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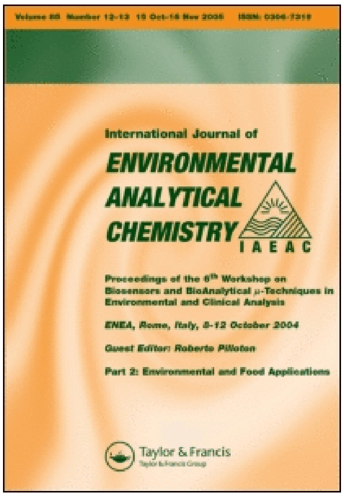

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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P. Burba[a]; P. G. Willmer[a]; M. Betz[b]; F. Fuchs[b]
[a] Institut für Spektrochemie, Dortmund, F.R.G. [b] Engler-Bunte-Institut, Karlsruhe, F.R.G.

To cite this Article Burba, P. , Willmer, P. G. , Betz, M. and Fuchs, F.(1983) 'Atomic Absorption Determination of Beryllium Traces in Natural Waters', International Journal of Environmental Analytical Chemistry, 13: 3, 177 — 191
To link to this Article: DOI: 10.1080/03067318308071592
URL: http://dx.doi.org/10.1080/03067318308071592

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Intern. J. Environ. Anal. Chem., 1983, Vol. 13, pp. 177–191
0306-7319/83/1303-0177 $06.50/0

Atomic Absorption Determination of Beryllium Traces in Natural Waters†

P. BURBA and P. G. WILLMER
Institut für Spektrochemie, D-4600 Dortmund, F.R.G.

and

M. BETZ and F. FUCHS
Engler-Bunte-Institut, D-7500 Karlsruhe, F.R.G.

(*Received April 22, 1982*)

Be traces in natural waters, especially in tap- and surface-water are increasingly subject to analytical control (e.g. by AAS, ICP-OES, fluorometry). In the present paper an analytical procedure is described for the atomic-absorption determination of Be in water. Be traces are quantitatively enriched on special cellulose ion-exchangers (Cellulose-Hyphan of the Riedel-de Haën AG, Hannover, G.F.R.), resp. cellulose-pyrogallol by a fast batch-technique. Dissolved matters like NaCl, Ca(II), Fe(III), humic acid or EDTA do not interfere in the separation. As radio-tracer experiments by means of Be-7 show, in this manner nanogram quantities of Be can be enriched by the factor 100–200 from tap-, river- and sea-water. Flame- respectively ETA-AAS are used for the determination of the enriched Be. Within the latter several atomizer systems and different coated tubes are applied. Accompanying ions, for example Ca^{2+}, cause partially high signal depressions. The detection limits (3σ) of the complete procedure are 50 ng/l Be (FAAS, s_r, 0.02) resp. 1 ng/l (GFAAS, s_r 0.09). With the developed method the Be content in natural waters including sea-water is determined.

KEY WORDS: Be traces, natural waters, atomic absorption spectrometry, cellulose ion-exchangers, selective separation.

1. INTRODUCTION

The determination of trace quantities of the toxic element Be in natural waters is gaining increased importance with the growing interest in

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†Presented at the 12th Annual Symposium on the Analytical Chemistry of Pollutants, Amsterdam, April 1982.

pollution of the environment. According to different national guidelines[1,2] the Be concentrations in tap- or surface water should not exceed a limit of 0.1 resp. 0.2 μg/l. However, average Be contents in such waters, e.g. in mineral- or sea water are by orders of magnitude below this level in the ng/l range.[3]

Different analytical techniques based on atomic absorption spectrometry (AAS),[3,4] optical emission spectrometry,[5] fluorometry,[6] spectrophotometry[7] or chelate gas chromatography[8] can be applied for the determination of Be traces. The flame-AAS (FAAS) resp. graphite furnace-AAS (GFAAS) commonly employed in water analysis makes possible detection limits (3σ) of 3 resp. 0.05 μg/l Be.[9] Therefore, Be contents of less than 0.1 μg/l and/or eventual matrix interferences often require suitable preconcentration techniques before their determination. Especially suitable for the Be enrichment and separation are methods based on liquid-liquid extraction with β-diketones,[3,7,10] coprecipitation with Fe(III)- resp. Al(III)-hydroxide[6,10,11] and partially on ion-exchangers.[3,12]

The aim of the present work was to enrich and separate Be traces from different natural waters (e.g. mineral- and surface waters) on chelating cellulose ion-exchangers.[13,14] These ion-exchangers contained special anchor groups for complex-forming with Be(II). Dissolved organic and/or inorganic matters in waters were suggested as matrix, possibily interfering the ion-exchange resp. the subsequent AAS. In connection with the latter, the effect of interfering matrix elements, especially of Ca^{2+} on the Be determination with GFAAS, was of particular interest. For this purpose, different graphite tubes and furnace systems were investigated.

