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Minimizing Chloride Interferences Produced by Combination Acid Digestion Using Palladium and Hydrogen as a Matrix Modifier in Graphite Furnace Atomic Absorption Spectrometry

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■ The use of $Pd/Mg(NO_3)_2$ and 5% H_2 as a modifier is evaluated as a method of reducing the chloride interferences produced by a mixed-acid digestion. The presence of 10 μL of 2% HCl produces suppressions which range from 15 to 90% for As, Sn, Pb, Cd, and Tl with the use of $Pd/Mg(NO_3)_2$ as the modifier. The use of $Pd/Mg(NO_3)_2$ along with 5% H_2 (during the dry and the char) reduces the suppression to less than 5% for Pb, Cd, and Tl. The use of Pd and 5% hydrogen as the matrix modifier for tin reduces the suppression caused by the HCl to less than 5%. In addition, if the 5% H_2 gas mixture is not adequately purged from the furnace prior to atomization, the selenium response is reduced by 18%.

Introduction

The use of palladium as a matrix modifier for graphite furnace atomic absorption spectrometry (GFAAS) is the subject of a number of recent publications (*1–15*). The interest in palladium is partially generated by its ability to thermally stabilize a number of elements, especially the semimetallics (*6*, *7*, *9*). The added thermal stability provides analytical utility by minimizing or eliminating matrix interferences during two of the steps common to most furnace programs. First, the Pd stabilizes the analyte and allows the removal of the sample matrix via the elevated (200–700 °C) charring temperatures. Second, the Pd raises the appearance temperature of the analyte during atomization thereby producing a warmer gas-phase temperature during atomization. The elevated gas-phase temperatures reduce the analyte-containing polyatomics formed during atomization (*5*, *16*, *17*).

The interaction Pd has with the various metals that results in the enhanced thermal stability is an area of current investigation (*7*). Wendl and Muller-Vogt have reported a Pb–Pd intermetallic complex using X-ray diffraction (*18*). Rettberg and Beach have indicated that the formation of intermetallic species between the analyte and the palladium may be the interaction that results in the added stability (*8*). Early investigations indicated that the performance of Pd as a modifier was significantly influenced by sample matrix. Strong oxidizing matrices resulted in poor modifier performance. The oxidation state (Pd needs to be in its reduced form) of the Pd plays a significant role in its overall performance (*7*, *9*). Methods for assuring that the Pd is in its reduced form include furnace pretreatment of the Pd, addition of an aqueous reducing agent along with the Pd, and addition of a gaseous reducing agent during the furnace cycle. The most effective means for assuring the Pd is in its reduced form has been reported to be the use of a 5% H_2/Ar gas mixture (*5*, *7*).

Various purge gases have been used in GFAAS to enhance sensitivity and/or minimize matrix effects (*19–30*). The use of hydrogen as a reducing agent for Pd (*5–7*) is recommended over the alternatives because it minimizes the contamination which often accompanies the addition of aqueous reducing agents. The use of hydrogen also affords a means of minimizing or eliminating halogen-induced suppressions. L'vov (*16*) has indicated that the relatively high bond dissociation energy of hydrogen halides allows the hydrogen under the correct conditions to effectively compete for free halide during atomization, thereby minimizing the halide interference in the gaseous state. The use of hydrogen as a matrix modifier for the elimination of chloride interferences has been reported for the determination of lead in steel (*25*, *30*).

The U.S. EPA has developed and approved methodology for both drinking water (1980) and wastewater (1979) analysis using graphite furnace AAS. This methodology requires the use of standard additions for sample analysis in order to correct for operative matrix suppression such as chloride on Tl. Digestion procedures which are amenable to graphite furnace analysis often preclude the use of HCl because of the chloride interferences on certain elements. This is somewhat problematic in that HCl is often used to solubilize certain metals as their chlorides. In addition, this implies that a single digestion procedure is not compatible with direct aspiration flame AAS, inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and GFAAS. The U.S. EPA has addressed these shortcomings with method 200.2, which is a mixed-acid digestion which is amenable to ICP-AES, ICP-MS, and GFAAS. This article describes the application of mixed-acid digestion to trace-metal determination by GFAAS. It focuses on the use of Pd as a "universal" modifier and the use of H_2 as a matrix modifier. The H_2 function is two-fold. First, it is an effective means of maintaining the Pd in its reduced form in the presence of oxidizing sample matrices. Second, the hydrogen minimizes or eliminates the HCl interference, which is unavoidable because of the mixed-acid digestion.

