Portable Elemental Analysis for Environmental Samples

（ ポータブル装置を用いた環境試料の元素分析 ）

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Preface

Many elemental analysis methods are utilized to determine the composition of elements in materials. It can be carried out in industry, laboratory, university or others institution research, or/and outside room such as at the mountain, sea, river, and so on. In the case of on-site analysis, the portable elemental analyzer is very useful to perform it simply and easily.

The aim of this thesis is to present the portable analyzer of Brix meter for measurement of viscosity and concentration of aqueous sucrose solution, desktop type of small X-ray fluorescence spectrometer for analysis of electric and electronic devices, and portable elemental analyzer of liquid electrode plasma optical emission spectrometry for the environmental samples. This thesis is based on the works of mentioned above. The contents are described as follows. Chapter 1 is the introduction of this thesis. Chapter 2 is the work of measurement of viscosity and sucrose concentration in aqueous sucrose solution using portable Brix meter. Chapter 3 is the work of analysis of rare and noble metals in electric devices by X-ray fluorescence spectrometry. Chapter 4 is the work of analysis of alkaline and alkaline earth metals in standard samples by liquid electrode plasma optical emission spectrometer. Chapter 5 is the work of quantitative analysis of alkaline metals in environmental samples using liquid electrode plasma optical emission spectrometer, and chapter 6 is summary of this thesis.

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Chapter 1

Introduction

Elemental analysis has been known as important process of accurately determining the composition of elements in materials. Elemental analysis can be qualitative (determining what elements are present), and it can be quantitative (determining how much of each are present). Several methods of elemental analysis such as inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), atomic absorption spectrometry (AAS), etc. are utilized.

Spectroscopic measurements are being used in many different applications, such as color measurement, concentration determination of chemical components or electromagnetic radiation analysis [1]. A refractometer is a kind of this apparatus that can be used to determine the identity of an unknown substance based on its refractive index, to assess the purity of a particular substance, or to determine the concentration of one substance dissolved in another. So, refractive index of a medium or a solution is a important characteristic parameter, and widely used in optical, chemical, and biomedical industries to determine the concentration of sugar such as in food, fruit juices, etc. as the Brix Value. In modern daily life, portable apparatus to determine the harvesting time of fruit and vegetable, quality of food ingredients such as honey or jam or sugar levels in beverages do it quickly and easily is needed. The commercially available Brix meter refers to the light refraction. A refractometer takes the refraction angles and correlates them to the refractive index values that have been established. Using these values, it can determine the concentrations of solutions [2]. With predefined formulas or concentration tables, the density meter converts the measured density value automatically into the desired concentration unit [3]. In this study, the Brix meter will be applied to the suitability portable viscometer by knowing the relationship between the measured value of concentration and viscosity of analyzed sample solution.

One of the most popular methods for elemental analysis is the XRF technique which has the capability of simultaneous, multi-elemental, non-destructive analysis and can be applied to many kinds of sample: liquid or solid (thick, intermediate or thin) and in many cases with sufficient sensitivity for the determination of many trace elements [4]. XRF analysis also has advantages such as the sort analysis time, the great depth of information, the accuracy of analysis, the simple operability, the economic efficiency and the possible high sample throughput [5]. Its applications cover a wide field such as analysis of metal, semiconductor, soil, glass, plastic, environmental samples, archaeological objects, work of arts, etc. Field portable XRF (FPXRF) technology has gained widespread acceptable in the environmental community as a viable analytical approach for on-site analysis of a variety of environmental samples [6].

How does XRF work? Figure 1.1 describes the XRF principle. When a primary X-ray excitation source from an X-ray tube or a radioactive source strikes a sample, an electron is ejected from the inner shells and creating vacancies. Another electron from the outer shells is transferred to an inner shell and this transferring process gives X-ray characteristic (X-ray fluorescence), that can be used to identify the presence of the elements in the sample [7].

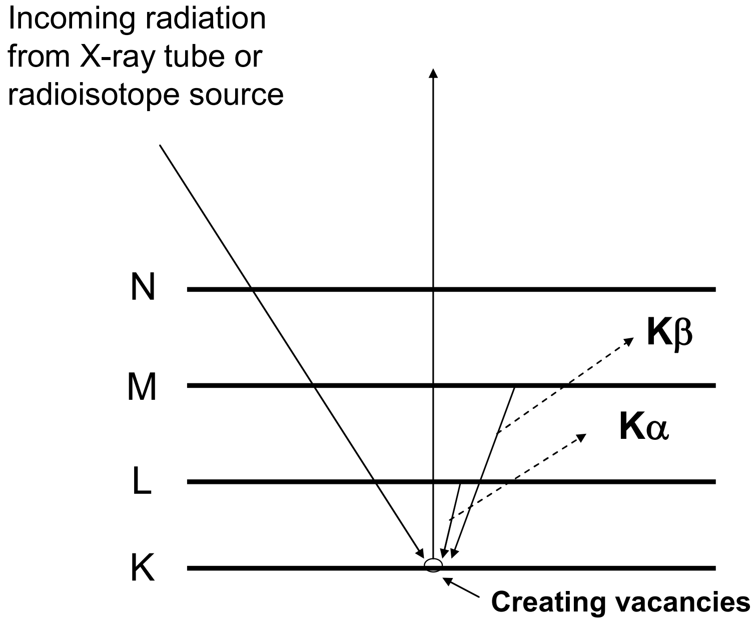


Figure 1.1. XRF process.

A portable total reflection X-ray fluorescence spectrometer for nanogram chromium detection limit was developed by Kunimura and Kawai [8], and illustrated at figure 1.2. The spectrometer mainly consists of a 1.5-W X-ray tube. With the simple arrangement and small size, the apparatus can detect some element such as chromium, calcium, iron, chlorine and tin. Kawai et. al [9] utilized the types of handy x-ray fluorescence spectrometers for their analysis. Their results obtained with a Niton spectrometer are presented as a goal to develop a laboratory-made spectrometer using an Amptek Cool-X pyroelectric x-ray generator, illustrated at figure 1.4. [10]. H. Ida and J. Kawai [11] present the applications of XRF analysis with a pyroelectric X-ray generator, namely Cool-X, for analysis of glass and ceramics. The pyroelectric X-ray generator is particularly suitable for portable XRF spectrometers because of the characteristics of small dimensions, light weight and dry battery drive.

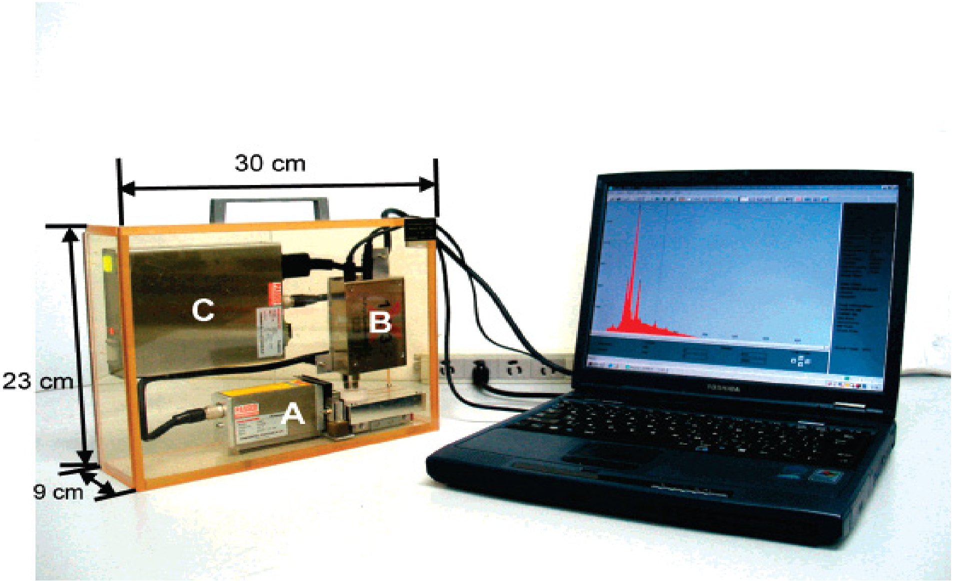


Figure 1.2. Portable TXRF spectrometer [8].

Figure 1.3. Portable Niton XRF spectrometer [9].

Figure 1.4. X-Ray emitter with pyroelectric crystal [10].

The others samples of portable analyzer can be shown at the figure 1.5 below. A pH meter is an electronic instrument used to measure the pH (acidity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). An ultraviolet (UV) light meter is useful for measuring UV radiation both in the field and the laboratory. The meter is also useful for determining the UV filtering capacity of transparent plastic and glass barriers that are commonly used to filter electric light sources.

Figure 1.5. Other samples of portable analyzer (a) pH meter (b) UV light meter.

Nowadays there are many electric and electronic appliances are used in our daily life. These goods are made by company using many variety kinds of materials such as ceramics, polymeric materials, composite materials or metals, including rare and noble metal. Material is identified as rare metal when its native on the earth is very rare, the ore cannot be economically significant enough to provide the metal and the metal cannot be pure enough scientifically and physically [12]. In many cases, noble metals were also be utilized to improve the performance quality of electric and electronic goods, because their properties that have resistance to corrosion and oxidation. The growing of electronic products will give the environmental problems in the future after unused. Electronics waste should be prevented, and older electronics should be reused and recycled. In order to perform this purpose, identifying their element content should be done. In this study, XRF is used to analyze rare and noble metal existence in electric and electronic devices.

Another method for elemental analysis is optical emission spectrometry (OES). OES that also known as atomic emission spectrometry (AES) remains one of the widely used analytical methods for the determination of the elements and their compounds in variety of types of samples and in differing concentrations. It derives analytical information from atomic spectra in the optical region of the electromagnetic spectrum. This optical region is the ultraviolet (UV) and the visible light. The atomic spectra in this region originate from energy transitions in outer electronic shells of free atoms or ions [13]. Using OES, we can determine the chemical composition of solids, like steel or wood or paint, and liquids, like oil or milk, and gases, like air or car exhausts. Knowing the content of materials, we can monitor changes in the environment, and improve production processes and product properties, such as strength, corrosion resistance and appearance. OES also can be used to monitor the deposition of layered devices used in the semiconductor industry, and the deposition of hard coatings on tools, etc [14].

Several analytical methods described above has really many advantages, but sometimes due to the high cost of the measuring equipment used, the expert technicians required, and the sheer size of the equipment involved, so that the miniaturization dimension of apparatus is applied in various application fields, including in analytical spectrometry. Miniaturized analytical devices have advantages such as small sample volumes involved, low power consumption, and portability [15].

Microplasma based on plasma emission technology and the principle of atomic/optical emission spectroscopy has been developed for effective detection method for miniaturized chemical analysis systems [16]. A novel type of portable elemental analyzer, namely liquid electrode plasma optical emission spectrometry (LEP-OES) has developed to detect trace metals contained in fluid samples. The portable size of the analyzer will make it possible to easily perform elemental analysis without having to use the large-scale analytical equipment required previously.

Recently, the development of suitable analytical methods have been downscaled and produced to minimize the amount of instrumentation used in order to maintain portability. A glow discharge optical emission spectroscopy (GD-EOS) has been demonstrated as an effective detection method suitable for integration with miniaturized gas chromatography (GC) systems [17, 18] and benefits not only from low detection limits but also allows atomic and molecular determination to aid analysis. The development of microwave microplasmas has attracted much attention in the last years. Several researchers at laboratories develop the powerful and robust microplasmas which can be integrated on a chip because plasmas in combination with separation techniques are widely used in analytical science. An electrolyte as a cathode discharge (ELCAD) developed by Jenkin and Manz [16] is known as the effective method for liquid sample introduction. In this glow discharge, the cathode was a liquid sample, which was delivered to the plasma region using a peristaltic pump. Recently, Iiduka et al. and their research group inducted by Takamura [19-21] have developed a novel type of portable elemental analyzer, namely liquid electrode plasma optical emission spectrometry (LEP-OES) comprised of a polydimethylsiloxane (PDMS) microchannel and electrodes. The plasma is generated by confined electric current through a sample solution in a microfluidic channel.

The detection principle of LEP-EOS is simple, and described at figure 1.6. [20] Sensitivity of this analyzer for measurement range was reported by Micro emission Ltd on May 2008 [22]. When voltage was applied in the micro-fluidic channel that was filled with sample electrolytic solution, H_2O gas bubble was formed by heating, and subsequently plasma emits light in the bubble. By analyzing the light, the atomic concentration in the sample solution can be determined. There are 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 this study, LEP-EOS is used to analyze some standard solution samples, bottle drinking water, grapefruit juice, soybean milk, coffee, and environmental samples of Lake Biwa water.

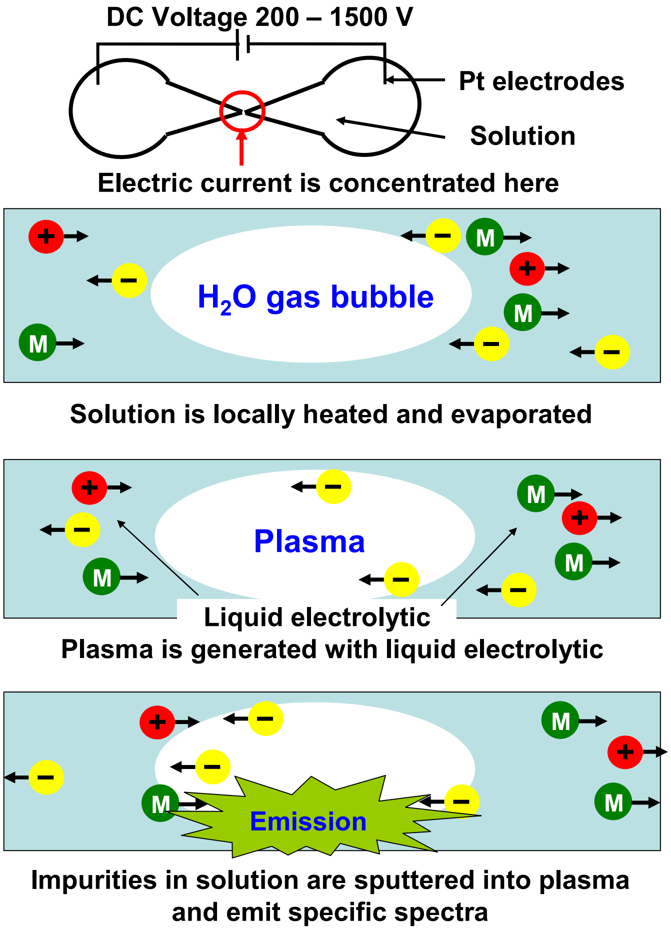
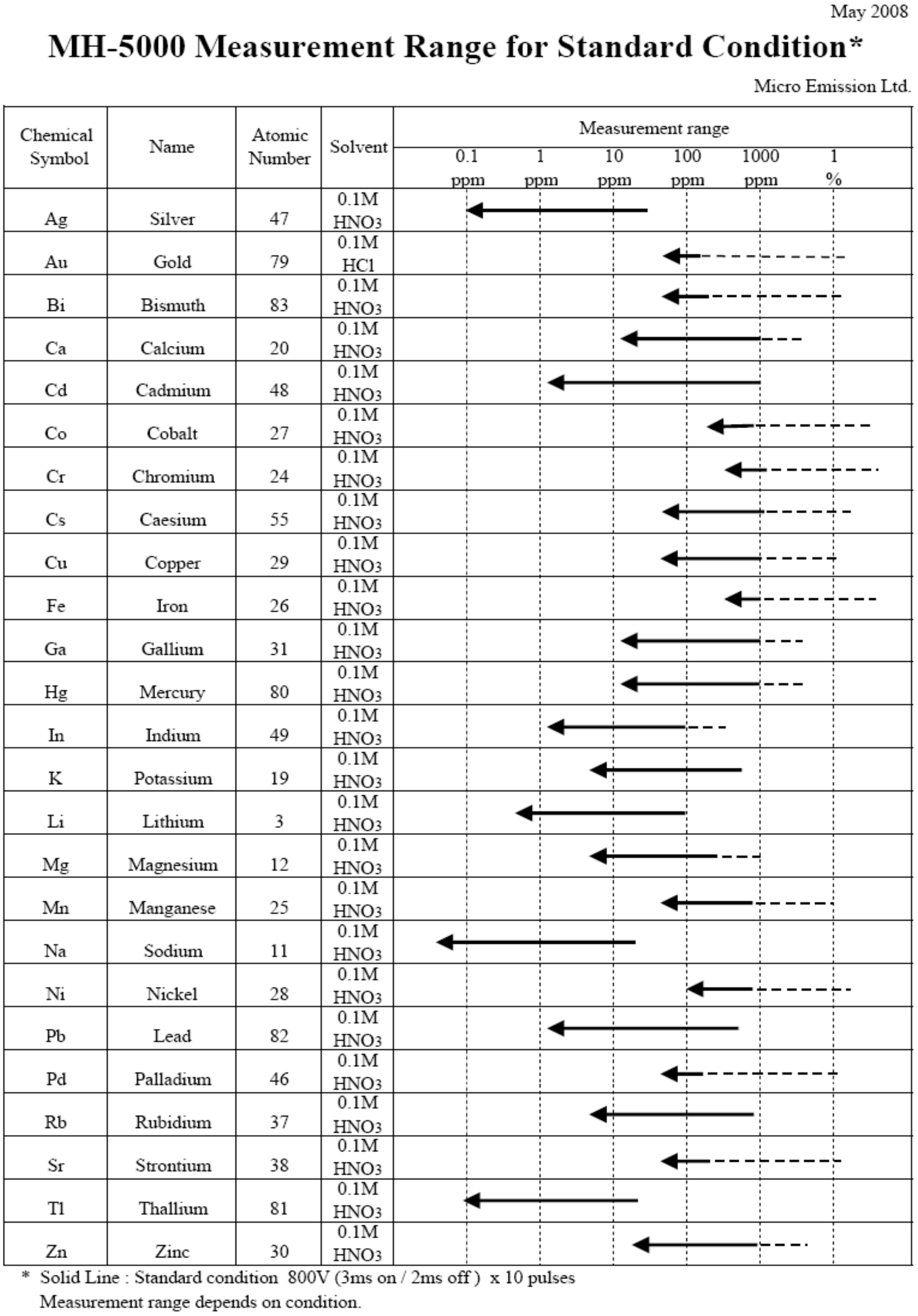


Figure 1.6. Schematics of confined liquid electrode plasma optical emission spectrometry (LEP-OES) [20].

