



Simultaneously determination of multi metal elements in water samples by liquid cathode glow discharge-atomic emission spectrometry



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ARTICLE INFO

Article history:

Received 13 April 2016

Received in revised form 25 May 2016

Accepted 25 May 2016

Available online 27 May 2016

Keywords:

Liquid cathode glow discharge (LCGD)

Atomic emission spectrometry (AES)

Determination

Metal elements

Water samples

ABSTRACT

In this work, a liquid cathode glow discharge-atomic emission spectrometry (LCGD-AES) was constructed for simultaneously determination of K, Na, Ca, Mg and Zn in water samples (tap water, mineral water, Yellow River water and waste water), in which the glow discharge plasma was produced between the needle-like Pt anode and electrolyte around a quartz capillary cathode. The effects of the supporting electrolyte, discharge voltage and organic additives on emission intensity were investigated in detail. The limits of detections (LODs) of metals were compared with those measured by the closed-type electrolyte-cathode discharge-atomic emission spectrometry (ELCAD-AES). In addition, the measured results of water samples using LCGD were verified by ICP. The results showed that the optimal operation conditions are pH = 1 HNO₃ as supporting electrolyte, addition of 0.15% formic acid and 650 V discharge voltage. The R² and the RSD are ranged from 0.9887 to 0.9990 and 1.10% to 2.19%, respectively. LODs of K, Na, Ca, Mg and Zn are 0.02, 0.04, 0.19, 0.04 and 0.05 mg L⁻¹, which are in agreement with the ELCAD-AES, and satisfied the recommended levels of the China standards for drinking water quality. The obtained results of Na, K, Ca, Mg and Zn in water samples by LCGD and ICP have certain difference. This result provides an alternative analytical method for the determination of metal elements in water samples.

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1. Introduction

The determination of metal elements in real water samples is a very hot topic, especially for environment monitoring and environmental protection. The well-known high-performance spectrometric instruments, such as inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS), are widely used to accurately, sensitively and rapidly measure the micro and trace metal elements in all kinds of water samples. However, these methods are commonly performed at laboratories, requiring complicated equipment and operation [1]. These defects limit their applications mainly to laboratory settings, and hinder their use for real-time and on-line analyses under field conditions [1,2]. To meet the requirements of field arrangement and rapid determination, more compact low-cost micro-plasma emission source are highly desirable for in situ, real-time and on-line monitoring of metal element [3,4].

Over the past two decades, electrolyte cathode discharge-atomic emission spectrometry (ELCAD-AES) has received a rapid development [1–5]. It is considered a very promising alternative miniaturized excitation source which possesses potential advantages over commercially and analytically successful plasma sources because of its more compact and portable instruments, lower power consumption (<75 W), no inert gas requirement and operation in atmospheric pressure air [6,7]. Also, ELCAD has been successfully employed for the real time and on-line simultaneously detection of multi-elements in aqueous solution [8,9].

For the ELCAD, the solution containing the metal elements is the cathode and above it (about 1–5 mm) a metal rod, i.e., W or Pt, is the anode [5]. When the applied voltage was sufficiently high, a glow discharge is produced between the anode and the cathode at atmospheric air pressure. The atomic lines of metals dissolved in water samples appear instantaneously in the spectrum emitted by the ELCAD, in this way the content of metals in water samples can be detected [10,11]. Glow discharge devices are typically used as primary atomic spectrometry atomization/excitation sources for direct solid analysis with favorable analytical features [12]. In 1887, the first glow discharge apparatus using solution as an electrode was described by Gubkin. Despite observations of atomic emissions from glow discharge electrolysis throughout the 1950s and 1960s, the electrolyte cathode glow discharge (ELCAD) as a glow discharge electrolysis-like system was successfully

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designed for metal analysis only in 1993 [13]. However, the devices and stability of discharge need to be further improved, and moreover, their higher limits of detections (LODs) do not meet the requirements for detection of trace metals in environmental and biological samples. In order to improve the analytical performance, enhance the emission efficiency, and increase the sensitivity of determination, many improvements for discharge structure of ELCAD have been established based on the original design by Cserfalvi group [13,14], including the solution-cathode glow discharge (SCGD) [15], liquid sampling-atmospheric pressure glow discharge (LS-APGD) [16], drop spark discharge (DSD) [17], direct current atmospheric pressure glow discharge (DC-APGD) [18], alternating-current electrolyte atmospheric liquid discharge (AC-EALD) [19], and liquid electrode discharge [20]. In addition, the excitation principle and fundamental feature of ELCAD were studied by many authors [21–23] and also reviewed in recent years [5,10,11].

