

Determination of Low levels of Lead in Tap, River, Ground and Snow Waters using $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ modifiers with Tungsten-treated Pyrolytic Graphite Furnace Atomic Absorption Spectrometry

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Abstract

The W-treated pyrolytic graphite (PG) furnace made it possible to enhance the precision (RSD <2%), calculated limit of detection (LOD) and sensitivity of Pb by a 100 μL injection with 5 μL of modifier of 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ and 1w/v% $(\text{NH}_4)_2\text{HPO}_4$. Using the phosphate modifier gave the LOD of 0.02 $\mu\text{g L}^{-1}$ with a hollow cathode lamp as a radiation source. The modification effect on sulfate matrices, such as Na_2SO_4 , K_2SO_4 and MgSO_4 remaining a severe interference for a Pd modifier, was extended to be the upper limit to 50, 50 and 10 mg L^{-1} as cation concentration for each matrix, respectively. The recoveries of 1.00 $\mu\text{g L}^{-1}$ of Pb added to tap, river and snow water samples were to be $104 \pm 1 \%$, $105 \pm 1 \%$ and $102 \pm 3 \%$ with 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ and to be $99 \pm 3 \%$, $99 \pm 2 \%$ and $101 \pm 4 \%$ with 1w/v% $(\text{NH}_4)_2\text{HPO}_4$, respectively. The Pb concentration of Pb in a certified reference material of river water (MNIJ CRM 7202-a) was agreement with the certified value ($1.01 \pm 0.02 \mu\text{g kg}^{-1}$)

Keywords : Lead, environmental water, atomic absorption spectrometry, matrix modifier

Introduction

Lead is an important element in toxic elements, presenting a serious environmental and health hazard to human and animals at low levels of exposure by water pollutions, because its usefulness. Since the acceptable maximum concentration levels of Pb are found to be $<10 \mu\text{g L}^{-1}$ in drinking water and environmental water because of its extremely toxicity, high sensitive and speedy analytical techniques are effective to monitoring the Pb concentration dissolved in water at low concentration levels.

The concentration levels such as a few and sub $\mu\text{g L}^{-1}$ are found in drinking water and fresh water, such as river, rain and snow. The level of Pb concentration was reported to be ranged from 0.5 to 6.2 $\mu\text{g L}^{-1}$ in snow, from 0.1 to 3.8 $\mu\text{g L}^{-1}$ in precipitation and from 0.04 to 0.7 $\mu\text{g L}^{-1}$ in stream water.¹ Background level of river water in Japan was reported to be ranged from 0.022 to 5.45 $\mu\text{g L}^{-1}$.² High sensitive and speedy analytical techniques are

necessary to determination of water samples including the low levels of Pb in waters for studies of public health or environmental science.

Since an electrothermal atomic absorption spectrometry (ETAAS) is a highly sensitive analytical technique than inductively coupled plasma-atomic emission spectrometry (ICP-AES) and has an economical merit than the ICP-mass spectrometry (MS), the ETAAS is used extensively for the direct analysis of water. The analysis of low levels of Pb in water is problematic because a time-consuming preconcentration is usually necessary and the reagents may cause contamination. In order to suppress the contamination from the experimental environment and decrease in pretreatment time, an on-line preconcentration techniques have been proposed. An electrodeless discharge lamp is necessary as a radiation source to the high sensitive analysis of Pb. Large volume injection technique in ETAAS with a W-treated pyrolytic graphite (PG) furnace is also one of highly sensitive and convenient methods, which is

effective to minimize the time for analysis and the contamination. Although the large volume injection can be effective to enhance the sensitivity, problems arise in an increase in interference from the concentrated matrix.

