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Determination of trace elements by ion chromatography

I. Beryllium

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ABSTRACT

A method for the determination of beryllium by ion-exchange chromatography followed by post-column derivatization with 4,5-dihydroxy-3-(8-hydroxy-3,6-disulpho-1-naphthylazo)naphthalene-2,7-disulphonic acid (Beryllon II) and spectrophotometric detection at 625 nm is described. With injection of 50 μl of the sample, the calibration graph was linear from 50 to 5000 μg/l of beryllium with a detection limit (3σ) of 42 μg/l. The detection limit for direct injection of a 500-μl volume is 2 μg/l. Typical relative standard deviations of 0.9–0.2% and 1.5–2.0% for 10 mg/l and 10 μg/l beryllium standards, respectively, were obtained. Freedom from interference from nine cations investigated is reported. The method was applied successfully to the determination of low levels of beryllium in environmental samples.

INTRODUCTION

Beryllium can be considered as a trace element, which occurs naturally in the earth's crust and in surface waters at μg/g and ng/l levels, respectively [1,2]. This element is used as a hardening agent in alloys, as a moderator in atomic energy reactors and as a compact fuel element for rockets [3].

The most significant feature of the biological activity of beryllium is the highly toxic character of the element and its compounds. Inhalation of beryllium can cause beryllosis, a serious disease which leads to weight loss, dyspnea, cough, chest pains, fatigue and general weakness [4].

Owing to its toxicological importance and unknown physiological activity, the development of a method to determine beryllium accurately at low levels in environmental and biological samples has attracted attention. Different methods based on atomic absorption [5,6], spectrophotometry [7,8] and spectrofluorimetry [9,10], etc., have been reported. Photometric and fluorimetric methods, predominantly based on coloured complex formation, are more popular owing to their simplicity.

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Some methods, although sensitive, suffer from interferences and pretreatment of the sample is generally required before determination [5–10].

The use of modern ion-exchange chromatographic techniques for trace metal determination is now well established, as is evident from the steady increase in the number of papers in this area reviewed recently [11,12]. However, few of these papers have dealt with the determination of the trace amounts of beryllium. Noda *et al.* [13] demonstrated the feasibility of gel permeation chromatography for the separation of mixed-ligand complexes of several beryllium(II) β-diketonates. Biswanath and Desay [14] separated beryllium as β-isopropyltropolone complexes on a reversed-phase column. Kondratjonok and Schwedt [15] recently found that the optimum separation conditions for beryllium ions on a polymer-coated cation-exchange column (polybutadiene–maleic acid on silica) are an eluent based on pyridine-2,6-dicarboxylic and citric acid with conductivity as the detection mode. With these methods quantitative separation and accurate determination of beryllium can be carried out, but a simpler method based on widely used instrumentation is required. As ion chromatographic (IC) techniques are potentially cost effective, as recently shown for anions and cations [13,16], and are suitable for studying metals and their speciation [13,17], we decided to develop a simpler and accurate method for low-level beryllium determination by IC.

This paper describes the use of ion-exchange chromatography followed by post-column derivatization using 4,5-dihydroxy-3-(8-hydroxy-3,6-disulpho-1-naphthylazo)naphthalene-2,7-disulphonic acid (Beryllon II) and spectrophotometric detection to determine beryllium at the μg/l level. Experimental conditions and analytical figures of merit including linear dynamic range, column efficiency and interferences are discussed. Results for the determination of beryllium in environmental certified reference materials are also presented.

EXPERIMENTAL

Instrumentation

A Dionex (Sunnyvale, CA, U.S.A.) Model 4500i ion chromatograph system equipped with a pressurized post-column reagent delivery module (RDM) and a UV–VIS detector (VDM II, Dionex) were employed. A Dionex AI-450 data system was used for data collection and processing and a Varian (Australia) DMS-300 spectrophotometer for spectrophotometric measurements.

The separations were carried out on an IonPac CS3 cation-exchange column (250 mm × 4.6 mm I.D.) used in conjunction with an IonPac CG3 guard column (50 mm × 4.6 mm I.D.).

