AD-A149 181 TRACE METALS ANALYSIS OF WASTEWATER BY ATOMIC ABSORPTION SPECTROSCOPY(U) ROCK ISLAND ARSENAL IL ENGINEERING DIRECTORATE T G TOWNS ET AL. AUG 84 1/1

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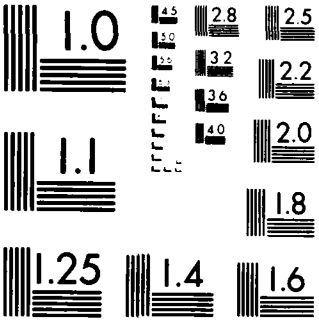

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TRACE METALS ANALYSIS OF WASTEWATER BY ATOMIC ABSORPTION SPECTROSCOPY

BY

THEODORE G. TOWNS, Ph.D.
and
KAREN L. FRANICH

AUGUST 1984

U.S. ARMY
AMCCOM

TECHNICAL REPORT

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

ENGINEERING DIRECTORATE
ROCK ISLAND ARSENAL
ROCK ISLAND, ILLINOIS 61299-5000

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
EN-84-11

2. GOVT ACCESSION NO.
AD-A149 181

3. RECIPIENT'S CATALOG NUMBER

4. TITLE *(and Subtitle)*
TRACE METALS ANALYSIS OF WASTEWATER BY ATOMIC ABSORPTION SPECTROSCOPY

5. TYPE OF REPORT & PERIOD COVERED
Technical Report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Theodore G. Towns, Ph.D. and Karen L. Franich

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Commander, Rock Island Arsenal
ATTN: SMCRI-ENM-E
Rock Island, IL 61299-5000

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Commander, Rock Island Arsenal
ATTN: SMCRI-EN
Rock Island, IL 61299-5000

12. REPORT DATE
August 1984

13. NUMBER OF PAGES
35

14. MONITORING AGENCY NAME & ADDRESS *(If different from Controlling Office)*

15. SECURITY CLASS. *(of this report)*
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*
Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

1. Atomic Absorption Spectroscopy	6. Calibration Curves
2. Effluent Water	7. Linear Regression
3. Wastewater	8. Multianalyte Reference Solutions
4. Trace Metals	9. Spiking of Wastewater
5. Quality Control	10. EPA Quality Control Samples

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The primary project objectives of upgrading effluent trace metals analysis by atomic absorption spectroscopy (AA), providing advanced AA instruction, and modeling a schedule for quality control data in the analyses have been successfully completed. The upgraded and automated system will meet the needs of wastewater analysis in an accurate and efficient manner that yields a high level of confidence.

DD FORM 1 JAN 73 **1473** EDITION OF 1 NOV 65 IS OBSOLETE

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FOREWORD

This report was prepared by Dr. Theodore G. Towns, Howard University, Washington, D.C. and Ms. Karen L. Franich, Rock Island Arsenal, Rock Island, Illinois. The work was accomplished during the Summer of 1983 while Dr. Towns was employed under the Historically Black College Program for professors.

The project was carried out in the Analytical Chemistry Laboratory, Engineering Directorate, Rock Island Arsenal. The authors would like to thank Mr. George Powers for his assistance in the experimentation.

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* Each standards curve has inset the result of linear regression performed on the data; A or M = slope, B = intercept, R = correlation coefficient.

LIST OF TABLES

1.0 INTRODUCTION

1.1 Problem Statement.

Erratic or inconsistent analytical results in atomic absorption (AA) analysis can usually be attributed to the occurrence of one or more of the following:

(a) Poorly prepared reference materials.

(b) Inadequate instrument optimization.

(c) Neglect of routine instrument maintenance.

The scope of work concerns the remediation of these occurrences. Point (a) generally results from either inadequate starting materials or inadequate laboratory technique in the preparation; the focus of this work has been on the laboratory technique. Of points (b) and (c), the latter is perhaps the more serious since it inevitably results in both an elevated minimum detectable limit, i.e., lost sensitivity, and a degradation of analytical accuracy, while the former leads principally to lost sensitivity. Instrument optimization is addressed in the form of a standard operating procedure with notes detailing the interplay and adjustment of the operating parameters of the Varian model AA-775 used at Rock Island Arsenal (RIA).

NOTE

> This operating procedure must in no way be construed to supersede the manufacturer's "Operations Manual." Rather, it represents a synopsis of procedures germane to the routine use of the instrument in the RIA Engineering Directorate and it provides elaboration for points briefly mentioned in the AA manual. [1]

1.2 Objectives.

The objectives of this report are to describe:

(a) The upgrade in capability of the Varian model AA-775 Atomic Absorption Spectrophotometer, with particular regard for the application to routine effluent trace metals analysis.

(b) The provision of advanced instruction on the use of Atomic Absorption Spectroscopy (AAS) in wastewater trace metals analysis.

(c) A model schedule for the accumulation and analysis of quality control data sufficient to meet or exceed extant effluent regulations and US Army Environmental Hygiene Agency (AEHA) Regulation No. 722-1, November, 1982. [2]

(d) The review of laboratory procedures for the purpose of noting those steps where appreciable uncertainties are usually introduced by personnel.

1.2 Miscellaneous.

The advanced instruction on the use of AA analysis constitutes the bulk of section 2.0, Discussion. In section 2.1, EPA Quality Control Samples for Trace Metals, are notes on the Environmental Protection Agency (EPA) quality control samples and their use; notes on laboratory techniques necessary for the routine detection of analytes in the concentration range below one part per million (ppm); notes on preparation of a calibration curve and its use; and notes on the statistical interpretation of the experimental data, choice of appropriate operating parameters, and maintenance. Notes on laboratory procedures are a major topic of sections 2.2 through 2.9.

Significant enhancement in the statistical accuracy and precision of the concentration measurement can be achieved with the attachment of both an autosampling accessory and remote output devices such as a chart recorder and a digital printer. Enhancement in the use of the attendant personnel's time may also accompany this upgrade of the "basic" instrument. Details on the use of selected accessories are found in section 2.6, The Instrument.

The quality control schedule is given and exemplified in section 3.0, Results. The data is taken from the prevailing effluent analysis load during the course of this study.

In addition, the term "absorbance" as used in all of the calibration curves for this report actually refers to the relative absorbance determined from the peak heights on the chart recorder measured in millimeters. The peak heights are directly proportional to the actual absorbance and, therefore, give a valid and useful calibration curve for the determination of sample concentration.

2.0 DISCUSSION

2.1 EPA Quality Control Samples for Trace Metals.

The EPA quality control (EPA QC) samples, available as multianalyte concentrates, are reference solutions which have been prepared and stored under exacting laboratory conditions. The individual analyte concentration is given both in terms of a "true" value defining the number of significant figures associated with its preparation, and in terms of statistical values (mean, $\bar{X}$; and standard deviation, σ) derived from the <u>amount detected</u> by a number of independent analytical laboratories. The quality control program is based on a 95 percent confidence interval, and thus, results for a QC sample are considered acceptable if they fall within $\bar{X} \pm 2\sigma$. The estimate of a QC analyte concentration derived from a working standards curve should be accompanied by its own standard deviation reflecting the variance in its determination. Laboratory procedures must be sufficiently exacting to give a detected analyte concentration, $\bar{X}'$, including its standard deviation, σ', within the QC sample limits. The acceptable range given by EPA takes this into account. The analytical situation is represented in Figure 1. Note that, for simplicity, the figure has been couched in terms of a distribution with $\bar{X} = 0$; other equivalent representations are achieved by shifting the origin along the abscissa by an amount equal to the non-zero mean value with no change in the shapes of or relationship between the two distributions.

EPA QC samples may be put to several uses: a control for the digestion efficiency; a check on the quality of prepared reference solutions; and a guide to sample analysis accuracy. As a check on the reference solutions, the EPA QC samples may be analyzed unadulterated (neat) and this should be done at least as often as "fresh" reference solutions are prepared. As a control on either the digestion or the analysis, the EPA QC sample or one of the prepared reference solutions is introduced as a "spike" in one of the unknown samples, either before or after the digestion process. When the digestion efficiency is not in question, and the chemical interferences in the sample matrix are known to be nominal or absent, the neat EPA QC sample is an adequate control. However, for samples with unknown history or for those with known interferring matrices, the EPA QC sample or one of the prepared reference solutions <u>must</u> be run as a spike. This use of a spike is preferred and recommended ideally in all cases, but it may be deferred as appropriate to the neat EPA QC sample in the interest of time and material savings.

2.2 The Calibration Curve.

If the EPA QC sample is considered the "heart" of a quality control program, the calibration, or standards, curve must be taken as the "mind;" the two must work together to provide the desired quality assurance. The

