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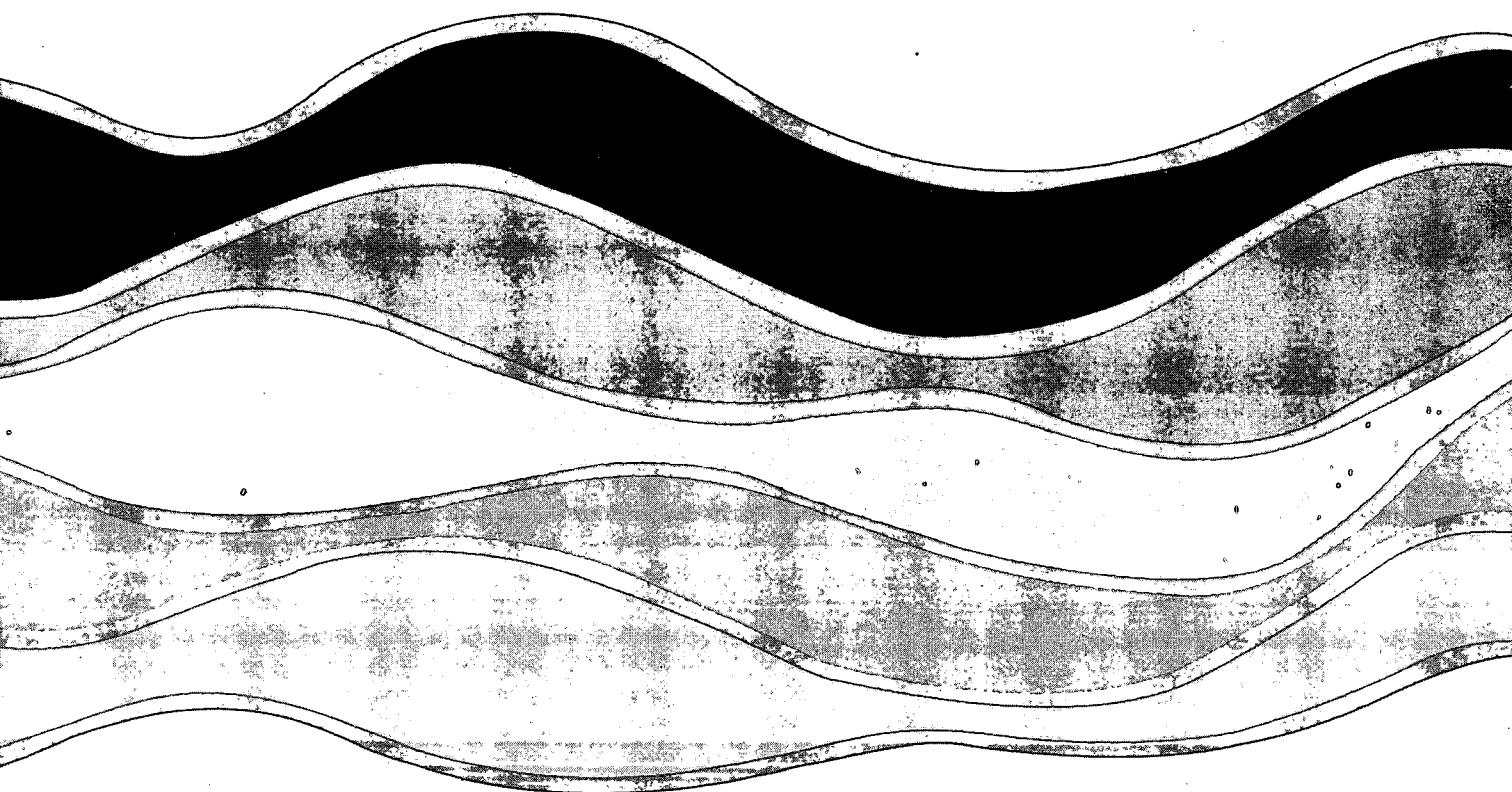WATER
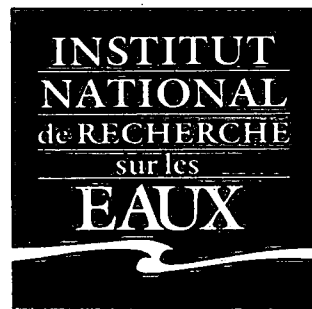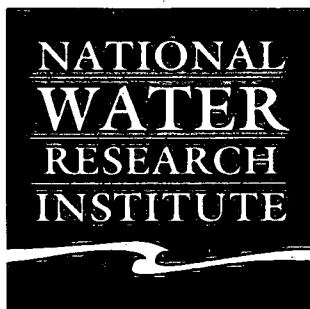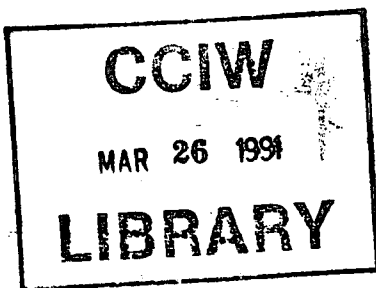RESEARCH
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DETERMINATION OF LEAD IN WATER BY FLAMELESS
ATOMIC ABSORPTION SPECTROMETRY AND
NICKEL-AMMONIUM-TARTRATE MODIFIER

