New methods for preconcentration and determination of heavy metals in natural water

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<u>Abstract</u> – Numerous instrumental methods are used to determine heavy metals in natural water, mainly with preconcentration, since the sensitivity of direct analysis is often insufficient. A number of such methods have been developed in the authors' laboratory. Highly selective solvent extraction separation of heavy metals (Ag, Cu, Hg) has been achieved by using macrocyclic extractants. The separated elements are determined by means of atomic absorption spectrometry and spectrophotometry. Heterochain polymer sorbents (polymeric thioether and tertiary amine) have been used to concentrate Se, Te, Hg, As, Cd, Pb and other heavy metals. Atomic absorption spectrometry and X-ray fluorescence analysis have been used to determine the elements in the concentrate. The methods are characterized by a high sensitivity and accuracy. Thin layer chromatography in combination with precontration of a group of metals by solvent extraction has been used for the analysis of surface waters. Chelates, mainly diethyldithiocarbamates, are extracted and separated in a thin layer. Visual or densitometric determination is possible. In a similar way tritium-labelled chelates have been used for radiometric determination of Pb, Cd and Hg. Several methods are based on using ion chromatography. Highly sensitive techniques have been proposed to determine As, Se, Te, Cr, Mo, W and V, as well as Cd, Cu, Mn, Ni and Pb; preconcentration is necessary only in some individual cases.

INTRODUCTION

It would seem that natural water should be comparatively easy to analyze, from the point of view of preconcentrating and determining its components, including the heavy metals. Several methods can be applied to separate the trace quantities of these metals from the matrix: evaporation of water, recovery of trace components by solvent extraction or sorption methods. However, heavy metals can exist in various states in natural water, and it is, therefore, necessary to take measures aimed at obtaining the forms suitable for a positive analytical effect to be reached. This is, for instance, true for mercury, which frequently forms methyl– and dimethylmercury and complexes with fulvic acids, or for arsenic, which is sometimes present in two oxidation states and in the form of different chemical compounds. Moreover, the analysis becomes a more complicated problem in the case of saline water and water containing a large amount of suspended particles. In the latter case, suspended particles are converted into a dissoved state, or else a precipitate is separated by filtration or centrifugation, it is then combined with the solid concentrate of the trace elements and analyzed. The stage of sample preparation is thus very important in analyzing natural water for heavy metals.

Why is it necessary in many cases to resort to the preconcentration of heavy metals? The main reason lies in the fact that direct determination frequently proves to be insufficiently sensitive. In addition to this, some methods require a solid sample. Other determination methods are sensitive to the forms in which the elements exist, and, when concentrated, the element is practically always converted into one compound.

By heavy metals we shall understand the most toxic elements, primarly lead, cadmium, mercury, arsenic, selenium, tellurium, as well as copper, nickel, cobalt, zinc, chromium, silver, and some other metals.

Extensive literature, including reviews (refs. 1–4), is devoted to concentration and determination of heavy metals in natural water.

METHODS FOR CONCENTRATING AND DETERMINING HEAVY METALS: A SUMMARY

The principal methods of preconcentration of heavy metals in the analysis of natural water are evaporation, solvent extraction and sorption techniques, but many others are also applied.

The methods based on water evaporation are suitable in numerous cases, since the losses of metals occurring with the boiling of water are usually not very high. Naturally, these methods are meant for concentrating a group of metals. Preconcentration by evaporation is unsuitable for sea or highly mineralized waters.

Solvent extraction is convenient both for group and selective concentration of heavy metals. As early as in 1953 Pohl (ref. 5) proposed concentrating 23 elements, not counting the rare-earth ones, in the analysis of natural water by extraction of chelates with 8-hydroxyquinoline, dithizone and diethyldithiocarbamate, with a step-wise change in pH, and using chroloform as the solvent. The obtained concentrate, after chloroform had been distilled off, was analyzed by the atomic emission method. Very many similar methods have been described since then, but in most of them one extractant is used, and the number of recovered metals is not so large. For instance, the ammonium pyrrolidinedithiocarbamate – methylisobutylketone system has gained very wide acceptance. There are examples of using extraction chromatography and gel extraction.

