

**Slurry sampling high-resolution continuum source electrothermal  
atomic absorption spectrometry for direct beryllium  
determination in soil and sediment samples after elimination of  
SiO interference by least-squares background correction**

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## **Abstract**

In this work a simple, efficient, and environmentally-friendly method is proposed for determination of Be in soil and sediment samples employing slurry sampling and high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS-ETAAS). The spectral effects originating from SiO species were identified and successfully corrected by means of a mathematical correction algorithm. Fractional factorial design has been employed to assess the parameters affecting the analytical results and especially to help in the development of the slurry preparation and optimization of measuring conditions. The effects of seven analytical variables including particle size, concentration of glycerol and HNO<sub>3</sub> for stabilization and analyte extraction, respectively, the effect of ultrasonic agitation for slurry homogenization, concentration of chemical modifier, pyrolysis and atomization temperature were investigated by a 2<sup>7-3</sup> replicate (n = 3) design. Using the optimized experimental conditions, the proposed method allowed the determination of Be with a detection limit being 0.016 mg kg<sup>-1</sup> and characteristic mass 1.3 pg. Optimum results were obtained after preparing the slurries by weighing 100 mg of a sample with particle size < 54 μm and adding 25 mL of 20% w/w glycerol. The use of 1 μg Rh and 50 μg citric acid was found satisfactory for the analyte stabilization. Accurate data were obtained with the use of matrix-free calibration. The accuracy of the method was confirmed by analysis of two certified reference materials (NIST SRM 2702 Inorganics in Marine Sediment and IGI BIL-1 Baikal Bottom Silt) and by comparison of the results obtained for ten real samples by slurry sampling with those determined after microwave-assisted extraction by inductively coupled plasma time of flight mass spectrometry (TOF-ICP-MS). The reported method has a precision better than 7 %.

**Keywords:** Beryllium determination; Soil and sediment analysis; High-resolution continuum source AAS; Electrothermal atomic absorption spectrometry; Slurry sampling; Fractional

factorial design; Microwave-assisted extraction; Inductively coupled plasma mass spectrometry

## 1. Introduction

Among trace elements with toxicological properties, Be is one of the most toxic elements in the periodic table [1] and has been increasingly recognised having a significant environmental impact [2, 3]. Because soil and other environmental samples are sources of Be for entering the food chain [1, 4, 5], the determination of Be in environmental matrices is of significant interest [6-18]. Beryllium concentrations in soil and sediments vary based on geology and anthropogenic inputs [1, 3]; in general in non-contaminated soils the concentration is within a range from 0.1–3 mg kg<sup>-1</sup> [7, 19, 20].

Many analytical methods [4, 6-18, 21-29] were employed for reliable quantification of trace Be in environmental and geological samples with atomic absorption spectrometry with electrothermal atomization (ETAAS) [7, 11-17, 21-23, 29-32] being still the most widely used in routine analytical practice for trace elements analysis. However, determination of Be in soils and sediments by ETAAS is not easy because of the complexity of the matrix [7, 12, 21, 22, 29, 31]. Prior to the analytical measurement, usually fusion or effective dissolution method must be utilized in order to release this element from challenging sample matrices containing refractory materials such as silicates and/or silicoaluminate and high-fired beryllium oxide [23, 31, 33]. Complete dissolution of samples for the determination of total Be thus usually requires time consuming heating of the samples with different mixtures of HF in combination with acids such as HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, etc. [7, 12, 13, 21, 23, 30, 31]. Moreover, due to the presence of other ions in the matrix of samples prepared this way, serious interference problems causing mainly light scattering and/or pre-atomization losses of Be during higher ashing temperature were previously reported [7, 12, 21, 22, 29]. To achieve an interference-free and accurate determination of Be in desired samples, separation/preconcentration methods have been widely employed [7, 12, 21, 22]. Moreover,

as shown by several authors [13, 29-31] setting the experimental conditions according to the stabilized temperature platform furnace concept (STPF) [34] with the use of appropriate chemical modifier enables significant reduction of the interference for direct analysis of Be in complex environmental matrices.

Compare to traditionally used digestion methods for preparation of sediments and soils, slurry sampling is better fitted for these powdered samples as it is significantly more time efficient, less costly, reduces the risk of contamination or analyte loss, and does not usually involve the use of hazardous reagents making it more in compliance with green chemistry trends [35-37]. However, while the more conventional wet digestion/extraction methods employ HF to remove/separate the complex and refractory matrix [7, 12, 13, 21, 23, 31], this matrix persists when solid samples are analyzed as slurries as this matrix cannot be removed by thermal pre-treatment [38, 39]. Consequently, spectral interference caused frequently by molecular absorption due to diatomic molecules with pronounced fine structure [38, 40, 41], may be the major obstacle in the application of this technique due to limited background correction capability of conventional line source atomic absorption spectrometers [38]. In several cases even the use of a highly efficient Zeeman effect background correction with a magnet at the atomizer is not useful for this purpose [41, 42]. The introduction of high resolution continuum source AAS (HR-CS-AAS) represented a significant change in this direction due to its unsurpassed background correction capabilities [38, 43]. Previously, a number of trace elements in a wide variety of complex sample matrices was successfully determined by HR-CS-ETAAS using direct solid sample analysis without any interference [35, 38, 40, 43]. However, according to the best our knowledge to this date no method has been published for the purpose of direct determination of Be in soils and sediments solids by the ETAAS method.

