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Analysis of Sodium, Potassium and Calcium using a Portable Liquid Electrode Plasma Optical Emission Spectrometer

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Abstract

Elements of sodium (Na), potassium (K) and calcium (Ca) in beverage samples and river water were analyzed with portable liquid electrode plasma - optical emission spectrometer (LEP-OES). The degree of reproducibility for emission intensities and individual variety of a disposal sample chip were investigated, and measuring conditions for quantitative analysis and the precision was discussed. The sensitivity for Na was higher than those for K and Ca by one or two orders of magnitude. Several ppm of Na and K, and several hundred of Ca in aqueous samples could be quantitatively analyzed with 2-30% of deviation without internal standard. The applied voltage was predominant factor for accurate quantitative analysis, and 800 V was found to be the best voltage estimation for quantitative analysis of alkaline metals contents.

Keywords*: liquid electrode plasma - optical emission spectrometer*

Abstrak

Telah dianalisis unsur-unsur sodium (Na), potassium (K) and kalsium (Ca) dalam sampel minuman dan air sungai menggunakan spektrometer emisi optic portabel - plasma elektroda cair. Tingkat reproduksibilitas untuk emisi radiasi dan variasi chip yang digunakan diukur, kemudian dibahas pula kondisi pengukuran dan presisinya untuk analisis kuantitatif. Sensitivitas Na lebih tinggi satu atau dua kali dari pada K dan Ca. Beberapa konsentrasi dari Na dan K (dalam ppm), serta beberapa ratus konsentrasi Ca (dalam ppm) dalam sampel air dapat dianalisis secara kuantitatif dengan deviasi 2-30% tanpa menggunakan standar internal. Tegangan yang diberikan merupakan faktor dominan untuk analisis kuantitatif yang akurat, dan didapatkan bahwa 800 V merupakan estimasi tegangan yang terbaik untuk analisis kuantitatif kandungan logam alkali.

Kata kunci*: plasma elektroda cair - spektrometer emisi optis*

INTRODUCTION

Recently, miniaturization of dimension of analytical instrument has been interest in a field of elemental analysis because of several advantages such as the lower power consumption, small size, light weight, and easy perform to on-site analysis. There are several methods to determine the composition of elements such as inductively coupled plasma (ICP), X-ray fluorescence spectrometry, atomic absorption spectrometry, ion chromatography, etc. Although a portable X-ray fluorescence spectrometer has been commercially available and utilized for on-site analysis, detection of light element is not easy because energy of these characteristic X-rays are low. Most of other kinds of apparatus are usually utilized at the fixed place.

Microplasma based optical emission spectroscopy has been attracted attention as for effective detection method for miniaturized elemental analysis systems [1-3]. Recently, Takamura and his research groups found light emission from solution in a micro channel when high voltage was applied from both sides. They subsequently investigated this phenomenon and developed as a novel type of portable elemental analyzer, namely liquid electrode plasma optical emission spectrometry (LEP-OES) [4-6]. The advances of this method are neither gas plasma nor nebulizer is required, lower power consumption (~0.3 W) and small sample amount (<<1 μL). The plasma generation in a micro channel was confirmed by Wu et al. [7] and Jo et al. [8].

The principle of LEP-OES is different from that of electrolyte-cathode discharge [9, 10], and the mechanism was proposed by Matsumoto et al. [5] as follows: (1) solution samples are introduced into a micro channel with the direct current applied voltage of 200-1500 volt from Pt electrodes inserted into the reservoir at both sides; (2) solution in the micro channel is locally heated and evaporated by concentrated electric current; (3) H_2O gas bubble is formed by this heating, and then plasma generates; (4) impurities in solution are sputtered into the plasma, and emit light with specific spectra depend on element contents in solution sample. Then, analysis of emitted light would give the quantitative and quantitative information of a sample solution. They reported that intensity ratio for Na and K emission lines corresponds to the atomic ratios[5], and lower detection limit for Cd in 0.1 M HNO_3 was 300 ppb [5]. Iizuka et al. [6] and Wu et al. [7] reported that lower pH values in acidic region gave more intense emission peaks due to increment of electric conductivity of a sample solution. Recently, Jo et al. [8] monitored behavior of a microplasma and a micro-bubble in a sealed micro-fluidic glass chip. They also reported in the same literature that intensity of Pb emission line 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. [11]. Since 2004, their work about this spectrometer has been appeared in three conference proceedings [4-6], but not in academic journals. In the present study, we measured emission spectra of alkaline-containing solution with various conditions, and assessed its reproducibility, accuracy and sensitivity for alkali and alkaline earth elements to apply it for qualitative and quantitative elemental analysis.