Chemical modification is preferred as a simple approach to overcome the matrix interferences encountered especially in the direct determination in samples including complex matrices, where various matrix modifiers have been used, including Pd, Pd-Mg, $\text{NH}_4\text{H}_2\text{PO}_4$ and ascorbic acid.³ A mix modifier such as Ni- $\text{NH}_4\text{H}_2\text{PO}_4$ ⁴ and Co- $\text{NH}_4\text{H}_2\text{PO}_4$ ⁵ was also reported to enhance the sensitivity. In the previous work, a Pd modifier was used to determination of Pb by ETAAS using the large volume injection combined with the W-treated PG furnace and a hollow cathode lamp as a radiation source, resulting the calculated limit of detection (LOD) of $0.02 \mu\text{g L}^{-1}$ (3s) in snow water matrix by integrated absorbance mode.⁶ The effectiveness of the modifier for sulfate matrix, such as Na_2SO_4 , K_2SO_4 and MgSO_4 , was acceptable up to 10, 10 and 5 mg L^{-1} as cation.

In the present work, the various modifiers were examined to the determination of Pb by the ETAAS using the large volume injection combined with the W-treated PG furnace and the hollow cathode lamp.

The $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ modifiers enhance the effectiveness of matrix modification to those sulfates with keeping the similar level of the LOD to the use of Pd modifier. Recovery test of Pb spiked with real samples was took place. The Pb concentration of Pb in a certified reference material of river water (MNIJ CRM 7202-a) was agreement with the certified value.

Experimental

Instrumentation

Atomic absorption was observed with a Hitachi model Z-7000 graphite furnace atomic absorption spectrometer equipped with a Zeeman-effect background corrector and a Hitachi model 180-0341 optical temperature controller (OTC) system (Hitachi, Marunouchi, Tokyo, Japan). A standard atomization conditions were summarized in Table 1. Lamp current, wavelength, bandwidth and time constant were 7.5 mA, 283.3 nm, 1.3 nm and 0.02 s, respectively. A hollow cathode lamp of Pb of Hitachi 208-2023 was used as a radiation source. Pyrolytic graphite furnace of Hitachi 190-6003 was utilized throughout.

Table 1
Standard atomization conditions

Stage	Temperature/ °C	Time / s	Ar / ml min ⁻¹
1 Dry	80 – 150	30	200
2 Pyrolysis	150 – 800	20	200
3 Pyrolysis	800 – 800	20	200
4 Atomizing ^a	2400 – 2400	4	0
5 Cleaning	2800 – 2800	3	200

^a optical temperature controller was used.

Gilson micropipettes (Gilson Medical Electronics, Villier-leBel, France) were used for sample injection. Portable clean booth of Iuchi model PC-100S (Tenman, Osaka, Japan) corresponding to class 100 with HEPA filter was used for sample preparations. A Milli-Q Academic system after deionized by an Elix 5 system (Millipore Co., Inc.) was used for water purification.

Reagents

A commercially available stock solution of 1000 mg L^{-1} Pb was used (Kanto Chemical Co., Nihonbashihocho, Tokyo, Japan). An aliquot of this solution was diluted as required before use. Aqueous solution of 0.1 mol L^{-1} of tungsten was prepared for the surface modification using by sodium tungstate (VI) dihydrate (Kanto Chemical Co.). An AAS-grade $\text{NH}_4\text{H}_2\text{PO}_4$ and analytical-reagent grade of $(\text{NH}_4)_2\text{HPO}_4$ and ascorbic

acid were used (Kanto Chemical Co.). Commercially available matrix modifier of 10000 ppm of Pd and Pd-Mg in HNO₃ were used (Kanto Chemical Co.). An AAS grade of nitric acid was used (Kanto Chemical Co.). Other solutions were prepared from analytical reagent grade chemicals (Kanto Chemical Co.).

Samples

Tap water samples were taken in Tokushima, Japan, the sample was taken after running the tap for a few minutes and used without further treatment. River water samples were collected from the clean rivers in Tokushima. Ground water samples were collected in Tokushima. Snow samples were collected in Morioka in North Japan. The samples were used for a recovery test without any treatment.

