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RELIABLE ANALYSES OF WATER BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Athens, Georgia 30601

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RELIABLE ANALYSES OF WATER BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY

by

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FOREWORD

Nearly every phase of environmental protection depends on a capability to identify and measure specific pollutants in the environment. As part of this Laboratory's research on the occurrence, movement, transformation, impact and control of environmental contaminants, the Analytical Chemistry Branch develops and assesses new techniques for identifying and measuring chemical constituents of water and soil.

Inductively coupled plasma emission spectrometry is a relatively new instrumental technique for the rapid, quantitative analysis of water for approximately two dozen trace elements. This report presents an initial evaluation of one commercial instrument that embodies the technique.

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ABSTRACT

Reduction of stray light in the inductively coupled plasma emission spectrometer (ICPES) has greatly increased its reliability as a technique for the multielemental analysis of water. Because of interferences introduced by matrix elements, reliable analysis of some less-sensitive elements has been impractical at concentrations of $\leq$ 200 ppb. After surfaces in the secondary optical system were painted to prevent light scatter and the aperture at the primary lens was reduced in the ICPES, some interference corrections were reduced by more than one order of magnitude. Reduced interferences in the ICPES along with improved corrections by adding exact concentrations of calcium and magnesium to reagent blanks run during sample analyses have definitely improved the accuracy of this multielement analysis system. Observed background changes caused by the presence of magnesium were compensated for by adding matrix elements to calibration standards. Alcohol was added to standards, reagent blanks, and samples to overcome problems of background change during analysis of samples of unknown organic content such as municipal sewage.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AA	-- atomic absorption
AERL	-- Athens Environmental Research Laboratory
ARL	-- Applied Research Laboratory
CF	-- correction factor
DEC	-- Digital Equipment Corporation
E+xx	-- 10^{xx}
EPA	-- Environmental Protection Agency
ERDA	-- Energy Research and Development Administration
IAG	-- interagency agreement
ICPES	-- inductively coupled plasma emission spectrometer
INAA	-- instrumental neutron activation analysis
kW	-- kilowatt
l/min	-- liters per minute
LQD	-- lowest qualitative determinable
MHz	-- megahertz
µm	-- micrometer
ml	-- milliliter
nm	-- nanometer
ppb	-- parts per billion
ppm	-- parts per million
RF	-- radio frequency

SYMBOLS

Ag	-- silver	Mo	-- molybdenum
Al	-- aluminum	Ni	-- nickel
As	-- arsenic	Pb	-- lead
B	-- boron	Sb	-- antimony
Ba	-- barium	Se	-- selenium
Be	-- berylium	Sn	-- tin
C	-- carbon	Sr	-- strontium
Ca	-- calcium	Ti	-- titanium
Cd	-- cadmium	V	-- vanadium
Co	-- cobolt	Y	-- yttrium
Cr	-- chromium	Zn	-- zinc
Cu	-- copper	$\leq$	-- equal to or less than
Fe	-- iron		
Hg	-- mercury	$\geq$	-- equal to or greater than
Mg	-- magnesium		
Mn	-- manganese		

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The cooperation of Drs. V. A. Fassel, R. K. Winge, and J. M. Katzenberger of the Ames Laboratory-ERDA and the Department of Chemistry of Iowa State University in helping to set up and operate the spectrometer is gratefully acknowledged. We are particularly indebted to Dr. Katzenberger for his modifications to the computer software used in this system. The work at the Ames Laboratory was performed under an interagency agreement (IAG-04-0417) with EPA.

Appreciation is also expressed to the Central Regional Laboratory of EPA Region V for its cooperation in supplying sewage samples and standards to permit comparison of data with other techniques and laboratories. The work of Ms. T. I. Sutton of the Athens ERL on this project is sincerely appreciated.

SECTION 1

INTRODUCTION

The Environmental Protection Agency's responsibilities in pollutant monitoring, enforcement proceedings, and surveys of the occurrence of trace elements require analytical capabilities at state-of-the-art levels. Evaluation of one presently available instrument for the rapid multielement analysis of water samples, the inductively coupled plasma emission spectrometer (ICPES), was conducted at the Athens Environmental Research Laboratory. Selected for the study was Applied Research Laboratory's model QA-137, which was considered to be the best commercially available ICPES based on the evaluation of such instruments by the Energy Research and Development Administration's Ames Laboratory under an interagency agreement with EPA (IAG-D6-0417).*

During initial evaluation of the instrument at Athens ERL, spark source mass spectrometer data were compared with IPES data following analysis of cross-check solutions from plating plants. Major differences were detected. Further evaluation attributed these differences to stray light from calcium and magnesium lines in the ICPES, and work was immediately begun to resolve the problem. This report describes the steps that were taken to improve the instrument's performance, describes the Ca and Mg correction procedures, and compares the improved ICPES with other analytical instruments in characterizing the same water samples.

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*Winge, R. K., J. M. Katzenberger, and V. A. Fassel. Development and Application of an Inductively Coupled Plasma Analytical System for the Simultaneous Multielement Determination of Trace Elemental Pollutants in Water. Annual progress reports for 1974-1976 to EPA under Interagency Agreement EPA-IAG-D6-0417. Energy Research and Development Administration, Ames, IA.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Changes initiated by the Athens ERL in the inductively coupled plasma emission spectrometer have resulted in more reliable analytical results for multielement analyses of water. Detection limits, in fact, have been improved for 15 of 23 elements routinely determined, including a 10-fold increase in sensitivity for titanium, vanadium, and yttrium. Because major matrix elements affect background signals at certain wavelengths, they must be included in all calibration standards for analyses that approach the lowest quantitatively determinable concentrations for trace impurities in water. Adding exact concentrations of matrix elements to the reagent blanks is the most precise and reliable technique available to correct interference and/or background shift. Addition of alcohol to waters of unknown organic content is an effective technique to compensate for background differences between calibration standards and real samples.

Because it is a precise, accurate, and rapid technique, IPES should be considered for routine multielement determinations in water. No rigorous preparations or preconcentrations of fresh waters are required to meet or surpass most EPA criteria limits for analysis of metals in water. If early model instruments are used, they should be updated by installing filters at lower wavelengths and/or holographic gratings to minimize required corrections caused by matrix element interference.

SECTION 3

EQUIPMENT

Excitation source for the QA-137 optical emission spectrometer evaluated in this study was an inductively coupled argon plasma device manufactured by the Applied Research Laboratory (ARL). Data readout and computation was performed by standard ARL equipment interfaced to a DEC PDP 11/05 minicomputer having an 8K core memory. The inductively coupled plasma source was powered by a radio frequency (RF) power supply, operating at 27 MHz with 3 kW rating. Initial ionization of the argon was started by a Tesla coil; continuous or sustained operation was maintained by induced heat from a two-turn induction coil that encircle the torch assembly. The QA-137 spectrometer was equipped with 31 exit slits (elements and wavelengths in Table 1); the grating was blazed for ≈ 300 nm. Wavelengths covered by this array ranged from 189.5 to 461.5 nm. Entrance and exit slitwidths were 12 μm and 50 μm, respectively. The electrical signal from each of the 31 photomultipliers was taken by the readout system and integrated on a capacitor for a given time. The charge on each capacitor was then converted to a concentration value from the calibration curves and stored in the PDP11/05 minicomputer. Concentration data were printed out using an ASR 33 teletype.

With the computer program used in this study, standard errors of concentration and intensity from calibration data can be printed out along with curve coefficients for curves, slopes, and intercepts. In addition, an error table can print out each element calibrated and each standard used, including concentration and intensity residuals. Linearity values for each standard are also printed in the error tables. The standard error tables and error tables for calibrations can be used by the operator as a control on reliability of analytical data.

