

## **Quantitative Elemental Analysis of Alkaline Metals in Environmental Samples using Liquid Electrode Plasma Optical Emission Spectrometer**

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### **Abstract**

*Element in bottle drinking water, 100% orange juice and coffee and unknown element and concentration in environmental sample were quantitatively analyzed using a portable elemental analyzer of liquid electrode plasma optical emission spectrometer. In order to carry out this purpose, calibration of known element sample was firstly prepared by measuring its emission intensity in various concentrations. Sodium and potassium were commonly detected by this spectrometer, however other elements such as calcium and magnesium were not detected due to the minimum detection limit. The detected element by this portable analyzer shows that its accuracy is enough for quantitative analysis of environmental samples.*

**Keywords:** *elemental analysis, liquid electrode plasma optical emission spectrometer*

### **Abstrak**

*Elemen dalam air minum kemasan, jus jeruk 100%, dan kopi serta elemen tak dikenal dan konsentrasinya pada sampel lingkungan dianalisis secara kuantitatif menggunakan analyzer elemen yang portabel pada spektrometer emisi optik jenis plasma elektroda cair. Untuk melakukan hal ini, pertama-tama harus dilakukan kalibrasi dari sampel elemen yang tak diketahui dengan pengukuran intensitas emisinya dalam berbagai konsentrasi. Pada umumnya sodium dan potassium terdeteksi dengan spektrometer ini, tetapi beberapa elemen lain seperti kalsium dan magnesium tidak terdeteksi disebabkan natasan minimum deteksinya. Dari elemen yang terdeteksi dengan analyzer portable ini menunjukkan bahwa akurasinya baik untuk analisis kuantitatif pada sampel lingkungan.*

**Kata Kunci:** *elemental analysis, liquid electrode plasma optical emission spectrometer*

### **INTRODUCTION**

Detection of element content in substances is an important issue, including in commercial beverage such as milk, juice, coffee, etc. Bao et.al. [1] analyzed trace elements using X-ray fluorescence in fruit juice characterized by a high content and other soluble solid substances. Some alkaline metals such as sodium and potassium are detected in muskmelon, pineapple and orange juice. Several alkaline earth metals such as magnesium, calcium and zirconium were also detected in their analyzed fruit juice samples. Barends [2] was determined the trace metal in fruit, juice and juice products using an axially viewed plasma of inductively coupled

plasma optical emission spectrometry. Several alkaline and alkaline metals such as sodium, potassium, and calcium were detected in analyzed samples.

In the particular case such as on-site or screening analysis, portable analyzer apparatus is required. A novel type of portable elemental analyzer, namely liquid electrode plasma optical emission spectrometry (LEP-OES) offers the possibility to easily perform elemental analysis, including monitoring for incoming food and beverages in industry, and health and medicine applications. LEP-OES is also suitable for analysis samples in environmental such as rain water, water in river, sea, lake, and so on. Iiduka et al. [3] reported

that LEP-OES have high sensitivity for “on-site analysis” in the detection of toxic element such as water, soil, and food.

Lake Biwa is located in Shiga Prefecture, east of Kyoto, and is the largest freshwater lake in Japan. Many scientific have been studied about Lake Biwa. Mito et al [4] were determined the concentration of dissolved elements Al, P, V, Cr, Mn, Fe, Ni, Zn, As, Y, W, and U using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS; JMS-Plasmax 1, JEOL, Tokyo, Japan). The concentrations of dissolved Mg, Si, Ca, and Sr were determined using an ICP-atomic emission spectrometer (ICAP-96-953, Nippon Jarrell Ash, Uji, Japan). Using this method, the spatial and temporal distributions of 16 elements were observed in Lake Biwa from May 1994 to December 1998. Moreover, to elucidate the budget of the dissolved elements, the concentrations in river water and rainwater samples were also determined. Another researcher, Sugiyama et al. [5] was determined the dissolved concentration of major and trace element in Lake Biwa water as follows: Na and K were determined with a Hitachi (Tokyo, Japan) model 180-80 Zeeman atomic absorption spectrometer. Mg, Ca, Sr, Ba, and Si were simultaneously and directly determined with a Japan Jarrell Ash (Uji, Japan) model ICAP-96-953 inductively coupled plasma atomic emission spectrometer (ICP-AES). V, Mo, Cu, Zn, Ni, and Fe were concentrated 250-fold through a solvent extraction method and determined using ICP-AES.

