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SIMULTANEOUS MULTIELEMENT ANALYSIS OF LIQUID SAMPLES

BY

INDUCTIVELY COUPLED ARGON PLASMA ATOMIC-EMISSION SPECTROSCOPY

AT

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION V

CENTRAL REGIONAL LABORATORY

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1.0 Scope and Application

1.1 This method is applicable to fresh water samples including drinking waters, surface waters, domestic and industrial waste effluents for the analyses of total and dissolved metals of the twenty elements listed in Table 1.

1.2 The detection limits for the 20 elements are listed in Table 2. These data represent the mean values determined on 5 days, over a 3 month period. Each individual detection limit was determined by averaging 10 consecutive 10 second exposures of each element. The numerical values are in µg/l and each is the concentration of that element necessary to produce a signal twice the standard deviation of the background noise.

The two sigma detection limit, defined above, is in common use and produces a figure of merit by which various analytical appproaches may be compared, but, like most detection limits, are almost never at a level that can be accurately reported. A more useful approach, which is similar to the Lower Optimum Concentration Range (LOCR) reported for atomic absorption use[1], is the Lowest Quantitative Determinable Concentration (LQD)[2]. The LQD is defined as the amount of material necessary to produce a signal that is 10X the standard deviation of the noise (i.e. 5X detection limit). The LQD for the 20 elements are also reported in Table 2

1.3 The relative standard deviation (RSD) of a 1 mg/l standard for all elements is of the order of 1% over 5-10 minute periods and 2-4% over the course of an 8 hour day. A typical set of RSDs is presented in Table 3 and demonstrates variations for 10 consecutive 10 second integration periods.

1.4 The working ranges for all twenty elements are from the LQD to above 100 ppm. An illustration of these ranges are presented in Table 4, the value reported is the average of four measurements made on the same day over an 8 hour period. In the case of calcium two elemental lines are simultaneously employed and the linear dynamic range is increased to at least 1000 mg/l. For all elements

the 100 mg/l upper limit doesn't represent the actual upper limit of linear instrumental response for any element. Instead the limiting value indicates to an operator the need for careful judgement to insure that overlapping effects from other elements are absent. (See Section 4) But this working range does define sample concentration values normally reported in day-to-day operation.

1.5 For those procedures and applications described in this manuscript, the degree of operator skill necessary to perform analysis using an ICAP-AES is similar to that required for operation of an atomic absorption spectrometer (AAS). However, the initial set up of an installation, reviewing of data and routine instrumental problem evaluation would probably still require ready access to an experienced spectroscopist.

1.6 Approximately 50 digested or otherwise prepared samples and 10 quality control samples can be run per hour. At this sample run rate a realistic analysis output of between 5000 and 8000 analysis per man day can be expected. These huge numbers assume all twenty elements are requested by the sample originator. This is almost never the case. Furthermore, thousands of analysis per day assume no sample pretreatment. In fact the majority of sample handling time is associated with sample digestion. This situation will not change with the implementation of the ICAP-AES. Lastly, the transfer of completed analyses from the teletype sheet to the report form currently being used will be no faster with the plasma system than it is now and constitutes a significant fraction of the operator's time.

2.0 Summary of the Method

Liquid samples are aspirated into a high temperature argon plasma produced by inductively coupling radio-frequency electromagnetic radiation to the argon gas.[3] The high temperature[4] of the plasma ($\sim$10,000^{o}K) causes desolvation, molecular breakdown, atomization, and/or ionization and excitation of the metals in solution. The resultant radiation produced as the excited atoms relax is passed

through the entrance slit of a dispersive device where it is separated into discrete wavelengths. The intensity of each of the characteristic wavelengths is associated with a metal and is measured by a photomultiplier tube. The photocurrent is transformed, by reference to standards, to concentration values which are recorded.

3.0 Sample Handling and Preservation

3.1 General

Samples are collected, filtered (for dissolved metals), preserved and digested according to approved EPA procedures.[1]

3.2 Sample Handling

Samples are collected in polyethylene containers, preserved with 10ml of 50% HNO_3/l and sealed with plastic caps, containing a polyethylene insert.

3.3 Sample Digestion

For total metal analysis[1] samples are digested by the addition of 3 ml of conc. HNO_3 to 100 ml of representative sample in a Griffin beaker. The beaker is covered with a ribbed watch glass and carefully heated to dryness on a hot plate. After cooling, 3 ml of conc. HNO_3 is added and the beaker is heated until the acid mixture is brought to a gentle boil. At this point, to improve sample disolution, 5 ml of 1:1 HCl is added to the warm HNO_3 mixture and the volumn is brought to 100 ml with distilled deionized water.

4.0 Interferences

4.1 Introduction

The ICAP is in many ways an ideal excitation source. The 10,000^{o}K operating temperature is twice as hot as any chemical flame and therefore produces significantly larger numbers of excited atoms. Further the plasma gas, argon, is chemically inert and spectroscopically simple. The combination of these characteristics afford the ICAP an interference free existence when compared with flames, arcs and sparks[2]. Still there are some concerns that must be considered in the installation and operation of ICAP spectrometer system. These are discussed below.

4.2 Chemical Interferences

The ICAP is virtually free of the classical chemical interferences[5,6] associated with both flame AAS and flame atomic emission spectroscopy (AES). Molecular formation among solution or gaseous atoms exposed to 10,000°K is not likely and has not been observed. Carrier gas induced chemical reactions are also very small because argon is inert.

4.3 Ionization Interferences

Changes in emission intensities due to the presence or absence of easily ionized material (i.e. Na, K, La) has not been reported[6,7] nor does this work indicate such problems exist.

4.4 Positional stability of radiation source

The positional stability of the plasma is a very important consideration because very small changes in plasma location can easily cause significant changes in analytical results. A partial list of variables which would cause the position or the area of the plasma to change is as follows:

1. Movement of plasma torch
2. Movement of coupling coils
3. Geometry of annular sample channel
4. Variations in either forward or reflected RF power
5. Gas pressure
6. Gas flow
7. Gas purity
8. Changes in inductance coupling
9. Solution viscosity changes
10. Changes in sample uptake rate
11. Unknown sources

In the thousands of analyses so far performed, none of these problems have proved to be significant. However, because these problems can be present, and can appear at any time, a comprehensive quality assurance audit procedure is included as a part of this method. The audits run to date show excellent long term precision and daily precision of a 1.0 mg/l solution for all elements to be less than 5% with no restandardization over a 10 hour period.