Extensive possibilities in the analysis of natural water are provided by the sorption methods of preconcentration, based on using organic ion exchangers, complex-forming sorbents, activated carbons, and other sorbents. The advantage of sorption methods is the possibility of performing the concentration from large volumes of solutions, especially when dynamic techniques – columns or sorption filters – are used. Sorption methods can provide very high heavy metal concentration coefficients, e.g., up to 10^4, whereas solvent extraction does not usually yield more than 10^2.

Out of the methods used to determine heavy metals in natural water of greatest importance at present are those of atomic absorption, X-ray fluorescence, spectrophotometry and voltammetry, with the latter two methods mainly used to determine a small number of elements. The X-ray fluorescence method is only used in combination with preconcentration. Atomic emission spectrometry in the version with inductively coupled plasma, as well as with the arc when the solution evaporation on the electrode is used, is in principle suitable without concentration; preconcentration, however, is mostly used in this case too. The same is true for the atomic absorption and the other above-mentioned methods.

Examples of heavy metals determination in natural water with the use of preconcentration are shown in Table 1.

At present an important problem of such determinations, especially those performed in a routine analysis, is their automation. Primarily suitable for this purpose is the flow injection analysis.

Examined below are the methods developed in the authors' laboratory.

METHODS USING SOLVENT EXTRACTION

Of interest for selective extraction concentration of heavy metals are macrocyclic compounds. Their possibilities can be illustrated as exemplified by silver extraction. The following two N,O-containing macrocycles have been synthesized and investigated: 8,9;18,19-dibenzo-1,7-dioxy-11,16-diazacyclononadeca-10,16-dien (1) and 8,9;18,19-dibenzo-1, 3,7-trioxa-11,16-diazacyclononadeca-10,16-dine (2).

(1)   (2)
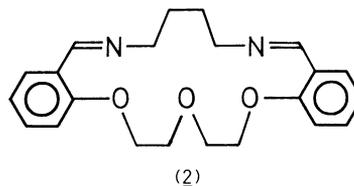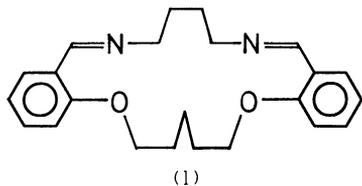
Out of a large group of investigated elements – Ag(I), Hg(II), Cd, Zn, Fe(III), Co(II), Cu(II) and Pb – these reagents interact only with silver. This metal is extracted in the form of complexes of AgLX composition, where L is the macrocycle and X is the counterion (ClO_4^-, picrate, and in the system with macrocycle (2) – dipicrylamine). Recovery increases with increasing hydrophobity of the counterion (ClO_4^-, Pi, DPA). On this basis an extraction atomic absorption method of determining silver in water has been developed with the use of reagent (1) (ref. 21). But of special interest is the extraction-photometric method of determining this element in water, involving the use of two reagents. For selective extraction of silver a macrocyclic reagent is used, and for photometric determination – thyrodin or rhodanin, introduced directly into the organic phase. In fact the sensitivity of this method proved to be "record-breaking": the molar absorption coefficient of the formed compound is higher than $9 \cdot 10^5$, one can determine silver in the amount of 0.06 μg/l.

(3)

(4)
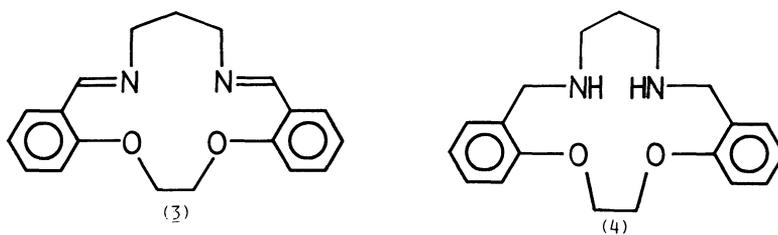
Selectivity of the interaction with heavy metals, when N,O-macrocyclic reagents are used, is determined not only by the size of the cavity but also by the conformational mobility of the molecule as a whole. Comparison of 5,6;14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-7, 12-dien (3) and 5,6;14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane (4) has shown the selectivity of reagent (3) to be considerably higher than that of macrocycle (4). The presence of double bonds makes the molecule of compound (3) substantially more rigid. Macrocycle (4) is distinguished by a higher conformational mobility (ref. 32).