In this work, investigation of molecular absorption under high resolution revealed a fine structure of SiO band directly interfering with the determination of Be at the resonance line 234.8605 nm. The correction of distinct molecular structures directly overlapping the analyte line was performed by applying the least squares background correction (LSBC) [43]. With the employment of the fractional factorial design an optimization of the sample preparation, dispensing, thermal pre-treatment and atomization parameters resulted in the development of a robust, fast, accurate and environmentally friendly method suited for routine direct determination of Be in soils and sediments by HR-CS-ETAAS.

## **2. Experimental**

### **2.1 Instrumentation**

The measurements were carried out using the model contrAA 600 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with transversely heated graphite furnace and autosampler MPE 60. Xenon short-arc lamp with a nominal power of 300 W, operating in a hot-spot mode was the light source. The double monochromator (prism and echelle grating) combined with a CCD array detector with 588 pixels ensures the unique resolution with a spectral bandwidth of below 2 pm/pixel. Peak area absorbance values were measured. The primary analytical line 234.8605 nm for Be was used for the measurement. Pyrolytically coated graphite tubes (Analytik Jena, Part no. 407–152.023 Schunk, Germany, Batch-No: 103074348-46/13) with preinstalled PIN platform and integrated contacts for transverse heating were used. Argon (99.999 %, Linde Gas, Inc., Czech Republic) was used as the sheating gas; the internal gas flow in the graphite tube was interrupted during the atomization step.

The microwave-assisted extraction of samples was carried out in the Speedwave<sup>TM</sup> MWS-3+ (Berghof, Germany) microwave system with the maximum total output of the

microwave generator 1450 W. The sample throughput of the MWS-3+ system was increased by using the Multitube System (MT) employed with the DAC-100S digestion vessels [44]. This arrangement allows simultaneous extraction/digestion of three samples in one DAC-100S PTFE vessel by placing three MT PFA tubes into each of the vessels.

Inductively coupled plasma time of flight mass spectrometer Optimass8000 (GBC Scientific Equipment Pty. Ltd., Australia) [45] was used in several cases for comparative measurements. Samples of slurries were sonicated using a Sonorex Super RK52 ultrasonic bath (35 kHz, RF-power 240 W; BANDELIN electronic GmbH & Co. KG, Germany). The turbidity was measured using a photometer Nephla LPG 239 (Dr. Lange GmbH, Germany) at the working wavelength of 860 nm. The scattered light is measured at a 90° angle through the bottom of the cell without reflection against a dark background and displayed digitally as a measured value. The measured values correspond to formazine nephelometric units (FNU) (measurement range: 0.001 to 1000 FNU) according to DIN EN 27027 or ISO 7027.

Powder X-ray diffraction data (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) were collected by an independent accredited analytical laboratory using the D8 Advance diffractometer (Bruker AXS, Germany) with Bragg-Brentano  $\Theta$ - $\Theta$  goniometer (radius 217.5 mm) equipped with a secondary beam curved graphite monochromator and Na(Tl)I scintillation detector. The generator was operated at 40 kV and 30 mA. The scan was performed at room temperature from 5 to 70° (2  $\Theta$ ) in 0.02° step with a counting time of 5 s per step.

## **2.2 Reagents and standards**

Beryllium solution of 1 g L<sup>-1</sup> Be in 3% HNO<sub>3</sub> was obtained from VUK Panenske Brezany Ltd. (Czech Republic). Nitric acid (65%, m/m) of Selectipur quality and glycerol (99.6%, p.a.) were purchased from (Lach-Ner, Neratovice, Czech Republic). Laboratory grade Triton X-100 (4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol) and silicon dioxide

(99.8%) were obtained from Sigma-Aldrich (USA). The solution of 1 g L<sup>-1</sup> of Rh in 10% v/v HCl was obtained from SCP Science (Canada). Solutions of 25 g L<sup>-1</sup> of citric acid (Lachema, Brno, Czech Republic) and that of 100 g L<sup>-1</sup> ammonium fluoride (Sigma-Aldrich, USA), were prepared by dissolving these pro-analysis grade salts in water. Solutions were prepared using deionised water of 0.05 µS cm<sup>-1</sup> conductivity using the UltraClear (SG, Germany) pure water system.

### **2.3 Quality assurance and quality control**

Commercially supplied quality control materials of SRM 2702-Inorganics in Marine Sediment and Baikal Bottom Silt BIL-1 (no. 7126-94) were purchased from National Institute of Standards & Technology, USA, respectively from Siberian Branch of Russian Academy of Sciences, Institute of Geochemistry, Russia. The certificates for the materials ensured a particle size smaller than 70 µm in SRM 2702 and smaller than 25 µm for the major fraction (92.3 %, m/m) in BIL-1.

