FLUORIMETRIC DETERMINATION OF BERYLLIUM WITH 3-HYDROXY-2-NAPHTHOIC ACID BY FLOW INJECTION ANALYSIS AFTER PRECONCENTRATION ON A SILICA GEL MICROCOLUMN

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A method was worked out for the selective determination of trace concentrations of beryllium by flow injection analysis (FIA) with fluorimetric detection using 3-hydroxy-2-naphthoic acid (λ_{ex} = 375 nm, λ_{em} = 455 nm) at c_L = 50 μmol l^{-1} in 0·1M ammonium acetate, pH 7·1. In injected sample volumes of 80 μl, Be can be determined in concentrations of 10 to 156 μg l^{-1} with relative standard deviations not exceeding 5%, after its selective sorption on a microcolumn (2 × 40 or 3 × 30 mm) of silica gel from a medium of 0·05M-EDTA and 0·1M tartaric acid followed by elution with 0·1M-HCl. After preconcentration from 5 to 15 ml volumes, Be can be determined under the same conditions in samples at concentrations of ϱ_{Be} = 0·5 to 4·6 or 0·1 to 0·8 μg l^{-1}, respectively, with s_r from 6 to 12%, the enrichment factor being as high as 200. The method was applied to beryllium bronzes and to dust from the atmosphere of the beryllium bronze foundry. The relative deviations of the beryllium content did not exceed 8% for the bronzes as compared to certified values, and 5% for the dust as compared to results obtained by ETA AAS.

In addition to morin (3,5,7,2',4'-pentahydroxyflavone), 3-hydroxy-2-naphthoic acid is the most frequently used reagent for the fluorimetric determination of beryllium[1-6]. A blue-fluorescing chelate with the composition Be : L = 1 : 1 (λ_m = = 470 nm) is formed at pH 3·5 to 10·5 in aqueous or aqueous alcoholic solutions[1]; at pH 10·5 to 12, the BeL_2 chelate is formed (λ_{ex} = 383 nm, λ_{em} = 370 nm). The reagent itself fluoresces with λ_{ex} = 360 nm, λ_{em} = 508 nm at pH 3 to 10·5 and with λ_{ex} = 360 nm, λ_{em} = 490 nm, at higher pH up to pH 12.

In the presence of 3-hydroxy-2-naphthoic acid in a concentration of 50 to 60 μmol . . l^{-1}, beryllium can be determined in concentrations of 0·1 to 10 μmol l^{-1} in 0·1M ammonium acetate at pH 7·1. Interferences from other ions and compounds can be eliminated by using a mixture of 0·02M-EDTA and 0·04M-Mg(II) ions or by separation on a silica gel column[1,7].

The present work is dedicated to the optimization of conditions of the selective determination of trace concentrations of Be(II) by flow injection analysis (FIA) using fluorimetric detection with 3-hydroxy-2-naphthoic acid in 0·1M ammonium acetate, following preconcentration and separation of Be(II) on a silica gel microcolumn (2 × 40 mm).

EXPERIMENTAL

Working solutions of $Be(ClO_4)_2$ were prepared daily by diluting a standard stock solution with water or $HClO_4$. The standard solution contained Be in a concentration of 29·4 mmol l^{-1} in 0·54M-$HClO_4$ (ref.[1]). Stock solution of quinine bisulfate in 0·05M-H_2SO_4 contained the pentahydrate (Merck, Darmstadt, F.R.G.) in a concentration of 100 μg l^{-1}. Stock solution of 3-hydroxy-2-naphthoic acid (Lachema, Brno), c_L = 1 mmol l^{-1} in 20% (v/v) ethanol, was prepared from the recrystallized preparation[1]. The remaining chemicals and solvents were commercial products (Lachema, Brno) of reagent grade purity. Bidistilled water was prepared in a quartz still.

Glass sorption microcolumns 7 × 25, 2 × 40 or 3 × 30 mm and a glass sorption column 7 × 250 mm fitted with glass frits or a glass microcolumn 3 × 30 mm encased in a metal jacket and closed at the two ends (Tessek, Prague) were packed with an aqueous slurry of washed (HCl 1 + 1) and decanted Kieselgel silica gel 0·05—0·1 mm grain size (Merck, Darmstadt, F.R.G.) or Silpearl silica gel 0·05—0·2 mm grain size (Kavalier, Votice). The silica gel column was activated by washing successively with 20 ml of water, 20 ml of 5M-HCl, 20 ml of water and 20 ml of 0·1M ammonium acetate.

