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### Title

Calcium fluoride as a dominating matrix for quantitative analysis by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS): A feasibility study

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3 1 **Calcium fluoride as a dominating matrix for quantitative analysis by laser ablation-inductively**  
4 **coupled plasma-mass spectrometry (LA-ICP-MS): a feasibility study**  
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20 Abstract

21 Calcium fluoride formed by the reaction between ammonium bifluoride and calcium chloride was  
22 investigated as a dominating matrix for quantitative analysis by laser ablation inductively coupled  
23 plasma mass spectrometry (LA-ICP-MS). Transformation from a solid sample to the calcium  
24 fluoride-based matrix permitted quantitative analysis based on calibration standards made from  
25 elemental standards. A low abundance stable calcium isotope, i.e.  $^{44}\text{Ca}^+$ , was monitored as the  
26 internal standard for quantitative analysis by LA-ICP-MS. Correlation coefficient factors for  
27 multiple elements were obtained with values over 0.999. The results for multiple elements in a  
28 certified reference material of soil (NIST SRM 2710a) agreed with the certified values in the range  
29 of expanded uncertainty, indicating the present method was valid for quantitation of elements in  
30 solid samples.

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32 *Keywords:* ammonium bifluoride, calcium fluoride, matrix-matching, calibration, LA-ICP-MS,  
33 quantitative analysis

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3 **36 1. Introduction**

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5 **37** Since the commercial availability in the early 1980s, inductively coupled plasma mass  
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7 **38** spectrometry (ICP-MS) has been increasingly adopted in inorganic chemical metrology as one of the  
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9 **39** most accurate quantitative analytical approaches [1]. The measurement by ICP-MS contributed to  
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11 **40** 56 out of 61 international comparisons organised by the working groups of Consultative Committee  
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13 **41** for Amount of Substance: Metrology in Chemistry and Biology (i.e. CCQM) since 1998. This  
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15 **42** could be attributed to the facts that ICP-MS has multiple merits for quantitative analysis, such as  
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17 **43** capability for simultaneous multi-elemental analysis with quite low instrumental detection limits,  
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19 **44** robustness permitting introduction of samples with various matrices, capability for overcoming  
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21 **45** spectral and non-spectral interferences, and so on. On the other hand, laser ablation (LA) had been  
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23 **46** applied to various research fields as an effective approach for introducing solid samples into the  
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25 **47** ICP-MS since the mid 1980s [2-11]. However, there are almost no reports on quantitative  
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27 **48** LA-ICP-MS analysis for chemical metrology activities, such as participating international  
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29 **49** comparisons or developing certified reference materials (CRMs). The major reason could be  
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31 **50** attributed to the fact that there was not a well-established calibration strategy applicable to a sample  
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33 **51** independent of the matrix [9], i.e. calibration strategy is still a key issue for quantitative elemental  
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35 **52** analysis by LA-ICP-MS.

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37 **53** External calibration (with or without internal standard), standard addition, and isotope dilution are  
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39 **54** major strategies for quantitative analysis by ICP-MS [12]. In solution-based quantitative elemental  
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41 **55** analysis, the solution uptake rate could be well controlled by using a stable nebulizer with or without  
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43 **56** the assist of a solution pump, while the samples and the standards could be made in the same matrix.  
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45 **57** Similarly, in solid-sample-based LA-ICP-MS quantitative elemental analysis, the  
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47 **58** sample-introduction rates between the sample and the standard should be identical or could be  
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49 **59** properly corrected with an internal standard. Furthermore, the matrix of the sample and the standard  
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51 **60** should be matched so that the signal responses between the sample and the standard are identical,  
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53 **61** thereby achieving accurate and precise results. Standards with an identical or similar matrix with  
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55 **62** the samples have been investigated for quantitative results of elements in various sample matrices by  
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57 **63** LA-ICP-MS, such as bones, minerals, and human teeth [13-17]. Lithium borate glasses had been  
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59 **64** investigated as a candidate calibrating strategy for analyzing samples of various matrix [18-22]. In  
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61 **65** these works, lithium borate acted as a dominating matrix and improved the capability for

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3 66 quantitative analysis by LA-ICP-MS. Due to a high temperature (around 950 to 1150 °C) is  
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5 67 required for making lithium borate glasses, crucibles made of platinum alloys are usually used as the  
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7 68 heating vessels for making lithium borate glasses. Contamination from the crucibles can be  
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9 69 problematic for quantitative analysis of some elements by LA-ICP-MS [19].

10 70 Strategies for quantitative analysis [23, 24] as well as for ablation mechanisms of various matrices  
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12 71 have been established for LA-ICP-MS [25-27]. Poly-methyl-methacrylate (PMMA) binder with  
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14 72 cesium as an internal standard and silicon-matrix standard solutions have been shown to be effective  
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16 73 for quantitative analysis of some elements in solid samples by LA-ICP-MS [23, 24]. However,  
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18 74 homogeneity of samples prepared with the PMMA binder needed to be improved for better  
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20 75 reproducibility [23], while calibration based on silicon-matrix solution standard required that the  
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22 76 concentration of silicon in the sample should be separately determined prior to the analysis of other  
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24 77 elements [24]. Slurry-based standard addition and isotope dilution had been reported as an  
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26 78 effective calibrating strategy for quantitative analysis of soil samples [28]. However, the principles  
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28 79 of standard addition and isotope dilution required to prepare multiple sub-samples (spiked and  
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30 80 non-spiked) for each sample and may limit the throughput of sample preparation.

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32 81 In this work, calcium fluoride was investigated as a dominating matrix for the quantitative  
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34 82 analysis of elements in soil samples by LA-ICP-MS based on elemental calibration standards made  
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36 83 from solution standards. Traceability confirmation and uncertainty evaluation of the results were  
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38 84 addressed for its potential application in chemical metrology. Multiple articles had presented  
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40 85 ammonium fluoride or ammonium bifluoride as a reagent for removing silica in solid samples prior  
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42 86 to the analysis [29-31]. In this work, ammonia bifluoride was used as a reagent providing fluoride  
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44 87 ion to form calcium fluoride.

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## 47 89 **2. Experimental**

### 48 49 90 **2.1. Instrumentations**

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51 91 The LA-ICP-MS measurements were carried out with a J200 LA instrument (Applied Spectra Inc.,  
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53 92 Fremont, CA) and an Aurora Elite model ICP-MS instrument (Bruker Cop., Bremen, Germany).  
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55 93 The J200 LA instrument was equipped with a 266 nm Nd:YAG laser. The operating conditions of  
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57 94 the LA -ICP-MS were selected after careful optimization of each parameter to obtain sufficient and  
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59 95 reproducible signal intensities for elements of interest. [In order to facilitate the measurement of](#)

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3 96 complex matrix samples, the ICP-MS was operated at normal sensitivity mode. An automatic  
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5 97 presser (3630 X-Press®, SPEX, Metuchen, NJ) with a 13.1 mm dia. die set were used for making  
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7 98 pellets of solid samples. A Lindberg/Blue M™ model electrical furnace (Thermo Fisher Scientific,  
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9 99 Asheville, NC) was used for heating during sample pretreatment. An analog vortex mixer from  
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11 100 VWR International (Radnor, PA) was used for mixing the sample and the chemicals during sample  
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13 101 pretreatment. A Delta Range® model electronic balance from Mettler Toledo (Columbus, OH) was  
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15 102 used for gravimetric sample preparation.  
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## 18 104 **2.2. Chemicals and materials**

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20 105 A certified reference material of soil (SRM 2710a) from the National Institute of Standard and  
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22 106 Technology (NIST, Gaithersburg, MD) was used for optimization of sample pretreatment procedure  
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24 107 as well as for confirming the validity of the proposed approach.

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26 108 High purity ammonium bifluoride (ABF, 99.999% trace metals basis) and calcium chloride  
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28 109 (anhydrous powder, 99.99 % trace metals basis) from Millipore Sigma Corp., (St. Louis, MO) were  
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30 110 used for producing calcium fluoride matrices. A multi-element standard solution (Supelco ICP  
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32 111 multi-element standard solution IV) was purchased from Millipore Sigma. The concentrations of  
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34 112 Mg, Al, Mn, and Fe were traceable to NIST SRMs 3131a, 3101a, 3132, and 3126a, respectively.

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36 113 Flat-bottom perfluoroalkoxy alkane (PFA) reaction vessel sets (7-mL vial with enclosure) from  
37  
38 114 Savillex (Eden Prairie, MN) were used for sample pretreatment.  
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## 41 116 **2.3. Procedure for sample pretreatment**

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43 117 Sample weighing was carried out with the electronic balance operated with a readability of 0.1 mg  
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45 118 and a maximum capacity of 101 g. Typical procedure for treatment of the samples is as follows.

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47 119 First, approximately 0.3 g of ABF and 0.05 g of initial solid sample (e.g. NIST SRM 2710a) were  
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49 120 respectively weighed and placed into the PFA vial. After the addition of 0.5 mL of pure water, the  
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51 121 PFA vial was firmly capped and placed on the vortex mixer for one minute. Then, approximately  
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53 122 0.65 g of 40 % (w/w) calcium chloride solution was added into the PFA vial, which was re-capped  
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55 123 and put on the vortex mixer for one additional minute. After that, the PFA vial was uncapped and  
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57 124 placed into the electrical furnace. Finally, the sample in the PFA vial was heated to 130 °C for two  
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59 125 hours followed by 230 °C for one hour.  
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126 After cooling, the sample was removed from the PFA vial and grounded to fine powder (with a  
127 diameter around or less than 10  $\mu\text{m}$ , confirmed with an optical microscope), which was pressed into  
128 a pellet at seven tons of pressure with holding time of four minutes. The sample pellet was  
129 analyzed for elemental content with LA-ICP-MS.

130 Samples for procedure blank were obtained in the same way as described above without the  
131 addition of the initial solid sample. Calibration standards with multiple concentration levels were  
132 also obtained in the same way by addition of various quantities of elemental standard solutions  
133 instead of the initial solid sample in the aforementioned procedure.