SECTION 4

EXPERIMENTAL PROCEDURES

Operating conditions for the inductively coupled plasma source were those recommended by the vendor:

1. RF power (forward), 1100 W and 1600 W
2. Reflected power, < 2 W
3. Plasma argon flowrate, 16 l/min
4. Auxiliary plasma argon flowrate, 1.4 l/min
5. Aerosol argon flowrate, 1 l/min
6. Integration time, 10 sec
7. Calibration, 7 concentrations for all elements except Ca and Mg, 3 concentrations for Ca and Mg
8. Warm up time, 1 hour
9. Adjustment of entrance slit placement to optimum each day

The addition of a microscope slide cover at the magnesium II, 279.55-nm exit slit reduced the interference of magnesium in the secondary optics. By decreasing the aperture at the primary lens to a 5-mm opening, the light allowed into the spectrometer from the torch was reduced.

Reduction of stray light caused by magnesium in the secondary optics was accomplished by covering bright surfaces with black paint. Baffles of black paper were also placed in the system to prevent reflections from reaching various detectors.

Correction factors (CF) for calcium and magnesium were determined and applied using either blank corrected intensity ratios or concentrations provided in the modified software. Originally, 12 CF's could be handled by the software, but the Ames Laboratory expanded this capability to 44.

Mixtures of acid, methyl alcohol, and ethyl alcohol were checked for the most favorable background levels for most elements.

No loss of operation time because of instrument down time occurred during the 6-month period of operation. Instrument

stability for day-to-day operations was remarkably good; calibration curves did not change more than 10% between successive days.

SECTION 5

RESULTS AND DISCUSSION

Results before and after modifications to the ICPES and changes in operating procedures are discussed in this section. Data listed in Table 2 are correction factors for interferences by calcium (column 1 and 2) and magnesium (column 3 and 4). Correction factors were calculated using data from 50-ppm calcium in one solution and 50-ppm magnesium in another; no other elements were added.

Ratios for the correction factors were calculated using the blank corrected intensity of the channel to be corrected in the numerator and the blank corrected intensity of the interfering element in the denominator as follows:

$$\text{CF ratio} = I_{Al}^{Ca} / I_{Ca} \qquad (1)$$

where I_{Al}^{Ca} is the intensity recorded for the aluminium channel, and

I_{Ca} is the intensity for calcium when aspirating the 50-ppm calcium solution.

These ratios were stored in the computer, and the corrections applied to the analyses are the product of equation 2.

$$\text{CF applied} = (I_{Al}^{Ca} / I_{Ca}) I_{Ca}^{U} \qquad (2)$$

where I_{Ca}^{U} is the blank corrected intensity of calcium found in the sample of question.

The modified software package supplied by Ames Laboratory allowed the correction to be applied to the analytical concentration data or the intensity correction as shown above.

Correction data in the first two columns of Table 2 show little or no change in calcium interference levels after painting the bright surfaces and adding the baffles. Data in columns 3 and 4 show some changes in magnesium interference correction data after painting and adding of some baffles in the secondary optics. The significant changes occurring with

magnesium corrections are at Cd, Cu, Sb, and V wavelengths. The changes, addition of the microscope slide and reduction of light at the primary lens, were made after the data in Table 2 were gathered. Correction factors calculated after the changes of the microscope slide and reduction of light at the primary lens are listed in Table 3. Comparison of the data in Table 3 with those of columns 1 and 3 in Table 2, reveals that significant reductions have been made in corrections to account for interferences caused by calcium. The data in Tables 2 and 3 show that the most advantageous changes in calcium corrections resulted from changes in the primary optics, whereas the best changes for magnesium corrections occurred in the secondary system.

When interference corrections of the magnitude listed in columns 1 and 3 of Table 2 were applied to data from analyses with concentrations of $\leq$ 0.05 ppm, results in many cases were unacceptable. Contributions from calcium and magnesium to analyses of other elements are shown in Table 4. Inspection of these interferences (Table 4) reveals the nonlinearity of interference of both calcium and magnesium. Using data from Table 4, the magnesium correction factor for arsenic is made using equation 1.

$$I_{As}^{Mg}/I_{Mg} = 0.104/50.0 = 2.08E-3$$

Then using equation 2 to correct an analysis containing 100 ppm Mg, we find this product.

$$(I_{As}^{Mg}/I_{Mg})\, I_{Mg}^{U} = 2.08E-3 \text{ X } 100 = 0.208E+0$$

Comparing this value (0.208E+0) to the observed value for the interference caused by 100 ppm magnesium at the arsenic wavelength (0.333E+0) reveals a difference of 0.125E+0 ppm that would be identified as arsenic. Now, to attempt a full correction for calcium and magnesium interference in arsenic analysis, magnesium correction (0.208E+0 ppm) and calcium correction (1.400 ppm = 1.608E+0 ppm) are calculated. Referring to Table 5 where 100 ppm each of calcium and magnesium was observed, the correction in fact should be 0.719E+0 ppm, showing an over correction of 0.889 ppm applied to the arsenic analysis. Calculated corrections for calcium and magnesium, as with those discussed for arsenic, are confounded even more as can be seen in Table 6. The corrections applied to the analyses by the software are algebraically added to either the intensity or the concentration data. Taking the values from calcium 50 ppm and magnesium 50 ppm columns in Table 6, the total for arsenic should be equal to the third column where 50 ppm each of calcium and magnesium were observed in the same solution. The total of the calcium and magnesium columns from Table 6 is 0.624E+0

compared with 0.461E+0 contribution with the two elements mixed, however, leaving an over correction of 0.163E+0 ppm.

Several elements such as Al_1, B, Cd, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pb_2, Sb, Se, Sn, Ti, V, and Zn show that calculations for corrections from pure solutions of calcium and magnesium are not applicable to multielement analysis. When the ratio of the Ca and/or Mg concentration to the analyte concentration reaches 1000, significant errors caused by interferences can be introduced at the analytical wavelengths for Al, As, Hg, Pb, Sb, Se, and Sn; errors for other elements become significant when this ratio reaches ≈ 10,000. Data listed in Table 7 show sodium and potassium to be only minor problems when compared to calcium and magnesium interferences.

Using ICPES, data from 10 runs of laboratory standard material were collected in the "as received" state (Table 8). Calibration of the ICPES was accomplished using no matrix elements (Ca and Mg) in the solutions containing the remainder of the elements. Calculated corrections were applied to correct data for the Ca and Mg in the analyses of the 10 determinations represented in Table 8. The ratio of Ca or Mg to the remaining elements is about 2000:1, 100 ppm each of Ca and Mg and 0.05 ppm for all other elements. After the modifications listed at the beginning of this section were made, the data listed in Tables 9 through 13 were collected. Calibration of the ICPES was done using standards containing the matrix elements of Ca and Mg; the corrections for Ca and Mg were done by using "blank" solutions containing equal concentrations of the Ca and Mg contained in the samples.

Examination of these data shows that the latter of the two techniques yields data that are more reliable when the ratio of Ca and Mg concentration to other elements approaches 1000. Detection limits calculated in our laboratory for the ICPES are listed in Table 14. Column 1 shows detection limits from data of the "as received" instrument; column 2 shows results after the modifications listed at the first of this section. In column 3, the detection limits are calculated from data while aspirating 100 ppm Ca and Mg. Column 4 is the lowest quantitatively determinable concentration, which is five times the detection limit. Comparing data in column 4 of Table 14 with those in Tables 9 through 13, one can see that the LQD concentration is a very conservative estimate for solutions containing up to 100 ppm each of Ca and Mg. Precision and accuracy data in Tables 12 and 13 show that As, Hg, Pb, Sb, Se, and Sn can be determined in those solutions at a concentration below the calculated LQD concentration. The precision of the analyses for the afore-mentioned elements is at least a factor of 10 greater than the remaining list of analytes.