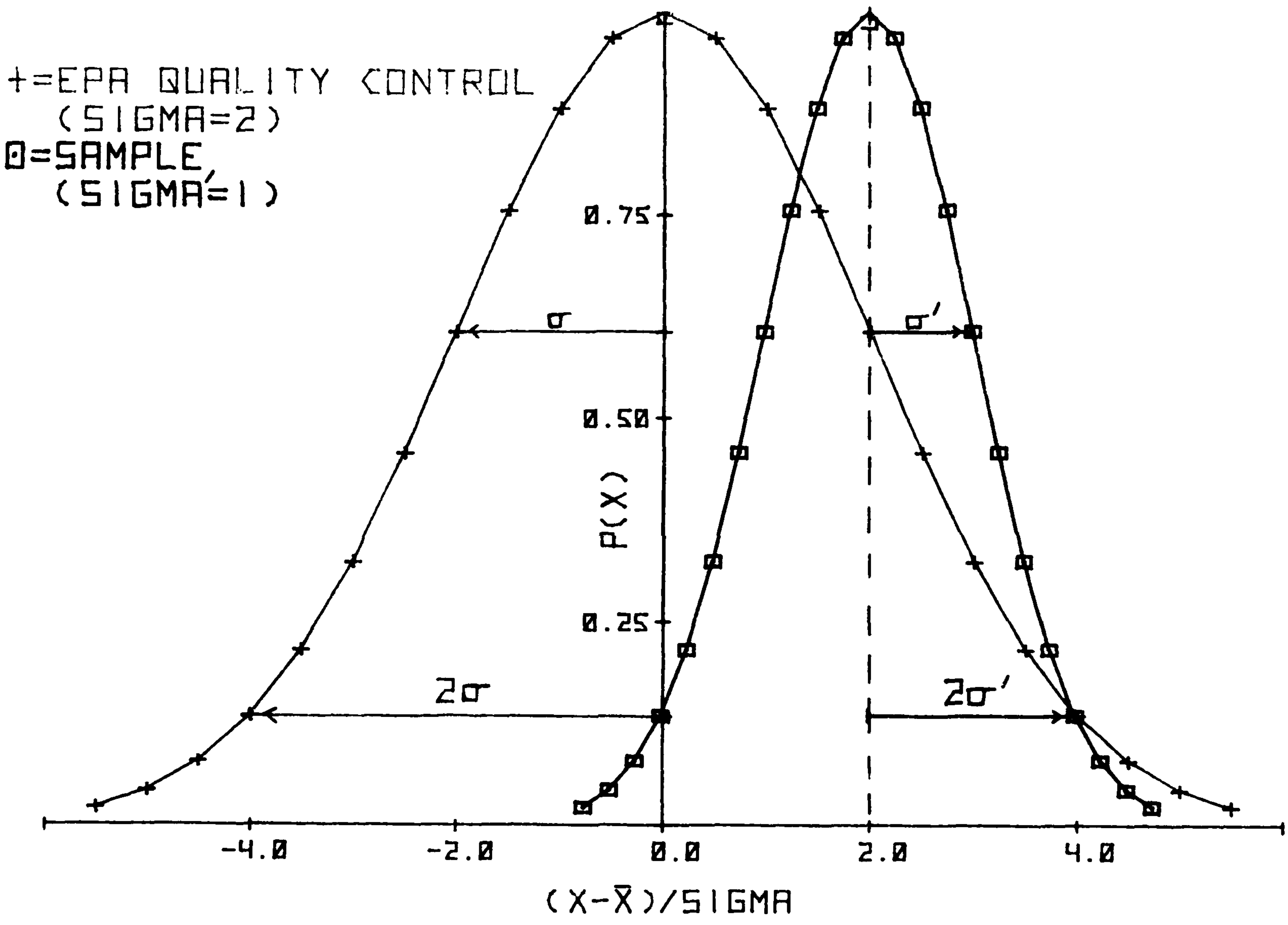


FIGURE 1

Distribution Curves for Quality Assessment.

efficacy of the standards curve will be determined in part by the care taken in its preparation and in part by the thoughtfulness of its use. The EPA QC sample concerns the laboratory technique exercised in the volumetric preparation of solutions, the calibration curve concerns the relationship between absorbance and concentration for a given analyte.

2.3 Preparation of Reference Solutions.

The primary trace metal stock solutions, typically available commercially as 1000 ppm ± 1 percent concentrates, must either be NBS certified standards or be traceable to such standards. The room temperature shelf life of the one pint (500 mL) volumes as supplied is at least one year, and probably longer. Secondary stocks and serial dilutions (hereafter referred to as "working standards") derived from the primary stock will have a considerably reduced shelf life which, however, can be maximized by the procedures given here. Degradation of working standards is generally attributed to two phenomena: thermal instabilities (minimized by refrigerated storage), and surface adsorption (minimized by prior "acid soaking" of the storage containers). The importance of this acid soaking procedure is often overlooked.

Before its use, the volumetric glassware (class A, borosilicate glass) including stoppers and any other containers destined for storage duty, must be soaked in one to one strong acid, <u>viz.,</u> nitric, phosphoric, or perchloric, for at least four hours. After soaking, the one to one acid can be returned to its own container for reuse over a period of approximately six months.

NOTE

> This presumes the glassware has already been scrupulously cleaned with a good quality laboratory detergent, e.g., Alconox, and rinsed with tap and then deionized water. The acid soaking solution must not be used as a cleaning solution for "dirty" glassware.

After emptying the acid solution, the vessels should be rinsed three times with deionized water, the excess shaken out, and dried. Drying may be omitted when the vessels are for immediate use, however, a recommended practice is to then make a final rinse with a small portion of the solvent or matrix used. Drying can be effected in several ways: evaporation at room temperature (air drying), rinsing with reagent grade acetone and shaken dry, or blown dry with a compressed air source; if this latter is used, care should be taken to remove the traces of lubricants which often contaminate air from such sources. When the empty vessels are to be shelved for later use, their openings should be either stoppered, using a short, 1/8 to 1/4 inch wide strip of lens paper between the ground glass surfaces, or covered with an inert material such as "Parafilm". Volumetric flasks thus pretreated can then be used for convenient, reliable preparation and storage of working standards.

Experience has shown that under the procedures given above:

(a) Secondary stocks of the order of 100 ppm are usable for at most six weeks.

(b) Serial dilutions in the range 0.1 to 10 ppm are usable for at most two weeks.

(c) Dilutions to below 0.1 ppm should not be kept for longer than five days.

As mentioned earlier, the working standards should be prepared as one or more serial dilutions of the secondary stock. Serial dilution affords a proven method for minimizing the uncertainties passed through the volumetric work, and provides a tractable design for assessing anomalous occurrences attributable to the standards. By the same token, serial dilution also demands that the same care be given the preparation of each in the series. The quality of the dilution will depend on two critical factors: temperature and the handling of the volumetric ware.

For very precise work, the glassware and reagents must all be at the ambient temperature of the volumetric vessel's calibration, typically specified as 20 deg C on the apparatus label (TD 20 deg C means to deliver at 20 deg C). Since 20 deg C is not always the room temperature of the laboratory, having the reagents and apparatus involved all at the same temperature, which is near that of the calibration, is sufficient. Considering the coefficient of thermal expansion of water in the neighborhood of room temperature (approximately 0.0002/deg C), there is a margin of about 5 deg C over which temperature variation will not introduce significant loss in accuracy or precision; that is, all else being equal, laboratory room temperature of, say, 25 deg C will introduce an error of less than 1 percent when using glassware calibrated at 20 deg C. The effect of temperature on the volumetric ware itself is also a consideration, but for good quality borosilicate glassware the effect of temperature is negligible.

If pipets are not dry before use, always rinse them to a point above the fiducial mark, with the solution to be transferred. A recommended practice is to wash one's hands before beginning the work, and then avoid handling any part of a pipet that will contact the reagents. Pipets should have a clean, dry surface on which to rest when not in hand. The fiducial mark must be at eye level when filling and the miniscus should "sit" on this mark. Volumetric pipets are calibrated either "to contain" (TC) or "to deliver" (TD); the two letter designation may be found on the glassware in the vicinity of its capacity marking. To deliver means that after gravity has withdrawn all but the last drop, the pipet tip is touched to the side of the receiver vessel to remove both the drop and a part of what remains in the tip. There will still be a small amount of liquid remaining inside the pipet tip, it is there by design, leave it. A TD pipet will be labeled as such. A TC pipet may or may not have an imprint; the absence of such a marking near the capacity label can be taken as to contain, which means that the last portion inside the tip should be blown out, after gravity has finished its work.

The amount of analyte transferred for each solution in the series should be as large as practicable; i.e., smaller volumes at high concentration, larger volumes at lower concentrations. After discharging the contents into a volumetric flask, the matrix is added to bring the liquid level to a point below the neck and the vessel is swirled a few times to insure mixing. The volume is then brought to the mark, the last half milliliter, mL, or so introduced dropwise taking care not to run drops down the side of the neck because this can lead to a false reading. After filling, the flask is stoppered and inverted at least twice. The solution is now ready for use.

Since the absorbance versus concentration relation is not often linear over more than an order of magnitude (decade) change in concentration, adequate characterization of the relationship requires at least five concentrations per decade span. For example, to cover the span 0.1 to 1.0 ppm, a representative schedule of standards is (0.1, 0.3, 0.5, 0.8, and 1.0 ppm). Serial dilution implies that each decade of concentration is prepared from the preceding decade. A representative schedule is:

(a) Begin with secondary stock of 100 ppm and pipet 10.0, 8.0, 5.0, and 3.0 mL aliquots per 100 mL to prepare the decade 10.0, 8.0, 5.0, and 3.0 ppm.

(b) Use 10 mL aliquots of each from step (a) per 100 mL to prepare 1.0, 0.8, 0.5, and 0.3 ppm.

(c) And so on until the desired limit is reached.

2.4 Multianalyte Reference Solutions.

This is a practical means of minimizing both the amount of glassware required for routine analysis over a wide concentration range and the amount of time devoted to standards preparation. The foremost concerns here are "chemical interferences" and "chemical (metathesis) reactions." A recommended practice, though not essential, is to compose standards solutions as free as possible from both of these influences. "Chemical interferences" is the phrase used to describe the suppression of an analyte's absorbance caused by the presence of another species in the matrix. For instance, chromium is known to suffer this interference from the presence of cobalt, iron, nickel, and some of the Group II-A elements; lead suffers no cationic interferences but is subject to anionic interference from concentrations of phosphate, carbonate, acetate, fluoride, and iodide in excess of ten times the concentration of lead. Iron on the other hand, while an interference for chromium, is itself typically subject to none. The kinds of "chemical interferences" for most of the common elements analyzed by the atomic absorption are well documented and available. [3-6] "Chemical reactions" are probable when the form in which the components are available as primary stock are unstable when mixed. Caution is in order only when a reaction removes analyte from solution, viz., precipitation. For example, while neither lead nor chromium exhibit any mutual "chemical interference," their form in our primary stock is as the nitrate and dichromate salts, respectively, and their mixture, at the 100 ppm level, leads within seconds to the formation of a flocculent, pale-orange precipitate (a thorough investigation of the nature of this precipitate was not feasible, but by its color and cursory solubility studies one of the lead oxides is a probable candidate; for all of them the solubility product constant is well below 100 ppm.)

