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ANALYSIS OF ALKALINE AND ALKALINE EARTH METALS IN STANDARD SAMPLES BY LIQUID ELECTRODE PLASMA OPTICAL EMISSION SPECTROMETER

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ABSTRACT---Sodium, potassium and calcium in standard sample solution were analyzed with a portable analyzer of liquid electrode plasma optical emission spectrometer (LEP-OES) to assess its validity for quantitative analysis. Reproducibility and sensitivity were investigated using different disposal sample chip and applied voltage. In the applied voltage of 800 V, there is no increasing period of emission intensity by consecutive measurement, and the relative standard deviation among chips was less than 20%. The sensitivity of emission intensity for Na and K were proportional to the applied voltage, but Ca was exponential. The sensitivity was different by kinds of element and applied voltage. According to its reproducibility, the spectrometer would be used for quantitative analysis.

1. Introduction

Optical emission spectrometry (OES) that also known as atomic emission spectrometry (AES) remains one of the most powerful methods for the determination of the elements and their compounds in variety of types of samples and in differing concentrations. Classical OES with arcs and sparks remains important for production and product control in industry. For the direct analysis of solids, however laser induced breakdown spectrometry is valuable alternative for aluminum alloys [1]. Direct current (DC) plasma was used to monitor aerosol samples [2] and alkaline metals in gas flow [3]. The development of DC and radio frequency (RF) as well as microwave microplasma has attracted for the suitability of the source for OES (atomic and molecular) species detection in air out of the carrying substrate [4]. The most commonly used radiation source for OES is the inductively coupled plasma (ICP). It is an important tool for the detection of molecular fragment and even for elemental analysis.

Recently, there is strong interest in miniaturization of analysis system to realize portability and to reduce instrument and operation cost. Miniaturized analytical devices also have advantages such as small sample volumes involved and low power consumption. Many prominent approaches have been performed to miniaturized plasma source [5-9] and OES for gas [5], liquid [6] and heavy metals samples [7]. A microplasma based on glow discharge optical emission spectroscopy has been demonstrated as effective detection method for miniaturized chemical analysis systems in aqueous analyts [10], and the benefits not only from low detection limit but also allows to atomic and molecular detection to aid analysis. Iiduka et al. and their research group inducted by Takamura [11-13] have recently developed a novel type of portable elemental analyzer, namely liquid electrode plasma optical emission spectrometry (LEP-OES).

Takamura and his groups find this principle of liquid electrode plasma by accident when their students apply too high voltage to separate ionic species in capillary electrophoresis, and light that identified as plasma is emitted. They consider that some elements are emitted from plasma. This phenomenon is applied to liquid electrode plasma. The principle of capillary electrophoresis is that charged molecules will migrate toward the opposite pole and separate from each other based on physical characteristics. The used apparatus and principle of capillary electrophoresis is similar to liquid electrode plasma, like as shown at figure 1.

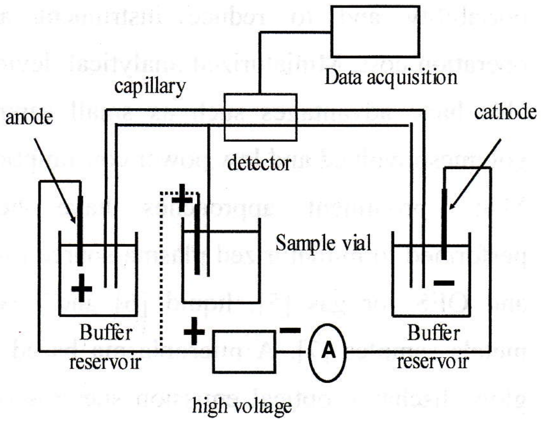

Figure 1. Instrumental set-up of capillary electrophoresis system [14].

