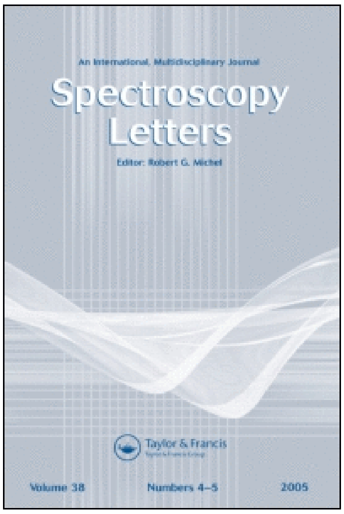

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Solid-Phase Spectrophotometric Determination of Beryllium at ng mL^{-1}

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SOLID-PHASE SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM AT ng mL^{-1}

Key Words: Solid-phase spectrophotometry, chromazurol S, beryllium, underground water, mining waste water, beryl.

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Abstract.

A microdetermination method at ng mL^{-1} level for beryllium by solid-phase spectrophotometry was been developed. Chrome Azurol S was used as chromogenic reagent to form a blue complex which was easily and strongly sorbed and concentrated on a dextran-type anion-exchange resin. The resin-phase absorbances at 594- and 800 nm were measured directly. Beryllium could be determined over the 1.5 - 15.0 ng mL^{-1} range with a RSD of 2.7 % by using 100 mL of sample solution. The detection limit was 0.21 ng mL^{-1}. By using only 10 mL of sample solution, the calibration graph was linear over the concentration range 10-85 ng mL^{-1}, the RSD

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being 1.2 %. The method was applied to the determination of beryllium in underground and mining waste water samples and in beryl mineral.

INTRODUCTION

Compounds of beryllium have a high toxicity and the tissues of mammalian species do not excrete it and, therefore, the effects are cumulative. It has been demonstrated that in humans beryllium damages the mucous membrane and the skin and its accumulation in the lungs originates berylliosis. Its presence in water is mainly due to the waste dumped by metallurgical and nuclear industries. The high toxicity mainly affects people who work in the areas of these industries[1]. For the determination of trace amounts of beryllium in water samples, enrichment of this element prior to the determination step is required in order to obtain reliable results. Some papers have described many enrichment techniques based on various principles such as liquid-liquid extraction[2], coprecipitation [3] and ion-exchange[4].

Numerous complexes of Be(II) with azo reagents, and triphenylmetane reagents (such as Beryllon II, Eriochrome Black T, p-nitrophenylazo-resorcinol and Chromal Blue G) have been used for spectrophotometric determination of berylium[5,6]. They exhibit moderate sensitivity but it can be increased by addition of a cationic surfactant.

Chrome Azurol S (CAS) has been used as chromogenic reagent for spectrophotometric determinations of beryllium. In presence of EDTA as masking agent, the Chrome Azurol S method is highly selective for berylium[7].

The aim of this work was to develop an analytical method for beryllium with CAS simultaneously based in a selective enrichment and determination by solid phase spectrophotometry (SPS). This technique enables determining analyte concentrations at ng mL^{-1} and, sometimes, at sub-ng mL^{-1} levels [8-11] without requiring an expensive instrumentation combining the measurements of solid-surface absorbance with using a solid support to preconcentrate selectively the analyte and measuring the absorbance directly in the solid phase with the aid of a chromogenic reagent. The proposed method joins to the intrinsic selectivity offerred by SPS that apported by using EDTA as masking agent.

EXPERIMENTAL

Reagents.

All reagents were of analytical-reagent grade and the water was doubly distilled.

Ion exchanger. Sephadex QAE A-25 (Aldrich), anion-exchange resin was used in the chloride form in original dry state as obtained from the supplier and without pretreatment.

Beryllium (II) standard solution 1000 mg L $^{-1}$, prepared by dissolving 19.660 g of beryllium sulfate tetrahydrate $BeSO_4 4H_2O$ (Merck) in doubly distilled water containing 5 mL of conc. H_2SO_4 and diluting the solution with doubly distilled water to 1000 mL. Beryllium (II) working solutions were made "in situ" by dilution with doubly distilled water.

