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Description	

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Determination of Trace Amounts of Sodium and Lithium in Zirconium Dioxide (ZrO_2) using Liquid Electrode Plasma Optical Emission Spectrometry

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Keywords: Liquid electrode plasma optical emission spectrometry; Zirconium dioxide; trace element detection; without interference

Abstract

This paper describes a quantitative measurement of trace elements (Na, Li) in high purity zirconium dioxide powder using liquid electrode plasma optical emission spectrometry (LEP-OES). Conventionally, for such type of measurements, inductively coupled plasma optical emission spectrometry (ICP-OES) is frequently employed. The detection limits of elements in zirconium by ICP-OES are degraded due to the spectra interference between the trace elements and zirconium of the matrix, because zirconium is a line rich element in spectra obtained by ICP-OES. LEP-OES is an elemental analysis method developed by the authors. The measurement principle is simple, as follows. Sample solution is put into a narrow channel on a small cuvette and voltage pulse is applied from both ends of the channel. At the center of the channel which is made narrower, the voltage and current are concentrated there, and plasma is generated. From the emission of the plasma, the quantitative analysis of the elements in the solution is achieved. The LEP-OES has the property that the emission of zirconium is relatively weak, so that highly sensitive measurement of trace elements in zirconium matrix can be conducted without interference. Sample solution is prepared by dissolving high purity zirconium dioxide powder and trace amounts of Na or Li with sulfuric acid. The voltage dependence and the pulse width dependence of optical emission spectra are also investigated. With increase of the voltage or the pulse width, the ratio of emission intensities of Na to those of hydrogen increases. This suggests that the ratio of sensitivity of two elements is variable, that means the element selectivity is controllable

to some extent by the measurement conditions in LEP-OES. In the case of Na and H, the ratio can be controlled from 7.4 to 21.6%. Finally, the detection limits (3 S.D.) of the trace elements, Na and Li, in 4000 $\mu g\ g^{-1}$ zirconium dioxide aqueous solution are found to be 0.02 $\mu g\ g^{-1}$ and 0.133 $\mu g\ g^{-1}$, respectively. These values correspond to 5 $\mu g\ g^{-1}$ for Na, 33.25 $\mu g\ g^{-1}$ for Li in original high purity zirconium dioxide powder. The correlation coefficient of calibration curve was 0.995 for Na, 0.985 for Li. Those are comparable to the literature values of detection limits using ICP-OES.

1. Introduction

Zirconium dioxide has outstanding chemical and physical properties such as heat-resistance, chemical resistance, high toughness, high strength and catalytic characterization, so that it is widely used in industry in piezoelectricity components, catalysts, solid electrolyte fuel batteries, and so on [1,2]. It is well-known that these properties of high purity zirconium dioxide are subject to change by very small amounts of impurity elements [2]. Therefore, the measurement of the impurity concentration in zirconium dioxide is important from the viewpoint of quality maintenance. Conventionally, for such measurement of the trace elements, inductively coupled plasma optical emission spectrometry (ICP-OES) has been employed [3, 4] as the most effective device. However, in zirconium dioxide matrix, high concentrate zirconium peak frequently interferes with impurity element peak, because zirconium is a line rich element in ICP-OES measurement. Therefore, the quantitative measurement of the trace element

in high purity zirconium dioxide is very difficult [2]. In order to improve the limit of detection, some studies have been reported [5-9]. One of them reports that the combination of a microwave-assisted digestion using H_2SO_4-$(NH_4)SO_4$ and the wavelet transform-based spectral interference correction allows fast and satisfactory determination of trace Fe, Hf, Mn , Na, Si and Ti in high-purity zirconium dioxide powders by ICP-OES [9]. The factor of the improvement for Na is, however, only about twice. Further improvement is preferable. On the other hand, we have developed an elemental analyzer method, namely liquid electrode plasma optical emission spectrometry (LEP-OES) [9-11]. The measurement principle is simple, as follows (Fig. 1). Sample solution is put into a narrow channel on a small cuvette and voltage pulse is applied from both ends of the channel (Fig.1-a). At the center of the channel which is made narrower, the voltage and current are concentrated there (Fig.1-b), and plasma is generated (Fig.1-c). From the emission of the plasma, the quantitative analysis of the elements in the solution is achieved. The LEP-OES has the property that the sensitivity strongly depends on the measurement conditions and the element. This means that LEP-OES has element selective property. In this case, the emission of zirconium in LEP-OES is very weak in typical measurement conditions, compared to its emission in ICP-OES, so that highly sensitive measurement of trace elements with low detection limits in zirconium matrix can be expected when using LEP-OES, without the zirconium peak interference.