This device was comprised from a polydimethylsiloxane (PDMS) micro channel and electrodes. The plasma is generated by confined electric current through a sample solution in a micro fluidic channel. The detection principle was as follows [12]. Solution samples introduced into a micro channel was applied with 20-1500 direct current voltage from Pt electrodes inserted into the reservoir at both sides. Solution at the micro channel is locally heated by concentrated electric current, and to form H_2O gas bubble, and subsequently generated plasma. Elements contained in a sample solution emit specific spectra by excitation by plasma, which was recorded with a compact micro spectrometer. The advances of this method are neither gas plasma nor nebulizer is required, no contamination from electrode because the electric field around the electrodes are low and plasma does not touch the electrodes, lower power consumption (~0.3W), small sample amount (<<1μL), handling and optical coupling are very easy because plasma is sealed in the channel, and ultra low background and high sensitivity.

They reported that intensity ratio for Na and K emission lines correspond to the molecular ratios [11], and lower detection limit for Cd in 0.1M HNO_3 was 300 ppb [12]. Dependencies of pH value of a sample solution were investigated by Iizuka et al. [12] and Wu et al. [15]. Lower pH values gave more intense emission peaks. Recently, Jo et al. [16] observed behavior of a microplasma and a micro-bubble in a sealed micro-fluidic glass chip, and reported that intensity of Pb emission line from the microplasma has a linear relationship in the 10-100 ppm regions.

The liquid electrode plasma optical emission spectrometry (LEP-OES) possesses a wide range of potential uses envisioned for the analyzer, including monitoring for harmful substances in drainage water and preliminary checks on soil or water quality, as well as the likes of process control in factories, incoming food inspections in the food distribution industry, and health and medicine applications. In 2007, the liquid electrode plasma optical emission spectrometer developed by Takamura's research group has been commercialized by Micro Emission Ltd [17]. In the present study, reproducibility and sensitivity were investigated to assess spectrometer's validity for quantitative analysis.

2. Experimental

The Handy Elemental Analyzer MH-5000 [16] (Micro Emission Ltd, Japan) was utilized for this experiment. The size and weight are 205 mm (L) x 115 mm (W) x 113 mm (H), and 1400 g, respectively. As a microscope, Ocean Optics miniature spectrometer USB 4000 was equipped. The experimental setup is shown in figure 1. A typical analytical procedure is as follows: The 40 μL of solution sample was put into a disposal chip, which is made from plastic. The high voltage of DC 600 V was applied by Pt electrodes for 10 ms for 10 times with 50 ms interval. This experiment was repeated 10 times. Some measurements were performed with 500-1200 V applied voltage and 5-100 ms supplied time.

The $NaNO_3$ (Nacalai, GR), 1000 ppm Ca standard solution ($CaCO_3$ in 1 M HCl; Nacalai), 1005 ppm K standard solution (KCl aqueous solution, Wako), 35% HNO_3 (Wako, GR) were utilized for preparation of standard and sample solution. The analyzed media is 0.1 M HNO_3 aqueous solution unless otherwise stated.

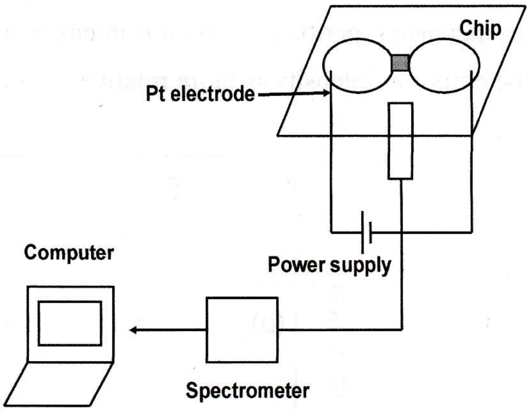

Figure 2. The experimental setup of handy liquid electrode plasma optical emission spectrometer [11-13].

