

## ANALYSIS OF NATURALLY OCCURRING WATERS FOR TOXIC METALS USING COMBINED ION EXCHANGE-SOLVENT EXTRACTION PROCEDURES

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Abstract- An analytical technique is described for the determination of cadmium, cobalt, copper, manganese, lead, uranium and zinc in samples of natural waters. After acidification of the water sample with hydrochloric acid, the diethyldithiocarbamates of the trace elements are isolated by extraction with a 2:5 mixture of acetone and chloroform at pH 5. Following this preconcentration step the metal ions are adsorbed on a column of the strongly basic anion-exchange resin Dowex 1 using as sorption solution a mixture (5:4:1, v/v) of tetrahydrofuran, methyl glycol and 6 M hydrochloric acid. Successive elution is effected with 6 M hydrochloric acid (Co, Cu, Mn and Pb), 1 M hydrochloric acid (U) and 2 M nitric acid (Cd and Zn); the metal ions in the eluates are determined by atomic-absorption spectrophotometry (except uranium, which is determined fluorimetrically). The procedure was used to determine the trace metals in water and snow samples collected in Austria and to analyse a sample of seawater from the Adriatic Sea.

### INTRODUCTION

Determinations of trace quantities of toxic metals in liquid environmental samples, as for example natural waters, are gaining importance with growing interest in pollution of the environment with elements such as lead, cadmium, copper, cobalt, manganese, zinc, and uranium.

Analytical techniques based on atomic-absorption spectrophotometry emission spectroscopy, fluorimetry, and spectrophotometry are often used here, frequently in combination with liquid-liquid extraction and/or ion-exchange to preconcentrate toxic metals so that improved detection limits and accuracy can be achieved.

### ANALYTICAL METHOD, EXPERIMENTAL RESULTS AND DISCUSSION

A technique in which a combination of preconcentration methods is employed was developed by the research group of the author and consists of the following steps:

- 1) The water sample (1 liter) is made 0.1 M in HCl by the addition of concentrated HCl and after adding sodium acetate (10 g) the pH is

adjusted to about 5 with 25 % NaOH solution.

2) After the addition of 1 g of sodium diethyldithiocarbamate the elements are extracted with two 15 ml portions of a 2:5 mixture of acetone and chloroform.

3) The combined extracts are evaporated under an infrared lamp, to the residue of the metal diethyldithiocarbamates a mixture consisting of 50 % tetrahydrofuran (THF), 40 % methyl glycol (MG) and 10 % 6 M HCl is added and the solution is evaporated to dryness.

4) The residue is dissolved in a small volume (30 ml) of the same THF-MG-HCl-mixture and passed through a column containing 4 g of the strongly basic anion exchange resin Dowex 1, X8 (100-200 mesh; chloride form). Then the resin bed is washed with 60 ml of the THF-MG-HCl-mixture.

5) Elution of Co, Cu, Mn, and Pb with 6 M hydrochloric acid (100 ml) and determination of the elements by atomic-absorption spectrophotometry.

6) Elution of U with 1 M hydrochloric acid (100 ml) and fluorimetric determination.

7) Elution of Cd and Zn with 2 M nitric acid (100 ml) and determination by atomic-absorption spectrophotometry.

Investigations with respect to the suitability of the 2:5 mixture of acetone and chloroform as an extractant for metal diethyldithiocarbamates showed that quantitative extraction of the seven elements is achieved at pH 5 in the presence of acetate. However, the sodium diethyldithiocarbamate must be added to the water sample immediately after this has been saturated with the extractant in order to take full advantage of the extraction efficiency of the chelating agent. At pH 5 the rate of the decomposition of diethyldithiocarbamate is relatively high (Ref.1).

Following evaporation of the combined extracts, the diethyldithiocarbamate complexes must be destroyed in the presence of THF-MG-HCl, otherwise many of the elements are retained incompletely on subsequent passage of the THF-MG-HCl sorption solution through the ion-exchange column. Thus, for instance Co is not adsorbed at all, and only 5, 10, 80 and 85 % of Cu, Pb, Mn and Zn, respectively, are adsorbed. After destruction of the diethyldithiocarbamates (by simple evaporation of the THF-MG-HCl-mixture), all elements are retained quantitatively by the anion-exchange resin from the THF-MG-HCl-mixture. The distribution coefficients shown in Table 1 were measured in the various media used for adsorption and elution. From these

TABLE 1. Distribution coefficients (1 g Dowex 1; 1 mg load)

Ion	THF-MG-HCl mixture	6 M HCl	1M HCl	2 M HNO <sub>3</sub>
Cd(II)	705	130	700	<1
Co(II)	6030	<10	<1	<1
Cu(II)	75	12	<1	<1
Mn(II)	200	<10	<1	<1
Pb(II)	250	<10	65	<10
UO <sub>2</sub> (II)	3510	250	<1	<1
Zn(II)	305	125	195	<1

results it is seen that the elements are strongly retained from the THF-MG-HCl-mixture and that successive applications of 6 M HCl, 1 M HCl and 2 M nitric acid give eluates which contain Co, Cu, Mn, and Pb, uranium, and Cd and Zn, respectively.