Table 1. Examples of heavy metals determination methods in natural waters with preconcentration

Metals determined	Water analysed	Preconcentration method	Determination method	Detection limit μg/ml	Ref.
Al,Ba,Ca, Cd,Co,Cr, Cu,Fe,K, Mg,Mn,Mo,Ni, Na,Pb,Sr,V Zn	Fresh waters	Evaporation	AES-ICP	0.03-4.8	(6)
As,Se	Water	Evaporation followed by the hydride generation	AES-ICP	0.02-0.03	(7)
As,Sb,Se	Natural waters	Same as above	–	–	(8)
Cu	River water	Extraction with caproic acid (1M) and benzylamine (0.5M) in heptane	AAS	0.3	(9)
Cd,Cu,Fe, Mn,Ni,Pb,Zn	Sea water	Sorption of metal 8-quinolinates on C_{18}-modified silica gel	AES-ICP	0.02	(10)
Sb,Sc		Soption of metal pyrrolidine-dithiocarbamates on C_{18}-modified silica gel	AAS-ETA	7.50	(11)
Au,Cd,Ir, Pd,Zn and other		Sorption on macroporous anion-exchanger IRA-900	AAS-ETA or mass spectrometry	–	(12)
Cd,Cu,Pb, Zn	Sea and tap water	Sorption on 2-mercaptobenzo-thiazole loaded on glass beads with the aid of collodion	Flame AAS	0.04-0.1	(13)
Cd,Co,Cu,Fe Ni,Pb,U,Zn	Sea water	Sorption on chelating sorbent Chelex-100	SSMS	–	(14)
Cd,Cu,Fe,Mn, Ni,Pb,Zn	Water	Sorption on chelating cellulose sorbent Hyphan	Flame AAS	–	(15)
U	Natural waters	Coprecipitation with iron dibenzyldithiocarbamate	XRF	0.4	(16)
Ag,Cd,Cr,Cu, Fe,Hg,Mo,Ni, Pb,Pd,Sn,Zn, Zr	Natural waters	Coprecipitation with cadmium or cobalt pyrrolidinedithio-carbamate	XRF	–	(17)
Ag,Bi,Cd,Co, Cu,Fe,Mo,Ni Pb,Sn,V,W,Zn	Natural waters	Coprecipitation with silver or nickel dibenzyldithio-carbamate	AES-ICP	–	(18)
Cd,Co,Cr,Cu, Mn,U,Zn	Sea water	Coprecipitation with 1-(2-pyridilazo)-2-naphthol	NAA	–	(19)
As,Cd,Co,Cu, Hg,Mo,Sb,Sn, Te,Ti,U,V,W	Natural waters	Flotation with combined collector iron (III) and ammonium pyrrolidinedithiocarbamate	NAA		(20)

Macrocyclic extractants have also been proposed for selective extraction of copper and mercury.

For the concentration and subsequent atomic absorption or atomic emission determination of silver, also of interest are the sulphur-containing neutral compounds previously described by us (ref. 23): isopropyl–N–methylthiocarbamate (IPMTC) and isopropyl–N–ethylthiocarbamate (6). These compounds, being used as flotation reagents, are readily available and cheap. Silver, however, is by no means the most important heavy metal to be determined in natural water.

$$
\begin{array}{ll}
\underset{H_3C}{\overset{H_3C}{>}}CH-O-\underset{\underset{S}{\|}}{C}-NHR & \underset{R}{\overset{R}{>}}Sn(NO_3)_2
\end{array}
$$

(5) R = CH_3 (7)

(6) R = C_2H_5

Very suitable for extraction concentration of arsenic are organotin compounds (7), where R is, e.g., nonyl.

