Liquid Cathode Glow Discharge as an Excitation Source for the Analysis of Complex Water Samples with Atomic Emission Spectrometry

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ABSTRACT: A liquid cathode glow discharge (LCGD) was developed as a low-power and miniaturized excitation source of atomic emission spectrometry (AES) for the determination of K, Na, Ca, and Mg in water samples from rivers and lakes. The discharge stability and parameter influencing the analytical performance of LCGD-AES were systematically examined. Moreover, the measurement results of water samples using LCGD-AES were verified by ion chromatography (IC). The results showed that the optimized operating parameters are a 660 V discharge voltage, pH = 1.0 HNO3 as the supporting electrolyte, and a 4.0 mL min⁻¹ solution flow rate. High concentrations of some metals may interfere with the detection of Ca and Mg. Low-molecular-weight organic substances do not have a remarkable enhancement on signal intensity. With the addition of 0.5% cetyltrimethylammonium chloride (CTAC), the emission intensity of elements can enhance significantly. However, it is not used to further evaluate the analytical performance due to instability of plasma after adding CTAC. The maximum power of LCGD is 52 W. The limits of detection and precision (RSD, in 1 mg L⁻¹) of K, Na, Ca, and Mg are 0.20, 0.02, 0.01, and 0.01 mg L⁻¹ and 0.9, 1.5, 0.6, and 1.2%, respectively. The measurement results of K, Na, Ca, and Mg in water samples by LCGD-AES are basically in agreement with the reference values measured by IC. The recovery of samples ranged from 84 to 113% except for Na, suggesting that the measurement results have high accuracy and reliability. All the results indicated that the LCGD-AES can provide an alternative analytical method for in situ, real-time, on-line determination of K, Na, Ca, and Mg in water samples from rivers and lakes.

1. INTRODUCTION

Direct elemental analysis of water samples is a crucial issue particularly for industry, agriculture, sanitation, and environmental protection.¹ Conventional analytical instruments, i.e., inductively coupled plasma-atomic emission spectrometer/mass spectrometer (ICP-AES/MS), atomic fluorescence spectrometer (AFS), and atomic absorption spectrometer (AAS), are the most effective tools for the determination of metals owing to their high sensitivity and stability.²⁻⁶ However, these commercial instruments are not suitable for in situ, real-time, and on-line continuous monitoring because they are bulky, expensive, with high energy consumption, and use inert/special gases.⁷⁻⁸ To meet the demands of in-field analysis, development of miniaturized and portable OES systems has already aroused great attention.²⁻⁶

In the last 20 years, electrolyte–cathode atmospheric glow discharge (ELCAD) as an alternative excitation source of atomic emission spectrometry (AES) has been developed to meet requirements of compact, portable, low cost, and on-site monitoring of metal elements.⁴⁻⁶ In ELCAD, the analyzed solution is bommbarded with the positive ions, and as a result of sample sputtering, the dissolved metals can be transferred to the plasma region where the excitation processes occur. Compared with ICP, ELCAD does not require support gas, operates in ambient air, consumes lower power (<75 W), and offers portable and low-cost instruments.⁴⁻⁵

ELCAD was first designed in 1993 by Cserfalvi et al. and then employed for direct multi-element analysis of solution samples.⁶⁻⁹ However, a drawback of this excitation source is the requirement for large sample consumption and a high flow rate (8–10 mL min⁻¹) because only in this way can the capillary surface be covered with solution for sustaining the continuous and steady discharge plasma.¹⁰⁻¹³ After that, in order to obtain miniaturized plasma sources, reduce the sample consumption, enhance discharge stability, and improve the detectability and emission efficiency, several similar discharge devices were developed by different groups.²,⁶,¹⁰ For example, Webb et al.¹⁴⁻¹⁵ reported a simplified device named solution cathode glow discharge (SCGD), which provided primarily a decrease in...
discharge volume (nearly 2 mm$^3$). With this new design, limits of detection (LODs) were greatly improved with most now in the ppb levels. Shekhar et al. designed a novel ELCAD setup that could generate plasma even at a 0.96 mL min$^{-1}$ flow rate using a V groove onto the capillary. Jamróz et al. constructed a miniaturized atmospheric pressure glow discharge (APGD) system in which the volume of the discharge was very small (6 mm$^3$). Marcus et al. proposed a liquid sampling-atmospheric pressure glow discharge (LS-APGD) for the analysis of solution samples, which could be operated at 0.3–1.0 mL min$^{-1}$ flow rates. Yu et al. developed a novel solution analysis system based on dielectric barrier discharge (DBD) in which the sample consumption was only 0.5 mL. Xiao et al. established an ac-electrolyte atmospheric liquid discharge (aEALD) system, which was operated at 0.1–0.8 mL min$^{-1}$ flow rates. In addition, György et al. reported that ELCAD could be used as an atom reservoir in atomic absorption spectrometry for analysis of the solution sample in which a significant increase in the sensitivity was found only with the addition of La solution.