Recommended procedure

The PG furnace surface modification was carried out by a single-drop coating method, viz., 100 μ L of the 0.1 mol L⁻¹ of W solution were introduced into the PG furnace and the standard atomization cycle was carried out.⁷

Five μ L of chemical modifier solution was introduced additionally into the W-treated PG furnace by manual pipetting after a 100 μ L of the sample solution had been introduced. The absorbance values corresponding to Pb were obtained during atomizing in the standard atomization cycle. During experiment, sample operations were carried out in the clean booth. The blank solution was tested for Pb contamination from the experimental environment. No contamination was observed during the period of the experiment.

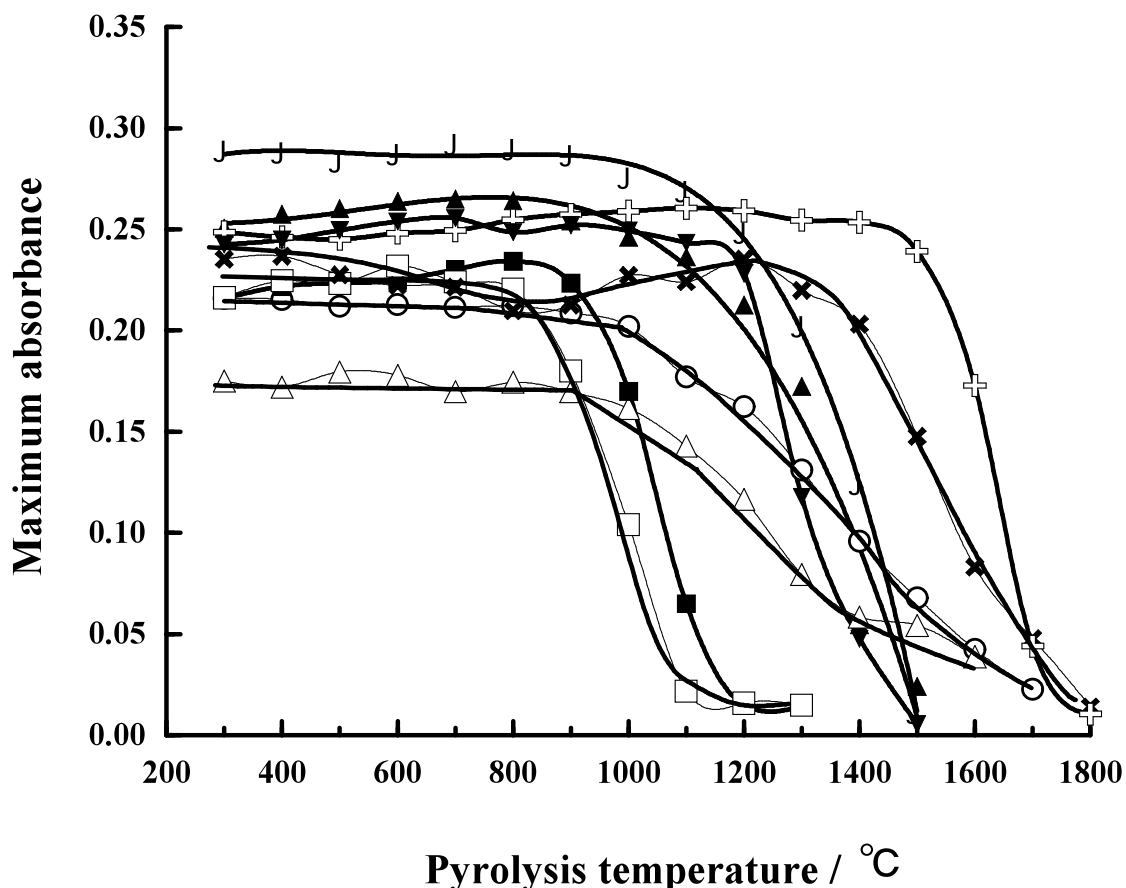


Figure 1

Effect of pyrolysis temperature on maximum absorbance for 5 μ g L⁻¹ of Pb using various matrix modifiers combined with the W-treated PG furnace.

