Optimization of lithium metaborate fusion and post-ultrasonic extraction for multi-element determination in graphite by ICP-AES

Liangcheng ZHAO,* Li WEI,* Yanqiao HU,* Qingzhi CHEN,* Wencui CHENG,* Jinming ZHANG,* Xing LI,* Ziyi AN,** Jianwei MENG,*† Huajie LIU,***†

* Key Laboratory of Mineral Resources and Ecological Environment Monitoring, Hebei Province, Hebei Research Center for Geoanalysis, Baoding 071051, China
** National Research Center for Geoanalysis, Beijing 100037, China
*** School of Life Sciences, Institute of Life Science and Green Development, Hebei University, Baoding 071002, China

† To whom correspondence should be addressed.
E-mail: mjw678@sina.com; liuhuajie@foxmail.com
Abstract

The existing methods cannot achieve rapid mass decomposition and multi-element analysis of graphite ore samples. In this study, it is found that molten lithium metaborate can destroy the structure of graphite, causing graphite C to be oxidized and decomposed in an oxygen environment. We have established a method system for testing graphite ore samples with lithium metaborate at 950°C melting-ultrasonic extraction-ICP-AES multi-element (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, and Ti) testing. The verification results of the national first-level reference materials show that the detection limit of this method is low and the accuracy and precision are good. The results of the measured samples show no significant difference between this method and the classical chemical analysis method. This method has the following advantages over the existing ones: simple operation process, faster decomposition and testing, less reagent usage, less sample contamination, and better results reproducibility.

Keywords: Graphite, lithium metaborate, decomposition, ultrasonic extraction, ICP-AES (Inductively coupled plasma-Atomic emission spectrometry)
Introduction

The rapid and accurate determination of multiple elements of graphite in large quantities plays an important role in its production and application. Graphite is a non-metallic material widely used in the fields of industry, military, and aerospace. Nevertheless, the current analysis technology cannot meet the requirements for rapid multi-element determination of graphite samples in large quantities. The reason is that graphite has stable chemical properties, and is difficult to be decomposed directly by alkali fusion and acid solution decomposition methods under normal temperature and pressure.

The main decomposition methods of graphite samples and their limitations are as follows. 1) The first approach is to burn graphite at high temperature and digest/fuse the ash with acid/alkali (JC/T1021.5-2007), in which the loss of elements under burning conditions will cause certain volatile trace elements to not be accurately detected. 2) Burning graphite sample in a platinum crucible with sodium potassium carbonate can avoid the loss of volatile elements, but K and Na cannot be detected. 3) Extraction with hydrochloric acid solution under heating conditions (GB/T3521-2008) can merely determine soluble Fe. 4) The disadvantages of microwave reflux digestion at ordinary pressure are that the operation is cumbersome and time-consuming, and the operation of multiple cooling and adding HNO₃ is easy to contaminate the sample. 5) The method of direct injection of sample for determination is poor in precision since the sample is directly measured without digestion.
It has been observed in previous experiments that lithium metaborate corrodes graphite crucibles. It means that this substance may be a good decomposition flux that meets the requirements for simultaneous determination of multiple elements in graphite ore samples. In fact, lithium metaborate has been widely reported in the decomposition of minerals such as soil, stream sediments and rocks, including some refractory rocks and minerals, but it has not been used in the decomposition of graphite samples so far. Some believe that lithium metaborate is a high-melting-point non-oxidizing flux, and some report that it has strong oxidizing properties. Research on the high temperature Raman spectrum and melt structure of lithium metaborate shows that lithium metaborate has a chain BO$_3$ triangle structure at room temperature, which gradually transforms into hexagonal ring ($\text{B}_3\text{O}_6$)$_3^-$ after melting. At high temperature, the chain and hexagonal ring structures are transformed into BO$_3$ to form a continuous random network structure, during which B can be reduced to boron carbide by C. Therefore, graphite existing in a hexagonal layered structure can react with lithium metaborate at high temperatures, and its structure varies and decomposes under the action of oxygen in the air. Furthermore, since this flux does not introduce any element to be tested, it has little contamination to the sample.

In this paper, the graphite samples were treated by lithium metaborate high temperature melting system, and multielement determination was carried out by ICP-AES. The research purpose is to solve the following problems: 1) Can the lithium metaborate alkali fusion method decompose graphite samples while meeting the
requirements of multi-element quantitative testing? 2) Establishing and optimizing the lithium metaborate alkali fusion-ICP-AES system for rapid mass determination of multiple elements in graphite samples. To our knowledge this is the first report on decomposition of graphite samples by lithium metaborate fusion.