The eluent and the post-column reagent solution (PCR) were mixed with the aid of a T-piece, positioned at the exit of the analytical column, followed by a packed-bed reaction coil of 100-μl volume.

Injections of 50, 100, 200 and 500 μl of the sample were performed.

Reagents and standards

Hydrochloric acid, glycine, sodium chloride and sodium hydroxide were Suprapur grade materials (Merck). Beryllon II [4,5-dihydroxy-3-(8-hydroxy-3,6-disulpho-1-naphthylazo)naphthalene-2,7-disulphonic acid] was obtained from Novachimica.

Ultra-pure water (18 MΩ/cm resistivity at 25°C) obtained treating doubly distilled water (Carlo Erba) in a UHQ system (Elga, U.K.), was used throughout.

Working standards were prepared by serial daily dilution of stock solutions, containing 1000 mg/l of Be(II), Ca(II), Mg(II), Cu(II), Ni(II), Al(III), Mn(II), Co(II), Cr(III) and Mo(VI) obtained from Merck.

National Bureau of Standards (NBS) Standard Reference Material SRM 1643b (water) was obtained from the NBS (Washington, DC, U.S.A.) and MESS-1 and BCSS-1 (Estuarine Sediment Reference Materials) from the National Research Council of Canada (Ottawa, Canada).

All standards, samples and reagents were prepared and stored in polyethylene containers previously cleaned and conditioned following a procedure for trace element determination [18].

Eluent solution

The final choice for the eluent solution was 190 m*M* hydrochloric acid, which was prepared fresh daily and used at a flow-rate of 1 ml/min.

Post-column reagent (PCR) solution

The PCR solution consisted of 0.01% (w/v) Beryllon II in glycine–sodium chloride–sodium hydroxide buffer at pH 12.6. The PCR solution was prepared daily by dissolving 100 mg of Beryllon II in 1 l of the above buffer. This buffer was obtained mixing 350 ml of a solution which was prepared by dissolving 7.507 g of glycine (the buffer substance) and 5.84 g of sodium chloride in 1 l of water, with 650 ml of 1 *M* sodium hydroxide solution. The PCR flow-rate varied between 0.2 and 1.5 ml/min, as will be explained in the following section.

RESULTS AND DISCUSSION

Complexing reagents for beryllium

Beryllium belongs to Group IIA of the Periodic System, but only complex ions of it are known [19]. Apart from fluoride, stable complexes are primarily obtained with ligands containing O and N donor atoms. Such ligands of analytical interest are hydroxy acids, β-diketones (acetylacetone), chromotropic acid azo derivatives (Beryllon II, III and IV), anthraquinone derivatives (quinalizarin) and triphenylmethane derivatives [20]. Among these dyes, Beryllon II, which is the product of coupling chromotropic acid with diazo H-acid, 4,5-dihydroxy-3-(8-hydroxy-3,6-disulpho-1-naphthylazo)naphthalene-2,7-disulphonic acid, is soluble in water. It turns red in acidic solution and violet in alkaline solution. In the pH range 11.5–14 it forms blue complexes with Be, Ca, Mg, Al, Cu, Co, Ni, Mn, Mo and Cr [21]. When performing normal colorimetric procedures, many of these interferences with beryllium determination must usually be eliminated by the addition of EDTA [19,20]. If this is not sufficient, beryllium has to be separated by extraction with acetylacetone [20] or by means of ion-exchange [22].

Detection conditions

Studies on the absorption of the PCR solution mixed with the eluent with and without the addition of beryllium were performed.

