

DETERMINATION OF BERYLLIUM IN VARIOUS TYPES OF NATURAL WATERS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The procedure for the reliable determination of Be in natural waters by ETAAS was elaborated. Various modifiers (EDTA, $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$ and the mixture of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$) for the determination of beryllium was examined. The applicability of the selected $\text{Mg}(\text{NO}_3)_2$ as the appropriate and generally used modifier for the determination of Be in the different types of natural waters by ETAAS has been confirmed. The accuracy of the method was verified by analyzing of the certified reference material of drinking water ("Trace Metals in Drinking Water"). The real drinking waters and waste waters with the reference values of Be concentration, spiked tap water, mineral waters and model river water were utilized for the determination of Be. Using $\text{Mg}(\text{NO}_3)_2$ for modification, the detection limit of $0.07 \mu\text{g L}^{-1}$, the quantification limit of $0.22 \mu\text{g L}^{-1}$ and characteristic mass of 3.7 pg of Be were obtained. The recovery was in the range 95–111% and (%) RSD value was less than 8%.

KEYWORDS: Beryllium, ETAAS, Magnesium nitrate, Chemical modifier, Natural waters.

INTRODUCTION

Beryllium is one of the most toxic elements in the periodic table. It is responsible for the often-fatal lung disease, Chronic Beryllium Disease (CBD) or berylliosis, and is listed as a Class A EPA carcinogen (Taylor *et al.*, 2003). Although, acute and chronic beryllium poisoning occurs mainly by the inhalation of industrial gases and dust, the determination of trace amounts of beryllium in natural waters is of interest as it can indicate environmental pollution and could provide some information of the metal uptake trough these sources. According to different national guidelines, the beryllium concentration in tap or surface water should not exceed a limit 0.1 resp. $0.2 \mu\text{g L}^{-1}$.

Different methods have been used for the determination of beryllium in waters. These include molecular spectrophotometry (Madrakian *et al.*, 2005; Amin 2001; Singh *et al.*, 1998; Chamsaz *et al.*, 2010), spectrofluorimetry (Rama *et al.*, 2004; Jiang and He, 2003), inductively coupled plasma atomic emission spectrometry (ICP–AES) (McAlister and Horwitz 2005; Okamoto *et al.*, 2002; Wu *et al.*, 2001), inductively coupled plasma mass spectrometry (ICP–MS) (Forrer *et al.*, 2001a; Forrer *et al.*, 2001b; Wen *et al.*, 2000), flame atomic absorption spectrometry (FAAS) (Yamini *et al.*, 2002; Afkhami *et al.*, 2001; Suvardhan *et al.*, 2006) or electrothermal atomic absorption spectrometry (ETAAS) (Peng and Kuo, 2000; Burguera *et al.*, 1999; Sun, 1999; Recknagel *et al.*, 1997; Korečková–Sysalová, 1997; Černohorský and Kotrlý, 1995; Kubová *et al.*, 1994; Nakamura *et al.*, 1994; Robles and Aller, 1994; Hiraide *et al.*, 1994; Yang and Ni, 1994; Burguera *et al.*, 2000; Vanhoe *et al.*, 1988; Fangruo *et al.*, 1990; Shan *et al.*, 1989; Lytle *et al.*, 1993). Among these methods, ETAAS offers relatively low cost, simplicity, high selectivity and sensitivity. In ETAAS, the use of various chemical modifiers such as magnesium nitrate (Burguera *et al.*, 1999; Korečková–Sysalová, 1997; Hiraide *et al.*, 1994; Vanhoe *et al.*, 1988; Fangruo *et al.*, 1990), ammonium phosphomolybdate (Lytle *et al.*, 1993), lanthanum nitrate (Fangruo *et al.*, 1990), calcium nitrate (Sun

1999; Fangruo *et al.*, 1990), aluminium nitrate (Sun 1999; Černohorský and Kotrlík, 1995; Fangruo *et al.*, 1990), strontium nitrate (Fangruo *et al.*, 1990), palladium nitrate (Yang and Ni, 1994), ammonium nitrate (Kubová *et al.*, 1994), isomorphous metals, such as Eu, Ir, Sm (Burguera *et al.*, 1999), Lu (Burguera *et al.*, 1999; Burguera *et al.*, 2000) and Zr (Castro *et al.*, 2009) have been reported for the determination of beryllium in biological and environmental samples.