**Experiment**

**Instruments and reagents**

VISTA-MPX Inductively coupled plasma-atomic emission spectrometer (ICP-AES, Varian Company): the instrument adopts a high-resolution echelle cross-dispersion optical system, a CCD solid detector, and a detachable three-layer quartz concentric torch. The optimal operating conditions of ICP-AES are listed in Table 1.

X-ray diffractometer: Rigaku SmartLab 9kW (Rigaku Corp.) equipped with a rotating copper target. The optimal operating conditions of X-ray diffractometer are listed in Table 1.

Supersonic cleaner: Desen DSA50-JY1-1.8L, power 50 W, frequency 40 kHz (Fuzhou Desen Precision Co., Ltd., Fuzhou, China)

Grinder: GJ-1 sealed laboratory sample preparation grinder (Nanchang laboratory prototype plant, Nanchang, China)

Inflatable temperature-controlled muffle furnace: TM-3014, a box-type furnace of 300×400×250 mm in size, equipped with 100 mL and 18 mL porcelain crucible (Michem Instrumentation Ltd., Beijing, China)
Standard solution and main reagents. Standard stock solution: The concentrations of standard stock solutions SiO₂, K₂O, Na₂O, Al₂O₃, CaO, MgO, Fe₂O₃, TiO₂, MnO, and P₂O₅ are 1 mg mL⁻¹.

Standard working solution for ICP-AES: According to the content of the sample and the content difference between the measured elements, the standard stock solution is gradually diluted to prepare a series of mixed standard working solutions. Specifically, SiO₂, Al₂O₃ and Fe₂O₃ are 0, 10, 50, 100 and 200 mg L⁻¹; CaO and MgO are 0, 1, 10, 20 and 50 mg L⁻¹; TiO₂, MnO, P₂O₅, K₂O and Na₂O are 0, 0.5, 1, 10 and 20 mg L⁻¹. The medium is a mixed solution of 0.008 g mL⁻¹ lithium metaborate and 5% hydrochloric acid.

Premium grade pure hydrochloric acid: 160718 (Beijing Institute of Chemical Reagents, Beijing, China)

Premium grade pure lithium metaborate: LiBO₂ ≥ 99.99%, Aladdin L101992-100g (Aladdin Industrial Co., Shanghai, China)

High purity water (resistivity≥18 MΩ·cm).

Standard graphite ore. Primary reference materials of China: GBW03118, GBW03119, and GBW03120; Canada: CDN-GR-2; Mongolia: CGL003.

Experimental method

After the graphite sample (particle size <74 μm) is crushed, it is dried in an oven at 105°C for 2-3 hours, and then transferred to a desiccator to cool to room temperature.

In the decomposition experiment, the graphite decomposition under various test
conditions is compared, such as different crucibles (porcelain, high aluminum, gold, silver, platinum, etc.), graphite sample weights, sample mass ratios (the mass ratio of lithium metaborate to graphite), melting conditions (sample melting temperature, melting duration, filling air and CO in the melting system), and extraction conditions (water extraction, acid extraction method, ultrasonic-assisted water extraction, ultrasonic-assisted acid extraction, acid dosage, ultrasonic vibration time). The details of the methods and materials are shown in each of the optimization experiments in the results and discussion section.

In the ICP-AES optimization experiment, the matrix effect and spectral line interference are detected to determine the detection limit and accuracy of the method. With the measured samples as materials, the results of the present method are compared with those of traditional chemical analysis methods (atomic absorption method, spectrophotometry, and volumetric method) described elsewhere. ²

Finally, the optimization process and parameters of the lithium metaborate alkali fusion decomposition of the graphite sample are determined as follows: Weigh 0.2500 g of the sample and place it into a platinum crucible covered with 1 g of lithium metaborate; mix the sample with the lithium metaborate by a thin plastic rod or platinum wire; cover the mixture with 1 g of lithium metaborate and put it into the muffle furnace; heat it to 950°C to melt for 2-3 h, and shake it 1-2 times during melting. Take it out after the melting is complete; after it cools down, put it in a PTFE beaker, and add about 150 mL of 5% hot hydrochloric acid for ultrasonic vibration extraction; after the extraction, take out the crucible and wash it with water; after the
solution cools, dilute it in a volumetric flask with water to 250 mL, with the acidity keeping at 5%; shake the final solution well for subsequent test. According to the methods described above, operation blanks of 0.008 g mL\(^{-1}\) of lithium metaborate were prepared by dissolving 2 g of lithium metaborate in 5% hydrochloric acid and diluting to 250 mL for ICP-AES determination.

