

Determination of beryllium trace contents in mineral waters after preconcentration on a chelating ion-exchanger

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Summary. A separation-preconcentration procedure for the determination of Be traces in mineral waters is described. The precision and the accuracy of the procedure were checked by the use of artificial as well as of real samples by AAS-ETA and AES-ICP. On the basis of the results and of their statistical evaluation, the proposed procedure allows to obtain reliable results with the necessary limit of determination and can provide important, till now not accessible information on Be-concentration in waters.

1 Introduction

General knowledge on beryllium as toxic element recently occurring in growing contents in the environment is modest. Due to the negative effect of this element on the human organism [1], it is necessary to investigate the causes for its distribution, as well as methods for its determination.

Beryllium occurs in nature in relatively low contents – in the earth's crust its average content is estimated to $3 \cdot 10^{-4}\%$ [2]. In the majority of cases it accompanies aluminium and silicon compounds. It penetrates into ground and surface waters by weathering and leaching of different rocks, e. g. granites and micas. Its dissolution is to a large extent enhanced by acid rain, generally contributing to a growing concentration of metals in water. Other sources of beryllium are the emissions from the combustion of lower quality coal or thermal treatment of ores.

Beryllium occurs in waters probably as hydroxy complexes or fluoro complexes [3]. From water it is relatively easily sorbed by clay particles and organic compounds. The beryllium content in waters has till now not been followed continuously. In several countries it has not yet been included in any maximum limits for drinking [4, 5]

or mineral [6] waters. In the Czechoslovak standard for drinking water (valid since 1991) a limiting value for Be of $0.2 \mu\text{g/l}$ has been stated [7]. According to published data, the beryllium content in waters varies in the range of $0.001 - 100 \mu\text{g/l}$ [8–11].

The most frequently used analytical methods for the determination of low beryllium contents in waters are: atomic absorption spectrometry with electrothermal atomization [12], atomic emission spectrometry with ICP [13], electrothermal evaporation in ICP [14] and mass spectrometry [15].

The direct determination of beryllium in mineral waters is however problematic, due to its low content and the large concentration of accompanying elements. In the majority of cases neither the AAS-ETA nor the AES-ICP methods recommended by the corresponding EPA [16] and DIN [17] standards achieve the required limit of detection. It is therefore necessary to apply methods enabling a preconcentration of beryllium traces with their simultaneous separation from interfering macrocomponents [18–20].

The aim of the present work is to present a method for the determination of beryllium in mineral waters after its separation and preconcentration on a chelating ion-exchanger.

2 Experimental

Reagents

The chemicals used were of analytical grade purity (MERCK, FRG and LACHEMA, CSFR). The concentration of the solutions used was checked gravimetrically or by chelatometric titration.

Solutions

HNO_3 (1 mol/l).
 CH_3COONa (1 mol/l).
Sodium salt of EDTA-Chelaton III (0.1 mol/l), pH 5.0–5.5.

Ammonium salt of EDTA (0.1 mol/l), pH 4.5.

Acetate buffer, pH 4.5 (57.9 g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} + 32.5\text{ ml } \text{CH}_3\text{COOH}$ in 1000 ml).

Washing solution, pH 6.0 (50 ml 1 mol/l $\text{CH}_3\text{COOH} + 100\text{ ml } 0.1\text{ mol/l}$ ammonium salt of EDTA in 1000 ml).

Chelating ion-exchanger Ostsorb Salicyl (Spolchemie, Ústí nad Labem, ČSFR), grain size 0.10–0.25 mm [18].

Apparatus

Prism spectrophotometer MOM 204 (Hungary).

Atomic absorption spectrometer, Perkin-Elmer 380 (USA).

Electrothermal graphite atomizer, Perkin-Elmer HGA-400 (USA).

Atomic emission spectrometer with inductively coupled plasma, sequential, PLASMAKON S35, KONTRON (FRG).

Working conditions for AAS-ETA

Wavelength: 234.9 nm
 Radiation source: Hollow cathode lamp – Be
 Working current: 20 mA
 Spectral slit width: 0.7 nm
 Background compensator: Deuterium lamp
 Dosage: 20 μl sample + 10 μl matrix modifier
 (0.20 mol/l NH_4NO_3)

Temperature program:

Step	Temperature $^{\circ}\text{C}$	Temperature growth $^{\circ}\text{C s}^{-1}$	Time s	Ar flow rate ml min^{-1}
1	110	8	20	300
2	220	10	18	300
3	1000	4	20	300
4	2250	0	6	50
5	2600	1	3	300