Buffer solution of pH 5.3, was made by dissolving 35.05 g of hexamethylenetetramine (HMTA) (Merck) and 25 mL of 4 M HCl in 500 mL of doubly distilled water and adjusting the pH with a few drops of HCl 4 M or NaOH 4 M. This solution was stored under refrigeration.

Chromazurol S (Aldrich) (CAS) buffered solution 1.7 x 10^{-4} M prepared by dissolving the necessary amount of the dye in the above HMTA buffer solution. This solution was stored under refrigeration. In this conditions the solution is stable for at least one month.

Ethylenediaminetetraacetic acid (Panreac) (EDTA) solution 1.72 x 10^{-2} M.

Apparatus.

A GBC 911 microcomputer-controlled UV-VIS spectrophotometer with glass cells (1-mm optical path length) was employed for all spectral measurements. The spectrophotometer was connected to a 80286 microcomputer by means of a serial port for data acquisition and data processing and fitted with GBC Scan Master Software V1.62 (from GBC). The spectra were registered with a scan rate of 250 nm/min. The pH measurements were made with a Crison Model 2002 pH-meter fitted with a glass-saturated calomel electrode assembly and a temperature probe. An

Agitaser 2000 rotating agitator and a desk centrifuge Selecta model S-240 were also used.

Absorbance measurements.

The absorbance (really attenuation) of the complex species sorbed on the resin was measured in a 1 mm glass cell at 594- (corresponding to the absorption maximum of the coloured species) and 800 nm (in a region where only the resin absorbs ligth). The net absorbance (A) for the complex was calculated from[11]:

$$A_c = A_{594} - A_{800} \qquad (1)$$

where: $A_{594} = A_{s594} - A_{b594}$ and $A_{800} = A_{s800} - A_{b800}$ and A_{sXXX} and A_{bXXX} are the absorbances of the sample and the blank (cell packed with resin equilibrated with blank solution) respectively at the indicated wavelength. In fact, the observed absorbance, A, at a given wavelength is obtained by[12]:

$$A = A_c + A_{soln} + A_R + A_{RL}$$

where A_c represents the absorbance of the complex species sorbed on the resin, A_{soln} that of the intersticial solution between the resin beads (it can be neglected), A_R that of the resin background ($A_{R800} \approx 1.000$) and A_{RL} that of the reagent in the solid phase. The packing of the resin in the cell beads affects the values of A_c, A_R and A_{RL}, but when the absorbance is measured at two different wavelengths, one corresponding to the absorption maximum of the coloured species (594 nm) and the other in a region where only the resin absorbs (800 nm), the absorbance difference, $A_{s594} - A_{s800}$, can be assumed to be constant under the similar packing conditions. On the other hand, if the absorbance of a blank resin is measured at the same two wavelengths, the absorbance difference, $A_{b594} - A_{b800}$, allows to estimate the absorbance of the complex, A_c (that is related with the concentration of analyte in the solution as it was shown by Yoshimura[12]) from the equation (1).

Procedures.

I) To 100 mL of sample solution containing 1.5-15.0 ng mL^{-1} of beryllium placed into a 1-l polyethylene bottle, 5 mL of 1.57 x10^{-2} M EDTA solution were added and then the solution was hot for 15 min at 80° C in a water bath. After coulding, 10 mL of 1.7 x 10^{-4} M CAS buffered solution and 30 mg of Sephadex QAE A-25 resin were added. The mixture was shaken mechanically for 15 min after which the resin beads were collected by filtration under suction through a sintered glass plate and with the aid of a pipette packed into a 1-mm cell together with a small volume of the aqueous solution. Then, the cell was centrifuged for 1 min at 5000 rpm. A blank solution containing all reagents except beryllium was prepared and treated in the same way as described for the sample. Absorbances (A_{s594}, A_{s800}, A_{b594} and A_{b800}) were measured before 30 min from collection of resin as described under "**Absorbance Measurements**". The calibration graph was constructed in the same way by using beryllium solutions of known concentration.