The layout of the FIA apparatus in the arrangements for the direct determination of beryllium and for its determination after separation and preconcentration on silica gel microcolumns with a facility for counter-current elution[8] is shown in Fig. 1. Carrier liquid was pumped with a Unipan 304 five-channel peristaltic pump (Zalimp, Poland) whose flow rate was variable from 0·1 to 18 ml min^{-1}, sample was delivered by means of an adapted chromatographic six-way valve (Development Workshop, Czechoslovak Academy of Sciences, Prague) with a minimal injection volume of 80 μl. Four-way and six-way medium-pressure chromatographic valves (Mikrotechna, Prague) served for controlling the sample flow direction and the eluting liquid flow. Teflon capillaries 0·5, 0·6, 0·7 and 1·0 mm i.d. (Technoplast, Chropyně, or Norton Chemplast, Wayne, U.S.A.) were used in the apparatus.

Fluorescence of the beryllium chelate with 3-hydroxy-2-naphthoic acid (λ_{ex} = 375 nm, λ_{em} = 455 nm) was measured on a PE 203 fluorometer (Perkin–Elmer, Norwalk, U.S.A.) with a double monochromator, fitted with an Osram XBO 150 W high-pressure xenon lamp. A flow cell made from a quartz tube 2 mm i.d., 3·8 mm o.d., was employed in the FIA mode; it was fixed in the original rotary cell holder supplied as accessory to the PE 203 instrument, using teflon gaskets. The volume of the measuring section of the cell was about 30 μl.

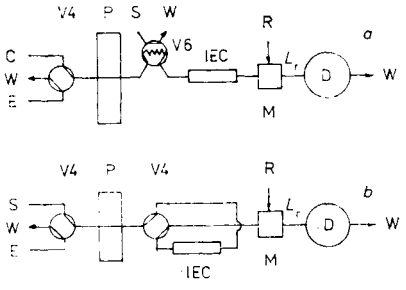

FIG. 1

Block diagram of flow injection analysis apparatus with separation (*a*) and preconcentration (*b*) on a silica gel microcolumn; C carrier medium, E eluting agent (0·1M-HCl), W waste, S sample, V4 four-way chromatographic valve, V6 six-way chromatographic injection valve (V_1 = 80 μl), P peristaltic pump, IEC silica gel microcolumn (2 × 40 mm), R 3-hydroxy-2-naphthoic acid solution in 0·1M ammonium acetate, M reaction detector, L_r reaction coil (18 cm), D fluorimetric detector

Analytical signals were evaluated by means of an EZ 3 recorder (Laboratorní přístroje, Prague). Acidity was measured with an OP 205/1 pH-meter (Radelkis, Budapest, Hungary) equipped with a G 202B glass electrode (Radiometer, Copenhagen, Denmark) and an OP 083OP saturated calomel electrode (Radelkis, Budapest, Hungary). The instrument was calibrated periodically using a phosphate buffer at pH 6·47 ± 0·01. The pH values measured in the water–ethanol mixed solvent were not corrected.

The fluorometer scale for various selector and sensitivity settings was standardized by continual addition of solutions of quinine bisulfate, ϱ = 0·01, 0·1 and 1·0 μg l^{-1} in 0·05M-H_2SO_4; λ_{ex} = = 355 nm, λ_{em} = 455 nm.

The concentrations of Be(II) were read from calibration plots of peak height or area vs c_{Be} for the constant volume added, viz. 80 μl or 5 or 15 ml.

Dust samples from the atmosphere of a beryllium bronze foundry (aspirated air volumes 100 to 1 000 l) were pretreated by dry mineralization of the organic matter of a Synpor 6 nitrocellulose membrane filter; a part of the filter was placed on the bottom of a platinum crucible, 1 ml of acetone was added, and after the "packing" of the organic matter of the filter and evaporation of the solvent, all organic matter was ashed for 1 h at 550°C in a muffle furnace. The non-combustible residue was boiled for 20 min in HNO_3 (1 + 1) and the solution was diluted to 10 ml.