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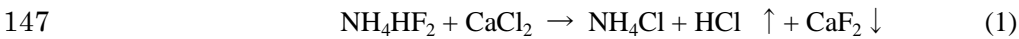
### 135 **3. Results and discussion**

#### 136 **3.1. Reaction in the procedure of sample pretreatment**

137 Calcium fluoride was chosen as the matrix for quantitative analysis by LA-ICP-MS because  
138 calcium has multiple low-abundance stable isotopes ( $^{42}\text{Ca}$ ,  $^{43}\text{Ca}$ ,  $^{44}\text{Ca}$ , and  $^{46}\text{Ca}$ ; 0.6 %, 0.1 %, 2 %, and 0.004 %, respectively), which could be measured as candidate internal standards for various  
139 sample-to-matrix mixing levels. Meanwhile, a stable precipitate of calcium fluoride could be easily  
140 obtained due to its quite low solubility product at a level of  $10^{-11}$  (mol/L)<sup>3</sup> order. In addition,  
141 calcium fluoride is a stable, non-hygroscopic (i.e. without swelling water from the air) compound  
142 and permits making a durable sample pellet for the analysis by LA-ICP-MS.

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144 As mentioned above, ABF and calcium chloride were added for sample pretreatment. The  
145 reaction between ABF and calcium chloride could be expressed with Eq. (1).

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149 In a preliminary experiment, it was found that the  $\text{CaCl}_2$  residue resulted in apparent swelling of  
150 the sample pellets by absorption of the water vapour from the air. Therefore, a slight (ca. 5 %, mole ratio) excess quantity of ABF in comparison to that of calcium chloride was added to  
151 completely convert calcium chloride to calcium fluoride. Based on the solubility product of  
152 calcium fluoride in water, the concentration of residual  $\text{F}^-$  and  $\text{Ca}^{2+}$  after precipitation reaction were  
153 both under mmol/L. Therefore, the production efficiency of calcium fluoride was over 99.9%  
154 considering the starting concentrations of  $\text{NH}_4\text{HF}_2$  and  $\text{CaCl}_2$ .

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3 156 After the reaction, water was evaporated to obtain a solid sample. Temperature for evaporation  
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5 157 was investigated in the range from 100 °C to 230 °C in steps of 10 °C. The results showed that  
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7 158 the evaporation at a temperature above 140 °C caused splashing of the sample. By contrast, a  
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9 159 temperature under 140 °C provided a mild evaporation without splashing of the sample but took a  
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11 160 longer time to obtain a dry solid sample. Therefore, the samples were heated at 130 °C for two  
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13 161 hours to evaporate the majority of water and further heated at 230 °C for one hour to obtain a dry  
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15 162 solid sample. Taking into consideration the melting temperature of the PFA material of the vial,  
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17 163 temperature over 240 °C was not investigated.

18 164 Raman spectroscopy was performed to confirm the chemical structure of the solid sample  
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20 165 obtained by the reaction outlined in Eq. (1). The spectra in Fig. 1 show that the typical peaks for  
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22 166 ABF (i.e., peaks at  $\sim 1685\text{ cm}^{-1}$ ) and calcium chloride (i.e., peaks at  $\sim 1638\text{ cm}^{-1}$  and  $\sim 3429$   
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24 167  $\text{cm}^{-1}$ ) disappeared after the reaction, while the peaks for calcium fluoride (i.e., peaks at  $\sim 321\text{ cm}^{-1}$ )  
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26 168 and ammonium chloride (i.e., peaks at  $\sim 1708\text{ cm}^{-1}$ ) were observed. These results indicate that the  
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28 169 major matrix after the reaction was a mixture of calcium fluoride and ammonium chloride, which  
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30 170 were independent of temperature for evaporation in the range from 100 °C to 230 °C.

31 171 In the present experiment, the reaction between  $\text{NH}_4\text{HF}_2$  and  $\text{CaCl}_2$  was dominating. The sample  
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33 172 powders were trapped by the resulting  $\text{NH}_4\text{Cl}$  and  $\text{CaF}_2$ .

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### 37 174 **3.2. Representative signal intensities for magnesium and calcium in a calibration standard**

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39 175 For quantitative analysis, chemical composition of the sample ablated should be representative of  
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41 176 the bulk sample. In order to confirm the minimum number of data points required for quantitative  
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43 177 analysis, the results for signal intensities of  $^{24}\text{Mg}^+$  and  $^{44}\text{Ca}^+$  in a calibration standard are plotted in  
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45 178 Figs. 2 (a) and (b), whereas the results for the signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  are plotted in  
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47 179 Fig. 2(c). The bars shown in Figs. 2 (a) to (c) indicate the standard uncertainties, which were  
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49 180 obtained by dividing the standard deviation with the square root of the number of data points. In  
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51 181 principle, the standard uncertainty of a mean value of measurement depends on the standard  
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53 182 deviation and the number of data, i.e. the more data, the less standard uncertainty. However, when  
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55 183 the number of data was large enough, the contribution of increased data points could be negligible.  
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57 184 The results all were obtained after a pre-ablation to exclude possible surface contamination of the  
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59 185 pellet.



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3 186 In Figs. 2 (a) to (c), the plots from the low number of data to the high number of data were  
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5 187 respectively obtained by considering 5 to 110 (with a step size of 5) sets of data. In Fig. 2 (a), the  
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7 188 results for  $^{24}\text{Mg}^+$  obtained with various numbers of data agreed with one another in the range of their  
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9 189 standard uncertainty. The standard uncertainty decreased with the increase in the number of data  
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11 190 from 5 to 60, whereas the improvement in standard uncertainty was quite slight with further increase  
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13 191 of the number of data from 60 to 110. The reason can be attributed to the contribution of number of  
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15 192 data, approximately  $0.45 (1/\sqrt{5})$ ,  $0.13 (1/\sqrt{60})$ , and  $0.10 (1/\sqrt{110})$  respectively for a number of 5, 60,  
16  
17 193 and 110. The results for  $^{44}\text{Ca}^+$  shown in Fig. 2 (b) were similar to the results for  $^{24}\text{Mg}^+$  in Fig. 2 (a).

18 194 In Fig. 2 (c), the results for signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  showed that a stable value with  
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20 195 a small uncertainty (relative uncertainty close to or lower than 1 %) could be obtained when the  
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22 196 number of data points was over 60. Therefore, each sample or standard in the following  
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24 197 experiment was analysed to obtain at least 60 sets of data for quantitative analysis.

25 198 Dependence of the relative standard uncertainty on the number of data points is plotted in Fig. 3.  
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27 199 As can be seen from Fig. 3, the relative standard uncertainty for each parameter decreased with the  
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29 200 increase of number of data points. The relative standard uncertainty for signal intensity ratio of  
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31 201  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  showed the lowest value for each number of data points over 40, indicating the  
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33 202 improvement of measurement precision by internal standard correction.  
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### 37 204 **3.3. Linearity of the calibration curves**

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39 205 The concentration of an element of interest in a solid sample was quantitated based on a  
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41 206 calibration curve established using multiple standards made from elemental solution standards.  
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43 207 The results for signal intensities of  $^{24}\text{Mg}^+$ ,  $^{27}\text{Al}^+$ ,  $^{55}\text{Mn}^+$ , and  $^{57}\text{Fe}^+$  in the calibration standards are  
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45 208 summarized in Table 2, along with the slope, the intercept, and the correlation factor for the  
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47 209 calibration curves.

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49 210 In Table 2, the signal intensities for each element in the calibration Standards 2 to 4 were  
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51 211 significantly higher than in Standard 1 (i.e. blank). The correlation factor for each element was  
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53 212 better than 0.999, showing very good linearity of the calibration curve. Detection limits were  
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55 213 calculated as the concentrations corresponding to 3-fold the standard deviations of 10-times  
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57 214 measurement of Standard 1. The method detection limits for Mg, Al, Mn, and Fe were respectively  
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59 215 2.0, 1.7, 0.8, and  $22 \mu\text{g g}^{-1}$ , giving the sample-to-Ca ratio was 0.1.

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5 217 **3.4. Analytical results of the elements in NIST SRM 2710a**

6 218 The method developed in this work was applied to the quantitative analysis of elements in a soil  
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8 219 CRM, i.e. NIST SRM 2710a. As the internal standard, the contribution of the contents of Ca in the  
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10 220 sample was also considered, which was negligible (< 0.5 %) in comparison to the contents of Ca  
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12 221 introduced as calcium chloride for sample preparation. The observed values for the elements in  
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14 222 NIST SRM 2710a are summarized in Table 3 with the certified values. In Table 3, both the  
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16 223 certified values and the observed values are given as the (Mean  $\pm$  expanded uncertainty), with a  
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18 224 coverage factor ( $k = 2$ ) corresponding to an interval having a level of confidence of approximately  
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20 225 95 %. Uncertainty estimation was carried out following the guide to the expression of uncertainty  
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22 226 in measurement [32]. The major factors considered for the uncertainties in the observed values  
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24 227 were the linearity of the calibration curve (the slope and the intercept) and the measurement of signal  
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26 228 intensity in the sample.

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28 229 In Table 3,  $\Delta M / \Sigma U$ , i.e.  $(M_o - M_c) / (U_o + U_c)$  is given as a parameter for evaluating the extent of  
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30 230 agreement between an observed value and a certified value. For this parameter,  $M_o$  and  $M_c$  are the  
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32 231 means of an observed value and a certified value, respectively, while  $U_o$  and  $U_c$  are the  
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34 232 expanded uncertainty of an observed value and a certified value, respectively. A value of  $\Delta$   
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36 233  $M / \Sigma U$  in the range of [-1, 1] indicates that the observed value was in good agreement with the  
37  
38 234 certified value.

39 235 In Table 3, two sets of observed values (A and B, respectively) were obtained with two  
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41 236 independent sample pellets made with different sample-to-Ca ratios. The  $\Delta M / \Sigma U$  values for Al  
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43 237 (set A), Mn (sets A and B), and Fe (sets A and B) were in the range of [-1, 1], indicating good  
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45 238 agreement between the observed values and the certified values. By contrast, the  $\Delta M / \Sigma U$  values  
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47 239 for Mg (sets A and B) and Al (set B) were out of the range of [-1, 1], indicating less agreement  
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49 240 between the observed values and the certified values. One of the reasons for such disagreement  
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51 241 might be the fact that only a minute portion (roughly 1/50 000) of the sample pellet was subjected to  
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53 242 the analysis by LA-ICP-MS, therefore, the inhomogeneity of different elements in the initial sample  
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55 243 powder may be ineligible. According to the certificate of NIST SRM 2710a, the homogeneity tests  
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57 244 were based on the analysis of at least 170 mg of sample powders, which was over 150 000 folds than  
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59 245 the quantity of sample used for obtaining one set of data in the present work. [Since the dominating](#)

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246 matrix in the present work was calcium fluoride with ammonium nitrate, the matrix effect due to a  
247 relative minor difference in sample mass could be negligible.