To demonstrate the applicability of techniques discussed above, sewage influent and effluent samples were analyzed by ICPES, INAA, and AA with resultant data presented in Tables 15 through 21. Data listed under the heading ICP-A were determined at the Athens Environmental Research Laboratory; INAA results are from the same laboratory at its Neutron Activation Facility. AA results are averages from 10 different state and Federal laboratories, and ICP-V results are from another EPA laboratory. Data in Tables 19 through 21 provide comparisons of standard samples and a spiked drinking water sample. In most cases, ICPES data and AA results are in excellent agreement, and each are in fair agreement with INAA results, both on real samples (sewage) and standard materials.

The ICP-A instrument was calibrated using standards containing matrix elements Ca and Mg. Corrections for Ca and Mg interferences during analyses were done by adding exact amounts of Ca and Mg to the blank solution, so the corrections are treated as a blank subtraction from sample data. When running samples that may have contained waste organics, 1 ml each of methyl alcohol and ethyl alcohol was added to all calibration standards and samples to compensate for changes in background levels caused by organic compounds. Background changes caused by organics can be significant in analyses that approach LQD concentrations. Two percent alcohol was added to assure that the overriding background changes resulting from possible organic contamination of samples was constant and therefore more correctly compensated for. When the 2% alcohol solution was added to water, there was a change in most background signals toward a smaller value.

The major findings of this evaluation report can be summarized as follows:

- Corrections for stray light are significant when the ratio of Ca or Mg to most analytes reaches 1000.
- Calibration standards should contain major impurity elements that occur in the real samples.
- Compensation for unknown organic impurities can be made by adding alcohol to the standards and blanks.

TABLE 1. SPECTROMETER LINE ARRAY

Element*	Wavelength, nm
Ag I	328.07
Al I	308.22
Al I	396.15
As I	193.76
B I	249.68
Ba II	455.40
Be II	313.04
C I	247.86
Ca II	315.89
Cd II	226.50
Co II	238.89
Cr II	267.72
Cu I	324.75
Fe II	259.94
Hg I	253.65
Mg II	279.55
Mn II	257.61
Mn I	403.08
Mo II	287.15
Ni II	231.60
Pb II	220.35
Pb I	405.78
Sb I	206.84
Se I	196.09
Sn I	303.41
Sr II	407.77
Ti II	334.90
V II	292.40
Y II	242.22
Y II	371.03
Zn I	213.86

* I denotes radiation originating from neutral atom.
II denotes radiation originating from singly ionized atoms.

TABLE 2. COMPARISON OF CORRECTION FACTORS

	I	II	III	IV
	Ca Correction		Mg Correction	
	Unpainted	Painted	Unpainted	Painted
Al	-3.62E-2	-4.14E-2	-1.68E-4	NC
As	-6.15E-3	-4.50E-3	-8.55E-4	-1.50E-4
B	-1.08E-3	-1.03E-3	-1.01E-3	-9.31E-4
Ba	-1.48E-2	-1.08E-2	-2.68E-4	NC
Be	NC	NC	-2.88E-4	NC
Cd	-3.57E-3	-2.61E-3	-1.20E-5	-1.55E-6
Co	-4.08E-3	-3.77E-3	-1.59E-4	-1.50E-4
Cr	-5.29E-3	-3.91E-3	-1.58E-3	-1.16E-3
Cu	-7.02E-3	-1.56E-3	-1.01E-4	NC
Fe	-1.93E-3	-2.04E-3	-1.51E-5	NC
Hg	-2.03E-3	-1.88E-3	-6.83E-4	-5.63E-4
Mn	-2.68E-4	-4.01E-4	-7.09E-4	NC
Mo	-3.30E-3	-2.30E-3	-5.02E-4	-2.50E-4
Ni	-4.29E-3	-4.77E-3	-1.70E-4	-1.87E-4
Pb	-3.76E-3	-4.22E-3	-3.14E-4	-3.90E-4
Sb	-1.49E-3	-1.71E-3	-1.75E-5	-3.55E-6
Se	-8.36E-3	-6.57E-3	-1.70E-4	-2.84E-4
Sn	-1.86E-3	-1.90E-3	-6.96E-5	-3.20E-5
Sr	NC	NC	-2.52E-4	NC
Ti	NC	NC	-2.86E-4	NC
V	-8.94E-3	-7.10E-3	-3.07E-2	-2.23E-3
Y	NC	NC	-2.85E-4	NC
Zn	-1.91E-3	-1.61E-3	-1.73E-4	-1.56E-4

NC - No correction required.

TABLE 3. CORRECTION FACTORS PRESENTLY REQUIRED ON ARL QA-137

	Calcium*	Magnesium*
Al	-1.61E-4	-2.38E-4
As	-1.96E-3	-1.01E-4
B	-7.17E-5	-1.10E-3
Ba	-9.87E-4	NC
Be	NC	NC
Cd	-2.15E-4	NC
Co	-1.21E-4	-1.13E-4
Cr	-1.15E-5	-1.54E-3
Cu	NC	NC
Fe	-1.12E-4	NC
Hg	-1.00E-4	-2.58E-4
Mn	-6.69E-4	NC
Mo	-3.73E-5	-2.10E-4
Ni	-2.46E-4	-2.00E-4
Pb	-4.39E-4	-2.26E-4
Sb	-5.51E-4	-3.00E-6
Se	-1.12E-3	-2.50E-4
Sn	-9.75E-5	NC
Sr	NC	NC
Ti	NC	NC
V	-3.44E-5	NC
Y	-8.90E-5	NC
Zn	-4.05E-4	-1.70E-4

* Calculated from 1000 µg/ml.
NC - No correction required.

TABLE 4. NONLINEARITY OF Ca AND Mg INTERFERENCE

	Mg *50 ppm	Mg *100 ppm	Ca *50 ppm	Ca *100 ppm
Al	0.245E-1	0.208E-1	0.367E-1	-0.205E-1
Al	0.843E-2	0.781E-2	0.186E+0	0.385E+0
As	0.104E+0	0.333E+0	0.520E+0	0.752E+0
B	0.469E-1	0.210E-1	-0.306E-2	0.984E-2
Ba	0.316E-2	0.705E-2	0.374E-2	0.744E-2
Be	0.900E-4	0.120E-3	0.200E-3	0.900E-4
Ca		0.157E+0		
Cd	0.355E-2	0.397E-2	0.508E-2	0.780E-2
Co	0.404E-2	0.706E-2	0.439E-2	0.685E-2
Cr	0.488E-2	0.718E-2	-0.320E-2	-0.990E-3
Cu	-0.138E-2	-0.322E-2	0.512E-2	-0.512E-2
Fe	0.425E-2	0.839E-2	0.288E-2	0.423E-2
Hg	0.187E-1	0.514E-1	0.308E-1	0.492E-1
Mn	0.109E-2	0.222E-2	0.310E-3	0.134E-2
Mn	0.571E-2	0.479E-2	-0.178E-1	0.175E-1
Mo	0.271E-1	0.388E-1	-0.257E-1	-0.927E-2
Ni	0.951E-2	0.206E-1	0.399E-2	0.254E-1
Pb	0.566E-1	0.104E+0	0.836E-1	0.188E+0
Pb	0.279E+0	0.409E+0	-0.477E-1	0.625E-1
Sb	0.546E-1	0.175E+0	0.192E+0	0.286E+0
Se	0.113E+0	0.288E+0	0.328E+0	0.451E+0
Sn	0.781E-1	0.583E-1	0.201E+0	-0.110E+0
Sr	0.800E-4	0.570E-3	0.334E-1	0.672E-1
Ti	0.160E-3	0.200E-3	-0.145E-2	-0.640E-3
V	0.760E-3	0.172E-1	-0.369E-2	-0.307E-2
Zn	0.229E-2	0.888E-2	0.218E-2	0.679E-2

Mean of 10 determinations for each element.
Units are equivalents in ppm.
ICP calibrated from ∿0.005 to ∿5 ppm for all elements except Ca and Mg.
* Concentrations of Mg or Ca in solution aspirated.

