Preconcentration of heavy metal impurities from water on chromatographic paper

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An attempt is made to employ the previously proposed method for preconcentration of nonvolatile impurities as a narrow zone on a TLC plate or on chromatographic paper for extraction of heavy metals from potable water. The method is based on vigorous evaporation of a volatile matrix (water) induced by a stream of hot air. The degree of preconcentration was determined using ICP MS analysis for lead, cobalt, and zinc. The concentrations of impurities increased by a factor of more than 200 over a period of 20—30 min.

Key words: preconcentration, inorganic impurities, aqueous solutions, thin layer chromatography, thermodesorption.

Determination of heavy metal impurities in water is a topical task. In order to increase the sensitivity of analysis, various methods of preconcentration, which are often cumbersome, for example, evaporation of large amounts of the material, are normally used.[1,2] Therefore, development of more facile methods for the enrichment of samples to be analyzed for their impurity components present considerable interest[3,4] for analytical chemistry.

Note that planar chromatography is an efficient tool for separation and analytical determination of various inorganic compounds.[1]

This study is aimed at extending the scope of application of the preconcentration technique proposed in our previous works.[5,6] The degrees of preconcentration and extraction of heavy metal impurities in potable water were estimated by inductively coupled plasma mass spectrometry.

The thermodesorption preconcentration of low-volatility impurities by planar chromatography is carried out in the following way.[5,6] A vessel with the sample to be analyzed is covered by a lid having a slit for a TLC plate or for a chromatographic paper strip in the middle. A liquid sample largely consisting of a volatile major component, for example, water, moves up over the plate or paper strip due to ordinary capillary forces. The front of the solvent (eluent) moves along the sorbent; however, as it has passed the lid, it enters an area of higher temperature, in which it is exposed to a vigorous directed stream of warm air and evaporates. Therefore, this area (somewhat above the slit) acts as a specific concentration zone in which the major volatile component is rapidly evaporated, while low-volatility components of the sample are accumulated as a relatively narrow band. The contents of nonvolatile and low-volatility inorganic impurities can be determined using conventional chromatographic separation followed by densitometric detection. The preconcentrated components can also be determined by other nonchromatographic methods.

In this study, the method of preconcentration by planar chromatography is employed for determining traces of heavy metals in potable water.

Experimental

Model mixtures were prepared using initial aqueous solutions of Pb^{2+}, Co^{2+}, and Zn^{2+} cations with concentrations of 20, 10, and 10 μg L^{-1}, respectively. Note that the maximum permissible concentrations of double-charged ions in potable water are higher than the concentrations we used in the model solution of Pb, Co, and Zn; they are 0.03, 0.1, and 1 mg L^{-1}, respectively.[7] A 100-μL sample of a standard solution of the corresponding salt (lead nitrate (20 mg L^{-1}) or cobalt or zinc nitrate (10 mg L^{-1})) was introduced with a syringe into a 100-mL measuring flask and diluted with 100 mL of deionized water (Milli-Q) to a required concentration.

A model solution or tap water (20 mL) was poured into a Petri dish covered with a lid having a narrow slit. One end of a 100×50-mm chromatographic paper strip (MH-218, Macherey-Nagel, Germany) was immersed in the water sample under analysis and the components were accumulated on the section of the strip exposed above the slit in the lid, which was arranged 10 mm above the surface of the liquid sample. The water moving along the paper strip was continuously evaporated by a stream of hot air (this was done using a household hairdrier). The time of preconcentration did not exceed 30 min.

After preconcentration, the working section of the paper (a 5-mm wide area having been subjected to efficient heating) was cut off, placed in a crucible, and washed with 2 mL of dilute nitric acid. An aliquot portion was analyzed on an HP 4500 ICP MS instrument.

The instrument was calibrated against standard solutions. It was found by the method of standard additives that the relative standard deviations do not exceed 0.01.

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Table 1. Contents of heavy metal ions in the initial solution to be analyzed (M_0) and degrees of concentration (K) and extraction (R) of heavy metal ions after preconcentration on a chromatographic paper strip from a model aqueous solution calculated in relation to the sample consumed

Ion	t/min	M_0/μg	K	R (%)
Pb^{2+}	0	0.004	—	—
	10	0.620	155	89
	30	1.140	285	92
Co^{2+}	0	0.002	—	—
	10	0.318	159	88
	30	0.620	305	90
Zn^{2+}	0	0.002	—	—
	10	0.310	155	85
	30	0.610	310	87

Results and Discussion

The parameters used to quantitatively evaluate the results of preconcentration were the degree of preconcentration K and the degree of extraction R (see Ref. 3).

The degree of preconcentration was calculated as $K = M_i/M_0$, where M_i is the amount of metal on the paper strip (in the area of accumulation formed after preconcentration) and M_0 is the content of metal on the paper after wetting in the initial solution (before the water front has passed through the section of the paper below the slit).

The degree of extraction R was found as the ratio of the experimental M_i value to the value calculated theoretically (M_{theor}); the latter was calculated based on the total content of the substance in the sample

$$R = (M_i/M_{\text{theor}}) \cdot 100\%.$$

Tables 1 and 2 present data on the degrees of preconcentration and extraction of heavy metals from the prepared model solutions and from tap water specimens.

It follows from the data of Table 1 that preconcentration for 10—30 min increases the contents of heavy ions on the paper by factors of several hundred. The degree of metal extraction from the solutions is 85—92%.

Similar results were obtained with tap water samples (see Table 2). The concentrations of lead, cobalt, and zinc on the paper increase 100—300-fold (see Table 2). The degree of extraction of the inorganic impurities from samples of tap water approaches 90%.

Table 2. Contents of heavy metal ions in the initial water (M_0) and degrees of concentration (K) and extraction (R) of heavy metal ions after preconcentration on a chromatographic paper strip from a tap water specimen calculated in relation to the sample consumed

Ion	t/min	M_0/μg	K	R (%)
Pb^{2+}	0	0.002	—	82
	5	0.037	18	86
	10	0.210	105	86
	20	0.360	180	87
	30	0.590	295	86
Co^{2+}	0	0.002	—	84
	5	0.036	18	88
	10	0.320	105	90
	20	0.350	175	88
	30	0.580	290	90
Zn^{2+}	0	0.003	—	83
	5	0.045	15	83
	10	0.190	95	86
	20	0.520	173	85
	30	0.840	280	86

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