Chem. Anal. (Warsaw), **41**, 483 (1996) **SHORT COMMUNICATION**

Determination of Heavy Metals in Natural Waters by Flame Atomic Absorption Spectrometry

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Key words: flame atomic absorption spectrometry, lead, cobalt, copper, manganese, water analysis

Methods for lead, cobalt, copper and manganese concentrated from natural water samples are suggested. Lead and cobalt are concentrated by adsorption with manganese(IV) oxide formed in the water sample analysed after an interaction of potassium permanganate and manganese sulphate. For manganese and copper the extraction with a solution of 8–hydroxyquinoline in chloroform is proposed.
Highly reproducible, selective and fast flame atomic absorption spectrometric (AAS) techniques for lead, cobalt, copper and manganese determination in natural water of Lithuania are sugested.

Zaproponowano metody zagęszczania ołowiu, kobaltu, miedzi i manganu z próbek wód naturalnych. Ołów i kobalt zagęszczano przez adsorpcję na tlenku manganu(IV), otrzymanym w próbce analizowanej wody w wyniku działania nadmanganianu potasu i siarczanu manganu(II). W przypadku manganu i miedzi zaproponowano ekstrakcję roztworem 8-hydroksychinoliny w chloroformie.
Do oznaczania ołowiu, kobaltu, miedzi i manganu w naturalnych wodach Litwy zaproponowano doskonale odtwarzalną, selektywną i szybką technikę płomieniowej atomowej spektrometrii absorpcyjnej.

Because of the extensive use of heavy metals, the evaluation of the water pollution with those materials is an important task of environmental researches. Many trace metals are natural constituents of the environment. Some of them are even necessary for the biological functions of organisms. At high concentration levels, however, all metals have negative impact, as they are easily accumulated.

The concentration of heavy metals in natural water is too low to be detected directly by flame atomic absorption spectroscopic techniques. Thus, various concentration methods are used and extraction seems to be the most common of them.

For example, Reichert [1] has examined cobalt extraction conditions using pyrrolidinedithiocarbamate and methyl isobutyl ketone as an extracting agent. Singh and Sharma [2] determined optimal lead and cobalt extraction conditions with an extractant methyl isobutyl ketone and a ligand hexametylenimine carbodithioate [2]. Vivoli and Mamcardi developed a method for lead, cadmium, nickel and cobalt using evaporation and extraction techniques [3].

This paper reports our method to concentrate lead and cobalt by adsorption with manganese(IV) oxide formed in the analysed water sample after interaction of potassium permanganate and manganese sulphate. For concentrating manganese and copper we suggest extraction with a solution of 8-hydroxyquinoline in chloroform. The results of this study are presented herein.

EXPERIMENTAL

Materials and apparatus

Potassium permanganate (chemical-reagent grade), manganese sulphate (chemical-reagent grade), sodium hydroxide (chemical-reagent grade), metals (purity ≥ 99,9%), nitric acid (especially pure), hydrochloric acid (especially pure), 8-hydroxyquinoline (chemical-reagent grade), and chloroform (analytical-reagent grade, redistilled) were used. For all the aqueous solutions bidistilled water was used.

Standard stock solutions of metals were prepared by dissolving the metal in the solution of nitric acid (1:1). Standard solutions of metals were prepared by dilution of the appropriate standard stock solution with doubly distilled water just before using.

Standard stock solutions of metals were prepared by dissolving the metal in the diluted nitric acid (1:1). Standard solutions of matals were prepared by dilution of the appropriate standard stock solution with bidistilled water just before using.

Absorbance measurements were made with Hitachi model 170-50 atomic absorption spectrometer (Japan). Conditions of metal determination are presented in Table 1. The pH of the solutions was determined by means of pH-meter pH-673M (Russia). For separation of chloroform from water a centrifuge CLN-2 (Russia) was used.

Table 1. Conditions of metal determination by flame AAS technique

Metal	Absorption line, nm	Electric current density, mA	Flame
Pb	283.3	10	propane–butane–air
Co	240.7	15	propane–butane–air
Cu	324.8	10	propane–butane–air
Mn	279.5	10	acetylene–air

Procedures

To obtain calibration curves for metal determination 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of appropriate metal standard solution (5 μg ml^{-1}) were pipetted into 50 ml graduated flask, 5 ml of 2 mol l^{-1} HCl solution were added into each flask and diluted to mark with water. The absorbances of obtained solutions with metal concentration from 0.05 to 0.5 μg ml^{-1} were measured under conditions presented in Table 1.