TABLE 5. INTERFERENCE OF Ca AND Mg MIXTURES

	5 ppm Ca 5 ppm Mg*	50 ppm Ca 50 ppm Mg*	100 ppm Ca 100 ppm Mg*
Al	-0.209E-1	-0.288E-1	0.421E-1
Al	0.440E-1	0.196E+0	0.392E+0
As	-0.422E-1	0.461E+0	0.719E+0
B	0.981E-2	-0.461E-2	0.219E-1
Ba	0.670E-3	0.593E-2	0.799E-2
Be	0.220E-3	0.120E-3	0.210E-3
Cd	0.131E-2	0.657E-2	0.151E-1
Co	0.663E-2	0.741E-2	0.164E-1
Cr	0.408E-2	0.398E-2	0.104E-1
Cu	0.202E-2	0.355E-2	0.102E-2
Fe	0.221E-2	0.403E-2	0.159E-1
Hg	0.101E-1	0.384E-1	0.810E-1
Mn	0.590E-3	0.186E-2	0.438E-2
Mn	0.413E-1	0.118E-1	0.501E-2
Mo	0.275E-1	0.215E-1	0.839E-1
Ni	0.767E-2	0.226E-1	0.345E-1
Pb	0.242E-1	0.133E+0	0.249E+0
Pb	0.169E+0	0.213E+0	0.594E+0
Sb	-0.149E-1	0.173E+0	0.305E+0
Se	-0.203E-1	0.342E+0	0.507E+0
Sn	0.195E+0	0.545E-1	0.246E+0
Sr	0.330E-2	0.335E-1	0.649E-1
Ti	0.185E-2	-0.400E-3	0.271E-2
V	0.120E-2	-0.400E-3	0.152E-2
Zn	0.280E-2	0.910E-2	0.209E-1

Mean of 10 determinations for each element.
Units are equivalents in ppm.
ICP calibrated from ∿0.005 to ∿5 ppm for all elements except Ca and Mg.
* Concentrations of Mg and Ca in solution aspirated.

TABLE 6. Ca-Mg CORRECTIONS VERSUS Ca-Mg MIXTURE

	50 ppm Ca*	50 ppm Mg*	50 ppm Ca 50 ppm Mg*
Al_1	0.367E-1	0.245E-1	-0.288E-1
Al	0.186E+0	0.843E-2	0.196E+0
As	0.520E+0	0.104E+0	0.461E+0
B	-0.306E-2	0.469E-1	-0.461E-2
Ba	0.374E-2	0.316E-2	0.593E-2
Be	0.200E-3	0.900E-4	0.120E-3
Cd	0.508E-2	0.355E-2	0.657E-2
Co	0.439E-2	0.404E-2	0.741E-2
Cr	-0.320E-2	0.488E-2	0.398E-2
Cu	0.512E-2	-0.138E-2	-0.355E-2
Fe	0.288E-2	0.425E-2	0.403E-2
Hg	0.308E-1	0.187E-1	0.384E-1
Mn	0.310E-3	0.109E-2	0.186E-2
Mn	-0.178E-1	0.571E-2	0.118E-1
Mo	-0.257E-1	0.271E-1	0.215E-1
Ni	0.399E-2	0.951E-2	0.226E-1
Pb	0.836E-1	0.566E-1	0.133E+0
Pb	-0.477E-1	0.279E+0	0.212E+0
Sb	0.192E+0	0.546E-1	0.173E+0
Se	0.328E+0	0.113E+0	0.342E+0
Sn	0.201E+0	0.781E-1	0.545E-1
Sr	0.334E-1	0.800E-4	0.335E-1
Ti	-0.145E-2	0.160E-3	-0.400E-3
V	-0.369E-2	0.760E-3	-0.400E-3
Zn	0.218E-2	0.229E-2	0.910E-2

Mean of 10 determinations for each element.
Units are equivalents in ppm.
ICP calibrated from ∿0.005 to ∿5 ppm for all elements except Ca and Mg.
* Concentrations of Mg and/or Ca in solution aspirated.

TABLE 7. INTERFERENCE OF MATRIX ELEMENTS AND MIXTURES

	50 ppm Na 50 ppm K*	100 ppm Na 100 ppm K*	50 Mg 20 K 100 ppm Na 100 ppm Ca*	100 ppm Na*	100 ppm Ca*	50 ppm Na*	50 ppm K*
Al	-0.111E-1	-0.251E-1	0.184E-1	-0.122E-1	-0.205E-1	-0.119E-1	+0.274E-1
Al	-0.660E-2	-0.308E-1	0.344E+0	-0.309E-2	0.385E+0	-0.507E-2	-0.586E-2
As	+0.199E-1	+0.105E-1	0.585E+0	+0.210E-1	0.752E+0	+0.232E-1	-0.235E-1
B	-0.127E-1	-0.508E-1	0.642E-2	-0.219E-2	0.984E-2	+0.720E-2	-0.989E-2
Ba	+0.360E-3	+0.480E-3	0.617E-2	+0.119E-2	0.744E-2	+0.370E-3	-0.900E-4
Be	-0.900E-4	-0.900E-4	0.220E-3	-0.800E-4	0.900E-4	-0.600E-4	+0.130E-3
Ca						+0.572E-1	+0.130E-3
Cd	-0.330E-3	-0.259E-2	0.909E-2	-0.172E-2	0.780E-2	-0.121E-2	+0.259E-2
Co	-0.930E-3	-0.603E-2	0.988E-2	-0.113E-2	0.685E-2	-0.117E-2	-0.840E-3
Cr	-0.109E-2	-0.726E-2	0.326E-2	-0.165E-2	-0.990E-3	-0.131E-2	-0.970E-3
Cu	-0.560E-3	-0.380E-3	-0.660E-3	-0.298E-2	-0.512E-2	-0.258E-2	-0.128E-2
Fe	-0.109E-2	-0.539E-2	0.653E-2	-0.520E-3	0.423E-2	-0.133E-2	-0.380E-3
Hg	-0.555E-2	-0.341E-1	0.502E-1	+0.130E-1	0.492E-1	-0.865E-2	-0.807E-2
Mg						-0.540E-3	-0.148E-2
Mn	-0.130E-3	-0.580E-3	0.262E-2	-0.600E-4	0.134E-2	-0.220E-3	-0.110E-3
Mn	-0.881E-2	-0.593E-1	0.328E-1	-0.930E-2	0.175E-1	-0.130E-1	-0.809E-2
Mo	-0.859E-2	-0.352E-1	0.196E-1	+0.419E-2	-0.927E-2	-0.812E-2	-0.983E-2
Ni	-0.481E-2	-0.141E-1	0.287E-1	-0.292E-2	0.254E-1	-0.390E-2	-0.398E-2
Pb	-0.196E-1	-0.380E-1	0.179E+0	-0.122E-1	0.188E+0	-0.803E-2	-0.212E-1
Pb	-0.718E-1	-0.241E+0	0.216E+0	-0.457E-1	0.625E-1	-0.425E-1	-0.239E-1
Sb	-0.116E-1	-0.150E-1	0.209E+0	-0.276E-1	0.286E+0	+0.271E-1	-0.125E-1
Se	-0.209E-1	+0.140E-1	0.391E+0	-0.139E-1	0.451E+0	+0.173E-1	-0.298E-1
Sn	-0.845E-1	-0.244E+0	0.553E-1	-0.302E-1	-0.110E+0	-0.662E-1	-0.275E-1
Sr	+0.170E-3	+0.430E-3	0.598E-1	+0.540E-3	0.672E-1	+0.210E-3	-0.200E-4
Ti	-0.450E-3	-0.184E-2	-0.310E-3	-0.160E-3	-0.640E-3	-0.290E-3	-0.380E-3
V	-0.251E-2	-0.464E-2	-0.154E-2	-0.232E-2	-0.307E-2	-0.740E-3	-0.215E-2
Zn	-0.338E-2	+0.680E-2	0.159E-1	-0.408E-2	0.679E-2	-0.246E-2	-0.549E-2