With the developed procedure, nanogram quantities of Be should be separated from polluted waters and determined by GFAAS in the ng/l range.

2. EXPERIMENTAL

Reagents and solutions

Chelating cellulose ion-exchangers. Several ion-exchangers on the basis of cellulose were used. Besides the commercially available Cellulose-Hyphan® (TM of the Riedel de Haën AG, Hannover/Seelze, F.R.G.) the ion-exchanger cellulose-pyrogallol was synthesized for this purpose in accordance with a previously described procedure.[15] For purification, the ion-exchangers were treated successively with 4 M hydrochloric acid, tridistilled water and reagent-grade acetone. The air-dried ion exchangers in the H^+-form were stable for months.

Reagents

A standard stock solution of Be (1 g/l) was obtained by dissolving a Titrisol® (Merck, Nr. 9922) in 2 M hydrochloric acid. For investigations of Be separation-parameters and analytical interferences the salts and acids used were of analytical suprapuregrade (such grades should be used preferentially if available). The humic acid (HS) used was taken from the Ruhr-river, similarly the lignin sulfonic acid (LS).

Solutions

All solutions were made by dilution with high-purity water to minimize blanks.

Apparatus and operating conditions

Several atomic-absorption spectrometers (Pye-Unicam SP 9, Beckman-Instruments 1272, Perkin-Elmer 4000) were employed with the following parameters:

Wavelength	234.9 nm
Slit	0.5 nm
Source	Be hollow-cathode lamp
Lamp current	5 mA
Burner (FAAS)	one-slit burner for the acetylene-nitrous oxide flame
Flame	C_2H_2/N_2O, stoichiometric
Background	D_2-background correction.

In the case of FAAS the samples (100 μl) were introduced by an injection method.[16] The resulting signals were evaluated by peak-heights. So detection limits (3σ) of 7 μg/l Be in 2 M hydrochloric acid could be reached.

Graphite furnace equipment

Different graphite furnaces (Perkin-Elmer HGA 74, HGA 76 B and HGA 500) were employed under similar conditions. They were flushed with argon. For all Be determinations the same optimized temperature program[17] was chosen, as shown in Table I.

Graphite tubes

Three kinds of graphite tubes were applied in connection with GFAAS-determinations of Be: Zr-coated tubes,[18] pyrolytically-coated tubes[19] and

TABLE I

Graphite-furnace program for the Be determination

Program step	Temperature/Time
Drying	100°C/30 s
Ashing	1000°C/20 s
Atomization[a]	2700°C/10 s(mini-flow)
Clean-up	2700°C/15 s

[a]With D_2-background correction.

normal graphite tubes. The Zr-coating of the tube was accomplished according to a described method,[20] the pyrolytic coating with a methane/argon mixture in a HGA 76 B system at 2100°C (three cycles per 3 min each).

Be-7 Tracer experiments

As Be radio-tracer, a sample of carrier-free Be-7 (half-time 53, 4 d, γ-energy 478 KeV) was used in 0.1 M hydrochloric acid solution. The specific activity of Be-7 was about 1.5 GBq/μg Be (produced by Amersham Buchler Ltd.). The tracer experiments could be carried out in an apparatus as described earlier.[21] Generally, the experimental solutions (200 ml) were marked with 1 ng/l Be-7. Thus, the kinetics of Be^{2+}-exchange could be determined by taking of 0.2 ml filtered samples after definite time intervals. The resulting γ-activity of the samples was measured in a NaJ(Tl)-scintillation counter.

Distribution coefficients and recovery rates

The distribution coefficients K_d (ml/g) of Be^{2+} and other ions (e.g. heavy-metal ions) on the discussed cellulose ion-exchangers could be determined by using the batch equilibrium method. For this purpose high-clean polyethylene containers were used. 200 ml samples containing 1 μg/l to 2 mg/l Be^{2+}, resp. 25 μg/l Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+} (each) and different salts (30 g/l NaCl, resp. 100 mg/l Na^{+}, Ca^{2+}) were equilibrated with 0.1 g ion-exchanger under magnetically stirring at appropriate pH-values. After reaching the equilibrium (1 h) the loaded ion-exchanger was separated by filtration, dried and the enriched metal traces eluted by 2 M hydrochloric acid. The metal content in the acid eluate was determined by FAAS (injection method). According to the formula

$$K_d = \frac{c_{ex}}{c_{sol}} \text{ [ml/g]}$$

the distribution coefficient was calculated (c_{ex}(μg/g) stands for the metal concentration in the exchanger phase, c_{sol}(μg/ml) for the metal concentration in the solution).

Storage of natural water samples

The storage resp. the pre-treatment of Be-containing natural waters was investigated in 1 l borosilicate glass- and polyethylene containers at pH 2 resp. 8.5. Carrier-free, high-specific activity Be-7 was used to prepare reaction solutions, containing 1 ng/l Be^{2+} and 30 g/l NaCl, in 1 l bottles. They were examined at daily intervals for loss of Be activity caused by adsorption on the container walls.