248 The metrological traceability of the results was ensured by using multiple concentration levels of  
249 calibration standards made from a multi-element standard solution with elemental concentrations  
250 traceable to NIST SRMs. All of the sample and standard pretreatment operations were carried out  
251 based on a gravimetric method by using an analytical balance.

252

253 **3.5. Comparison of quantitation strategy used in the present work and selected references**

254 A comparison of quantitation strategies used in this work with those used in multiple literature  
255 references is summarized in Table 4. It is notable that the standards for calibration curves described  
256 in Refs. 13 to 17 were respectively matrix-matched with the samples to ensure better quantitative  
257 results. By contrast, calcium fluoride was introduced as an additional matrix for the measurement  
258 of soil sample in this work; calibration standards made from elemental solutions could be used for  
259 quantitative analysis of the elements in soil sample. The precision and correlation coefficient of  
260 calibration curves measured in this work were comparable to or better than the values previously  
261 reported.

262

263 **4. Conclusions**

264 Calcium fluoride was investigated as a dominating matrix for quantitative analysis of elements in  
265 solid samples by LA-ICP-MS. Transformation from a soil sample to the calcium fluoride matrix  
266 permitted quantitative analysis based on calibration standards made from elemental solutions. A  
267 low abundance stable calcium isotope, i.e.  $^{44}\text{Ca}^+$  providing moderate signal intensity comparable to  
268 the elements of interest, was measured and used as the internal standard for quantitative analysis by  
269 LA-ICP-MS. Linearity with good correlation coefficient ( $> 0.999$ ) was obtained for the calibration  
270 curves of multiple elements. The results for a soil sample, NIST SRM 2710a, agreed with the  
271 certified values, indicating that the present method could be a reliable candidate for quantitative  
272 analysis of the elements in solid sample by LA-ICP-MS. The possibility of ensuring metrological  
273 traceability and evaluating uncertainty of the results permits the application for chemical metrology  
274 purposes.

275 The whole process of the present method takes several hours, which is longer or comparable to

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2  
3 276 lithium borate fusion and microwave-assisted acid digestion. Due to a relatively lower temperature  
4  
5 277 is required for heating, the present method permits the use of PFA and PTFE vessels for sample  
6  
7 278 preparation, which contributes to a better control of procedure blank. The solid samples are more  
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9 279 stable and have a much smaller size than a sample solution obtained by acid digestion; this feature is  
10  
11 280 a merit for long term monitoring and remeasurement for quality control.

12  
13 281 Calcium was used as the internal standard in the present work. Special attention should be paid  
14  
15 282 to spectral interferences of calcium isotopes to ensure the accuracy of the results. The  
16  
17 283 concentration of calcium in the sample should be negligible in comparison to the quantity of calcium  
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19 284 introduced as the matrix or precisely quantified and considered for internal standard correction.

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21 285 Four elements, i.e. Mg, Al, Mn, and Fe, were discussed in the present work from the viewpoint of  
22  
23 286 quantitative analysis. Based on the results obtained by adding multiple levels of sample quantities  
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25 287 (i.e. sample to CaF<sub>2</sub> ratio), good linearity with a correlation coefficient value over 0.999 was also  
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27 288 observed for Sc (5.3 %), Ti (0.8 %), V (0.9 %), Cr (3.6 %), Co (4.8 %), Ni (2.1 %), Cu (1.3 %), Zn  
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29 289 (2.0 %), Ge (2.6 %), Rb (2.4 %), Sr (1.1 %), Y (4.6 %), Zr (5.7 %), Ru (9.7 %), Pd (8.9 %), Ag  
30  
31 290 (1.2 %), Cd (1.1 %), In (2.2 %), Ba (1.5 %), La (3.3 %), Ce (5.8 %), Pr (4.7 %), Nd (7.0 %), Sm  
32  
33 291 (5.5 %), Eu (2.2 %), Gd (2.9 %), Tb (5.9 %), Dy (7.2 %), Tl (3.8 %), Pb (1.4 %), Th (3.9 %), and U  
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35 292 (1.6 %), respectively, where the value in the parentheses following each element is the typical  
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37 293 relative standard deviation of the signal intensity observed in the same conditions as those used for  
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39 294 “Observed value B” in Table 3. However, due to the range of concentrations for these elements,  
40  
41 295 additional optimization of the calibrating standards is required for quantitative analysis. The works  
42  
43 296 about quantitative analysis of these elements are still in progress and the authors will try to publish  
44  
45 297 the results in the near future.

46 298

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48  
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402 Table 1  
403 Operating conditions of LA -ICP-MS.

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405	<b>Laser ablation</b>	<b>J200 LA</b>
406	Wavelength	266 nm
407	Energy per pulse	20 mJ
408	Beam diameter	80 $\mu\text{m}$
409	Pulse repetition rate	10 Hz
410	Scan rate	100 $\mu\text{m s}^{-1}$
411	Line-to-line distance	400 $\mu\text{m}$
412	Pre-ablation	45 s
413	Lines per pellet	6
414	Line-to-line delay	15 s
415	<b>ICP-MS</b>	<b>Aurora Elite</b>
416	RF power	1400 W
417	Plasma gas flow rate	Ar 14 L min <sup>-1</sup>
418	Auxiliary gas flow rate	Ar 1.00 L min <sup>-1</sup>
419	Carrier gas flow	Ar 1.4 L min <sup>-1</sup>
420	Scanning mode	Peak hopping
421	Dwell time per isotope	5 ms
422	Data acquisition mode	Time resolved (TRA)

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Table 2  
Signal intensities for the elements in calibration standards obtained by LA-ICP-MS.

Standard	Element-to-Ca ratio ( $\times 10^{-6}$ )	Signal intensity <sup>a</sup> / CPS (after internal standard correction by using <sup>44</sup> Ca <sup>+</sup> signal intensity)			
		<sup>24</sup> Mg <sup>+</sup>	<sup>27</sup> Al <sup>+</sup>	<sup>55</sup> Mn <sup>+</sup>	<sup>57</sup> Fe <sup>+</sup>
1	0.000	23300 ± 500	1500 ± 100	1600 ± 300	46100 ± 1400
2	0.401	2449000 ± 11000	727000 ± 8000	3584000 ± 170000	689000 ± 7000
3	0.839	5189000 ± 28000	1523000 ± 10000	7839000 ± 387000	1393000 ± 18000
4	1.251	7684000 ± 66000	2266000 ± 12000	10970000 ± 769000	2000000 ± 11000
5	1.663	9954000 ± 58000	2975000 ± 19000	14437000 ± 219000	2609000 ± 17000
Slope		6011000	1793000	8685000	1542000
Intercept		65910	8979	150800	66620
Correlation factor		0.9998	0.9999	0.9992	0.9998

a, Mean ± standard uncertainty.

Table 3  
Analytical results of the elements in NIST SRM 2710a.

Element	Concentration <sup>a</sup> / %			$\Delta M / \Sigma U$ <sup>d</sup>		
	Certified value		Observed value A <sup>b</sup>	Observed value B <sup>c</sup>	Observed value A	Observed value B
Mg	0.734	± 0.038	0.654 ± 0.038	0.657 ± 0.030	-1.05	-1.12
Al	5.95	± 0.05	5.92 ± 0.29	5.53 ± 0.28	-0.09	-1.27
Mn	0.214	± 0.006	0.166 ± 0.077	0.172 ± 0.052	-0.58	-0.72
Fe	4.32	± 0.08	4.33 ± 0.12	4.37 ± 0.13	0.07	0.25

a. Mean ± expanded uncertainty,  $k = 2$ . b. Sample-to-Ca ratio, 0.100. c. Sample-to-Ca ratio, 0.150.

d.  $\Delta M / \Sigma U$ , i.e.  $(M_o - M_c) / (U_o + U_c)$ ;  $M_o$  and  $M_c$ , Means of observed value and certified value, respectively;  $U_o$  and  $U_c$ , Expanded uncertainty of observed value and certified value, respectively.

Table 4

A comparison of the present work with reported methods for quantitation analysis.

Ref. No.	Element	Sample	Standard	Process for making calibrating standard	Typical precision / RSD	Correlation coefficient of calibration curve
Ref. 13	Pb	Bone	Bone CRM	Pressed pellets	10-20%	NA <sup>a</sup>
Ref. 14	Co, Ni, Cu, Ga, Zn, Se, Pb	Iron sulphide	Element + Pyrite (iron sulfide)	Welding and re-solidification	<15%	NA <sup>a</sup>
Ref. 15	Mg, Al, V, Mn, Zn, As, Sr, Rb, Cd, Ba, Hg, Pb	Fish dorsal spine	Hydroxyapatite (calcium phosphate)	Coprecipitation and pressed pellets	1.6-24%	0.9690-0.9997
Ref. 16	Al, Ba, La, Sr	Human teeth	Elements + Human teeth	Solution-standard spiking, drying, and pressed pellets	2.1-4.2%	0.9991-0.9996
Ref. 17	Rare earth elements	Scheelite (calcium tungstate)	Elements + Tungstate	Solid-state reaction and pressed pellets	<4%	>0.9999
Present work	Mg, Al, Cu, Fe	Soil+CaF <sub>2</sub>	Elements + CaF <sub>2</sub>	Coprecipitation and pressed pellets	<5%	>0.999

a. Not available.