Experimental Section

Reagents. Modifiers. (a) Palladium/Magnesium Nitrate Modifier. The palladium powder (Johnston Matthey, Material Technology, Royston, England) used was 99.998% pure and was found to contain trace amounts of silver. The palladium modifier solution is made by dissolving 30 mg of palladium in 100 μL of concentrated nitric acid. The modifier solution is then gently warmed on a hot plate (in a 10-mL graduated cylinder) until the palladium powder has complete dissolved. To date, it has not been necessary to add HCl in order to achieve complete dissolution of the palladium powder. The resulting solution is diluted to 5 mL, and 20 mg of magnesium nitrate hexahydrate (99% minimum purity, EM Science, Gibbstown, NJ) is added. After the magnesium nitrate has been added, the solution is diluted to the mark with ASTM type I water.

(b) Palladium Modifier. Palladium modifier solution is made by dissolving 30 mg of palladium in 100 μL of concentrated nitric acid. The solution is gently warmed on a hot plate until the palladium is dissolved. The solution is then diluted to 10 mL.

Table I. Graphite Furnace Operating Conditions[a-c]

element	wavelength, nm	slit, nm	pyrolysis temp, °C	atom., °C
As[d]	193.7	0.7	1300	2200
Cd	228.8	0.7	800	1600
Pb	283.3	0.7	1200	2000
Se[d]	196.0	2.0	1000	2000
Sn	286.3	0.7	1400	2300
Tl	276.8	0.7	1000	1600

[a] Matrix modifier, 0.015 mg of Pd + 0.01 mg of $Mg(NO_3)_2$ or 0.015 mg of Pd. [b] A 5% H_2 in Ar gas mix is used during the dry and char steps at 300 mL/min for all elements. The 5% H_2 is part of the matrix modifier but is added during specific furnace cycles as mentioned in the text. [c] All determinations are based on integrated peak areas. [d] An electrodeless discharge lamp was used for this element.

Standard Solutions. The working standards were prepared by diluting the 1000 μg/mL stock standard solution (made according to the procedure reported in EPA method 200.7) with 1% HCl (v/v) and 2% HNO_3 (v/v) such that the resulting standard represented the high point on the calibration curve; subsequent dilutions were performed by the autosampler. All working standard solutions were stored in Nalgene (HDPE) plastic bottles.

Nitric Acid/Hydrochloric Acid. The nitric acid used was Ultrex Baker analyzed (J. T. Baker Inc., Phillipsburg, NJ). The hydrochloric acid used was Ultrex Baker analyzed (J. T. Baker Inc.).

Instrumentation. Graphite Furnace. The graphite furnace AA spectrometer used was a Perkin-Elmer 5100 equipped with Zeeman background correction. The Perkin-Elmer AA spectrometer was equipped with an HGA 600 furnace and an AS-60 autosampler. The capability of using an alternative purge is a standard option with the 5100 and is software controlled. L'vov platforms were used throughout this study. The furnace operating parameters are listed in Table I. It is important to realize that when the Perkin-Elmer 5100 furnace purge gas is electronically changed to the alternative gas there is a time lag before the furnace gaseous environment is completely converted. This time lag was determined using a helium leak detector. The time lag for initial detection of hydrogen was ~20 s while an additional 5 s was required to completely purge the tube. In order to compensate for this time lag, an additional 30-s furnace step at 20 °C was inserted after the purge gases were switched to ensure the graphite tube contained the appropriate gas.

Sample Preparation. The sample preparation procedure utilized a mixed-acid digestion, which is described in detail in EPA method 200.2. Briefly, method 200.2 involves the addition of 1.0 mL of (1 + 1) HCl (v/v) and 2 mL of (1 + 1) HNO_3 (v/v) to a 100-mL aqueous sample. The sample is then evaporated (without boiling, 85 °C) to approximately 20 mL, at which point it is covered with a watch glass and allowed to reflux for 30 min. The sample is allowed to cool and is transferred into a 50-mL volumetric flask for final dilution with ASTM type I water.