Over the past 10 years, ELCAD-type has been widely employed for the detection of various real samples, including brines, mineral water, and brass samples as well as tea leaves, high-salinity well waters, tap water and snow, honeys, human hair and stream sediments, colloidal silica, titanium dioxide, and zirconoys. However, as far as we know, the LODs of the proposed method, the detection of K, Na, Ca, and Mg in water solutions of 1000 mg L$^{-1}$ K, Na, Ca, and Mg were obtained by National Center for Certified Reference Materials, Beijing, China. Methanol, ethanol, formic acid, acetic acid, and cetyltrimethylammonium chloride (CTAC) were analytical reagents purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Stock standard solutions of 1000 mg L$^{-1}$ K, Na, Ca, and Mg were obtained from Shanghai Chemical Reagent Corporation. All water samples were taken from West Lake, East Lake, Poyang Lake, Xixi Wetland, Yellow River, and Yangtze River.

The spectral resolution of the monochromator was 0.05 nm, the detectable spectral range was 200–800 nm, the grating was 1800 grooves mm$^{-1}$, and the PMT was running at −1000 V.

2. Reagents and Samples. HCl, HNO$_3$, and H$_2$SO$_4$ were of superior reagent grade and received from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Stock standard solutions of 1000 mg L$^{-1}$ K, Na, Ca, and Mg were obtained from National Center for Certified Reference Materials, Beijing, China. Methanol, ethanol, formic acid, acetic acid, and cetyltrimethylammonium chloride (CTAC) were analytical reagents purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Stock standard solutions of 1000 mg L$^{-1}$ K, Na, Ca, and Mg were obtained from Shanghai Chemical Reagent Corporation. All water samples were taken from West Lake, East Lake, Poyang Lake, Xixi Wetland, Yellow River, and Yangtze River.

2.3. Solution Preparation and Measurement Procedure. The pH of the solutions was measured with a pH meter (PHS-3E, INESA, Shanghai, China). The blank solution of pH = 1.0 was prepared with concentrated HNO$_3$. Single-element working standard solutions were prepared by dilution of stock solutions with high-purity water, adjusted to pH = 1.0, and then used to optimize the operating parameters. In order to assess the interference by coexisting ions, they were applied at 100 mg L$^{-1}$ in single-element working standards. Single-element working standard solutions with 3% (v/v) low-molecular-weight organic substances (i.e., HCOOH, CH$_3$COOH, CH$_3$OH, and CH$_2$CH$_2$OH) and a 0.5% (m/v) surfactant (i.e., CTAC) were used to investigate the effects of organic additives on the emission intensity. All water samples, including West Lake, East Lake, Poyang Lake, Xixi Wetland, Yellow River, and Yangtze River, were filtered with a 0.45 μm microfiltration membrane of cellulose acetate, diluted with deionized water, acidified with HNO$_3$ to pH = 1.0, then analyzed for three independent solutions, and averaged by LCGD-AES and IC.

The samples and standards were introduced by the peristaltic pump at a 4.0 mL min$^{-1}$ flow rate. The discharge was powered by a power supply operated at 660 V. After the emission signal was stabilized, a steady signal was recorded, and the average of 11 successively measured values of the emission intensity was used for evaluation. The background subtraction was achieved by determination of a blank solution (pH = 1.0 HNO$_3$). In all cases, LODs were defined as 3σ/$s$, where σ is the standard deviation corresponding to 11 blank measurements, and s is the
slope of the calibration curve. Relative standard deviations (RSDs) were calculated from the average and standard deviation produced from 11 repeated integrations of the signal.

The diluted water samples were also determined by an ICS-1500 ion chromatograph ( Dionex, USA) with a conductivity detector and eluent degassing module. Cations were separated with a CS12A ion-exchange column (250 mm × 4 mm, Analytic) and CG12A guard column (50 mm × 4 mm, Guard). The cation suppressor was a CSRS 300. Isocratic elution was employed for K+, Na+, Ca2+, and Mg2+ determination with 20 mmol L−1 methyl sulfonic acid (MSA) as the eluent (1.0 mL min−1). The injection volume was 25 μL, and the run time was set to 15 min.