RESULTS AND DISCUSSION

The influence of some metals on lead, cobalt, manganese and copper AAS determination was examined. Ratios interfering metal/analyte are considered as limiting when the determination error is ±10%. The results obtained are presented in Table 2. According to the results the ratios interfering metal/analyte are very large, thus there is no selectivity problem for natural water analysis by AAS.

Table 2. Limiting ratios of the interfering metal to the determined metals concentrations

Interfering M	M:Pb	M:Co	M:Cu	M:Mn
Na	40000:1	4800:1	12000:1	40000:1
K	4000:1	10000:1	20000:1	40000:1
Ca	4000:1	5000:1	12000:1	4000:1
Mg	2400:1	10000:1	40000:1	10000:1
Fe	4000:1	10000:1	2000:1	10000:1
Pb	–	24000:1	12000:1	10000:1
Co	1600:1	–	24000:1	4000:1
Cu	1600:1	40000:1	–	40000:1
Mn	10000:1	20000:1	2000:1	–

For successful determination of lead and cobalt in natural water the concentration conditions were examined. To 100 ml of hot (~70°C) bidistilled water 1 ml of metal standard solution (0.01 mg ml^{-1}) and different volumes of potassium permanganate solution (4 mg ml^{-1}) were added at the constant volume of manganese sulphate solution (10 mg ml^{-1}). The solutions obtained were stirred and filtered through a glass filter No 4. The precipitates on the filter were dissolved by adding in small portions 5 ml of HCl solution (1:1), the filter was rinsed with bidistilled water and the solution with metals dissolved was collected in 50 ml volume glass beaker. After that the solution was heated until boiling, cooled, transferred into 25 ml graduated flask, diluted to mark with bidistilled water, absorbance for lead and cobalt was measured (Fig. 1) and an optimal volume of potassium permanganate was established. The influences of manganese sulphate and water volumes on concentrating of lead and cobalt were examined in the same way. The optimal volumes of potassium permanganate and manganese sulphate solutions were in both cases above 0.4 ml and the water volume should not exceed 200–1000 ml (Fig. 2).

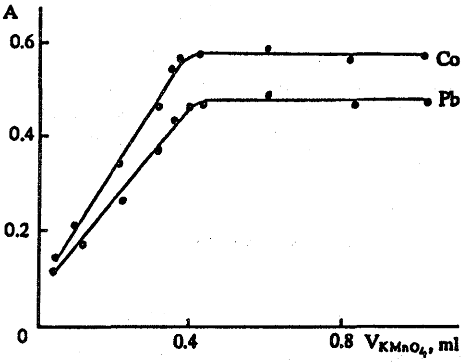

Figure 1. An influence of potassium permanganate volume on lead and cobalt absorbance from water. $C_{Pb} = C_{Co} = 0.4$ µg ml^{-1}; $C_{KMnO_4} = 4$ mg ml^{-1}; $C_{MnSO_4} = 10$ mg ml^{-1}; $V_{H_2O} = 500$ ml; $V_{MnSO_4} = 0.5$ ml

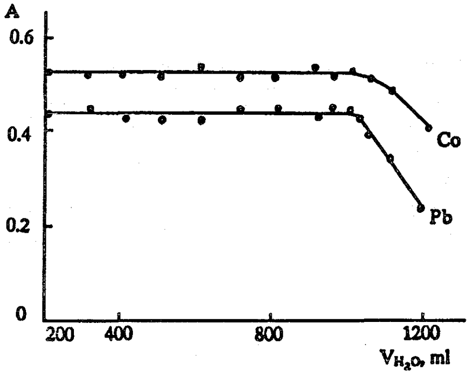

Figure 2. Dependence of lead and cobalt absorbance on the water volume. $C_{Mn} = C_{Cu} = 0.4$ µg ml^{-1}; $C_{MnSO_4} = 10$ mg ml^{-1}; $C_{KMnO_4} = 4$ mg ml^{-1}; $V_{MnSO_4} = V_{KMnO_4} = 0.5$ ml

The lead and cobalt concentrating technique was applied for the analysis of natural water. To 500 ml of natural water 0.5 ml of potassium permanganate solution and 0.5 ml of manganese sulphate solution were added. The further procedure of analysis is the same as described above.

For manganese and copper concentrating extraction with 8-hydroxyquinoline solution in chloroform is suggested. The optimal extraction conditions were determined. The influence of pH of the aqueous phase on manganese and copper absorbance was examined (Fig. 3). According to these results pH range 9.0–10.5 for manganese and 6.5–8.0 for copper was found to be optimal. The extraction time and extractant volume were studied. The minimal extraction time being 1 min and an extractant volume of 10 ml being sufficient for complete extraction of manganese and copper chelates. An influence of the volume of the aqueous phase on manganese and copper absorbance was examined, and under indicated conditions (when 15 ml of chloroform) the water volume should not exceed 200 ml (Fig. 4).