In this paper we investigated the applied voltage dependence and the pulse width

dependence of the emission intensity of spectra, and we calculated and suggest the detection limits, coefficients of variation (C.V), and correlation coefficients, using the calibration curve of sodium and lithium, respectively.

2 Experimental section

2.1 Reagent

Zirconium dioxide powder (NEWMET KOCH, Germany) was used for zirconium dioxide aqueous solution. Nitric acid (KANTO CHEMICAL, Japan) was used for washing chips and a beaker was used when dissolving zirconium dioxide powder. Sulfuric acid (KANTO CHEMICAL, Japan) and Ammonium sulfate (NAKARAITESUKU, Japan) was used for dissolving zirconium dioxide powder. Sodium standard solution (KANTO CHEMICAL, Japan) and lithium standard solution (KANTO CHEMICAL, Japan) were spiked into zirconium dioxide solution as analyte. Water purified with Milli Q Labo system (Millipore) was used throughout the experiments.

2.2 Apparatus

Spectroscope (Andor, Japan Model No SR-3031-A) and CCD (Andor, Japan Newton) were used to measure optical emission. Oscilloscope (Tektronix, Japan TDS 2002 TWO CHANNEL DIGITAL) was used for confirming electric current (Fig. 2).

2.3 Sample preparation

At first for decontamination a quartz glass beaker and a transfer pipette were washed

with 10% (v/v) nitric acid diluted with the purified water at room temperature (RT), and dried by nitrogen gas. Subsequently, a medical spoon made of plastic was washed with the purified water, and dried by nitrogen gas. After these washing procedures, zirconium dioxide (0.4 g) was weighed and transferred into the clean quartz glass beaker with 4.0 g of ammonium sulfate, and 10 ml concentrated sulfuric acid. This mixture was heated at 350 °C for 1 h using hotplate while stirring. After cooling to RT, the sample solution was diluted to 4000 $\mu g g^{-1}$ zirconium dioxide, and 1.8 M sulfuric acid, using 100 ml by the purified water [10]. In addition, for preparation of standard solutions, 1000 $\mu g g^{-1}$ sodium and lithium standard solutions were diluted into zirconium dioxide solution, 0,0.2, 0.6, 1.0, 5, 10, 15, 20 $\mu g\ g^{-1}$ for sodium and 0, 0.3, 2, 3, 5, 10, 15, 20, 25 $\mu g\ g^{-1}$ for Li respectively.

2.4 Experimental setup for evaluation of LEP-OES characteristics

The experimental setup for evaluation of LEP-OEP characteristics is shown in Fig. 2. The chip washed with the purified water was immersed in the purified water overnight at RT. These were immersed in 10% (v/v) nitric acid for 5 minutes and washed with the purified water. For evaluation of the characteristics, the sample solution was injected into the chip using syringe carefully. In addition, during a sample injection, air bubbles were prevented from entering the device. The platinum wires were immersed in the device, and the voltage was applied using high-voltage power supply. The emission spectrum was measured by spectroscope (Andor), and the current was confirmed by oscilloscope.

3 Results and discussion

3.1 The voltage dependency of Na spectrum

The 10 μg g^{-1} sodium containing 4000 μg g^{-1} zirconium dioxide in sulfuric acid (1.8 M) aqueous solution was used as sample solution for evaluation of voltage dependency. For evaluation of voltage dependency, measurements were carried out using the following experimental conditions. Voltage was applied as three pulses. Each pulse width was 80 μsec. Periods between pulses are 2 ms. Each pulse height is one of 500, 600, 700, 800, 900 and 940 V. The measurement was carried out three times at each voltage. These data measured 3 times were averaged and the data is shown in Fig. 3. Emission lines of Na and H are clearly observed. Hydrogen spectrum must be a peak of water origin. The sodium and hydrogen intensities increase with the applied voltage could be observed. This increase is plotted as a function of voltage in Fig.4. At low applied voltage (500-700 V), the sodium optical emission intensity is intensive as that of hydrogen. In addition, at high applied voltage (800-940 V) the hydrogen optical emission intensity was much more intensive than sodium optical emission intensity. These facts mean that the sensitivities of each element in LEP-OES are changeable by the operation condition such as applied voltage. This element-selective feature of LEP-OES is advantageous in case of trace impurity measurements in high concentrate matrix.

