Combined Nickel and Phosphate Modifier for Lead Determination in Water by Electrothermal Atomic Absorption Spectrometry

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The effectiveness of nickel nitrate plus ammonium dihydrogenphosphate as a combined modifier for the determination of lead in a variety of water samples by ETAAS was evaluated. Optimization of the temperature program, modifier mass and pyrolysis hold time for the determination of lead was carried out. The results indicate that the combined modifier allows the quantitative stabilization of Pb in water samples up to 1200 °C during the pyrolysis step. In comparison, the maximum pyrolysis temperature without the modifier is 900 °C or lower. The modifier further reduces the background absorbance caused by sample matrices and significantly enhances the sensitivity of Pb determination. The observed detection limit is 0.14 µg l^{-1} with a sample volume of 10 µl. The characteristic mass or sensitivity of the proposed method is 7 pg. The tolerable amounts of various interferents such as chloride, sulfate and carbonate in the presence of the modifier are high enough for the determination of lead in a variety of waters. The recoveries of spiked Pb in tap water and waters from variably contaminated waters from a ditch, a lake and a river in the Chicago area were 89–101%. The proposed method has several advantages over commonly used methods with H_3PO_4 or $Mg(NO_3)_2 + NH_4H_2PO_4$ as modifiers.

Keywords: *Lead; chemical modifier; atomic absorption spectrometry; water; interferences*

Lead is toxic to humans and animals, especially to young children. As a result of worldwide accumulation, Pb presents a serious environmental and health hazard.[1] In natural waters, Pb concentrations often range from 1 to 30 µg l^{-1}.[2] Hence highly sensitive analytical techniques are necessary to determine the Pb concentrations in these waters. Because of its sensitivity, versatility, speed and specificity, ETAAS has been extensively utilized in the direct analysis of water for numerous elements.[3] In recent decades, ETAAS has been the US Environmental Protection Agency (USEPA) method of choice for elemental analysis including Pb in water samples.[4,5] However, problems arise in analyzing samples composed of complex matrices. Chemical interference encountered in a pulse-heated electrothermal atomizer frequently causes depression of absorbance signals due to the co-volatilization of the analyte with the matrices.[6] Currently available ways of reducing such interferences include platform atomization,[7] probe atomization,[8] Zeeman effect background correction[9] and chemical treatment of the sample in the graphite furnace.[10,11] Chemical modification is preferred as a simple approach to alleviating interferences encountered especially in the direct determination of volatile elements in samples with significant amounts of matrices. The modifiers can act as pyrolysis aids and delay the vaporization of the analyte before the graphite tube is nearly isothermal,[12] the ideal condition for atomization. To date, a variety of modifiers have been suggested for Pb, including palladium,[13] palladium plus magnesium,[3] ammonium phosphate,[14] ascorbic acid,[15] lanthanum[16] and others.[17–20] Despite considerable efforts having been made to search for valid Pb modifiers in the past, only limited success has been reported for modifiers that meet some or all the criteria

of a suitable modifier.[3,13–20] These criteria include suppression of the interference associated with sample matrices, increase of pyrolysis temperature without Pb loss and enhancement of Pb signals. Therefore, further work in this area is deemed necessary.

In this work, we investigated the effectiveness of a combined nickel nitrate and ammonium dihydrogenphosphate modifier for the determination of Pb in natural waters. The objective was to develop a valid and feasible analytical scheme for the direct measurement of Pb in drinking and surface waters with complex matrices, some of which interfere with Pb determination.

EXPERIMENTAL

Instrumentation and Reagents

A Perkin-Elmer (Norwalk, CT, USA) Model 503 atomic absorption spectrometer equipped with an HGA-2100 graphite furnace controller and a deuterium arc background corrector was used for all atomic absorption measurements. Collection of absorbance signals and peak integration were achieved with PeakSimple II software via a data acquisition board (SRI Instruments, Torrance, CA, USA). The wavelength, spectral bandwidth and lamp current used for Pb determination were set according to the recommendations of the instrument manufacturer. Pyrolytic graphite-coated graphite tubes (Perkin-Elmer, Part No. B0135653) with a L'vov graphite platform (Perkin-Elmer, Part No. B0121091) were utilized throughout. When chemical modifiers were used, they were injected separately from sample solutions.

