Sensitive Determination of Trace Lead In Lake and Drinking Waters With Etaas Using Ni-NH$_4$H$_2$PO$_4$-NaOH Modifier

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SENSITIVE DETERMINATION OF TRACE LEAD IN LAKE AND DRINKING WATERS WITH ETAAS USING Ni-NH₄H₂PO₄-NaOH MODIFIER

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A method has been developed for the direct determination of trace lead in Lake Michigan and two sources of drinking water. This method uses electrothermal atomic absorption spectrometry with platform atomization and a combined modifier of nickel, ammonium dihydrogenphosphate and sodium hydroxide (Ni-NH₄H₂PO₄-NaOH). The optimal temperature program and modifier mass allowed quantitative stabilization of lead in water solution up to 1400°C. The characteristic mass and detection limit of the proposed method are 3.4 pg and 0.038 μg/l for a 20 μl sample. The detection limit is 20 times lower than the USEPA standard method and 17.6 times lower than the manufacturer's recommended method (without modifier). The detection method can also tolerate interference of 0.6 mg/ml Cl⁻, 0.8 mg/ml SO_4^{2-} and 0.7 mg/ml CO_3^{2-}. The recoveries of lead spiked in the samples from Lake Michigan, a commercial spring water and a fountain were between 85% and 97%. The lead concentrations in these samples were found to be in the range of 0.12–0.25 μg/l and 0.11–0.30 μg/l when sample volumes of 10 and 20 μl were used, respectively. Because of the low detection limit and the tolerance to interference, the proposed method offers a low-cost solution to the determination of trace lead in drinking and natural waters.

Keywords: Lead; drinking water; detection; ETAAS

INTRODUCTION

Water in the ecosystem is vulnerable to metal contamination and can provide direct access of contaminants to the food chain[1]. Lead, as a cumulative element with a biological half life of greater than 20 years[2], presents a more serious environmental and health hazard than any other elements[3]. It is generally recognized that dietary intake is the main factor contributing to the uptake of trace

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metals including lead by human[4]. The current worldwide concern about the quality of drinking water is, to a large extent, prompted by a growing awareness of large-scale environmental pollution through the spread of trace elements and their mobilization. Over the past 15 years, local authorities and water utilities have increasingly demanded the analysis of trace elements in drinking and surface waters[5]. Generally, the concentrations of trace elements including lead in environmental water samples are in the ppb (μg/l) or sub-ppb levels[6]. The low background levels of trace and ultratrace elements necessitate low minimum detection limits. Separation and preconcentration procedures were previously utilized by analysts prior to the element determination in order to improve the detection limits for trace elements[7–10]. These procedures have several disadvantages including potential contamination[11]. In many cases, a direct and fast method without any matrix separation or preconcentration is desirable for trace-metal analysis of water. Electrothermal atomization atomic absorption spectrometry (ETAAS) is one of the few analytical techniques which meet the requirements of trace-metal analysis, and is the technique most frequently used[11]. With a stabilized temperature platform furnace (STPF), optimal analytical conditions and chemical modifiers for complex samples, this technique can be used directly to quantify the trace element level in water[11]. However, the loss of analyte in the pyrolysis stage, especially for the determination of volatile elements like lead, usually leads to the deterioration of analytical characteristics[12]. Therefore, it is essential for an effective ETAAS method to stabilize the volatile elements at high pyrolysis temperatures and to achieve a better sensitivity.

The main purpose of the current work is to develop a rapid and reliable approach for the direct determination of trace lead (Pb) in drinking and natural waters using a $Ni-NH_4H_2PO_4-NaOH$ modifier under routine ETAAS analytical conditions.

EXPERIMENTAL

Apparatus

All absorbance measurements were obtained using a Perkin-Elmer atomic absorption spectrophotometer (503) fitted with a HGA-2100 graphite furnace and a deuterium background corrector as described earlier[13]. The Pb absorbance was measured at the 283.3-nm line. The Pb hollow-cathode lamp (VMR Scientific, West Chester, USA) was operated at 7 mA. The slit width was 0.7 nm. The setting of other parameters was based on the recommendation of the in-

TABLE I   Graphite furnace program for the direct determination of Pb in waters by platform and matrix modification technique.

