Editorial:


Editors: Wei Guo, Zhaochu Hu, Wei Hang, and Xian-Hua Li

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Journal Overview

The *Atomic Spectroscopy* (ISSN 0195–5373; e-ISSN 2708-521X) is a peer-reviewed international journal started in 1962 by Dr. Walter Slavin. It is dedicated to advancing the analytical methodology & applications, instrumentation & fundamentals, and the science of reference materials in the fields of atomic spectroscopy. Publishing frequency: Six issues per year.

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Guidelines for Authors

Scope: The ATOMIC SPECTROSCOPY (AS) is a peer-reviewed international journal started in 1962 by Dr. Walter Slavin and now is published by Atomic Spectroscopy Press Limited (ASPL), Hongkong, P.R. China. It is intended for the rapid publication of original Articles, Reviews, and Letters/Editorials in the fields of elements, elemental speciation and isotopic analysis by AAS, AFS, ICP-OES, ICP-MS, GD-MS, TIMS, SIMS, AMS, LIBS, XRF, SEM-EDX, EMPA, NNA, and SR-related techniques. Manuscripts dealing with (i) instrumentation & fundamentals, (ii) methodology development & applications, and (iii) standard reference materials (SRMs) development can be submitted for publication.

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Text should be formatted at US letter size, with sufficient margins on either side, and all pages numbered sequentially. The lines should be double spaced, in a single, left justified, column. Special characters, chemical formulae or mathematical equations should be carefully typeset. Spelling should follow the conventions of British or American English, but not a mixture of these. All tables and figure captions to be added at the end of the text.

Figures and Graphic Abstract submitted separate from the text. Since most graphs/charts/diagrams will be reduced for publication to a single column width, authors should ensure that a sufficiently large point size is chosen for symbols, annotation, and weight of lines so that these features will be distinguishable in the reduced version. Use a JPG or TIFF file (resolution > 300 dpi, size < 2 M) as the image for the figure and graphic abstract.

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In 1962, Dr. Walter Slavin founded the “Atomic Absorption Newsletter” (AANL), used to demonstrate the utility of the early PerkinElmer atomic absorption spectrometer (AAS) instruments (e.g., Model 214 and 303) to users and potential customers. In 1980, with the development of the Inductively coupled plasma (ICP) related techniques, such as ICP-optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS), Dr. Walter Slavin changed the name of the journal to “Atomic Spectroscopy” (AS). In 1990, Dr. Anneliese Lust officially became the Editor-in-Chief of the journal and had overall responsibility for operations until the end of 2019. Since 2020, the ownership of this journal has been transferred to Atomic Spectroscopy Press Limited (ASPL), Hong Kong, China. A Chinese team took over and ushered in a new era, expanding its publication scope from the AAS and ICP related techniques to the whole field of atomic spectroscopy. In the past three years, the journal’s academic influence has improved significantly. AS has become one of the most important international journals in the atomic and mass spectroscopy field.

Organized by Xian-Hua Li (Institute of Geology and Geophysics, CAS), Wei Hang (Xiamen University), Zhaochu Hu (China University of Geosciences, Wuhan), Shenghong Hu (China University of Geosciences, Wuhan), and Wei Guo (China University of Geosciences, Wuhan), the 60th Anniversary for Atomic Spectroscopy (AS) celebrations were held on April 20-22, 2023 at the China University of Geosciences, Future City Campus, Wuhan. Atomic Spectroscopy & Mass Spectrometry
(ASMS) is a powerful tool that enables chemical information of elements and isotopes related investigations into their bulk and/or in-situ distribution in various samples. ASMS is a classic yet a vibrant and rapidly developing area of research that attracts scientists from numerous fields including life sciences, environmental sciences, earth and planetary sciences, food safety, semiconductors and high-purity materials, forensics, instrumentation development, and beyond. This conference was timely and highly successful, with 125 invited researchers (Fig. 1) from multiple disciplines and academic, industrial, government labs and analytical instrument companies in attendance. The conference was comprised of three parts, including celebrating the 60th anniversary of AS, academic actives, and the future development of AS journal.

In the first section of the celebration (Fig. 2), AS received warm blessings, memories, and expectations from Dr. Walter Slavin (founding Editor-in-Chief, 1962-1989), Dr. Anneliese Lust (former Editor-in-Chief, 1990-2019), Professor Xian-Hua Li (current Editor-in-Chief, 2020-), Professor Shucheng Xie (Academician of the CAS), Professor Shaoyong Jiang (Assistant Principle of China University of Geosciences, Wuhan), and Dr. Bing Zhu (Vice President of PerkinElmer). AS also received the online blessings from AS distinguished authors including Professor Benli Huang (Academician of the CAS), Professor Zhifang Chai (Academician of the CAS), and Professor Guibin Jiang (Academician of the CAS).

The focus of the academic activities (the 2nd section) was on “New Technology of Atomic & Mass Spectrometry: New Developments & Applications, R&D of Instrument and Microanalytical Techniques for Extraterrestrial Samples.” A total of 14 invited lectures (Fig. 3) and four short talks led to active discussions about current state-of-the-art technologies, key challenges, and emerging applications in the field of ASMS.

Professor Hang Wei (Associate Editor) chaired the 3rd session of this conference (Fig. 4). After Professor Guo Wei (Executive Editor) reported on the development status of the AS journal over the past three years, the AS editorial board members and invited experts had an in-depth discussion of the future development, challenges, and suggestions for this journal. Finally, Editor-in-Chief Professor Xian-Hua Li stressed that improving the scientific and cultural spirit of journals is as important as journal quality.

Many attendees also enjoyed the informal and relaxing environment of the AS Conference, with ample opportunities to mingle and interact with the conferees over a coffee break or an evening reception session. The pleasant weather, crystal-clear lake, and built-in free time during Sunday afternoons encouraged the exploration of the beautiful scenery in the surrounding area. The meeting ended with a sumptuous lunch featuring the expectations and wishes of the atomic spectroscopy researchers.
In closing, the conference organizers appreciated the AS Editorial Board Members and invited experts for supporting this meeting on such a timely and important topic. We thanked the State Key Laboratory of Biogeology and Environmental Geology (BEGE), China University of Geosciences, PerkinElmer company and other analytical instrument manufacturers for the financial support. It was also important to acknowledge the hard work of the 26 volunteers during the entire planning process and their help in making the conference proceed smoothly. We thanked all the conference attendees for their participation and for making the meeting a great success.

Fig. 3 Academic activities on the topic “New Technology of Atomic Spectroscopy & Mass Spectrometry”.

Fig. 4 An in-depth discussion of the future development, challenges, and suggestions for AS journal.
AUTHOR INFORMATION

Wei Guo received his B.S. degree in Chemistry (2003), M.S. degree in Analytical Chemistry (2007), and Ph.D. degree in Geochemistry (2011) from the China University of Geosciences, Wuhan. He is a professor at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan. His research focused the analytical techniques of elemental and isotopic analysis and their applications to biogeochemistry and environment geology. He is working as Executive Editor for Atomic Spectroscopy. He published over 60 peer-reviewed scientific papers in SCI journals.

Zhaochu Hu received his B.S. degree in Chemistry (1998) and M.S. degree in Analytical Chemistry (2001) from China University of Geosciences, Wuhan, and completed Ph.D. in Geochemistry from the Northwest University, China. He is a professor at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. His research focused on the in situ analysis of elements and isotopes, the preparation of geological samples, the research and development of reference materials, and the chemical composition of the continental crust. He is working as an associate editor for Atomic Spectroscopy. He is the recipient of the National Science Fund for Distinguished Young Scholars (2019), and the leading talent of the National "Ten Thousand People Plan"(2019). He is working as an associate editor for Atomic Spectroscopy. He has published more than 100 papers in SCI journals, including about 60 first/corresponding author papers published in Analytical Chemistry, JAAS, Chemical Geology, GGR, etc.

Wei Hang received his BSc in 1988 from Zhejiang University, and PhD in 1994 from Xiamen University. He is a professor in Chemistry Department at Xiamen University. His work covers a range of topics, from fundamental studies on plasma sources, such as laser ablation & ionization, glow discharge, and ICP, to the development of mass spectrometric instrumentation. He is working as an associate editor for Atomic Spectroscopy. He has published over 180 papers in SCI journals.

Xian-Hua Li received his BSc in 1983 from the University of Science and Technology of China, and his Ph.D. in 1988 from the Institute of Geochemistry, Chinese Academy of Sciences (CAS). He is a research professor of geochemistry at the Institute of Geology and Geophysics, CAS. His major research interests are isotope geochronology, geochemistry, isotopic microanalysis and their applications to igneous petrogenesis, chemical geodynamics, and the evolution of the Earth and Moon. He has been working as Editor-in-chief of Atomic Spectroscopy, associate editor of Precambrian Research, Geological Magazine, and American Journal of Science, and member of editorial committee in many other academic journals. Xian-Hua Li is the author or co-author of over 450 articles published in peer-reviewed scientific journals, with an h-index of 102 (Web of Science). He was elected as a Fellow of the Geological Society of America in 2007, Academician of CAS in 2019, and named as Clarivate Analytics Global Highly Cited Scientist, ESI Global Highly Cited Scholar, and Elsevier China Highly Cited Scholar.

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The authors declare no competing financial interest.
Advances in the Multi-elemental Analysis of Solder by ETV-ICPOES for the Discrimination of Forensic Evidence

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ABSTRACT: Lead-tin solder is a useful piece of evidence from a crime scene and may be examined for information related to the construction or source of an improvised explosive device (IED). A technique based on electrothermal vaporization into inductively coupled plasma optical emission spectrometry was improved for the direct quantification of trace and major elements in solder (Ag, As, Bi, Cr, Fe, Sb, Sn). NIST 1728, a tin-alloy certified reference material, was used for external calibration and achieve a direct, fully solid-sampling procedure using only 0.5–3.0 mg of sample. Point-by-point internal standardization with Ar 404.442 nm was performed to compensate for sample loading effects on the plasma, and a background correction technique was introduced to improve the overall efficiency of analysis. As solder was observed to change composition during some mock scenarios of IED preparation, which limits how solder can be examined in forensics, different soldering conditions (temperature, solder size, cleaning of the soldering tip or not between subsequent samples) were studied using an Fe-tip soldering device. Statistical analyses including Student’s t-tests and a one-way analysis of variance revealed that none of these conditions resulted in contamination of the melted solder sample, hence confirming the viability of the mock procedure used to replicate IED soldering in research. A new qualitative discrimination method is introduced and demonstrated in a blind trial for matching and discriminating lead-tin solders. This method represents an improvement from past research and has potential for use in evaluating other forensic evidence involving ferrous-alloys.

INTRODUCTION

Improvised explosive devices (IEDs), colloquially known as “homemade bombs”, form a broad category of crude yet sophisticated weapons systems that are designed to “destroy, incapacitate, harass, or distract”. The design systems of IEDs are highly variable and may be modified depending on the destructive impact or intended campaign target; however, one identified commonality in these design systems is solder. Lead-tin solder is a fusible metal alloy used to bond workpieces in an electrical circuit. Most lead-tin solders contain a rosin core to aid with melting and solder wetting (i.e., adherence to other metal surfaces), providing an attractive option for reliable electric sequencing in the initiation or detonation of an explosive device.

Lead-tin solder has been identified as a promising piece of physical evidence from a crime. A variety of trace impurities exist in solders because of: (1) individual manufacturer preferences for solder, and/or (2) the absence of control regulations in the manufacturing process. As a result, solder may be accurately distinguished and implied in crime; if solder salvaged from a crime scene is compared to solder from a suspect, a match between elemental fingerprints may identify a guilty party. This possibility has been harnessed by researchers who have discriminated solders, and successfully matched solders, on trace and major element concentrations (Bi, Cu, Sb, Ni, Pb, and Sn).

Solder analysis as a forensic technique has gained momentum in the past five years since the discovery that rosin may facilitate the contamination of elements from the soldering gun to the solder (during the melting process, “soldering”). After melting solders with a Cu-tip soldering gun, a melted portion exhibited higher
investigate contamination of the major tip elements from an Fe current r extra protection against corrosion. layer of Fe at the working surface, with additional layers of Cr as mechanical and thermal properties.

Tips are pop other soldering tips exhibit the same pattern of contamination in Fe). Based tip for sample melting, only Cu, As, Ag, Sb, and Bi were solder tips, namely tips with Fe sample size. Involved melting with a cons additional investigation into the contamination process. To date, of solder, and thus the e discrimination from its unmelted pair (i.e., solder from a suspect's IED soldering.

This possibility for melting to distort the elemental fingerprint of solder, and thus the efficacy of sample matching, warrants additional investigation into the contamination process. To date, contamination by melting has been replicated in limited settings and under fixed variable conditions; current method designs involved melting with a constant soldering gun temperature and sample size.5,5 There is also limited work on the effects of other solder tips, namely tips with Fe-plating. In a study using an Fe-Al-based tip for sample melting, only Cu, As, Ag, Sb, and Bi were measured in the samples, rather than the major tip elements (Al or Fe). It is therefore inconclusive whether the major elements from other soldering tips exhibit the same pattern of contamination in rosinsolders. This is an important avenue to explore as Fe-plated tips are popular given their added durability and balance of mechanical and thermal properties.6 These tips contain a plated layer of Fe at the working surface, with additional layers of Cr as extra protection against corrosion.7 This literature inspires the current research interests: expand the elemental profile (Fe, Cr) to investigate contamination of the major tip elements from an Fe-

In addition, this research will investigate the impact of cleaning the solder tip during sample melting. In past research designs, reiterative cleaning of the soldering tip was done between melting samples, either by wiping with 10% HNO3 (v/v)8 or by sanding, soaking in 10% (v/v) HNO3 acid bath, and further wiping with doubly deionized water (DDW).9 There are two problems with tip cleaning. Firstly, an individual producing an IED is unlikely to employ routine cleaning measures. Secondly, trace metals (such as Fe) can be easily etched and soluble in acid and acid mixtures; several applications of etching with dilute HNO3 have been done.8 Cleaning with acid may (1) etch the surface of the soldering tip, thus preventing contamination to a sample during melting, or (2) remove trace metal residue leftover from previous solder sample melts, preventing contamination from one solder sample to another. These reasons may explain why no significant increases in other elements beyond Cu were observed after melting.5 This introduces the final goal of the research: investigate the significance of tip cleaning and improve the mock procedure for IED soldering.

This research will use electrothermal vaporization (ETV) for sample introduction into inductively coupled plasma optical emission spectrometry (ICPOES) for multi-elemental analysis, which has been applied in numerous forensic,10–12 archaeological,13–16 and environmental applications.17–18 These applications share a short analysis time, up to 85 s per sample, and study materials, artifacts, and/or evidence that is limited in mass (0.1–5 mg). In each application, an optimized temperature program is configured to resistively vaporize a sample up to 2700–2800°C. ETV replaces the need for sample digestion, which has been a reported cause of interference and analyte precipitation in past determinations of solder.5 Additional coupling to Ar-based ICPOES allows for the passive measurement of up to 70 elements with sub-parts-per-billion detection limits.19 As a result, ETV-ICPOES offers an effective approach for a direct, sensitive and robust trace element analysis.

### EXPERIMENTAL

#### Instrumentation and operating conditions.

Research was conducted using an ARCOS inductively coupled plasma optical emission spectrometer (SPECTRO Analytical Instruments, Kleve, Germany). An electrothermal vaporization system (ETV 4000C, Spectral Systems, Furstenfeldbruck, Germany) was coupled in broad user conditions including soldering gun temperature and solder sample size.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>idle power (KW)</td>
<td>1.70</td>
</tr>
<tr>
<td>Ar plasma gas flow rate (L min⁻¹)</td>
<td>14.5</td>
</tr>
<tr>
<td>Ar auxiliary gas flow rate (L min⁻¹)</td>
<td>3.50</td>
</tr>
<tr>
<td>Plasma view</td>
<td>Lateral</td>
</tr>
<tr>
<td>Signal scan mode</td>
<td>Transient</td>
</tr>
<tr>
<td>Integration time (ms)</td>
<td>10</td>
</tr>
<tr>
<td>Sampling rate (Hz)</td>
<td>10</td>
</tr>
<tr>
<td>Observation height (mm)</td>
<td>10</td>
</tr>
<tr>
<td>ETV</td>
<td></td>
</tr>
<tr>
<td>Ar bypass gas flow rate (L min⁻¹)</td>
<td>0.5</td>
</tr>
<tr>
<td>Ar carrier gas flow rate (L min⁻¹)</td>
<td>0.15</td>
</tr>
<tr>
<td>CF₃ reaction gas flow rate (mL min⁻¹)</td>
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<tr>
<td>Step</td>
<td>Temperature (°C)</td>
</tr>
<tr>
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<tr>
<td>Cleaning</td>
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<tr>
<td>Cooling</td>
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<td>Temperature program for sample analysis</td>
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<tr>
<td>Initial temperature</td>
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<td>Pyrolysis</td>
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<td>Cooling</td>
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<tr>
<td>Vaporization</td>
<td>2300</td>
</tr>
<tr>
<td>Cooling</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 1: Operating conditions for ETV-ICPOES, based on optimized conditions from Scheffler et al.20

This literature inspires the current research interests: expand the elemental profile (Fe, Cr) to investigate contamination of the major tip elements from an Fe-plated soldering tip, and identify if this contamination varies under broad user conditions including soldering gun temperature and solder sample size.
Table 2. Certified reference materials and solder samples used in this work

<table>
<thead>
<tr>
<th>Material ID</th>
<th>Use in project</th>
<th>Material</th>
<th>Bulk composition</th>
<th>Rosin core</th>
</tr>
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<tr>
<td>SRM 1728</td>
<td>Calibration</td>
<td>Tin alloy</td>
<td>90:3:0.5 Sn:Cu:Ag</td>
<td>No</td>
</tr>
<tr>
<td>CRM 1131</td>
<td>Reference</td>
<td>Solder</td>
<td>40:60 Sn:Pb</td>
<td>No</td>
</tr>
<tr>
<td>C2416</td>
<td>Reference</td>
<td>Bullet lead</td>
<td>99% Pb</td>
<td>No</td>
</tr>
<tr>
<td>K2</td>
<td>Sample</td>
<td>Solder</td>
<td>Unknown</td>
<td>Yes</td>
</tr>
<tr>
<td>ON-003</td>
<td>Sample</td>
<td>Solder</td>
<td>60:40 Sn:Pb</td>
<td>Yes</td>
</tr>
<tr>
<td>EDM-3</td>
<td>Sample</td>
<td>Solder</td>
<td>Unknown</td>
<td>No</td>
</tr>
<tr>
<td>EDM-2</td>
<td>Sample</td>
<td>Solder</td>
<td>60:40 Sn:Pb</td>
<td>Yes</td>
</tr>
<tr>
<td>EDM-1</td>
<td>Sample</td>
<td>Solder</td>
<td>50:50 Sn:Pb</td>
<td>No</td>
</tr>
<tr>
<td>Dura-Pure 17657</td>
<td>Sample</td>
<td>Solder</td>
<td>50:50 Sn:Pb</td>
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</tr>
<tr>
<td>Electrosol 17664</td>
<td>Sample</td>
<td>Solder</td>
<td>60:40 Sn:Pb</td>
<td>Yes</td>
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<tr>
<td>Oatey 48317</td>
<td>Sample</td>
<td>Solder</td>
<td>60:40 Sn:Pb</td>
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</tbody>
</table>

For tests of soldering iron temperature, a soldering iron and thermocouple were connected to a PL512 Mantle Minder Temperature Controller (GLAS-COL Apparatus Company, Terre Haute, USA). The thermocouple was contacted to the soldering tip to monitor iron temperature immediately preceding melting. Slight deviations in temperature are expected due to reported precision limits (±1.5% of full scale)\(^2\) from the manufacturer.

The following analyte emission lines were monitored in samples: Ag I (328.068 nm), As I (189.042 nm), Bi I (223.061 nm), Cu I (324.754 nm), Fe I (373.486 nm), Pb II (172.680 nm), Sb I (217.581 nm), and Sn II (175.790 nm). These emission lines were selected based on maximum sensitivity and intensity, minimum spectroscopic interference, and day-to-day reproducibility.

**Standard reference materials, gases, and samples.** A variety of standard reference materials (SRMs) and commercially available solders were used in this project (Table 2). SRM 1728, a tin-alloy material, was used for matrix-matched external calibration. SRM C2416 and CRM 1131 were used for routine validation of the calibration and quality control. All SRMs in this research were obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

Pure argon (99.996%, MEGS Specialty Gases, Ottawa, ON, Canada) is used for all gas flows of the ICP, and for the carrier and bypass gases of the ETV assembly. Carbon tetrafluoride (MEGS Specialty Gases) reaction gas supplemented the carrier gas flow to increase analyte volatility and transport efficiency.

**Melting procedures.** Solder samples were melted by contacting the tip of the soldering iron with a solder sample only until solder wetting was visible, between 2–10 s, depending on the sample thickness and alloy melting point. Between melting different samples, the tip of the soldering iron was cleaned with 10% (v/v) HNO\(_3\) (prepared through dilution of 68.0%–70.0% (assay) HNO\(_3\) from Anachemia, VWR International LLC) then DDW purified to a resistivity of 18.2 M\(\Omega\) cm (Arium Pro UV/DI, Sartorius Stedim Biotech, Göttingen, Germany).

When testing for the effect of sample size on contamination, solder samples Electrosol, Oatey, and Dura-Pure were cut into portions of 0.5 cm, 1.0 cm, 2.0 cm, and 3.0 cm. The temperature of the soldering iron was held at 350°C for these tests. When testing different soldering temperature conditions, solder samples Electrosol, Oatey, and Dura-Pure were cut into portions of 1 cm and melted at 200°C, 300°C, and 400°C. When testing for contamination between solder samples, 0.5-cm portions of solders Electrosol, Oatey, and Dura-Pure were melted in sequence with the temperature of the iron held at 350°C and without intermediate cleaning.

**Analysis procedure.** Solder sub-samples were cut into small chippings (approximately 1.5 mg) using a number 11 scalpel blade (Feather Safety Razor Co., Osaka, Japan). Five chippings of each sample were prepared for replicate measurements. External calibration curves were constructed using five chippings of SRM 1728, in weights ranging from 1.0 mg to 3.0 mg. Samples were loaded into individual graphite boats and introduced into the graphite furnace for a 100 s, 5-step analysis program (Table 1). Graphite boats were individually cleaned in the ETV furnace using a programmed cleaning cycle (Table 1). This was done preceding an analysis, and between analyses of different samples, to ensure the boats were clear of sample residue.

**Data processing, internal standardization, and background correction.** Transient signal profiles were collected for studied analytes and exported to Excel for processing. For each analyte signal, point-by-point internal standardization was done with the Ar I (404.442 nm) emission line. This technique compensates for sample loading effects on the plasma and instrument drift. Other Ar emission lines may be used for internal standardization in ETV-ICPOES; Ar I (415.859 nm), Ar I (763.511 nm), and Ar I (430.010 nm)\(^2\) have been used in various applications. Ar I (404.442 nm) was selected for this research as it demonstrated day-to-day stability and the same signal suppression (an artefact of sample loading) among sample matrices.

A background correction technique was then applied to
eliminate the positive bias from background emission, as proposed by Maung and Beauchemin. This replaces the blank subtraction method used conventionally with ETV-ICPOES where the average signal from 10 blank samples (i.e., empty graphite boats) is subtracted from analyte profiles. Background correction instead takes the average signal before and/or after the analyte peak and subtracts this point-by-point from transient profiles; in this work, the signal immediately preceding vaporization (e.g., time 0–50 s) was sufficient as the average background. To complete data processing, the peak area was integrated over the 30 s vaporization time step.

RESULTS AND DISCUSSION

Effect of background correction on analysis. Conventionally, the average blank signals from 10 empty graphite boats is used for blank subtraction. In this work, background signals obtained during the analysis of calibration standards were taken in place of blank signals because great variability and even contamination often resulted during the analysis of empty graphite boats, as illustrated in Fig. 1. This affected the integrated signal, as shown in Fig. 2, where background correction systematically resulted in more analyte signal. The benefit of background correction versus blank subtraction is particularly striking for Fe, Pb and Sb. Background correction thus improves sample analysis in several ways: (1) increasing the total signal integration of analytes, and therefore improving LODs (not shown), (2) preventing negative signal integration in the case of trace determinations with high background or using contaminated graphite boats, and (3) decreasing analysis time by 10 analyses, which are otherwise required to generate an average blank signal (n=10).

Method validation. Four SRMs were analyzed routinely for validation of the calibration and analytical method. SRM 1131 and C2416 contained matrices highly similar to those of solder samples and enabled the validation of elements within the linear dynamic range. SRM 8437 and SRM 2710, both agricultural samples, were added exclusively to monitor Fe and Cr, respectively. These materials contain Fe and Cr concentrations that mirror those observed in solder and have established material homogeneity that is suitable for quality control in this research. All elements, with the exception of Cu and Pb, agree with the certified values. These exceptions are due to the large discrepancies in concentrations between the calibration SRM and the reference SRMs; for example, there is a 1102-fold difference of Cu concentration with SRM 1131, and a 47-fold difference of Pb with C2416. They were thus omitted from Table 3. The relative standard deviation (RSD) ranges from 11% (for Fe in SRM 8437) to 38% (for As in SRM 2710), which is typical of solid-sampling ETV analysis of mg aliquots. In fact, 1.5 mg is significantly less than the representative amount indicated on the certificates and thus reflects inhomogeneity of the materials at the mg level. However, this does not prevent accurate analysis down to 1 mg aliquots, as previously demonstrated by Becker, and evident in Table 4. These RSDs are acceptable in exchange for a fast, simple, and convenient direct analysis method.

The method was also cross-verified by comparing most element concentrations for solder samples previously analyzed by inductively coupled plasma mass spectrometry (ICPMS) (Table 5). A Student’s t-test at the 95% confidence interval indicates agreement for Sb, Bi and Sn (p = 0.08–0.91), thereby confirming the accuracy of the proposed analytical method. The disagreement for Cu and Pb was anticipated due to the aforementioned concentration discrepancies between standards and samples. This does not prevent qualitative analysis using these elements, as will be seen in the Alternative discrimination model section, which is even simpler. Hence, alternative calibration strategies to enable quantitative determination of these elements were not pursued.
Table 3. Average concentrations (% mean ± standard deviation, n = 5) obtained for selected elements in SRMs. Elements with no reported values were either not certified or were beyond the linear dynamic range of calibration.