Natural water samples (saline and non-saline) were freshly collected in pre-cleaned polyethylene bottles. After separation of suspended matter (0.45 μm filtration) they were acidified to $pH < 2$ with concentrated suprapure nitric acid (2 ml HNO_3 per 1 l sample).

For polluted surface waters an UV-irradiation as described elsewhere[22] was applied as sample pre-treatment (Hg-low-pressure lamp, 70 W, 1 h at 45°C in a quartz-reactor). It led to the release of Be-species that are bound to dissolved organic matter into species well accessible to ion-exchange.

Be separation from natural waters

Batch-method: To 200 ml of the stored water sample 0.1 g cellulose-pyrogallol were added. Then, under magnetically stirring, the pH of the solution was adjusted to 8.5 with 2 M sodium hydroxide solution and fixed at this value by addition of 5 ml borate buffer solution. After at least 45 minutes, the loaded ion-exchanger was filtered on a filter-paper, washed and dried at 90°C. The enriched Be traces could be eluted with 2 ml 2 M hydrochloric acid, suprapure, which were subjected to AAS-determinations.

Column-method: 0.3 g Hyphan- resp. pyrogallol-cellulose (capacity 0.4 mmol/g), suspended in high-pure water, was loaded into a glass column with an inner diameter of 1 cm. The ion-exchanger had a volume of about 2.5 ml in the wet state resulting in a filling height of approximately 3 cm. On the column prepared Be traces were separated from 0.5 to 1 l samples.

The pH of the solution was adjusted to pH 8.5 by adding 5 to 10 ml borate buffer of pH 8.5. The flow rate was 5 ml/min. After the separation step and washing with 10 ml high-pure water, the enriched Be traces could be quantitatively eluted with 5 ml 2 M hydrochloric acid, suprapure.

Quantitative determination of Be

Be traces enriched by the factor 100 were determined by FAAS resp. GFAAS under the operating conditions already described.

In the case of FAAS calibration curves could be obtained by aspirating (resp. injection) of synthetic Be standards on the basis of 2 M hydrochloric acid. Calibration by the standard addition method was necessary in the case of GFAAS.

Reagent blanks were run through the whole analytical procedure. If necessary, they could be deducted from the Be content found in the sample.

3. RESULTS AND DISCUSSION

Immobilized chelating agents, especially chelating ion-exchangers, are gaining increased importance for the preconcentration of metal traces from dilute aqueous or organic solutions. Cellulose as support material for such ion-exchangers offers a number of desirable properties.[23] So it has a high-porous, hydrophilic structure and remarkably low blank values of metal traces.

Expecially oxygen- and hydroxyl-containing reagents are to be used as chelating groups for Be-selective cellulose ion-exchangers. Be(II) as strong Lewis acid prefers the coordination with oxygen as donor atom. The use of such complexing agents in the fluid-extraction of Be traces is a clear parallel.

The analytical enrichment of Be traces (5 μg/l) from saline solutions (200 ml of 0.5 M NaCl-solution) on different cellulose materials (0.1 g) by a simple batch-technique is shown in Figure 1 as relation between recovery and pH-value. Below pH 4 the ion-exchangers practically do not enrich dissolved Be traces. Between pH 5 and 8.5, the recovery rate is strongly affected by the H^+-concentration. The highest recovery rates can generally be reached at $pH \geqq 8.5$. Already natural cellulose, the support material of the ion-exchangers, enriches the Be traces by the factor 10^3. On the basis of the cellulose especially the pyrogallol-exchanger reaches recovery rates of >90%. Fe(III)-loaded ion-exchangers (20 mg Fe(III)/g exchanger) show the highest Be recoveries. It can be suggested that in these cases Be(II) is

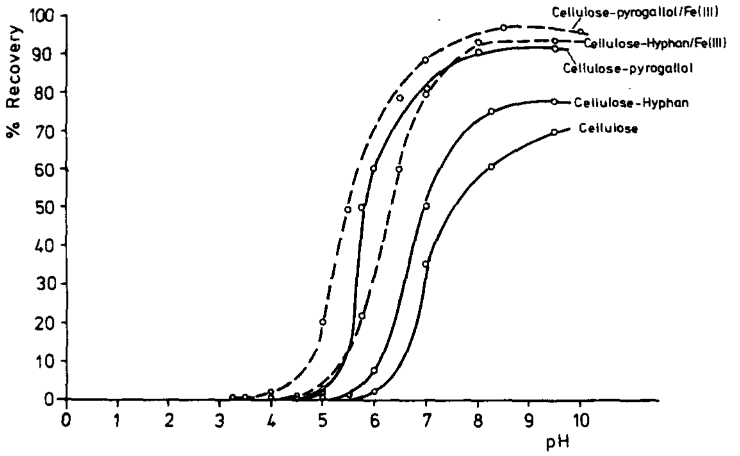

FIGURE 1 % Be recovery (5 μg/l) on different cellulose materials (0.1 g, each) from 0.5 M NaCl solution (200 ml) as function of pH.

bound to the Fe(III) fixed on the ion-exchanger. Therefore, Fe(III) abundant in natural waters, does not disturb the separation method.