II) To 10 mL of sample solution containing 10-85 ng mL^{-1} of beryllium placed into a 20-mL glass test tube with stopper 1 mL of 1.57 x10^{-2} M EDTA solution were added and then the solution was hot for 15 min. at 80° C in a water bath. After coulding, 2 mL of 5.78 x 10^{-4} M CAS buffered solution and 30 mg of Sephadex QAE A-25 resin were added. The mixture was shaken mechanically for 5 min after which the resin beads were collected by suction with the aid of a pipette, packed into a 1-mm cell and centrifuged as above. Absorbances measurements was carried out as described in procedure I).

Treatment of Samples.

a) Waters.

From the guidelines indicated in bibliography[13], water samples were filtered through a membrane filter (Millipore) with a pore size of 0.45 µm and collected in a polyethylene container which had previously been carefully cleaned with a (1:1) nitric acid solution and rinsed with bidestilled water. Samples were stored at 4°C and the analyses were performed with the least possible delay (during the 24 h following their collection). The usual general precautions were taken to avoid contamination.

b) Beryl.

A suitable weight of sample (500 mg) was treated in a teflon crucible with 15 mL of a concentrate acid $HF/H_2SO_4/HNO_3$ solution mixture (prepared according to

Shapiro and Brannock[14]). The crucible was covered with a teflon cover, placed in a steam bath and heated overnight. Then, the cover was removed and crucible heated until acid fumes were no longer emitted. The content was transferred to a Vycor beaker using a minimum of water and heated until SO_3 evolve. Finally, the solution was cool to room temperature and diluted to 250 mL in a volumetric flask.

RESULTS AND DISCUSSION

Absorption Spectra in resin phase.

CAS reacts with Be(II) to originate a coloured complex in solution (570 nm, $\epsilon = 2.4 \times 10^4$ L $mol^{-1} cm^{-1}$). The optimum pH for the complex formation is about 4.5 - 5.0 [15, 16]. Between pH = 3.0 - 7.5 this complex is sorbed on an anion-exchange resin showing the absorption maximum at 594 nm. Figure 1 shows the spectra of the coloured species in solution and resin phase from which the strong increase of the sensitivity in solid phase as compared with solution becomes self-evident.

Study of experimental variables.

pH dependence.

At pH values below 4.0 and above 5.8, the absorbance value at 594 nm in resin phase decreases significatively. We chosed pH 5.3 as the best pH value for following experiences due to the strong increase in absorbance shown by the fixed CAS on the resin below pH 5 (Fig. 2). The pH could be satisfactorily adjusted by addition of a 0.5 M HMTA/HCl buffer solution. By using this buffer solution, a significative increase in absorbance was observed with respect to use other buffers solutions (i.e. a 20% if acetic acid / acetate buffer was used).

Reagent concentration.

Absorbance increases with an increasing CAS concentration, a plateau occurring from a molar ratio [CAS]/[Be(II)] = 12 and 10 (for 100- and 10 mL sample

