DETERMINATION OF BARIUM IN WATERS
BY ATOMIC ABSORPTION SPECTROMETRY
AFTER ION-EXCHANGE CHROMATOGRAPHY SEPARATION

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A method was developed for the determination of low contents of barium in medium mineralized waters. The element determined is separated from a large sample volume by its selective sorption on the strongly acidic cation-exchanger Dowex 50W X8 from cyclohexanediamine-N,N,N′,N′-tetraacetic acid at pH 5·5. After the washing of the column, elution with 4M-HNO_3, and further treatment of the eluate, barium is determined by atomic absorption spectrometry in the flame acetylene–air. The method allows the determination of barium in concentrations down to 0·01 mg/l.

The determination of low concentrations of Ba^{2+} ions in waters has not yet been solved to full satisfaction. Of the usual analytical procedures, the methods of emission[1] and absorption[2] flame spectrometry are suitable for the determination of barium, as an alkali earth element; other methods, *e.g.* photometry or polarography, cannot be used due to their low sensitivity and selectivity. A direct determination of barium by atomic absorption spectrometry (AAS) in waters is also not possible without a preliminary concentration and isolation because of the interfering effect of other elements (Ca, Al) and the not very high sensitivity, particularly when the usual combination of the fuels — air and acetylene — is used. The characteristic concentration for 1% absorption is 10 mg Ba/l. In the recent years, according to published data[3], a considerable lowering of that limit has been achieved by using hot flames (N_2O–acetylene); we did not find, however, such an increase of sensitivity and besides it is accompanied by the appearance of additional interfering effects due to ionization.

A suitable method for the separation and enrichment of the Ba^{2+} ions from large volumes is their selective sorption on a column of a strongly acidic cation exchanger from the medium of a complexing agent, developed in our laboratory[4,5] and used also by other authors for the determination of barium in sea water[6]. A method for the determination of barium in waters in concentrations down to 0·01 mg/l was worked out by adapting that separation procedure and combining it with the final determination by AAS.

EXPERIMENTAL

Apparatus and Chemicals

The AAS determination of barium was carried out on an instrument Perkin-Elmer 306 with the recorder Hitachi, threeslot burner, and hollow-cathode Ba lamp (Intensitron, filled with argon, 20 mA) in the flame acetylene–air; slit width 0·3 mm, damping 2. A pH-meter PHM 26 (Radiometer) with a glass and calomel electrode of the same make was used for the pH control. Chromatographic separations were carried out on columns of the usual form, 30 cm long with the inner diameter 12 mm, with a sealed-in frit and the packing of 10 ml swelled resin.

The strongly acidic cation-exchange resin Dowex 50W X8 (50—100 mesh), Fluka, was — after the usual treatment (swelling, decantation, multiple recyclization) — converted to the NH_4^+-form by washing with $1M$-NH_4Cl. Standard solution of Ba^{2+}, 1 mg/ml: 1·4369 g $BaCO_3$ (Specpure, Johnson-Matthey) dried at 110°C was dissolved in 40 ml HCl (1 : 4) and brought to the volume of 1 000 ml. Additive solutions of Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Fe^{3+}, and Al^{3+} were prepared from the corresponding carbonates and chlorides of the highest purity available. 1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid (DCTA), 0·2M: 69·28 g of the chemical (Lachema) was dissolved, under the addition of 60 ml conc. NH_4OH, in 1 000 ml water. All the other chemicals were p.a. purity.

RESULTS

Determination of Barium by the AAS Method

The aim of this part of the work was to find the conditions for the measurements of the light absorption by Ba in diluted HNO_3 (1 : 10), obtained by treating the eluate after the separation on the ion exchanger. A particular attention was paid to the selection of the burner, ratio of the flow rates of the gases, and flame profile, from which the optimum height over the burner top was determined. The use of the three-slot burner brings about — besides a sensitivity enhancement (c. by 50%) — an increase of the measurement stability due to the broadening of the reaction zone; thus the absorbed radiation is not affected by the instability of the peripheral parts of the flame.