The evaluation was performed by the peak height

Working conditions for AES-ICP

Wavelength: Be II 313.042 nm, BG 312.960 nm
 Be I 234.861 nm, BG 234.912 nm
 Ar flow rates: outer 14.5 l min^{-1}
 inner 0.7 l min^{-1}
 carrier 1.2 l min^{-1}
 Plasma power: 1.5 kW
 Observation height: 12 mm above the load coil
 Integration time: 5 s
 Sample uptake rate: 1.2 ml min^{-1} (peristaltic pump)
 Nebulizer: concentric, glass, Meinhard Type B
 Computer: KDT CPU Z 80 A

Influence of the sample acidity on the sorption of Be

A solution containing 5 ml HCl (1 mol/l) and 5 mg Be^{2+} was diluted to 200 ml with deionized water. The acidity of

the solution was adapted to the required pH using NH_4OH (1 mol/l) and diluted to 250 ml with deionized water. The sorbent Ostsorb Salicyl was placed in a column (7.6 \times 111 mm) and washed with 50 ml ammonium acetate (0.02 mol/l) of the same pH-value. The sample was passed through this column with a rate of 0.6 ml/min. Fractions of 2 ml were taken and evaluated spectrophotometrically as follows: To each fraction 2 ml acetate buffer (pH 4.6), 0.5 ml Chelaton III (5%) and 1 ml 0.16% Chromazurol S were added. The solution was diluted to 50 ml with deionized water and its absorbance measured at 569 nm in a 2 cm cuvette. From the data obtained break-through curves for different pH-values were constructed and the usable capacity of the sorbent calculated. The maximum usable capacity was found at pH 4.5 ($Q_b = 26.6\text{ }\mu\text{mol/ml}$) and this pH-value was then used for further investigations.

Working procedure

Samples of mineral waters are taken in polyethylene vessels previously leached with 10% HCl and deionized water. Immediately after sampling the pH-value is adjusted to 1.6–1.8 with HCl (6 mol/l). An aliquot part of the sample is boiled for 15 min with an addition of 1–5 ml 30% H_2O_2 . After cooling the sample, a solution of Chelaton III (0.1 mol/l, pH 5.5) is added in an amount exceeding approximately two times the molar concentration of the present alkaline earth metals and iron. This amount is necessary for their masking and simultaneously for the improvement of the selectivity and usable capacity of the sorbent. The acidity of the sample solution is then adjusted to pH 4.5 by addition of sodium acetate (2 mol/l). 5 ml of Ostsorb Salicyl in Na form are placed in a column (7.6 \times 111 mm) and before the sorption of Be the exchanger is washed with 10 ml acetate buffer of pH 4.5. The sample solution is passed through the column at a rate of 1.0–1.5 ml/min. After consumption of the whole sample solution, the vessel and the exchanger are rinsed three times with 10 ml deionized water. Beryllium is finally eluted with HNO_3 (0.1 mol/l) passed through the column at a rate of 0.5 ml/min. For a total elution 10 ml acid are sufficient. The first 2 ml of the effluent are discarded and the rest is collected in a measuring flask and diluted to 25 ml with deionized water.

3 Results and discussion

Influence of mineral water macrocomponents on the Be sorption

This influence was investigated with a model solution containing in 1000 ml a known amount of salts, 100 ml Chelaton III (0.1 mol/l), 10 ml acetate buffer of pH 4.5 and 50 $\mu\text{g Be}^{2+}$. The beryllium content in the eluate was determined spectrophotometrically with Chromazurol S. Quantitative sorption was found from NaCl solutions ranging from 1.15 to 68.97 g Na^+/l and from MgSO_4 solutions up to 170 mg Mg^{2+}/l .

From a model solution containing a two-fold amount of Chelaton III (i.e. 200 ml), the sorption was quantita-

tive up to a concentration of 267 mg Mg²⁺/l, from CaCl₂ solutions up to 240 mg Ca²⁺/l or from Fe(NO₃)₃ solutions up to 36 mg Fe³⁺/l.

Experimental results show the possibility to increase the concentration of Be in the effluent 10 to 100 times, still achieving the simultaneous separation of components which could interfere in the AAS-ETA or AES-ICP determination.

Precision and accuracy

The precision and the accuracy of the proposed procedure were determined by analysing a model sample whose composition is shown in Table 1. With a known content of 0.150 µg/l Be²⁺ an arithmetical mean of 0.154 µg/l was calculated from 20 repeated AAS-ETA determinations (corrected by the blank value).

According to Student's test, the calculated value $t = 1.016$ is smaller than the theoretical one $t_k = 2.093$ ($\gamma = 19$, $\alpha = 0.05$). The method can therefore be considered to be free from systematic error. For the calculation of the limit of determination the blank value and its standard deviation were determined by analysis of the model sample.

If we use the following definition for the limit of determination [21]

$$L_q = x_0 + 10 s_0$$

where x_0 is the arithmetical mean of the blank value for AAS-ETA or background for AES-ICP, and s_0 is standard deviation of these values both calculated from 20 measurements, then the limit of determination obtained under the described conditions is 0.01 µg/l Be for AAS-ETA and 0.25 µg/l Be for AES-ICP.