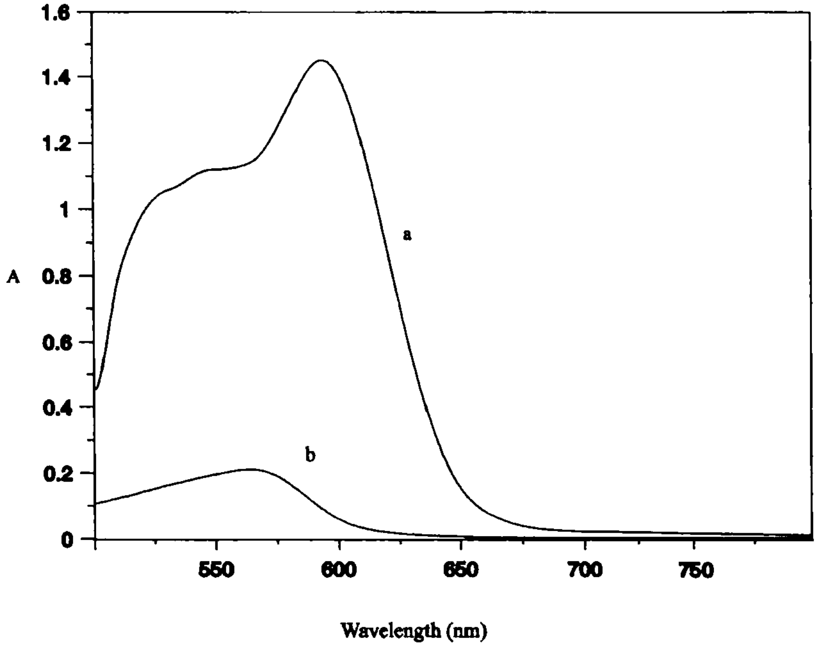

FIG. 1. Net absorption spectra of Be(II)-CAS species:(a) on the resin (blank resin as reference). [CAS] = 2.2×10^{-5} M, [Be(II)] =2.6×10^{-6} M , 0.030 g of resin, 1 mm optical path length, sample volume 100 ml, stirring time 15 min, pH=5.0 (b) in aqueous solution, [CAS]= 8.9×10^{-5} M, [Be(II)] = 8.9×10^{-6} M, 10 mm optical path length, pH=5.0 (blank as reference).

volume respectively). It seems that the excess of free ligand competes with the complex for sorption on the resin phase and it originates these plateaus. 1.7 x 10^{-5} M, and 1.15 x 10^{-4} M reagent concentrations were chosen for 100- and 10 mL sample volumes, respectively (molar [CAS]/[Be(II)] ratio 15 and 13).

Other experimental conditions.

The use of a large amount of resin (m_r, g) reduces, as usually[11] the absorbance values (Fig. 3b). Absorbance decreases according to the empirical

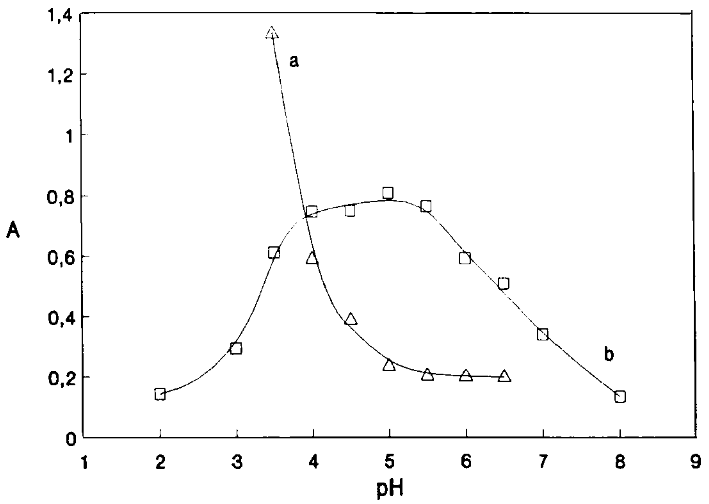

FIG. 2. pH influence: a) on CAS absorbance; b) on Be(II)-CAS net absorption 0.030 g of resin, [Be(II)] = 1.6×10^{-6} M, [CAS] = 1.7×10^{-5} M, 1 mm optical path length, stirring time 20 min, sample volume 100 mL.

equation: $\log A = -1.611 - 1.008 \lg m_r$ ($r = 0.9987$), that is: $A m_r^{1.008} = 0.0245$. The empirical exponent 1.008 indicates that the hyperbole obtained is equilateral and, hence, the absorbance decreases inversely to amount of resin used (Fig. 3a). This result is similar to those obtained in other cases [8-11]. 30 mg of dry resin were used as a compromise between the highest absorbance and ease of handling.