<table>
<thead>
<tr>
<th>SRM</th>
<th>As</th>
<th>Bi</th>
<th>Cr</th>
<th>Fe</th>
<th>Sb</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1131</td>
<td>Measured: 0.0094 ± 0.0011</td>
<td>0.0587 ± 0.0099</td>
<td>–</td>
<td>–</td>
<td>0.485 ± 0.076</td>
<td>44.9 ± 8.1</td>
</tr>
<tr>
<td></td>
<td>Certified: 0.01</td>
<td>0.06</td>
<td>–</td>
<td>–</td>
<td>0.43</td>
<td>39.3</td>
</tr>
<tr>
<td>C2416</td>
<td>Measured: 0.065 ± 0.013</td>
<td>0.10 ± 0.03</td>
<td>–</td>
<td>–</td>
<td>0.83 ± 0.11</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Certified: 0.056 ± 0.001</td>
<td>0.10 ± 0.01</td>
<td>–</td>
<td>–</td>
<td>0.79 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>8437</td>
<td>Measured: –</td>
<td>–</td>
<td>0.0040 ± 0.00045</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Certified: –</td>
<td>–</td>
<td>(0.0000026)</td>
<td>0.0031 ± 0.0006</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>2710</td>
<td>Measured: 0.073 ± 0.028</td>
<td>0.0041 ± 0.0013</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Certified: 0.0626 ± 0.0038</td>
<td>–</td>
<td>(0.0039)</td>
<td>3.38</td>
<td>0.0038 ± 0.0003</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4. Comparison of current ETV-ICPOES data (n = 5) to ICPMS data (n = 6) from Huang et al. for solder samples. Elements in agreement have concentrations that are not significantly different (at the 95% confidence interval) between ICPMS and ETV-ICPOES methods.

<table>
<thead>
<tr>
<th>Solder</th>
<th>Elements in agreement (p &lt; 0.05)</th>
<th>Elements not in agreement (p ≥ 0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDM-3</td>
<td>Sb, Bi, Sn</td>
<td>Cu, Pb</td>
</tr>
<tr>
<td>K2</td>
<td>Sb, Bi, Sn</td>
<td>Cu, Pb</td>
</tr>
<tr>
<td>ON-003</td>
<td>Sb, Bi, Sn</td>
<td>Cu, Pb</td>
</tr>
<tr>
<td>EDM-1</td>
<td>Sb, Bi, Sn</td>
<td>Cu, Pb</td>
</tr>
</tbody>
</table>

![Fig. 3](image-url) Element concentrations (n = 5, except n = 3–5 for Fe and Cr in Electrisol) in unmelted and melted portions of various sizes of solders Dura-Pure (top), Oatey (middle) and Electrisol (bottom).

Effect of solder size. An increased length of solder may facilitate etching of trace elements from the soldering iron tip during the melting process because of the additional time required to melt the larger area of solder, therefore increasing the contact time between the soldering tip and sample. To assess the significance of etching, element concentrations among four sample groups—unmelted solder (control), 0.5-cm solder melt, 1.0-cm solder melt, 2.5-cm solder melt, 3.0-cm solder melt—were compared (Fig. 3). A one-way analysis of variance (ANOVA) was used to assess if there was a significant change in element concentration after melting. This process was repeated for three types of solder. No significant statistical difference resulted among the groups for all solders tested (Table S1). Hence, etching does not vary with solder size.

Comparisons were additionally performed between the control group and a single melted experimental group. This would resolve possible etching that may occur in one specific size condition rather than another, which may not be isolated when examining differences holistically using an ANOVA test. Comparisons were done for each element using an unpaired Student’s t-test at the 95% confidence interval. The results for Dura-pure solder (Table S2) show that all elements agree between the unmelted portion and each melted size portion (p = 0.3–0.9). Similar results (not shown) were obtained for Electrisol and Oatey solders.

Effect of soldering temperature. The temperature of the soldering iron was varied to assess if temperature leads to significant change in element concentration. In previous work, soldering temperature was held constant at 350°C for all samples (with the exception of sample ON-003, which was melted at 300°C), which produced no significant change in concentration for elements Ag, As, Bi, Cu, Pb, Sb and Sn. In this study, three melting temperatures were tested to examine contamination from the Fe-tip soldering iron: 200°C, 300°C, and 400°C. The results are shown for three solders in Fig. 4. For each solder, an ANOVA test confirmed no significant difference among element concentrations between each test condition (Table S3). A Student’s t-test between control and individual test conditions (unmelted vs. 200°C, unmelted vs. 300°C, unmelted vs. 400°C) of solder Dura-Pure further confirmed no significance difference (p = 0.19–0.95) in element concentrations after melting between any two test...
Table 5. Blind test for identification of unknown solder (Dura-pure 17657) using mass-corrected element signals that were integrated and computed as a range (mean ± 1 standard deviation) for comparison; T = match (i.e., element range overlaps), F = no match (i.e., element ranges do not overlap). A sample is identified when all ranges overlap.

<table>
<thead>
<tr>
<th>Unknown solder (Dura-pure 17657)</th>
<th>Ag</th>
<th>As</th>
<th>Bi</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Sb</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRM 1131</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>K2</td>
<td>T</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
</tr>
<tr>
<td>ON-003</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
</tr>
<tr>
<td>EDM-1</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>EDM-2</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>EDM-3</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>F</td>
<td>T</td>
<td>F</td>
<td>F</td>
<td>T</td>
</tr>
<tr>
<td>Dura-Pure 17657</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Electrisol 17664</td>
<td>T</td>
<td>T</td>
<td>F</td>
<td>T</td>
<td>F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Oatey 48317</td>
<td>T</td>
<td>F</td>
<td>F</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The la...conditions (Table S4). This result is consistent among solders Electrisol and Oatey (not shown).

The lack of significant contamination after melting may be due to the increased corrosion resistance of the Fe-based soldering tip. The Fe-plated tip used in this research, and in many other Fe or stainless-steel soldering tips, contains an appreciable fraction of Cr (between 12 to 30%, depending on the grade) to allow the formation of a Cr-rich surface oxide film. This film behaves as a shield against corrosion, and may be a factor for why the solder does not leach any of the trace and major elements tested. Even in the case of rosin-core solders, which have been shown to leach trace metals due to their acidity, etching from the Fe-tip soldering gun did not measurably occur.

Contamination between soldering samples. One final possibility for etching is between solder samples as they are melted in series, with no cleaning intervention. Past solder research has involved some frequent cleaning of the soldering tip, which may directly etch the surface of the tip to prevent contamination to a sample, or perhaps remove deposit leftover from melting solder, thus preventing cross-contamination between one solder to another. To test if contamination by either mean is persistent, three solders, Electrisol, Oatey, and Dura-Pure, were melted in sequence without cleaning the soldering tip.

If contamination did occur from a lack of cleaning, it would be evident in either Oatey or Electrisol, which were melted later in the sequence. However, a Student’s t-test at the 95% confidence interval (Table S5) confirmed no significant change in concentration between unmelted and melted fractions, even for the latter two solders ($p = 0.06–0.61$). This provides evidence that no significant cross-contamination occurs when melting different solders in series without a cleaning step. Furthermore, a melted solder (Dura-Pure) from a clean tip produced an average relative standard deviation (RSD) of $19.8 \pm 4.9\%$ compared to an average RSD of $15.4 \pm 8.1\%$ when the same sample was melted with an uncleaned tip. Expectedly, an F-test confirmed no significant difference in precision when a sample was melted with either tip ($F$ values ranging from $1.34–2.92$, $F_{0.00} = 4.11$). In future work, no cleaning of the soldering tip is necessary when studying the soldering procedure, which will decrease analysis time and remove the need to obtain acid or acidic solutions.

Alternative discrimination model. In past research, the discrimination of solder has been achieved using a model developed by Suzuki et al., which compares trace and major element concentrations among solders. This model assigns each element concentration as a range (mean ± 2 standard deviations), and ranges that overlap are tabulated as a match. When the ranges

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Note: The image containing the table and figures is not transcribed due to the limitations of the text-based interface.
of all elements match, solders are considered to be the same. This has been harnessed to correctly match a melted sample with its unmelted pair amongst a bank of various lead-tin solders. Both works demonstrate the need for only 3 elements for successful discrimination.

Though this technique by Suzuki et al. is effective, it requires the construction of an external calibration curve for each monitored element and complete quantitative interpolation of a dataset. In this work, a new procedure focused solely on qualitative elemental data is proposed. To this end, one sample of solder was randomly selected from a bank of 8 solder materials and assigned as the test unknown. Five replicates of each sample, including the unknown sample, were measured. Instead of computing element concentrations, element peak areas were integrated and mass-corrected. The average of five replicates provided a range (mean ± 1 standard deviation) for element-by-element comparison. The results of this blind test are compiled in Table 5. As shown, there is only one sample for which all element ranges match with the unknown; this confirms that the unknown was correctly and discretely identified as Dura-Pure 17657. As no calibration was required, analytes Pb II (172.680 nm) and Cu I (324.754 nm) could be incorporated into the analysis. Impressively, most elements alone could achieve discrimination of two-thirds of solders within the sample bank (6 out of 9 samples). The element with the least amount of discrimination power was Pb, which excluded 3/9 solders in the blind trial. Though only one element (Bi) was sufficient to discriminate all but the unknown in this limited solder bank, at a minimum, 2–3 elements should be used in the discrimination model.

CONCLUSION

This study determined trace and major elements of solder when melting under varying user conditions of sample size and temperature. Melting solder of different sizes (0.5–3 cm) or increasing the temperature of the soldering iron caused no significant change in concentrations after melting. These observations are consistent for solders with or without rosin, and indicate the absence of significant etching of the major tip elements when using a Fe-tip soldering iron. This is in contrast to melting rosin-containing solders using a Cu-tip soldering iron, which etched Cu.

Present research observations provide additional context for solder contamination, which adds to the knowledge-base for the forensic analysis of solders. The background correction technique eases the procedure for analyzing trace alloyed materials or other forensic evidence by replacing blank subtraction, which also improves LODs and decreases overall analysis time. Eliminating solder-tip cleaning better aligns with how IEDs are realistically produced. Qualitative discrimination using mass-corrected peak areas is a simpler and faster approach for solder discrimination and may be suitable as an alternative to conventional quantitative strategies to understand and anticipate how a salvaged solder sample can be properly paired with its reference, and how changes (or lack thereof) in concentration implicate specific soldering tools (on the basis of soldering tip material). Most importantly, there is added assurance that these predictions are robust despite inherent user variations in soldering conditions, such as soldering temperature or solder size. The use of ETV-ICPOES is a promising analytical technique for the discrimination of solders, and including elements like Fe and Cr makes this approach suitable for the analysis of stainless steels or other ferrous-alloys. It can thus be applied to a variety of crime-related devices (e.g., tools, weapons, cordage, etc.) as well as other artefacts and fragments (e.g., debris, geological materials or soils, automobile parts).

In the future, multivariate statistical analyses such as linear discriminant analysis (LDA) and/or principal component analysis (PCA) will be explored to aid in discriminating solders and identify which variables affect discrimination most based on simple, visual classifications. These techniques have been applied in past forensic research (hair analysis, automotive paint analysis) to achieve high discrimination, and in some cases, up to 100% probability or prediction success. This would facilitate solder analysis as some methods of multivariate analysis (e.g., LDA) do not require quantitative analysis, but instead rely on peak integration.

ASSOCIATED CONTENT

The supporting information (Tables S1–S5) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION

Diane Beauchemin received her Ph.D. in 1984 from Université de Montréal. She is a professor (Full) at Queen’s University. Her research efforts are focused on inductively coupled plasma mass spectrometry (ICPMS) and ICP optical emission spectrometry (OES) from both fundamental and application perspectives, and expanding the range of application of ICPMS/OES to geochemical exploration, risk assessment of food safety, characterization of nanoparticles, and forensic analysis. She has been working as member of editorial board for Atomic Spectroscopy. Diane Beauchemin won the Alan Date Memorial Award (1988) from VG.
Elemental, the Distinguished Service Award (2001) from Spectroscopy Society of Canada, the Maxxam Award (2017) and Clara Benson Award (2019) from Canadian Society for Chemistry, and the Gerhard Herzberg Award (2018) from the Canadian Society for Analytical Sciences and Spectroscopy. She is author or co-author of over 160 articles published in peer-reviewed scientific journals.

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**Notes**

The authors have no conflicts to declare.

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**REFERENCES**


A Quantity Chalcopyrite Reference Material for In Situ Sulfur Isotope Analysis

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ABSTRACT: Secondary ion mass spectrometry (SIMS) for sulfur isotope analysis in chalcopyrite is an essential technique with exceptional spatial resolution, which enables precise constraints on mineralization mechanisms. However, the scarcity of matrix-matched chalcopyrite reference materials (RM) for SIMS hinders its accuracy and reliability. This study introduces a large-grained natural chalcopyrite RM (IGSD) for precise sulfur isotope analysis ($\delta^{34}$S) using SIMS and laser ablation multicollector-inductively coupled plasma mass spectrometry (LA-MC-ICPMS). Petrographic examination and electron microprobe analysis (EMPA) results confirm the homogeneity of major elements in the IGSD chalcopyrite grains. The results of in situ analysis at four SIMS laboratories and one LA-MC-ICPMS laboratory and bulk analysis confirm the homogeneity of the S isotope composition in the IGSD chalcopyrite grains. The in situ analysis result is consistent with the result of isotope ratio mass spectroscopy (IRMS), which falls within the same range of uncertainty. This supports the suitability of the IGSD chalcopyrite RM for in situ S isotope analysis. The recommended $\delta^{34}$S value of the IGSD chalcopyrite RM, based on IRMS, is 4.21 ± 0.23‰ (2SD, n = 30).

INTRODUCTION

Sulfur is widely distributed throughout the lithosphere, biosphere, hydrosphere, and atmosphere. Because of its multiple valence states and large differences in relative atomic masses, sulfur isotopes exhibit significant fractionation. Therefore, the sulfur isotopic systems are a valuable for tracing sulfur sources and constraining various geochemical processes.\(^1\)\(^-\)\(^4\)

In recent years, in situ microanalysis techniques, such as LA-ICP-MS and SIMS have been widely adopted for sulfur isotope analysis.\(^5\)\(^-\)\(^15\) Compared to traditional bulk methods, e.g., RIGS, TIMS, and MC-ICPMS, in situ microanalysis offers several advantages, including increased efficiency, convenience, and notably, superior spatial resolution down to the micrometre scale, all while maintaining high precision.

SIMS-based sulfur analysis is a versatile and widely used in situ technique. It is characterized by high sensitivity and extremely high spatial resolution (1–20 μm),\(^11\)\(^-\)\(^14\),\(^16\),\(^17\) which has a unique advantage in analyzing minerals with complex intergrown, heterogeneous, or zoning isotopic compositions. Therefore, sulfur isotope analysis through SIMS has proven to be a powerful tool for obtaining precise measurements of sulfur isotopes in minerals. This has enabled researchers to address a wide array of geological problems with high precision (~ 0.2‰),\(^12\),\(^14\),\(^15\),\(^18\)\(^-\)\(^23\) However, instrumental mass fractionation (IMF) is a significant restraint factor for SIMS-based isotopic ratio analysis. Because of IMF, a systematic difference exists between the instrumentally measured
Table 1. The published δ³⁴S values in different sulfides (in-house standards or reference materials) for in situ Sulfur isotope analysis

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Material</th>
<th>δ³⁴S value with 2SD ‰ (method)</th>
<th>In-situ method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrite</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAV-18</td>
<td>Natural material</td>
<td>9.62 ± 0.27 (LA-MC)</td>
<td>LA-MC</td>
<td>Cradock et al. 12</td>
</tr>
<tr>
<td>PPP-1</td>
<td>Natural material</td>
<td>5.3 ± 0.2 (IRMS)</td>
<td>LA-MC and SIMS</td>
<td>Gilbert et al. 13</td>
</tr>
<tr>
<td>Py1</td>
<td>Natural material</td>
<td>−0.6 ± 0.6 (IRMS)</td>
<td>LA-MC</td>
<td>Molsnár et al. 14</td>
</tr>
<tr>
<td>Py2</td>
<td>Natural material</td>
<td>−0.4 ± 1 (IRMS)</td>
<td>LA-MC</td>
<td>Molsnár et al. 14</td>
</tr>
<tr>
<td>10^−1</td>
<td>PSPT</td>
<td>5.33 ± 0.27 (IRMS)</td>
<td>LA-MC</td>
<td>Feng et al. 15</td>
</tr>
<tr>
<td>PSPT-2</td>
<td>PSPT</td>
<td>32.48 ± 0.29 (SN-MC)</td>
<td>LA-MC</td>
<td>Bao et al. 16</td>
</tr>
<tr>
<td>G18.007267</td>
<td>RPP</td>
<td>3.46 ± 0.18 (SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 11</td>
</tr>
<tr>
<td>PAS-Py</td>
<td>PAS</td>
<td>18.22 ± 0.07 (IRMS)</td>
<td>LA-MC</td>
<td>Feng et al. 16</td>
</tr>
<tr>
<td>RPPY</td>
<td>RPP</td>
<td>3.66 ± 0.24 (IRMS)</td>
<td>LA-MC</td>
<td>Lv et al. 17</td>
</tr>
<tr>
<td>Balmat</td>
<td>Natural material</td>
<td>15.1 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
<tr>
<td>Ruttan</td>
<td>Natural material</td>
<td>1.2 ± 1 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
<tr>
<td>CAR 123</td>
<td>Natural material</td>
<td>1.4 ± 0.4 (Unknown)</td>
<td>SIMS</td>
<td>Moffat et al. 16</td>
</tr>
<tr>
<td>UWPy-1</td>
<td>Natural material</td>
<td>16.39 ± 0.40 (IRMS)</td>
<td>SIMS</td>
<td>Kozdon et al. 12</td>
</tr>
<tr>
<td>SPAJN</td>
<td>Natural material</td>
<td>−2.95 ± 0.56 (Unknown)</td>
<td>SIMS</td>
<td>Kitayama et al. 40</td>
</tr>
<tr>
<td>Sonora</td>
<td>Natural material</td>
<td>1.61 ± 0.16 (IRMS)</td>
<td>SIMS</td>
<td>Farquhar et al. 13</td>
</tr>
<tr>
<td>Py-1117</td>
<td>Natural material</td>
<td>0.3 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Zhang et al. 17</td>
</tr>
<tr>
<td>CS01</td>
<td>Natural material</td>
<td>4.6 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Zhang et al. 17</td>
</tr>
<tr>
<td>Sierra</td>
<td>Natural material</td>
<td>2.17 ± 0.28 (IRMS)</td>
<td>SIMS</td>
<td>LaFlamme et al. 14</td>
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<td><strong>Chalcopyrite</strong></td>
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<td>CPY-1</td>
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<td>−0.7 ± 1.0 (IRMS)</td>
<td>LA-MC</td>
<td>Molsnár et al. 14</td>
</tr>
<tr>
<td>PSPT-1</td>
<td>PSPT</td>
<td>−0.73 ± 0.09 (SN-MC)</td>
<td>LA-MC</td>
<td>Bao et al. 16</td>
</tr>
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<td>VN411-m</td>
<td>Glass</td>
<td>0.37 ± 0.24 (SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 15</td>
</tr>
<tr>
<td>GC</td>
<td>Natural material</td>
<td>−0.63 ± 0.12 (IRMS)</td>
<td>LA-MC</td>
<td>Chen et al. 15</td>
</tr>
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<td>LA-MC</td>
<td>Chen et al. 15</td>
</tr>
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<td>TC1725</td>
<td>Natural material</td>
<td>12.78 ± 0.16 (IRMS)</td>
<td>LA-MC</td>
<td>Bao et al. 16</td>
</tr>
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<td>PAS-Cpyy</td>
<td>PAS</td>
<td>10.58 ± 0.33 (IRMS)</td>
<td>LA-MC</td>
<td>Feng et al. 16</td>
</tr>
<tr>
<td>GBW07268</td>
<td>RPP</td>
<td>−0.57 ± 0.24 (SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 16</td>
</tr>
<tr>
<td>Norikib</td>
<td>Natural material</td>
<td>8.0 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
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<td>Trou Lake</td>
<td>Natural material</td>
<td>0.3 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
<tr>
<td>OMP</td>
<td>Natural material</td>
<td>2.29 ± 0.56 (Unknown)</td>
<td>SIMS</td>
<td>Kitayama et al. 40</td>
</tr>
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<td>Nityh-b</td>
<td>Natural material</td>
<td>−3.58 ± 0.44 (IRMS)</td>
<td>SIMS</td>
<td>LaFlamme et al. 14</td>
</tr>
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<td>HTS4-6</td>
<td>Natural material</td>
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<td>SIMS</td>
<td>Li et al. 44</td>
</tr>
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<td>CPY-1</td>
<td>Natural material</td>
<td>1.4 ± 0.04 (Unknown)</td>
<td>SIMS</td>
<td>Li et al. 44</td>
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<td>NBS 123</td>
<td>PPP</td>
<td>17.09 ± 0.19</td>
<td>LA-MC</td>
<td>Pribil et al. 45</td>
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<td>PSPT-3</td>
<td>PSPT</td>
<td>26.40 ± 0.21 (SN-MC)</td>
<td>LA-MC</td>
<td>Bao et al. 17</td>
</tr>
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<td>PAS-GBW07270</td>
<td>PAS</td>
<td>−5.44 ± 0.18 (IRMS)</td>
<td>LA-MC</td>
<td>Nie et al. 46</td>
</tr>
<tr>
<td>SPI-1</td>
<td>RPP</td>
<td>−7.13 ± 0.41 (IRMS)</td>
<td>LA-MC</td>
<td>Lv et al. 17</td>
</tr>
<tr>
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<td>Natural material</td>
<td>14.3 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
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<td>Chishol</td>
<td>Natural material</td>
<td>1.5 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
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<td>BT-4</td>
<td>Natural material</td>
<td>15.42 ± 0.14 (IRMS)</td>
<td>SIMS</td>
<td>Kozdon et al. 12</td>
</tr>
<tr>
<td>JG-14</td>
<td>Natural material</td>
<td>4.9 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Zhang et al. 17</td>
</tr>
<tr>
<td>MY99-12</td>
<td>Natural material</td>
<td>3.1 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Zhang et al. 17</td>
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<td><strong>Galena</strong></td>
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<tr>
<td>CBI-3</td>
<td>Natural material</td>
<td>28.4 ± 0.36 (SN-SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 47</td>
</tr>
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<td>RPP-Gn</td>
<td>RPP</td>
<td>−0.94 ± 0.36 (SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 11</td>
</tr>
<tr>
<td>NWU-GN</td>
<td>RPP</td>
<td>28.27 ± 0.17 (IRMS)</td>
<td>LA-MC</td>
<td>Lv et al. 17</td>
</tr>
<tr>
<td>UWGal-1</td>
<td>Natural material</td>
<td>16.61 ± 0.16 (IRMS)</td>
<td>SIMS</td>
<td>Kozdon et al. 12</td>
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<td><strong>Pyrhotite</strong></td>
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<td>Po-10</td>
<td>Natural material</td>
<td>6.0 ± 0.1</td>
<td>LA-MC</td>
<td>Gilbert et al. 13</td>
</tr>
<tr>
<td>Polo</td>
<td>Natural material</td>
<td>5.6 ± 1.2 (IRMS)</td>
<td>LA-MC</td>
<td>Molsnár et al. 14</td>
</tr>
<tr>
<td>Anderson</td>
<td>Natural material</td>
<td>1.4 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
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<td>Enon</td>
<td>Natural material</td>
<td>0.90 ± 0.56 (unknown)</td>
<td>SIMS</td>
<td>Kitayama et al. 40</td>
</tr>
<tr>
<td>Alexo</td>
<td>Natural material</td>
<td>5.23 ± 0.40 (IRMS)</td>
<td>SIMS</td>
<td>LaFlamme et al. 14</td>
</tr>
<tr>
<td>YP316</td>
<td>Natural material</td>
<td>1.5 ± 0.1 (IRMS)</td>
<td>SIMS</td>
<td>Li et al. 46</td>
</tr>
<tr>
<td>JC-Po</td>
<td>Natural material</td>
<td>0.06 ± 0.33 (IRMS)</td>
<td>SIMS</td>
<td>Chen et al. 47</td>
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<td><strong>Pentlandite</strong></td>
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<tr>
<td>Norikib</td>
<td>Natural material</td>
<td>7.9 ± 0.2 (IRMS)</td>
<td>SIMS</td>
<td>Crowe et al. 16</td>
</tr>
<tr>
<td>KA8</td>
<td>Natural material</td>
<td>2.21 ± 0.56 (unknown)</td>
<td>SIMS SIMS</td>
<td>Kitayama et al. 40</td>
</tr>
<tr>
<td>VMSo</td>
<td>Natural material</td>
<td>3.22 ± 0.51 (IRMS)</td>
<td>SIMS</td>
<td>LaFlamme et al. 14</td>
</tr>
<tr>
<td>JC-Pn</td>
<td>Natural material</td>
<td>−0.09 ± 0.15 (IRMS)</td>
<td>SIMS</td>
<td>Chen et al. 47</td>
</tr>
<tr>
<td><strong>Arsenopyrite</strong></td>
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<td></td>
<td></td>
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<tr>
<td>RPP-Apy</td>
<td>RPP</td>
<td>−1.05 ± 0.15 (SN-MC)</td>
<td>LA-MC</td>
<td>Chen et al. 11</td>
</tr>
<tr>
<td>JYS-65</td>
<td>Natural material</td>
<td>−1 (IRMS)</td>
<td>SIMS</td>
<td>Xie et al. 30</td>
</tr>
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</table>

Note: RPP: Resin-preserved powders; PSPT: pressed sulfide powder tablets; PAS: plasma-activated sintering synthesized; LA-MC: LA-MC-ICPMS; SN-MC: SN-MC-ICPMS.
and real values, which is intrinsically restrained by the composition and crystallographic orientation of the material under specific instrumental conditions.\cite{14,24,26} This indicates that IMF is ubiquitous and cannot be entirely eliminated. Thus far, the only reliable means of correction for IMF has been the use of homogeneous matrix-matched standards.\cite{12,27,28} Thus, well-characterized, matrix-matched RMs for SIMS calibration are crucial for obtaining accurate sulfur isotopes.\cite{14,29} The in-house standards and reference materials of different sulfides for in situ sulfur isotope analysis were compiled in Table 1. There are many synthetic and natural RMs for most sulfides. However, as a high-resolution surface analysis method, operating under ultra-high vacuum conditions, SIMS places considerable demands on the surface morphology. Moreover, SIMS is also affected by the crystal orientation of analyte.\cite{12,13,30} Therefore, synthetic standards (such as the resin-preserved powders or pressed powder pellet standards), which were used in LA-MC-ICPMS,\cite{31} may not be suitable for SIMS. Thus, the optimal sulfur isotopic standards for SIMS are natural minerals with homogeneous isotopic compositions. However, these natural RMs are relatively rare and limited for most sulfide minerals (Table 1).

