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DETERMINATION OF BERYLLIUM IN NATURAL WATERS USING ATOMIC ABSORPTION SPECTROMETRY WITH TANTALUM-COATED GRAPHITE TUBE

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In the present paper a method for direct determination of beryllium in natural waters, especially in surface waters, using atomic absorption spectrometry with graphite furnace is described. Two procedures are compared, using an ordinary graphite tube and matrix modifier $\text{Mg}(\text{NO}_3)_2$, and using a tantalum coated tube without any modifier added. The detection limit (3σ) of the proposed method using the tantalum-coated tube is proved to be $0.02 \mu\text{gBe/l}$. With the developed method the Be content in natural water samples collected from highly polluted and reference regions of Bohemia were determined. A certified reference material (IAEA/W-4) was also analysed to prove the accuracy of proposed method.

Keywords: Beryllium determination; atomic absorption spectrometry; electrothermal atomisation; natural waters

INTRODUCTION

Concentrations of Be in surface waters are usually about $0.01\text{--}1 \mu\text{g/l}$,^[1] whereas in tap-, lake-, and mineral- waters are in the range of $1\text{--}55 \text{ ng/l}$.^[2] Unfortunately, in some areas the contents of Be can be much more high due to high environmental pollution. Several problems exist in the northern part of Bohemia with toxic elements (As, Be, Cd, Pb) due to large coal combustion in local power stations or heating plants. Since beryllium is a highly toxic metal it is necessary to control its content even at very low levels.^[3] A method sensitive enough and

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most frequently used is atomic absorption spectrometry with electrothermal atomisation.

The beryllium determination using graphite furnace brings some problems, namely matrix interferences, memory effects and bad reproducibility.^[2-5] In order to overcome these problems the use of a suitable matrix modifier, mostly $\text{Mg}(\text{NO}_3)_2$, is recommended.^[6-8] The mechanism of atomisation of Be in the presence of magnesium was studied by Styris and Redfield in detail.^[9] Graphite tubes treated by zirconium,^[3,4] thorium^[5] or lanthanum^[6] were also used to improve reproducibility, sensitivity and interferences in the determination of beryllium. Zátka^[10] firstly proposed the impregnation of the graphite atomiser with a tantalum oxalate solution. Hocquet and Labeyrie^[11] and Fritzsche et al.^[12] found that tantalum coated tubes influenced the atomisation process of tin positively. The increase in the sensitivity and lower memory effects were observed by Wahab and Chakrabarti^[13] when atomised yttrium from tantalum treated graphite tube. Tantalum coated platforms were also tested for tin, selenium and rhodium in the presence of some interfering cations by Michaelis et al.^[14]

This paper describes a reliable method for the determination of Be in surface waters from 0.02 $\mu\text{g/l}$. The accuracy was tested by analysis of a certified reference material simulated fresh water (IAEA/W-4) and by the method of standard additions. The proposed method was applied to analysis of surface waters taken from a polluted area in the north part of Bohemia (Řolava) and from a reference area in the south part of the country (Trnávka). Two experimental procedures are compared: using an ordinary graphite tube and $\text{Mg}(\text{NO}_3)_2$ as a matrix modifier, and using a tantalum treated tube without any modifier added.

EXPERIMENTAL

Instrumentation

All results were obtained using an atomic absorption spectrometer Perkin-Elmer, model 4000, equipped with a graphite furnace atomiser, model HGA 500, and an autosampler AS-40 (Perkin-Elmer). Absorption signals were recorded using a Perkin-Elmer Data System 3500 and results were registered using a PRS-10 printer-sequencer. The volume of the injected samples or calibration solutions was 20 μl , the volume of a matrix modifier was 10 μl . Absorbance was measured at a wavelength of 234.9 nm using a bandpass of 0.7 nm and a beryllium hollow-cathode lamp operated at 30 mA. Ordinary graphite and tantalum-coated tubes^[10] were applied throughout the measurements. Deuterium-arc background corrected peak-height absorbances were measured. Ultrapure water was prepared

by Nanopure System (Barnstead, FRG), a quartz still (Acidest, Heraeus, FRG) was used for the preparation of nitric acid of high-purity.