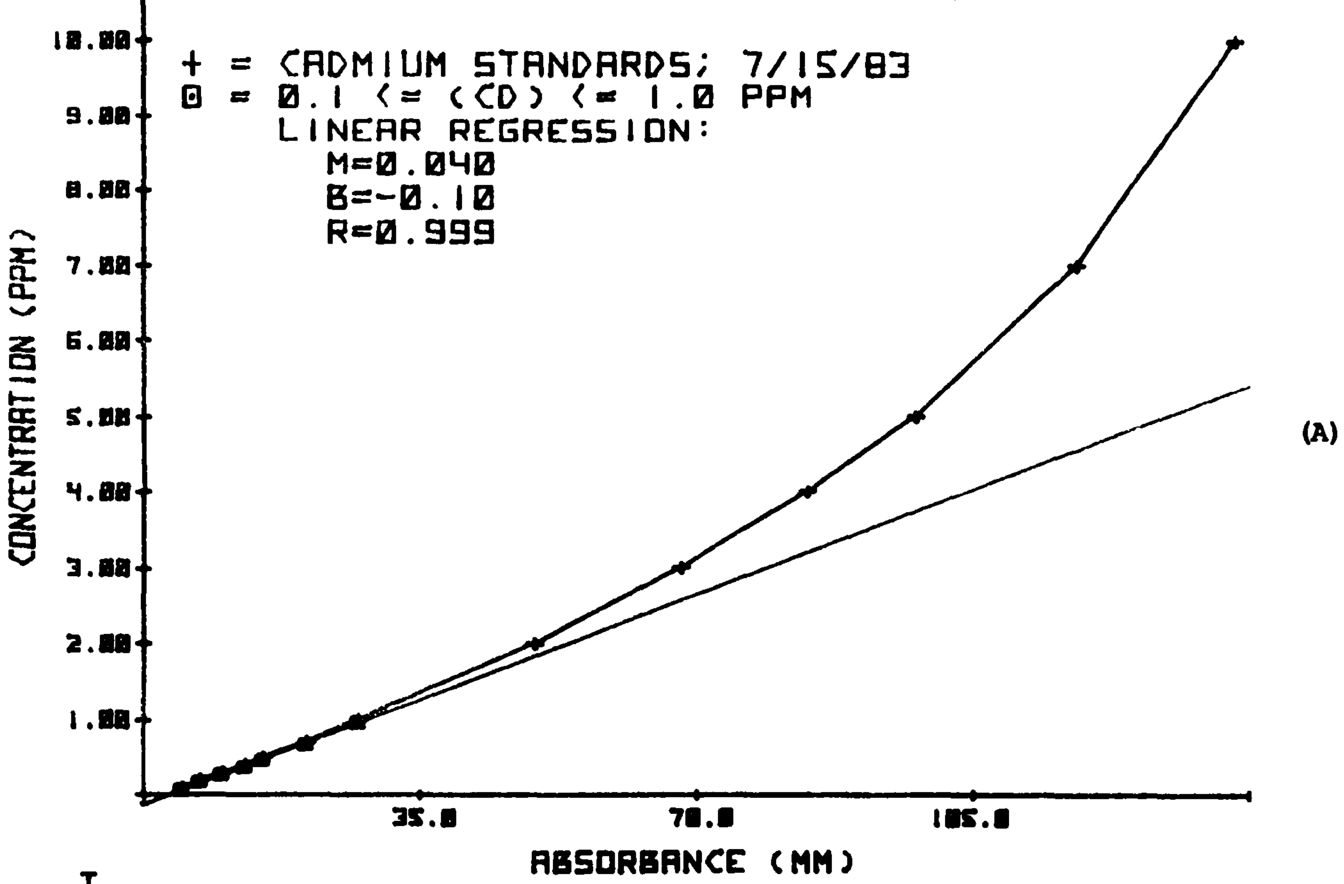
2.5 Absorbance versus Concentration.

The atomic absorption method is essentially a single wavelength ultraviolet or visible (UV/VIS) experiment. The quantitative use is based on the well known Beer-Lambert Law, $A = a \cdot b \cdot c$, where a = absorptivity (an intensive property of the absorber which is wavelength dependent), b = optical path length, and c = concentration. The law defines a linear relationship which passes through the origin between absorbance A (an extensive property) and concentration. However, inherent in the derivation of the law are two principal assumptions, the second of which has significant bearing on the preparation and use of the calibration curve: that the absorptivity at a given wavelength is constant; and that the absorbing species are non-interacting. While the absorptivity is appreciably dependent on the absorber's environment, in the present application (flame photometry) the first assumption is appropriate. The second assumption clearly presents no conflict at very low concentrations (parts per billion (ppb) or smaller). But just as clearly, every element or absorber must exhibit a concentration level at which this assumption becomes entirely untenable. Indeed, positive and negative deviations from the Beer-Lambert Law expectation over a wide concentration range are quite common; the interactions gain sufficient magnitude to significantly affect the "constancy" of the absorptivity. Thus a realistic expectation for the shape of the calibration (or standards) curve is not a straight line from the origin out to the highest concentration of interest, thereby requiring but a few (two or three) reference solutions spanning perhaps three or four orders of magnitude in concentration. Rather, it is a linear portion in the dilute region and a concentration level at which decided curvature sets in, thus requiring groups of several (ideally five) reference solutions where each group spans only one order of magnitude change in concentration. An empirical standards curve for cadmium is representative of the situation and is given in Figure 2(A). The feature of note is that there is a quite good linear correlation up to about one ppm, but thereafter, the relation is indeed a standards "curve."

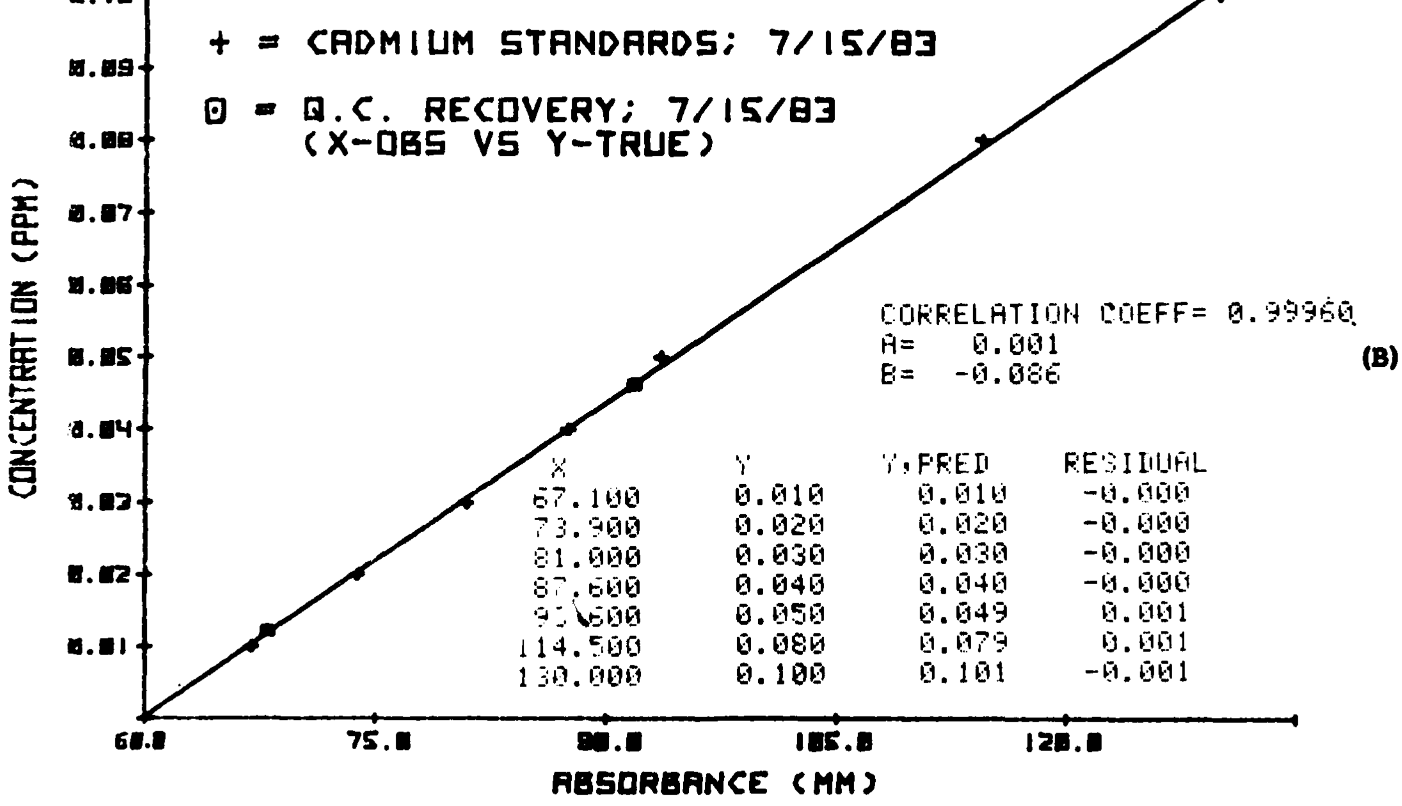
What is essential for the analysis is that the unknown sample concentration be bracketed by reference solutions. The remarks of the preceding paragraph are intended to provide insight into the number and value of reference concentrations needed to achieve an analytically useful

FIGURE 2

Generalized Calibration Curve (data for Cd).



Cadmium Standards (low ppb level)



CORRELATION COEFF= 0.99960
A= 0.001
B= -0.086

X	Y	Y,PRED	RESIDUAL
67.100	0.010	0.010	-0.000
73.900	0.020	0.020	-0.000
81.000	0.030	0.030	-0.000
87.600	0.040	0.040	-0.000
93.600	0.050	0.049	0.001
114.500	0.080	0.079	0.001
130.000	0.100	0.101	-0.001

calibration curve. For example, when one is working in a region of the absorbance function which as been found to be inherently linear, i.e., less than one ppm for the metals of current interest, the number of bracketing standards may be taken as a minimum of three, spanning an approximate order of magnitude change in concentration. When working in a non-linear region, concentration intervals must be made sufficiently small to achieve practical linearity or else a non-linear curve-fit must be used.

2.6 The Instrument.

The Varian model AA-775 is a thoroughly modern atomic absorption spectrometer offering several capabilities that facilitate routine analyses for trace metals. There are input and output ports for simultaneous operation of an autosampler and chart recorder and digital printer. Benefits from these automating accessories accrue both to the precision of the analytical method and to the flexibility of the operator's time. An internal microprocessor provides, among other features, an automatic calibration curve based on up to five reference solutions and subsequent direct output of sample concentration.

The automatic calibration curve can, for highly controlled samples, offer substantial time savings in the conversion of absorbance to concentration. However, its use requires a judicious choice of reference solutions since there is no "automatic" correction for any inherent curvature over the range of standards used. Consequently, its range must be limited and its practical utility as the sole output device for unknowns of highly variable composition is questionable.

The sample introduction process is an important part of the AA analysis and can be conveniently described in terms of a "sampling time," the period over which a sample is aspirated, and a "settling time," the period between successive samplings. Adequate sample time allows: the establishment in the flame of a steady-state condition reflecting the true analyte concentration; and sufficient time for an integrated response to be made by the instrument. Adequate settle time allows: the previous sample to be cleared from the nebulizer capillary; and the instrument response to return to its baseline. Efficient use of time requires minimization of these two parameters; however, they should not be made too short and the same set of values for samples and standards alike is desirable.