3.2 Applied voltage time dependency of Na spectrum

The 10 μg g^{-1} sodium containing 4000 μg g^{-1} zirconium dioxide in sulfuric acid (1.8 M) aqueous solution was used as sample solution for this experiment. For the voltage application time, the measurements were carried out using the following experimental conditions. Voltage was applied as three pulses. Each pulse width (t_w) is one of the following: 40, 80, 120, 200, 400 and 800 μsec. Periods between pulses was 2 msec. Each pulse height was 600 V. The measurement was carried out eight times at each voltage application time. The averaged spectrum is shown in Figure 5. The hydrogen spectrum must be a peak of water origin. In Figure 5, the sodium and hydrogen optical emission intensities, and the heat emission increase depending on the width of the pulse for the applied voltage can be observed. These increases of the sodium and hydrogen spectra are shown in Fig. 6. It is found that the optical emission intensities of sodium and hydrogen for voltage application time increases such as logarithmic functions. At the $t_w < 80$ μsec, sodium spectrum is intense than hydrogen spectrum. However, $t_w > 80$ μsec, hydrogen spectrum was more intense than sodium spectrum. That means that the t_w can also change the element-selectivity. Each average CV of sodium and hydrogen spectrum intensity, excluding the maximum value and the minimum value of the eight measurements, were calculated. The average CV's were 11.3% for hydrogen and 14.1% for sodium. It is confirmed that the CV of the emission intensity for each applied voltage time (40, 80, 120, 200, 400, and 800 μsec) were 13.4, 14.6, 21.6, 10.6, 12.3 and 11.9% for sodium, and 18.7, 15.0, 8.2, 10.6, 7.4 and 7.6% for hydrogen. The differences of the CV originating from the applied voltage time were not observed.

3.3 Measurement of trace amount of sodium in zirconium dioxide

In order to make the calibration curve of sodium, the sodium aqueous solution was spiked into the dissolved zirconium dioxide solution so that the spiked sodium concentrations in the samples were 0, 0.2, 0.6, 1.0, 5, 10, 15 and 20 μg g^{-1}. These samples at each sodium concentration were measured in the following experimental conditions. Voltage was applied as ten pulses. Each pulse width was 80 μsec. Period between pulses was 2 msec. Each pulse height was all 600 V. For evaluation of reproducibility, the sample solution was measured eight times at each sodium concentration. As a result, the sodium emission intensity increased with sodium concentration for both low (0, 0.2, 0.6 and 1.0 μg g^{-1}) and high (0, 5, 10, 15 and 20 μg g^{-1}) concentration of the sodium (Fig. 7). The calibration curve is shown in Fig. 8. The CV is calculated to be 15.8% for sodium concentrations of 0, 0.2, 0.6, and 1.0 μg g^{-1}, to be 19.9% for sodium concentrations of 0, 5, 10, 15 and 20 μg g^{-1} by the sodium calibration curve. The correlation coefficients were calibrated to be 0.998 for sodium concentrations of 0, 0.2, 0.6 and 1.0 μg g^{-1}, and to be 0.985 for sodium concentrations of 0, 5, 10, 15 and 20 μg g^{-1} by the sodium calibration curve. It is calculated that the sodium detection limit (3σ) is 0.02 μg g^{-1} from the calibration curve (Fig. 8). The detection limit of the trace element in zirconium dioxide powder is equal to the value which doubled the sodium detection limit in 4000 μg g^{-1} zirconium dioxide 250. Therefore, it is found that the detection limits of sodium in the zirconium dioxide

powder were 5 μg g^{-1} in LEP-OES. In the previous work [9], the detection limit of sodium in the zirconium dioxide powder by ICP-AES is reported as 8.8 μg g^{-1} with conventional open-system digestion coupled off-peak correction method, and as 4.5μg g^{-1} with microwave-assisted digestion coupled wavelet transform correction. The value of 5 μg g^{-1} by our simple system is considered to be comparable to those values.

