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Determination of copper, nickel, zinc, cobalt and manganese in seawater by chelation ion chromatography

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ABSTRACT

Preconcentration and determination of trace elements in seawater by chelation ion chromatography (CIC) was studied. For the retention of metal ions (0.25–0.30 *M*), ammonium acetate (at pH 4.8–5.1) and macroporous iminodiacetate chelating resin were used. This system (CIC) permits trace and ultra-trace determination of metals in a variety of complex matrices, in particular those with a high content of alkali and alkaline earth metals. Detection limits range from 0.1 to 0.5 ng. Satisfactory results are obtained in the range 0.05–0.5 μg/l when 60 ml of sample are preconcentrated. In this work the contents of zinc, copper, nickel, cobalt and manganese in seawater from the Venice lagoon are presented. The results obtained by chelation ion chromatography are compared with those obtained using preconcentration of metals with dithizone and ammonium pyrrolidinedithiocarbamate in chloroform and analysed by graphite furnace atomic absorption spectrometry.

INTRODUCTION

The determination of trace metals at μg/l levels in seawater is hampered by the matrix effect due to the high alkali and alkaline earth metal concentration. This high cation concentration makes it impossible to concentrate metal cations by conventional cation-exchange methods. Unlike conventional ion-exchange concentration methods that are typically not selective for ions of the same valency [1], chelation concentration is a selective concentration method.

Chelation ion chromatography (CIC) is a new method that combines analyte concentration and matrix elimination with analytical separations and selective detection for transition metals [2].

In recent years ion-exchange resin has been used for trace metal determinations in combination with on-line chromatographic detection. For this reason, iminodiacetate chelating resin (Chelex-100), which for many years has been used with success in batch analysis for the determination of many metals in complex matrices [3,4], was packed in a column and eluent forced through at 1–2 ml/min. The results showed that in these conditions only partial recovery of some trace metals is achieved. After many attempts to improve the metal retention on Chelex-100 chelating resin, it was concluded that the low recovery of metal ions was caused by a physical degradation of the resin under pressure because of low degree of cross-linking of microporous polystyrene–divinylbenzene (PS–DVB) supporting polymer. For this reason, Dionex has developed a more highly cross-linked macroporous PS–DVB containing the iminodiacetate functional group that allows operation at high pressure without physical degradation (Met Pac CC-1 column) [2]. Using this resin high recoveries of several metals has been obtained with complex matrices.

In the present work a chelating column (Met Pac CC-1) was used to preconcentrate trace elements starting from a sample volume ranging from 5 to 60 ml.

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Alkali metals and anions are not retained by the chelating column during the sample loading. Alkaline earth metals are removed by the chelating column and selectively eluted to waste by a 2 *M* ammonium acetate pH 5.5 buffer.

The concentrated transition metals are then eluted with 0.5 *M* nitric acid and sent to a second concentrator column. The concentrated metals are then separated in an analytical column by pyridine-2,6-dicarboxylic acid (PDCA).

Detection is accomplished by visible absorbance after post-column derivatization with a metallochromic indicator, 4(2-pyridylazo) resorcinol mono sodium salt hydrate (PAR) [5,6].

EXPERIMENTAL

Materials

Chromatographic equipment. The ion chromatography (IC) system consisted of a Model 2020i chromatograph with eluent degas module (EDM) and reagent-delivery module (RDM), a gradient pump module (GPM), a DQP-1 sample pump and a variable-wavelength detector module (VDM).

An advanced computer interface (ACI) was in series with a 386 Uni Bit PC.

Columns. The column used for chelation, containing a macroporous PS–DVB iminodiacetate chelating resin, was from Dionex (Met-Pac CC-1). The column has a capacity of 0.45 mequiv.

A second concentrating column, TMC-1 (sulphonated PS–DVB cation-exchange resin), with high capacity (2.2 mequiv./ml), a CS5 separation column, a CG5 precolumn (packed with a mixed-bed ion-exchange resin) and GPM programme (for CIC) were from Dionex [7].

Reagents. Ammonium acetate 2 *M*, pH 5.4 ± 0.1, PDCA, PAR and ammonium nitrate 0.1 *M*, pH 3.5 ± 0.1, were purchased from Dionex.

Nitric acid was Aristar grade (BDH); bidistilled water was obtained using a Milli-Q Plus system from Millipore.

Chloroform was GPR grade (BDH); ammonium pyrrolidinedithiocarbamate (APDC) and dithizone were, respectively, Spectrasol and AnalaR grade (BDH).

Analytical conditions.

Fig. 1 shows a scheme of the chelation concentration chromatography system.

Ammonium acetate 2 *M* was used for chelation on the CC-1 column.

In order to stabilize the samples for storage, both samples and standards were acidified to pH 2 with nitric acid. Before concentration, to ensure the complete recoveries of trace metals, the solutions were buffered with 2 *M* ammonium acetate pH 5.4.