Chalcopyrite (CuFeS\textsubscript{2}) is an important source of copper and a primary copper sulfide in various types of deposits from magmatic (Cu-Ni sulfide systems) to various hydrothermal systems.\cite{34,35,36,37,38,39,40,41,42,43} Therefore, the characteristics of chalcopyrite sulfur isotopes (\(\delta^{34}\)S) have been extensively exploited for tracing metal sources and constraining the mineralization mechanism.\cite{14,22,23,58,66} There are many natural and synthetic chalcopyrite RMs for LA-MC-ICPMS, as listed in Table 1. However, natural chalcopyrite references for SIMS are rare. Only few RMs are reported as working RMs for chalcopyrite SIMS-based sulfur isotope microanalysis, such as Trout Lake and Norilsk,\cite{38,39} OPM,\cite{40} CPY-1, and CPY-2 (in-house standards),\cite{34,44} Nifty-b,\cite{14} and HST-4-6.\cite{44} However, the limited quantities of these RMs hindered their widely share and abroad application. Moreover, all these standards are selected from samples obtained from hydrothermal systems, where chalcopyrite grains are usually small and always precipitate with other sulfides, such as pyrite, sphalerite, galena, and pyrrhotite. As it can be challenging to isolate chalcopyrite grains for analysis, this is a significant limitation for microanalysis. Additionally, the softness of chalcopyrite crystals can make it difficult to achieve a smooth surface during polishing, particularly for small standards. Thus, there is an urgent need for a large quantity, high purity, and adequate size of the chalcopyrite standard that can address these challenges.

In this study, we provided a pure and large-grained chalcopyrite standard (IGSD) for sulfur isotope analysis (\(\delta^{34}\)S) through SIMS and LA-MC-ICPMS. The chalcopyrite is less impure in other minerals (only a few pyrrhotite or pentlandite grains are observed) owing to the origin of the high-temperature magmatic system. The chalcopyrite standards were tested in several laboratories (four SIMS and one LA-ICPMS laboratories), and high homogeneity in \(\delta^{34}\)S was observed. This study provides evidence that chalcopyrite samples (IGSD) are adequately homogeneous to serve as a suitable RM for in situ microanalysis. Furthermore, sufficient quantity (~ 500 g) of this material is available and laboratories around the world can request it for their use.

**EXPERIMENTAL**

**Sample description and preparation.** Chalcopyrite samples were collected from the McCreedy West deposit on the North Range of the Sudbury Igneous Complex (SIC) in Ontario, Canada (Fig. 1). SIC is a structure formed by meteorite impact at 1850 Ma.\cite{67} It comprises three major components: (1) the main mass sequence containing quartz-earing norites, a gabbroic zone, and a granophyric zone, (2) the contact sublayer marked by small and inclusion-filled gabbronoritic bodies, and (3) the offset sublayer containing numerous dikes. The contact and offset sublayer zones are the major hosts for world-class magmatic Ni-Cu-PGE sulfide mineralization. The McCreedy West deposit is located in the western part of the Onaping-Levack Ni-Cu-PGE sulfide mineralized zone. The sulfide mineralization at the McCreedy West is massive, semi-massive, and disseminated, with sulfide assemblages of chalcopyrite, cubanite, pentlandite, pyrrhotite, and minor pyrite. Sudbury brecciated footwall contains several chalcopyrite-rich massive sulfide veins. The IGSD sample used in this study was collected from one of these veins, which is predominantly composed of almost pure chalcopyrite with a small amount of pyrrhotite or pentlandite (Fig. 2a).

The IGSD sample (~ 50 g) was crushed into small fragments. Under a microscope, chalcopyrite grains of high purity were carefully handpicked. Some chalcopyrite grains were selected and prepared for bulk analysis. Different sizes of chalcopyrite grains were cast into round epoxy mounts (diameter of 25.4 mm) with other RM (HTS4-6) (Figs. 2b and 2c). All the epoxy mounts were carefully polished several times with a diamond paste, and the grain size was gradually reduced. All the mounts were first washed in ethanol, followed by deionized water, and then heated in an oven for 3 h at 40 °C. Subsequently, several mounts were sent to SIMS and LA-MC-ICPMS laboratories to investigate the homogeneity of IGSD chalcopyrite.

**Analytical techniques**

**EMPA.** The major elemental composition was obtained using a JEOL JXA8530F-plus microprobe at the State Key Laboratory of Ore Deposit Geochemistry (SKLODG), Institution of Geochemistry, Chinese Academy of Sciences, China. The electron microprobe was equipped with five spectrometers. An acceleration voltage of 15 kV and a probe current of 20 nA with a
Fig. 1 Geological map of the Sudbury Igneous Complex showing the location of the McCreedy West deposit (Modified from ref. 67).

Fig. 2 (a) Photograph of IGSD chalcopyrite. (b) Mounts of different grains of IGSD chalcopyrite. (c) Typical BSE map of IGSD chalcopyrite.

beam diameter of 5 μm was applied. The following sulfides were used as standards: CuFeS₂ (Fe, Cu, and S), ZnS (Zn), Cd (Cd), SnO₂ (Sn), FeAsS (As), Ge (Ge), GaAs (Ga), Sb₂S₃ (Sb), InP (In), PbS (S), and Ag (Ag).

IRMS. The bulk sulfur isotopic compositions (δ³⁴S) of IGSD chalcopyrite were obtained using a MAT253 isotope ratio mass spectrometer coupled with an elemental analyzer (EA-IRMS) at SKLODG. The IGSD sample was crushed into several grains and sieved under a microscope to ensure high purity. The grains were then crushed to a 200-mesh using an agate mortar. The chalcopyrite (~ 180 μg) was reacted with copper wire and tungsten trioxide at 1020 °C under a vacuum pressure of 9 × 10⁻⁷ Pa, and the product SO₂ was measured using a MAT253 mass spectrometer. The analytical precision was better than 0.3 (2SD) as calculated from repeated analyses of the IAEA international standards IAEA-S-1 (δ³⁴S = −0.37‰, n = 4), IAEA-S-2 (δ³⁴S = 22.67‰, n = 5) and IAEA-S-3 (δ³⁴S = −32.49‰, n = 5).

SIMS. Four sets of SIMS measurements were performed to determine the homogeneity of the IGSD. In situ sulfur isotope analysis of IGSD chalcopyrite grains was performed using a CAMECA NanoSIMS 50 L instrument at SKLODG. The sample mounts were cleaned and then coated with a ~ 20 nm thick gold layer before analysis. A primary beam of ~ 150 pA Cs⁺ with an impact energy of 16 keV was rastered on an area of 7 × 7 μm² for
150 s as the pre-sputtered time to remove the gold coating and possible contaminations, followed by a secondary ion beam (SIB) auto-centering process. Both the $^{32}$S and $^{34}$S ions were measured using a Faraday cup with a $1 \times 10^{11}$ Ω preamplifier resistor for 300 cycles, with a cycle duration of 0.54 s each. The total analysis time, including pre-sputtering, was approximately 7 min per measurement. Other instrumental settings, including the baseline correction method, were similar to those reported by Chen et al. Typical count rates obtained for $^{32}$S were ~ 1.4 × 10^8 cps, and the internal precision of $^{34}$S/$^{32}$S for single analysis was typically 0.2‰ (2 Standard Error, 2SE). The chalcopyrite RM HTS4-6 ($δ^{34}$S = 0.63 ± 0.16‰,44) was used to correct the IMF at the beginning of the measurement. The repeatability of HTS4-6 in the test was approximately 0.3‰ (2SD, n = 10).

Another sulphur analysis was conducted at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), using a CAMECA IMS 1280-HR instrument. The analytical parameters were similar to those described by Li et al. and are briefly summarized here. A primary Cs+ ion beam (~ 3.3 nA current and 20 keV total impact energy) was focused on the sample surface. The beam size was approximately 15 μm. A pre-sputtering step lasting 40 s was conducted to remove the gold coating prior to analysis. The magnetic field was stabilized during analysis using an NMR field sensor. $^{32}$S and $^{34}$S were simultaneously measured using two movable Faraday cups of the multi-collector system (L1 and H’2), with resistors of $1 \times 10^{10}$ Ω and $1 \times 10^{11}$ Ω, respectively. The mass resolving power was set at approximately 5000 to avoid isobaric interference in the measurement. The total analysis time for each spot was typically 4 min. Typical count rates obtained for $^{32}$S were ca. 2.6 × 10^8 cps, and the internal precision of $^{34}$S/$^{32}$S for the analysis spot was typically 0.05‰ (2SE). The calibration reference material used for IMF correction was HTS4-6 chalcopyrite on the same mount. The repeatability of HTS4-6 in the test was approximately 0.2‰ (2s, n = 8).

The homogeneity of sulfur isotopic compositions of the IGSD was tested using a CAMECA IMS 1280 SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The sample mounts were cleaned, and gold coated before SIMS analysis. Cesium ions were used as primary ions, and the background obtained was ~ 0.2‰ (2s, n = 29, 2SD) was consistent with the recommended value for the sample surface. The beam size was approximately 15 μm. A pre-sputtering step lasting 40 s was conducted to remove the gold coating prior to analysis. The magnetic field was stabilized during analysis using an NMR field sensor. $^{32}$S and $^{34}$S were simultaneously measured using two movable Faraday cups of the multi-collector system (L1 and H’2), with resistors of $1 \times 10^{10}$ Ω and $1 \times 10^{11}$ Ω, respectively. The mass resolving power was set at approximately 5000 to avoid isobaric interference in the measurement. The total analysis time for each spot was typically 4 min. Typical count rates obtained for $^{32}$S were ca. 2.6 × 10^8 cps, and the internal precision of $^{34}$S/$^{32}$S for the analysis spot was typically 0.05‰ (2SE). The calibration reference material used for IMF correction was HTS4-6 chalcopyrite on the same mount. The repeatability of HTS4-6 in the test was approximately 0.2‰ (2s, n = 8).

Time for each measurement cycle was 1 s. Typical count rates obtained for $^{32}$S were ~ 5.0 × 10^6 cps, and the internal precision of $^{34}$S/$^{32}$S for the analysis spot was typically 0.1‰ (2SE). The homogeneity test of the IGSD was also conducted at the China University of Geosciences (CUG), Wuhan, China by using the CAMECA NanoSIMS 50 L instrument. To remove the gold coating and possible contaminations, a primary beam of 200 pA Cs+ with an impact energy of 16 keV was rastered on an area of $12 \times 12$ μm² for 120 s as the pre-sputtered time, followed by an SIB auto-centering process. Two Faraday cups with $1 \times 10^{11}$ Ω preamplifier resistors were used for collecting data for 200 cycles with a cycle duration of 0.54 s each. The total analysis time, including pre-sputtering, was approximately 7 min per measurement. Typical count rates obtained for $^{32}$S were ~ 1.7 × 10^8 cps, and the internal precision of $^{34}$S/$^{32}$S for single analysis was typically 0.2‰ (2SE).

LA-ICP-MS. In situ S isotopic analyses were conducted with a high-resolution Nu 1700 MC-ICP-MS in combination with a RESOLution S155-LR excimer ArF laser ablation system (ASI, Australia) at the State Key Laboratory of Continental Dynamics (SKLCD), Northwest University in Xi’an, China.

The laser was operated in the aperture mode with a spot size of 53 μm and a signal intensity of approximately 10 V ($^{32}$S signal). Argon and ultra-high He were used as auxiliary and carrier gases, respectively, and their flow rates were set at 950 and 280 mL min⁻¹, respectively. Time-resolved mode was used to determine S isotopic ratios with an integration time of 0.3 s. Each measurement lasted for 125 s, including 20 s of background measurement, 45 s of data acquisition, and 60 s of washout. The background obtained for $^{32}$S was less than 200 mV. Low laser energy (3.5 J/cm²) and laser repetition rate (3 Hz) were used to obtain a relatively stable signal intensity.

The setting of the instrument and the mass bias correction were similar to those in the reference. In-house chalcopyrite (CPY-1) (chalcopyrite, $δ^{34}$S = 4.3 ± 0.2‰) was used as the bracketing calibration for the $δ^{34}$S ratios. During the analysis, a reference (TC1725 chalcopyrite, $δ^{34}$S = 12.78 ± 0.16‰) was employed to monitor IMF. The $δ^{34}$S value obtained from this standard (12.85 ± 0.32‰, n = 29, 2SD) was consistent with the recommended value within the margin of error.

In this study, all the measured $^{34}$S/$^{32}$S ratios were normalized using Vienna-Canyon Diablo Troilite (V-CDT) standard compositions ($^{34}$S/$^{32}$S-V-CDT = 0.0441626) as $δ^{34}$Sraw (%) = \left[ \frac{\left(^{34}\text{S}_{\text{sample}} / ^{32}\text{S}_{v-\text{CDT}}\right)}{^{34}\text{S}_{v-\text{CDT}}} \right] - 1 \times 1000. For SIMS, the IMF factor was calculated for each analysis using the relation IMF = $δ^{34}$Sraw $−δ^{34}$Sraw. Subsequently, the IMF was used to calculate the $δ^{34}$Sraw of the unknown sample using the relation $δ^{34}$Sraw = $δ^{34}$Sraw + IMF. The $δ^{34}$S value was reported with the associated analytical uncertainty (SE) and standard deviation (SD), which were estimated.
as the square sum of the standard deviation of the measurement and the uncertainty of the IMF of the reference sample. The uncertainties for the RMs in the test have been propagated to the absolute $\delta^{34}$S of the IGSD.

### RESULTS AND DISCUSSION

#### Chemical composition of RM.
To evaluate their major element characteristics and chemical homogeneity, the chemical compositions of the IGSD were measured by EMPA. The results are shown as the average values in Table 2. The detailed data of the individual measurements are listed in Supporting Information. The homogeneity of the chemical composition of IGSD chalcopyrite was assessed through the intermediate precision of the mean (2SD) of all measurements performed on the sample.

The EMPA results show that the IGSD exhibited a high degree of chemical homogeneity. The concentration of Fe varied between 29.60% and 31.64%, with an average value of 30.55% ± 0.36‰ (n=250, 2SD). Similarly, the Cu concentration ranged from 31.54% to 34.65%, with an average of 34.15% ± 0.49‰ (n=250, 2SD). The concentration of S was found to be between 35.00% and 36.01%, with an average value of 35.47% ± 0.34‰ (n=250, 2SD). The Zn content of the IGSD was found to be very low (< 0.14%). The concentrations of other elements (including Cd, Sn, As, Ge, Ga, Sb, Ln, Ph, and Ag) were also found to be very low, with values close to the detection limit (0.02 wt %). These results indicate that the IGSD is a highly homogeneous sample with respect to major element mass fraction. This can also be confirmed from the typical backscatter electron (BSE) map (Fig. 2c) and homogeneous wavelength dispersive X-ray (WDX) mapping with an area of 250 μm × 250 μm (Fig. 3), with no internal growth or zoning and mineral inclusions.

#### $\delta^{34}$S characteristic of IGSD.
The $\delta^{34}$S value of the IGSD was determined by both bulk and in situ analyses. The summarized data of the sulfur isotopes ($\delta^{34}$S) are listed in Table 3. Detailed data can be found in Supporting Information.

#### $\delta^{34}$S determined by EA-IRMS.
For bulk isotope analyses, two sessions were conducted. In session 1 (November 2020), nine fragments were selected from three main parts of the IGSD (three grains each). The $\delta^{34}$S values of the IGSD ranged from 4.14‰ to 4.34‰ (Fig. 4), yielding a mean $\delta^{34}$S value of 4.21 ± 0.12‰ (2SD, n = 9).

In session 2 (October 2022), 15 fragments were randomly selected from three different parts of the IGSD chalcopyrite. Every sample was separated into two subsamples for $\delta^{34}$S. The $\delta^{34}$S values of IGSD in this session ranged from 4.03‰ to 4.53‰ (Fig. 4), yielding a mean $\delta^{34}$S value of 4.21 ± 0.23‰ (2SD, n = 30).
bulk δ34S of the IGSD in two different sessions are almost the same, confirming the reliability of the result.

δ34S determined by in situ analysis. To determine the δ34S value and investigate the homogeneity of the S isotopes of IGSD chalcopyrite, a total of 395 SIMS and LA-MC-ICP-MS measurements were performed on three mounts.

The δ34S measurements were conducted on three large grains with crossing points in steps of 20–60 μm on NanoSIMS. A total of 282 measurements were performed with a δ34S of 4.4 ± 0.5‰ (2SD) (Fig. 5a). A total of twenty-nine δ34S measurements were also performed on 15 grains in GGIGCAS with a δ34S of 4.0 ± 0.1‰ (2SD) (Fig. 5b).

Two sessions were carried out for the δ34S measurements on three random large grains on Nu 1700 in SKLCD (Fig. 5c). During session 1 (January 2021), thirty measurements were performed with a homogeneous value of δ34S = 4.1 ± 0.3‰ (2SD). However, during session 2 (January 2023), fifty-four measurements were obtained with a homogeneous value of δ34S = 4.3 ± 0.2‰ (2SD).

All the δ34S values determined by in situ methods are consisted within 2SD uncertainty intervals, also confirming the reliability of the result.

Homogeneity of RM. Homogeneity is a fundamental requirement for a material to qualify as an RM. Both the bulk and in situ δ34S measurement at five different laboratories show that the δ34S values of IGSD chalcopyrite follow a Gaussian distribution with high analysis repetition (with 2SD < 0.3‰, except for the measurements by NanoSIMS (Fig. 5). Notably, the in-situ measurement on NanoSIMS possess with lower analysis repetition (~ 0.5‰) may be due to slight detector drift during a long period (~ 35 h). This indicates that the IGSD is homogeneous in δ34S characteristics.

As suggested by the key international guide for the characterization of RMs (ISO Guide 35), the F-test was also conducted to examine the homogeneity of the IGSD in sulfur isotopes. The F-test for the comparison of two population variances was applied using one-way analysis of variance (ANOVA statistics). The F ratio is defined as the ratio of the between-unit variance ($S^2_{between}$) to the within-unit variance ($S^2_{within}$) according to the regulations of the ISO Guide 35(2017) and JJF 1343-2022.

$$F = \frac{S^2_{between}}{S^2_{within}}$$

where $S^2_{between}$ is the ratio of between-unit sums of squares ($SS_{between}$) to associated degrees of freedom ($ν_{between}$), and $S^2_{within}$ is the ratio of between-unit sums of squares ($SS_{within}$) to associated degrees of freedom ($ν_{within}$).

$$ν_{between} = m - 1$$

$$ν_{within} = N - m$$

Fig. 5 Measurement and probability density curves of δ34S values for IGSD in different laboratories. The range bar for a single analysis is 2SD (a,b and c). The range bar for a single analysis in homogeneity test is 2SE (d and e).
Recommended in situ sulfur analysis.

Bulk isotope analysis. Laboratories and methods were consistent within 2SD uncertainty for sulfur isotopic compositions determined at different laboratories and methods were consistent within 2SD uncertainty intervals, which were 4.4 ± 0.5‰ for NanoSIMS at SKLODG, 4.0 ± 0.1‰ for SIMS at GIGCAS, and 4.1 ± 0.3‰ and 4.3 ± 0.2‰ for LA-MC-ICPMS at SKLCD. These values were also consistent with the result of the bulk sulfur isotope analysis (4.21 ± 0.12‰ in session 1 and 4.21 ± 0.23‰ in session 2), confirming the accuracy of sulfur isotopic compositions. Therefore, the δ34S value of 4.21 ± 0.23‰ (2SD, n = 30) of IRMS is the recommended value for IGSD chalcopyrite.

CONCLUSION

This study demonstrated that the IGSD chalcopyrite sample is homogeneous with respect to major element and δ34S compositions. This sulfide mineral is suitable as an RM for S isotope microanalysis through SIMS and LA-MC-ICPMS. The best recommended value of δ34S is 4.21 ± 0.23‰ (2SD) of IRMS for IGSD chalcopyrite.

Currently, approximately 500 g of the IGSD grains is stored in the NanoSIMS laboratory at SKLODG and is available for distribution. Interested parties may request access to the material from the first author of this article.

ASSOCIATED CONTENT

The supporting information (Detailed data) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION

Youwei Chen received B.S. degree in geochmistry from Nanjing university in 2005 and Ph.D. degree in geochmistry of ore deposit from institution of geochmistry, Chinese Academy of Sciences (IGCAS) in 2010. He is an associate professor of geochmistry at the IGCAS and currently in charge of the NanoSIMS laboratory. His interest on microanalysis was initiated since 2017 at LA-

Table 4. ANOVA statistics for homogeneity testing of Sulfur isotope compositions of IGSD

<table>
<thead>
<tr>
<th></th>
<th>Bulk measurement with EA-IRMS</th>
<th>In situ measurement with NanoSIMS</th>
<th>In situ measurement with SIMS (GIGCAS)</th>
</tr>
</thead>
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<tr>
<td>m</td>
<td>15</td>
<td>3</td>
<td>14</td>
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<td>SSWithin</td>
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<td>vWithin</td>
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<tr>
<td>F</td>
<td>1.44</td>
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<tr>
<td>Fcritical</td>
<td>2.42</td>
<td>3.03</td>
<td>2.55</td>
</tr>
</tbody>
</table>

All ANOVA results were calculated using the Microsoft Excel software. The results are listed in Table 4.

Bulk isotope analysis. To test the homogeneity of the isotope ratios, 15 fragments of IGSD chalcopyrite were randomly selected from three large parts (Fig. 2a) (five to each). Two subsamples were then taken from each fragment, with each being treated as an independent sample. F-testing demonstrates that the bulk IRMS results of the IGSD samples have very good homogeneity at a confidence level of 95% [F < Fcritical for α = 0.05, where α represents the sample significance level].

In situ sulfur analysis. Two F-tests of in situ analysis were performed to examine the homogeneity of IGSD in sulfur isotopes. In the first test, three large grains (~8 mm) from different parts of the IGSD were selected and measured by NanoSIMS (SKLODG) in one session. In total, 91–96 analysis spots were distributed in a crossing pattern spaced at intervals of approximately 20–60 µm on each grain. A total of 282 measurements were performed over ~35 h. Each grain was treated as a sample, and the measurements on each grain were treated as replicated measurements to calculate the ANOVA statistics.

For the second test, 15 grains of the IGSD were also selected and measured by SIMS (GIGCAS). A total 28 measurements were performed by two measurements on each grain (a pair of measurements was rejected because of the bad position of one of the two measurements).

The F ratios of the samples in both of the in situ homogeneity tests were less than the Fcritical (Table 4) value of α = 0.05, demonstrating that the in situ analyses of the IGSD samples exhibited outstanding homogeneity at a confidence level of 95%.

Therefore, both the F-test on bulk and in situ analyses demonstrated the homogeneity of IGSD chalcopyrite, indicating that IGSD chalcopyrite can be considered as a RM for in situ δ34S analysis.

Recommended δ34S values of IGSD. Previous homogeneous tests proved that the IGSD is homogeneous in δ34S. Additionally, the sulfur isotopic compositions determined at different laboratories and methods were consistent within 2SD uncertainty.
MC-ICPMS. Then he started working on NanoSIMS in 2020. His major research interests are SIMS methods development, NanoSIMS application on ore deposit, and the formation of the uranium deposit, etc.

Jianfeng Gao received his BSc in 1999 and MSc in 2005 from Nanjing University, and PhD in 2013 from the University of Hong Kong. He is a research professor of geochemistry at the Institute of Geochemistry, Chinese Academy of Sciences. His major research interests are analytical techniques of elemental and isotopic analysis and their applications to igneous petrogenesis, and magmatic-hydrothermal mineralization systems. He has been working as a member of editorial board for Atomic Spectroscopy.

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REFERENCES


Precise and Accurate Mass-independent Chromium Isotope Measurement by Total Evaporation Mode on Thermal Ionization Mass Spectrometry (TE-TIMS) at 200 ng Level

Li-Juan Xu, Ke Zhu, Qian-Ru Man, Jamie Lewis, Haibo Ma, and Sheng-Ao Liu

ABSTRACT: Mass-independent chromium (Cr) isotope ratios measurements have been widely used in dating early solar system events and tracing the genetic relationships between different solar system, as well as terrestrial materials. Current analytical techniques need relatively large sample sizes, and this limits the application of Cr isotopes on precious mission return samples and some Cr-poor samples (e.g., BCR-2 with Cr contents of ~15 ppm). This paper reports a novel analytical method for mass-independent Cr isotopic ratios measurements using a Thermal Ionization Mass Spectrometer (TIMS) operated in total evaporation (TE) mode. A three-step cation column (AG 50W-X12 resin, 200–400 mesh) chemistry is used to purify Cr in various samples, including chondrites, basalts and peridotites, and the Cr yield is better than 92%. Residual organics from column resins is detrimental to Cr ionization on filaments, we demonstrate that this can be effectively removed by treating samples with H2O2 at 40 °C on hotplate. Single Cr measurements on rhenium filaments consume 15 to 20 ng of Cr and sustain 53Cr of ~10V for 10 to 20 minutes. Generally, for one sample of 200 ng Cr, 10–15 ng repeated measurements can be made and 2-standard error precisions of ~ 0.05 and ~ 0.10 for ε53Cr and ε54Cr, respectively can be achieved. The reproducibility (the 2-standard deviation) for ε53Cr and ε54Cr is 0.05 and 0.07, respectively, tested by multiple measurements for DTS-2b (USGS dunite) and NWA 7734 (ordinary chondrite). Concentration and doping test (mainly for Fe) have also been conducted. These tests show that the Fe/Cr must be < 5 % and the measured 54Fe/52Cr< 1 % in order to achieve accurate ε54Cr. Finally, the ε53Cr and ε54Cr values measured by normal method on TIMS are systematically higher than those measured by total evaporation method on TIMS, which is potentially caused by non-kinetic mass-dependent fractionation during Cr evaporation and ionization on TIMS. The TE method could reduce this effect that may cause inaccurate mass-independent Cr isotope data on TIMS.