Matrix modifier: ■ 1w/v% ascorbic acid, □ 4w/v% ascorbic acid, ● 1w/v% NH₄H₂PO₄, ○ 4w/v% NH₄H₂PO₄, ▲ 1w/v% (NH₄)₂HPO₄, △ 4w/v% (NH₄)₂HPO₄, × 1000 ppm Pd, + 1000 ppm Pd-1000 ppm Mg, ▼ absent.

Results and Discussion

Figure 1 shows that the effect of pyrolysis temperature on the maximum absorbance for $5 \mu\text{g L}^{-1}$ of Pb with the W-treated PG furnace with various matrix modifiers according to the standard atomization condition except for the atomization temperature of $3000 \text{ }^\circ\text{C}$. The maximum volume of matrix modifier injected into the commercially available PG furnace was $5 \mu\text{L}$ after deposition of $100 \mu\text{L}$ of sample solution. When the modifier was absent, a constant value of absorbance was observed in the temperature range $300 - 1100 \text{ }^\circ\text{C}$ and above $1200 \text{ }^\circ\text{C}$ that was decreased. Using the ascorbic acid

modifiers gave a constant value of absorbance in the range $300 - 900 \text{ }^\circ\text{C}$ and above $1000 \text{ }^\circ\text{C}$ that was decreased. Using the $\text{NH}_4\text{H}_2\text{PO}_4$ and the $(\text{NH}_4)_2\text{HPO}_4$ modifiers gave a constant value of absorbance in the range $300 - 900 \text{ }^\circ\text{C}$ and above $1000 \text{ }^\circ\text{C}$ that was decreased. For the Pd, the absorbance was decreased above $1300 \text{ }^\circ\text{C}$. When the Pd-Mg modifier was used, a constant value of absorbance was observed in the range $300 - 1400 \text{ }^\circ\text{C}$. Thus, the temperature of $800 \text{ }^\circ\text{C}$ was selected as the pyrolysis temperature in the standard atomization conditions. At these pyrolysis temperatures, a constant absorbance was observed with a hold time of $20 - 80 \text{ s}$.