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NWRI CONTRIBUTION 91-106

MANAGEMENT PERSPECTIVE

Lead and its compounds are a serious cumulative body poison. Reliable and accurate data about the presence of lead in the environment are very important. The analytical methodology for the determination of such highly toxic element is far from simple and still presents many unresolved problems. Atomic absorption spectrometry continues to be the method of choice for the determination of lead in environmental samples and has been used more frequently than any other technique. However, it is prone to serious errors if other interfering elements are present.

The improved method described in this report is based on the application of atomic absorption spectroscopy, using a tungsten furnace. It was found that the addition of nickel-ammonium tartrate to the sample significantly contributed toward eliminating interferences usually observed with other methods for lead determination. The use of this "matrix modifier" also brings improvement in terms of accuracy and precision of the analytical data. The method requires simple and inexpensive instrumentation. It is efficient and economical for the determination of trace levels of lead in various water samples.

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Le plomb et ses composés sont un poison à effet cumulatif dangereux pour l'organisme. Il est très important de disposer de données fiables et précises sur la présence de plomb dans le milieu. Les méthodes d'analyse pour le dosage de cet élément très toxique sont loin d'être simples et il existe encore de nombreuses questions non résolues. La spectrométrie d'absorption atomique est toujours la méthode privilégiée de dosage du plomb dans les échantillons du milieu, et elle a été utilisée plus souvent que toute autre technique. Toutefois, elle est sujette à de graves erreurs en présence d'autres éléments interférants.

La méthode modifiée décrite dans le présent rapport repose sur l'application de la spectroscopie d'absorption atomique, à l'aide d'un four au tungstène. Les chercheurs ont constaté que l'addition de tartrate d'ammonium et de nickel à l'échantillon a éliminé considérablement les interférences généralement observées lorsque l'on applique d'autres méthodes de dosage du plomb. L'utilisation de "modificateur de matrice" a également accru la précision et la justesse des données d'analyse. La méthode nécessite des instruments simples et peu coûteux. Elle est efficace et économique pour le dosage du plomb à l'état de trace dans divers échantillons d'eau.

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ABSTRACT

This report describes a method for the determination of low concentrations of lead in water samples. The method is based on the application of atomic absorption spectrophotometry using a Zeeman modulated tungsten ribbon furnace. Analytical interferences are eliminated by the addition of ammonium tartrate-nickel [II] nitrate to the samples to act as a matrix modifier and adjust the pH. The results show the superior performance of this modifier over other types used conventionally. A detection limit of 1 ppb with a relative standard deviation of less than 10% was achieved. When a multiple injection procedure is used, a detection limit as low as 0.1 ppb can be obtained. The method requires simple instrumentation and is economical and efficient for the determination of lead in variety of water samples.