The Varian model 51 Autosampler provides a highly reproducible means of regimenting the sample introduction; and the sampling and settling times can be varied to optimize the sensitivity for a given analyte and concentration range. The sample time should be three to four times the integration period and the settle time should be equal to or greater than the sample time. We have found that a sampling time of about eight seconds (with integration periods up to two seconds) provides adequate resolution of concentrations down to about 0.1 ppm for the metals of interest here. At lower concentrations sample times as great as 12 to 14 seconds have been necessary.

The actual time savings that results from the use of an autosampler depends on the number and nature of samples (unknowns, standards, and quality controls) and is difficult to quantify. However, we can be certain that an automatic device will perform the sample introduction more reproducibly and no slower than a person, so that whatever the time required here, it does not involve personnel attendance; that is, personnel may engage in other analytical activity (e.g., standards preparation, paperwork, etc.) while sampling proceeds unattended. The full (50 samples) model 51 carousel may be set up in about 10 to 15 minutes and will cycle in about 14 minutes at a combined sample and settle time of 16 seconds, or in about 24 minutes at a combined sample and settle time of 28 seconds. The individual sample cup volume (six mL) is sufficient for three to five metal analyses, depending on the sample time, so that reduced manual handling of the aspiration tube minimizes the opportunity for sample contamination.

There are several advantages to using a chart recorder as an output device. Principal among them are: such output affords a more accurate estimate of the noise level and hence the true signal strength; any drift or change in the baseline (zero calibration) is more readily evident and accountable; the shape of the absorption peaks provides a useful guide both to the adequacy of the selected operating parameters (specifically, the sample and settle times and the integration time) and to the need for maintenance activity; and, the full scale Recorder Span (mV) and the absorbance assigned to it can be selected to allow collection at one time of a wider range of data than could be effectively used by the autocalibration feature alone.

For highly controlled samples, that is, for unknowns whose concentrations all fall within one linear region of the calibration curve, use of the internal autocalibration feature with a digital printer and chart recorder can realize appreciable timesavings for data processing. For example with cadmium (see Figure 2A), over the range 0.1 to 5.0 ppm the calibration curve is non-linear, but this interval may be divided into two sufficiently linear ranges (0.1 to 1.0 ppm and 1.0 to 5.0 ppm), only one of which at a time could be used for the autocalibration curve outputing to the digital printer. On the other hand, the dynamic range of the chart recorder at REC RANGE = 0.5 A and Recorder Span = 500 mV will allow calibration data to be collected over the whole range (0.1 to 5.0 ppm). The internal calibration curve may be used to process unknowns in, say, the lowest concentration range; the digital printer will then output values for all unknowns in that range directly. The chart output can then be used to 'manually' determine unknowns that fall outside the automatic calibration curve. Obviously, for those cases when all unknowns are within the range selected for the internal processor, there is no 'residual' processing to be done by the operator.

The full scale recorder deflection in absorbance units (REC RANGE), the recorder sensitivity in mV (Recorder Span), the recorder time constant (REC FAST, REC NORM, REC DAMPED), and the integration period (TIME SEC) are all chosen in consort to achieve adequate signal to noise at the desired sensitivity. Signal to noise (S/N) ratios of less than three to four are of marginal quantitative use.

The treatment of the recorder output is straightforward. Baseline and peak height lines should be drawn parallel to the time axis of the chart and should be placed in the "middle" of their respective noise levels, that is, so that equal excursions of magnitude and duration occur both above and below the line. When the baseline is very stable, one line may be drawn from the beginning to the end of the sequence, otherwise it should be drawn between the average noise levels on either side of each peak. When the baseline must be drawn for each peak, it will likely not be parallel to the time axis, and the height must be measured from the midpoint of the peak base width.

The noise level (sensitivity) can be affected by excessive turbulence in the burner compartment. In this connection, the exhaust system draft may be too vigorous. The draft is simply controlled by closing the stack damper in, say, 10 to 15 degree increments until an optimum draft is obtained. This would be a one time adjustment for the current exhaust system configuration.

When one encounters unexpectedly high unknown concentrations which are off-scale at the current recorder setting, one may choose: an alternate, less sensitive analytical wavelength; reduced sensitivity settings (i.e., increase REC RANGE or the Recorder Span); or a rotation of the burner head to yield an absorbence reading of less than 1.0 in the most concentrated sample. In any case the change should be made at the end of the initially programmed sample sequence, and standards must be run until the unknowns are bracketed by at least three references forming a linear segment of the calibration curve.

2.7 Maintenance.

The cleanliness of the burner head and nebulizer assembly has pronounced influence on the noise level and thus the sensitivity. The presence of (carbon) deposits in the burner slot is evident by irregularities in the peak-line of the inner flame profile. Small deposits are easily removed, after turning off the flame, with an unwanted business card or a soft metal (e.g., copper or brass) strip. A good practice at the end of a sample run, before shutting down the instrument, is to aspirate 25 to 50 mL of deionized water as a flush for the nebulizer and spray chamber.

The burner head should be dismantled periodically for a thorough internal scrubbing with soap and water. A plastic domestic dish scrubber or one of the copper mesh (not steel) variety is appropriate for removing encrustation inside the burner. Hard metal implements (e.g. screwdrivers, razor blades, etc.) must not be used for cleaning; also, acids or other harsh chemical cleansers or abrasives should not be used. <u>Take care while cleaning not to immerse the interlock socket.</u> The spray chamber should be removed periodically and cleaned with soap and water. The aspiration capillary hose should be replaced whenever it becomes cloudy or otherwise visibly encrusted on its interior walls. When fitting the fresh tubing one must take care that the (sharp) metal edge of the nebulizer entrance tube does not gouge the wall of the capillary hose and thereby create blockage.

There are only three optical surfaces that require regular inspection, and cleaning as necessary: the hollow cathode lamp window and the entrance and exit windows to the burner compartment. These surfaces must be free of fingerprints and dust or other smudges and debris. They must be cleaned only with quality lense paper and optical grade solvent, e.g., spectrograde ethanol, methanol, or acetone.

Gas supply hoses must be inspected regularly for both physical integrity (major cracking or deterioration) and secure fit. When acetylene supply tank pressure gets below 100 psi, a fresh supply should be fitted. Below this pressure the acetone used as stabilizer in the tank gains sufficient concentration in the gas supply to pose both a serious safety hazard and an increase in flame instability.

The autosampler sample cups must not be allowed to dry out when they contain sample; they should be rinsed several times with deionized water, shaken out and allowed to dry secure from contact with metal containing apparatus and particulate fallout.

Gas supply filters (whether for fuel or oxidant, particularly air) should be changed according to the manufacturer's instructions or when substantial deviations from usual S/N levels are noticed. The replacement date of such filters should be noted for future reference. This presumes that the reduced S/N cannot be traced to some other alignment or matrix problem.

2.8 Instrument Alignment.

Instrument alignment response and analytical performance are as intimately tied to the care in setting up the instrument as they are to the quality of the reference solutions used. Diligence and patience are the keywords here; an instrument may be stable at less than optimum performance. While manufacturers make every effort to make operation as "user friendly" as possible, one must remember that the ultimate friendliness is only achieved through familiarity and practice with the exercise of the key operator qualities. (This is particularly important to the adjustment of the burner position and flame composition.) To set up the instrument, proceed as follows:

(a) Check that gas supplies and lamp current switches are OFF.

(b) Power ON; check that the following conditions have been automatically selected:

ABSorbance operating mode;
INTegrate REPeat readout mode;
Background Correction OFF
RECorder NORMal
RECorder RANGE = 1.0 (absorbance unit)
TIME SEConds = 1.0 (second)

NOTE

CAL ZERO light will be flashing; both display and meter indications are meaningless.

(c) Fit burner; connect interlock; exhaust ON; gas supplies ON.

(d) Fit lamp; adjust current to specification.

NOTE

The current given on the specification card accompanying each lamp is 'recommended' (not absolute); somewhat higher currents may improve the signal to noise ratio and thereby afford greater sensitivity. For example, operation of the iron lamp at 10 mA showed signficant improvement in the signal to noise ratio for the analysis of this element. The current selected must not exceed the maximum specified. Once the desired current is selected, the lamp should be allowed to warm up for a period of 15 to 20 minutes, in the interest of maximum stability and minimum noise at the chosen setting.

(e) Adjust the burner vertical and horizontal positions so that the lamp light spot, intercepted at the midpoint of the burner slot, is approximately two to four mm above the slot and centered. Adjust the angular position so that the light spot is centered when alternately intercepted at the ends of the burner slot. These adjustments can be conveniently made with the use of a business card for example.

(f) Set the monochrometer wavelength and slit at the values recommended for the concentration range of interest; select Single Beam (SB) and adjust the gain so that the meter reading is about half scale. Using the gain adjustment to keep the meter reading on scale, maximize the signal by fine adjustment of a) the wavelength selector, and b) the lamp focus, with the two knurled thumbscrews on the sector base.

(g) Select Double Beam (DB); light the flame.

At this point the coarse alignment of the instrument has been effected; fine tuning is achieved (in DB) as follows:

(a) Aspirate the matrix or analytical blank; select CAL ZERO

(b) Aspirate a solution known to give ABS = 0.4, while adjusting:

(1) Horizontal, vertical, and angular burner position.

(2) Fuel and oxidant flow.

(3) Glass bead position (nebulizer).

(4) Burner vertical position again.

NOTE

Analyte	ppm giving ABS=0.4	ABS (best observed at given ppm)
Cd	2.0	0.518
Cr	10.0	0.504
Fe	7.0	0.489
Pb	10.0	0.400

NOTE

Steps (1),(2), and (3) above, are all crucially interdependent; here, perhaps more than any other step in the procedure, diligence and patience must prevail. The flame configuration, physical position, gas volume ratio, and nebulization rate will "make or break" the AA analysis.

Step (2) represents the optimization of the "flame stoichiometry" or composition, which will be determined by the nature of both the analyte and the matrix. For the digestion process prescribed by the US EPA, i.e., for a given matrix, the identity of the analyte will be the deciding factor. Flame composition for best performance is given for each element as either oxidizing (lean), reducing (rich), or stoichiometric (intermediate). Oxidizing flames are the hottest and appear non-luminous white with a slight bluish hue in the body of the flame profile. Reducing flames are the coolest and appear luminous with red to pink hue in the flame profile. The exact composition of the flame must be found during aspiration of the appropriate standard solution; a previously achieved set of index numbers (as shown on the AA-775 control panel) should be taken only as a guide.