INTRODUCTION

Mass-independent chromium (Cr) isotope fractionation plays central in understanding the formation of terrestrial planets and early Solar System evolution. Cr isotopes (mass-independent) are fractionated on radiogenic, nucleosynthetic and cosmogenic effects. The short-lived radionuclide 53Mn, with a half-life of 3.7 ± 0.2 Myrs, decays to 53Cr and was present in the early Solar System. Therefore, the 53Mn-to-53Cr decay system is a useful chronometer to date early Solar System events such as chondrule (precursor) formation, differentiation of planets/asteroids, as well as chondrite parent body processes. Injection of Supernova material potentially caused 54Cr isotopic heterogeneity among different groups of meteorites originating in different regions of the solar protoplanetary disk. The variation of 54Cr isotopic anomalies provides a robust means for tracing the kinship...
between Solar System materials, including the origin of Earth-Moon system,\textsuperscript{24} chondrule formation,\textsuperscript{6,10,25,26} terrestrial impact events,\textsuperscript{27,28} the relationships between different groups of chondrite (e.g., CV-CK, CB-CH and CO-CM),\textsuperscript{21} planetary mantle heterogeneity,\textsuperscript{14} and the number the meteorite parent bodies.\textsuperscript{15} The cosmogenic Cr isotope ingrowth is mainly found in the material with high Fe/Cr ratios and long cosmic ray exposure ages, including metal phases in chondrites,\textsuperscript{20} iron meteorites\textsuperscript{20,29} and lunar samples.\textsuperscript{30}

The application of Cr isotopes for unravelling these planetary and cosmochemical issues is based on making both highly precise and highly accurate mass-independent Cr isotope measurements. Thermal ionization mass spectrometry (TIMS) is the technique of choice for mass-independent Cr isotopic ratios measurements\textsuperscript{31,32}, as the specificity of ionization in TIMS ion source can effectively avoid the isobaric interferences from $^{56}$Fe on $^{54}$Cr, as well as $^{54}$V and $^{59}$Ti on $^{56}$Cr.\textsuperscript{33} However, it appears that there are small residual mass-dependent fractionations that cannot be corrected for. This residual fractionation is evident in the correlation of $^{53}$Cr and $^{64}$Cr (where $^{53}$Cr and $^{64}$Cr are the per 10’000 mass-independent isotope deviations in $^{53}$Cr-$^{52}$Cr and $^{54}$Cr-$^{52}$Cr ratios relative to NIST 3112a.) for multiple measurements of standards,\textsuperscript{20,27,34} which should otherwise show no correlation. In detail, the $^{53}$Cr and $^{54}$Cr vary from -0.2 to 0.2 and from -0.4 to 0.4, respectively, with a slope of ~2.62 that is confirmed by the theoretical calculation about the slope (2.61) of $^{53}$Cr and $^{64}$Cr variation based on different Cr oxides and different mass fractionation laws.\textsuperscript{23} This apparent mass dependent Cr isotope fractionation during TIMS measurement is explained by the use of an unsuitable correction law (using exponential law) for correcting the mass-dependent equilibrium isotope fractionation between multiple Cr oxide species e.g., CrO and CrO\textsubscript{2}.\textsuperscript{23,34} Hence, the effect of different mass fractionation behaviors of Cr and its oxide species greatly hampers both the precision and accuracy of Cr isotope measurements by TIMS. Another problem for Cr isotopes measurements on TIMS is the presence of organics from the ion exchange resins used in the Cr separation. If these organics are not sufficiently broken down (oxidized) following separation, then their presence on the filament has been shown to be deleterious to Cr ionization.

Alongside thermal ionization mass spectrometry mass-dependent Cr isotopes can also be measured by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Plasma based techniques have the advantage there is no Cr evaporation process during ionization and using samples standard bracketing techniques it MC-ICP-MS has produced higher precisions (~0.03 and ~0.06 for $^{53}$Cr and $^{64}$Cr, respectively) than those on TIMS (~0.06 and ~0.12 for $^{53}$Cr and $^{64}$Cr, respectively), when giving same measurement times.\textsuperscript{14,15,22,23,35,36} However, due to the poor specificity of the ICP ion source more rigorous chemical purification (e.g., a four-step column chemistry) is needed to separate Cr from matrix elements, especially the isobaric elements for Cr, i.e., Fe, Ti and V.\textsuperscript{23,35,36}

In addition to elemental isobaric interference, mass-independent Cr isotope measurements on MC-ICP-MS also need optimizing to avoid Ar based polyatomic interference on the isotopes of interest, e.g., $^{40}$Ar$^{12}$C (on $^{53}$Cr), $^{40}$Ar$^{14}$N (on $^{54}$Cr) and $^{40}$Ar$^{16}$O (on $^{54}$Fe that is used to correct $^{54}$Fe). Such interferences are typically dealt with by operating the MC-ICP-MS in medium mass resolution ($m/Δm > 5,000$) and mass resolving the interference. However, operating in medium mass resolution comes at a cost of sensitivity and mass-independent Cr isotope measurements on MC-ICP-MS and, also the typical TIMS measurements requires at least 500 ng of loading Cr for high-precision measurement,\textsuperscript{25,31,36,37} and up to 8-10 μg.\textsuperscript{38} This relatively large sample size limits the application of Cr isotopes in some Cr-poor and precious samples. For instance, small samples such as micro-drilled chondrules, chondritic refractory inclusions; low-Cr content samples including tektites, carbonates and Fe-Mn nodules and precious samples from sample return missions, e.g., Chang’E, Hayabusa, Martian Moon eXploration (MMX) and OSIRIS-Rex missions.

The method of total evaporation (TE) on TIMS may developed for mass-independent Cr isotope measurements. Total evaporation method attempt to evaporate all sample loaded onto the filament over a relatively short period of time and aims to effectively decrease the mass fractionation of a sample. For example, Fiedler et al.\textsuperscript{39} reported that the standard deviation of repeated $^{239}$Pu/$^{239}$Pu ratio analyses decreased from 0.038% to 0.008% when TE-TIMS was applied compared to standard measurements. For Cr the TE-TIMS method requires only ~ 15 ng of Cr and can be run using the single filament configuration. This means that the absolute amount of organics on each filament can be decreased, assuming the amount of residual organics from column separation is independent of the amount sample, and hence the amount of Cr processed. Similar TE-TIMS method for Cr isotope measurements has already been used in previous studies,\textsuperscript{10,13,15,26} but the detailed methodology has not been systematically reported. Furthermore, during data acquisition, the some of the previous TE-TIMS Cr work calculated the isotope ratios for every measured cycle and then took the mean, rather than calculating the isotope ratios from mean signals over all cycles,\textsuperscript{10,13,26} which does not follow the theory of total evaporation.

For mass-independent isotope ratio measurements, the yield of Cr column chemistry should be taken into consideration. This is because a low yield (e.g., < 80%) may result in non-exponential mass-dependent isotope fractionation of Cr and this cannot be corrected for during measurement unless the exact style of the mass-dependent fractionation is known.\textsuperscript{31} Here, a high-yield (> 90%) three-step Cr column chemistry is developed that can be used for a various of samples (e.g., chondrites, basalts and peridotites). Additionally, a novel and effective method for
removing the residual organics from the resin is described, which may also help improve the TIMS method for the mass-dependent Cr isotope fractionation. We report the detailed methodology for mass-independent Cr isotope measurements using TE-TIMS, including the tests for concentration effect and Fe-doping.

EXPERIMENTAL

Chemical reagents and materials. All chemical procedures were carried out in laminar flow hoods (Class 100) in a clean room (Class 1000) with filtered air. Ultrapure water (Milli-Q) with a resistivity of 18.2 MΩ·cm was used for diluting reagents. All optima-grade grade (BV-III) acids (hydrochloric acid (HCl), nitric acid (HNO₃), and hydrofluoric acid (HF) which are from Beijing chemical factory), were further purified twice using a sub-boiling distillation system (Savillex DST-1000 Minnetonka, USA). Boric acid (99.99%) and silicon dioxide (99.99%) with alumina doping are obtained from Sigma-Aldrich (701491). NIST SRM 3112a Cr (1000 ppm) is used as isotopic reference standard whilst GSB-Ti, Fe, V, K, Na, Ca, Mg and Mn ultrapure standard solutions of 1000 ppm are from the China Iron and Steel Research Institute.

PFA beakers (Savillex) were cleaned with BV-III 7 M HNO₃ and/or 5.5 M HCl for 8 h on a hot plate at 130 °C, followed by distilled 7 M HCl and ultrapure water at 130 °C for 8 h. TIMS filaments (single filament) are made from rhenium ribbon (99.99% purity, 0.014 mm thick, 0.28 mm wide, H. Cross company).

Rock standard samples: rock powders of BHVO-2 (basalt), BCR-2 (basalt), DTS-2b (dunite) were obtained from the United States Geological Survey (USGS), The Rock powders of JP-1 (peridotite) are from Geological Survey of Japan (GSJ). In addition, a carbonaceous chondrite, Murchison [CM2] and an ordinary chondrite, Northwest Africa [NWA] 7734 [H4], Allende [CV3] were also analyzed in this study.

Sample preparation and digestion. Sample powders (~50 mg) were digested with concentrated HF (29 M) and HNO₃ (14 M) in PFA beakers at 150 °C on hotplates for more than seven days for most terrestrial geological reference materials (DTS-2b, JP-1) and meteorites samples (Murchison CM2, NWA 7734 [H4]) and then evaporated to dryness. Samples were then digested in concentrated aqua regia (HCl:HNO₃ = 3:1) for more than seven days and then evaporated to dryness at 130 °C. The samples were then redissolved in 0.5 ml of concentrated HCl (11 M) afterwards evaporated to dryness on a hot plate at ~100 °C. Finally, the samples were re-dissolved in 0.2 ml 6 M HCl in preparation for column chemistry.

Column chemistry. In this study a three step, high Cr yield chromatography procedure is developed using AG 50W-X12 (Bio-Rad) resin. AG 50W-X12 resin was used in the chromatography procedure as it as a higher cross-linkage, smaller wet bead size, and smaller molecular weight limits than the Bio-Rad AG50W-X8 (200 ~ 400 mesh), which will give better separation of Cr and Mg. The column chromatography used in this study is described in Table 1 and an example elution curve for the BHVO-2 reference material is shown in Fig. 1.

In order to achieve high Cr yields in column chromatography, it

<table>
<thead>
<tr>
<th>Step</th>
<th>Acid volumes</th>
<th>Acid</th>
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</thead>
<tbody>
<tr>
<td>Wash resin</td>
<td>5 mL</td>
<td>6 M HCl</td>
</tr>
<tr>
<td>Wash resin</td>
<td>2 mL</td>
<td>MQ</td>
</tr>
<tr>
<td>Pre-condition</td>
<td>3 ml</td>
<td>1 M HCl</td>
</tr>
<tr>
<td>Load sample#</td>
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<td>1 M HCl</td>
</tr>
<tr>
<td>Collect Cr</td>
<td>3.5 ml</td>
<td>1 M HCl</td>
</tr>
<tr>
<td>Elute matrix and collect residual Cr</td>
<td>3 ml</td>
<td>6 M HCl</td>
</tr>
</tbody>
</table>

Note: Before the column 2, the matrix collected by 3ml 6 M HCl should repeat column 1, then the mixed total Cr load together for the column 2.

Fig. 1 The Cr elution curve of BHVO-2 for column 1 and column 2 using AG50W-X12 resin (200 ~ 400 mesh). The column 1 is 4 mm in diameter and 10 cm in length and column 2 is 4 mm in diameter and 3 cm in length (Table 1). Concentrations of eluting elements were analyzed on Elemental XR ICP-MS in the Isotope Geochemistry Lab of the China University of Geosciences, Beijing.
is essential to control the oxidation state of the Cr in solution. Therefore, prior to loading on the first ion exchange column, samples are refluxed overnight in 0.2 ml of 6 M HCl at 130 °C to promote the formation of Cr$^{3+}$-Cl species (mainly Cr(H$_2$O)$_6$Cl$^{2+}$ / CrCl$_3$(H$_2$O)$_9$), which have a low affinity to the cation resin and are eluted early.$^{33,42}$ The first column uses 1 ml of AG50W-X12 resin in 4 mm diameter columns. Before loading the samples on the column, the resin was cleaned with 5 ml of 6 M HCl and 3 ml MQ water, then conditioned with 3 ml of 1 M HCl. Samples, in 0.2 ml of 6 M HCl, were diluted to 1 M HCl with 1 ml of ultrapure water then immediately loaded onto columns followed by 3.5 (1 + 1 + 1.5) ml of 1 M HCl to collect Cr. In this step, Cr was separated from most major elements, e.g., Fe, Mg, Mn, Ni, and V (Fig. 1). This chromatography also has a good separation of Cr from V and Mg which has been a problem for previous column chromatography using 0.5 M HNO$_3$ matrices, which have high (99 %) Cr yield but required a fourth TODGA column and still do not achieve adequate V separation on basaltic V-rich matrices.$^{23,36,26,42}$

In order to improve the chromatography yield for the first column, following the collection of the main ~85% Cr elution the remaining ~15% Cr and sample matrix was collected using 3 (1 + 1 + 1) ml of 6 M HCl.$^{15}$ This aliquot was then evaporated at 130 °C to reduce the sample volume and promote CrCl$_3$(H$_2$O)$_9$ formation and reloaded on to the first column which was cleaned with 5 ml of 6 M HCl and reconditioned with 3 ml of 1 M HCl. In this way, Cr is well separated from V and Mg and a high Cr yield is maintained. The Cr yield is around 97% after the first and second columns. The Cr from these two steps were then recombined and re-digested in 0.5 M HNO$_3$ before loading on the third column.

As with columns 1 and 2 control over the oxidation state of Cr in solution is critical. Prior the third column samples are dried down three times in 0.1 ml of concentrated HNO$_3$ to convert to nitrate form. Samples are then re-dissolved in 250 μl of 2 M HNO$_3$, and then diluted with 730 μl MQ water to achieve ~1 ml of ~0.5 M HNO$_3$. This solution was heated on a hotplate at 130 °C for two hours, in order to promote the formation of Cr$^{3+}$ and equilibrium for the different species. After that, 20 μl of 30% H$_2$O$_2$ is added and the solution kept at room temperature for 48 h, in order to maximise the promotion of Cr$^{3+}$.

The third column contains 0.33 ml of Bio-Rad AG50W-X12 (200 ~ 400 mesh) cation exchange resins.$^{41}$ The resin was cleaned with 2 ml of 6 M HCl and 1 ml MQ water, then preconditioned with 1 ml of 0.5 M HNO$_3$. Samples are loaded in 1 ml of 0.5 M HNO$_3$, followed by 2.5 ml of 1 M HF to effectively remove residual Ti, Al, Fe and V, and 6 (3 + 3) ml of 1 M HCl to remove remaining Mg, K and Ca, and Na. Finally, Cr was collected with 1.6 (0.4 + 0.4 + 0.4 + 0.4) ml of 6 M HCl. The yield of this column is higher than 95%. Compared to 3 ml of 6 M HCl for final Cr collection with the same columns in previous study,$^{31}$ less acid is used in this step and this should lead to less organics in the sample from the resin, but also will not lose Cr.

<table>
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<th>Element</th>
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<tr>
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<td>50Ti</td>
<td>50Cr</td>
<td>50V</td>
<td>52Cr</td>
<td>53Cr</td>
<td>54Cr</td>
<td>56Fe</td>
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</tbody>
</table>

The total recovery of Cr for diverse samples from the three-column cation-exchange chromatography procedure is higher than 90%. For example, the total Cr recovery for BCR-2 ([Cr] = 15 ppm), BHVO-2 ([Cr] = 280 ppm), and DTS-2b ([Cr] = 15 000 ppm) of this study are 92%, 92%, and 98%, respectively. Total chemistry blanks for the column separation procedures are less than 0.5 ng, which are negligible compared to more than 200 ng quantities of Cr isolated from each sample of this study.

### Thermal ionization mass spectrometry-Total Evaporation (TE)

Chromium isotope ratios were analyzed on a Thermo Fisher Scientific TRITON Plus (TIMS) in the Isotope Geochemistry Lab of the China University of Geosciences, Beijing. Samples were loaded on outgassed Re filaments and narrow paraffin dams were used on the Re filaments to constrain the samples solution while loading, which was performed at 1 A current. Samples were loaded as 1 μl containing 15 ng of Cr and a further 1 μl of mixture of Al-bearing silica gel and concentrated H$_2$BO$_3$ (1:1) was then loaded the mixture was then dried by heating quickly to 1.5 A, and then increase the current to ~ 2.2 A until the filament showing dull red for 1 s to form a glass. We have tested that compared to the typical slow drying at 0.5 A current,$^{33}$ and the fast drying in this study will not affect the final Cr data.

During a measure procedure, total evaporation (TE) mode was chosen in the method file. The cup configuration for Cr isotope measurements is listed in Table 2. The following parameters are set: idle time of 3 s; heat-slope of 3 mA/cycle; the pilot signal (on $^{50}$Cr) of 10 000 mV; number of cycles 1960 and an integration time of 1.049 s. No baseline measurements were taken during measurement as this will result in lost signal and compromise the total evaporation. In fact, we process the data in the TE mode, i.e., calculate the sum of the signals from all measurement cycles. Compared to the sum of all the signals, e.g., ~3000 V for $^{54}$Cr (the Cr isotope with the lowest abundance), the noise of faraday cups (mostly lower than 10$^{-3}$ V) can be neglected. Isobaric interferences from Ti$^{+}$ and V$^{+}$ and Fe$^{+}$ on Cr$^{+}$ were corrected assuming natural isotope ratios,$^{49}$ Ti$^{50}$Ti = 1.0185, $^{51}$V/$^{50}$V = 399.0 and $^{54}$Fe/$^{56}$Fe = 15.698, and the mass-dependent Cr isotope fractionation from the instrument and column were all normalized by $^{50}$Cr/$^{52}$Cr = 0.051859 using an exponential law.$^{6,43}$

All the measurements were run automatically in a sequence that includes 21 filaments. In detail, six NIST 312a filaments and three other samples of five individual filaments are run in a day with a NIST 312a filaments run for every three sample filaments. Sequences were started after a five-hour pump down, when the source pressure is lower than 5 × 10$^{-7}$ Pa, without using any liquid nitrogen to further increase the vacuum. The automatic filament
heating program increases the stable $^{52}\text{Cr}^{+}$ beams to 6 V (we set automatic signal tuning at 0.01 V and 1 V for $^{52}\text{Cr}$ beam), and finally the measurement will also stop when the signal decreases below 6 V. Each sample was analyzed for 10 – 15 times (with 10 – 15 filaments, and each filament is only for one measurements), until the 2SE uncertainties for $\varepsilon_{53}\text{Cr}$ and $\varepsilon_{54}\text{Cr}$ are lower than or close to ~0.05 and ~0.10, respectively, and typical 15 ng Cr loads of NIST 3112a or from sample purification usually achieves 800 ~ 1800 cycles of data.

For data collection, measurements with less than 600 cycles are not considered and $^{56}\text{Fe}/^{54}\text{Cr}$ ratio > 1 $\times$ 10$^{-3}$ (see discussion in the doping test later) are not considered valid. The final sum $^{54}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios (sum of total 800 ~ 1960 cycles) is used to calculate epsilon Cr values, which is different from the previous studies using the mean $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios of each cycle.$^{5,10,26}$ Considering the mass-dependent fractionation on the TIMS, we calculate the sample data relative to the mean of the NIST 3112a measurements ($n = 6$) in a same turret. All the $^{53}\text{Cr}/^{52}\text{Cr}$ and $^{54}\text{Cr}/^{52}\text{Cr}$ ratios of the samples are expressed as the epsilon notations relative to the reference material NIST 3112a:

$$
\varepsilon_{x}\text{Cr} = \left( \frac{\text{sample}^{54}\text{Cr}}{\text{sample}^{52}\text{Cr}} \right) \times \frac{\text{NIST}^{52}\text{Cr}}{10000} (1)
$$

where $x = 53$ or 54.

**Minimizing of organic matter.** Organics from the column resin has always been considered to be a significant impediment for obtaining stable Cr ionization on TIMS.$^{33,37,44,45}$ Although less acid was used in the third-column Cr collecting step (see section “Column chemistry”) and total evaporation method (see section “Thermal ionization mass spectrometry-Total Evaporation (TE)”) can effectively reduce the amount of organics introduced onto the filaments, further reduction in organics can be achieved by chemical treatment of the sample following chromatography. Perchloric acid (HClO$_4$), ultraviolet radiation, aqua regia, HNO$_3$, or H$_2$O$_2$ are usually used to eliminate organic matter.$^{20,23,26,41,45}$ (Table 3). The HClO$_4$ is a strong acid, and a powerful oxidizer when hot, which should effectively oxidize and remove the organics. However, the HClO$_4$ may result in loss of Cr by forming volatile CrO$_2$Cl$_2$ during the subsequent evaporation to dryness, as the boiling point temperature of CrO$_2$Cl$_2$ is significantly less that the temperature required to effectively evaporate HClO$_4$.$^{44,46,47,48}$ Liu et al.$^{41}$ used 30 μl of HClO$_4$ and 500 μl of HNO$_3$ to effectively eliminate organic matter at low temperature and avoided the volatilization of CrO$_2$Cl$_2$. However, it needs long time (two weeks). Also considering the explosive risk for HClO$_4$ at high temperatures, this method is not recommended. Van Kooten et al.$^{26}$ used concentrated aqua regia followed by concentrated HNO$_3$ to remove the organics in Cr from the column and needed about 10 days.

We have also tested HNO$_3$ and H$_2$O$_2$ for their ability to remove the organics from Cr solutions following chemistry. We have found that repeated evaporation to dryness in concentrated HNO$_3$ and heat the samples in concentrated HNO$_3$ (1 ml) overnight are insufficient to totally remove organics. We observe in Cr-poor samples such as BHVO-2 and BCR-2, where organics are not as effectively diluted on when loading onto filament, the Cr ion beams on TIMS are have low intensity and rapidly decrease. H$_2$O$_2$ is widely used when digesting organic matter for isotope measurements. Johnson and Bullen$^{49}$ firstly employed H$_2$O$_2$ on a 70 °C hot plate, under ultraviolet rays for decomposing H$_2$O$_2$. Although the relatively high temperature could potentially increase the oxidative ability, we found 70 °C also increase the speed of decomposition of H$_2$O$_2$, which intensively generates oxygen bubbles. The breaking of these bubbles could splash the sample outside of the beakers. Since we found that H$_2$O$_2$ alone can effectively remove organics, it is not necessary to use ultraviolet rays for decomposing the H$_2$O$_2$ to H$_2$O and O$_2$ and hence we did not follow this method. In this study, 100 μl of H$_2$O$_2$ was used to eliminate organic compounds with low temperature, i.e., 40 °C for two-three hours which prevented rapid decomposition of the H$_2$O$_2$ and sample splash. During the process, the Cr solution are observed to turn purple in colour that could be due to the oxidation of Cr to CrO$_2$$^{2+}$. After drying down the H$_2$O$_2$ samples are redissolved in 0.5 ml conc. HCl to reduce the Cr to Cr$^{3+}$. Following the H$_2$O$_2$ treatment signals for the solution standards, geological reference materials and meteorites (15 ~ 20 ng Cr) are all stable at 10 V for 1000 ~ 1800 cycles (integration time of 1.049 s) after above eliminating organics procedure.

Another way to minimize the organics is using a tiny column with less resin, which will introduce less organics from the resin.$^{13}$ All the organics affecting the Cr ionization should from the last wash.

### Table 3. Reported methods for organic component eliminated of Cr by TIMS

<table>
<thead>
<tr>
<th>Material used</th>
<th>Methods</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>100 μl of H$_2$O$_2$ to dryness and purple at 40 °C</td>
<td>This study</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>100 μl of concentrated HNO$_3$ for three times</td>
<td>Zhu et al.$^{16}$; Qin et al.$^{20}$</td>
</tr>
<tr>
<td>HClO$_4$ + HNO$_3$</td>
<td>two weeks at room temperature</td>
<td>Liu et al.$^{19}$</td>
</tr>
<tr>
<td>Ultraviolet radiation/H$_2$O$_2$</td>
<td>100 μl of 30% H$_2$O$_2$ to dryness at 70 °C</td>
<td>Johnson and Bullen$^{45}$</td>
</tr>
<tr>
<td>H$_2$O$_2$ + HNO$_3$</td>
<td>100 μl of H$_2$O$_2$ and 100 μl of HNO$_3$</td>
<td>Chrastny et al.$^{47}$</td>
</tr>
<tr>
<td>Aqua regia + HNO$_3$</td>
<td>aqua regia for one week and HNO$_3$ for three days</td>
<td>Van Kooten et al.$^{26}$</td>
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</table>
Table 4. The ε<sup>53</sup>Cr and ε<sup>54</sup>Cr for the mixture of NIST 3112a and GSB Fe with different Fe/Cr ratios (0.01 ~ 1)

<table>
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<th>ε&lt;sup&gt;53&lt;/sup&gt;Cr (measured)</th>
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<th>2SE</th>
<th>ε&lt;sup&gt;54&lt;/sup&gt;Cr (measured)</th>
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<th>2SE</th>
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<tbody>
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<td>1.11</td>
<td>0.49</td>
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</table>

RESULTS AND DISCUSSION

Isobaric interference and doping test. Fe, Ti, and V are the major isobaric interferences on the isotopes of Cr (54Fe-54Cr and 50V-50Ti-50Cr). However, Ti and V have high first ionization potentials, and are typically not ionized under the same conditions as Cr with the emitters of silica gel and H3BO3 by TIMS<sup>39,46</sup>. In addition, our three-step column chromatography procedure provides an effective separation of Cr from Ti and V, hence we do not perform doping tests for Ti and V. However, Fe is a major element and rich in both rock samples and the environment (causing a high Fe in blank), and Fe can be ionized in the presence of silica gel and H3BO3 emitters at slightly higher temperature (> 1350 °C)<sup>41</sup> than that of Cr which is usually between 1100 °C and 1400 °C. Therefore, it is still important to examine the potential influence of isobaric interference from 54Fe on 54Cr with the total evaporation of TIMS. The ε<sup>53</sup>Cr and ε<sup>54</sup>Cr values on a mixture of NIST SRM 3112a and GSB Fe were analyzed for the Fe/Cr ratios ranged from 0.001 to 1. As shown in the Table 4 and Fig. 2, the ε<sup>54</sup>Cr values of these mixtures with different Fe/Cr ratios are identical within our precision (-0.02 ± 0.06 ~ 0.02 ± 0.06, 2 SE, n= 9-14), so addition of Fe has no effect on ε<sup>54</sup>Cr data. However, ε<sup>54</sup>Cr values of these mixtures are increases with higher Fe/Cr, which are range from -0.01 ± 0.10 (54Fe/54Cr = 0.0002) to 1.11 ± 0.13 (54Fe/54Cr = 0.017) caused by the isobaric interference from 54Fe on 54Cr after corrected by isobaric interferences from Fe<sup>+</sup> on Cr<sup>+</sup> with 56Fe/54Fe = 15.698 as that of other samples. From these data, it is clear that interference from 54Fe on 54Cr can be sufficiently corrected for when 56Fe/54Cr ratios lower than 0.0009 (Table 4 and Fig. 2), which is evidenced by the similar ε<sup>54</sup>Cr values among the doped samples with 56Fe/54Cr = 0.0002 (ε<sup>54</sup>Cr = -0.01 ± 0.10), 56Fe/54Cr = 0.0009 (ε<sup>54</sup>Cr = 0.01 ± 0.11), and pure NIST 3112a (ε<sup>54</sup>Cr = 0.04 ± 0.06; 2SD, N = 4) (Table 5). As for the routine measurements, 56Fe/54Cr ratios are usually less than 5 × 10<sup>-4</sup>.