Barium, as well as other elements forming low-dissociable oxides, is sensitive to the ratio of the flow rates of the gases. The formation of oxides, lowering the absorption of radiation by free atoms, can be suppressed by adjusting strong reducing conditions in the flame. On the other hand, the sensitivity increase, achieved by raising the fuel-to-oxidant ratio, is limited by the instability of the measurement in the luminous flame. The flow rates 3·6 and 20·3 l/min for acetylene and air, resp., were therefore chosen as the optimum values, based on experimental data. As a result of the kinetics of the processes occurring in the flame, the atomic absorption depends on the distance of the measured flame layer from the burner top, particularly for those elements, whose absorption depends highly on the character of the flame. It follows from Fig. 1 that under the experimental conditions chosen, the maximum

absorption of Ba occurs at the distance of 6 mm above the burner top. Under the optimum conditions it is possible to determine 5 µg Ba^{2+} in the volume of 5·5 ml diluted HNO_3 1 : 10 (which is the final volume of the sample solution after the enrichment by the chromatographic procedure). Fig. 2 represents the record of the measurements of reference solutions containing $5-50$ µg Ba/5·5 ml with a thirty-fold expansion of the recorder scale.

Separation and Enrichment of Ba^{2+} *by Ion-Exchange Chromatography*

Chromatographic separation served two purposes: concentration of Ba^{2+} ions from a large solution volume, and their separation from interfering elements, particularly Ca^{2+} and the possibly present Al^{3+}. The selective retention of Ba^{2+} on a strongly acidic cation exchangers from the medium of a complexing agent is accounted for by its high affinity towards that exchange resin[7] $(K_H^{1/2Ba} = 4·02)$ and, in comparison with other elements (Mg, Ca, Sr), a low stability constant[7] of the complex with DCTA ($\log K = 8·0$). It has been proved theoretically[7] as well as experimentally[3,4] that the Ba^{2+} ions do not pass the resin column even at pH 7·5, whereas other ions, including Mg^{2+}, Ca^{2+}, and Sr^{2+}, pass the column at the pH values as low as 6. An essential portion of the alkali metal ions and ammonium ions, bound in the used form of the exchanger, remains, however, retained on the column. The high selectivity coefficient of Ba^{2+} accounts for the possibility of separating those components by washing the column with a diluted mineral acid. On the other hand, the high affinity of Ba^{2+} makes its quantitative elution from the resin column slightly more difficult.
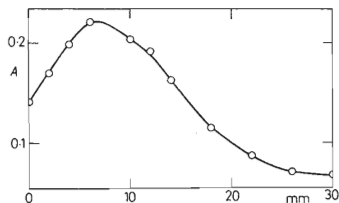

Fig. 1

Flame Profile of Barium

    Flow rates: acetylene 3·6 l/min, air 20·3 l/min; three-slot burner; 200 mg Ba/l added, diluted HNO_3 (1 : 10).
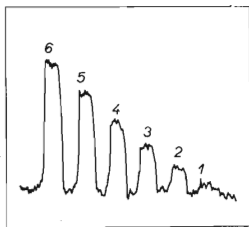
Fig. 2

Scannings of Measurements of Ba Reference Samples

    For conditions *cf.* text; scale expansion 30×; 5·5 ml HNO_3 1 : 10 contained *1* 0·005, *2* 0·010, *3* 0·020, *4* 0·030, *5* 0·040, *6* 0·050 mg.

The various steps of the chromatographic procedure were followed separately:

Elution of Ba *from the column*: 4M-HNO$_3$ was chosen as the most efficient for the elution[8]. For the quantitative elution of the Ba^{2+} ions in the amount of $0.05-10$ mg (sorbed on the exchange resin in the H$^+$ form from 0.01M-HCl), 50 ml of that acid is sufficient at the flow rate $40-50$ ml/h. As the sensitivity of the AAS determination of barium using the fuel gases acetylene–air is not very high, as mentioned, a high enrichment in the final step is substantial for the lowering of the determination limit. The most suitable is a cautious evaporation of the eluate on a sand bath to dryness, dissolving of the residue in 0.5 ml conc. HNO$_3$, and its dilution with 5 ml H$_2$O. Experiments comparing the measured values of samples subjected to evaporation with those of standards prepared in HNO$_3$ comfirmed a perfect agreement of the results. Therefore this method, lowering, in addition, the possibility of corrosion of metallic parts of the nebulizer and the burner, was used in all the following procedures.