### **2.4 Samples**

Ten samples of soils and sediment from the bottom of the surface water system of the Elbe River were obtained from the Institute of Environmental and Chemical Engineering of the University of Pardubice and Water management laboratories, Ltd. (Pardubice) respectively, and collected in the neighborhood of Pardubice (Czech Republic). The dried samples were subjected to a grinding process in a mortar and then sieved through nylon (polyester) sieves for a particle size of < 200, 90 and 54 µm and kept in sealed plastic vials until analysis.

### **2.5 Procedure for slurry analysis**

The slurries, similarly as all the other samples investigated in this study, were prepared in triplicate. The slurries were prepared using the following procedure. An accurately weighed amount of about 100.0 mg of sample (fractions < 200, 90 or 54  $\mu\text{m}$ ) was transferred into a 25 mL calibrated flask and two drops of Triton X-100 were added to ensure wetting of the sample. Suitable amounts of glycerol and/or nitric acid were added to give a final solution containing 5, 10, 20 % (w/w) glycerol and 0.1, 5 and 10 % (w/w)  $\text{HNO}_3$ . The slurries were then sonicated for 1, 3 or 5 min in an ultrasonic bath. Thereafter, approximately 1 mL of the slurry was transferred into the autosampler cup and then only manual shaking was necessary a few moments before the injection. Finally, 25  $\mu\text{L}$  of the slurry plus 0–10  $\mu\text{L}$  of the chemical modifier mixture containing 0.5  $\text{g L}^{-1}$  of Rh and 25  $\text{g L}^{-1}$  of citric acid were injected into the graphite furnace by means of the auto-sampler and subjected to the heating program presented in Table 1. The preparation of the reagent blank was subjected to the procedure as outlined above, to correct for any possible trace amount of the analyte in the reagents used for slurry preparation.

While the calibration using five aqueous standards within a range of 0–20  $\mu\text{g L}^{-1}$  of Be was performed by means of the instrument software, the calibration relative to a certified reference material using five standards was manually pre-mixed using Baikol Bottom Silt BIL-1 quality control material containing 2.7 ( $\pm 0.4$ )  $\text{mg kg}^{-1}$  of Be using the following way: the portions of material (25.0–100.0 mg) were transferred into a 25 mL volumetric flask, two drops of Triton X-100 were added and then diluted to final volume with 20% (m/m) glycerol. The resulting mixtures were shaken vigorously prior to analysis.

## **2.6 Procedure for microwave extraction**

For comparative purposes, an adapted microwave-assisted procedure [44] was used. Sample mass of 10.0 mg was weighed into the MT-tubes and 5 mL of 100  $\text{g L}^{-1}$  of  $\text{NH}_4\text{F}$  was

added. These MT-tubes were placed into the outer digestion vessel, where 20 mL of 100 g L<sup>-1</sup> NH<sub>4</sub>F were added to ensure that the level of NH<sub>4</sub>F was higher in the outer vessel than in the PFA tubes. The evaporation of the solution from the PFA tubes was thus prevented by compensation of the vapour pressures [44]. The extractions were performed at the temperature of 190 °C held for 15 minutes with a ramp set at 5 min at 50 % power of the MWS-3+. The resulting solutions were diluted to 10 mL with deionised water. Before analysis all solutions were filtrated through a 0.45 µm Nylon syringe filters (Whatman Autovial).

Determination of Be in the extracts by a reference oTOF-ICP-MS method was done using standard quantitative calibration with aqueous standards and Rh as an internal standard [45].

## **2.7 Sedimentation study**

The sedimentation curves were obtained by monitoring the amount of the light scattered by the suspended solid particles at an angle of 90° with respect to the light beam axis during a time interval of 140 s by a nephelometer. The suspension concentration was 0.4% (w/w) with particle fractions < 200, 95, and 50 µm in 0–40% (w/w) glycerol. The final volume of all suspensions was set to 25 mL and the samples were transferred into a beaker. The scan started (time 0) right after a 2-min stirring of the sample using a magnetic stirrer. All measurements were made in cylindrical cuvettes with a 25-ml suspension. The formazine nephelometric unit (FNU) as a function of time was divided by the initial signal (FNU<sub>0</sub>) to obtain the modified sedimentation curves.

