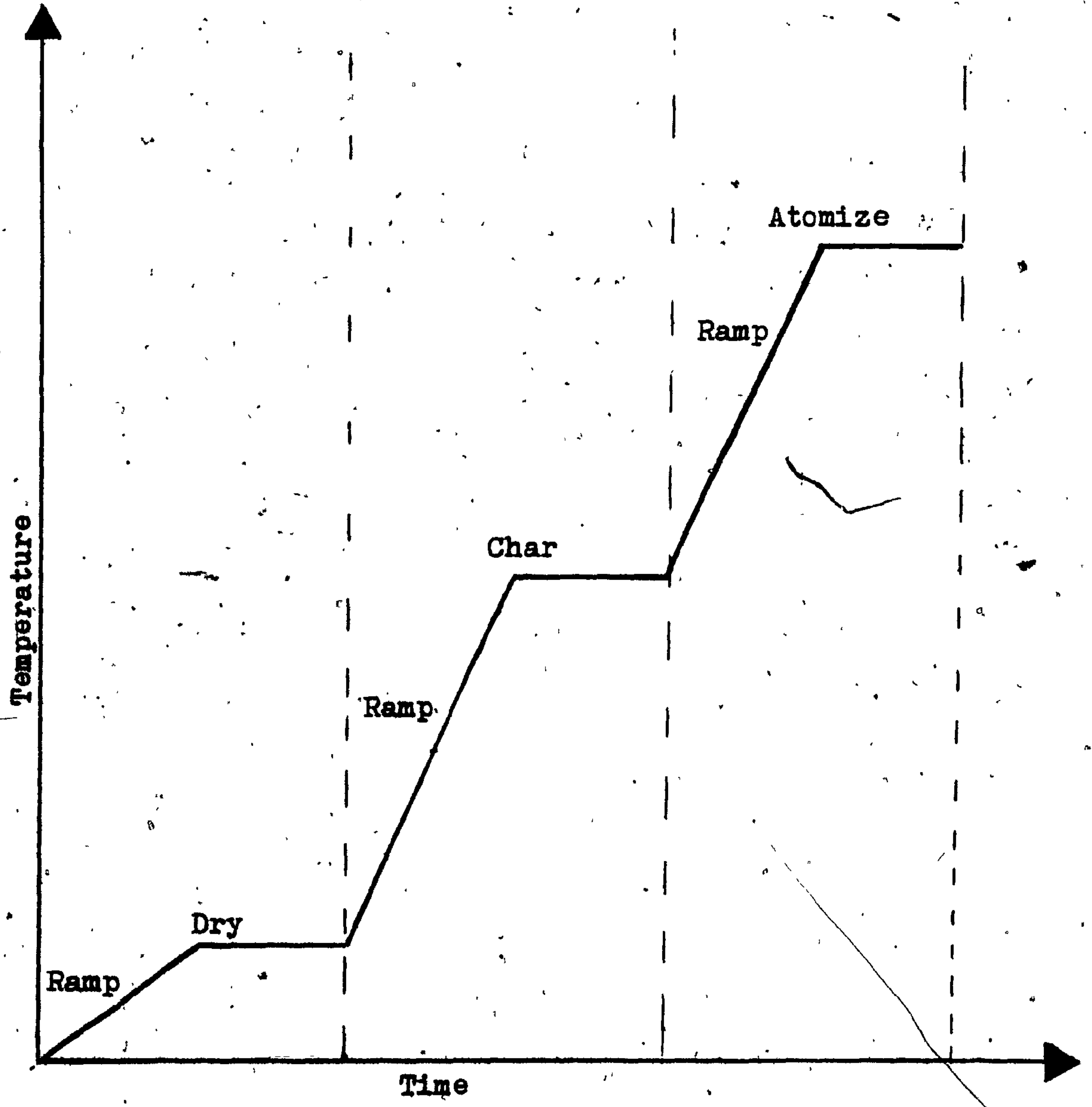


FIGURE 2.5 TIME/TEMPERATURE PROGRAMMING CYCLES WITH RAMPING

Ramp-drying allows for complete evaporation of solvent, and hence prevents any subsquent spattering. Ramp-charring permits more complete destruction of matrix materials (e.g. organic interferents, salts, etc). Ramp-atomization can assist in seperating spectral interferents which have different volatilities from that of the analyte. Figure 2.6 indicates the separation of an interferent peak from an analyte peak. Recorder operation is timed to yield only the analyte peak.

The HGA control programmer has controls permitting temperature settings for the drying, charring and atomizing cycles. Timers are also provided for setting the time duration for each temperature cycle. The ramp programmer, when used has controls permitting for setting of ramping time for the drying, charring and atomizating cycles. The complete analysis cycle series can be initiated by a single control. The proper settings for time and temperature depend on the solution matrix, and are usually determined experimentally.

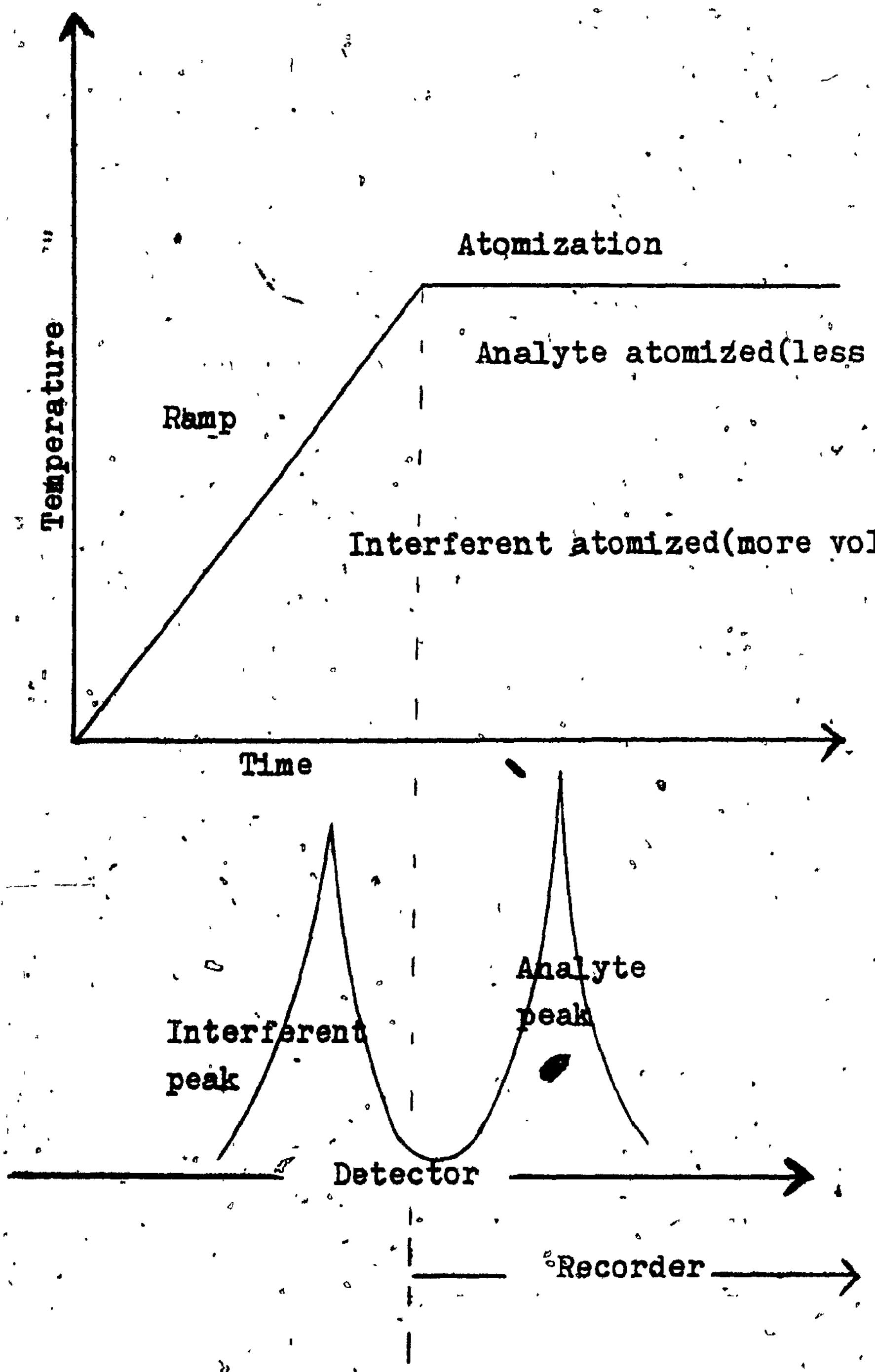


FIGURE 2.6 SEPARATION OF INTERFERENT BY RAMP-ATOMIZATION

3 PROCEDURES

3.1 General Oil Sample Preparation Procedures (Ashing and Acid Take-up) ASTM 3327/74T

3.1.1 Ashing

About five gram of the oil sample is weighed into a clean 50 ml glazed porcelain crucible. About 20 volume % of 20 % (weight per volume) of benzenesulfonic acid in butanol* is added. The mixture, swirled, is then heated over a burner until the sample ignites. Flame is applied to the edge of the crucible to sustain burning of the sample. The temperature is increased when the sample burn-off approaches completion, and heating is continued until smoke no longer appears. The crucible is then transferred to a muffle furnace and heated at 540°C. The sample is then removed from the muffle furnace when all of the carbon residue has disappeared (usually five to ten hours is required).

3.2.2 Acid Take-up

About 5 ml of 1:1 hydrochloric acid is added to the crucible, and the resulting mixture is heated gently under a glazed procelain cover, using a hot plate. After completion of dissolution, the cover is removed, washed down with water and the crucible contents are evaporated down to about 2 ml. The final volume is quantitatively transferred to a 25.00 ± 0,03 ml volumetric flask containing 2.0 ml of potassium buffer solution*, and is diluted to the mark with distilled water. All final solutions should contain about 80 ppm of potassium from the ionization buffer and about 4 % hydrochloric acid.

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* Procedures for the preparation of these solutions can be found in Appendix A.

3.2 Operational Conditions

3.2.1 Flame Technique

The elements involved in this study which were analysed by flame method include nickel, vanadium, iron, copper and zinc. Based on the relatively simple aqueous matrix involved, the operational conditions applied were exactly those suggested by Perkin Elmer (52). No investigation into the optimization of the operational conditions was required.

Linear ranges and sensitivities* were also taken from Perkin Elmer Manual (52) and calibration standards were made up accordingly.

The operational conditions as to the radiation source, wavelength used, etc, for each element are shown in Table 3.1. The sensitivity and absorbance/concentration linear limit for each element are shown in Table 3.2, and are those indicated by the Perkin Elmer operational manual.

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* Sensitivity is represented by the concentration of the analyte at its analytical wavelength which yields 1 % absorption (0.044 absorbance unit).

TABLE 3.1

OPERATIONAL CONDITIONS OF THE ATOMIC ABSRPTION(FLAME TECHNIQUE)

Element	Radiation source	Wavelength (nm)	Slit(nm)	Background corrector	Burner type	Digital readout of absorbance	Fuel	Oxidant
V	Hollow cathode lamp	318.4	0.7	Double beam	High temperature 2 in. slot	3 sec. integration	C_2H_2	N_2O
Ni	Hollow cathode lamp	232.0	0.2	Double beam	Regular 4 in. slot	3 sec. integration	C_2H_2	Air
Fe	Hollow cathode lamp	248.3	0.2	Double beam	Regular 4 in. slot	3 sec. integration	C_2H_2	Air
Cu	Hollow cathode lamp	324.8	0.7	Double beam	Regular 4 in. slot	3 sec. integration	C_2H_2	Air
Zn	Hollow cathode lamp	213.9	0.7	Double beam	Regular 4 in. slot	3 sec. integration	C_2H_2	Air

TABLE 3.2

LINEARITY AND SENSITIVITY FOR THE FLAME TECHNIQUE

Element	Linearity (ppm)	Sensitivity (ppm)	Standard solutions* (ppm)
V	150	1.7	20, 40, 60, 80 and 100
Ni	5	0.15	1, 2, 3, 4 and 5
Fe	5	0.12	1, 2, 3, 4 and 5
Cu	5	0.09	1, 2, 3, 4 and 5
Zn	1	0.018	0.2, 0.4, 0.6, 0.8 and 1.0

* Procedures for the preparation of these solutions can be found in Appendix A

3.2.2 Graphite Furnace Flameless Technique

Elements involved for the graphite furnace flameless study were vanadium, nickel, chromium, cobalt, iron, molybdenum, manganese and copper. The general temperature settings for each cycle were adjusted to values approximating those suggested by Perkin Elmer (47)(48)(49).

For the temperature/time cycles, the drying temperature was always set at 100°C (i.e. for aqueous matrix). The charring temperatures were set at 200°C below the maxima suggested to avoid loss of analyte. Maximum atomization temperatures were used as suggested to achieve the best possible sensitivity. The time settings were adjusted according to the minimum requirements for 20 ul sample injections, with the ramping time occupying half of the total time for each cycle.

The operational conditions as to the radiation source, wavelength used, cycle temperatures, etc, for each element are shown in Tables 3.3 and 3.4.

TABLE 3.3

GNERAL OPERATIONAL CONDITIONS FOR GRAPHITE FURNACE ATOMIZATION TECHNIQUE

Element	Radiation source	Wavelength (nm)	Slit (nm)	Sample size(ul)	Digital readout	Tube type	Background corrector	Carrier gas/ flow rate
V	Hollow cathode lamp	318.4	0.7	20	Peak maximum	Pyrolytic	D_2 beam	Nitrogen/ 100 cc/min
Ni	Hollow cathode lamp	232.0	0.2	20	Peak maximum	Pyrolytic	D_2 beam	Nitrogen/ 100 cc/min
Cr	Hollow cathode lamp	357.9	0.7	20	Peak maximum	Regular	D_2 beam	Nitrogen/ 100 cc/min
Co	Hollow cathode lamp	240.7	0.2	20	Peak maximum	Pyrolytic	D_2 beam	Nitrogen/ 100 cc/min
Fe	Hollow cathode lamp	248.3	0.2	20	Peak maximum	Regular	D_2 beam	Nitrogen 100 cc/min
Mn	Hollow cathode lamp	279.5	0.2	20	Peak maximum	Pyrolytic	D_2 beam	Nitrogen 100 cc/min
Mo	Hollow cathode lamp	313.3	0.7	20	Peak maximum	Pyrolytic	D_2 beam	Nitrogen 100 cc/min
Cu	Hollow cathode lamp	324.7	0.7	20	Peak maximum	Regular	D_2 beam	Nitrogen 100 cc/min

TABLE 3.4

TIME/TEMPERATURE PROGRAMMING FOR GRAPHITE FURNACE ATOMIZATION TECHNIQUE

	Drying		Charring		Atomizing	
	time(sec.) ramp/hold	temp.(C^{o}) max.	time(sec.) ramp/hold	temp.(C^{o}) max.	time(sec.) ramp/hold	temp.(C^{o}) max.
V	10/10	100	10/10	1600	5/5	2800
Ni	10/10	100	10/10	800	5/5	2700
Cr	10/10	100	10/10	900	5/5	2700
Co	10/10	100	10/10	800	5/5	2700
Fe	10/10	100	10/10	900	5/5	2700
Mn	10/10	100	10/10	900	5/5	2700
Mo	10/10	100	10/10	1600	5/5	2700
Cu	10/10	100	10/10	700	5/5	2500

Linear ranges and sensitivities were also taken from those suggested by Perkin Elmer and standard solutions were made up accordingly. The linear limits and sensitivities are shown in Table 3.5.

The HGA 2100 graphite furnace is equipped with two gas flow modes, normal and interrupt. For the interrupt mode, nitrogen flow gas to the graphite furnace is stopped during the atomization cycle. This provides for the highest sensitivity by prolonging the atom vapour resident time inside the furnace tube. However it also induces higher memory effect and therefore poorer precision.

The normal mode provides for reduction in the flow of nitrogen during the atomization cycle and, although lower sensitivity is obtained, better precision results.

For the major portion of the graphite furnace methodology, the normal mode was used. The interrupt mode was applied only with respect to certain manganese determinations (i.e. very low manganese content).

TABLE 3.5

LINEARITY AND SENSITIVITY FOR THE GRAPHITE FURNACE TECHNIQUE*

Element	Linearity (ppb)	Sensitivity (ppb)	Standard solutions** (ppb)
V	1000	19	200, 500, 700 and 800
Ni	350	7.5	100, 200 and 300
Cr	100	1.5	10, 20, 30 and 40
Co	60	3	10, 20, 30 and 40
Fe	75	1.5	20, 40 and 60
Mn(normal)	30	0.5	5, 10, 15, 20 and 25
(interrupt)	10	0.15	2, 4, 6 and 8
Mo	500	4.5	100, 200 and 300
Cu	150	2.5	40, 80 and 120

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* Based upon 20 ul sample injection.

** Procedures for the preparation of these standard solutions can be found in Appendix

3.3 Weathering Procedures

The weathering procedures used in this study were of small scale in comparison with those applied by the U.S. Coast Guard (29)(30). In these latter procedures, actual weathering conditions are closely simulated, through the use of actual sea water, and the exposure of the oil weathering system to natural conditions (e.g. sunlight radiation, normal air circulation, wave action simulation, etc).

In this study, because of the lack of equipment and budgetary restrictions, weathering was carried out on a very small scale. The system applied was scaled-down simulation of the system used by the U.S. Coast Guard (30). The system does provide, however a means of altering the original oil composition, as the results obtained will indicate. For "fingerprinting" technique as applied to environmental spill and source samples, it is not so much a matter of precision and accuracy for each individual elemental determination as it is a matter of the determination of the consistency of the elemental ratios used through the unweathered and weathered sample conditions. Where consistency can be established, the method serves well for the purpose of matching and mismatching spill and source samples.

Most privately owned laboratories will not have the facilities to perform the elaborate weathering procedures as suggested by the U.S. Coast Guard (i.e. a constant supply of sea water is almost impossible inshore). The weathering set-up used in this study should therefore provide a downscaled scheme for artificial weathering. More elaborate budgets will permit refinements to this scheme.

The general and simplified weathering scheme applied is shown in Figure 3.1, and depends largely on the loss of volatile components over the exposure period.

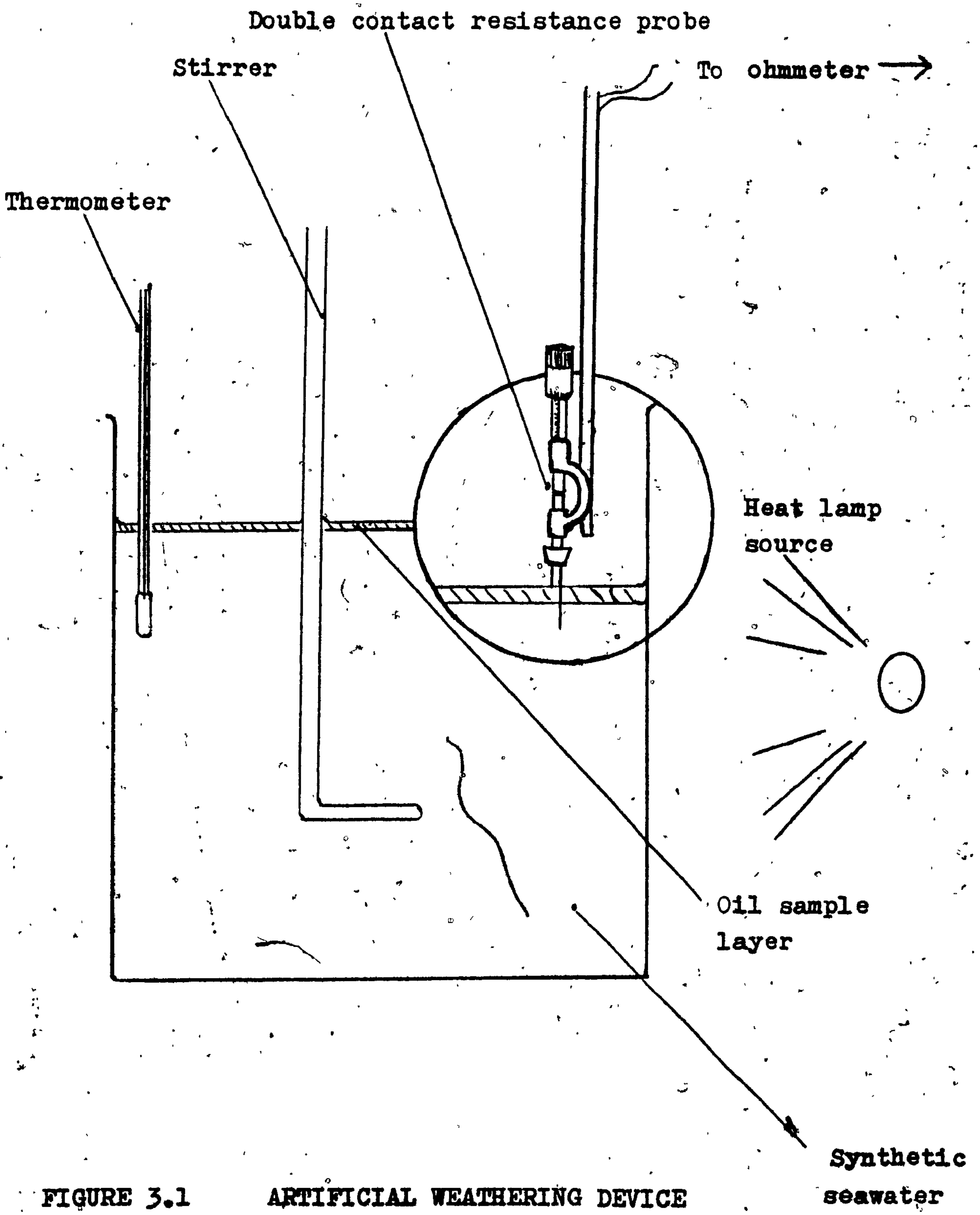

FIGURE 3.1 ARTIFICIAL WEATHERING DEVICE

The general weathering procedures involved the following:-

2.3 liter of synthetic sea water (53) was added to a 3 liter beaker. Approximately 100 ml of the original sample oil was floated on the sea water. The thickness of the oil layer (and its thickness for subsequent measurements) was measured using a double-contact resistance probe according to the method outlined by Dick and Feldman (54).

Stirring of the oil and seawater layers was commenced and continued during the weathering period. The heat lamp source operated on the basis of twelve hours on (during the day) and twelve hours off (during the night). The day temperature achieved was about 25°C, while ambient temperatures were obtained (around 20°C) at night.

For the first four hours of each weathering test, the oil layer thickness was determined every hour. For the next eight hours, the thickness was determined every two hours. For the ensuing period of weathering, the thickness was determined every twelve hours (at the start and the close of the day-testing period). Each test was continued for a total period of 96 hours.

For each oil weathered, a plot of layer thickness expressed as percent volume loss against testing time was obtained.

Figures 3.2 and 3.3 indicate typical percent volume loss versus weathering time plots. It will be noted that near the close of the weathering test period, the sample volume shows a definite tendency to plateau-out. It was assumed, at this point, that furthering weathering would not radically increase the loss of volatile components. Total volume losses for the various test oils varied according to the type of oil, being about 20 percent for the crudes and about 4 percent for the bunker oils.