To investigate the effect of volume of the water sample on the recovery and accuracy of the determinations of the trace elements, varying volumes of tap water were analysed for the seven elements. The results showed that the volume of water has no effect in the volume range of 0.25 to 1.0 liter, but for accurate determinations of most elements not less than one liter of water sample should be used.

Since iron is the only major constituent of natural waters extractable with diethyldithiocarbamate under the conditions employed, the effect of foreign metal ions on the extraction and anion-exchange separation of the seven elements was studied with respect to the behavior of iron only. According to the results obtained, up to 10 mg of iron did not affect the recovery of the trace elements, except for uranium, of which much lower contents were found in the presence of 2 and 10 mg of iron. This is because 60 ml of the THF-MG-HCl-mixture are not sufficient to remove iron completely from the anion-exchanger so that some iron accompanies uranium into the 1 M HCl eluate and causes quenching of the uranium fluorescence. Complete removal of iron can be achieved by increasing the volume of THF-MG-HCl solution to 100-200 ml. Some of the copper will then pass into the effluent, however, because of its relatively low distribution coefficient of 75 (see Table 1).

Application of the procedure to the determination of the seven elements in numerous Austrian waters showed that their complete recovery was achieved in all cases. Furthermore, the results indicated clearly that Cd, Co and Pb cannot be determined without preliminary preconcentration by the extraction and anion-exchange methods because of the very low contents (usually much less than 1  $\mu\text{g}$  / liter ) of these metals in the waters analysed. Determinations of the seven trace elements in four snow samples gave results from which it was evident that the trace element contents decrease invariably with increasing distance of the sampling site from the highway except for uranium which shows virtually the same concentration in all the snow samples, because uranium is not contained in the exhaust fumes of cars; its presence in the samples (0.1  $\mu\text{g}$  U/liter) can be attributed to its removal (with the dust) from the air by the snow fall.

In order to investigate if the method is also applicable to the analysis of saline waters, a sample of seawater from the Adriatic Sea was analysed. The results shown in Table 2 indicate that none of the trace elements in the sample can be determined by direct atomic-absorption measurements (see column A of Table 2). The uranium determinations agreed very well with those obtained after anion-exchange separation of uranium thiocyanate.

It should be mentioned finally that the trace elements can also be concentrated quantitatively on a 4-g column of the strongly acid cation-exchanger Dowex 50 from one liter of the water sample which is 0.1 M in hydrochloric acid. Following adsorption, the trace elements, together with the coadsorbed main constituents are eluted with 6 M hydrochloric acid and, after evaporation of the eluate the anion-exchange separation described before is

carried out. However, this cation exchange separation method was abandoned in favor of the more rapid extraction method so that this technique is more suitable for the routine determination of trace elements in natural waters.

TABLE 2. Results of determinations of trace elements in a sample of seawater<sup>x</sup>

Element	Contents ( $\mu\text{g}/\text{liter}$ )		
	A	B	C
Cadmium	22.1	0.10	0.05 (0.5)
Cobalt	98.4	0.15	0.15 (0.5)
Copper	26.7	2.30	2.10 (4.5)
Manganese	28.6	3.80	4.20 (5.0)
Lead	95.2	0.35	0.37 (0.5)
Uranium	0.9 <sup>xxx</sup>	2.35	2.40 (2.5)
		2.25 <sup>xx</sup>	2.36 (1.0) <sup>xx</sup>
Zinc	28.8	0.55	0.75 (1.0)

A = Direct atomic-absorption determination without preliminary separation by extraction and anion-exchange

B = Determination after preliminary isolation by extraction and anion-exchange

C = Results obtained after preliminary isolation by extraction and anion-exchange and deduction of the known amounts of trace elements added as spikes before the separations. The number in parentheses gives the amount of spike added.

<sup>x</sup> Sample taken from the Adriatic Sea in October 1974 at the shore near Lignano Pineta, Italy.

<sup>xx</sup> Results obtained after anion-exchange separation of uranium thiocyanate (Ref.2).

<sup>xxx</sup> Determination by direct fluorimetry.

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