Reagents

Standard beryllium solution. A solution containing 10 mg/l of beryllium was prepared from a stock solution of 1000 mg/l (Merck, FRG) by dilution with 0.3% HNO₃. This solution was further diluted to the desired concentrations of calibration curve by ultrapure water with the addition of 0.5 ml HNO₃ per 100 ml. Calibration solutions were prepared freshly every week kept in polypropylene flasks.

Matrix modifier Mg(NO₃)₂·6 H₂O. A solution containing 10 g/l of magnesium was prepared by dissolving magnesium nitrate (Merck, Suprapur) in demineralised water and acidified with 0.5 ml HNO₃ to 100 ml. This solution was further diluted to lower concentrations.

Tantalum oxide Ta₂O₅ (spectral grade) 20% water suspension was prepared for tantalum-treated graphite tubes.^[11] For investigation of interferences all analytical-reagent grade chemicals were used.

Coating Process

Fifty microliters of 20% water suspension of Ta₂O₅ are introduced into the ordinary graphite tube and treated following the recommended temperature programme (dry at 100°C, ramp 25s, hold 5s, ash at 1000°C, ramp 20s, hold 30s, atomise at 2700°C, ramp 1s, hold 10s, gas stop). After three repetitions of this procedure the surface has a goldish appearance.

Water Samples

Surface water samples were collected in 1 liter pre-cleaned polyethylene bottles. After filtration on a 0.1 μm membrane filter, samples were acidified with high-purity nitric acid 5 ml to each 1 liter of sample. Bottles were stored at +4°C until the measurement.

Determination of Beryllium by GF AAS

For the case of measurement with an ordinary graphite tube the standard temperature programme recommended by Perkin-Elmer^[15] was suitable. When a matrix modifier or tantalum-coated tube were used a new temperature pro-

TABLE I Temperature programme for the determination of Be in natural waters using an ordinary graphite tube with 100 mg Mg/l as modifier, or Ta-coated tube without modifier.

	Step			
	Dry	Char	Atomise	Clean
Temperature, °C				
Ta-coated tube	120	1200	2600	2700
ordin.tube + Mg	120	1000	2600	2700
Ramp time, s				
Ta-coated tube	20	20	0	2
ordin.tube + Mg	20	25	0	2
Hold time, s				
Ta-coated tube	10	20	3	2
ordin.tube + Mg	20	20	3	2
Ar flow, ml/min	300	300	20	300

gramme was derived, given in Table I. During the atomisation step the mode "max power heating" was in operation for all measurements. The influence of heating rate on signal of 20 pg of Be from Ta-coated tube is seen in Figure 1.

RESULTS AND DISCUSSION

Interferences

The interference effects of main surface water components were studied on the beryllium signal in concentration up to 200 mg/l. Results are listed in Table II. As follows from it all investigated ions cause the enhancements of 1 $\mu\text{g/l}$ Be

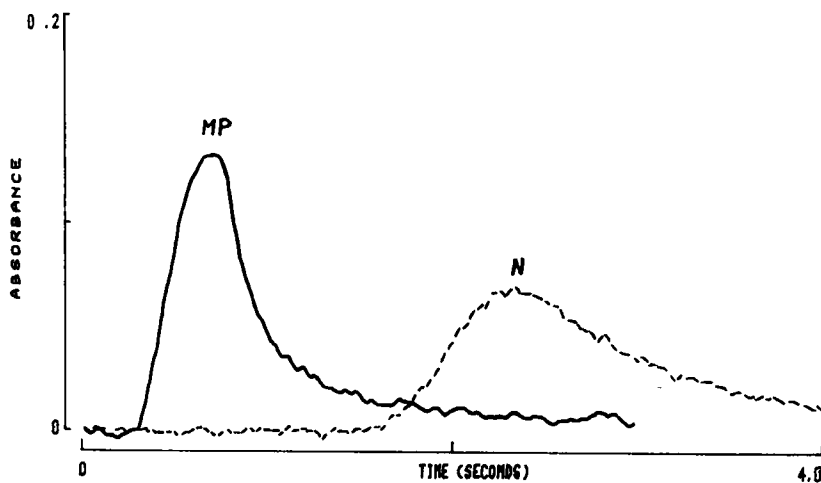


FIGURE 1 The influence of heating rate on the atomisation signal of 20 pg of Be using Ta-coated tube: a) fast heating rate (MP), b) normal heating rate (N).