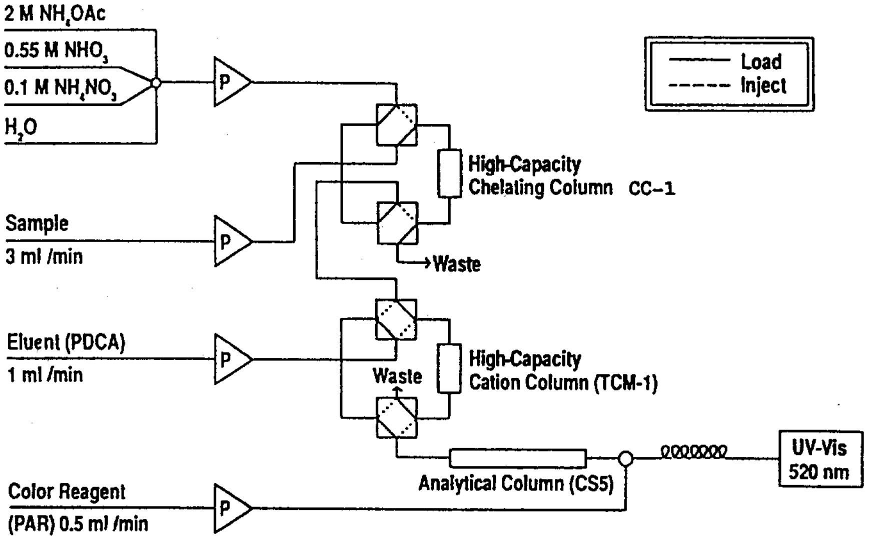

Fig. 1. Scheme of the chelation concentration method for the determination of transition metals.

The recommended analytical conditions were as follows: ammonium acetate final concentration between 0.25 and 1 *M* and final pH 5.4 ± 1 [7].

Variation of the pH, by addition of 2 *M* ammonium acetate was followed in bidistilled water and seawater acidified to pH 2.2 and in seawater that had not been acidified. The recommended pH for 100 ml of seawater is achieved by addition of 90–100 ml of ammonium acetate, resulting in a solution of about 1 *M* ammonium acetate. However, dilution of the sample and the high cost of the large amount of ammonium acetate used preclude the application of the method in these conditions. For this reason the final ammonium acetate concentration was 0.25–0.30 *M* (final pH 4.8–5.1), depending on whether standard or seawater solution was used. This was achieved by addition of 10–20 ml of ammonium acetate for every 100 ml of standard or sample solution.

Nitric acid 0.35 *M* was used to elute metals in the preconcentration column (TMC-1). Before the metals preconcentrated in the TMC-1 column [7] can be injected into the analytical stream, the TMC-1 must be converted from the acid (H^+) form to the ammonium (NH_4^+) form. This is accomplished by pumping 0.1 *M* ammonium nitrate (at pH 3.5) into the TMC-1 column.

RESULTS AND DISCUSSION

Fig. 2 shows a typical chromatogram of a standard solution of trace metals analysed by chelation concentration when 6 m*M* pyridine-2,6-dicarboxylic acid (PDCA) was used.

We also studied the variation in the retention time of copper, nickel, zinc, cobalt and manganese and noted a very low variation when many analyses were performed.

To assure the validity of the analytical data, the evaluation of analytical blanks using chelation concentration was performed.

To minimize the influence of the metals on the blank, analytical-grade reagents and glassware were used and all parts of the system were thoroughly washed with 0.1 *M* oxalic acid. Care was taken to minimize reagent and sample contamination during preparation and handling.

Generally, iron and zinc are the most common metal contaminants, while a small amount of copper may also be observed. Fig. 3 shows a typical level of background contaminant in a blank run.

The average values of the blank, when 60 ml of bidistilled water were preconcentrated, were 0.1, 0.05 and 0.30 ppb for copper, nickel and zinc, respectively. When several blanks (n = 8) were analysed, the observed R.S.D.s were 1.1, 0.7, and 2.1% for copper, nickel and zinc, respectively. Cobalt and manganese peaks do not occur on blank chromatograms.

To verify the linearity of the CIC method in relation to the volume of lagoon water used (after purification with Chelex 100 resin [4]), copper, nickel, zinc, cobalt and manganese at 1, 2, 2, 2, 2 μg/l, respectively, were added and 5, 10, 20 and 40 ml of sample were preconcentrated.

To evaluate the linearity with the increase in metal concentrations in saline matrix, the method of additions was carried out on Venice lagoon water. In the both cases the excellent linearity of the method was confirmed.

To evaluate the precision of the method at ppb levels, analysis of standards was repeated a number

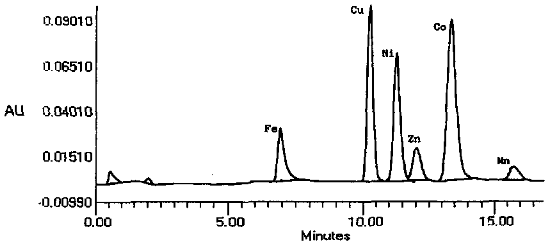

Fig. 2. Typical chromatogram of a standard solution of copper, nickel, cobalt (1 μg/l), zinc and magnanese (2 μg/l) by chelation concentration when 60 ml of solution were preconcentrated and 6 m*M* pyridine-2,6 dicarboxylic acid (PDCA) was used.