Properly installed, the glass bead will be about one mm from the nebulizer orifice and its adjustment should be small, less than one full turn of its adjusting screw. The adjustment should be made for maximum absorbance and stability. The effect seen from this adjustment can be

> quite significant particularly if the setting has been moved grossly out of range. The best sensitivity has been found for sample uptake rates of three to six mL/minute. [6]

Since the adjustments of steps (2) and (3) will have a major effect on the vertical geometry of the flame profile, step (4) is essential as the last step in optimizing the "flame configuration".

(c) Aspirate the matrix or analytical blank; select CAL ZERO; aspirate the optimization standard to check performance.

(d) Select an ABSorbance EXPansion factor (1.0 usually) and an integration period (TIME SEConds = 1.0, usually).

NOTE

> The expansion factor will only affect the digital display; it is not presented to the input-output ports. The factor affects both the signal and the noise; to be practically useful factors greater than one must be accompanied by substantially increased integration times and consequently greater sampling times. For this reason a preferred scale expansion technique is outlined in the final note under Recorder Setup.
>
> An integration period of one second will provide a relatively noise-free signal for metal concentrations down to about 0.5 ppm for all the metals of interest here. Longer periods may be used to smooth out the noise inherently encountered when working at the tens of ppb level. The only caution here is that the sampling time should be on the order of three to four times the integration period.

2.0 Recorder Setup.

Power/ON; Select full scale (f/s) = 1 V; Select standby. Allow to warm up, for example, while setting up the AA-775.

Select INT REP, TIME SEC = "x" (x greater than or equal to 3).

Select BAR GRAPH; when pen comes to rest, you have "x" seconds to set the baseline with the ZERO POS potentiometer (10 turn). If you miss, simply select bar graph again.

Select REC RANGE; pen will deflect to or near f/s; you have as much time as you please to set the pen to exactly f/s with the RECORDER ADJUST potentiometer (one turn). When completed, go on to the next step.

NOTE

The number in the digital display after selecting REC RANGE will be the f/s deflection in absorbence units and at this point has no bearing on the zero and f/s positioning of the pen.

Select REC NORM, REC FAST or REC DAMPED.

NOTE

After selecting, for example, REC NORM, the pen will come to rest at a position determined by the status of the CAL ZERO function. That is:

(a) If CAL ZERO is assigned (LED on) and the AA-775 is aspirating the assignment, then the pen will rest at zero position established above.

(b) If CAL ZERO is assigned and the AA-775 is aspirating anything other than the assignment, the pen will rest at a position up- or down-scale from the original selection according to the difference in absorbance between the assignment and what is being aspirated.

(c) If CAL ZERO is not assigned (LED flashing), the pen will behave as based on the last previous assignment.

The assignment should be whichever (matrix or air) has the lower absorbance, most likely air for wastewater analysis. When the difference in absorbance between matrix and air is small, the baseline position is not critical. When this difference is substantial, as for lead, the baseline position established must be able to accomodate the pen excursion due to the air aspirated between samples. For Pb, if the assignment was air, pen moves up-scale when aspirating matrix; if the assignment was matrix, pen moves down-scale when aspirating air.

Select the desired recorder SPAN; a decrease from f/s = 1 V may equire a small final adjustment of the baseline position with the ZERO OS control, unless the recorder functions are perfectly alanced/calibrated.

NOTE

The choice of recorder SPAN in concert with the choice of REC RANGE determines the magnitude of the pen displacement for a given analyte absorbance value. For example, if the pen response to a given absorbance value is, say, 14 mm at

REC RANGE = 1 A and recorder SPAN = 1 V, then nominally the same (14 mm) response can be achieved with REC RANGE = 2.0 A and SPAN = 500 mV. By the same token, an effective two-fold amplification of the "readability" of the recorded signal (i.e., 28 mm) is achieved either by halving the SPAN at the original REC RANGE or by the converse; if both initial parameters are divided by two, the enhancement is four-fold (i.e., 56 mm). Remember that such enhancements apply to both the signal level and noise level; however, we have found empirically with the present system that increases in recorder sensitivity (decreased SPAN) generally tend to produce somewhat higher noise levels than the corresponding change in the REC RANGE. The relevance of these comments to the above note is that at analyte concentrations above one ppm settings of REC RANGE = 1 A and SPAN = 1 V are quite adequate and render nominal the difference in absorbance between matrix and air, thereby mitigating the choice of baseline position. Also, at concentration levels below one ppm where more sensitive settings are required, a judicious choice of both parameters may eliminate the concern with baseline position.

3.0 RESULTS

The data and analyses given in this section are based on the techniques set forth in section 2.0, Discussion. During the summer weeks when the daytime, ambient laboratory temperature was consistently above 90 deg F (32 deg C), all secondary stocks and glassware were allowed to equilibrate at the temperature of the instrument room (approximately 26 deg C), and volumetric preparations were performed therein. Flame methods were used without simultaneous use of the background correction (deuterium) lamp and absorbance was outputted to the Varian Model 9176 chart recorder. Peak heights were measured to the nearest 0.1 millimeter and a linear regression was performed (using a Hewlett-Packard 34C hand held calculator) as concentration versus absorbance on typically four or five points spanning not more than an order of magnitude change in concentration. When necessary the end-points were varied to achieve a linear correlation coefficient of not less than 0.999. Additional program code was entered in the calculator to allow a determination of the standard deviations for the regression slope, regression intercept, and the interpolated unknown concentration. (The formulae on which the additional program code is based may be found in the appendix.)

The data in Table I is a representative, abridged listing of an original series of unknowns analyzed for chromium using an oxidizing air and acetylene flame. The certified concentration of chromium in "QC-6" is: true value, 250 ppb; reported 242 ± 46 ppb. There are two sets of data in Table I: the left three columns result from instrumental conditions posted at the table foot; the right three columns result from sampling under identical conditions except that REC RANGE = 0.6 and Recorder Span = 1 V (i.e., lower sensitivity). Table II is a listing of statistical data obtained by linear regression analysis of the data in Table I.

As for the QC sample results, the values when derived from standards numbered one through seven are within the acceptable range, and the precision of their measurement, in terms of the relative estimate of variance (s = 100*s/X), is below the maximum value (eight percent) established for chromium by AEHA. [2] That the amount detected is, in fact, in the low part of the acceptable range may be attributed in large measure to matrix mismatch between standards and sample; particularly the relatively high concentration of iron (900 ppb in the QC sample, along with other metals). That the QC results, when derived from standards numbered six through twelve, are outside their expected range and low is attributed to extrapolation error and to the negative curvature in the calibration curve (c.f. Figure 4).

For samples whose concentration is less than 80 ppb, the results are given as such since standards below 80 ppb were not used during the sample

TABLE I

Chromium AA Analysis

Sample Name	Chart Peak Height (mm)	Concentration (ppb ± 2σ)	Sample Name	Chart Peak Height (mm)	Concentration (ppb ± 2σ)
std. 1	6.8	80	std. 6	21.9	800
std. 2	9.9	100	std. 7	28.2	1000
std. 3	15.5	200	std. 8	51.8	2000
std. 4	27.7	400	std. 9	75.2	3000
std. 5	32.0	500	std. 10	117.6	5000
std. 6	51.8	800	std. 11	169.5	8000
std. 7	66.0	1000	std. 12	208.5	10000
QC-6	15.2	204 ± 18	QC-6	7.0	146 ± 68
QC-6	15.2	204 ± 18	QC-6	6.7	134 ± 68
18,19 (204)	4.6	< 80	--	--	--
18,19 (208)	2.8	< 80	--	--	--
19	109.0	1703 ± 56	19	47.1	1818 ± 34

The QC samples were bracketed by a matrix "wash" which itself gave peak height = 1.8 mm.

Instrument Conditions: Lamp current, 5 mA; wavelength, 357.6 nm; slit, 0.2 nm; (oxidant:fuel), (48:20); A(max), 0.500 at 10.0 ppm; REC RANGE, 0.5 A; TIME SEC, 1.0; sample time=settle time, 8 sec; Recorder Span, 500 mV; chart speed, 2.5 cm/min.

TABLE I (Con't)

Chromium AA Analysis

Sample Name	Chart Peak Height (mm)	Concentration (ppb ± 2σ)	Sample Name	Chart Peak Height (mm)	Concentration (ppb ± 2σ)
19WT	192.0	3030 ± 110	19WT	82.0	3271 ± 224
20,21 (204)	3.6	<80	--	--	--
20,21 (208)	7.6	83 ± 20	--	--	--
20	95.5	1487 ± 46	20	39.8	1514 ± 34
20WT	91.4	1422 ± 44	20WT	38.5	1459 ± 34
21	89.7	1394 ± 42	21	37.1	1401 ± 36
21WT	66.3	1020 ± 28	--	--	--
22,24 (204)	54.9	838 ± 22	--	--	--
22,24 (208)	38.6	578 ± 16	--	--	--
22	50.8	773 ± 20	--	--	--
QC-6	15.7	212 ± 16	QC-6	6.2	113 ± 70

The QC samples were bracketed by a matrix "wash" which itself gave peak height = 1.8 mm.

Instrument Conditions: Lamp current, 5 mA; wavelength, 357.6 nm; slit, 0.2 nm; (oxidant:fuel), (48:20); A(max), 0.500 at 10.0 ppm; REC RANGE, 0.5 A; TIME SEC, 1.0; sample time=settle time, 8 sec; Recorder Span, 500 mV; chart speed, 2.5 cm/min.

TABLE II

Statistical Evaluation for Table I Data

Data Pairs (Conc. Range)	7(0.08 to 1.0 ppm)	5(0.8 to 5.0 ppm)
Slope of Conc. vs Abs.	0.016	0.044
Variance on Slope	0.0003	0.0009
Intercept	-0.039	-0.235
Variance on Intercept	0.012	0.064
Correlation Coefficient	0.999	0.999

run. However, there is sufficient sensitivity or readability under the conditions listed to detect approximately 20 ppb before the analyte peak becomes lost in the matrix or background signal.

For samples whose concentration is not bracketed by standards one through seven, confident determination of the concentration requires bracketing standards seven through eleven, even though the extrapolated result is only about 10 percent different. While one can expect this difference will become less as higher concentration levels are approached, extrapolation to lower levels leads to much greater uncertainties and errors, and must be avoided.