**Results and Discussion**

*Possible mechanism of graphite decomposition by lithium metaborate*

The successful decomposition of graphite samples by lithium metaborate in the molten state may be explained by two mechanisms. First, the chain-like BO\(_3\) triangle structure of lithium metaborate is transformed into a hexagonal ring (B\(_3\)O\(_6\))^3-structure at high temperatures, and the continuous random network structure formed is conducive to the reduction of B by C and the formation of boron carbide.\(^{20-21}\) In other words, under the action of lithium metaborate alkali fusion, the following reaction may occur:

\[
\text{B} + \text{C} \rightarrow \text{B}_4\text{C} + \text{CO} \quad (1)
\]

This chemical reaction can destroy the ordered hexagonal layered structure of graphite and contribute to the decomposition of graphite samples.

To verify this hypothesis, the X-ray diffraction (XRD) analysis results of 8 samples with sample mass ratio (ratio of lithium metaborate to graphite: 0.33, 0.5, 1.0, 2.0, 3.0, 5.0, 10.0 and 20.0) under four melting durations (0.5 h, 1 h, 2 h and 3 h) were cross-compared at the melting temperature of 950°C. The results show that a few
obvious C-B diffraction peaks are observed for the melt with the sample mass ratio greater than 2.0 and the melting duration less than 2 h (Fig. 1). Under other treatment conditions, although graphite samples tend to be completely decomposed, no obvious C-B diffraction peaks are found for their melts. This demonstrates that lithium metaborate destroys the hexagonal layered structure of graphite at high temperature, causing graphite easy to be oxidized.

Second, in the molten state of lithium metaborate, graphite C may react with the O$_2$ in the air to decompose graphite. To verify this hypothesis, an inflatable temperature-controlled muffle furnace is used to cross-compare the melting effect under two gas environments (aerobic environment: filled with air; anaerobic environment: filled with 5 L min$^{-1}$ of CO gas) and two air-contacting area gradients. The air-contacting area gradient is achieved by the following steps: place 0.5000 g of spectral pure graphite powder in 100 mL and 18 mL porcelain crucibles respectively; add 2 g of lithium metaborate to mix well with the sample, and then cover the surface with 1 g of lithium metaborate. All samples were heated in a 900°C temperature-controlled muffle furnace for 3 hours, and then taken out and cooled to room temperature. The observation showed that in an aerobic environment, the sample in large crucible was completely decomposed, and the sample in small crucible had a small amount of graphite residue, which was further decomposed after an extended time period. By contrast, in an oxygen-free environment, the decomposition of samples in both large and small crucibles was not complete, and the corresponding residual ratio of melts were 94.51% and 94.58%, respectively. This
proves that O$_2$ in the air plays an important role in the decomposition of graphite samples by molten lithium metaborate.

In summary, it is believed that the oxidation of graphite carbon by molten lithium metaborate and O$_2$ in the air can destroy the molecular structure of graphite as well as promote the decomposition of graphite samples.

**Optimization of graphite decomposition conditions**

In order to improve the decomposition and recovery efficiency of graphite samples, and to reduce the interference of sample contamination on spectroscopy in the ICP-AES test, the following optimization experiments were carried out regarding the decomposition conditions of graphite samples.

*The selection of crucible.* In the proposed graphite decomposition method, the crucible material should ensure that no new elements will be introduced after the melting of lithium metaborate. Contrast experiments were performed on crucibles made from various materials such as porcelain, high aluminum, gold, silver, and platinum. The non-metallic crucible like porcelain and high aluminum were not chosen because they could be corroded by the lithium metaborate solvent, and therefore resulting in potential contamination of the measured elements. The melting points of gold, silver and other metal crucibles cannot meet the high-temperature requirements, and such crucibles worn out easily. Although platinum crucible did not have the above shortcomings, its direct contact with graphite at 950°C might lead to corrosion of platinum crucible.$^{20}$

In order to eliminate the possibility of graphite eroding the platinum crucible, a
"sandwich method" was adopted. A layer of lithium metaborate was laid on the platinum crucible’s bottom, and the graphite powder sample was placed in the middle of the bottom for high temperature burning. After that, lithium metaborate was added and stirred slightly, and then a layer of lithium metaborate was covered on it for direct melting. In this way, after the lithium metaborate is melted, graphite can be effectively decomposed without corroding the platinum crucible.