Evaluation of concentration effect. We also did evaluation of concentration effects is to test 1) if samples and standards measured at different signals, whether it causes inaccurate data; 2) whether more loading samples and higher signals result in more precise data. Usually, 15 ~ 20 ng Cr of geological reference materials and meteorites were loaded on the Re filament in this study (Table 5). We have also tested the effect of loading a range of different Cr masses on filaments with 7.5 ng (with pilot signal

![Fig. 2](link) Measured Cr isotope ratios for the mixture of NIST3112a and GSB Fe with different Fe/Cr ratios (0.01 ~ 1). a): the ε<sup>53</sup>Cr and ε<sup>54</sup>Cr for the mixture of NIST SRM 3112a and GSB Fe with different doped Fe/Cr ratios (0.01 ~ 1). b): the ε<sup>54</sup>Cr vs. 54Fe/54Cr (measured ratios by TIMS) for the mixture of NIST SRM 3112a and GSB Fe. The error bar of ε<sup>54</sup>Cr and ε<sup>53</sup>Cr is 2SE, which are not higher than 0.06 and 0.12, respectively (Table 4).

(eluting Cr) of 3 ml 6M HCL through third column (also the third step in this study) with 0.33 ml cation resin. Zhu et al.<sup>13</sup> used a smaller column with only 0.1 ml of cation resin in the column. Since the resin is less, the volume of the wash acid (6M HCL) also decreases to 1 ml. Hence, using 3.3 times less resin and 3 times less acid results in ~10 times (3.3×3) less organics introduced to the final purified Cr. Note that, the 0.1 ml column will only allow maximum ~5 mg silicate samples were loaded and purified, relative to ~10 mg mg of column with 0.33 ml resin. It will be useful to use the tiny columns to process small but Cr-rich samples, e.g., the chondrules.<sup>19</sup> Less resin and acid also introduces less Cr blanks.
isotope measurements. However, as for the accuracy, the 50 ng of 7 V for $^{52}$Cr, 15 ng (with pilot signal of 10 V for $^{52}$Cr) and 50 ng (with pilot signal of 30 V for $^{52}$Cr) loads of NIST 3112a being tested (Table 5 and Fig. 3). Note that, all individual filaments have to 800 to 1800 cycles of measurement, and the data are all relative to 15 ng loading of NIST 3112a. The uncertainty for both $e^{53}$Cr and $e^{54}$Cr values do not vary with the mass of Cr loaded and the pilot signal set for the TE measurement, so high signal measurements cannot improve the data precision. By comparison, using 7.5 ng Cr loads and setting a lower TE voltage is not detrimental to precision, so for some samples, total 100 ng Cr could also be enough for a high-precision mass-independent Cr isotope measurements. However, as for the accuracy, the 50 ng (with pilot signal of 30V) measurements show non-zero $e^{53}$Cr values, indicating mismatch (more than three times) of the signals between samples and standards will lead to inaccurate $e^{53}$Cr data.

**Precision and accuracy of Cr isotope data.** The Cr isotopic composition of both pure and doped NIST SRM 3121a, four terrestrial geological reference materials and three meteorites have each been analyzed between 5 and 15 times (Table 5 and Fig. 4). The external reproducibility is assessed as a pooled standard deviation across all reference material processed through column chromatography. The pooled standard deviation for $e^{53}$Cr and $e^{54}$Cr is 0.055 and 0.076, respectively (2 SD) and this reproducibility is comparable with what has previously been reported by TIMS16 and high precision MC-ICP-MS data.23,24 This figure encapsulates the reproducibility of multiple individually processed reference material aliquots and in the case of NWA7734

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<th>2SE</th>
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<th>2SD</th>
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**Notes:** *1: The pure solution standard of NIST 3112a was analyzed after the column chemistry with the mixture of 5 μg of pure NIST 3112a and matrix (50 μg of Fe + Mn + Ca + Al (1:10) and 5 μg of Ti + V + Mn + Ni + Na + K (1:1)). These matrix elements were from ultrapure GSB standards of the China Iron and Steel Research Institute. *2: The pure solution standard of NIST 3112a was analyzed after the column chemistry. All the data are measured from different sessions. Table 5. The $e^{53}$Cr and $e^{54}$Cr of terrestrial geological reference materials and meteorites standards in this study.
Fig. 3 Measured Cr isotope ratios for the NIST 3112a with different loaded samples contents (7.5 ng, 15 ng, 50 ng). The Cr loading for 7.5 ng, 15 ng, 50 ng on each filament are analyzed on 7 V, 10V, and 30 V for $^{52}$Cr signal, respectively. The error bar of $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr is 2SE, which are not higher than 0.06 and 0.12, respectively (Table 5).

Fig. 4 The $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr of geological reference materials and meteorites standards measured by TE-TIMS in this study (“large red circles” is abbreviated to “LC”) and the literatures (“small grey circles” is abbreviated to “SC”). The error bar of $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr is 2 SE respectively (Table 5). The gray bars are the average $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr values for bulk silicate Earth from Zhu et al. 23

As a further test of to assess whether column chemistry fractionates mass-independent Cr isotope compositions, two NIST SRM 3112a standards that have been passed through all the columns have been measured. One (*1 in Table 5), is the mixture of 5 μg of pure NIST 3112a with 50 μg of Fe, Mn, Ca and Al (1:10) and 5 μg of Ti, V, Mn, Ni, Na and K (1:1), from GSB elemental standards. The second (2* in Table 5) is pure NIST 3112a. Following measurements against unprocessed NIST SRM 3112a, the $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr values of these two standards after column chemistry are 0 within our reproducibility. The well consistent data for columned NIST 3112a suggests that our column chemistry does not shift the $\varepsilon^{53}$Cr and $\varepsilon^{54}$Cr values (Table 5) of samples (e.g., through inducing non-kinetic mass-dependent fractionation).

Comparison of TE method with normal method. Table 6 and Fig. 5 show the comparison between Cr isotopes measured by
normal and TE-TIMS methods for same purified samples (from same columns and digestion) of Allende (a CV3 chondrite). All the measurements are performed on Triton TIMS housed at Freie Universität Berlin. The TE data have been published in Zhu et al.\(^{16}\) It can be found that both the \(\varepsilon^{54}\)Cr and \(\varepsilon^{56}\)Cr values of normal measurements are systematically higher than the TE data. The differences for \(\varepsilon^{54}\)Cr and \(\varepsilon^{56}\)Cr values between two methods are ~0.09 and ~0.16 and the differences in the paired measurements lie on a line with a slope close to 2. We interpret this systematic difference as the non-kinetic Cr isotope fractionation between different Cr species (e.g., Cr\(^{3+}\), CrO\(_2\), CrO\(_3\) and CrO\(_4^2-\)) during Cr evaporation and ionization on TIMS. The details have been discussed in Zhu et al.\(^{23}\) and Bourdon and Fitoussi.\(^{48}\) However, TE mode aims to minimize this effect, because each measurement will evaporate all the Cr on one filament. The \(\varepsilon^{53}\)Cr (0.10 ± 0.04, 2SD) and \(\varepsilon^{54}\)Cr (0.92 ± 0.07, 2SD) data (Fig. 5, Grey bars) are another Allende dissolution (passed through 4 columns) measured by MC-ICP-MS. These values are slightly higher than the TE-TIMS data, which can be caused by sample heterogeneity.

### CONCLUSION

We report on a total evaporation TIMS method for mass-independent Cr isotope measurements. This novel method can 1) decrease the Cr quantity needed in the measurements, which is significant for precious samples from sample return missions and some Cr-poor samples. We find that ~200 ng of Cr is enough to achieve a high-precision measurements, with 2 SE uncertainties for \(\varepsilon^{53}\)Cr and \(\varepsilon^{54}\)Cr are ~0.05 and ~0.10 respectively; 2) minimize the TIMS instrumental mass fractionation of Cr isotopes achieving a better data accuracy. Based on literature study, we developed a three-step column chemistry to purify Cr from a various of samples, including basalts, peridotites and chondrites, which can also achieve a high yield (> 90%). We found H\(_2\)O\(_2\) at low temperature, i.e., on hot plate of 40 °C, can effectively remove the organics from the column resin.

### AUTHOR INFORMATION

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Notes
The authors declare no competing financial interest.

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Fe-Ni@ACC Nanocomposite for Magnetic Dispersive Micro Solid-phase Extraction of Cu (II) From Food and Hair Samples

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ABSTRACT: Fe-Ni@ACC nanocomposite was synthesized by hydrothermal method and characterized using scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FT-IR). Fe-Ni@ACC was used as adsorbent for magnetic dispersive micro solid-phase extraction (M-D-μSPE) procedure for separation and preconcentration of trace level of copper at trace levels before its determination by microsampling flame atomic absorption spectrometry (FAAS). The effects of various parameters such as pH, amount of adsorbent, eluent type and eluent volume, and sample volume on the recoveries of copper on Fe-Ni@ACC were optimized. The presented method is accurate, inexpensive and environmentally friendly and due to magnetic properties of the adsorbent, the separation process is very simple and fast. The method presents limit of detection (LOD)(3s/m) of 0.69 μg L\textsuperscript{-1}, limit of quantification (LOQ)(10s/m) of 2.29 μg L\textsuperscript{-1}, preconcentration factor of 40 and relative standard deviation (RSD %) (s/x) 1.18%. The accuracy of the method was confirmed by the analysis of TMDA-53.3 fortified water and TMDA-64.2 fortified water certified reference materials and addition-recovery tests to real samples. The present M-D-μSPE method was successfully applied to determination of copper level of tap water, cigarette, human hairs and black teas samples.

INTRODUCTION

Trace levels of heavy metals, which have significant positive and negative effects on the ecosystem and human health, are released into the environment through natural activities and/or human activities.\textsuperscript{1,2} Copper at trace levels is of vital importance due to its duties in the biological systems of living things, on the other hand, high doses cause serious problems due to its toxicity. In the deficiency of copper which plays an important role in living metabolism, causes problems such as anemia, decrease in body resistance, weakness, fatigue, decreased growth, iron deficiency, fragile bones, skin scars, eczema, mitochondrial destruction, DNA breakage, injury to neuronal cells and deterioration in different enzymes.\textsuperscript{4-7} The high amounts of copper can cause liver metabolic disorders, nausea, vomiting, diarrhea, stomach cramps, hepatic neurosis, gastrointestinal bleeding, hypertension, dermatitis, Alzheimer's, Parkinson's, schizophrenia, depression, autism, epilepsy, liver or kidney damage, and even death occurs.\textsuperscript{8-12} Copper enters the environment as a result of natural events such as volcanoes, forest fires and aerosol particles from sea spray. Its amount in the environment increases as a result of human activities in industrial areas such as electricity-electronics, paper, petroleum, rayon, water treatment, wood and leather preservative, mining, fertilizer, construction, transportation, industrial equipment, chemistry, jewelry and paint industry.\textsuperscript{2,13,14} Due to the fundamental significance and hazardous effects of copper on the ecosystem and living things, accumulating on biological, nutritional and environmental samples by being released into the environment; It is of great importance to determine copper at trace levels with accurate, sensitive, precise, economical, environmentally friendly and fast analytical instrumental methods.
Many analytical techniques such as FAAS, GF-AAS, ICP-OES, ICP-MS, SEC-ICP-MS, AES, voltammetry and spectrophotometry/derivative spectrophotometry have been developed for the determination of copper and the other metals amount in various samples.\textsuperscript{15-22} Flame atomic absorption spectrometry (FAAS) is a sturdy technique that gives accurate, sensitive and precise measurements found in many laboratories due to its low cost and ease of use.\textsuperscript{23,24} However, generally separation and enrichment are required prior to flame atomic absorption measurements due to low concentrations of trace level analytes and/or complex sample matrix. Thus, the analyte of interest is determined more precisely and with lower detection limit values.\textsuperscript{25-27} Many sample preparation methods such as solid phase extraction (SPE), liquid-liquid extraction (LLE), and cloud point extraction (CPE) have been developed for separation and enrichment of copper from complex matrix media.\textsuperscript{28-31} However, all these classical methods have initiated to leave their position to microextraction methods because of the disadvantages such as time consuming, laborious, expensive, toxic, insufficient preconcentration factor, high organic solvent volume and secondary waste.\textsuperscript{32-33} For these disadvantages to eliminate, microextraction techniques developed such as liquid phase micro extraction (LPME) and magnetic dispersive micro solid-phase extraction (M-D-μSPE), which offer the advantages of environmentally friendly, simple, fast, cheap, high preconcentration factor, high analyte recovery, minimal analyte loss and low volume toxic solvent use.\textsuperscript{2,34-36}

The usage of new adsorbent on SPME of trace metal ions is one of the attractive parts of analytical chemistry. The Activated carbon cloth (ACC) is one of them. It has some advantages: mechanical robustness and resistance, higher surface area, easy handling, modification and regeneration compared to the other activated carbon products.\textsuperscript{37-44} All these features make ACC an economical and highly efficient an adsorbent that can be used in solid phase extraction and dispersive micro solid-phase extraction methods. The synthesis and characterization of new nanocomposites containing ACC is one of the new working areas of our working group to improve adsorption properties of ACC. Fe-Ni@ACC nanocomposite is one of them, it was firstly synthesized and used for SPME of copper (II). The adsorption mechanism related with physical interaction between Fe-Ni@ACC nanocomposite and analyte ion.

In this study, Fe-Ni@ACC nanocomposite was synthesized and characterized and used as an adsorbent in the separation and enrichment of Cu (II) in various samples by SPME method. The analytical parameters (pH, adsorbent amount, eluent volume, sample volume, foreign ion effect, etc.) affecting the quantitative recoveries of copper were optimized.

**EXPERIMENTAL**

Characterization of Fe-Ni@ACC Nanocomposite. A nanocomposite of activated carbon cloth with Ni-Fe was prepared by a one-step hydrothermal method and this nanocomposite was used as a sorbent in the microextraction of trace levels of Cu (II). The activated carbon cloth and the obtained nanocomposite were characterized using SEM (Fig. 1), EDX (Fig. 2), SEM mapping (Fig. 3) and FT-IR (Fig. 4). When the SEM images with the same
Effect of pH. pH of the working solution is one of the most important variables controlling which the adsorption of metals to sorbent materials, hence the percentage recovery and SPME efficiency. The effect of pH on the SPME method was studied in the range of 2.0-11.0 using a model solution in which other parameters were kept constant. The results are presented in Fig. 5a. The quantitative recovery values between pH 8.0-10.0 were obtained. The recoveries were not quantitative in the neutral and acidic pH. All subsequent work was done at pH 9.0 using phosphate buffer solution.

Effect of Fe-Ni@ACC Amount. The amount of sorbent in SPME methods is another important parameter that affects the quantitative recovery values of the analyte elements. The effects of Fe-Ni@ACC amounts on the recoveries of copper(II) were investigated in the range of 1.0-20.0 mg. The results are depicted in Fig. 5b. It is seen that the quantitative recovery values were obtained as from 5.0 mg sorbent. In further works, 5.0 mg of Fe-Ni@ACC was used. The Fe-Ni@ACC adsorbent was stable to acids and bases and it was used at least 20 times without any loss of its adsorption properties.

Effect of Eluent Type and Concentration on recoveries of copper(II). The most suitable eluent to desorb metal ions on the surface of the adsorbent should be determined. The desorption occurs when the desorption power of the eluent is higher than the adsorption force that keeps Cu (II) ions on the sorbent. In the presented study, 1, 1.5, 2, 3 M HNO₃ and 1, 1.5, 2 M HCl were tested as eluent. The results are given in Fig. 5c. It was observed that a quantitative % recovery was obtained with 2 M and 3M HNO₃. So, 2 M HNO₃ was selected in further studies.

Effect of Eluent Volume. The effect of eluent volume on the recoveries of copper(II) was studied using 2 M HNO₃ in the range of 0.5-2.0 mL. The results are presented in Fig. 5d. The maximum and quantitative recovery of Cu (II) ion is at volumes of 0.75 mL and higher. Therefore, the optimum eluent volume was determined as 0.75 mL.

Effect of sample volume. The determining the maximum sample volumes is an important goal to achieve high preconcentration factor in the extraction processes of trace element analysis. The effect of sample volume on the method was investigated using model solutions in the range of 10.0-50.0 mL. The results given in

Table 1. SEM-EDX results of Fe-Ni@ACC nanocomposite

<table>
<thead>
<tr>
<th>Elements</th>
<th>Weight (%)</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.34</td>
<td>84.31</td>
</tr>
<tr>
<td>O</td>
<td>18.55</td>
<td>14.99</td>
</tr>
<tr>
<td>Fe</td>
<td>1.36</td>
<td>0.32</td>
</tr>
<tr>
<td>Ni</td>
<td>1.74</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Fig. 4 FT-IR spectrum of ACC and Fe-Ni@ACC nanocomposite.

The FT-IR spectrum of the 4000-5000 cm⁻¹ infrared spectral region of Fe-Ni@ACC is presented in Fig. 4. The peaks at ~2978 cm⁻¹ and ~2896 cm⁻¹ are due to the C-H stretchings in the (-CH₃) and (-CH₂) groups. The peak at ~2100 cm⁻¹ corresponds to the C=C bond stretching, and the peak at ~1043 cm⁻¹ corresponds to the C-O stretching vibration. In the FT-IR spectrum at fingerprint region, while the peak of the FeO bond is seen between 500-750 cm⁻¹, the peak of the NiO bond is seen between 500-550 cm⁻¹.

The FT-IR spectrum of the 4000-5000 cm⁻¹ infrared spectral region of Fe-Ni@ACC is presented in Fig. 4. The peaks at ~2978 cm⁻¹ and ~2896 cm⁻¹ are due to the C-H stretchings in the (-CH₃) and (-CH₂) groups. The peak at ~2100 cm⁻¹ corresponds to the C=C bond stretching, and the peak at ~1043 cm⁻¹ corresponds to the C-O stretching vibration. In the FT-IR spectrum at fingerprint region, while the peak of the FeO bond is seen between 500-750 cm⁻¹, the peak of the NiO bond is seen between 500-550 cm⁻¹.
The recovery of the analyte and the efficiency of the extraction ions in real samples are a problem that significantly affects the volume was 0.75 mL. The maximum sample volume was chosen as 30 mL and the preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL. The preconcentration factor was calculated as 40 when the final volume was 0.75 mL.

The effect of some foreign ions on the % recovery efficiency of Cu (II) ions (pH: 9, FeNi@ACC amount: 5 mg, eluent type: 2M HNO$_3$, eluent volume: 0.75 mL, N=3)

Table 2. The effect of foreign ions on the % recovery efficiency of Cu (II) ions (pH: 9, FeNi@ACC amount: 5 mg, eluent type: 2M HNO$_3$, eluent volume: 0.75 mL, N=3)

<table>
<thead>
<tr>
<th>Foreign Ions</th>
<th>Added as</th>
<th>Conc. (µg mL$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>CaCl$_2$</td>
<td>250</td>
<td>93 ± 2</td>
</tr>
<tr>
<td>F$^-</td>
<td>NaF</td>
<td>500</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>NaNO$_3$</td>
<td>250</td>
<td>92 ± 1</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>Mn(NO$_3$)$_2$·4H$_2$O</td>
<td>10</td>
<td>94 ± 2</td>
</tr>
<tr>
<td>Pt$^{4+}$</td>
<td>Pt(NO$_3$)$_4$</td>
<td>5</td>
<td>93 ± 1</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>10</td>
<td>97 ± 1</td>
</tr>
<tr>
<td>K$^+$</td>
<td>KCl</td>
<td>1500</td>
<td>95 ± 1</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>MgCl$_2$·6H$_2$O</td>
<td>100</td>
<td>95 ± 1</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>5</td>
<td>92 ± 1</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>NaSO$_4$</td>
<td>2000</td>
<td>96 ± 2</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>Na$_2$CO$_3$</td>
<td>2500</td>
<td>95 ± 3</td>
</tr>
</tbody>
</table>

Table 3. Analysis of water certified reference materials (CRMs) with the developed M-D$_3$SPE method (pH: 9, FeNi@ACC amount: 5 mg, eluent type: 2M HNO$_3$, eluent volume: 0.75 mL, N=3)

<table>
<thead>
<tr>
<th>Water CRMs</th>
<th>Certification value (µg L$^{-1}$)</th>
<th>Found value (µg L$^{-1}$)</th>
<th>Relative Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMDA-53.3</td>
<td>308</td>
<td>312 ± 12</td>
<td>1.3</td>
</tr>
<tr>
<td>TMDA-64.2</td>
<td>274</td>
<td>273± 8</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Fig. 5e shows that up to 30 mL of quantitative % recovery was achieved. The maximum sample volume was chosen as 30 mL and the preconcentration factor was calculated as 40 when the final volume was 0.75 mL.

Matrix effects. The levels of foreign ions accompanying analyte ions in real samples are a problem that significantly affects the % recovery of the analyte and the efficiency of the extraction procedure. In Table 2, the effects of some foreign ions on the method at the specified concentrations are examined. The obtained quantitative % recovery values show that foreign ions do not affect the developed method at the specified concentrations.

Analytical performance of the method. Analytical data, which are indicators of analytical performance, were obtained under optimum experimental conditions and 10 parallel blank samples were prepared and the developed method was applied to determine the limit of detection (LOD) and limit of quantification (LOQ). Recovery for copper up to sample volume of 30 mL is quantitative and since the final volume was 0.75 mL, the preconcentration factor was calculated as 40. The limit of detection (LOD) of the method was calculated as 0.69 µg L$^{-1}$ at 3s/m, and the limit of quantification (LOQ) was calculated as 2.29 µg L$^{-1}$ at 10s/m. The 40-fold enrichment factor was taken into account in the calculations. Relative standard deviation (%RSD) was calculated as 1.18% from the formula 100$(s / x)$ (N=10). The calibration curve obtained for the method, $y = 0.0772x + 0.0009$ (y=concentration, x=absorbance) and R$^2$ is 0.9997. The obtained % recovery values in real sample applications of the method are in the range of 94-103 (s: standard deviation of the blank signals (N=10), m: slope of the calibration curve).

To evaluate the accuracy of the developed SPME method, the method was applied to Environment Canada TMDA-64.2 Fortified water and Environment Canada TMDA-53.3 Fortified Water certified reference materials and the results are presented in Table 3. When the obtained results are compared with the Cu (II)
concentration in the certified reference material, it is seen that both are compatible.

**Real samples analysis.** Addition and recovery studies were carried out on tap water, cigarette, human hairs and black teas samples for to investigate the applicability of the developed SPME method. A known amount of analyte was added to these samples and the developed method was applied. The results are presented in Table S1 and Table S2. As can be seen from the tables, recoveries ranging from 94-103% were obtained, which is an acceptable range for trace analysis.

**Comparison with other methods.** This developed method was compared with other studies in the literature in which AAS/FAAS was used in terms of preconcentration factor, detection limit, relative standard deviation values and other data, and the data are presented in Table S3. It has been seen that the data in the Table and the obtained data are comparable. 2,6,38,60-65

**CONCLUSION**

A new method magnetic dispersive micro solid-phase extraction has been developed which includes a combination of M-D-μSPE and FAAS for the separation, preconcentration and determination of trace level Cu (II) founds in various black tea, cigarette, human hair and water samples. The analytical parameters effective on the method have been optimized and the results are presented above. In order to test the accuracy of the developed method, both addition-recovery studies and certified reference material analyzes were carried out. The main advantages of the method can be listed as follows: offers low LOD and LOQ, High reproducibility and microextraction efficiency, the accuracy of the method has been demonstrated by the application to certified reference materials. The used amount of adsorbent and the volume of eluent are at a minimum level, can be analyzed by micro-injection, Completion of all steps of the method in a short time and easily, it can be applied to samples with different matrix (Black tea, water, cigarette and hair). An effective enrichment can be made with milligram-level adsorbent and this adsorbent can be used at least 20 times, etc.

**AUTHOR INFORMATION**

Prof. Mustafa Soylak is working on Environmental Analytical Chemistry, Nanotechnology, Nanomaterials, Nanocomposites, Separation/Preconcentration Techniques including Solid Phase Extraction, Coprecipitation, Cloud point extraction, membrane filtration, speciation and microextraction of trace organic and inorganic species. Dr. Soylak has an h-index of 111 (Web of science). He has over 725 papers in Web of Science, 8 book chapters and reviews, two textbooks (in Turkish), one textbook on microextraction techniques (Elsevier, 2020). He is Editor-in-Chief of Comprehensive Sampling and Sample Preparation (Elsevier, 2022). He was visiting professor at King Saud University- Saudi Arabia on 2010-2016 and at Near East University-Cyprus on 2018-2019. He is now Professor at Erciyes University, Department of Chemistry, Kayseri-Turkey. He is the editorial board member of *Atomic Spectroscopy*, *Journal of Hazardous Materials*, *International Journal of Environmental Analytical Chemistry*, *Arabian Journal of Chemistry*, *Turkish Journal of Chemistry* and *Journal of Nanostructure in Chemistry*. He has TÜBİTAK (Turkish Scientific and Technological Research Council) Encouragement Award in 2001. He is the recipient of the highest prestigious science award in Turkey, TÜBİTAK Science Award in 2020. He has also İlim Yayma Award from İlim Yayma Foundation in 2021. He has been a principal member of the Turkish Academy of Sciences (TÜBA) since 2020. He has obtained a TÜBİTAK 2247-A National Fellowship for Outstanding Researchers (2021).

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**REFERENCES**


**ASSOCIATED CONTENT**

The supporting information (Tables S1–S3) is available at www.at-spectrosc.com/as/home.