3.1 Spiked Samples.

As mentioned in paragraph 2 of section 2.1, EPA Quality Control Samples for Trace Metals, quality control should be effected by the use of spiked samples. The spike can be a convenient aliquot of one of the reference solutions added to a duplicate of one of the unknowns; an equal aliquot of matrix should be added to the same volume of unspiked sample so that the base or background concentrations will be the same, thereby simplifying the data reduction. The calculation is based on the following:

$$C = X \cdot \left[\frac{S}{Y-X}\right]$$

where,

X = observed concentration of the analyte in unknown sample duplicate;
Y = observed concentration of the analyte in the spiked unknown sample;
S = true concentration of spike as milligrams added per total volume of spiked sample; and
C = corrected concentration of unknown sample.

The quotient in brackets above represents an enhancement or suppression factor which will be applicable to correct other determinations of the same metal under the same conditions at the same time (i.e., during that sample run). This factor is determined ad hoc and is transferable neither from day to day nor from analyte to analyte. Acceptable values for this factor are in the range 0.5 to 1.5 (i.e., 50% enhancement or 50% suppression); factors outside this range indicate a serious matrix mismatch which must be corrected. The correction need not be applied to the unknown sample determinations if the factor is in the range 0.9 to 1.1.

3.2 Sampling Sequence.

A recommended sampling sequence is: three to five standards, two neat quality control solutions (EPA certified), duplicate unknown, spiked unknown, five to six samples, standard number one, five to six samples, standard number two, and so on, alternating five to six samples with one of the initial standards until the calibration curve has been reproduced.

End the sequence with a known (QC, spike or standard). If all of the subsequent responses for the standards are within approximately 10% of their initial value, there is no problem.

4.0 CONCLUSIONS

Establishing a limit of detection, while straight-forward, is not quite as simple, procedurally, as extending one's calibration curve to the lowest concentration level for which signal response can be distinguished from noise. Statistically meaningful quantitation cannot be made at the limit of detection [7] . As a functional rule of thumb, detectability should be at a level at least 50% below the desired level of quantitation. For example, if one desires to determine an element at the 0.1 ppm level, detection should be evident at the 0.05 ppm level. Figures 2(B) through 6 are presented simply as empirical evidence that under the procedures outlined herein routine detectability with high confidence can be acheived for the metals of current interest. A definitive determination of the Limit of Detection must await the results of subsequent experiments designed expressly for such purpose.

There is currently sufficient capability, and facility, to detect the required maximum allowable level of cadmium, chromium, iron, and lead in RIA effluent by flame atomic absorption methods (c.f. Table III).

(a) Without any special procedures, the detection limits for cadmium, chromium (both tri- and hexavalent) and iron are about an order of magnitude lower than are needed to meet the present effluent specification.

(b) With special procedures, the detection limit for lead in samples can be brought down to the current required specification (100 ppb maximum permitted). Special procedures could be the concentration of the sample during the acid digestion procedure and flame AA analysis, the use of electrothermal atomization (graphite furnace), solvent extraction techniques, or combinations of these.

NOTE

Maximum care in the preparation of reference solutions is essential.

(c) Reference solutions (working standards and certified EPA quality control samples) must be prepared in acid soaked glassware and stored under refrigeration.

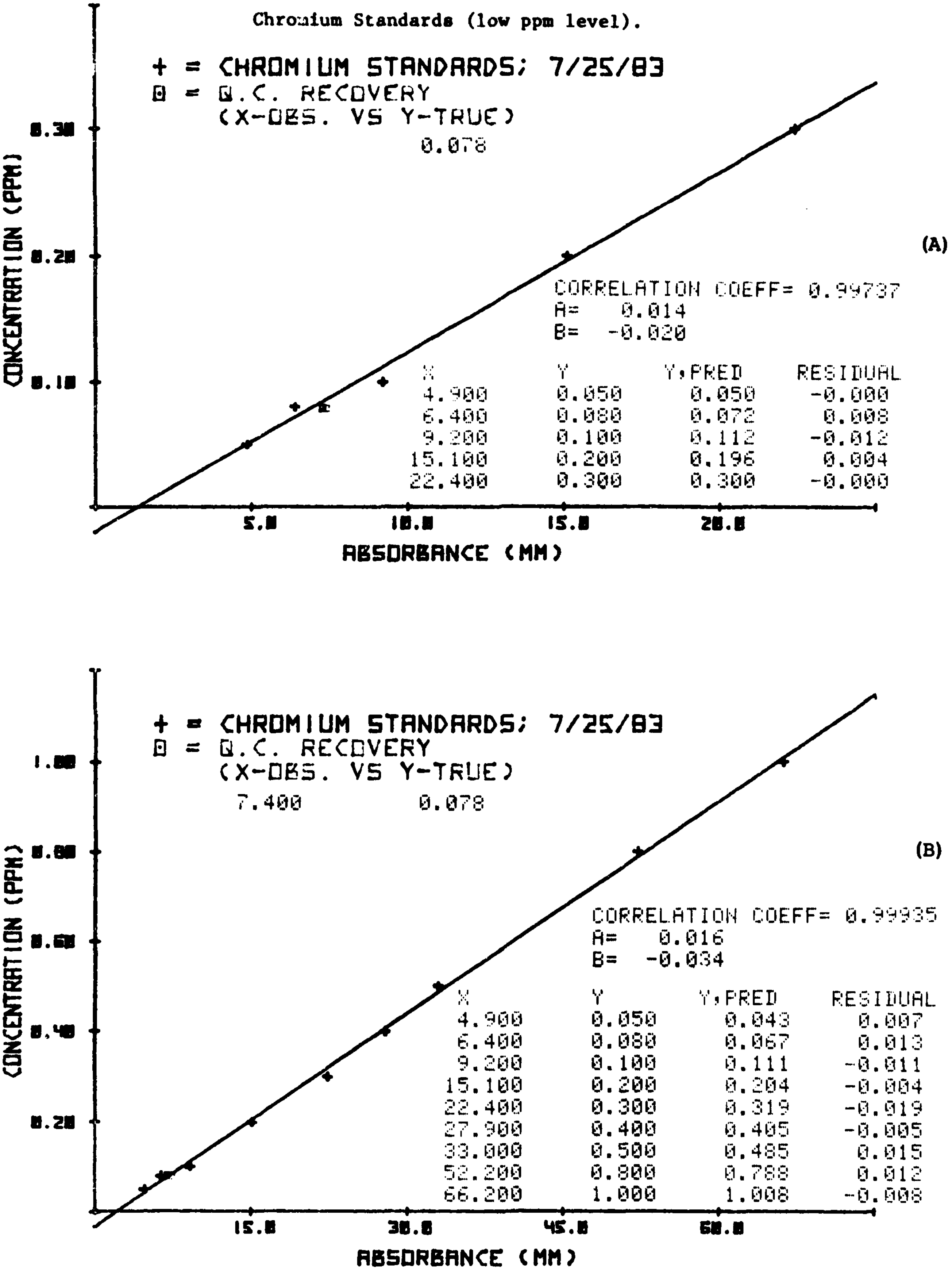
(d) Lack of adequately climatized (thermally stable) environment for reference solution preparation will introduce significant error and non-reproducibility in analytical results, particularly at the concentration levels needed for effluent analysis.

NOTE

Maximum care in the construction and use of calibration curves is essential.

FIGURE 3

Chromium Standards (low ppm level).



(A)

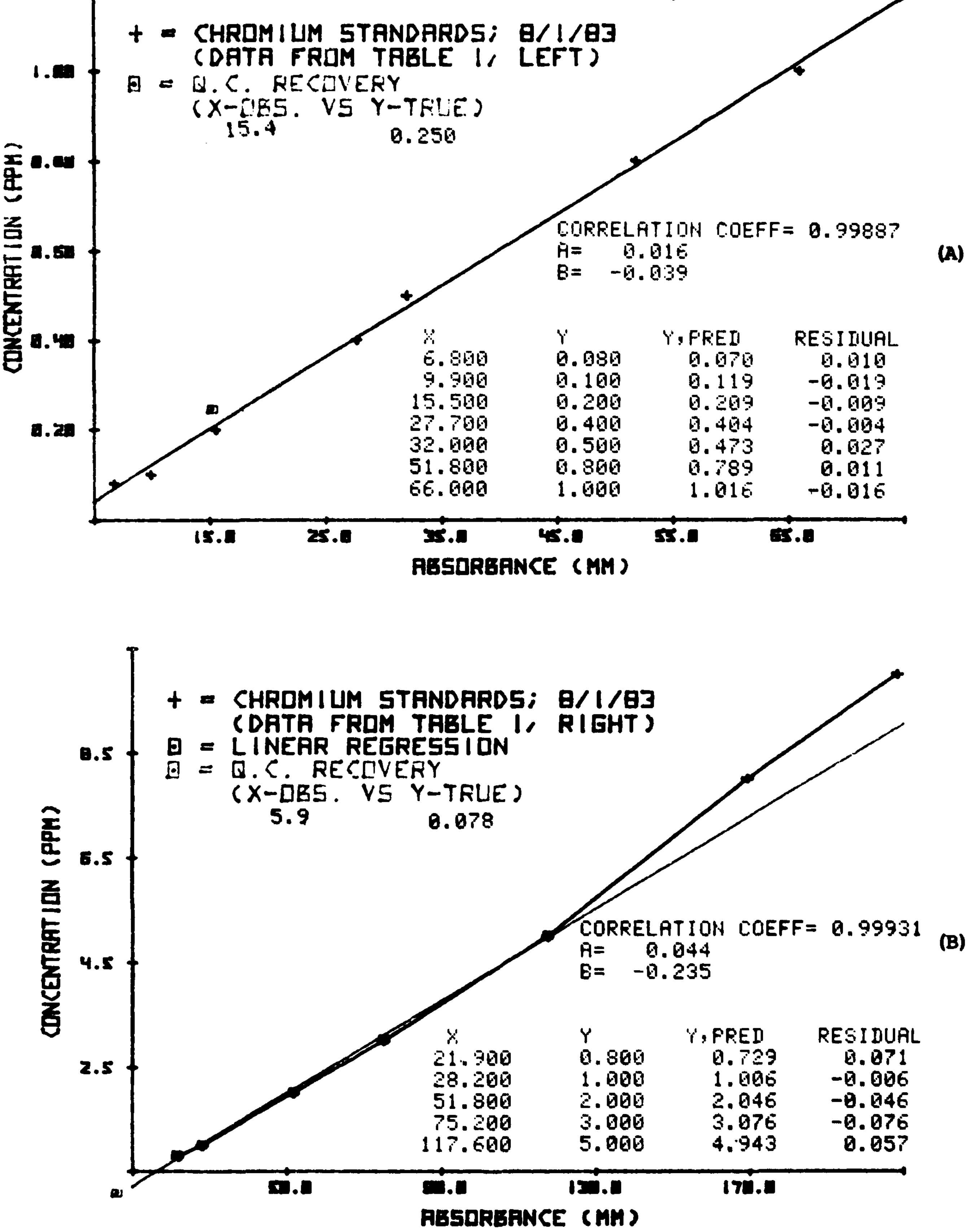
```
CORRELATION COEFF= 0.99737
A=    0.014
B=   -0.020
      X          Y          Y,PRED     RESIDUAL
   4.900      0.050      0.050      -0.000
   6.400      0.080      0.072       0.008
   9.200      0.100      0.112      -0.012
  15.100      0.200      0.196       0.004
  22.400      0.300      0.300      -0.000
```