Separation of alkali metal ions from the Ba^{2+}-*ions*. The sorption of $0.1-1.0$ mg Ba^{2+} from 200 ml 0.01$-$1M-HCl on the ion-exchanger in the H$^+$-form and subsequent elution with 50 ml 4M-HNO$_3$ proved that Ba^{2+} is retained quantitatively on the column even from 1M-HCl, hence no losses would occur on washing the column with that acid. In order to test the completness of the elution of monovalent ions, the exchange column in the H$^+$ form was converted to the form of the corresponding ion (Na$^+$, K$^+$, NH$_4^+$) by washing with 1M solution of the chloride; the column was then washed with 200 ml 1M-HCl and eluted with 50 ml 4M-HNO$_3$. Less than 20 µg of all the ions tested was found in the eluate.

Sorption of Ba *from large volumes*. The dependence of the efficiency of the retention of the Ba^{2+} ions on the column of the resin in the NH$_4^+$ form on pH of the solution from the volume of 1 000 ml was followed in the medium of a 0.01M excess of DCTA. For the content of barium, 0.5 mg, the results given in Table I were obtained, indicating that the sorption of Ba^{2+} itself from large volumes proceeds in accordance with theoretical considerations.

Separation of Ba *from associate elements*. The following series of experiments served for testing the effect of other elements, currently present in mineralized waters, on the sorption of Ba^{2+}, and the efficiency of their separation. A solution containing 1 000 mg Ca^{2+}, 500 mg Mg^{2+}, 100 mg Sr^{2+}, 2 000 mg Na$^+$, 500 mg K$^+$, 5 mg Fe^{3+}, 1 mg Al^{3+}, and 0.5 mg Ba^{2+} (all as chlorides) in 1 000 ml water was prepared. The volume of 0.2M-DCTA added, corresponding to the 0.01M excess with respect to the ions present (except for Na$^+$ and K$^+$), amounted 285 ml. In this case the retention of Ba^{2+} was found to be complete only after decreasing pH of the sorbed solution down to 5.5 (Table I). Some other ions are partly sorbed at that pH, too. They are, however, eluted completely by washing with 200 ml 0.01M-DCTA, pH 7.2,

TABLE I

Dependence of Efficiency of Ba^{2+} Sorption on pH

Volume 1 000 ml. I 0·5 mg Ba^{2+}, II 0·5 mg Ba^{2+}, 2000 mg Na^+, 500 mg K^+, 1 000 mg Ca^{2+}, 500 mg Mg^{2+}, 100 mg Sr^{2+}, 5 mg Fe^{3+}, and 1 mg Al^{3+}.

pH of the solution	Found Ba^{2+}, %	
	I	II
5·5	—	100·5
6·0	—	98·0
6·5	100·0	73·0
7·0	102·0	58·0
7·5	100·0	—
8·0	70·0	—
8·5	28·5	—

TABLE II

Efficiency of Chromatographic Separation

Starting volume 1 000 ml. 2000 mg Na^+, 500 mg K^+, 1 000 mg Ca^{2+}, 500 mg Mg^{2+}, 100 mg Sr^{2+}, 5 mg Fe^{3+}, and 1 mg Al^{3+} added, NH_4^+ eluted from the ion-exchanger.

Ion	Found in the eluate	
	μg	%
Na^+	16	$8 . 10^{-4}$
K^+	4	$8 . 10^{-4}$
Ca^{2+}	0	0
Mg^{2+}	0·5	$1 . 10^{-4}$
Sr^{2+}	0	0
Fe^{3+}	1·5	0·03
Al^{3+}	< 5	<0·5
NH_4^+	<20	—

while the sorption of Ba^{2+} remains unaffected. The efficiency of that procedure is illustrated by the data of Table II, where the contents of the various elements in the final eluate are given; a very sharp separation occurs for all the elements. A complete separation of Ca^{2+} ions is extremely important, with regard to the final determination of barium by atomic absorption spectrometry.

Testing of the method. In order to test the reliability and efficiency of the new technique developed, barium was determined in model solutions and in samples

of natural waters by using the complete separation process. The detailed analytical procedure as follows is recommended for the determination of Ba in medium mineralized waters: 0·2M-DCTA in a 0·01M excess with respect to the bivalent ions present (the total of those ions is determined by titrating an aliquot of the sample with 0·2M-DCTA, thymolphthalexone indication) is added to 1000 ml of the water sample (Tables III, IV). The pH value is adjusted to 5·5 by means of a solution of diluted NH_4OH (1 : 4) or HCl (1 : 4) under the potentiometric control. The solution obtained is run through the resin column in the NH_4^+ form with the flow rate 70—80 ml/h.

TABLE III

Determination of Barium in Synthetic Samples of Waters
  Volume 1000 ml.