Results and Discussion

GFAAS is prone to chloride-induced suppressions; therefore, a preliminary investigation focused on the effects of HCl on certain metals via the formation of volatile chlorides or the formation of chlorides during atomization. This investigation involved pipeting a known amount of analyte on the platform and subsequently adding various volumes (3, 5, 10, 15, and 20 μL) of 2% HCl. The modifier used in this investigation was a mixture of palladium and magnesium nitrate. Figure 1 is a plot of normalized integrated absorbance vs microliters of 2% HCl for Pb, Cd, As, Sn, and Tl. Figure 1 was generated using a pure argon purge gas throughout the furnace program. Figure 1 indicates that the presence of HCl in the sample matrix does suppress the signal relative to 1% HNO_3. The actual magnitude of the interference varies considerably, but in all cases, the addition of the first 5 μL of 2% HCl produces a greater suppression proportionally than the addition of the next 15 μL. The suppression, which is evident for Pb, Cd, As, Sn, and Tl, is most pronounced for Cd and Tl. The Cd and Tl signals are suppressed by over 85% with the addition of 5 μL of 2% HCl.

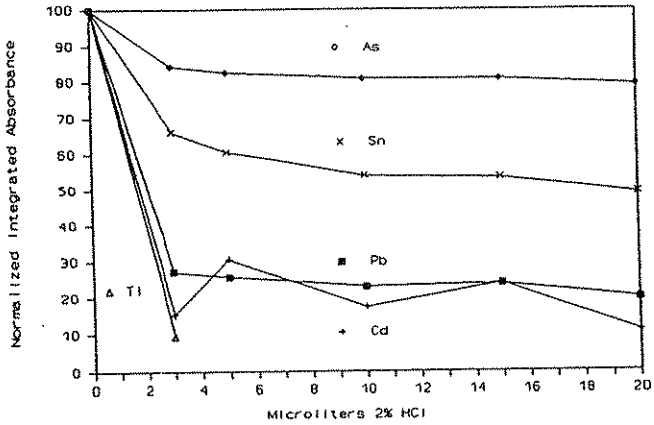

Figure 1. Effectiveness of $Pd/Mg(NO_3)_2$ as a modifier in the presence of up to 2% HCl. (% RSD of individual points 2–3%.)

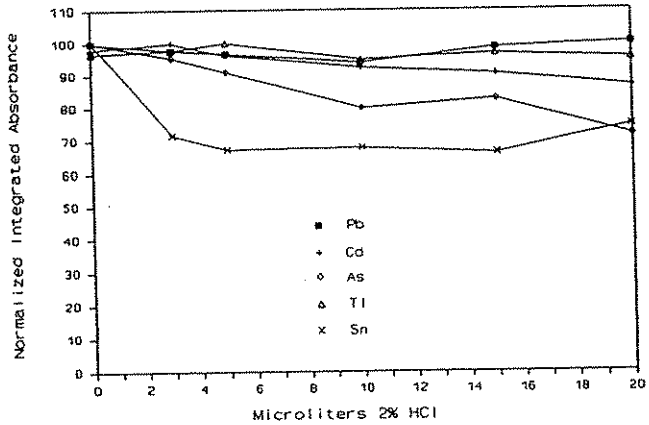

Figure 2. Effectiveness of $Pd/Mg(NO_3)_2$ and H_2 as a modifier in the presence of up to 2% HCl. (% RSD of individual points 2–3%.)

Two of the most common methods for the removal of chloride interferences are (1) the formation of a volatile chloride species at a reduced temperature and/or (2) addition of a modifier that has a greater affinity for the free chloride and can favorably compete with the analyte for the free chloride during atomization. Argon/hydrogen gas mixtures have been reported to decrease the interferences produced by chlorides (*24*, *30*).