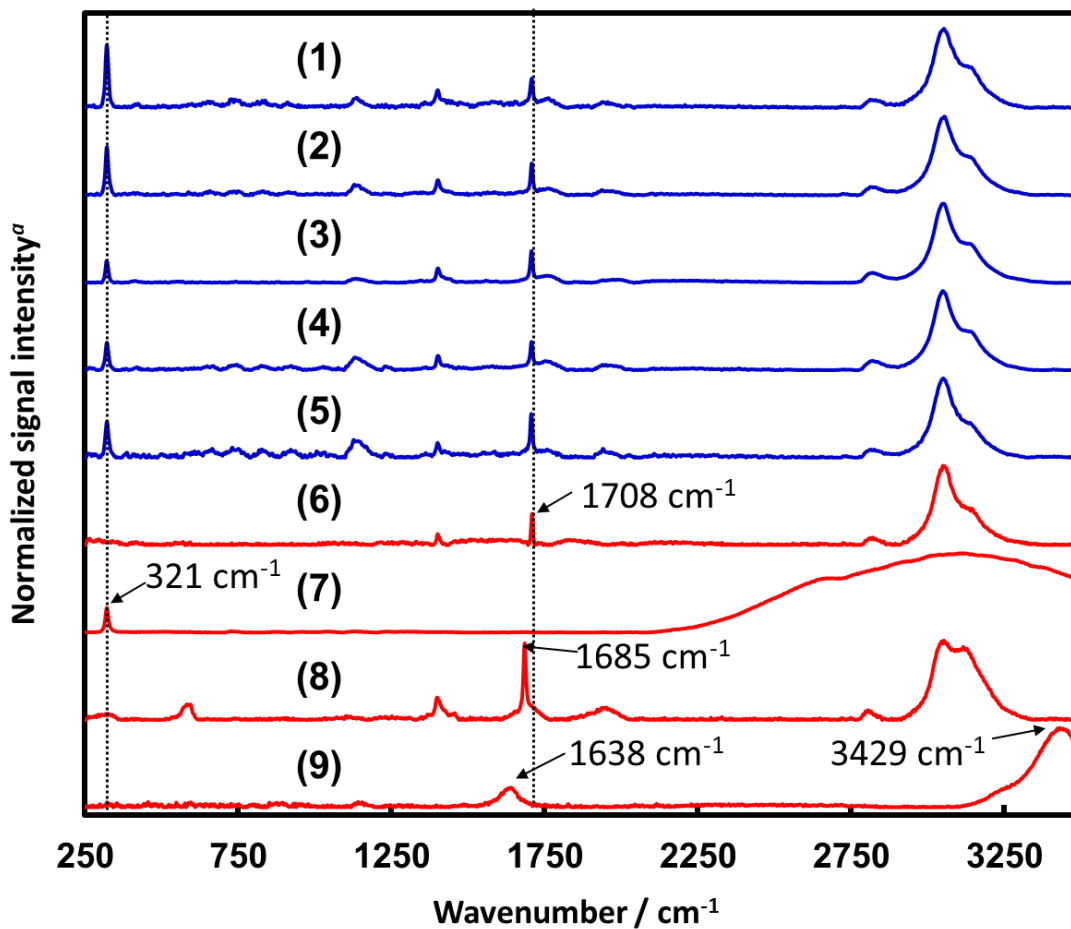


Fig. 1 Raman spectroscopic results of solid samples obtained in the present work at different evaporating temperatures. (1) Sample, evaporating temperature, 100 °C; (2) Sample, evaporating temperature, 140 °C; (3) Sample, evaporating temperature, 170 °C; (4) Sample, evaporating temperature, 200 °C; (5) Sample, evaporating temperature, 230 °C; (6) Standard,  $\text{NH}_4\text{Cl}$ ; (7) Standard,  $\text{CaF}_2$ ; (8) Standard, ABF; (9) Standard,  $\text{CaCl}_2$ .

<sup>a</sup>The signal intensity for each sample was normalized to its largest signal intensity.

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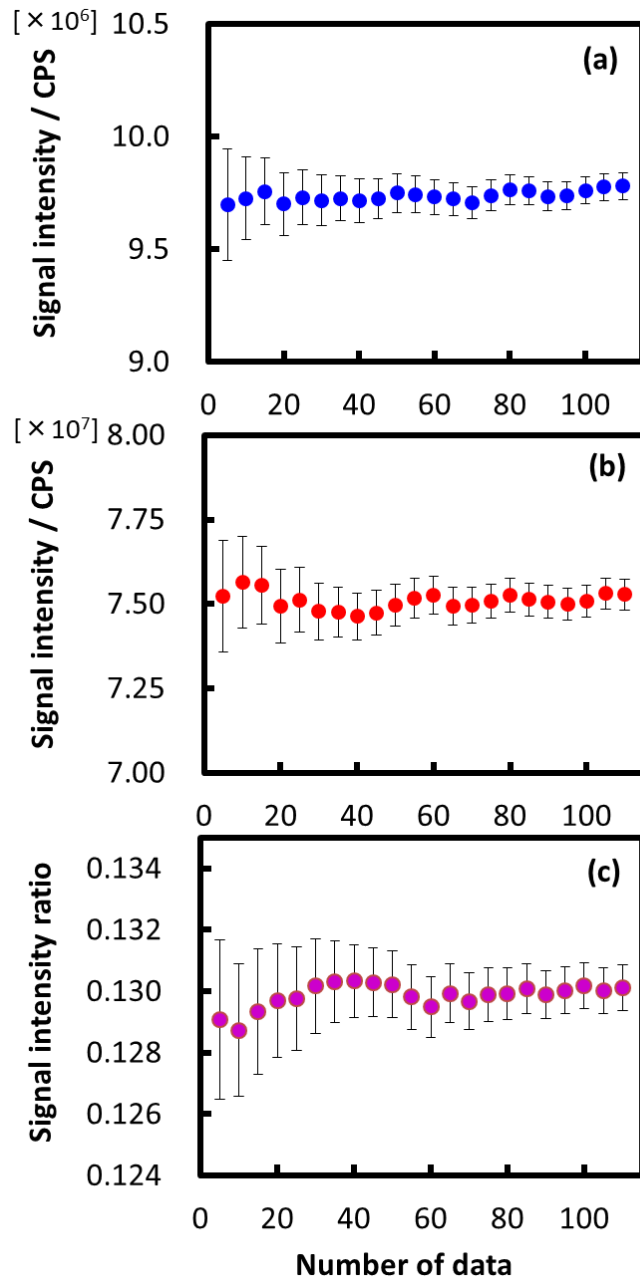


Fig. 2 Results for  $^{24}\text{Mg}^+$  and  $^{44}\text{Ca}^+$  in a calibration standard measured by LA-ICP-MS (bar, standard uncertainty).

(a) Signal intensity of  $^{24}\text{Mg}^+$ , (b) Signal intensity of  $^{44}\text{Ca}^+$ , (c) Signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$ .

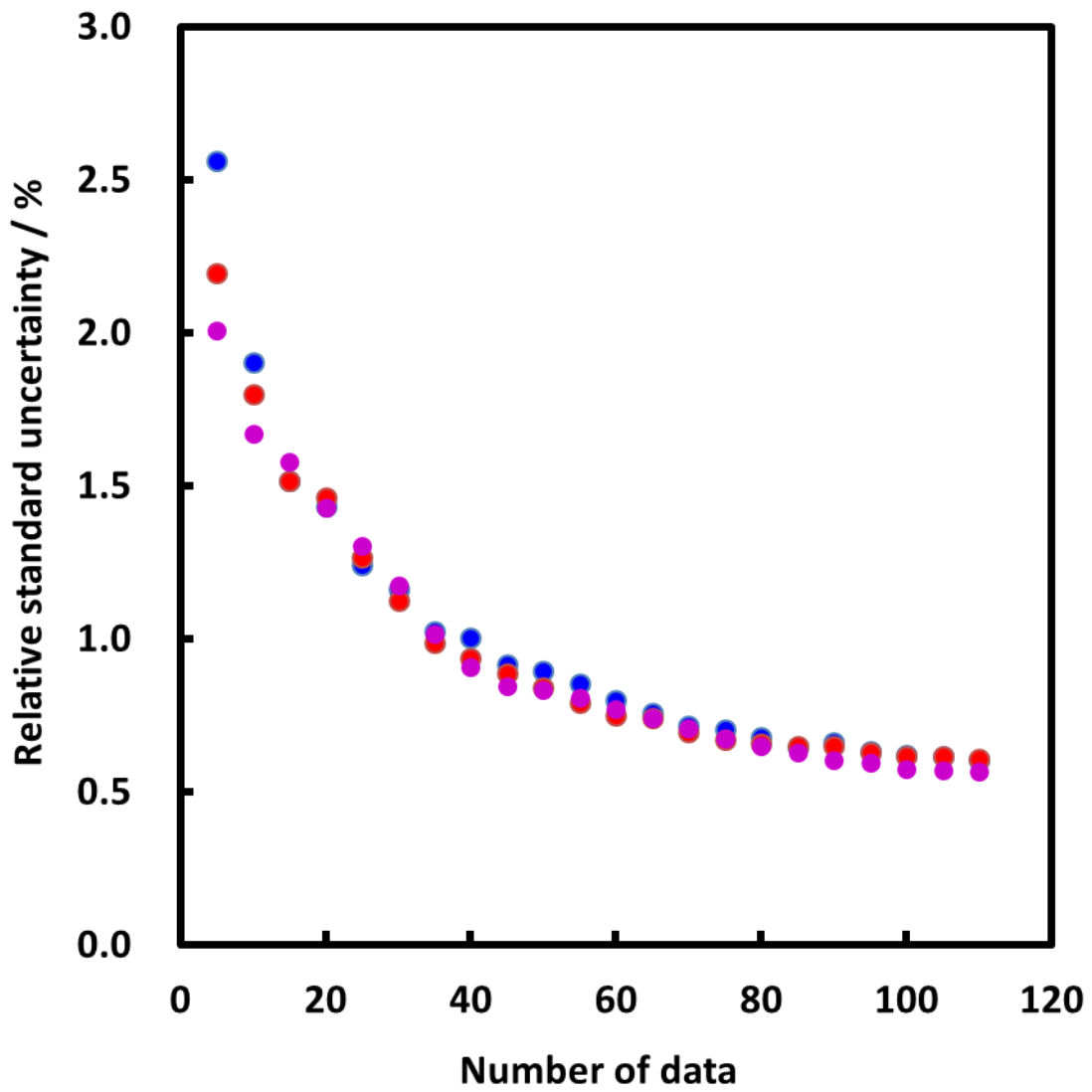


Fig. 3 Dependence of relative standard uncertainty on the number of data points.