Ion added mg	0·2M-DCTA ml	Ba^{2+} added mg	Ba^{2+} content, mg		Difference %
			calc.	found	
—	50	0·02	0·02	0·021	+ 5·0
—	50	0·05	0·05	0·051	+ 2·0
—	50	0·10	0·10	0·102	+ 2·0
—	50	0·50	0·50	0·50	± 0
5 000 Na^+	50	—	0	0	—
2 000 Na^+	50	0·10	0·10	0·098	− 2·0
5 000 Na^+	50	0·10	0·10	0·103	+ 3·0
10 000 Na^+	50	0·10	0·10	0·088	−12·0
1 000 Ca^{2+}	175	—	0	0·012	—
1 000 Ca^{2+}	175	0·10	0·112	0·110	− 1·8
2 000 Ca^{2+}	300	0·10	0·124	0·119	− 4·0
3 000 Ca^{2+}	425	0·10	0·136	0·131	− 3·7
1 000 SO_4^{2-}	50	—	0	0·004	—
1 000 SO_4^{2-}	50	0·05	0·054	0·059	+ 9·3
1 000 SO_4^{2-}	50	0·10	0·104	0·110	+ 5·8
2 000 SO_4^{2-}	50	0·03	0·038	0·035	− 7·9
2 000 SO_4^{2-}	50	0·05	0·058	0·061	+ 5·2
a	285	—	0	0·044	—
a	285	0·05	0·094	0·095	+ 1·1
a	285	0·10	0·144	0·147	+ 2·1
a	285	0·20	0·244	0·250	+ 2·4
a	285	0·50	0·544	0·530	− 2·6
a	285	1·00	1·044	1·050	+ 0·6
b	250	—	0	0·011	—
b	250	0·02	0·031	0·034	+ 9·7
b	250	0·10	0·111	0·107	− 3·6

^{a} 2000 mg Na^+, 500 mg K^+, 1000 mg Ca^{2+}, 500 mg Mg^{2+}, 100 mg Sr^{2+}, 5 mg Fe^{3+}, and 1 mg Al^{3+} as chlorides; ^{b} volume 5000 ml.

The column is washed with 200 ml washing solution (0·01M-DCTA, pH 7·2) and with 200 ml 1M-HCl, and the Ba^{2+} retained is eluted with 50 ml 4M-HNO_3 with the flow rate 40—50 ml/h. The eluate in 100 ml beakers is cautiously evaporated on a sand bath to dryness, the residue is dissolved in 0·5 ml conc. HNO_3 and diluted with 5 ml H_2O. The content of barium is determined by the AAS method on the instrument PE using the air and acetylene flow rates 20·3 and 3·6 l/min, resp., and the height above the burner top 6 mm. The results are evaluated by means of a calibration curve obtained by measuring reference solutions containing 0·005—0·2 mg Ba^{2+} in 5·5 ml HNO_3 (1 : 10), with a thirtyfold expansion of the recorder scale, or 0·1—1 mg Ba^{2+} under the same conditions with a threefold scale expansion.

TABLE IV
Determination of Barium in Natural Water Samples

Sample	Volume analyzed ml	Number of determinations	Average Ba^{2+} content mg/l	Standard deviation
Oravská Polhora	50—100	6	17·63	0·288
Garden spring, Carlsbad	1 000	12	0·027	0·0015
Prague water mains	1 000	2	0·054	—

The results of determination of barium in synthetic samples are given in Table III. The Ba contents can be determined reliably for sodium concentrations up to 5000 mg/l, higher Na^+ contents displace barium from the column. The presence of Ca^{2+} up to 3000 mg/l does not prevent the quantitative determination, it requires, however, a disproportionally large amount of the complexing agent. Sulfates up to the content of 2000 mg/l do not interfere in the chromatographic procedure and the final determination, although the thermodynamic solubility product of $BaSO_4$ is exceeded. The results of determinations of 0·02 and 0·1 mg Ba^{2+} in 5 l distilled water (*i.e.*, concentrations 0·004 and 0·02 mg Ba^{2+}/l, resp.) are given in addition for the examination of the sorption efficiency and the accuracy of the complete procedure.

Samples of natural waters were further analyzed in order to test the reliability of the method. Typical examples are given in Table IV. The values found prove the high sensitivity, reliability, and accuracy of this analytical method for the determination of barium in medium mineralized waters.

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