The data in Figure 2 represent an initial evaluation of the use of 5% H_2 in argon along with $Pd/Mg(NO_3)_2$ as a method of eliminating the chloride interference. The data in Figure 2 were collected using the same experimental procedure as Figure 1 except that the furnace was purged with a gas mixture of 5% H_2 in Ar during the dry and char steps. Figure 2 indicates that the most severe suppressions observed in Figure 1 are minimized or eliminated in the case of Pb, Tl, and Cd. In Figure 1 the Tl signal is suppressed by over 90% with the addition of 5 μL of 2% HCl while in Figure 2 this suppression is reduced to 5% with the addition of the 5% H_2 purge gas. However, the use of 5% H_2 along with $Pd/Mg(NO_3)_2$ recovered only 5–10%

Table II. Effects of Different Furnace Gas Programs on Reducing the Chloride Interference on Lead

exp	sample[a]	furnace[b] temp	time	gas	abs $\bar{x} \pm 2\sigma$
1	1% HNO_3	120	50	Ar	0.102 ± 0.004
		1200	30	Ar	
		20	30	Ar	
2	2% HCl	120	50	Ar	0.009 ± 0.004
		1200	30	Ar	
		20	30	Ar	
3	2% HCl	120	50	Ar	0.067 ± 0.003
		20	30	Ar	
4	2% HCl	120	50	Ar	0.100 ± 0.002
		20	30	H_2	
5	2% HCl	120	50	Ar	0.007 ± 0.003
		1200	30	Ar	
		20	30	H_2	
6	2% HCl	120	50	H_2	0.081 ± 0.008
		20	30	Ar	
7	2% HCl	120	30	H_2	0.050 ± 0.018
		20	30	Ar	
		1200	30	Ar	
		20	30	Ar	
8	2% HCl	120	50	H_2	0.102 ± 0.004
		200	30	H_2	
		20	30	Ar	
		1200	30	Ar	
		20	30	Ar	
9	2% HCl	120	50	H_2	0.099 ± 0.002
		1200	30	H_2	
		20	30	Ar	
10	2% HCl	120	50	H_2	0.100 ± 0.002
		1200	30	H_2	
		20	30	H_2	

[a] A 10-μL aliquot of 50 μg/L Pb standard for each experiment. Sample size, 10 μL. [b] All furnace programs have an atomization step of 2200 °C under stop-flow conditions. Temperature in degrees centigrade; time in seconds.

of the As and Sn signal relative to $Pd/Mg(NO_3)_2$ modifier. The results shown in Figure 2 raise some interesting questions in regard to how the hydrogen eliminates the chloride interference on Pb but only marginally on Sn.

Lead was used to further investigate where in the furnace program the 5% hydrogen gas mixture is most effective in eliminating or minimizing the interference produced by the chloride. The results from this investigation are tabulated in Table II.

The first experiment shown in Table II gives the Pb response in the absence of HCl. The second experiment indicates the suppressive effect of HCl on Pb signal under identical furnace conditions. In the third experiment the 1200 °C char has been removed from the furnace program. A comparison of the Pb response in experiments 2 and 3 indicates a partial loss of Pb during the 1200 °C char. The fourth experiment investigates the effectiveness of hydrogen in eliminating the chloride interference during atomization. The addition of hydrogen during atomization should reduce the Pb suppression by effectively competing with Pb for the free chloride (*16*). A comparison of the relative responses in experiments 3 and 4 indicates that the presence of hydrogen during atomization does reduce the chloride interference. In experiment 5, the hydrogen purge gas is used prior to atomization along with a 1200 °C char. The resulting Pb response is suppressed similar to experiment 2. The results from experiments 2–5 indicate that if a 1200 °C char is used the chloride must be removed or the Pb will be lost during the char. Experiments 6–8 are designed to evaluate the effectiveness of hydrogen in removing the chloride interference during the drying cycle. The sixth experiment utilizes the hydrogen mixture in the dry. In addition, the char step in the furnace program has been eliminated. The Pb response in experiment 6 is 80% of that in experiment 1. A comparison of experiments 3 and 6 may indicate a marginal reduction in the chloride interference if the hydrogen is used in the dry without a 1200 °C char. In experiment 7, the hydrogen is used in the dry along with a 1200 °C char. A comparison of experiments 2 and 7 indicates that the hydrogen does remove some of the chloride interference during the dry. The comparison of experiments 2 and 7 may be a better gauge of the effectiveness of the hydrogen to remove the chloride during the dry because the 1200 °C char removes the Pb prior to atomization and thereby eliminates any reduction in the chloride interference which may occur due to the platform's ability to reduce the chloride interference. In the eighth experiment, a 200 °C prechar furnace step has been added in which hydrogen is used as the purge gas. This demonstrates that the hydrogen can be used to eliminate the chloride interference with furnace temperature of less than 210 °C. Experiments 9 and 10 were designed to determine if the chloride interference could be eliminated prior to atomization with the use of hydrogen in the dry and a 1200 °C char. Experiment 9 indicates that the use of hydrogen during the dry and the char will eliminate the chloride interference. The combination of experiments 9 and 10 indicates that if the chloride interference is eliminated prior to atomization the addition of hydrogen during the cool-down cycle is not necessary.