The best stirring times were 15 min and 5 min for 100- and 10 mL sample volumes, respectively (Fig. 4). The fixed complex is stable for 30 min after equilibration.

The order of addition of the reagents affects significatively the results obtained; the best order was: EDTA solution the first (for masking interferent ions such as Al(III) and Fe(III)). Second, the buffered CAS solution, then the sample and the last, the resin.

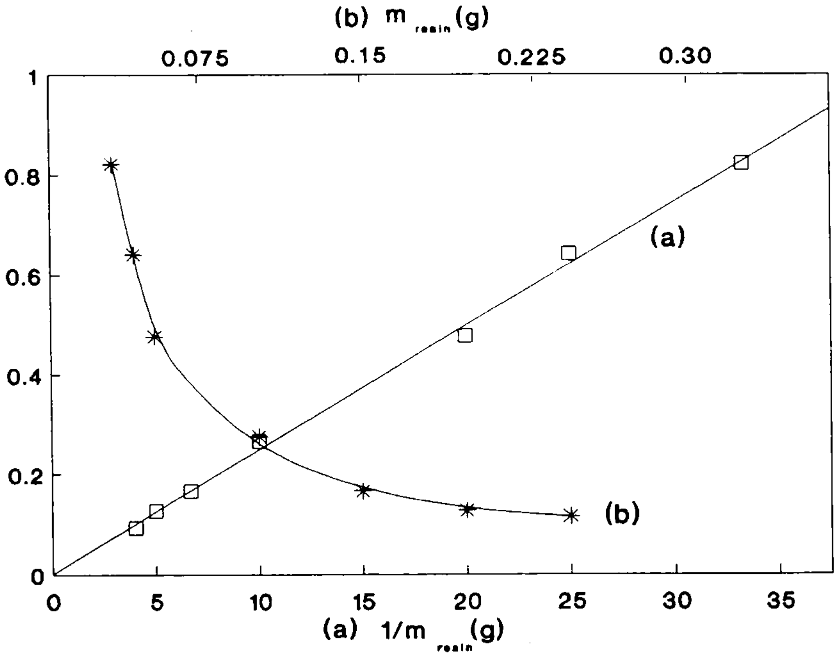

FIG. 3. Resin amount dependence. [CAS] = 1.7x10^{-5} M, [Be(II)] = 1.3x10^{-6} M, pH = 5.3, 1 mm optical path length, sample volume 100 ml, stirring time 30 min.

Distribution measurements.

CAS buffered solution and 30 mg of Sephadex QAE A-25 resin were added to a 100 mL water solution containing 200 nmole of Be(II). After 15 min equilibration, the resin was separated by filtration. Then, the equilibrium concentration of Be(II) in solution was determined as described in the 100 mL volume procedure (procedure I) . The distribution ratio, D, (mmole of Be(II) sorbed per g of resin/mmole of Be(II) per mL of solution) was calculated from the initial and equilibrium concentrations in the solution. An average value of (4.7 ± 0.7) x 10^3 mL g^{-1} was obtained from four replicate determinations. In the same conditions, the distribution ratio for CAS was (19.1 ± 0.8) x 10^4 mL g^{-1}.

