Evaluation of ammonium fluoride for quantitative microwave-assisted extraction of silicon and boron from different solid samples

Lenka Husáková, Iva Urbanová, Tereza Šídová, Tereza Cahová, Tomáš Faltys and Jitka Šrámková

Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Pardubice CZ-532 10, Czech Republic

(Received 1 December 2014; accepted 9 June 2015)

A novel, simple, efficient and environmentally friendly closed-microwave-assisted extraction (MAE) method of silicon and boron from a variety of industrial and environmental samples using ammonium fluoride as an extractant was developed. This method avoids handling the corrosive and toxic HF and prevents the potential risk of analyte loss due to the creation of volatile SiF$_4$ and BF$_3$ in the presence of HF. Atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry were employed for the subsequent analysis of the resulting supernatant for determination of Si and B, respectively. Certified reference material BCR$^\text{®}$-032 Natural Moroccan Phosphate Rock (phosphate fertiliser) was taken to optimise the extraction parameters such as the sample amount, extraction temperature and time and the volume of the extractant. The optimum extraction parameters evaluated using a fractional factorial design were as follows: 50 mg of the sample extracted with 5 mL of 100 g L$^{-1}$ NH$_4$ F for 15 min at 180°C. The optimised MAE procedure was successfully applied to nine different matrix reference materials intended primarily for validation of methods for determination of components in fertilisers, sludge, plants and fly ash. The obtained results were in a good agreement with the certified or comparative values with an overall precision better than 10% in all cases. The proposed method is recommended for fast and reliable preparation of samples with silicon content <8.2% (w/w). However, further decreasing the sample mass to 10 mg enabled the quantitative extraction of silicon from fly ashes at levels of 23% (w/w).

Keywords: silicon; boron; microwave-assisted extraction; ammonium fluoride; flame atomic absorption spectrometry; inductively coupled plasma optical emission spectrometry; fractional factorial design

1. Introduction

The quantification of silicon and boron in multiple solid industrial, environmental and biological samples by more rapid and accurate methods is being requested more frequently as both element are widely employed for material processing and industrial applications and are important to living organisms [1–5]. For this purpose, direct analytical methods like X-ray fluorescence analysis (XRF) [6,7], laser-induced breakdown spectroscopy (LIBS) [8] and laser sampling technique combined with inductively coupled plasma mass spectrometry (LA-ICP-MS) [7] are especially suitable to avoid laborious and time-consuming sample dissolution procedures. Application of LA-ICP-MS in routine analytical practice remains limited because of the high cost of the instrumentation, the difficulties for generating reliable data for the calibration model.
and its validation still being a challenge for LIBS [8]. Although the limits of detection for ultralight elements are dropping consistently with new XRF spectrometer developments, allowing better analysis of difficult elements [6], the most common methods for the determination of Si and B concentration in solid matrices are still spectrophotometry [3–5,9,10], inductively coupled plasma optical emission spectrometry (ICP-OES) [3,4,11–16], atomic absorption spectrometry (AAS) [3,4,17–19] and ICP-MS [3–5,20] employed after dry ashing and alkaline fusion [3,4,12,13,15,17], gravimetry [21] or acid wet digestion (in open or closed arrangement with or without the employment of microwave heating) [3,4,12–14,20]. From the literature data presented in the last years [5,8] it is evident the demand for development of the methods for quantification of difficult elements like silicon or boron in environmental and geochemical samples. Sample decomposition/preparation still draws attention [22]. The AOAC (Association of Official Analytical Chemist) Official Methods [23], which are based on gravimetry requires several gram test portions, are time-consuming and extremely laborious; involve numerous steps in the analytical sequence, which also increases the risks of systematic errors. Instrumental neutron activation analysis, a primary method very useful for development of CRMs suffers from several interferences and needs the determination of P and Al for appropriate corrections, enables to analyse three samples per hour and is applicable to samples containing at least 5 g kg$^{-1}$ of Si [24–26]. Among a large number of published nuclear reaction methods only prompt-γ spectrometry has a practical use relating to the determination of boron [3]. However, this method is not suitable for detection of low levels of B and is time-consuming, similarly as thermal ionisation mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS) [3,4]. Although positive-TIMS (PTIMS) has been reported as the most precise, and the negative-TIMS (NTIMS) as the most sensitive, they require extensive sample preparation and purification, which limits their usefulness for routine analyses [3–5]. In addition, TIMS, similarly as conventional ICP-MS methods, suffer from spectral interferences, mass fractionation and memory effects [5].

Alkali fusion and borate fusion are effective techniques for the decomposition of rocks that contain acid-resistant accessory minerals [27,28]. The later one cannot be used when boron should be the analyte of interest. Alkali fusion is traditionally used to analyse the major elements in geological samples [29] as its employment results in high solid environment of the fused materials which may be responsible for matrix interferences and represents a risk of contamination due to the necessity of large amounts of concentrated reagents [30].