Table 1.1. MH-5000 measurement range for standard condition [22].



May 2008

MH-5000 Measurement Range for Standard Condition*

Micro Emission Ltd.

Chemical Symbol	Name	Atomic Number	Solvent
Ag	Silver	47	0.1M HNO_3
Au	Gold	79	0.1M HCl
Bi	Bismuth	83	0.1M HNO_3
Ca	Calcium	20	0.1M HNO_3
Cd	Cadmium	48	0.1M HNO_3
Co	Cobalt	27	0.1M HNO_3
Cr	Chromium	24	0.1M HNO_3
Cs	Caesium	55	0.1M HNO_3
Cu	Copper	29	0.1M HNO_3
Fe	Iron	26	0.1M HNO_3
Ga	Gallium	31	0.1M HNO_3
Hg	Mercury	80	0.1M HNO_3
In	Indium	49	0.1M HNO_3
K	Potassium	19	0.1M HNO_3
Li	Lithium	3	0.1M HNO_3
Mg	Magnesium	12	0.1M HNO_3
Mn	Manganese	25	0.1M HNO_3
Na	Sodium	11	0.1M HNO_3
Ni	Nickel	28	0.1M HNO_3
Pb	Lead	82	0.1M HNO_3
Pd	Palladium	46	0.1M HNO_3
Rb	Rubidium	37	0.1M HNO_3
Sr	Strontium	38	0.1M HNO_3
Tl	Thallium	81	0.1M HNO_3
Zn	Zinc	30	0.1M HNO_3

* Solid Line : Standard condition 800V (3ms on / 2ms off) x 10 pulses
Measurement range depends on condition.

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Chapter 2

Measurement of Viscosity and Sucrose Concentration in Aqueous Sucrose Solution using Portable Brix Meter

The viscosity of aqueous sucrose solution in various concentrations and the sugar content were measured by using an Ostwald viscometer and a commercial available of portable Brix meter respectively. The increasing of the concentration of sucrose would also followed by increasing viscosity of the solution. Depending on their concentration, the measured value of viscosity of solution would be automatically confirmed into the desired concentration unit. The suitability of Brix meter for other application will be checked.

2.1 Introduction

Viscosity is a fundamental characteristic property of all liquid. Viscosity of aqueous electrolyte solutions is of considerable interest due to its importance in both natural and industrial processes. When a liquid flows, it has an internal resistance to flow. The viscosity depends on temperature, pressure and the type and composition of the material. The measurement of viscosity is significant importance in both industry and academia. Accurate knowledge of viscosity is necessary for various industrial processes. In industry, viscosity allows distinguish directly the quality of the final product such as lubricating oils, fuels, inks, paints, and so on. Another importance of viscosity in industry is to control the progress of physicochemical reactions during manufacturing. In the food processing, knowing the viscosity of the product is beneficial in that viscosity indicates consistency, pour-ability, concentration, and firmness to define product quality. In petroleum, all the range possibilities make the vibrating viscometers as efficient on light fuels as on bitumen [1].

The viscosity depends on temperature, pressure and the type and composition of the material. It may also depend on the shear rate and can change with time by the process of flow itself. For special systems the viscosity is influenced by external electrical fields [2]. Commonly, viscosity is measured by the viscosity apparatus directly. The relationship between concentration of sucrose solution and its viscosity will be shown at the figure 2.1. The data of viscosity is taken from the references [3]. Increasing of concentration will influence on viscosity. From the relationship, if we know the concentration of solution, we can know its viscosity.

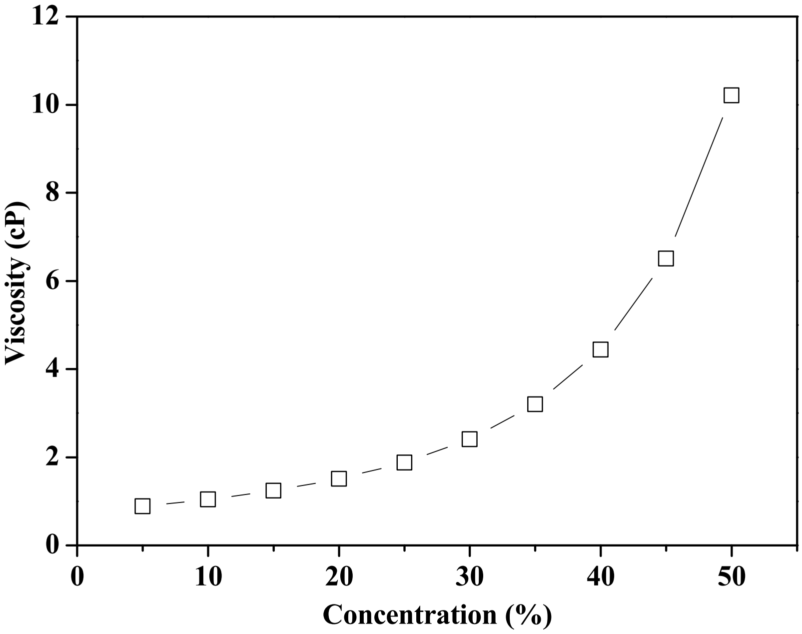


Figure 2.1. Viscosity of sucrose aqueous solution at 30^0C [3].

There are several types of viscometers classified into seven categories by their measurement principle as follows [4]: capillary, orifice, high temperature, rotational, falling-ball, vibrational, and ultrasonic viscometer. The vibration-type viscometer, the working principle is based on the vibration, either torsion, either translation, at resonance or controlled frequency of a module immerged in a liquid. The falling-ball viscometer, the working principle is based on measure of the time of the fell of a module placed in a vertical tube which contained a sample [1].

Capillary viscometer is most widely used for measuring viscosity. A common type of this capillary is called the "Ostwald" with simple in operation, require a small volume of sample liquid, temperature control is simple and inexpensive. In capillary viscometer, viscosity is measured noting the time required for a known volume of liquid to flow through a small capillary between two marked lines.

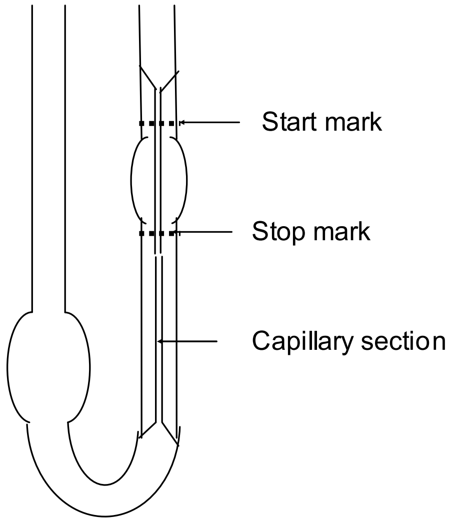


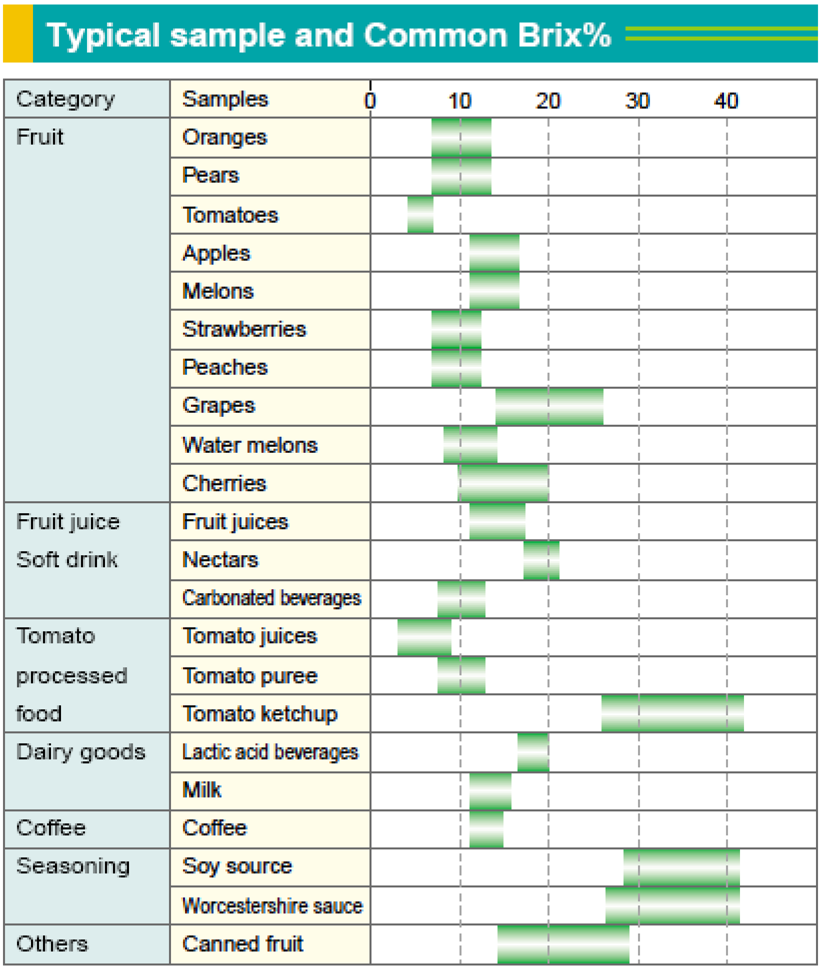
Figure 2.2. Ostwald viscometer

Refractive index of a medium or a solution is a very important characteristic parameter and some associated parameters such as temperature, concentration, viscosity, etc., may be estimated from it. Those parameters are used very often in optical, chemical, and biomedical industries. A simple and direct measurement of reflectivity could provide the refractive index of the test medium by using only Fresnel's equation, it is related to the measurement of light intensity variations [5]. The refractive index correlates closely to the molar fractions of the components in solution, and constant for a substance under standard conditions of temperature and pressure. The refractive index has been widely used to determine the concentration of sugar such as in food, fruit juices, etc. as the Brix Value (BV) [6-8].

The commercially available Brix Meter refers the light refraction. A refractometer takes the refraction angles and correlates them to the refractive index values that have been established. Using these values, it can determine the concentrations of solutions [9]. With predefined formulas or concentration tables, the density meter converts the measured density value automatically into the desired concentration unit [10]. The Brix measuring ranges for several samples are listed in Table 2.1. [11].

The purpose of this study is to apply the suitability of this Brix meter to other portable viscometer by knowing the relationship between the measured value of concentration and viscosity of analyzed sample solution.

Table 2.1. Brix measuring range for several samples [11]



Typical sample and Common Brix%

Category	Samples
Fruit	Oranges
	Pears
	Tomatoes
	Apples
	Melons
	Strawberries
	Peaches
	Grapes
	Water melons
	Cherries
Fruit juice Soft drink	Fruit juices
	Nectars
	Carbonated beverages
Tomato processed food	Tomato juices
	Tomato puree
	Tomato ketchup
Dairy goods	Lactic acid beverages
	Milk
Coffee	Coffee
Seasoning	Soy source
	Worcestershire sauce
Others	Canned fruit

2.2 Experimental

The viscosity of sucrose was be determined by using Ostwald viscometer (Sougo Rikagaku Galasu Seisakusho, Kyoto, Japan). The distilled water obtained by Elix 5 is used for preparation of sucrose ($C_{12}H_{22}O_{11}$; Nacalai Tesque, Inc Kyoto Japan; GR grade) standard solution. The viscosity is determined by measuring its rate of flow through a capillary tube. At a constant temperature of 303 K, the sucrose solution is added from the pipette to the Ostwald viscometer as illustrated at Figure 2.3 (a). With the aid of a piece of rubber tubing or pipette filler, the liquid is sucked up the capillary arm of the viscometer until the surface of the liquid is above the upper mark as illustrated at Figure 2.3 (b). The liquid is then allowed to flow down the arm. The time required for the surface of the liquid to pass from the upper mark to the lower mark is noted, as illustrated at Figure 2.3 (c).

Sucrose solution in many various concentrations are made by using mass formula of [$\frac{\text{mass of sucrose}}{\text{mass of sucrose} + \text{water}}$]. Then viscosity could be calculated using Poiseuille equation. The concentration of sucrose solution was measured by portable Brix meter of RA-250HE (Kyoto Electronics Manufacturing Co. Ltd.) by dropping the sample onto the prism, then pressing the read key and the result will appeared on the display, like as illustrated at figure 2.4. It can be calibrated with a drop of distilled water and cleaned by rinsing or wiping.

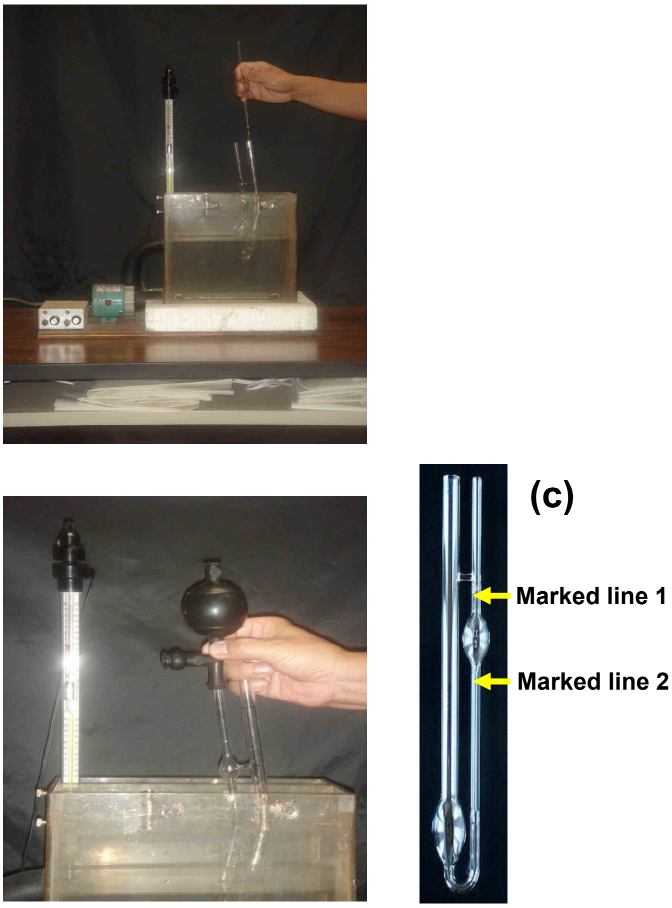


Figure 2.3. Measurement of viscosity of sucrose solution using Ostwald viscometer.

(a) adding solution; (b) sucking up solution; (c) measuring time

Figure 2.4. Measurement of concentration of sucrose solution using portable Brix meter.

2.3 Results and discussion

Standard pure water that used to determine the capillary constant has the density and the viscosity are 0.99571 g/cm^3 and 0.00798 g/cm.s respectively [12]. Using the equation: $\eta = \rho kt$, and the time required for the surface of the liquid to pass from the upper mark to the lower mark, the capillary constant is 4.1286 x 10^{-5} cm^2/s^2. The time required for sucrose solution is also noted, then its viscosity in various concentrations can be calculated and experimental value is compared to the reference. Table 2.2 shows the concentration values of sucrose solution by direct preparing using mass formula of $[\frac{\text{mass of sucrose}}{\text{mass of sucrose} + \text{water}}]$ and the measured values using portable Brix meter and the measured value of concentration of sucrose solution by portable Brix meter and by direct preparing is nearly similar, that describe at figure 2.5. It was seen at the figure 2.5 that there is relationship between the concentration and the viscosity. It was shown that increasing the concentration of sucrose solution gives rise to increasing viscosity. With this tendency, the value of solution viscosity can be predicted base on the read value of concentration on this portable Brix meter. So that, the Brix meter is applicable to other uses than concentration measurement.

Table 2.2. Concentration and viscosity of sucrose solution*

DP	Concentration (Brix %)			Viscosity (cP)			
	Measurement by PBM			Theo.	Measurement		
	Ave	SD	RSD	[10]	Ave	SD	RSD
5	4.9	0.12	2.37	0.8872	0.8994	0.0022	0.2509
10	9.7	0.21	2.15	1.0389	1.0539	0.0019	0.1774
15	14.6	0.23	1.58	1.2380	1.2418	0.0040	0.3261
20	19.6	0.17	0.88	1.5055	1.5077	0.0029	0.1948
25	24.6	0.21	0.85	1.8760	1.9020	0.0029	0.1516
30	29.5	0.17	0.59	2.4068	2.4480	0.0024	0.0987
35	34.6	0.21	0.60	3.1987	3.2786	0.0052	0.1581
40	39.5	0.21	0.53	4.4397	4.5696	0.0021	0.0471
45	44.4	0.26	0.60	6.5050	6.7306	0.0235	0.3493
50	49.4	0.23	0.47	10.2094	10.7237	0.1138	1.0612

*DP: sucrose concentration by direct preparing, PBM: sucrose concentration by portable Brix meter; Ave: average value of concentration and viscosity in 3 times measurements, SD: standard deviation of measurement, RSD: relative standard deviation (%) of measurement, Theo.: theoretical value of sucrose viscosity [3].