*Optimization of sample melting temperature and time.* First, 0.2500 g of graphite ore sample was weighed and placed in a platinum crucible that had been evenly padded with 1.0000 g of lithium metaborate. Subsequently, the two substances are stirred well, and then covered with 1.0000 g of lithium metaborate. The prepared sample was used to compare the melting conditions under 5 melting temperature gradients (700°C, 800°C, 850°C, 900°C and 1000°C). The results showed that after 3 hours of melting, the samples under all treatments with a melting temperature of below 850°C were not completely melted or even not melted, the solution after ultrasonic extraction was turbid; as the temperature rose, the sample tended to melt further. When the temperature reached 950°C, the sample melted completely, and the analysis results of standard graphite ore were good.

At a melting temperature of 950°C, the sample was taken out every 0.5 h for observation, and the melt was extracted by ultrasonic vibration for element determination. According to the results, when the melting duration was less than 2 h, the sample decomposition was incomplete, and the element determination results were low; whereas when the melting duration was longer than 2 h, the sample was
completely decomposed and the solution extracted by ultrasound was clear. Thus, the melting duration was determined to be 2.5 h, and the melting temperature 950°C.

*Optimization of sample weight and constant volume.* Appropriate sample weight and constant volume can shorten the melting duration of samples and improve the accuracy of element determination. In this study, the graphite samples with different contents were adopted for optimization test of sample weight and constant volume. According to the content range of the elements to be measured in the sample, the sample weight was determined to be 0.1000-0.5000 g, and the constant volume 250 mL.

The sample mass ratio optimization test was carried out with standard graphite as the test material. 0.2500 g of graphite standard was weighed and prepared into 7 samples with different sample mass ratio gradients (the mass ratio of lithium metaborate to graphite: 1.6, 3.2, 4.0, 6.0, 8.0, 10.0 and 12.0). Then these samples were melting in a platinum crucible at 950°C for 3 h. The results showed that the samples with a melting ratio of <4.0 cannot be completely melted, leaving obvious black carbon particles. Some samples became transparent spheres, but the solution was not clear after ultrasonic vibration. The sample with a mass ratio of 4.0 was basically decomposed, and the black particles were not obvious. When the sample mass ratio rose to 8.0, the graphite was thoroughly decomposed, and the standard substance test results after the ultrasonic extraction solution was clarified could satisfy the quality specifications. The decomposition results of higher sample mass ratio and the measured content of each element were not significantly different from those when
the mass ratio was 8.0. Thus, the final sample mass ratio was determined to be 8.0.

Optimization of ultrasonic extraction conditions. The graphite melt after alkali fusion of lithium metaborate adheres to the crucible wall and can be extracted by ultrasonic. There\textsuperscript{12-13} have been reports about the ultrasonic extraction of graphite melt, but not involve the extraction of graphite from lithium metaborate melt. Thus, in this study, four melt extraction methods (boiling water extraction, acid extraction, ultrasonic-assisted water extraction and ultrasonic-assisted acid extraction) commonly used in chemical laboratories were compared. The results showed that the ultrasonic-assisted acid extraction method had the best effect: the crucible melt can be completely dissolved in 200 mL 2.5\% HCl solution by ultrasonic vibration for 2 h, and there were very few flocs. Ultrasonic-assisted water extraction, however, had poor performance: after sonicating in a PTFE beaker containing 200 mL of hot water for 2 to 3 hours, the melt peeled off in lumps and was basically insoluble; the melt could still not be dissolved after ultrasonic oscillation for over 4 h. Furthermore, the boiling water extraction and acid extraction are also not suitable for melt extraction. The former had slow reaction and low efficiency (extraction time> 4 h), and the latter was easy to produce silicic acid precipitation which would interfere with the experimental results.

In order to optimize the acid concentration of the ultrasonic-assisted acid extraction method, the crucible melt was directly placed in a PTFE beaker pre-filled with 200 mL hot HCl solution to compare the ultrasonic vibration time required for the melt to completely dissolve under 6 HCl concentration treatments (2.5\%, 5\%,
10%, 15%, 20% and 30%). The results showed that the ultrasonic vibration time declined with the rising HCl concentration, from 2 h (under 2.5% HCl concentration treatment) to 10 min (under 30% HCl concentration treatment; Fig. 2); but the occurrence probability of flocs (mostly silicic acid) in the extracted solution increased with the rising acid concentration.