3. RESULTS AND DISCUSSION

3.1. Spectral Characteristics of the LCGD-AES. The emission spectra of the LCGD-AES with a blank (a) and a 20 mg L−1 mixed solution of K, Ca, Na, and Mg (b) are presented in Figure 2. As can be seen on Figure 2a, the bands from 262.0 to 309.0 nm are ascribed to the OH (A′Σ′ → XΠI) 31 the lines at 656.3 and 486.1 nm are assigned to Hα and Hβ, and many lines from 410.0 to 470.1 nm are assigned to O II. All these active species are coming from the cathode sputtering of the electrode.32 In addition, the bands from 315 to 406 nm are attributed to the C3Πu → B3Πg of N2 because the discharge is operated in atmospheric air.33,34

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However, as shown in Figure 2b, the new lines of K I, Ca I, Na I, and Mg I appear at 766.6/770.1, 422.8, 589.1/589.7, and 285.4 nm, respectively. Moreover, the intensities of K I 766.6 nm and Na I 589.1 nm are higher than those of K I 770.1 nm and Na I 589.7 nm, respectively. In addition, the emission lines at 766.6 (K I), 422.8 (Ca I), 589.1 (Na I), and 285.4 nm (Mg I) are clearly isolated from the blank emission spectra. Therefore, the analytical lines at 766.6, 422.8, 589.1, and 285.4 nm are selected for qualitative determination of K, Ca, Na, and Mg in water samples.

3.2. Optimization of the Operating Parameters. The optimization of operating parameters is described in the Supporting Information (section S1), and the optimized values are given in Table 1.

3.3. Influence of Interfering Matrix Components. The matrix concentration affected the accuracy of the measuring result in liquid-sampling atmospheric pressure glow discharge (LS-APGD).20 So, it is not astonishing that the matrix concentration can also influence the determination of the element by LCGD-AES. Wang et al.29 found that different concomitants presented in sample solutions above certain levels can influence the electric conductivity of solutions.

3.3.1. Interference by Metal Ions. Jamróz et al.18 reported that the discharge in the APGD system was suppressed in the presence of relatively high concentrations of Mg (>100 mg L−1) and Na (>500 mg L−1). Therefore, further efforts are needed to decrease the matrix effect in complex samples. In this work, the effect of coexisting ions on the detection of 5 mg L−1 K, Ca, Mg, and 2 mg L−1 Na was investigated. The criterion for interference was defined as a tolerable error not exceeding ±15% in the detection of Na, K, Ca, and Mg. It is found in Figure 3 that 100 mg L−1 coexisting ions have no significant effect on the detection of K and Na, but 100 mg L−1 Ni2+, Cu2+, Co2+, Na+, K+, and Cr3+ have a remarkable effect on the detection of Ca. Meanwhile, 100 mg L−1 Ni2+, Co2+, and Cr3+ can also affect the detection of Mg. These results indicate that matrix elements present at high concentrations may seriously interfere with the determination of Ca and Mg.

3.3.2. Effects of Organic Additives. Many studies showed that the low-molecular-weight organic substances and surfactants may reduce the emission intensity of OH and only enhance metals that can be readily converted into volatile forms.23,24,27,36 So, the influence of adding low-molecular-weight organic substances on the recovery was also examined with pH = 1.0 HNO3 as the electrolyte solution. As shown in Figure 4, adding 3% (v/v) low-molecular-weight organic substances, i.e., HCOOH, CH3COOH, CH3OH, and CH3CH2OH, could not have a remarkable enhancement on emission intensity (unchanged the emission intensity for K and Na, even a slight decline in the intensity of Ca and Mg). So, we can say that the low-molecular-weight organic substances could not interfere with the detection of K I, Na I, Ca I, and Mg I. However, the signal intensities of each element increased dramatically with addition of 0.5% (m/v) CTAC (1.6-fold for Na, 5.6-fold for K, 1.9-fold for Ca, and 1.7-fold for Mg). Meanwhile, higher discharge current and unstable discharge plasma were observed in sample solutions with CTAC than in solutions without CTAC. This is because the presence of CTAC may increase the viscosity and decrease the surface tension of the solution, which could change the formation of cathode sputtering in the glow discharge.6,27,36 Unfortunately, due to instability of discharge plasma with addition of 0.5% CTAC, it was not used for further evaluation of analytical performance. The detailed mechanism of enhancing the emission intensity and evaluation of analytical characteristics by using CTAC are worthy of further investigation.