Optimisation of the experimental conditions for AAS-ETA

The dependence of the Be signal on the atomisation temperature was investigated using a model sample contain-

ing 60 pg Be²⁺ in 0.1 mol/l HNO₃ and 0.02 mol/l NH₄NO₃ (dosage: 50 µl). It has been found that in tubes with pyrolytical coating a temperature of 2250 °C is satisfactory for the atomisation of Be. The influence of the temperature of the sample pyrolysis on the Be signal intensity was investigated and the results showed that the optimum for the thermal decomposition of the sample was 1000 °C. In pyrolytical tubes with an effluent volume of 10 ml and a dosage of 20 µl, the calibration curve is linear in the range of 0–50 ng Be.

Optimisation of the experimental conditions for AES-ICP

In order to achieve a maximal signal-to-background relation, the dependence of this parameter on the observation height, plasma power and carrier gas-flow rate was investigated. The optimal values found are included in the experimental part.

Measurements on mineral water samples after application of the described separation-preconcentration procedure were performed at the spectral lines Be II 313.042 nm and Be I 234.861 nm. Possible spectral interferences, i. e. effect of vanadium and titanium on the ionic line and of iron on the atomic line were not observed. The precision obtained with the more sensitive ionic line was two-times worse ($s_r = 4.32\%$) as compared with the line Be I 234.861 nm ($s_r = 2.39\%$).

By the comparison of spectral scans performed on both lines we found that the worse precision could be explained by the interfering complex spectrum of the blank caused by the presence of OH bands [21] in the neighbourhood of the line Be II 313.042 nm.

Checking the accuracy of the proposed procedure

The accuracy of the Be determination in real samples of mineral waters was determined by comparing two independent analytical methods – AAS-ETA and AES-ICP. The results are presented in Table 2. Some insignificant differences are shown by samples from the source Mlýnský, where the volume of the original sample was 3 ml

Table 1. Composition of the mineral water model sample (volume 1 l)

Component	c (mg/l)	
Na ⁺	767.0	F ⁻ , Br ⁻ , J ⁻ , HPO ₄ ²⁻ ,
Ca ²⁺	93.3	HBO ₃ ²⁻ , Cl ⁻ , NO ₃ ⁻
Mg ²⁺	48.0	
K ⁺	70.2	
Fe ²⁺	6.8	Be ²⁺ 0.150 µg/l
NH ₄ ⁺	3.0	
Li ⁺	2.04	
Rb ⁺	2.07	
Cs ⁺	1.97	
Sr ²⁺	0.45	
$x = 0.154 \mu\text{g/l Be}$		$n = 20$ (with correction on blank)
$s = 0.017 \mu\text{g/l}$		
Student's t-test		$t = 1.016$
		$t_k = 2.093$ ($\gamma = 19$, $\alpha = 0.05$)

Table 2. Content of beryllium in mineral waters from the Czech Republic

Locality	Spring	Determined (µg/l)	
		AAS-ETA	AES-ICP
Bílina	V 1	6.8	6.8
Dolní Kramolín	Ilsano II	1.00	0.98
Jánské Lázně	Černý	0.07	0.07
Jánské Lázně	Jan	0.07	0.07
Karlovy Vary	Mlýnský (colonade)	85.5	79.1
Karlovy Vary	Mlýnský (filled)	48.6	41.4
Karlovy Vary	Sadový	94.5	81.6
Louka	Magnesia	0.34	0.34
Vratislavice n. Nisou	TV 4	24.9	24.9

and after separation of the basic matrix by the proposed procedure the final volume of the effluent was 25 ml, which means that the Be content in the real sample was diluted 8.3 times. The Be concentration was also determined in the original sample without application of the proposed separation-preconcentration procedure using AES-ICP and the results were identical with those originally obtained, i.e. lower than the results obtained by AAS-ETA. We therefore suppose that the signal for Be measured by AAS-ETA can be increased in spite of the fact that great attention was paid to the prevention of the memory effect accompanying the determination of Be.

Other samples of the investigated mineral waters were preconcentrated from the original volume of 500–800 ml to a final volume of the effluent of 25 ml. In these cases the results obtained by both methods agree very well.

4 Conclusion

A procedure for the determination of Be traces in mineral waters by selective preconcentration on the ion-exchanger Ostsorb Salicyl was worked out. The precision and accuracy of the procedure was checked on model as well as real samples. Comparison of the results obtained by two independent analytical methods (AAS-ETA and AES-ICP) and their statistical valuation proved that the proposed method gives reliable results with a determination limit of 0.01 µg/l. It can thus contribute to gaining important but till now not easily accessible information concerning Be contents in waters.

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