## **2.8 Experimental design and statistical data treatment**

Two-level 2(k-p) fractional factorial design (where k is the number of factors investigated, and p describes the size of the fraction of the full factorial used), with seven

factors, one central point (C) and with three replicates ( $n = 3$ ), was used to find the optimal conditions for the extraction and to evaluate the significance of the factors (variables), as well as the interactions between them [46, 47]. The fractional factorial experimental design  $2^{7-4} + 1$  C ( $n = 3$ ) was used because of its reduced number of experiments (27 against 384 experiments using the full design) but also because no loss of significant information occurred. The studied factors were: (1) glycerol concentration (% w/w), (2)  $\text{HNO}_3$  concentration (% w/w), (3) sonification time, (4) particle size, (5) pyrolysis temperature, (6) atomization temperature, (7) concentration of modifier. All factors were evaluated at two levels, low (denoted as  $-1$ ) and high (denoted as  $+1$ ). The central point of the design space (middle value denoted as  $0$ ), i.e. the experiment, in which all the parameters have a value which is the average between their low and high level, was also added to the experiment. Table 2 summarizes the levels for the experimental design. The responses for each experiment were calculated as the average mean of integrated absorbance obtained for Be in real sediment sample and the resulting data are summarized in Table S1.

The Statistica 12 computer program (StatSoft, Inc., USA) and QC Expert<sup>TM</sup> 2.5, TriloByte Statistical Software, (Pardubice, Czech Republic) were used for data processing.

### **3. Results and discussion**

#### **3.1 Evaluation of spectral interference on Be determination**

As it is demonstrated in Fig. 1a, where the wavelength-resolved absorbance spectrum as collected on ContrAA<sup>®</sup>600 during the atomization of a slurry of NIST SRM 2702 (blue line) is shown, there is a well-structured background in the vicinity of the analytical line for Be at 234.8605 nm. This structured background may be attributed to the diatomic molecule SiO caused by silicates as this corresponds both to the reference SiO spectrum obtained from the molecule spectra database in the software (Fig. 1a, red line) and also to the spectrum

recorded with SiO<sub>2</sub>. The structured background caused by silicates is thus recognized to be the main spectral interference in the determination of Be in soil and sediment solids by ETAAS.

In such a case when the molecules causing fine-structured background at the analyte wavelength position are known, the structured background can be corrected using the HR-CS-ETAAS instrument software by the so-called least-squares background correction (LSBC) using reference spectra [43]. The SiO reference spectrum was recorded using 100 µg of SiO<sub>2</sub> which was introduced into the graphite furnace via the injection of 25 µL of 0.4 % (w/w) SiO<sub>2</sub> slurry together with the chemical modifier. The reference spectrum was stored in the method and subtracted from the sample spectrum, which removed essentially all the molecular absorption structures, as is shown in Fig. 1b. The amount of 100 µg of SiO<sub>2</sub> corresponded to the hypothetical situation when the slurry samples of 0.4 % (w/w) concentration prepared according to the description in section 2.5 would contain nothing but SiO<sub>2</sub>. The robustness of the method for the correction of spectral effect is hugely important in this particular case as not only the concentration of silicate matrix significantly varies among the analysed soil and sediment samples, but also different forms of silicate matrix are present as can be seen from available XRD spectra (see Fig. S1). In contrast to the instrumentation equipped with conventional correction system, the visibility of the spectral environment at high resolution in HR-CS-AAS may be used as a diagnostic tool in order to recognize and control the spectral interference. Moreover, the concentration values of matrix component for least-squares background correction to correct for structured background need not to necessarily match those in the respective samples. However, the concentration values must be high enough for mean value spectra to clearly show extinction values.

### **3.2 Optimization of the experimental conditions for slurry analysis**

The factors of interest in optimizing the slurry sampling included particle size, pyrolysis and atomization temperature, concentration of chemical modifier, concentration of stabilizing and extracting agent, and ultrasonic agitation. All of these factors have been according to the stabilized-temperature platform furnace (STPF) concept [34] previously reported [36, 48] as the most important in terms of influencing the accuracy of the analytical procedure when using the slurry technique.

The Box Hunter & Hunter fractional factorial design was employed to investigate the influence of all the above mentioned seven variables onto the analytical results. The maximum and minimum levels of the variables being investigated are shown in Table 2. These values were chosen following the recommendations given in the literature and according to the preliminary experiments. In order to establish the influence of the tested variables, Be integrated absorbance as the response was studied, moreover, for the resulting data presented in Table S1 also the repeatability expressed as RSD (%) is included.

The effects and significance of the variables in the extraction process were evaluated using Pareto's charts, which included a vertical line that corresponded to the 95% limit indicating statistical significance. As can be seen from Fig. 2, the analytical response is improved by increasing the atomization temperature (Factor 6) and glycerol concentration (Factor 1), as well as by reducing the analyzed particle size (Factor 4) and employed pyrolysis temperature (Factor 5). Increasing the glycerol concentration has a promoting effect onto the stabilization of the suspension; this effect is more pronounced for the fraction < 50  $\mu\text{m}$  (see Fig. S3). The suspension can be stabilized for time longer than 10 s when using the glycerol concentration up to 40 % (Fig. S3). However, huge fuming during the thermal program is observed for such a high glycerol concentration and thus for DOE experiments the investigated amount was decreased to 20 % as similarly to 40 %, 20 % glycerol concentration enables the stabilization of the suspension up to 5s which is enough to ensure a representative