3. Results and discussion

Figure 3 shows emission spectra of 0.1 M HNO_3 and 5 ppm Na in 0.1 M HNO_3. In the absence of Na^+, only two emission lines were observed at 309 and 656 nm due to OH groups and atomic H emission, respectively. By adding of 5 ppm Na into 0.1 M HNO_3, another emission line of sodium was observed at the wavelength of 589 nm.

The reproducibility of this spectrometer was examined by consecutive measurements using 3 disposal chips in different applied voltage. Figure 4 shows the reproducibility of sodium emission intensities at 589 nm for series of 10 ppm Na. At the applied voltage of 600 V, the relative standard deviation (RSD) for each chip is 17%, 23% and 27% respectively. It seems that at the first few measurement number there is increasing period of emission intensity with the sequential measurement. At applied voltage of 800 Volt, since the first to the last measurement, there is no increasing period of emission intensity and the emission intensity is more relative constant. The RSD for each chip is 15%, 17% and 18% respectively. The averaged value of 15 times measurements using 3 disposal chips could reflect on the absolute value of the sample with relative standard deviation less than 20% can be used for quantitative analysis. Of course that %RSD value is useful for some cases of quantitative analysis such as on-site or screening analysis, where easy, simple and fast analysis methods are be more emphasized than accuracy value, not for all cases of quantitative analysis.

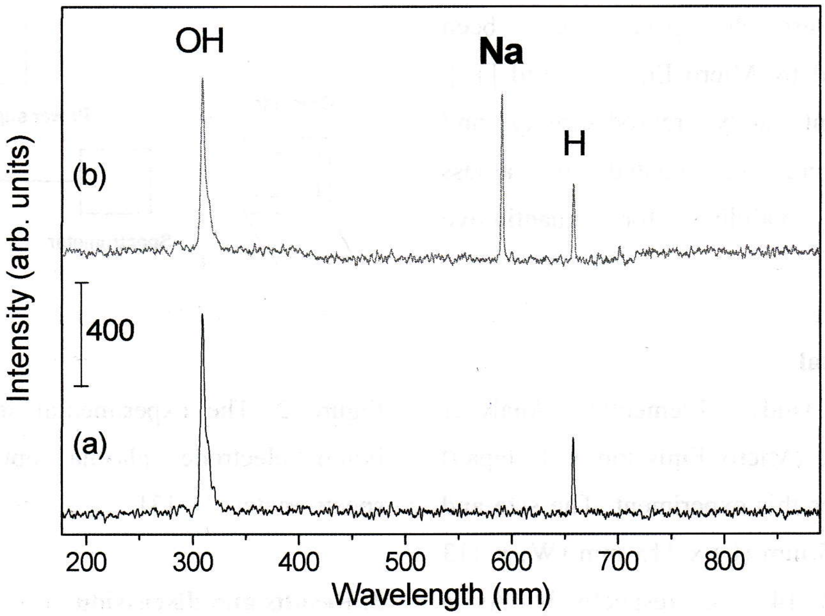

Figure 3.

Emission spectra of (a) 0.1 M HNO_3 (b) 5 ppm Na standard solution. Applied voltage: 600 V, 1 ms.