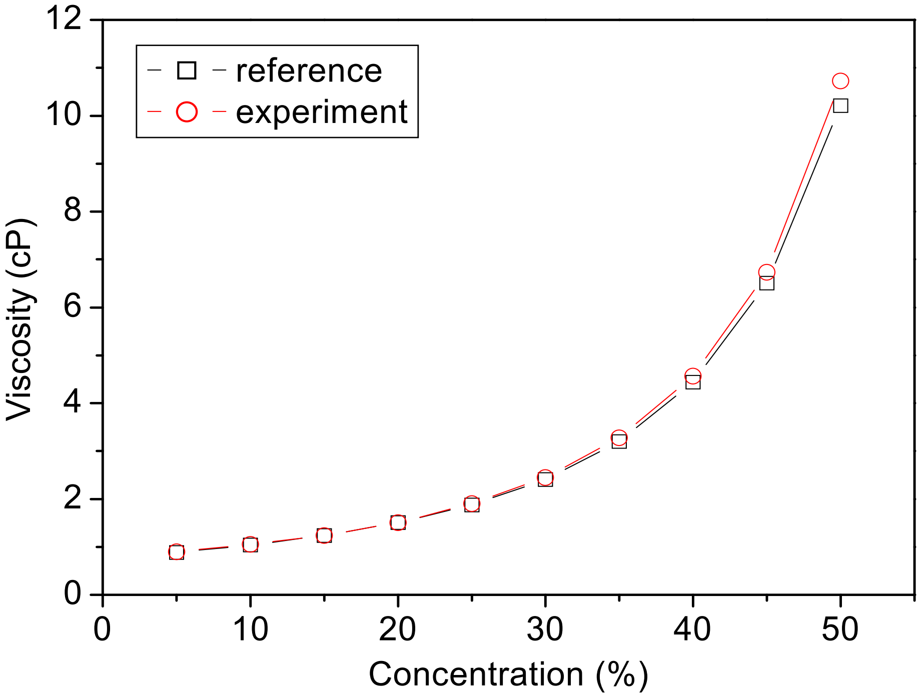


Figure 2.5. Viscosity of sucrose solution in various concentrations at 303 K.

2.4 Conclusions

By using the easy and simply measurement of the viscosity of aqueous sucrose solution in various concentrations and the sugar content using an Ostwald viscometer and a commercial of portable Brix meter, the relationship between these parameters can be known. The experiment results indicate that increasing of the concentration of sucrose would followed by increasing viscosity. Depending on their concentration, the measured value of viscosity of solution would be automatically confirmed into the desired concentration unit. With this tendency, the value of solution viscosity can be predicted base on the read value of concentration on this portable Brix meter. So that, portable Brix meter is applicable to other uses than concentration measurement.

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Chapter 3

Analysis of Rare and Noble Metals in Electric Devices by X-Ray Fluorescence Spectrometry

Rare and noble metals contained in electric and electronic devices were analyzed by a commercially available energy dispersive X-ray fluorescence spectrometer. Several kinds of rare and noble metals such as nickel, cobalt, tungsten, zirconium, gold, silver, and bismuth were detected by analysis of the samples at inside part after removal of the package or crushing. Both bromine and antimony were detected in the most electronic part which contains plastics. The classification of elements contained and the procedures for identification of emission peaks in X-ray fluorescence spectrum were explained.

3.1 Introduction

Many electronic and electric appliances are recently used in our modern daily life. These appliances are mainly composed from various metals including rare and noble metals. As the production and the use of electronic and electric products continue to increase dramatically throughout both business and public sectors, the challenges of disposal and recovery of materials are becoming significant. Discarding the used products of rare and noble metals can lead natural resources to be exhausted. Whereas, providing of rare and noble metal sources are very limited, so that collecting and converting rare elements into reusable materials are needed. Collecting and recycling of rare and noble metal included in electric and electronic scrap is one of the important problems, because the necessity of reducing quantity of metal used and metal recycled are recently advocated by some factors such as the idea to use the resources effectively, depletion of resource and increasing of price [1, 2].

In January 2008, Komei Halada of National Institute for Materials Science released on the press about the amount of metals which have been accumulated in Japan to date which are recyclable for use as metal resources in the future with the title of "Japan’s ‘Urban Mines’ are Comparable to the World’s Leading Resource Nations, Calculating the Scale of the Urban Mines Accumulated in Japan" [3]. These metals, called “urban mines,” are found in a wide range of products, but are generally not recycled when products are discarded. The results of this study revealed that Japan’s urban mines have reached a scale comparable to natural reserves of the world’s leading resource nations. According to these calculations, Japan’s urban mines of many metals exceed 10% of world reserves, including gold, (approx. 6,800 tons, or about 16% of the world’s current reserves of 42,000 tons), silver (60,000 tons, or 22%), indium (61%), tin (11%), and tantalum (10%). Many metals are used in parts for electronic devices such as cell phone and personal computer (Table 3.1), and many consumers replace their cell phone and PC when new designs and models appear. Because about 21 million cell phones are replaced and no longer needed, the amount of gold available for recycling can be calculated at as much as 150 kg a year. However, many of these used cell phones are thrown out as trash and incinerated or buried in landfill, left in the drawer or kept as a memento. Only about 1/4 are recovered, that means approximately 100 kg of gold is lost without use each year. The content of the press released mentioned above was published recently [4].

Table 3.1. Main metals used in products [4]

Products	Metal applied
Plastic products	Sb, Sn
Coated and plated steel products	Zn, Sn
Integrated circuit	Au
Liquid crystal devices	In
Electronic parts	Au, In, Ta, Sn
Automobiles	Fe, Pt
Electronic equipment	Fe, Pt, Ag

Shiratori and Nakamura [5-7] propose the concept of artificial mineral deposit to calculate the typical metal content of circuit board for personal computer, official automation equipments, general equipment, CRT and LCD. For example, metal content in the circuit board of personal computer is calculated as follows: Au 500 g/t, Ag 2000 g/t, Pd 50 g/t, Pt 10 g/t, Cu 15 %, Zn 2%, Pb 2%, Sn 2 %, Ta 0.3 %, Bi 0.04%, Ni 2%, Sb 0.04 %, Co 0.2 % and Ba 0.4%. The recycling process and technology of the noble metal from electric and electronic apparatus is introduced by this journal in 2007 [8-10]. However, the recycling is not so active [11], many disposal printed wiring boards were not recycled due to the processing expense [12]. According to Nakano, there are four kinds of metals: copper, silver, gold and palladium are recycled from a mobile telephone, but the recovery factor of itself is low, and the other rare metals are not recycled again [13]. Shiratori et al. estimated the quantity of rare and noble metal as the mean of whole board [6]. The recycling efficiency is can be expected if the element kind and the density of individual device are understood, and the parts of devices are sorted according to the object element.

In the present chapter, we introduce the analysis of rare and noble metal in electric and electronic device using X-ray fluorescence spectrometry. The metal element contained in the discarded home electronic appliances product can be analyzed by removal the package, cutting or crushing. The advantage of elemental analysis by X-ray fluorescence is not necessary to choose the form of the sample, and the measurement of solid sample is possible. In addition, automation of the quick measurement is possible. The analysis from about several microns to millimeters is possible from the surface of the sample depends on x-ray energy, the kind of element composition, and density of the solid sample in the measurement. When analyzing of sample is performed at the outer layer or the bulk, non destructive analysis is possible [14-16].

3.2 Experimental

Measurement of X-ray fluorescence spectrum was performed in the air using the energy dispersive X-ray fluorescence of Rayny EDX-800 (Shimazu). The X-ray tube is rhodium (Rh) target, and as for the detector is Si (Li) semiconductor detector. The X-ray tube was operated at 50 kV, electric current was automatically adjusted at the maximum of 1 mA, so that the dead time for detector became 25%. Measuring time is made for 100 seconds. This measurement is not use the filter. The used sample in this experiment such as integrated circuit, resistor, diode, transistor and the other electronic parts are mainly got from the waste electric and electronic equipment. Samples were analyzed at both outside and inside. Analyzing at inside part of device was done by cutting or crushing of samples.

3.3 Results and discussion

3.3.1 Computer memory

X-ray fluorescence spectrum of computer memory of desktop type is shown at Figure 3.1. Nickel, silver, copper, bromine, titanium, antimony, lead, tin and strontium were detected from this sample. Besides X-ray fluorescence of the element origin in the sample, Rh Kα originated from X-ray tube (anode) and Rh KαC originated from the Compton scattering were observed. Therefore, analyzing the rhodium contained in the device sample is impossible, and it is necessary to use the different X-ray tube. The energy of X-ray characteristic is specific to each element, but due to there are many elements whose similar type in the emission line, it has become complicated one. The function of peak identification is automatically attached to the commercial X-ray fluorescence analyzer. However, it is necessary to assign the decided peak, because maybe there is a wrong when assign the peak with similar energy especially in the low energy range of K and L line.

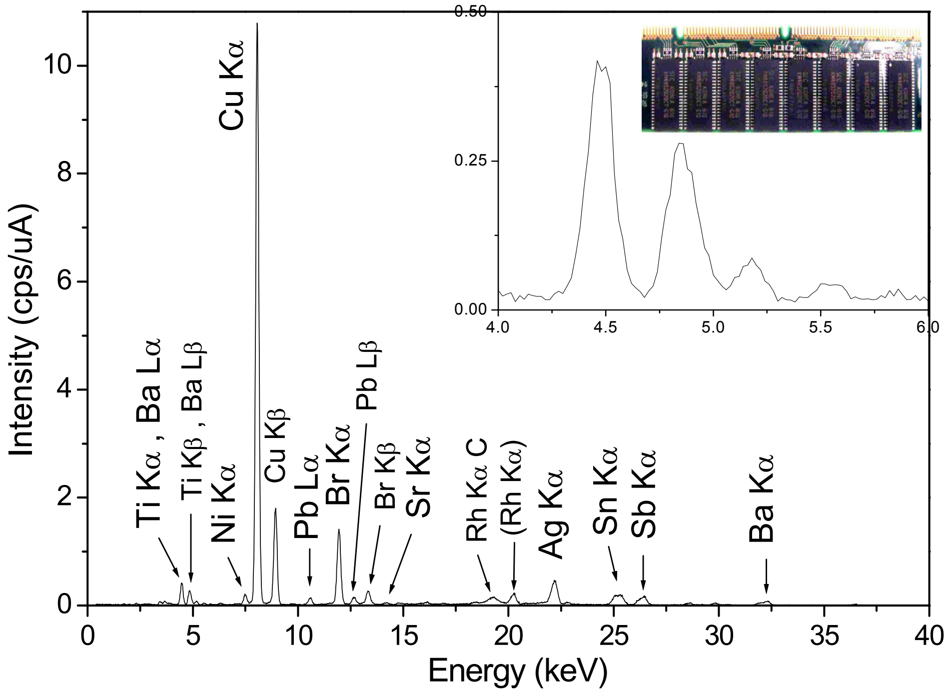

Figure 3.1. XRF spectrum of computer memory.

There are two vicinity peaks of 4.5 and 4.9 keV here. The X-ray characteristic energy of Sc Kβ (4.46 keV), Ti Kα (4.51 keV) and Ba Lα (4.46 keV) with the almost same energy in the vicinity of 4.5 keV cannot be separated by detector installed in X-ray fluorescence analyzer. The same cases were happened in the vicinity of 4.9 keV which Ti Kβ (4.93 keV), VKα (4.95 keV) and Ba Lβ (4.83 keV) have the almost same energy. The intensity ratio for Kα and Kβ line in 3d transition metal is about 10:1. It is judged that there is no scandium origin peak corresponding to the Sc Kα line observed at 4.1 keV. Intensity ratio at the peak of 4.5 keV and 4.9 keV is remarkably large in this spectrum like as the peak of Cu Kα and Cu Kβ line. Therefore, there are two independent peaks: Ti Kα and Ti Kβ line, not a single peak. This sample is not contain vanadium corresponding to the fact that there is no observed peak at 5.43 keV which suitable with VKβ. In addition, this sample contains barium corresponding to Ba Kα line is observed at 32 keV peak. The intensity ratio of Ba Kα (32 keV) relatives to Ba Lα (4.5 keV) is larger than XRF spectrum in other barium compounds that measured in the same condition, and it is clear that 4.5 keV peak has some kind of overlapping peaks. Therefore, these two peaks near 4.5 keV and 4.9 keV are judged as overlapping of Ti K and Ba L line.

3.3.2 Integrated Circuit

Figure 3.2 (a) shows XRF spectrum of the analyzed integrated circuit chip from the outside part. Antimony, bromine, titanium, and small amount of iron were detected from this sample. X-ray characteristic of rare and noble metals were not confirmed in the outside analysis. The XRF spectrum of the integrated circuit chip at inside part by removing package section is shown in Figure 3.2 (b). The analyzed part is enclosed with a round sign in the insertion photograph. The internal spectrum shows the great difference if compared with the outside, and the peak of nickel and gold were detected. Silicon (Si Kα) was observed with a remarkably small peak.

Silicon is a main element of the integrated circuit, and also the most widely used for material in semiconductor devices. It is thought that silicon is a main ingredient in this system, but its low energy is absorbed in the air, and Si Kα peak is remarked with small peak. Moreover, gold might be used as contact point. Antimony and bromine were also detected at inside part of integrated circuit but the relative strength is lower than outside. The package of this integrated circuit chip is covered with plastic. The detected bromine here might be as bromine compound such as plybrominated diphenyl ether (PBDE) and polybrominated biphenyls (PBBs) that usually used as flame retardants in plastics, textiles and furnishing to make them difficult to burn. In addition, antimony trioxide is also used together with bromine compound as materials that resist to the spread of fire in the plastic. Furthermore, bromine and antimony are simultaneously detected in many of samples that covered with plastics.

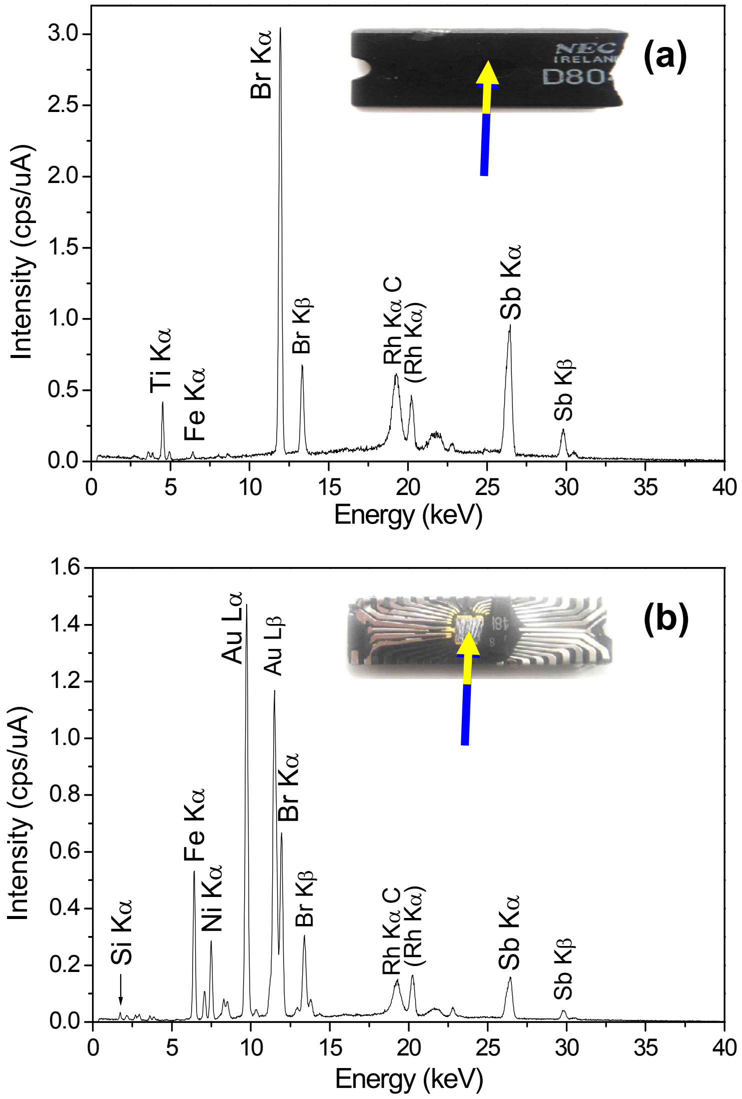

Figure 3.2. XRF spectrum of an integrated circuit at outside part (a) and inside part (b).

3.3.3 Resistor

XRF spectrum of a metal film resistor of 470 Ω at outside and the cut section (inside) are shown in Figure 3.3 (a) and (b) respectively. The peak of varieties elements such as copper, tin, chrome, zinc, titanium and barium were observed both at outside and inside, and Fe Kα line is the strongest peak. Barium and strontium as alkaline earth elements and ceramic foundation were strongly detected from the inside part. The measured cross section area of the cutting resistor at Figure 3.3 (b) is remarkably smaller than the outside. Therefore, the peak intensity is weaker than the outside.

3.3.4 Peltier device

X-ray fluorescence spectrum of the ceramic type small Peltier element of 1.5 cm was observed with extremely small peaks, except for tin (Figure 3.4). The peak of Al Kα line is small, but aluminum oxide is actually the prominent ingredient of these materials. The outside ceramic part of alumina type used as insulator in Peltier device absorbs the incident X-ray and X-ray fluorescence. The X-ray loses its intensity via interactions with material, and X－ray absorption coefficient of aluminum will decrease smoothly with high energy. Only Sn Kα peak with high energy and low absorption was observed by the measurement from outside ceramic part. When the ceramic part is removed and the inside part was directly measured, various transition metal elements such as bismuth and tellurium that widely used as a thermoelectric material are detected (Figure 3.5).