3.4 Measurement of trace amount of lithium in zirconium dioxide

The lithium aqueous solution is spiked into the dissolved zirconium dioxide solution, so that the spiked lithium concentrations in the samples are 0, 0.3, 1.0, 2, 3, 5, 10, 15 and 20 μg g^{-1}. These samples at each lithium concentration are measured in the following experimental conditions (Voltage was applied as ten pulses. Each pulse width was 80 μsec. Period between pulses was 2 msec, Each pulse height was all 600 V). We use 670.784 nm as analytical line for lithium. The samples were measured eight times at each sodium concentration. These data are averaged, as shown in Figure.9. The increase of continuous spectrum for optical emission intensity in low concentrations of lithium 0, 0.3, 1.0, 2, 3, 5 μg g^{-1} in aqueous solutions is greater than the increase in high concentrations of lithium 0, 5, 10, 15 and 20 μg g^{-1} in aqueous solutions. The lithium emission intensity increases with lithium concentration at both low (0, 0.3, 1, 2, 3 and 5 μg g^{-1}) and high (0, 5, 10, 15 and 20 μg g^{-1}) concentrations of lithium (Fig. 9). The CV is calculated to be 10.4% for lithium at low concentrations (0, 0.3, 1, 2, 3 and 5 μg g^{-1}), to be 12.4% for lithium at high concentrations (0, 5, 10, 15 and 20 μg g^{-1}) by the lithium

calibration curve. The correlation coefficient is calibrated at 0.985 for lithium at low concentration and 0.993 for lithium at high concentration using the lithium calibration curve. It is calculated that the lithium detection limit (3σ) is 0.13 μg g^{-1} from the calibration curve (Fig.10). The detection limit of lithium in zirconium dioxide powder is equal to the value which doubled the lithium detection limit in a 4000 μg g^{-1} zirconium dioxide 250. Therefore, it is found that the detection limit of lithium in the zirconium dioxide powder was 33 μg g^{-1}.

4. Conclusion

We achieved the quantitative measurement of trace elements (Na, Li) in high purity zirconium dioxide powder by LEP-OES, utilizing its unique property that the emission intensity of zirconium is weak in LEP-OES.

It is also confirmed that the sensitivity of to each element in LEP-OES depends on the measurement conditions of the applied voltage and the width of pulse. In the cases of Na and H measurement the dependency varied by elements and emission peaks. This fact suggests that element-selective measurement, such as that of Na in zirconium powder mentioned above, can be extended to another pair of elements by carefully choosing the measurement conditions.

Finally, in this work, the current detection limits of Na and Li in 4000 μg g^{-1} zirconium dioxide aqueous solution are determined to be 0.02 μg $g^{-1}$and 0.13 μg g^{-1}, respectively. These values correspond to 5 μg g^{-1} for Na and 33 μg g^{-1} for Li in high purity zirconium dioxide powder.

References

[1] O.J.Kond, K.Domen, I.J. Maruyak, Faraday Trans. 88 (1992) 2095

[2] R.M. Li, Z.S. Li, Y.F. Xin, Appl. Sci. Technol. 9 (2001) 52.

[3] A.F. Kiera, S. S. Lehr, M. Song, N.H. Bings, J.A.C. Broekaert, Spectrochimica Acta Part B 63 (2008) 287-292

[4] A. Ikem, J. Egilla, Food Chemistry^{-1}10 (2008) 301-309

[5] P. Taylor, P. Schutyser, Spectrochim. Acta 41B (1986) 81.

[6] X.G. Ma, Z.X. Zhang, Spectrosc. Spectral Anal. 14 (1994) 55.

[7] E.Poussel, Spectrochim. Acta 51B (1996) 75.

[8] E.H. Evans, J.A. Day, C.D. Palmer, WJ. Price, C.M.M. Smith, J.F. Tyson, J. Anal. At. Spectrom.20 (2005) 562

[9] X. Ma, Y. Li, Analytica Chimica Acta 579 (2006) 47-52

[10] H. Matsumoto, A. Iiduka, T. Yamamoto, E. Tamiya, Y. Takamura Proceedings of microTAS 2005 Conference, 1, pp 427-429, Boston. Transducer Research Foundation (2005)

[11] A. Iiduka, Y. Morita, E. Tamiya, Y. Takamura, Micro Total Analysis Systems 2004, 1, pp 423-425, Cambridge. The Royal Society of Chemistry (2004) .