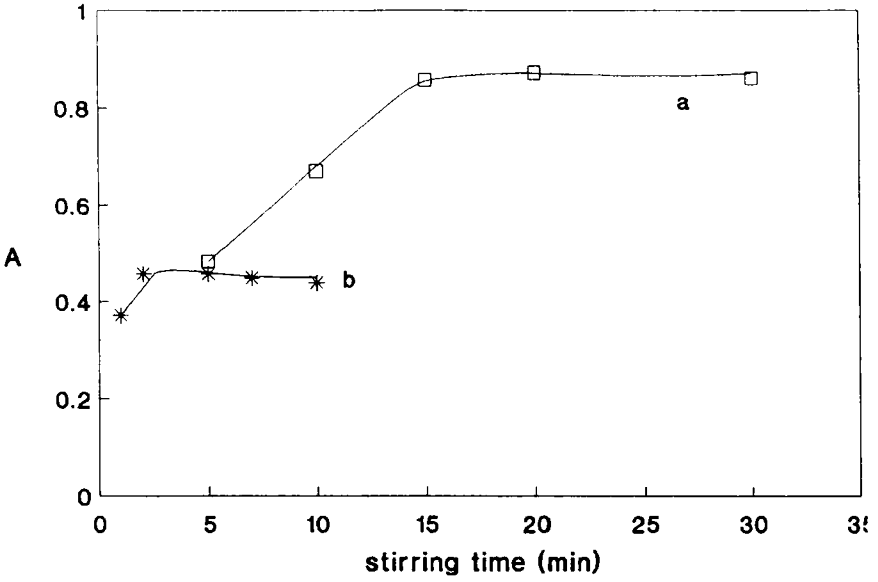

FIG. 4. Stirring time dependence on color development in resin-fase.

0.030 g of resin, pH = 5.3

(a) 100 ml of sample, [CAS] = 1.7×10^{-5} M. [Be(II)]= 1.6×10^{-6} M

(b) 10 ml of sample, [CAS] = 1.2×10^{-4} M [Be(II)]= 4.4×10^{-6} M

Nature of the fixed complex.

The probable composition of the fixed Be(II)-CAS complex on Sephadex was stablished at the working pH 5.3 using the Job[17] and the equilibrium shift[18] methods. Job method showed a ratio [CAS]/[Be(II)] = 1. The graph of log $(A/(A_{max}-A))$ vs log [CAS] (equilibrium shift method) gave a slope of 0.96 (r=0.9979). Consequently, results indicated that a 1:1 (CAS:Be(II)) anionic complex is fixed on the anionic exchanger. These results agree with those found in aqueous solution[19].

Figures of merit

In the above mentioned conditions, the main figures of merit of the two SPS procedures proposed (for 2 different sample volumes of Beryllium) have been established. Table I summarizes the values found for the linear dynamic range, calibration line (equation and correlation coefficient), sensitivity, limit of detection and determination and reproducibility.

The reproducibility was calculated in terms of the variation coefficient (per cent relative standard deviation) from the absorbance of 10 independent measurements of a same sample at the concentration levels of 10 ng mL^{-1} and 70 ng mL^{-1}, for 100- and 10-mL sample, respectively. It was possible verifiying that the reproducibility is improved when the cells packed with the resin were centrifuged, during 1 min at 5000 rpm, previously the spectrophotometric measurements and the absorbance values were increased about 15%. Centrifugation time beyond 1 min does not increase absorbance values.

The limit of detection ($K = 3$)[20] and the quantification limit ($K = 10$)[21] were established from the standard deviation of the absorbance measurements of ten independent blanks (average values were 0.0020 and 0.0014) for each procedure and the standard deviation values were 6.86×10^{-2} and 5.1×10^{-3} absorbance units for 100- and 10- mL sample volumes, respectively.

The sensitivity was obtained for the slope of the calibration line and expressed as apparent molar absorptivity. As can be seen, and it is intrisic to Solid Phase Spectrophotometric methodology, sensitivity is enhanced by increasing the sample volume used in the determination. Thus, for 100 mL sample volume, sensitivity is about 6-fold higher than for 10 mL of sample.

In Table 2 the sensitivity, expressed as apparent molar absorptivity, of the proposed procedures is compared with that of spectrophotometric procedures (including extractive procedures and formation of ternary complexes with surfactants) described in the literature for beryllium. It is observed that SPS methodology using CAS gives a very noticeable increase in sensitivity in relation to procedures in