Beryllium bronze samples B1—B3 (10 to 50 mg) were dissolved[9] in 1 ml of hot concentrated HCl containing H_2O_2 and evaporated to dryness, and the residue was dissolved in 0·5 ml of HCl (1 + 1) and diluted with water to 1 000 ml.

Sample aliquots (1 to 10 ml) were diluted with water, 70 ml of an EDTA–tartaric acid masking mixture (20 ml of 0·5M tartaric acid and 50 ml of 0·1M-EDTA) and 10 ml of 1M ammonium acetate were added, and pH was adjusted to 7·1 if necessary. The solution was diluted to 100 ml with water, and a volume of 80 μl for beryllium bronzes or 5 to 15 ml for dust samples was injected on the microcolumn.

RESULTS AND DISCUSSION

Beryllium ions are sorbed on silica gel quantitatively and selectively[1] from a medium of 0·05M-EDTA and 0·1M tartaric acid at pH 4·5 to 9·5. Amounts of 10 to 2 250 ng Be(II) can be sorbed[1] on a 7 × 250 nm column from 10 to 200 ml volumes of solution in 0·1M ammonium acetate at pH 7·1.

The eluting efficiency was checked by injecting 10 ml of solution with c_{Be} = = 11·6 μmol l^{-1} on a 7 × 25 mm silica gel column, washing the latter with 20 ml of water at a flow rate of F_m = 0·5 ml min^{-1}, and eluting the analyte with hydrochloric acid at pH 1·1, 2·1, 3·1 or 4·1 or using a 1 + 1 mixture, or with 3-hydroxy-2--naphthoic acid solution at a concentration of 50 or 100 μmol l^{-1}. Fractions of 0·5 ml were collected and treated to obtain ϱ_{Be} = 0 to 520 μg l^{-1}, c_L = 50 μmol l^{-1} in 0·1M ammonium acetate at pH 7·1, and injected into a continuous stream of distilled water as the carrier liquid in a simple one-channel FIA equipment (F_m = 0·7 ml . . min^{-1}, L_r = 30 cm, 0·5 mm i.d.

Hydrochloric acid as the eluting agent gave the best results. The retention curves with HCl (Fig. 2) demonstrate that at concentrations $c_{HCl} \geqq 10$ mmol l^{-1} the elution is sufficently efficient, the majority (85—95%) of beryllium being eluted in the first 3—4 ml.

The corresponding calibration plot was linear over the range of $\varrho_{Be} = 3$ to 92 μg . l^{-1}; repeatability was $s_r = 11{\cdot}7$ and 2·1% for $\varrho_{Be} = 10{\cdot}4$ and 52·0 μg l^{-1}, respectively, using 10 independent measurements, the peak heights were 22 to 35 and 125 to 150 mm, respectively. The limit of determination defined as $10s_0$ (for ten independent measurements of the standard deviation of the recorder noise, s_0) was 1·3 μg l^{-1}.

It was hoped that the determination could be simplified and the reaction detector eliminated by using 3-hydroxy-2-naphthoic acid as the eluent, but the elution with this reagent at $c_L = 50$ or 100 μmol l^{-1} was not quantitative. Moreover, at $c_L =$ $= 100$ μmol l^{-1} the reagent caused quenching of fluorescence.

Optimization of Reaction Detector Parameters

When injecting 80 μl of solution of Be(II) at concentrations $\varrho_{Be} \leqq 836$ μg l^{-1} into the stream of the 0·1M-HCl carrier liquid ($F_m = 0{\cdot}7$ ml min^{-1}), the sample zone was mixed with a continuous stream of a solution of 3-hydroxy-2-naphthoic acid, $c_L = 50$ μmol l^{-1} in the medium of 0·1M ammonium acetate and 0·1M-NH_3 ($F_R =$ $= 0{\cdot}7$ ml min^{-1}). The reaction mixture, with a resultant pH 7·1 ± 0·1, was fed at a flow rate of $F_m = 1{\cdot}4$ ml min^{-1} through the reaction coil ($L_r = 30$ to 500 mm, 1·0 mm i.d.) to the flow cell.