Figure 2 indicated that the interference produced by chloride on Sn is not totally eliminated by the use of hydrogen in the dry and the char. In an attempt to eliminate the chloride interference, the hydrogen gas mixture was added to the preatomization cycle. The addition of hydrogen during atomization should reduce the Sn suppression by effectively competing with Sn for the free chloride (*16*). The use of hydrogen throughout the furnace program produced results similar to those reported in Figure 2 for Sn. Further investigation indicated that the $Mg(NO_3)_2$ in the modifier was influencing the trend in the Sn response shown in Figures 1 and 2. The suppression on Sn by the presence of HCl was further investigated using Pd alone [without $Mg(NO_3)_2$]. The use of Pd (without the hydrogen gas mixture) as a modifier for Sn produced a Sn response vs microliters of 2% HCl plot similar to that of Cd in Figure 1. The use of Pd along with hydrogen in the dry and the char produced a Sn response vs microliters of 2% HCl plot similar to that of Cd in Figure 2.

The use of Pd alone as a modifier for Sn was further investigated in order to evaluate where in the furnace program the hydrogen eliminates the interference. Table III summarizes a series of furnace programs used to investigate the chloride interference on Sn. The first experiment shown in Table III gives the Sn response in the absence of HCl. The second experiment indicates the suppressive effects of HCl on Sn under identical furnace conditions. In the third experiment, the 1400 °C char was eliminated. The relative response indicates that some of the Sn is lost during the char. The fourth experiment utilizes the same furnace program except hydrogen is present just prior to atomization. It is worth noting that, due to the purge gas delay inherent in the instrument, the hydrogen was present in the furnace for approximately 5–10 s prior to atomization in experiment 4. This may indicate that hydrogen is competing with the Sn for the chloride during atomization and thereby minimizing the

Table III. Effects of Different Furnace Gas Programs on Reducing the Chloride Interference on Tin

exp	sample[a]	furnace[b] temp	time	gas	abs $\bar{x} \pm 2\sigma$
1	1% HNO_3	120	50	Ar	0.152 ± 0.002
		1400	30	Ar	
		20	30	Ar	
2	2% HCl	120	50	Ar	0.016 ± 0.004
		1400	30	Ar	
		20	30	Ar	
3	2% HCl	120	50	Ar	0.079 ± 0.009
		20	30	Ar	
4	2% HCl	120	50	Ar	0.137 ± 0.009
		20	30	H_2	
5	2% HCl	120	50	H_2	0.132 ± 0.007
		20	30	Ar	
6	2% HCl	120	50	H_2	0.132 ± 0.005
		20	30	Ar	
		1400	30	Ar	
		20	30	Ar	
7	2% HCl	120	50	H_2	0.135 ± 0.002
		1400	30	H_2	
		20	30	Ar	
8	2% HCl	120	50	H_2	0.147 ± 0.004
		1400	30	H_2	
		20	30	H_2	

[a] A 5-μL aliquot of 250 μg/L Sn standard for each experiment. Sample size, 10 μL. [b] All furnace programs have a stop-flow atomization at 2300 °C and a cleanout cycle at 2600 °C. Temperature in degrees centigrade; time in seconds.