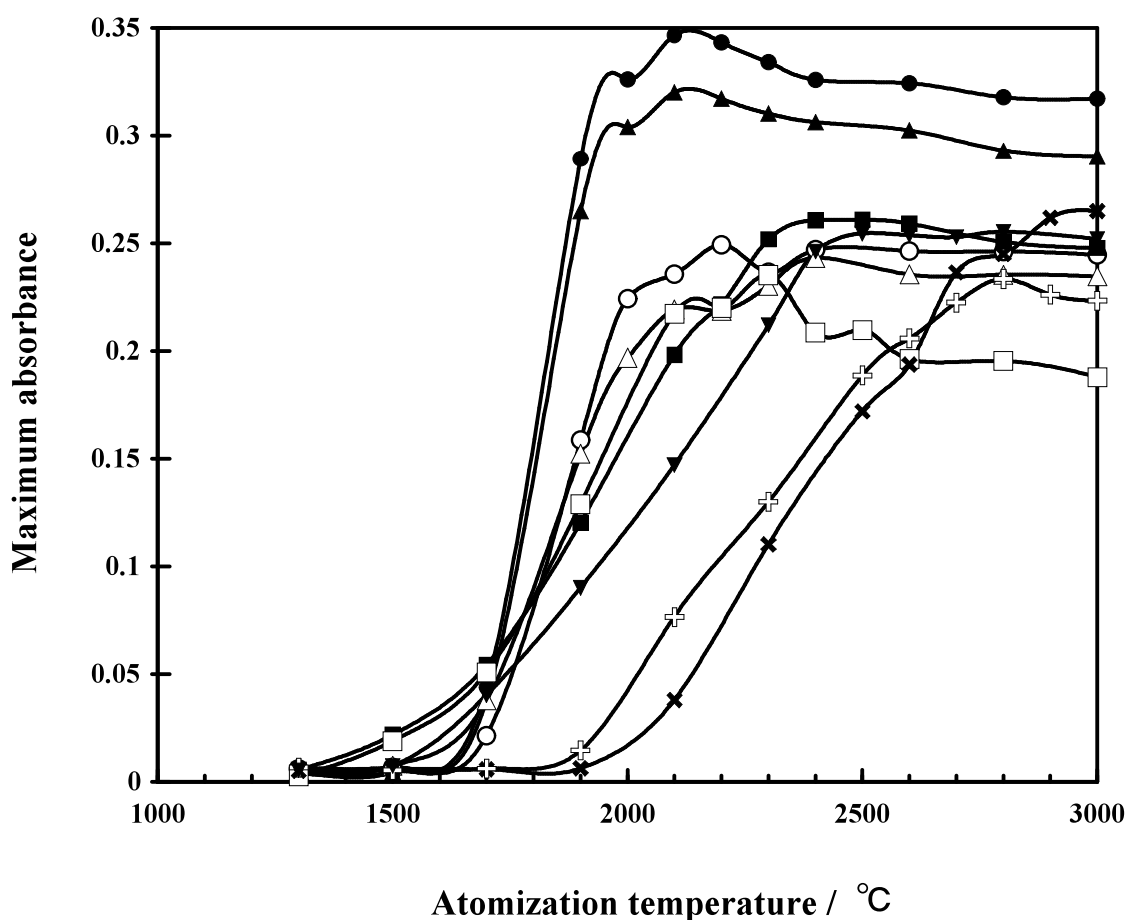


Figure 2

Effect of atomization temperature on maximum absorbance for $5 \mu\text{g L}^{-1}$ of Pb using various matrix modifiers combined with the W-treated PG furnace.

Matrix modifier: ■ 1w/v% ascorbic acid, □ 4w/v% ascorbic acid, ● 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$, ○ 4w/v% $\text{NH}_4\text{H}_2\text{PO}_4$, ▲ 1w/v% $(\text{NH}_4)_2\text{HPO}_4$, △ 4w/v% $(\text{NH}_4)_2\text{HPO}_4$, × 1000 ppm Pd, + 1000 ppm Pd-1000 ppm Mg, ▼ absent.

Figure 2 shows that the effect of atomization temperature on the maximum absorbance for $5 \mu\text{g L}^{-1}$ of Pb with the W-treated PG furnace with various matrix modifiers according to the standard atomization condition. A constant value of maximum absorbance was observed in temperatures above $2400 \text{ }^\circ\text{C}$, $2300 \text{ }^\circ\text{C}$, $2300 \text{ }^\circ\text{C}$, $2300 \text{ }^\circ\text{C}$, $2900 \text{ }^\circ\text{C}$ and $2800 \text{ }^\circ\text{C}$ with the absence, ascorbic acid,

$\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, Pd and Pd-Mg modifiers, respectively. The optimum atomization temperature was selected to be $2700 \text{ }^\circ\text{C}$, $2800 \text{ }^\circ\text{C}$, $2400 \text{ }^\circ\text{C}$, $2400 \text{ }^\circ\text{C}$, $3000 \text{ }^\circ\text{C}$ and $3000 \text{ }^\circ\text{C}$, respectively. Comparing the absorbance data in Fig. 1 and 2 indicates the better sensitivity for the modifiers of $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ and $1\text{w/v}\%$ $(\text{NH}_4)_2\text{HPO}_4$.

Table 2
Analytical performance for various matrix modifiers

Matrix modifier	LOD ^a $/\mu\text{g L}^{-1}$	RSD ^b $/\%$
Non	0.07	5.4
1w/v% ascorbic acid	0.06	3.0
4 w/v% ascorbic acid	0.07	1.7
1 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$	0.02	1.0
4 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$	0.05	1.6
1 w/v% $(\text{NH}_4)_2\text{HPO}_4$	0.02	2.0
4 w/v% $(\text{NH}_4)_2\text{HPO}_4$	0.04	2.0
1000 ppm Pd	0.04	2.5
1000 ppm Pd -1000 ppmMg	0.08	1.3

^a Calculated limit of detection defined as a concentration for 3 s.