To investigate the relationship between the SiO₂ content in graphite samples and the probability of silicic acid flocculation in the solution of ultrasonic-assisted acid extraction, the extraction of graphite ore samples (including certified reference materials and self-mined samples) with various SiO₂ contents was compared. The weight of each graphite ore sample was 0.2500 g, the melting ratio was 8.0, 200 mL 5% hot HCl solution was added during ultrasonic acid extraction, and the ultrasonic oscillation time was 2 h. It was found out that no precipitation was observed in case of a SiO₂ content ≤50%, but for graphite ore samples with a higher SiO₂ content, the precipitation was obvious.

In conclusion, ultrasonic-assisted acid extraction is the best method for extracting the graphite melt. In this method, the concentration of HCl is 5% and the amount of acid is 200 mL. It should be noted that for graphite ore samples with SiO₂ content over 50%, the sample weight should be reduced moderately to avoid precipitation.

*Optimization of ICP-AES conditions*

In the proposed method, lithium metaborate can induce a significant matrix effect. To be specific, it can introduce a large amount of easily ionized Li⁺ into the
extraction solution, destroy the ionization equilibrium in the plasma, and alter the excitation efficiencies of the elements to be measured in the plasma, thereby affecting the determination of the elements to varying degrees. Research has shown that the presence of Li\(^+\) only has a great impact on the test results of Na in the sample, and its influence on other elements are insignificant.\(^{22}\) Besides, in the case of low Na content, the increase in the amount of flux will reduce the accuracy of test results. To eliminate the potential interference of Li, the soluble salt concentration is reduced, so that the sample matrix can be matched to calibration curve. The medium is a mixed solution of 0.008 g mL\(^{-1}\) lithium metaborate and 5% hydrochloric acid.

In ICP-AES determination, the spectral line parameters recommended by the instrument as well as the interference deduction program installed on the instrument is used to select the spectral lines of the measured elements and to eliminate the background interference. The observation direction is radial in evaluating the interference. The spectral lines of the elements are given in Table 2.

**Method evaluation**

*Method detection limit.* According to the optimized method (see Subsection 1.2 for details), element test were on the operation blank. Under optimum operating conditions of the instrument, the standard deviation \(\sigma\) for 10 consecutive measurements is calculated. Then the detection limit can be obtained through multiplying \(3\sigma\) by the dilution factor of 1000.\(^{13}\) Table 2 shows that the detection limit of this method meets the detection requirements.

*Accuracy and precision of the method.* In order to investigate the accuracy and
precision of this method, 10 rounds of detection were performed respectively with the national primary reference materials (GBW03118, GBW03119 and GBW03120), Canadian CDN-GR-2 and Mongolia CGL003 according to the analysis steps of this method. The relative error (RE) and relative standard deviation (RSD) calculated are shown in Table 3. It can be seen from Table 3 that the measured values are consistent with the reference values, and both RE and RSD are below 8.00%, indicating that the accuracy and precision of this method meet the experimental requirements.

**Contrast test of measured samples and methods.** A total of 3 samples of low-carbon, medium-carbon and high-carbon graphite were determined respectively by the present method and conventional chemical methods. In the chemical methods, the volumetric method is used for Al₂O₃ determination; the volumetric method is used for samples with CaO and MgO contents over 5%, whereas the atomic absorption method for those below 5%; TiO₂, P₂O₅ and Fe₂O₃ determination adopts spectrophotometry; MnO, K₂O and Na₂O are determined by the atomic absorption method. The results of the proposed method are in rough agreement with those of chemical methods (Table 4).

**Conclusions**

It is found that the molten lithium metaborate and O₂ can oxidize the carbon in graphite samples and decompose the graphite samples at high temperature.

The paper proposes a method of lithium metaborate melting—ultrasonic extraction—ICP-AES for the decomposition of graphite ore samples and the
The determination of multiple elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Si and Ti). The verification results based on national primary reference materials demonstrated that the detection limit of the proposed method was low, and the precision met the requirements for the accurate determination of major elements in graphite samples. The results of the proposed method were roughly consistent with those of classical chemical methods. Moreover, compared with other existing methods, this method system has the advantages of simple operation, rapid decomposition and detection, low reagent consumption, less sample contamination, and good reproducibility of analysis results. It is an efficient approach for the quantitative analysis of multi-elements in graphite ore samples in large quantities.