Mean of 10 determinations for each element. ICP calibrated ~0.005 to ~5 ppm for each element except Ca and Mg. * Concentrations of Ca, Mg, Na, and K in solution aspirated.

TABLE 8. ORIGINAL ATTEMPTS TO CORRECT FOR Ca AND Mg INTERFERENCE

Element	$\bar{X}$ 10 Runs	Variance	Standard Deviation
Al	0.0472	0.000025	0.0050
As	0.0804	0.0082	0.029
B	0.0771	0.0035	0.0188
Ba	0.0482	0.0000015	0.0012
Be	0.0504	0.0000072	0.0027
Ca	98.90	0.281	0.53
Cd	0.0565	0.000011	0.0033
Co	0.0542	0.000011	0.0034
Cr	0.0512	0.0000097	0.0031
Cu	0.0471	0.000035	0.0059
Fe	0.0531	0.000011	0.0033
Hg	0.0816	0.00099	0.031
Mg	98.77	0.0415	0.20
Mn	0.0502	0.0000005	0.0007
Mo	0.0524	0.000096	0.0098
Ni	0.0648	0.00014	0.0118
Pb	Overcorrected		
Sb	0.0909	0.0129	0.114
Se	0.1030	0.0021	0.0464
Sn	0.0768	0.0015	0.0384
Sr	0.0514	0.0000035	0.0019
Ti	0.0373	0.000021	0.0046
V	0.0499	0.0000020	0.0014
Y	0.0500	0.0000005	0.0007
Zn	0.0312	0.0000007	0.0008

Ca and Mg concentration is 100 ppm each, other elements 0.050 ppm.

TABLE 9. MATRIX 20 ~1 RATIO*

	Mean	Variance	Standard Deviation	Added	Difference	% Error
Al	0.468E+1	0.982E-3	0.313E-1	0.486E+1	-0.18E+0	-4
Al	0.488E+1	0.266E-3	0.163E-1	0.486E+1	+0.20E-1	+0.4
As	0.101E+2	0.256E-2	0.506E-1	0.996E+1	+0.14E+0	+1.0
B	0.516E+1	0.137E-2	0.370E-1	0.515E+1	+0.10E-1	+0.2
Ba	0.492E+1	0.119E-2	0.345E-1	0.498E+1	-0.60E-1	-1
Be	0.504E+1	0.137E-2	0.370E-1	0.514E+1	-0.10E+0	-2
Cd	0.505E+1	0.101E-2	0.319E-1	0.499E+1	+0.60E-1	+1
Co	0.509E+1	0.461E-3	0.215E-1	0.499E+1	+0.10E+0	+2.0
Cr	0.512E+1	0.228E-3	0.151E-1	0.508E+1	+0.40E-1	+0.8
Cu	0.501E+1	0.407E-3	0.202E-1	0.503E+1	-0.20E-1	- .4
Fe	0.524E+1	0.244E-3	0.156E-1	0.515E+1	+0.21E+0	+4.0
Hg	0.494E+1	0.257E-2	0.507E-1	0.500E+1	-0.60E-1	-1
Mn	0.504E+1	0.163E-3	0.128E-1	0.503E+1	+0.10E-1	+2
Mn	0.503E+1	0.222E-3	0.149E-1	0.503E+1	+0.00E+0	0
Mo	0.511E+1	0.418E-3	0.204E-1	0.500E+1	+0.11E+0	+2
Ni	0.501E+1	0.118E-2	0.344E-1	0.499E+1	+0.20E-1	+0.40
Pb	0.102E+2	0.367E-2	0.606E-1	0.996E+1	+0.20E+0	+2.0
Pb	0.103E+2	0.579E-2	0.761E-1	0.996E+1	+0.34E+0	+3
Sb	0.523E+1	0.722E-3	0.269E-1	0.511E+1	+0.12E+0	+2
Se	0.243E+2	0.201E-1	0.142E+0	0.2423E+2	+0.10E+0	+ .41
Sn	0.103E+2	0.154E-2	0.393E-1	0.996E+1	+0.34E+0	+3
Sr	0.506E+1	0.190E-3	0.138E-1	0.522E+1	-0.16E+0	-3.0
Ti	0.487E+1	0.391E-3	0.198E-1	0.495E+1	-0.80E-1	-2
V	0.382E+1	0.521E-3	0.228E-1	0.398E+1	-0.16E+0	-4.0
Zn	0.515E+1	0.472E-3	0.217E-1	0.510E+1	+0.50E-1	+1

Data from 10 determinations. * Ca and Mg concentrations 100 ppm each.

TABLE 10. MATRIX 100 ∿1 RATIO*

	Mean	Variance	Standard Deviation	Added	Difference	% Error
Al	0.101E+1	0.443E-3	0.211E-1	0.973E+0	+ .370E-1	+3.8
Al	0.954E+0	0.231E-4	0.480E-2	0.973E+0	-0.190E-1	-2
As	0.197E+1	0.848E-3	0.291E-1	0.1992E+1	- .220E-1	-1.1
B	0.106E+1	0.268E-4	0.518E-2	0.1029E+1	+0.310E-1	+3.0
Ba	0.990E+0	0.932E-5	0.305E-2	0.996E+0	-0.600E-2	-0.6
Be	0.102E+1	0.185E-4	0.430E-2	0.1027E+1	-0.700E-2	-0.7
Cd	0.988E+0	0.134E-4	0.366E-2	0.998E+0	-0.100E-1	-1.0
Co	0.981E+0	0.168E-4	0.410E-2	0.998E+0	-0.170E-1	-1.7
Cr	0.103E+1	0.175E-4	0.418E-2	0.1015E+1	+0.150E-1	+1.5
Cu	0.997E+0	0.610E-5	0.247E-2	0.1006E+1	-0.900E-2	-0.9
Fe	0.101E+1	0.142E-4	0.377E-2	0.1030E+1	-0.200E-1	-2
Hg	0.971E+0	0.531E-4	0.728E-2	0.1001E+1	-0.300E-1	-3
Mn	0.101E+1	0.124E-4	0.352E-2	0.1006E+1	+0.400E-2	+0.4
Mn	0.987E+0	0.607E-4	0.779E-2	0.1006E+1	-0.190E-1	-2
Mo	0.102E+1	0.575E-4	0.758E-2	0.1000E+1	+0.200E-1	+2
Ni	0.101E+1	0.443E-4	0.665E-2	0.997E+0	+0.130E-1	+1.3
Pb	0.200E+1	0.593E-3	0.243E-1	0.1992E+1	+0.800E-2	+0.4
Pb	0.197E+1	0.240E-2	0.490E-1	0.1992E+1	-0.220E-1	-1.1
Sb	0.101E+1	0.451E-3	0.212E-1	0.1022E+1	-0.120E-1	-1.2
Se	0.491E+1	0.127E-2	0.356E-1	0.4845E+1	+0.650E-1	+1.3
Sn	0.209E+1	0.190E-2	0.436E-1	0.1992E+1	+0.980E-1	+5
Sr	0.117E+1	0.292E-4	0.540E-2	0.1043E+1	+ .127E+0	+12.2
Ti	0.994E+0	0.441E-5	0.210E-2	0.989E+0	-0.500E-2	- .5
V	0.988E+0	0.848E-5	0.291E-2	0.978E+0	+0.100E-1	+1.0
Zn	0.102E+1	0.326E-4	0.571E-2	0.1019E+1	+0.1E-2	+1

Data from 10 determinations. *Ca and Mg concentrations 100 ppm each.