^b Relative standard deviation (n=5) at $5 \mu\text{g L}^{-1}$.

Table 2 shows the calculated limit of detection (LOD) defined as a concentration of Pb corresponding to 3s for blank solution together with the relative standard deviation (RSD) at $5 \mu\text{g L}^{-1}$. The matrix modifier of $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ and $1\text{w/v}\%$ $(\text{NH}_4)_2\text{HPO}_4$ was indicated the better LOD values and the better reproducibility. The slope of calibration graph was 0.0692 and $0.0676 \text{ abs } \mu\text{g}^{-1} \text{ L}$ with $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ and $1\text{w/v}\%$ $(\text{NH}_4)_2\text{HPO}_4$, respectively. Xu and Liang⁴ reported the LOD of $0.14 \mu\text{g L}^{-1}$ using by Ni- $\text{NH}_4\text{H}_2\text{PO}_4$ modifier. Shirasaki et. al.⁵ reported the LOD of $0.03 \mu\text{g L}^{-1}$ using by Co- $\text{NH}_4\text{H}_2\text{PO}_4$ modifier. In the previous report, Imai et. al.⁶ reported the LOD of $0.02 \mu\text{g L}^{-1}$ using by Pd modifier with a higher pyrolysis temperature of $1400 \text{ }^\circ\text{C}$ and the integrated absorbance mode. In this work, the LOD can be reached to $0.02 \mu\text{g L}^{-1}$ using by a simple modifier of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ with a conventional pyrolysis temperature of $800 \text{ }^\circ\text{C}$ and a maximum absorbance mode.

Table 3 shows tolerable matrix concentrations

with various modifiers. The chemical modifiers of 1000ppm Pd and $1000\text{ppmPd}+1000\text{ppmMg}$ were also tested according to the recommended procedure. For the Pd modifier, the tolerable limit was reduced to 5 mg L^{-1} for Na_2SO_4 , K_2SO_4 and MgSO_4 , 50 mg L^{-1} for MgCl_2 , 10 mg L^{-1} for CaCl_2 . For the Pd+Mg modifier, that was reduced to 10 mg L^{-1} for Na_2SO_4 and K_2SO_4 , 5mgL^{-1} for MgSO_4 , K_2SO_4 and MgSO_4 was observed by the use of Pd modifier, respectively.

Table 4 shows the effect of the $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ and the $1\text{w/v}\%$ $(\text{NH}_4)_2\text{HPO}_4$ modifiers on the maximum absorbance of Pb in the presence of various alkali and alkaline earth metals, which are commonly found in water of tap, river, rain and snow, where a pyrolysis temperature of $800 \text{ }^\circ\text{C}$. Interferences were observed in the absence of the modifier, whereas in its presence, they were suppressed. Using the Pd modifier at $1400 \text{ }^\circ\text{C}$ pyrolysis reported was limited up to 10 , 10 and 5 mg L^{-1} for Na_2SO_4 , K_2SO_4 and MgSO_4 matrix, respectively.⁷ The effectiveness of the $1\text{w/v}\%$

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$\text{NH}_4\text{H}_2\text{PO}_4$ and the 1w/v% $(\text{NH}_4)_2\text{HPO}_4$ modifiers for Na_2SO_4 , K_2SO_4 and MgSO_4 matrix, respectively. was extended the upper limit to 50, 50 and 10 mg L^{-1}

Table3
Tolerable matrix concentration with various modifiers for 5 $\mu\text{g L}^{-1}$ of Pb

Matrix	Matrix modifier				
	1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$	1w/v% $(\text{NH}_4)_2\text{HPO}_4$	1000ppm Pb	Pd @1400°C Pyrolysis	1000ppm + 1000ppm Pd + Mg
MgCl_2	100	100	50	50	50
CaCl_2	100	100	10	100	100
Na_2SO_4	50	50	5	10	10
K_2SO_4	50	50	5	10	10
MgSO_4	10	10	50	5	5