EXPERIMENTAL

The Handy Elemental Analyzer MH-5000 [11] (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. The electric power is supplied by a 9 V dry battery which is accommodated inside the package. A disposal sample chip is made of plastic, the size of which is 200 μm in width and 70 μm in height. As a microscope, Ocean Optics miniature spectrometer USB4000 is equipped. A typical analytical procedure is as follows: (1) the 40 μL of a solution sample put into a disposal sample chip; (2) the high voltage of DC 800 V is applied by Pt electrodes for 3 ms, and repeated 10 times with 5 ms interval for one measurement; (3) Successive ten sets of procedure (2) are carried out using the same chip. Some measurements were performed with 500-1200 V applied voltage.

The $NaNO_3$ (Nacalai, GR), $Ca(NO_3)_2 \cdot 4H_2O$ (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 set as 0.1 M HNO_3 aqueous solution unless otherwise stated.

RESULTS AND DISCUSSION

Dependency of applied voltage

Figure 1 shows emission spectra of 0.1 M HNO_3 and 893 ppm Ca^{2+} in 0.1 M HNO_3 sample at the applied voltage of 800 V. In the absence of Ca^{2+}, intense two lines due to OH (309 nm) and atomic H (656 nm) emission were mainly observed. A broad band around 515 nm is assigned as C_2 species so called Swan bands [12], which might result from plastics utilized in disposal sample chip. The presence of Ca^{2+} in the sample solution gave additional atomic emission line at 423 nm and two CaOH molecular emission lines [12] at 553 and 623 nm.

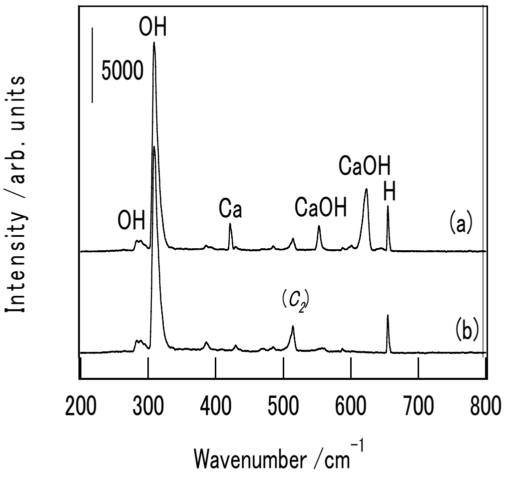

Figure 1. Emission spectra of (a) 893 ppm Ca solution in 0.1 M HNO_3 and (b) 0.1 M HNO_3 at the applied voltage of 800 V.

Figure 2 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. Note that the aqueous media is 0.1 M HCl for once because the original standard Ca solution purchased has been prepared by dissolving of $CaCO_3$ in 1 M HCl. At the 500 V of applied voltage, single emission line due to Na at 589 nm was confirmed along with OH and H emission intensities. The higher applied voltage resulted in higher emission lines, as well as cases reported by Matsumoto et al. [5]. Complicated many emission lines appeared at the applied voltage above 900 V. All the intensities enhanced with the voltage increasing.

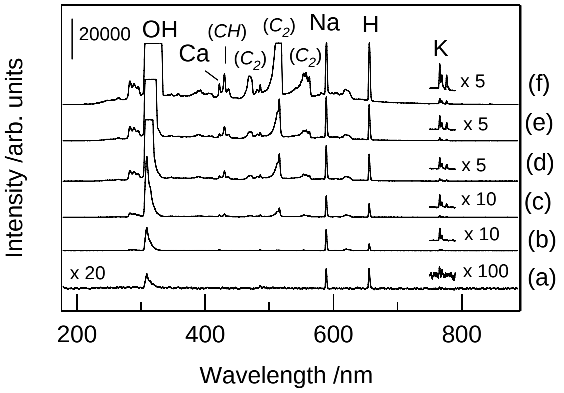

Figure 2. Emission spectra of Na, K and Ca containing standard sample solutions at different applied voltage. Applied voltage: (a) 500, (b) 700, (c) 800, (d) 900, (e) 1000 and (f) 1200 V. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, media: 0.1 M HCl.