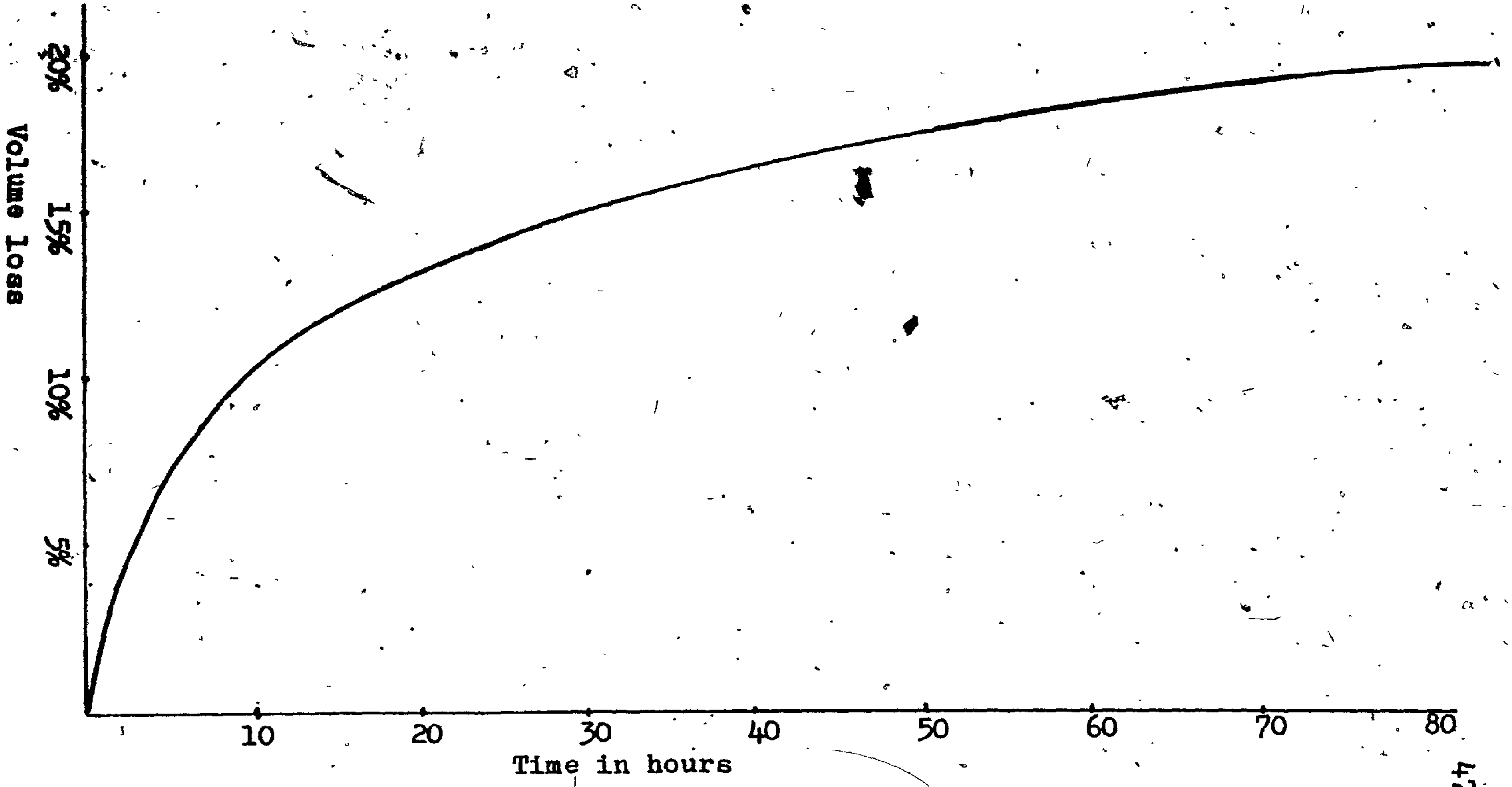

FIGURE 3.2 VOLUME LOSS AGAINST TIME / A CANADIAN CRUDE

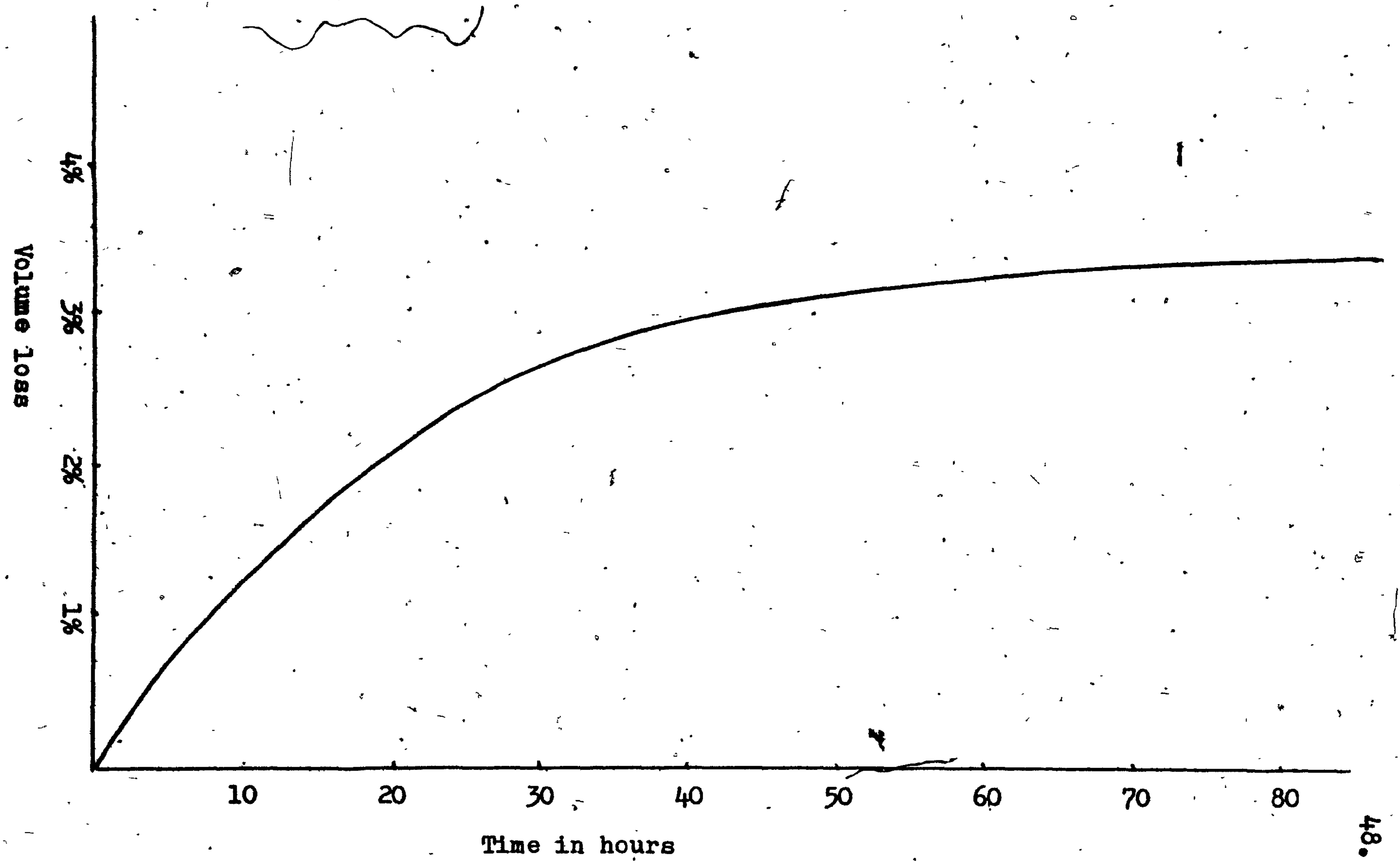

FIGURE 3.3 VOLUME LOSS AGAINST TIME / THIN FILM BUNKER

3.4 Testing of the Analytical Methodology Using ASTM/NBS Standard Oil Material GM-5

Owing to the extensive data collected, only the final results are shown here. Details concerning methodology and calculation are shown in Appendix B.

The standard tested was ASTM/NBS Oil Standard Material GM-5. The analysis for nickel involved the dimethylglyoxime precipitation method, while that for vanadium involved the tungstic acid technique (55). Seventeen (17) results were reported to the ASTM by their contracted analysts, and the average values and standard deviations were:-

Nickel	$93.^{0} \pm 1.^{2}$ ppm
Vanadium	$79.^{0} \pm 1.^{2}$ ppm

The following results, calculated from the methodologies and data outlined in Appendix B were obtained:-

Standard solution calibration basis

Nickel	$90.^{6} \pm 0.^{8}$ ppm
Vanadium	$81.^{1} \pm 1.^{9}$ ppm

Spiking solution basis

Nickel	$92.^{4} \pm 2.^{5}$ ppm
Vanadium	$78.^{3} \pm 4.^{8}$ ppm

Overall basis

Nickel	$91.^{5} \pm 2.^{0}$ ppm
Vanadium	$79.^{7} \pm 3.^{4}$ ppm

Absolute relative error of overall basis results

Nickel	1.6 %
Vanadium	0.9 %

It will be noted that the ASTM/NBS results and the atomic absorption results generally agree within the range of one (1) standard deviation, although the precision for the atomic absorption technique is at a lower order.

It will also be noted that the spiking and the standard calibration methods practically give the same result within a one (1) standard deviation spread, although the spiking method gives poorer precision than the standard calibration method.

4. RESULTS AND DISCUSSIONS RELATIVE TO THE ANALYSES ON THE TEST OILS

4.1 Difference between Spiking and Standard Calibration Techniques

The ten samples were supplied by Shell Canada Limited and involved:-

Crude oils

(1) Venezuelan Largomar
(2) Venezuelan Largotrica
(3) A Canadian Crude
(4) A Second Canadian Crude

Bunker oils

(5) Bunker C
(6) Low Sulphur Bunker
(7) Thin Film Bunker
(8) Bunker Fuel No. 4
(9) Bunker Fuel No. 5
(10) Bunker B

For simplicity, the oil samples will be referred to by their numbers as assigned.

For the original samples, spiking techniques were applied where elemental contents were sufficiently elevated.

The results for both the spiking and standard calibration techniques are presented in Appendix C Tables 1 to 20. From the results obtained, it can be observed that:-

(a) With the exception of the manganese analyses, and within the limit of a one standard deviation spread, for any particular analyte and sample, the spiking and standard calibration techniques, in general, yield the same results.

(b) Generally, within the limit of a one standard deviation spread, standard calibration and spiking techniques yield identical result. However, the precision for the standard calibration technique are superior to those for the spiking technique. This can be attributed to the fact that the spiking technique involves dilution of the original sample and the addition of small but exact volumes of standard solution, and is therefore more susceptible to manipulative errors. Using nickel as an example, the tabulated results clearly show the difference in the precisions but the similarity in the results for the spiking and standard calibration techniques. Table 4.1 shows data from Tables 1 to 6 of Appendix C.

(c) For manganese, the spiking and the standard calibration techniques show a difference in the results beyond one standard deviation. Table 4.2 shows the relevant data from Tables 5, 6, 9 and 10 of Appendix C.

Such a difference occurs because of the fact that the manganese analytical line (279.48 nm) is known to be overlapped by an iron resonance line (279.47 nm) (56)(57). This line is not particularly strong in intensity. but is noted when a comparison is made of the relative contents of iron and manganese in the oil samples. It is apparent that the iron content in these samples is of a magnitude of fifty to one hundred times greater than that of the manganese. Even though the iron resonance line at 279.47 nm is not strong, absorption of manganese source radiation (279.48 nm) by iron will be significant compared with that arising out of manganese itself. This explains why the results for manganese are much higher using the standard calibration technique than those obtained when using the spiking technique. Incidentally these results reinforce the credibility of the spiking technique as a mean of compensating for matrix interference. Table 4.3 shows the relevant data from Tables 5, 6, 9 and 10 of Appendix C.

(d) Finally it can be observed that the precision for results obtained by the graphite furnace atomization technique is generally poorer than that by the flame technique. This is due largely to a lack of reproducibility relative to the graphite furnace atomization as based on;-

(i) Memory effect: Penetration of the sample atom vapour as it takes place into the graphite furnace wall. This gives rise to what is known as the "memory effect". The penetrated residual analyte may enter more or less into the next cycle of atomization giving variable absorbance values.

(ii) Sampling: Injection of the sample solution by micropipette is never as accurate and as reproducible as continuous nebulization and aspiration. Some tendency of the sample solution to creep out of the graphite furnace results in variable losses of analyte.

(iii) The absorption response is a factor of the condition and age of the graphite furnace tube, and a tube used after fifty to one hundred injection cycles will provide less sensitivity than a new one.

TABLE 4.1

RESULTS (PPM) AND STANDARD DEVIATIONS FOR NICKEL ANALYSES ON THE ORIGINAL OIL SAMPLES NUMBERS 1 TO 6 - SPIKING AND STANDARD CALIBRATION TECHNIQUES

Oil sample No.	1	2	3
Standard calibration	16.0 ± 0.1	18.7 ± 0.4	$3.8^{7} \pm 0.2^{2}$
Spiking technique	16.9 ± 0.4	18.9 ± 0.9	$4.0^{7} \pm 0.3^{8}$

Oil sample No.	4	5	6
Standard calibration	14.1 ± 0.2	34.3 ± 0.7	$30.^{2} \pm 1.^{5}$
Spiking technique	13.9 ± 0.5	$35.^{4} \pm 1.^{0}$	$30.^{7} \pm 1.^{7}$

TABLE 4.2

RESULTS (PPB) AND STANDARD DEVIATIONS FOR MANGANESE ANALYSES ON THE ORIGINAL OIL SAMPLES 5, 6, 9 AND 10 - SPIKING AND STANDARD CALIBRATION TECHNIQUES

Oil sample No.	5	6	9	10
Standard calibration	$25^6 \pm 2^4$	$37^6 \pm 2^4$	$13^2 \pm 1^6$	$32^8 \pm 1^7$
Spiking technique	$14^9 \pm 1^6$	$26^8 \pm 3^4$	$81.^9 \pm 4.^5$	$24^8 \pm 2^4$

TABLE 4.3

RESULTS AND STANDARD DEVIATIONS FOR IRON (PPM) AND MANGANESE (PPB) ON THE ORIGINAL OIL SAMPLES 5, 6, 9 AND 10 - SPIKING AND STANDARD CALIBRATION TECHNIQUES

Oil sample No.	5	6	9	10
Iron (ppm)				
Standard calibration	13.2 ± 0.1	26.9 ± 0.2	$7.3^{3} \pm 0.1^{6}$	24.0 ± 0.5
Spiking technique	12.8 ± 0.5	$26.^{6} \pm 1.^{3}$	$7.4^{3} \pm 0.1^{9}$	24.5 ± 0.5
Manganese (ppb)				
Standard calibration	$25^{6} \pm 1^{4}$	$37^{6} \pm 2^{4}$	$12^{3} \pm 1^{6}$	$32^{3} \pm 1^{7}$
Spiking technique	$14^{9} \pm 1^{9}$	$26^{8} \pm 3^{4}$	$81.^{9} \pm 4.^{5}$	$24^{8} \pm 2^{5}$

4.2 Comparison of the Metal Contents between the Original and Weathered Oil Samples and the Calculation of Metal Content Ratios

Subsequent to weathering, the oils were re-analysed for all of the analytes of importance. The determinations of manganese were made on the samples using the spiking technique to reduce the matrix interference effect imposed by the presence of iron.

In order to reduce the time for the analyses, and since precisions had been found to be better, the standard calibration technique was applied for all the other elements.

Table 4.4 through Table 4.13 shows the analytical results, and the data involved were abstracted from Tables 1 to 20 of Appendix G.

TABLE 4.4

ANALYTICAL RESULTS FOR VENEZUELAN LARGOMAR CRUDE

	Original **	Weathered **	Difference % *		
			Ave.	Min.	Max.
V	162 ± 2 ppm	216 ± 6 ppm	33	28	39
Ni	16.5 ± 0.1 ppm	19.7 ± 0.4 ppm	19	16	22
Cr	$32.^{6} \pm 3.^{1}$ ppb	$45.^{2} \pm 1.^{6}$ ppb	39	22	59
Co	$58.^{2} \pm 2.^{6}$ ppb	$65.^{5} \pm 7.^{5}$ ppb	13	-5	31
Fe	0.44 ± 0.07 ppm	0.62 ± 0.05 ppm	41	12	81
Mo	$36.^{3} \pm 2.^{1}$ ppb	$62.^{5} \pm 4.^{6}$ ppb	72	51	91
Mn	$3.^{3} \pm 1.^{2}$ ppb	$3.9^{8} \pm 0.1^{7}$ ppb	21	-15	98
Zn	$0.38^{3} \pm 0.03^{0}$ ppb	10.3 ± 0.3 ppb	excessive		
Cu	0.44 ± 0.08 ppm	0.71 ± 0.08 ppm	61	21	119

* The average and the possible range of difference.

e.g. Vanadium: 162 ± 2 ppm (160 → 164) ppm (Original oil)

216 ± 6 ppm (210 → 222) ppm (Weathered oil)

$$\text{Average difference} = \frac{(216-162)}{162} = 33\ \%$$

$$\text{Maximum difference} = \frac{(222-160)}{160} = 39\ \%$$

$$\text{Minimum difference} = \frac{(210-164)}{164} = 28\ \%$$

** Based on volume loss, original to weathered = 17 %

TABLE 4.5

ANALYTICAL RESULTS FOR VENEZUELAN LARGOTRICA CRUDE

	Original*	Weathered*	Difference %		
			Ave.	Min.	Max.
V	142 ± 2 ppm	190 ± 4 ppm	34	29	38
Ni	18.7 ± 0.4 ppm	$23.^{3} \pm 1.^{0}$ ppm	25	17	33
Cr	$31.^{5} \pm 6.^{4}$ ppb	$44.^{9} \pm 3.^{3}$ ppb	42	10	92
Co	$98.^{2} \pm 4.^{9}$ ppb	117 ± 6 ppb	19	8	32
Fe	0.45 ± 0.09 ppm	0.59 ± 0.05 ppm	31	0	77
Mo	$35.^{3} \pm 2.^{0}$ ppb	$11^{5} \pm 1^{0}$ ppb	excessive		
Mn	$2^{5} \pm 1^{1}$ ppb	$17.^{7} \pm 2.^{3}$ ppb	-29	-57	43
Zn	$0.37^{6} \pm 0.02^{8}$ ppm	$3.1^{4} \pm 0.4^{4}$ ppm	excessive		
Cu	0.38 ± 0.07 ppm	0.50 ± 0.04 ppm	32	3	74

* Based on volume loss, original to weathered = 16 %

TABLE 4.6

ANALYTICAL RESULTS FOR A CANADIAN CRUDE

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	2.34 ± 0.08 ppm	$3.0^{0} \pm 0.1^{9}$ ppm	28	16	41
Ni	$3.8^{7} \pm 0.2^{2}$ ppm	$4.7^{5} \pm 0.1^{2}$ ppm	23	13	33
Cr	not detectable	not detectable	not available		
Co	$10.^{0} \pm 1.^{5}$ ppb	$12.^{6} \pm 1.^{8}$ ppb	26	-13	69
Fe	$0.11^{1} \pm 0.06^{2}$ ppm	$4.2^{2} \pm 0.1^{3}$ ppm	excessive		
Mo	not detectable	not detectable	not available		
Mn	not detectable	not detectable	not available		
Zn	not detectable	3.25 ± 0.07 ppm	not available		
Cu	not detectable	not detectable	not available		

* Based on volume loss, original to weathered = 21 %

TABLE 4.7

ANALYTICAL RESULTS FOR A SECOND CANADIAN CRUDE

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	30.^{9} ± 1.^{9} ppm	37.^{1} ± 1.^{1} ppm	20	10	32
Ni	14.1 ± 0.2 ppm	16.9 ± 0.2 ppm	20	17	23
Cr	65.^{0} ± 4.^{3} ppb	79.^{5} ± 3.^{7} ppb	22	9	37
Co	20.3 ± 0.8 ppb	23.4 ± 0.1 ppb	15	10	20
Fe	0.22^{0} ± 0.04^{6} ppm	0.36 ± 0.04 ppm	64	18	135
Mo	13^{6} ± 2^{5} ppb	15^{4} ± 3^{2} ppb	13	-24	68
Mn	7.52 ± 0.03 ppb	5.^{3} ± 1.^{4} ppb	-30	-48	-11
Zn	0.12^{0} ± 0.03^{8} ppm	3.1^{1} ± 0.1^{4} ppm	excessive		
Cu	not detectable	0.61 ± 0.02 ppm	not available		

* Based on volume loss, original to weathered = 16 %

TABLE 4.8

ANALYTICAL RESULTS FOR BUNKER C

	Original*	Weathered*	Difference %		
			Ave.	Min.	Max.
V	270 ± 7 ppm	288 ± 4 ppm	7	2	11
Ni	34.3 ± 0.7 ppm	36.6 ± 0.4 ppm	7	3	10
Cr	44^0 ± 1^8 ppb	47^5 ± 6^1 ppb	8	-10	27
Co	19^7 ± 1^5 ppb	18^7 ± 1^5 ppb	-5	-19	21
Fe	13.2 ± 0.1 ppm	13.7 ± 0.4 ppm	4	0	8
Mo	27^2 ± 2^0 ppb	29^3 ± 4^8 ppb	8	-16	35
Mn	14^9 ± 1^6 ppb	17^1 ± 1^8 ppb	15	-7	42
Zn	1.2^2 ± 0.1^0 ppm	4.2^7 ± 0.3^2 ppm	excessive		
Cu	0.6^0 ± 0.1^0 ppm	0.7^5 ± 0.1^1 ppm	25	-8	72

* Based on volume loss, original to weathered = 0 %

TABLE 4.9

ANALYTICAL RESULTS FOR LOW SULPHUR BUNKER

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	143 ± 3 ppm	156 ± 6 ppm	9	3	16
Ni	$30.^{2} \pm 1.^{5}$ ppm	30.0 ± 0.5 ppm	-1	-7	6
Cr	$110^{4} \pm 3^{1}$ ppb	$101^{1} \pm 3^{8}$ ppb	-8	-14	2
Co	161 ± 8 ppb	$18^{5} \pm 1^{2}$ ppb	15	2	29
Fe	26.9 ± 0.2 ppm	26.1 ± 0.2 ppm	-3	-4	-2
Mo	$28^{6} \pm 1^{4}$ ppb	$31^{8} \pm 2^{6}$ ppb	11	-3	26
Mn	$26^{8} \pm 3^{4}$ ppb	$29^{3} \pm 3^{9}$ ppb	9	-36	42
Zn	$2.0^{4} \pm 0.2^{0}$ ppm	$2.5^{0} \pm 0.1^{9}$ ppm	22	3	46
Cu	1.08 ± 0.08 ppm	1.02 ± 0.08 ppm	-6	-19	10

* Based on volume loss, original to weathered = 0 %

TABLE 4.10

ANALYTICAL RESULTS FOR THIN FILM BUNKER

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	177 ± 5 ppm	173 ± 1 ppm	-2	-5	1
Ni	17.1 ± 0.2 ppm	16.8 ± 0.1 ppm	-2	-3	0
Cr	$46.^{9} \pm 1.^{6}$ ppb	$48.^{8} \pm 5.^{8}$ ppb	4	-11	20
Co	$89.^{4} \pm 1.^{2}$ ppb	$64.^{9} \pm 3.^{7}$ ppb	-27	-32	-22
Fe	$1.7^{5} \pm 0.1^{0}$ ppm	1.79 ± 0.02 ppm	2	-4	10
Mo	not detectable	not detectable	not available		
Mn	$16.^{7} \pm 2.^{2}$ ppb	$15.^{9} \pm 1.^{8}$ ppb	-5	-25	22
Zn	$0.23^{9} \pm 0.02^{8}$ ppm	$5.2^{0} \pm 0.1^{0}$ ppm	excessive		
Cu	$0.09^{3} \pm 0.01^{2}$ ppm	0.63 ± 0.08 ppm	excessive		

* Based on volume loss, original to weathered = 0 %

TABLE 4.11

ANALYTICAL RESULTS FOR BUNKER FUEL NO. 4

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	35.0 ± 0.9 ppm	34.3 ± 0.9 ppm	-2	-7	3
Ni	7.72 ± 0.07 ppm	7.88 ± 0.07 ppm	2	0	4
Cr	$44.^{1} \pm 4.^{2}$ ppb	40.1 ± 0.4 ppb	-9	-18	2
Co	$32.^{8} \pm 3.^{8}$ ppb	$25.^{0} \pm 1.^{7}$ ppb	-24	-36	-8
Fe	$0.22^{6} \pm 0.01^{1}$ ppm	$0.21^{0} \pm 0.02^{4}$ ppm	-7	-22	9
Mo	not detectable	not detectable	not available		
Mn	$14.^{1} \pm 1.^{6}$ ppb	$9.^{1} \pm 1.^{1}$ ppb	-35	-49	-18
Zn	$0.26^{3} \pm 0.01^{9}$ ppm	1.32 ± 0.04 ppm	excessive		
Cu	$0.034^{5} \pm 0.002^{1}$ ppm	$0.28^{9} \pm 0.01^{8}$ ppm	excessive		

* Based on volume loss, original to weathered = 3 %

TABLE 4.12

ANALYTICAL RESULTS FOR BUNKER FUEL NO. 5

	Original*	Weathered*	Difference %		
			Ave.	Min.	Max.
V	108 ± 3 ppm	104 ± 2 ppm	-4	-8	1
Ni	19.2 ± 0.2 ppm	19.5 ± 0.4 ppm	2	-2	5
Cr	$47^{0} \pm 1^{4}$ ppb	$55^{0} \pm 3^{5}$ ppb	17	6	28
Co	130 ± 1 ppb	$13^{6} \pm 1^{6}$ ppb	5	-8	18
Fe	$7.3^{3} \pm 0.1^{6}$ ppm	7.10 ± 0.07 ppm	-3	-6	0
Mo	120 ± 9 ppb	$12^{1} \pm 4^{6}$ ppb	1	-42	50
Mn	$81.^{9} \pm 4.^{5}$ ppb	$89.^{1} \pm 7.^{9}$ ppb	0	-6	25
Zn	$0.76^{5} \pm 0.02^{5}$ ppm	1.41 ± 0.05 ppm	excessive		
Cu	$0.13^{4} \pm 0.01^{6}$ ppm	0.60 ± 0.04 ppm	excessive		

* Based on volume loss, original to weathered = 4 %

TABLE 4.13

ANALYTICAL RESULTS FOR BUNKER B

	Original *	Weathered *	Difference %		
			Ave.	Min.	Max.
V	152 ± 4 ppm	153 ± 4 ppm	1	-4	6
Ni	29.0 ± 0.3 ppm	29.2 ± 0.4 ppm	1	-2	3
Cr	$107^{6} \pm 4^{5}$ ppb	$92^{6} \pm 1^{8}$ ppb	-14	-19	-8
Co	198 ± 5 ppb	178 ± 9 ppb	-10	-2-	-3
Fe	24.0 ± 0.5 ppm	25.1 ± 0.5 ppm	4	0	9
Mo	$11^{7} \pm 1^{1}$ ppb	$35^{0} \pm 8^{0}$ ppb	excessive		
Mn	$24^{8} \pm 2^{5}$ ppb	$24^{2} \pm 1^{0}$ ppb	-2	-15	13
Zn	1.73 ± 0.03 ppm	$1.9^{9} \pm 0.1^{1}$ ppm	15	7	24
Cu	$0.32^{1} \pm 0.03^{9}$ ppm	0.67 ± 0.03 ppm	excessive		

* Based on volume loss, original to weathered = 0 %

Comparison of the results reveals the following:-

(a) For copper and zinc, and especially with zinc, there are unrealistic differences in the metal contents between the original and weathered sample oils. The above trend can also be observed to be associated with molybdenum (with the exception of samples 5 and 6), with manganese on the crude oils (samples 1 to 4) and with iron (samples 3 and 4). The reason for these disparate differences is thought to be contamination of oil during the weathering process. Such contamination could well have arisen out of impurities in the reagents used to prepare the synthetic seawater, since the total analysis was not available for these reagents. This is suspected to be particularly the situation for zinc and copper differences. For manganese and iron, satisfactory results were obtained whenever the metallic contents were high enough (i.e. as in the bunker oils) to render contamination insignificant. Molybdenum is not a common source of reagent contaminant, however the experimental differences could easily have been caused by the lack of sensitivity for the molybdenum absorption at the detection levels involved.

(b) The crude oils, after weathering, show a much greater increase in their metal contents than do the bunker oils. This can be attributed to the fact that the total volume loss for the bunker oils by evaporation is much less due to the removal as distillates of the non-volatile componants of the parent crude.

In determining the useable ratios, the copper, zinc and molybdenum analyses must be ignored as suspect. Manganese would be omitted for the crude oils (samples 1 to 4) and iron will be omitted for samples 3 and 4. In addition, the following rules were always observed in order to provide valid subsquent "fingerprinting" comparisons.

(a) Order of elements in general terms of quantity and analytical reliability is vanadium, nickel chromium, cobalt, iron and manganese.

(b) In accordance with the general range of compositions for the elements, the concentration unit for vanadium, nickel and iron is expressed as ppm, whilst that for chromium, cobalt and manganese is expressed as ppb.

(c) The deviation ΔR (error of ratio) associated with each ratio will be calculated based upon the standard deviations of the two values involved in the ratio as propagation of indeterminate errors (58).

$$R = \frac{A}{B} \quad \text{and} \quad \Delta R = R\sqrt{(\Delta A/A)^2 + (\Delta B/B)^2} \quad \ldots\ldots (1)$$

where:-

R = the ratio

ΔA and ΔB = the standard deviations for the values A and B

Example; Venezuelan Largomar crude (original sample)

V; 162 ± 2 ppm

Ni: 16.5 ± 0.1 ppm

$$\text{Ratio} = \frac{162}{16.5}$$

$$= 9.8^2$$

$$\Delta R = 9.82\sqrt{(2/162)^2 + (0.1/16.5)^2}$$

$$= 0.1^3$$

$$\text{Ratio} \pm \Delta R = 9.8^2 \pm 0.1^3$$

Tables 4.14 to 4.23 show the calculated metal content ratio values and their errors (ΔR) using available analytical data from Tables 4.4 to 4.13 of Section 4.