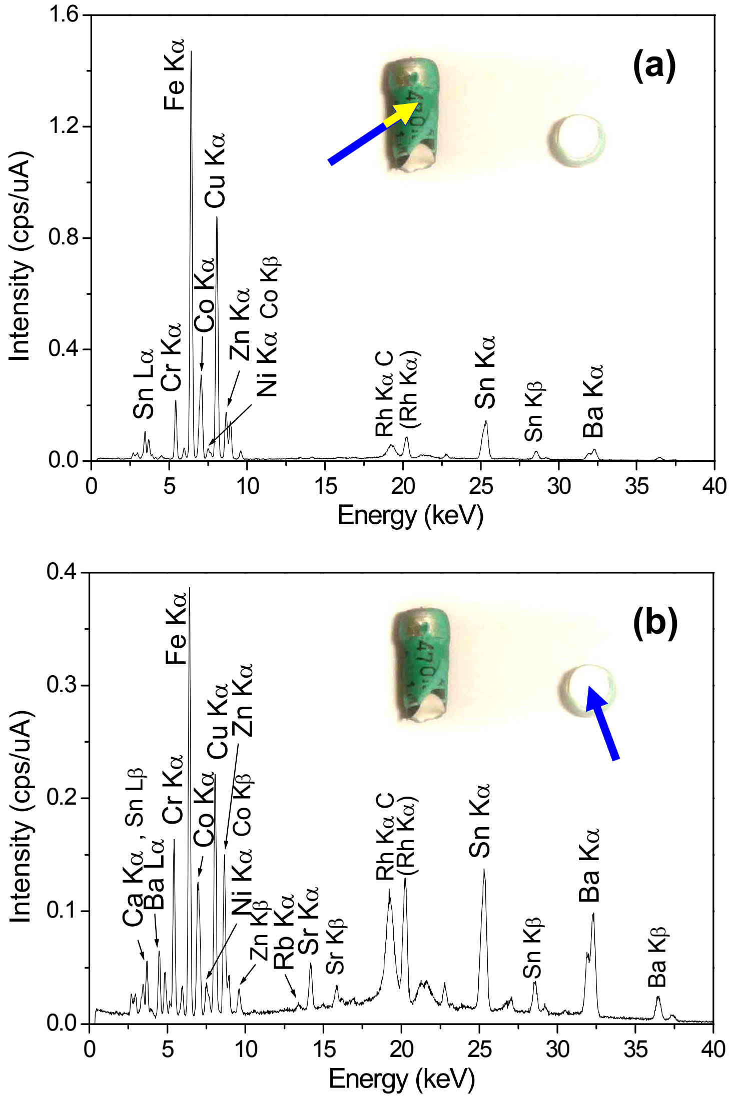

Figure 3.3. XRF spectrum a metal film resistor at outside part (a) and inside part (b).

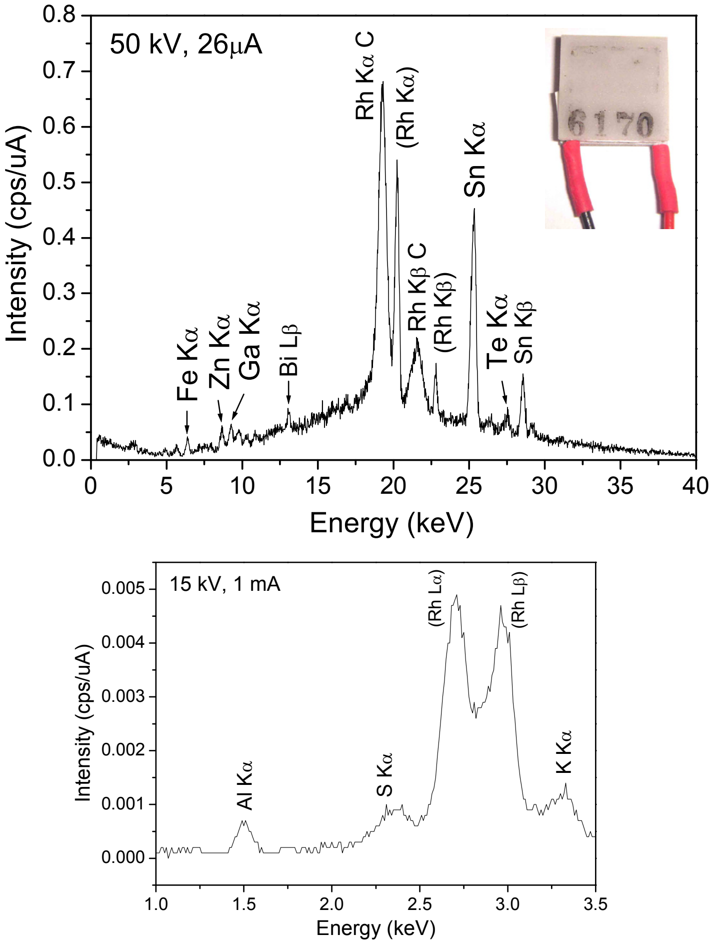

Figure 3.4. XRF spectrum of a peltier device at outside part.

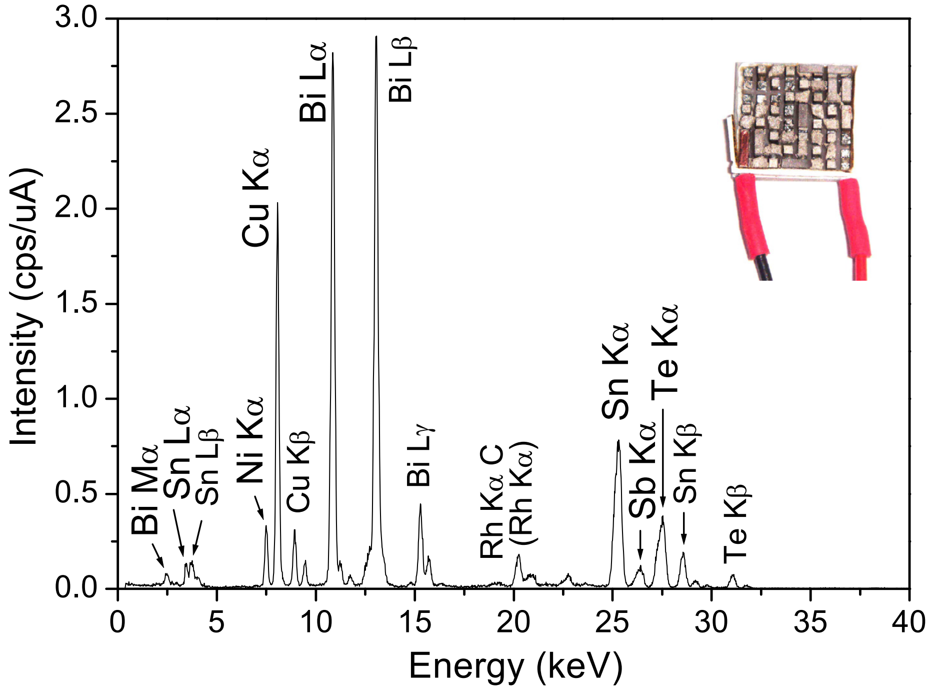

Figure 3.5. XRF spectrum of a peltier device at inside part.

3.3.5 Memory card (microdisk)

The XRF spectrum of the small sized memory card for mobile telephone is shown in Figure 3.6. Tungsten and gold were detected from this sample. Other peak such as silicon, titanium, copper, antimony, and bromine was detected. Plastic part at outside of this sample is thin compared with integrated circuit chip. Therefore, gold and tungsten can be analyzed although from outside.

3.3.6 Other devices

The XRF spectrum of magnetic train ticket card, hard disk of desktop type computer, and incandescent light bulb are shown in Figure 3.7-3.9. The other devices spectra are shown at Figure 3.10-3.20. A lot of titanium and iron were detected from the magnetic train ticket card, and also a small amount of niobium was detected. Nickel, cobalt and phosphorus were detected in a hard disk. Krypton was detected as well as on calcium, silicon, and strontium which are seemed as the glass ball component from an incandescent lamp. The krypton is the inert gas which is enclosed in an electric bulb to prevent the sublimation of the filament. In this spectrum, Kr $K\alpha$ line is overlaps with Pb $L\beta$ line.

The measurement results of other electronic and electric devices parts were together summarized in Table 3.2. The results for bipolar transistor, PN diode, mylar capacitor, ceramic capacitor, and floppy disk are analyzed at inside, and for flash disk, micro disk, electric plug and solder, analysis was done from the outside. Various rare and precious metals were detected from these devices. In addition, antimony and bromine were detected from many plastic covered of electronic parts.

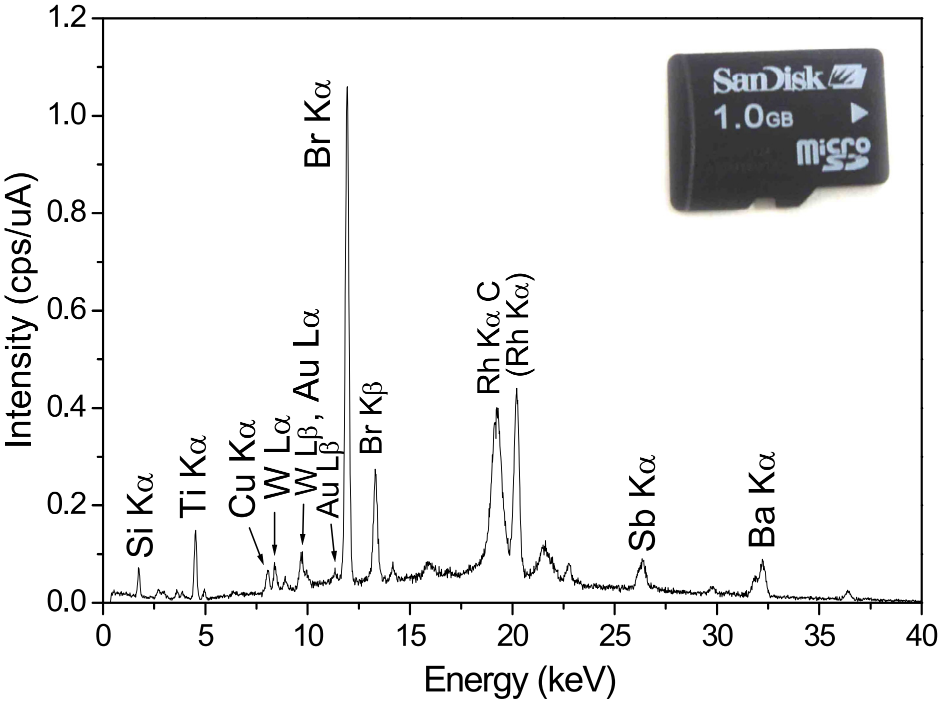

Figure 3.6. XRF spectrum of a memory card.

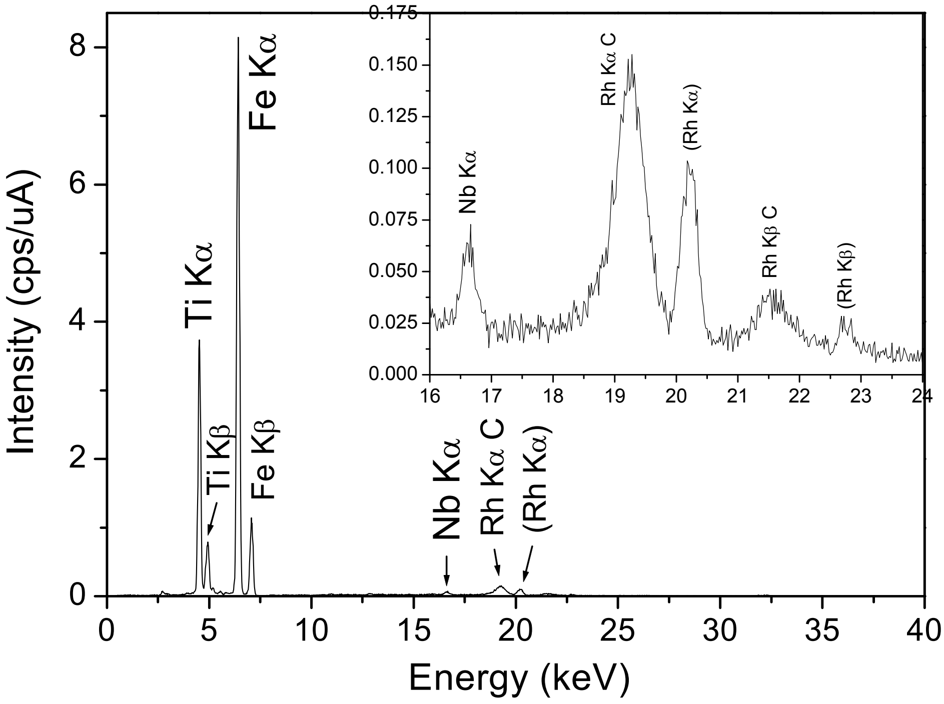

Figure 3.7. XRF spectrum of a train ticket card.

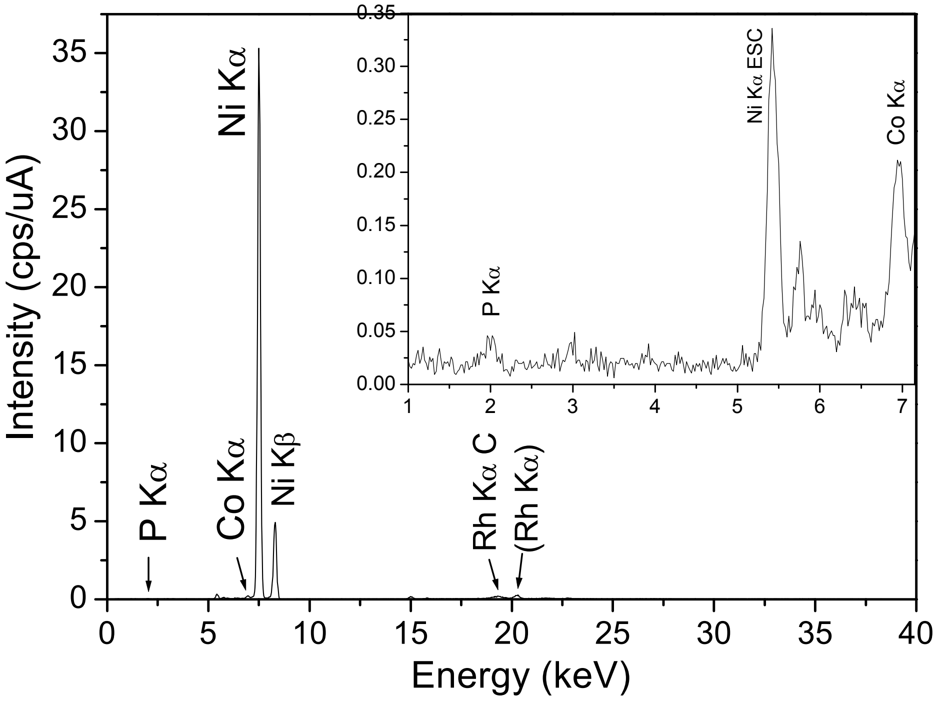

Figure 3.8. XRF spectrum of computer hard disk.

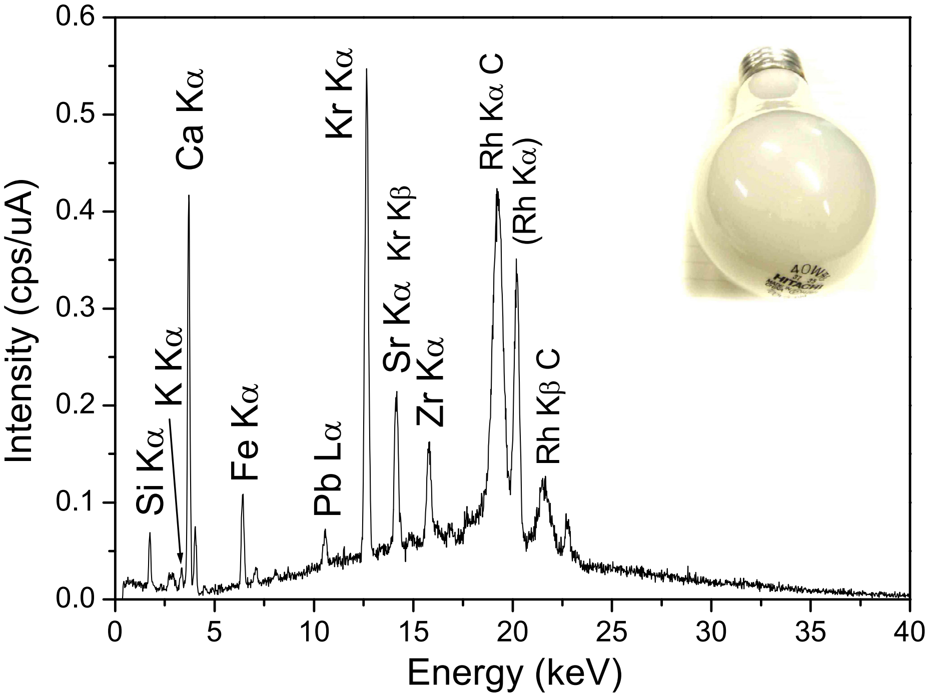

Figure 3.9. XRF spectrum of an incandescent light bulb.