aliquot of the sample to be injected into the cuvette when it is manually shaken prior to the sampling. The particle size and atomization temperature have the biggest effect on the analytical response (see Fig. 2). The benefit from smaller particles sizes when working with slurry sampling may be due to the fact that the smaller particles are both easily stabilized but also easily evaporated from the graphite furnace [36]. Although sonication is currently well established in analytical practice to provide optimum homogenization of the slurry before analysis [36] and/or to support analyte extraction, no significant influence of sonication time onto the analytical signal was observed in this study. Similarly, the concentration of nitric acid in the slurry solution within the investigated range did not affect the rate of the extraction of the analyte nor the precision of the signal measurement. Rhodium with citric acid chemical modifier was applied to the determination of Be; this chemical modifier is currently well established in our laboratory [49]. Although to this date this chemical modifier has not been recommended for stabilization of Be, it enables its stabilization up to 1400° C (see Figure S4), similarly as different chemical modifiers recommended for this purpose previously [15, 30, 31, 50]. It can be seen from the data presented in Fig. S5 that already 1 µg of Rh with 50 µg of citric acid impacts positively both the sensitivity and also the precision of the Be determination in real sample analysis. The increasing amount of chemical modifier mixture did not further increase the analytical response meaning that the lowest investigated amount was adequate for the analyte stabilization.

The experimental data presented in Table S1 were subjected to multiple regression analysis. All possible subsets regressions available in QC.Expert™ program were performed to find the best mathematical model that correlates the variables and the analytical response. For each possible combination of model terms the following criteria were monitored: F-statistic, coefficient of determination (also referred to as the R<sup>2</sup> value), Akaike's information criterion (AIC) or MEP (mean squared prediction error). A good model should have a large

value of F and  $R^2$ , small AIC value and small MEP value [51]. Based on these criteria a resulting model which presented a  $R^2 = 0.989$  and best fitted the data was found (see Table S2). The number of statistical parameters and tests which measure the quality and appropriateness of the final model fit to a set of data are presented in Table S3.

The optimization procedure was performed using the graphical approach and evaluated for factors which were revealed (see Fig. 2) to be significant. 3D surface plots for overall response desirability were built to show the effects of two variables within their studied ranges and visualize the tendency of important factors to influence the analytical response (see Fig. S6).

The optimization plot illustrated in Fig. 3 provides the optimum solution for the contributing variable combinations. The dashed lines and solid lines indicate the means and the standard deviations at 95% confidence limit for each factor, respectively. The highest value of integrated absorbance for each factor shows its optimum value. As shown on the top right hand side of Fig. 3 the desirability values for the analytical response (integrated absorbance) were set 0 for minimum (0.287), 0.5 for middle (0.5747) and 1.0 for maximum (0.8616). These values were set based on the experimental data presented in Table S1.

The individual desirability score of 1.0 selected as the target value for the optimization of the dependent factors is demonstrated at the bottom of Fig. 3 and the overall analytical response of the illustrated plots with the observed level of factors is depicted at the top (left) of Fig. 3. The analysis has shown that setting parameter 2 and 3 to the low level and parameter 1 and 4 to the high level produces the maximum attribute response. The optimum conditions thus were as follows: 20% (m/m) of glycerol, particle size < 54  $\mu\text{m}$ , pyrolysis and atomization temperature 1100  $^{\circ}\text{C}$  and 2700  $^{\circ}\text{C}$ , respectively.

### **3.3 Figures of merit**

As the slopes of the calibration lines of the matrix matched standards evaluated under the optimized conditions differ less than 10 % from that of the aqueous standard, which means that the effect of matrix was under a good control at the conditions described, the later calibration was used for quantification. This yields a model described by the following equation:  $Q_A = 8.52 \cdot 10^{-2} (9.6 \cdot 10^{-4}) [\text{Be}]$  (where  $Q_A$  = integrated absorbance and  $[\text{Be}]$  is the concentration of the analyte in  $\mu\text{g L}^{-1}$ ; standard deviation of the slope is given in parentheses). R-squared which indicates the percentage of variation that can be explained by the regression equation equals 99.96 %.

The limit of detection (LOD) and limit of quantification (LOQ) defined as the concentration that gives an integrated absorbance equal to three times and ten times of the standard deviation of ten measurements of a sample with Be concentration close to the blank were  $0.063 \mu\text{g L}^{-1}$  and  $0.209 \mu\text{g L}^{-1}$ , respectively. These values, corresponding to  $0.016 \text{ mg kg}^{-1}$  and  $0.053 \text{ mg kg}^{-1}$  of Be in the original sample, are sufficiently low so that Be content in rocks, soils and sediments samples [20] could be determined. Moreover, the LOD attained is lower approximately by two orders than the maximum limits established for Be by Czech legislation. Characteristic mass value of 1.29 pg was achieved. It was calculated using the equation  $m_0 = (0.0044 \times V) / m$ , where  $V$  is the injection volume ( $25 \mu\text{L}$ ) and  $m$  is the calibration slope. This value is comparable to the one reported for Be previously by Bettinelli et al. ( $m_0 = 1.3 \text{ pg}$ ) [31] during direct analysis of soil and sediment samples after acid dissolution. On the other hand, our value is less favorable in comparison with the value  $0.42 \text{ pg}$  published by Castro et al. [13] for coal fly ash. However, it is worthwhile to note the attained sensitivity will be impacted by the differences in the graphite furnace design. This may be confirmed by the fact that the same value of  $1.3 \text{ pg}$  achieved also in our study was reported by Welz et al. [52] to be typical for Be at the most sensitive analytical line of  $234.861 \text{ nm}$  for HR-CS-ETAAS with transversely heated graphite tube atomizer.