TABLE 4.14

METAL CONTENT RATIO VALUES FOR VENEZUELAN LARGOMAR CRUDE

Ratio	Original	Weathered
V/Ni	$9.8^2 \pm 0.1^4$	$10.9^6 \pm 0.3^8$
V/Cr	$4.9^7 \pm 0.4^8$	$4.7^8 \pm 0.2^2$
V/Co	$2.7^8 \pm 0.1^3$	$3.3^0 \pm 0.3^9$
V/Fe	$36^8 \pm 5^9$	$34^8 \pm 3^0$
Ni/Cr	$0.50^6 \pm 0.04^8$	$0.43^6 \pm 0.01^8$
Ni/Co	$0.28^3 \pm 0.01^2$	$0.30^1 \pm 0.03^5$
Ni/Fe	$37.^5 \pm 6.^0$	$31.^8 \pm 2.^6$
Cr/Co	$0.56^0 \pm 0.05^9$	$0.69^0 \pm 0.08^3$
Cr/Fe	$7^4 \pm 1^4$	$72.^9 \pm 6.^4$
Co/Fe	$13^2 \pm 2^2$	$10^6 \pm 1^5$

TABLE 4.15

METAL CONTENT RATIO VALUES FOR VENEZUELAN LARGOTRICA CRUDE

Ratio	Original	Weathered
V/Ni	$7.5^{9} \pm 0.1^{9}$	$8.1^{5} \pm 0.3^{9}$
V/Cr	$4.5^{1} \pm 0.9^{2}$	$4.2^{3} \pm 0.3^{2}$
V/Co	$1.44^{6} \pm 0.07^{5}$	$1.62^{4} \pm 0.09^{0}$
V/Fe	$31^{6} \pm 6^{3}$	$32^{2} \pm 2^{8}$
Ni/Cr	$0.5^{9} \pm 0.1^{2}$	$0.51^{8} \pm 0.04^{4}$
Ni/Co	$0.19^{0} \pm 0.01^{0}$	$0.19^{9} \pm 0.01^{3}$
Ni/Fe	$41.^{6} \pm 8.^{4}$	$39.^{5} \pm 3.^{8}$
Cr/Co	$0.32^{1} \pm 0.06^{7}$	$0.38^{4} \pm 0.03^{4}$
Cr/Fe	$7^{0} \pm 2^{0}$	$76.^{1} \pm 8.^{5}$
Co/Fe	$21^{8} \pm 4^{5}$	$19^{8} \pm 2^{0}$

TABLE 4.16

METAL CONTENT RATIO VALUES FOR A CANADIAN CRUDE

Ratio	Original	Weathered
V/Ni	$0.60^{5} \pm 0.04^{0}$	$0.63^{2} \pm 0.04^{3}$
V/Co	$0.23^{4} \pm 0.03^{6}$	$0.23^{8} \pm 0.03^{7}$
Ni/Co	$0.38^{7} \pm 0.06^{2}$	$0.37^{7} \pm 0.05^{5}$

TABLE 4.17

METAL CONTENT RATIO VALUES FOR A SECOND CANADIAN CRUDE

Ratio	Original	Weathered
V/Ni	$2.1^{9} \pm 0.1^{4}$	$2.19^{5} \pm 0.07^{0}$
V/Cr	$0.47^{5} \pm 0.04^{3}$	$0.46^{7} \pm 0.02^{6}$
V/Co	$1.5^{2} \pm 0.1^{1}$	$1.58^{5} \pm 0.04^{8}$
Ni/Cr	$0.21^{7} \pm 0.01^{5}$	$0.21^{2} \pm 0.01^{0}$
Ni/Co	$0.69^{5} \pm 0.02^{9}$	$0.722^{2} \pm 0.009^{1}$
Cr/Co	$3.2^{0} \pm 0.2^{5}$	$3.4^{0} \pm 0.1^{6}$

TABLE 4.18

METAL CONTENT RATIO VALUES FOR BUNKER C

Ratio	Original	Weathered
V/Ni	$7.8^{7} \pm 0.2^{6}$	$7.8^{7} \pm 0.1^{4}$
V/Cr	$0.61^{4} \pm 0.03^{0}$	$0.60^{6} \pm 0.07^{8}$
V/Co	$1.3^{7} \pm 0.1^{1}$	$1.5^{4} \pm 0.1^{2}$
V/Fe	$20.4^{5} \pm 0.5^{5}$	$21.0^{2} \pm 0.6^{8}$
V/Mn	$1.8^{1} \pm 0.2^{0}$	$1.6^{8} \pm 0.1^{8}$
Ni/Cr	$0.078^{0} \pm 0.003^{6}$	$0.077^{0} \pm 0.009^{9}$
Ni/Co	$0.17^{4} \pm 0.01^{4}$	$0.19^{6} \pm 0.01^{6}$
Ni/Fe	$2.59^{8} \pm 0.05^{6}$	$2.67^{1} \pm 0.08^{3}$
Ni/Mn	$0.23^{0} \pm 0.02^{5}$	$0.21^{4} \pm 0.02^{3}$
Cr/Co	$2.2^{3} \pm 0.1^{9}$	$2.5^{4} \pm 0.3^{8}$
Cr/Fe	$33.^{3} \pm 1.^{4}$	$34.^{7} \pm 4.^{6}$
Cr/Mn	$2.9^{5} \pm 0.3^{4}$	$2.7^{8} \pm 0.4^{6}$
Co/Fe	$14.^{9} \pm 1.^{1}$	$13.^{6} \pm 1.^{1}$
Co/Mn	$1.3^{2} \pm 0.1^{7}$	$1.0^{9} \pm 0.1^{4}$
Fe/Mn	$0.088^{6} \pm 0.009^{5}$	$0.080^{1} \pm 0.008^{8}$

TABLE 4.19

METAL CONTENT RATIO VALUES FOR LOW SULPHUR BUNKER

Ratio	Original	Weathered
V/Ni	$4.7^4 \pm 0.2^6$	$5.2^0 \pm 0.2^2$
V/Cr	$0.129^5 \pm 0.004^5$	$0.154^3 \pm 0.008^2$
V/Co	$0.88^8 \pm 0.04^8$	$0.84^3 \pm 0.06^4$
V/Fe	$5.3^2 \pm 0.1^2$	$5.9^8 \pm 0.2^3$
V/Mn	$0.53^4 \pm 0.06^9$	$0.53^2 \pm 0.07^4$
Ni/Cr	$0.027^4 \pm 0.001^6$	$0.029^7 \pm 0.001^2$
Ni/Co	$0.18^8 \pm 0.01^3$	$0.16^2 \pm 0.01^1$
Ni/Fe	$1.12^3 \pm 0.05^6$	$1.14^9 \pm 0.02^1$
Ni/Mn	$0.11^3 \pm 0.01^5$	$0.10^2 \pm 0.01^4$
Cr/Co	$6.8^6 \pm 0.3^9$	$5.4^6 \pm 0.4^1$
Cr/Fe	$41.^0 \pm 1.^2$	$3.8^7 \pm 1.^5$
Cr/Mn	$4.1^2 \pm 0.2^4$	$3.4^5 \pm 0.4^8$
Co/Fe	$5.9^8 \pm 0.3^0$	$7.0^9 \pm 0.4^6$
Co/Mn	$0.60^1 \pm 0.08^2$	$0.63^1 \pm 0.09^3$
Fe/Mn	$0.10^0 \pm 0.01^3$	$0.08^9 \pm 0.01^2$

TABLE 4.20

METAL CONTENT RATIO VALUES FOR THIN FUEL BUNKER

Ratio	Original	Weathered
V/Ni	$10.3^5 \pm 0.3^2$	10.30 ± 0.08
V/Cr	$3.7^7 \pm 0.1^7$	$3.5^4 \pm 0.4^2$
V/Co	$1.98^0 \pm 0.06^2$	$2.6^7 \pm 0.1^5$
V/Fe	$101.^1 \pm 6.^4$	$96.^6 \pm 1.^2$
V/Mn	$10.^6 \pm 1.^4$	$10.^9 \pm 1.^2$
Ni/Cr	$0.36^4 \pm 0.01^3$	$0.34^4 \pm 0.04^1$
Ni/Co	$0.191^3 \pm 0.003^4$	$0.25^9 \pm 0.01^5$
Ni/Fe	$9.7^7 \pm 0.5^7$	$9.3^8 \pm 0.1^2$
Ni/Mn	$1.0^2 \pm 0.1^4$	$1.0^6 \pm 0.1^2$
Cr/Co	$0.52^4 \pm 0.01^9$	$0.75^2 \pm 0.09^9$
Cr/Fe	$26.^8 \pm 1.^8$	$27.^3 \pm 3.^2$
Cr/Mn	$2.8^1 \pm 0.3^8$	$3.0^7 \pm 0.5^0$
Co/Fe	$51.^1 \pm 3.^0$	$36.^2 \pm 2.^1$
Co/Mn	$5.3^5 \pm 0.7^1$	$4.0^8 \pm 0.5^2$
Fe/Mn	$0.10^5 \pm 0.01^5$	$0.11^2 \pm 0.01^3$

TABLE 4.21

METAL CONTENT RATIO VALUES FOR BUNKER FUEL NO. 4

Ratio	Original	Weathered
V/Ni	$4.5^{3} \pm 0.1^{2}$	$4.3^{5} \pm 0.1^{2}$
V/Cr	$0.79^{3} \pm 0.07^{8}$	$0.85^{5} \pm 0.02^{4}$
V/Co	$1.0^{7} \pm 0.1^{3}$	$1.3^{7} \pm 0.1^{0}$
V/Fe	$154.^{9} \pm 8.^{5}$	$16^{3} \pm 1^{9}$
Ni/Cr	$0.17^{5} \pm 0.01^{7}$	$0.196^{5} \pm 0.002^{6}$
Ni/Co	$0.23^{5} \pm 0.02^{7}$	$0.31^{5} \pm 0.02^{2}$
Ni/Fe	$34.^{2} \pm 1.^{7}$	$37.^{5} \pm 4.^{5}$
Cr/Co	$1.3^{4} \pm 0.2^{0}$	$1.6^{0} \pm 0.1^{1}$
Cr/Fe	$19^{5} \pm 2^{1}$	$19^{1} \pm 2^{2}$
Co/Fe	$14^{5} \pm 1^{8}$	$11^{9} \pm 1^{6}$

TABLE 4.22

MEATAL CONTENT RATIO VALUES FOR BUNKER FUEL NO. 5

Ratio	Original	Weathered
V/Ni	$5.6^{3} \pm 0.1^{7}$	$5.3^{3} \pm 0.1^{5}$
V/Cr	$0.229^{8} \pm 0.009^{4}$	$0.18^{9} \pm 0.01^{2}$
V/Co	$0.83^{1} \pm 0.02^{4}$	$0.76^{4} \pm 0.09^{1}$
V/Fe	$14.7^{3} \pm 0.5^{2}$	$14.6^{5} \pm 0.3^{2}$
V/Mn	$1.31^{9} \pm 0.08^{1}$	$1.1^{7} \pm 0.1^{0}$
Ni/Cr	$0.040^{8} \pm 0.001^{3}$	$0.035^{4} \pm 0.002^{4}$
Ni/Co	$0.147^{7} \pm 0.001^{9}$	$0.14^{3} \pm 0.01^{7}$
Ni/Fe	$2.61^{9} \pm 0.06^{3}$	$2.74^{6} \pm 0.06^{2}$
Ni/Mn	$0.23^{4} \pm 0.01^{3}$	$0.21^{9} \pm 0.02^{0}$
Cr/Co	$3.6^{2} \pm 0.1^{1}$	$4.0^{4} \pm 0.5^{4}$
Co/Fe	$64.^{1} \pm 2.^{4}$	$77.^{5} \pm 5.^{0}$
Cr/Mn	$5.7^{4} \pm 0.3^{6}$	$6.1^{7} \pm 0.6^{7}$
Co/Fe	$17.7^{4} \pm 0.4^{1}$	$19.^{2} \pm 2.^{3}$
Co/Mn	$1.58^{7} \pm 0.08^{8}$	$1.5^{3} \pm 0.2^{2}$
Fe/Mn	$0.089^{5} \pm 0.005^{3}$	$0.079^{7} \pm 0.007^{1}$

TABLE 4.23

METAL CONTENT RATIO VALUES FOR BUNKER B

Ratio	Original	Weathered
V/Ni	$5.2^{4} \pm 0.1^{5}$	$5.2^{4} \pm 0.1^{5}$
V/Cr	$0.141^{3} \pm 0.007^{0}$	$0.165^{2} \pm 0.005^{4}$
V/Co	$0.76^{8} \pm 0.02^{8}$	$0.86^{0} \pm 0.04^{9}$
V/Fe	$6.3^{3} \pm 0.2^{1}$	$6.1^{0} \pm 0.2^{0}$
V/Mn	$0.61^{3} \pm 0.06^{4}$	$0.63^{2} \pm 0.03^{1}$
Ni/Cr	$0.027^{0} \pm 0.001^{2}$	0.0318 ± 0.0008
Ni/Co	$0.146^{5} \pm 0.004^{0}$	$0.164^{0} \pm 0.008^{6}$
Ni/Fe	$1.20^{8} \pm 0.02^{8}$	$1.16^{3} \pm 0.02^{8}$
Ni/Mn	$0.11^{7} \pm 0.01^{2}$	$0.120^{7} \pm 0.005^{2}$
Cr/Co	$5.4^{3} \pm 0.2^{7}$	$5.2^{0} \pm 0.2^{8}$
Cr/Fe	$44.^{8} \pm 2.^{1}$	$36.^{9} \pm 1.^{0}$
Cr/Mn	$4.3^{3} \pm 0.4^{7}$	$3.8^{3} \pm 0.1^{7}$
Co/Fe	$8.2^{5} \pm 0.2^{7}$	$7.0^{9} \pm 0.3^{8}$
Co/Mn	$0.79^{8} \pm 0.08^{3}$	$0.73^{6} \pm 0.04^{8}$
Fe/Mn	$0.09^{7} \pm 0.01^{0}$	$0.103^{7} \pm 0.004^{8}$

4.3 Test for the Reliability (Probability of Success) of the Metal Ratios in "Fingerprinting" Oils

From the six elements, a total of fifteen ratio groups can be obtained, and these ratio groups are listed in Tables 4.24 to 4.38.

Ratio group	Number of ratio pairs involved based on available analytical data
V/Ni	10
V/Cr	9
V/Co	10
V/Fe	8
V/Mn	5
Ni/Cr	9
Ni/Co	10
Ni/Fe	8
Ni/Mn	5
Cr/Co	9
Cr/Fe	8
Cr/Mn	5
Co/Fe	8
Co/Mn	5
Fe/Mn	5

Tables 4.24 to 4.38 show data from Tables 4.14 to 4.23 of Section 4.

TABLE 4.24

METAL CONTENT RATIO VALUES FOR V/Ni

Oil No.	Original	Weathered
1	$9.8^{2} \pm 0.1^{4}$	$10.9^{6} \pm 0.3^{8}$
2	$7.5^{9} \pm 0.1^{9}$	$8.1^{5} \pm 0.3^{9}$
3	$0.60^{5} \pm 0.04^{0}$	$0.63^{2} \pm 0.04^{3}$
4	$2.1^{9} \pm 0.1^{4}$	$2.19^{5} \pm 0.07^{0}$
5	$7.8^{7} \pm 0.2^{6}$	$7.8^{7} \pm 0.1^{4}$
6	$4.7^{4} \pm 0.2^{6}$	$5.2^{0} \pm 0.2^{2}$
7	$10.3^{5} \pm 0.3^{2}$	10.30 ± 0.08
8	$4.5^{3} \pm 0.1^{2}$	$4.3^{5} \pm 0.1^{2}$
9	$5.6^{3} \pm 0.1^{7}$	$5.3^{3} \pm 0.1^{5}$
10	$5.2^{4} \pm 0.1^{5}$	$5.2^{4} \pm 0.1^{5}$

TABLE 4.25

METAL CONTENT RATIO VALUES FOR V/Cr

Oil No.	Original	Weathered
1	$4.9^{7} \pm 0.4^{8}$	$4.7^{8} \pm 0.2^{2}$
2	$4.5^{1} \pm 0.9^{2}$	$4.2^{3} \pm 0.3^{2}$
4	$0.47^{5} \pm 0.04^{3}$	$0.46^{7} \pm 0.02^{6}$
5	$0.61^{4} \pm 0.03^{0}$	$0.60^{6} \pm 0.07^{8}$
6	$0.129^{5} \pm 0.004^{5}$	$0.154^{3} \pm 0.008^{2}$
7	$3.7^{7} \pm 0.1^{7}$	$3.5^{4} \pm 0.4^{2}$
8	$0.79^{3} \pm 0.07^{8}$	$0.85^{5} \pm 0.02^{4}$
9	$0.229^{8} \pm 0.009^{4}$	$0.18^{9} \pm 0.01^{2}$
10	$0.141^{3} \pm 0.007^{0}$	$0.165^{2} \pm 0.005^{4}$

TABLE 4.26

METAL CONTENT RATIO VALUES FOR V/Co

Oil No.	Original	Weathered
1	$2.7^{8} \pm 0.1^{3}$	$3.3^{0} \pm 0.3^{9}$
2	$1.44^{6} \pm 0.07^{5}$	$1.62^{4} \pm 0.09^{0}$
3	$0.23^{4} \pm 0.03^{6}$	$0.23^{8} \pm 0.03^{7}$
4	$1.5^{2} \pm 0.1^{1}$	$1.58^{5} \pm 0.04^{8}$
5	$1.3^{7} \pm 0.1^{1}$	$1.5^{4} \pm 0.1^{2}$
6	$0.88^{8} \pm 0.04^{8}$	$0.84^{3} \pm 0.06^{4}$
7	$1.98^{0} \pm 0.06^{2}$	$2.6^{7} \pm 0.1^{5}$
8	$1.0^{7} \pm 0.1^{3}$	$1.3^{7} \pm 0.1^{0}$
9	$0.83^{1} \pm 0.02^{4}$	$0.76^{4} \pm 0.09^{1}$
10	$6.3^{3} \pm 0.2^{1}$	$6.1^{0} \pm 0.2^{0}$

TABLE 4.27

METAL CONTENT RATIO VALUES FOR V/Fe

Oil No.	Original	Weathered
1	$36^{8} \pm 5^{9}$	$34^{8} \pm 3^{0}$
2	$31^{6} \pm 6^{3}$	$32^{2} \pm 2^{3}$
5	$20.4^{5} \pm 0.5^{5}$	$21.0^{2} \pm 0.6^{3}$
6	$5.3^{2} \pm 0.1^{2}$	$5.9^{8} \pm 0.2^{3}$
7	$101.^{1} \pm 6.^{4}$	$96.^{6} \pm 1.^{2}$
8	$154.^{9} \pm 8.^{5}$	$16^{3} \pm 1^{9}$
9	$14.7^{3} \pm 0.5^{2}$	$14.6^{5} \pm 0.5^{2}$
10	$6.3^{3} \pm 0.2^{1}$	$6.1^{0} \pm 0.2^{0}$

TABLE 4.28

METAL CONTENT RATIO VALUES FOR V/Mn

Oil No.	Original	Weathered
5	$1.8^{1} \pm 0.2^{0}$	$1.6^{8} \pm 0.1^{8}$
6	$0.53^{4} \pm 0.06^{9}$	$0.53^{2} \pm 0.07^{4}$
7	$10.^{6} \pm 1.^{4}$	$10.^{9} \pm 1.^{2}$
9	$1.31^{9} \pm 0.08^{1}$	$1.1^{7} \pm 0.1^{0}$
10	$0.61^{3} \pm 0.06^{4}$	$0.63^{2} \pm 0.03^{1}$

TABLE 4.29

METAL CONTENT RATIO VALUES FOR Ni/Cr

Oil No.	Original	Weathered
1	$0.50^{6} \pm 0.04^{8}$	$0.43^{6} \pm 0.01^{8}$
2	$0.5^{9} \pm 0.1^{2}$	$0.51^{8} \pm 0.04^{4}$
4	$0.21^{7} \pm 0.01^{5}$	$0.21^{2} \pm 0.01^{0}$
5	$0.078^{0} \pm 0.003^{6}$	$0.077^{0} \pm 0.009^{9}$
6	$0.027^{4} \pm 0.001^{6}$	$0.029^{7} \pm 0.001^{2}$
7	$0.36^{4} \pm 0.01^{3}$	$0.34^{4} \pm 0.04^{1}$
8	$0.17^{5} \pm 0.01^{7}$	$0.196^{5} \pm 0.002^{6}$
9	$0.040^{8} \pm 0.001^{3}$	$0.035^{4} \pm 0.002^{4}$
10	$0.027^{0} \pm 0.001^{2}$	0.0315 ± 0.0008

TABLE 4.30

METAL CONTENT RATIO VALUES FOR Ni/Co

Oil No.	Original	Weathered
1	$0.28^{3} \pm 0.01^{2}$	$0.30^{1} \pm 0.03^{5}$
2	$0.19^{0} \pm 0.01^{0}$	$0.19^{9} \pm 0.01^{3}$
3	$0.38^{7} \pm 0.06^{2}$	$0.37^{7} \pm 0.05^{5}$
4	$0.69^{5} \pm 0.02^{9}$	$0.722^{2} \pm 0.009^{1}$
5	$0.17^{4} \pm 0.01^{4}$	$0.19^{6} \pm 0.01^{6}$
6	$0.18^{8} \pm 0.01^{3}$	$0.16^{2} \pm 0.01^{1}$
7	$0.191^{3} \pm 0.003^{4}$	$0.25^{9} \pm 0.01^{5}$
8	$0.23^{5} \pm 0.02^{7}$	$0.31^{5} \pm 0.02^{2}$
9	$0.147^{7} \pm 0.001^{9}$	$0.14^{3} \pm 0.01^{7}$
10	$0.146^{5} \pm 0.004^{0}$	$0.164^{0} \pm 0.008^{6}$

TABLE 4.31

METAL CONTENT RATIO VALUES FOR Ni/Fe

Oil No.	Original	Weathered
1	$37.^{5} \pm 6.^{0}$	$31.^{8} \pm 2.^{6}$
2	$41.^{6} \pm 8.^{4}$	$39.^{5} \pm 3.^{8}$
5	$2.59^{8} \pm 0.05^{6}$	$2.67^{1} \pm 0.08^{3}$
6	$1.12^{3} \pm 0.05^{6}$	$1.14^{9} \pm 0.02^{1}$
7	$9.7^{7} \pm 0.5^{7}$	$9.3^{8} \pm 0.1^{2}$
8	$34.^{2} \pm 1.^{7}$	$37.^{5} \pm 4.^{5}$
9	$2.61^{9} \pm 0.06^{3}$	$2.74^{6} \pm 0.06^{2}$
10	$1.29^{8} \pm 0.02^{8}$	$1.16^{3} \pm 0.02^{8}$

TABLE 4.32

METAL CONTENT RATIO VALUES FOR Ni/Mn

Oil No.	Original	Weathered
5	$0.23^{0} \pm 0.02^{5}$	$0.21^{4} \pm 0.02^{3}$
6	$0.11^{3} \pm 0.01^{5}$	$0.10^{2} \pm 0.01^{4}$
7	$1.0^{2} \pm 0.1^{4}$	$1.0^{6} \pm 0.1^{2}$
9	$0.23^{4} \pm 0.01^{3}$	$0.21^{9} \pm 0.02^{0}$
10	$0.11^{7} \pm 0.01^{2}$	$0.120^{7} \pm 0.005^{2}$

TABLE 4.33

METAL CONTENT RATIO VALUES FOR Cr/Co

Oil No.	Original	Weathered
1	$0.56^{0} \pm 0.05^{9}$	$0.69^{0} \pm 0.08^{3}$
2	$0.32^{1} \pm 0.06^{7}$	$0.38^{4} \pm 0.03^{4}$
4	$3.2^{0} \pm 0.2^{5}$	$3.4^{0} \pm 0.1^{6}$
5	$2.2^{3} \pm 0.1^{9}$	$2.5^{4} \pm 0.3^{8}$
6	$6.8^{6} \pm 0.3^{9}$	$5.4^{6} \pm 0.4^{1}$
7	$0.52^{4} \pm 0.01^{9}$	$0.75^{2} \pm 0.09^{9}$
8	$1.3^{4} \pm 0.2^{0}$	$1.6^{0} \pm 0.1^{1}$
9	$3.6^{2} \pm 0.1^{1}$	$4.0^{4} \pm 0.5^{4}$
10	$5.4^{3} \pm 0.2^{7}$	$5.2^{0} \pm 0.2^{8}$

TABLE 4.34

METAL CONTENT RATIO VALUES FOR Cr/Fe

Oil No.	Original	Weathered
1	$7^{4} \pm 1^{4}$	$72.^{9} \pm 6.^{4}$
2	$7^{0} \pm 2^{0}$	$76.^{1} \pm 8.^{5}$
5	$33.^{3} \pm 1.^{4}$	$34.^{7} \pm 4.^{6}$
6	$41.^{0} \pm 1.^{2}$	$38.^{7} \pm 1.^{5}$
7	$26.^{8} \pm 1.^{8}$	$27.^{3} \pm 3.^{2}$
8	$19^{5} \pm 2^{1}$	$19^{1} \pm 2^{2}$
9	$64.^{1} \pm 2.^{4}$	$77.^{5} \pm 5.^{0}$
10	$44.^{8} \pm 2.^{1}$	$36.^{9} \pm 1.^{0}$

TABLE 4.35

METAL CONTENT RATIO VALUES FOR Cr/Mn

Oil No.	Original	Weathered
5	$2.9^5 \pm 0.3^4$	$2.7^8 \pm 0.4^6$
6	$4.1^2 \pm 0.2^4$	$3.4^5 \pm 0.4^8$
7	$2.8^1 \pm 0.3^8$	$3.0^7 \pm 0.5^0$
9	$5.7^4 \pm 0.3^6$	$6.1^7 \pm 0.6^7$
10	$4.3^4 \pm 0.4^7$	$3.8^3 \pm 0.1^7$

TABLE 4.36

METAL CONTENT RATIO VALUES FOR Co/Fe

Oil No.	Original	Weathered
1	$13^{2} \pm 2^{2}$	$10^{6} \pm 1^{5}$
2	$21^{8} \pm 4^{5}$	$19^{8} \pm 2^{0}$
5	$14.^{9} \pm 1.^{1}$	$13.^{6} \pm 1.^{1}$
6	$5.9^{8} \pm 0.3^{0}$	$7.0^{9} \pm 0.4^{6}$
7	$51.^{1} \pm 3.^{0}$	$36.^{2} \pm 2.^{1}$
8	$14^{5} \pm 1^{8}$	$11^{9} \pm 1^{6}$
9	$17.7^{4} \pm 0.4^{1}$	$19.^{2} \pm 2.^{3}$
10	$8.2^{5} \pm 0.2^{7}$	$7.0^{9} \pm 0.3^{8}$

TABLE 4.37

METAL CONTENT RATIO VALUES FOR Co/Mn

Oil No.	Original	Weathered
5	$1.3^{6} \pm 0.1^{7}$	$1.0^{9} \pm 0.1^{4}$
6	$0.60^{1} \pm 0.08^{2}$	$0.63^{1} \pm 0.09^{3}$
7	$5.3^{5} \pm 0.7^{1}$	$4.0^{8} \pm 0.5^{2}$
9	$1.58^{7} \pm 0.08^{8}$	$1.5^{3} \pm 0.2^{2}$
10	$0.79^{8} \pm 0.08^{3}$	$0.73^{6} \pm 0.04^{8}$

TABLE 4.38

METAL CONTENT RATIO VALUES FOR Fe/Mn

Oil No.	Original	Weathered
5	$0.088^{6} \pm 0.009^{5}$	$0.080^{1} \pm 0.008^{8}$
6	$0.10^{0} \pm 0.01^{3}$	$0.08^{9} \pm 0.01^{2}$
7	$0.10^{5} \pm 0.01^{5}$	$0.11^{2} \pm 0.01^{3}$
9	$0.089^{5} \pm 0.005^{3}$	$0.079^{7} \pm 0.007^{1}$
10	$0.09^{7} \pm 0.01^{0}$	$0.103^{9} \pm 0.004^{8}$

To test for the reliability of these ratio groups, a simple scoring test was used. A score of one unit was assigned for every correct match of identical oil or for every correct mismatch of non-identical oils. No score was assigned when the above criteria were not satisfied.