● Signal intensity of  $^{24}\text{Mg}^+$ , ● Signal intensity of  $^{44}\text{Ca}^+$ , ● Signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$ .

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1     **Calcium fluoride as a dominating matrix for quantitative analysis by laser ablation-inductively**  
2     **coupled plasma-mass spectrometry (LA-ICP-MS): a feasibility study**

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20 Abstract

21 Calcium fluoride formed by the reaction between ammonium bifluoride and calcium chloride was  
22 investigated as a dominating matrix for quantitative analysis by laser ablation inductively coupled  
23 plasma mass spectrometry (LA-ICP-MS). Transformation from a solid sample to the calcium  
24 fluoride-based matrix permitted quantitative analysis based on calibration standards made from  
25 elemental standards. A low abundance stable calcium isotope, i.e.  $^{44}\text{Ca}^+$ , was monitored as the  
26 internal standard for quantitative analysis by LA-ICP-MS. Correlation coefficient factors for  
27 multiple elements were obtained with values over 0.999. The results for multiple elements in a  
28 certified reference material of soil (NIST SRM 2710a) agreed with the certified values in the range  
29 of expanded uncertainty, indicating the present method was valid for quantitation of elements in  
30 solid samples.

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32 *Keywords:* ammonium bifluoride, calcium fluoride, matrix-matching, calibration, LA-ICP-MS,  
33 quantitative analysis

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3 **36 1. Introduction**

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5 **37** Since the commercial availability in the early 1980s, inductively coupled plasma mass  
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7 **38** spectrometry (ICP-MS) has been increasingly adopted in inorganic chemical metrology as one of the  
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9 **39** most accurate quantitative analytical approaches [1]. The measurement by ICP-MS contributed to  
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11 **40** 56 out of 61 international comparisons organised by the working groups of Consultative Committee  
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13 **41** for Amount of Substance: Metrology in Chemistry and Biology (i.e. CCQM) since 1998. This  
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15 **42** could be attributed to the facts that ICP-MS has multiple merits for quantitative analysis, such as  
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17 **43** capability for simultaneous multi-elemental analysis with quite low instrumental detection limits,  
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19 **44** robustness permitting introduction of samples with various matrices, capability for overcoming  
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21 **45** spectral and non-spectral interferences, and so on. On the other hand, laser ablation (LA) had been  
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23 **46** applied to various research fields as an effective approach for introducing solid samples into the  
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25 **47** ICP-MS since the mid 1980s [2-11]. However, there are almost no reports on quantitative  
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27 **48** LA-ICP-MS analysis for chemical metrology activities, such as participating international  
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29 **49** comparisons or developing certified reference materials (CRMs). The major reason could be  
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31 **50** attributed to the fact that there was not a well-established calibration strategy applicable to a sample  
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33 **51** independent of the matrix [9], i.e. calibration strategy is still a key issue for quantitative elemental  
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35 **52** analysis by LA-ICP-MS.

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37 **53** External calibration (with or without internal standard), standard addition, and isotope dilution are  
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39 **54** major strategies for quantitative analysis by ICP-MS [12]. In solution-based quantitative elemental  
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41 **55** analysis, the solution uptake rate could be well controlled by using a stable nebulizer with or without  
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43 **56** the assist of a solution pump, while the samples and the standards could be made in the same matrix.  
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45 **57** Similarly, in solid-sample-based LA-ICP-MS quantitative elemental analysis, the  
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47 **58** sample-introduction rates between the sample and the standard should be identical or could be  
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49 **59** properly corrected with an internal standard. Furthermore, the matrix of the sample and the standard  
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51 **60** should be matched so that the signal responses between the sample and the standard are identical,  
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53 **61** thereby achieving accurate and precise results. Standards with an identical or similar matrix with  
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55 **62** the samples have been investigated for quantitative results of elements in various sample matrices by  
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57 **63** LA-ICP-MS, such as bones, minerals, and human teeth [13-17]. Lithium borate glasses had been  
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59 **64** investigated as a candidate calibrating strategy for analyzing samples of various matrix [18-22]. In  
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61 **65** these works, lithium borate acted as a dominating matrix and improved the capability for

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3 66 quantitative analysis by LA-ICP-MS. Due to a high temperature (around 950 to 1150 °C) is  
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5 67 required for making lithium borate glasses, crucibles made of platinum alloys are usually used as the  
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7 68 heating vessels for making lithium borate glasses. Contamination from the crucibles can be  
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9 69 problematic for quantitative analysis of some elements by LA-ICP-MS [19].

10 70 Strategies for quantitative analysis [23, 24] as well as for ablation mechanisms of various matrices  
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12 71 have been established for LA-ICP-MS [25-27]. Poly-methyl-methacrylate (PMMA) binder with  
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14 72 cesium as an internal standard and silicon-matrix standard solutions have been shown to be effective  
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16 73 for quantitative analysis of some elements in solid samples by LA-ICP-MS [23, 24]. However,  
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18 74 homogeneity of samples prepared with the PMMA binder needed to be improved for better  
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20 75 reproducibility [23], while calibration based on silicon-matrix solution standard required that the  
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22 76 concentration of silicon in the sample should be separately determined prior to the analysis of other  
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24 77 elements [24]. Slurry-based standard addition and isotope dilution had been reported as an  
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26 78 effective calibrating strategy for quantitative analysis of soil samples [28]. However, the principles  
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28 79 of standard addition and isotope dilution required to prepare multiple sub-samples (spiked and  
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30 80 non-spiked) for each sample and may limit the throughput of sample preparation.

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32 81 In this work, calcium fluoride was investigated as a dominating matrix for the quantitative  
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34 82 analysis of elements in soil samples by LA-ICP-MS based on elemental calibration standards made  
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36 83 from solution standards. Traceability confirmation and uncertainty evaluation of the results were  
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38 84 addressed for its potential application in chemical metrology. Multiple articles had presented  
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40 85 ammonium fluoride or ammonium bifluoride as a reagent for removing silica in solid samples prior  
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42 86 to the analysis [29-31]. In this work, ammonia bifluoride was used as a reagent providing fluoride  
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44 87 ion to form calcium fluoride.

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## 47 89 **2. Experimental**

### 48 49 90 **2.1. Instrumentations**

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51 91 The LA-ICP-MS measurements were carried out with a J200 LA instrument (Applied Spectra Inc.,  
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53 92 Fremont, CA) and an Aurora Elite model ICP-MS instrument (Bruker Cop., Bremen, Germany).  
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55 93 The J200 LA instrument was equipped with a 266 nm Nd:YAG laser. The operating conditions of  
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57 94 the LA -ICP-MS were selected after careful optimization of each parameter to obtain sufficient and  
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59 95 reproducible signal intensities for elements of interest. In order to facilitate the measurement of

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3 96 complex matrix samples, the ICP-MS was operated at normal sensitivity mode. An automatic  
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5 97 presser (3630 X-Press®, SPEX, Metuchen, NJ) with a 13.1 mm dia. die set were used for making  
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7 98 pellets of solid samples. A Lindberg/Blue M™ model electrical furnace (Thermo Fisher Scientific,  
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9 99 Asheville, NC) was used for heating during sample pretreatment. An analog vortex mixer from  
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11 100 VWR International (Radnor, PA) was used for mixing the sample and the chemicals during sample  
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13 101 pretreatment. A Delta Range® model electronic balance from Mettler Toledo (Columbus, OH) was  
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15 102 used for gravimetric sample preparation.  
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## 18 104 **2.2. Chemicals and materials**

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20 105 A certified reference material of soil (SRM 2710a) from the National Institute of Standard and  
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22 106 Technology (NIST, Gaithersburg, MD) was used for optimization of sample pretreatment procedure  
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24 107 as well as for confirming the validity of the proposed approach.

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26 108 High purity ammonium bifluoride (ABF, 99.999% trace metals basis) and calcium chloride  
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28 109 (anhydrous powder, 99.99 % trace metals basis) from Millipore Sigma Corp., (St. Louis, MO) were  
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30 110 used for producing calcium fluoride matrices. A multi-element standard solution (Supelco ICP  
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32 111 multi-element standard solution IV) was purchased from Millipore Sigma. The concentrations of  
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34 112 Mg, Al, Mn, and Fe were traceable to NIST SRMs 3131a, 3101a, 3132, and 3126a, respectively.

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36 113 Flat-bottom perfluoroalkoxy alkane (PFA) reaction vessel sets (7-mL vial with enclosure) from  
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38 114 Savillex (Eden Prairie, MN) were used for sample pretreatment.  
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## 41 116 **2.3. Procedure for sample pretreatment**

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43 117 Sample weighing was carried out with the electronic balance operated with a readability of 0.1 mg  
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45 118 and a maximum capacity of 101 g. Typical procedure for treatment of the samples is as follows.

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47 119 First, approximately 0.3 g of ABF and 0.05 g of initial solid sample (e.g. NIST SRM 2710a) were  
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49 120 respectively weighed and placed into the PFA vial. After the addition of 0.5 mL of pure water, the  
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51 121 PFA vial was firmly capped and placed on the vortex mixer for one minute. Then, approximately  
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53 122 0.65 g of 40 % (w/w) calcium chloride solution was added into the PFA vial, which was re-capped  
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55 123 and put on the vortex mixer for one additional minute. After that, the PFA vial was uncapped and  
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57 124 placed into the electrical furnace. Finally, the sample in the PFA vial was heated to 130 °C for two  
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59 125 hours followed by 230 °C for one hour.  
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3 126 After cooling, the sample was removed from the PFA vial and grounded to fine powder (with a  
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5 127 diameter around or less than 10  $\mu\text{m}$ , confirmed with an optical microscope), which was pressed into  
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7 128 a pellet at seven tons of pressure with holding time of four minutes. The sample pellet was  
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9 129 analyzed for elemental content with LA-ICP-MS.