The recovery rate of Be traces is nearly constant at 90 to 95% in the concentration range of 1 ng/l to 1 mg/l Be, also in the presence of earth-alkali ions (200 mg/l Ca^{2+}).

The high-selective separation and enrichment of Be traces is important for the subsequent determination step. Well known is the interfering influence of many ions (e.g. of Ca^{2+}) on the GFAAS-determination of Be.[17,19,20] Under this aspect some attempts were made to prevent the co-enrichment of other trace constituents of liquid environmental samples, for instance heavy-metal ions. Thus, the effect of the complexing agent EDTA on the distribution coefficients K_d of different ions (Be^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}) on cellulose-pyrogallol was investigated. The Figure 2 shows the influence of EDTA on some element distribution-coefficients at constant pH (8.5) and in the presence of Ca^{2+} (100 mg/l) and Na^+ (300 mg/l). In the range 1 to 10 mg/l EDTA no depressing influence on the Be^{2+}-distribution coefficient is detectable. Constantly the K_d-values of Be^{2+} on the pyrogallol-cellulose amounts to 5×10^4 (ml/g), even in the presence of higher EDTA-concentrations (50 mg/l). As expected, the decreasing effect of EDTA on the other distribution coefficients is very large. Under the reaction conditions the investigated K_d-values are lowered by about 3 orders of magnitude. Even some 100 μg/l EDTA show this intense effect. It is evident that this reaction can successfully be used for masking of many

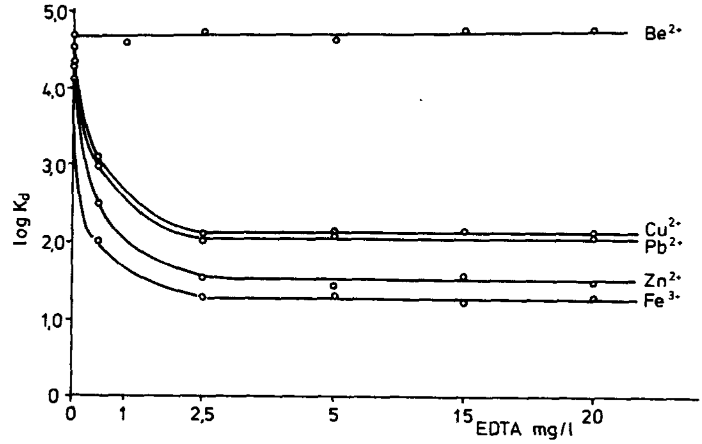

FIGURE 2 Distribution coefficient K_d (ml/g) of some ions (5 µg/l Be^{2+}, 25 µg/l Cu^{2+}, Fe^{3+}, Pb^{2+}, Zn^{2+}, each. Matrix: 100 mg/l Ca^{2+}, 300,g/l Na^{+}) in the presence of EDTA (pH 8.5).

interfering ions. The resulting separation factors between Be^{2+} and other ions are about 10^3.

Occasionally, pretreatment and storage of sample has an important influence on the accuracy and/or reproducibility of water analysis in the trace range. Loss or contamination risks during storage is a well known problem.[24,25] Especially in the case of Be, a loss of traces from neutral solutions is possible, e.g. by precipitation or adsorption on the container walls. For the reasons mentioned above, experiments were carried out to study the adsorption behaviour of Be traces in different containers (glass, polyethylene) at the ng/l-level. Carrier-free, high-specific activity of Be-7 was used to prepare 1 ng/l Be*-solutions in saline water (30 g/l NaCl). In Figure 3 the storage under different conditions over a relatively long time is shown. As may be seen from that figure, the loss of Be traces reaches about 30% in glass containers at pH 8.5 within 24 h. It is remarkable, that it decreases to only 10% after the elapse of 8 days. In comparison, the polyethylene (PE) container adsorbs less Be, but it shows a similar adsorption characteristic after ten days. No measurable loss of Be traces over twenty days can be detected at pH 2 in polyethylene containers. Therefore, all liquid environmental samples (after 0.45 µm-filtration of the suspended matter) were acidified in pre-cleaned polyethylene bottles with concentrated nitric acid to pH $\leqq 2$.