Step	Drying	Charring	Atomizing	Cleaning
Temperature/°C	130	1000‡	2400§	2650
Ramp time /s*	5	5	1	1
Hold time /s	40	40	7	3
Gas flow / ml.min^{-1}	300	300	Stop†	300

*Estimated values
†Continuous-flow purge gas and tube-wall used for EPA method 7421.[14]
‡500°C for EPA and no-modifier methods
§2100°C for no-modifier method

strument manufacturer. Pyrolytically coated graphite tubes with a pyrolytically coated graphite platform were utilized throughout the study.

An Eppendorf pipette fitted with metal-free disposable polypropylene tips was used to introduce sample solutions into the graphite furnace. Sample and modifier aliquots were 10 μl in all cases unless otherwise indicated. When chemical modifiers were used, they were injected *separately* from sample solutions. The internal gas flow was interrupted during the atomization stage except for the EPA method of 7421[14]. The pyrolysis and atomization temperatures were set to 500°C and 2100°C, respectively, for sample analysis without modifiers. The details of the graphite furnace temperature program used in the determination of lead in water samples are given in Table I.

Reagents

Chemicals of analytical-reagent grade or better were used to make up solutions in Milli-Q ultrapure water. The ultrapure water came from a centralized reverse osmosis system. The water then passed through five treatment columns including one activated charcoal column and four exchange resin columns (Cole Parmer, USA). The water from these columns was further treated with a Milli-Q Plus ultrapure water system (Millipore, USA). The concentration of metals in the final water is expected to be less than 1 pg/ml[15]. Calibration standard solutions were made from the commercial stock solution of 1 mg/ml prepared from Pb(NO$_3$)$_2$ (VWR Scientific, West Chester, USA). Working standard solutions were obtained by further dilution with ultrapure water.

The matrix modifier solution of 1 mg/ml nickel was prepared from analytical reagent grade nickel nitrate (Aldrich Chemical Co., Wisconsin, USA). Ammonium dihydrogenphosphate with a purity of 99.999% (Aldrich Chemical Co., Wisconsin, USA) was dissolved in ultrapure water to prepare a 20 mg/ml solution. All reagents involved in this work have been tested prior to experimentation, and no detectable amounts of lead were found.

Water Samples

One water sample was taken from a public drinking fountain on the campus of the University of Illinois at Chicago. Another sample was taken from a bottle of Dannon® commercial natural spring water, purchased from a supermarket. The third sample was collected from the coast of Lake Michigan, near the Adler Planetarium in Chicago. The lake water was filtered on site through a 0.2 μm syringe filter (Gelman Sciences, USA) using a syringe filter assembly (VWR scientific, USA). The samples were kept at 4°C for less than one week before analysis.

RESULTS AND DISCUSSION

Previous studies[13,16] and preliminary experiments led us to choose the mixed Ni-NH$_4$H$_2$PO$_4$-NaOH as the chemical modifier for the determinations of lead in the drinking and lake waters.