[12] K. W. Jo, M.G Kim, S.M. Shin, and J. H. Lee, APPLIED PHYSICS LETTERS 92, 011503 (2008)

Figures caption

Fig.1 The sample solution was introduced into the narrow part of flow channel in the chip, with no air bubbles. The platinum electrode is inserted into both end of the flow channel. The voltage was applied to the platinum electrode (a).The detail of narrow part of the chip is shown (b). The voltage and current are concentrated there, and plasma is generated (c).

Fig.2 Experimental set up

Fig. 3 The applied voltage dependence of the spectrum, The solution condition is Na 10ppm sulfuric acid 1.8M and ZrO_2 4000 μg g-1. Voltage is applied as three pulses, each pulse width is 80 μs, Period between pulses is 2ms.

Fig. 4 The optical intensity rates of sodium (wavelength value is 588.9 nm and hydrogen (wavelength value is 656.5 nm) for the applied voltage.

Fig.5 The voltage application time dependence for the spectrum, The solution conditions are Na 10 μg g-1, sulfuric acid 1.8M, ZrO_2 4000 μg g-1. Voltage is 600 V, and Voltage is applied as three pulses. Period between pulses is 2ms.

Fig.6 The optical intensity of sodium (wavelength value is 588.9 nm) and hydrogen (wavelength value is 656.5 nm) for the voltage application time.

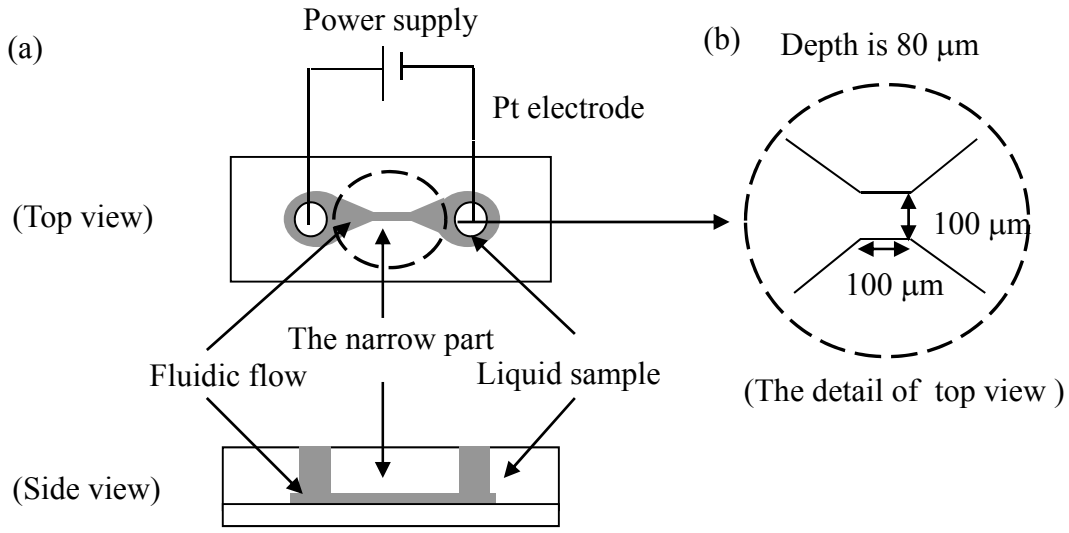
Fig. 7 Trace sodium element (a) 0-1 μg g-1, (b) 0-15 μg g-1 spectrum in 4000 μg g-1 zirconium dioxide. The solution condition is sulfuric acid 1.8M. The applied voltage condition is voltage 600V, the number of pulse, 10, the pulse width, 80

msec, the period between pulse, 2msec.

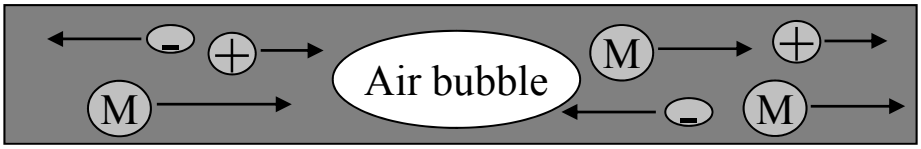
Fig. 8 The calibration curve of sodium optical intensity.