TABLE 1

Analytical Figures of Merit

Parameter		Volume of sample system (mL) 100	Volume of sample system (mL) 10
calibration line	intercept	0.002 (8.75×10^{-4})[*]	- 0.017 (2.6×10^{-3})[*]
	slope (mL ng^{-1})	6.61×10^{-2} (1.25×10^{-3})[*]	1.14×10^{-2} (4.32×10^{-4})[*]
	corr coeff	0.9992	0.9996
	LDR[a] (ng mL^{-1})	1.5 - 15.0	10 - 85
sensitivity[*] (L $mol^{-1}cm^{-1}$)		5.96×10^{6}	1.03×10^{6}
DL[b] (ng mL^{-1})		0.21	1.4
QL[c] (ng mL^{-1})		0.71	4.4
RSD (%) (n=10)		2.7	1.2

[*] Standard deviation of three independents calibrations

[**] Expressed as apparent molar absorptivity (Absorbance value of the species sorbed on the resin from a 1M aqueous solution of Be(II) and supposing that it was measured in a 10-mm optical path length)

[a] LDR, linear dynamic range. [b] DL, Detection limit. [c] QL, quantification limit

homogeneous solution and extractive methods using conventional spectrophotometry. On the other hand, matrix effects, can be reduced by diluting the samples, taking into account the sensitivity of the method proposed and the dependence of the sensitivity on the sample volume (Fig. 5).

Effect of foreign ions

In Table 3 the effect of various potentials interferent species, commonly found in the water, on the determination of 60 ng mL^{-1} of Be(II) is listed. This effect was investigated by adding a known amount of the test ion to the beryllium solution. A

TABLE 2

Comparison of Sensitivity of some Beryllium Conventional Spectrophotometric Methods

Reagent	Molar absorptivity (λ_{max})	Reference
Beryllon II	1.20x10^{4} (630)	22
Thoron I	1.36x10^{4} (523)	23
Sulphochrome	1.40x10^{4}	7
Eriochrome Cyanine R	1.50x10^{4} (525)	24
Chrome Azurol S	2.40x10^{4} (569)	16
Chromal Blue G	3.10x10^{4}	7
Eriochrome Black T [a]	5.50x10^{4}	7
Eriochrome Cyanine R / CTA [b]	8.65x10^{4} (590)	25
Chrome Azurol S / PDA [b]	9.01x10^{4} (605)	26
Chromal Blue G / CTA	9.40x10^{4} (626)	27
Chrome Azurol S / CTA [b]	9.45x10^{4} (615)	28
Chrome Azurol S (10 mL) [c]	1.03x10^{6} • (594)	This paper
Chromazurol S (100 mL) [c]	5.96x10^{6} • (594)	This paper

[a] extractive procedure

[b] ternary complexes, CTA: Cetyltrimetilamonium chloride

[c] Solid-Phase Spectrophotometry

• Apparent molar absorptivity: Absorbance value of the complex sorbed on the resin from a 1 M aqueous solution of Be(II) and measured in a 10 mm optical path length cell.

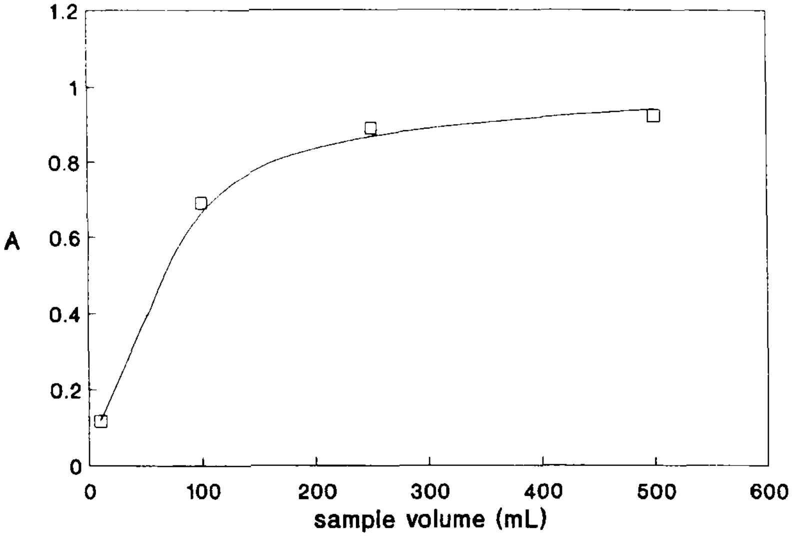

FIG. 5. Effect of volume on sensitivitiy.