In short, for this study, when a ratio value for a particular weathered oil sample matched that of the original oil sample or mismatched any ratio value other than that of the original oil sample, a score of one unit was assigned.

The reliability is then expressed as a percentage representing the total score versus the total number of tests.

For a ratio group of N ratio pairs (original ratio - weathered ratio), the tests will be performed in a N x N matrix as indicated below:-

$$\begin{array}{cccccc}
A_o-A_w & B_o-A_w & C_o-C_w & \cdots & \cdots & A_o-N_w \\
A_o-B_w & B_o-B_w & C_o-B_w & \cdots & \cdots & \cdots \\
A_o-C_w & B_o-C_w & C_o-C_w & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
A_o-N_w & \cdots & \cdots & \cdots & \cdots & N_o-N_w
\end{array}$$

For N number of ratio pairs, in theory there will be N correct matches and $(N^2 - N)$ correct mismatches. However the statistical weight for a correct match or a correct mismatch is the same, since the purpose of oil spill identification is as much not to accuse the innocent party of spilling oil as to accuse the spiller.

The criterium for the matching was based upon the ΔR for the ratios.

For example:-

<u>V/Ni ratios of Venezuelan Largotrica crude oil.</u>

Original = $7.5^9 \pm 0.1^9$
Weathered = $8.1^5 \pm 0.3^9$

The ratios can also be expressed as possible ranges dictated by their ΔR factors.

Order of ΔR	Original	Weathered
½	7.50 - 7.68	7.96 - 8.34
1	7.40 - 7.78	7.76 - 8.54
1½	7.30 - 7.88	7.56 - 8.74
2	7.21 - 7.97	7.37 - 8.93

The possible range of values for the original and weathered ratios overlap at one order of ΔR, therefore at one order of ΔR, these two ratios match each other.

The comparisons and scoring were done with the aid of a computer program PETRO1. This program provides inputs for values of ratio pairs and their ΔR values, and includes the various orders of ΔR values at which comparisons would be carried out. The algorithm of the program is to take the difference of the two ratio values (RDF) and compare it with the sum of the ΔRs multiplied by the order of ΔR(TE). For a correct match TE must be greater or equal to RDF. For a correct mismatch TE must be less than RDF. The algorithm is illustrated in Figure 4.1.

The outputs of the program are the total number of comparisons carried out, total scoring and percentage success of the tested ratio group. The program also has outputs for all ratio pairs which fail to score for manual checking purpose.

Comparisons were carried out for each ratio group at ½, 1, 1½, 2, 2½ and 3 orders of ΔR.

The probability of success was tabulated against order of ΔR. Table 4.39 shows data from Appendix D.

```
LNH
00100 PROGRAM PETRO1(INPUT,OUTPUT)
00110 DIMENSION NN(10),OR(10),OE(10),WR(10),WE(10)
00120 PRINT 1
00130 1 FORMAT(2X,*ENTER THE NUMBER OF RATIO PAIRS*)
00140 READ,N
00150 PRINT 2
00160 2 FORMAT(2X,*ENTER THE RATIO VALUES AND THE MPES*)
00170 PRINT 6
00180 6 FORMAT(1X,*SAMPLE NO  ORIGINAL RATIO   WEATHERED RATIO*)
00190 DO 10 I=1,N
00200 READ,NN(I),OR(I),OE(I),WR(I),WE(I)
00210 10 CONTINUE
00220 11 PRINT 12
00230 12 FORMAT(2X,*ENTER THE ORDER OF MPE FOR THE TEST*)
00240 READ,TO
00250 IF (TO.EQ.0.0) GO TO 13
00260 S=0.0
00270 PRINT 7
00280 7 FORMAT(2X,*RATIO PAIRS WHICH FAIL TO SCORE*)
00290 PRINT 8
00300 8 FORMAT(1X,*NO   ORIGINAL RATIO        NO   WEATHERED RATIO*)
00310 DO 20 J=1,N
00320 DO 30 K=1,N
00330 RD=OR(J)-WR(K)
00340 RDF=ABS(RD)
00350 TE=TO*(OE(J)+WE(K))
00360 IF (J.EQ.K) GO TO 40
00370 IF (TE.GE.RDF) GO TO 50
00380 S=S+1
00390 GO TO 30
00400 50 PRINT 9,NN(J),OR(J),OE(J),NN(K),WR(K),WE(K)
00410 9 FORMAT(1X,I2,3X,2F8.4,5X,I2,3X,2F8.4)
00420 GO TO 30
00430 40 IF(TE.LT.RDF) GO TO 50
00440 S=S+1
00450 30 CONTINUE
00460 20 CONTINUE
00470 NT=N**2
00480 PER=S*100/NT
00490 PRINT 3,NT
00500 3 FORMAT (10X,*TOTAL NUMBER OF TESTS IS*,2X,I3)
00510 PRINT 4,S
00520 4 FORMAT(10X,*TOTAL SCORING IS*,2X,F4.1)
00530 PRINT 5,PER
00540 5 FORMAT(10X,*PERCENTAGE IS*,1X,F6.2,////)
00550 GO TO 11
00560 13 STOP
00570 END
READY.
```

At one order of ΔR

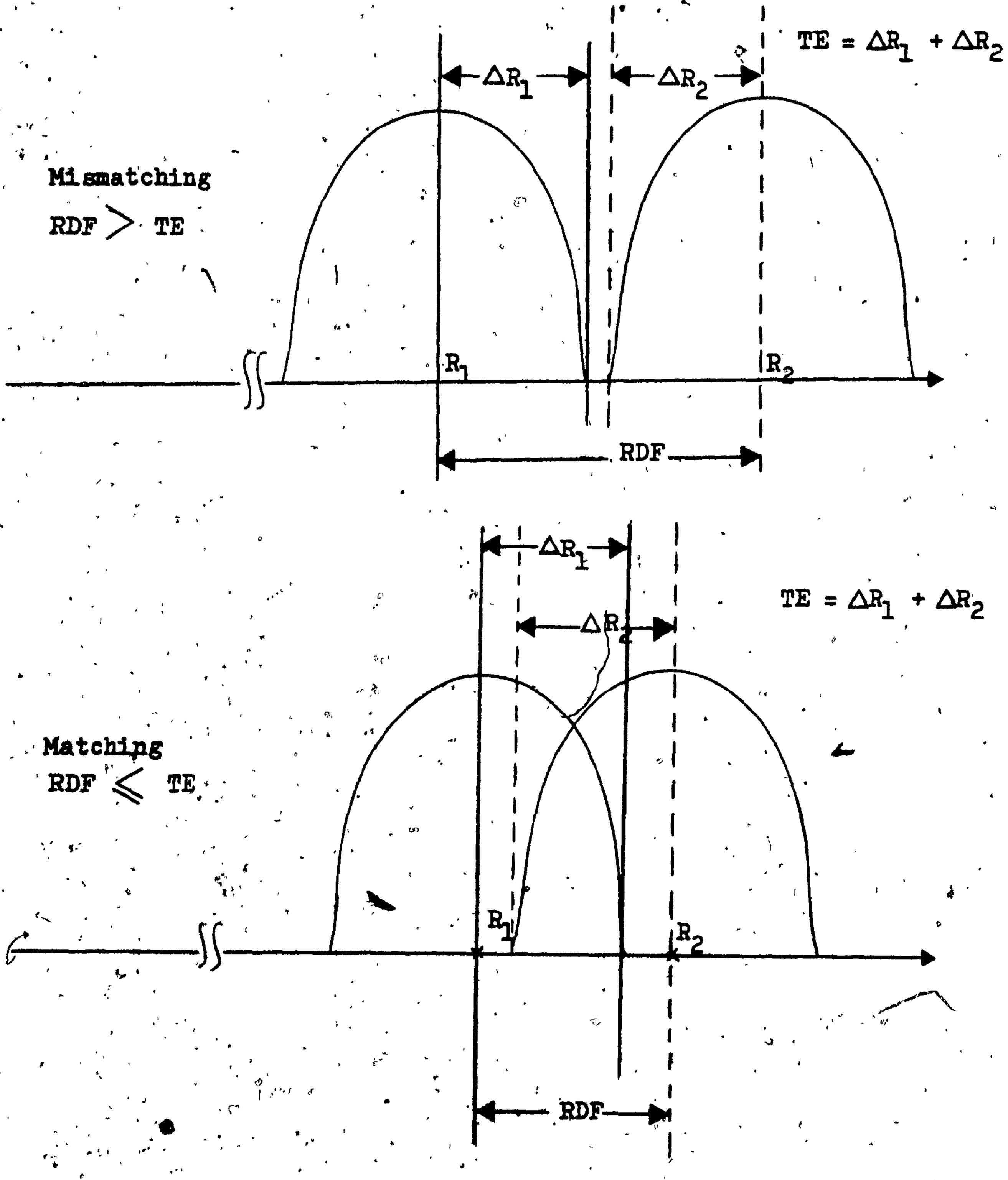

FIGURE 4.1 COMPARISON OF RATIOS USING THEIR ΔR'S

TABLE 4.39

PERCENT PROBABILITY OF SUCCESS OF THE RATIO GROUPS AT DIFFERENT ORDERS OF ΔR

Ratio group	Order of ΔR					
	½	1	1½	2	2½	3
V/Ni	92.0	94.0	89.0	88.0	88.0	86.0
V/Cr	93.8	90.1	87.6	90.1	90.1	86.4
V/Co	87.0	88.0	85.0	84.0	82.0	79.0
V/Fe	93.8	93.8	93.8	93.8	90.6	89.1
V/Mn	96.0	92.0	88.0	88.0	84.0	84.0
Ni/Cr	92.6	93.8	92.6	88.9	86.4	81.5
Ni/Co	86.0	80.0	73.0	68.0	60.0	50.0
Ni/Fe	82.8	84.4	84.4	84.4	84.4	84.4
Ni/Mn	92.0	84.0	84.0	84.0	84.0	76.0
Cr/Co	90.1	95.1	91.4	88.9	80.2	77.8
Cr/Fe	89.1	90.6	79.7	70.3	65.6	62.5
Cr/Mn	84.0	76.0	68.0	48.0	44.0	40.0
Co/Fe	87.5	93.8	90.6	84.4	84.4	84.4
Co/Mn	92.0	88.0	84.0	84.0	72.0	64.0
Fe/Mn	72.0	52.0	20.0	20.0	20.0	20.0

4.3.1 Single Ratio Approach

It will be observed that with an order of ΔR greater than two, the probability of success for the ratio groups is rather low. This can be explained by the fact that, at such a high inclusion of ΔR, the chance of incorrect mismatchings will be high, causing a decline in the probability of success.

Furthermore, the ratio groups involving manganese have, in general, a much lower success probability. This can be attributed to the insufficient number of tests carried out with the manganese-involved ratios, and also to the higher order of ΔR associated with these ratios.

The overall probability of the "Metal Ratio Fingerprinting Technique" at different orders of ΔR can be calculated by taking the average of the probability of success of all of the ratio groups within an order of ΔR. Using data from Table 4.39, we obtain data for Table 4.40.

From Table 4.40 it is apparent that the manganese-involved ratios should be excluded. The "Metal Ratio Fingerprinting Technique", using any one of the ten ratios as listed:- V/Ni, V/Cr, V/Co, V/Fe, Ni/Cr, Ni/Co, Ni/Fe, Cr/Co, Cr/Fe and Co/Fe, will have a 90.4 ± 4.9 % chance of correctly identifying a match or a mismatch between the oil spill and a suspect source, using an order of one for the ΔR.

TABLE 4.40

OVERALL PERCENT PROBABILITY OF SUCCESS OF THE METAL RATIO FINGERPRINTING TECHNIQUE AT VARIOUS ORDERS OF ΔR FOR THE RATIOS*

	Order of R			
	½	1	1½	2
Mn-involved ratios included	$88.^{7} \pm 6.^{0}$	$8^{6} \pm 1^{1}$	$8^{1} \pm 1^{8}$	$7^{8} \pm 2^{0}$
Mn-involved ratios not included	$89.^{5} \pm 3.^{7}$	$90.^{4} \pm 4.^{9}$	$86.^{7} \pm 6.^{4}$	$84.^{1} \pm 8.^{4}$

* Standard deviations shown as ± values

4.3.2 Multi-ratio Approach

The probability of success using a single ratio approach as determined by this study is about 90 % at one order of ΔR. However this confidence can be improved significantly where a multi-ratio approach is adopted.

For example, with the V/Ni and Ni/Co ratios used simultaneously, the ratio pairs (original - weathered) which are matched or mismatched incorrectly are listed for:-

One order of ΔR out of one hundred possible combinations each

V/Ni (94 %)	Ni/Co (80 %)	
1-1	1-7	6-6
2-5	1-8	7-2
5-2	2-5	7-5
7-1	3-1	7-7
10-6	3-8	8-2
10-9	5-2	8-5
	5-6	8-7
	5-10	8-8
	6-2	10-9
	6-5	10-10

Only 2-5, 5-2 and 10-9 are incorrectly mismatched in the overall picture. Hence the probability of success for two ratios used simultaneously is:-

$$\frac{\text{Total number of tests} - \text{Number of tests which fail in the overall picture}}{\text{Total number of tests}} \quad \ldots (2)$$

$$= \frac{200 - 6}{200}$$

$$= 97.0\ \%$$

If the V/Co ratio is added, at one order of ΔR out of one hundred possible combinations each:-

V/Ni (94 %)	Ni/Co (80 %)		V/Co (88 %)
1-1	1-7	7-5	1-7
2-5	1-8	7-7	2-2
5-2	2-5	8-2	2-5
7-1	3-1	8-5	2-8
10-6	3-8	8-7	4-2
10-9	5-2	8-8	4-5
	5-6	10-9	4-8
	5-10	10-10	5-8
	6-2		6-9
	6-5		7-7
	6-6		8-8
	7-2		9-6

Only 2-5 fails in the overall picture, so the probability of success is:-

$$\frac{300 - 3}{300} = 99.0\ \%$$

Hence, by using three ratios, the probability of a correct match or a correct mismatch is 99 % and this can be considered as excellent.

However, in real life there must be cases where, in a multi-ratio approach not all of the ratios reach an identical conclusion. For example, in the instance just provided, if the ratios V/Ni and V/Co identify a match while that for Ni/Co identifies a mismatch, the probability exists that it is a match rather than a mismatch situation, but at what statistical criteria?

To resolve such a difficulty it would be necessary to explore a more advanced statistical approach, or to explore the suspect spill/source samples by a technique or techniques other than atomic absorption methodology.

4.4 Conclusions and Suggestions for Further Research

Oil spill identification by "Metal Ratio Fingerprinting Technique" using atomic absorption spectrometry was found to be reliable as an identification tool providing that the spill and source oils are non-distillates.

The probability of success as determined with one order of ΔR for the single ratio approach is 90 ± 5 %, while with the multi-ratio approach (V/Ni, V/Co and Ni/Co) it is 99 %. This compares with the probability of the "fingerprinting" methods as listed by the U.S. Coast Guard (59) of:-

Gas Chromatography (GC)	91 ± 3 %
Fluorescence Spectroscopy (FS)	91 ± 2 %
Thin-layer Chromatography (TLC)	63 ± 4 %
Infrared Spectroscopy (IR)	94 ± 3 %
All Four Methods Combined	99.9 %

The metal ratio method is superior to TLC, and with only a single ratio approach, just slightly inferior to the other methods.

It is not implied that the atomic absorption analysis approach can replace the other "fingerprinting" techniques. It is recommended that this technique be used as a precursor to and a support for existing established "fingerprinting" techniques, particularly and singularly where non-distillate oils are involved.

Technically this method offer advantages over the other techniques, while providing, at the same time, certain disadvantages. The major disadvantage is that the experimental work is time-consuming in that the elements have to be determined separately and calibration standards have to be prepared. The time-consuming disadvantage is particularly apparent where graphite furnace atomization techniques are involved. The time factor is often a large multiple of that required for other spectroscopic techniques (IR, UV and Fluorescence).

One of the main advantages of the atomic absorption methodology is the simple interpretation of the analytical results, as opposed to the interpretation of complicated IR, UV and Fluorescence spectra and complex chromatograms. The computation of ratio values and comparisons are simple and can often be carried out by simple manual calculation.

For GC, IR and Fluorescence work, comparison (pattern recoginition) is always difficult and usually impossible by simple calculation. Computer-assisted interpretation at very sophisticated statistical criteria is often involved. Advanced computer technology will render the above method less time-consuming, but the cost of computer time and the initial cost of setting up the algorithm is quite significant.

In a small scale laboratory where expensive computers and data banks are not available, the "Metal Ratio Fingerprinting Technique" should provide an effective tool for the identification of crude oils, bunker oils and other non-distillate oils.

The following are suggested as areas for further research which would be relevant to this study.

(a) As mentioned before, atomic absorption suffers from the fact that it is time-consuming. Further work involving simultaneous multi-element analysis should be explored. This would include sequential multi-channel atomic absorption spectrometry (60)(61), Echelle grating atomic absorption spectrometry (62) and continnum-source atomic absorption spectrometry (63). In addition the use of other optical techniques which offer comparable sensitivity and precision to atomic absorption spectrometry, but with multi-element capacity, such as atomic fluorescence spectrometry (64)(65) and inductive-couple plasma emission spectrometry (66)(67) should be explored.

(b) With ample budget and facilities, weathering of oils should be carried out on a large scale and under conditions parelleling those suggested by the U.S. Coast Guard (30), and involving larger number of samples as to obtain a general increase in the reliability of the probability t

of success in matching/mismatching.

(c) The method should also be applied to real-life oil spills versus suspected sources and a comparison made of results obtained against those obtained by established "fingerprinting" techniques.

(d) More sophisticated statistical approaches could be investigated. For example, instead of taking the ratio of two elements, it might be worthwhile to explore the value of ratios such as A/A+B+C where A, B and C are different metallic contents. Also attempts can be made to resolve the problem as described in Section 4.3, where with the multi-ratio approach, the ratios do not reach the same conclusion.

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APPENDIX A

PREPARATION OF SOLUTIONS USED IN THIS STUDY

(1) Potassium Buffer Solution

Weigh 1.9068 ± 0.0002 g of reagent grade potassium chloride into a 250 ml beaker, dissolve with distilled water, transfer to a 1 liter volumetric flask, dilute to the mark with distilled water.

$$\text{Solution Strength} = \frac{1.9068 \pm 0.0002 \text{ g} \times 39.102}{1 \text{ liter} \qquad \times 74.56}$$

$$= 1000 \text{ mg/liter}$$

$$= 1000 \text{ ppm K}$$

(2) 20 % Benzenesulfonic Acid in Butanol

Weigh 100.0 ± 0.2 g of benzenesulfonic acid into a 250 ml beaker. Transfer to a 1 liter beaker containg 400.0 ± 0.2 g of n-butanol, mix well and store.

(3) Preparation of Standard Solutions for Flame Atomic Absorption Analysis

(3-a) Nickel

100 ppm Ni standard solution:
Pipette 10.00 ± 0.02 ml of 1000 ppm Ni (Fisher standard) solution into a 100.00 ± 0.08 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 100.0 ppm Ni

1, 2, 3, 4 and 5 ppm Ni standard solutions:
Measure 1.00 ± 0.02 ml, 2.00 ± 0.02 ml, 3.00 ± 0.02 ml, 4.00 ± 0.02 ml and 5.00 ± 0.02 ml of the 100 ppm Ni standard solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 1.00, 2.00, 3.00, 4.00 and 5.00 ppm Ni.

(3-b) Copper

100 ppm Cu standard solution:
Pipette 10.00 ± 0.02 ml of 1000 ppm Cu (Fisher standard) solution into a 100.00 ± 0.08 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 100.0 ppm Cu

1, 2, 3, 4 and 5 ppm Cu standard solutions:
Measure 1.00 ± 0.02 ml, 2.00 ± 0.02 ml, 3.00 ± 0.02 ml, 4.00 ± 0.02 ml and 5.00 ± 0.02 ml of the 100 ppm Cu standard solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 1.00, 2.00, 3.00, 4.00 and
5.00 ppm Cu

(3-c) Iron

100 ppm Fe standard solution:
Pipette 10.00 ± 0.02 ml of 1000 ppm Fe (Fisher standard) solution into a 100.00 ± 0.08 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 100.0 ppm Fe

1, 2, 3, 4 and 5 ppm Fe standard solutions:
Measure 1.00 ± 0.02 ml, 2.00 ± 0.02 ml, 3.00 ± 0.02 ml, 4.00 ± 0.02 ml and 5.00 ± 0.02 ml of the 1000 ppm Fe standard solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 1.00, 2.00, 3.00, 4.00 and
5.00 ppm Fe

(3-d) Zinc

20 ppm Zn standard solution:
Pipette 2.00 ± 0.01 ml of 1000 ppm Zn (Fisher standard) solution into a 100.00 ± 0.08 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 20.0 ppm Zn

0.2, 0.4, 0.6, 0.8 and 1.0 ppm Zn standard solutions:
Measure 1.00 ± 0.02, 2.00 ± 0.02, 3.00 ± 0.02, 4.00 ± 0.02 and 5.00 ± 0.02 ml of the 20.0 ppm Zn standard solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 0.200, 0.400, 0.600, 0.800
and 1.00 ppm Zn

(3-e) Vanadium

20, 40, 60, 80 and 100 ppm V standard solutions:
Measure 2.00 ± 0.02, 4.00 ± 0.02, 6.00 ± 0.02, 8.00 ± 0.02 and 10.00 ± 0.02 ml of 1000 ppm V (Fisher Standard) solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 20.0, 40.0, 60.0, 80.0 and
100 ppm V

(4) Preparation of Standard Solutions for Graphite Furnace Atomization Atomic Absorption Analysis

(4-a) Vanadium

200, 500, 700 and 800 ppb V standard solutions:
Measure 1.00 ± 0.02, 2.50 ± 0.02, 3.50 ± 0.02 and 4.00 ± 0.02 ml of 20.0 ppm vanadium standard solution prepared according to (3-e) into four different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 200, 500, 700 and 800 ppb V

(4-b) Nickel

10 ppm Ni standard solution:
Pipette 5.00 ± 0.02 ml of the 1000 ppm Ni (Fisher standard) solution into a 500.0 ± 0.2 ml volumetric flask, diluted to the mark with distilled water.

Solution strength: 10.00 ppm Ni

100, 200 and 300 ppb Ni standard solutions:
Measure 1.00 ± 0.02, 2.00 ± 0.02 and 3.00 ± 0.02 ml of the 10.00 ppm Ni standard solution into three different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 100, 200 and 300 ppb Ni

(4-c) Chromium

1 ppm Cr standard solution:
Pipette 1.000 ± 0.006 ml of 1000 ppm Cr (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 1.000 ppm Cr

10, 20, 30 and 40 ppb Cr standard solutions:
Measure 1.00 ± 0.02, 2.00 ± 0.02, 3.00 ± 0.02 and 4.00 ± 0.02 of the 1.000 ppm Cr standard solution into four different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 10.0, 20.0, 30.0 and 40.0 ppb Cr

(4-d) Cobalt

1 ppm Co standard solution:
Pipette 1.000 ± 0.006 ml of 1000 ppm Co (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 1.000 ppm Co

10, 20, 30 and 40 ppb Co standard solutions:
Measure 1.00 ± 0.02, 2.00 ± 0.02, 3.00 ± 0.02 and 4.00 ± 0.02 ml of 1.000 ppm Co standard solution into four different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 10.0, 20.0, 30.0 and 40.0 ppb Co

(4-e) Iron

1 ppm Fe standard solution:
Pipette 1.000 ± 0.006 ml of the 1000 ppm Fe (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.
Solution strength: 1.000 ppm Fe

20, 40 and 60 ppb Fe standard solutions:
Measure 2.00 ± 0.02, 4.00 ± 0.02 and 6.00 ± 0.02 ml of the 1.000 ppm Fe standard solution into three 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 20.0, 40.0 and 60.0 ppb Fe

(4-f) Manganese

10 ppm Mn standard solution:
Pipette 10.00 ± 0.02 ml of 1000 ppm Mn (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 10.00 ppm Mn

100 ppb Mn standard solution:
Pipette 10.00 ± 0.02 ml of the 10.00 ppm Mn standard solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 100.0 ppb Mn

5, 10, ,5, 20 and 25 ppb Mn standard solutions:
Pipette 5.00 ± 0.01, 10.00 ± 0.02, 15.00 ± 0.03, 20.00 ± 0.03 and 25.00 ± 0.03 ml of the 100.0 ppb Mn standard solution into five different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 5.00, 10.00, 15.00, 20.00
and 25.00 ppm Mn

2, 4, 6 and 8 ppb Mn standard solutions:
Measure 2.00 ± 0.02, 4.00 ± 0.02, 6.00 ± 0.02 and 8.00 ± 0.02 ml of 100.0 ppb Mn standard solution into four different 100.00 ± 0.08 ml volumetric

flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 2.00, 4.00, 6.00 and 8.00 ppb Mn

(4-g) Molybdenum

10 ppm Mo standard solution:
Pipette 10.00 ± 0.02 ml of 1000 ppm Mo (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 10.00 ppm Mo

100, 200 and 300 ppb Mo standard solutions:
Measure 1.00 ± 0.02, 2.00 ± 0.02 and 3.00 ± 0.02 ml of the 10.00 ppm standard Mo solution into three 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 100, 200 and 300 ppb Mo

(4-h) Copper

4 ppm Cu standard solution
Pipette 4.00 ± 0.02 ml of 1000 ppm Cu (Fisher standard) solution into a 1000.0 ± 0.3 ml volumetric flask, dilute to the mark with distilled water.

Solution strength: 4.00 ppm Cu

40, 80 and 120 ppb Cu standard solutions: Measure 1.00 ± 0.02, 2.00 ± 0.02 and 3.00 ± 0.02 ml of 4.00 ppm Cu standard solution into three different 100.00 ± 0.08 ml volumetric flasks, to each flask add 4.00 ± 0.04 ml hydrochloric acid and 8.00 ± 0.04 ml of 1000 ppm K solution, dilute to the mark with distilled water.

Solution strength: 40, 80 and 120 ppb Cu

(5) Preparation of Substitute Sea Water (50)

(5-a) Stock Solution I

Dissolve the indicated amounts of the following in distilled water, dilute to 7.0 liters and store in a well-stoppered glass container.

$MgCl_2 \cdot 6H_2O$	3889 g
$CaCl_2$(anhydrous)	406 g
$SrCl_2 \cdot 6H_2O$	14.8 g

(5-b) Stock Solution II

Dissolve the indicated amounts of the following in distilled water, dilute to 7.0 liters and store in a well-stoppered glass container.

KCl	486 g
$NaHCO_3$	141 g
KBr	70.4 g
H_3BO_3	19.0 g
NaF	2.1 g

(5-c) Stock Solution III

Dissolve the indicated amounts of the following in distilled water, dilute to 10.0 liters and store in a well-stoppered glass container.