Emission intensities for three kinds of elements were plotted as a function of applied voltage in Figure 3. It should be noted that the intensity for Na is proportional to the voltage, while that for Ca is exponential. The relative sensitivity depends on not only kinds of elements, but also the applied voltage due to differences in their excitation energy. In a case of Ca emission line at 422 nm, the intensity increased with the applied voltage; however, the degree of increment in the adjacent CH emission line was also remarkable. Overlapping of the two emission lines was negligible at the applied voltage of 800 V. As a result, the higher applied voltage does not always increase the signal to background ratio, especially in the low concentration. Note that the equipped spectroscope could count below 30,000 arbitrary units as shown in Figure 2. Then, the suitable applied voltage should be determined individually for a target element, the concentration and coexisting substrates.

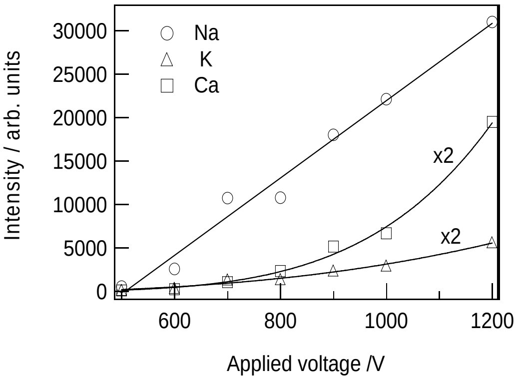

Figure 3. Dependency of applied voltage on emission spectra. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, 0.1 M HCl.

Reproducibility

The variation from lot to lot of a disposal chip, and effects of consecutive measurements on the emission intensity were next investigated. Successive measurement of 10 ppm Na containing 0.1 M HNO_3 sample gave randomly varied peak intensities. The relative standard deviations for 10 times measurement at the applied voltage of 800 V were 9-26 % against eight times runs. Each disposal chip also gave different emission intensity. However, the deviation of the averaged analytical results (22 % for eight chips) was the same level as those for individual consecutive measurements. It should be noted that systematic increment of the emission intensity throughout successive measurements were often confirmed at the applied voltage of 600 V, while any systematic increment was not confirmed in cases for 800 V. The typical results are shown in Figure 4. At the applied voltage of 600 V, averaged peak counts for the first five times measurements were smaller than those for the following five measurements in most cases (7 times occurred in eight times measurements). The reason for this increment behavior is not sure. One possible reason is results from its low applied voltage; i.e., the 600 V might not be enough to reach equilibrium for one measurement. In the present study, we confirmed that averaged value of 80 times measurements at the applied voltage of 800 V using 8 disposal chips (10 times measurements for each chip) could reflect on an absolute value o with 2-30 % of the accuracy.

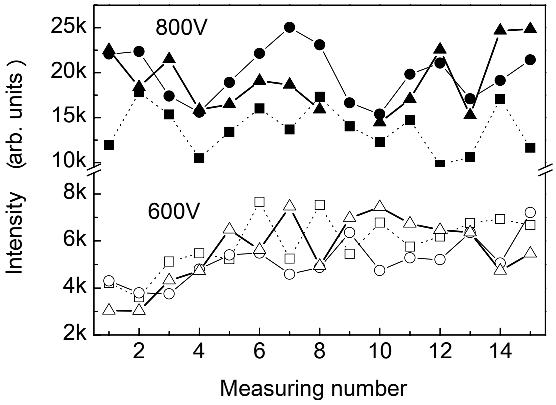

Figure 4. Variation of intensity for Na emission line throughout consecutive measurements with individual sample chip. Sample: 10 ppm Na in 0.1 M HNO_3. Applied voltage: 600 or 800 V.

Quantitative elemental analysis

Figure 5 shows intensities of emission lines for Na, K and Ca species at various concentrations. For each concentration, we adopted averaged values of the corresponding 50-80 measurements using 5-8 chips at the applied voltage of 800 V. It is obvious that sensitivity quite differs with elements, and each element gave linear relationship between the concentration and emission lines. Differences of relative sensitivity for each element are mainly results from the specific excitation energy and/or dissociation energy of the corresponding M-O and M-OH bonding. The relative sensitivities of K and Ca to Na per weight were ca. 1/25 and 1/700 at 800 V. Note that an emission spectrum for 20 ppm Ca solution gave a tiny peak due to Ca emission at 422 nm, but the intensity was too weak for its evaluation at the measuring condition.