[CAS] = 1.7×10^{-5} M, [Be(II)] = 1.2×10^{-6} M, pH = 5.3, amount of resin = 0.030 g, stirring time = 15 - 120 min.

TABLE 3

Effect of Foreign Ions on the Determination of 60 ng mL^{-1} of Beryllium

Foreign ion or species	Tolerance level (ng mL^{-1})
Ca(II), Cu(II), Mg(II), Fe(II)*, Fe(III)* Al(III)*, Na(I), Cl^-, NO_3^-, $SO_4^=$	2000
$CO_3^=$	1000
Zn(II), Pb(II)	500
$HPO_4^=$, UO_2(II), F^-	100

* In the presence of EDTA

2000 ng mL^{-1} maximum level of potentially interfering ions were tested firstly and if the interference occurred, the concentration of interferent was reduced progressively until interference ceased. Higher concentrations than 2000 ng mL^{-1} were not tested. Tolerance level is defined as the foreign ion concentration that produces not more than ± 5% spectrophotometric error in the recovery of Be(II).

Analytical applications.

The proposed method has been applied to the determination of beryllium content in underground and mining waste waters and a beryl mineral. In water samples, a study of recovery was also undertaken.

Water samples.

The method was applied to the determination of beryllium in water samples by standard addition calibration graph method by using 100 mL sample volume (Table 4).

a) **Underground water** from Ciudad Rodrigo city (Salamanca province).

b) **Uranium mining waste water** from Ciudad Rodrigo city (Salamanca province).

The loss of sensitivity caused by the matrix effect could be evaluated from the ratio of slopes of the standard addition calibration graph and the standard calibration graph: the ratios were 1.220 (from underground water) and 0.501 (from uranium mining waste water). It is seen that the matrix effect in these waters is noticeable. We attribute this strong matrix effect to the high ionic content, principally Ca(II) and $SO_4^{=}$ in the second water. Results, including recovery study were satisfactory.

Mineral.

The method was applied to the determination of beryllium in a mineral sample (beryl) by standard addition calibration graph method using 10 mL sample volume. A minor matrix effect was observed in this case: 0.908 was the ratio of slopes. Results were also satisfactory (Table 4).

TABLE 4 Analytical Applications

Sample	Amount added (ng mL^{-1})	Amount found (ng mL^{-1})	Recovery (%)	Amount found by ETAAS (ng mL^{-1})
Underground water[a]	0.00	4.6 ± 0.2	--	4.7 ± 0.2
	2.00	6.5	97.0	
	5.00	9.6	100.4	
Mining waste water[a]	0.00	10.8 ± 0.5	--	11.0 ± 0.4
	5.00	15.6	96.8	
	10.00	20.6	98.0	
Beryl[b]	--	4.30 ± 0.09[*]		4.4 ± 0.1[*]

[a] Standard addition calibration graph method. 100 mL sample volume

[b] Standard addition calibration graph method. 10 mL sample volume

[*] Amount expressed as % BeO

Values are average of three determinations

CONCLUSIONS

Beryllium can be analyzed with accuracy and precision at ng·mL^{-1} by SPS with CAS as chromogenic reagent and Sephadex QAE A-25 anion exchange resin as solid support.

Although the proposed method seems to be tedious, it is a very sensitive one-step method which allows to determinate Be(II) from 1.5 to 80 ng·mL^{-1} without requiring an expensive and sophisticate instrumentation such as HPLC, ICP, ETAAS. However, a larger sample volume is required.

The method here developed shows a sensitivity up to 25 times higher than the same procedure in solution but using only 0.1 cm of optical path length instead of 1 cm (conventional spectrophotometry). Moreover, precision is similar to that of the usual spectrophotometry in spite of measurements are obtained on a solid support.

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