Using the recommended procedure, the recoveries for 1.00 $\mu\text{g L}^{-1}$ of Pb added to various samples such as tap, river and snow were studied for 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ and 1w/v% $(\text{NH}_4)_2\text{HPO}_4$ modifiers. The volume of 900 μL of water sample was mixed with the 100 μL of volume of a Pb standard solution (0 or 10 $\mu\text{g L}^{-1}$) in a micro-test tube. The Pb concentration was determined with a calibration graph. Analytical results were summarized in Table

5 and 6 with for 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ and 1w/v% $(\text{NH}_4)_2\text{HPO}_4$ modifiers, respectively. In the case of 1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$, the recoveries of Pb added were to be 104±1 %, 105±1 % and 102±3 % for tap, river and snow samples, respectively. For the 1w/v% $(\text{NH}_4)_2\text{HPO}_4$, those were to be 99±3 %, 99±2 % and 101±4 % for tap, river and snow samples, respectively.

Table 4
Relative value of the maximum absorbance of 5 $\mu\text{g L}^{-1}$ of Pb with and without matrix modifier

Matrix	Matrix conc. / mg L^{-1} as cation	Absence	Matrix modifier	
			1w/v% $\text{NH}_4\text{H}_2\text{PO}_4$	1w/v% $(\text{NH}_4)_2\text{HPO}_4$
Cd only	0	1.00	1.00	1.00
NaNO_3	100	1.09	0.93	0.93
KNO_3	100	0.87	0.96	0.93
$\text{Mg}(\text{NO}_3)_2$	100	0.86	1.01	0.94
$\text{Ca}(\text{NO}_3)_2$	100	1.02	0.99	1.03
NaCl	100	0.62	0.94	0.94
KCl	100	0.85	0.96	0.95
MgCl_2	100	0.86	1.01	0.96
CaCl_2	100	0.96	1.00	0.99
Na_2SO_4	50	0.52	0.99	1.02
K_2SO_4	50	0.49	0.91	0.97
MgSO_4	10	0.81	0.99	0.93

Determination of Pb in the certified reference material of river water including $0.1 \text{ mol L}^{-1} \text{ HNO}_3$ (MNIJ CRM 7202-a) was carried out according to the recommended procedure. This material was prepared by the addition of Pb to $1.01 \pm 0.02 \mu\text{g kg}^{-1}$ into a clean river water. In this sample, concentrations of major elements such as Na, K, Mg and Ca were 3.68 , 0.85 , 1.24 and $4.67 \mu\text{g kg}^{-1}$, respectively. The concentration of Pb observed $1.01 \pm 0.01 \mu\text{g kg}^{-1}$ and $1.01 \pm 0.01 \mu\text{g kg}^{-1}$ with $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ and $1\text{w/v}\%$ $(\text{NH}_4)_2\text{HPO}_4$ modifiers, respectively. These value were in agreement with

the certified value.

The determination of Pb in 23 of taps and 7 of snow was carried out according to the recommended procedure. The analytical results are summarized in Table 7.

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Table 5
Recoveries of $1.00 \mu\text{g L}^{-1}$ Pb added to the various water samples
with the $1\text{w/v}\%$ $\text{NH}_4\text{H}_2\text{PO}_4$ modifier

Sample	Pb spiked $/ \mu\text{g L}^{-1}$	Sample		Found $/ \mu\text{g L}^{-1}$	Recovery $/ \%$
		Blank -added $/ \mu\text{g L}^{-1}$	Pb -added $/ \mu\text{g L}^{-1}$		
Tap	1.00	0.12	1.18	1.06	106
Tap	1.00	5.57	6.60	1.03	103
Tap	1.00	0.26	1.30	1.04	104
Tap	1.00	0.31	1.33	1.02	102
Tap	1.00	0.34	1.38	1.04	104
River	1.00	0.32	1.38	1.06	106
River	1.00	0.27	1.33	1.06	106
River	1.00	0.09	1.14	1.05	105
Ground	1.00	0.26	1.30	1.04	104
Ground	1.00	0.02	1.02	1.00	100
Ground	1.00	0.00	1.05	1.05	105
Ground	1.00	0.03	1.08	1.04	104
Ground	1.00	0.03	1.05	1.02	102
Snow	1.00	0.35	1.03	1.38	103
Snow	1.00	0.57	1.63	1.06	106
Snow	1.00	0.50	1.52	1.02	102
Snow	1.00	0.83	1.80	0.97	97
Snow	1.00	1.03	2.03	1.00	100
Snow	1.00	4.54	5.53	0.99	99
Snow	1.00	1.95	3.00	1.05	105
Snow	1.00	2.47	3.48	1.01	101
Snow	1.00	0.11	1.16	1.05	105
Snow	1.00	0.63	1.62	0.99	99
Snow	1.00	0.72	1.76	1.04	104