The enrichment of Be traces from natural waters was carried out on the discussed ion-exchangers according to the batch-equilibrium method. In

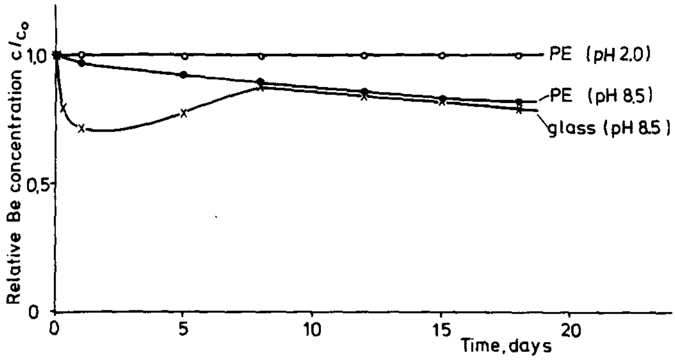

FIGURE 3 Loss of Be traces (1 ng/l Be-7) from saline solution (30 g/l NaCl) in different containers (glass, polyethylene) at pH 2 resp. 8.5.

this case, besides high distribution coefficients for Be, fast ion-exchange kinetics are necessary when the traces are to be separated from relatively large sample volumes (200 ml) on little amounts of ion-exchanger (0.1 g). The kinetics of the Be separation on cellulose ion-exchangers can be measured by using the radioactive tracer Be-7. Typical results for the Be-sorption on cellulose-pyrogallol are shown in Figure 4, concerning the separation of 1 ng/l Be* from sea-water (North Sea) at pH 8.5. The sorption curve consists of two exponential components. The half-times for sorption of Be traces by cellulose-pyrogallol are: step 1 with 10 s, step 2 with 6 min. The first step with a half-time of the order of 10 s is attributed to exchange of Be(II) on pyrogallol anchor-groups near the surface of the exchanger. The rate of the second step is possibly controlled by the diffusion of the Be(II) into the inner part of the cellulose ion-exchanger. Within 10 minutes, more than 90% of the Be traces are separated from the saline sample. A similar exchange behaviour of pyrogallol-cellulose could be found out at the Be*-separation from river water (Ruhr-river, Germany) and drinking-water (Dortmund, Germany) under the same conditions.

In all cases a practically quantitiative separation of Be traces is possible within 30 minutes. As the present experiments show, the described batch-method on the basis of cellulose-pyrogallol can be used for the fast, simple and reliable analytical enrichment of Be traces from both, saline and non-saline waters. The Be recoveries generally are in the range of 92 to 97%, even in the presence of considerable contents of complex-forming humic acid and lignin sulfonic acid (20 mg/l HS + 10 mg/l LS). After elution with hydrochloric acid the final concentrate contains the Be traces enriched by

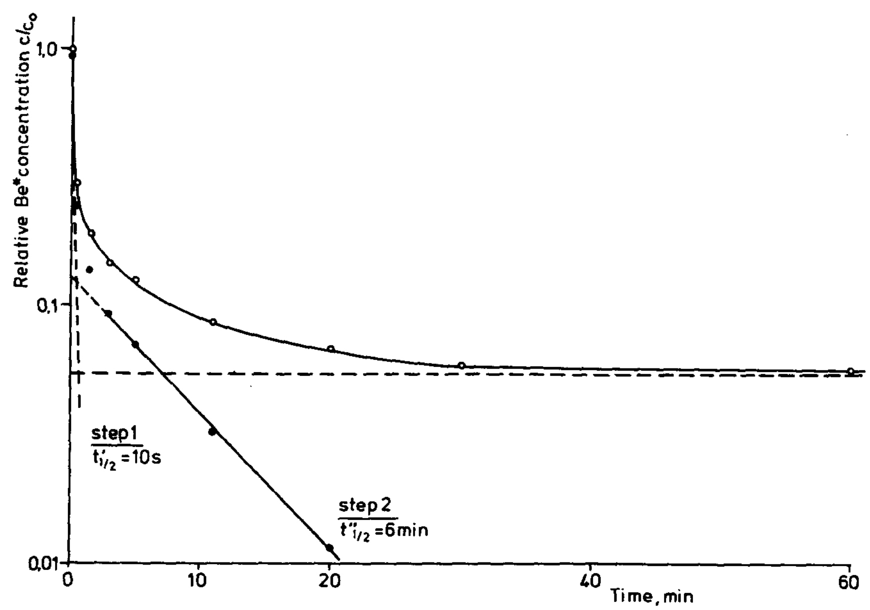

FIGURE 4 Separation of Be (1 ng/l Be-7) from North-Sea water (200 ml sample, pH 8.5) on cellulose-pyrogallol (0.1 g) as function of time.

the factor of 100. A higher preconcentration of the Be can be achieved, if large sample volumes (1–2 l) are passed through little Hyphan- or pyrogallol-cellulose columns.