TABLE 11. MATRIX 200 ∿l RATIO*

	Mean	Variance	Standard Deviation	Added	Difference	% Error
Al	0.546E+0	0.312E-3	0.177E-1	0.486E+0	+0.6E-1	+12
Al	0.517E+0	0.262E-4	0.511E-2	0.486E+0	+0.31E-1	+6.4
As	0.915E+0	0.416E-3	0.204E-1	0.996E+0	-0.81E-1	-8.1
B	0.520E+0	0.134E-4	0.367E-2	0.515E+0	-0.5E-2	+1
Ba	0.498E+0	0.526E-5	0.229E-2	0.498E+0	0	0
Be	0.517E+0	0.517E-5	0.227E-2	0.514E+0	+0.3E-2	+0.6
Cd	0.514E+0	0.665E-5	0.258E-2	0.499E+0	+0.15E-1	+0.6
Co	0.512E+0	0.543E-5	0.233E-2	0.499E+0	+0.13E-1	+2.6
Cr	0.512E+0	0.487E-5	0.221E-2	0.508E+0	+0.4E-2	+0.8
Cu	0.498E+0	0.352E-5	0.188E-2	0.503E+0	-0.5E-2	-1
Fe	0.528E+0	0.394E-5	0.199E-2	0.515E+0	+0.5E-2	+1
Hg	0.520E+0	0.182E-3	0.135E-1	0.500E+0	+0.2E-1	+4.0
Mn	0.505E+0	0.267E-5	0.163E-2	0.503E+0	+0.2E-2	+0.4
Mn	0.468E+0	0.691E-4	0.831E-2	0.503E+0	-0.35E-1	-7
Mo	0.500E+0	0.270E-4	0.520E-2	0.500E+0	0	0
Ni	0.501E+0	0.117E-4	0.341E-2	0.499E+0	+0.2E-2	+0.4
Pb	0.101E+1	0.102E-2	0.319E-1	0.996E+0	+0.14E-1	+1.4
Pb	0.104E+1	0.154E-2	0.393E-1	0.996E+0	+0.44E-1	+4.4
Sb	0.495E+0	0.145E-3	0.120E-1	0.511E+0	-0.16E-1	-3.1
Se	0.241E+1	0.991E-3	0.315E-1	0.2423E+1	-0.13E-1	-0.5
Sn	0.106E+1	0.156E-2	0.395E-1	0.966E+0	+0.64E-1	+6.4
Sr	0.592E+0	0.721E-5	0.268E-2	0.522E+0	+0.7E-1	+13.4
Ti	0.501E+0	0.144E-5	0.120E-2	0.495E+0	+0.6E-2	+1.2
V	0.495E+0	0.216E-5	0.147E-2	0.498E+0	-0.3E-2	-0.6
Zn	0.540E+0	0.323E-4	0.568E-2	0.510E+0	+0.3E-1	+5.9

Data from 10 determinations. *Ca and Mg concentrations 100 ppm each.

TABLE 12. MATRIX 1000 ∿1 RATIO*

	Mean	Variance	Standard Deviation	Added	Difference	% Error
Al	0.113E+0	0.449E-3	0.212E-1	0.97E-1	+0.16E-1	+16
Al	0.109E+0	0.166E-4	0.407E-2	0.97E-1	+0.12E-1	+12
As	0.125E+0	0.584E-3	0.242E-1	0.199E+0	-0.74E-1	-37
B	0.113E+0	0.784E-5	0.280E-2	0.103E+0	+0.10E-1	+10
Ba	0.102E+0	0.615E-6	0.784E-3	0.100E+0	+0.20E-2	+20
Be	0.104E+0	0.230E-6	0.480E-3	0.103E+0	+0.10E-2	+10
Cd	0.106E+0	0.137E-5	0.117E-2	0.100E+0	+0.60E-2	+6
Co	0.108E+0	0.113E-5	0.106E-2	0.100E+0	+0.80E-2	+8
Cr	0.115E+0	0.183E-5	0.135E-2	0.102E+0	+0.13E-1	+13
Cu	0.113E+0	0.599E-6	0.774E-3	0.101E+0	+0.12E-1	+12
Fe	0.109E+0	0.132E-5	0.115E-2	0.103E+0	+0.60E-2	+6
Hg	0.113E+0	0.131E-3	0.114E-1	0.100E+0	-0.13E-1	-13
Mn	0.103E+0	0.313E-6	0.559E-3	0.101E+0	+0.20E-2	+2
Mn	0.143E+0	0.724E-4	0.851E-2	0.101E+0	+0.42E-1	+42
Mo	0.122E+0	0.250E-4	0.500E-2	0.100E+0	+0.22E-1	+27
Ni	0.104E+0	0.502E-5	0.224E-2	0.100E+0	+0.40E-2	+4
Pb	0.200E+0	0.169E-3	0.130E-1	0.99E+0	+0.10E-2	+5
Pb	0.277E+0	0.809E-3	0.284E-1	0.199E+0	+0.78E-1	+39
Sb	0.712E-1	0.424E-3	0.206E-1	0.102E+0	-0.31E-1	+30
Se	0.428E+0	0.231E-3	0.152E-1	0.485E+0	-0.57E-1	-12
Sn	0.345E+0	0.899E-3	0.300E-1	0.398E+0	-0.53E-1	-13
Sr	0.131E+0	0.424E-5	0.651E-3	0.120E+0	+0.11E-1	+9
Ti	0.107E+0	0.281E-6	0.449E-3	0.990E-1	+0.80E-2	+8
V	0.280E-1	0.719E-7	0.268E-3	0.350E-1	-0.70E-2	-20
Zn	0.106E+0	0.734E-6	0.857E-3	0.102E+0	+0.40E-2	+4

Data from 10 determinations. *Ca and Mg concentrations 100 ppm each.