(B)

```
CORRELATION COEFF= 0.99935
A=    0.016
B=   -0.034
      X          Y          Y,PRED     RESIDUAL
   4.900      0.050      0.043       0.007
   6.400      0.080      0.067       0.013
   9.200      0.100      0.111      -0.011
  15.100      0.200      0.204      -0.004
  22.400      0.300      0.319      -0.019
  27.900      0.400      0.405      -0.005
  33.000      0.500      0.485       0.015
  52.200      0.800      0.788       0.012
  66.200      1.000      1.008      -0.008
```

FIGURE 4

Chromium Standards (for data in Table I).



(A)

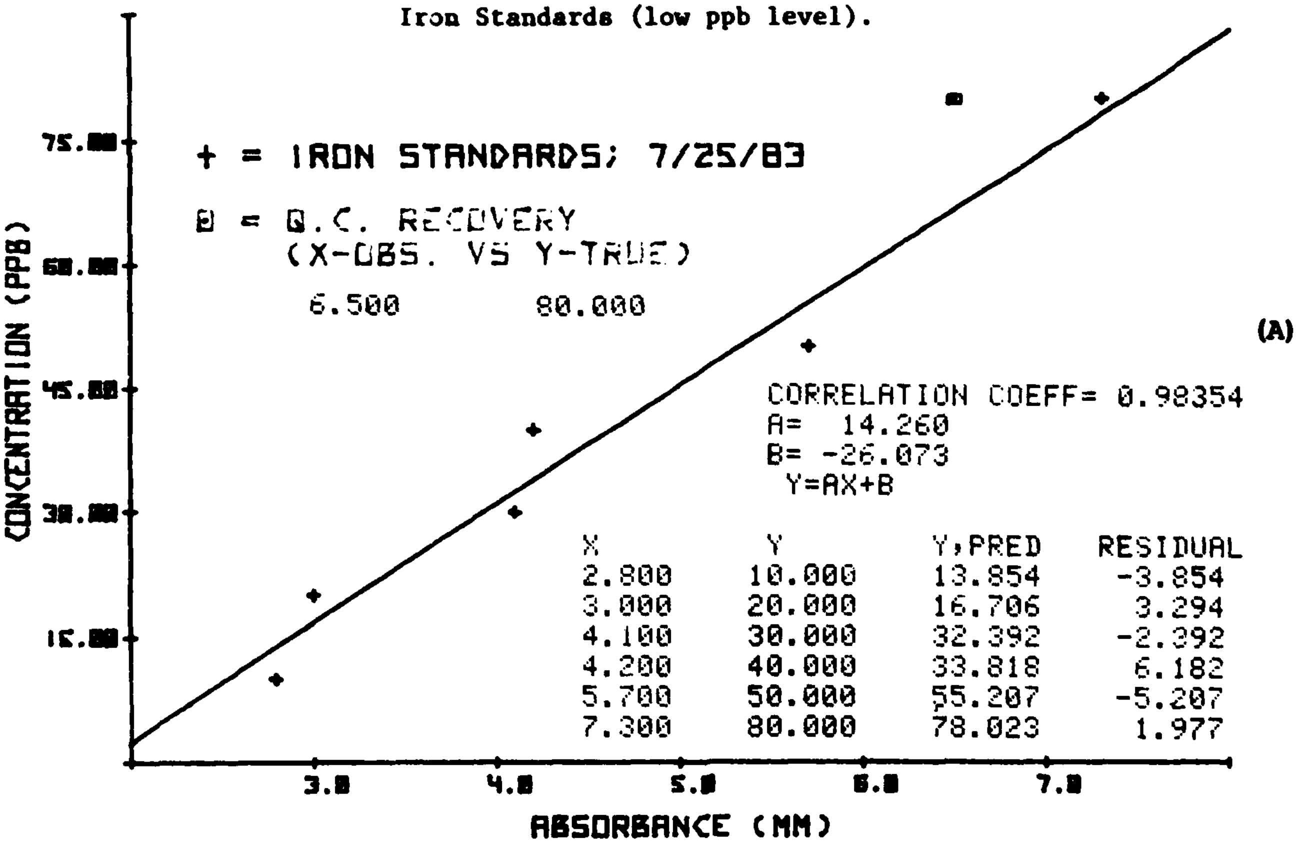
X	Y	Y,PRED	RESIDUAL
6.800	0.080	0.070	0.010
9.900	0.100	0.119	-0.019
15.500	0.200	0.209	-0.009
27.700	0.400	0.404	-0.004
32.000	0.500	0.473	0.027
51.800	0.800	0.789	0.011
66.000	1.000	1.016	-0.016

(B)

X	Y	Y,PRED	RESIDUAL
21.900	0.800	0.729	0.071
28.200	1.000	1.006	-0.006
51.800	2.000	2.046	-0.046
75.200	3.000	3.076	-0.076
117.600	5.000	4.943	0.057

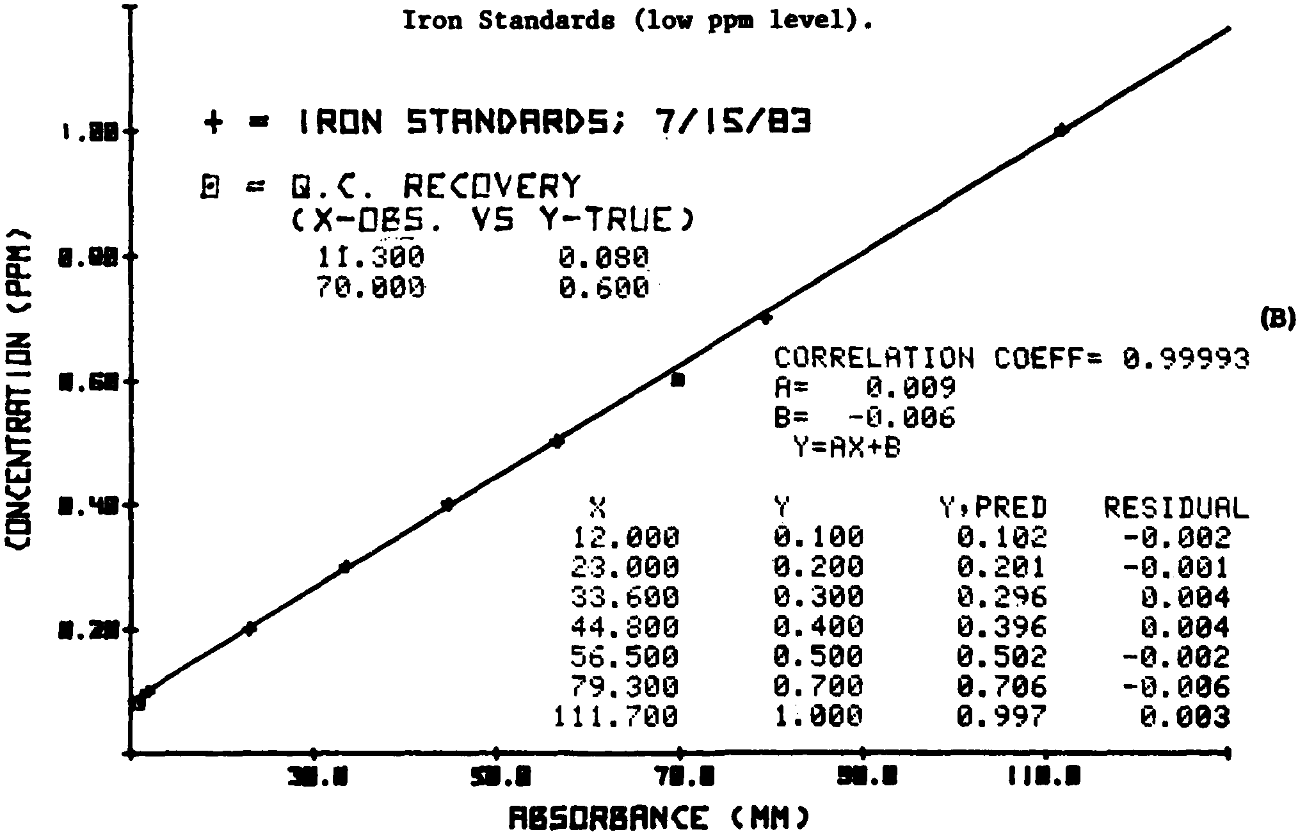
FIGURE 5

Iron Standards (low ppb level).