RÉSUMÉ

Le présent rapport décrit une méthode de dosage de faibles
concentrations de plomb dans des échantillons d'eau. La méthode est fondée
sur l'application de la spectrophotométrie d'absorption atomique utilisant un
four à ruban de tungstène à modulation Zeeman. Les interférences dues à
l'analyse sont éliminées par l'addition de tartrate d'ammonium et de nitrate
de nickel (II) aux échantillons qui servira de modificateur de matrice et à
ajuster le pH. Les résultats montrent la performance supérieure de ce
modificateur par rapport à d'autres types utilisés de façon classique. On a
enregistré une limite de détection de 1 partie par milliard avec un écart type
inférieur à 10 %. Lorsque l'on utilise l'injection multiple, une limite de
détection d'à peine 0,1 partie par milliard peut être obtenue. La méthode
exige des instruments simples, elle est économique et efficace pour le dosage
du plomb dans divers échantillons d'eau.

INTRODUCTION

The determination of lead in water is of great importance due to its well documented and recognized toxicity to the aquatic environment and the entire ecosystem. The technique most commonly used for this determination has been based on Electrothermal Atomic Absorption Spectroscopy. The problem of the method is that severe interference attributed to the "Matrix Effect" is usually encountered. Many procedures for the elimination of this interference have been reported (1-10). The methods have been subject of debate and dissatisfaction among environmental scientists for many years.

The term and concept of "Matrix Modification" was first introduced to the Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) by Edinger in 1975 (2). The aim of matrix modification is to permit high enough pyrolysis temperature to remove the bulk of the interfering substances during the thermal pretreatment (ashing) without losing the analyte element prior to the atomizing stage. The matrix modifier is a compound or a mixture of compounds that is added to the sample before the analysis to eliminate matrix interference. An efficient matrix modifier reduces spectral interference such as the screening of molecular or atomic lines caused by substances present in the sample and the scattering of radiation by non-volatized particles. It also reduces or removes volatization and vapor phase interference (3).

Several matrix modifiers are recommended and used in GF-AAS (4-7). Ascorbic acid was used for the determination of lead in drinking water (8). Ammonium nitrate is recommended for the determination of lead in seawater (9). Ammonium phosphate is the most recommended and accepted modifier for the determination of lead by GF-AAS (10-15). A combination of palladium and magnesium nitrate has been proposed as the universal modifier for GF-AAS (3). The introduction of the platform technique to GF-AAS brought further improvement in respect to Pb determination (15,16). It has been reported that some organic compounds when added to the sample enhance the signal of lead during GF-AAS analysis. Fuller (17) used oxalic, succinic and glutaric acids, whereas Regan

(18) studied ascorbic and tartaric acids. The best results for the determination of Pb in drinking water have been obtained with tartaric acid used as a modifier (9). Dolinsek et al. (19) found that complexing reagents enhance the sensitivity of lead determination. Campell and Ottaway (20,21) reported that the carbon of the carbon furnace plays a major role in the formation of the atomic vapor by assisting the reduction of metal oxides.

Several metal-based electrothermal atomization devices have been used as substitutes for the conventional graphite-based systems. The reason for this is to overcome the problems encountered with atomization of analytes forming graphite-metal compounds of low volatility and the "memory effect " of the graphite furnace. The Tungsten Furnace Atomic Absorption Spectrophotometry (TF-AAS) proved to be the best technique (22-26). The TF-AAS differs from GF-AAS in the material (tungsten vs. graphite) and in the geometry of the furnace (V-shaped ribbon vs. tube). Most informations dealing with the determination of lead by the electrothermal atomization have been oriented toward the GF-AAS and are not directly applicable to the TF-AAS. A search of the literature did not bring any information about the matrix modifiers suitable for TF-AAS.