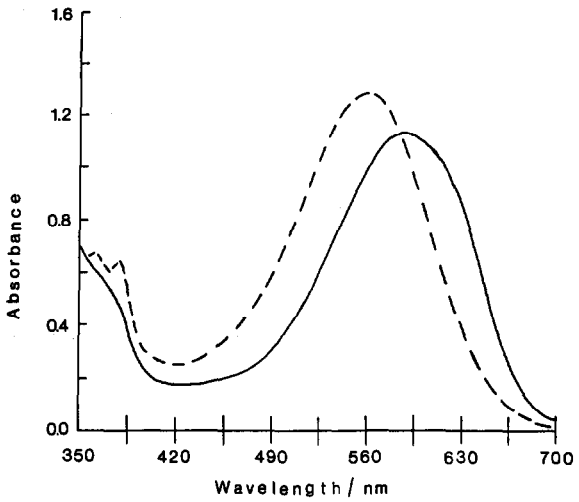

Fig. 1. Absorption spectra of the PCR–eluent mixture from the chromatographic cell without (dashed line) and with (solid line) the addition of 10 mg/l of beryllium.

The effluent from the spectrophotometric cell of the ion chromatograph was collected and a known amount of beryllium added. The spectrum of the effluent without the addition of beryllium (Fig. 1, dashed line) showed a maximum absorption at 560 nm, as reported for Beryllon II in alkaline solutions [19,20].

When adding beryllium to the effluent solution, the spectrum which was measured *vs.* the PCR–eluent mixture presented the maximum absorption of the Be–Beryllon II complex at 626.5 nm (Fig. 1, solid line). pH values about 2 units lower and higher than 12.6 caused a decrease in the sensitivity of the beryllium determination. In this investigation a wavelength of 625 nm was used.

Separation conditions

The feasibility of beryllium separation on a low-capacity divinylbenzene–styrene sulphonated copolymer cation-exchange column [23], using hydrochloric acid as eluent, was investigated. Six different concentrations of hydrochloric acid between 50 and 220 mM at a flow-rate of 1 ml/min for the elution of a 10 mg/l beryllium standard were tested.

For all the mobile phase concentrations, the column efficiency, N, using 10 mg/l of beryllium was evaluated. A comparison of the data obtained shows that there was no statistical difference, at the 99% confidence interval, using the different concentrations for the mobile phase, thus indicating that the beryllium peak has similar column efficiencies ($N = 1120 \pm 50$), irrespective of the eluent concentration used.

The retention time of beryllium ions was found to be linearly dependent ($r = -0.99982$) on the eluent concentration. For concentrations below 100 mM the retention times were unacceptably long. In order to minimize the analysis time and avoid overlap with potential interferent ions (*i.e.*, Mg^{2+}), 190 mM was found to be the best concentration for the hydrochloric acid mobile phase.

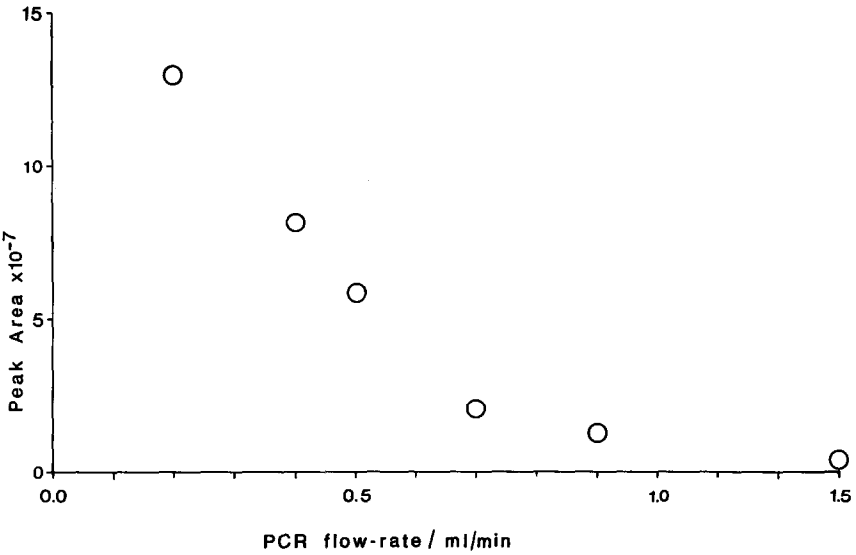

Fig. 2. Effect of the PCR flow-rate on the analytical response (peak area) of 10 mg/l of beryllium. Injection volume 50 μl.