In the present work, we modified and designed a system termed as liquid cathode glow discharge-atomic emission spectrometry (LCGD-AES) based on the principle and characteristics of ELCAD, in which the glow discharge plasma was produced between the needle-like Pt anode and electrolyte around a quartz capillary cathode. This improvement of excitation source makes the solutions flow over the top of the capillary to be exhausted at any time by many grooves on the graphite carbon rod, results in conductive state of the circuit, and thereby increases the discharge plasma stability. Moreover, it can operate in air under atmospheric pressure. All these features make it attractive as a field instrument for metal element analysis and determination. In order to demonstrate the method's feasibility, direct determination of K, Na, Ca, Mg and Zn in water samples (tap water, mineral water, Yellow River water and waste water) by using LCGD-AES was chosen as the subjects. The effects of the supporting electrolyte, discharge voltage and addition of organic substances on emission signal were investigated in detail. The limits of detections (LODs) of metal elements were calculated and then compared with closed-type ECLAD-AES techniques. In addition, the measured results of water samples using LCGD were verified by ICP.

2. Experimental

2.1. The setup of LCGD system

The experiment setup of LCGD system is shown in Fig. 1. It contains DC high voltage power supply, sample introduction, glow discharge

system, and spectral detection. The DC high voltage source was a DH 1722-6 power supply (Beijing Dahua radio factory, Beijing, China) providing the voltage of 0–1000 V and the current of 0–0.5 A.

Water samples were introduced into the LCGD system by a quartz capillary (internal diameter 1 mm, external diameter 1.2 mm) with the aid of a peristaltic pump (Beijing Dongnan yicheng Laboratory Equipment Co., Ltd., YZ1515x) and its flow rate was controlled at 4.5 mL min^{-1} . To decrease signal fluctuations of glow discharge, several knots were tied in rubber tubing of peristaltic-pump. The discharge system mainly consists of two parts: a pointed platinum anode with a diameter of 1 mm was sealed into a quartz tube, while the water samples were pumped through the quartz capillary and flowed over the top of the capillary which in turn was served as the cathode. The quartz capillary was passed through a hole on the graphite rod. The excess part of capillary with graphite carbon rod was 2.5 mm. The graphite rod was fixed on the plug of reservoir. The discharge gap between the tip of the platinum and the top of the quartz capillary was about 2 mm. The solution, which overflowed from the tip of quartz capillary, was flowed into the reservoir by means of many grooves on the graphite rod. When the voltage was sufficiently high, the glow discharge plasma was produced between the electrolyte around quartz capillary cathode and needle-like Pt anode.

The glow discharge system was mounted on a manual precision translation stage with three orthogonal micrometer screw gauges, which could be controlled precisely in the x, y, and z directions to adjust position of the glow discharge plasma, obtain the maximum signal output and focus the discharge image into the entrance slit of monochromator (Zolix Instruments Co., Ltd., Omni-λ500) with a 1800 grooves/mm holographic grating. The discharge photographs were taken by ICCD camera of Andor technology (MN: DH334T-18U-03; SN: ICCD-05703). The emission spectrometry of discharge plasma was imaged with a quartz lens onto the vertical adjustable entrance slit of the monochromator. A PMTH-S1-CR131 photomultiplier tube (PMT) biased at -1000 V was used as the detector. Spectral resolution of the spectrometer is 0.05 nm.

2.2. Reagents and samples

HNO_3 , HCl and H_2SO_4 were of superior-reagent grade. KCl, NaCl, CaCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ were all of analytical reagent grade. De-ionized water ($>18 \text{ M}\Omega \text{ cm}$ resistivity) was obtained by a water

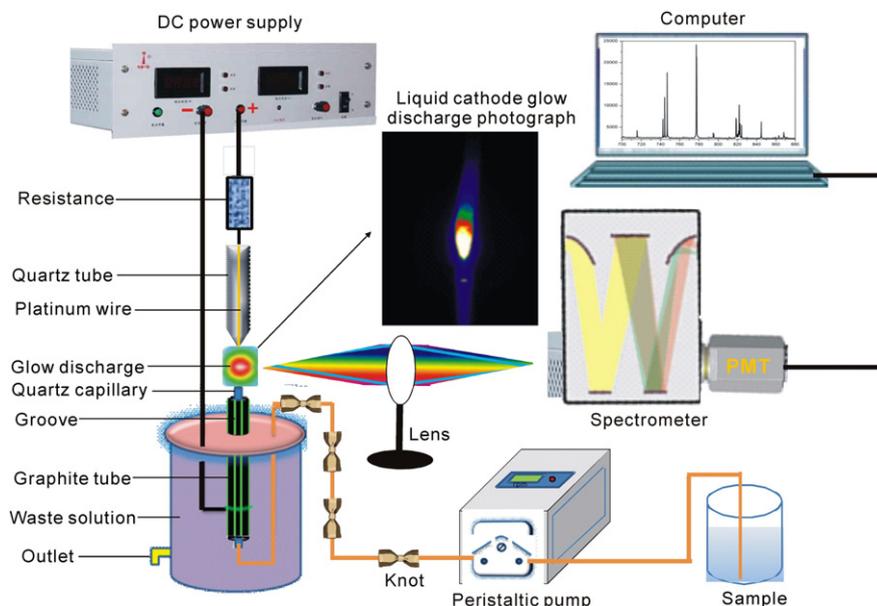


Fig. 1. Schematic diagram of the LCGD.

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