In the present work, five various chemical modifiers (EDTA, $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, and the combination of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$) were compared and the selection of the chemical modifier, suitable for all types of waters was made and applied.

METHODS

Instrumental

The determination of Be was performed on a Perkin–Elmer (Norwalk, Connecticut, USA) model 5100 PC atomic absorption spectrometer with Zeeman background correction, equipped with an HGA–700 graphite furnace and an AS–71 autosampler. Pyrolytically coated THGA graphite tubes (Perkin–Elmer, USA) with pre–inserted pyrolytic L'vov platforms were employed. Measurements were made using a Be hollow cathode lamp (Perkin–Elmer, USA) at 234.9 nm with a 0.7 nm spectral bandwidth and an operating current of 30 mA. Modifiers were injected (10 μL) after sample injection (20 μL). Argon was used as a furnace sheath gas. Measurements were performed in the integrated absorbance mode. Temperature program for the determination of Be in water samples by ETAAS is shown in Table 1.

Reagents and samples

All reagents were of analytical grade. Concentrated HNO_3 , concentrated HCl, standard stock solution of 1000 mg L^{-1} for Be ($\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ in 0.5 mol L^{-1} HNO_3), stock solution of 10 g L^{-1} for Pd ($\text{Pd}(\text{NO}_3)_2$ in 0.5 mol L^{-1} HNO_3), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, EDTA, $\text{Fe}(\text{NO}_3)_3$, KCl, NaCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ were obtained from Merck (Darmstadt, Germany).

Certified reference material (CRM) “Trace metals in drinking water” (TMDW) with certified value of Be concentration was obtained from High–Purity Standards (Charleston, Canada). Waste waters (WW4, WW5) and drinking waters (DW4, DW5) with reference values of Be concentrations were obtained from Aslab (Water Research Institute, Prague, Czech Republic).

Deionized water (PRO–PS Labconco system, Kansas City, Kansas, USA) was used to prepare all the solutions and to rinse the previously cleaned laboratory ware.

Working standard solutions of Be (1–10 $\mu\text{g L}^{-1}$) were prepared by suitable dilution of the standard stock solution in 0.2% (v/v) HNO_3 .

Modifiers were also prepared in 0.2% (v/v) HNO_3 . Masses of the used modifiers were: 15 μg of $\text{Mg}(\text{NO}_3)_2$, 5 μg of Pd, 50 μg of $\text{Ca}(\text{NO}_3)_2$, 100 μg of EDTA, and 5 μg of Pd + 15 μg of $\text{Mg}(\text{NO}_3)_2$ in 10 μL .

A model sample of synthetic river water (SRW) was prepared by dissolving 294 mg of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 216 mg of NaCl, 8.6 mg of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 9.5 mg of KCl and 7.3 mg of $(\text{NH}_4)_2\text{HPO}_4$ in 1 L of deionized water (Chakraborti *et al.*, 1987).

Tap water (TW) was collected in our laboratory (Bratislava, Slovakia). Commercial mineral waters “Korytnica” sparkling (MWS) and “Korytnica” quiet (MWQ) were also used for analyses. Natural water samples (tap and mineral waters) were after sampling acidified by addition of 5 mL of 65% (w/v) nitric acid to 1 L of water sample.

RESULTS AND DISCUSSION

Temperature program optimization

Without the addition of any modifier, Be was gradually lost at temperatures above 1100°C. Five various modifiers (EDTA, $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, and the combination of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$) were used and compared in this work. In the presence of these modifiers, higher pyrolysis temperatures were achieved (Figure 1).