Optimization of Temperature Program and Modifier Mass

The main functions of chemical modifiers for element analysis with ETAAS is to stabilize the elements of high and medium volatility at high pyrolysis temperatures, to reduce matrix interference, and to control the chemical environment in graphite furnaces[17]. In our study, experiments with and without modifiers were first carried out to optimize pyrolysis and atomization temperatures. The curves of pyrolysis and atomization are shown in Figure 1. These curves were determined using 0.02 ng Pb with the Ni-NH$_4$H$_2$PO$_4$-NaOH modifier and 0.05 ng Pb without the modifier. When 100 μg NH$_4$H$_2$PO$_4$, 1 μg Ni and 1 μg NaOH were added to the platform, the pyrolysis temperature can be as high as 1400°C without a significant lead loss (curve A in Figure 1). In the absence of modifiers, the Pb signal decreases significantly when the pyrolysis temperature is over 900°C (curve C in Figure 1). In addition, the sensitivity of the Pb determination with the modifier is about four times as high as that without any modifier. Figure 1 also shows that the absorbance does not change significantly in the atomization temperature range of 2200°C to 2600°C (curves B and D). These optimization tests indicate that the combined Ni-NH$_4$H$_2$PO$_4$-NaOH modifier can stabilize Pb to a great extent and enhance Pb detection significantly. Considering the diffusional effect existing at high atomization temperatures[18] and possible matrix interference in samples, an atomization temperature of 2400°C and a pyrolysis temperature of 1000°C were used for the subsequent experiments.
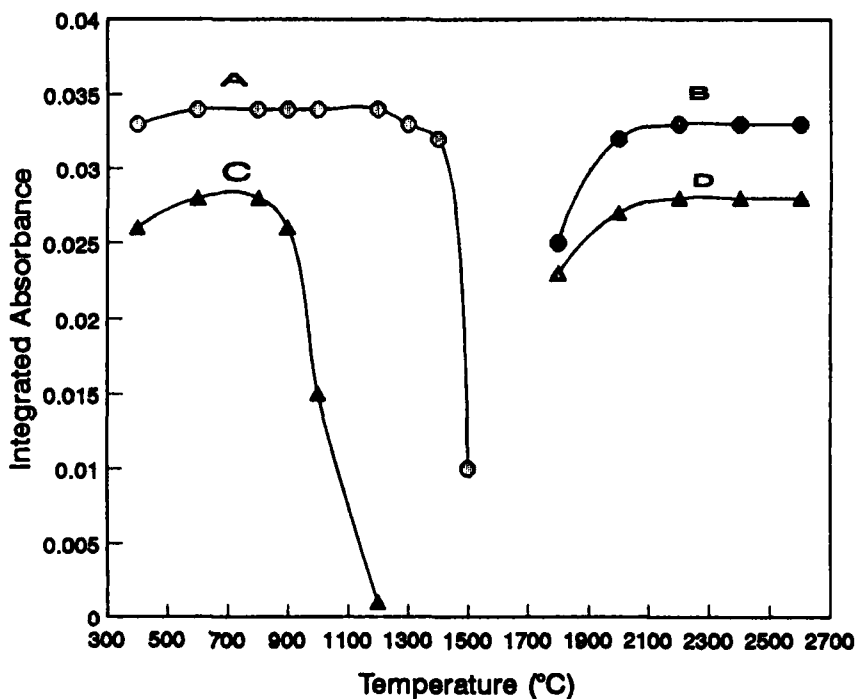
FIGURE 1   Effects of matrix modifiers on the pyrolysis and atomization temperatures for Pb deter-
mination. Pyrolysis (A) and atomization (B) curves of 0.02 ng Pb with 1 μg Ni + 10 μg $NH_4H_2PO_4$
+ 1μg NaOH modifier; and pyrolysis (C) and atomization (D) of 0.05 ng Pb with no modifiers.
Atomization temperature of 2400°C was set for pyrolysis curves, and pyrolysis temperature of 500°C
was set for atomization curves.

Modifier mass is known to have a bilateral effect on element determination[19–
21]. In order to achieve a balance between sensitivity and thermal stability for
Pb determination, the amounts of Ni and $NH_4H_2PO_4$ optimized in our previous
work[13] were employed. The optimal mass of NaOH obtained in this study was
1 μg.

Interference

The Ni-$NH_4H_2PO_4$-NaOH modifier, under the optimal ETAAS operating con-
ditions, can tolerate Cl^-, SO_4^{2-} and CO_3^{2-}. These anions have been found to
interfere with Pb determination[22,23]. The maximum permissible concentrations
of Cl^-, SO_4^{2-} and CO_3^{2-} in the presence of the proposed modifier are 0.60,
0.81 and 0.68 mg/ml, respectively. At these concentrations and below, the in-
terferents cause less than a 10% depression to the signal generated by 0.02 ng

TABLE II   Results of interference studies. All results are % recovery with the absorbance of the matrix-free reference solution being 100%. ($\pm$ Standard Deviation, SD, is calculated from four replicates).

Interference	Compound used	Permissible Conc. (mg/ml)	Recovery of 0.02 ng Pb
Cl^-	NaCl	0.6	90 $\pm$ 4
SO_4^{2-}	Na_2SO_4	0.81	92 $\pm$ 6
CO_3^{2-}	Na_2CO_3	0.68	97 $\pm$ 3

Pb (see Table II). The tolerable concentrations of interferents appear to be higher than those in many types of drinking and natural waters.