Effect of PCR flow-rate on the peak area of beryllium

The effect of the PCR flow-rate on the response of beryllium while keeping the eluent flow-rate constant was investigated. As shown in Fig. 2, the chromatographic response (peak area) was found to be dependent on the PCR flow-rate. An excellent linearity ($r = -0.99998$) was obtained in the range 0.2–0.5 ml/min. On increasing the PCR flow-rate, the peak area decreased. This behaviour could be used for increasing the dynamic range, so that high concentrations can be determined without diluting the sample.

Linearity and detection limit

For a PCR flow-rate of 0.2 ml/min, excellent linearity ($r = -0.99998$) over two orders of magnitude from 50 to 5000 μg/l (5.5–556 μM) of beryllium, on injecting 50-μl samples, was found. The linear range can be extended using the PCR flow-rate (as mentioned above) or using smaller injection volumes, thus avoiding sample dilution in some instances. The detection limit, calculated by using the definition of three times the standard deviation (3σ), was 42 μg/l on injection of 50 μl. Concentrations lower than 1 μg/l (0.1 μM) can be determined by increasing the injection volume, or by means of the on-line preconcentration technique.

Reproducibility

Using two different PCR flow-rates (0.4 and 0.2 ml/min) and 190 mM hydrochloric acid as the eluting agent, data on the reproducibility of the peak area and the retention time were obtained by performing ten injections of 50 μl of a 10 mg/l beryllium standard solution on four separate occasions.

The relative standard deviations (R.S.D.) for the peak area varied from 0.20 to

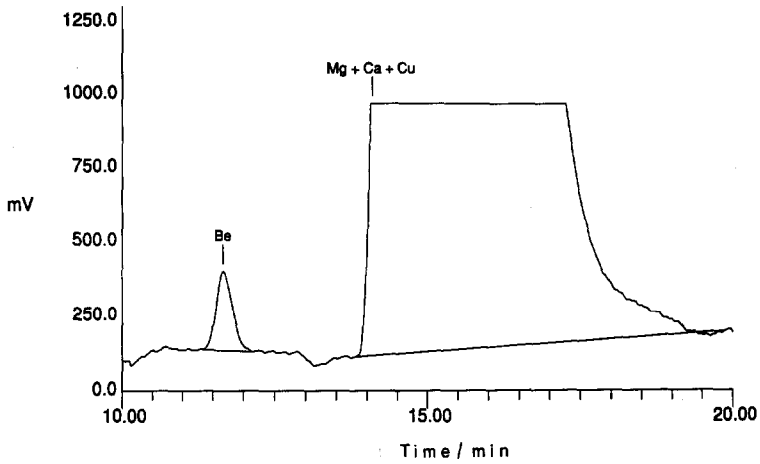

Fig. 3. Chromatogram obtained on injecting 200 μl of a solution containing 40 μg/l of beryllium together with 10 mg/l of Mg(II), Ca(II) and Cu(II).

0.73% for a 0.4 ml/min PCR flow-rate and from 0.44 to 0.90% for a 0.2 ml/min PCR flow-rate. The R.S.D. values for the retention time varied from 0.13 to 0.40% and from 0.10 to 0.33% for PCR flow-rates of 0.4 and 0.2 ml/min, respectively. Thus, both peak area and retention time data were indicative of a stable and reproducible system.

Interferences

Beryllon II, at alkaline pH, is not a specific spectrophotometric reagent for beryllium. Therefore, interferences are possible if other species elute at similar retention times to beryllium. This was investigated by analysing a solution containing 0.5 mg/l of beryllium and increasing amounts of interferents from 10 to 100 mg/l. The interferents tested were Mg(II), Ca(II), Cu(II), Ni(II), Al(III), Mn(II), Cr(III), Mo(VI) and Co(II). It was found that using 190 m*M* hydrochloric acid as mobile phase only three cations, Mg(II), Ca(II) and Cu(II), had retention times in the vicinity of beryllium, *viz.*, 14.3, 14.8 and 15.9 min, respectively. However, they could not interfere in the determination of beryllium even at the highest concentration ratio tested, as shown in Fig. 3, where the chromatogram obtained for a sample containing 40 μg/l of beryllium together with 10 mg/l of Mg(II), Ca(II) and Cu(II) is illustrated.