TABLE II Effect of chosen ions on signal of 1 μg Be/l in an ordinary graphite tube (with or without modifier) and in Ta-coated tube.

<i>Interferent</i>		<i>Change of Be signal (%)</i>		
		<i>Ordinary graphite tube</i>		<i>Ta-coated tube</i>
<i>200 mg/l</i>	<i>Compound</i>	<i>no modifier</i>	<i>modifier Mg 100 mg/l</i>	
Na ⁺	NaCl	+27	-1.3	0
Ca ²⁺	CaCl ₂	+34	-3.9	-2.6
Ca ²⁺	Ca(NO ₃) ₂	+31	-3.9	-3.3
Mg ²⁺	MgCl ₂	+46	-4.2	+1.2
Mg ²⁺	Mg(NO ₃) ₂	+52	-5.3	+1.7
Fe ³⁺	FeCl ₃	+23	+1.4	+4.6
NO ₃ ⁻	KNO ₃	+19	-2.6	0
SO ₄ ²⁻	Na ₂ SO ₄	+15	-5.9	+2.6

signal. Since the influence of Mg(NO₃)₂ shows the greatest effect it was studied in detail. The dependence of Be signal on the concentration of Mg is shown in Figure 2, the maximum signal being obtained in the presence of 100 mg/l of Mg. With the increasing concentration of Mg there is a time/temperature shift in the appearance of the Be signal to higher values which shows the thermal stabilization of Be in the tube. This thermal stabilization explains the decrease of studied interferences. The modifier Mg(NO₃)₂ at two concentration levels of 100 mg/l and 1000 mg/l, respectively, was investigated, with respect to the elimination of interferences. It was found that interferences examined were removed already at 100 mg/l of Mg (Table II). If concentration of main components in waters are higher a suitable modifier concentration should be investigated again.

The second possibility of elimination of the above mentioned interference effects is the use of tantalum-coated graphite tubes (Table II). This way of elimination of interferences is preferable because the Ta-coated tube allows higher charring temperatures, and no Be blank is introduced when magnesium nitrate is used as modifier. The preparation of Ta-coated tubes is very simple and the surface is stable that any renovation is not necessary during the analysis of more than 100 samples.

The atomisation mechanisms for beryllium described in the literature^[9,16] occur by thermal decomposition of adsorbed oxides which are rather thermostable. The improvement in sensitivity of Be in the tantalum treated atomiser is possibly caused by decrease in the free oxygen concentration in the gas phase and the atomisation is then more effective.

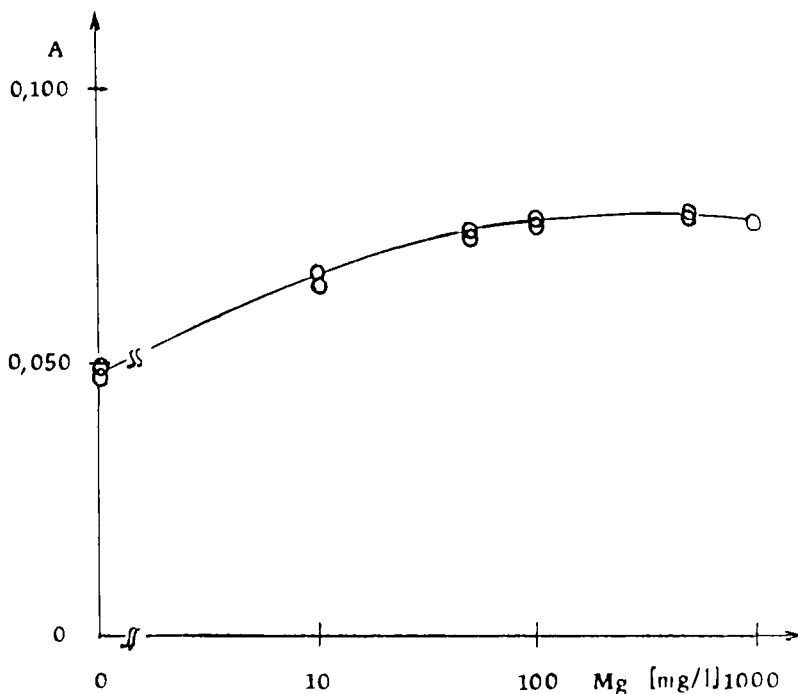


FIGURE 2 Effect of Mg-ions on the Be signal of 1 $\mu\text{g/l}$ in an ordinary graphite tube (RSD is 3.73% – 4.01% for 10 mg Mg/l to 1000 mg Mg/l, respectively, $n = 3$).