Aliquots used for the samples and modifiers were 10 µl in all cases except when indicated otherwise. The internal gas flow was interrupted during the atomization stage. The graphite furnace temperature program for Pb determination is given in Table 1. Chemicals with the highest available purity but at least of analytical-reagent grade were used to prepare solutions in deionized water. Standard solutions were made from a commercial stock standard solution of 1000 mg l^{-1} prepared from $Pb(NO_3)_2$ (VWR Scientific, Chicago, IL, USA). Working standard solutions were obtained by dilution to volume with deionized water.

Chemical modifier solutions of Ni, La and Mg were prepared from their nitrate salts. Palladium modifier solutions were prepared by diluting a 5% $Pd(NO_3)_2$ stock solution with deionized water. Modifier solutions of ammonium dihydrogenphosphate ($NH_4H_2PO_4$) were prepared by dissolving the salt

Table 1 ETAAS temperature program for Pb determination in water samples using the $Ni(NO_3)_2 + NH_4H_2PO_4$ modifier

Step	1	2	3	4
Temperature/°C	130	1000	2400	2650
Ramp time/s*	2	2	1	1
Hold time/s	40	50	5	5
Ar gas flow/ml min^{-1}	300	300	0†	300

* Estimated.

† A continuous flow of 300 ml min^{-1} was used for the USEPA Method 7421.

in deionized water. The above chemicals were obtained from Aldrich (Madison, WI, USA) and had a purity of 99.999%. All the reagents and deionized water were tested for Pb prior to the experiments and no detectable amounts of Pb were found.

Water Samples and Their Characterization

Three surface water samples were taken from the Lake Calumet area, 15 miles south of downtown Chicago, IL, USA. The surface and ground waters in the area have been substantially contaminated with slag wastes from local steel companies. In addition to the slag wastes, other solid waste materials such as household trash, demolition debris and fly ash were used as fill materials to convert the extensive coastal marshes into usable industrial and residential properties. The wastes were also disposed of in several landfills in the area. Interstate Highway 94 lies immediately to the west of the area, where it receives road deicing agents and automobile exhaust fumes from the highway. Lake Calumet connects Lake Michigan through the Calumet River.

One sample was taken directly from Lake Calumet, a second from the Calumet River and the third from a ditch near the highway. The ditch water appeared to have come from surface runoff, although mixing with the groundwater is possible before the water was discharged to the ditch. These samples were filtered through 0.2 μm syringe filters (Gelman, Ann Arbor, MI, USA) using a syringe filter assembly (VWR Scientific, USA). They were kept at 4 °C for a brief period of time before analysis. The tap water used in this study was taken from the campus of the University of Illinois at Chicago. The source of the water is Lake Michigan. The water sample was taken after running the tap for a few minutes and analyzed without further treatment. All the samples were analyzed for their pH values with an Orion (Cambridge, MA, USA) pH meter and their concentrations of F^-, Cl^-, SO_4^{2-}, PO_4^{3-} and NO_3^- with a DX100 Ion Chromatograph (Dionex, Sunnyvale, CA, USA). No phosphate was detectable in the samples.

RESULTS AND DISCUSSION

Selection of Chemical Modifiers

Several preliminary experiments were conducted to select a valid chemical modifier for the measurement of Pb in the water samples. The modifiers tested include commonly used Pd, Pd + Mg, phosphate, La and Ni. In view of their stabilization and the enhancement effects on the Pb signal in standard solutions and the water samples, $Ni(NO_3)_2$ and $NH_4H_2PO_4$ were selected as a combined modifier for further investigation. An initial screening of various concentrations of $Ni(NO_3)_2$ and $NH_4H_2PO_4$ was done to provide an adequate combination for the optimization of the temperature program discussed below.

Optimization of ETAAS Conditions

Temperature program

The temperatures of pyrolysis and atomization were first optimized using a Pb standard solution of 5 μg l^{-1} in both the presence and absence of modifiers. The optimization results are shown in Fig. 1. For the optimization of the pyrolysis temperature, an atomization temperature of 2400 °C was used. When 100 μg ml^{-1} $Ni(NO_3)_2$ with 10 mg ml^{-1} $NH_4H_2PO_4$ was added to the standard solution, a pyrolysis temperature up to 1200 °C could be used without Pb loss (curve A in Fig. 1). In comparison, pyrolysis temperatures over 900 °C in the absence of the modifier (curve C) resulted in significant Pb loss. In addition, the sensitivity of Pb determination with the addition of $Ni(NO_3)_2$ and $NH_4H_2PO_4$ was enhanced about twofold or more compared with Pb determination without the modifier. In order to optimize the atomization temperature, a fixed pyrolysis temperature of 600 °C was used. In the presence