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11 130 Samples for procedure blank were obtained in the same way as described above without the  
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13 131 addition of the initial solid sample. Calibration standards with multiple concentration levels were  
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15 132 also obtained in the same way by addition of various quantities of elemental standard solutions  
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17 133 instead of the initial solid sample in the aforementioned procedure.  
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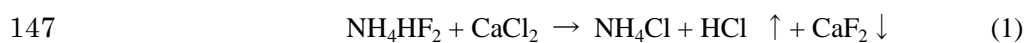
### 20 135 **3. Results and discussion**

#### 21 22 136 **3.1. Reaction in the procedure of sample pretreatment**

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24 137 Calcium fluoride was chosen as the matrix for quantitative analysis by LA-ICP-MS because  
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26 138 calcium has multiple low-abundance stable isotopes ( $^{42}\text{Ca}$ ,  $^{43}\text{Ca}$ ,  $^{44}\text{Ca}$ , and  $^{46}\text{Ca}$ ; 0.6 %, 0.1 %, 2 %,  
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28 139 and 0.004 %, respectively), which could be measured as candidate internal standards for various  
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30 140 sample-to-matrix mixing levels. Meanwhile, a stable precipitate of calcium fluoride could be easily  
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32 141 obtained due to its quite low solubility product at a level of  $10^{-11}$  (mol/L)<sup>3</sup> order. In addition,  
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34 142 calcium fluoride is a stable, non-hygroscopic (i.e. without swelling water from the air) compound  
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36 143 and permits making a durable sample pellet for the analysis by LA-ICP-MS.

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38 144 As mentioned above, ABF and calcium chloride were added for sample pretreatment. The  
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40 145 reaction between ABF and calcium chloride could be expressed with Eq. (1).

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47 149 In a preliminary experiment, it was found that the  $\text{CaCl}_2$  residue resulted in apparent swelling of  
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49 150 the sample pellets by absorption of the water vapour from the air. Therefore, a slight (ca. 5 %,   
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51 151 mole ratio) excess quantity of ABF in comparison to that of calcium chloride was added to  
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53 152 completely convert calcium chloride to calcium fluoride. Based on the solubility product of  
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55 153 calcium fluoride in water, the concentration of residual  $\text{F}^-$  and  $\text{Ca}^{2+}$  after precipitation reaction were  
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57 154 both under mmol/L. Therefore, the production efficiency of calcium fluoride was over 99.9%  
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59 155 considering the starting concentrations of  $\text{NH}_4\text{HF}_2$  and  $\text{CaCl}_2$ .

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3 156 After the reaction, water was evaporated to obtain a solid sample. Temperature for evaporation  
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5 157 was investigated in the range from 100 °C to 230 °C in steps of 10 °C. The results showed that  
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7 158 the evaporation at a temperature above 140 °C caused splashing of the sample. By contrast, a  
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9 159 temperature under 140 °C provided a mild evaporation without splashing of the sample but took a  
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11 160 longer time to obtain a dry solid sample. Therefore, the samples were heated at 130 °C for two  
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13 161 hours to evaporate the majority of water and further heated at 230 °C for one hour to obtain a dry  
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15 162 solid sample. Taking into consideration the melting temperature of the PFA material of the vial,  
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17 163 temperature over 240 °C was not investigated.

18 164 Raman spectroscopy was performed to confirm the chemical structure of the solid sample  
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20 165 obtained by the reaction outlined in Eq. (1). The spectra in Fig. 1 show that the typical peaks for  
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22 166 ABF (i.e., peaks at  $\sim 1685\text{ cm}^{-1}$ ) and calcium chloride (i.e., peaks at  $\sim 1638\text{ cm}^{-1}$  and  $\sim 3429$   
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24 167  $\text{cm}^{-1}$ ) disappeared after the reaction, while the peaks for calcium fluoride (i.e., peaks at  $\sim 321\text{ cm}^{-1}$ )  
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26 168 and ammonium chloride (i.e., peaks at  $\sim 1708\text{ cm}^{-1}$ ) were observed. These results indicate that the  
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28 169 major matrix after the reaction was a mixture of calcium fluoride and ammonium chloride, which  
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30 170 were independent of temperature for evaporation in the range from 100 °C to 230 °C.

31 171 In the present experiment, the reaction between  $\text{NH}_4\text{HF}_2$  and  $\text{CaCl}_2$  was dominating. The sample  
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33 172 powders were trapped by the resulting  $\text{NH}_4\text{Cl}$  and  $\text{CaF}_2$ .  
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### 37 174 **3.2. Representative signal intensities for magnesium and calcium in a calibration standard**

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39 175 For quantitative analysis, chemical composition of the sample ablated should be representative of  
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41 176 the bulk sample. In order to confirm the minimum number of data points required for quantitative  
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43 177 analysis, the results for signal intensities of  $^{24}\text{Mg}^+$  and  $^{44}\text{Ca}^+$  in a calibration standard are plotted in  
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45 178 Figs. 2 (a) and (b), whereas the results for the signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  are plotted in  
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47 179 Fig. 2(c). The bars shown in Figs. 2 (a) to (c) indicate the standard uncertainties, which were  
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49 180 obtained by dividing the standard deviation with the square root of the number of data points. In  
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51 181 principle, the standard uncertainty of a mean value of measurement depends on the standard  
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53 182 deviation and the number of data, i.e. the more data, the less standard uncertainty. However, when  
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55 183 the number of data was large enough, the contribution of increased data points could be negligible.  
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57 184 The results all were obtained after a pre-ablation to exclude possible surface contamination of the  
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59 185 pellet.

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3 186 In Figs. 2 (a) to (c), the plots from the low number of data to the high number of data were  
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5 187 respectively obtained by considering 5 to 110 (with a step size of 5) sets of data. In Fig. 2 (a), the  
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7 188 results for  $^{24}\text{Mg}^+$  obtained with various numbers of data agreed with one another in the range of their  
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9 189 standard uncertainty. The standard uncertainty decreased with the increase in the number of data  
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11 190 from 5 to 60, whereas the improvement in standard uncertainty was quite slight with further increase  
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13 191 of the number of data from 60 to 110. The reason can be attributed to the contribution of number of  
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15 192 data, approximately  $0.45 (1/\sqrt{5})$ ,  $0.13 (1/\sqrt{60})$ , and  $0.10 (1/\sqrt{110})$  respectively for a number of 5, 60,  
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17 193 and 110. The results for  $^{44}\text{Ca}^+$  shown in Fig. 2 (b) were similar to the results for  $^{24}\text{Mg}^+$  in Fig. 2 (a).

18 194 In Fig. 2 (c), the results for signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  showed that a stable value with  
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20 195 a small uncertainty (relative uncertainty close to or lower than 1 %) could be obtained when the  
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22 196 number of data points was over 60. Therefore, each sample or standard in the following  
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24 197 experiment was analysed to obtain at least 60 sets of data for quantitative analysis.

25 198 Dependence of the relative standard uncertainty on the number of data points is plotted in Fig. 3.  
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27 199 As can be seen from Fig. 3, the relative standard uncertainty for each parameter decreased with the  
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29 200 increase of number of data points. The relative standard uncertainty for signal intensity ratio of  
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31 201  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$  showed the lowest value for each number of data points over 40, indicating the  
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33 202 improvement of measurement precision by internal standard correction.  
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### 37 204 **3.3. Linearity of the calibration curves**

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39 205 The concentration of an element of interest in a solid sample was quantitated based on a  
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41 206 calibration curve established using multiple standards made from elemental solution standards.  
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43 207 The results for signal intensities of  $^{24}\text{Mg}^+$ ,  $^{27}\text{Al}^+$ ,  $^{55}\text{Mn}^+$ , and  $^{57}\text{Fe}^+$  in the calibration standards are  
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45 208 summarized in Table 2, along with the slope, the intercept, and the correlation factor for the  
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47 209 calibration curves.

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49 210 In Table 2, the signal intensities for each element in the calibration Standards 2 to 4 were  
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51 211 significantly higher than in Standard 1 (i.e. blank). The correlation factor for each element was  
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53 212 better than 0.999, showing very good linearity of the calibration curve. Detection limits were  
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55 213 calculated as the concentrations corresponding to 3-fold the standard deviations of 10-times  
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57 214 measurement of Standard 1. The method detection limits for Mg, Al, Mn, and Fe were respectively  
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59 215 2.0, 1.7, 0.8, and  $22 \mu\text{g g}^{-1}$ , giving the sample-to-Ca ratio was 0.1.

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**3.4. Analytical results of the elements in NIST SRM 2710a**

The method developed in this work was applied to the quantitative analysis of elements in a soil CRM, i.e. NIST SRM 2710a. As the internal standard, the contribution of the contents of Ca in the sample was also considered, which was negligible (< 0.5 %) in comparison to the contents of Ca introduced as calcium chloride for sample preparation. The observed values for the elements in NIST SRM 2710a are summarized in Table 3 with the certified values. In Table 3, both the certified values and the observed values are given as the (Mean ± expanded uncertainty), with a coverage factor ( $k = 2$ ) corresponding to an interval having a level of confidence of approximately 95 %. Uncertainty estimation was carried out following the guide to the expression of uncertainty in measurement [32]. The major factors considered for the uncertainties in the observed values were the linearity of the calibration curve (the slope and the intercept) and the measurement of signal intensity in the sample.

In Table 3,  $\Delta M / \Sigma U$ , i.e.  $(M_o - M_c) / (U_o + U_c)$  is given as a parameter for evaluating the extent of agreement between an observed value and a certified value. For this parameter,  $M_o$  and  $M_c$  are the means of an observed value and a certified value, respectively, while  $U_o$  and  $U_c$  are the expanded uncertainty of an observed value and a certified value, respectively. A value of  $\Delta M / \Sigma U$  in the range of [-1, 1] indicates that the observed value was in good agreement with the certified value.

In Table 3, two sets of observed values (A and B, respectively) were obtained with two independent sample pellets made with different sample-to-Ca ratios. The  $\Delta M / \Sigma U$  values for Al (set A), Mn (sets A and B), and Fe (sets A and B) were in the range of [-1, 1], indicating good agreement between the observed values and the certified values. By contrast, the  $\Delta M / \Sigma U$  values for Mg (sets A and B) and Al (set B) were out of the range of [-1, 1], indicating less agreement between the observed values and the certified values. One of the reasons for such disagreement might be the fact that only a minute portion (roughly 1/50 000) of the sample pellet was subjected to the analysis by LA-ICP-MS, therefore, the inhomogeneity of different elements in the initial sample powder may be ineligible. According to the certificate of NIST SRM 2710a, the homogeneity tests were based on the analysis of at least 170 mg of sample powders, which was over 150 000 folds than the quantity of sample used for obtaining one set of data in the present work. Since the dominating



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246 matrix in the present work was calcium fluoride with ammonium nitrate, the matrix effect due to a  
247 relative minor difference in sample mass could be negligible.