TABLE 13. MATRIX 2500 ∿1 RATIO *

	Mean	Variance	Standard Deviation	Added	Difference	% Error
Al	0.246E-1	0.152E-4	0.390E-2	0.200E-1	+0.46E-2	+23
As	0.275E-1	0.432E-3	0.208E-1	0.400E-1	-0.125E-1	-31
B	0.374E-1	0.244E-5	0.156E-2	0.400E-1	-0.26E-2	-6
Ba	0.217E-1	0.429E-7	0.207E-3	0.200E-1	+0.17E-2	+8
Be	0.227E-1	0.224E-7	0.150E-3	0.210E-1	+0.17E-2	+8
Cd	0.233E-1	0.131E-5	0.115E-2	0.200E-1	+0.33E-2	+16
Co	0.234E-1	0.142E-5	0.119E-2	0.200E-1	+0.34E-2	+17
Cr	0.254E-1	0.134E-5	0.116E-2	0.200E-1	+0.54E-2	+27
Cu	0.208E-1	0.424E-6	0.651E-3	0.200E-1	+0.8E-3	+4
Fe	0.227E-1	0.512E-6	0.716E-3	0.200E-1	+0.27E-2	+14
Hg	0.438E-1	0.736E-4	0.858E-2	0.400E-1	+0.38E-2	+19
Mn	0.222E-1	0.405E-7	0.201E-3	0.200E-1	+0.22E-2	+11
Mo	0.324E-1	0.166E-4	0.407E-2	0.400E-1	-0.76E-2	-12
Ni	0.237E-1	0.666E-5	0.258E-2	0.200E-1	+0.37E-2	+18
Pb	0.569E-1	0.257E-3	0.160E-1	0.400E-1	+0.169E-1	+42
Sb	0.447E-1	0.262E-3	0.162E-1	0.400E-1	+0.47E-2	+12
Se	0.126E+0	0.967E-4	0.984E-2	0.100E+0	+0.26E-1	+26
Sn	0.105E+0	0.128E-2	0.358E-1	0.104E+0	+0.1E-2	+1
Sr	0.267E-1	0.204E-7	0.143E-3	0.210E-1	+0.57E-2	+27
Ti	0.220E-1	0.153E-6	0.391E-3	0.200E-1	+0.20E-2	+10
V	0.621E-2	0.566E-7	0.238E-3	0.500E-2	+0.121E-2	+24
Zn	0.147E-1	0.205E-5	0.143E-2	0.100E-1	+0.47E-2	+47

Data from 10 determinations. *Ca and Mg concentrations 100 ppm each.

TABLE 14. DETECTION LIMITS (µg/l) QA-137 SYSTEM*

		1*	2*	3*	4*
Al	396.15	7	4	4	20
As	193.76	50	50	50	250
B	249.68	4	3	3	15
Ba	455.40	0.2	0.1	0.1	0.5
Be	313.04	0.06	0.1	0.1	0.5
Cd	226.50	1	1	2	10
Co	238.89	2	1	1	5
Cr	267.72	2	1	1	5
Cu	324.75	2	0.6	1	5
Fe	259.94	1	0.8	0.6	3
Hg	253.65	20	15	15	45
Mn	257.61	0.3	0.2	0.1	0.5
Mo	287.15	7	6	6	30
Ni	231.60	4	4	4	20
Pb	220.35	20	20	20	100
Sb	206.84	20	20	20	100
Se	196.09	20	20	20	100
Sn	303.41	80	50	50	250
Sr	407.77	0.1	0.05	0.01	0.05
Ti	334.90	6	0.5	0.4	2
V	292.40	5	0.3	0.2	1
Y	371.03	5	0.5	0.5	2
Zn	213.86	3	3	3	6

* Detection limit is the analyte concentration required to produce a signal two times the standard deviation at the analytical line.

1. Values before modifications.
2. Values after modifications.
3. Values with 100 µg/ml Ca and Mg matrix.
4. LQD is the lowest quantitatively determinable concentration or five times the detection limit.

TABLE 15. SEWAGE EFFLUENT V-11

	ICP-A	INAA	AA	ICP-V
Ag	<5E-9	*NR	NR	NR
Al	1.51E-6	1.6E-6	1.53E-6	9.20E-7
As	<5E-8	6.0E-9	NR	NR
B	2.30E-7	NR	NR	NR
Ba	1.3E-8	NR	NR	NR
Be	<5E-9	NR	NR	NR
Ca	4.29E-5	3.2E-5	NR	NR
Cd	4.7E-8	4.8E-8	4.8E-8	4.3E-8
Co	3E-9	1.2E-9	NR	NR
Cr	1.09E-7	6.2E-8	1.18E-7	1.27E-7
Cu	7.0E-8	NR	1.09E-7	1.05E-7
Fe	6.08E-7	6.3E-7	6.05E-7	6.24E-7
Hg	1.1E-8	1.6E-8	NR	NR
Mg	1.42E-5	1.3E-5	NR	NR
Mn	1.38E-7	1.4E-7	1.38E-7	1.28E-7
Mo	<5E-9	2.6E-9	NR	NR
Ni	3.17E-7	NR	3.06E-7	2.68E-7
Pb	2.20E-7	NR	2.50E-7	1.93E-7
Sb	2.2E-8	2.6E-7	NR	NR
Se	<5E-8	NR	NR	NR
Sn	<5E-8	NR	NR	NR
Sr	1.97E-7	2.5E-7	NR	NR
Ti	<5E-9	NR	NR	NR
V	<5E-9	NR	NR	NR
Y	<5E-9	NR	NR	NR
Zn	2.19E-7	2.0E-7	2.16E-7	2.27E-7

*NR - Not reported.

TABLE 16. SEWAGE EFFLUENT V-12

	ICP-A	INAA	AA	ICP-V
Ag	<5E-9	NR	NR	NR
Al	1.72E-6	1.8E-6	1.74E-6	1.07E-6
As	<5E-8	7.8E-9	NR	NR
B	2.71E-7	NR	NR	NR
Ba	1.6E-8	2.8E-8	NR	NR
Be	<5E-9	NR	NR	NR
Ca	51.6E-5	4.0E-5	NR	NR
Cd	5.9E-8	5.1E-8	5.8E-8	5.0E-8
Co	1.1E-8	1.4E-9	NR	NR
Cr	1.29E-7	8.2E-8	1.39E-7	1.44E-7
Cu	9.0E-8	NR	1.17E-7	1.20E-7
Fe	6.59E-7	5.8E-7	7.23E-7	7.32E-7
Hg	2.0E-8	1.6E-8	NR	NR
Mg	1.60E-5	1.4E-5	NR	NR
Mn	1.58E-7	1.7E-7	1.55E-7	1.50E-7
Mo	1.0E-8	2.7E-9	NR	NR
Ni	3.71E-7	NR	3.43E-7	3.17E-7
Pb	2.91E-7	NR	3.00E-7	2.26E-7
Sb	1.8E-8	3.4E-9	NR	NR
Se	<5E-8	NR	NR	NR
Sn	<5E-8	NR	NR	NR
Sr	2.25E-7	2.5E-7	NR	NR
Ti	5E-9	NR	NR	NR
V	<5E-9	NR	NR	NR
Y	<5E-9	NR	NR	NR
Zn	2.71E-7	2.2E-7	2.51E-7	2.62E-7

NR - Not reported.

TABLE 17. SEWAGE INFLUENT V-13

	ICP-A	INAA	AA	ICP-V
Ag	1.1E-8	1.8E-8	NR	NR
Al	3.54E-6	6.6E-6	3.094E-6	3.133E-6
As	9.1E-8	6.6E-9	NR	NR
B	2.21E-7	NR	NR	NR
Ba	1.60E-7	1.4E-7	NR	NR
Be	<5E-9	NR	NR	NR
Ca	5.72E-5	4.4E-5	NR	NR
Cd	1.37E-7	1.4E-7	1.39E-7	1.30E-7
Co	5.0E-8	4.7E-9	NR	NR
Cr	4.67E-7	3.2E-7	4.55E-7	4.33E-7
Cu	4.58E-7	NR	4.72E-7	4.62E-7
Fe	6.30E-6	6.0E-6	6.230E-6	6.539E-6
Hg	1.40E-7	4.7E-8	NR	NR
Mg	1.87E-5	1.8E-5	NR	NR
Mn	2.85E-7	3.0E-7	2.94E-7	2.70E-7
Mo	<5E-8	1.5E-8	NR	NR
Ni	1.052E-6	NR	1.075E-6	1.037E-6
Pb	7.85E-7	NR	8.09E-7	6.91E-7
Sb	4.2E-8	1.2E-8	NR	NR
Se	<5E-8	1.1E-9	NR	NR
Sn	<5E-8	NR	NR	NR
Sr	2.62E-7	3.6E-7	NR	NR
Ti	5.7E-8	NR	NR	NR
V	<5E-8	8.0E-9	NR	NR
Y	<5E-8	NR	NR	NR
Zn	1.309E-6	1.0E-6	1.211E-6	1.170E-7

NR - Not reported.