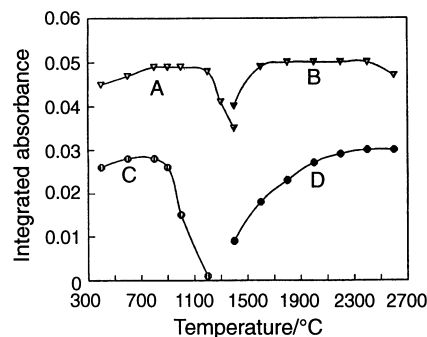**Fig. 1** Effects of chemical modifier on the pyrolysis and atomization temperatures for the analysis of 5 μg l^{-1} Pb standard solution. Combined modifier, 100 μg ml^{-1} $Ni(NO_3)_2$ + 10 mg ml^{-1} $NH_4H_2PO_4$. Curves A and C show the relationship between integrated Pb peak absorbance and pyrolysis temperature with a fixed atomization temperature of 2400 °C, (A) with and (C) without the modifier. Curves B and D depict the relationship between Pb signal and atomization temperature with a fixed pyrolysis temperature of 600 °C, (B) with and (D) without the modifier.

of the combined modifier, no significant differences for the Pb signal were observed with atomization temperatures between 1800 and 2400 °C (curve B in Fig. 1). However, the integrated absorbance of Pb without the modifier increased with increase in atomization temperature (curve D). Considering the diffusion effect at high atomization temperatures,[21] an atomization temperature of 2400 °C and a pyrolysis temperature of 1000 °C appear to be the optimum for Pb determination. These temperatures were adopted in subsequent experiments, including Pb determinations in water samples and recoveries of spiked Pb from the samples.

Pyrolysis time

The hold time for pyrolysis in routine analysis is usually set at about 30–40 s. However, complex matrices in some water samples produce high background absorption that can be beyond the correction capacity of a Zeeman effect corrector.[17,22] Therefore, it often requires a longer hold time for the determination of trace volatile elements (e.g., Pb) in these water samples. The approach of increasing the pyrolysis time has been found to be successful in many cases and has overcome the problem of background absorption.[5,23] However, the validity of using this approach depends on the effectiveness of chemical modifiers in stabilizing the analyte during the pyrolysis. The relationship between Pb recovery and pyrolysis hold time is depicted in Fig. 2 for 2 ng Pb-spiked ditch water (the sample with the most complex matrix) in the presence of $Ni(NO_3)_2$ plus $NH_4H_2PO_4$ as the modifier. The recovery was in the range 85–94% when the hold time increased from 30 to 110 s. The maximum recovery of 94% occurred at a hold time of 70 s. Therefore, a pyrolysis time of 70 s was adopted in subsequent work.
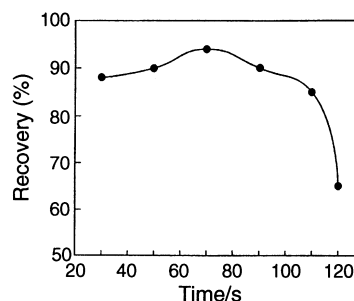

Fig. 2 Influence of pyrolysis time on the recovery of 2 ng lead-spiked ditch water. The maximum recovery of 94% occurs at 70 s.