For the liberation of silicon and boron from different solid samples and the digestion of siliceous materials and resistant materials containing boron, handling of dangerous hydrofluoric acid alone or in combination with other strong acids like HNO$_3$, HCl, HClO$_4$, H$_2$SO$_4$ is usually required [3,4,13,14,19,20,31,32]. As HF is extremely corrosive and toxic, several authors have explored new, safe and effective digestion methods for geological materials utilising ammonium compounds. For this purpose the mixtures of ammonium fluoride or NH$_4$HF$_2$ with nitric acid alone [22,29,33] or with hydrogen peroxide [34] or aqua regia [35] were successfully used to determine different major, minor and trace elements. Both in open [29,33–35] and in a closed high-pressure [22] digestion arrangement these methods are rather time-consuming as they are aimed to enable complete sample digestion to achieve reproducible and accurate analytical results. As the attention of the above referred works [22,33–35] was aimed at the capability of the various mixtures for a total destruction of the refractory matrix of different geological materials, no information is provided relating to the results of silicon concentrations in the investigated digested samples, although this information could be also important in the analytical task. Similarly, no analytical results were
provided related to the capability of the utilised methods [22,29,33–35] relating to the determination of boron.

Reaction of HF with samples containing silicon and boron produces volatile SiF₄ and BF₃ [3,4,13]. If Si or B are the target analytes, the formation of these volatile compounds implies a high risk of analyte loss after the vessel is opened, even if the decomposition of the sample has taken place in a closed system [3,4,13]. However, this problematics is much more complex and what reaction products will be finally created is strongly dependent on the experimental conditions [36,37]. The addition of mannitol and glycerol was reported to be somewhat efficient for suppression of the volatilisation and for the stabilisation of boron; KF solution was however found to be more suitable for this purpose [37]. As potassium is a major element in most geological samples, only HF is needed for the stabilisation of boron in most geological sample solutions and attaining accurate analytical results [36]. As reviewed in the literature [38,39], different reaction products are created in the reaction of silicon or boron and its compounds (oxides, hydroxides, salts, etc.) if ammonium fluoride or ammonium hydrogen fluoride are the reagents. Ammonium fluorides (anhydrous or in aqueous solution) react with many substances including elements, oxides, hydroxides, salts, etc. by the formation of ammonium fluorometallates or oxofluorometallates. Silicon and its compounds form ammonium hexafluorosilicate, which decompose above 300°C [38]. The reaction of a mixture of SiO₂ and NH₄HF₂ begins at a temperature of about 100°C and takes place exothermally to give (NH₄)₂SiF₆×NH₄F [38]. The fluorination of boron and its compounds by ammonium fluorides depending on the reaction conditions gives NH₄BF₄, mixtures of (NH₄)₂BOF₃, (NH₄)₃B₂O₅F₆ and other ammonium oxo- and hydroxofluoroborates [38,39]. What is important in the analytical point of view is that the above-mentioned resulting products are in contrast to SiF₄ and BF₃ more thermally stable, which is a prerequisite for utilisation of NH₄F in a sample preparation step and replacement of the hydrofluoric acid with all their handicaps.

In this work, the potential of ammonium fluoride for extraction of silicon and boron from different solid samples was investigated for the first time. In combination with a closed vessel microwave-assisted extraction (MAE), with the flexibility of vessel options, choices of sample size, temperature, amounts of solvent and number of samples [40], simple, rapid and high-throughput method was developed for silicon and boron extraction that can be applied to multiple matrices like plants, fertilisers, sludge samples or coal-fly ash. Using the described method, the use of some other reagents like mineral acids, being usually necessary for complete sample digestion, are not needed which is in agreement with green chemistry trends [41].

2. Experimental
2.1. Reagents and solutions
Reagents of analytical grade or higher quality were used. All solutions were prepared from deionised water, which was purified by means of the UltraClear (SG, Germany) pure water system to the final conductivity of 0.05 µS cm⁻¹. All plastic ware were immersed in 2 mol L⁻¹ nitric acid for 24 hours and then rinsed with deionised water. The stock solutions of 1 g L⁻¹ Si (H₂O/0.4% F⁻) and B (3% HNO₃) were obtained from SCP Science Ltd. (Canada) and VUK Panenske Brezany Ltd. (Czech Republic), respectively. The standard solutions as well as the calibration solutions were prepared by appropriate dilution with deionised water. Nitric acid (65%, w/w) was of Selectipur quality (Lach-Ner, Neratovice, the Czech Republic). Ammonium fluoride was of pro-analysis grade (p.a.) and obtained from Sigma-Aldrich (USA).
2.2. Quality assurance and quality control
The commercially supplied reference materials: BCR®-032 Natural Moroccan Phosphate Rock (Institute for Reference Materials and Measurements, IRMM, Belgium), intended primarily for use in verification and calibration of methods and apparatus, respectively, for determining components in fertilisers, Sludge from city water treatment WT-H No. 12–3-14 (Slovak Institute of Metrology, Bratislava, Slovakia), BCR®-060 Aquatic Plant (Lagarosiphon major) (IRMM), Reference material (RM) No.12–2-03 P-Alfalfa Essential and toxic elements in Lucerne (Slovak Institute of Metrology), NCS DC 73350 Leaves of Poplar (China National Analysis Center for Iron and Steel, Beijing, China), GBW 07602 and GBW 07603 Bush branches and leaves (Institute of Geophysical and Geochemical Exploration, Langfang, China), Constituent Elements in Coal Fly Ash Standard Reference Material® 1633b (National Institute of Standards & Technology, USA) and certified reference material Fine Fly Ash CTA-FFA-1 (Institute of Nuclear Chemistry and Technology, Warszawa, Poland) were analysed.

