Determination of potassium and sodium ions with diaphragm glow discharge plasma in aqueous solution

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Abstract. In the present work, a new apparatus of diaphragm glow discharge emission spectroscopy was described for the determination of potassium and sodium ions in aqueous solution. The discharge was formed in a pin hole on a dielectric diaphragm interposed between two submerged graphite electrodes. Effects of pH and applied voltage on the determination have been examined. It was found that decreasing the solution pH and increasing the applied voltage were favorable for the determination performance. Limits of detection for Na and K were 0.002 and 0.05 mg L⁻¹ under the optimum conditions, respectively. It demonstrates that the diaphragm glow discharge emission spectroscopy is a promising technique in measurements of metal ions in aqueous solution, because no optical interferences from the electrodes were found.

1. Introduction

Recently, electrolyte as cathode glow discharge (ELCAD) has been extensively investigated as a novel analytical tool to determine the concentrations of trace metals in aqueous solutions [1-8]. In ELCAD, a rod anode is placed over the surface of an aqueous solution, and a sheath of plasma is sustained between the anode tip and the solution as a high DC voltage is applied to the system. During ELCAD, the metal ions in the solution were sputtered to the plasma zone and were excited by three body reactions. These excited atoms will spontaneously radiate the characteristic atomic lines. As the intensity of these lines was often proportional to the concentration of the metal ions in the solution, ELCAD can be used for the quantitatively analyses of metal elements in liquids [3-8]. The most obvious advantage of ELCAD is its instrumental simplicity and high sensitivity. However, this process uses tungsten or platinum as the working electrode, which interfere the determination because of thermal radiation [9]. Previously, we designed a new diaphragm glow discharge plasma reactor in which the electrodes do not directly contact with the highly reactive plasma. The discharge mode used was termed as liquid diaphragm glow discharge (LDGD) [10]. Experimental results showed that the LDGD reactor could be operated in electrolytic solution with no direct electrode contact. Considering the problem of ELCAD, we attempted to use LDGD for the detection of aqueous Na and K.

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2. Experimental

Experimental apparatus consisting of a discharge reactor, a dc power supply and a series of measuring instruments were shown in figure 1.

![Experimental apparatus for the optical determination of Na and K.](image)

The discharge reactor was a quartz cylinder with 60 mm inner diameter containing two electrodes. The anode was a graphite rod (diameter: 0.5 cm) put into a quartz tube with a pin hole in the tube, which was immersed in 100 ml of dilute sulfuric acid solution. The cathode was placed in the reactor and was separated from the anode by the quartz tube.

A dc voltage varied from 0 to 1000 V was applied across the anode and the cathode. The bulk solution in the reactor was maintained at 293±2 K by running cooling water in the outer water jacket, in order to avoid the variation in discharge characteristics. A quartz fiber probe was located 10 mm vertically from the pin hole of the quartz tube, where the optical intensity emitting from the discharge was measured using a photo-multichannel analyzer (PMA–11, Hamamatsu Photonics Co., Ltd) with a wavelength ranging from 200 to 900 nm, where the measurement was repeated 20 times and the average value was recorded.

3. Results and discussion

3.1 Emission spectra

When the voltage was applied to electrodes, emissions were observed by the PMA–11 when the applied voltage was over 700 V. The emission spectra between 200 and 900 nm in 0.04 M H₂SO₄ solution containing 200 mg L⁻¹ K⁺ and 100 mg L⁻¹ Na⁺ at applied voltage of 850 V were shown in figure 2.

As indicated in figure 2, there are several lines and bands present in the spectra. The bands in the wavelength from 250 to 340 nm are due to the emissions of excited OH radicals. The main transitions of the OH radicals generated in the discharge are from A²Σ⁺ → X²Π [9]. The emission line at 656.3 nm were ascribed to the Hα (n=3 to n=2). Emission lines at 589 and 766.5 nm were attributed to the radiations of Na (2p⁶3p→2p⁶3s) and K (3p⁶4p→3p⁶4s) atoms [11].

H and OH are generated from the decomposition of H₂O. Although a high concentration of SO₄²⁻ ions are present in the solution, no emissions from S or SO were observed in the emission spectra. At the same time, no thermal emission was observed from the electrode [9]. The present investigation indicated that LDGD is a good tool for detection of aqueous metal ions because the discharge is simple...
and no emissions of the supporting electrolyte and of the electrodes were present.