4.5 Unwanted Light Interferences

There are two classes of light interferences which may affect each channel of the instrument. They are:

1. Direct spectral overlaps.
2. Indirect and/or stray light additions.

In emission spectroscopy the possibility of two or more elements having overlapping lines is an important consideration. In a direct reader this spectral type of interference is predictable and can be empirically identified by measuring the highest reported concentration of a particular element in the absence of all other elements. The effect on all other elements is thus recorded. If problems are observed these data can then be factored into the calculations.

A more uncommon type of direct spectral interference happens when two lines are extremely close but do not normally overlap unless one of the elements is extremely concentrated. The line broadening or reversal problem is identified in the same manner as a direct spectral interference and can be controlled by a careful specification of linear dynamic ranges.

The second class of light interference addresses itself to the observation that any extraneous light[3] introduced into the system may create poor results. The most serious problems are associated with the introduction of unwanted light which is unique to the sample and not the blank. For example an emission resulting from a concentrated sample might reflect from some shiny surface within the direct reader and cause an error. Any photomultiplier tube which detects any of this "stray" light will read that intensity as element intensity and therefore concentration. Stray problems of this nature stem from three principle sources:

1. An imperfection in grating.
2. A reflective surface is exposed inside the spectrometer.
3. A mechanical breakdown or lack of some internal light shielding.

In those cases where it has been determined that spectral corrections of the type stated above are needed, they have been made. Generally speaking these corrections are small, apply to only a few elements, and are easily verified.

5.0 Apparatus

5.1 Direct Reader

The Jarrell-Ash Plasma Atom Comp 750 equipped with exit slits listed in Table 1 comprises the basic direct reader. Each slit is observed by a photomultiplier (PM) with associated power supply and picoampmeter. The details of the spectrometer are included in J-A Manual Model 75 Atom Comp section A1 and D1.

5.2 Plasma Assembly

The plasma assembly is composed of a nebulizer[9], spray chamber[10], torch[11], coupling box and power supply. The power supply and coupling box are supplied by the CCA Corporation and Henry Radio Corporation, respectively, through Jarrell-Ash Division of Fisher Scientific Company. The nebulizer is a right angle pneumatic aerosol generator constructed of teflon and glass (with external brass fittings). The plasma torch is all quartz and of standard design which separates coolant argon, plasma argon and accepts nebulized solution. The spray chamber is modeled after the conical chamber described by Fassel.[10]

5.3 Argon Gas

Argon is supplied from a liquid tank (Linda GP45). The use of liquid is preferable because it is cheaper, less labor is involved in moving tanks and the quality of argon is superior to that from low grade gaseous tanks.

6.0 Reagents

6.1 Water and Acids

Distilled deionized water is used in all cases. All acids are analytical grade.

6.2 Standards

Standards are prepared monthly (or as needed) by the addition of 0.500ml of 1000 mg/l stock solutions of all metals in Table 1 (except Ag which is handled separately) to a 500 ml volumetric flask. The solutions (except Ag) are acidified with 25 ml of 1:1 HCl. Silver is prepared daily in 5% HNO_3. A blank is prepared and run with reference to distilled water. Generally, no differences between the prepared blank and distilled water have been observed and therefore samples are run by reference to distilled water.

7.0 Procedure

7-1 Turn on argon gas

7-2 Turn on cooling water

7-3 Turn on R-F power supply (10 min. warm up)

7-4 Ignite plasma using Tesla coil

7-5 Adjust forward power to 1.0KW

7-6 Adjust reflected power to less than one W.

7-7 Turn on teletype

7-8 Adjust entrance refractor plate such that Hg-#13 reads a maximum on profile meter.

7-9 Choose a Basic Data Set to be used and set time and date.

7-10 With plasma light blocked measure the dark currents of all channels to be used.

7-11 With plasma light blocked measure the white light response of system.

7-12 Uncover plasma, redo 7-6 and record in intensity units blank water being aspirated.

7-13 Use the two point standardization procedure.

a. List standards needed - command L
b. Clear computer memory - command J
c. Run each standard in duplicate - command EGG
d. Record each standard - command N

e. Standardize spectrometer for all standards - command S
f. Record gains and offsets of standard curves - command W
g. Run (EGC) and record the 1000µg/l standard. This standard should read 1000 ± 2% for all elements. If any element does not read within the specified range repeat sequence 7-13.

7-14 Create the operating commands for the days work (i.e. QEGIGIAC will run a sample twice and print both runs in raw intensity and average both runs and print the average in concentration units).

7-15 Run the 1000µg/l standard using the operating command for that day.

7-16 Run the blank used. Check against distilled water.

7-17 Run a sample - allow at least a 50 second wash.

7-18 Every 1/2 hour or 30 samples rerun 1000 ug/l standard.

Every 1 hour or 60 samples rerun 1000 ug/l standard and blank.

7-19 During every day of operation collect in addition to the data called for above:

a. A complete 10 x 10 sec. evaluation of dark current.
b. A complete 10 x 10 sec. evaluation of white light.
c. A complete 10 x 10 sec. evaluation of detection limits.
d. Compile and update the data collected in 7-18.

8.0 Calculations

8.1 Basic Approach

Intensity data for the blank and the mixed 1000µg/l standard are stored in the computer after being entered by procedures outlined in section 7. A value of "zero" is assigned to the intensity associated with the blank and a value of 1000µg/l for the intensity corresponding to that solution. By reference to these data the computer then assigns concentration values to unknown intensities. The linear range and validity of this approach can be seen in Table 4. Background corrections are made by reference to the standard Dynamic Background Correction package supplied by the vendor. The use of an Internal Standard(s) is also a possibility but none were used in these comparisons because no improvements in results have been observed.

8.2 Readout of Computation

The photocurrent output is frequently sampled (60/sec) and digitized by a PDP8M computer. The computer can print intensity (I), ratioed intensity (R) baseline corrected intensity (B) or concentration (C) using a standard SR33 teletype. The format of the output and other details are defined by a Basic Data Set. All pertinent details necessary for the creation and use of the Basic Data Set are defined in Operation Instructions for 8K Mark II System (C01-08P-B001, 08T, 08D, 08B).