$Ba(NO_3)_2$	0.994 g
$Mn(NO_3)_2 \cdot 6H_2O$	0.546 g
$Cu(NO_3)_2 \cdot 3H_2O$	0.396 g
$Zn(NO_3)_2 \cdot 6H_2O$	0.151 g

$Pb(NO_3)_2$	0.066 g
$AgNO_3$	0.0049 g

(5-e) Substitute Sea Water

Dissolve 61.3 g of NaCl and 10.23 g of Na_2SO_4 in 2.0 liters of distilled water, add slowly with vigorous stirring 50.0 ml of stock solution I, then 25.0 ml of stock solution II and 2.50 ml of stock solution III, dilute to 2.5 liters with distilled water, adjust to PH 8.2 with 0.1 N NaOH solution.

(5-f) Chemical Composition of Substitute Sea Water ASTM 1141/74

Compound	Concentration (g/liter)
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003
$Ba(NO_3)_2$	0.0000994
$Mn(NO_3)_2$	0.0000340
$Cu(NO_3)_2$	0.0000308
$Zn(NO_3)_2$	0.0000096
$Pb(NO_3)_2$	0.0000066
$AgNO_3$	0.00000049

APPENDIX B

ANALYSIS OF ASTM/NBS STANDARD OIL MATERIAL GM-5 BY ATOMIC ABSORPTION METHODS

For this study, quintuplicate samples of the standard oil were taken and the sample weights were recorded as follows:-

Sample No.	Weight (gram)
1	1.0872 ± 0.0002
2	0.8015 ± 0.0002
3	1.4888 ± 0.0002
4	1.3222 ± 0.0002
5	1.1499 ± 0.0002

The samples were treated according to the general procedures listed in Section 3.1. The final volume was 25.00 ± 0.03 ml.

The nickel and vanadium calibration standard solutions were prepared according to the procedures outlined in Appendix (i.e. procedures (3-a) and (4-a).

Nickel

(a) Standard solution calibration data and use

Standard solution (ppm)	Absorbance	Ave. abs. ± ave. dev.
Blank	0.000 0.000 0.000	0.000 ± 0.000
1.00	0.023 0.023 0.023	0.023 ± 0.000
2.00	0.047 0.046 0.045	0.046 ± 0.001
3.00	0.067 0.069 0.071	0.069 ± 0.001
4.00	0.092 0.092 0.092	0.092 ± 0.001
5.00	0.115 0.115 0.115	0.115 ± 0.000

Regression analysis

Regression coefficient (r) = 1.0000

Intercept (b) = 0.000

Slope (m) = 0.0230

Equation of calibration line

$$\text{Content (in ppm)} = \frac{\text{Absorbance}}{0.0230}$$

Using this equation and the absorbance data of the sample solutions the following data were obtained.

Sample No.	Ave. abs. ± ave. dev.*	Solution concentration (ppm)
1	0.091 ± 0.000	3.96
2	0.067 ± 0.000	2.91
3	0.122 ± 0.001	5.30
4	0.111 ± 0.001	4.83
5	0.096 ± 0.000	4.17

The equation for converting the metal content in the sample solutions to metal content in the residual oil samples is:-

$$\text{ppm (elemental content)} = \frac{C \times Vol^{**}}{W} \quad ..... \quad (B\text{-}1)$$

where:-

C = Metal concentration calculated in sample solution (ppm)

Vol = Volume of sample solution (25.00 ± 0.03 ml)

W = Sample weight in grams

Using the recorded sample weights, the nickel content of the five samples was calculated using equation (B-1).

* Average absorbance ± average deviation based on three readings for the digital integration output.

** For aqueous matrix, 1 ppm is assumed to be equivalent to 1 ug/ml.

Sample No.	Nickel content in residual oil (ppm)
1	91.0
2	90.9
3	89.1
4	91.2
5	90.7

Average ± standard deviation = 90.6 ± 0.8 ppm

(b) Standard additions (spiking technique)

For each of the five samples, these solutions were prepared:-

S-0 2.00 ± 0.01 ml of the sample solution was pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark (dilution factor: 5.00).

S-1 2.00 ± 0.01 ml of the sample solution and 1.00 ± 0.01 ml of 10.00 ppm Ni standard were pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark.

S-2 2.00 ± 0.01 ml of the sample solution and 2.00 ± 0.01 ml of 10.00 ppm Ni standard were pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark.

All samples were diluted to the mark with a solution containing 4 % hydrochloric acid and 80 ppm potassium ionization buffer. Amount of nickel added to solution S-0 was 0.0 ug, to S-1 was 10.0 ug and to S-2 was 20.0 ug.

For sample No.1

Spike-solution	Average absorbance ± average deviation
S-0	0.018 ± 0.000
S-1	0.042 ± 0.000
S-3	0.063 ± 0.000

For convenience, with the regression analysis, the amount of standard added can be plotted against absorbance. The intercept (b) on the y axis (amount of standard added) is obviously the amount of unknown, present. Figure B-1 shows the system.

Regression analysis

r = 0.9993

m = 44.38

b = -8.19

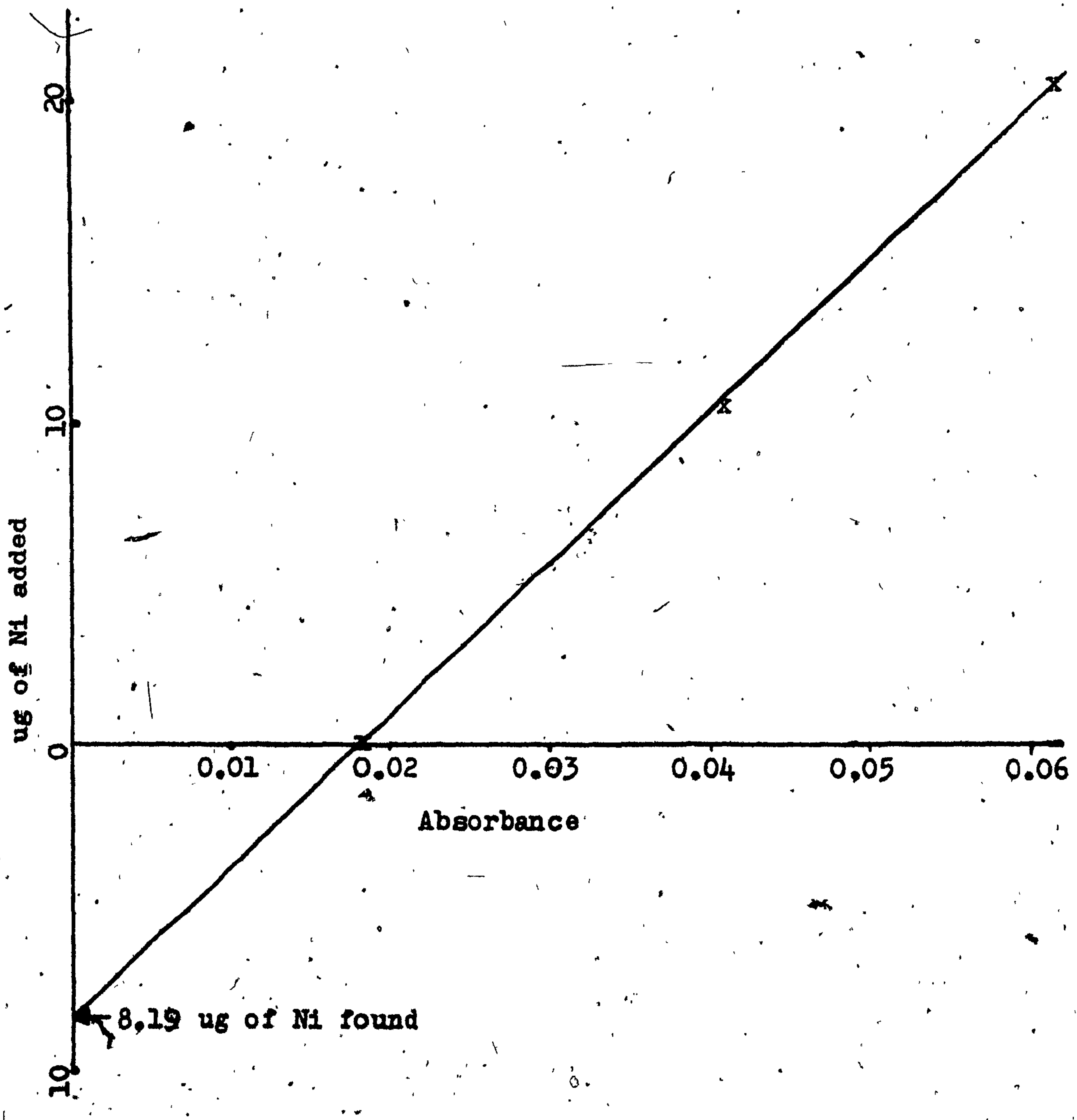

FIGURE B-1 SPIKING TECHNIQUE Ni ANALYSIS/SAMPLE NO. 1

Therefore ug Ni in sample solution = 8.19

Concentration of Ni in sample solution = 0.819 ppm

Ni (ppm) in residual oil

$$= \frac{\left\{\begin{array}{c}\text{ppm in sample solution x dilution factor} \\ \text{x original sample volume (ml)}\end{array}\right\}}{\text{Sample weight in gram}} \quad \ldots\ldots \quad \text{(B-2)}$$

$$= \frac{0.820 \times 5.00 \times 25.00}{1.0872}$$

$$= 94.3$$

For sample No. 2

Spike-solution	Average absorbance ± average deviation
S-0	0.014 ± 0.000
S-1	0.037 ± 0.001
S-2	0.060 ± 0.000

$r = 1.0000 \quad b = -6.09 \quad m = 43.48$

ppm in sample solution = 0.609

ppm in residual oil sample = 95.0

For sample No. 3.

Spike-solution	Average absorbance ± average deviation
S-0	0.024 ± 0.000
S-1	0.048 ± 0.000
S-2	0.070 ± 0.001

r = 0.9997 b = -10.56 m = 43.45

ppm in sample solution = 1.056

ppm in residual oil sample = 88.7

For sample No. 4

Spike-solution	Average absorbance ± average deviation
S-0	0.022 ± 0.000
S-1	0.045 ± 0.000
S-2	0.067 ± 0.000

r = 0.9999 b = -9.85 m = 44.44

ppm in sample solution = 0.985

ppm in residual oil sample = 93.1

For sample No. 5

Spike-solution	Average absorbance ± average deviation
S-0	0.019 ± 0.000
S-1	0.041 ± 0.000
S-2	0.064 ± 0.000

r = 0.9999   b = -8.37   m = 44.44

ppm in sample solution = 0.837

ppm in residual oil sample = 91.0

Average ± average deviation = 92.^{4} ± 2.^{5} ppm
(Ni content in residual oil GM-5)

Vanadium

Vanadium analyses on the GM-5 residual oil sample were carried out by the graphite furnace atomization technique. The sample solutions, made up according to the procedures as listed in Section 3.1, were first diluted five-fold (2.00 ± 0.01 ml to 10.00 ± 0.02 ml, dilution factor: 5.00) for the calibration standard method.

(a) Standard solution calibration data and use

Standard solution (ppm)	Absorbance			Ave. abs. ± ave. dev.
Blank	0.000	0.000	0.000	0.000 ± 0.000
0.200	0.021	0.022	0.023	0.022 ± 0.001
0.400	0.040	0.042	0.043	0.042 ± 0.042
0.600	0.066	0.059	0.062	0.062 ± 0.002
0.800	0.086	0.082	0.081	0.083 ± 0.002
1.000	0.102	0.105	0.108	0.105 ± 0.002

Regression analysis

$r = 0.9998$

$m = 0.104$

$b = 0.000^{3}$

Equation of calibration line:-

$$\text{Content (in ppm)} = \frac{\text{Absorbance} - 0.000^{3}}{0.104}$$

Using the calibration line and the absorbance data for the five sample solutions, together with equation (B-2),

$$\left\{ \text{ppm in residual oil} = \frac{\left\{\begin{array}{c}\text{ppm in sample solution x dilution factor} \\ \text{x original sample volume (ml)}\end{array}\right\}}{\text{Sample weight in grams}} \right\}$$

the following data were obtained.

Sample No.	Ave. abs. ± ave. dev.	Concentration (ppm)	
		in sample solution	in residual oil sample
1	0.071 ± 0.001	0.68^{0}	$78.^{2}$
2	0.055 ± 0.003	0.52^{6}	$82.^{0}$
3	0.100 ± 0.002	0.95^{9}	$80.^{5}$
4	0.090 ± 0.000	0.86^{2}	$81.^{5}$
5	0.080 ± 0.004	0.76^{6}	$83.^{3}$

Average ± standard deviation = $81.^{1} \pm 1.^{9}$ ppm
(vanadium content in residual oil GM-5)

(b) Standard additions (spiking technique)

For each of the five samples, these solutions were prepared as follows:-

S-0 1.00 ± 0.01 ml of the sample solution was pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark (dilution factor: 10.00).

S-2 1.00 ± 0.01 ml of the sample solution and 2.00 ± 0.01 ml of 1 ppm vanadium standard were pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark.

S-4 1.00 ± 0.01 ml of the sample solution and 4.00 ± 0.01 ml of 1 ppm vanadium standard were pipetted into a 10.00 ± 0.02 ml volumetric flask and diluted to the mark.

All solutions were diluted to the mark with a solution containing 80 ppm potassium ionization buffer and 4 % hydrochloric acid. Amount of vanadium added to the spike-solution S-0 was 0.00 ug, to S-2 was 2.00 ug and to S-4 was 4.00 ug.

For sample No.1

Spike-solution	Average absorbance ± average deviation
S-0	0.036 ± 0.001
S-2	0.058 ± 0.001
S-4	0.080 ± 0.001

r = 1.0000 b = -3.27 m = 9.0909

ppm in sample solution = 0.327

ppm in residual oil sample = 75.2

For sample No.2

Spike-solution	Average absorbance ± average deviation
S-0	0.026 ± 0.002
S-2	0.048 ± 0.000
S-4	0.070 ± 0.001

r = 1.0000 b = -2.36 m = 9.0909

ppm in sample solution = 0.236

ppm in residual oil sample = 73.7

For sample No. 3

Spike-solution	Average absorbance ± average deviation
S-0	0.048 ± 0.000
S-2	0.070 ± 0.000
S-4	0.090 ± 0.001

r = 0.9996 b = -4.60 m = 9.5166

ppm in sample solution = 0.460

ppm in residual oil sample = 77.^{3}

For sample No. 4

Spike-solution	Average absorbance ± average deviation
S-0	0.044 ± 0.000
S-2	0.066 ± 0.002
S-4	0.085 ± 0.001

r = 0.9991 b = -4.33 m = 9.7387

ppm in sample solution = 0.433

ppm in residual oil sample = 81.^{9}

For sample No. 5

Spike-solution	Average absorbance ± average deviation
S-0	0.040 ± 0.002
S-2	0.062 ± 0.002
S-4	0.082 ± 0.002

$r = 0.9996$ $b = -3.84$ $m = 9.5166$

ppm in sample solution = 0.384

ppm in residual oil sample = $83.^{5}$

Average ± standard deviation = $78.^{3} \pm 4.^{8}$ ppm.

(vanadium content in residual oil GM-5)

APPENDIX C

ANALYSIS OF TEST OILS

TABLE 1

VENEZUELAN LAGOMAR-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	162 ± 2 ppm
	Flame(spiking)	176 ± 8 ppm
Ni	Flame(standard calibration)	16.5 ± 0.1 ppm
	Flame(spiking)	16.9 ± 0.4 ppm
Cr	Furnace(standard calibration)	$32.^{6} \pm 3.^{1}$ ppb
Co	Furnace(standard calibration)	$58.^{2} \pm 2.^{6}$ ppb
	Furnace(spiking)	$54.^{9} \pm 3.^{0}$ ppb
Fe	Furnace(standard calibration)	0.44 ± 0.07 ppm
Mo	Furnace(standard calibration)	$36.^{3} \pm 2.^{1}$ ppb
Mn	Furnace(standard calibration)	$3.^{3} \pm 1.^{2}$ ppb
Zn	Flame(standard calibration)	$0.38^{3} \pm 0.03^{0}$ ppm
Cu	Flame(standard calibration)	0.44 ± 0.08 ppm

TABLE 2

VENEZUELAN LAGOTRICA-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	142 ± 2 ppm
	Flame(spiking)	$14^4 \pm 1^2$ ppm
Ni	Flame(standard calibration)	18.7 ± 0.4 ppm
	Flame(spiking)	18.9 ± 0.9 ppm
Cr	Furnace(standard calibration)	$31.^5 \pm 6.^4$ ppb
Co	Furnace(standard calibration)	$98.^2 \pm 4.^9$ ppb
	Furnace(spiking)	$9^7 \pm 1^2$ ppb
Fe	Furnace(standard calibration)	0.45 ± 0.09 ppm
Mo	Furnace(standard calibration)	$35.^3 \pm 2.^0$ ppb
Mn	Furnace(standard calibration)	$2^5 \pm 1^1$ ppb
Zn	Flame(standard calibration)	$0.37^6 \pm 0.02^8$ ppm
Cu	Flame(standard calibration)	0.38 ± 0.07 ppm

F

TABLE 3

A CANADIAN CRUDE-ELEMENTAL ANALYSIS

Element	Method	Result
V	Furnace(standard calibration)	2.34 ± 0.08 ppm
	Furnace(spiking)	$2.7^{0} \pm 0.1^{0}$ ppm
Ni	Flame(standard calibration)	$3.8^{7} \pm 0.2^{2}$ ppm
	Furnace(spiking)	$4.0^{7} \pm 0.3^{8}$ ppm
Cr	Furnace(standard calibration)	N.D.
Co	Furnace(standard calibration)	$10.^{0} \pm 1.^{5}$ ppm
Fe	Furnace(standard calibration)	$0.11^{1} \pm 0.06^{2}$ ppm
Mo	Furnace(standard calibration)	N.D.
Mn	Furnace(standard calibration)	N.D.
Zn	Flame(standard calibration)	N.D.
Cu	Furnace(standard calibration)	N.D.

TABLE 4

A SECOND CANADIAN CRUDE-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	$30.^{9} \pm 1.^{9}$ ppm
Ni	Flame(standard calibration)	14.1 ± 0.2 ppm
	Flame(spiking)	13.9 ± 0.5 ppm
Cr	Furnace(standard calibration)	$65.^{0} \pm 4.^{3}$ ppb
	Furnace(spiking)	$6^{9} \pm 1^{2}$ ppb
Co	Furnace(standard calibration)	20.3 ± 0.8 ppb
Fe	Furnace(standard calibration)	$0.22^{0} \pm 0.04^{6}$ ppb
Mo	Furnace(standard calibration)	$13^{6} \pm 2^{5}$ ppb
Mn	Furnace(standard calibration)	7.52 ± 0.03 ppb
Zn	Flame(standard calibration)	$0.12^{0} \pm 0.03^{8}$ ppm
Cu	Furnace(standard calibration)	N.D.

TABLE 5

BUNKER C-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	270 ± 7 ppm
	Flame(spiking)	$28^3 \pm 1^7$ ppm
Ni	Flame(standard calibration)	34.3 ± 0.7 ppm
	Flame(spiking)	$35.^4 \pm 1.^0$ ppm
Cr	Furnace(standard calibration)	$44^0 \pm 1^8$ ppb
	Furnace(spiking)	$45^6 \pm 2^5$ ppb
Co	Furnace(standard calibration)	$19^7 \pm 1^5$ ppb
	Furnace(spiking)	$18^8 \pm 2^8$ ppb
Fe	Flame(standard calibration)	13.2 ± 0.1 ppm
	Flame(spiking)	12.8 ± 0.5 ppm
Mo	Furnace(standard calibration)	$27^2 \pm 2^0$ ppb
	Furnace(spiking)	$26^2 \pm 3^4$ ppb
Mn	Furnace(standard calibration)	$25^6 \pm 2^4$ ppb
	Furnace(spiking)	$14^9 \pm 1^6$ ppb
Zn	Flame(standard calibration)	$1.2^2 \pm 0.1^0$ ppm
Cu	Flame(standard calibration)	$0.6^0 \pm 0.1^0$ ppm

TABLE 6

LOW SULPHUR BUNKER-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	143 ± 3 ppm
	Flame(spiking)	146 ± 6 ppm
Ni	Flame(standard calibration)	$30.^{2}$ ± $1.^{5}$ ppm
	Flame(spiking)	$30.^{7}$ ± $1.^{7}$ ppm
Cr	Furnace(standard calibration)	110^{4} ± 3^{1} ppb
	Furnace(spiking)	110^{0} ± 3^{4} ppb
Co	Furnace(standard calibration)	161 ± 8 ppb
	Furnace(spiking)	152 ± 8 ppb
Fe	Flame(standard calibration)	26.9 ± 0.2 ppb
	Flame(spiking)	$26.^{6}$ ± $1.^{3}$ ppb
Mo	Furnace(standard calibration)	28^{6} ± 1^{4} ppb
	Furnace(spiking)	27^{5} ± 8^{0} ppb
Mn	Furnace(standard calibration)	37^{6} ± 2^{4} ppb
	Furnace(standard calibration)	26^{8} ± 3^{4} ppb
Zn	Flame(standard calibration)	2.0^{4} ± 0.2^{0} ppm
Cu	Furnace(standard calibration)	1.08 ± 0.08 ppm

TABLE 7

THIN-FILM BUNKER-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	177 ± 5 ppm
	Flame(spiking)	174 ± 4 ppm
Ni	Flame(standard calibration)	17.1 ± 0.2 ppm
	Flame(spiking)	17.2 ± 0.4 ppm
Cr	Furnace(standard addition)	46.^{9} ± 1.^{6} ppb
	Furnace(spiking)	48.^{3} ± 3.^{3} ppb
Co	Furnace(standard addition)	89.^{4} ± 1.^{2} ppb
	Furnace(spiking)	90.^{0} ± 3.^{7} ppb
Fe	Flame(standard calibration)	1.7^{5} ± 0.1^{0} ppm
Mo	Furnace(standard calibration)	N.D.
Mn	Furnace(standard calibration)	16.^{7} ± 2.^{2} ppb
Zn	Flame(standard calibration)	0.23^{9} ± 0.02^{8} ppm
Cu	Furnace(standard calibration)	0.09^{3} ± 0.01^{2} ppm

TABLE 8

BUNKER FUEL NO 4-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	35.0 ± 0.9 ppm
Ni	Flame(standard calibration)	7.72 ± 0.07 ppm
	Flame(standard calibration)	$7.7^{3} \pm 0.1^{5}$ ppm
Cr	Furnace(standard calibration)	$44.^{1} \pm 4.^{2}$ ppb
	Furnace(standard calibration)	$45.^{7} \pm 3.^{0}$ ppb
Co	Furnace(standard calibration)	$32.^{8} \pm 3.^{8}$ ppb
Fe	Furnace(standard calibration)	$0.22^{6} \pm 0.01^{1}$ ppm
Mo	Furnace(standard calibration)	N.D.
Mn	Furnace(standard calibration)	$14.^{1} \pm 1.^{6}$ ppb
Zn	Flame(standard calibration)	$0.26^{3} \pm 0.01^{9}$ ppm
Cu	Furnace(standard calibration)	$0.034^{5} \pm 0.002^{1}$ ppm

TABLE 9

BUNKER FUEL NO 5-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	108 ± 3 ppm
	Flame(spiking)	105 ± 7 ppm
Ni	Flame(standard calibration)	19.2 ± 0.2 ppm
	Flame(spiking)	19.2 ± 0.4 ppm
Cr	Furnace(standard calibration)	$47^{0} \pm 1^{4}$ ppb
	Furnace(spiking)	$46^{7} \pm 3^{0}$ ppb
Co	Furnace(standard calibration)	130 ± 1 ppb
Fe	Flame(standard calibration)	$7.3^{3} \pm 0.1^{6}$ ppm
	Flame(spiking)	$7.4^{3} \pm 0.1^{9}$ ppm
Mo	Furnace(standard calibration)	120 ± 9 ppb
Mn	Furnace(standard calibration)	$12^{3} \pm 1^{6}$ ppb
	Furnace(spiking)	$81.^{9} \pm 4.^{5}$ ppb
Zn	Flame(standard calibration)	$0.76^{5} \pm 0.02^{5}$ ppm
Cu	Flame(standard calibration)	$0.13^{4} \pm 0.1^{6}$ ppm

TABLE 10

BUNKER B-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	152 ± 4 ppm
	Flame(spiking)	153 ± 6 ppm
Ni	Flame(standard calibration)	29.0 ± 0.3 ppm
	Flame(spiking)	29.7 ± 0.7 ppm
Cr	Furnace(standard calibration)	$107^{6} \pm 4^{5}$ ppb
	Furnace(spiking)	$106^{0} \pm 9^{3}$ ppb
Co	Furnace(standard calibration)	198 ± 5 ppb
Fe	Flame(standard calibration)	24.0 ± 0.5 ppm
	Flame(spiking)	24.5 ± 0.5 ppm
Mo	Furnace(standard calibration)	$11^{7} \pm 1^{1}$ ppb
Mn	Furnace(standard calibration)	$32^{8} \pm 1^{7}$ ppb
	Furnace(spiking)	$24^{8} \pm 2^{5}$ ppb
Zn	Flame(standard calibration)	1.73 ± 0.03 ppm
Cu	Flame(standard calibration)	$0.32^{1} \pm 0.03^{9}$ ppm

TABLE 11

VENEZUELAN LAGOMAR(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	216 ± 6 ppm
Ni	Flame(standard calibration)	19.7 ± 0.4 ppm
Cr	Furnace(standard calibration)	45.^{2} ± 1.^{6} ppb
Co	Furnace(standard calibration)	65.^{5} ± 7.^{5} ppb
Fe	Flame(standard calibration)	0.62 ± 0.05 ppm
Mo	Furnace(standard calibration)	62.^{5} ± 4.^{6} ppb
Mn	Furnace(standard calibration)	3.9^{8} ± 0.1^{7} ppb
Zn	Flame(standard calibration)	10.3 ± 0.2 ppm
Cu	Flame(standard calibration)	0.71 ± 0.08 ppm

TABLE 12

VENEZUELAN LAGOTRICA(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	190 ± 4 ppm
Ni	Flame(standard calibration)	23.^{3} ± 1.^{0} ppm
Cr	Furnace(standard calibration)	44.^{9} ± 3.^{3} ppb
Co	Furnace(standard calibration)	117 ± 6 ppb
Fe	Furnace(standard calibration)	0.59 ± 0.05 ppm
Mo	Furnace(standard calibration)	11^{5} ± 1^{0} ppb
Mn	Furnace(standard calibration)	17.^{7} ± 2.^{3} ppb
Zn	Flame(standard calibration)	3.1^{4} ± 0.4^{4} ppm
Cu	Flame(standard calibration)	0.50 ± 0.04 ppm

TABLE 13

A CANADIAN CRUDE(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Furnace(standard calibration)	$3.0^{0} \pm 0.1^{9}$ ppm
Ni	Flame(standard calibration)	$4.7^{5} \pm 0.1^{2}$ ppm
Cr	Furnace(standard calibration)	N.D.
Co	Furnace(standard calibration)	$12.^{6} \pm 1.^{8}$ ppb
Fe	Flame(standard calibration)	$4.2^{2} \pm 0.1^{3}$ ppm
Mo	Furnace(standard calibration)	N.D.
Mn	Furnace(standard calibration)	N.D.
Zn	Flame(standard calibration)	3.25 ± 0.07 ppm
Cu	Furnace(standard calibration)	N.D.