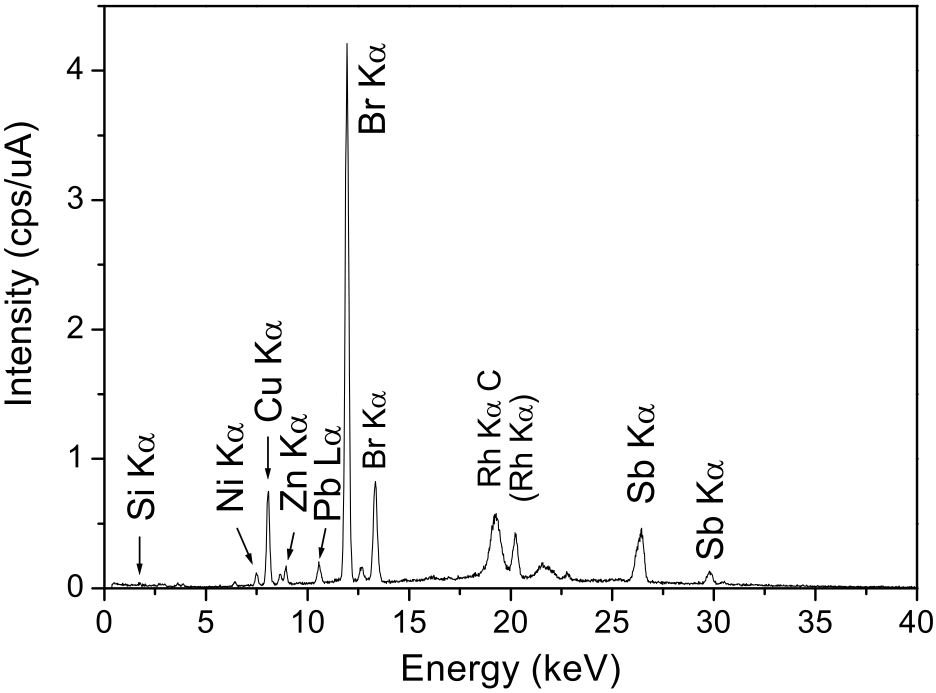

Figure 3.10. XRF spectrum of bipolar transistor.

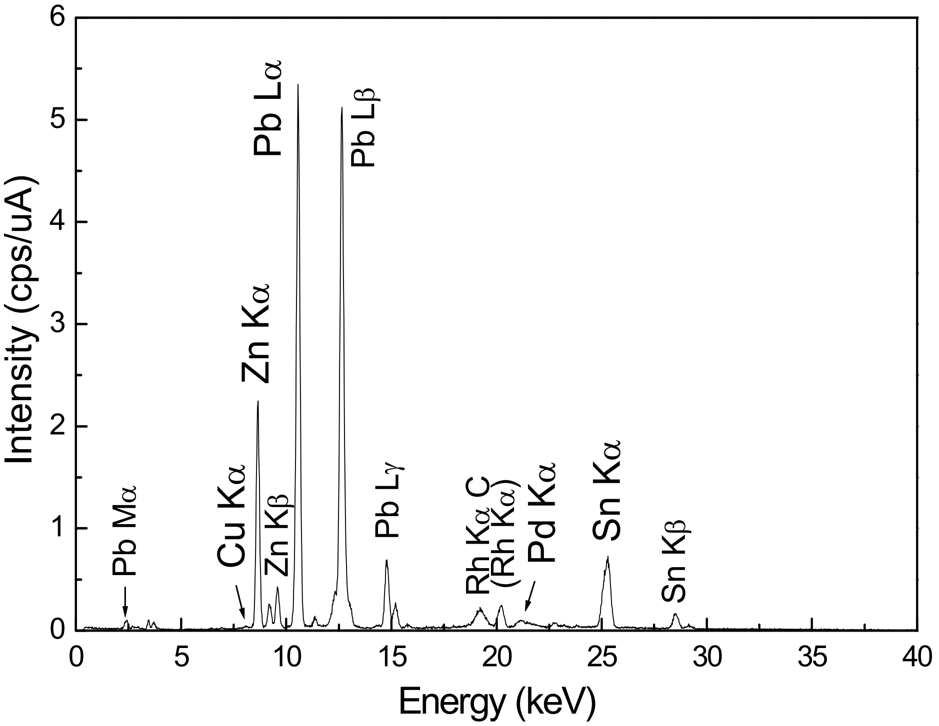

Figure 3.11. XRF spectrum of mylar capacitor.

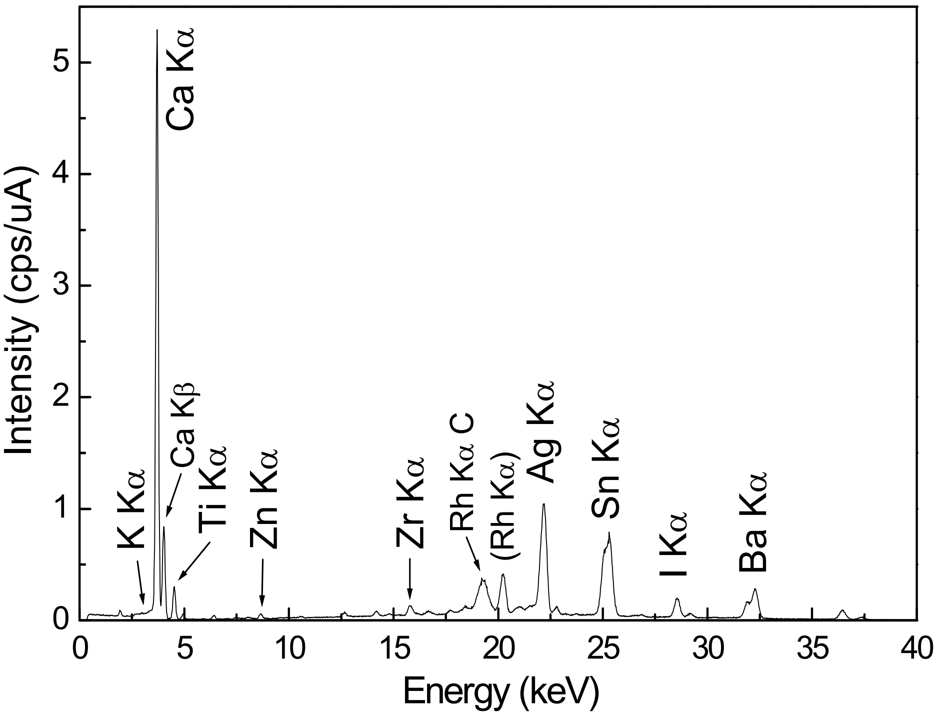

Figure 3.12. XRF spectrum of ceramic capacitor.

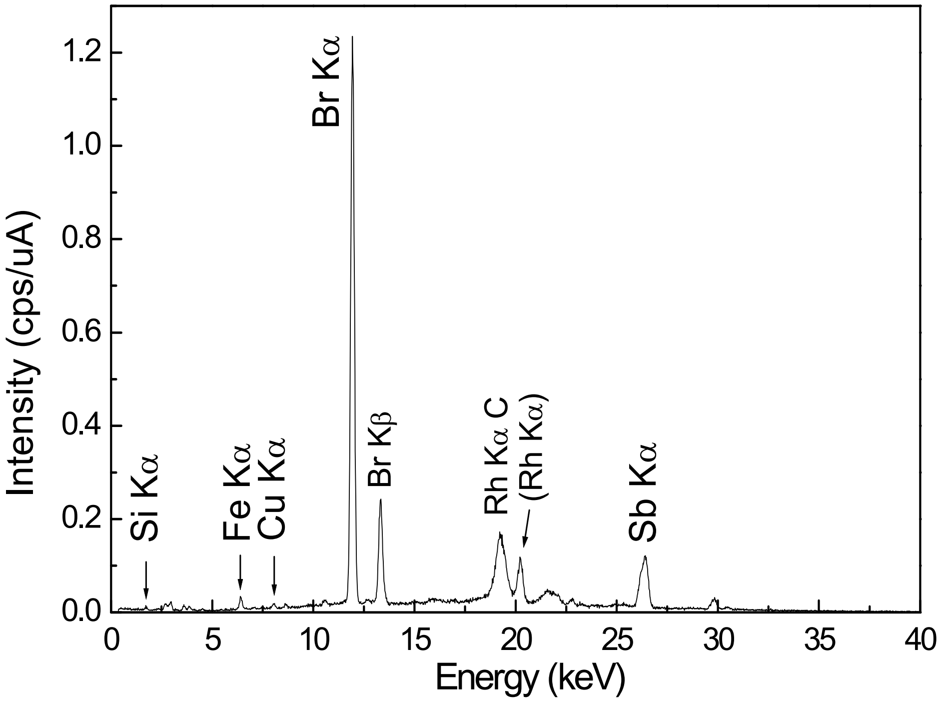

Figure 3.13. XRF spectrum of PN diode.

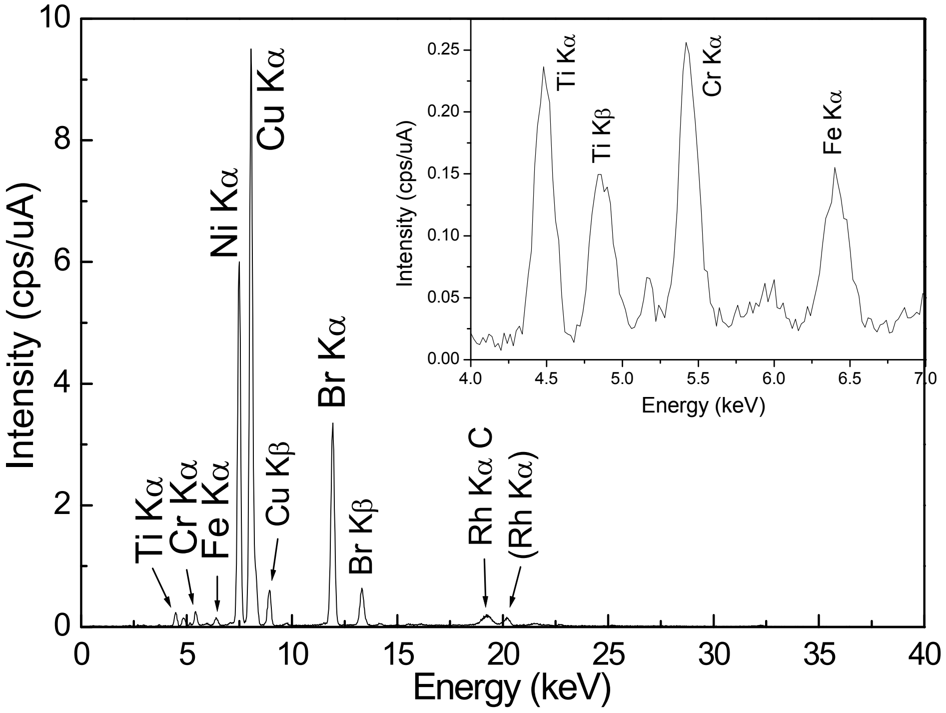

Figure 3.14. XRF spectrum of flash disk.

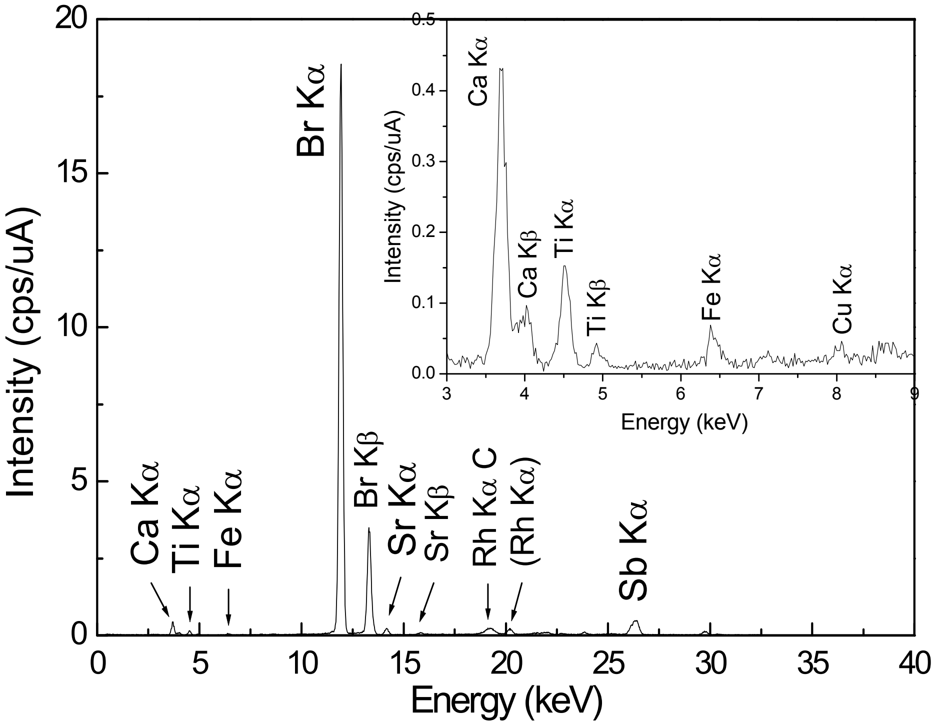

Figure 3.15. XRF spectrum of electric plug.

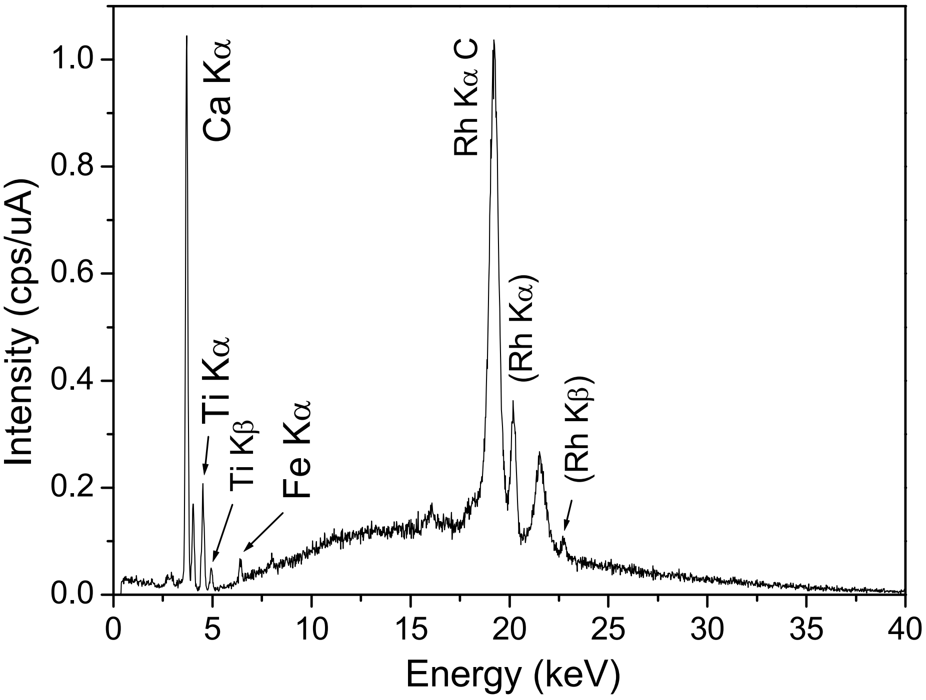

Figure 3.16. XRF spectrum of toggle switch.

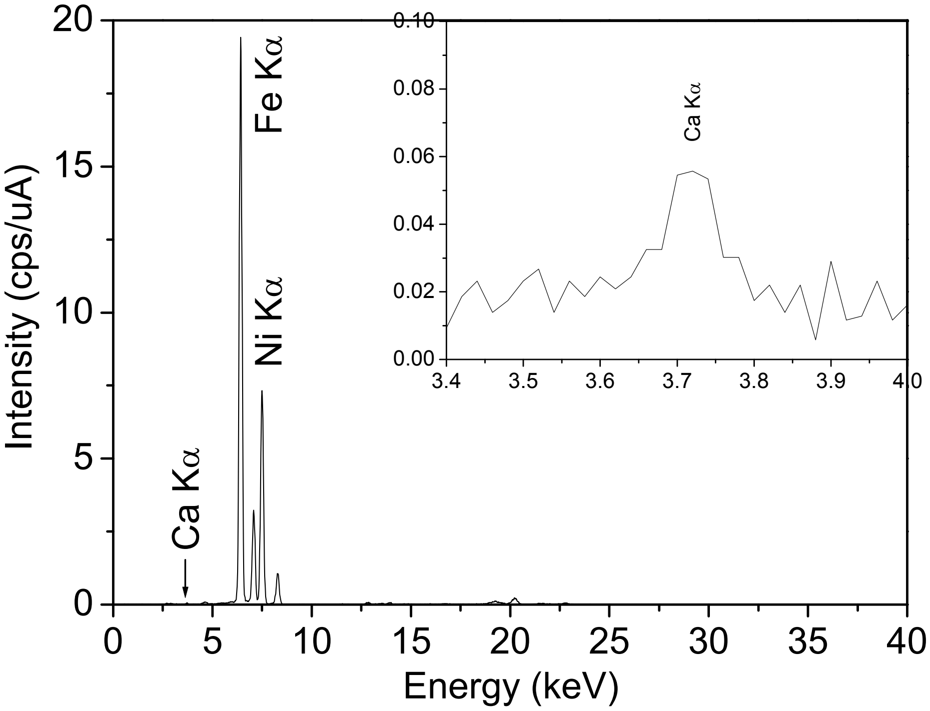

Figure 3.17. XRF spectrum of alkaline battery.