9.0 Comparability Data

9.1 Accuracy

The accuracy for 15 of the 20 elements has been verified by reference to "standard" water samples supplied to our laboratory by the U.S. EPA, the U.S. Geological Survey (U.S.GS) and the National Bureau of Standards (NBS). The U.S. EPA comparisons for 13 metals in 5 different solutions are presented in Tables 5, 6, 7, 8 and 9. No problems from the LQD to the upper concentrations present were observed. Note that any value below the LQD is presented here only for comparison and would not normally be reported. A similar conclusion can be drawn from the summary of data on two U.S.GS samples for 15 elements presented in Table 10 and the 6 elements in the NBS material presented in Table 11. The U.S.GS material was certified by a round robin evaluation and precision measurements are reported with the mean value. The U.S. EPA and NBS reference materials do not have such precision values available at this time. A fourth material analyzed is the AQC spike or reference sample used by the Metals Section of the CRL to ascertain daily performance. These data are presented in Table 12. Again the comparison between referee and proposed analytical method results is acceptable for all metals analyzed.

9.2 Comparability to Reference Method

The reference materials used in the accuracy studies were prepared in relatively pure waters and might not properly reflect problems associated with real samples. Direct comparison to AAS was accomplished by two studies called Study I and II. In the first study to compare the results of ICAP to the AAS reference methods 18 elements were investigated. (No reference method exists for Yttrium and Boron was referenced to the Curcumin Method.[1]) In this approach four different water matrices (laboratory, lake, river and effluent water) were spiked with the 18 metals at two concentration levels. Concentrations were chosen to fall into the optimum range for AAS analyses. The samples were chosen to cover a broad spectrum of sample types to approximate samples encountered in our NPDES work. The samples were digested following EPA procedures[1] and spiked at two concentration levels. After standing for 48 hours the samples were filtered to insure that homogenous aliquots could be taken. A set of 8 aliquots were analyzed by AAS for each element on 3 different days over approximately 6 weeks. An equivalent set was analyzed by an ICAP on 6 different days over the same period. The results of this study are presented in Tables 13 through 32. Two total study summaries are also presented in Tables 33 and 34. The average recovery data in the latter Table would clearly indicate no problems with these data. The linear correlation presented in Table 33 is the linear slope of a plot of results by AAS (y) vs. ICAP (x). An ideal match would result in a slope of 1.00 and have an intercept of 0. The data document a satisfactory comparison of the two methods.

In the second study of comparability 22 pairs of samples which were part of the normal laboratory AQC program were reanalyzed by an ICAP. Each sample pair is a sample and that sample spiked with the routine AAS spike solution. This

spike solution contains Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The results reported in Tables 35 to 57 represent a comparison of ICAP to AAS for all metals in the AQC spike requested by the sample originator for that sample. All sample and spike pairs investigated are included. The total Study II comparison in terms of percent recovery is given in Table 57. As is the case in the previous studies, the methods are comparable.

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Table No.

Study II - Samples and Spiked Samples

35	STP #1070
36	STP #3392
37	STP #01142
38	STP #01172
39	STP #1298
40	STP #13757
41	STP #21361
42	STP #21324
43	STP #3443
44	Electric Power Generating #1227
45	Electric Power Generating #1248
46	Dirty River #21507
47	Military Arsenal #1346
48	Drinking Water #1130
49	General Industrial #1290
50	General Industrial #1324
51	Automotive Industry #7484
52	General Industrial #1249
53	Tire Company #8446
54	Paper Industry #7007
55	Communications Industry #0018
56	Communications Industry #3494
57	Summary of % Recovery in Study II

	Name	λ in nm		Name	λ in nm
Ag	Silver	328.1	Mg	Magnesium	279.6
Al	Aluminum	396.2	Mn	Manganese	257.6
B	Boron	249.7	Mo	Molybdenum	203.8
Ba	Barium	233.5	Ni	Nickel	341.5
Ca(1)	Calcium	393.4	Pb	Lead	220.3
Ca(2)	Calcium	364.4			
Cd	Cadmium	226.5	Sn	Tin	190.0
Co	Cobalt	238.9	Ti	Titanium	334.7
Cr	Chromium	267.7	V	Vanadium	309.3
Cu	Copper	324.8	Y	Yttrium	417.8
Fe	Iron	259.5	Zn	Zinc	213.9

ELEMENT LIST AND ANALYTICAL LINES

TABLE I

A list of the elements currently analyzed by the CRL ICAP-AES instrument and the emission line chosen for each element.

	D.L. µg/l	LQD µg/l		D.L. µg/l	LQD µg/l
Ag	4	20	Mg	<0.5	1
Al	7	35	Mn	1	5
B	3	15	Mo	5	25
Ba	1	5	Ni	15	75
Ca	<0.5	1	Pb	12	60
Cd	2	10	Sn	12	60
Co	4	20	Ti	1	5
Cr	1	5	V	1	5
Cu	1	5	Y	~1	5
Fe	2	10	Zn	1	5

*Five Runs over Three Months

MEAN* DETECTION LIMITS

AND LOWEST QUANTITATIVELY DETERMINABLE CONCENTRATIONS (LQD)

TABLE 2

The detection limit (D.L.) is the amount of material that will produce a signal that is twice as large as the standard deviation of the noise. The lowest quantitative determinable concentration (LQD) is 5 times the D.L. and is the lowest concentration one can expect to report.

	% RSD		% RSD
Ag	1.8	Mg	1.1
Al	0.8	Mn	1.1
B	0.8	Mo	1.0
Ba	0.9	Ni	0.5
Ca	0.5	Pb	0.4
Cd	0.9	Sn	1.2
Co	1.0	Ti	1.1
Cr	0.8	V	1.1
Cu	1.2	Y	1.0
Fe	1.0	Zn	0.8

TYPICAL RELATIVE STANDARD DEVIATION

AT 1 mg/l

TABLE 3

These RSDs are typical variations for 10 consecutive intergration periods. Data of this type is recorded at the beginning and end of each day's operation.