In the present study, bottle drinking water, 100% orange juice, coffee and environmental samples of Adogawa river and Lake Biwa water in various depths were quantitatively measured by using a handy elemental analyzer of liquid electrode plasma

optical emission spectrometer (LEP-OES).

## EXPERIMENTAL

40  $\mu$ L of solution sample was put into a chip. The high voltage of DC 800-900 V was applied by Pt electrodes with 3-10 ms supplied time. The bottle drinking water, 100% orange juice, coffee and environmental sample of Adogawa river and Lake Biwa water were utilized for analyzed samples. Water samples were taken at four locations of Lake Biwa with various depths of 0m, 1m, 5m and 50m. The analyzed media is 0.1 M HNO<sub>3</sub> aqueous solution unless otherwise stated.

## RESULTS AND DISCUSSION

Figure 1 shows the calibration curve for sodium and potassium at various concentrations. The tendency of applied voltage and concentration effect are similar, compared to before use a new disposal chip (before May 2008). The curve shows that the higher concentration will result the higher emission intensity too. The relative sensitivity for Na/K is about 20, it means that emission intensity of sodium would be detected about 20 times larger than potassium.

Figure 2 shows emission spectrum of the bottle drinking water. The indicated element contents in the bottle drinking water are as follows: Na 11.9 mg/1000 ml, Ca 12.6 mg/1000 ml, Mg 2.9 mg/1000 ml, K 5.7 mg/1000 ml and SiO<sub>2</sub> 77.9 mg/1000 ml. The strongest emission intensity is sodium (Na) at 589 nm about 11500 arbitrary units. Another observed spectral line of the element is potassium (K) at 766 nm, but its intensity is quite small about 200 arbitrary units. The spectral line of OH<sup>-</sup> and H<sup>+</sup> are observed at 306 nm and 656 nm respectively. The spectral line of element for calcium (Ca) and magnesium (Mg) are not observed. If these spectral lines exist, they will be

observed at the wavelength of 422 nm and at 285 nm that correspond to Ca and Mg. Although the concentration of calcium in the indicated elements contents is larger than sodium, but Ca line is not observed at this spectrum, due to the minimum detection limit for calcium using this portable analyzer is about 15-20 ppm. The quantitatively detected sodium and potassium are about  $13 \pm 3$  and  $3 \pm 1$  ppm respectively, almost the same to the indicated element contents. This means that the accuracy is enough for quantitative analysis.

The emission spectrum of 100% orange juice is shown at figure 3. The indicated element content is only sodium 2 mg/1000 ml, but other spectral line of the element of potassium at 766 nm was observed more clearly than sodium with the emission intensity about 4 times larger than sodium in arbitrary units. The spectral band of H is also observed at 486 nm, but more weak than at 656 nm. The quantitatively detected sodium and potassium are about  $1.7 \pm 0.6$  and  $145 \pm 37$  ppm respectively. It was known that commonly in some fruit, potassium content is much larger than sodium. Bao et al. [1] reported that potassium content in orange juice is about 825 ppm (analyzed by XRF) and 795 ppm (analyzed by AAS), and sodium content is only about 88 ppm (analyzed by XRF) and 85 ppm (analyzed by ICP-AES).

The similar case is shown at the spectrum of coffee (figure 4). The indicated element content of coffee is only sodium with 0 mg/1000 ml. The quantitatively detected element is sodium about  $0.2 \pm 0.1$  and potassium about  $400 \pm 64$  ppm. Although there is no indicated potassium content, but the spectrum of potassium is also observed in this sample.

Commonly as qualitative analysis, the spectral line of sodium and/or potassium were observed with strong emission intensity. Meanwhile, the

emission efficiency of different element in the same group is related to its excitation energy [6]. OH<sup>-</sup> and H<sup>+</sup> that resulted from water ionization in the solution were always observed at the spectral line of 306 nm and 656 nm. In addition the emission intensity OH<sup>-</sup> is stronger than H<sup>+</sup>.