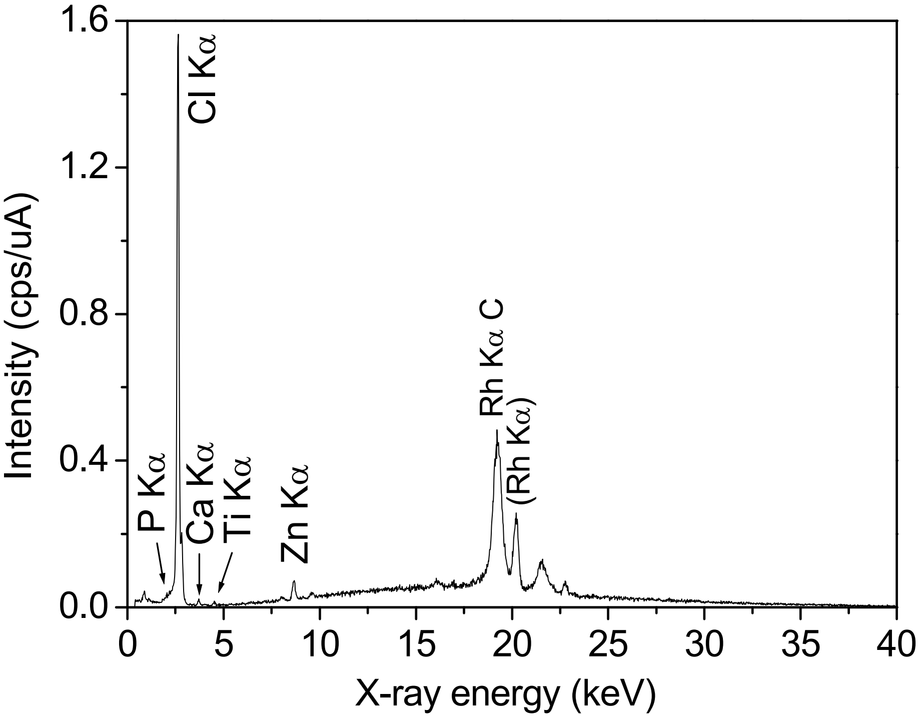

Figure 3.18. XRF spectrum of crocodile clip connector.

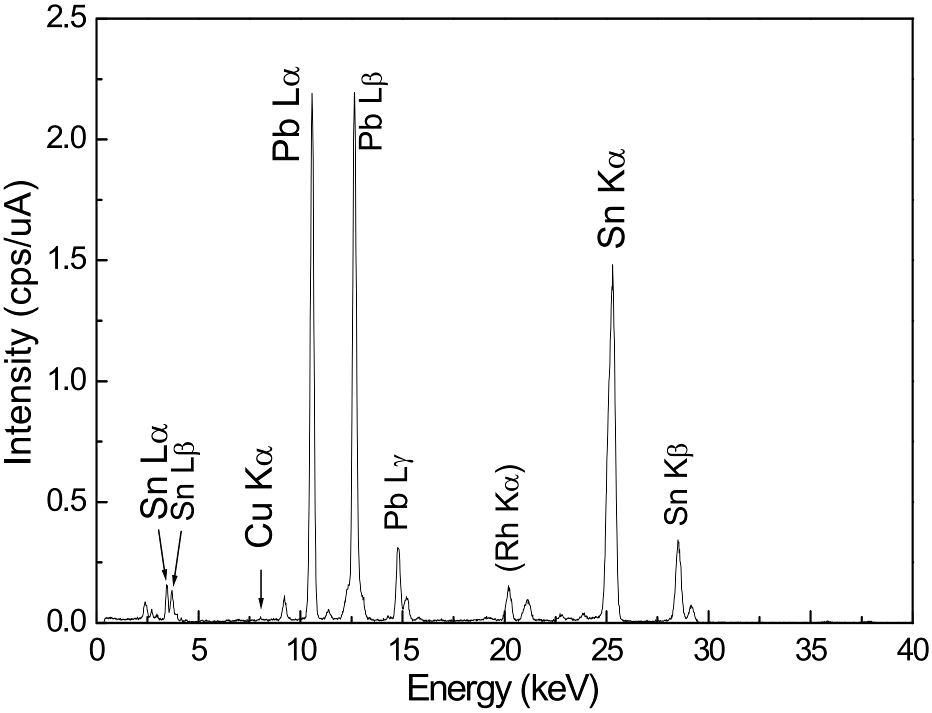

Figure 3.19. XRF spectrum of soldering material.

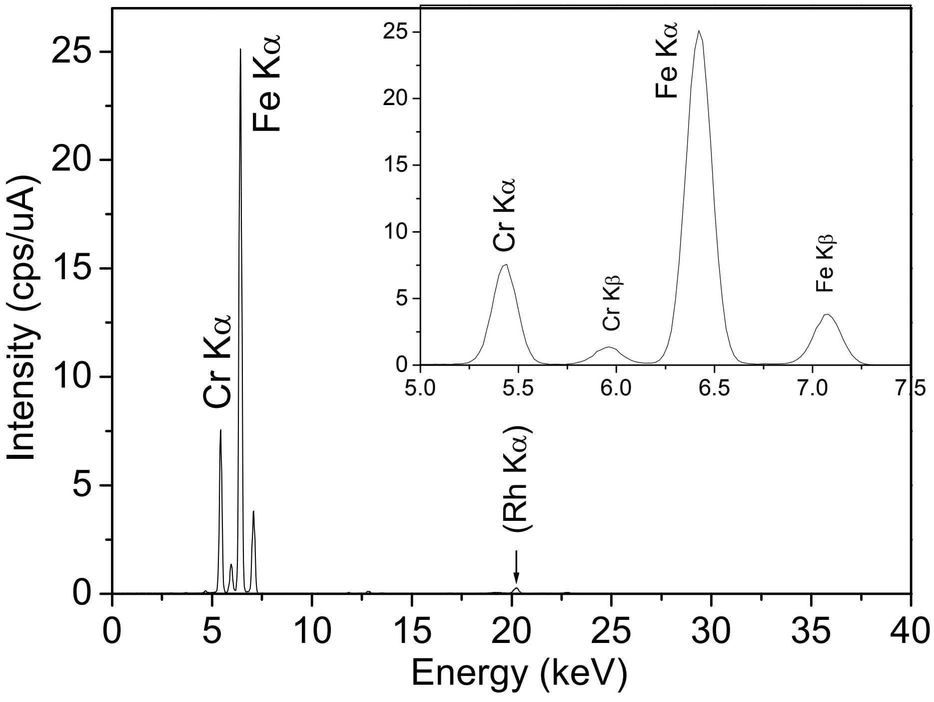

Figure 3.20. XRF spectrum of floppy disk.

Table 3.2. Detected elements by XRF analysis of various devices.

Samples name	Elements detected
Integrated circuit (outside)	Ti, Fe, Br, Sb
Integrated circuit (inside)	Si, Fe, Ni, Br, Sb, Au
Metal film resistor (outside)	Cr, Fe, Co, Ni, Cu, Zn, Sn, Ba, Zr
Metal film resistor (inside)	Ca, Cr, Fe, Co, Ni, Cu, Zn, Sr, Rb, Sn, Ba
Bipolar transistor	Si, Ni, Cu, Zn, Br, Sb, Pb
Mylar capacitor	Cu, Zn, Sn, Pd, Pb
Ceramic capacitor	K, Ca, Ti, Zn, Zr Ag, Sn, I, Ba
PN diode	Si, Fe, Cu, Br, Sb
Computer memory	Ti, Ni, Cu, Br, Sr, Ag, Sn, Sb, Pb
Flash disk	Ti, Cr, Fe, Ni, Cu, Br
Memory card (microdisk)	Si, Ti, Cu, Br, Sb, Ba, W, Au
Peltier device (outside)	Al, K, S, Sn
Peltier device (inside)	Ni, Cu, Sn, Sb, Te, Bi
Computer hard disk	P, Co, Ni
Electric plug	Ca, Ti, Fe, Cu, Br, Sr, Sb
Toggle switch	Ca, Ti, Fe
Alkaline battery (outside)	Ca, Fe, Ni
Crocodile clip connector	Cl, P, Ca, Ti, Zn
Soldering material	Cu, Sn, Pb
Floppy disk	Cr, Fe
Incandescent light bulb	K, Si, Ca, Fe, Kr, Sr, Pb
Train ticket card	Ti, Fe, Nb

3.4 Conclusions

X-ray fluorescence spectra of electric and electronic devices were measured with a commercial EDXRF spectrometer, and the result of analyzing contained rare and noble metals were described above. The outside part of many devices was covered with plastic, conductive polymer, ceramic, etc, so that it was difficult to get elemental information by the measurement through the package. When the inside part of device was directly measured by removing or breaking the package, the contained rare and noble metals were able to be detected. Pretreatment such as breaking or crushing sample in this measurement is a simple and easy operation if compared with chemical process such as elution or liquation.

X-ray fluorescence analysis offers many advantages such as the short analysis time, simple and easy in operation, able to know the information of element component/content within once measurement (simultaneous), automatic, and good reproducibility. The various portable of X-ray fluorescence analyzer was marketed, and further study would be aimed to miniaturization with high sensitivity [17]. Attached software in this commercial device can automatically identify elements in a sample and quantitative information based upon a library of X-ray data. However analytical process should be performed in order to get accurately results [15-17].

Understanding of what kind of element contained is an important thing that should be performed in recycling process of rare and noble metal, and X-ray fluorescence analysis is effective technique for this purpose. In addition, the restricted harmful element in the manufacture of various types of electronic and electrical equipment is detected at the same time. In this report, measurement was performed in the air, but if measurement was done in vacuum or helium, or the distance between detector and sample was shortened, light element such as Mg, Al, Si, P and Cl became easier detected.

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Chapter 4

Analysis of Alkaline and Alkaline Earth Metals in Standard Samples by Liquid Electrode Plasma Optical Emission Spectrometer

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.

4.1 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 4.1.

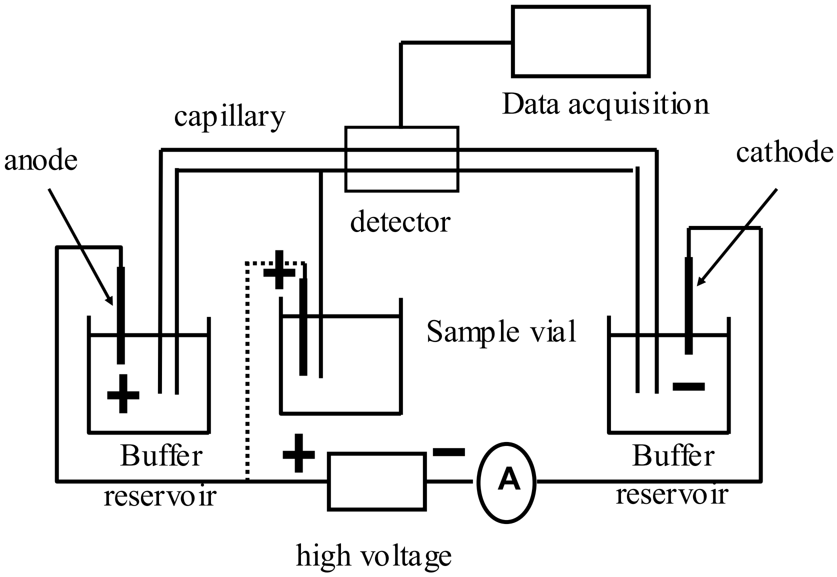

Figure 4.1. Instrumental set-up of capillary electrophoresis system [14].

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.

4.2 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 4.1. 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.

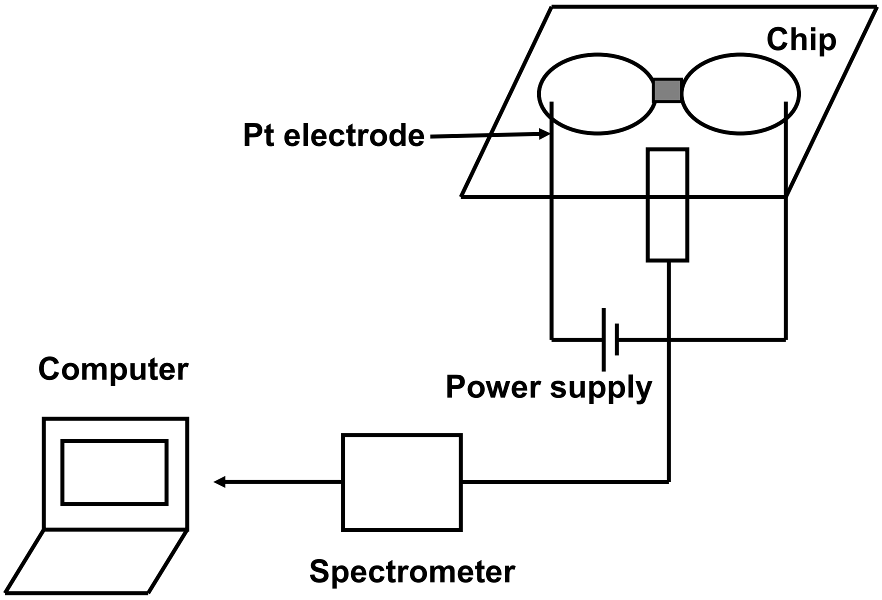

Figure 4.2. The experimental setup of handy liquid electrode plasma optical emission spectrometer [11-13].

4.3 Results and discussion

Figure 4.3 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 4.4 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.

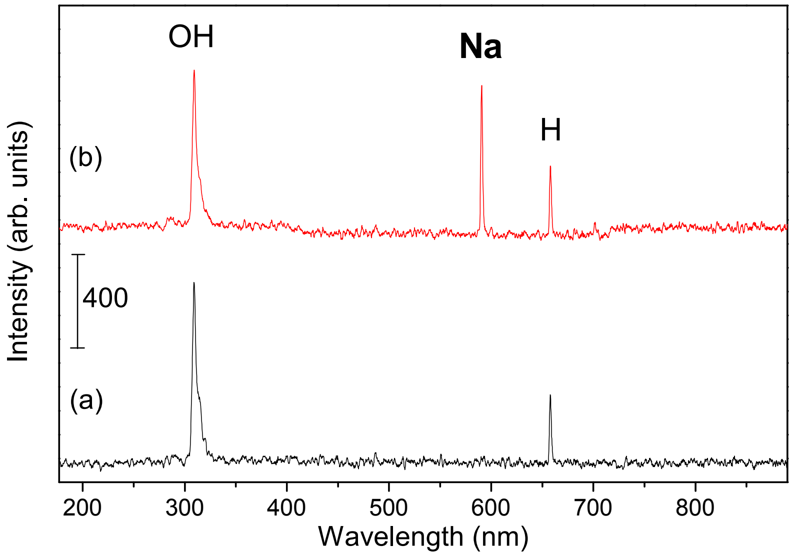

Figure 4.3. Emission spectra of (a) 0.1 M HNO_3 (b) 5 ppm Na standard solution. Applied voltage: 600 V, 1 ms.

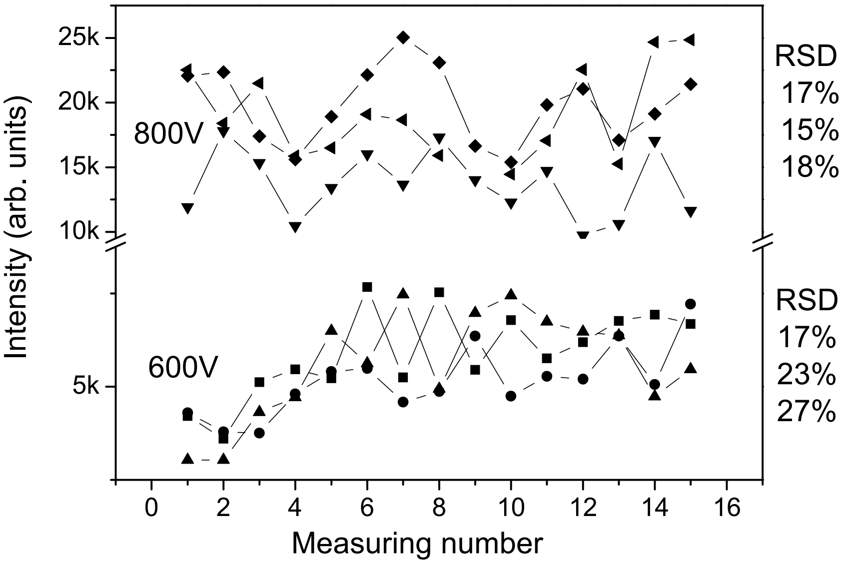

Figure 4.4. Reproducibility of sodium emission intensity lines. Sample: 10 ppm Na in 0.1 M HNO_3, Applied voltage: 600 V and 800 V

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 4.5 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.

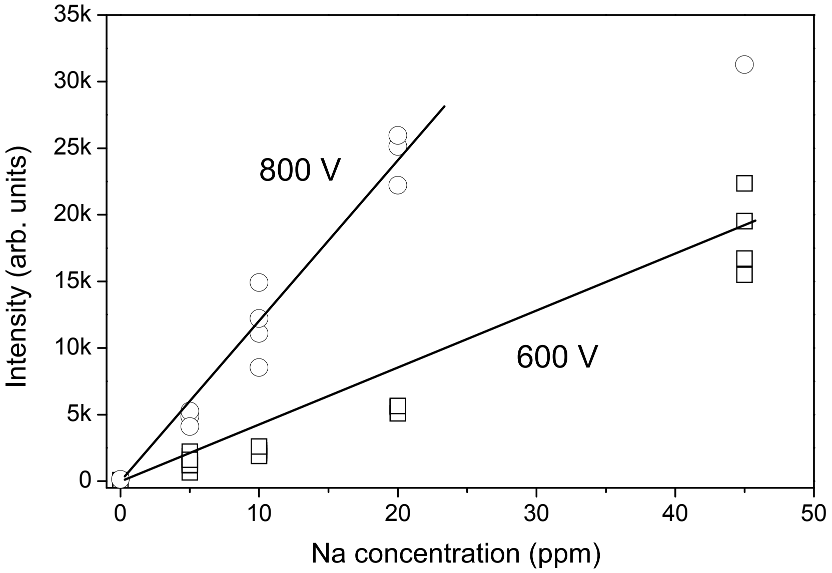

Figure 4.5. Calibration curves for Na emission lines in 0.1 M HNO_3. Applied voltage: 600 and 800 V, 10 ms.