	100 mg/l			100 mg/l
Ag	96 ± 1		Mg	106 ± 2
Al	95 ± 1		Mn	99 ± 3
B	100 ± 1		Mo	102 ± 2
Ba	106 ± 3		Ni	100 ± 1
Ca(1)	97 ± 1		Pb	104 ± 1
Ca(2)	989 ± 2 *			
Cd	105 ± 4		Sn	105 ± 4
Co	97 ± 3		Ti	100 ± 1
Cr	96.2 ± 0.4		V	99 ± 5
Cu	95 ± 7		Y	100 ± 2
Fe	94 ± 2		Zn	96 ± 2

* Ca(2) at 1000mg/l

Average of 4 runs over 6 hours

Overall Average 100 ± 4 ppm

DEMONSTRATION OF LINEAR RANGE

TABLE 4

	USEPA µg/l	ICAP µg/l		USEPA µg/l	ICAP µg/l
Ag			Mg		
Al	25	16	Mn	13	12
B			Mo		
Ba			Ni		
Ca			Pb	28	39
Cd	1.8	<2	Sn		
Co			Ti		
Cr	9.2	4.2	V		
Cu	9.0	6			
Fe	18	16.0	Zn	10	9.9

U.S. EPA REFERENCE MATERIAL 1171 - 1

TABLE 5

	USEPA µg/l	ICAP µg/l		USEPA µg/l	ICAP µg/l
Ag			Mg		
Al	575	520	Mn	96	96
B			Mo		
Ba			Ni		
Ca			Pb	92	98
Cd	16	14	Sn		
Co			Ti		
Cr	83	82	V		
Cu	67	66			
Fe	402	435	Zn	79	81

U.S. EPA REFERENCE MATERIAL 1171 - 2

TABLE 6

All reference material run as a single blind experiment.

	USEPA ug/l	ICAP ug/l		USEPA ug/l	ICAP ug/l
Ag			Mg		
Al	1100	1030	Mn	449	465
B			Mo		
Ba			Ni		
Ca			Pb	350	350
Cd	73	75	Sn		
Co			Ti		
Cr	406	400	V		
Cu	314	313			
Fe	769	842	Zn	367	371

U.S. EPA REFERENCE MATERIAL 1171 - 3

TABLE 7

All reference material run as a single blind experiment.

	ICAP µg/l	A.A.S. Region V µg/l	US EPA µg/l		ICAP µg/l	A.A.S. Region V µg/l	US EPA µg/l
Ag				Mg	12.3*	11.9*	12
Al	649	650	700	Mn	368	350	350
B				Mo			
Ba				Ni	273	260	250
Ca	36.4*	37.5*	36.7	Pb	254	260	250
Cd	54	49	50	Sn			
Co	522	510	500	Ti			
Cr	157	150	150	V	731	760	750
Cu	252	260	250				
Fe	676	610	600	Zn	206	190	200

U.S. EPA REFERENCE MATERIAL 475-1

TABLE 8

	ICAP µg/l	A.A.S. Region V µg/l	US EPA µg/l		ICAP µg/l	A.A.S. Region V µg/l	US EPA µg/l
Ag				Mg	2.7*	2.5*	2.6
Al	75	<200	60	Mn	17	<20	15
B				Mo			
Ba				Ni	52	<60	30
Ca	7.3*	7.2*	7.2	Pb	25	<60	24
Cd	8	<20	2.5	Sn			
Co	19	<40	20	Ti			
Cr	14	<40	10	V	69	<400	70
Cu	14	<20	11				
Fe	41	<60	20	Zn	18	<20	16

U.S. EPA REFERENCE MATERIAL 475-2

TABLE 9

*Nutrient Sample #475
Conc. are in mg/l

All reference material run as a single blind experiment.

	USGS µg/l	ICAP µg/l		USGS µg/l	ICAP µg/l
Ag	6.4 ± 0.9	5.7	Mg	18.3 ± 0.9*	18.7
Al	71 ± 35	66.4	Mn	159 ± 14	160
B	92 ± 29*	113	Mo	56.6 ± 4.6	62.5
Ba			Ni	9.3 ± 6	<15
Ca	69.5±2.5*	65.7	Pb	23 ± 11	15.5
Cd	4.7 ±1.4	6.9	Sn		
Co	5.1 ± 0.6	<4	Ti		
Cr	16.5 ± 6	19.7	V		
Cu	391 ± 24	379			
Fe	87 ± 16	80	Zn	347 ± 28	346

* Ref. Material 47 - conc mg/

USGS REFERENCE MATERIAL 49 and 47

TABLE 10

The USGS value represents the average and standard deviation of all laboratories who participated in the Analytical Evaluation Program for Standard Reference Water Samples 49 and 47 through May, 1975.

All reference material run as a single blind experiment.

	NBS µg/l	ICAP µg/l		NBS µg/l	ICAP µg/l
Ag			Mg		
Al			Mn	42	44
B			Mo		
Ba			Ni		
Ca			Pb	47	20
Cd	14	12	Sn		
Co			Ti		
Cr	47	49	V		
Cu	807	848			
Fe			Zn	4893	4770

NBS REFERENCE MATERIAL (PRELIMINARY)

TABLE 11

The NBS values are preliminary and represent uncertified theoritical values supplied by NBS for their first mixed heavy metals in water standard reference material.

All reference material run as a single blind experiment.

	ICAP Ave. µg/l	AAS Ave. µg/l		ICAP Ave. µg/l	AAS Ave. µg/l
Ag			Mg		
Al	2257	2610	Mn	503	494
B			Mo		
Ba	1267	1210	Ni	1229	1242
Ca			Pb	1298	1281
Cd	506	492	Sn		
Co			Ti		
Cr			V		
Cu	462	470			
Fe	1312	1296	Zn	483	486

** Average 1 year (~100 runs)

***Average 2 months (14 runs)

IN-HOUSE CHECK STANDARD COMPARISON

OF AAS** AND ICAP***

TABLE 12

STUDY I

COMPARISON OF ICAP AND AAS AT

mg/l CONCENTRATIONS

IN

DISTILLED WATER (Digested as Any Sample)

LAKE MICHIGAN (A Clean Lake)

SEWAGE TREATMENT PLANT (Processing Industrial & Residential Wastes)

CALUMET RIVER (A Dirty River)

FOR

A SIX WEEK PERIOD TO SHOW PRECISION

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.260	0.254	Mg	9.9	9.8
Al	10.0	10.0	Mn	1.02	0.99
B	0.50	0.51*	Mo	25.7	26
Ba	9.4	9.1	Ni	5.1	4.96
Ca	25.8	26.4	Pb	5.25	5.0
Cd	0.252	0.249	Sn	10.0	10.
Co	0.97	1.03	Ti	10.0	10.6
Cr	1.04	1.02	V	9.9	9.5
Cu	1.00	1.02			
Fe	1.18	1.05	Zn	0.55	0.50