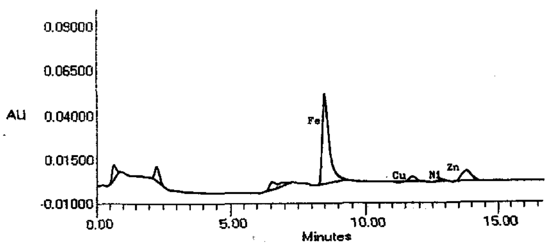

Fig. 3. Typical level of background using chelation concentration. Copper, nickel and zinc are 0.060, 0.040 and 0.20 μg/l, respectively. In this case we did not calculate the blank of iron.

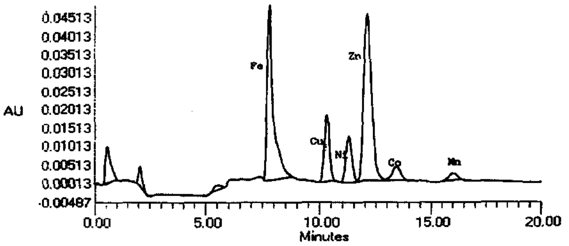

Fig. 4. Typical chromatogram of Venice lagoon seawater when 60 ml of sample were preconcentrated. Copper, nickel, zinc, cobalt and manganese levels are 0.3, 0.35, 4.2, 0.09 and 0.36 μg/l respectively. In this case we did not calculate the iron level.

of times and R.S.D.s calculated. When 60 ml of copper, nickel, zinc, cobalt and manganese standard samples were preconcentrated R.S.D.s of 0.26, 2.3, 16.2, 0.41 and 4.6%, respectively, were obtained. The data confirm that the precision of the method at the ppb level is good.

Finally, analysis of Venice lagoon seawater was performed to control the level of trace metals in the channel connecting the lagoon with the sea. A 60-ml sample of the lagoon seawater was sampled at 3.5 m depth, filtered through a 0.45-μm cellulose filter, immediately loaded on the preconcentrating column and analysed. Fig. 4 shows a typical chromatogram of Venice lagoon seawater.

The results obtained by chelation ion chromatography are compared with those acquired using preconcentration of metals with dithizone (diphenylthiocarbazone) and APDC absorption spectrometry in chloroform and analysed by graphite furnace atomic absorption spectrometry (AAS) after re-extraction in acid solution [8]. The data obtained with the two methods are very similar; only the manganese concentration is different because during the loading phase a part of it is not quantitatively retained on the preconcentrating column. It has been verified that, during the washing phase with ammonium acetate, about 15% of manganese is lost when the rate of sample loading is 3 ml/min. This is not a problem since the percentage of manganese eluted during this elution process is constant.

The linear range calculated for the system using a seawater matrix was from 0.1 ng (detection limit) to at least 250 ng for the metals studied. The detection limits for copper, nickel, zinc, cobalt and manganese in seawater, when 60 ml of sample were preconcentrated, were 0.05, 0.05, 0.15, 0.05 and 0.1 μg/l, respectively.

The data obtained from many successive analyses of Venice lagoon seawater show low variations of copper, nickel and cobalt, while zinc is a highly variable because of the changes of the chemical composition of water flowing in the channel. A higher degree of uncertainty was found for manganese, which in some analyses was below the detection limit.

Regarding the iron concentration, this was not determined because of the high levels of iron found in the blank during the analytical procedure.

CONCLUSIONS

The CIC method shows high validity. This technique allows the analysis of many metals at trace levels in a few minutes and it is possible to eliminate completely the salty matrix interferences.

Alkali metals and anions are not retained by the chelating column. Alkaline earth metals are selectively eluted to the waste when 2 *M* ammonium acetate is pumped through the chelating column.

Up to 100 ml of seawater were concentrated on the chelating column without significant loss of the transition metals.

The precision of CIC at the low-ppb level is very good. Zinc typically shows a higher relative standard deviation. This mainly results from the higher blank value. The reliability of the method is very high.

Table I shows the comparison between the CIC method and a preconcentration method by APDC

TABLE I

CHARACTERIZATION OF VENICE LAGOON WATER BY GRAPHITE FURNACE AAS AND CIC

Element	AAS	CIC
Copper	0.55	0.58
Nickel	0.73	0.71
Zinc	2.0	1.93
Cobalt	0.04	0.08
Manganese[a]	1.90	1.15

[a] During the elution process with ammonium acetate some manganese (15%) is eluted.

or dithizone extraction and graphite furnace AAS analysis.

The analysis of Venice lagoon water in the zone examined shows rather low heavy metal values. Only for zinc are the values higher as a result of both different environmental conditions and a greater probability of contamination by this element. Analysis of heavy metals for environmental monitoring in Venice lagoon, utilizing the CIC technique, was also taken in account. Some problems related to the filtration equipment and the automatic sample treatment present (particularly for zinc), at this moment, a limitation to the application of the monitoring system.

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