For the optimized reaction capillary length of $L_r = 180$ mm the calibration plot was linear over the entire range of $\varrho_{Be} \leqq 836$ μg l^{-1}. Repeatability of determination for 10 independent measurements at $\varrho_{Be} = 200$ or 700 μg l^{-1} was $s_r = 5{\cdot}5$ or 2·0%, respectively, the peak heights being 25 to 30 and 120 to 130 mm, respectively; the limit of determination for the $10s_0$ criterion was 10·2 μg l^{-1}, which corresponds to an approximate value of the dispersion coefficient of $D \approx 10$.

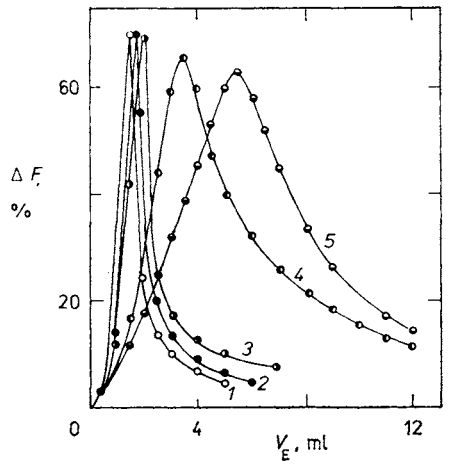

FIG. 2

Elution of beryllium from a silica gel column (7 × 25 mm) with hydrochloric acid after injection of 10 ml of solution with $c_{Be} =$ $= 11{\cdot}6$ μmol l^{-1}; pH: *1* HCl 1 + 1, *2* 1·2, *3* 2·1, *4* 3·1, *5* 4·2. ΔF (%) fluorescence of eluate after subtraction of blank fluorescence

Determination of Beryllium by Flow Injection Analysis after Preconcentration and Separation on a Microcolumn

The breakthrough capacity was determined for the 2 × 40 mm microcolumn and a Be amount of 83 ng by repeated injection of 80 μl of a solution with $\varrho_{Be} = 52\ \mu g\ l^{-1}$ to a continuous stream of 0·1M ammonium acetate, pH 7·1, till the microcolumn saturation. The breakthrough capacity was identified with the amount of Be(II) ions causing the appearance of the first measurable peaks at the maximum sensitivity of measurement. The first peaks recorded were very disperse and poorly reproducible; the corresponding total volume of injected solution of Be(II) was about 1·7 ml. The breakthrough capacity of the microcolumn was independent of the injection flow rate over the region of $F_m = 0{\cdot}1$ to 0·9 ml min^{-1}.

Sorption of Be(II) ions on the 2 × 40 mm microcolumn was examined by injecting 80 μl of Be(II) solution at concentrations $\varrho_{Be} = 0$ to 200 $\mu g\ l^{-1}$ in 0·1M ammonium acetate, pH 7·1. After each addition of sample, the microcolumn was washed thoroughly with 3 ml of distilled water, and the Be(II) ions sorbed were eluted with 0·1M-HCl until the recorder zero line was attained for the optimum parameters of the reaction detector ($F_m = F_E + F_R = 0{\cdot}7 + 0{\cdot}7$ ml min^{-1}, $L_r = 180$ mm, 1 mm i.d.).

The sorption of Be(II) ions from 0·1M ammonium acetate either alone or in mixture with the massing solution of 0·05M-EDTA + 0·1M tartaric acid at pH 7·1 ± 0·1 was quantitative over the entire region of breakthrough capacity of the microcolumn. Elution with 0·1M-HCl was rapid and quantitative, a volume of 0·5 ml being sufficient for complete elution.

In both cases, the calibration plots were linear over the region of $\varrho_{Be} = 10$ to 156 $\mu g\ l^{-1}$ for the injected volume of 80 μl. Repeatability of determination s_r for 10 measurements was $s_r = 5{\cdot}3$ or 5·1% for $\varrho_{Be} = 40\ \mu g\ l^{-1}$ (peak heights 45 to 50 mm and 30 to 45 mm, respectively), and $s_r = 3{\cdot}4$ or 3·2% for $\varrho_{Be} = 150\ \mu g\ l^{-1}$ (peak heights 170 to 180 mm and 160 to 170 mm, respectively). The limit of determination was 1·7 and 1·9 $\mu g\ l^{-1}$ for sorption from 0·1M ammonium acetate alone and in mixture with the masking solution, respectively.