LOW CONCENTRATION IN DISTILLED WATER

TABLE 13

	ICAP $\pm\sigma$ mg/l	AAS $\pm\sigma$ mg/l		ICAP $\pm\sigma$ mg/l	AAS $\pm\sigma$ mg/l
Ag	0.007	0.002	Mg	0.2	0.2
Al	0.3	0.1	Mn	0.02	0.02
B	0.02	0.02*	Mo	0.8	1
Ba	0.2	0.3	Ni	0.1	0.03
Ca	0.5	0.1	Pb	0.08	0.2
Cd	0.006	0.002	Sn	0.2	1
Co	0.02	0.02	Ti	0.3	0.8
Cr	0.01	0.01	V	0.2	0.2
Cu	0.02	0.06			
Fe	0.03	0.02	Zn	0.01	0.01
n	6	3	n	6	3

over 6 weeks

PRECISION STUDY - LOW CONCENTRATION
IN DISTILLED WATER

* Curcumin Method

TABLE 14

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.52	0.52	Mg	15.0	14.8
Al	15.3	14.4	Mn	2.05	1.95
B	1.00	0.99 *	Mo	52.1	52
Ba	14.1	13.7	Ni	10.3	9.9
Ca	49.8	52.9	Pb	10.4	9.9
Cd	0.512	0.50	Sn	19.7	20.6
Co	1.94	2.04	Ti	19.6	20.1
Cr	2.07	2.07	V	19.6	18.5
Cu	2.00	2.05			
Fe	2.26	2.02	Zn	1.06	0.99

HIGH CONCENTRATION IN DISTILLED WATER

TABLE 15

	ICAP ± σ mg/l	AAS ±σ mg/l		ICAP ± σ mg/l	AAS ± σ mg/l
Ag	0.02	0.004	Mg	0.3	0.2
Al	0.2	0.1	Mn	0.02	0.03
B	0.04	0.01*	Mo	0.7	2
Ba	0.1	0.8	Ni	0.2	0.1
Ca	0.4	0.8	Pb	0.2	0.1
Cd	0.006	0.01	Sn	0.5	0.2
Co	0.02	0.05	Ti	0.2	0.1
Cr	0.05	0.08	V	0.05	0.4
Cu	0.01	0.11			
Fe	0.04	0.02	Zn	0.01	0.02
n	6	3		6	3

(over 6 weeks

PRECISION STUDY - HIGH CONCENTRATION IN DISTILLED WATER

*Curcumin Method

TABLE 16

	ICAP %	AAS %		ICAP %	AAS %
Ag	105	108	Mg	102	100
Al	106	88	Mn	103	96
B	100	96 *	Mo	105	103
Ba	94.6	93	Ni	102	98
Ca	96	106	Pb	102	97
Cd	104	100	Sn	97	113
Co	97	101	Ti	96	95
Cr	103	105	V	97	90
Cu	100	103			
Fe	108	97	Zn	102	98

* Curcumin Method

RELATIVE RECOVERY STUDY

IN

DISTILLED WATER

TABLE 17

$$\text{Relative Recovery} = \frac{\text{High Conc.} - \text{Low Conc.}}{\text{Spike Conc.}} \times 100$$

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.262	0.258	Mg	21.2	20.9
Al	10.6	10.3	Mn	1.02	0.98
B	0.54	0.55 *	Mo	26.3	21
Ba	9.5	9.1	Ni	5.2	5.02
Ca	62.3	64.1	Pb	5.40	5.1
Cd	0.258	0.252	Sn	10.3	10.4
Co	0.97	1.02	Ti	9.9	10.6
Cr	1.05	1.03	V	10.1	9.5
Cu	1.02	1.04			
Fe	1.37	1.20	Zn	0.56	0.50

LOW CONCENTRATION IN LAKE MICHIGAN WATER

TABLE 18

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ±σmg/l	AAS ±σmg/l
Ag	0.009	0.005	Mg	0.4	0.3
Al	0.3	0.1	Mn	0.03	0.02
B	0.04	0.04 *	Mo	0.9	1
Ba	0.2	0.3	Ni	0.1	0.07
Ca	0.4	0.4	Pb	0.09	0.1
Cd	0.008	0.003	Sn	0.3	1
Co	0.03	0.02	Ti	0.3	0.8
Cr	0.02	0.01	V	0.3	0.2
Cu	0.03	0.09			
Fe	0.02	0.01	Zn	0.01	0.02
n	6	3	n	6	3

over 6 week

PRECISION STUDY - LOW CONCENTRATION - LAKE MICHIGAN

TABLE 19

* Curcumin Method

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.52	0.52	Mg	25.6	25.7
Al	15.6	14.4	Mn	2.02	1.95
B	1.01	1.03*	Mo	51	52
Ba	13.9	13.7	Ni	10.2	9.83
Ca	83.3	83.8	Pb	10.3	9.9
Cd	0.51	0.51	Sn	19.6	21.8
Co	1.90	2.02	Ti	19.5	20.1
Cr	2.06	2.01	V	19.4	18.5
Cu	1.98	2.05			
Fe	2.28	2.07	Zn	1.05	0.98

HIGH CONCENTRATION IN LAKE MICHIGAN WATER

TABLE 20

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ± σ mg/l	AAS ±σmg/l
Ag	0.02	0.01	Mg	0.4	0.2
Al	0.3	0.1	Mn	0.04	0.02
B	0.07	0.03*	Mo	1	2
Ba	0.2	0.8	Ni	0.2	0.03
Ca	0.5	0.6	Pb	0.2	0.2
Cd	0.01	0.01	Sn	0.6	0.2
Co	0.04	0.05	Ti	0.4	0.1
Cr	0.05	0.07	V	0.4	0.4
Cu	0.05	0.08			
Fe	0.06	0.03	Zn	0.02	0.02
n	6	3	n	6	3

(over 6 wee

PRECISION STUDY - HIGH CONCENTRATION - LAKE MICHIGAN

TABLE 21

*Curcumin Method

	ICAP %	AAS %			ICAP %	AAS %
Ag	103	104		Mg	88	96
Al	100	88		Mn	100	97
B	94	96*		Mo	101	103
Ba	90	93		Ni	99	96
Ca	104	98		Pb	98	96
Cd	100	104		Sn	93	113
Co	93	100		Ti	96	95
Cr	101	98		V	93	90
Cu	96	101				
Fe	91	87		Zn	98	96