2.3. Instrumentation and procedures

2.3.1. Microwave-assisted extraction
The MAE of samples was carried out in Speedwave™ MWS-3+ (Berghof, Germany) microwave system with the maximum total output of the microwave generator 1450 W. To increase the sample throughput of the MWS-3+ system, Multitube System (MT) was used in combination with DAC-100S digestion vessels [42]. Using this, three MT PFA tubes can be placed into a standard DAC-100S PTFE vessel; thereby it is possible to digest/extract 3 samples simultaneously in one DAC-100S digestion vessel.

For optimisation purposes a 50, 100 or 150 mg portion of the sample was weighed and placed into a 10-mL PFA tube to which 2, 5 or 7 mL of 100 g L⁻¹ of NH₄F was added. After that, the tube was placed into a 100-mL pressure resistant PTFE vessel, whereupon 20 mL of 100 g L⁻¹ of NH₄F was added to ensure higher liquid level in the outer DAC-100S vessel than in each MT tube providing that the vapour pressures are compensated and the evaporation of the solution from the MT-vessel is prevented [42]. This is also a requirement to prevent any contamination of the sample since three replicas are extracted in one vessel at a time [43,44]. The schematic representation of the MAE system is depicted in Figure 1. The samples were extracted using the following programme: 5, 10 or 15 min at 140, 160 or 180°C (with a ramp set at 3 min). After that, 10 minutes were needed for the vessel to cool down. The resulting extract was filtered through a 0.45-μm syringe filter (Whatman Autovial) and diluted with deionised water to the volume of 10 mL. The solutions were analysed by flame atomic absorption spectrometry (FAAS) or ICP-OES for Si and B determination, respectively, along with a blank containing the same amount of ammonium fluoride and prepared in the same way as the samples. Before the analysis, the samples were diluted with deionised water in various ratios depending on the level of the analyte.

2.3.2. AAS measurement
The determination of Si was carried out using an Avanta P double beam atomic absorption spectrometer (GBC Scientific Equipment Pty. Ltd., Australia) with deuterium arc background correction in the flame absorption mode. GBC flame atomisation system contained solid inert polymer-mixing chamber and nitrous oxide-acetylene titanium burner construction designed to reduce carbon build up. Sample solutions were introduced to the spectrometer through a
standard GBC pneumatic nebuliser. The nebuliser has a platinum-iridium capillary and tantalum venture for resistance to different corrosive agents attack. The hollow cathode lamp obtained from Photron Pty. (Australia) was used with the wavelength set at 251.6 nm. A lamp current and spectral resolution of 14 mA and 0.2 nm, respectively, was used. The gas flame mixture was formed with 10.0 L min$^{-1}$ nitrous oxide and 5.1 L min$^{-1}$ acetylene (99.5%, from Linde Gas, Inc., Czech Republic).

Five aqueous standards ranging from 0 to 100 mg L$^{-1}$ of Si were used to obtain the calibration curves, from which all calculations were made in one analytical run. All calibration plots were linear in the investigated concentration ranges with the correlation coefficients better than 0.999. When the method of standard additions was used, two additions were applied in the linear range of calibration. The correlation coefficients were better than 0.99 in all cases.

2.3.3. ICP-OES measurement
The quantification of boron was performed by an independent analytical laboratory using ICP-OES method as this method provides higher sensitivity and lower detection capability for B determination than it is possible to obtain by FAAS even when nitrous oxide/acetylene flame is used. In addition, ICP-OES was accepted as standard method ISO 11885:1996. Boron quantifications were performed with an ICP atomic emission spectrometer Integra XL 2 (GBC
Scientific Equipment Pty. Ltd., Australia). The used emission lines of boron were B I 249.773 nm, B I 249.678 nm and B I 208.959 nm. The first line as the most sensitive line was used for the quantification and the other two to check for any possible spectral interference. The plasma power supply was 1.1 kW, observation height 6 mm, plasma gas flow 11 L min\(^{-1}\), auxiliary gas flow 1.5 L min\(^{-1}\), nebuliser gas flow 0.6 L min\(^{-1}\), photomultiplier voltage 600 V, sample uptake rate 1.0 mL min\(^{-1}\) and integration time 2 s.

The concentrations of boron were evaluated from the linear calibration lines constructed based on the analysis of solutions ranged from 0 to 1 mg L\(^{-1}\) of B.

Further details of the method being previously thoroughly validated for the determination of boron are given in Ref [16].