Real sample analysis

The method investigated was used to determine beryllium in three different certified reference materials: NBS SRM 1643b (trace metals in water) and National Research Council of Canada MESS-1 and BCSS-1 (estuarine sediment reference materials for trace elements).

The chromatograms obtained for SRM 1643b (a) before and (b) after the addition of 50 μg/l of beryllium are shown in Fig. 4.

In order to leach the total metal concentration, the estuarine sediment samples were treated with nitric acid by refluxing for 2 h, following the procedure described by Langston [24].

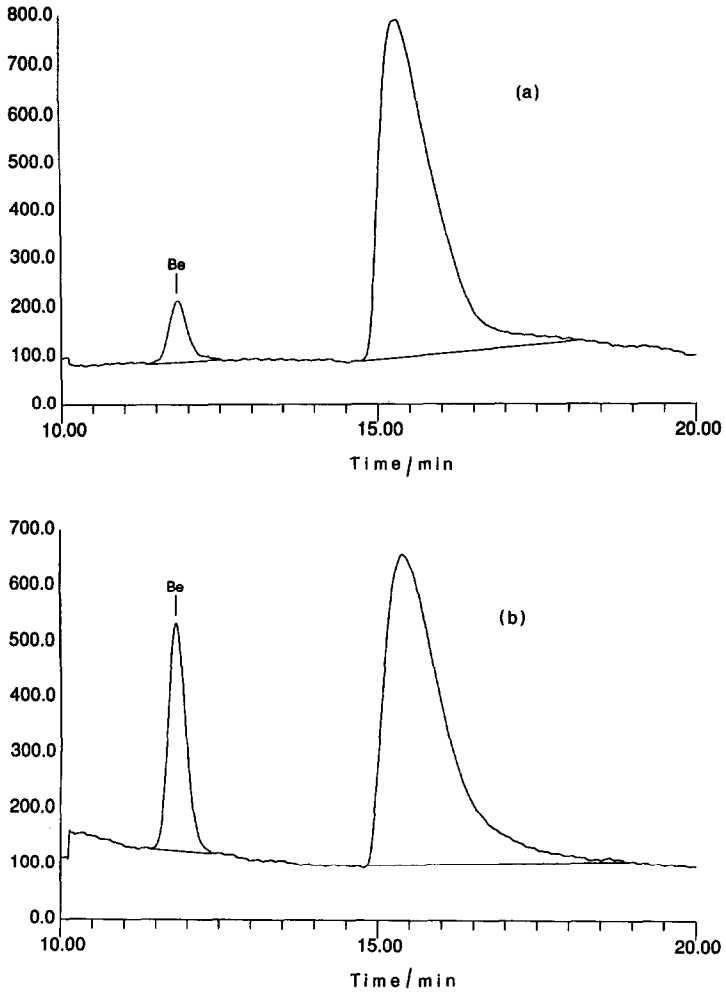

Fig. 4. Chromatograms obtained for direct injection of 200 μl of SRM 1643b (a) before and (b) after the addition of 50 μg/l of beryllium.

TABLE I

RECOVERY OF BERYLLIUM IN CERTIFIED REFERENCE MATERIALS

Sample	Certified Be content ± S.D. (ng/g)	Concentration determined ± S.D. (n = 10) (ng/g)	Recovery (%)
SRM 1643b	19	19.2 ± 0.36	101
MESS-1	1900 ± 200	1879 ± 20	98
BCSS-1	1300 ± 300	1307 ± 20	100.5

For all three reference materials tested, the beryllium concentrations obtained using the standard addition method were found to concur with the certified values, as reported in Table I.

CONCLUSIONS

A simple, rapid and accurate method based on ion-exchange chromatography with post-column derivatization has been developed to determine beryllium in the μg/l–mg/l range. The possibility of obtaining lower detection limits by means of on-line preconcentration techniques is under investigation.

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