* Curcumin Method

RELATIVE RECOVERY

IN

LAKE MICHIGAN WATER

TABLE 22

$$\text{Relative Recovery} = \frac{\text{High Conc.} - \text{Low Conc.}}{\text{Spike Conc.}} \times 100$$

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.26	0.274	Mg	41.6	42.5
Al	13.5	12.6	Mn	1.18	1.15
B	1.15	1.2 *	Mo	25.7	26
Ba	9.3	9.2	Ni	5.30	4.99
Ca	80.0	82.6	Pb	5.46	5.2
Cd	0.284	0.279	Sn	9.9	11.2
Co	0.98	1.04	Ti	9.8	10.5
Cr	1.30	1.29	V	10.1	9.5
Cu	1.18	1.22	Zn	1.19	1.14
Fe	7.55	7.1			

LOW CONCENTRATION IN A STP

(Industrial & Residential Wastes)

TABLE 23

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ±σmg/l	AAS ±σmg/l
Ag	0.01	0.007	Mg	0.8	0.6
Al	0.1	0.3	Mn	0.01	0.02
B	0.06	0.1 *	Mo	0.4	1
Ba	0.1	0.4	Ni	0.06	0.02
Ca	0.4	0.6	Pb	0.07	0.2
Cd	0.004	0.001	Sn	0.2	0.8
Co	0.01	0.02	Ti	0.1	0.4
Cr	0.04	0.01	V	0.1	0.2
Cu	0.01	0.08	Zn	0.05	0.05
Fe	0.05	0.1			
n	6	3	n	6	3

over 6 weel

PRECISION STUDY - LOW CONCENTRATION - STP

TABLE 24

* Curcumin Method

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.52	0.529	Mg	46	47.6
Al	17.6	16.2	Mn	2.13	2.10
B	1.65	1.73*	Mo	49.6	51
Ba	13.7	13.7	Ni	10.2	9.66
Ca	84.7	83.7	Pb	10.0	9.7
Cd	0.52	0.53	Sn	18.9	22
Co	1.90	2.04	Ti	18.9	19.1
Cr	2.27	2.29	V	28.5	27.9
Cu	2.09	2.19			
Fe	8.9	8.5	Zn	1.67	1.64

HIGH CONCENTRATIONS IN A STP

(Industrial & Residential Wastes)

TABLE 25

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ±σmg/l	AAS ±σmg/l
Ag	0.02	0.004	Mg	2	0.4
Al	0.4	0.4	Mn	0.04	0.04
B	0.09	0.05*	Mo	0.9	4
Ba	0.3	0.7	Ni	0.3	0.08
Ca	0.5	0.4	Pb	0.2	0.2
Cd	0.01	0.02	Sn	0.4	1
Co	0.04	0.06	Ti	0.4	0.6
Cr	0.08	0.08	V	0.6	0.8
Cu	0.04	0.08			
Fe	0.1	0.2	Zn	0.02	0.04
n	6	3	m	6	3

(over 6 weel

PRECISION STUDY - HIGH CONCENTRATION - STP

* Curcumin Method

TABLE 26

	ICAP %	AAS %		ICAP %	AAS %
Ag	104	102	Mg		
Al	83	72	Mn	95	95
B	100	104*	Mo	95	102
Ba	88	90	Ni	99	93
Ca			Pb	91	91
Cd	94	100	Sn	90	104
Co	92	100	Ti	90	85
Cr	97	100	V	94	92
Cu	91	97			
Fe	130	137	Zn	96	100

* Curcumin Method

RELATIVE RECOVERY IN A

STP (INDUSTRIAL & RESIDENTIAL WASTES)

TABLE 27

$$\text{Relative Recovery} = \frac{\text{High Conc.} - \text{Low Conc.}}{\text{Spike Conc.}} \times 100$$

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.257	0.259	Mg	23.7	24.0
Al	11.0	9.9	Mn	1.15	1.14
B	0.56	0.55*	Mo	25.7	26
Ba	9.2	9.0	Ni	5.24	5.04
Ca	122	125	Pb	5.37	5.1
Cd	0.258	0.249	Sn	10.1	10.2
Co	1.90	2.02	Ti	9.7	10.6
Cr	1.03	0.99	V	9.9	9.5
Cu	1.02	1.04			
Fe	2.59	2.37	Zn	0.600	0.55

LOW CONCENTRATION IN THE CALUMET RIVER

TABLE 28

(The Calumet River is very polluted, its waters resemble discharges from industrial steel mill plants.)

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ±σ mg/l	AAS ±σmg/l
Ag	0.009	0.008	Mg	0.8	0.7
Al	0.2	0.06	Mn	0.02	0.02
B	0.03	0.04 *	Mo	0.7	2
Ba	0.2	0.3	Ni	0.09	0.08
Ca	0.9	1	Pb	0.08	0.3
Cd	0.005	0.004	Sn	0.2	0.4
Co	0.04	0.02	Ti	0.3	0.8
Cr	0.03	0.01	V	0.3	0.3
Cu	0.02	0.08			
Fe	0.04	0.03	Zn	0.009	0.03
n	6	3	n	6	3

(over 6 week

PRECISION STUDY - LOW CONCENTRATION - CALUMET RIVER

* Curcumin Met

TABLE 29

	ICAP mg/l	AAS mg/l		ICAP mg/l	AAS mg/l
Ag	0.49	0.50	Mg	37	37.9
Al	15.2	13.9	Mn	2.06	2.02
B	1.02	1.10 *	Mo	50	51
Ba	13.8	14.0	Ni	9.7	9.43
Ca	119.1	119.6	Pb	9.7	9.5
Cd	0.49	0.50	Sn	18.7	21.4
Co	2.8	3.0	Ti	18.4	19.3
Cr	1.96	1.98	V	18.6	18.3
Cu	1.90	2.01	Zn	1.02	0.97
Fe	3.5	3.24			