The incorporation of the "Zeeman Effect" technique improved the performance characteristics of the AAS. The Zeeman effect (27) refers to the splitting of atomic spectral lines in a strong magnetic field. As a result, it is possible to differentiate between atomic absorption and the absorption caused by molecular absorbers, nonspecific absorbers and particulate scattering effect. The condition of sequential turning the magnetic field on and off is referred to as Zeeman Modulation. The AAS equipped with this feature subtracts the field-on peak area from the field-off peak area of the absorption curve (28). TF-AAS instruments with Zeeman Modulation are relatively inexpensive, easy to operate, compact and highly automated.

The objective of this study was to develop an interference free method for the determination of low concentration of lead in water samples using TF-AAS.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade. Stock solutions prepared by weight were standardized by appropriate standard analytical procedures. Standard and working solutions were prepared from respective stock solutions by dilution with distilled deionized water. The "cocktail" - the solution so referred to in the text was prepared by dissolving appropriate amount of salts in water and acidified to pH 1 with nitric acid. It contained the following ions in ppm amounts : $Ca^{2+}(100)$, $Mg^{2+}(20)$, $Fe^{3+}(2)$, $Al^{3+}(2)$, $Mn^{2+}(2)$, $Zn^{2+}(2)$, $Na^{+}(120)$, $K^{+}(80)$, $NO_3^{-}(560)$, $SO_4^{2-}(140)$, $F^{-}(5)$, $PO_4^{3-}(140)$, $CO_3^{2-}(80)$ and $Cl^{-}(220)$. All samples and solutions were preserved by the acidification to pH 1 with nitric acid.

Because the ammonium tartrate salt contained significant level of lead, purification was required. The procedure consisted of the precipitation of PbS by the addition of a solution of Na_2S and by removing the excess of sulfide by the addition of a the bismuth solution. After filtration, the solution of ammonium tartrate was shown to contain non-detectable concentration of lead (29).

The combinations of nickel [II] nitrate with ascorbic, citric, artaric and oxalic acids and with ammonium, sodium and potassium tartrates were tested as the matrix modifiers. The composition of these solutions was 5% nickel and 10% tartrate. Other compounds tested as matrix modifiers were ammonium and phosphate, citric, tartaric, ethylenediaminetetra-acetic, diethylenetriaminepenta-acetic acids, thiourea and hydroxylamine hydrochloride. Palladium and magnesium were the cations included in the tests.

Instrumentation

A Scintrex AAZ-2 Zeeman Modulated Atomic Absorption Spectrophotometer controlled by an Apple IIc computer and using a tungsten foil ribbon as heat

transducer was the principle instrument. The low mass ribbon permits a high rate of temperature rise (3000°C/s). Figure 1 is a typical plot of the absorbance vs. time obtained in the analysis of a 10 μL sample containing 10 ppb of lead. A temperature cycle of 140°C for drying, 700°C for ashing and 1600°C for atomizing was used. The signals were recorded at 283.8 nm. Comparative data were generated with a Perkin-Elmer "Zeeman 5100" graphite furnace AAS.

All glass and plastic ware was thoroughly cleaned with 1:1 nitric acid and rinsed with deonized distilled water. Only teflon containers were used for samples and standards preparation and storage.

RESULTS and DISCUSSION

The preliminary experiments were designed to prove the necessity of adding a matrix modifier as part of the sample preparation for the determination of lead by TF-AAS. A second aim was to evaluate the applicability of the various modifiers used by GF-AAS for the TF-AAS. All the samples chosen, standards and blanks were analyzed, spiked with known amount of lead and reanalyzed. The values obtained for peak areas were converted to the concentration units (ppb) on the basis of calibration curves. A typical calibration curve is shown in Fig. 2. The values of the recoveries (%) are summarized in Tables 1 and 2.