3.4. Analytical Performance. To estimate the detection performance of the LCGD-AES method, calibration curves at a concentration ranging from 1 to 10 mg L−1 were established

Table 1. Typical Operating Parameters of the LCGD-AES

| parameters          | values |
|---------------------|--------|
| discharge gap (mm)  | 2.0    |
| capillary diameter (mm) | 1.0    |
| discharge voltage (V) | 660    |
| supporting electrolyte | HNO3  |
| pH of the electrolyte | 7 = 1.0  |
| solution flow rate (mL·min−1) | 4.0    |
| spectral resolution (nm) | 0.05   |
| number of replicates | 11     |
under the optimized operation parameters. The power, calibration curve, $R^2$, LOD, and RSD are listed in Table 2. It is clear that LCGD-AES offers high sensitivity (the sensitivities of K, Na, Ca, and Mg are $1.8 \times 10^5$, $7.6 \times 10^5$, $1.2 \times 10^5$, and $4.9 \times 10^5$, respectively). The LODs of K, Na, Ca, and Mg at 660 V are 0.20, 0.02, 0.01, and 0.01 mg L$^{-1}$, respectively. The precision (RSD, $n = 11$ in 1 mg L$^{-1}$) is better since the RSDs varied in the range of 0.6–1.5%. The $R^2$ and power consumptions ranged from 0.9818 to 0.9997 and from 46 to 52 W, respectively. All results indicated that detection of metal elements by LCGD-AES has high sensitivity and precision and low LOD and power consumption. Therefore, LCGD-AES can be as an efficient excitation source for the detection of metal elements.

A comparison of the LODs obtained by the proposed method with other closed-type ELCAD-AES$^{1,5,9,14,18,29,36}$ for the determination of K, Ca, Na, and Mg is summarized in Table 3. As shown in Table 3, the LODs obtained with LCGD-AES are basically inferior to those of similar methods. This is mainly owing to the sacrifice of analytical performances to decrease the cost of the instrument (the total cost of LCGD-AES including sample introduction, excitation source, and spectral detection system is only about $14,000$). In addition, a high-resolution spectrometer with excellent performance, i.e., a Shamrock SR-500i equipped with an intensified charge-coupled device detector, could also improve the analytical performance and LODs.$^{5,37}$ It is worth mentioning that the LCGD excitation source is a portable instrument with low cost and power.

### Table 2. Analytical Performance of LCGD-AES for K, Na, Ca, and Mg at 660 V

| analytical line | voltage (V)/current (mA) | power (W) | calibration equation (dynamic range) | $R^2$ | sensitivity (mg L$^{-1}$) | LOD (mg L$^{-1}$) | RSD (%)$^a$ |
|----------------|--------------------------|-----------|-------------------------------------|-------|--------------------------|------------------|-------------|
| K I 766.6 nm   | 660/(70–75)              | 48.8–51.5 | $I = 3.4 \times 10^7 + 1.8 \times 10^6$ (1–10 mg L$^{-1}$) | 0.9997 | $1.8 \times 10^5$       | 0.20             | 0.9         |
| Na I 589.1 nm  | 660/(70–75)              | 48.8–51.5 | $I = 8.9 \times 10^7 + 7.6 \times 10^6$ (1–10 mg L$^{-1}$) | 0.9844 | $7.6 \times 10^5$       | 0.02             | 1.5         |
| Ca I 422.8 nm  | 660/(74–78)              | 48.8–51.5 | $I = 9.0 \times 10^7 + 1.2 \times 10^6$ (1–10 mg L$^{-1}$) | 0.9994 | $1.2 \times 10^5$       | 0.01             | 0.6         |
| Mg I 285.4 nm  | 660/(74–78)              | 48.8–51.5 | $I = 3.2 \times 10^7 + 4.9 \times 10^6$ (1–10 mg L$^{-1}$) | 0.9818 | $4.9 \times 10^5$       | 0.01             | 1.2         |

$^a$Standard concentration: 1 mg L$^{-1}$, $n = 11$. 

Figure 3. Influence of 100 mg L$^{-1}$ coexisting ions on the recovery of K, Na, Ca, and Mg (solution concentration: 5 mg L$^{-1}$ K, Ca, Mg, and 2 mg L$^{-1}$ Na, and other experimental conditions are the same as in Figure 2).