For the determination of the enriched Be the FAAS (injection method when possible) and GFAAS was employed. In the first case, the analytical advantages can be seen in relatively small interferences, simple technique resp. calibration and low time-consumption. But for the Be determination in the lower ng/l-range the much more sensitive GFAAS is inevitable.

The GFAAS procedure of Be determination could be carried out in different furnace systems (HGA 74, HGA 76 B, HGA 500) and graphite tubes (Zr-coated, pyrolytically coated and uncoated tubes). In good agreement with other reports[17,19,20] the optimization program established the parameters given in Table I. The ashing behaviour of Be (10 ng/ml) in 2 M hydrochloric acid was largely depending on ashing-temperature and -time. The maximum temperature above which ashing losses of Be intensively occurred after 30 s was 1000°C. An ashing time of 20 s was considered to be sufficient to remove any acid. Commonly, an atomization temperature of 2700°C brought the maximum Be signal similar to that given in the literature.[17,19]

Another severe problem which is encountered in the flameless atomic-absorption determination of Be is the abundance of matrix-specific interferences.[19,20] Such interferences are caused by many cations and anions, but particularly by Ca^{2+}-ions abundant in natural waters.[17,20] Thus, 0.5 mg/ml Ca^{2+} can cause 50% signal depressions in Zr-coated graphite tubes.[20]

From this point of view the influence of Ca^{2+}-ions on the Be-signal was investigated in different graphite tubes (Zr-, pyrolytically coated and uncoated tubes) and furnace systems (HGA 74, 76 B resp. 500) using the same temperature program as dicussed above. The results are compiled in Figures 5 and 6.

As may be seen from the first diagram (Figure 5) the Ca^{2+}-ions have a severely decreasing effect on the Be-signal in Zr-coated tubes as reported by other authors.[19,20] So 0.5 mg/ml Ca^{2+} cause a signal depression of 80%. On the other hand, practically no Ca^{2+}-influence on the Be-signal can be detected in the pyrolytically coated tubes. However, these tubes have the disadvantage of lowered reproducibility of the Be response. In the absence of Ca^{2+} the Be response in the three investigated tube sorts show approximately equal peak heights (c. 200 mm with 10 ng/ml Be, 20 μl). Figure 6 demonstrates the influence of different furnace systems, which only differ in the heating rate during the atomization step, on the Be response in presence of Ca^{2+}-ions according to a constant furnace

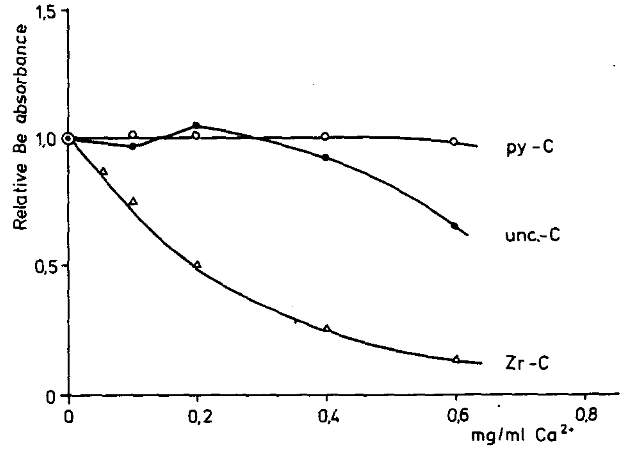

FIGURE 5 Effect of Ca^{2+} on the Be atomic-absorption (10 ng/l Be, 20 μl) in different graphite tubes (pyrolytically coated-, uncoated-, Zr-coated tubes). Furnace program parameters: drying at 100°C/30 s, ashing at 1000°C/20 s, atomization at 2700°C/15 s, spectrometer Perkin-Elmer 4000/HGA 500, D_2-background correction.

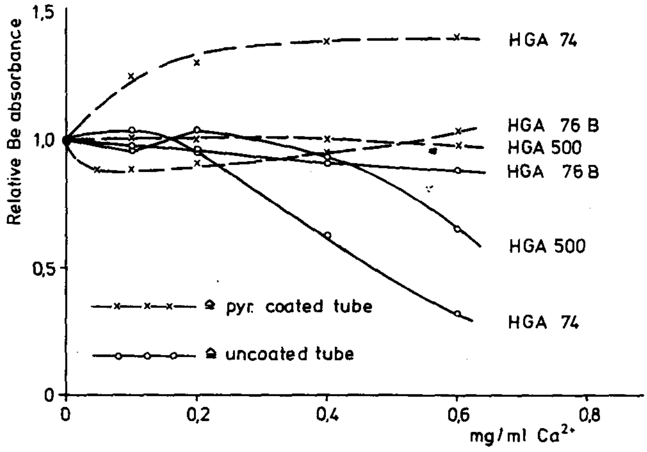

FIGURE 6 Relative Be atomic-absorption (10 ng/ml Be, 20 μl) as function of Ca^{2+} concentration in different furnace systems (Perkin-Elmer HGA 74, 76 B resp. 500). Furnace program: drying at 100°C/30 s, ashing at 1000°C/20s, atomizing 2700°C/15 s).