Concentration and ratio of modifiers

The modifier concentration has been known to influence significantly the sensitivity of metal determinations.[22–24] In addition to increasing the possibility of contamination of the graphite tube, a high modifier concentration generally depresses the absorbance signal owing to secondary adsorption at the cooler ends of the graphite tube.[25,26] On the other hand, a higher modifier concentration stabilizes the analyte to higher pyrolysis temperatures.[27] Therefore, careful optimization of the modifier concentration is essential in overcoming the problems while achieving higher sensitivity and thermal stability. In this work, a standard Pb solution of $5 \mu g \, l^{-1}$ was used to examine the influence of increasing concentrations of $Ni(NO_3)_2$ and $NH_4H_2PO_4$ on the Pb absorbance signals. The results are shown in Fig. 3. It should be noted that the optimization of $Ni(NO_3)_2$ and $NH_4H_2PO_4$ concentrations was accomplished separately. During the optimization of the $Ni(NO_3)_2$ concentration the $NH_4H_2PO_4$ concentration was fixed at $10 \, mg \, ml^{-1}$ and during the optimization of $NH_4H_2PO_4$ concentration the $Ni(NO_3)_2$ concentration was fixed at $100 \, \mu g \, ml^{-1}$. For the purpose of comparison, the Pb absorbance without any modifier is also shown in Fig. 3. These results show that the maximum signal enhancement is achieved at an $Ni(NO_3)_2$ concentration of $100 \, \mu g \, ml^{-1}$ and an $NH_4H_2PO_4$ concentration of $10 \, mg \, ml^{-1}$. The combined modifier provides much higher signal enhancement than an $Ni(NO_3)_2$ or $NH_4H_2PO_4$ modifier alone. The effect of $Ni(NO_3)_2$ concentrations greater than $25 \, \mu g \, ml^{-1}$ on the integrated Pb absorbance is not very significant. Similarly, $NH_4H_2PO_4$ concentrations in the range $8–20 \, mg \, ml^{-1}$ have almost an equivalent effect on the signal enhancement. In the light of this finding, $100 \, \mu g \, ml^{-1}$ $Ni(NO_3)_2$ and $10 \, mg \, ml^{-1}$ $NH_4H_2PO_4$ were chosen as the combined modifier for the interference tests below.

Non-spectral Interferences

The frequently encountered non-spectral interferent ions and compounds on the signal of the analyte element were investigated in this work. Various interferent ions were added to a $5 \mu g \, l^{-1}$ Pb standard solution, and the Pb recovery was measured for each interferent. The results are given in Table 2, where the RSD was calculated from four replicates. Apparently, the combined modifier of $100 \, \mu g \, ml^{-1}$ $Ni(NO_3)_2$ and $10 \, mg \, ml^{-1}$ $NH_4H_2PO_4$ can tolerate sulfate up to $1.01 \, mg \, ml^{-1}$ with only a 5–10% depression of the signal generated by $5 \mu g \, l^{-1}$ Pb. Sulfate is one of the most troublesome interferent ions for Pb determination.[17,28] The above modifier appears to

Table 2 Test of interferences in the determination of Pb in $5 \mu g \, l^{-1}$ Pb standard solutions spiked with selected interferent ions. The recovery is the calculated percentage based on the integrated absorbance. The recovery of the interference-free standard solution was 100%. Standard deviations were calculated from four replicates

Interferent	Compound used	Interferent concentration/ $mg \, ml^{-1}$	Recovery (%)
Cl^-	NaCl	0.91	93 ± 7
SO_4^{2-}	Na_2SO_4	1.01	89 ± 5
ClO_4^-	$Fe(ClO_4)_3$	0.84	94 ± 5
CO_3^{2-}	Na_2CO_3	0.68	91 ± 8

have the ability to reduce the impact of sulfate anions in natural waters. The reaction mechanism between the modifier and sulfate is unknown. In addition to sulfate, the modifier can also effectively tolerate up to $0.91 \, mg \, ml^{-1}$ Cl^-, $0.84 \, mg \, ml^{-1}$ ClO_4^- and $0.68 \, mg \, ml^{-1}$ CO_3^{2-}. The high recovery of $93 \pm 7\%$ for Cl^- in Table 2 indicates that the modifier would be effective for Pb determination in chloride-rich water samples.

Limit of Detection and Characteristic Mass

The detection limit for the proposed method is $0.14 \, \mu g \, l^{-1}$, calculated as three times the standard deviation of a $10 \, \mu l$ blank solution for 10 determinations. The characteristic mass or sensitivity of Pb detection, defined as the mass of Pb which yields an integrated absorbance signal of 0.0044, is 7 pg.

Sample Analyses and Method Comparison

Using the proposed method, we determined the Pb concentrations in and recoveries from tap water and three surface water samples from the Lake Calumet area in Chicago. Table 3 gives the results for Pb in various water samples and the concentrations of some major anions in the samples. The samples were found to have Pb concentrations in the range $0.78–2.48 \, \mu g \, l^{-1}$. The recoveries of 2 ng of Pb added to the samples were 89–101%.