2.3.4. **Experimental design and statistical data treatment**

Three-level \(3^{(k-p)}\) fractional factorial design, with four factors \((3^{(4-1)})\), 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 [45,46]. The studied factors were: sample mass \((A)\), volume of the extraction agent \((B)\), extraction temperature \((C)\) and time \((D)\). All factors were evaluated at three levels, low (denoted as \(-1\)), middle (denoted as \(0\)) and high (denoted as \(+1\)). The levels for the experimental design are summarised in Table 1. The fractional factorial experimental design was chosen for the optimisation not only because of its reduced number of experiments (27 against 81 experiments using full design) but also because no loss of significant information occurs. Additionally, mechanism of the reaction with NH\(_4\)F may result in various products depending on the experimental conditions used, which makes it difficult to calculate even an approximate amount of the NH\(_4\)F that should be used. The reaction mechanism influences the temperature range that can be used for the extraction; moreover, the temperature is also limited by the instrumental properties of the MWS-3\(^+\) system. In order to reliably detect the temperature within the reaction vessel by the IR sensor of the MWS-3\(^+\) system, the environment inside the vessel has to reach at least 120°C and cannot exceed 230°C, which is a maximum allowable temperature that the multi-tubes can withstand.

The responses for each experiment were calculated as the arithmetic mean of concentrations obtained for Si in BCR®-032 Natural Moroccan Phosphate Rock CRM (see Table S1). Optimisations were performed for Si as in contrast to B the concentration of Si in all investigated samples is typically several order higher, so it can be expected that the high Si content will mainly limit the extraction conditions.

A second-order polynomial model was fitted to correlate the relationship between independent variables and response. The data were processed using the Statistica 12 computer program (StatSoft, Inc., USA) and QC Expert™ 2.5, TriloByte Statistical Software, (Pardubice, Czech Republic).

| Variables                  | \(-1\) | 0   | \(+1\) |
|----------------------------|--------|-----|--------|
| Sample mass (mg)           | \(A\)  | 50  | 100    | 150   |
| Volume of 100 g L\(^{-1}\) NH\(_4\)F (mL) | \(B\)  | 2   | 5      | 7     |
| Extraction temperature (°C) | \(C\)  | 140 | 160    | 180   |
| Extraction time (min)      | \(D\)  | 5   | 10     | 15    |

Table 1. Variables and levels investigated using the fractional factorial experimental design.
3. Results and discussion

3.1. Optimisation of the experimental conditions for microwave extraction

The effects and significance of the variables in the extraction process were evaluated using Pareto’s charts, including a vertical line that corresponds to the 95% limit which indicates statistical significance. As can be seen from Figure 2, for the extraction of silicon, the extraction efficiency is improved by improving the reagent amount (Factor B) and temperature (Factor C), as well as by reducing the sample mass to be extracted (Factor A). The volume of the extractant has the most positive effect on the extraction efficiency. No significant interactions between the investigated factors were observed.

In order to find the best mathematical model that correlates the variables and the analytical response, all possible subsets regression available in QC.Expert™ program were performed. For each possible combination of model terms the following criteria: \( F \)-statistic, coefficient of determination (also referred to as the \( R^2 \) value), Akaike’s information criterion (AIC) or MEP (mean squared prediction error) were monitored, as a good model should have large value of \( F \) and \( R^2 \), small AIC value and small MEP value [47,48]. Based on these criteria, a second-order (quadratic) polynomial was shown to fit the data and the reality of the situation the best. The equation of the model with the use of only statistically significant parameters is

\[
-1.32 (0.28)B^2 - 0.84 (0.18)A - 0.56 (0.20)B + 0.51 (0.18)C + 10.04 (0.55),
\]

![Figure 2](image_url)

Figure 2. Pareto chart of the standardised effects in the fractional factorial design \(3^{4-1}\) for the study of variables (A) sample mass, (B) volume of the extraction agent, (C) extraction temperature, (D) time and their interactions on silicon extraction. The L and Q letters indicate linear and quadratic effect of the factor, respectively.
where \( B \) is the volume of NH\(_4\)F (100 g L\(^{-1}\)) in mL, \( A \) sample mass in mg and \( C \) extraction temperature in °C. Standard deviations of the estimates are given in parentheses. The number of statistical parameters and tests which measures the quality and appropriateness of the final model fit to a set of data are presented in Table S2 in the Supplementary material.

Three response surfaces were obtained from the results of the 3\(^{4-1}\) design and these are illustrated in Figure 3. Each plot shows the effects of two variables within their studied ranges and visualises the tendency of each factor to influence the silicon extraction efficiency.

As can be seen from the plots, relating to the volume of extraction agent, the best agreement between the certified and analysed concentration of silicon was achieved for 5 mL of the extractant. Lower or higher volumes caused a small decrease; similarly, increasing sample mass influences negatively the analytical results. The decrease in the signal observed when 7 mL of NH\(_4\)F was used may be caused by higher pressure of the gaseous phase above the solution in the closed vessel compared to when only 2 or 5 mL were used. Increase in the extraction time did not lead to any further increase in extraction efficiency. With respect to the extraction temperature, it is clear that the quantitative extraction was achieved from the temperature being at least 160°C. In order to ensure the most robust conditions for the utilisation of the method to various sample matrices with the necessity of using low sample quantities, experimental conditions were finally selected as follows: sample mass of 50 mg, 5 mL of the extractant, 180°C extraction temperature held for 15 min.