The lowest reproducibly measurable concentrations of Be(II) ions were determined by adding 80 μl volumes of Be(II) solutions at $\varrho_{Be} = 1$ to 15 $\mu g\ l^{-1}$ in 0·1M ammonium acetate at pH 6·3 to a continuous stream of 0·1M ammonium acetate at pH 7·1, washing the 2 × 40 mm microcolumn with 3 ml of water and eluting the analyte with 0·1M-HCl till the recorder zero line was reached. Samples with $\varrho_{Be} = 1$ to 7 $\mu g\ l^{-1}$ gave irreproducible and disperse peaks, and only at $\varrho_{Be} \geqq 10\ \mu g\ .\ l^{-1}$ the results were reproducible enough, with repeatabilities $s_r \leqq 9{\cdot}2\%$ (peak height 7 to 12 mm); the repeatability of blank measurements was $s_r = s_0 = 3{\cdot}5\%$, peak height 2 to 5 mm. (The repeatabilities are for 10 independent measurements with sample or water.)

In the same conditions, counter-current elution of the sorbed Be(II) ions using the FIA equipment shown in Fig. 1*b* led to a negligible improvement in the sensitivity of determination (by approximately 5%), in contrast to the results obtained on microcolumns with chelating sorbents[8]. This is apparently due the different nature of the sorption processes on the microcolumns of the two types. For the determination, the simpler concurrent FIA apparatus was therefore used.

Table I gives the limiting concentrations of interferents (C_X) for the selective sorption of 80 μl of Be(II) solution at $\varrho_{Be} = 58\ \mu g\ l^{-1}$ from a masking mixture of 0·05M-EDTA + 0·1M tartaric acid in 0·1M ammonium acetate, pH 7·1, containing the interferent under study. The limiting concentration ratios giving a relative change in fluorescence of $\Delta F \leqq 2\%$ were determined graphically[1] from the plots of $\Delta F = f(c_X)$. The data demonstrate that the determination of beryllium after its preconcentration and separation on a microcolumn of pretreated silica gel is highly selective.

Owing to the quantitativeness of sorption of Be(II) ions on microcolumns of silica gel over wide regions of beryllium concentrations and sample injection flow rates ($\varrho_{Be} < 10\ \mu g\ l^{-1}$, $F_m = 0{\cdot}1$ to $0{\cdot}9$ ml min^{-1}), the preconcentration is feasible from highly dilute solutions of Be(II) ions in 0·1M ammonium acetate, alone or in mixture with a masking solution of 0·05M-EDTA and 0·1M tartaric acid. The enrichment factor was determined by injecting a constant amount of 4·48 ng of Be(II) ions in differently concentrated solutions, prepared by adding 80 μl of Be(II) solution, $\varrho_{Be} = 58\ \mu g\ l^{-1}$, to 5–15 ml of the solvent system.

The sensitivity of determination for approximately 60 or 200 fold dilutions and injection of 5 to 15 ml of Be(II) solution is 10 and 15%, respectively, lower than for the direct injection of the Be(II) chelate of 3-hydroxy-2-naphthoic acid in the simple one-channel FIA equipment, and 5 and 6%, respectively, lower than for the on-column injection of 80 μl of Be(II) solution, $\varrho_{Be} = 58\ \mu g\ l^{-1}$, using the reaction detector. The change in sensitivity is identical for the determination by peak height and peak area measurements.

By preconcentration on the silica gel microcolumn 2 × 40 mm from 0·1M ammonium acetate at pH 7·1 in the presence of the masking mixture, Be can be determined in concentrations of 0·5 to 4·6 μg l^{-1}, with $s_r = 9{\cdot}8$ or 6·3% at $\varrho_{Be} = 0{\cdot}5$ and 4·6 μg . l^{-1}, respectively, and the total sample volume 5 ml (peak heights 7 to 15 and 120 to 125 mm). When injecting 15 ml of sample, beryllium can be determined in concentrations of 0·08 to 0·78 μg l^{-1}. The repeatability of determination ($n = 10$) was $s_r = 10{\cdot}8$ and 8·2% for $\varrho_{Be} = 0{\cdot}1$ and 0·7 μg l^{-1}, respectively (peak heights 6 to 12 and 110 to 120 mm, respectively).