Accuracy, Precision and Detection Limit

The accuracy of proposed methods was tested by the analysis of a certified reference material simulated fresh water IAEA/W-4 (International Atomic Energy Agency, Austria) and by the method of standard additions for the analysis of surface waters from exposed area in the northern Bohemia (Rolava) and from a reference area in the southern Bohemia (Trnávka). Results summed in Table III corresponds with a certified value very well. In Table IV results include the correlation of values obtained for filtrated and non-filtrated samples.

TABLE III Beryllium analysis of the certified reference material simulated fresh water IAEA/W-4.

Found, $\mu\text{g/l}$		Certified, $\mu\text{g/l}$
<i>ordinary graphite tube with $\text{Mg}(\text{NO}_3)_2$ as modifier</i>	<i>Ta-treated tube</i>	
1.21 ± 0.046	1.23 ± 0.037	1.25

$n = 3$

TABLE IV Results of the beryllium determination ($\mu\text{g/l}$) in chosen surface water samples from both investigated regions analysed by two suggested procedures and by standard additions.

Sample	Ordinary tube		Ta-coated tube		
	with modifier $\text{Mg}(\text{NO}_3)_2$	standard additions	calibration line	standard additions	
ROLAVA					
Nw	11 f	2.51	2.66	2.62	2.70
	n	2.48	2.74	2.68	2.76
Nw	12 f	3.49	3.56	3.50	3.58
	n	3.47	3.48	3.46	3.54
Nw	13 f	3.24	3.26	3.22	3.26
	n	3.10	3.20	3.06	3.02
Nw	14 f	2.90	2.97	3.08	3.00
	n	2.84	2.75	2.98	3.04
TRNÁVKA					
Sw	111 f	< 0.02	< 0.02	< 0.02	< 0.02
Sw	112 f	0.29	0.30	0.27	0.30
Sw	113 f	0.07	0.09	0.08	0.08
Sw	114 f	< 0.02	< 0.02	< 0.02	< 0.02
Sw	115 f	< 0.02	0.03	< 0.02	0.02

f...filtrated samples (0.1 μm membrane)

n...not filtrated samples

From the results shown in Table IV a good agreement between values obtained directly from calibration curves and by the technique of standard additions can be seen. From the results it can be concluded that for the studied types of waters the membrane filtration (0.1 μm) of samples did not influence either the concentrations found or the precision of the analysis.

Standard deviation was calculated from 11 parallel measurements of water sample with concentrations of 0.29, 1.25 and 3.48 $\mu\text{gBe/l}$. This standard deviations were found to be 6.37%, 3.80% and 2.52%, respectively, when measured with a normal graphite tube and modification of samples by addition of 100 mg/l of Mg. For measurement with Ta-coated tube the standard deviations found for the same samples were 6.13%, 3.01% and 1.78%, respectively.

The detection limit was calculated as three times the standard deviation of the blank (3σ). It was determined from ten values. A tantalum-coated tube yields a detection limit 0.02 $\mu\text{gBe/l}$ while an ordinary graphite tube with a matrix modifier only 0.07 $\mu\text{gBe/l}$. The higher detection limit originates from a beryllium blank of the magnesium nitrate.

Numerous samples of natural waters, e.g. surface- and rain water, were analysed by the procedures described above. Examples of the results found are given in Table IV. Considering that according to different national guidelines^[17,18] the beryllium concentration should not exceed a limit of 0.2 $\mu\text{g/l}$, the results found show very high environmental pollution in the north area of Bohemia. Similar results were obtained in case of rain waters taken from the investigated regions.

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