Dependency of applied voltage on each emission lines was investigated in more detail. Figure 4.6 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 4.7. 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.

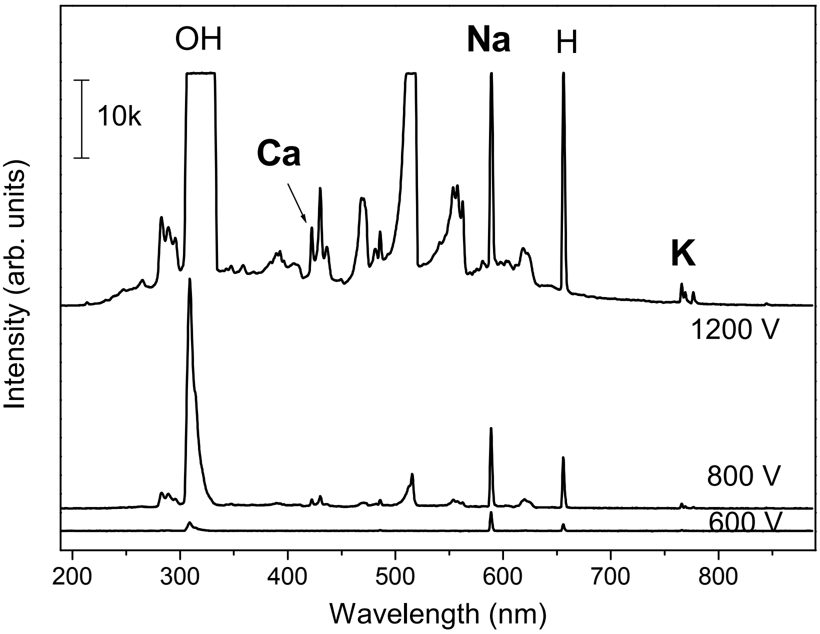

Figure 4.6. Dependency of applied voltage on emission spectra. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, 0.1 M HCl. Applied voltage: 600, 800 and 200 V, 5 ms.

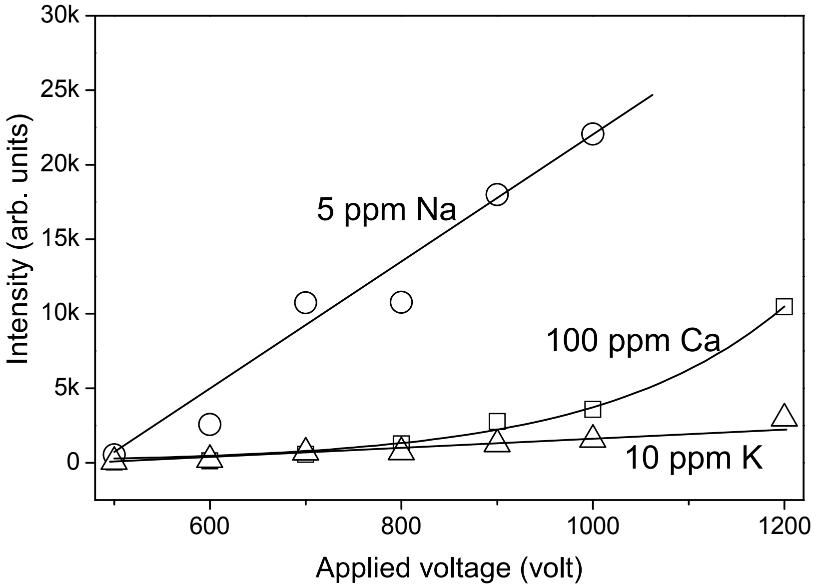

Figure 4.7. Emission intensities for Na, K and Ca lines with different applied voltage. Sample: Na 5 ppm, K 10 ppm, Ca 100 ppm, 0.1 M HCl. Applied voltage: 500-1200 V, 5 ms.

4.4 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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Chapter 5

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

Indicated element in commercially available such as 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 screening quantitative analysis of environmental samples.

5.1. 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. Barens [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.

Table 5.1. Comparison of the results (µg/ml) obtained by different methods [1].

Analyte	Muskmelon juice		Pineapple juice		Orange juice	
	XRF	ICP-AES	XRF	ICP-AES	XRF	ICP-AES
Na	239	245	75	80	88	85
Mg	33	35	66	63	29	33
Si	31	28	33	29	23	26
K	1930	1890[a]	702	724[a]	825	795[a]
Ca	44	46	67	62	52	46
Mn	0.20	0.20	0.56	0.49	0.20	0.25
Fe	1.7	1.8	7.6	7.2	4.9	4.3
Ni	0.10	0.12	0.11	0.13	0.10	0.08
Cu	0.19	0.22	0.15	0.13	0.13	0.11
Zr	0.10	0.11	0.22	0.21	0.12	0.13

[a] Obtained with AAS

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 Jarrel 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. Their results can be listed at Table 5.2. [5]. Sodium and potassium are the detected major element both at north and south basin. Wavelength emission lines for some elements for ICP analysis was listed at Table 5.3. [6].

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).

Table 5.2. Dissolved concentrations of major and trace elements in water from Lake Biwa [5].

	North basin		South basin	
Element	Concentration		Concentration	
Na	286 μmol/l	6.58 ppm	305 μmol/l	7.01 ppm
Ca	273 μmol/l	10.92 ppm	274 μmol/l	10.96 ppm
Mg	85.3 μmol/l	0.07 ppm	84.8 μmol/l	2.06 ppm
K	44.4 μmol/l	1.74 ppm	47.5 μmol/l	1.86 ppm
Si	18.7 μmol/l	0.53 ppm	27.3 μmol/l	0.76 ppm
Sr	478 nmol/l	41.87 ppb	502 nmol/l	43.96 ppb
Ba	57.7 nmol/l	7.90 ppb	71.2 nmol/l	9.75 ppb
Mn	25.1 nmol/l	1.38 ppb	129 nmol/l	7.09 ppb
Fe	24.5 nmol/l	1.37 ppb	80.5 nmol/l	4.51 ppb
Cu	7.9 nmol/l	0.50 ppb	9.6 nmol/l	0.61 ppb
Zn	4.2 nmol/l	0.27 ppb	6.1 nmol/l	0.39 ppb
Ni	3.6 nmol/l	0.21 ppb	3.6 nmol/l	0.21 ppb
Mo	2.9 nmol/l	0.27 ppb	3.7 nmol/l	0.35 ppb
V	2.3 nmol/l	0.12 ppb	4.0 nmol/l	0.20 ppb

North basin: Ie-1 at a depth of 73 m, and south basin: Nb-5 (3.5 m) and Na-3 (2 m).

Table 5.3. Some emission line of elements for ICP analysis [6]

Element	Wavelength emission (nm)	Detection limit (ng/ml)
Ag	328.068	1
Al	396.152	5
Au	242.795	3
Ba	455.403	0.2
Bi	223.061	5
C	193.366	10
Ca	393.366	0.1
Co	228.802	1
Cr	205.552	2
Cu	324.754	0.5
Fe	259.940	0.8
K	769.896	50
Mg	279.553	0.1
Mn	257.610	0.3
Mo	202.030	1
Na	588.995	2
Ni	221.647	3
Pb	220.353	20
Pt	214.423	10
S	180.600	20
Si	251.611	5
Sr	407.771	0.1
V	309.311	1
Zn	213.856	1
Zr	213.198	2

5.2. Experimental

Experimental setup was similar to those at chapter 4. The 40 μL 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 Ie-1, Kc-3, Lc-4 and Lc-2 (figure 5.1) in various depths of 0m, 1m, 5m and 50m on May 5th, 2008. The analyzed media is 0.1 M HNO_3 aqueous solution unless otherwise stated.

Since May 2008, a new type of disposal chip had been available, and calibration curve for known standard solution of sodium and potassium were prepared again by measuring of various concentrations.

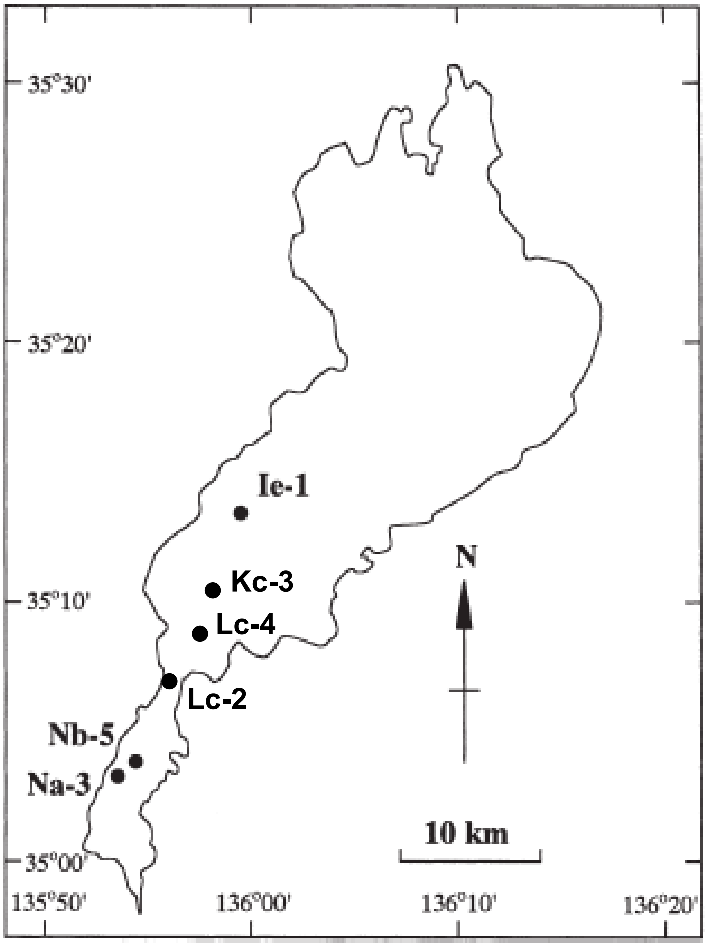

Figure 5.1. Sampling locations on Lake Biwa

(Figure 5.1. is cited from [5], with additional sampling location at Kc-3, Lc-4 and Lc2)

5.3. Results and Discussion

Figure 5.2 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 5.3 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_2 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^- and H^+ 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 (Table 1.1 Chapter 1). The quantitatively detected sodium and potassium are about 13±3 and 3±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 5.4. 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±0.6 and 145±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 5.5). The indicated element content of coffee is only sodium with 0 mg/1000 ml. The quantitatively detected element is sodium about 0.2±0.1 and potassium about 400±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. Generally, the emission efficiency of an alkaline metal is higher than an alkaline earth metal. Meanwhile, the emission efficiency of different element in the same group is related to its excitation energy [7]. OH^- and H^+ 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^- is stronger than H^+.

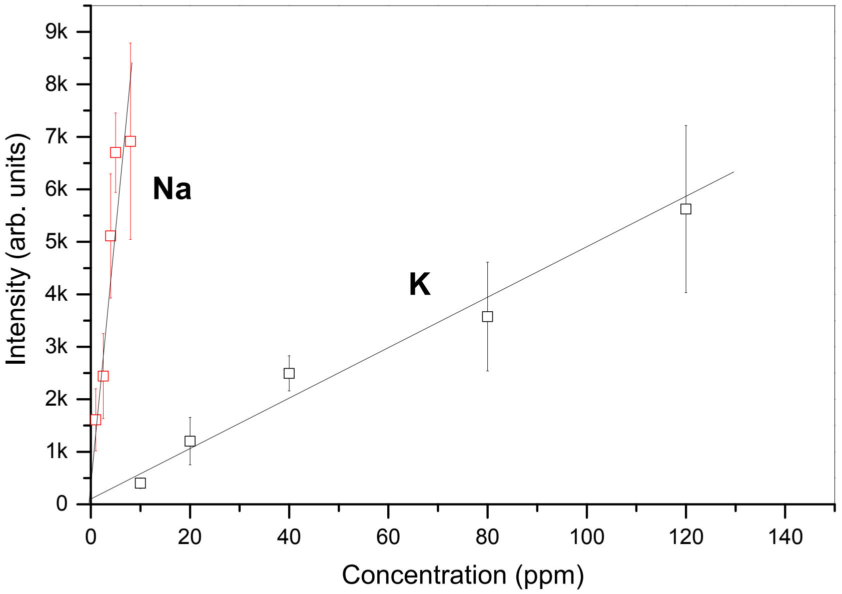

Figure 5.2. Calibration curve of Na and K

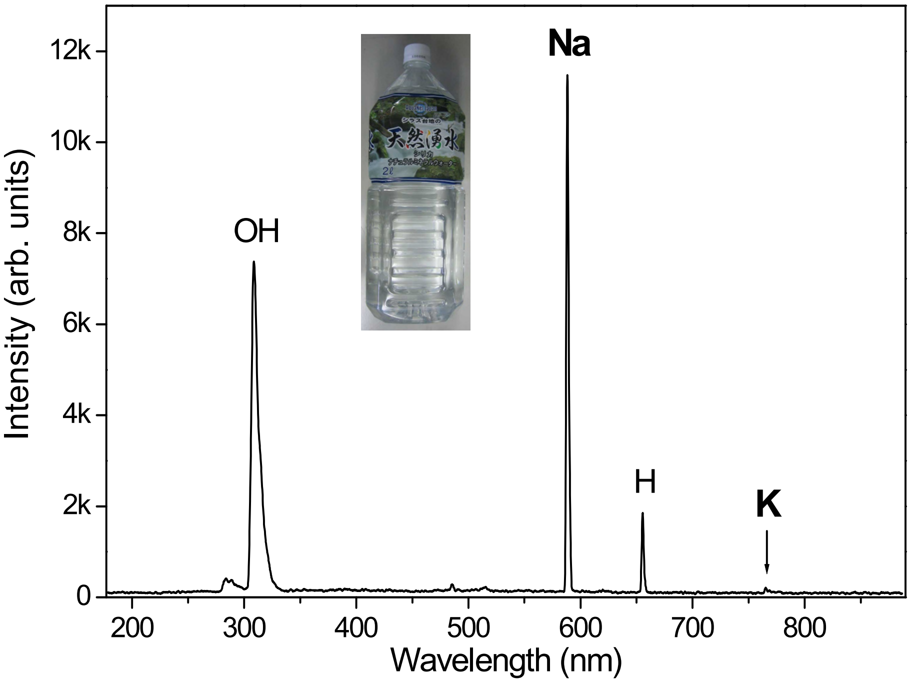

Figure 5.3. Emission spectrum of the bottle drinking water.

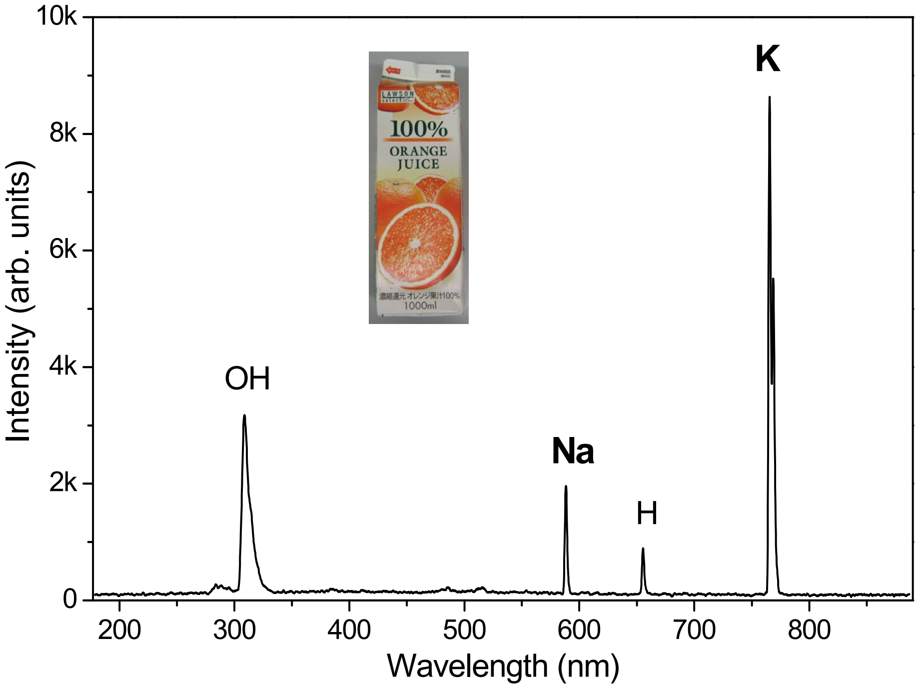

Figure 5.4. Emission spectrum of 100% orange juice.