### 3.2. Analytical figures of merit

#### 3.2.1. Limits of detection and quantification

After the optimisation of the MAE extraction parameters, the analytical characteristics were evaluated for the proposed method with the use of FAAS and ICP-OES for Si and B quantification, respectively. Limits of detection (LOD) and limits of quantification (LOQ) defined as the concentration which is given by an integrated absorbance equal to 3 times and 10 times of the standard deviation of 10 measurements of a sample blank are combined in Table 2. As ammonium fluoride is available in high purity, problems with contamination were observed neither for the determination of Si nor for B even for high concentrations of ammonium fluoride (see Table 2) and no significant differences were observed for LODs and LOQs values obtained based on the measurement of the sample blank without and with the presence of NH\(_4\)F.

#### 3.2.2. Matrix effects

As the ammonium fluoride matrix can have a considerable effect on the progress of the analysis and the quality of the obtained results, a calibration curve using aqueous standard samples with those containing ammonium fluoride in the same concentrations as used for sample preparation was constructed for both Si and B determination. The overall descriptive statistics for individual calibration curves for the Si and B analytes are presented in Table 2. There is a high degree of linearity for all the calibration curves used as the average coefficient of determination for all calibration curves subsequently estimates to 0.999. The results of the Chow test point to the deduction that there is no significant difference between the matrix-matched and solvent-only calibration types, statistically proving the superiority of the use of matrix-free calibration standards. The slopes of calibration lines of the standard additions method for ammonium fluoride extracts from both investigated samples were very close to that of the aqueous standard (within 10%), which means that the effect of the matrix was under a good control at the conditions described; direct aqueous calibration was used for quantification.
Figure 3. Response surfaces from $3^{4-1}$ design.
3.2.3. Trueness and precision

Different types of certified reference materials (Natural Moroccan Phosphate Rock BCR®-032, Sludge WT-H No. 12-3-14, Aquatic Plant BCR®-060, Lucerne CSRM No.12-2-03, Leaves of Poplar NCS DC 73350, Bush branches and leaves GBW 07602 and GBW 07603, Coal Fly Ash NIST SRM 1633b and Fine Fly Ash CTA-FFA-1) were analysed in order to prove the trueness and precision. As seen from Table 3, good agreement between the results obtained using an aqueous calibration for quantification was achieved by the proposed microwave-extraction method and the declared values. With the exception of Si determination in Aquatic Plant BCR®-060, recovery values for Si were found to be in the range of 93–103%. Recovery for Si in BCR®-060 of 84% is related to the indicative value that is provided by the producer of the reference material. The determined value (24.0 ± 0.7 g kg⁻¹) is however close to the mean value reported previously (24.9 ± 0.4 g kg⁻¹) by Sucharova and Suchara [14]. In order to achieve quantitative extraction of Si at relatively high levels of about 23% (w/w) from Coal Fly Ash NIST SRM 1633b and Fine Fly Ash CTA-FFA-1, sample mass taken for the extraction had to be decreased to 10 mg. In order to analyse such low sample masses, homogeneity must be assured as a representative sample, i.e. sample with evenly distributed analytes is needed [49,50]. If a sample with insufficient homogeneity is available, it can be homogenised by several techniques such as cutting or grinding (e.g. using vibration mills or ball mills). During our measurements, the samples of fly ash have been analysed after extracting three separate portions, which were taken from different parts of the flask. As can be seen from the results in Table 3, the relative standard deviations (RSD) of these analyses were less than 4%, which suggests that the materials were sufficiently homogenous even at such low sample masses.

As the analyte losses due to the creation of volatile SiF₄ and BF₃ are frequently debated problem in the literature [3,4,13] relating to the determination of both analytes in the presence of HF, two of the available certified reference samples were extracted using HF in order to compare the relevant data with those obtained with NH₄F. The MAE was performed using the same way as described in the Section 2.3.1 when using the NH₄F. The amount of HF was equimolar to that of NH₄F. Concentrations of silicon (mean value ± 2SD, n = 3) in GBW 07602

| Silicon, FAAS | Boron, ICP-OES |
|--------------|----------------|
| **Slope (1/mg L⁻¹)** | **Aqueousᵃ** | **NH₄Fᵇ** | **Aqueousᵃᶜ** | **NH₄Fᵇᶜ** |
| Standard deviation of slope | | | | |
| Interceptᵈ | 6.16 × 10⁻⁵ | 1.44 × 10⁻⁴ | 6.20 × 10⁻⁵ | 6.65 × 10⁻⁵ |
| Standard deviation of intercept | | | | |
| Coefficient of determination R² | 0.9999 | 0.9999 | 0.9998 | 0.9995 |
| LOD (µg L⁻¹) | 500 | 470 | 4 | 5 |
| LOQ (µg L⁻¹) | 1700 | 1600 | 13 | 17 |
| LOD (mg kg⁻¹) | 100 | 94 | 0.8 | 1.0 |
| LOQ (mg kg⁻¹) | 340 | 320 | 2.6 | 3.4 |