The results obtained from this study were compared with those from two commonly used ETAAS methods for Pb determination (Table 3). The first is the standard method recommended by the USEPA.[5] It involves the addition of $10 \, \mu l$ in a 1 ml sample of H_3PO_4 as the modifier and a $20 \, \mu l$ sample injection with continuously flowing purge gas in the absence of a platform. The second method uses $2 \, \mu g \, Mg(NO_3)_2 + 10 \, \mu g$ $NH_4H_2PO_4$ as a combined modifier.[29] The maximum ashing temperature was found to be about 1000 °C under the instrumental conditions used in this study. When used to analyze $5 \mu g \, l^{-1}$ Pb standard solution at an ashing temperature of 900 °C and an atomization temperature of 2000 °C, the latter method has a detection limit of $0.39 \, \mu g \, l^{-1}$ and a characteristic mass of 15 pg. These values were significantly higher than those obtained in this study. The analytical performances of these two methods with the water samples used in this study are shown in Table 3. The Pb concentrations and recoveries measured for the four water samples with the USEPA method were $1.01–2.57 \, \mu g \, l^{-1}$ and 79–90%, respectively. For the ditch water with a complex matrix, the recovery with the USEPA method is significantly lower than that with the proposed method. The method using the $Mg(NO_3)_2 + NH_4H_2PO_4$ modifier also gives significantly lower recoveries of 2 ng of Pb added to the water samples. In particular, the method cannot overcome the interference from the complex matrix of the ditch water. As a result, the peaks obtained during the analyses were not sufficiently well resolved to give meaningful results. This comparison demonstrates the effectiveness and applicability of the proposed modifier for the direct determination of Pb in natural waters with complex matrices.
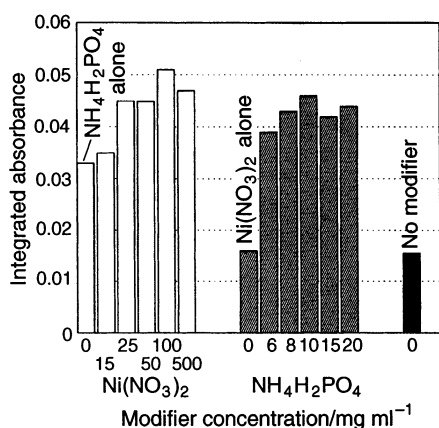

Fig. 3 Signal enhancement in response to the amount of modifier used for the determination of Pb in $5 \mu g \, l^{-1}$ standard solution. A fixed concentration of $10 \, mg \, ml^{-1}$ $NH_4H_2PO_4$ was used in $Ni(NO_3)_2$ optimization (left columns) and a fixed concentration of $100 \, \mu g \, ml^{-1}$ $Ni(NO_3)_2$ was used in $NH_4H_2PO_4$ optimization (middle columns). The far right column is the Pb signal without any modifier.

Table 3 Lead concentrations and recoveries of 2 ng Pb added to natural waters from various sources. Standard deviations were calculated from four replicates. Anion concentrations were obtained from ion chromatographic analyses. No phosphate was detected.

Sample	Pb found*/μg l^{-1}			Recovery* (%)			pH	SO$_4{}^{2-}$/mg l^{-1}	Cl$^-$/mg l^{-1}	F$^-$/mg l^{-1}	NO$_3{}^-$/mg l^{-1}
	A	B	C	A	B	C					
Lake Calumet	1.37±0.09	1.39±0.13	1.59±0.21	89±4	84±6	70±9	7.74	56.8	50.4	0.59	6.3
Calumet River	0.78±0.12	1.01±0.17	ND†	101±8	89±5	78±8	7.58	44.8	38.8	0.25	6.4
Ditch water	1.41±0.12	1.29±0.19	—‡	93±8	79±9	—‡	7.79	564	216	17.2	3.9
Tap water	2.48±0.04	2.57±0.22	3.82±0.37	95±2	90±6	85±7	7.78	28.1	12.5	1.27	1.5

* A, This method; B, EPA Method 7421; C, 2 μg Mg(NO$_3$)$_2$ + 10 μg NH$_4$H$_2$PO$_4$.[29]
† ND = not detected.
‡ Pb peaks too complex to resolve.

CONCLUSION

It is reasonable to suggest that Ni(NO$_3$)$_2$ plus NH$_4$H$_2$PO$_4$ can act as an effective chemical modifier for the determination of Pb in several types of waters by ETAAS. Based on the experimental results, the pyrolysis temperature can be set to as high as 1200 °C, which is compatible with or higher than those used with the most common chemical modifiers such as Pd and Pd + Mg. The combined Ni(NO$_3$)$_2$ + NH$_4$H$_2$PO$_4$ modifier also enhances the Pb signal and reduces matrix interferences. The recovery data for different water samples appear to verify the effectiveness and applicability of the proposed method for the direct measurement of Pb in water samples with complex matrices.

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