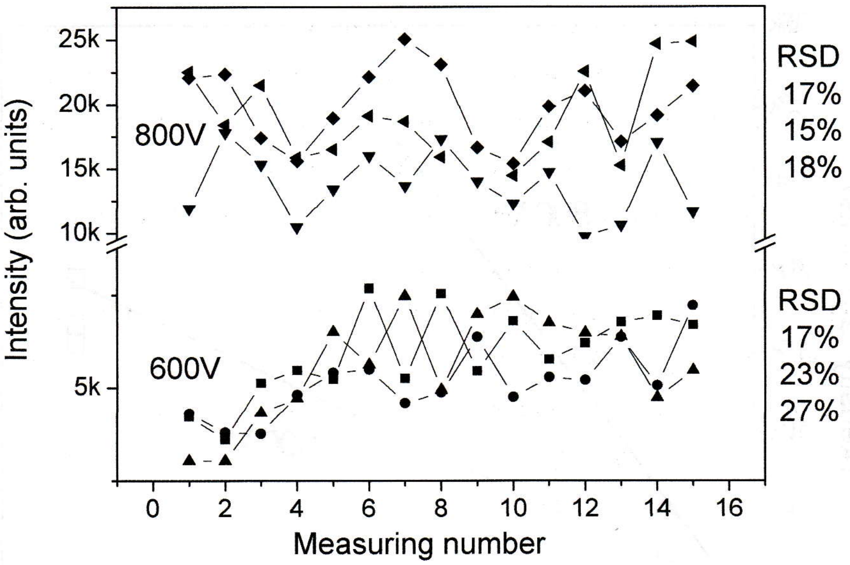

Figure 4.

Reproducibility of sodium emission intensity lines. Sample: 10 ppm Na in 0.1 M HNO_3, Applied voltage: 600 V and 800 V

Although the reasons why the emission intensity changes throughout successive measurement are not clear, one possible reason is assumed might be due to end-of-life of a disposal sample chip because the micro channel is pruned by plasma. The deformation of the micro channel might influence character of plasma. Another possible reason of the increment of emission peak intensities is assumed to be caused by somewhat changes in nature of the plasma caused by air bubble. The air small bubble in sub-millimeter diameter was confirmed even after the first measurement, and the size of remained bubble and the number increased with consecutive measurements. The existence of air bubble would reduce volume of solution where plasma generates.

Figure 5 shows calibration curves for Na emission. The higher applied voltage resulted in higher emission lines, as well as cases reported by Matsumoto et al. [12]. A linear relation was confirmed in 0-45 ppm region at the applied voltage of 600 V, but the region was limited below 20 ppm at the applied voltage of 800 V. This is because the equipped spectroscope could count below 30000 arbitrary units, and a calibration curve is saturated where the intensity reaches 30000 arbitrary units. Then, a dynamic range for an element would expand by choice of the suitable applied time and/or measuring time.

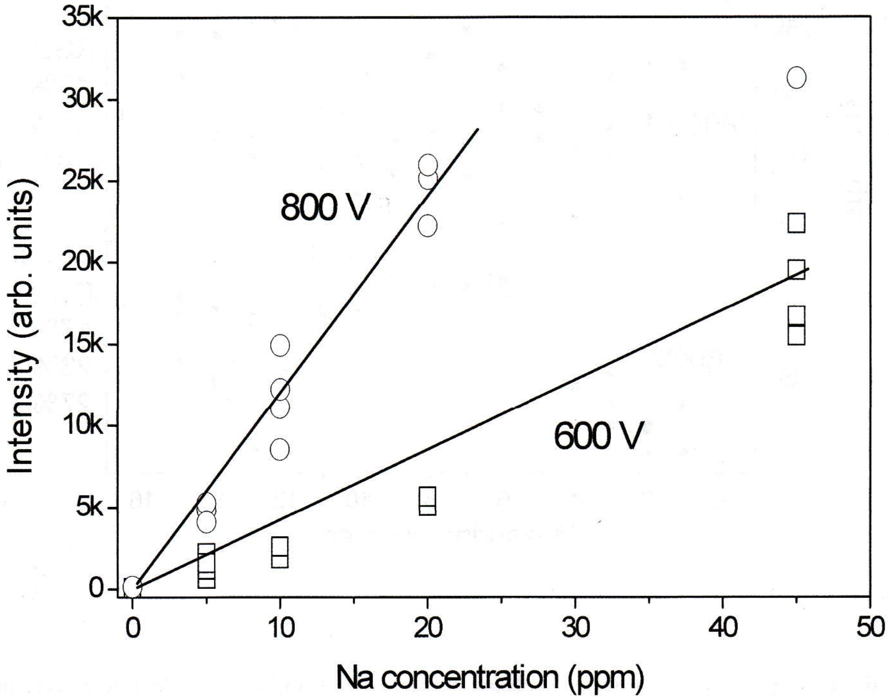

Figure 5.