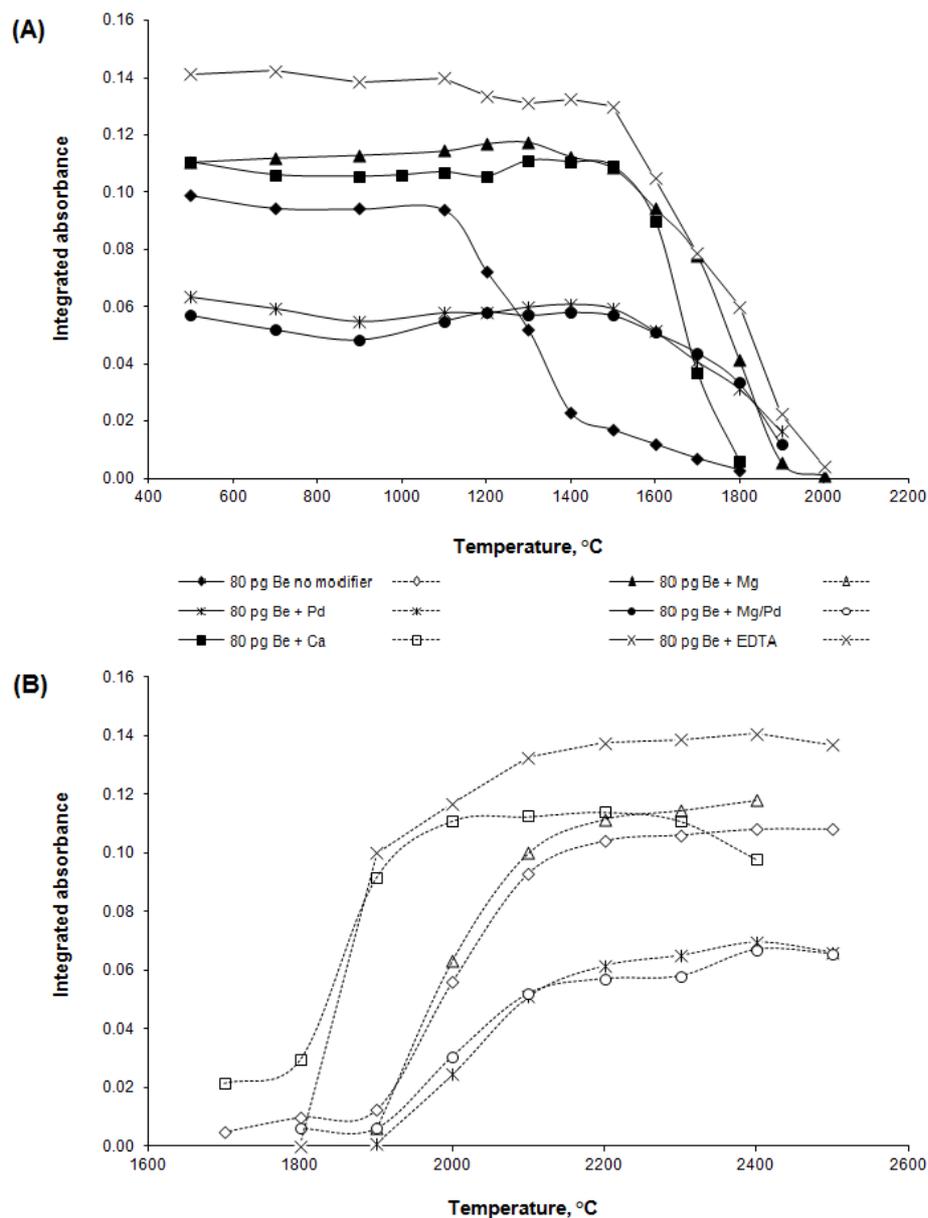


Figure 1. Pyrolysis curves (compact lines) (A) and atomization curves (broken lines) (B) for Be (80 pg) without and with chemical modification

The optimum pyrolysis temperatures selected for the used modifiers are introduced in Table 1. The optimum atomization temperature was used the same (2300 °C) in all cases.