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Table 6
Recoveries of 1.00 $\mu\text{g L}^{-1}$ Pb added to the various water samples with the 1w/v% $(\text{NH}_4)_2\text{HPO}_4$ modifier

Sample	Pb spiked $/ \mu\text{g L}^{-1}$	Sample		Found $/ \mu\text{g L}^{-1}$	Recovery $/ \%$
		Blank -added $/ \mu\text{g L}^{-1}$	Pb -added $/ \mu\text{g L}^{-1}$		
Tap	1.00	0.07	1.06	0.99	99
Tap	1.00	5.17	6.18	1.01	101
Tap	1.00	0.06	1.07	1.01	101
Tap	1.00	0.04	1.05	1.01	101
Tap	1.00	0.06	0.94	0.94	94
River	1.00	0.05	1.05	1.00	100
River	1.00	0.04	1.00	0.96	96
River	1.00	0.03	1.03	1.00	100
Ground	1.00	0.06	1.07	1.01	101
Ground	1.00	0.06	0.98	0.96	96
Ground	1.00	0.02	1.07	1.05	105
Ground	1.00	0.02	1.00	0.98	98
Ground	1.00	0.02	1.05	1.03	103
Snow	1.00	0.08	1.02	0.94	94
Snow	1.00	0.28	1.27	0.99	99
Snow	1.00	0.12	1.06	0.94	94
Snow	1.00	0.48	1.47	0.99	99
Snow	1.00	0.69	1.68	0.99	99
Snow	1.00	4.56	5.62	1.06	106
Snow	1.00	1.65	2.71	1.06	106
Snow	1.00	2.38	3.41	1.03	103
Snow	1.00	0.13	1.18	1.05	105
Snow	1.00	0.44	1.50	1.06	106
Snow	1.00	0.68	1.72	1.04	104

Table 7
Analytical results of Pb in water with the 1 w/v% $\text{NH}_4\text{H}_2\text{PO}_4$ modifier

Sample	Pb / $\mu\text{g L}^{-1}$	Sample	Pb / $\mu\text{g L}^{-1}$	Sample	Pb / $\mu\text{g L}^{-1}$
Tap	0.05 ± 0.01	Tap	0.02 ± 0.01	Snow	3.80 ± 0.13
Tap	0.30 ± 0.02	Tap	0.25 ± 0.03	Snow	1.61 ± 0.06
Tap	0.05 ± 0.01	Tap	0.23 ± 0.01	Snow	2.30 ± 0.14
Tap	0.31 ± 0.04	Tap	1.21 ± 0.02	Snow	0.18 ± 0.01
Tap	0.97 ± 0.05	Tap	ND ^a	Snow	0.46 ± 0.07
Tap	0.18 ± 0.03	Tap	1.67 ± 0.05	Snow	0.67 ± 0.08
Tap	0.29 ± 0.02	Tap	1.37 ± 0.03	Snow	4.63 ± 0.11
Tap	0.16 ± 0.02	Tap	0.68 ± 0.02		
Tap	0.04 ± 0.00	Tap	0.71 ± 0.03		
Tap	0.21 ± 0.02	Tap	0.20 ± 0.02		
Tap	0.20 ± 0.02	Tap	0.41 ± 0.04		

^a less than LOD.

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