Notes:ᵃCalibration with matrix-free standards (n = 5). ᵇCalibration containing 50 g L⁻¹ NH₄ F in each standard (n = 5). ᵈThe results are evaluated for 249.773 nm B line. ᵉParameter is statistically insignificant at significance level 0.05 as its p-value is above 0.05.
Table 3. Determination of total silicon and boron in various reference materials using the developed MAE method.

| Reference material                        | Silicon       | Boron         |
|------------------------------------------|---------------|---------------|
|                                          | Certified     | Obtained\(a\) | R\(^b\) RSD\(^c\) | Certified     | Obtained\(^{a,d}\) | R\(^b\) RSD\(^c\) |
| Natural Moroccan Phosphate Rock BCR®-032 | 9.8 ± 0.56    | 9.9 ± 0.3     | 101 1.5          | 22.6 ± 2.2    | 21.7 ± 1.0       | 96  2.3           |
| Sludge WT-H No. 12–3–14                  | 82 ± 12       | 77.4 ± 1.3    | 94  1.0          | 31 ± 8        | 31.1 ± 5.7      | 100 9.2           |
| Aquatic Plant BCR®-060                   | 28.5\(^{e}\)  | 24.0 ± 0.7    | 84  1.5          | 25\(^{e}\)    | 24.7 ± 1.7      | 99  3.5           |
| Lucerne CSRM No.12–2–03                  | 3\(^{e}\)     | 3.1 ± 0.3     | 103 4.8          | 30\(^{e}\)    | 28.9 ± 1.3      | 96  2.3           |
| Leaves of Poplar NCS DC 73350            | 7.1 ± 0.8     | 6.6 ± 0.3     | 93  2.2          | 53 ± 5        | 57.4 ± 3.0      | 108 2.6           |
| Bush Branches and Leaves GBW 07602       | 5.8 ± 0.4     | 5.7 ± 0.2     | 98  1.8          | 38 ± 6        | 39.8 ± 2.7      | 105 3.4           |
| Bush Branches and Leaves GBW 07603       | 6.0 ± 0.7     | 5.8 ± 0.2     | 97  1.7          | 34 ± 7        | 35.3 ± 3.4      | 104 4.8           |
| Coal Fly Ash NIST SRM 1633b              | 230.2 ± 0.8   | 230 ± 18      | 100 3.9          |               |               |                |
| Fine Fly Ash CTA-FFA-1                   | 224.8 ± 9.2   | 216.3 ± 4.1   | 96  1.0          |               |               |                |

Notes: \(^a\)Mean ± 2 S.D. \((n = 3)\).
\(^b\)Recovery (%) expressed as \((\text{the ratio of observed value obtained from an analytical process via a calibration graph/ the reference value}) \times 100\).
\(^c\)RSD of three independent analyses.
\(^d\)Results of boron content are evaluated from spectral line B I 249.773 nm.
\(^e\)Informative value.
\(^f\)Not certified.
Bush branches and leaves and BCR 032 Natural Moroccan Phosphate Rock after the MAE with HF was $4.4 \pm 1.2 \text{ g kg}^{-1}$ and $6.5 \pm 0.4 \text{ g kg}^{-1}$, respectively. When compared with the data being presented in Table 3, significantly lower values were obtained than those being declared or those found after the MAE with NH$_4$F. Unfortunately, no relevant data are available for B determination as samples containing HF cannot be analysed directly by ICP-OES to avoid chemical attack of the torch. In this special case, the excess of HF must be complexed with H$_3$BO$_3$, which makes it impossible to quantify boron in these samples. These problems however are not related to the use of different ammonium fluorides; on the contrary, several fluorides were proved to minimise memory effects during ICP-OES boron determination [3,4].

The precision of the proposed method was evaluated in term of intra-day comparison. For this purpose, all reference sample materials were analysed in three replicates during the same day, within each series, every solution was analysed in five replicate. The RSD values were typically below 5% for silicon determination or 10% for boron determination, which shows that the precision of the method was satisfactory. The results of this study are given in Table 3. The results presented in Table 3 demonstrate the capabilities of the proposed extraction procedure for obtaining quality results for Si and B in the tested samples (plants, phosphate fertilisers, sludge and fly ash).

3.2.4. Sample throughput

Using the full capacity of the 8-position carousel of the MWS-3$^+$ microwave oven and the PFA multitube system [42], three MT PFA tubes can be placed into a standard DAC-100S PTFE vessel; thereby it is possible to extract three samples simultaneously in one DAC-100S digestion vessel and therefore up to 24 samples in one microwave run. The total time needed for the microwave procedure is 30 min (including extraction and cooling down of the reaction vessel) for 24 samples. The sample preparation, i.e. weighing, pipetting of the extractant, diluting etc., takes approximately 90 min for 24 samples. With this set-up, it is possible to prepare and analyse a minimum of 96 samples in an 8 h working day, which equals to 12 samples h$^{-1}$.