HIGH CONCENTRATION IN THE CALUMET RIVER

TABLE 30

	ICAP ±σmg/l	AAS ±σmg/l		ICAP ±σmg/l	AAS ±σmg/l
Ag	0.01	0.008	Mg	2	0.
Al	0.4	0.2	Mn	0.09	0.006
B	0.05	0.03*	Mo	2	3
Ba	0.5	0.7	Ni	0.3	0.06
Ca	0.5	0.6	Pb	0.2	0.2
Cd	0.02	0.01	Sn	0.6	0.6
Co	0.1	0.2	Ti	0.8	0.6
Cr	0.06	0.09	V	0.9	0.6
Cu	0.08	0.09	Zn	0.3	0.1
Fe	0.1	0.08			
n	6	3	n	6	3

(over 6 week

PRECISION STUDY - HIGH CONCENTRATION - CALUMET RIVER

*Curcumin Meth

TABLE 31

	ICAP %	AAS %		ICAP %	AAS %
Ag	93	96	Mg	89	92
Al	84	80	Mn	91	88
B	92	110 *	Mo	98	100
Ba	92	100	Ni	89	88
Ca			Pb	87	88
Cd	93	100	Sn	86	100
Co	90	98	Ti	87	87
Cr	93	99	V	88	87
Cu	88	97			
Fe	91	87	Zn	86	84

* Curcumin Method

RELATIVE RECOVERY

IN THE

CALUMET RIVER

TABLE 32

$$\text{Relative Recovery} = \frac{\text{High Conc.} - \text{Low Conc.}}{\text{Spike Conc.}} \times 100$$

	Slope	INTCP µg/l			Slope	INTCP µg/l
Ag	1.02	+0.003		Mg	1.05	-0.925
Al	0.87	+0.800		Mn	0.97	+0.003
B	1.07	-0.035	*	Mo	1.02	-0.479
Ba	1.03	-0.458		Ni	0.96	+0.003
Ca	1.00	1.36		Pb	0.98	+0.159
Cd	1.03	-0.014		Sn	1.11	-0.995
Co	1.08	-0.019		Ti	0.98	+0.958
Cr	1.02	-0.048		V	0.99	+0.398
Cu	1.07	-0.039				
Fe	0.97	-0.126		Zn	1.01	-0.067

* Curcumin Method

$$\text{Slope} = \frac{\Delta AAS}{\Delta ICAP}$$

TOTAL STUDY I COMPARISON

LINEAR CORRELATION

TABLE 33

This data is the least squares slope and intercept of all data collected in Study I. The AAS Values are plotted on the y axis v.s. the ICAP values on the x axis.

	ICAP %	AAS %			ICAP %	AAS %
Ag	101 ±4	104 ± 3		Mg	93 ± 8	96 ± 4
Al	93 ±12	83 ± 7		Mn	97 ± 5	94 ± 4
B	97 ±4	101 ± 7	*	Mo	100 ± 4	102 ± 1
Ba	91 ±3	94 ± 4		Ni	97 ± 6	94 ± 4
Ca	100 ±6	102 ± 6		Pb	95 ± 7	93 ± 4
Cd	98 ±5	101 ± 2		Sn	95 ± 8	108 ± 7
Co	92 ±5	100 ± 1		Ti	92 ± 4	90 ± 5
Cr	99 ±5	100 ± 3		V	93 ± 4	90 ± 2
Cu	94 ±5	100 ± 3				
Fe	106 ±17	102 ±24		Zn	96 ± 7	94 ± 7

* Curcumin Method

TOTAL STUDY I COMPARISON

OF

RELATIVE RECOVERY

TABLE 34

The recovery presented is the average(and σ) for the observed recovery in each of the four water types in Study I.

STUDY II

COMPARISON OF ICAP AND AAS

FOR

SAMPLE AND SPIKED SAMPLE PAIRS

FROM

NORMAL LABORATORY AQC PROGRAM

WITH

ALL SAMPLES CHOSEN AT RANDOM

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	<14	132	672	940	84	101
Ba						
Cd	< 4	15	208	205	102	95
Cr	41	40	244	239	101	99.5
Cu	23	32	211	232	94	100
Fe	609	579	1715	1586	110	101
Mn	62	65	271	267	104	101
Ni	<30	16	181	256	91	120
Pb	19	22	218	231	99	104
Zn	203	219	404	422	100	102

STP #1070

TABLE 35

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	96	328	986	1140	111	102
Ba	119	104	1004	932	111	104
Cd	<4	10	228	203	112	97
Cr	11	4	230	177	109	86
Cu	50	49	250	237	100	94
Fe	1290	1128	2550	2243	126	111
Mn	52	48	282	250	115	101
Ni	<30	22	203	236	102	107
Pb	26	37	250	241	112	102
Zn	113	109	332	295	109	93

STP #8392

TABLE 36

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	730	1020	1549	1828	102	101
Ba						
Cd	<4	7	199	213	100	103
Cr	9	10	201	204	96	100
Cu	10	12	189	206	90	98
Fe	156	141	1240	1144	108	100
Mn	54	54	259	261	103	103
Ni	<30	22	173	232	87	105
Pb	15	26	209	228	97	101
Zn	36	40	225	232	95	96

STP # 01142

TABLE 37

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd	<4	6	211	199	104	97
Cr	11	10	215	185	102	97
Cu	9	10	199	210	95	100
Fe	565	496	1774	1515	121	102
Mn	61	55	276	259	107	102
Ni	<30	30	180	233	90	102
Pb	26	26	238	220	106	96
Zn	60	46	270	246	105	100

STP #01170

TABLE 38

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	706	804	1425	1528	90	91
Ba						
Cd	< 4	9	192	214	96	103
Cr	40	35	231	222	96	94
Cu	19	26	204	223	93	99
Fe	1650	1744	2744	2768	109	102
Mn	162	179	367	386	103	104
Ni	<30	26	181	222	91	98
Pb	46	67	248	264	97	99
Zn	193	213	393	415	100	101

STP #1298

TABLE 39

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd	<4	7	212	196	106	95
Cr	8	5	213	180	103	90
Cu	26	28	228	232	101	97
Fe	611	506	1734	1474	112	96
Mn	153	142	372	342	109	100
Ni	<30	20	199	216	99.5	108
Pb	31	50	253	264	111	107
Zn	93	108	287	307	97	100

STP #13757

TABLE 40

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	830	800	1552	1634	95	103
Ba	117	120	852	872	92	95
Cd	17	20	209	203	93	96
Cr	275	261	468	449	87	94
Cu	164	216	339	366	88	92
Fe	7132	7100	8516	8400		
Mn	241	255	444	458	102	102
Ni	228	248	415	438	94	95
Pb	155	150	331	346	88	98
Zn	567	708	896	889	114	90