Figure 4. Influence of adding 3% (v/v) methanol, ethanol, formic acid, and acetic acid, and 0.5% (m/v) CTAC on the recovery of K, Na, Ca, and Mg (solution concentration: 5 mg L$^{-1}$ K, Ca, Mg, and 2 mg L$^{-1}$ Na, and other experimental conditions are the same as in Figure 2).
Table 3. Comparison of the LODs Obtained by LCGD-AES with Other Closed-Type ELCAD-AES for the Detection of K, Ca, Na, and Mg

| methods      | LOD (mg L$^{-1}$) | reference |
|--------------|-------------------|-----------|
|              | K                 | Na        | Ca        | Mg        |
| LCGD         | 0.20              | 0.01      | 0.02      | 0.01      | this work |
| SCGD         | 0.00049           | 0.011     | 0.00014   | 0.0055    | 1         |
| SCGD         | 0.00066           | 0.45      | 0.0005    | 0.34      | 5         |
| ELCAD        | 0.2               | 0.4       | 0.06      | 0.8       | 9         |
| SCGD         | 0.013             | 0.023     | 0.0008    | 0.019     | 14        |
| APGD         | 0.004             | 0.09      | 0.002     | 0.04      | 18        |
| SCGD         | 0.0002            | 0.011     | 0.00008   | 0.0002    | 29        |
| APGD         | 0.0004            | 0.36      | 0.002     | 0.1       | 36        |

To demonstrate long-term stability/repeatability of the proposed method, the emission intensity of K, Na, Ca, and Mg was continuously monitored at 766.6, 589.1, 422.8, and 285.4 nm, respectively. Figure 5 shows the change of emission intensity for 5 mg L$^{-1}$ mixed solution (experimental conditions are the same as in Figure 2).

3.5. Analysis of Natural Water Samples. It is found that direct determination of K, Na, Ca, and Mg in certified reference materials is not successful because the inherent analyte concentrations in certified reference materials are far below the LODs of LCGD-AES. To confirm the reliability of results obtained with this method, water samples from West Lake, East Lake, Poyang Lake, Xixi Wetland, Yellow River, and Yangtze River were selected and analyzed by LCGD-AES. The accuracy of LCGD-AES for the determination of K, Na, Ca, and Mg in water samples was also assessed by comparison with a reference method using IC. Due to the 1–10 mg L$^{-1}$ linear range of the calibration equation for K, Na, Ca, and Mg, water samples must be diluted appropriately (not diluted for K determination, diluted five times for Na determination, diluted 10 times for Ca determination, and diluted 2.5 times for Mg determination) by ultrapure water before determination. The measured results are summarized in Table 4. As shown in Table 4, rough agreement of the results obtained with two methods is achieved, demonstrating that measurement results using the LCGD-AES are accurate and reliable.

In addition, to verify the repeatability of the results obtained with the LCGD-AES, the recovery was implemented according to the standard addition method (2 mg L$^{-1}$ spiked concentrations of K, Na, Ca, and Mg in the diluted water samples). The results are listed in Table 5. It is found that all water samples have acceptable recoveries (84%–113%) except Na in all samples (recovery<90%). So, the results measured by LCGD-AES are accurate and reliable. Lower recovery of Na in all samples is not yet clear but indicates there are other interferences.

The $t$ test is used for calculating the $p$ value to find the statistical significance of the test. $p < 0.05$ suggests that the group means are different; otherwise, $p > 0.05$ indicates that both groups have identical means. The statistical results between LCGD-AES and IC are listed in Table 6. Almost all values of $t$ do not go over $t_{0.05} = 2.78$ ($t$ test for a confidence level of 95%). Meanwhile, most of the $p$ values (significant level) are higher than that of 0.05 (Table 6). The results suggested that

Table 4. Measurement Results of K, Na, Ca, and Mg in Real Water Samples by LCGD-AES and IC (mg L$^{-1}$)