4. Conclusions

In this work, a novel method employing NH$_4$F for MAE of Si and B from multiple solid materials was developed. The clear advantage of the proposed method is avoiding handling of the very corrosive and toxic HF, the relative low price of NH$_4$F compared to HF, no significant waste generation and speed of MAE. The method thus contributes to the green chemistry. Combination of MAE with FAAS or ICP-OES method allows the quantification of Si and B at approximately 100 mg kg$^{-1}$ and 1 mg kg$^{-1}$, respectively, which was sufficient for analysis of environmental and industrial solid samples such as plants, phosphate fertilisers, sludge and fly ash. However, if necessary, combination of the proposed MAE method with the use of alternative analytical methods like atomic absorption spectrometry with electrothermal atomisation or inductively coupled plasma mass spectrometry can be expected to further improve the analytical performance relating to the detection power. Nevertheless, some problems relating to the detection limits may be observed depending on the purity of the NH$_4$F used. What can be further expected is a possible employment of the proposed MAE extraction for other elements. These expectations need to be solved in further study.

Disclosure statement

No potential conflict of interest was reported by the authors.
Funding
Financial support from the University of Pardubice [project number SGFChT06/2014] is gratefully acknowledged.

Supplemental data
Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/03067319.2015.1070409.

ORCID
Lenka Husáková  http://orcid.org/0000-0003-0639-5122

References
[1] F. Chainet, C.-P. Lienemann, M. Courtiaud, J. Ponthus and O.F.X. Donard, J. Anal. Atom Spectrom. 26, 30 (2011). doi:10.1039/COJA00152J.
[2] S.J. Lugowski, D.C. Smith, J.Z. Lugowski, W. Peters and J. Semple, Fresen J. Anal. Chem. 360, 486 (1998). doi:10.1007/s002160050745.
[3] R.N. Sah and P.H. Brown, Microchem. J. 56, 285 (1997). doi:10.1016/mchj.1997.1428.
[4] R.N. Sah and P.H. Brown, Plant Soil. 193, 15 (1997). doi:10.1023/A:1004251606504.
[5] A. Farhat, F. Ahmad and H. Arafat, Desalination. 310, 9 (2013). doi:10.1016/j.desal.2011.12.020.
[6] S. Reidinger, M.H. Ramsey and S.E. Hartley, New Phytol. 195, 699 (2012). doi:10.1111/j.1469-8137.2012.04179.x.
[7] C.-F. Wang, F.-H. Tu, S.-L. Jeng and C.-J. Chin, J. Radioanal Nucl. Ch. 242, 97 (1999). doi:10.1007/BF02345899.
[8] P.F. De Souza, D. Santos, G.G.A. De Carvalho, L.C. Nunes, M.D. Gomes, M.B.B. Guerra and F.J. Krug, Spectrochim. Acta. B. 83-84, 61 (2013). doi:10.1016/j.sab.2013.02.004.
[9] Q.-Z. Zhai and C.-M. Zhao, Instrum. Sci. Technol. 37, 472 (2009). doi:10.1080/10739140903087980.
[10] J.M.T. Carneiro, A.L.R.M. Rossete, G.S. Oliveira and J.A. Bendassolli, Commun. Soil Sci. Plan. 38, 1411 (2007). doi:10.1080/00103620701377245.
[11] G. Kaiser, A. Meyer, M. Friess, R. Riedel, M. Harris, E. Jacob and G. Tölg, Fresen. J. Anal. Chem. 352, 318 (1995). doi:10.1007/BF00322228.
[12] M.B. Haysom and Z.A. Ostatek-Boczynski, Commun. Soil Sci. Plan. 37, 2299 (2006). doi:10.1080/00103620600819420.
[13] S. Mann, D. Geilenberg, J.A.C. Broekaert and M. Jansen, J. Anal. Atom Spectrom. 12, 975 (1997). doi:10.1039/a701446e.
[14] J. Sucharová and I. Suchara, Anal. Chim. Acta. 576, 163 (2006). doi:10.1016/j.aca.2006.06.004.
[15] A. Krushevskia and R.M. Barnes, Analyst. 119, 131 (1994). doi:10.1039/an9941900131.
[16] A. Krejčová and T. Čermohorský, Food Chem. 82, 303 (2003). doi:10.1016/S0308-8146(02)00566-6.
[17] R.A. Burdo and W.M. Wise, Anal. Chem. 47, 2360 (1975). doi:10.1021/ac60364a025.