Acknowledgements

This research was funded by the Geological Survey Project of China Geological Survey (DD20160095-20).
References

1. The Editorial Committee of Handbook of Industrial Requirements for Mineral Resources, “Handbook of Industrial Requirements for Mineral Resources”, ed. Q. N. Shao and W. P. Tao, 2010, Geological Publishing House, Beijing, China, 310.

2. National Development and Reform Commission, “JC/T1021.5—2007 Methods for Chemical Analysis of Graphite” in “Methods for Chemical Analysis of Nonmetal Mineral and Rock”, 2007, China Building Materials Press, Beijing, China, 1.

3. L. C. Zhao, X. P. Guo, Y. Q. Hu, W. C. Cheng, L. Wang and H. C. Ma, Rock and Mineral Analysis, 2015, 34, 308.

4. General Administration of Quality Supervision, Inspection and Quarantine of PRC and Standardization Administration of PRC, “GB/T3521—2008 Method for chemical analysis of graphite”, 2008, Standards Press of China, Beijing, China, 1.

5. M. Watanabe and A. Narukawa, Analyst, 2000, 125, 1189.

6. U. Schäffer and V. Krivan, Fresenius Journal of Analytical Chemistry, 2001, 371, 859.

7. Y. Koshino and A. Narukawa, Analyst, 1992, 117, 967.

8. H. Yamaguchi, S. Itoh, S. Igarashi, K. Naitoh and R. Hasegawa, ISIJ International, 2000, 40, 779.

9. K. Watanabe and J. Inagawa, Analyst, 1996, 121, 623.

10. Y. Koshino and A. Narukawa, Analyst, 1993, 118, 827.

11. H. S. Mahanti and R. M. Barnes, Analytical Chemistry, 1983, 55, 403.

12. K. Yin, “Lithium metaborate graphite crucible mine Ultrasonic
extraction--ICP-MS method for the determination of 19 kinds of elements in rocks and stream sediment”, 2012, The Master's degree thesis of Jilin University.

13. H. Liu, J. Li, D. P. Du and L. Z. Xie, Rock and Mineral Analysis, 2010, 29, 387.

14. S. F. Ma, H. L. Wen, A. H. Gong, W. J. Qu and Y. P. Cao, Rock and Mineral Analysis, 2009, 28, 535.

15. H. P. Chen, Y. M. Sha, X. P. Zhao, M. J. Wang, L. P. Guo and Z. L. Fan, Rock and Mineral Analysis, 2009, 28, 367.

16. D. G. Zhao, S. H. Wang and P. Zhao, Journal of Iron and Steel Research, 2012, 24, 19.

17. Z. B. Guo, Y. N. Zhang, Z. Dai and X. Wang, Rock and Mineral Analysis, 2015, 34, 55.

18. H. S. Liu, N. F. Wang, M. Liu and X. Y. Wang, Spectroscopy and Spectral Analysis, 1996, 16, 66.

19. The Editorial Committee of Rock and Mineral Analysis, “Rock and Mineral Analysis (Fourth Edition: Volume (IV)”, ed. M. Yin and J. X. Li, 2011, Geological Publishing House, Beijing, China, 1271.

20. P. Li, Y. L. Wang, J. F. Yang, J. Q. Gao and Z. H. Jin, Bulletin of the Chinese Ceramic Society, 1994, 6, 4.

21. Q. Wen, J. L. You, S. P. Huang, B. K. Yu, G. C. Jiang and C. D. Zhou, Spectroscopy and Spectral Analysis, 2000, 20, 694.

22. L. S. Wang, H. Hao, G. Z. Wang and J. P. Hu, Rock and Mineral Analysis, 2008, 27, 287.
### Table 1  Optimal operating conditions of ICP-AES and X-ray diffractometer

| Parameter                     | Set value | Parameter                     | Set value |
|-------------------------------|-----------|-------------------------------|-----------|
| Power/kW                      | 1.2       | Integral time/s               | 10        |
| Plasma gas flow rate/L min⁻¹  | 15.0      | Washing time/s                | 15        |
| Auxiliary gas flow rate/L min⁻¹ | 1.50      | Sample delay time/s           | 15        |
| Nebulizer pressure/kPa        | 200       | Instrument stabilization delay/s | 15        |
| Observation height/mm        | 12        | Reading times                 | 3         |