Table 1. Temperature program for the determination of beryllium in waters by ETAAS

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (mL min ⁻¹)
Drying	110	1	20	250
Drying	130	5	30	250
Pyrolysis	1100 ^a /1300 ^b /1400 ^c	10	20	250
Atomization	2300	0	5	0
Cleaning	2400	1	2	250

^ameasurements without the addition of any modifier; ^bmeasurements with Ca(NO₃)₂, Mg(NO₃)₂ and EDTA; ^cmeasurements with (Pd(NO₃)₂ and Pd(NO₃)₂+Mg(NO₃)₂

Analytical figures of merit

Analytical characteristics of the methods with the various chemical modifiers, including characteristic mass calculated as $m_0=0.0044 \times 20/a$, where a is the slope of the calibration curve and sample volume is 20 μL , the limit of detection (LOD) calculated as $3SD/a$, where a is the slope of the calibration curve and SD the standard deviation of 10 consecutive measurements of blank solutions, the limit of quantification (LOQ) calculated on the basis of $10SD/a$ (Currie, 1999) and precision (RSD, evaluated by ten replicate analyses of solutions containing 80 μg of beryllium) are summarized in Table 2.

Sensitivity is increasing in order: $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2 < \text{Pd}(\text{NO}_3)_2 < \text{Ca}(\text{NO}_3)_2 < \text{no modifier} < \text{Mg}(\text{NO}_3)_2 < \text{EDTA}$. Precision is increasing in order: $\text{Pd}(\text{NO}_3)_2 < \text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2 < \text{no modifier} < \text{Ca}(\text{NO}_3)_2 < \text{Mg}(\text{NO}_3)_2 < \text{EDTA}$.

Table 2. Analytical characteristics

Used modifier	a^a	m_0^b (pg)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	RSD (%)
no modifier	0.0251	3.5	0.08	0.25	4.7
$\text{Pd}(\text{NO}_3)_2$	0.0137	6.4	0.09	0.29	7.2
$\text{Mg}(\text{NO}_3)_2$	0.0280	3.1	0.07	0.22	3.1
$\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$	0.0132	6.7	0.10	0.32	5.7
EDTA	0.0324	2.7	0.05	0.18	2.2
$\text{Ca}(\text{NO}_3)_2$	0.0232	3.8	0.07	0.23	4.3

^aslope of the calibration curve for Be standard solutions without and with addition of modifiers; ^bcharacteristic mass; LOD–Limit of detection; LOQ–Limit of quantification; RSD–Relative standard deviation

Determination of Be in waters

Determination of Be in the CRM “Trace metals in drinking water” and in the spiked synthetic river water without the addition of any modifier and in the presence of the studied modifiers.

CRM “Trace metals in drinking water” (TMDW) with certified value of Be concentration obtained from High–Purity Standards (Charleston, Canada) was used to verify the accuracy of the method. The evaluation of beryllium was done by calibration curve method and also by standard addition method (Table 3). Relative analytical errors (in %) were different depending on the used modifier and evaluation method. Using no modifier and standard addition method for evaluation, the analytical error for the CRM sample was relatively the same as using calibration curve method for evaluation and $\text{Mg}(\text{NO}_3)_2$ as the chemical modifier.

The synthetic river water was chosen as the sample with very complex matrix. For the determination of Be in the synthetic river water, various chemical modifiers were applied and the selection of the modifier was done. After spiking Be ($4 \mu\text{g L}^{-1}$) to the sample, evaluation of beryllium was done by calibration curve method and also by standard addition method (Table 4).