interference. The improvement in the Sn response found when experiment 3 is compared to 4 is similar to the response difference found in Table II for Pb. The fifth experiment indicates that the chloride interference can be reduced by the use of hydrogen in the dry, possibly due to the enhancement of HCl formation during the dry. The Sn response in experiment 6 indicates that the Sn response can be preserved using a 1400 °C char provided hydrogen is used during the dry. The degree to which the Sn response is preserved in experiment 6 would not be predicted on the basis of the Pb response from experiment 7 in Table II. Experiment 7 utilizes the hydrogen gas mixture in both the dry and the char. The Sn signal is 86% of that in 1% HNO_3 standard. This may indicate that the use of hydrogen in the dry and the char does not completely remove the chloride interference. Experiment 8 utilizes an all-hydrogen gas furnace program and the Sn signal is 97% of that in experiment 1.

It has been reported that the use of hydrogen as a reducing agent suppresses the selenium response due to the formation of selenium hydride (*30*). Initially we experienced a similar selenium suppression with the use of the argon/hydrogen gas mixture. Table IV is a summary of furnace programs used to investigate the selenium suppression. Experiment 1 utilizes a 40-s purge with argon prior to atomization. The second experiment has a 30-s purge with argon prior to atomization, and the selenium response is 98% of that in experiment 1. The third experiment has a 20-s purge with argon, and the selenium signal is 92% of experiment 1. The fourth experiment utilizes a 10-s purge with argon, and the selenium response is 82% of experiment 1. The fifth experiment eliminates the argon purge prior to atomization. The selenium response is similar to experiment 4. Through the use of a helium leak detector it was determined that the Ar/H_2 gas would begin to be purged from the furnace at ~20 s after the electronic valve had been actuated. The furnace would be completely purged of H_2 in about 25–30 s. Therefore,

Table IV. Effect of the Presence of Hydrogen Gas in the Furnace during Selenium Atomization

exp	sample[a]	furnace[b] temp	time	gas	abs $\bar{x} \pm \sigma$
1	1% HNO_3	130	35	H_2	0.179 ± 0.003
		900	30	H_2	
		20	40	Ar	
2	1% HNO_3	130	35	H_2	0.175 ± 0.002
		900	30	H_2	
		20	10	H_2	
		20	30	Ar	
3	1% HNO_3	130	35	H_2	0.164 ± 0.001
		900	30	H_2	
		20	20	H_2	
		20	20	Ar	
4	1% HNO_3	130	35	H_2	0.148 ± 0.003
		900	30	H_2	
		20	30	H_2	
		20	10	Ar	
5	1% HNO_3	130	35	H_2	0.148 ± 0.002
		900	30	H_2	
		20	40	H_2	

[a] A 10-μL aliquot of 100 μg/L Se standard for each experiment. Sample size, 10 μL. [b] All furnace programs have an atomization step of 2300 °C under stop-flow conditions. Temperature in degrees centigrade; time in seconds.

Table V. Precision and Recovery Data for Drinking Water

element	av conc, ng/mL	% RSD	fortif conc,[a] ng/mL	% RSD at fortif conc[b]	av % rec
As[c]	0.5	10.5	10	0.6	88
Cd	<0.05[d]	*e*	0.5	6.3	105
Pb	<0.7[d]	*e*	10	4.0	101
Se[c]	<0.6[d]	*e*	25	1.5	89
Sn[c]	<1.7[d]	*e*	50	0.4	101
Tl	<0.7[d]	*e*	20	2.8	95

[a] Fortified sample concentrations based on 100-mL sample volumes. [b] RSD reported on 50-mL sample volumes. [c] Electrodeless discharge lamps were used. [d] Sample concentration less than the established method detection limit. [e] Not determined on sample concentration less than the method detection limit.

with purge times of less than 20 s, the Se signal may be suppressed due to the presence of H_2 during atomization. The presence of H_2 may cause the formation of selenium hydride during atomization (*29*). Purging times greater than ~30 s provide a pure argon gas-phase environment in which the formation of hydride species is inhibited.

