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Evaluation of flow injection-solution cathode glow discharge-atomic emission spectrometry for the determination of major elements in brines



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ABSTRACT

A new method for the determination of major metal elements in high salinity brines was developed by solution cathode glow discharge (SCGD) with flow injection analysis (FIA). The matrix interferences of major cations and anions in brines have been evaluated. It was found that high concentration of Na⁺ and K⁺ could interfere each other, K⁺ at a concentration of 400 mg L⁻¹ enhanced the signal intensity of Na⁺ more than 20%. The effect of the anions was observed and it was noted that the signal intensity of both Ca²⁺ and Mg²⁺ were suppressed significantly when the SO₄²⁻ reached 100 mg L⁻¹. It was demonstrated that some low molecular weight organic substances such as formic acid, glycerol and ascorbic acid could eliminate interference of SO₄²⁻ even with volume percentages of 0.5%. Under the optimized condition, the proposed FIA-SCGD can determine K, Na, Ca and Mg with the limits of detection of 0.49 (K), 0.14 (Na), 11 (Ca) and 5.5 (Mg) ng mL⁻¹. The proposed method has been successfully applied to the analysis of 5 salt lake samples and compared with those obtained with inductively coupled plasma atomic emission spectrometry (ICP-AES). The advantages of small size, low energy consumption, good stability and repeatability indicated that the SCGD is promising for the determination of major ions in brine samples.

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1. Introduction

Liquid discharge microplasmas have evolved to meet the requirement of compact, low cost and portable methods for the detection and measurement of metal elements [1–6]. The first use of the liquid discharge microplasmas incorporating a solution as the cathode for analytical atomic spectroscopy was reported in 1993 by Cserfalvi et al. [1] who later named this source as an electrolyte cathode glow discharge (ELCAD). ELCAD is an atmospheric-pressure glow discharge between a metal anode and the surface of a flowing electrolyte sample solution. The atomic lines of metals dissolved in the solution appear immediately in the spectrum emitted by the liquid discharge; in this way, the concentration of metals in a sample solution can be determined. Following this pioneering study, significant variations of the ELCAD design have been developed, including liquid sampling-atmospheric pressure glow discharge (LS-APGD) [7,8], solution cathode glow discharge (SCGD) [9–13], liquid electrode plasma

atomic emission spectroscopy (LEP-AES) [14–16], alternating current electrolyte atmospheric liquid discharge (ac-EALD) [17,18] etc.

Compared with ICP-AES [19], liquid discharge microplasmas such as the ELCAD or SCGD, offer several advantages in not requiring a gas source or solution nebulizer and being small and inexpensive. In addition, they produce relatively simple spectra largely devoid of ionic spectral lines and a low background with no strong continuum [4,20]. With such advantages the technique offers interesting possibilities for on-site or in-field application and some portable device have been invented such as LEP-AES (Micro Emission, Japan) [16], liquid electrode spectral emission chip (LEd-SpEC) [21], liquid-film dielectric barrier discharge (LFDBD) [22]. In recent years, liquid discharge microplasmas have been applied for the analysis of several real samples including water samples [17, 23–27], human hair [28], stream sediment [28], honeys [29], tuna fish [30], aquatic plant [30], colloidal silica [31], titanium dioxide [32], zircalloys [33,34], soils and spruce needles [26] etc. It was also demonstrated that adding low molecular weight organic compounds [17,24,30,33], (e.g., formic, acetic acids and ethylalcohol) results in varying enhancement of signals of several elements (Hg, Ag, Pb, Cd, Ni, Co, Fe, Mn, Mg, Cu, Ca and Se)

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in ELCAD. A similar signal enhancement was also achieved by adding non-ionic [25,26,29,35] (Triton X-45, Triton X-100, Triton X-114, Triton X-405 and Triton X-705), ionic [28] (cetyltrimethylammoniumchloride, CTAC) surfactants or the combination of a surfactant (Triton X-114) and potassium iodide [25]. All these studies demonstrated that ELCAD or SCGD could be used successfully for the determination of elements in various samples. It has also been confirmed that chemical interferences, such as the binding of calcium by phosphate, are also notable in ELCAD though effects can be mitigated by the addition of lanthanum [4]. Despite these progresses, to the best of our knowledge, liquid discharge has rarely been applied in high salinity samples [27], perhaps because of its complicated matrix. Brines represent a natural liquid mineral resource since it contains many useful components such as potassium, boron, lithium, strontium, and sodium. Many hypersaline lakes and underground brines are exploited for raw materials used in industry, agriculture and medicine [36]. Conventional analytical tools such as ICP-AES [19] and inductively coupled plasma mass spectrometry (ICP-MS) [37] are the most effective ways to determine these metal ion content. However, it is not easy to introduce high salinity solutions, since the salinity load may cause plasma instability, spectral interferences, and signal suppression and even nebulizers blocking. Flame atomic absorption spectrometry (AAS), which typically has a linear range of only about two orders of magnitude, is a particular problem [38,39] for the analysis of brines with wide concentration range and can only determine one element each time. Flame photometry is very simple and less time consuming method for determining mineral content but it needs a gas supply [40]. In contrast, for ELCAD/SCGD, the analyte is directly introduced to the plasma without the use of nebulizer, which results in reduced memory effects and avoids the problem of deposits blocking the system. Therefore, it is well suited to the analysis of brine samples.