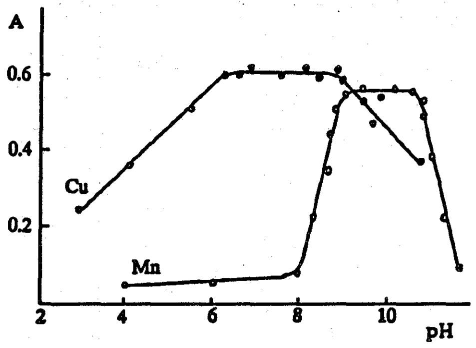

Figure 3. Dependence of manganese and copper absorbance on the pH of aqueous phase. $C_{Mn} = C_{Cu} = 0.4\ \mu g\ ml^{-1}$; $C_{8\text{-hydrox.}} = 0.1\ mol\ l^{-1}$; $V_{CHCl_3} = 10\ ml$; $t_{extr.} = 120\ s$

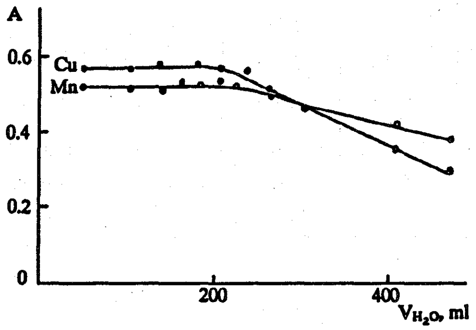

Figure 4. Dependence of manganese and copper absorbance on the water volume. $C_{Mn} = C_{Cu} = 0.4\ \mu g\ ml^{-1}$; $C_{8\text{-hydrox.}} = 0.1\ mol\ l^{-1}$; pH(Mn) = 10; pH(Cu) = 7; $V_{CHCl_3} = 15\ ml$; $t_{extr.} = 60\ s$

On the basis of optimal extraction conditions a methodology for manganese and copper determination in natural water was worked out. To 100 ml of natural water sample 5 ml of buffer solution (pH~10 for manganese and pH~7 for copper) were added. The solution was shaken with 15 ml of 0.1 mol l^{-1} 8-hydroxyquinoline solution in chloroform for 60 s. The extract was evaporated until dryness, 10 ml of 2 mol l^{-1} HNO_3 solution were added and an absorbance was measured under conditions mentioned in Table 1. Manganese and copper concentrations were found from calibration curves.

The results of lead, cobalt, copper and manganese determination in natural water obtained according to the suggested methodologies are shown in Table 3. Concentration of the metals examined do not exceed the limiting values for natural water. The techniques are selective and fast. The relative standard deviations are between 1.0% and 5.0% and the recoveries are between 96.5% and 104.5%.

Table 3. Results of metal determination in natural water ($n = 5, P = 0.95$)

Station	Element	Amount determined mg l^{-1}	RSD %	Amount added mg l^{-1}	Total amount determined mg l^{-1}	Recovery %
Prienai reg. Balbieriškis village Bore No 12 (depth 63 m)	Mn	0.044	1.0	0.100	0.148	102.7
	Co	0.025	5.0	0.500	0.545	102.8
	Cu	0.31	4.5	0.100	0.42	102.4
	Pb	0.011	2.8	0.500	0.508	99.4
Alytus reg. Kaniūkai village Bore No 65 (depth 70 m)	Mn	0.028	1.7	0.100	0.125	97.6
	Co	0.058	3.1	0.500	0.454	97.7
	Cu	0.33	3.8	0.100	0.45	102.2
	Pb	0.014	4.2	0.500	0.525	104.0
Anykščiai reg. Kairiai village. Well	Mn	0.065	2.8	0.100	0.171	103.6
	Co	0.055	1.9	0.500	0.571	102.8
	Cu	0.33	2.8	0.100	0.46	104.5
	Pb	0.014	3.4	0.500	0.525	102.1
Varėna-2. Bore No 5 (depth 70 m)	Mn	0.013	3.6	0.100	0.116	102.6
	Co	0.021	4.8	0.500	0.503	96.5
	Cu	0.12	4.6	0.100	0.22	100.0
	Pb	0.010	1.9	0.500	0.505	99.0

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Received September 1995
Accepted February 1996