248 The metrological traceability of the results was ensured by using multiple concentration levels of  
249 calibration standards made from a multi-element standard solution with elemental concentrations  
250 traceable to NIST SRMs. All of the sample and standard pretreatment operations were carried out  
251 based on a gravimetric method by using an analytical balance.

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253 **3.5. Comparison of quantitation strategy used in the present work and selected references**

254 A comparison of quantitation strategies used in this work with those used in multiple literature  
255 references is summarized in Table 4. It is notable that the standards for calibration curves described  
256 in Refs. 13 to 17 were respectively matrix-matched with the samples to ensure better quantitative  
257 results. By contrast, calcium fluoride was introduced as an additional matrix for the measurement  
258 of soil sample in this work; calibration standards made from elemental solutions could be used for  
259 quantitative analysis of the elements in soil sample. The precision and correlation coefficient of  
260 calibration curves measured in this work were comparable to or better than the values previously  
261 reported.

262

263 **4. Conclusions**

264 Calcium fluoride was investigated as a dominating matrix for quantitative analysis of elements in  
265 solid samples by LA-ICP-MS. Transformation from a soil sample to the calcium fluoride matrix  
266 permitted quantitative analysis based on calibration standards made from elemental solutions. A  
267 low abundance stable calcium isotope, i.e.  $^{44}\text{Ca}^+$  providing moderate signal intensity comparable to  
268 the elements of interest, was measured and used as the internal standard for quantitative analysis by  
269 LA-ICP-MS. Linearity with good correlation coefficient ( $> 0.999$ ) was obtained for the calibration  
270 curves of multiple elements. The results for a soil sample, NIST SRM 2710a, agreed with the  
271 certified values, indicating that the present method could be a reliable candidate for quantitative  
272 analysis of the elements in solid sample by LA-ICP-MS. The possibility of ensuring metrological  
273 traceability and evaluating uncertainty of the results permits the application for chemical metrology  
274 purposes.

275 The whole process of the present method takes several hours, which is longer or comparable to

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276 lithium borate fusion and microwave-assisted acid digestion. Due to a relatively lower temperature  
277 is required for heating, the present method permits the use of PFA and PTFE vessels for sample  
278 preparation, which contributes to a better control of procedure blank. The solid samples are more  
279 stable and have a much smaller size than a sample solution obtained by acid digestion; this feature is  
280 a merit for long term monitoring and remeasurement for quality control.

281 Calcium was used as the internal standard in the present work. Special attention should be paid  
282 to spectral interferences of calcium isotopes to ensure the accuracy of the results. The  
283 concentration of calcium in the sample should be negligible in comparison to the quantity of calcium  
284 introduced as the matrix or precisely quantified and considered for internal standard correction.

285 Four elements, i.e. Mg, Al, Mn, and Fe, were discussed in the present work from the viewpoint of  
286 quantitative analysis. Based on the results obtained by adding multiple levels of sample quantities  
287 (i.e. sample to CaF<sub>2</sub> ratio), good linearity with a correlation coefficient value over 0.999 was also  
288 observed for Sc (5.3 %), Ti (0.8 %), V (0.9 %), Cr (3.6 %), Co (4.8 %), Ni (2.1 %), Cu (1.3 %), Zn  
289 (2.0 %), Ge (2.6 %), Rb (2.4 %), Sr (1.1 %), Y (4.6 %), Zr (5.7 %), Ru (9.7 %), Pd (8.9 %), Ag  
290 (1.2 %), Cd (1.1 %), In (2.2 %), Ba (1.5 %), La (3.3 %), Ce (5.8 %), Pr (4.7 %), Nd (7.0 %), Sm  
291 (5.5 %), Eu (2.2 %), Gd (2.9 %), Tb (5.9 %), Dy (7.2 %), Tl (3.8 %), Pb (1.4 %), Th (3.9 %), and U  
292 (1.6 %), respectively, where the value in the parentheses following each element is the typical  
293 relative standard deviation of the signal intensity observed in the same conditions as those used for  
294 “Observed value B” in Table 3. However, due to the range of concentrations for these elements,  
295 additional optimization of the calibrating standards is required for quantitative analysis. The works  
296 about quantitative analysis of these elements are still in progress and the authors will try to publish  
297 the results in the near future.

298

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304 Laboratory.

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402 Table 1  
403 Operating conditions of LA -ICP-MS.

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405	<b>Laser ablation</b>	<b>J200 LA</b>
406	Wavelength	266 nm
407	Energy per pulse	20 mJ
408	Beam diameter	80 $\mu\text{m}$
409	Pulse repetition rate	10 Hz
410	Scan rate	100 $\mu\text{m s}^{-1}$
411	Line-to-line distance	400 $\mu\text{m}$
412	Pre-ablation	45 s
413	Lines per pellet	6
414	Line-to-line delay	15 s
415	<b>ICP-MS</b>	<b>Aurora Elite</b>
416	RF power	1400 W
417	Plasma gas flow rate	Ar 14 L min <sup>-1</sup>
418	Auxiliary gas flow rate	Ar 1.00 L min <sup>-1</sup>
419	Carrier gas flow	Ar 1.4 L min <sup>-1</sup>
420	Scanning mode	Peak hopping
421	Dwell time per isotope	5 ms
422	Data acquisition mode	Time resolved (TRA)

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Table 2  
Signal intensities for the elements in calibration standards obtained by LA-ICP-MS.

Standard	Element-to-Ca ratio ( $\times 10^{-6}$ )	Signal intensity <sup>a</sup> / CPS (after internal standard correction by using <sup>44</sup> Ca <sup>+</sup> signal intensity)			
		<sup>24</sup> Mg <sup>+</sup>	<sup>27</sup> Al <sup>+</sup>	<sup>55</sup> Mn <sup>+</sup>	<sup>57</sup> Fe <sup>+</sup>
1	0.000	23300 ± 500	1500 ± 100	1600 ± 300	46100 ± 1400
2	0.401	2449000 ± 11000	727000 ± 8000	3584000 ± 170000	689000 ± 7000
3	0.839	5189000 ± 28000	1523000 ± 10000	7839000 ± 387000	1393000 ± 18000
4	1.251	7684000 ± 66000	2266000 ± 12000	10970000 ± 769000	2000000 ± 11000
5	1.663	9954000 ± 58000	2975000 ± 19000	14437000 ± 219000	2609000 ± 17000
Slope		6011000	1793000	8685000	1542000
Intercept		65910	8979	150800	66620
Correlation factor		0.9998	0.9999	0.9992	0.9998

a, Mean ± standard uncertainty.



Table 3  
Analytical results of the elements in NIST SRM 2710a.

Element	Concentration <sup>a</sup> / %						$\Delta M / \Sigma U$ <sup>d</sup>	
	Certified value		Observed value A <sup>b</sup>		Observed value B <sup>c</sup>		Observed value A	Observed value B
Mg	0.734	± 0.038	0.654	± 0.038	0.657	± 0.030	-1.05	-1.12
Al	5.95	± 0.05	5.92	± 0.29	5.53	± 0.28	-0.09	-1.27
Mn	0.214	± 0.006	0.166	± 0.077	0.172	± 0.052	-0.58	-0.72
Fe	4.32	± 0.08	4.33	± 0.12	4.37	± 0.13	0.07	0.25

a. Mean ± expanded uncertainty,  $k = 2$ . b. Sample-to-Ca ratio, 0.100. c. Sample-to-Ca ratio, 0.150.

d.  $\Delta M / \Sigma U$ , i.e.  $(M_o - M_c) / (U_o + U_c)$ ;  $M_o$  and  $M_c$ , Means of observed value and certified value, respectively;  $U_o$  and  $U_c$ , Expanded uncertainty of observed value and certified value, respectively.

Table 4

A comparison of the present work with reported methods for quantitation analysis.

Ref. No.	Element	Sample	Standard	Process for making calibrating standard	Typical precision / RSD	Correlation coefficient of calibration curve
Ref. 13	Pb	Bone	Bone CRM	Pressed pellets	10-20%	NA <sup>a</sup>
Ref. 14	Co, Ni, Cu, Ga, Zn, Se, Pb	Iron sulphide	Element + Pyrite (iron sulfide)	Welding and re-solidification	<15%	NA <sup>a</sup>
Ref. 15	Mg, Al, V, Mn, Zn, As, Sr, Rb, Cd, Ba, Hg, Pb	Fish dorsal spine	Hydroxyapatite (calcium phosphate)	Coprecipitation and pressed pellets	1.6-24%	0.9690-0.9997
Ref. 16	Al, Ba, La, Sr	Human teeth	Elements + Human teeth	Solution-standard spiking, drying, and pressed pellets	2.1-4.2%	0.9991-0.9996
Ref. 17	Rare earth elements	Scheelite (calcium tungstate)	Elements + Tungstate	Solid-state reaction and pressed pellets	<4%	>0.9999
Present work	Mg, Al, Cu, Fe	Soil+CaF <sub>2</sub>	Elements + CaF <sub>2</sub>	Coprecipitation and pressed pellets	<5%	>0.999

a. Not available.