A Step-by-step Classification Method of Coal and Miscellaneous Materials by Laser-induced Breakdown Spectroscopy

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ABSTRACT: The miscellaneous materials, including gangue, plastic, and wood commonly present in coal. These miscellaneous materials affect the reliability of coal analysis using laser-induced breakdown spectroscopy in power plants, but have significantly distinct spectral characteristics from coal. Hence, this paper proposes a step-by-step classification method to screening the false spectra of miscellaneous materials. The first step aims to identify the plastic and wood spectra by determining the existence of specific characteristic spectral lines using the standard deviation (SD) values. The spectral lines Si I 288.16 nm with the SD value of more than 850 counts and Li I 670.78 nm with SD value of more than 1750 counts were used as the distinguishing markers. The classification accuracy of first step was 100%. Due to the high similarity between gangue and coal, the second step utilized the random forest (RF) classification model to identify the gangue spectra. The number of trees and random variables in the RF model was optimized. The accuracy of classification model without and with the proposed step-by-step method was 98.30 and 99.96%, respectively. To assess the necessity of spectra classification, a set of calorific value analysis was performed by adding false spectra of different proportions, which were compared with analysis after removing the false spectra. The root mean square error of prediction (RMSEP) was 0.42 MJ kg⁻¹ (after removing), compared with 0.50 MJ kg⁻¹ (mixing with 10% gangue spectra), 0.56 MJ kg⁻¹ (mixing with 20% gangue spectra) and 0.57 MJ kg⁻¹ (mixing with 30% gangue spectra). The results demonstrated that the proposed step-by-step classification method could effectively identify the spectra of coal and miscellaneous materials and improve the accuracy of coal analysis.

INTRODUCTION

Recently, China has set the goal of reaching carbon peaking and carbon neutrality, making the transition to a new energy structure imperative. In this context, the flexibility of thermal power generation and its ability to regulate peak shaving will become more prominent. The ultimate and proximate analysis of coal is crucial to support the data needs of power plants in optimizing combustion. Knowing the coal property prior to utilization is helpful for flexible peak shaving. Commercial analytical devices based on prompt gamma neutron activation analysis (PGNAA) and X-ray fluorescence (XRF) technology already exist. However, PGNAA requires bulky equipment and must be operated under strict safety regulations. XRF cannot measure low atomic number elements which are essential measurements. Laser-induced breakdown spectroscopy (LIBS) is a type of frontier atomic emission spectroscopy that has been extensively applied in the ultimate and proximate analysis of coal. LIBS has advantages of quick, simultaneous multi-element, and online detection. Measurement equipment based on LIBS can be installed on the coal conveyor belt to provide fast measurement and timely data, supporting the need for flexible peak shaving of power plants.
However, LIBS spectra are highly sensitive to the analyzed sample, and the spectra of different samples can vary significantly. During coal mining, transportation, and storage, various miscellaneous materials, such as gangue, plastic, and wood can mix with the coal, which can affect the accuracy of coal analysis using LIBS. It is essential to screen the miscellaneous materials on the conveyor belts in the power plants. Visual recognition combined with machine learning has been successfully used to classify coal and miscellaneous materials, with effective outcomes reported in previous studies.\textsuperscript{10-13} However, this method requires the introduction of various devices, which can adversely affect the convenience and efficiency of LIBS for coal analysis in power plants.

LIBS combining various classification methods has also been applied to screen the substances.\textsuperscript{14} Especially the machine learning algorithms show better performance for samples with similar compositions, such as coal and gangue. Lin \textit{et al.}\textsuperscript{15} tested four classification models, including Naïve Bayes, K-nearest neighbor (KNN), decision tree (DT), and random forest (RF) combined with LIBS to differentiate metal additive manufacturing (AM) parts, and results showed that the RF model performed best. Sheng \textit{et al.}\textsuperscript{16} compared the performance of support vector machines (SVM) and RF in classifying iron ores and concluded that RF exhibited a better level of classification prediction. Janovszky \textit{et al.}\textsuperscript{17} tested three statistical methods, including classification tree (CT), linear discriminant analysis (LDA), and RF, for classifying mineral particles and found that the accuracy of both RF and LDA was better than 92%. Rzecki \textit{et al.}\textsuperscript{18} used seven classifiers, including DT, RF, KNN, SVM, probabilistic neural network (PNN), multilayer perceptron (MLP), and generalized regression neural network (GRNN), to classify paper and ink samples. The results showed that the RF classifier had the highest recognition accuracy. The above studies suggest that LIBS combined with RF is a highly effective classification method. Additionally, our group developed a method to check whether the characteristic spectral lines were reliably present that used its standard deviation (SD) values. Bai \textit{et al.}\textsuperscript{19} chose Si 288.16 nm as the analysis line and used its SD value to identify invalid breakdown spectra from all the particle stream spectra. Similarly, Yao \textit{et al.}\textsuperscript{20} calculated the SD value of C 247.86 nm to judge whether the coal is effectively excited. This method can be effectively applied as a basis for classification when the elemental composition of different samples differs significantly.

In summary, the presence of false spectra generated by miscellaneous materials can affect the accuracy of coal analysis using LIBS. It is necessary to screen the false spectra, which has not yet been investigated. This work proposes a step-by-step classification method based on the characteristic spectral lines and the RF model for coal and false spectra. The SD values of specific spectral lines were used to screen the spectra of plastic and wood. Then, the RF model was adopted to screen the spectra of gangue. To assess the efficacy and necessity of this classification method, a set of calorific value analysis was performed by retaining false spectra of different proportions.

**METHODS**

**Step-by-step classification method.** Fig. 1 compares typical
LIBS spectra of coal, gangue, plastic, and wood samples obtained by averaging 300 spectra collected from each sample. The figure highlights seven characteristic spectral lines of major elements that may be used to distinguish the spectra. The elemental composition of plastic and wood differs significantly from that of coal, making their spectra, especially for some characteristic spectral lines, entirely different. Therefore, the presence of several specific spectral lines can be used to screen the plastic and wood spectra. In contrast, the element composition in coal and gangue is highly similar. The differences in elemental content are reflected in the intensity of spectral lines, such as the 350–450 nm band in Fig. 1. However, the fluctuation of the LIBS spectrum makes the spectral intensity highly uncertain, and it is difficult to classify the coal and gangue spectra by comparing the SD values of specific spectral lines.

Therefore, a step-by-step classification method for coal and miscellaneous materials is proposed, which includes three steps. First, the classification model based on the characteristic spectral lines is applied to screen the plastic and wood spectra. Second, the spectra of coal and gangue are preprocessed by reducing the data dimensionality. Finally, the random forest model is used to identify the spectra of coal and gangue. Fig. 2 illustrates the scheme, and the following sections will discuss the basic principles and descriptions of these three steps in detail.

**Characteristic spectral lines classification model.** In this study, plastic and wood sample spectra were screened by checking the existence of specific spectral lines using their SD values. SD can be calculated as:

$$SD = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (X_i - \bar{X})^2}$$  \hspace{2cm} (1)

where $SD$ is the standard deviation of the spectral line intensity, $X_i$ is the intensity of the $i$th pixel in the peak of spectral line, $\bar{X}$ is the average intensity of all the pixels in the peak of spectral line, and $N$ is the pixel number in the peak of spectral line. The value of $N$ is set to 5 in this work.

After screening, all spectra would be classified into two kinds: coal and gangue, and plastic and wood. The selection of the analyzed spectral lines was based on the principle that their intensity and corresponding the content of elements were significantly different in two kinds of samples. Two ways were used to choose the analyzed spectral line: selecting the main elements of each sample or selecting trace elements with significant differences in the samples. While the main elements for all samples were evident, including C for coal, Al and Ca for gangue, C for plastic, and O for wood. They were also found in other samples, often in substantial amounts. As shown in Fig. 1, the high intensities of characteristic spectral line of these primary elements were common in all spectra with minor differences, rendering them unsuitable for the analyzed spectral lines. Thus, trace elements that only existed in coal and gangue, such as Si and Li, were selected for analysis.

As shown in Fig. 3, the characteristic spectral lines of Si I 288.16 nm and Li I 670.78 nm were significantly different between the spectra of the two kinds of samples, and they would be used as analyzed spectral lines for the classification model. The SD values of these spectral lines were calculated one by one and used to identify plastic and wood spectra. The minimum SD values of coal and gangue were larger than the maximum SD values of plastic and wood. Thus, the SD thresholds of these spectral lines were determined and used to completely distinguish the plastic and wood from coal and gangue. The SD thresholds of the intensities of Si I 288.16 nm and Li I 670.78 nm are 850 and 1750 counts, respectively. Fitted lines with SD values set as the thresholds were included in Fig. 3 to demonstrate how the classification model works. As mentioned before, the peak of spectral line consisted of five pixels in this work. It was assumed that the spectral intensities of the first- and fifth-pixel points were equal to the intensities of wood spectra’s corresponding points. The shape of the characteristic peaks was composed of two axisymmetric diagonal lines, and the SD values of the characteristic peaks were used as thresholds to draw the fitted lines. The specific spectral lines in coal and gangue spectra were more prominent and distinct than the fitted line, resulting in their SD values being greater than the thresholds. Conversely, the plastic and wood spectra exhibited opposite results.

**Data dimensionality reduction.** The high-dimensional nature of LIBS spectra results in a large amount of redundant information, which translates to a long computation time when input into the model. To address this issue, feature selection and principal component analysis (PCA) were used to reduce the dimensionality of LIBS spectra and extract valid information when establishing the RF model for coal and gangue classification. Since coal and gangue constituent elements are remarkably similar, this work concentrated on several elements with notable differences in
Random forest classification model. Random forest is an integrated learning method composed of a series of classifiers, or ‘trees’, which work together to make decisions and achieve an optimal result. Randomness is observed in the selection of each tree’s training set using the Bagging method, and a certain number of features are randomly chosen from the attributes. The random forest model is popular in LIBS spectrum classification modeling due to its ability to prevent overfitting, resistance to noise, and capacity for parallel processing.\cite{16}

In this study, the RF model was applied to classify the spectra of coal and gangue after data preprocessing, with 5100 spectra in the calibration set and 2100 spectra in the validation set. The number of trees and random variables were optimized to maximize the classification accuracy.

The classification model performance was assessed by the accuracy, which can be defined as follows:

\[
\text{accuracy} = \frac{N_c}{N_t}
\]

where \(N_c\) and \(N_t\) are the number of correct classified spectra and the total number of spectra in the validation set, respectively.

### EXPERIMENTAL

Samples. To simulate the proportion of raw coal blended with miscellaneous materials in the power plant, 27 samples were collected from the power plant site. Following the procedure of ASTM standard methods,\cite{23} the collected coal and miscellaneous materials were ground into powders at 0.2 mm particle size and dried at 45 °C for 4 h to minimize the influence of moisture on the spectral measurements. Then the powder of 3 g was compressed into compact and flat pellets with a diameter of 24 mm using a tablet machine (Pike Technologies Crushir) to reduce the impacts of physical matrix effects. In particular, 19 coal samples were numbered C1 to C19, 5 gangue samples were numbered G1 to G5, 2 plastic samples were numbered N1 and N2, and 1 wood sample were numbered N3. 14 coal samples, 3 gangue samples, and 1 plastic sample were randomly selected to form the calibration set, while the remaining 5 coal samples, 2 gangue samples, 1 plastic sample, and 1 wood sample formed the validation set. \(\text{Table 2}\) provides calorific values ranging from 18.23 to 25.92 MJ kg\(^{-1}\) of 19 coal samples on air dried basis, which were analyzed by the ASTM standard method.\cite{23} The chemical composition of gangue is similar to that of coal, with a slightly lower carbon content and a significantly higher concentration of metallic elements than coal.\cite{24,25} In contrast, plastics and wood differ significantly from coal in elemental composition. The collected plastic samples are mostly made of polypropylene (PP) and polyethylene (PE), which mainly composed of C and Al.\cite{26} The wood primarily contains O, Ca, K, P, and S.\cite{27}

LIBS experimental setup. The LIBS experimental system’s description has been provided in detail in the literature.\cite{28} The ablation source was a Q-switched Nd:YAG laser (Quantel Brilliant Easy, USA) emitting at 1064 nm with the pulse duration of 5 ns. The repetition frequency was set to 2 Hz and the laser energy was adjusted to 55 mJ/pulse to obtain a better spectrum. A lens with a focal length of 150 mm was employed to concentrate the laser onto the sample surface to produce a plasma. Then the four-channel spectrometer (Avantes, Netherlands), which had a nominal resolution of 0.08-0.10 nm and spanned the wavelength range of 178 to 827 nm, received the plasma emission by an optical fiber. The integration time was set to 1.05 ms and the delay time was adjusted to 1 μs. To simulate the collection condition of LIBS performing on the coal conveyor belt, the samples were placed on a motorized translation table. The table was controlled to move the samples in the XY plane at a speed of 3 mm/s. 1 spectrum was taken at each of the 300 locations on the sample surface for each sample.

### RESULTS AND DISCUSSION

Characteristic spectral lines classification model. Fig. 4 displays a scatter plot of all samples’ SD values of line intensity of C, Ca, Al, and O. These four elements were chosen by using the strategy of selecting the main elements of each sample. Fig. 4(a) shows that the SD value distribution of C and Ca spectral lines was similar for all spectra, making it difficult to classify the

### Table 1. Selected feature for the RF model

<table>
<thead>
<tr>
<th>Selected Feature</th>
<th>Wavelength/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C I</td>
<td>247.86</td>
</tr>
<tr>
<td>Si I</td>
<td>251.61 and 288.16</td>
</tr>
<tr>
<td>Fe I</td>
<td>275.61 and 373.49</td>
</tr>
<tr>
<td>Al I</td>
<td>308.22, 309.28, 394.40 and 396.15</td>
</tr>
<tr>
<td>O I</td>
<td>777.19</td>
</tr>
</tbody>
</table>
Table 2. Calorific value of samples in this study

<table>
<thead>
<tr>
<th>Calibration set</th>
<th>Validation set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Calorific value (ad)/MJ kg⁻¹</td>
</tr>
<tr>
<td>C1</td>
<td>21.66</td>
</tr>
<tr>
<td>C2</td>
<td>23.72</td>
</tr>
<tr>
<td>C3</td>
<td>25.03</td>
</tr>
<tr>
<td>C4</td>
<td>23.18</td>
</tr>
<tr>
<td>C5</td>
<td>24.57</td>
</tr>
<tr>
<td>C6</td>
<td>25.92</td>
</tr>
<tr>
<td>C7</td>
<td>25.60</td>
</tr>
<tr>
<td>C8</td>
<td>23.97</td>
</tr>
<tr>
<td>C9</td>
<td>24.39</td>
</tr>
</tbody>
</table>

Figure 5 The scatter plot of the SD values of Si I 288.16 nm and Li I 670.78 nm, and their thresholds have been marked with red lines.

Table 3. Comparison of the classification accuracy using different characteristic spectral lines

<table>
<thead>
<tr>
<th>Characteristic spectral lines</th>
<th>Accuracy/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si I 288.16 nm</td>
<td>82.04</td>
</tr>
<tr>
<td>Li I 670.78 nm</td>
<td>99.70</td>
</tr>
<tr>
<td>Si I 288.16 nm and Li I 670.78 nm</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 4. Comparison of the RF classification accuracy before and after data dimensionality reducing

<table>
<thead>
<tr>
<th>Preprocessing methods</th>
<th>Coal spectra/%</th>
<th>Gangue spectra/%</th>
<th>All spectra/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw spectra</td>
<td>99.87</td>
<td>94.17</td>
<td>98.24</td>
</tr>
<tr>
<td>Feature selection and PCA</td>
<td>99.87</td>
<td>99.67</td>
<td>99.81</td>
</tr>
</tbody>
</table>

spectra by setting a threshold. Fig. 4(b) indicates that the SD values of the O and Al spectral lines were mixed together to some extent. Relying solely on these two spectral lines made it difficult to completely distinguish two kinds of samples.

Figure 5 is a scatter plot of the SD values of Si I 288.16 nm and Li I 670.78 nm. It shows that the plastic and wood were distinguished from coal and gangue spectra. Orange points represents the plastic and wood spectra that are close to the origin of the axis, while grey points indicates that coal and gangue are farther from it. Obviously, the SD values of these spectral lines are an effective way to separate spectra of different samples. As previously mentioned, the SD values of two characteristic spectral lines, Si I 288.16 nm and Li I 670.78 nm, were used as the basis for classification in this model. Table 3 compares the accuracy of the classification model using these criteria separately and in combination. The accuracy of classification model using the spectral line of Si I 288.16 nm and Li I 670.78 nm was 96.26% and 99.70%, respectively. However, the accuracy of the model using the combination of the spectral lines of Si I 288.16 nm and Li I 670.78 nm reached 100%, with all plastic and wood spectra being screened out.

Random forest classification model. After successfully eliminating all plastic and wood spectra, an RF classification model was built to classify coal and gangue using the remaining 4200 spectra of coal and 900 spectra of gangue in the calibration set as input. The model's performance was checked by inputting the remaining 1500 coal and 600 gangue spectra from the validation set. In addition, data preprocessing methods of feature selection combined with PCA were applied to reduce the dimensionality of the raw spectral data and extract the valid information. Table 4 compares the classification accuracy of RF models without and with data dimensionality reduction. The number of trees (ntree) and random variables (mtry) used in the RF model were empirically set to 200 and 3, respectively. The results demonstrated that the raw spectra combined with the RF model already provided a high classification level. However, the model calculation was time-consuming and unsuitable for LIBS's fast and online measurements. It was necessary to reduce the raw data dimensionality. The feature selection combined with PCA was an effective method, obtaining a classification accuracy of 99.81%. Therefore, in the subsequent RF model optimization, the feature selection combined with PCA was applied throughout the process.

To further optimize the model, the classification accuracy of the RF model was contrasted as a function of ntree at different levels of mtry, as shown in Fig. 6(a). The model achieved the highest
Fig. 6 Relationship of (a) step-by-step and (b) non-step-by-step classification accuracy with $n_{tree}$ and $m_{try}$.

Fig. 7 The results of the calorific value analysis using 4 inputs: (a) experimental group, (b) control group A, (c) control group B, (d) control group C.

accuracy of 99.95% when $m_{try}$ was set to 2 and $n_{tree}$ was set to 380, 480, and 500, with only one spectrum in the validation set being incorrectly classified. The ideal value of $n_{tree}$ was 380 to accelerate the model calculation. Combining the characteristic spectral lines and RF classification model, the step-by-step classification method achieved an accuracy of 99.96%.

Figure 6(b) illustrates the classification results without employing the step-by-step classification method. Here, all preprocessed spectra of miscellaneous materials and coal were
used as input to construct the classification model. The validation set contained 9 samples with 2700 spectra. The classification accuracy was 98.30% with 46 spectra misclassified. This may be due to the large spectral differences and the preprocessing methods reducing the information contained in the spectra. In comparison, the model without employing the step-by-step classification method was slower to calculate and had a lower accuracy. These results demonstrated that the proposed step-by-step classification method was effective.

**Calorific value quantitative analysis.** To assess the necessity of spectral classification in coal analysis, a comparative experiment was performed for calorific value analysis. This was done by adding false spectra generated by gangue with varying proportions and comparing them with classified spectra. The raw coal production process typically yields 15% to 30% associated gangue production. Based on the degree of spectral interference, three control groups were formed. Control group A had 300 spectra of each sample with a random substitution of 10% gangue spectra for coal spectra, resulting in the ratio of coal and gangue spectra was 9:1. The ratios of coal and gangue spectra in control groups B and C were 8:2 and 7:3, respectively. The blended gangue spectra were randomly selected from all spectra of gangue samples. The blending ratio of each gangue sample was the same, and all spectra did not repeat each other. The spectra of plastic and wood were effectively excluded, so their effect was not considered here.

In the practical application of LIBS to coal analysis in power plants, the quantitative model for calorific value is typically built from laboratory data. Then the data collected in the field is fed into the model to predict the calorific value. In this work, the LIBS data from coal samples of the calibration set was used as the independent variable to build the quantitative analysis model, and the dependent variable was the calorific value. Because of the complicated and intimate relationship between calorific value and the content of various elements in coal, the full LIBS spectra were utilized for quantitative analysis. A quantitative analysis model for calorific value was built based on partial least square (PLS) to minimize the spectral dimensionality. When predicting elemental content in LIBS, PLS is a regression analysis method that contains correlation analysis and was frequently used in LIBS predicting elemental content. Three averaged spectra were input for each sample while modeling the spectra of the calibration set coals to reduce the influence of data fluctuations on the calorific value prediction. For the quantitative model of control groups, the spectra of each coal sample and the blended gangue spectra were first divided into three equally. Then the spectra were averaged, which means the blending ratio of the gangue spectra of 3 averaged spectra was the same.

The performance of quantitative analysis model of the calorific value was assessed by the determination coefficient ($R^2$), the root mean square error of prediction (RMSEP), the average absolute error (AAE), and the average relative error (ARE), which has been introduced detailed in literature.15

Figure 7(a)-(d) compares the prediction results of calorific value using spectral data from the experimental group, control group A, control group B, and control group C, respectively. As can be seen, the $R^2$ remained unchanged at 0.99, the RMSEP increased from 0.42 MJ kg$^{-1}$ (after removing) to 0.50 MJ kg$^{-1}$ (mixing with 10% gangue spectra), 0.56 MJ kg$^{-1}$ (mixing with 20% gangue spectra), and 0.57 MJ kg$^{-1}$ (mixing with 30% gangue spectra), the AAE increased from 0.42 MJ kg$^{-1}$ (after removing) to 0.50 MJ kg$^{-1}$ (mixing with 10% gangue spectra), 0.54 MJ kg$^{-1}$ (mixing with 20% gangue spectra), and 0.54 MJ kg$^{-1}$ (mixing with 30% gangue spectra), and the ARE increased from 1.80% (classified spectra) to 2.14% (mixing with 10% gangue spectra), 2.35% (mixing with 20% gangue spectra), and 2.35% (mixing with 30% gangue spectra).

Since the model was built from the same calibration set, $R^2$ remained unchanged at 0.99. However, the value of RMSEP , AAE, and ARE increased with the proportion of doping in the gangue spectra. This is because the LIBS spectra of both coal and gangue contains emission lines such as C, H, and O and the mineral elements Si, Al, and Ca, but the content of which differs significantly. The maceral and mineral makeup of the coal affects the calorific value as a coal-rank metric. In actuality, the calorific value drops as the mineral matter rises due to the endothermic breakdown processes and the heat capacities of such minerals during burning. Still, it increases as the carbon content does. Therefore, the kinds of samples profoundly affected LIBS spectra and the calorific value prediction. The results demonstrated that the proposed step-by-step classification method was effective in eliminating the interference of the miscellaneous materials spectra and improving the accuracy of calorific value prediction.

Furthermore, the conventional method of coal analysis utilized in power plants requires sampling from the conveyor belt, sample preparation, and analysis employing a calorimeter in the laboratory. In contrast, the step-by-step classification method proposed in this study requires less than 5 s to classify the entire spectra. When integrated with the LIBS measurement device installed on the coal conveyor belt, the entire process from spectrum acquisition and screening to coal analysis can be completed within an average of 1 minute. Therefore, the proposed classification method in conjunction with LIBS measurement resolves the issues of time-intensive analysis and poor sample representativeness associated with conventional methods to satisfy the substantial demand for flexible peak-shaving in power plants.

**CONCLUSION**

A step-by-step classification method to effectively screen the miscellaneous materials spectra was proposed to improve power...
plants' coal analysis on the conveyor belt. The spectra of plastic and wood were screened using the SD values of specific characteristic spectral lines, and the classification accuracy reached 100%. Subsequently, after reducing the data dimensionality using feature selection combined with PCA, an RF classification model was used to classify the gangue and coal spectra. The accuracy was 99.95%, with only one gangue spectrum misclassified by optimizing the number of trees and random variables. Finally, PLS was employed as the calibration model to compare the predicted performance of calorific value using the spectra without and with classification as input. Compared to spectra mixed with coal and gangue, the classified spectra resulted in optimal RMSEP, AAE, and ARE values, which were 0.42 MJ kg⁻¹, 0.42 MJ kg⁻¹, and 1.8%, respectively. The results confirmed the need to identify coal and miscellaneous materials' spectra and provided an experimental basis for practical application. The proposed step-by-step spectral classification method can further improve the accuracy of coal analysis and support the flexible peak-shaving in power plants.

**AUTHOR INFORMATION**

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


X-ray Fluorescence Analysis of Snow Cover Solid Phase for Investigation of Emissions by Aluminum Industry and Combined Heat and Power Complex

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ABSTRACT: X-ray fluorescence method was proposed for a determination of major elements in samples of snow cover solid phase collected in the urban areas of the Irkutsk region near aluminum smelter and combined heat and power plant. The limitation of the analyzed sample mass, which in some cases does not exceed 50 mg, as well as the features of the elemental composition (high Al and low Si contents) require a special methodological approach to quantitative elemental analysis. Due to the lack of matrix-matched certified reference materials, the calibration set includes certified reference materials of igneous and sedimentary rocks as well as aluminum ore samples. Results of X-ray fluorescence method were compared with the results obtained by reference methods including atomic absorption, atomic emission and spectrophotometry methods. It showed that it is necessary to use samples of snow cover solid phase analyzed by reference methods as a calibration set for X-ray fluorescence analysis, which ensures the quantitative determination of major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe). These elements are important for environmental pollution investigation. Al was discovered as a main pollutant produced by aluminum smelter, Si, Ca, Ti, Mn, and Fe - by combined heat and power plant.

INTRODUCTION

The aluminum industry has significant environmental and health impact. Aluminum is a neurotoxic substance that has been found in high levels in the brain tissues of Alzheimer’s disease, epilepsy, and autism patients, as well as premature infants and ones with renal failure, who are at the risk of developing the central nervous system and bone toxicity.1 Besides alumina, air pollutions from aluminum smelters includes coke dust, particulate and gaseous fluorides, and sodium dioxide, as well as organic compounds.2–5 Aluminum production facilities are often supplied by combined heat and power (CHP) plants which emit nitrogen dioxide, organic compounds, sulphur dioxide, as well as inorganic dust with toxic elements.5 Air pollution control, identification of pollution areas and sources of potentially toxic elements, minimization of negative impacts on the environment and living organisms in the areas influenced by aluminum production and CHP facilities are current environmental problems. Fast and accurate methods for recognizing the effects of industrial emissions are required.

Snow cover is an important source of data for environmental pollution studies due to its accumulation of atmospheric dust particles.7–21 During a snowfall, snow captures gaseous substances and solid particles suspended in the atmospheric air. When the snowfall stops, snow cover collects dry precipitation of particles and dust from the atmosphere. The study of the mineral and elemental composition of snow cover solid phase is important for a better understanding of the migration routes of pollutants and determining their impact on biological objects, including humans.