Analytical Figureures of Merit

The characteristic mass (m_0) and the detection limit of the proposed method are given in Table III. The characteristic mass is defined as the mass of analyte which yields an integrated absorbance signal of 0.0044 A.s, whereas the calculation of the detection limit is based on the variability of a blank solution (3σ of 11 replicates). The m_0 values of the proposed method are 3.6 and 3.4 pg for a sample volume 10 and 20 μl, respectively. In comparison, the U.S. Environmental Protection Agency (USEPA) method 7421[14] yields an m_0 value of 14.7 pg using our instrument. The m_0 value of the manufacturer recommended method (with no modifiers) is 12.1 pg. The detection limits of the proposed method are 0.065 and 0.038 μg/L with 10 and 20 μl samples, respectively. By contrast, the detection limits for the USEPA and no-modifier methods are 0.76 and 0.67 μg/L, respectively. The characteristic mass and detection limits of the proposed method are significantly lower than the reported method using a Ni-$NH_4H_2PO_4$ modifier or other similar modifiers[13]. The addition of NaOH apparently increases the sensitivity of Pb detection in the current method. One possible mechanism for the sensitivity enhancement is that Pb is concentrated from solution to a Pb phosphate mineral called hydroxypyromorphite prior to the drying step. Hydroxypyromorphite (formula $Pb_5(PO_4)_3OH$) precipitates very quickly in alkaline solution under the experimental conditions[16].

TABLE III   Characteristic masses and detection limits.

	This work	This work	EPA method	No modifier
Injection volume (μl)	10	20	20	20
Characteristic mass, m_0 (pg)	3.6	3.4	14.7	12.1
Detection limit (μ/l)	0.065	0.038	0.76	0.67

TABLE IV   Recoveries (%) of Pb spiked in water samples ($\pm$ SD from four replicates).

	This method	This method	EPA method	No Modifier
Sample volume (μl)	10	20	20	20
Lead added (μg/l)	2	1	2.5	2
Lake Michigan	88 $\pm$ 7	90 $\pm$ 5	89 $\pm$ 4	101 $\pm$ 5
Spring water	93 $\pm$ 6	85 $\pm$ 4	103 $\pm$ 5	113 $\pm$ 7
Fountain water	97 $\pm$ 5	86 $\pm$ 3	106 $\pm$ 8	88 $\pm$ 6

Water Analysis

Comparative studies of the Pb recoveries from different samples were undertaken in order to evaluate the applicability and effectiveness of the procedures to the analysis of water samples. The Pb recoveries of the three water samples are listed in Table IV, which shows the recovery of 0.02 ng Pb spiked in the samples of Lake Michigan, spring and fountain waters ranging from 85% to 97%. Meanwhile, the recoveries of Pb spiked in the above water samples are 87–103% by the USEPA method[14] and 88–115% by the manufacturer listed method (no modifier). The precisions of all three methods are between 4–10%. The good recoveries for the three methods points to the simple matrices of these samples, in which very low concentrations of chloride and sulfate were detected in our laboratory with a Dionex 100 ion chromatography.

The Pb concentrations of the water samples are presented in Table V, based on *direct* determinations using the proposed method under optimal conditions. Table V shows that the analytical results with 10 and 20 μl sample aliquots are comparable, and that the Pb concentrations in the three samples are in the range of 0.11–0.30 μg/l. The precisions are generally less than 15%. In comparison, the USEPA method with and without a modifier cannot detect any discernible absorbance peaks for the samples, presumably because the Pb concentrations are below the detection limits of the latter methods (see Table III).

In conclusion, the proposed ETAAS method with the Ni-NH$_4$H$_2$PO$_4$-NaOH modifier could be used in the direct determination of trace Pb in drinking and natural waters without the need of sample separation or preconcentration. This

TABLE V   Determination of Pb by ETA-AAS with platform and matrix modification, in comparison with other methods ($\pm$ SD from four replicates). All concentrations are in μg/l.

Sample volume (μl)	This method	This method	EPA method	No Modifier
	10	20	20	20
Lake Michigan	0.12 $\pm$ 0.015	0.11 $\pm$ 0.020	B.D.*	B.D.
Spring water	0.19 $\pm$ 0.026	0.15 $\pm$ 0.017	B.D.	B.D.
Fountain water	0.25 $\pm$ 0.021	0.30 $\pm$ 0.011	B.D.	B.D.

*Below detection limit.

method is relatively free from matrix interference. It can be easily incorporated into routine analysis and monitoring of Pb in waters with health concerns.

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