It is obvious from the obtained results, that the determination of lead by TF-AAS without the addition of the modifier is not reliable and does not produce meaningful and useful data. The results from analyses incorporating the addition of various modifiers showed considerable discrepancies with published data. The explanation could be that the data from the literature were generated with GF-AAS and not with TF-AAS. The additions of sodium and potassium tartrate, EDTA, DPTA and thiourea produce distorted and irreproducible signals. The values obtained have not been reported in the tables. Nickel and palladium modifiers were the best performers. Various combinations of nickel [II] with several organic compounds were used to determine their matrix modifying efficiency. The data summarized in Table 3 indicate that the most efficient modifier was the

combination of Ni with an ammonium tartrate solution. The mixture of sodium and potassium tartrate with Ni showed also significant improvement of the signal but had a smaller effect than the ammonium tartrate - Ni combination.

No literature reference about the use of the ammonium tartrate and/or its combination with metal ions as modifier was found. Due to the buffering property of the ammonium tartrate, experiments were conducted to establish the function of this compound during the matrix modifying process. The most complex sample (cocktail) was treated with the addition of sodium tartrate - Ni solution, acidified with nitric acid to pH 1 and analyzed. As increasing amounts of ammonium hydroxide were added to this sample, the pH was monitored and the TF-AAS signal was measured. Similar tests were repeated with a mixture of potassium tartrate and tartaric acid substituted for the sodium tartrate - Ni solution. The results represented in Fig. 3 show a low level signal in the acid range of the pH scale. The level of the signal increases as the pH is raised to reach a plateau from pH 3 to pH 10. To determine the cause of the changes in the response (is it the addition of ammonia or the changes of the pH ?), the following tests were conducted. In the first test, the pH of the solution spiked with Pb and containing the ammonium tartrate - Ni modifier was adjusted to 1.0 with nitric acid and increased to 10.0 by the addition of ammonium hydroxide. Nitric acid was than added till the pH decreased to 1.0. During the second experiment the variation of the pH from 1.0 to 10 and back to 1.0 was achieved by the successive addition of sodium hydroxide and nitric acid, respectively. Again, the signal of Pb was monitored at each step. The results as represented in Fig. 4 are similar to those in Fig.3, showing a sharp decline of the response below pH 3.0 and maintaining a constant value from pH 3.0 to 10.0. These results confirm the importance of pH for the analytical system. It is necessary to adjust and maintain the pH of the sample above a value of 3.0. If the pH of the sample after the addition of the modifier is lower than 3.0, it must be adjusted to a value in the range 3.0 to 4.0 by the addition of the ammonium hydroxide. Values of pH higher than 4.0 may cause the precipitation of metal hydroxides and distortion of the results.

The results of the tests establishing the most effective composition of the modifier are summarized in Figures 5 and 6. In both graphs, peak areas

are plotted against the increasing content of one component, whilst keeping the other constant. In another experiment, the peak areas were measured relatively to the increasing amount of added modifier (see Fig. 7). The optimal composition of the modifier was found to be the mixture of 20% ammonium tartrate with 5% nickel [II] nitrate solutions. This modifier is added to the sample in the ratio 1 : 10 by volume.

The results of test designed to compare the performance of the ammonium tartrate - Ni, Pd - Mg nitrate modifiers and their individual components are presented in Table 4. The best results were obtained with ammonium tartrate - Ni modifier. The Pd - Mg nitrate solution was confirmed to be a viable modifier, although the recoveries were less consistent than in the test using the ammonium tartrate - Ni modifier. Also the high price of palladium nitrate ($50/g) vs. nickel nitrate ($0.2/g) cannot be ignored when comparing the two modifiers. The effectiveness of the ammonium tartrate - Ni the Pd - Mg modifiers was further tested by analyzing samples containing various potentially interfering compounds. As can be seen in Table 5, the Pd - Mg modifier gave poor results in the presence of sulfate and aluminum ions. The recovery of Pb from the seawater sample was 7% only. By contrast, the ammonium tartrate - Ni modifier performed very well in all cases. The low recovery (50%) was obtained only with the seawater sample.

The relative standard deviation of ten replicate measurements was found to be 6% at non-detectable Pb level, 5% at the 15 ppb, and 4% at the 30 and 50 ppb concentrations of Pb. The practical detection limit with a 10.0 uL sample injection was 1.0 ppb.