program (Table I). In the furnaces (HGA 74, 76 B, 500) pyrolytically coated and uncoated tubes were employed. From the different curves it can be concluded that the speed of the heating plays a very important role for the Be atomization in the particular tubes. The greatest effect of Ca^{2+} on the Be signal can be seen in the two tube types, if connected with the relatively slow heating HGA 74. Thus, the Be response is clearly increased in the pyrolytically coated tube but severely decreased in the uncoated tube. In the latter case 0.5 mg/ml Ca^{2+} cause above 50% signal depression. These results are in agreement with those of another report.[19] In contrast to this case rapid heating during the atomization step, as it is possible in the modern HGA 76 B resp. 500 system,[26] seems to remove the interferences on the Be signal caused by Ca^{2+}-ions.

The described results give practical guidelines about the calibration of Be determination by GFAAS. To avoid systematic errors, the standard addition method should be used generally.

The enrichment of Be traces on cellulose ion-exchangers connected with FAAS resp. GFAAS was characterized as combined method for the determination of Be in the nanogram range. On the basis of a 100-fold Be-enrichment the detection limits (3σ) of the procedure were 50 ng/l (FAAS) resp. 1 ng/l (GFAAS) of Be, the relative standard deviations 0.02 ($N=10$, 1 μg/l) resp. 0.08 ($N=10$, 0.02 μg/l).

Numerous samples of natural waters, e.g. sea- and mineral water, surface-, tap- and waste water, were analyzed by the procedures described above. Good agreement was obtained between results for spiked (e.g. 20 ng/l Be) and unspiked samples. In general, the Be recovery from the water samples was 90% (e.g. North-Sea) to 95% (e.g. Rhine-water). The results of the Be analyses are summarized in Table II.

TABLE II

Be determinations in different waters by the combined procedure (using GFAAS)

Type	Origin	Content of Be (ng/l)	Enrichment
Sea-Water	North-Sea	$\leqq 1$	Cellulose-pyrogallol
Mineral water	Bad Pyrmont/F.R.G.	55.8	Cellulose-pyrogallol
Mineral water	Essen/F.R.G.	9.0	Cellulose-pyrogallol
River water	Rhine (Maxau, 6.2.80)	4.5	Cellulose-Hyphan
River water	Rhine (Maxau, 10.2.80)	11.0	Cellulose-pyrogallol
River water	Rhine (Köln, 6.2.80)	4.0	Cellulose-Hyphan
River water	Ruhr (Dortmund, 10.3.80)	7.2	Cellulose-pyrogallol
River water	Ruhr (Dortmund, 23.1.81)	5.2	Cellulose-pyrogallol
River water	Ruhr (Dortmund, 2.2.81)	4.3	Cellulose-pyrogallol
River water	Ruhr (Schwerte, 28.1.81)	4.5	Cellulose-pyrogallol
River water	Ruhr (Schwerte, 4.3.81)	3.3	Cellulose-pyrogallol
River water	Neckar (Heilbronn, 11.2.81)	14.0	Cellulose-pyrogallol
River water	Danube (Leipheim, 11.2.81)	6.0	Cellulose-pyrogallol
Tap water	Dortmund/F.R.G. (3.3.80)	$\leqq 1$	Cellulose-pyrogallol
Tap water	Karlsruhe/F.R.G. (16.9.80)	1.5	Cellulose-pyrogallol
Tap water	Leipheim/F.R.G. (11.2.81)	$\leqq 1$	Cellulose-pyrogallol
Waste water	Dortmund/F.R.G. (4.3.81)	5.2	Cellulose-pyrogallol

For sea-water (North-Sea) results only below the 3σ-detection limit ($\leqq 1$ ng/l Be) were obtained, while in the number of analyzed mineral waters relatively high Be contents (to about 50 ng/l, e.g. Bad Pyrmont/F.R.G.) could be determined in agreement with the range of 10 to 100 ng/l Be, quoted in the literature.[3] In the natural surface waters of Germany (e.g. Rhine-, Ruhr-, Danube-, Neckar-river) investigated, relatively low Be contents were found ranging from 4 to 14 ng/l. As the series of Be analyses in the German river Ruhr at different times and places shows, the content of dissolved Be (3 to 7 ng/l) can be rather constant. Only in the case of Neckar water, well known for its heavy-metal pollution,[27] a Be content worth mentioning (14 ng/l) was obtained. But in comparison to a discussed Be limit of 100 ng/l in different waters, it seems to be moderate. The tap- resp. drinking waters partly originating from river water (e.g. Dortmund/Ruhr, Leipheim/Danube) did not show detectable Be concentration ($\leqq 1$ ng/l).