### 3.4 Accuracy and precision

Certified reference materials BIL-1 Baikal Bottom Silt and SRM 2702 Inorganics in Marine Sediment were analysed to test the accuracy and precision of the proposed method (see Table 3). It can be seen from the data presented in Table 3 that good agreement was achieved between the certified values and those values determined by the HR-CS-ETAAS and the reference TOF-ICP-MS method. By applying the paired *t*-test no statistical difference at the 95% confidence level was observed between the values found by both methods ( $p = 0.0903$ ). The trueness of the developed method for analyzing the real samples was evaluated also by determination of Be in real soil and sediment samples and comparison of the results with those found by the TOF-ICP-MS method after the microwave assisted extraction (see Table 4). To reveal valuable information about proportional, constant, and random error via the slope, intercept, and standard deviation of the residuals ( $S_{y/x}$ ), respectively [53], the data were compared by linear regression. A regression line between comparative values ( $x$ ) obtained by TOF-ICP-MS and results by HR-CS-ETAAS ( $y$ ) was  $y = (0.967 \pm 0.207) x + (0.208 \pm 0.397)$  with  $R^2 = 0.732$ . Additionally, Student *t*-test was applied for comparison of the results obtained by both methods at the significance level of 0.05. The results obtained using both procedures for the determination of Be were not significantly different for a 95% confidence level ( $p = 0.437$ ) and thus both methods are comparable.

The precision of the method was assessed in terms of intra-day and inter-day comparison. The analysis of the slurry sample three times during the same day was performed in order to determine the intra-day precision. Inter-day precision was calculated after the analysis of the same sample on three different days during one week. Within each series, every sample was analysed in three replicates to assess the relative standard deviation (RSD).

The RSD values of intra-day and inter-day studies typically found to be below 7 % show that the precision of the method was satisfactory (see Table 3 and Table 4).

#### **4. Conclusions**

With its ability to apply a least-squares background correction algorithms HR-CS-ETAAS has been proved as very effective to overcome the interferences occurring during the direct slurry sample analysis of Be in soils and sediments. The interference caused due to the electron excitation spectra of SiO molecules was considered to be the most serious.

Optimization by design of experiment techniques resulted in assessing experimental conditions that have enabled an environmentally friendly, fast, sensitive, interference-free, accurate and precise analysis of Be in all types of investigated samples with concentration of Be above  $0.016 \text{ mg kg}^{-1}$ . The proposed method offers an effective and simple solution of the problem which up to date has not been successfully solved in analytical practice and which is easy to follow for analytical laboratories. It can be expected that the robust and sensitive instrument solution will furthermore allow simple reliable analysis of some other trace elements strongly sensitive to the presence of silicate matrix.

Additionally, the proposed method performs very well in comparison with other techniques used in the direct analysis of solid samples or slurries for beryllium determination in environmental and geological samples, such as secondary ion mass spectrometry [54, 55], laser induced breakdown spectrometry [56] or inductively coupled plasma mass spectrometry when coupled with laser ablation [55, 57]. In comparison with works which can be found in the literature, the presented method is clearly the simplest with minimal sample preparation (e.g., no need to prepare pellets, etc.) [54, 56, 57], interference-free and does not need an internal standard [57]. Other benefits include its speed, cost-effectivity [54, 55, 57], smaller dependence on the size and structure of the particles to be analyzed [54, 57], better limit of

detection [55-58] and analytical precision at low levels [54, 55]. It also enables constructing the calibration curve with aqueous standard solutions, which is very unusual for above mentioned techniques [54, 56, 57]. On the other hand it lacks when compared in terms of linear dynamic range [54, 55, 57] or capabilities for performing depth profiling analysis and elemental mapping or real-time beryllium monitoring using portable equipment [56, 59].

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## Figure captions

**Fig. 1.** Wavelength-resolved absorbance spectra in the vicinity of the 234.8605 nm analytical line using HR-CS-GFAAS recorded for NIST SRM 2702 (a) without correction (blue line) and (b) after correction using LSBC and SiO<sub>2</sub> as a reference spectrum in the presence of 1 µg Rh + 50 µg citric acid. Pyrolysis and atomization temperatures were 1000 and 2400 °C, respectively. Molecule spectrum of SiO obtained from method library is also included (Fig. 1a, red line).