TABLE 14

A SECOND CANADIAN CRUDE(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	$37.^{1}$ ± $1.^{1}$ ppm
Ni	Flame(standard calibration)	16.9 ± 0.2 ppm
Cr	Furnace(standard calibration)	$79.^{5}$ ± $3.^{7}$ ppb
Co	Furnace(standard calibration)	23.4 ± 0.1 ppb
Fe	Furnace(standrad calibration)	0.36 ± 0.04 ppm
Mo	Furnace(standard calibration)	15^{4} ± 3^{2} ppb
Mn	Furnace(standard calibration)	$5.^{3}$ ± $1.^{4}$ ppb
Zn	Flame(standard calibration)	3.1^{1} ± 0.1^{4} ppm
Cu	Flame(standard calibration)	0.61 ± 0.02 ppm

TABLE 15

BUNKER C(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	288 ± 4 ppm
Ni	Flame(standard calibration)	36.6 ± 0.4 ppm
Cr	Furnace(standard calibration)	$47^5 \pm 6^1$ ppb
Co	Furnace(standard calibration)	$18^7 \pm 1^5$ ppb
Fe	Flame(standard calibration)	13.7 ± 0.4 ppm
Mo	Furnace(standard calibration)	$29^3 \pm 4^8$ ppb
Mn	Furnace(standard calibration)	$23^1 \pm 4^5$ ppb
	Furnace(spiking)	$17^1 \pm 1^8$ ppb
Zn	Flame(standard calibration)	$4.2^7 \pm 0.3^2$ ppm
Cu	Flame(standard calibration)	$0.7^5 \pm 0.1^1$ ppm

TABLE 16

LOW SULPHUR BUNKER(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	156 ± 6 ppm
Ni	Flame(standard calibration)	30.0 ± 0.5 ppm
Cr	Furnace(standard calibration)	$101^{1} \pm 3^{8}$ ppb
Co	Furnace(standard calibration)	$18^{5} \pm 1^{2}$ ppb
Fe	Flame(standard calibration)	26.1 ± 0.2 ppm
Mo	Furnace(standard calibration)	$31^{8} \pm 2^{6}$ ppb
Mn	Furnace(standard calibration)	$29^{3} \pm 2^{1}$ ppb
	Furnace(spiking)	$29^{3} \pm 3^{9}$ ppb
Zn	Flame(standard calibration)	$2.5^{0} \pm 0.1^{9}$ ppm
Cu	Flame(standard calibration)	1.02 ± 0.08 ppm

TABLE 17

THIN FILM BUNKER(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	173 ± 1 ppm
Ni	Flame(standard calibration)	16.8 ± 0.1 ppm
Cr	Furnace(standard calibration)	48.^{8} ± 5.^{8} ppb
Co	Furnace(standard calibration)	64.^{9} ± 3.^{7} ppb
Fe	Flame(standard calibration)	1.79 ± 0.02 ppm
Mo	Furnace(standard calibration)	N.D.
Mn	Firnace(standard calibration)	15.^{9} ± 1.^{8} ppb
Zn	Flame(standard calibration)	5.2^{0} ± 0.1^{0} ppm
Cu	Flame(standard calibration)	0.63 ± 0.08 ppm

TABLE 18

BUNKER FUEL NO. 4(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	34.3 ± 0.9 ppm
Ni	Flame(standrad calibration)	7.88 ± 0.07 ppm
Cr	Furnace(standard calibration)	40.1 ± 0.4 ppb
Co	Furnace(standard calibration)	$25.^{0}$ ± $1.^{7}$ ppb
Fe	Furnace(standard calibration)	0.21^{0} ± 0.02^{4} ppm
Mo	Furnace(standrad calibration)	N.D.
Mn	Furnace(standard calibration)	$9.^{1}$ ± $1.^{1}$ ppb
Zn	Flame(standard calibration)	1.32 ± 0.04 ppm
Cu	Flame(standard calibration)	0.28^{9} ± 0.01^{8} ppm

TABLE 19

BUNKER FUEL NO. 5(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	104 ± 2 ppm
Ni	Flame(standard calibration)	19.5 ± 0.4 ppm
Cr	Furnace(standard calibration)	55^{0} ± 3^{5} ppb
Co	Furnace(standrad calibration)	13^{6} ± 1^{6} ppb
Fe	Flame(standard calibration)	7.10 ± 0.07 ppm
Mo	Furnace(standrad calibration)	12^{1} ± 4^{6} ppb
Mn	Furnace(standard calibration)	$99.^{0}$ ± $6.^{0}$ ppb
	Furnace(spiking)	$89.^{1}$ ± $7.^{9}$ ppb
Zn	Flame(standard calibration)	1.41 ± 0.05 ppm
Cu	Flame(standard calibration)	0.60 ± 0.04 ppm

TABLE 20

BUNKER B(WEATHERED)-ELEMENTAL ANALYSIS

Element	Method	Result
V	Flame(standard calibration)	153 ± 4 ppm
Ni	Flame(standard calibration)	29.2 ± 0.4 ppm
Cr	Furnace(standard calibration)	$92^6 \pm 1^8$ ppb
Co	Furnace(standard calibration)	178 ± 9 ppb
Fe	Flame(standard calibration)	25.1 ± 0.5 ppm
Mo	Furnace(standard calibration)	$35^0 \pm 8^0$ ppb
Mn	Furnace(standard calibration)	$25^8 \pm 2^0$ ppb
	Furnace(spiking)	$24^2 \pm 1^0$ ppb
Zn	Flame(standard calibration)	$1.9^9 \pm 0.1^1$ ppm
Cu	Flame(standard calibration)	0.67 ± 0.03 ppm