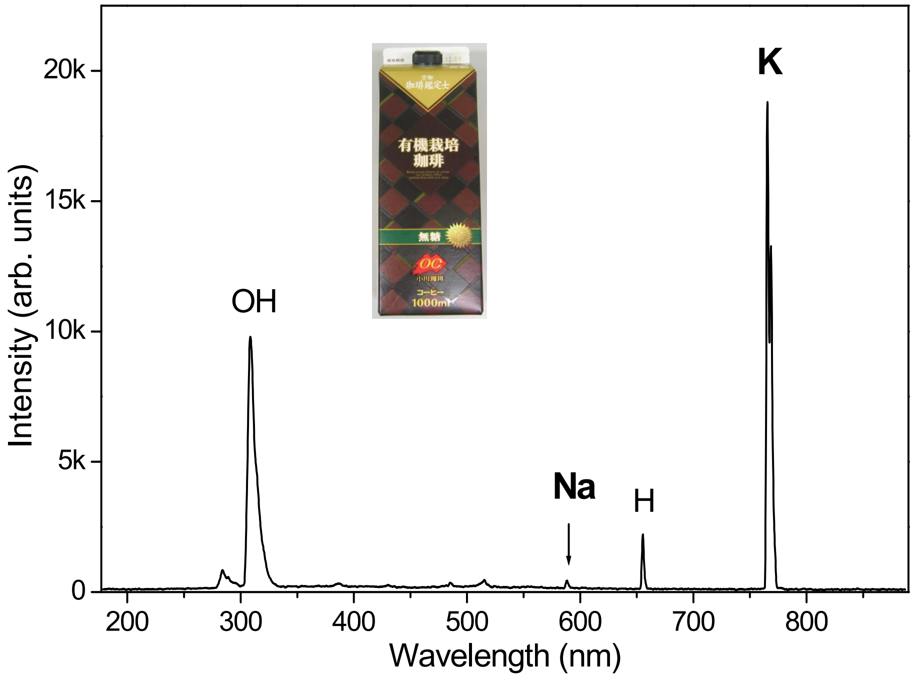

Figure 5.5. Emission spectrum of coffee.

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 5.6 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 5.7-5.13. As a qualitative analysis, most of spectra show that only sodium was observed at 589 nm. The strongest line is OH^- at 306 nm, followed by Na and H^+ 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 [8] 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.

It was reported by Micro emission Ltd. [8] 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. Undetectable some indicated element content is caused to its detection limit for each element. So that, in the future measurement, choosing the analytical parameters such as applied voltage and applied measuring time are important thing should be done. Matsumoto et al. [9] 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.

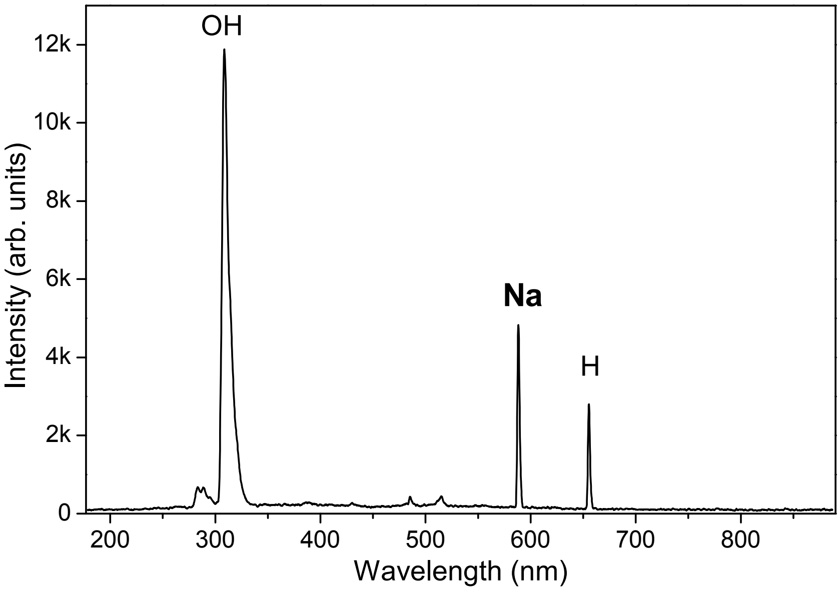

Figure 5.6. Emission spectrum of Adogawa river water

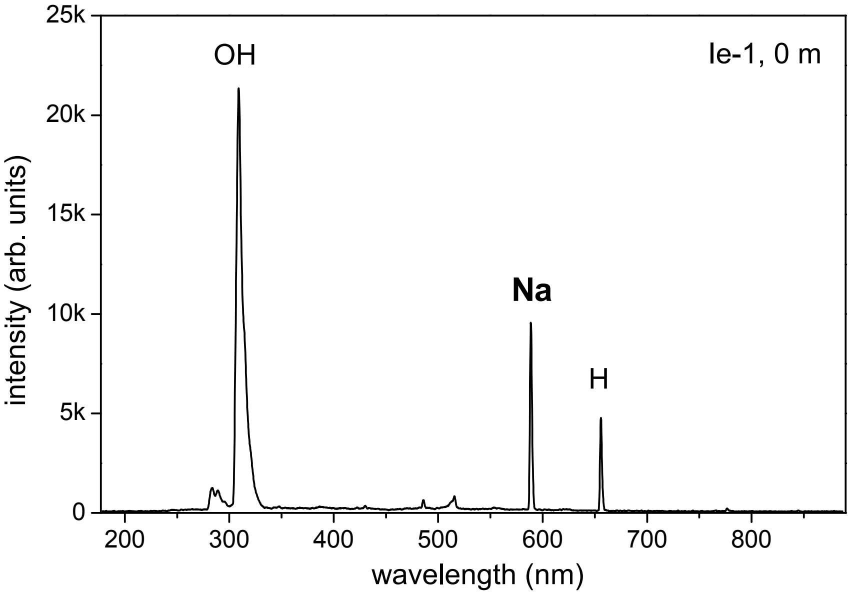

Figure 5.7. Emission spectrum of Lake Biwa water in depth of 0 m (Ie-1).

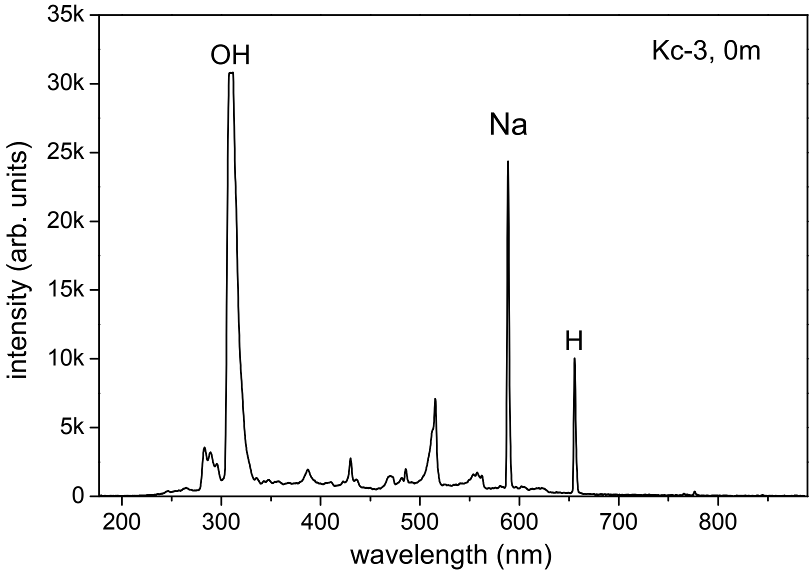

Figure 5.8. Emission spectrum of Lake Biwa water in depth of 0 m (Kc-3).

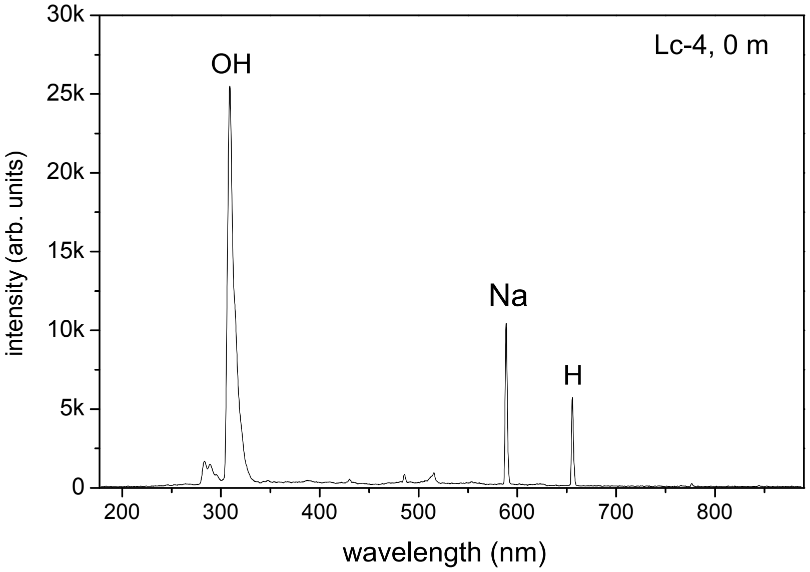

Figure 5.9. Emission spectrum of Lake Biwa water in depth of 0 m (Lc-4).

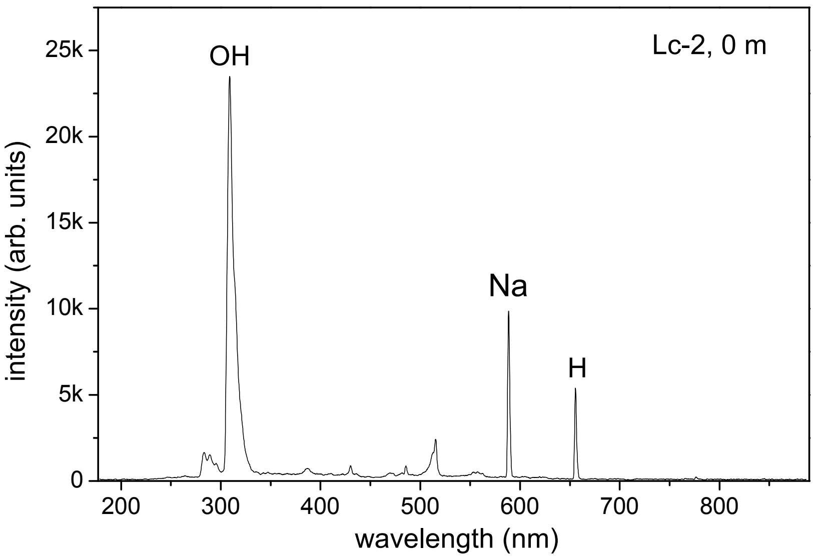

Figure 5.10. Emission spectrum of Lake Biwa water in depth of 0 m (Lc-2).

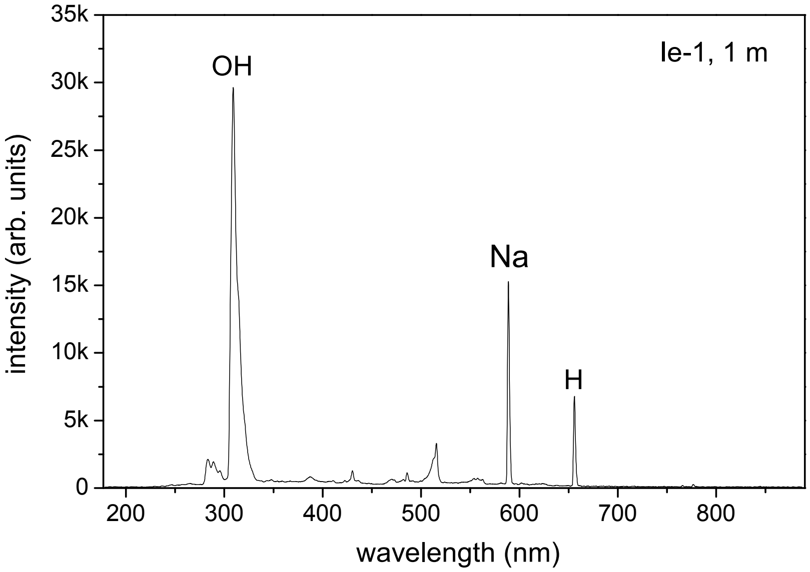

Figure 5.11. Emission spectrum of Lake Biwa water in depth of 1 m.

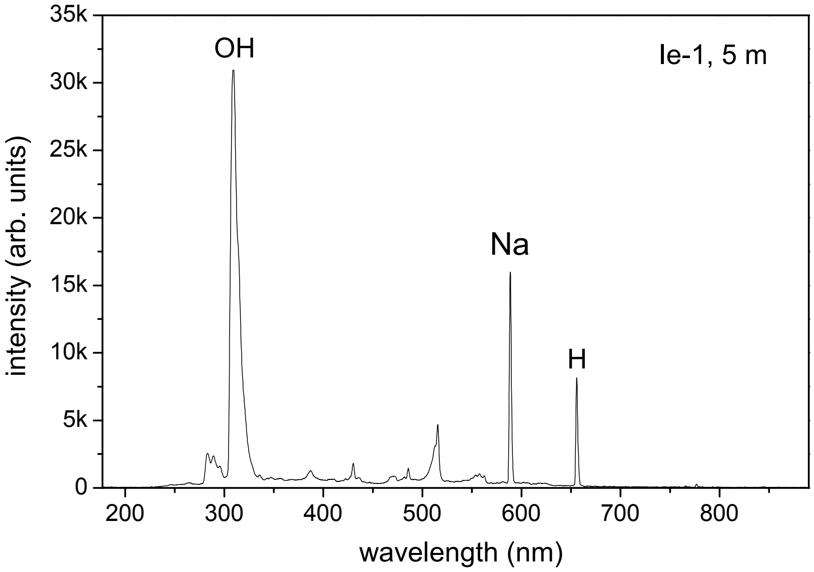

Figure 5.12. Emission spectrum of Lake Biwa water in depth of 5 m.

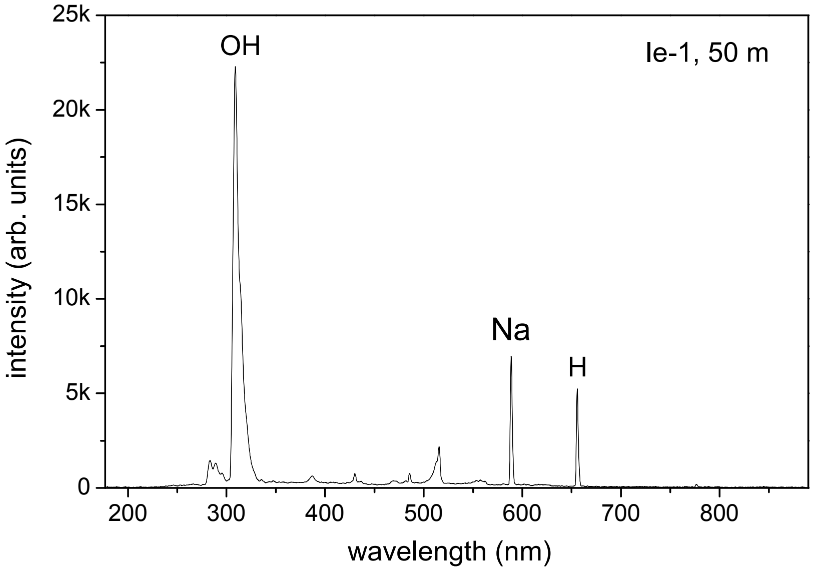

Figure 5.13. Emission spectrum of Lake Biwa water in depth of 50 m.

5.4. Conclusions

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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Chapter 6

Summary

It was known that elemental analysis has important role in the determining of elements composition of materials. Many elemental analysis methods such as inductively coupled plasma (ICP), X-ray fluorescence spectrometry (XRF), atomic absorption spectrometry (AAS), etc. are utilized in industry, laboratory, university or others. Usually, these methods require skills/experiences and large space/size. Then, in order to anticipate these problems, the portable analyzer is recently developed to miniaturize the dimensions of apparatus. Miniaturization was developed to carry out on-site analysis at the place where samples are located, rather than moving the sample to the laboratory.

In this study, several application of portable Brix meter, desktop type of small X-ray fluorescence spectrometer and portable elemental analyzer of liquid electrode plasma optical emission spectrometer were carried out. The results obtained in this study are summarized as follows.

Chapter 2

The viscosity of aqueous sucrose solution in various concentrations and the sugar content were measured by using an Ostwald viscometer and a commercial available of portable Brix meter respectively. The viscosity is determined by measuring its rate of flow through a capillary tube of Ostwald viscometer, the time required for sucrose solution is also noted, then its viscosity in various concentrations can be calculated and experimental value is compared to the reference. The concentration of aqueous sucrose solution was measured by using portable Brix meter. There is relationship between the concentration and the viscosity. Increasing of concentration gives rise to increasing viscosity. With this tendency, by knowing concentration value, its viscosity can be estimated. So that, the Brix meter can be applied to other uses than concentration measurement.

Chapter 3

Rare and noble metals contained in electric and electronic devices were analyzed by a commercially available energy dispersive X-ray fluorescence spectrometer. The used samples in this experiment such as integrated circuit, resistor, diode, transistor and the other electronic parts were mainly got from the waste electric electronic equipment. Several kinds of rare and noble metals such as nickel, cobalt, tungsten, zirconium, gold, silver, and bismuths were commonly detected by analysis of the samples at inside part after removal of the package or crushing. However, various rare and noble metals were detected from outside part of devices, such as gold was detected in memory card. The outside part of many devices was covered with plastic, conductive polymer, ceramic, etc, so that it was difficult to get elemental information by the measurement through the package. Both bromine and antimony were detected in the most electronic part which contains plastics. When the inside part of device was directly measured by removing or breaking the package, the contained rare and noble metals were able to be detected.

Understanding of what kind of element contained in electric and electric devices is an important thing that should be performed in recycling process of rare and noble metal. X-ray fluorescence analysis with the short analysis time, simple and easy in operation is an effective technique for this purpose.

Chapter 4

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 600 V, at the first few measurement number, there is increasing period of emission intensity by consecutive measurement, and the relative standard deviation (RSD) among chips was 17%, 23% and 27%. When applied voltage was changed to 800 V, there is no increasing period since the first to the last measurement, emission intensity has more relative constant, relative standard deviation 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.

Chapter 5

The commercially available samples such as bottle drinking water, 100% orange juice and coffee and unknown element and concentration in environment samples of Adogawa river water and Lake Biwa water 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 screening quantitative analysis of environmental samples. The presence of element contents in these samples are easily detected by this analyzer with just taking a sample, putting in the chip, applying voltage, emission, spectra, then qualitative or quantitative analysis can be performed.