**Fig. 2** Pareto chart of the standardized effects in the fractional factorial design  $2^{7-3}$  for the study of variables (1) glycerol concentration, (2) HNO<sub>3</sub> concentration, (3) sonification time, (4) particle size, (5) pyrolysis temperature, (6) atomization temperature and (7) volume of chemical modifier.

**Fig. 3.** Profiles for predicated values and desirability function evaluated for integrated absorbance of Be obtained from repeated (n = 3) real sample analysis using the slurry sampling technique. Dashed line indicated current values after optimization.

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Table 1 Electrothermal program

Step	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold (s)	Gas flow (L min <sup>-1</sup> )
Drying 1 <sup>a</sup>	100	20	40	2.0
Drying 2	280	10	5	2.0
Pyrolysis	1100 <sup>b</sup>	100	1	2.0
	1100 <sup>b</sup>	0	10	0.0
Atomization	2700 <sup>b</sup>	3000	2	0.0
Cleaning	2800	500	1	2.0

<sup>a</sup> Injection of 25 µL of a sample together with appropriate volume of mixture of 25 g L<sup>-1</sup> citric acid with 0.5 g L<sup>-1</sup> Rh. The slurry was manually shaken in the autosampler cup using a polypropylene tip a few moments before collecting.

<sup>b</sup> The pyrolysis and atomization temperatures, similarly as the volume of the chemical modifier mixture used for the measurements varied according to the scheme presented in Table 2.

Table 2 Variables and levels investigated using the fractional factorial experimental design

Variables	-1	0	+1
1 Glycerol concentration (% w/w)	5	10	20
2 HNO <sub>3</sub> concentration (% w/w)	0.1	5.0	10
3 Sonification time (min)	1	3	5
4 Particle size (μm)	< 54	< 90	< 200
5 Pyrolysis temperature (°C)	900	1200	1500
6 Atomization temperature (°C)	2300	2500	2700
7 Chemical modifier (μL) <sup>a</sup>	2	6	10

<sup>a</sup> Volume of a mixture containing 25 g L<sup>-1</sup> of citric acid and 0.5 g L<sup>-1</sup> of Rh.

Table 3 Concentrations of Be in soil and sediment reference samples determined by HR-CS-ETAAS and TOF-ICP-MS methods

	Certified (mg kg <sup>-1</sup> )	Found (mg kg <sup>-1</sup> ) <sup>a</sup>		RSD (%)	
		TOF-ICP-MS	HR-CS-AAS	Intra-day	Inter-day
BIL-1	2.7 ± 0.4	2.4 ± 0.2	2.7 ± 0.1	2.1	3.5
SRM 2702	3.0 <sup>b</sup>	2.5 ± 0.4	2.90 ± 0.06	1.0	0.1

<sup>a</sup> Mean of triplicate determinations with 95% confidence level.

<sup>b</sup> Indicative value.

Table 4 Determination of Be in soils and sediments: comparison of methods

Sample	Concentration <sup>a</sup> (mg kg <sup>-1</sup> )		RSD (%) <sup>b</sup>	
	TOF-ICP-MS	HR-CS-ETAAS	Intra-day	Inter-day
1	1.89 ± 0.19	1.65 ± 0.13	3.9	2.1
2	1.78 ± 0.15	1.9 ± 0.2	4.7	5.0
3	1.72 ± 0.14	1.88 ± 0.08	2.2	5.3
4	2.42 ± 0.12	2.65 ± 0.09	1.7	1.3
5	2.24 ± 0.10	2.7 ± 0.2	3.7	0.2
6	1.85 ± 0.17	1.94 ± 0.09	2.4	3.2
7	2.13 ± 0.50	2.16 ± 0.07	1.7	6.9
8	1.77 ± 0.09	2.11 ± 0.01	0.3	3.4
9	2.13 ± 0.12	2.04 ± 0.09	2.3	3.5
10	0.99 ± 0.07	1.24 ± 0.07	3.0	4.6

<sup>a</sup> Each value is the mean ± 2 SD (n = 3).