Calibration curves for Na emission lines in 0.1 M HNO_3. Applied voltage: 600 and 800 V, 10 ms.

Dependency of applied voltage on each emission lines was investigated in more detail. Figure 6 shows emission spectra of Na, K and Ca-containing samples with different applied voltage. The concentration of Na, K, and Ca are 5, 10, and 100 ppm, respectively. With increasing the applied voltage, emission peak intensities for each emission line also increased. Intensities for these three emission lines were plotted as a function of applied voltage in Figure 7. It should be noted that emission intensity for Na and K is proportional to the voltage, but the emission intensity of Ca is assumed like parabola or exponential function. The relative sensitivity much differs by not only kinds of elements, but also the applied voltage due to differences of their excitation energy. The evaluated relative sensitivities of K and Ca to Na per weight were 1/30 and 1/400 at 600 V, 1/30 and 1/200 at 800 V, and 1/20 and 1/60 at 1200 V, respectively

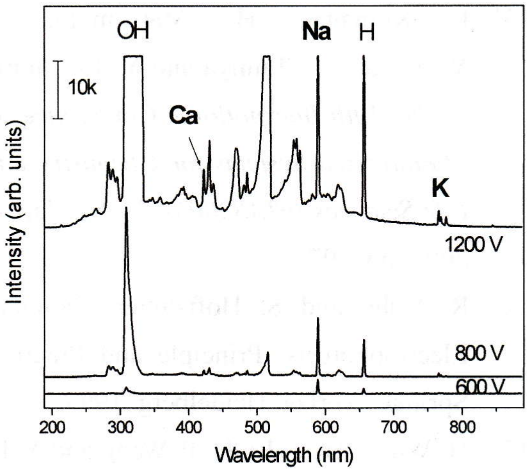

Figure 6. Dependency of applied voltage on emission spectra. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, 0.1 M HCl. Applied voltage: 600, 800 and 200 V, 5 ms.

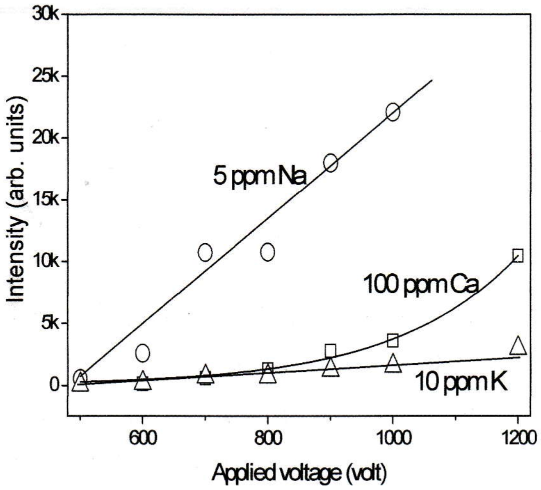

Figure 7.

Emission intensities for Na, K and Ca lines with different applied voltage. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, 0.1 M HCl. Applied voltage: 500-1200 V, 5 ms.

4. Conclusions

Sodium, potassium and calcium in indicated standard sample solution were analyzed with a portable analyzer of liquid electrode plasma optical emission spectrometer (LEP-OES) to assess its validity for quantitative analysis. Reproducibility and sensitivity were investigated using different disposal sample chip and applied voltage. At applied voltage of 800 V, there is no increasing period of emission intensity with the sequential measurement, and the relative standard deviation (RSD) among chips was less than 20%. The sensitivity of emission intensity for Na and K were proportional to the applied voltage, but Ca was exponential. The relative sensitivity much differs by not only kinds of elements, but also the applied voltage due to differences of their excitation energy. The evaluated relative sensitivities of Na/K/Ca were 200/6/1 at applied voltage of 800 V. According to its reproducibility and sensitivity, the spectrometer would be used for quantitative analysis.

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