APPENDIX D

```
LNH

00100 PROGRAM PETRO1(INPUT,OUTPUT)
00110 DIMENSION NN(10),OR(10),OE(10),WR(10),WE(10)
00120 PRINT 1
00130 1 FORMAT(2X,*ENTER THE NUMBER OF RATIO PAIRS*)
00140 READ,N
00150 PRINT 2
00160 2 FORMAT(2X,*ENTER THE RATIO VALUES AND THE MPES*)
00170 PRINT 6
00180 6 FORMAT(1X,*SAMPLE NO  ORIGINAL RATIO   WEATHERED RATIO*)
00190 DO 10 I=1,N
00200 READ,NN(I),OR(I),OE(I),WR(I),WE(I)
00210 10 CONTINUE
00220 11 PRINT 12
00230 12 FORMAT(2X,*ENTER THE ORDER OF MPE FOR THE TEST*)
00240 READ,TO
00250 IF (TO.EQ.0.0) GO TO 13
00260 S=0.0
00270 PRINT 7
00280 7 FORMAT(2X,*RATIO PAIRS WHICH FAIL TO SCORE*)
00290 PRINT 8
00300 8 FORMAT(1X,*NO   ORIGINAL RATIO       NO   WEATHERED RATIO*)
00310 DO 20 J=1,N
00320 DO 30 K=1,N
00330 RD=OR(J)-WR(K)
00340 RDF=ABS(RD)
00350 TE=TO*(OE(J)+WE(K))
00360 IF (J.EQ.K) GO TO 40
00370 IF (TE.GE.RDF) GO TO 50
00380 S=S+1
00390 GO TO 30
00400 50 PRINT 9,NN(J),OR(J),OE(J),NN(K),WR(K),WE(K)
00410 9 FORMAT(1X,I2,3X,2F8.4,5X,I2,3X,2F8.4)
00420 GO TO 30
00430 40 IF(TE.LT.RDF) GO TO 50
00440 S=S+1
00450 30 CONTINUE
00460 20 CONTINUE
00470 NT=N**2
00480 PER=S*100/NT
00490 PRINT 3,NT
00500 3 FORMAT (10X,*TOTAL NUMBER OF TESTS IS*,2X,I3)
00510 PRINT 4,S
00520 4 FORMAT(10X,*TOTAL SCORING IS*,2X,F4.1)
00530 PRINT 5,PER
00540 5 FORMAT(10X,*PERCENTAGE IS*,1X,F6.2,////)
00550 GO TO 11
00560 13 STOP
00570 END
READY.
```

```
TEST FOR V/NI *DEL*

RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 10
  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 1         9.82   0.14       10.96  0.38
? 2         7.59   0.19       8.15   0.39
? 3         0.605  0.040      0.632  0.043
? 4         2.19   0.14       2.195  0.070
? 5         7.87   0.26       7.87   0.14
? 6         4.74   0.26       5.20   0.22
? 7         10.35  0.32       10.30  0.08
? 8         4.53   0.12       4.35   0.12
? 9         5.63   0.17       5.33   0.15
? 10        5.24   0.15       5.24   0.15


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5

  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  1      9.8200    .1400      1     10.9600    .3800
  2      7.5900    .1900      2      8.1500    .3900
  5      7.8700    .2600      2      8.1500    .3900
  6      4.7400    .2600      6      5.2000    .2200
  8      4.5300    .1200      8      4.3500    .1200
  9      5.6300    .1700      9      5.3300    .1500
 10      5.2400    .1500      6      5.2000    .2200
 10      5.2400    .1500      9      5.3300    .1500
            TOTAL NUMBER OF TESTS IS  100
            TOTAL SCORING IS  92.0
            PERCENTAGE IS  92.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  1      9.8200    .1400      1     10.9600    .3800
  2      7.5900    .1900      5      7.8700    .1400
  5      7.8700    .2600      2      8.1500    .3900
  7     10.3500    .3[illegible]      1     10.9600    .3800
 10      5.2400    .1500      6      5.2000    .2200
 10      5.2400    .1500      9      5.3300    .1500
            TOTAL NUMBER OF TESTS IS  100
            TOTAL SCORING IS  94.0
            PERCENTAGE IS  94.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
```

```
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1       9.8200    .1400     1    10.9600    .3800
 2       7.5900    .1900     5     7.8700    .1400
 5       7.8700    .2600     2     8.1500    .3900
 6       4.7400    .2600     8     4.3500    .1200
 6       4.7400    .2600     9     5.3300    .1500
 6       4.7400    .2600    10     5.2400    .1500
 7      10.3500    .3200     1    10.9600    .3800
 9       5.6300    .1700     6     5.2000    .2200
 9       5.6300    .1700    10     5.2400    .1500
10       5.2400    .1500     6     5.2000    .2200
10       5.2400    .1500     9     5.3300    .1500
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  89.0
          PERCENTAGE IS  89.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1       9.8200    .1400     1    10.9600    .3800
 2       7.5900    .1900     5     7.8700    .1400
 5       7.8700    .2600     2     8.1500    .3900
 6       4.7400    .2600     8     4.3500    .1200
 6       4.7400    .2600     9     5.3300    .1500
 6       4.7400    .2600    10     5.2400    .1500
 7      10.3500    .3200     1    10.9600    .3800
 8       4.5300    .1200     6     5.2000    .2200
 9       5.6300    .1700     6     5.2000    .2200
 9       5.6300    .1700    10     5.2400    .1500
10       5.2400    .1500     6     5.2000    .2200
10       5.2400    .1500     9     5.3300    .1500
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  88.0
          PERCENTAGE IS  88.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1       9.8200    .1400     7    10.3000    .0800
 2       7.5900    .1900     5     7.8700    .1400
 5       7.8700    .2600     2     8.1500    .3900
 6       4.7400    .2600     8     4.3500    .1200
 6       4.7400    .2600     9     5.3300    .1500
 6       4.7400    .2600    10     5.2400    .1500
 7      10.3500    .3200     1    10.9600    .3800
 8       4.5300    .1200     6     5.2000    .2200
 9       5.6300    .1700     6     5.2000    .2200
 9       5.6300    .1700    10     5.2400    .1500
10       5.2400    .1500     6     5.2000    .2200
10       5.2400    .1500     9     5.3300    .1500
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  88.0
          PERCENTAGE IS  88.00
```

```
 ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO       NO   WEATHERED RATIO
 1      9.8200   .1400     7   10.3000   .0800
 2      7.5900   .1900     5    7.8700   .1400
 5      7.8700   .2600     2    8.1500   .3900
 6      4.7400   .2600     8    4.3500   .1200
 6      4.7400   .2600     9    5.3300   .1500
 6      4.7400   .2600    10    5.2400   .1500
 7     10.3500   .3200     1   10.9600   .3800
 8      4.5300   .1200     6    5.2000   .2200
 8      4.5300   .1200     9    5.3300   .1500
 8      4.5300   .1200    10    5.2400   .1500
 9      5.6300   .1700     6    5.2000   .2200
 9      5.6300   .1700    10    5.2400   .1500
10      5.2400   .1500     6    5.2000   .2200
10      5.2400   .1500     9    5.3300   .1500
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  86.0
          PERCENTAGE IS  86.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU      0.823 UNTS.

RUN COMPLETE.
```

```
TEST FOR V/CR *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 9

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO   ORIGINAL RATIO    WEATHERED RATIO
? 1          4.97   0.48       4.78   0.22
? 2          4.51   0.92       4.23   0.32
? 4          0.475  0.043      0.467  0.026
? 5          0.614  0.030      0.606  0.078
? 6          0.1295 0.0045     0.1543 0.0082
? 7          3.77   0.17       3.54   0.42
? 8          0.793  0.078      0.855  0.024
? 9          0.2298 0.0094     0.189  0.012
? 10         0.1413 0.0070     0.1652 0.0054



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO         NO   WEATHERED RATIO
  2     4.5100   .9200        1     4.7800   .2200
  6      .1295   .0045        6      .1543   .0082
  8      .7930   .0780        8      .8550   .0240
  9      .2298   .0094        9      .1890   .0120
 10      .1413   .0070       10      .1652   .0054
         TOTAL NUMBER OF TESTS IS    81
         TOTAL SCORING IS  76.0
         PERCENTAGE IS  93.83


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO         NO   WEATHERED RATIO
  1     4.9700   .4800        2     4.2300   .3200
  2     4.5100   .9200        1     4.7800   .2200
  2     4.5100   .9200        7     3.5400   .4200
  6      .1295   .0045        6      .1543   .0082
  7     3.7700   .1700        2     4.2300   .3200
  9      .2298   .0094        9      .1890   .0120
 10      .1413   .0070        6      .1543   .0082
 10      .1413   .0070       10      .1652   .0054
         TOTAL NUMBER OF TESTS IS    81
         TOTAL SCORING IS  73.0
         PERCENTAGE IS  90.12
```

```
 ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       4.9700     .4800      2      4.2300    .3200
 2       4.5100     .9200      1      4.7800    .2200
 2       4.5100     .9200      7      3.5400    .4200
 4        .4750     .0430      5       .6060    .0780
 6        .1295     .0045      6       .1543    .0082
 7       3.7700     .1700      2      4.2300    .3200
 8        .7930     .0780      5       .6060    .0780
 9        .2298     .0094      9       .1890    .0120
10        .1413     .0070      6       .1543    .0082
10        .1413     .0070     10       .1652    .0054
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  71.0
          PERCENTAGE IS  87.65


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       4.9700     .4800      2      4.2300    .3200
 1       4.9700     .4800      7      3.5400    .4200
 2       4.5100     .9200      1      4.7800    .2200
 2       4.5100     .9200      7      3.5400    .4200
 4        .4750     .0430      5       .6060    .0780
 7       3.7700     .1700      2      4.2300    .3200
 8        .7930     .0780      5       .6060    .0780
10        .1413     .0070      6       .1543    .0082
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  73.0
          PERCENTAGE IS  90.12


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       4.9700     .4800      2      4.2300    .3200
 1       4.9700     .4800      7      3.5400    .4200
 2       4.5100     .9200      1      4.7800    .2200
 2       4.5100     .9200      7      3.5400    .4200
 4        .4750     .0430      5       .6060    .0780
 7       3.7700     .1700      2      4.2300    .3200
 8        .7930     .0780      5       .6060    .0780
10        .1413     .0070      6       .1543    .0082
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  73.0
          PERCENTAGE IS  90.12


 ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       4.9700     .4800      2      4.2300    .3200
 1       4.9700     .4800      7      3.5400    .4200
 2       4.5100     .9200      1      4.7800    .2200
```

```
 2     4.5100   .9200     7     3.5400   .4200
 4      .4750   .0430     5      .6060   .0780
 5      .6140   .0300     4      .4670   .0260
 7     3.7700   .1700     1     4.7800   .2200
 7     3.7700   .1700     2     4.2300   .3200
 8      .7930   .0780     5      .6060   .0780
10      .1413   .0070     6      .1543   .0082
10      .1413   .0070     9      .1890   .0120
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  70.0
          PERCENTAGE IS  86.42


  ENTER THE ORDER OF MPE FOR THE TEST
 ? 0.0

 SRU       0.766 UNTS.

 RUN COMPLETE.
```

```
TEST FOR V/CO *DEL*


RNH

   ENTER THE NUMBER OF RATIO PAIRS
 ? 10

   ENTER THE RATIO VALUES AND THE MPES
  SAMPLE NO   ORIGINAL RATIO    WEATHERED RATIO
 ? 1          2.78    0.13      3.30    0.39
 ? 2          1.446   0.075     1.624    0.090
 ? 3          0.234   0.036     0.238   0.037
 ? 4          1.52    0.11      1.585   0.048
 ? 5          1.37    0.11      1.54    0.12
 ? 6          0.888   0.048     0.843   0.064
 ? 7          1.980   0.062     2.67    0.15
 ? 8          1.07    0.13      1.37    0.10
 ? 9          0.831   0.024     0.764   0.091
 ? 10         6.33    0.21      6.10    0.20




   ENTER THE ORDER OF MPE FOR THE TEST
 ? 0.5
   RATIO PAIRS WHICH FAIL TO SCORE
  NO   ORIGINAL RATIO      NO   WEATHERED RATIO
   1     2.7800   .1300     1     3.3000   .3900
   1     2.7800   .1300     7     2.6700   .1500
   2     1.4460   .0750     2     1.6240   .0900
   2     1.4460   .0750     5     1.5400   .1200
   2     1.4460   .0750     8     1.3700   .1000
   4     1.5200   .1100     5     1.5400   .1200
   5     1.3700   .1100     5     1.5400   .1200
   5     1.3700   .1100     8     1.3700   .1000
   7     1.9800   .0620     7     2.6700   .1500
   8     1.0700   .1300     8     1.3700   .1000
   9      .8310   .0240     6      .8430   .0640
   9      .8310   .0240     9      .7640   .0910
  10     6.3300   .2100    10     6.1000   .2000
           TOTAL NUMBER OF TESTS IS  100
           TOTAL SCORING IS  87.0
           PERCENTAGE IS  87.00


   ENTER THE ORDER OF MPE FOR THE TEST
 ? 1.0
   RATIO PAIRS WHICH FAIL TO SCORE
  NO   ORIGINAL RATIO      NO   WEATHERED RATIO
   1     2.7800   .1300     7     2.6700   .1500
   2     1.4460   .0750     2     1.6240   .0900
   2     1.4460   .0750     5     1.5400   .1200
   2     1.4460   .0750     8     1.3700   .1000
   4     1.5200   .1100     2     1.6240   .0900
   4     1.5200   .1100     5     1.5400   .1200
   4     1.5200   .1100     8     1.3700   .1000
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```
 5       1.3700    .1100          8       1.3700    .1000
 6        .8880    .0480          9        .7640    .0910
 7       1.9800    .0620          7       2.6700    .1500
 8       1.0700    .1300          8       1.3700    .1000
 9        .8310    .0240          6        .8430    .0640
           TOTAL NUMBER OF TESTS IS  100
           TOTAL SCORING IS  88.0
           PERCENTAGE IS  88.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO          NO    WEATHERED RATIO
 1       2.7800    .1300          7       2.6700    .1500
 2       1.4460    .0750          4       1.5850    .0480
 2       1.4460    .0750          5       1.5400    .1200
 2       1.4460    .0750          8       1.3700    .1000
 4       1.5200    .1100          2       1.6240    .0900
 4       1.5200    .1100          5       1.5400    .1200
 4       1.5200    .1100          8       1.3700    .1000
 5       1.3700    .1100          2       1.6240    .0900
 5       1.3700    .1100          4       1.5850    .0480
 5       1.3700    .1100          8       1.3700    .1000
 6        .8880    .0480          9        .7640    .0910
 7       1.9800    .0620          7       2.6700    .1500
 8       1.0700    .1300          6        .8430    .0640
 8       1.0700    .1300          9        .7640    .0910
 9        .8310    .0240          6        .8430    .0640
           TOTAL NUMBER OF TESTS IS  100
           TOTAL SCORING IS  85.0
           PERCENTAGE IS  85.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO          NO    WEATHERED RATIO
 1       2.7800    .1300          7       2.6700    .1500
 2       1.4460    .0750          4       1.5850    .0480
 2       1.4460    .0750          5       1.5400    .1200
 2       1.4460    .0750          8       1.3700    .1000
 4       1.5200    .1100          2       1.6240    .0900
 4       1.5200    .1100          5       1.5400    .1200
 4       1.5200    .1100          8       1.3700    .1000
 5       1.3700    .1100          2       1.6240    .0900
 5       1.3700    .1100          4       1.5850    .0480
 5       1.3700    .1100          8       1.3700    .1000
 6        .8880    .0480          9        .7640    .0910
 7       1.9800    .0620          7       2.6700    .1500
 8       1.0700    .1300          5       1.5400    .1200
 8       1.0700    .1300          6        .8430    .0640
 8       1.0700    .1300          9        .7640    .0910
 9        .8310    .0240          6        .8430    .0640
           TOTAL NUMBER OF TESTS IS  100
           TOTAL SCORING IS  84.0
           PERCENTAGE IS  84.00


 ENTER THE ORDER OF MPE FOR THE TEST
```

```
? 2.5
 RATIO PAIRS WHICH FAIL  TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       2.7800    .1300       7       2.6700    .1500
 2       1.4460    .0750       4       1.5850    .0480
 2       1.4460    .0750       5       1.5400    .1200
 2       1.4460    .0750       8       1.3700    .1000
 4       1.5200    .1100       2       1.6240    .0900
 4       1.5200    .1100       5       1.5400    .1200
 4       1.5200    .1100       8       1.3700    .1000
 5       1.3700    .1100       2       1.6240    .0900
 5       1.3700    .1100       4       1.5850    .0480
 5       1.3700    .1100       8       1.3700    .1000
 6        .8880    .0480       9        .7640    .0910
 7       1.9800    .0620       2       1.6240    .0900
 7       1.9800    .0620       5       1.5400    .1200
 7       1.9800    .0620       7       2.6700    .1500
 8       1.0700    .1300       5       1.5400    .1200
 8       1.0700    .1300       6        .8430    .0640
 8       1.0700    .1300       9        .7640    .0910
 9        .8310    .0240       6        .8430    .0640
               TOTAL NUMBER OF TESTS IS  100
               TOTAL SCORING IS  82.0
               PERCENTAGE IS   82.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
 RATIO PAIRS WHICH FAIL  TO SCORE
NO    ORIGINAL RATIO          NO    WEATHERED RATIO
 1       2.7800    .1300       7       2.6700    .1500
 2       1.4460    .0750       4       1.5850    .0480
 2       1.4460    .0750       5       1.5400    .1200
 2       1.4460    .0750       8       1.3700    .1000
 4       1.5200    .1100       2       1.6240    .0900
 4       1.5200    .1100       5       1.5400    .1200
 4       1.5200    .1100       8       1.3700    .1000
 5       1.3700    .1100       2       1.6240    .0900
 5       1.3700    .1100       4       1.5850    .0480
 5       1.3700    .1100       8       1.3700    .1000
 6        .8880    .0480       9        .7640    .0910
 7       1.9800    .0620       1       3.3000    .3900
 7       1.9800    .0620       2       1.6240    .0900
 7       1.9800    .0620       5       1.5400    .1200
 7       1.9800    .0620       7       2.6700    .1500
 8       1.0700    .1300       2       1.6240    .0900
 8       1.0700    .1300       4       1.5850    .0480
 8       1.0700    .1300       5       1.5400    .1200
 8       1.0700    .1300       6        .8430    .0640
 8       1.0700    .1300       9        .7640    .0910
 9        .8310    .0240       6        .8430    .0640
               TOTAL NUMBER OF TESTS IS  100
               TOTAL SCORING IS  79.0
               PERCENTAGE IS   79.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU      0.931 UNTS.

RUN COMPLETE.
```

```
TEST FOR V/FE *DEL*



RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 8

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO   WEATHERED RATIO
? 1          368     59        348     30
? 2          316     63        322     28
? 5          20.45   0.55      21.02   0.68
? 6          5.32    0.12      5.98    0.23
? 7          101.1   6.4       96.6    1.2
? 8          154.9   8.5       163     19
? 9          14.73   0.52      14.65   0.32
? 10         6.33    0.21      6.10    0.20



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  2   316.0000 63.0000      1   348.0000 30.0000
  6     5.3200   .1200      6     5.9800   .2300
  7   101.1000  6.4000      7    96.6000  1.2000
 10     6.3300   .2100     10     6.1000   .2000
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  60.0
          PERCENTAGE IS  93.75


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1   368.0000 59.0000      2   322.0000 28.0000
  2   316.0000 63.0000      1   348.0000 30.0000
  6     5.3200   .1200      6     5.9800   .2300
 10     6.3300   .2100      6     5.9800   .2300
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  60.0
          PERCENTAGE IS  93.75


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1   368.0000 59.0000      2   322.0000 28.0000
```

```
 2   316.0000 63.0000        1   348.0000 30.0000
 6     5.3200   .1200        6     5.9800   .2300
10     6.3300   .2100        6     5.9800   .2300
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  60.0
          PERCENTAGE IS  93.75


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1  368.0000 59.0000        2   322.0000 28.0000
  2  316.0000 63.0000        1   348.0000 30.0000
  2  316.0000 63.0000        8   163.0000 19.0000
 10    6.3300   .2100        6     5.9800   .2300
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  60.0
          PERCENTAGE IS  93.75


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1  368.0000 59.0000        2   322.0000 28.0000
  2  316.0000 63.0000        1   348.0000 30.0000
  2  316.0000 63.0000        8   163.0000 19.0000
  6    5.3200   .1200       10     6.1000   .2000
  7  101.1000  6.4000        8   163.0000 19.0000
 10    6.3300   .2100        6     5.9800   .2300
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  58.0
          PERCENTAGE IS  90.63


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1  368.0000 59.0000        2   322.0000 28.0000
  1  368.0000 59.0000        8   163.0000 19.0000
  2  316.0000 63.0000        1   348.0000 30.0000
  2  316.0000 63.0000        8   163.0000 19.0000
  6    5.3200   .1200       10     6.1000   .2000
  7  101.1000  6.4000        8   163.0000 19.0000
 10    6.3300   .2100        6     5.9800   .2300
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  57.0
          PERCENTAGE IS  89.06


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.673 UNTS.

RUN COMPLETE.
```

```
TEA *DEL*
TEST FOR V/MN *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 5

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO   ORIGINAL RATIO    WEATHERED RATIO
? 5          1.81    0.20      1.68    0.18
? 6          0.534   0.069     0.532   0.074
? 7          10.6    1.4       10.9    1.2
? 9          1.319   0.081     1.17    0.10
? 10         0.613   0.064     0.632   0.031



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO    WEATHERED RATIO
  9     1.3190    .0810      9      1.1700   .1000
            TOTAL NUMBER OF TESTS IS    25
            TOTAL SCORING IS  24.0
            PERCENTAGE IS  96.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO    WEATHERED RATIO
  6      .5340    .0690     10       .6320   .0310
 10      .6130    .0640      6       .5320   .0740
            TOTAL NUMBER OF TESTS IS    25
            TOTAL SCORING IS  23.0
            PERCENTAGE IS  92.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO    WEATHERED RATIO
  6      .5340    .0690     10       .6320   .0310
  9     1.3190    .0810      5      1.6800   .1800
 10      .6130    .0640      6       .5320   .0740
            TOTAL NUMBER OF TESTS IS    25
            TOTAL SCORING IS  22.0
            PERCENTAGE IS  88.00


  ENTER THE ORDER OF MPE FOR THE TEST
```

```
? 2.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  6       .5340    .0690    10       .6320    .0310
  9      1.3190    .0810     5      1.6800    .1800
 10       .6130    .0640     6       .5320    .0740
              TOTAL NUMBER OF TESTS IS   25
              TOTAL SCORING IS  22.0
              PERCENTAGE IS  88.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  5      1.8100    .2000     9      1.1700    .1000
  6       .5340    .0690    10       .6320    .0310
  9      1.3190    .0810     5      1.6800    .1800
 10       .6130    .0640     6       .5320    .0740
              TOTAL NUMBER OF TESTS IS   25
              TOTAL SCORING IS  21.0
              PERCENTAGE IS  84.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  5      1.8100    .2000     9      1.1700    .1000
  6       .5340    .0690    10       .6320    .0310
  9      1.3190    .0810     5      1.6800    .1800
 10       .6130    .0640     6       .5320    .0740
              TOTAL NUMBER OF TESTS IS   25
              TOTAL SCORING IS  21.0
              PERCENTAGE IS  84.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU      0.597 UNTS.

RUN COMPLETE.
```

```
TEST FOR NI/CR *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 9
  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 1         0.506    0.048    0.436    0.013
? 2         0.59     0.12     0.518    0.044
? 4         0.217    0.015    0.212    0.010
? 5         0.0780   0.0036   0.0770   0.0099
? 6         0.0274   0.0016   0.0287   0.0012
? 7         0.364    0.013    0.344    0.041
? 8         0.175    0.017    0.1965   0.0026
? 9         0.0408   0.0013   0.0354   0.0024
? 10        0.0270   0.0012   0.0315   0.0008



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      1       .4360   .0130
  1       .5060   .0480      2       .5180   .0440
  6       .0274   .0016      6       .0297   .0012
  8       .1750   .0170      8       .1965   .0026
  9       .0408   .0013      9       .0354   .0024
 10       .0270   .0012     10       .0315   .0008
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  75.0
          PERCENTAGE IS  92.59


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      1       .4360   .0130
  1       .5060   .0480      2       .5180   .0440
  8       .1750   .0170      8       .1965   .0026
  9       .0408   .0013      9       .0354   .0024
 10       .0270   .0012     10       .0315   .0008
          TOTAL NUMBER OF TESTS IS   81
          TOTAL SCORING IS  76.0
          PERCENTAGE IS  93.83


  ENTER THE ORDER OF MPE FOR THE TEST
```

```
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      2        .5180   .0440
  2       .5900   .1200      1        .4360   .0130
  4       .2170   .0150      8        .1965   .0026
  8       .1750   .0170      4        .2120   .0100
 10       .0270   .0012      6        .0297   .0012
 10       .0270   .0012     10        .0315   .0008
           TOTAL NUMBER OF TESTS IS    81
           TOTAL SCORING IS  75.0
           PERCENTAGE IS  92.59


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      2        .5180   .0440
  1       .5060   .0480      7        .3440   .0410
  2       .5900   .1200      1        .4360   .0130
  2       .5900   .1200      7        .3440   .0410
  4       .2170   .0150      8        .1965   .0026
  6       .0274   .0016     10        .0315   .0008
  8       .1750   .0170      4        .2120   .0100
 10       .0270   .0012      6        .0297   .0012
 10       .0270   .0012     10        .0315   .0008
           TOTAL NUMBER OF TESTS IS    81
           TOTAL SCORING IS  72.0
           PERCENTAGE IS  88.89


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      2        .5180   .0440
  1       .5060   .0480      7        .3440   .0410
  2       .5900   .1200      1        .4360   .0130
  2       .5900   .1200      7        .3440   .0410
  4       .2170   .0150      7        .3440   .0410
  4       .2170   .0150      8        .1965   .0026
  6       .0274   .0016      9        .0354   .0024
  6       .0274   .0016     10        .0315   .0008
  8       .1750   .0170      4        .2120   .0100
 10       .0270   .0012      6        .0297   .0012
 10       .0270   .0012      9        .0354   .0024
           TOTAL NUMBER OF TESTS IS    81
           TOTAL SCORING IS  70.0
           PERCENTAGE IS  86.42


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1       .5060   .0480      2        .5180   .0440
  1       .5060   .0480      7        .3440   .0410
  2       .5900   .1200      1        .4360   .0130
  2       .5900   .1200      4        .2120   .0100
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  2       .5900   .1200        7        .3440   .0410
  4       .2170   .0150        7        .3440   .0410
  4       .2170   .0150        8        .1965   .0026
  6       .0274   .0016        9        .0354   .0024
  6       .0274   .0016       10        .0315   .0008
  7       .3640   .0130        1        .4360   .0130
  7       .3640   .0130        2        .5180   .0440
  8       .1750   .0170        4        .2120   .0100
  8       .1750   .0170        7        .3440   .0410
 10       .0270   .0012        6        .0297   .0012
 10       .0270   .0012        9        .0354   .0024
           TOTAL NUMBER OF TESTS IS   81
           TOTAL SCORING IS  66.0
           PERCENTAGE IS  81.48


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.757 UNTS.

RUN COMPLETE.
```

```
TEST FOR NI/CO *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
?01*DEL*
   10
  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO   WEATHERED RATIO
? 1         0.283  0.012      0.301   0.035
? 2         0.190  0.010      0.199   0.013
? 3         0.387  0.062      0.377   0.055
? 4         0.695  0.029      0.7222  0.0091
? 5         0.174  0.014      0.196   0.016
? 6         0.188  0.013      0.162   0.011
? 7         0.1913 0.0034     0.259   0.015
? 8         0.235  0.027      0.315   0.022
? 9         0.1477 0.0019     0.143   0.017
? 10        0.1465 0.0040     0.1640  0.0086


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  2        .1900    .0100     5        .1960   .0160
  4        .6950    .0290     4        .7222   .0091
  5        .1740    .0140     5        .1960   .0160
  5        .1740    .0140     6        .1620   .0110
  5        .1740    .0140    10        .1640   .0086
  6        .1880    .0130     2        .1990   .0130
  6        .1880    .0130     5        .1960   .0160
  6        .1880    .0130     6        .1620   .0110
  7        .1913    .0034     2        .1990   .0130
  7        .1913    .0034     5        .1960   .0160
  7        .1913    .0034     7        .2590   .0150
  8        .2350    .0270     8        .3150   .0220
 10        .1465    .0040     9        .1430   .0170
 10        .1465    .0040    10        .1640   .0086
            TOTAL NUMBER OF TESTS IS  100
            TOTAL SCORING IS  86.0
            PERCENTAGE IS  86.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1        .2830    .0120     7        .2590   .0150
  1        .2830    .0120     8        .3150   .0220
  2        .1900    .0100     5        .1960   .0160
  3        .3870    .0620     1        .3010   .0350
  3        .3870    .0620     8        .3150   .0220
  5        .1740    .0140     2        .1990   .0130
  5        .1740    .0140     6        .1620   .0110
```

```
   5     .1740   .0140      10      .1640   .0086
   6     .1880   .0130       2      .1990   .0130
   6     .1880   .0130       5      .1960   .0160
   6     .1880   .0130       6      .1620   .0110
   7     .1913   .0034       2      .1990   .0130
   7     .1913   .0034       5      .1960   .0160
   7     .1913   .0034       7      .2590   .0150
   8     .2350   .0270       2      .1990   .0130
   8     .2350   .0270       5      .1960   .0160
   8     .2350   .0270       7      .2590   .0150
   8     .2350   .0270       8      .3150   .0220
  10     .1465   .0040       9      .1430   .0170
  10     .1465   .0040      10      .1640   .0086
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  80.0
          PERCENTAGE IS  80.00


   ENTER THE ORDER OF MPE FOR THE TEST
 ? 1.5
   RATIO PAIRS WHICH FAIL TO SCORE
  NO   ORIGINAL RATIO       NO   WEATHERED RATIO
   1     .2830   .0120       3      .3770   .0550
   1     .2830   .0120       7      .2590   .0150
   1     .2830   .0120       8      .3150   .0220
   2     .1900   .0100       5      .1960   .0160
   2     .1900   .0100       6      .1620   .0110
   2     .1900   .0100      10      .1640   .0086
   3     .3870   .0620       1      .3010   .0350
   3     .3870   .0620       8      .3150   .0220
   5     .1740   .0140       2      .1990   .0130
   5     .1740   .0140       6      .1620   .0110
   5     .1740   .0140       9      .1430   .0170
   5     .1740   .0140      10      .1640   .0086
   6     .1880   .0130       2      .1990   .0130
   6     .1880   .0130       5      .1960   .0160
   6     .1880   .0130       9      .1430   .0170
   6     .1880   .0130      10      .1640   .0086
   7     .1913   .0034       2      .1990   .0130
   7     .1913   .0034       5      .1960   .0160
   7     .1913   .0034       7      .2590   .0150
   8     .2350   .0270       1      .3010   .0350
   8     .2350   .0270       2      .1990   .0130
   8     .2350   .0270       5      .1960   .0160
   8     .2350   .0270       7      .2590   .0150
   8     .2350   .0270       8      .3150   .0220
   9     .1477   .0019       6      .1620   .0110
  10     .1465   .0040       6      .1620   .0110
  10     .1465   .0040       9      .1430   .0170
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  73.0
          PERCENTAGE IS  73.00


   ENTER THE ORDER OF MPE FOR THE TEST
 ? 2.0
   RATIO PAIRS WHICH FAIL TO SCORE
  NO   ORIGINAL RATIO       NO   WEATHERED RATIO
   1     .2830   .0120       3      .3770   .0550
   1     .2830   .0120       7      .2590   .0150
   1     .2830   .0120       8      .3150   .0220
   2     .1900   .0100       5      .1960   .0160
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 2      .1900   .0100       6      .1620   .0110
 2      .1900   .0100       9      .1430   .0170
 2      .1900   .0100      10      .1640   .0086
 3      .3870   .0620       1      .3010   .0350
 3      .3870   .0620       7      .2590   .0150
 3      .3870   .0620       8      .3150   .0220
 5      .1740   .0140       2      .1990   .0130
 5      .1740   .0140       6      .1620   .0110
 5      .1740   .0140       9      .1430   .0170
 5      .1740   .0140      10      .1640   .0086
 6      .1880   .0130       2      .1990   .0130
 6      .1880   .0130       5      .1960   .0160
 6      .1880   .0130       9      .1430   .0170
 6      .1880   .0130      10      .1640   .0086
 7      .1913   .0034       2      .1990   .0130
 7      .1913   .0034       5      .1960   .0160
 7      .1913   .0034       7      .2590   .0150
 8      .2350   .0270       1      .3010   .0350
 8      .2350   .0270       2      .1990   .0130
 8      .2350   .0270       3      .3770   .0550
 8      .2350   .0270       5      .1960   .0160
 8      .2350   .0270       6      .1620   .0110
 8      .2350   .0270       7      .2590   .0150
 8      .2350   .0270      10      .1640   .0086
 9      .1477   .0019       6      .1620   .0110
 9      .1477   .0019      10      .1640   .0086
10      .1465   .0040       6      .1620   .0110
10      .1465   .0040       9      .1430   .0170
          TOTAL NUMBER OF TESTS IS  100
          TOTAL SCORING IS  68.0
          PERCENTAGE IS  68.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1       .2830   .0120      3      .3770   .0550
 1       .2830   .0120      7      .2590   .0150
 1       .2830   .0120      8      .3150   .0220
 2       .1900   .0100      1      .3010   .0350
 2       .1900   .0100      5      .1960   .0160
 2       .1900   .0100      6      .1620   .0110
 2       .1900   .0100      9      .1430   .0170
 2       .1900   .0100     10      .1640   .0086
 3       .3870   .0620      1      .3010   .0350
 3       .3870   .0620      5      .1960   .0160
 3       .3870   .0620      7      .2590   .0150
 3       .3870   .0620      8      .3150   .0220
 5       .1740   .0140      2      .1990   .0130
 5       .1740   .0140      6      .1620   .0110
 5       .1740   .0140      9      .1430   .0170
 5       .1740   .0140     10      .1640   .0086
 6       .1880   .0130      1      .3010   .0350
 6       .1880   .0130      2      .1990   .0130
 6       .1880   .0130      5      .1960   .0160
 6       .1880   .0130      9      .1430   .0170
 6       .1880   .0130     10      .1640   .0086
 7       .1913   .0034      2      .1990   .0130
 7       .1913   .0034      5      .1960   .0160
 7       .1913   .0034      6      .1620   .0110
 7       .1913   .0034      7      .2590   .0150
 7       .1913   .0034      9      .1430   .0170
 7       .1913   .0034     10      .1640   .0086
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 8      .2350   .0270       1        .3010   .0350
 8      .2350   .0270       2        .1990   .0130
 8      .2350   .0270       3        .3770   .0550
 8      .2350   .0270       5        .1960   .0160
 8      .2350   .0270       6        .1620   .0110
 8      .2350   .0270       7        .2590   .0150
 8      .2350   .0270       9        .1430   .0170
 8      .2350   .0270      10        .1640   .0086
 9      .1477   .0019       6        .1620   .0110
 9      .1477   .0019      10        .1640   .0086
10      .1465   .0040       5        .1960   .0160
10      .1465   .0040       6        .1620   .0110
10      .1465   .0040       9        .1430   .0170
         TOTAL NUMBER OF TESTS IS  100
         TOTAL SCORING IS  60.0
         PERCENTAGE IS  60.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1      .2830   .0120      3       .3770   .0550
  1      .2830   .0120      7       .2590   .0150
  1      .2830   .0120      8       .3150   .0220
  2      .1900   .0100      1       .3010   .0350
  2      .1900   .0100      3       .3770   .0550
  2      .1900   .0100      5       .1960   .0160
  2      .1900   .0100      6       .1620   .0110
  2      .1900   .0100      7       .2590   .0150
  2      .1900   .0100      9       .1430   .0170
  2      .1900   .0100     10       .1640   .0086
  3      .3870   .0620      1       .3010   .0350
  3      .3870   .0620      2       .1990   .0130
  3      .3870   .0620      5       .1960   .0160
  3      .3870   .0620      7       .2590   .0150
  3      .3870   .0620      8       .3150   .0220
  5      .1740   .0140      1       .3010   .0350
  5      .1740   .0140      2       .1990   .0130
  5      .1740   .0140      3       .3770   .0550
  5      .1740   .0140      6       .1620   .0110
  5      .1740   .0140      7       .2590   .0150
  5      .1740   .0140      9       .1430   .0170
  5      .1740   .0140     10       .1640   .0086
  6      .1880   .0130      1       .3010   .0350
  6      .1880   .0130      2       .1990   .0130
  6      .1880   .0130      3       .3770   .0550
  6      .1880   .0130      5       .1960   .0160
  6      .1880   .0130      7       .2590   .0150
  6      .1880   .0130      9       .1430   .0170
  6      .1880   .0130     10       .1640   .0086
  7      .1913   .0034      1       .3010   .0350
  7      .1913   .0034      2       .1990   .0130
  7      .1913   .0034      5       .1960   .0160
  7      .1913   .0034      6       .1620   .0110
  7      .1913   .0034      7       .2590   .0150
  7      .1913   .0034      9       .1430   .0170
  7      .1913   .0034     10       .1640   .0086
  8      .2350   .0270      1       .3010   .0350
  8      .2350   .0270      2       .1990   .0130
  8      .2350   .0270      3       .3770   .0550
  8      .2350   .0270      5       .1960   .0160
  8      .2350   .0270      6       .1620   .0110
  8      .2350   .0270      7       .2590   .0150