The technique of multiple sample injection is used to increase the sensitivity of the measurement. It involves several injections with ✗ drying and ashing steps between each injection followed by one final atomization step. The limitation of the procedure is the build-up of interfering substances on the tungsten ribbon. The results accomplished with this technique are shown in Figure 8. The detection limit of 0.1 ppb of Pb with a relative standard deviation (RSD) of 5% was achieved by 10 consecutive injections of 10 uL of the sample.

The performance of the ammonium tartrate – Ni modifier was also tested using Perkin-Elmer Mo. 5100 Graphite Furnace AAS with Zeeman Modulation. The analytical results obtained with standards, blanks, synthetic and actual samples indicated full applicability of this modifier to the Graphite Furnace instrumentation.

CONCLUSIONS

The accomplishment of this study is the improvement of the AAS determination of low concentration of lead in water samples. The use of ammonium tartrate – nickel modifier developed during the course of this study significantly improves the performance of the TF-AAS by limiting the matrix related interference. The necessity of adjusting the pH of the sample to the range of 3.0 to 4.0 to obtain optimum results constitutes an important finding. It has been established that a relatively inexpensive, robust, compact and easy to operate TF-AAS instrument is fully appropriate for applying the methodology. The method is sensitive, selective, simple and practical for the routine analysis of a variety of water samples for low concentration of lead.

APPENDIX A

**Operation procedure for the determination of Pb in water
by TF-AAS using Ammonium tartrate - Nickel [II] modifier.**

This manual is written in the form suitable for the incorporation into the "Operational Procedures of Water Quality National Laboratory," Inland Waters Directorate.

1.0 Scope and Application

1.1 This atomic absorption method is applicable to the determination of lead in a wide variety of water samples.

1.2 The detection limit is 0.001 mg/L by the single injection and 0.0001 mg/L by the multiple injection procedure.

2.0 Principle and Theory

2.1 See " Metals : General."

3.0 Interferences

3.1 See " Metals : General."

4.0 Sampling Procedure and Storage

4.1 See " Metals : General."

5.0 Apparatus

5.1 Tungsten Furnace Atomic Absorption Spectrophotometer with Zeeman Modulation - Scintrex AAZ-2, or equivalent.

5.2 Pb hollow cathode lamp.

5.3 Wavelength 283.3 nm.

5.4 pH indicator strips -pH range 2 -5.

5.5 All glass and plasticware rinsed with 1:1 nitric acid and deionized distilled water.

5.6 Fuel : 92% argon and 8% hydrogen welding grade mixture.

6.0 Reagents

6.1 Deionized distilled water.

6.2 Nitric acid special grade for atomic absorption analysis.

6.3 Stock lead solution, 1000 mg/L Pb : dissolve 1.599 g anhydrous lead nitrate in deionized water. Add 10 mL of conc. nitric acid and dilute in a volumetric flask to 1.0 L with deionized water.

6.4 Standard lead solution : Prepare calibration standards to cover the desired range by appropriate dilution of the stock solution.

6.5 Matrix modifier solution : Dissolve 100 g of supra-pure or purified ammonium tartrate and 25 g of nickel [II] nitrate in 500 mL of deionized distilled water.

7.0 Procedure

7.1 The analyst should follow the manufacturer's operating instruction for the particular instrument.

7.2 Pipette 10 mL of the sample into teflon test-tubes.

7.3 Prepare a blank and sufficient standards to cover the expected range of samples.

7.4 Add 1.0 mL of the matrix modifier solution to each and mix. Inspect the pH and adjust if necessary by diluted ammonium hydroxide to the value higher than pH 5.

7.5 Insert test tubes into the automated sampler and initiate the cycle.

8.0 Calculation

8.1 Prepare a calibration curve derived from the peak heights or peak areas obtained with the standard solutions.

8.2 Determine the concentration of Pb in the sample by comparing samples peak hights or areas with the calibration curve.