For analytical chemist, an analysis of snow cover solid phase is
not a simple task. Since the sample mass is limited and often does not exceed 50 mg, it is necessary to apply methods which do not require a large sample mass of the analyzed material, for example, inductively coupled plasma mass-spectrometry,\textsuperscript{10,17,19,22} opto-emission spectrometry,\textsuperscript{15,23} atomic emission analysis,\textsuperscript{15,16,19} or atomic absorption analysis.\textsuperscript{9,24} The X-ray fluorescence (XRF) method is widely used for the determination of elemental composition of various objects\textsuperscript{25,26} for different studies, including environmental investigation.\textsuperscript{27-34} However, despite the relatively low cost and high productivity, XRF method has not been applied for snow cover solid phase analysis. The experience of using X-ray methods in the analysis of this object is often limited to the study of individual particles by the electron probe microanalysis.\textsuperscript{20,35-41} Common XRF techniques usually require a relatively large sample mass (from 500 mg), however a quantitative analysis of small sample mass is also possible.\textsuperscript{42,43}

One of the problems in the study of snow cover solid phase is a specific phase composition of investigated samples. Wet chemistry methods based on the acid digestion procedure are almost free of influence of sample matrix, however the modern methods (including XRF) usually require matrix matched certified reference materials (CRMs) for quantitative analysis. There are no CRMs of snow cover solid phase, therefore specific techniques for the sample preparation are required. In contrast to the time-consuming acid leaching procedure, the fusion method can be used for XRF analysis to minimize the influence of the difference in phase composition between the analyzed and calibration samples.\textsuperscript{44,45} Due to the development of facilities for a sample preparation to the XRF analysis it is possible to reduce the analyzed sample mass.\textsuperscript{46-50} The limitations of the fusion sample preparation technique are: determination of volatile elements (S, F), which may be partially or completely lost during fusion process; determination of element content less than 0.1 wt. % due to the high degree of dilution with flux that significantly reduces the sensitivity of technique.

Other issues are specific elemental composition of investigated samples and, consequently, necessity for matrix effects correction. Two main approaches for the matrix effects correction in the XRF analysis are (1): the fundamental parameters (FP) model based on the physical model of X-ray radiation interaction with a sample and (2) the empirical influence coefficients (EIC) based on regression equations.\textsuperscript{51-53} Application of FP requires knowledge of the bulk chemical composition of sample, while the construction of reliable empirical regression equations requires a large number of matrix-matched calibration samples. Due to the differences in contents and ratios of analytes in snow cover solid phase samples and the lack of matrix-matched CRMs, the selection of matrix effects correction method is also the important task.

This study presents the application of the XRF method with a fusion sample preparation procedure for the quantitative determination of major elements in snow cover solid phase sample with a limited mass. The purpose of this work is to assess environmental pollution of areas influenced by the aluminum production facilities and CHP plants emissions. This study also includes the selection of calibration samples and matrix effects correction approach in the conditions of the lack of matrix-matched CRMs and specific phase and elemental composition of industrial emissions.

**EXPERIMENTAL**

**Instrumentation.** Major components of emissions from the aluminum industry (Na, Al) and the CHP plants (Mg, K, Si, Ti, Ca) were considered as the elements of interest. Investigation was carried out using the equipment of the Center of isotopic and geochemical Research (Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russian Federation).\textsuperscript{54} The measurements were performed using an S4 Pioneer wavelength-dispersive X-ray fluorescence spectrometer (Bruker AXS, Germany) equipped with Rh-anode X-ray tube and Soller optical scheme. Table 1 shows the conditions for measuring analytical lines: X-ray tube voltage and current, crystal monochromator (lithium fluoride LiF, pentaerythritol PET, synthetic multilayer crystal OVO-55), collimator and detector (SD – scintillation detector, GFPD – gas-flow proportional detector). The instrumental uncertainty is less than 0.3% rel. The measurement time for one sample was about 15 min.

Matrix effects correction was carried out using two methods, described in the Introduction section. The correction by FP method (“variable alphas” option of the spectrometer software) was applied using the following equation:

\[
C_i^* = C_i \cdot (1 + \sum_j \alpha_{ij} \cdot C_j)
\]

(1)

where \(C_i^*\) – corrected content of analyte, \(C_i\) – content of the matrix element; \(\alpha_{ij}\) - matrix correction coefficients.

The EIC method was applied using the following equation:

\[
C_i^* = C_i \cdot (1 + \sum_j \alpha_{ij} \cdot I_j)
\]

(2)

where \(I_j\) – intensity of the influencing element.

<table>
<thead>
<tr>
<th>Table 1. Instrumental operating conditions for analytical lines</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analytical line</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Na, Mg, K</td>
</tr>
<tr>
<td>Al, Si, K, P</td>
</tr>
<tr>
<td>K, Ca, Co, Ti, Ca</td>
</tr>
<tr>
<td>Fe, Mn, Cu</td>
</tr>
</tbody>
</table>

Notes: SD – scintillation detector, GFPD – gas-flow proportional detector.
Cluster analysis (CA) and principal component analysis (PCA) has been applied using Statistica 12 software. Maps were prepared in the QGIS 3.16 software. Spatial data processing algorithms of the SAGA GIS 7 integrated into QGIS software were used to build the spatial distribution of elements.

**Materials and sample preparation.** Samples of the snow cover solid phase were collected from Irkutsk region urbanized territories: Irkutsk and Shelekhov cities and their suburbs, where the main sources of high levels of air pollution are the Irkutsk Aluminum Smelter (including CHP plant, silicon, and cable production) and the Novo-Irkutsk CHP plant. The sampling scheme was drawn up considering the physical and geographical conditions, including the wind rose, the location of industrial enterprises and the terrain (Fig. 1). Samples were collected at the end of the stable snow cover season during the period of its maximum accumulation before the onset of thawing (late February and early March, from 2020 to 2022). Sampling was carried out to the entire depth of the snow layer, except for a 5-cm layer above the soil, using special polyvinyl samplers in plastic bags, while measuring the area and depth of the pit.

Snow samples were thawed at room temperature, and the melt water was filtered. The mass of obtained solid samples varied from 0.1 g to 2.0 g. According to the XRD data, collected samples consist of oxide phases containing aluminum and iron, presumably of technogenic origin: mainly corundum, mullite, and hematite, as well as natural minerals (quartz, anorthite, muscovite, phlogopite). According to the previous studies using electron probe microanalysis, samples collected from the same area also could contain microparticles of aluminum oxides and carbides and metal spherules of iron sulfides.\textsuperscript{35-37,39} Fig. 2 shows spectra of snow cover solid phase samples collected near aluminum smelter (a), CHP plant (b) and out of investigated area (c). The most intense lines are related with the presence of high Al (1.5 keV), Fe (6.4 keV), Ca (3.7 keV) and Si (1.7 keV) content. These major elements were considered as potential pollutants.

The phase composition of the samples was studied by X-ray powder diffractometry (XRD) using a D8 Advance powder diffractometer (Bruker AXS, Germany). The approved analytical methods of atomic emission spectroscopy (Kolibri-2 multichannel spectrometer, VMK-Optoelektronika, Russia), atomic absorption spectroscopy (M403 spectrometer, Perkin-Elmer, USA) and spectrophotometry (SF-56 spectrophotometer, OKB Spectr, Russia) were used as reference methods.

Obtained results were processed by CA and PCA to classify samples with different composition. The “Eigenvalues scree Plot” was used to determine two optimal principal components. Calculations showed that the first two principal components represent 86% of the total variance (factor 1 = 70.6%, factor 2 = 15.4%). Score and loading scatter plots were constructed in
Table 2. Analysis of snow cover solid phase samples by reference methods

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration range, wt. %</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.10-1.79</td>
<td>Atomic emission spectroscopy</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.12-3.02</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>MgO</td>
<td>0.11-1.99</td>
<td>Atomic absorption spectroscopy</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.54-73.07</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>CaO</td>
<td>0.51-5.26</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>MnO</td>
<td>0.03-0.10</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.36-6.40</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>SiO₂</td>
<td>6.63-48.26</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.06-0.20</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.07-0.77</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>Loss on ignition (LOI)</td>
<td>5.22-21.53</td>
<td>Gravimetry</td>
</tr>
</tbody>
</table>

Fig. 3 PCA results based on the elemental composition of snow cover solid phase samples obtained by reference methods: score scatter plot (a) and loading scatter plot (b) for two factors.

Projections on the first and the second factors (Fig. 3) to study the relationship of all variables. The most significant variables for the first factor are Al, Si, Ti, Mn, and Fe. The second factor divides the samples by the content of Na.

The score scatter plot shows a clear differentiation of samples collected near Novo-Irkutsk CHP plant (samples 1 and 4) and Irkutsk aluminum smelter (other 10 samples). The main difference in chemical composition caused by the variations of Na and K or Al and LOI (including F and C) contents in aluminum smelter emissions and Ca content in CHP plant emissions. The data obtained showed that sources of pollution are various in different fields of investigated area. According to a visual assessment of PCA graphs, 12 samples were divided into two groups.

Calibration samples. The calibration set was selected according to the ranges of elements’ contents determined for the samples of snow cover solid phase by reference methods (Table 2). We used CRMs of igneous and sedimentary rocks produced by the Vinogradov Institute of Geochemistry (Irkutsk, Russia): SDU-1 (dunit), SKD-1 (quartz diorite), SGG-2 (gabbro), SG-3 and SG-4 (granites), GBPg-1 (garnet-biotite plagiogneiss); West Siberian Testing Center (Yekaterinburg, Russia): SO-12 (granite); International Association of Geoanalysts (IAG): DBC-1 (GeoPT-33, soil), UoKLoess (GeoPT-13, loess) and SdAR-1 (GeoPT-31, modified river sediment); CRMs of aluminum raw materials produced by Research Institute of Applied Physics (Irkutsk, Russia): SB-1 and SB-2 (bauxite), SNS-1 (nepheline ore) and The Center for Mineral Technology (CETEM, Brazilia): BXSP-1, BXMG-1, BXMG-3, BXMG-5, BXPA-2 and BXGO-1 (bauxites). CRMs contain high aluminum concentrations due to the presence of minerals—aluminum hydroxides (boehmite, diaspor, gibbsite) and aluminum silicates (kaolinite, zeolite). The data on elemental and phase composition was taken from GeoREM database (http://georem.mpch-mainz.gwdg.de), websites of IAG (https://www.geoanalyst.org/geopt) and CETEM (https://www.cemet.gov.br/antigo/crm).

Calibration set and analyzed samples were preliminarily calcined for 4 hours in a muffle furnace at a temperature of 950 °C. Because elements’ contents are usually increasing during calcination (when LOI values related to water and carbon compounds), we recalculated elements’ contents to calcined samples using certified (for CRMs) and determined by gravimetric technique (for collected samples) LOI values. Calcined samples with a mass of 110 mg were fused with 1.1 g of lithium metaborate (Merck) with the addition of seven drops of a 4% LiBr solution in platinum crucibles in a TheOX electric furnace (Claisse, Canada) at a temperature of 1050 °C. The melt was poured onto platinum substrates and glass discs with a diameter of 10–12 mm were formed.

Validation. To assess the difference between results obtained by the XRF method and reference methods, the standard deviation (SD) value was calculated as follows:

\[
SD = \sqrt{\frac{\sum (C_{XRF} - C_{ref})^2}{n}}
\]

where \(C_{XRF}\) and \(C_{ref}\) - concentrations obtained by XRF and reference methods, \(n\) - the number of samples. The relative standard deviation (RSD) was calculated as follows:

\[
RSD = \sqrt{\frac{\sum \frac{(C_{XRF} - C_{ref})^2}{C_{ref}}}{n}}
\]

To compare the results obtained by XRF and reference methods, \(Z\)-score was calculated as follows:

\[
Z = \frac{C_{XRF} - C_{ref}}{0.02 \cdot (C_{ref})^{0.4895}}
\]

Assessment of pollution level. The assessment of the pollution level was performed by a comparison of the obtained results with the values accepted as a regional background. As this study deals with a unique geosystem of the Baikal region, the methodology
for determining the local background parameters differs from the generally accepted ones. Several background samples are taken outside the study area, 20 km away from the emission source. This is a background area identical to the emission source area in terms of climatic parameters, geological structure, relief, and soil cover. The sampling location satisfies the minimum urbanization of the surrounding area. After statistical processing of the data, the content of the elements, conventionally taken as the background, was determined (presented in supplementary files, Table S3). Pollution level was assessed using coefficients of elements’ concentrations:

\[ K_c = \frac{C}{C_b} \quad (6) \]

where \( C \) – content of element in sample; \( C_b \) – background content of element.

**RESULTS AND DISCUSSION**

Since the phase composition of the calibration set and analyzed samples is significantly different, and the calibration set does not include matrix-matched CRMs, we considered several options for constructing calibration equations.

I. CRMs listed in the Experimental section were used as a calibration set. For each analyte, the calibration range was chosen based on the data obtained by reference techniques for samples in Table 1. The number of calibration samples varied from nine to seventeen. Matrix effects were corrected in two ways: FP method (eq. (1)) or EIC method (eq. (2)). For EIC method the main elements of emission (Al, Si, Fe) were considered as influencing elements. The information about calibration samples and influencing elements are presented in supplementary files (Table S2).

II. According to the PCA (Fig. 3), samples of snow cover solid phase analyzed by the reference techniques were divided into two groups. Two samples (10 and 12), collected near aluminum smelter, and one sample (4), collected near Novo-Irkutsk CHP plant were chosen for a validation. Other nine samples were used as a calibration set. Two methods for matrix effects correction were also considered.

Table 3 shows the ranges of analytes, limit of detection (LOD) and root mean square (RMS) values, characterizing scatter of points relative to calibration curves (\( n \) varied from 9 to 17) and calculated as:

\[ RMS = \sqrt{\frac{\sum (C^{cert} - C^{XRF})^2}{n}} \quad (7) \]

where \( C^{cert} \) – certified content in CRM, \( C^{XRF} \) – content in CRM calculated using calibration curve.

EIC method allows to significantly reduce the RMS value for aluminum and silicon compared to the theoretical correction, while for the other elements the difference is insignificant. To assess the accuracy and select the optimal calibration equation, three test samples were analyzed according to the variants of equations I and II. Results were recalculated to uncalcined sample. Results are presented in supplementary files (Table S4). Table 4 shows obtained values of SD, RSD (\( n=3 \)) and Z-score.

According to the data given in Table 4, the use of snow cover solid phase samples analyzed by reference techniques as a calibration set enables to reduce the error for Al, Si, and Ca by more than 3 times and for Mg by more than 2 times, while the accuracy is almost the same for Na, K, Ti. According to the Z-criterion, the results of the determination of Al, Si, and Fe in all three samples by the reference methods (II) can be accepted as satisfactory (\(|Z|<2\)). For XRF analysis using CRMs (I), the results
can be considered as doubtful only for Al (2<|Z|<3). In total, out of thirty samples, the results for only eight samples can be considered as satisfactory and for other eight samples as doubtful obtained by equations I. Using of the calculation by equations II, the results for twenty samples can be accepted as satisfactory and for six samples as doubtful. Thus, it is preferable to use the samples for a calibration purposes preliminary analyzed by approved methods. Results of quantitative XRF analysis were used for further assessment of pollution level in the investigated area. According to the proposed methodology, 150 samples were collected in the area near the Irkutsk aluminum smelter and Novo-Irkutsk CHP plant (points of sampling are shown in Fig. 1) and analyzed from 2020 to 2022. Fig. 4 shows results of CA for 72 samples collected in 2020.

As can be seen from Fig. 4, the contents of LOI, Al and Na are strictly correlated with each other, which corresponds to the studies, established that the main (with content more than 10 wt. %) components of gas and dust emissions from Irkutsk Aluminum smelter are aluminum oxide, carbon, cryolite Na3AlF6 and chloleite Na3AlF14. This suggests a technogenic source of these elements. A closely related association of Mn, Ca, Ti, Si, K, and Mg probably characterizes emissions from the CHP plants. Table 5 shows ranges and average values of elements concentration coefficient as well as percentage of polluted (Kc>1) samples (Kc).

As can be seen from the Table 5, there is no significant pollution of snow cover solid phase by Na, Mg, and P (Kc values was more than 1 only for one sample for P, two samples for Mg, and 3 samples for Na). Even though Na, along with Al, is one of the main components of emissions from the aluminum industry, only 4% of samples contain Na, exceeding the background values. The reason is that some elements can be completely dissolved during the sample preparation procedure and remain in the water after filtration. According to a study conducted for other aluminum smelter located in same region, only about 10% of Na remains in snow cover solid phase, while for Al this value reaches 100%.

High values of Kc for Al related with Irkutsk aluminum smelter emissions, which settling on the Shelekhov city territory.

| Table 4. Comparison of two calibration sets for XRF analysis |
|---|---|---|---|---|---|---|---|---|---|
| No. | C calc, wt. % | Na2O | MgO | Al2O3 | SiO2 | P2O5 | K2O | CaO | TiO2 | MnO | Fe2O |
| 4 | 0.14 | 1.48 | 20.98 | 36.21 | 48.26 | 0.16 | 0.38 | 5.26 | 0.77 | 0.09 | 7.38 |
| 6 | -1.20 | -9.68 | 1.96 | -3.88 | -5.62 | -2.79 | 4.05 | -2.53 | -2.70 | 2.78 |
| 9 | 2.69 | -4.51 | 0.29 | -1.14 | 0.40 | -0.31 | 0.67 | -2.74 | 5.07 | 0.26 |
| 10 | 0.17 | 1.58 | 36.37 | 37.75 | 0.15 | 2.12 | 2.35 | 0.45 | 0.95 | 4.78 |
| 12 | 3.57 | 3.16 | 2.71 | -2.40 | -9.02 | -0.36 | -2.24 | -2.90 | -17.9 | 1.41 |
| 15 | 2.37 | 3.13 | -0.83 | -0.48 | -2.64 | 0.84 | -0.25 | 4.17 | 0.09 | 0.94 |
| SD | 0.05 | 0.20 | 1.19 | 1.30 | 0.02 | 0.05 | 0.20 | 0.02 | 0.03 | 0.29 |
| SDu | 0.02 | 0.08 | 0.28 | 0.39 | 0.01 | 0.07 | 0.03 | 0.03 | 0.01 | 0.09 |
| RSD | 4.55 | 13.88 | 5.81 | 3.28 | 19.73 | 3.82 | 4.35 | 5.24 | 41.54 | 5.47 |
| RSDu | 5.03 | 6.34 | 0.78 | 0.92 | 4.49 | 3.38 | 0.74 | 4.86 | 16.21 | 2.00 |

**Fig. 4** Results of CA of elemental composition of snow cover solid phase samples.

| Table 5. Minimal, maximum, and average values of elements concentration coefficients, percentage of polluted samples |
|---|---|---|---|---|
| Kc<sub>min</sub> | Kc<sub>max</sub> | Kc<sub>average</sub> | Kc<sub>percent</sub> |
| Na | 0.2 | 1.9 | 0.4 | 4 |
| Mg | 0.1 | 1.1 | 0.6 | 3 |
| Al | 0.9 | 2.8 | 1.5 | 92 |
| Si | 0.1 | 1.2 | 0.8 | 47 |
| P | 0.1 | 1.4 | 0.6 | 1 |
| K | 0.1 | 3.7 | 0.9 | 13 |
| Ca | 0.2 | 2.0 | 1.0 | 51 |
| Ti | 0.1 | 1.8 | 1.1 | 57 |
| Mn | 0.1 | 1.7 | 0.9 | 51 |
| Fe | 0.2 | 6.1 | 1.1 | 60 |
Quantification of Al in snow cover solid phase by the XRF method allows us to clearly assess the pollution areas and find the level of pollution by aluminum industry as high. The obtained distribution is in a good agreement with the distribution of F obtained for investigated area. Spatial distribution of Na is presented in supplementary materials (Fig. S1).

Figure 6 shows the spatial distribution for other elements (Si, K, Ca, Ti, Mn, Fe) in snow cover solid phase samples in the suburban areas of Shelekhov and Irkutsk cities.

High values of $K_c$ for Si, Ca, Fe, Mn, and Ti related with the CHP plant emission, settling on the Irkutsk city territory according to the wind rose. As can be seen for Fe distribution (Fig. 6f), extremal values of $K_c$ are observed near aluminum smelter, where several facilities (cable production, asphalt plant) are located. This anomaly has also been observed for Mn for several years and can be associated both with operation of CHP plant or city heaters, and with the repair of railways. High $K_c$ values for Ca and K may be associated with anti-icing treatment of roads. Thus, the proposed method allows to assess the degree of industrial pollution of the snow cover.

CONCLUSION

The proposed XRF method allows to quantify major elements (Na, Mg, Al, Si, P, K, Ca, Ti, Mn, Fe) in samples of snow cover polluted by industrial emissions. The work showed that the construction of calibration curves should be carried out using the preliminary analyzed samples of snow cover solid phase by reference methods. The RSD values, presenting the comparison of XRF and certified techniques (atomic absorption spectrometry, spectrophotometry, atomic emission spectrometry) data, did not exceed 1 rel. % for Al, Si, Ca, 2 rel. % for Fe, and 7 rel. % for other elements (except for Mn, which content did not exceed 0.1% in the samples). Spatial distribution of elements in the investigated area allowed us to discover the main pollution elements produced by the aluminum smelter (Al) and CHP plant (Si, Ca, Ti, Mn, Fe). XRF method has the advantage of being simple, cheap, and fast method that can be used for studying environmental pollution.

ASSOCIATED CONTENT

The supporting information (Tables S1–S4, and Fig S1) is available at www.at-spectrose.com/as/home

AUTHOR INFORMATION

Alena Amosova received her specialty engineer-nanotechnologist in 2014 from the Irkutsk State Technical University, she graduated from the postgraduate course in 2018 in the direction of Chemical Sciences (focus of Analytical Chemistry) and PhD in 2019 from the Vinogradov Institute of Geochemistry (Siberian Branch of the Russian Academy of Sciences). She is a researcher at laboratory of X-ray methods of analysis in the Vinogradov Institute of Geochemistry. Her major research interests are X-ray fluorescence analysis of geological objects (bottom and peat sediments, rocks, ores, rocks), geochemistry, application of X-ray spectrometry for paleoclimatic studies. She has been working in DIMA (Developing Innovative Multi-Proxy Analyses) Network.
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In-situ Online Detection of Atmospheric Volatile Organic Compounds Based on Laser Induced Breakdown Spectroscopy: A Review

Ye Fei, Jun Feng, Junyi Zhu, Guanhua Xing, and Yuzhu Liu

ABSTRACT: This review's main purpose is to provide a succinct overview of recent developments in the field of volatile organic compounds (VOCs) detection based on Laser-induced breakdown spectroscopy (LIBS). VOCs are important air pollutants, which have great harm to the environment and human body. It is of great significance to realize the rapid detection of VOCs in the atmospheric environment. LIBS is a novel atomic emission spectroscopy technology, which can achieve the rapid in-situ detection of substances and shows great potential in the online monitoring of atmospheric VOCs. To illustrate the development and difficulties of LIBS technology in atmospheric VOCs detection, some typical cases for various aspects are listed, including the detection of harmful elements in VOCs, source tracing of VOCs, the identification of isomers, and the detection of VOCs in living environment.

INTRODUCTION

In recent years, air pollution has emerged as one of the most pressing environmental challenges for all countries across the world, attracting wide attention of the international community. VOCs are a class of harmful organic pollutants that have high chemical reactivity and volatility in atmospheric environments. The definition of VOCs may vary depending on the country or organization. The World Health Organization (WHO) defines VOCs as a general term for certain VOCs that have a melting point below room temperature and a boiling point between 50 and 260 °C. VOCs can typically be categorized into five groups: non-methane hydrocarbons (NMHCs), halogenated hydrocarbons, oxygen-containing organic compounds, nitrogen-containing organic compounds, and sulfur-containing organic compounds. As one of the precursors to the formation of ozone and PM2.5, VOCs could increase tropospheric ozone concentration, urban gray haze, photochemical smog, and other harmful environmental effects, leading to significant damage to the environment. Additionally, VOCs exhibit physiological toxicity, leading to cancer, deformity, and organ damage in the human body. The sources of VOCs are diverse and can be classified into two categories: natural sources and artificial sources. Natural sources include emissions from wetlands, forests, and oceans, while artificial sources include emissions from industry, agriculture, homes, and transportation vehicles. Among them, industrial and vehicle emissions are the primary causes of VOCs. VOCs emissions have significantly increased due to the rapid industrialization and urbanization, posing a serious threat to the environment.

To implement effective control measures against these pollutants, a technology that can perform real-time quantitative monitoring of components in the moving air in an open environment is required. Currently, gas chromatography (GC), gas chromatography-mass spectrograph (GC-MS) and high-performance liquid chromatography (HPLC) are commonly used for the detection of VOCs. However, these methods require...
the mirrors and burns to form a plasma. The light emitted by the laser emitted from the laser converges on the sample gas through a delay trigger device, and a computer. During the experiment, the light is focused by a pulsed laser, which consists of a LIBS system used for the detection of atmospheric VOCs. The LIBS experimental system is shown in Fig. 1, which is a schematic diagram of the LIBS experimental setup.

**Fig. 1** The schematic diagram of the LIBS experimental setup.

The LIBS technology has been developed in the detection of pollutants, and many effective detection methods have been invented. Due to its advantages such as fast detection, high sensitivity, multi-component measurement, and little damage to the sample, LIBS is expected to emerge as a powerful tool for monitoring ambient air quality. Currently, the LIBS technology has been relatively mature in the detection of metal elements, but there are still many studies on substances that comprise non-metallic elements, such as VOCs. Hence, there is a considerable space for development in this area.

This paper mainly introduces the progress and challenges of LIBS technology in the detection of atmospheric VOCs. From the four levels of the detection of harmful elements in VOCs, source tracing of VOCs, identification of isomers, and VOCs detection in living environment, relevant cases are included to demonstrate the remarkable achievements and great development potential of LIBS in this field.