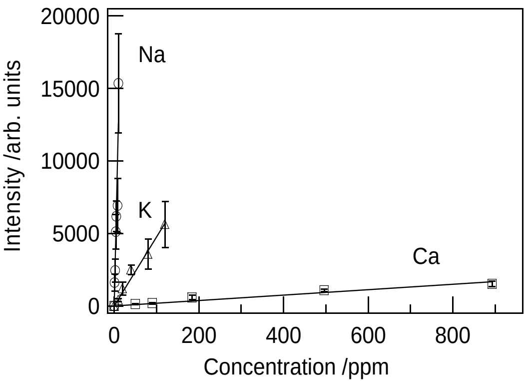

Figure 5. Emission intensities for Na, K and Ca species at various concentrations in 0.1 M HNO_3. Applied voltage: 800 V.

The bottled drinking water and orange juice samples are commercially available one, and the contents of some elements have been indicated at the outside part of the package. Although we did not confirm the contents using other methods such as ion chromatography or ICP-OES spectrometry, the indicated values were also listed in the table as an authorization value. The measured emission spectra are shown in Figure 6. The emission spectrum of orange juice possesses intense lines due to K and Na, accompanied with emissions for OH and H. In spectra of two kinds of bottled drinking water, emission lines for potassium were weak or trace level, but those of sodium were evident in both spectra. A bottled drinking water contains plenty amount of alkaline earth elements of Ca and Mg, and then an atomic emission line due to Mg was confirmed at 284 nm overlapping with a broad band due to OH. Estimated values for bottled drinking water A were half or one-third of the authorized values, but the orders were consistent. Results for bottled drinking water B and orange juice were well consistent with the authorization ones. Note that bottled drinking water B contains 77.9 ppm of SiO_2 according to the authorization value; however, any emission lines due to Si were not confirmed because of its insufficient sensitivity. Finally, we analyzed one river water (Adogawa river, Shiga, Japan) as for an unknown environmental samples. As shown in Figure 6, only sodium emission line was detected accompanied with those for H and OH. The contents of other elements such as K and Ca were below detection limit. The detected sodium can be quantitatively estimated as 3.7 ppm.

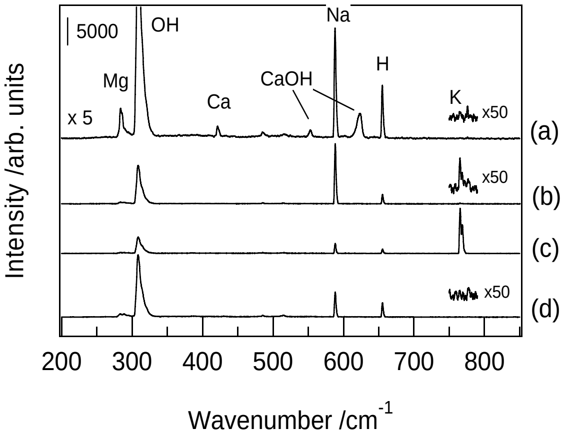

Figure 6. Emission spectra of (a) bottled drinking water A, (b) bottled drinking water B, (c) orange juice, and (d) Adogawa river water. The 1 M HNO_3 aqueous solution was added to each sample to set as 0.1M. Each sample was addedd Applied voltage: 800 V.

CONCLUSION

The emission spectra of Na, K and Ca species were recorded with a handy liquid electrode plasma optical emission spectrometer, and the measuring conditions for quantitative analysis were investigated. The emission intensity depended on the applied voltage of liquid electrode, and the dependency differed by elements. The relative sensitivities of K and Ca to Na per weight were ca. 1/25 and 1/700 at 800 V. The intensity of Na emission line increased with a sequential measurement at the applied voltage of 600 V, but the increment did not occur at the voltage of 800 V. Even in a continuous analysis using the same sample chip, emission intensity changed randomly with the relative standard devization of Ca 20 % throughout ten measurements. Every disposal chip also gave different emission intensity, but the accuracy was improved by averging procedure for some dozen times measurements using several chips. In a case for 10 ppm Na in 0.1 M HNO_3 at the applied voltage of 800 V using disposal chips, the relative standard deviation for 80 times measurements ushing 8 chips was 22 % without using any internal standards. The accuracy would be improved by use of appropriate internal standard.

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