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 8       .2350   .0270      9       .1430   .0170
 8       .2350   .0270     10       .1640   .0086
 9       .1477   .0019      5       .1960   .0160
 9       .1477   .0019      6       .1620   .0110
 9       .1477   .0019     10       .1640   .0086
10       .1465   .0040      5       .1960   .0160
10       .1465   .0040      6       .1620   .0110
10       .1465   .0040      9       .1430   .0170
              TOTAL NUMBER OF TESTS IS  100
              TOTAL SCORING IS  50.0
              PERCENTAGE IS  50.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       1.279 UNTS.

RUN COMPLETE.
```

```
TEST FOR NI/FE *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 8
  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 37 *DEL*
  1          37.5    6.0        31.8    2.6
? 2          41.6    8.4        39.5    3.8
? 5          2.598   0.056      2.671   0.083
? 6          1.123   0.056      1.149   0.021
? 7          9.77    0.57       9.38    0.12
? 8          34.2    1.7        37.5    4.5
? 9          2.619   0.063      2.746   0.062
? 10         1.208   0.28       1.163   0.028



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  1     37.5000   6.0000     1     31.8000  2.6000
  1     37.5000   6.0000     2     39.5000  3.8000
  1     37.5000   6.0000     8     37.5000  4.5000
  2     41.6000   8.4000     8     37.5000  4.5000
  5      2.5980    .0560     5      2.6710   .0830
  6      1.1230    .0560    10      1.1630   .0280
  7      9.7700    .5700     7      9.3800   .1200
  8     34.2000   1.7000     8     37.5000  4.5000
  9      2.6190    .0630     5      2.6710   .0830
  9      2.6190    .0630     9      2.7460   .0620
 10      1.2080    .2800     6      1.1490   .0210
           TOTAL NUMBER OF TESTS IS    64
           TOTAL SCORING IS  53.0
           PERCENTAGE IS  82.81


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  1     37.5000   6.0000     2     39.5000  3.8000
  1     37.5000   6.0000     8     37.5000  4.5000
  2     41.6000   8.4000     1     31.8000  2.6000
  2     41.6000   8.4000     8     37.5000  4.5000
  6      1.1230    .0560    10      1.1630   .0280
  8     34.2000   1.7000     1     31.8000  2.6000
  8     34.2000   1.7000     2     39.5000  3.8000
  9      2.6190    .0630     5      2.6710   .0830
  9      2.6190    .0630     9      2.7460   .0620
 10      1.2080    .2800     6      1.1490   .0210
```

```
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO     WEATHERED RATIO
  1      37.5000   6.0000     2      39.5000   3.8000
  1      37.5000   6.0000     8      37.5000   4.5000
  2      41.6000   8.4000     1      31.8000   2.6000
  2      41.6000   8.4000     8      37.5000   4.5000
  5       2.5980    .0560     9       2.7460    .0620
  6       1.1230    .0560    10       1.1630    .0280
  8      34.2000   1.7000     1      31.8000   2.6000
  8      34.2000   1.7000     2      39.5000   3.8000
  9       2.6190    .0630     5       2.6710    .0830
 10       1.2080    .2800     6       1.1490    .0210
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO     WEATHERED RATIO
  1      37.5000   6.0000     2      39.5000   3.8000
  1      37.5000   6.0000     8      37.5000   4.5000
  2      41.6000   8.4000     1      31.8000   2.6000
  2      41.6000   8.4000     8      37.5000   4.5000
  5       2.5980    .0560     9       2.7460    .0620
  6       1.1230    .0560    10       1.1630    .0280
  8      34.2000   1.7000     1      31.8000   2.6000
  8      34.2000   1.7000     2      39.5000   3.8000
  9       2.6190    .0630     5       2.6710    .0830
 10       1.2080    .2800     6       1.1490    .0210
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO     WEATHERED RATIO
  1      37.5000   6.0000     2      39.5000   3.8000
  1      37.5000   6.0000     8      37.5000   4.5000
  2      41.6000   8.4000     1      31.8000   2.6000
  2      41.6000   8.4000     8      37.5000   4.5000
  5       2.5980    .0560     9       2.7460    .0620
  6       1.1230    .0560    10       1.1630    .0280
  8      34.2000   1.7000     1      31.8000   2.6000
  8      34.2000   1.7000     2      39.5000   3.8000
  9       2.6190    .0630     5       2.6710    .0830
 10       1.2080    .2800     6       1.1490    .0210
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38
```

```
  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1    37.5000  6.0000      2     39.5000  3.8000
  1    37.5000  6.0000      8     37.5000  4.5000
  2    41.6000  8.4000      1     31.8000  2.6000
  2    41.6000  8.4000      8     37.5000  4.5000
  5     2.5980   .0560      9      2.7460   .0620
  6     1.1230   .0560     10      1.1630   .0280
  8    34.2000  1.7000      1     31.8000  2.6000
  8    34.2000  1.7000      2     39.5000  3.8000
  9     2.6190   .0630      5      2.6710   .0830
 10     1.2080   .2800      6      1.1490   .0210
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.795 UNTS.

RUN COMPLETE.
```

```
TEST N *DEL*

TEST FOR NI/MN *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 5

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO   WEATHERED RATIO
? 5         0.230  0.025     0.214  0.023
? 6         0.113  0.015     0.102  0.014
? 7         1.02   0.14      1.06   0.12
? 9         0.234  0.013     0.219  0.020
? 10        0.117  0.012     0.1207 0.0052



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  5       .2300   .0250      9       .2190   .0200
  6       .1130   .0150     10       .1207   .0052
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  23.0
          PERCENTAGE IS  92.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  5       .2300   .0250      9       .2190   .0200
  6       .1130   .0150     10       .1207   .0052
  9       .2340   .0130      5       .2140   .0230
 10       .1170   .0120      6       .1020   .0140
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  21.0
          PERCENTAGE IS  84.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  5       .2300   .0250      9       .2190   .0200
  6       .1130   .0150     10       .1207   .0052
  9       .2340   .0130      5       .2140   .0230
 10       .1170   .0120      6       .1020   .0140
```

```
                TOTAL NUMBER OF TESTS IS   25
                TOTAL SCORING IS  21.0
                PERCENTAGE IS  84.00


      ENTER THE ORDER OF MPE FOR THE TEST
    ? 2.0
      RATIO PAIRS WHICH FAIL TO SCORE
     NO    ORIGINAL RATIO       NO   WEATHERED RATIO
      5       .2300   .0250      9       .2190   .0200
      6       .1130   .0150     10       .1207   .0052
      9       .2340   .0130      5       .2140   .0230
     10       .1170   .0120      6       .1020   .0140
                TOTAL NUMBER OF TESTS IS   25
                TOTAL SCORING IS  21.0
                PERCENTAGE IS  84.00


      ENTER THE ORDER OF MPE FOR THE TEST
    ? 2.5
      RATIO PAIRS WHICH FAIL TO SCORE
     NO    ORIGINAL RATIO       NO   WEATHERED RATIO
      5       .2300   .0250      9       .2190   .0200
      6       .1130   .0150     10       .1207   .0052
      9       .2340   .0130      5       .2140   .0230
     10       .1170   .0120      6       .1020   .0140
                TOTAL NUMBER OF TESTS IS   25
                TOTAL SCORING IS  21.0
                PERCENTAGE IS  84.00


      ENTER THE ORDER OF MPE FOR THE TEST
    ? 3.0
      RATIO PAIRS WHICH FAIL TO SCORE
     NO    ORIGINAL RATIO       NO   WEATHERED RATIO
      5       .2300   .0250      9       .2190   .0200
      6       .1130   .0150      5       .2140   .0230
      6       .1130   .0150     10       .1207   .0052
      9       .2340   .0130      5       .2140   .0230
     10       .1170   .0120      5       .2140   .0230
     10       .1170   .0120      6       .1020   .0140
                TOTAL NUMBER OF TESTS IS   25
                TOTAL SCORING IS  19.0
                PERCENTAGE IS  76.00


      ENTER THE ORDER OF MPE FOR THE TEST
    ? 0.0

    SRU       0.616 UNTS.

    RUN COMPLETE.
```

```
TEST FOR CR/CO *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 9

  ENTER THE RATIO VALUES AND THE MPES.
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 1         0.560  0.059      0.690  0.083
? 2         0.321  0.067      0.384  0.034
? 4         3.20   0.25       3.40   0.16
? 5         2.23   0.19       2.54   0.38
? 6         6.88   0.39       5.46   0.41
? 7         0.524  0.019      0.752  0.099
? 8         1.34   0.20       1.60   0.11
? 9         3.62   0.11       4.04   0.54
? 10        5.43   0.27       5.20   0.28




  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  1        .5600    .0590    1       .6900    .0830
  2        .3210    .0670    2       .3840    .0340
  5       2.2300    .1900    5      2.5400    .3800
  6       6.8600    .3900    6      5.4600    .4100
  7        .5240    .0190    7       .7520    .0990
  8       1.3400    .2000    8      1.6000    .1100
  9       3.6200    .1100    9      4.0400    .5400
 10       5.4300    .2700    6      5.4600    .4100
            TOTAL NUMBER OF TESTS IS    81
            TOTAL SCORING IS  73.0
            PERCENTAGE IS  90.12


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO   WEATHERED RATIO
  6       6.8600    .3900    6      5.4600    .4100
  7        .5240    .0190    7       .7520    .0990
  9       3.6200    .1100    4      3.4000    .1600
 10       5.4300    .2700    6      5.4600    .4100
            TOTAL NUMBER OF TESTS IS    81
            TOTAL SCORING IS  77.0
            PERCENTAGE IS  95.06
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```
 ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1        .5600    .0590     7        .7520   .0990
 4       3.2000    .2500     5       2.5400   .3800
 4       3.2000    .2500     9       4.0400   .5400
 6       6.8600    .3900     6       5.4600   .4100
 7        .5240    .0190     7        .7520   .0990
 9       3.6200    .1100     4       3.4000   .1600
10       5.4300    .2700     6       5.4600   .4100
              TOTAL NUMBER OF TESTS IS   81
              TOTAL SCORING IS  74.0
              PERCENTAGE IS  91.36
```

```
 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1        .5600    .0590     2        .3840   .0340
 1        .5600    .0590     7        .7520   .0990
 4       3.2000    .2500     5       2.5400   .3800
 4       3.2000    .2500     9       4.0400   .5400
 7        .5240    .0190     1        .6900   .0830
 8       1.3400    .2000     7        .7520   .0990
 9       3.6200    .1100     4       3.4000   .1600
10       5.4300    .2700     6       5.4600   .4100
10       5.4300    .2700     9       4.0400   .5400
              TOTAL NUMBER OF TESTS IS   81
              TOTAL SCORING IS  72.0
              PERCENTAGE IS  88.89
```

```
 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1        .5600    .0590     2        .3840   .0340
 1        .5600    .0590     7        .7520   .0990
 2        .3210    .0670     1        .6900   .0830
 4       3.2000    .2500     5       2.5400   .3800
 4       3.2000    .2500     9       4.0400   .5400
 5       2.2300    .1900     8       1.6000   .1100
 5       2.2300    .1900     9       4.0400   .5400
 6       6.8600    .3900    10       5.2000   .2800
 7        .5240    .0190     1        .6900   .0830
 8       1.3400    .2000     1        .6900   .0830
 8       1.3400    .2000     5       2.5400   .3800
 8       1.3400    .2000     7        .7520   .0990
 9       3.6200    .1100     4       3.4000   .1600
 9       3.6200    .1100     5       2.5400   .3800
10       5.4300    .2700     6       5.4600   .4100
10       5.4300    .2700     9       4.0400   .5400
              TOTAL NUMBER OF TESTS IS   81
              TOTAL SCORING IS  65.0
              PERCENTAGE IS  80.25
```

```
  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  1       .5600    .0590     2        .3840   .0340
  1       .5600    .0590     7        .7520   .0990
  2       .3210    .0670     1        .6900   .0830
  2       .3210    .0670     7        .7520   .0990
  4      3.2000    .2500     5       2.5400   .3800
  4      3.2000    .2500     9       4.0400   .5400
  5      2.2300    .1900     8       1.6000   .1100
  5      2.2300    .1900     9       4.0400   .5400
  6      6.8600    .3900    10       5.2000   .2800
  7       .5240    .0190     1        .6900   .0830
  7       .5240    .0190     2        .3840   .0340
  8      1.3400    .2000     1        .6900   .0830
  8      1.3400    .2000     5       2.5400   .3800
  8      1.3400    .2000     7        .7520   .0990
  9      3.6200    .1100     4       3.4000   .1600
  9      3.6200    .1100     5       2.5400   .3800
 10      5.4300    .2700     6       5.4600   .4100
 10      5.4300    .2700     9       4.0400   .5400
           TOTAL NUMBER OF TESTS IS   81
           TOTAL SCORING IS  63.0
           PERCENTAGE IS  77.78


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.799 UNTS.

RUN COMPLETE.
```

```
TEST FOR CR/FE *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 8

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 1         74     14         72.9  6.4
? 2         70     20         76.1  8.5
? 5         33.3   1.4        34.7  4.6
? 6         41.0   1.2        38.7  1.5
? 7         26.8   1.8        27.3  3.2
? 8         195    21         191   22
? 9         64.1   2.4        77.5  5.0
? 10        44.8   2.1        36.9  1.0



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1    74.0000 14.0000      2     76.1000  8.5000
  1    74.0000 14.0000      9     77.5000  5.0000
  2    70.0000 20.0000      1     72.9000  6.4000
  2    70.0000 20.0000      9     77.5000  5.0000
  6    41.0000  1.2000      6     38.7000  1.5000
  9    64.1000  2.4000      9     77.5000  5.0000
 10    44.8000  2.1000     10     36.9000  1.0000
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  57.0
          PERCENTAGE IS  89.06



  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1    74.0000 14.0000      2     76.1000  8.5000
  1    74.0000 14.0000      9     77.5000  5.0000
  2    70.0000 20.0000      1     72.9000  6.4000
  2    70.0000 20.0000      9     77.5000  5.0000
  9    64.1000  2.4000      9     77.5000  5.0000
 10    44.8000  2.1000     10     36.9000  1.0000
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  58.0
          PERCENTAGE IS  90.63



  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
```

```
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1    74.0000 14.0000       2    76.1000  8.5000
 1    74.0000 14.0000       9    77.5000  5.0000
 2    70.0000 20.0000       1    72.9000  6.4000
 2    70.0000 20.0000       5    34.7000  4.6000
 2    70.0000 20.0000       6    38.7000  1.5000
 2    70.0000 20.0000       9    77.5000  5.0000
 5    33.3000  1.4000       7    27.3000  3.2000
 6    41.0000  1.2000       5    34.7000  4.6000
 7    26.8000  1.8000       5    34.7000  4.6000
 9    64.1000  2.4000       1    72.9000  6.4000
 9    64.1000  2.4000       2    76.1000  8.5000
 9    64.1000  2.4000       9    77.5000  5.0000
10    44.8000  2.1000      10    36.9000  1.0000
              TOTAL NUMBER OF TESTS IS    64
              TOTAL SCORING IS  51.0
              PERCENTAGE IS  79.69


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1    74.0000 14.0000       2    76.1000  8.5000
 1    74.0000 14.0000       9    77.5000  5.0000
 2    70.0000 20.0000       1    72.9000  6.4000
 2    70.0000 20.0000       5    34.7000  4.6000
 2    70.0000 20.0000       6    38.7000  1.5000
 2    70.0000 20.0000       7    27.3000  3.2000
 2    70.0000 20.0000       9    77.5000  5.0000
 2    70.0000 20.0000      10    36.9000  1.0000
 5    33.3000  1.4000       6    38.7000  1.5000
 5    33.3000  1.4000       7    27.3000  3.2000
 5    33.3000  1.4000      10    36.9000  1.0000
 6    41.0000  1.2000       5    34.7000  4.6000
 6    41.0000  1.2000      10    36.9000  1.0000
 7    26.8000  1.8000       5    34.7000  4.6000
 9    64.1000  2.4000       1    72.9000  6.4000
 9    64.1000  2.4000       2    76.1000  8.5000
10    44.8000  2.1000       5    34.7000  4.6000
10    44.8000  2.1000       6    38.7000  1.5000
10    44.8000  2.1000      10    36.9000  1.0000
              TOTAL NUMBER OF TESTS IS    64
              TOTAL SCORING IS  45.0
              PERCENTAGE IS  70.31


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 1    74.0000 14.0000       2    76.1000  8.5000
 1    74.0000 14.0000       5    34.7000  4.6000
 1    74.0000 14.0000       6    38.7000  1.5000
 1    74.0000 14.0000       9    77.5000  5.0000
 1    74.0000 14.0000      10    36.9000  1.0000
 2    70.0000 20.0000       1    72.9000  6.4000
 2    70.0000 20.0000       5    34.7000  4.6000
 2    70.0000 20.0000       6    38.7000  1.5000
 2    70.0000 20.0000       7    27.3000  3.2000
 2    70.0000 20.0000       9    77.5000  5.0000
```

```
  2    70.0000 20.0000     10    36.9000  1.0000
  5    33.3000  1.4000      6    38.7000  1.5000
  5    33.3000  1.4000      7    27.3000  3.2000
  5    33.3000  1.4000     10    36.9000  1.0000
  6    41.0000  1.2000      5    34.7000  4.6000
  6    41.0000  1.2000     10    36.9000  1.0000
  7    26.8000  1.8000      5    34.7000  4.6000
  9    64.1000  2.4000      1    72.9000  6.4000
  9    64.1000  2.4000      2    76.1000  8.5000
 10    44.8000  2.1000      5    34.7000  4.6000
 10    44.8000  2.1000      6    38.7000  1.5000
 10    44.8000  2.1000     10    36.9000  1.0000
           TOTAL NUMBER OF TESTS IS    64
           TOTAL SCORING IS  42.0
           PERCENTAGE IS  65.63


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO         NO   WEATHERED RATIO
  1    74.0000 14.0000      2    76.1000  8.5000
  1    74.0000 14.0000      5    34.7000  4.6000
  1    74.0000 14.0000      6    38.7000  1.5000
  1    74.0000 14.0000      7    27.3000  3.2000
  1    74.0000 14.0000      9    77.5000  5.0000
  1    74.0000 14.0000     10    36.9000  1.0000
  2    70.0000 20.0000      1    72.9000  6.4000
  2    70.0000 20.0000      5    34.7000  4.6000
  2    70.0000 20.0000      6    38.7000  1.5000
  2    70.0000 20.0000      7    27.3000  3.2000
  2    70.0000 20.0000      8   191.0000 22.0000
  2    70.0000 20.0000      9    77.5000  5.0000
  2    70.0000 20.0000     10    36.9000  1.0000
  5    33.3000  1.4000      6    38.7000  1.5000
  5    33.3000  1.4000      7    27.3000  3.2000
  5    33.3000  1.4000     10    36.9000  1.0000
  6    41.0000  1.2000      5    34.7000  4.6000
  6    41.0000  1.2000     10    36.9000  1.0000
  7    26.8000  1.8000      5    34.7000  4.6000
  9    64.1000  2.4000      1    72.9000  6.4000
  9    64.1000  2.4000      2    76.1000  8.5000
 10    44.8000  2.1000      2    76.1000  8.5000
 10    44.8000  2.1000      5    34.7000  4.6000
 10    44.8000  2.1000      6    38.7000  1.5000
           TOTAL NUMBER OF TESTS IS    64
           TOTAL SCORING IS  40.0
           PERCENTAGE IS  62.50


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU      0.888 UNTS.

RUN COMPLETE.
```

```
TESTF *DEL*
  *DEL*


TEST FOR CR/MN *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 5

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO   ORIGINAL RATIO    WEATHERED RATIO
? 5          2.95    0.34      2.78    0.46
? 6          4.12    0.24      3.45    0.48
? 7          2.81    0.38      3.07    0.50
? 9          5.74    0.36      6.17    0.67
? 10         4.34    0.47      3.83    0.17


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  5     2.9500    .3400      7     3.0700    .5000
  6     4.1200    .2400      6     3.4500    .4800
  7     2.8100    .3800      5     2.7800    .4600
 10     4.3400    .4700     10     3.8300    .1700
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  21.0
          PERCENTAGE IS  84.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO        NO    WEATHERED RATIO
  5     2.9500    .3400      6     3.4500    .4800
  5     2.9500    .3400      7     3.0700    .5000
  6     4.1200    .2400     10     3.8300    .1700
  7     2.8100    .3800      5     2.7800    .4600
  7     2.8100    .3800      6     3.4500    .4800
 10     4.3400    .4700      6     3.4500    .4800
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  19.0
          PERCENTAGE IS  76.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
```

```
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 5      2.9500   .3400      6      3.4500   .4800
 5      2.9500   .3400      7      3.0700   .5000
 6      4.1200   .2400      7      3.0700   .5000
 6      4.1200   .2400     10      3.8300   .1700
 7      2.8100   .3800      5      2.7800   .4600
 7      2.8100   .3800      6      3.4500   .4800
10      4.3400   .4700      6      3.4500   .4800
10      4.3400   .4700      7      3.0700   .5000
         TOTAL NUMBER OF TESTS IS   25
         TOTAL SCORING IS  17.0
         PERCENTAGE IS  68.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 5      2.9500   .3400      6      3.4500   .4800
 5      2.9500   .3400      7      3.0700   .5000
 5      2.9500   .3400     10      3.8300   .1700
 6      4.1200   .2400      5      2.7800   .4600
 6      4.1200   .2400      7      3.0700   .5000
 6      4.1200   .2400     10      3.8300   .1700
 7      2.8100   .3800      5      2.7800   .4600
 7      2.8100   .3800      6      3.4500   .4800
 7      2.8100   .3800     10      3.8300   .1700
10      4.3400   .4700      5      2.7800   .4600
10      4.3400   .4700      6      3.4500   .4800
10      4.3400   .4700      7      3.0700   .5000
10      4.3400   .4700      9      6.1700   .6700
         TOTAL NUMBER OF TESTS IS   25
         TOTAL SCORING IS  12.0
         PERCENTAGE IS  48.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL RATIO        NO   WEATHERED RATIO
 5      2.9500   .3400      6      3.4500   .4800
 5      2.9500   .3400      7      3.0700   .5000
 5      2.9500   .3400     10      3.8300   .1700
 6      4.1200   .2400      5      2.7800   .4600
 6      4.1200   .2400      7      3.0700   .5000
 6      4.1200   .2400      9      6.1700   .6700
 6      4.1200   .2400     10      3.8300   .1700
 7      2.8100   .3800      5      2.7800   .4600
 7      2.8100   .3800      6      3.4500   .4800
 7      2.8100   .3800     10      3.8300   .1700
10      4.3400   .4700      5      2.7800   .4600
10      4.3400   .4700      6      3.4500   .4800
10      4.3400   .4700      7      3.0700   .5000
10      4.3400   .4700      9      6.1700   .6700
         TOTAL NUMBER OF TESTS IS   25
         TOTAL SCORING IS  11.0
         PERCENTAGE IS  44.00



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```
 ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
 RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO         NO    WEATHERED RATIO
  5      2.9500    .3400        6     3.4500    .4800
  5      2.9500    .3400        7     3.0700    .5000
  5      2.9500    .3400       10     3.8300    .1700
  6      4.1200    .2400        5     2.7800    .4600
  6      4.1200    .2400        7     3.0700    .5000
  6      4.1200    .2400        9     6.1700    .6700
  6      4.1200    .2400       10     3.8300    .1700
  7      2.8100    .3800        5     2.7800    .4600
  7      2.8100    .3800        6     3.4500    .4800
  7      2.8100    .3800       10     3.8300    .1700
  9      5.7400    .3600        6     3.4500    .4800
 10      4.3400    .4700        5     2.7800    .4600
 10      4.3400    .4700        6     3.4500    .4800
 10      4.3400    .4700        7     3.0700    .5000
 10      4.3400    .4700        9     6.1700    .6700
          TOTAL NUMBER OF TESTS IS    25
          TOTAL SCORING IS  10.0
          PERCENTAGE IS  40.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.718 UNTS.

RUN COMPLETE.
```

```
TEST FOR CO/FE *DEL* .


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 8

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 1          132 2 22          106    15
? 2          218   45          198    20
? 5          14.9  1.1         13.6   1.1
? 6          5.98  0.30        7.09   0.46
? 7          51.1  3.0         36.2   2.1
? 8          145   18          119    16
? 9          17.74 0.41        19.2   2.3
? 10         8.25  0.27        7.09   0.38



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1   132.0000 22.0000      1   106.0000 15.0000
  1   132.0000 22.0000      8   119.0000 16.0000
  5    14.9000  1.1000      5    13.6000  1.1000
  6     5.9800   .3000      6     7.0900   .4600
  7    51.1000  3.0000      7    36.2000  2.1000
  8   145.0000 18.0000      8   119.0000 16.0000
  9    17.7400   .4100      9    19.2000  2.3000
 10     8.2500   .2700     10     7.0900   .3800
        TOTAL NUMBER OF TESTS IS    64
        TOTAL SCORING IS  56.0
        PERCENTAGE IS  87.50


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO   ORIGINAL RATIO       NO   WEATHERED RATIO
  1   132.0000 22.0000      8   119.0000 16.0000
  6     5.9800   .3000      6     7.0900   .4600
  7    51.1000  3.0000      7    36.2000  2.1000
 10     8.2500   .2700     10     7.0900   .3800
        TOTAL NUMBER OF TESTS IS    64
        TOTAL SCORING IS  60.0
        PERCENTAGE IS  93.75


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
```

```
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  1    132.0000 22.0000       8    119.0000 16.0000
  5     14.9000  1.1000       9     19.2000  2.3000
  7     51.1000  3.0000       7     36.2000  2.1000
  8    145.0000 18.0000       1    106.0000 15.0000
  8    145.0000 18.0000       2    198.0000 20.0000
 10      8.2500   .2700      10      7.0900   .3800
          TOTAL NUMBER OF TESTS IS    64
          TOTAL SCORING IS  58.0
          PERCENTAGE IS  90.63


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  1    132.0000 22.0000       2    198.0000 20.0000
  1    132.0000 22.0000       8    119.0000 16.0000
  2    218.0000 45.0000       1    106.0000 15.0000
  2    218.0000 45.0000       8    119.0000 16.0000
  5     14.9000  1.1000       9     19.2000  2.3000
  6      5.9800   .3000      10      7.0900   .3800
  7     51.1000  3.0000       7     36.2000  2.1000
  8    145.0000 18.0000       1    106.0000 15.0000
  8    145.0000 18.0000       2    198.0000 20.0000
 10      8.2500   .2700       6      7.0900   .4600
          TOTAL NUMBER OF TESTS IS    64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  1    132.0000 22.0000       2    198.0000 20.0000
  1    132.0000 22.0000       8    119.0000 16.0000
  2    218.0000 45.0000       1    106.0000 15.0000
  2    218.0000 45.0000       8    119.0000 16.0000
  5     14.9000  1.1000       9     19.2000  2.3000
  6      5.9800   .3000      10      7.0900   .3800
  7     51.1000  3.0000       7     36.2000  2.1000
  8    145.0000 18.0000       1    106.0000 15.0000
  8    145.0000 18.0000       2    198.0000 20.0000
 10      8.2500   .2700       6      7.0900   .4600
          TOTAL NUMBER OF TESTS IS    64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  1    132.0000 22.0000       2    198.0000 20.0000
  1    132.0000 22.0000       8    119.0000 16.0000
  2    218.0000 45.0000       1    106.0000 15.0000
  2    218.0000 45.0000       8    119.0000 16.0000
  5     14.9000  1.1000       9     19.2000  2.3000
```

```
 6     5.9800   .3000       10     7.0900   .3800
 8   145.0000 18.0000        1   106.0000 15.0000
 9   145.0000 18.0000        2   198.0000 20.0000
 9    17.7400   .4100        5    13.6000  1.1000
10     8.2500   .2700        6     7.0900   .4600
          TOTAL NUMBER OF TESTS IS   64
          TOTAL SCORING IS  54.0
          PERCENTAGE IS  84.38


 ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU        0.736 UNTS.

RUN COMPLETE.
```

```
TEST FOR CO/MN *DEL*


RNH_

  ENTER THE NUMBER OF RATIO PAIRS.
? 5

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 5         1.32   0.17       1.09   0.14
? 6         0.601  0.082      0.631  0.093
? 7         5.35   0.71       4.08   0.52
? 9         1.587  0.088      1.53   0.22
? 10        0.798  0.083      0.736  0.048



  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  5      1.3200    .1700      5      1.0900    .1400
  7      5.3500    .7100      7      4.0800    .5200
           TOTAL NUMBER OF TESTS IS    25
           TOTAL SCORING IS  23.0
           PERCENTAGE IS  92.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  5      1.3200    .1700      9      1.5300    .2200
  7      5.3500    .7100      7      4.0800    .5200
 10       .7980    .0830      6       .6310    .0930
           TOTAL NUMBER OF TESTS IS    25
           TOTAL SCORING IS  22.0
           PERCENTAGE IS  88.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  5      1.3200    .1700      9      1.5300    .2200
  6       .6010    .0820     10       .7360    .0480
 10       .7980    .0830      5      1.0900    .1400
 10       .7980    .0830      6       .6310    .0930
           TOTAL NUMBER OF TESTS IS    25
           TOTAL SCORING IS  21.0
           PERCENTAGE IS  84.00
```

```
 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL  RATIO        NO   WEATHERED RATIO
 5    1.3200    .1700        9    1.5300   .2200
 6     .6010    .0820       10     .7360   .0480
10     .7980    .0830        5    1.0900   .1400
10     .7980    .0830        6     .6310   .0930
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  21.0
          PERCENTAGE IS  84.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL  RATIO        NO   WEATHERED RATIO
 5    1.3200    .1700        9    1.5300   .2200
 6     .6010    .0820        5    1.0900   .1400
 6     .6010    .0820       10     .7360   .0480
 9    1.5870    .0880        5    1.0900   .1400
10     .7980    .0830        5    1.0900   .1400
10     .7980    .0830        6     .6310   .0930
10     .7980    .0830        9    1.5300   .2200
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  18.0
          PERCENTAGE IS  72.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO   ORIGINAL  RATIO        NO   WEATHERED RATIO
 5    1.3200    .1700        6     .6310   .0930
 5    1.3200    .1700        9    1.5300   .2200
 5    1.3200    .1700       10     .7360   .0480
 6     .6010    .0820        5    1.0900   .1400
 6     .6010    .0820       10     .7360   .0480
 9    1.5870    .0880        5    1.0900   .1400
10     .7980    .0830        5    1.0900   .1400
10     .7980    .0830        6     .6310   .0930
10     .7980    .0830        9    1.5300   .2200
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS  16.0
          PERCENTAGE IS  64.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU      0.651 UNTS.

RUN COMPLETE.
```

```
TEST FOR FE/MN *DEL*


RNH

  ENTER THE NUMBER OF RATIO PAIRS
? 5

  ENTER THE RATIO VALUES AND THE MPES
 SAMPLE NO  ORIGINAL RATIO    WEATHERED RATIO
? 5         0.0886 0.0095     0.0801  0.0088
? 6         0.100  0.013      0.089   0.012
? 7         0.105  0.015      0.112   0.013
? 9         0.0895 0.0053     0.0797  0.0071
? 10        0.097  0.010      0.1037  0.0048


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.5
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  5        .0886    .0095       6        .0890    .0120
  6        .1000    .0130       7        .1120    .0130
  6        .1000    .0130      10        .1037    .0048
  7        .1050    .0150      10        .1037    .0048
  9        .0895    .0053       6        .0890    .0120
  9        .0895    .0053       9        .0797    .0071
 10        .0970    .0100       6        .0890    .0120
         TOTAL NUMBER OF TESTS IS    25
         TOTAL SCORING IS  18.0
         PERCENTAGE IS  72.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 1.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO        NO    WEATHERED RATIO
  5        .0886    .0095       6        .0890    .0120
  5        .0886    .0095       9        .0797    .0071
  6        .1000    .0130       5        .0801    .0088
  6        .1000    .0130       7        .1120    .0130
  6        .1000    .0130      10        .1037    .0048
  7        .1050    .0150       6        .0890    .0120
  7        .1050    .0150      10        .1037    .0048
  9        .0895    .0053       5        .0801    .0088
  9        .0895    .0053       6        .0890    .0120
 10        .0970    .0100       5        .0801    .0088
 10        .0970    .0100       6        .0890    .0120
 10        .0970    .0100       7        .1120    .0130
         TOTAL NUMBER OF TESTS IS    25
         TOTAL SCORING IS  13.0
         PERCENTAGE IS  52.00


  ENTER THE ORDER OF MPE FOR THE TEST
```

```
? 1.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO        NO   WEATHERED RATIO
 5        .0886   .0095      6       .0890   .0120
 5        .0886   .0095      7       .1120   .0130
 5        .0886   .0095      9       .0797   .0071
 5        .0886   .0095     10       .1037   .0048
 6        .1000   .0130      5       .0801   .0088
 6        .1000   .0130      7       .1120   .0130
 6        .1000   .0130      9       .0797   .0071
 6        .1000   .0130     10       .1037   .0048
 7        .1050   .0150      5       .0801   .0088
 7        .1050   .0150      6       .0890   .0120
 7        .1050   .0150      9       .0797   .0071
 7        .1050   .0150     10       .1037   .0048
 9        .0895   .0053      5       .0801   .0088
 9        .0895   .0053      6       .0890   .0120
 9        .0895   .0053      7       .1120   .0130
 9        .0895   .0053     10       .1037   .0048
10        .0970   .0100      5       .0801   .0088
10        .0970   .0100      6       .0890   .0120
10        .0970   .0100      7       .1120   .0130
10        .0970   .0100      9       .0797   .0071
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS   5.0
          PERCENTAGE IS  20.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.0
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO        NO   WEATHERED RATIO
 5        .0886   .0095      6       .0890   .0120
 5        .0886   .0095      7       .1120   .0130
 5        .0886   .0095      9       .0797   .0071
 5        .0886   .0095     10       .1037   .0048
 6        .1000   .0130      5       .0801   .0088
 6        .1000   .0130      7       .1120   .0130
 6        .1000   .0130      9       .0797   .0071
 6        .1000   .0130     10       .1037   .0048
 7        .1050   .0150      5       .0801   .0088
 7        .1050   .0150      6       .0890   .0120
 7        .1050   .0150      9       .0797   .0071
 7        .1050   .0150     10       .1037   .0048
 9        .0895   .0053      5       .0801   .0088
 9        .0895   .0053      6       .0890   .0120
 9        .0895   .0053      7       .1120   .0130
 9        .0895   .0053     10       .1037   .0048
10        .0970   .0100      5       .0801   .0088
10        .0970   .0100      6       .0890   .0120
10        .0970   .0100      7       .1120   .0130
10        .0970   .0100      9       .0797   .0071
          TOTAL NUMBER OF TESTS IS   25
          TOTAL SCORING IS   5.0
          PERCENTAGE IS  20.00


 ENTER THE ORDER OF MPE FOR THE TEST
? 2.5
 RATIO PAIRS WHICH FAIL TO SCORE
NO    ORIGINAL RATIO        NO   WEATHERED RATIO
 5        .0886   .0095      6       .0890   .0120
```

```
  5        .0886    .0095       7       .1120    .0130
  5        .0886    .0095       9       .0797    .0071
  5        .0886    .0095      10       .1037    .0048
  6        .1000    .0130       5       .0801    .0088
  6        .1000    .0130       7       .1120    .0130
  6        .1000    .0130       9       .0797    .0071
  6        .1000    .0130      10       .1037    .0048
  7        .1050    .0150       5       .0801    .0088
  7        .1050    .0150       6       .0890    .0120
  7        .1050    .0150       9       .0797    .0071
  7        .1050    .0150      10       .1037    .0048
  9        .0895    .0053       5       .0801    .0088
  9        .0895    .0053       6       .0890    .0120
  9        .0895    .0053       7       .1120    .0130
  9        .0895    .0053      10       .1037    .0048
 10        .0970    .0100       5       .0801    .0088
 10        .0970    .0100       6       .0890    .0120
 10        .0970    .0100       7       .1120    .0130
 10        .0970    .0100       9       .0797    .0071
           TOTAL NUMBER OF TESTS IS    25
           TOTAL SCORING IS   5.0
           PERCENTAGE IS  20.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 3.0
  RATIO PAIRS WHICH FAIL TO SCORE
 NO    ORIGINAL RATIO       NO   WEATHERED RATIO
  5        .0886    .0095       6       .0890    .0120
  5        .0886    .0095       7       .1120    .0130
  5        .0886    .0095       9       .0797    .0071
  5        .0886    .0095      10       .1037    .0048
  6        .1000    .0130       5       .0801    .0088
  6        .1000    .0130       7       .1120    .0130
  6        .1000    .0130       9       .0797    .0071
  6        .1000    .0130      10       .1037    .0048
  7        .1050    .0150       5       .0801    .0088
  7        .1050    .0150       6       .0890    .0120
  7        .1050    .0150       9       .0797    .0071
  7        .1050    .0150      10       .1037    .0048
  9        .0895    .0053       5       .0801    .0088
  9        .0895    .0053       6       .0890    .0120
  9        .0895    .0053       7       .1120    .0130
  9        .0895    .0053      10       .1037    .0048
 10        .0970    .0100       5       .0801    .0088
 10        .0970    .0100       6       .0890    .0120
 10        .0970    .0100       7       .1120    .0130
 10        .0970    .0100       9       .0797    .0071
           TOTAL NUMBER OF TESTS IS    25
           TOTAL SCORING IS   5.0
           PERCENTAGE IS  20.00


  ENTER THE ORDER OF MPE FOR THE TEST
? 0.0

SRU       0.856 UNTS.

RUN COMPLETE.
SAVE

 PETRO1 ALREADY PERMANENT.
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