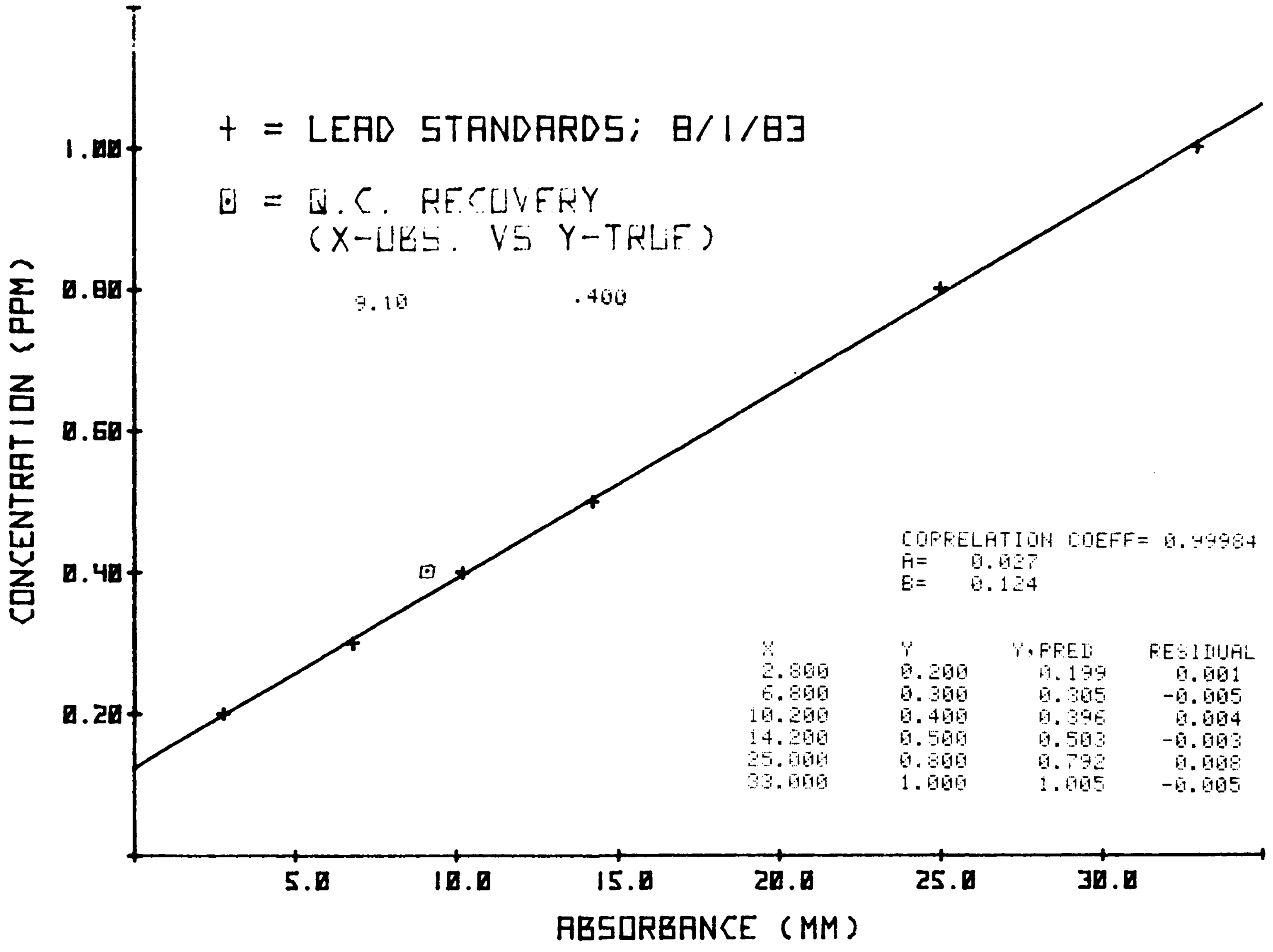


```
+ = IRON STANDARDS; 7/25/83

⊞ = Q.C. RECOVERY
   (X-OBS. VS Y-TRUE)

   6.500        80.000

CORRELATION COEFF= 0.98354
A=   14.260
B= -26.073
 Y=AX+B

     X           Y          Y,PRED    RESIDUAL
   2.800      10.000      13.854     -3.854
   3.000      20.000      16.706      3.294
   4.100      30.000      32.392     -2.392
   4.200      40.000      33.818      6.182
   5.700      50.000      55.207     -5.207
   7.300      80.000      78.023      1.977
```

Iron Standards (low ppm level).



```
+ = IRON STANDARDS; 7/15/83

⊞ = Q.C. RECOVERY
   (X-OBS. VS Y-TRUE)
    11.300         0.080
    70.000         0.600

CORRELATION COEFF= 0.99993
A=    0.009
B=   -0.006
 Y=AX+B

     X           Y          Y,PRED    RESIDUAL
   12.000      0.100       0.102     -0.002
   23.000      0.200       0.201     -0.001
   33.600      0.300       0.296      0.004
   44.800      0.400       0.396      0.004
   56.500      0.500       0.502     -0.002
   79.300      0.700       0.706     -0.006
  111.700      1.000       0.997      0.003
```



```
CORRELATION COEFF= 0.99984
A=    0.027
B=    0.124

   X          Y          Y.PRED     RESIDUAL
  2.800     0.200       0.199      0.001
  6.800     0.300       0.305     -0.005
 10.200     0.400       0.396      0.004
 14.200     0.500       0.503     -0.003
 25.000     0.800       0.792      0.008
 33.000     1.000       1.005     -0.005
```

FIGURE 6

Lead Standards (low ppm level).

TABLE III

Current Limits for RIA Effluent (ppm)

Element	(1) C Max.	(2) LOD	(3) LODA
Cd	0.15	0.0005	0.010
Cr(III)	1.0	0.005	0.05
Cr(VI)	0.3	0.005	
Fe (Total)	2.0	0.003	0.01
Fe (Dissolved)	0.5	0.003	
Pb	0.1	00.01	0.2

(1) City of Rock Island maximum allowable.
(2) Limit of Detection, from literature (c.f. reference 10).
(3) Limit of Detection attempted here.

(e) The determination of unknown concentrations must be bracketed by the determination of known concentrations.

(f) The actual magnitude of the reference concentrations and the intervals between them will be determined by the behavior of the calibration curve in the region of interest.

NOTE

Quality assurance procedures must be applied to both reference solutions and analysis of unknowns.

(g) A neat EPA certified quality control sample, prepared to specifications, is a bona fide control for reference solutions, and in special cases can be also an adequate control for the analysis of unknowns.

(h) A spiked unknown, with unknown duplicate, is in all cases a bona fide control for the analysis of unknowns.

Automated sampling and output accessories, when used routinely, facilitate more reliable or reproducible data and better use of personnel time.

5.0 GENERAL RECOMMENDATIONS

A certified EPA quality control sample, one for each concentration range of interest, should be analyzed with every set of unknown samples.

(a) Results should be maintained only for as long as a given set of secondary stock solutions is in use.

(b) When secondary stock is replenished, the mean recovery and variance may be computed and subjected to control charting procedures if desired.

A spiked sample with duplicate unknown should be included in every set of samples analyzed. The spike result need not be retained beyond the data reduction stage for the sample set of which it was a part.

Analytes should be determined at a level of 50% below the requirement and results reported to two significant figures or simply as less than the required limit.

The Hewlett-Packard Model 82905-B Digital Printer should be acquired and installed as an additional output device for the Varian model AA-775.

Volumetric preparation of reference solutions should be consistently performed in an environment where the temperature is consistently as near 20 deg C as practicable.

6.0 CONTINGENT RECOMMENDATIONS

If the current analysis load is subject to increase, in terms of either the number of samples per week or the number of analyses per sample or both, consideration should be given to the permanent placement of at least a one-half time laboratory assistant for maintaining glassware.

If the results from daily effluent sampling sites are to be correlated with the operation of any production function (e.g., for the sake of optimizing production procedures), that is, if daily unknown sample results are to be subjected to control charting procedures, then steps should be taken to establish computer collection, processing and transmittal (in digital or hard copy format) of AA data.

7.0 REFERENCES

[1] AA-775 Series Atomic Absorption Spectrophotometers: Operations Manual; Varian Techtron Publication No. 85 - 100301 - 00.

[2] US Army Environmental Hygiene Agency, REG 702-1; November, 1982, Appendix-H.

[3] Analytical Methods for Flame Spectroscopy, June, 1978; Varian Techtron Publication No. 85 - 100009 - 00.

[4] Methods for the Chemical Analysis of Water and Wastes, March, 1979; EPA - 600/4 - 79 - 020.

[5] Slavin, Morris, *Chemical Analysis, Vol. 25: Atomic Absorption Spectroscopy,* John Wiley & Sons, New York 1978.

[6] Price, W.J., *Spectrochemical Analysis by Atomic Absorption,* Heyden & Son, Philadelphia, 1979.

[7] Parsons, M.L.; Major, S; and Forster, A.R; *Appl. Spectrosc.,* 37 (1983), 411-418.

[8] US Army, AMCP 706-110.

[9] Ewing, Galen W., *Instrumental Methods of Chemical Analysis,* 4th Ed., McGraw-Hill, New York, 1975.

[10] Kolthoff, I.M. et al., *Quantitative Chemical Analysis,* 4th Ed., Macmillan, New York, 1969; p. 397 ff.

APPENDIX

The variance associated with the slope and the intercept derived from linear regression equations are useful variables for defining the confidence limits for the linear relationship. The variance associated with the value interpolated from regression parameters is also a useful quantity for defining the confidence limit on the interpolation. These variances can all be computed from the same set of factors used to compute the slope, intercept and correlation coefficient (particularly regarding hand-held calculators).

The equations given here are excerpted from reference 8, chapter five.

Definitions:

given: n, Σy, Σy^2, Σx, Σx^2, and Σxy

$S(xx) = [\Sigma x - (\Sigma x)^2/n]$ $\qquad$ $S(yy) = [\Sigma y^2 - (\Sigma y)^2/n]$

$S(xy) = [\Sigma xy - (\Sigma x) \cdot (\Sigma y)/n]$ $\qquad$ $S(y) = [S(yy) - S(xy)^2/S(xx)]/(n-2)$

the estimated variance of the slope,

$$s_m^2 = S^2(y)/S(xx)$$

the estimated variance of the intercept,

$$s_b^2 = S^2(y) \cdot [(1/n) + (\bar{X})^2/S(xx)] = [S^2(y)/n^2] \cdot [n + (\Sigma x)^2/S(xx)]$$

the estimated variance of a value, Y', interpolated from x = X',

$$s_Y^2(X') = S^2(y) \cdot [(1/n) + (X' - \bar{X})^2/S(xx)].$$

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TRACE METALS ANALYSIS OF WASTEWATER BY ATOMIC ABSORPTION SPECTROSCOPY
by Theodore G. Towns, Ph.D. and Karen L. Franich

Report EN-84-11, August 1984, 35 p, incl. figures and tables. Unclassified report.

The primary project objectives of upgrading effluent trace metals analysis by atomic absorption spectroscopy (AA), providing advanced AA instruction, and modeling a schedule for quality control data in the analyses have been successfully completed. The upgraded and automated system will meet the needs of wastewater analysis in an accurate and efficient manner that yields a high level of confidence.

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