In most cases the natural waters contain very low dissolved Be traces. This is due to the relative insolubility of the oxide and hydroxide of Be and its intense adsorption on suspended matter resp. sediments in waters, as it is shown in this study for the polymeric plant material cellulose. In the latter case the Be enrichment seems to be of the order 10^3, neutral pH-values presupposed. Moreover, in the weathering processes Be traces are concentrated in hydrolysates, similar to the element aluminium.

Sometimes, burdened surface waters can be polluted by a variety of strong-complexing dissolved organic matter[28] interfering the analytical procedures of water analysis. So many 1,3-diketones and 1,2-diphenols form relatively stable chelates with Be(II). Such possible interferences on the analytical enrichment of Be traces can be eliminated, if necessary, in a simple manner by anUV- irradiation[22] on oxidizing conditions (addition of H_2O_2).

The described analytical procedure consisting of a fast UV irradiation, selective one-step Be enrichment on cellulose ion-exchangers and detection by atomic-absorption (FAAS, GFAAS) can be used for rapid and well reproducible Be determinations in natural waters at the lower ng/l-level.

Acknowledgement

This work was supported by the "Ministerium für Wissenschaft und Technologie des Landes Nordhein-Westfalen" and the "Bundesministerium für Forschung und Technologie".

References

1. Deutscher Verein von Gas- und Wasserfachmännern: Arbeitsblatt W 151, Eschborn 1975.
2. Predel'no dopustimye koncentracci vrednych veščesstv v vodoemov sanitarno-bytovogo vodosnabženija, Moscow (USSR) 1970.
3. J. Korkisch, A. Sorio and I. Steffan, *Talanta* **23**, 289 (1976).
4. U.S. Environmental Protection Agency Manual: Methods for Chemical Analysis of Water and Wastes, Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, Ohio, EPA-625/6-74-003, 1974, p. 99.
5. R. K. Winge, *Appl. Spectroscopy* **33**, 206 (1979).
6. C. W. Sill and C. P. Willis, *Anal. Chem.* **31**, 598 (1959).
7. J. R. Merill, M. Honda and J. R. Arnold, *Anal. Chem.* **32**, 1420 (1960).
8. G. Kaiser, E. Grallath, P. Tschöpel and G. Tölg, *Z. Anal. Chem.* **259**, 257 (1972).
9. B. Welz, Atomic Absorption Spectroscopy, p. 62, Verlag Chemie, Weinheim/F.R.G. 1975.
10. H. A. Laitinen and P. Kivalo, *Anal. Chem.* **24**, 1467 (1952).
11. D. I. Eristavi, F. I. Brouchek and V. D. Eristavi, *Tr. Gruzinsk. Politekn. Inst. 1966* **3**, (108), 41 (in Russian).
12. J. Korkisch and A. Sorio, *Anal. Chim. Acta* **82**, 311 (1976).
13. P. Burba, K. H. Lieser, V. Neitzert and M. Röber, *Z. Anal. Chem.* **291**, 273 (1978).
14. P. Burba and P. G. Willmer, *Vom Wasser* **55**, 227 (1980).
15. P. Burba, M. Röber and K. H. Lieser, *Angew. Makromolekulare Chem.* **66**, 131 (1978).

16. H. Berndt and E. Jackwerth, *Atomic-Absorption Newsl.* **15,** 109 (1976).
17. P. Geladi and F. Adams, *Anal. Chim. Acta* **105,** 219 (1979).
18. J. H. Runnels, R. Merryfield and H. B. Fisher, *Anal. Chem.* **47,** 1258 (1975).
19. B. Neidhart and Ch. Lippmann, *Z. Anal. Chem.* **306,** 259 (1981).
20. Th. Stiefel, K. Schulze and G. Tölg, *Anal. Chim. Acta* **87,** 67 (1976).
21. K. H. Lieser and G. Zuber, *Angew. Makromolekulare Chem.* **57,** 183 (1977).
22. P. Burba and P. G. Willmer, *Z. Anal. Chem.* **311,** 222 (1982).
23. W. Wegscheider and G. Knapp, Preparation of chemically modified cellulose exchangers and their use for the preconcentration of trace elements CRC Critical Reviews in Analytical Chemistry, pp. 79–102 (1981).
24. L. Mart, *Z. Anal. Chem.* **296,** 350 (1979).
25. E. S. Gladney and W. E. Goode, *Anal. Letters* **10,** 619 (1977).
26. W. Slavin, D. C. Manning and G. R. Carnick, *Atomic Spectroscopy* **2,** 137 (1981).
27. U. Förstner and G. Müller, Schwermetalle in Flüssen und Seen als Ausdruck der Umweltverschmutzung, Springer-Verlag, Berlin–Heidelberg–New York, 1974.
28. T. M. Florence, *Water Research* **11,** 681 (1977).