**X-ray diffractometer**

| Parameter                     | Set value | Parameter                     | Set value |
|-------------------------------|-----------|-------------------------------|-----------|
| Accelerating voltage/kV       | 40        | Scan speed/° min⁻¹            | 5         |
| Applied current/mA            | 200       | Scan width/°                  | 0.02      |
| Scan range/°                  | 5-80      |                               |           |

### Table 2  Spectral lines and detection limits of the elements

| Elements  | Spectral line/nm | Detection limit, mass% | Elements  | Spectral line/nm | Detection limit, mass% |
|-----------|------------------|------------------------|-----------|------------------|------------------------|
| K₂O       | 766.491          | 0.070                  | Fe₂O₃     | 259.940          | 0.019                  |
| Na₂O      | 589.592          | 0.050                  | TiO₂      | 336.122          | 0.056                  |
| Al₂O₃     | 237.312          | 0.024                  | MnO       | 257.610          | 0.0056                 |
| CaO       | 317.933          | 0.011                  | P₂O₅      | 213.618          | 0.035                  |
| MgO       | 280.270          | 0.0077                 | SiO₂      | 251.611          | 0.089                  |
Table 3  Accuracy and precision of the method tested using certified reference materials of graphite

| Code     | Element concentration, mass% |
|----------|-------------------------------|
|          | K2O  | Na2O  | Al2O3 | CaO  | MgO  | Fe2O3 | TiO2 | MnO  | P2O5 | SiO2 |
|          |      |       |       |      |      |       |      |      |      |      |
| GBW 03118 | Certified | 2.54 | 1.6  | 12.93 | 9.37 | 6.10 | 6.73 | 0.57 | 0.084 | 0.13 | 49.84 |
|          | Measured | 2.56 | 1.62 | 12.45 | 9.42 | 6.18 | 6.80 | 0.55 | 0.082 | 0.12 | 48.74 |
|          | RE, %   | 0.78 | 1.25 | -3.71 | 0.53 | 1.31 | 1.04 | -3.51 | -2.38 | -7.69 | -2.21 |
|          | SD      | 0.0374 | 0.0792 | 0.0797 | 0.118 | 0.105 | 0.114 | 0.006 | 0.000 | 0.005 | 0.829 |
|          | RSD, %  | 1.46 | 4.89 | 0.64 | 1.25 | 1.70 | 1.68 | 1.15 | 1.04 | 4.23 | 0.829 |
|          | GBW 03119 | Certified | 2.17 | 1.56 | 13.03 | 5.34 | 5.35 | 6.99 | 0.64 | 0.054 | 0.14 | 49.34 |
|          | Measured | 2.14 | 1.65 | 12.87 | 5.30 | 5.47 | 7.05 | 0.63 | 0.056 | 0.13 | 49.96 |
|          | RE, %   | -1.38 | 5.77 | -1.23 | -0.75 | 0.93 | 0.86 | -1.56 | -1.85 | -7.14 | 1.26 |
|          | SD      | 0.0867 | 0.0328 | 0.495 | 0.0567 | 0.237 | 0.389 | 0.007 | 0.001 | 0.006 | 2.718 |
|          | RSD, %  | 6.80 | 1.99 | 3.85 | 1.07 | 4.39 | 5.52 | 1.21 | 1.22 | 5.00 | 5.44 |
|          | GBW 03120 | Certified | 0.99 | 0.23 | 5.60 | 0.74 | 0.50 | 1.48 | 0.55 | 0.022 | 0.16 | 10.34 |
|          | Measured | 1.02 | 0.22 | 5.64 | 0.70 | 0.49 | 1.42 | 0.54 | 0.021 | 0.15 | 10.73 |
|          | RE, %   | 3.03 | -4.35 | 0.71 | 5.41 | -2.0 | -4.05 | -1.82 | -4.55 | -1.88 | 3.77 |
|          | SD      | 0.0296 | 0.0076 | 0.147 | 0.0094 | 0.016 | 0.036 | 0.013 | 0.001 | 0.004 | 0.486 |
|          | RSD, %  | 2.90 | 3.47 | 2.61 | 1.35 | 3.47 | 2.56 | 2.12 | 2.12 | 5.00 | 5.44 |
|          | Canada CDN-GR-2 | Certified | 2.90 | 0.20 | 7.90 | 11.6 | 1.90 | 3.30 | 0.30 | <0.10 | 57.5 |
|          | Measured | 2.81 | 0.19 | 7.72 | 11.79 | 2.00 | 3.47 | 0.32 | -0.31 | 57.91 |
|          | RE, %   | -3.10 | -5.00 | -2.28 | 1.64 | 5.26 | 5.15 | 6.67 | 0.71 |
|          | SD      | 0.0160 | 0.0076 | 0.0988 | 0.191 | 0.030 | 0.023 | 0.007 | 3.017 |
|          | RSD, %  | 0.57 | 4.00 | 1.28 | 1.62 | 1.53 | 0.67 | 2.33 | 5.21 |
|          | Mongolia CGL003 | Certified | 2.54 | 0.47 | 9.33 | 7.05 | 1.94 | 3.48 | 0.57 | 0.030 | 0.100 | 52.20 |
|          | Measured | 2.45 | 0.51 | 9.12 | 6.74 | 1.97 | 3.64 | 0.54 | 0.028 | 0.093 | 52.53 |
|          | RE, %   | -3.54 | 8.51 | -2.25 | -4.4 | 1.55 | 4.60 | -5.26 | -6.67 | -7.00 | 0.63 |
|          | SD      | 0.0762 | 0.0146 | 0.0529 | 0.215 | 0.049 | 0.148 | 0.006 | 0.000 | 0.006 | 3.913 |
|          | RSD, %  | 3.11 | 2.87 | 0.58 | 3.19 | 2.52 | 4.06 | 1.29 | 2.96 | 6.46 | 7.45 |