TABLE 18. SEWAGE INFLUENT V-14

	ICP-A	INAA	AA	ICP-V
Ag	1.3E-8	1.9E-8	NR	NR
Al	4.273E-6	8.1E-6	4.515E-6	3.735E-6
As	1.15E-7	4.4E-9	NR	NR
B	2.55E-7	NR	NR	NR
Ba	1.86E-7	1.6E-7	NR	NR
Be	<5E-9	NR	NR	NR
Ca	6.62E-5	4.6E-5	NR	NR
Cd	1.59E-7	1.6E-7	1.61E-7	1.52E-7
Co	5.5E-8	5.8E-9	NR	NR
Cr	5.42E-7	3.9E-7	5.26E-7	5.59E-7
Cu	5.43E-7	NR	5.74E-7	5.40E-7
Fe	7.482E-6	6.7E-6	7.090E-6	7.617E-6
Hg	1.43E-7	8.8E-9	NR	NR
Mg	2.17E-5	2.2E-5	NR	NR
Mn	3.31E-7	3.6E-7	3.32E-7	3.15E-7
Mo	<5E-8	8.8E-9	NR	NR
Ni	1.282E-6	NR	1.250E-6	1.220E-6
Pb	8.95E-7	NR	9.57E-7	8.04E-7
Sb	1.4E-8	1.4E-8	NR	NR
Se	<5E-8	1.4E-9	NR	NR
Sn	<5E-8	NR	NR	NR
Sr	3.04E-7	4.4E-7	NR	NR
Ti	6.5E-7	7.7E-7	NR	NR
V	<5E-9	1.2E-8	NR	NR
Y	<5E-9	NR	NR	NR
Zn	1.518E-6	1.3E-6	1.404E-6	1.339E-6

NR - Not reported.

TABLE 19. STANDARD V-15

	ICP-A	INAA	AA	ICP-V
Ag	<5E-9	NR	NR	NR
Al	7.83E-7	8.1E-7	7.00E-7	7.00E-7
As	1.14E-7	7.8E-8	8.8E-8	NR
B	1.4E-8	NR	NR	NR
Ba	8E-9	NR	NR	NR
Be	<5E-9	NR	NR	NR
Ca	NR	2.9E-5	NR	NR
Cd	2.0E-8	2.2E-8	2.0E-8	1.8E-8
Co	4E-9	4.4E-10	NR	NR
Cr	9.7E-8	7.5E-8	9.7E-8	1.00E-7
Cu	9.4E-8	NR	7.8E-8	8.0E-8
Fe	6.21E-7	6.2E-7	6.27E-7	5.90E-7
Hg	1.5E-8	1.2E-8	NR	NR
Mg	NR	NR	NR	NR
Mn	1.23E-7	1.3E-7	1.15E-7	1.20E-7
Mo	<5E-9	NR	NR	NR
Ni	9E-9	NR	NR	<2.0E-8
Pb	1.36E-7	NR	1.12E-7	9.5E-8
Sb	2.0E-8	6.8E-10	NR	NR
Se	<5E-8	1.7E-8	1.9E-8	NR
Sn	<5E-8	NR	NR	NR
Sr	<5E-9	NR	NR	NR
Ti	<5E-9	NR	NR	NR
V	<5E-9	NR	NR	NR
Y	<5E-9	NR	NR	NR
Zn	1.13E-7	1.2E-7	1.01E-7	1.02E-7

NR - Not reported.

TABLE 20. ICP REFERENCE SAMPLE

	ICP	INAA
Ag	1.51E-7	1.4E-7
Al	9.83E-7	NR
As	7.5E-8	6.8E-10
B	4.91E-7	NR
Ba	9.77E-7	7.8E-7
Be	8.8E-8	NR
Ca	2.08E-5	2.7E-5
Cd	4.23E-7	3.8E-7
Co	4.58E-7	3.3E-7
Cr	3.06E-7	1.8E-7
Cu	5.04E-7	NR
Fe	2.430E-6	2.4E-6
Hg	7.6E-8	2.9E-8
Mg	4.73E-6	NR
Mn	4.30E-7	4.6E-7
Mo	1.074E-6	7.2E-7
Ni	5.48E-7	NR
Pb	5.409E-6	NR
Sb	<5E-9	1.2E-9
Se	5.8E-8	NR
Sn	3.70E-7	3.2E-7
Sr	2.9E-8	NR
Ti	6.02E-7	NR
V	5.33E-7	4.1E-7
Y	2.27E-5	NR
Zn	3.08E-6	2.1E-6

NR - Not reported.

TABLE 21. 124 DRINKING WATER

	ICP	INAA
Ag	<5E-9	NR
Al	2.4E-8	4.5E-8
As	<5E-8	NR
B	1.50E-7	NR
Ba	8.31E-6	7.4E-6
Be	<5E-9	NR
Ca	5.46E-5	3.8E-5
Cd	<5E-9	NR
Co	<5E-9	2.6E-9
Cr	<5E-9	1.3E-9
Cu	3.6E-8	NR
Fe	5.9E-8	3.2E-7
Hg	<5E-9	3.0E-8
Mg	2.20E-5	2.1E-5
Mn	<5E-9	1.8E-9
Mo	<5E-9	NR
Ni	<5E-9	NR
Pb	<5E-8	NR
Sb	<5E-9	3.5E-10
Se	<5E-8	NR
Sn	<5E-8	NR
Sr	3.24E-6	3.2E-6
Ti	<5E-9	NR
V	<5E-9	NR
Y	<5E-9	NR
Zn	9.5E-8	9.0E-8

NR - Not reported.

BIBLIOGRAPHY

Dickinson, G. W., and V. A. Fassel. 1969. Emission Spectrometric Detection of the Elements at the Nanogram per Milliliter Level Using Induction Coupled Plasma Excitation. Analytical Chemistry. 41: 1021.

Padobnik, B., et al. 1965. The Flame Photometric Determination of Li, Na, K, Ca, Mg, and Sr in Natural and Mineral Waters. Mikrochim Acta. 1074.

Steiner, R. L. 1969. Rapid Direct Reading Determination of Elements in Industrial Waste Water. Environmental Science Technology. 3: 1192.

Wendet, R. H., and V. A. Fassel. 1965. Induction Coupled Plasma Spectrometric Excitation Source. Analytical Chemistry. 37: 920.

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16. ABSTRACT

Reduction of stray light in the inductively coupled plasma emission spectrometer (ICPES) has greatly increased its reliability as a technique for the multielemental analysis of water. Because of interferences introduced by matrix elements, reliable analysis of some less-sensitive elements has been impractical at concentrations of ≤ 200 ppb. After surfaces in the secondary optical system were painted to prevent light scatter and the aperture at the primary lens was reduced in the ICPES, some interference corrections were reduced by more than one order of magnitude. Reduced interferences in the ICPES along with improved corrections by adding exact concentrations of calcium and magnesium to reagent blanks run during sample analyses have definitely improved the accuracy of this multielement analysis system. Observed background changes caused by the presence of magnesium were compensated for by adding matrix elements to calibration standards. Alcohol was added to standards, reagent blanks, and samples to overcome problems of background change during analysis of samples of unknown organic content such as municipal sewage.

17. KEY WORDS AND DOCUMENT ANALYSIS

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