![Emission spectra of LDGD](image)

**Figure 2.** Emission spectra of LDGD ([H$_2$SO$_4$]: 0.04 M; [K$^+$]: 200 mg L$^{-1}$; [Na$^+$]: 100 mg L$^{-1}$; voltage: 850 V; current: 340 mA)

3.2 Effects of experimental variables on the determination

The emission intensities of the K (766.5 nm) and Na (589 nm) increased with the concentration of these ions contained in the solution. As the emission intensity seems to increase linearly with the concentration in solution, the emission intensity with the concentration was fitted with the following equation:

$$I = A + Sc$$

where $I$ denote the emission intensity (counts) and $c$ is the concentration of metal ion in the solution. $A$ is the background emission intensity and $S$ is the detection sensitivity. The results at applied voltage 850 V are shown in figure 3.

![Calibration curve of the emission intensity versus concentration of K or Na ions in the solution](image)

**Figure 3.** Calibration curve of the emission intensity versus concentration of K or Na ions in the solution ([H$_2$SO$_4$]: 0.04 M; voltage, 850 V; current, 340 mA).

As shown in figure 3, straight lines with good correlation were obtained for both the K and Na ions.
The square regression coefficients $R^2$ were all close to 1 suggests that the emission intensity at 589 and 766.5 nm changed linearly to the concentration of sodium ion and potassium ion. So, the emission intensity at 589 and 766.5 nm can be used as the analytical signal for the determination of Na ion and K ion in the solution, respectively.

In order to ensure the maximum possible sensitivity and accuracy, effects of experimental variables on the determinations of Na and K were examined. The effects of applied voltage on the determinations of Na and K ions were shown in table 1.

**Table 1.** Effects of applied voltage on the determination of Na and K ions ([H$_2$SO$_4$]: 0.04 M)

| Voltage and current (V/ mA) | Determination of [Na$^+$] (mg L$^{-1}$) | Determination of [K$^+$] (mg L$^{-1}$) |
|-----------------------------|----------------------------------------|---------------------------------------|
| Calibration curve           | $R^2$                                  | Detection limit (mg L$^{-1}$)         |
|                             | Detection limit (mg L$^{-1}$)         |                                       |
| Calibration curve           | $R^2$                                  | Detection limit (mg L$^{-1}$)         |
|                             | Detection limit (mg L$^{-1}$)         |                                       |
| 750/254                     | 63 + 135 c                             | 0.997                                 |
|                             | 0.08                                   |                                       |
| 800/310                     | 137 + 253 c                            | 0.998                                 |
|                             | 0.01                                   |                                       |
| 850/340                     | 171 + 398.2 c                          | 0.999                                 |
|                             | 0.004                                  |                                       |
| 900/410                     | 183 + 431.4 c                          | 0.998                                 |
|                             | 0.002                                  |                                       |
| 950/460                     | 194 + 442.6 c                          | 0.997                                 |
|                             | 0.002                                  |                                       |

As indicated in table 1, all the determination sensitivities increased with increasing applied voltage. For example, when the applied voltage increased from 750 to 950 V, the determination sensitivity of Na at 589 nm increased from 63 to 194 counts per mg L$^{-1}$, while the sensitivity of K at 766.5 nm increased from 32 to 79 counts per mg L$^{-1}$. The detection limits can be obtained at 900 V, where 0.002 mg L$^{-1}$ for Na and 0.05 mg L$^{-1}$ for K.

Cserfalvi et al. [2] observed that the emission intensity of the lines depend strongly on pH of the water sample in ELCAD. Since the plasma generation mechanism is similar to that of ELCAD, effects of pH on the detection sensitivity were shown in figure 4.

**Figure 4.** Effects of pH on the detection sensitivity of Na and K ions (Applied voltage, 850 V; current, 340 mA).

As indicated in figure 4, the determination sensitivity decreased with increasing pH. However,
sensitivity did not increase further when the pH decreased to 1.0. Therefore, pH=1.0 maybe the optimum condition in the present investigations.

4. Conclusions
Decreasing the solution pH and increasing the applied voltage were favorable for the determination performance. Limits of detection for Na and K were 0.002 and 0.05 mg mg L⁻¹ under conditions of 900 V and pH < 1. The diaphragm glow discharge emission spectroscopy was a promising technique in measurements of metal ions in aqueous solution, because no optical interferences from the electrodes were present and the good detection sensitivity.

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