Fig. 1

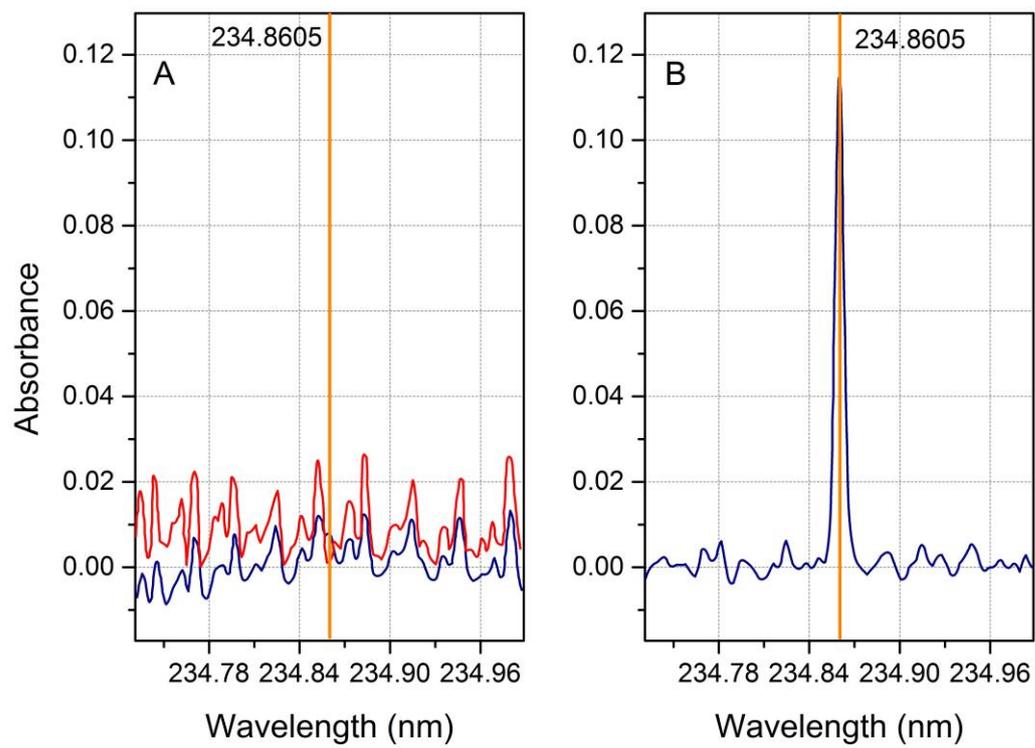


Fig. 2

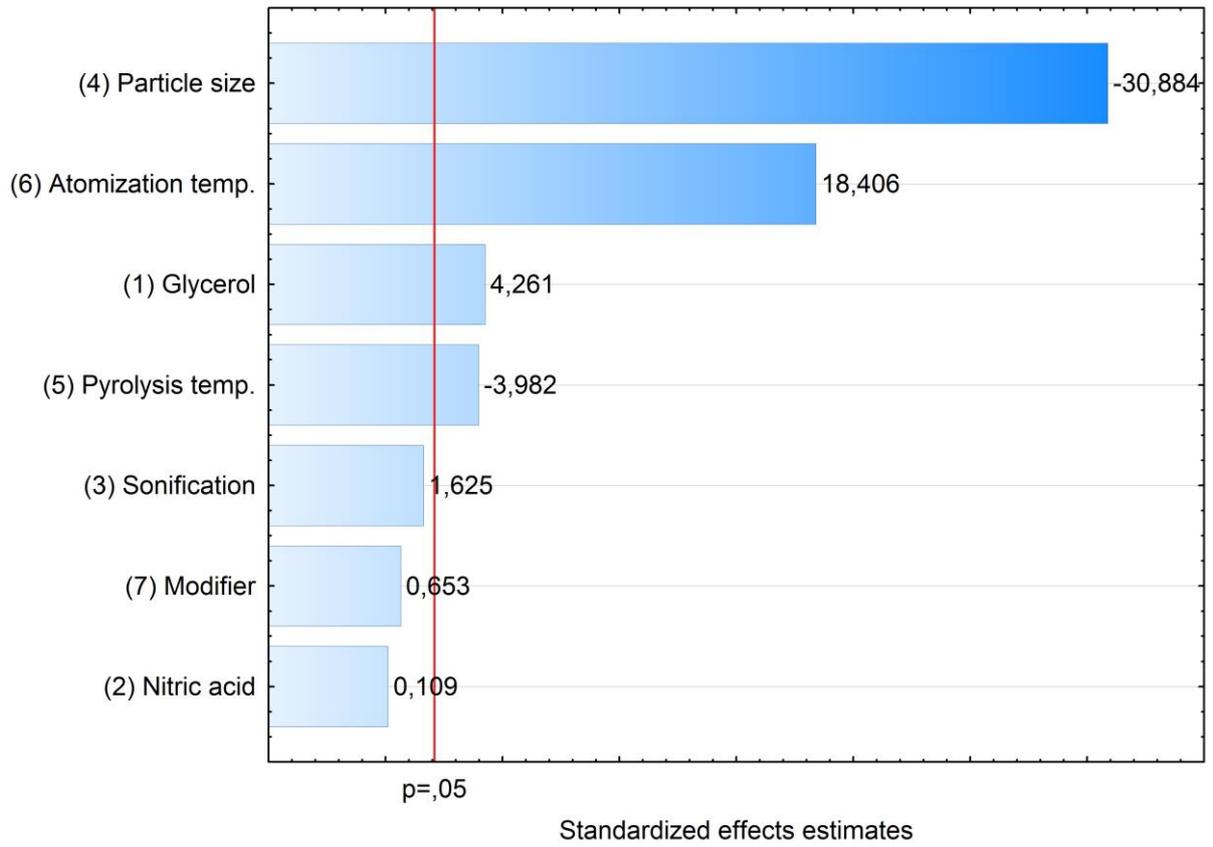


Fig. 3