These compounds extract anionic forms of arsenic (V): AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^{-}$, as well as the corresponding forms of arsenic (III). The extraction process is formally that of ion exchange (nitrate substitution by arsenate), but actually a complex-formation is taking place, because the arsenate enters into the first coordination sphere of tin, attaching itself to the central atom via the oxygen atoms.

The preconcentration method allows extracting arsenic (V) out of solutions from pH 6 to 5 M HNO_3. Arsenic is determined in the extract by the atomic absorption method using air–acetylene or nitrous oxide–acetylene flame, and in the version without a flame – using a graphite platform –graphite furnace atomizer. The proposed extraction atomic absorption method makes it possible to determine $1 \cdot 10^{-5}$ % of arsenic and less (ref. 24).

METHODS USING HETEROCHAIN SORBENTS

Among the methods of preconcentrating heavy metals, used in the analysis of natural water, of considerable importance are the sorption methods. Different types of sorbents, including the complex-forming ones, are used. Among them, heterochain polymers in which the complex-forming heteroatom enters into the polymer chain have exhibited a good performance. These sorbents differ from the conventional complex-forming sorbents by the concentration of their functional groups: it is much higher in this case. Subsequent determination of elements can be made by means of various methods.

Among the compounds of this class, at present already quite extensive, the ones that have been studied in greatest detail and found practical application are S– and N–containing polymers, especially the polymeric thioether $(-CH_2-S-)_n$ ($\sim 60\%$ of sulphur) (ref. 25). This polymer allows one to separate selectively, depending on the solution acidity, a large number of elements (ref. 26), including gold (III) in the region of 0.1–6 M, selenium and tellurium from 1–3 M, arsenic from 1 M HCl solutions, silver and mercury at pH 1–3, cadmium and tin at pH 6–7. The high distribution coefficients, the purity and homogeneity of obtained concentrate, its easy mouldability and solubility provide for the possibility of subsequent spectroscopic determination of elements both directly in the solid concentrate and after its dissolution. This made it possible to develop a number of sorption-spectroscopic methods of determining these elements.

A simple and fast method has been proposed to concentrate mercury from natural water without decomposition of the organic complexes of mercury (ref. 27) (the thioether quantitatively isolates mercury present both in the ionic form and in the form of methylmercury, as well as fulvic complexes most widely occurring in natural waters) (Table 2). Preconcentration is easily achieved in the field, directly at the sites where water samples are taken. The sorbent is added to the analyzed solution with pH 1–3, after 10 min of shaking the concentrate is filtered off, subsequent determination is performed by means of the atomic absorption of cold vapour. The method makes it possible to determine 0.01–0.02 µg/ml, the relative standard deviation is 0.10–0.11. The method has the advantage that the concentrate can be stored for a long time and easily transported, which is important when large territories are investigated for mercury pollution. The method has been applied to determine mercury in natural water bodies and waste waters.

TABLE 2. Determination of mercury by AAS after sorption
concentration of its different form

Mercury form	Without concentration				After sorption on polymer thioether	
	Without decomposition of organic matter		After decomposition of organic matter			
	µg/50ml	Recovery, %	µg/50ml	Recovery, %	µg/50ml	Recovery, %
Hg^{2+}	0.20	100	–	–	0.20	100
Fulvate complex	0.43	86	0.50	100	0.50	100
Methylmercury-acetate $CH_3HgOCOCH_3$	0.43	33	1.30	100	1.30	100

A method just as simple and fast is that of concentrating Ag, Cd and Pb. In the case of Cd and Pb, a weighted sample of sorbent (50–100 mg) is added to the water sample (0.1–0.5 l, pH 6–7) heated to boiling and the mixture is boiled for 30 min. Silver is quantitatively isolated at pH 1 and room temperature. The concentrate is filtered off, washed, dried with acetone and diethylether, and analyzed. Determination is possible, both directly in the concentrate obtained and after its dissolution, with the use of electrothermal and flame atomic absorption methods (refs. 28,29). The low detection limits that could be achieved in the case of the electrothermal method – 0.005 and 0.02 µg/ml for cadmium and lead, respectively (ref. 28) and 0.01 µg/ml for silver – make it possible to use these techniques successfully for the analysis of natural water, as well as for highly refined geochemical investigations. Examples of the analysis of different types of water are given in Table 3.