[18] J.A. Bowman and J.B. Willis, Anal. Chem. 39, 1210 (1967). doi:10.1021/ac60255a014.
[19] E. Kiss, Anal. Chim. Acta. 140, 197 (1982). doi:10.1016/S0003-2670(01)95465-0.
[20] X.B. Feng, S.L. Wu, A. Wharmby and A. Wittmeier, J. Anal. Atom Spectrom. 14, 939 (1999). doi:10.1039/a804683b.
[21] R. Matilainen and J. Tummavuori, Fresen J. Anal. Chem. 364, 700 (1999). doi:10.1007/s002160051417.
[22] Z.C. Hu, S. Gao, Y.S. Liu, S.H. Hu, L.S. Zhao, Y.X. Li and Q. Wang, J. Anal. Atom Spectrom. 25, 408 (2010). doi:10.1039/b921006g.
[23] R.L. Beine, AOAC Official Methods of Analysis (AOAC International, Rockville, 2011).
[24] E.S. Gladney, P.E. Neifert and N.W. Bower, Anal. Chem. 61, 1834 (1989). doi:10.1021/ac00192a010.
[25] J.D. Jones, P.B. Kaufman and W.L. Rigot, J. Radioanal Chem. 50, 261 (1979). doi:10.1007/BF02519963.
[26] L. Tobler, V. Furrer and A. Wytenbach, J. Radioanal Nucl. Ch. Le. 153, 85 (1991). doi:10.1007/BF02164869.
[27] T.T. Chao and R.F. Sanzolone, J. Geochem. Explor. 44, 65 (1992). doi:10.1016/0375-6742(92)90048-D.
[28] M. Totland, I. Jarvis and K.E. Jarvis, Chem. Geol. 95, 35 (1992). doi:10.1016/0009-2541(92)90042-4.
[29] Z.C. Hu, W. Zhang, Y.S. Liu, H.H. Chen, R.M. Gaschnig, K.Q. Zong, M. Li, S. Gao and S.H. Hu, Chem. Geol. 355, 144 (2013). doi:10.1016/j.chemgeo.2013.06.024.
[30] Z.S. Yu, P. Robinson and P. McGoldrick, Geostandard Newslett. 25, 199 (2001). doi:10.1111/j.1751-908X.2001.tb00596.x.
[31] H. Matusiewicz, Mikrochim. Acta. 111, 71 (1993). doi:10.1007/BF01240169.
[32] W.J. Price and P.J. Whiteside, Analyst. 102, 664 (1977). doi:10.1039/an977000664.
[33] W. Zhang, Z.C. Hu, Y.S. Liu, H.H. Chen, S. Gao and R.M. Gaschnig, Anal. Chem. 84, 10686 (2012). doi:10.1021/ac302327g.
[34] C. Mariet, O. Belhadj, S. Leroy, F. Carrot and N. Métrich, Talanta. 77, 445 (2008). doi:10.1016/j.talanta.2008.07.007.
[35] Z.C. Meng and N. Zhang, Anal. Lett. 45, 2086 (2012). doi:10.1080/00032719.2012.680060.
[36] Z. Hu and S. Gao, Chem. Geol. 253, 205 (2008). doi:10.1016/j.chemgeo.2008.05.010.
[37] S. Kozono, M. Yagi and R. Takashi, Anal. Chim. Acta. 368, 275 (1998). doi:10.1016/S0003-2670(98)00211-6.
[38] E.G. Rakov and E.I. Mel’nicenko, Usp Khim+. 53, 1463 (1984).
[39] E.G. Rakov and E.I. Mel’nicenko, Russian Chem. Rev. 53, 851 (1984). doi:10.1070/RC1984v053n09ABEH003126.
[40] M.V.B. Krishna, K. Chandrasekaran and D. Karunasagar, Anal Methods-Uk. 4, 1401 (2012). doi:10.1039/c2ay25084e.
[41] P.T. Anastas and M.M. Kirchhoff, Accounts Chem. Res. 35, 686 (2002). doi:10.1021/ar010065m.
[42] Berghof Products & Instruments GmbH, Multi Tube System for DAC-100 (Eningen, 2004).
[43] G.C.L. Araujo, A.R.A. Nogueira and J.A. Nóbrega, Analyst. 125, 1861 (2000). doi:10.1039/b003872p.
[44] L.C. Trevizan, A.R.A. Nogueira and J.A. Nóbrega, Talanta. 61, 81 (2003). doi:10.1016/S0039-9140(03)00220-0.
[45] D.C. Montgomery, Design and Analysis of Experiments (John Wiley & Sons, New York, 1991).
[46] G.E.P. Box, W.G. Hunter and S.J. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building (John Wiley & Sons, New York, 1978).
[47] M. Meloun, J. Militký and M. Forina, Chemometrics for Analytical chemistry. Volume 2: PC-Aided Regression and Related Methods (Ellis Horwood, Chichester, 1994).
[48] K. Kupka, QC. Expert Professional, Handbook (TriloByte Statistical Software, Ltd., Pardubice, 2013).
[49] B. Markert, Sci. Total Environ. 176, 45 (1995). doi:10.1016/0048-9697(95)04829-4.
[50] G.L. Donati, M.C. Santos, A.P. Fernandes and J.A. Nóbrega, Spectrosc. Lett. 41, 251 (2008). doi:10.1080/00387010802225138.