| samples       | K               | Na               | Ca               | Mg               |
|---------------|-----------------|-----------------|-----------------|-----------------|
| LCGD          | IC              | LCGD            | IC              | LCGD            | IC              |
| East Lake     | 6.0 ± 0.2       | 5.3 ± 0.4       | 15.7 ± 0.1      | 15.8 ± 0.1      | 19.9 ± 1.7      | 25.4 ± 3.0      | 8.2 ± 0.2       | 7.9 ± 0.1       |
| West Lake     | 3.1 ± 0.2       | 2.4 ± 0.4       | 10.3 ± 0.7      | 11.5 ± 0.5      | 17.6 ± 1.5      | 23.1 ± 3.2      | 3.1 ± 0.1       | 2.9 ± 0.1       |
| Poyang Lake   | 5.3 ± 0.3       | 4.7 ± 0.2       | 8.8 ± 1.0       | 7.0 ± 0.9       | 47.6 ± 2.2      | 53.1 ± 3.4      | 16.0 ± 0.1      | 15.7 ± 0.3      |
| Xixi Wetland  | 4.3 ± 0.5       | 5.1 ± 0.2       | 10.2 ± 1.7      | 6.4 ± 1.7       | 28.4 ± 2.5      | 35.2 ± 3.4      | 4.7 ± 0.4       | 5.7 ± 0.5       |
| Yangtze River | 1.8 ± 0.1       | 1.9 ± 0.1       | 32.7 ± 2.5      | 14.7 ± 1.5      | 26.3 ± 2.1      | 31.2 ± 2.6      | 8.4 ± 0.1       | 8.2 ± 0.1       |
| Yellow River  | 2.1 ± 0.3       | 1.6 ± 0.2       | 22.1 ± 1.0      | 23.4 ± 0.8      | 36.6 ± 2.2      | 42.5 ± 3.1      | 11.7 ± 1.7      | 14.0 ± 0.7      |

Table 5. Recoveries (%) of K, Na, Ca, and Mg Determined in Water Samples by LCGD-AES (2 mg L$^{-1}$ K, Na, Ca, and Mg Was Added into All Water Samples, Respectively)

| elements   | East Lake | West Lake | Poyang Lake | Xixi Wetland | Yellow River | Yangtze River |
|------------|-----------|-----------|-------------|--------------|--------------|---------------|
| K          | 85.3      | 101.1     | 88.3        | 94.4         | 84.6         | 86.2          |
| Na         | 124.6     | 68.9      | 87.0        | 76.8         | 131.2        | 88.8          |
| Ca         | 91.2      | 89.9      | 85.7        | 90.2         | 84.4         | 96.1          |
| Mg         | 112.9     | 86.1      | 105.8       | 100.6        | 103.9        | 103.8         |
AES has the enormous potential for the determination of many elements in complex samples. Therefore, the developed LCGD-AES demonstrated that the results measured by LCGD-AES are roughly accurate and reliable. Therefore, the developed LCGD-AES has the enormous potential for the determination of many elements in complex samples.

4. CONCLUSIONS

The LCGD-AES system was successfully designed and established as a miniaturized excitation source for detection of K, Na, Ca, and Mg in water samples from rivers and lakes. High concentrations of some metals may interfere with the detection of Ca and Mg. Low-molecular-weight organic substances do not have a remarkable enhancement on signal intensity. When the surfactant of 0.5% CTAC was added into the solution, the emission intensities of elements can increase remarkably. The analytical performances obtained with LCGD-AES are basically inferior to those of similar methods. This is mainly owing to the sacrifice of analytical performances to decrease the cost of the instrument. The measurement results of LCGD were roughly consistent with the reference values of IC. Compared with other ELCAD-type, the LCGD-AES has low energy consumption, high excitation efficiency, and low cost. It can be developed as a promising portable, inexpensive, and simple instrument for continuous monitoring of metal elements under field conditions with further improvement.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01906.

Table 6. t Test and p Values between the Analytical Results Obtained by LCGD-AES and IC (n = 3)

| sample          | K     | Na     | Ca     | Mg     |
|-----------------|-------|--------|--------|--------|
| East Lake       | 2.74 (0.052) | 2.13 (0.100) | 2.76 (0.051) | 2.22 (0.091) |
| West Lake       | 2.65 (0.057) | 10.67 (0.0004) | 2.56 (0.063) | 2.65 (0.057) |
| Poyang Lake     | 2.76 (0.051) | 2.76 (0.051) | 2.77 (0.0502) | 2.74 (0.052) |
| Xizi Wetland     | 2.60 (0.060) | 1.83 (0.141) | 2.71 (0.054) | 2.29 (0.084) |
| Yellow River     | 2.75 (0.052) | 2.63 (0.058) | 2.74 (0.052) | 1.79 (0.148) |
| Yangtze River    | 2.60 (0.060) | 2.37 (0.077) | 2.36 (0.078) | 1.25 (0.279) |

*p<0.05 indicated that there were significant differences between IC and LCGD-AES.

Notes
The authors declare no competing financial interest.

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