Table 3. Determination of beryllium in the CRM^a “Trace metals in drinking water” without the addition of any modifier and in the presence of studied modifiers

Modifier	Determined beryllium concentration ($\mu\text{g L}^{-1}$)			
	CCM	E (%)	SAM	E (%)
No modifier	34.4±1.12	72	19.3±1.39	4
$\text{Pd}(\text{NO}_3)_2$	26.2±2.08	31	17.5±2.22	13
$\text{Mg}(\text{NO}_3)_2$	19.4±1.25	3	19.6±1.28	2
$\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$	22.6±2.09	13	23.0±1.47	15
EDTA	19.5±2.41	3	21.0±1.57	5
$\text{Ca}(\text{NO}_3)_2$	18.8±0.61	6	19.3±1.27	3

^a certified content of beryllium: $20.0 \pm 5.0 \mu\text{g L}^{-1}$; CCM–Calibration curve method; E–Relative analytical error; SAM–Standard addition method

The results in Table 4 show fundamental differences between these modifiers when they are applying for the determination of Be in synthetic river water by ETAAS. Recoveries were different

depending on the used modifier and the evaluation method. Using standard addition method for evaluation without modifier, recoveries for the spiked samples were in the range 99–111%. Using calibration curve method for evaluation without modifier, recoveries for the spiked synthetic river water were around 248%. Using $\text{Mg}(\text{NO}_3)_2$ as the chemical modifier and calibration curve method for evaluation, recovery for the spiked sample of synthetic river water was 104%.

Table 4. Determination of beryllium in the spiked synthetic river water ($4 \mu\text{g L}^{-1}$) without the addition of any modifier and in the presence of studied modifiers

Modifier	Determined beryllium concentration ($\mu\text{g L}^{-1}$)			
	CCM	R (%)	SAM	R (%)
No modifier	9.92±0.51	248	4.45±0.28	111
$\text{Pd}(\text{NO}_3)_2$	6.97±0.18	174	4.37±0.10	109
$\text{Mg}(\text{NO}_3)_2$	4.15±0.31	104	3.97±0.29	99
$\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$	4.45±0.07	111	4.02±0.24	102
EDTA	4.80±0.05	120	4.08±0.49	102
$\text{Ca}(\text{NO}_3)_2$	4.11±0.12	103	4.16±0.08	104

CCM–Calibration curve method; R–Recovery; SAM–Standard addition method

In spite of the fact that also EDTA seems to be the appropriate chemical modifier leading to an increased sensitivity, precision and lower LODs values (Table 2), similar accuracy (Tables 3 and 4), worst recoveries compared to $\text{Mg}(\text{NO}_3)_2$ (see Table 4) were observed. We have concluded that Mg (as the generally used “ashing aid” for pyrolysis step) is more appropriate chemical modifier, universal for all types of the studied waters. Magnesium nitrate as the modifier stabilized beryllium and inhibits the formation of the relatively volatile $\text{Be}(\text{OH})_2$. Further experiments for the determination of Be in tap water, synthetic river water and mineral waters and for determination of Be in drinking waters and waste waters were done without modifier and using $\text{Mg}(\text{NO}_3)_2$ as the selected chemical modifier.

Determination of Be in the tap water, synthetic river water and mineral waters

Concentrations of Be in the tap water and analyzed mineral waters (MWQ and MWS) were found to be < LOD. In this case spiking of Be was also done. After spiking Be ($1 \mu\text{g L}^{-1}$ or $4 \mu\text{g L}^{-1}$) to the tap water, synthetic river water and mineral waters, evaluation of beryllium was made by calibration curve method and also by standard addition method (Table 5). Using no modifier and standard addition method for evaluation, recoveries for the all spiked samples were in the range 95–114%. Using $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier, recoveries were in the range 97–113% in any case of evaluation for the all spiked mineral waters. Using calibration curve method without the use of chemical modifier very high (%) relative analytical errors or (%) recoveries were performed, probably because of the matrix interferences.