8.3 The instrument equipped with the computer control produces directly the results in concentration units.

9.0 Precision and Accuracy

9.1 Calibration curve is typically linear to 0.100 mg/L.

9.2 Relative standard deviation at the lead level of 0.001 mg/L was 10%, and 5% and 4% at the levels 0.01 and 0.001 mg/L respectively.

9.3 Limit of detection is 0.001 mg/L with 10.0 uL injection and 0.0001 mg/L with 10 sequential 10,0 uL injections 0.05 mg/L respectively.

9.4 The total analytical time for 50 samples is approximately 3 1/2 h. The corresponding operator time is approximately 1 h, assuming automatic data calculation.

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TABLE 1

Recoveries (%) of Pb from water samples using different matrix modifiers.

Sample	no MF	NH_4NO_3	$NH_4H_2PO_4$	Asc. Ac.	$Ni(NO_3)_2$	$Pd(NO_3)_2$
A	19	62	78	70	93	98
B	42	62	24	56	63	97
C	17	30	92	70	98	103
D	84	77	58	70	112	102
E	60	114	69	79	106	109
F	49	66	101	46	45	92
G	36	104	89	70	80	97
H	23	55	75	63	82	98
I	95	103	99	101	104	100

All samples were analyzed, spiked (30 ppb) and re-analyzed.

A = Magnesium chloride (5,800 ppm)
B = Potassium chloride (1,000 ppm)
C = Manganese sulfate (250 ppm)
D = Potassium fluoride (50 ppm)
E = Cocktail
F = Tap water
G = Burlington Bay
H = Roseland Creek
I = Blank

TABLE 2

Recoveries (%) of Pb using different matrix modifiers.

Sample I.D.	No Modif.	Asc. Ac.	Citr. Ac.	Tart. Ac.	Amm. Tartr.	Oxal. Ac.	Hydrox. Amine
A	60	79	3	41	0	28	64
B	19	53	28	105	61	80	56
D	95	97	99	102	103	96	104
E	17	35	17	41	19	35	71
G	36	69	49	81	40	59	100
H	23	91	32	58	12	70	87
I	49	48	49	76	43	86	75

All samples were analyzed, spiked (30 ppb) and re-analyzed.

A = Cocktail
B = Magnesium chloride (5,800 ppm)
D = Blank
E = Sodium sulfate   (250 ppm)
G = Burlington Bay
H = Hidden Valley Creek
I = Tap Water

TABLE 3

Recoveries (%) of Pb using Ni - org. compound modifiers

MODIFIER & Ni(NO$_3$)$_2$	SAMPLES						
	A	B	D	E	G	H	I
No MF	106	93	103	98	80	82	45
Asc. Ac.	77	108	104	104	107	82	81
Citr. Ac.	67	89	104	60	109	97	80
Tart. Ac.	77	66	96	77	90	109	82
Amm. Tartr.	101	96	103	101	100	104	97
Pot. Tartr.	101	70	100	103	93	97	80
Sod. Tartr.	97	66	100	98	101	109	77
Oxal. Ac.	0	103	99	61	25	0	43
Hydroxyl Amine	0	101	101	0	23	8	36

All samples were analyzed, spiked (30 ppb) and re-analyzed.

A = Cocktail
B = Magnesium chloride (5,800 ppm)
D = Blank
E = Sodium sulfate   (250 ppm)
G = Burlington Bay
H = Hidden Valley Creek
I = Tap water

TABLE 4

Recoveries (%) of 30 ppb Pb using Ni and Pd modifiers

S. I.D.	Asc. Ac.	$Mg(NO_3)_2$	$Pd(NO_3)_2$	$Pd(NO_3)_2$ $Mg(NO_3)_2$	$Ni(NO_3)_2$	Amm. Tartr	Amm. Tartr. (Ni)
A	104	63	102	111	73	18	102
B	95	53	82	108	47	58	94
E	102	40	100	109	67	54	96 .
G	99	46	102	108	63	45	105
H	97	43	108	102	66	25	107
I	93	43	81	82	72·	46	99
D	99	100	98	101	100	99	102

All samples were analyzed, spiked (30 ppb) and re-analyzed.