The method of preconcentration and separation of Be(II) ions on a microcolumn from the medium of 0·1M ammonium acetate, 0·1M tartaric acid and 0·05M-EDTA was applied to beryllium bronze specimens containing 1, 3 and 6% Be, each represented by three samples, using 10 independent injections of 80 μl of sample solution.

The results (Table II) agree well with certified values; the relative differences for the three contents were 8·0, 6·7 and 4·0% for artificially prepared specimens of beryllium bronzes S1 – S3 containing 97, 95 and 92% Cu, respectively, and 0·4% of Al, Ni, Fe and Co. For beryllium bronze standards B1 – B3 the relative differences from certified values were 3·2, 4·1 and 2·0% for beryllium contents of 0·8, 2·0 and 2·5%, respectively; the specimens contained 97·5, 95·0 and 94·0% Cu, respectively, and 0·1 to 1·5% other metals[9].

TABLE I

Limiting interferent-to-beryllium molar concentration ratios for a relative change in fluorescence $\Delta F = 2\%$; $V_{sample} = 80\ \mu l$, $\varrho_{Be} = 58\ \mu g\ l^{-1}$, 0·1M tartaric acid, 0·05M EDTA, 0·1M ammonium acetate at pH 7·1

Interferent X	$c(X)/c(Be)$
F^-	5
Al(III), Cr(III)	600
Cu(II), Ni(II)	1 000
Cd(II)	2 000
Fe(III), Co(II), Ca(II), Mg(II), CO_3^{2-}	5 000
Zn(II)	5 300
PO_4^{3-}	7 000
Cl^-, NO_3^-, SO_4^{2-}, $(COO^-)_2$	15 000

TABLE II

Comparison of results of determination of beryllium FIA determination in 0·1M ammonium acetate at pH 7·1, 0·1M tartaric acid and 0·05M-EDTA; $V_{sample} = 80\ \mu l$ or 5 to 15 ml,column 2 × 40 mm, F_m[a] = (0·7 + 0·7) ml min^{-1}, $c_L = 50\ \mu mol\ l^{-1}$, elution with 0·1M-HCl, $n = 10$

Sample[b]	ϱ, $\mu g\ l^{-1}$		$\Delta(\varrho)$ %	Sample[c]	ϱ, $\mu g\ l^{-1}$		$\Delta(\varrho)$ %
	Certified	FIA			ETA AAS	FIA	
S1	25·0	27·0 ± 8·4	8·0	1	11·7 ± 0·9	12·0 ± 1·3	2·5
S2	75·0	80·0 ± 7·2	6·7	2	26·6 ± 1·5	26·1 ± 1·7	−1·9
S3	150·0	144·0 ± 6·9	−4·0	3	96·1 ± 5·3	98·4 ± 5·5	2·4
B1	92·5 ± 3·2	95·5 ± 4·7	3·2	4	16·2 ± 1·1	17·0 ± 1·5	4·9
B2	173·0 ± 5·6	180·1 ± 5·1	4·1	5	43·3 ± 3·3	42·1 ± 4·0	−2·8
B3	190·0 ± 4·1	186·2 ± 3·3	−2·0	6	112·2 ± 7·2	109·9 ± 5·1	−2·0

[a] $F_m = F_E + F_R$, the flow rates of eluent and reagent; [b] beryllium bronzes after separation; [c] foundry dust samples after preconcentration and separation on a silica gel microcolumn.

The results of determination of beryllium in dust samples from the atmosphere of the beryllium bronze foundry, taken at various sites of the working area and at the outlet of the dust separator, are in a very good agreement with those obtained by ETA AAS on an AA 175 ABQ instrument interfaced to a CRA 90 electrothermal atomizer (both Varian, Switzerland); the relative differences lay within the region of 2–5%.

The FIA method with fluorimetric detection using 3-hydroxy-2-naphthoic acid after preconcentration and separation on a microcolumn of pretreated silica gel thus appears suitable for the determination of trace quantities of beryllium in industrial samples. The interfering effect of copper and other matrix components[9] is eliminated by the use of the silica gel microcolumn, as evidenced by the frequency of positive and negative relative deviations of concentrations for the samples analyzed. The accuracy and precision of determination are comparable to those attained by the ETA AAS technique.

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