Determination of Be in drinking waters and waste waters

Drinking waters and waste waters with reference values of Be concentrations obtained from Aslab (Water Research Institute, Prague, Czech Republic) were used to verify the accuracy of the methods. Also in this case, the different methods were used for the determination of Be in the waters (measurement without the addition of any modifier and measurement with $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier). Relative analytical errors in Be determination are shown in Table 6. Using no modifier and calibration curve method for evaluation, determined Be concentrations were around 2.5 times more compared with the reference values for the drinking waters, around 3.5 times more compared with the reference values for the waste waters. Using no modifier and standard addition method, relative analytical errors in Be determination were in the range 3–11%. Using $\text{Mg}(\text{NO}_3)_2$ as the matrix modifier, relative analytical errors in Be determination were in the range 5–9% in any case of evaluation.

Table 5. Determination of beryllium in the spiked tap water, synthetic river water and mineral water without the addition of any modifier and in the presence of $Mg(NO_3)_2$

Sample	Be added ($\mu g L^{-1}$)	Determined beryllium concentration ($\mu g L^{-1}$)							
		No modifier				$Mg(NO_3)_2$			
		CCM	R (%)	SAM	R (%)	CCM	R (%)	SAM	R (%)
TW	0	ND				ND			
	1	1.22±0.23	122	1.14±0.15	114	1.08±0.08	108	1.05±0.11	105
	4	4.58±0.35	115	4.32±0.22	108	3.95±0.25	99	4.28±0.31	107
SRW	0	ND				ND			
	1	2.31±0.18	231	0.95±0.11	95	1.13±0.15	113	0.99±0.23	99
	4	9.92±0.51	248	4.45±0.28	111	4.15±0.31	104	3.85±0.29	96
MWQ	0	ND				ND			
	1	1.34±0.30	134	1.10±0.15	110	0.97±0.13	97	0.99±0.21	99
	4	5.14±0.18	129	3.88±0.28	97	4.19±0.29	105	3.92±0.17	98
MWS	0	ND				ND			
	1	1.76±0.22	176	1.12±0.20	112	1.09±0.20	109	1.03±0.19	103
	4	6.62±0.35	166	3.96±0.14	99	4.12±0.18	103	3.78±0.28	95

CCM—Calibration curve method; R—Recovery; SAM—Standard addition method; TW—Tap water; SRW—Synthetic river water; MWQ—Mineral water “Korytnica” quiet; MWS—Mineral water “Korytnica” sparkling; ND—Not detected

Table 6. Determination of beryllium in the drinking waters and waste waters without the addition of any modifier and in the presence of $Mg(NO_3)_2$

Sample	Reference content ($\mu g L^{-1}$)	Determined beryllium concentration ($\mu g L^{-1}$)							
		No modifier				$Mg(NO_3)_2$			
		CCM	E (%)	SAM	E (%)	CCM	E (%)	SAM	E (%)
DW4	1.57	4.03±0.18	157	1.62±0.38	3	1.67±0.12	6	1.46±0.21	7
DW5	1.67	4.00±0.23	139	1.49±0.12	11	1.79±0.27	7	1.54±0.17	8
WW4	1.52	4.66±0.29	207	1.38±0.24	9	1.66±0.18	9	1.40±0.19	8
WW5	5.00	17.1±0.44	242	4.80±0.19	4	4.55±0.15	9	4.76±0.28	5

CCM—Calibration curve method; E—Relative analytical error; SAM—Standard addition method; DW—Drinking water; WW—Waste water

CONCLUSIONS

The results presented in this work have confirmed the applicability of $Mg(NO_3)_2$ as the chemical matrix modifier for the determination of Be in the different types of waters by ETAAS. Magnesium nitrate as the modifier stabilized beryllium and inhibits the formation of the relatively volatile $Be(OH)_2$. In this case, both evaluation methods (calibration curve method and standard addition method) can be used with satisfactory result. Sensitivity and precision are increased compared with the determination without the addition of any modifier. For the determination of Be in natural waters without modifier, the evaluation of a standard addition method is necessary. The described method using $Mg(NO_3)_2$ as a matrix modifier can be used for rapid and reliable determination of Be in different types of waters (such as tap, river, mineral and waste waters).

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