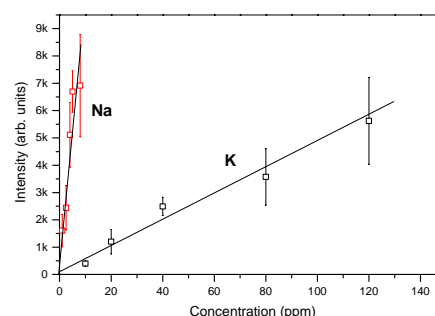


Figure 1. Calibration curve of Na and K.

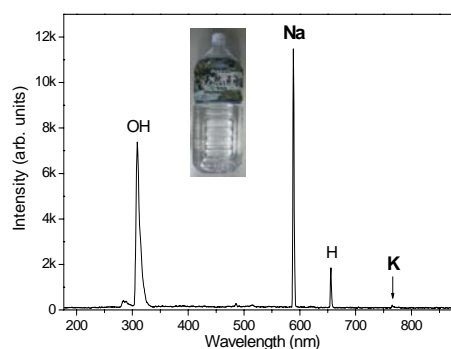


Figure 2. Spectrum of the bottle drinking water.

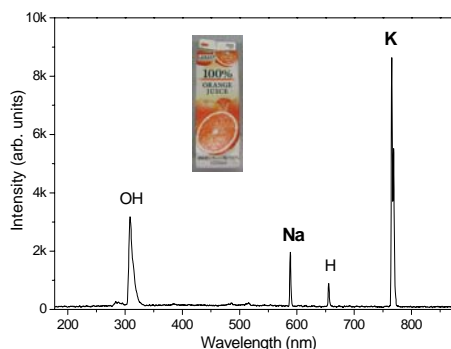


Figure 3. Spectrum of 100% orange juice.

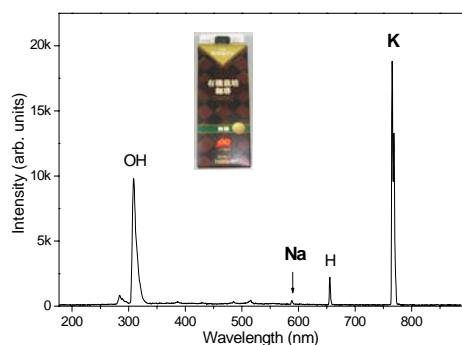


Figure 4. Spectrum of coffee.

In the last part, unknown element and concentration in environmental samples of Adogawa river and Lake Biwa water were measured. Unknown sample in environment such as rain water, river water, sea water, lake water, and so on can be quantitatively analyzed using this portable spectrometer with comparing the calibrated known samples. Figure 5 shows emission spectrum of Adogawa river water. The detected sodium can be quantitatively estimated as 4.7 ppm, according to the calibration curve know sample previously. Other unknown samples of Lake Biwa water in different location and depth were analyzed.

The emission spectra of Lake Biwa water is shown at figure 6-9. As a qualitative analysis, most of spectra show that only sodium was observed at 589 nm. The strongest line is OH<sup>-</sup> at 306 nm, followed by Na and H<sup>+</sup> at 656 nm. Others alkaline and/or alkaline earth metals were not observed by using this analyzer. The quantitatively detected sodium in north basin (Ie-1) of Lake Biwa is 7.01 ppm (0 m), 11.16 ppm (1 m), 11.63 ppm (5 m) and 5.06 ppm (50 m). In south basin (Kc-3, Lc-4, Lc-2 at the depth of 0 m), the detected sodium is 17.68 ppm, 7.59 ppm and 7.18 ppm respectively. The detected sodium by this portable analyzer is nearly similar with Sugiyama et al. It means that accuracy of this portable analyzer is enough for quantitative analysis. According to Sugiyama et al. [5],

sodium concentration in Lake Biwa is 6.58 ppm at north basin (Ie-1 at the depth of 73 m) and 7.01 ppm at south basin (Nb-5 at the depth of 3.5 m and Na-3 at the depth of 2 m). The detection limit of portable analyzer according to Micro Emission Ltd on May 2008 [7] for sodium is about 0.08 ppm. So, sodium is detectable element by this portable analyzer. Potassium with 1.74 ppm at north basin and 1.76 ppm at south basin is undetectable element by this portable analyzer because detection limit for potassium is from the range 8 ppm. Other elements with below the MH-5000 measurement range cannot be detected by this analyzer. Calcium concentration in Lake Biwa at north and south basin are 10.92 and 10.96 ppm respectively [5], but calcium cannot be detected by this analyzer, because the measurement range of MH-5000 for calcium is from about 15-20 ppm. Differences of sampling location and depth variation have not much influence in the kind of element detected by this analyzer.