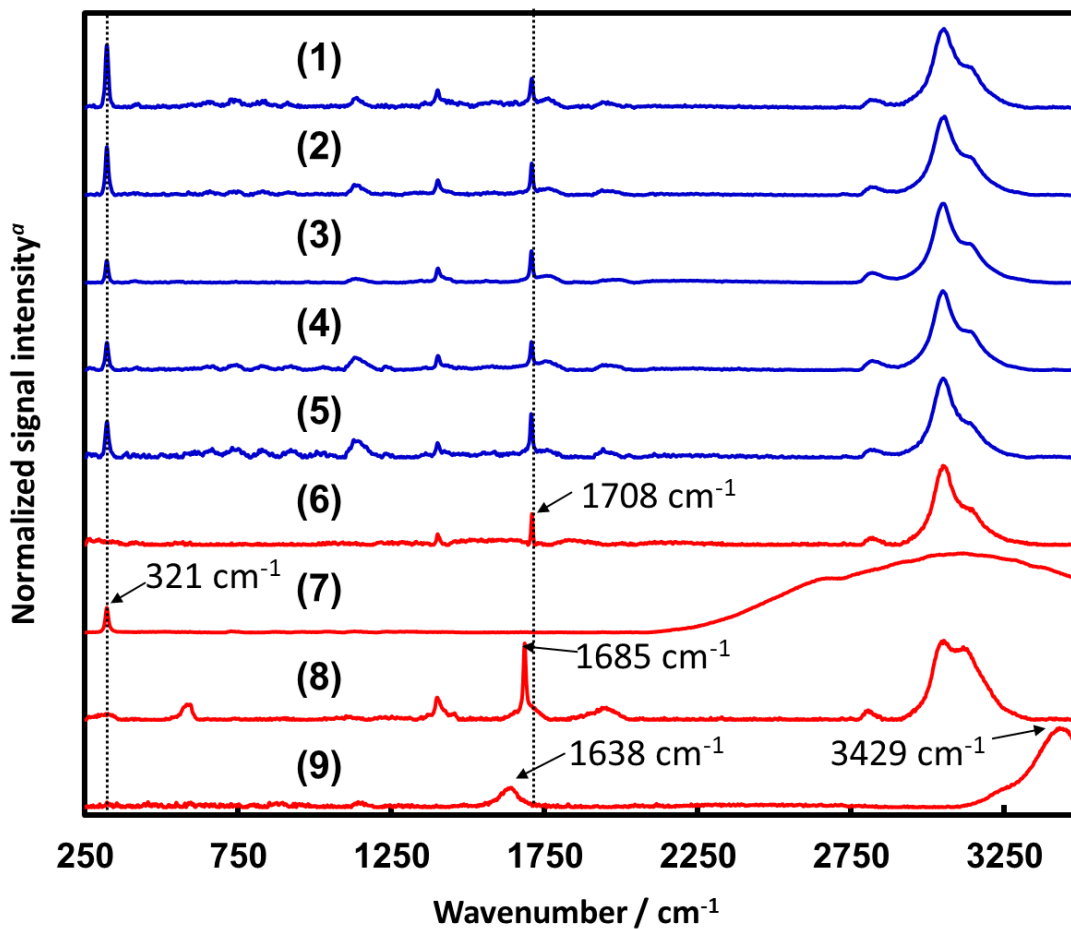


Fig. 1 Raman spectroscopic results of solid samples obtained in the present work at different evaporating temperatures. (1) Sample, evaporating temperature, 100 °C; (2) Sample, evaporating temperature, 140 °C; (3) Sample, evaporating temperature, 170 °C; (4) Sample, evaporating temperature, 200 °C; (5) Sample, evaporating temperature, 230 °C; (6) Standard,  $\text{NH}_4\text{Cl}$ ; (7) Standard,  $\text{CaF}_2$ ; (8) Standard, ABF; (9) Standard,  $\text{CaCl}_2$ .

<sup>a</sup>The signal intensity for each sample was normalized to its largest signal intensity.

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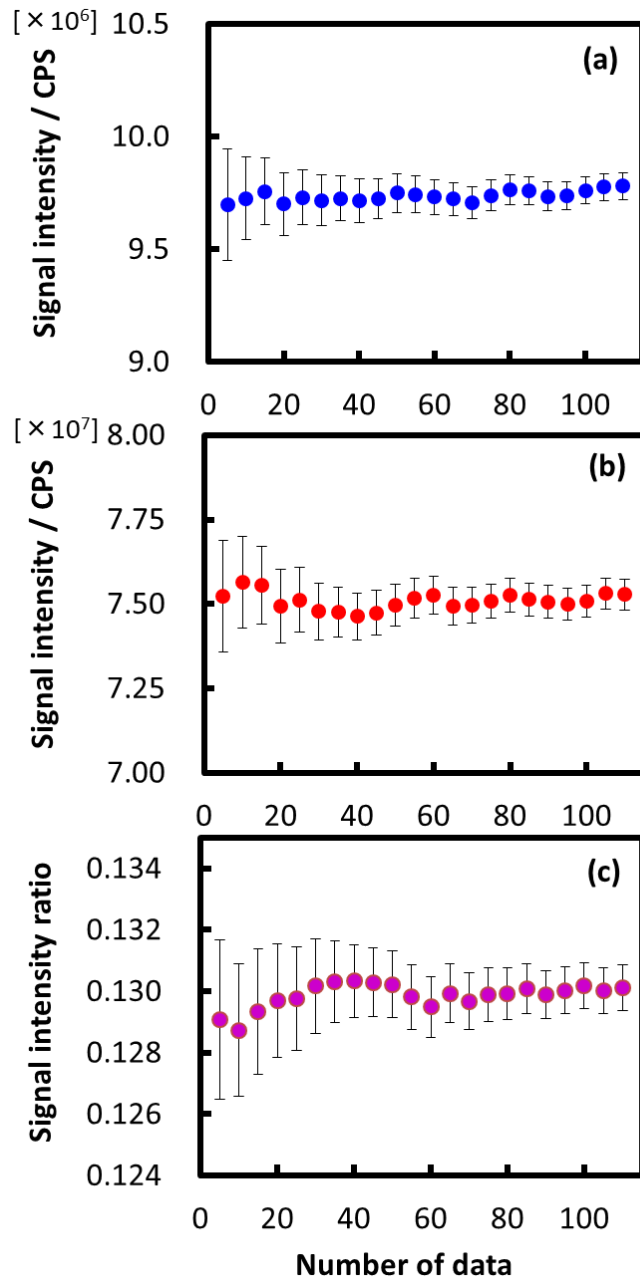


Fig. 2 Results for  $^{24}\text{Mg}^+$  and  $^{44}\text{Ca}^+$  in a calibration standard measured by LA-ICP-MS (bar, standard uncertainty).

(a) Signal intensity of  $^{24}\text{Mg}^+$ , (b) Signal intensity of  $^{44}\text{Ca}^+$ , (c) Signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$ .

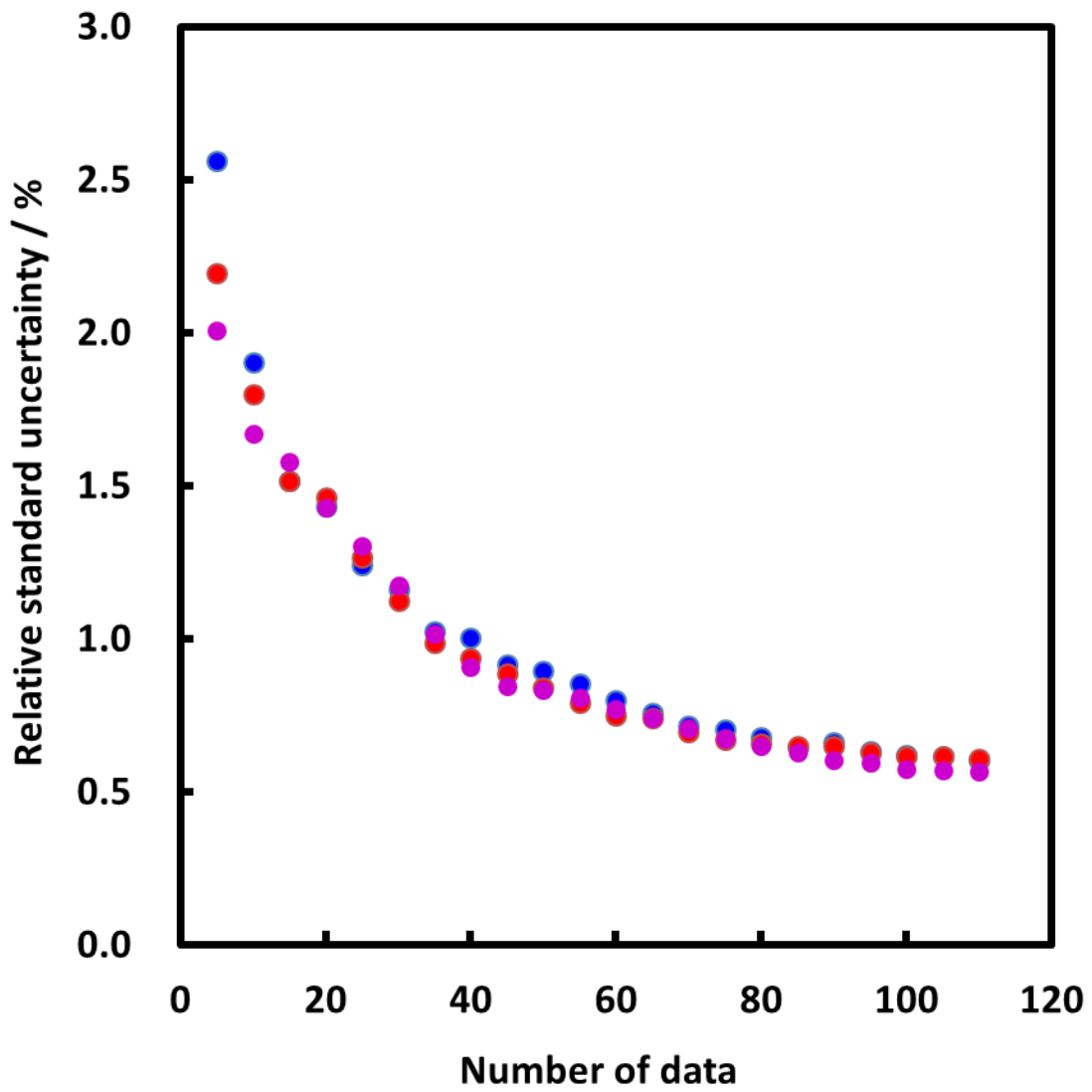


Fig. 3 Dependence of relative standard uncertainty on the number of data points.

● Signal intensity of  $^{24}\text{Mg}^+$ , ● Signal intensity of  $^{44}\text{Ca}^+$ , ● Signal intensity ratio of  $^{24}\text{Mg}^+$  to  $^{44}\text{Ca}^+$ .