A sorption – X-ray fluorescence method has been developed to determine selenium, tellurium, and arsenic. The method is characterized by a high reproducibility: the relative standard deviation in determining 300–1000 µg of metal per 1.2 g of sorbent amounts to 0.02–0.03. The detection limit, for 500 ml of the analyzed solution, amounts to $5.2 \cdot 10^{-3}$ – $4.7 \cdot 10^{-2}$ µg/ml. The sorbents extract the metals from water characterized by a high content of salts, e.g., containing NaCl ~60, $CaCl_2$ ~16, $MgCl_2$ ~3 and $SrCl_2$ ~0.45 g/l (ref. 30).

New prospects are opened up by the use of heterochain polymeric sorbents in the form of fibres, which makes it possible to perform the preconcentration by means of filtration. This, in its turn, facilitates concentration from large volumes of natural water. A study has been carried out to compare the sorption properties of powdered thioether and thioether in the form of fibre, as examplified by the sorption of gold (III) and mercury (II) from hydrochloric acid solutions. It has shown that the efficiency (in the chemical sense) of a fibrous sorbent, as compared with the powder, on the whole does not change, and the fibrous sorbent can really be used in the form of a sorption filter. In both cases the concentrate can be analyzed by the X-ray fluorescence and atomic absorption methods.

The investigation has also shown that quantitative separation of mercury (II) is possible with the use of fibrous thioether. Extensive potentialities are offered by using another investigated sorbent of the same type – polymeric tertiary amine. At the first stage of sorption this polymer manifests itself in acid solutions as a typical ion exchanger. However, the complex formation takes place on the second stage.

TABLE 3. Determination of cadmium and lead in surface waters

Sample	Metal concentration ranges in samples analyzed	
	Cd, µg/ml	Pb, µg/ml
River waters (40 samples)	0.012–0.85	0.050–12.0
Sea waters (30 samples)	0.008–0.30	0.03 – 5.0

METHODS USING ION CHROMATOGRAPHY

Ion chromatography is known to be a promising method for the analysis of natural water.   It is the best method of determining anions in aqueous solutions (ref. 31).   The method is also suitable for determining heavy metals.   Highly sensitive dual-column techniques have been developed to determine metals in different types of water, with the separation according to both the cation- and the anion-exchange mechanism.

In the first case Cd, Cu, Mn, Ni, Pb, Sr and Zn have been separated by elution with ethylenediammonium chloride or ethylendiammonium tartrate solutions and determined with a conductometric detector (ref. 32).   The detection limits amount to 0.3-6.0 μg/ml.   Precision of determining 20 μg/ml of these metals is characterized by the relative standard deviation equal to 0.015-0.050.

When determinations are made by the anion-exchange mechanism, the metals (As, Cr, Mo, Se, Te, V and W) are first converted into oxoanions, and the separation is conducted on columns with "Dionex" low-capacity anion-exchange resin; the elution is performed with sodium carbonate solution (ref. 33).   As an example, Fig. 1 shows the chromatogram of a mixture of SeO_4^{2-}, MoO_4^{2-}, AsO_4^{3-}, WO_4^{2-} and CrO_4^{2-}.   The linear range of determined contents amounts to 0.05-500 μg/ml.   The mean relative standard deviation within this interval does not exceed 0.05.   The minimal determined concentrations of the investigated metals do not exceed their maximum permissible concentrations in water even without the use of a concentrating column. Using a concentrating column one can reduce the detection limit value by another two orders of magnitude.   The method has been used to determine tungsten, molybdenum and chromium in waste water (Table 4).   The results obtained are in good agreement with the data of atomic emission (W), atomic emission with inductively coupled plasama (Mo) and spectrophotometric (Cr) methods.