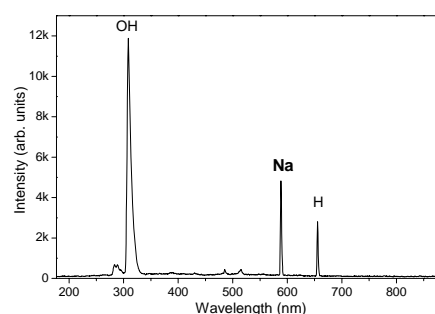


Figure 5. Spectrum of Adogawa river water

It was reported by Micro emission Ltd. [7] that the lowest detection limit of this analyzer is 0.1 ppm for silver, sodium and thallium. The detection limit for potassium and magnesium are about 7-8 ppm. In addition, the detection limit for calcium and zinc are about 15-20 ppm.

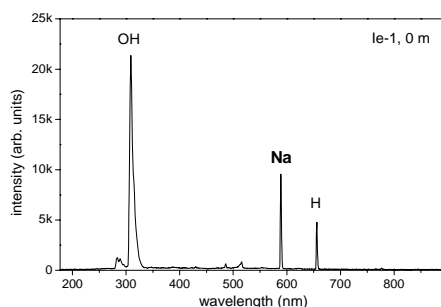


Figure 6. Spectrum of Lake Biwa water in depth of 0 m.

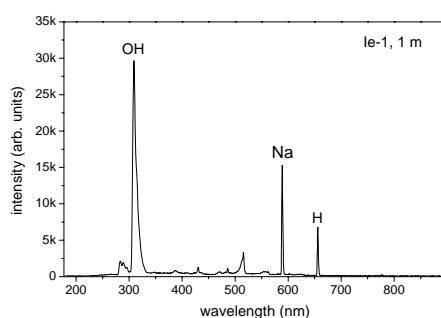


Figure 7. Spectrum of Lake Biwa water in depth of 1 m.

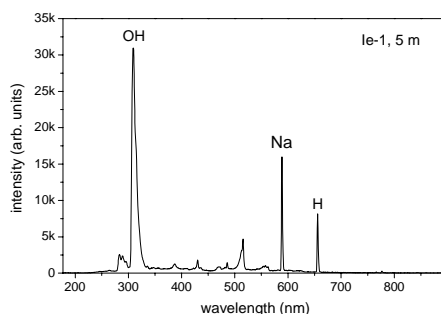


Figure 8. Spectrum of Lake Biwa water in depth of 5 m.

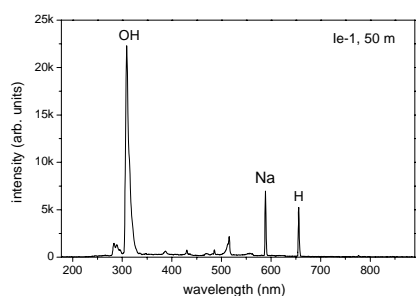


Figure 9. Spectrum of Lake Biwa water in depth of 50 m.

Undetectable some indicated element content is caused to its detection limit for each element. Matsumoto et al. [8] reported that sensitivity and stability for various elements, improvement of detection limit and reproducibility are dependence on channel length, support electrolyte concentration, applied voltage and pulse width.

#### 4. Conclusion

A portable elemental analyzer of liquid electrode plasma optical emission spectrometer was utilized to quantitative analysis of commercially available and environmental samples. Calibration of sodium and potassium should be performed for this purpose. The relative sensitivity for Na/K was 20, and it would be used for quantitative analysis. Sodium and potassium were commonly detected by this analyzer, however other elements such as calcium and magnesium were not detected due to the minimum detection limit. The detected element by this portable analyzer shows that its accuracy is enough for screening quantitative analysis of environmental samples.

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