In this study, we evaluated the determination of major metal elements in brines by solution cathode glow discharge atomic emission spectrometry with flow injection analysis (FIA). The matrix interference of major anions and cations in brines have been studied noting that some organic substances could eliminate

the interference of SO_4^{2-} , which could otherwise suppress the signals of Mg^{2+} and Ca^{2+} . The proposed method was successfully applied in the determination of K, Ca, Na and Mg in 5 salt lake samples. The analytical performance and results are comparable to traditional ICP-AES.

2. Experimental section

2.1. Instrumentations

A diagram of the experimental setup of FIA-SCGD-AES is presented in Fig. 1. It consists of sample introduction system, excitation source and spectrometer. The SCGD cell is composed of a tungsten rod electrode (2 mm diameter \times 60 mm length) and a reservoir (60 mm diameter \times 30 mm length) containing a graphite electrode with a quartz capillary (0.3 mm i.d) at the bottom. Samples are introduced into SCGD cell through the quartz capillary using a peristaltic pump with a six-way valve. The injection valve is fitted with a 100 μL sample loop. The carrier channel delivered 1.8 mL min^{-1} aqueous solution (pH 0.7; adjusted with HCl). Although the continuous sample introduction offers high sensitivity, FIA maintains the discharge and reduces memory effects of potassium and sodium or matrix interference when changing solutions. To reduce fluctuations caused by the peristaltic pump, an improvise pulse damper was included between the pump and the SCGD. This damper consists of a length of peristaltic pump tubing (1.52 mm inner diameter tygon tube) of 45 cm length coiled into a small volume. The distance between the top of the quartz and the tip of the tungsten electrode is $\sim 2 \text{ mm}$. A 5 k Ω ballast resistor is immersed in the electric circuit of the discharge to stabilize the discharge current, the discharge being powered by a Kepco (Flushing, NY) BHK 2000–0.1MG high-voltage power supply operated in constant-current mode at 65 mA with output voltage $\sim 1100 \text{ V}$. The cell was mounted on a platform built with three independent micrometer screw gauges, allowing precise adjustment in the x, y and z directions in order to obtain the maximum signal output. The discharge was imaged 2.5:1 with a fused-silica

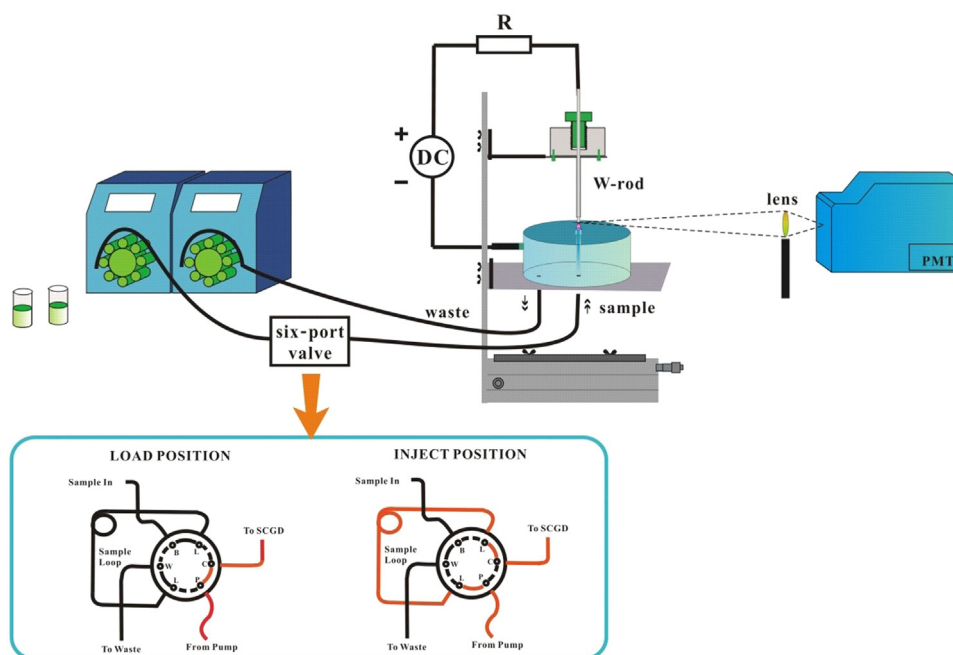


Fig. 1. A schematic diagram of the solution-cathode glow discharge cell used in this study generated in contact with a six-port valve. Sample or load solutions flow connections leading to the solution-cathode glow discharge dominated by six-port valve. The red line represents the solution flowing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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