In the case of determining selenium in the form of SeO_4^{2-} the use of a concentrating column made it possible to decrease the detection limit 10 times (ref. 34).   Without enrichment the minimal determined selenium concentration amounted to 10 μg/l, while as a result of concentration it decreased to 0.01 μg/l, which makes it possible to determine this element in natural water.   Selenium was determined, e.g., in the Moskva River water.
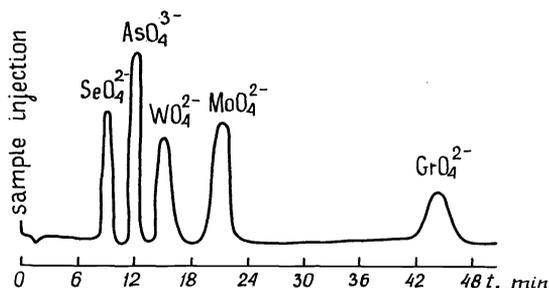

Fig. 1.   Chromatogram of a mixture of selenium(IV), molybdenum(VI), arsenic(V), tungsten(VI) and chromium(VI) oxoanions.   Separating brine column 3 x 500 mm; suppressing column 6 x 250 mm;   eluent $3 \cdot 10^{-3}$ M Na_2CO_3; eluent supply rate 230 ml/h.

TABLE 4.   Determination of chromium, molybdenum and tungsten in waste water (number of determination = 5; γ=0.95)

Element	Determined by ion chromatography, ppm	Determined by other methods, ppm
Cr	17.1 ±1.1	17.6
Mo	8.2 ±0.4	8.3
W	11.3 ±0.3	11.3

METHODS USING A COMBINATION OF SOLVENT EXTRACTION AND THIN LAYER CHROMATOGRAPHY

Combined with preliminary solvent extraction concentration of groups of metals in the form of chelates, TLC is quite suitable for the analysis of surface waters, which was demonstrated by determining heavy metals in river water samples (ref. 35). The scheme of analysis includes: solvent extraction preconcentration of metals with the use of sodium diethyldithiocarbamate, separation of chelates on commercially available plates with a thin silica gel layer, and visual or densitometric determination of the separated complexes directly in the chromatographic zones.

In preparation of this scheme a number of theoretical aspects of the chromatography of chelates was studied. The influence of the structure of chelates on their behaviour in the conditions of liquid adsorption chromatography was investigated. Recommendations have been given on the choice of a convenient chelate-forming reagent (class of chelates) from the point of view of solvent extraction recovery of a group of metals and their selective chromatographic separation (ref. 36). The possibilities of improving the analytical characteristics of the method have been estimated, especially of extending the range of determined chelate contents towards smaller quantities by taking into account all the factors that affect the retention parameters of complexes and keeping them invariable.

The absolute detection limits of metals in the form of diethyldithiocarbamates lie within the range from 1 to 10 ng, which allows their quantitative determination down to 0.05 µg/ml. The relative standard deviation in determining Co, Cu, Cr, Fe, Ni, Pb and Zn at a level of their maximum permissible concentrations lies within 0.1.
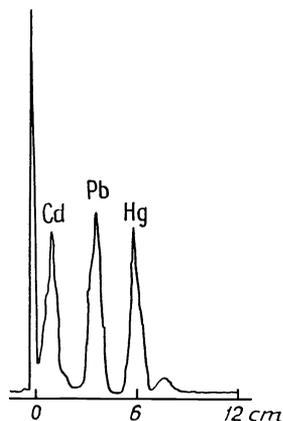

Fig. 2. Radiochromatogram of the extract of lead, cadmium and mercury ^{3}H-dipropyldithiophosphates (Silufol/toluene)

Interesting prospects are opened up by using TLC of chelate-forming reagents labelled with tritium (ref. 37). Converting the determined metals into their tritium-labelled complexes makes it possible to accomplish their radiometric determination in a thin layer, and with much lower absolute detection limits. Figure 2 shows a radio-chromatogram of an extract obtained after the extraction of cadmium, lead and mercury with ^{3}H-dipropyldithiophosphate solution in CCl_4. When a liquid scintillation counter is used, the detection limits for these metals amount to $9 \cdot 10^{-7} - 2 \cdot 10^{-6}$M. The calibration plots are linear on the average from $1 \cdot 10^{-7}$ to $2 \cdot 10^{-5}$M.

The methods developed thus make it possible to solve some problems of concentrating and determining heavy metals in natural water.

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