Note: Relative error RE = (Cj - Cs)/Cs × 100%, where Cj is the average value of 10 measurements of the reference material, and Cs is the suggested value; SD denotes “standard deviation”. RSD denotes “relative standard deviation”.
Table 4  Comparison of analytical results between traditional chemical methods and the present method

| Sample | Method           | Content, mass% |
|--------|-----------------|----------------|
|        |                 | K2O  | Na2O  | Al2O3 | CaO  | MgO   | Fe2O3 | TiO2  | MnO   | P2O5  | SiO2  |
| 1      | Chemical method | 2.32 | 3.38  | 13.84 | 8.79 | 7.82  | 13.41 | 2.39  | 0.17  | 0.94  | 44.60 |
|        | SD              | 0.0573 | 0.0746 | 0.119 | 0.167 | 0.134 | 0.129 | 0.0183 | 0.0119 | 0.0270 | 0.161 |
|        | The present method | 2.30 | 3.43  | 13.79 | 8.82 | 7.75  | 13.37 | 2.43  | 0.18  | 0.92  | 44.49 |
|        | SD              | 0.0564 | 0.0441 | 0.0662 | 0.0570 | 0.0632 | 0.0436 | 0.0104 | 0.0181 | 0.136 |
| 2      | Chemical method | 1.13 | 0.73  | 8.36  | 1.29 | 0.45  | 0.68  | 0.35  | 0.018 | 0.11  | 14.50 |
|        | SD              | 0.0374 | 0.0278 | 0.120 | 0.0493 | 0.0183 | 0.0260 | 0.0155 | 0.00155 | 0.00925 | 0.138 |
|        | The present method | 1.19 | 0.75  | 8.30  | 1.28 | 0.48  | 0.71  | 0.37  | 0.017 | 0.12  | 14.31 |
|        | SD              | 0.0373 | 0.0266 | 0.0972 | 0.0471 | 0.0196 | 0.0297 | 0.0160 | 0.00128 | 0.00834 | 0.0807 |
| 3      | Chemical method | 0.21 | 0.079 | 1.10  | 0.39 | 0.68  | 1.14  | 0.015 | 0.0079 | 0.44  | 3.25  |
|        | SD              | 0.0125 | 0.00481 | 0.0468 | 0.0220 | 0.0318 | 0.0380 | 0.00160 | 0.000618 | 0.00325 | 0.0571 |
|        | The present method | 0.22 | 0.080 | 1.05  | 0.41 | 0.71  | 1.12  | 0.017 | 0.0078 | 0.45  | 3.26  |
|        | SD              | 0.0131 | 0.00456 | 0.0396 | 0.0203 | 0.0283 | 0.0399 | 0.00181 | 0.000641 | 0.00352 | 0.0711 |

Note: SD denotes "standard deviation"
Fig. 1  XRD peaks of a sample melted for (1 h) at 950°C with sample mass ratio of lithium metaborate:graphite = (2.0)

Fig. 2  Correlation between HCl concentration in solution and the ultrasonic dissolution time