STP #21361

TABLE 41

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	1074	1152	1897	1960	103	101
Ba	112	<100	852	848	93	94
Cd	29	34	219	219	95	93
Cr	158	142	347	329	94	94
Cu	195	216	371	398	88	91
Fe	7488	7700	8824	8400		
Mn	203	212	404	408	100	98
Ni	248	282	447	480	100	99
Pb	162	172	362	376	100	102
Zn	822	844	1027	1109	102	88

STP #21324

TABLE 42

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd						
Cr						
Cu						
Fe	153	173	1079	1142	93	97
Mn						
Ni						
Pb						
Zn						

STP #8443

TABLE 43

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	238	444	969	1268	92	103
Ba						
Cd	< 4	<10	198	203	99	102
Cr	10	10	202	191	96	91
Cu	10	8	179	204	87	98
Fe	339	338	1397	1304	106	97
Mn	24	27	226	234	101	104
Ni	<30	21	186	219	93	99
Pb	<24	22	216	227	100	103
Zn	17	10	208	198	96	99

ELECTRIC POWER GENERATING PLANT #1227

TABLE 44

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	549	516	1476	1300	116	98
Ba	98	80	551	516		
Cd	< 4	11	216	214	107	102
Cr	16	14	225	210	104	98
Cu	11	19	206	222	98	102
Fe	224	240	1416	1254	120	101
Mn	15	16	237	228	111	107
Ni	<30	35	208	237	104	101
Pb	34	34	239	237	102	102
Zn	19	20	232	226	106	103
V	158	K100	2195	2272	102	112

ELECTRIC POWER GENERATING PLANT #1248

TABLE 45

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd	<4	<10	193	206	95	102
Cr	13	<20	199	166	93	77
Cu	14	17	192	212	89	98
Fe	1877	1800	2751	2600		
Mn						
Ni	<30	34	181	235	90.5	100
Pb	39	<40	227	234	94	100
Zn	29	24	218	229	95	103

POLLUTED RIVER #21507

TABLE 46

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd						
Cr	3	<20	179	198	88	96
Cu	<2	<10	160	204	80	98
Fe	908	862	1668	1850	76	99
Mn	7	<10	183	212	88	102
Ni						
Pb	<24	<40	172	230	86	101
Zn	22	56	230	263	104	104

MILITARY ARSENAL #1346

TABLE 47

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	<20	20	622	768	78	94
Ba						
Cd						
Cr	4	4	208	183	102	90
Cu						
Fe						
Mn						
Ni						
Pb						
Zn						

DRINKING WATER #1180

TABLE 48

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	<14	136	672	940	84	102
Ba						
Cd	< 4	<10	201	210	101	98
Cr	9	<20	204	189	95	94
Cu	14	16	193	218	88	91
Fe	186	184	1272	1200		
Mn	91	92	297	300	103	105
Ni	<40	<30	168	219	84	102
Pb	19	<40	214	238	98	98
Zn	24	25	224	227	99	100

GENERAL INDUSTRIAL #1290

TABLE 49

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	<14	<100	591	904	74	102
Ba						
Cd	< 4	< 10	181	197	90	98
Cr	3	< 20	183	193	90	94
Cu	3	10	164	201	30	96
Fe	77	64	1024	1085	95	102
Mn	7	8	194	217	93	104
Ni	23	< 30	202	206	90	102
Pb	<24	< 40	187	226	94	98
Zn	19	17	190	215	86	90

GENERAL INDUSTRIAL #1324

TABLE 50

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al Ba	132	132	792	924	83	99
Cd Cr	10	<20	224	173	107	86
Cu Fe						
Mn Ni						
Pb Zn						

AUTOMOTIVE INDUSTRIAL #7484

TABLE 51

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al Ba						
Cd Cr	< 4 25	9 16	192 212	198 206	95 94	95 95
Cu Fe	17 1613	24 1960	198 2684	222 3184	90 107	99 123
Mn Ni	<30	77	196	283	98	103
Pb Zn						

GENERAL INDUSTRIAL #1249

TABLE 52

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al	<14	36	539	840		101
Ba						
Cd						
Cr						
Cu	35	35	206	224	86	95
Fe						
Mn						
Ni						
Pb	<24	30	220	205	110	104
Zn						

TIRE COMPANY #8446

TABLE 53

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd	<4	< 10	184	201	92	96
Cr	20	< 20	200	224	90	105
Cu	166	200	341	403	88	101
Fe	1296	1380	2287	2430	99	105
Mn						
Ni	59	75	236	277	89	101
Pb	55	40	237	232	91	102
Zn	208	229	394	418	93	95

PAPER INDUSTRY #7007

TABLE 54

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd						
Cr						
Cu	4	<10	204	204	100	102
Fe	178	162	1286	1160	111	100
Mn	61	58	277	262	108	102
Ni	13	<30	210	224	99	102
Pb	<24	<40	194	216	97	100
Zn	39	12	238	209	100	99

COMMUNICATIONS INDUSTRY #0018

TABLE 55

	Sample		Spiked Sample		Recovery	
Element	ICAP µg/l	AAS µg/l	ICAP µg/l	AAS µg/l	ICAP %	AAS %
Al						
Ba						
Cd	9	6	103	107	94	101
Cr						
Cu						
Fe	5.6	5.6	6.2	6.1		
Mn						
Ni						
Pb						
Zn						

COMMUNICATIONS INDUSTRY #8494

TABLE 56

	ICAP % ± σ	AAS % ± σ	# Samples		ICAP % ± σ	AAS % ± σ	# Samples
Ag				Mg			
Al	106 ± 12	100 ± 4	14	Mn	103 ± 7	103 ± 2	14
B				Mo			
Ba	98 ± 11	98 ± 6	3	Ni	94 ± 6	103 ± 6	16
Ca				Pb	99 ± 8	101 ± 3	17
Cd	99 ± 6	98 ± 4	16	Sn			
Co				Ti			
Cr	98 ± 6	93 ± 6	18	V	102	112	1
Cu	91 ± 6	97 ± 3	18				
Fe	105 ± 13	101 ± 9	16	Zn	100 ± 7	98 ± 5	15

SUMMARY OF % RECOVERY

IN

STUDY II

TABLE 57