A = Cocktail
B = Magnesium chloride (5,800 ppm)
D = Blank
E = Sodium sulfate   (250 ppm)
G = Burlington Bay
H = Hidden Valley Creek
I = Tap water

TABLE 5

Recoveries of 30 ppb Pb

Compound (ppm)	Orig. Pb ppb	No Modif. ppb	%	Pd-Mg Modif. ppb	%	Ni-Tart. Mod. ppb	%
Dist. W.	> 0.1	32.8	109	29.4	98	30.8	103
$Mg(NO_3)_2$ (1,000)	1.9	18.7	56	29.3	92	32.1	101
$MgCl_2$ (5,000)	0.1	0.4	1	31.3	104	30.4	101
$Ca(NO_3)_2$ (2,000)	1.8	5.2	11	31.8	100	31.0	97
$Fe(NO_3)_3$ (100)	1.3	28.0	93	30.7	98	32.3	103
$Al(NO_3)_3$ (150)	1.1	25.9	84	25.8	83	31.9	103
$MnSO_4$ (275)	1.3	5.2	13	31.9	102	32.8	105
$Cu(NO_3)_2$ (150)	2.6	21.8	77	30.0	92	29.4	90
$NaNO_3$ (7,500)	1.5	19.1	59	32.4	103	32.1	102
$KHCO_3$ (500)	1.6	18.3	56	30.6	97	31.1	98
KF (150)	> 0.1	18.5	62	29.7	99	30.1	100
Na_3PO_4 (1,750)	2.4	21.1	59	30.1	93	31.8	98
Humic Ac. (sat.)	2.7	15.9	44	29.4	90	32.8	100
Seawater	0.8	1.0	1	2.1	7	15.7	50

Fig. 1

ABSORPTION (%) VS TIME (SEC)

Fig. 2

QUADRATIC (FIT=.998 PTS=13)

CONC(PPB)

Figure 3
Peak area vs. pH (ammonia)

peak area

pH

		1	2	3	4	5	6	7	8	9	10
Na-tartrate	——	50	75	105	110	110	110	110	110	110	110
Tartaric acid	—+—	55	85	105	112	114	115	118	119	120	120
K-tartrate	—*—	65	100	110	116	120	120	120	120	120	120

Figure 4

Peak area vs. pH (ammonia-nitric acid)

Peak area	30	60	90	105	110	112	112	113	114	113	113	112	111	110	109	109	105	70	30
pH	1	2	3	4	5	6	7	8	9	10	9	8	7	6	5	4	3	2	1

Figure 5
Peak area vs. Nickel addition

Ni %	Blank	Distilled water	Tap water
0.0	3	103	40
0.1	4	103	100
0.2	5	104	120
0.3	5	104	127
0.4	6	105	128
0.5	6	106	128
0.6	7	107	128
0.7	7	107	129
0.8	8	108	129
0.9	9	109	129
1.0	9	109	130

peak area

Ni %

Blank ——
Distilled water —+—
Tap water —*—

Figure 6
Peak area vs. Tartrate addition

peak area

	0.0	0.5	1.0	1.5	2.0	2.5	3.0
Blank	3	4	5	6	6	7	7
Distilled water	50	80	100	104	105	106	108
Tap water	41	100	120	128	129	128	128

Tartrate %

Figure 7
Peak area vs. Modifier addition

peak area

Modifier %

	0.0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Blank ————	3	4	5	5	6	6	7	8	9
Distilled water —+—	52	78	100	104	105	107	108	108	109
Tap water —*—	45	93	121	126	128	128	127	126	127

Figure 8
Multi-injection Technique

peak area

	No. of Injection	0	5	10	15	20
Blank	—	0	5	10	15	20
Distilled water	+	3	30	50	70	90
Tap water	*	10	65	108	145	158
Rain water	□	18	81	115	145	155

No. of Injection