The results obtained in Figure 2 indicated that the use of $Pd/Mg(NO_3)_2$ and 5% H_2 at least minimized the suppressions produced by the presence of HCl. The use of $Pd/Mg(NO_3)_2$ and 5% H_2 was then applied to the analysis of surface water, groundwater, and drinking water. The evaluation involved taking nine samples from each sample type (drinking, well, pond) and digesting them according to the mixed-acid digestion procedure EPA method 200.2. Four of the nine samples were fortified with the metals such that an absorbance of 0.1 would be produced by the added metal. The HCl concentration in the digested sample was 1.0%. Table V represents the results obtained from the analysis of drinking water. The percent relative standard deviations (% RSD) for fortified samples are approximately 1–7%. The average percent recoveries for drinking water ranged from 88 to 105%. Table VI contains the results obtained for the well water sample. The percent relative standard deviations for the fortified concentration for well water are in the 1–5% range. The average percent recoveries ranged from 95 to 110% for the well water

Table VI. Precision and Recovery Data for Well Water

element	av conc, ng/mL	% RSD	fortif conc,[a] ng/mL	% RSD at fortif conc[b]	av % rec
As[c]	0.9	14.2	10	2.1	102
Cd	1.8	11.9	0.5	4.6	109
Pb	<0.7[d]	*e*	25	0.7	102
Se[c]	<0.6[d]	*e*	25	1.2	96
Sn[c]	<1.7[d]	*e*	50	3.0	106
Tl	<0.7[d]	*e*	50	1.4	98

[a] Fortified sample concentration based on 100-mL sample volume. [b] RSD reported on 50-mL sample volume. [c] Electrodeless discharge lamps were used. [d] Sample concentration less than the established method detection limit. [e] Not determined on sample concentration less than the method detection limit.

Table VII. Precision and Recovery Data for Pond Water

element	av conc, ng/mL	% RSD	fortif conc,[a] ng/mL	% RSD at fortif conc[b]	av % rec
As[c]	3.2	4.1	10	0.8	101
Cd	<0.5[d]	*e*	0.5	4.5	99
Pb	1.2	20.5	25	1.8	102
Se[c]	<0.6[d]	*e*	25	1.6	98
Sn[c]	<1.7[d]	*e*	50	3.3	118
Tl	<0.7[d]	*e*	50	5.2	101

[a] Fortified sample concentration based on 100-mL sample volumes. [b] RSD reported on 50-mL sample volumes. [c] Electrodeless discharge lamps were used. [d] Sample concentration less than the established method detection limit. [e] Not determined on sample concentrations less than the method detection limit.

samples. Table VII contains the data obtained for the pond water sample. The percent relative standard deviations for the fortified samples are 1–6% with the average percent recoveries ranging from 97 to 118%.

Conclusion

The use of $Pd/Mg(NO_3)_2$ and 5% H_2 as a modifier for graphite furnace AAS virtually eliminates the chloride interference from a mixed-acid digestion for Cd, Pb, and Tl. The chloride interference on Pb can be eliminated using a 5% H_2 gas purge and furnace temperatures of 120–200 °C. The removal of the chloride must occur before the use of a 1200 °C char for Pb. The use of the 5% hydrogen gas mixture during the preatomization furnace cycle does reduce the chloride interference on Pb and Sn provided the chloride interference has not been removed via the dry and char. The chloride interference is not eliminated by the use of $Pd/Mg(NO_3)_2$ and 5% H_2 modifier for As and Sn. The use of Pd and 5% hydrogen as a modifier for Sn eliminates the chloride interference. Selenium, response is suppressed by the use of hydrogen as a modifier if the hydrogen is not adequately purged from the furnace prior to atomization. The use of a mixed-acid digestion is amenable to graphite furnace AAS for the analysis of pond water, groundwater, and drinking water samples if the hydrogen is used in order to minimize the chloride-induced suppression.

Registry No. As, 7440-38-2; Cd, 7440-43-9; Pb, 7439-92-1; Se, 7782-49-2; Sn, 7440-31-5; Tl, 7440-28-0; Pd, 7440-05-3; water, 7732-18-5.

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