**INSTRUMENTATION**

The LIBS experimental system is shown in Fig. 1, which is a typical LIBS system used for the detection of atmospheric VOCs. It consists of a pulsed laser, mirrors, a detector, a spectrometer, a delay trigger device, and a computer. During the experiment, the laser emitted from the laser converges on the sample gas through the mirrors and burns to form a plasma. The light emitted by the plasma is collected by the detector and coupled to the spectrometer, and the spectral information is then displayed on the computer. The laser is the core component of the device, as the plasma excited by it is key to obtaining sample element information, and the laser parameters will affect plasma formation. The spectrometer determines the range and resolution of the spectrum. Different types of lasers and spectrometers need to be selected according to the detection object. The delay trigger device is located between the laser and the spectrometer. By adjusting the delay time, the signal-to-noise ratio of the spectrum can be improved. In addition, when detecting gaseous samples, air pumps are sometimes used to control the gas flow and improve the laser hit rate.

**CASE STUDIES**

**Detection of harmful elements in VOCs.** Halogenated hydrocarbons and sulfur compounds are typical classes of VOCs in the atmosphere. Unlike other VOCs composed of carbon, hydrogen, oxygen, and nitrogen, the halogen and sulfur atoms in these compounds can be important features for spectral analysis. However, halogen and sulfur atoms have high ionization energy, and their most intense emission lines lie in the Vacuum UltraViolet (VUV) or Near-Infrared (NIR) region, which makes it difficult for LIBS to detect these elements. In the past few decades, many researchers have modified the experimental environment and samples to improve the detection performance.

For the detection of halogens, it is effective to improve the intensity of halogen lines by conducting experiments in an inert gas environment. Compared with the spectral lines of N, H and O, the intensities of halogen spectral line are relatively weak. But in the environment of inert gas, the spectral line intensity is significantly increased. Usually, helium is used as an ambient gas with better results. Asimellis et al. detected F and Cl qualitatively and quantitatively under controlled helium gas ambient atmosphere. After optimizing the experimental parameters, the spectral lines of F and Cl could be clearly observed in the upper visible and in the NIR (650–850 nm) region. In the later work, they studied the effect of the ambient atmosphere (pressure and gas species) on Br emission lines. The results showed that the signal-to-noise ratio was best in helium under 100 mbar, and the 827.24 nm Br atomic line shifted and expanded asymmetrically when the ambient atmosphere changed. In addition, Barbier et al. performed LIBS detection on flame retardants in plastics under different plasma conditions. It was found that the strength of Br line and Cl line was improved under the helium buffer. However, the enhanced halogen lines in the inert gas atmosphere are mainly located in the NIR region, which requires the spectrometer detection performance to be high. Furthermore, the detection needs to be carried out in the laboratory as it is difficult to create a...
controllable inert gas environment in an open environment, limiting the application of LIBS technology in the detection of atmospheric VOCs.

Another common approach is to use molecular emission bands. The intensity of some alkali-halogen molecular bands is stronger than that of halogen emission lines. By replacing the detection of halogen atoms with the detection of molecules formed by alkali metal elements (usually Ca or Ba) and halogens, the sensitivity of detection can be effectively improved, which helps to achieve the quantitative detection of halogens in samples. Fernandez-Menendez et al. investigated the spatial and temporal distribution of CaF emission in samples containing Ca and F. Under optimized conditions, the sensitivity of F detection was increased by more than 4 times. Gaif et al. obtained and evaluated the spectral signals of halogenated alkali metal compounds such as CaF, CaCl, BaBr, CaI. The results showed that the spectra of halogens combined with alkali-earth elements was easier to be detected than F and Cl atomic lines. Tang et al. realized the quantitative detection of F in copper ore based on SrF or CaF molecular emission bands. When there are no alkali metal elements in the sample that can form molecular emission bands with halogens, the sample may require certain manipulation to introduce these elements. The alkali metal elements and halogens combine into molecules in the plasma and can be detected by detectors. Alvarez-Llamas et al. developed a novel approach to quantitatively detect F in calcium-free samples based on molecular CaF bands. By spraying a calcium solution on the surface of the sample, an intense CaF molecular signal was detected via LIBS system. Mendez-Lopez et al. nebulized an aqueous solution of NaF onto the Ca-containing pellets to obtain molecular emission bands of CaF. This method was used to detect fluorine content in solids, and the experimental accuracy deviation of the three mouthwashes measured was less than 10%. In addition to solids and liquids, the use of molecular emission bands is also feasible in aerosols. Niu et al. detected the spectra of CaCl and CaF radicals in aerosols, which implies the possibility of this method in gas detection. Besides, since the detection of non-metallic elements may be difficult, combining LIBS technology with other technologies can help improve the detection ability to a certain extent. Naghi et al. applied LIBS-MLIF method to detect Cl atoms in concrete samples as a further development of molecular emission applications. It was found that the detection sensitivity of LIBS-MLIF was better than that of MLIBS. Although molecular emission bands can achieve quantitative and qualitative detection of halogens in samples, it is not a good choice for detecting halogens in atmospheric VOCs. Atmospheric VOCs almost do not contain alkali metal elements. Sample must be processed to obtain the molecular emission bands, which will hinder real-time detection in the actual environment.

Since the LIBS signal intensity of metallic elements is usually much higher than that of halogens, Duerst et al. proposed a new method to confirm the presence of halogens in mineral samples based on the relative intensity ratio of halogens and alkali metals. The LIBS spectra of more than twenty alkali metals and halogens were obtained and the relative intensity ratios of halogen/alkali metal were calculated in the experiment. When testing unknown samples, the peak intensity of alkali metal in the sample can be multiplied by the relative intensity ratio to determine the possible intensity of F, Cl, Br, and I, thus reducing the interference of noise on element identification. Although this method is not yet very mature, it undoubtedly provides a new way of identifying halogen spectral lines in LIBS spectra.

To achieve online direct detection of halogens in atmospheric VOCs, Zhang et al. applied LIBS system combined with a self-designed single particle aerosol mass spectrometry (SPAMS) to detect halogen atoms in three typical VOCs (Halon 2402, Freon R11, iodomethane) in the atmospheric environment. The laser used in the experiment had a wavelength of 1064 nm and an energy of 200 mJ. The time delay was set to 2.5 μs and the time integration was set to 2 ms. From the obtained LIBS and SPAMS spectra, the characteristic peaks of corresponding halogens in different samples were observed. Fig. 2 shows the LIBS spectrum and SPAMS spectrum of a Freon R11 sample, in which the LIBS characteristic spectral lines and mass spectrum of Cl can be seen. Using mass spectrum as a supplementary analysis, the detection accuracy was improved. Meanwhile, mass spectrum could distinguish halogen isotopes, and the source of pollutants could be traced by calculating the isotope abundance ratio. The Halon 2402 samples were tested by Raman spectroscopy to obtain molecular structure information, as shown Fig. 3. The characteristic peaks corresponding to several vibration modes could be considered as “spectral fingerprints” of the Halon 2402 molecule. Similarly, using the same method, Zhang et al. successfully captured the LIBS and SPAMS spectra of halogen atoms in halogenated hydrocarbons. The LIBS spectrum of C3H5BrF obtained by the
experiment is shown in Fig. 4. By comparing the theoretical and experimental Raman spectra, two rotational conformations of C₂H₄BrF were identified. It provides reference for rapid identification of halogenated hydrocarbons.

There are similar challenges with halogens when detecting sulfur in samples by LIBS system. Therefore, most researchers select the emission lines of sulfur located in the NIR or VUV region as the research object, with only a few studies using spectral lines in the VIS region. In addition, the experiment has certain environmental requirements to enhance the intensity of the characteristic sulfur lines. Asimellis et al. efficiently determined sulfur concentrations in samples with different concentrations in a helium gas atmosphere under controlled pressure using the NIR spectral lines of sulfur at 869.46 nm. The optimal ambient pressure measured experimentally was slightly lower than 100 mbar. Weritz et al. investigated sulfur in building materials via LIBS in air, argon, and helium atmospheres. According to the results, the resolution of sulfur spectral lines in the NIR region was best in the helium atmosphere under the same conditions. Jasik et al. employed VUV-LIBS to detect trace elements in polyethylene in a 2 mbar Ar atmosphere. Two atomic lines of sulfur were detected at 180.7 and 182.0 nm and the limit of detection (LOD) in the experiment was 50 μg/g.

Some researchers have also introduced double-pulse technology to improve the sensitivity of LIBS systems. Ma et al. quantitatively analyzed sulfur in coal under helium atmosphere using DP-LIBS technique. Two orthogonally configured nanosecond laser were utilized in the system. The first laser was used to ablate the sample, creating a plasma. The second laser reheated the plasma with a certain time interval. The parameters of the two laser beams were different. Compared with SP-LIBS, the mean strength of the sulfur lines captured by DP-LIBS was 2.3 times higher, and the interference of the oxygen atomic lines was also reduced due to the use of helium gas. The calibration curves were established to quantitatively calculate sulfur concentration. It was found that the best results were obtained when S I 921.3 nm was used. Gaft et al. tested and compared the performance of SP-LIBS and DP-LIBS in detecting sulfur concentrations in different minerals. For different kinds of samples and sulfur concentrations, different LIBS devices and detection bands need to be selected. Gondal et al. used DP-LIBS system to detect sulfur in the reinforced concrete structures. The sulfur ionic line was detected at 545.38 nm, which was used as the indicator of sulfur concentration in the sample. The LOD in the experiment was about 38 μg/g. In addition, Ma et al. used indirect laser-induced breakdown spectroscopy (ID-LIBS) to improve the detection sensitivity of Cl and S elements. Ag and Ba reacted with chloride and sulfate respectively in water to form precipitation. The indirect detection of Cl and S was achieved by measuring the remaining Ag and Ba in water. The results showed that this method could greatly improve the detection sensitivity.

However, most of the current studies using LIBS to detect sulfur are focused on solid samples (coal, steel, ore, etc.), because sulfur content is an important standard to measure the quality of industrial production and pollutant emission. There are few studies on the detection of sulfur in gaseous samples. Due to the high mobility of gases in open space, pollutants in the air may be relatively thin. Therefore, the speed and sensitivity of detection are critical, which makes many methods used to detect sulfur in solid samples no longer effective for detecting gases. Researchers are also exploring new ways to achieve accurate measurement of sulfur in atmospheric VOCs.
Zhang et al. investigated dimethyl sulfide (DMS), a major volatile sulfur-containing organic compound, under normal atmospheric conditions. The element information of DMS was obtained in this work by using LIBS and Raman techniques, and its molecular configuration. Different volumes of DMS liquid samples were added into the sample cell to fully volatilize to simulate different levels of air pollution. The outlet of the sample cell was placed near the laser focus to ensure that the concentration of the experimentally measured DMS was equal to the concentration of the prepared sample. Under the excitation of laser in 1000 mJ, several ionic lines of sulfur appeared in the 535−570 nm region of the LIBS spectrum. As is shown in Fig. 5, with the increase of DMS concentration, the spectral line intensity of sulfur also increases linearly. The calibration curve of sulfur in air was obtained based on the S II 545.383 nm peak, and the coefficient of determination $R^2$ was 0.986. In this experiment, the LOD was 46 mg·L$^{-1}$, which could meet the requirement for sulfur detection in real atmospheric environment. In addition, obvious sulfur ionic lines can be seen in the visible region when detecting gas samples, but often cannot be seen in solid detection. In order to verify whether the sample state influences the intensity of sulfur ionic lines, the LIBS spectra of gas and liquid DMS sample were compared in the experiment. It was found the sulfur ionic lines in gas sample were more easily detected when the experimental conditions were the same except for the sample state.

Chen et al. performed LIBS-SPAMS technology on the direct in-situ detection of sulfur in the atmosphere. Through the detection of CS$_2$ samples in different states, it was found that the characteristic lines of sulfur ions appeared in the LIBS spectrum of gaseous sample at 540−570 nm, and the signal-to-noise ratio was 28.0±1.2 dB, as shown in Fig. 6. In the aerosol spectrum, the
resolution of the corresponding spectral lines became worse and the signal-to-noise ratio decreased to 17.1±4.2 dB, but the sulfur lines could still be seen faintly. However, in the liquid sample, sulfur lines could not be detected at all in this band. It is also proved that gaseous samples are more easily excited into ionic states under the action of high-energy laser. LIFBASE software was used to calculate the temperature of CN molecular band. It was found that the vibration temperature and rotation temperature of CN molecular band in gaseous CS₂ experiment were higher than that in aerosol CS₂ experiment, indicating that the increase of plasma temperature was more conducive to the detection of sulfur than the increase of concentration. Besides, the three isotopes of sulfur were well distinguished in the mass spectrum of CS₂. The isotopic abundance ratio of sulfur in the sample was calculated and found to be very close to the natural abundance ratio.

The two examples above confirmed the feasibility of LIBS in detecting harmful elements in atmospheric VOCs. In fact, accurate identification and quantitative detection of these elements is a crucial part in the analysis of VOCs in the atmosphere, which is the basis for the classification of VOCs and the judgment of molecular structure in the follow-up work.

**Source tracing of VOCs.** Source tracing of VOCs is a crucial step in managing atmospheric VOCs pollution. Only by identifying the sources of atmospheric VOCs can different pollution sources be accurately managed. The types of VOCs produced by different pollution sources are different. If different VOCs in the air can be identified, its possible sources can be determined. Then specific measures are taken to control the emission of pollutants. In previous studies, SPAMS is often used to trace the source of air pollutants. According to the mass spectrum information of particulate matter, the clustering algorithm (ART-2a, K-medians, K-means, Fuzzy clustering, etc.) is used to classify particulate matter into different categories according to the similarity of mass spectrum characteristics, so as to distinguish the source of particulate matter. In this review, another tracing method based on LIBS combined with machine learning algorithms will be introduced, which can realize the rapid detection and differentiation of atmospheric VOCs.

Machine learning is an important technology in the field of artificial intelligence, which can automatically improve the prediction and decision-making abilities of computers through data or experience. Since the 1950s, machine learning has gone through multiple stages of development and has gradually matured. Many classical algorithms, such as Logistic Regression (LR), K-Nearest Neighbor (KNN), Classification and Regression Tree (CART), Error Back Propagation (BP), Artificial Neural Network (ANN), Convolutional Neural Network (CNN), Support Vector Machine (SVM), Adaptive Boosting (AdaBoost), Random Forest (RF), have been produced successively, promoting machine learning to penetrate into more different fields. At present, machine algorithms can be roughly divided into three categories: supervised learning, unsupervised learning, and reinforcement learning. They play a crucial role in many application scenarios such as image recognition, natural language processing, traffic prediction, medical diagnosis and so on. In recent years, LIBS combined with machine learning algorithms has become a hot topic. Chen et al. proposed a new method to identify inferior charcoal based on LIBS technology. Principle Component Analysis (PCA) was used to reduce the dimension of spectral data. On this basis, combined with the optimized KNN and SVM methods, the classification accuracy of fruit charcoal, mechanism charcoal and bamboo charcoal reached 96.0% and 97.3%, respectively. Liu et al. used the LIBS-HIS technology combined with machine learning algorithms to build recognition models of rice geographical origin. In the experiment, the recognition accuracy of the Partial Least Squares Discriminant Analysis (PLS-DA), the SVM, and the Extreme Learning Machine (ELM) algorithms reached 99.08%, 99.85% and 99.47%, respectively. Rzecki et al. tested the classification effect of seven machine learning algorithms (DT, KNN, RF, SVM, PNN, MLP, GRNN) on LIBS spectra of paper-ink samples, and the results showed that the RF algorithm had the best classification effect, with an accuracy of 99.08%.

Lu et al. proposed a method of atmospheric VOCs source tracing based on LIBS combined with machine learning algorithms. The source tracing model of VOCs is shown in Fig. 7. The five haloalkanes used in the experiment were C₂H₄BrCl, C₂H₄Cl₂, C₂H₄Cl, C₂H₄I and CH₃I. To simulate environmental pollution, liquid reagents were added to a closed box filled with air at atmospheric pressure and heated to accelerate the evaporation of the reagent until the gas in the box became stable. Firstly, LIBS were used to detect the polluted air. Atomic lines of Cl, Br and I, ionic lines of Br and I, CN molecular emission bands and some common elements in the air were respectively observed in different samples. For different VOCs samples, 300 spectra were selected and the data was standardized to carry out PCA. When the entire spectral region was selected for PCA, the data sets corresponding to different VOCs overlapped significantly on the two-dimensional plane composed of PC1 and PC2. When the bands of C, H, Cl, Br and CN were selected for PCA, different VOCs could be well separated on the two-dimensional plane.
composed of PC1 and PC2. The analysis results are shown in Fig. 8. On this basis, BP-ANN was used to establish the classification model of VOCs. 1500 pieces of spectral data were divided into training set and test set, with the training set accounting for 80% and the test set accounting for 20%. There were 5 neurons in the output layer of the model by using one-hot encoding. A hidden layer was established. After model training, the recognition accuracy could be calculated by comparing the label predicted and the actual ones. It was found that the recognition accuracy was highest when the number of neurons in the hidden layer was 4. In order to better evaluate the performance of the model, ten times ten-fold cross-validation was adopted, and the average value was taken as the final recognition accuracy. When the number of hidden layer neurons was 4, the recognition accuracy reached 99.77%.

Identification of isomers. Cis-trans isomers, also known as geometric isomers or E and Z isomers, are a type of stereoisomers that have the same molecular formula and bond connectivity but differ in the spatial arrangement of substituents around a double bond.99 There are also many isomers in VOCs. The structures of VOC isomers are different, and their degree of atmospheric pollution may vary. The study of isomers is important in many fields, including chemistry,94,95 biochemistry,96,97 and pharmacology,98,99 as they can have different physical, chemical, and biological properties.

Recent research on cis-trans isomers has focused on developing new methods for their synthesis, separation, and characterization. For example, advances in spectroscopic techniques, such as NMR and IR spectroscopy, have enabled researchers to distinguish between cis and trans isomers more accurately. Saman et al. characterized a highly-thermoresistant POSS, the octa(aminophenyl)silsesquioxane (OAPS) by using IR and NMR spectra.100 Abikhodr et al. demonstrated a method in which ion fragments produced by collision-induced dissociation (CID) are separated using IMS and identified using the vibrational fingerprints of only a few standards.101 In addition to infrared spectroscopy, there are some other spectral determination methods. Buhrow et al. measured the concentrations of endoxifen and its metabolites Z-and E-isomers in the plasma of estrogen receptor-positive breast cancer patients by liquid chromatography-mass spectrometry.102 Additionally, computational methods, such as molecular modeling and quantum chemistry calculations, have been used to predict the stability and properties of cis and trans isomers. Zhang et al. studied the effect of molecular structure on oxidation properties of propanol isomers at elevated pressure.103 Anthony et al. studied the internal rotation splitting in the spectra of three NT isomers to analyze the influence of isomers on the internal rotation barrier.104

In recent years, a new method has been proposed to determine and classify the isomers of VOCs in the atmosphere by LIBS technology. Zhang et al. studied rapid identification of VOCs and their isomers in the atmosphere.105 LIBS technology was developed to online distinguish VOCs and their isomers in the air. In this work, dibromoethane and fluorobromobenzene were used as experimental subjects. Dibromoethane and fluorobromobenzene are important commodity chemicals and indispensable synthetic intermediates in modern chemistry. There are two isomers of dibromoethane, 1,1-dibromoethane and 1,2-dibromoethane. Fluorobromobenzene has three isomers, such as,
2-fluorobromobenzene, 4-fluorobromobenzene, and 3-fluorobromobenzene. Their structure diagram is shown in Fig. 9. LIBS technology combined with machine learning was used to classify and identify isomers in the work. Firstly, the LIBS spectra of dibromoethane and fluorobromobenzene were quickly identified by machine learning. The recognition results are shown in Fig. 10. The point cluster distribution of fluorobromobenzene samples is relatively concentrated, and the scores of both principal components in the distribution area are negative. The distribution of data points for dibromoethane is relatively scattered, and the principal component score of the distribution area is positive.

Secondly, the LIBS spectra of the isomers of dibromoethane and fluorobromobenzene are classified by machine learning, and the results are shown in Fig. 11. Based on PCA algorithm, BP-ANN is used for accurate identification and classification. The following data come from BP-ANN algorithm. The optimal recognition accuracy of dibromoethane is 98.25%, and the precision and recall rate are 96.08% and 97.5%, respectively. The optimal recognition accuracy of fluorobromobenzene is 81.25%. The PCA distribution maps of the two isomers of p-fluorobromobenzene in Fig. 11 are highly overlapped, but the best recognition rate after combining BP-ANN is still higher than 80%. The precision and recall are 74.63% and 71.25%, respectively.

From the results, the classification of VOCs isomers by LIBS technology combined with machine learning is successful.

**VOCs detection in living environment.** On a global scale, the contribution of natural sources to the atmospheric VOCs is relatively large, but the natural sources are beyond the scope of human control. Thus, it is difficult to alter their emissions in the atmosphere, and artificial sources should be given special attention. VOCs emission objects in artificial sources are complex. In addition to transportation and industrial production, which are two of the most familiar sources of emissions, many common household items also emit VOCs, causing local air pollution and damaging human health. Therefore, it is significant to apply LIBS detection technology to the monitoring of VOC sources in daily life. In this review, two common types of VOCs in living environments are presented as examples, as shown in Fig. 12.
Mothballs are one of the important sources of indoor VOCs. Mothballs can be divided into natural camphor (the main component is $C_{10}H_{16}O$) and synthetic mothballs (the main component is $C_6H_4Cl_2$ or naphthalene, which is harmful to human health)\cite{106-108}. Since the production of natural camphor is relatively low, synthetic mothballs is commonly used as a substitute in the market. However, the smell of the two species is so similar that it’s difficult to distinguish them directly via sensory means. Therefore, a technique for identifying mothball species is needed.

Sun et al. successfully realized the distinction between two kinds of mothballs (camphor and p-dichlorobenzene) via LIBS combined with machine learning algorithm (PCA-SVC).\cite{109} It could be seen from the experimental results that the LIBS spectra of the two samples were similar, but the intensity of C and CN lines in the synthetic mothballs spectra were significantly higher. C, CN, Hα, Na and Cl spectra lines were used as the original features of PCA to reduce their dimensions. The principal component contribution rate and cumulative contribution rate is shown Fig. 13(a). On the two-dimensional plane formed by PC1 and PC2, the samples of air, natural camphor and synthetic mothballs could be distinguished, as shown in Fig. 13(b). The SVC data showed that the recognition accuracy could reach 98.33%. C$_2$ free radicals were also detected in high concentrations of synthetic mothballs volatile gases. In addition, Raman spectra of natural camphor and synthetic mothballs indicated that the characteristic peaks of the molecular vibration modes could be used as spectral fingerprints to distinguish mothballs.

Pesticide is an important means to control pests and diseases and maintain food production, which is widely used in modern agricultural production.\cite{110,111} Because many pesticides need to be applied in the form of spraying, the VOCs in them can easily enter the atmosphere, contaminating the ambient air and harming human health.\cite{112,113} Therefore, it is necessary to monitor the air near farmland.

Zhang et al. detected and analyzed the LIBS spectra of clean air, pesticide Decis and its active ingredient deltamethrin ($C_{22}H_{19}Br_2NO_3$, CAS:52918-63-5).\cite{114} CN molecular band, C$_2$ molecular band and Ca atomic line (422.672 nm) were detected in both pesticides and deltamethrin, as shown in Fig. 14 and Fig. 15. Two Br atomic lines (827.294 nm and 833.470 nm) were also seen in the spectrum of deltamethrin. In the above two spectra, it is found that some characteristic lines cannot be caught in the air, which indicates that it is feasible to use LIBS technology to monitor pesticide aerosols or VOCs emitted by pesticides.
CONCLUSION

Air pollution is a significant environmental challenge that affects human health and well-being. As nations worldwide become more aware of the impact of air pollution, there is an urgent need for advanced methods to prevent and control it. VOCs are one of the main air pollutants. The detection and source tracing of VOCs is essential to implementing control measures effectively. In this review, a method for detecting atmospheric VOCs based on LIBS is introduced. LIBS is a new method for material element analysis. Although it has been used more frequently to detect solid and liquid samples, its advantages of high sensitivity, high efficiency and requiring no sample pretreatment also make it ideal for the online detection of gas samples.

In this review, applications of VOCs in online detection based on LIBS technique are briefly introduced, and accurate qualitative analysis of halogenated hydrocarbons and sulfur-containing compounds was achieved by the spectra of halogen and sulfur elements, respectively. Then, according to the spectral characteristics of different VOCs, LIBS is combined with machine learning algorithm to successfully realize the source tracing of VOCs. In addition, in the listed cases, it is proposed that there are also differences in the spectra between isomers, and good classification results are obtained by LIBS combined with machine learning. Finally, the application of this technology to life scenes (detection of mothballs and pesticides) is briefly described.

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Notes

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--- Atomic Spectroscopy ---

**Description**
Quantitative analysis of trace and ultratrace elements in various samples

**Application**
Environment, Food, Medicine, Chemical, Materials, Biology

**Feature**
- Any application, any user, any location
- High sensitivity, high stability, high safety, simple operation, easy maintenance

**Description**
Qualitative and quantitative analysis of minor and trace elements in various samples

**Application**
Environment, Food, Chemical, Materials, Geology, Medicine

**Feature**
- Vacuum spectrometer, no purge gas required
- All wavelength acquisition and assistant functions
- 95% Ar for routine work, mini-touch with lower gas consumption, less cost

**Description**
Qualitative and quantitative analysis of trace and ultratrace elements in various samples. Available for LC-ICP-MS and LA-ICP-MS

**Application**
Food, Environment, Medicine, Biology, Chemical, Materials

**Feature**
- Excellent analytical performance, simple operation, easy maintenance
- 95% Ar for routine work, mini-touch with lower gas consumption, less cost

**Description**
Qualitative and quantitative analysis of trace and major elements in various samples

**Application**
Materials, Automobiles, Geology, Environment, Chemical, Medicine

**Feature**
- No pretreatment, non-destructive analysis
- Wide measuring range: 6ng–92μg, ppm–100%
- Air / Vacuum / Helium atmosphere, available for solid/powder/liquid

**Description**
AA-7800 Atomic Absorption Spectrophotometer

**Description**
ICPE-9820 Inductively Coupled Plasma Optical Emission Spectrometer

**Description**
ICPMS-2030 Inductively Coupled Plasma Mass Spectrometer

**Description**
EDX-8100 Energy Dispersive X-ray Fluorescence Spectrometer
We Want Images But We Make It Faster!

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LA-LIBS-ICP-TOFMS/μXRF

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- LIBS module for simultaneous in situ spectroscopy and mass spectrometry imaging
- μXRF nondestructive elemental imaging

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Customized Femto LA (for testing service only)
imageGEO193 (washout 1ms)
ESLumen LIBS Module
Nu Vitesse TOF-ICP-MS
TofWerk icpTOF R
Horiba XGT-9000 (15 μm resolution)

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