Fig. 9 Spectra of trace element of lithium (Wave length value is 670.78 nm) (a) 0-5 μg g-1, (b) 0-20 μg g-1 in 4000 μg g-1 zirconium dioxide solution. The solution condition is sulfuric acid 1.8M. The applied voltage condition is voltage 600V, the number of pulses,10, the width of pulse, 80 μsec, the period between pulse, 2 msec, the number of measurement, 8.

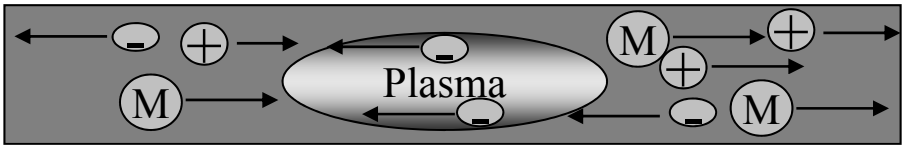
Fig. 10 The calibration curve of lithium optical intensity.



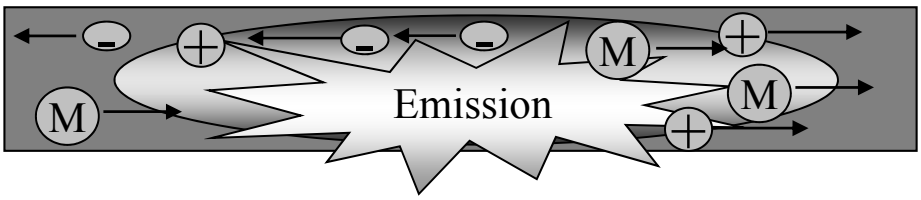
(c)



The sample solution was boiled in the narrow part of the chip, and an air bubble was generated.

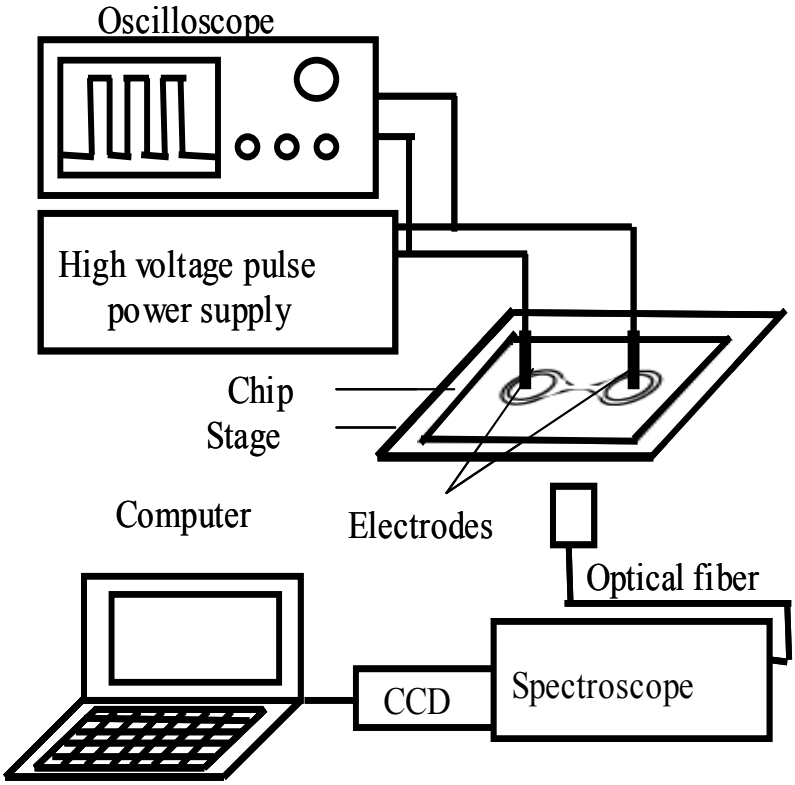


Strong electric field was applied to the air bubble, and plasma was generated.



The atoms in the solution entered the plasma, and light was emitted.

Fig.1 The sample solution was introduced into the narrow part of flow channel in the chip, with no air bubbles. The platinum electrode is inserted into both end of the flow channel. The voltage was applied to the platinum electrode (a).The detail of narrow part of the chip is shown (b). The voltage and current are concentrated there, and plasma is generated (c).



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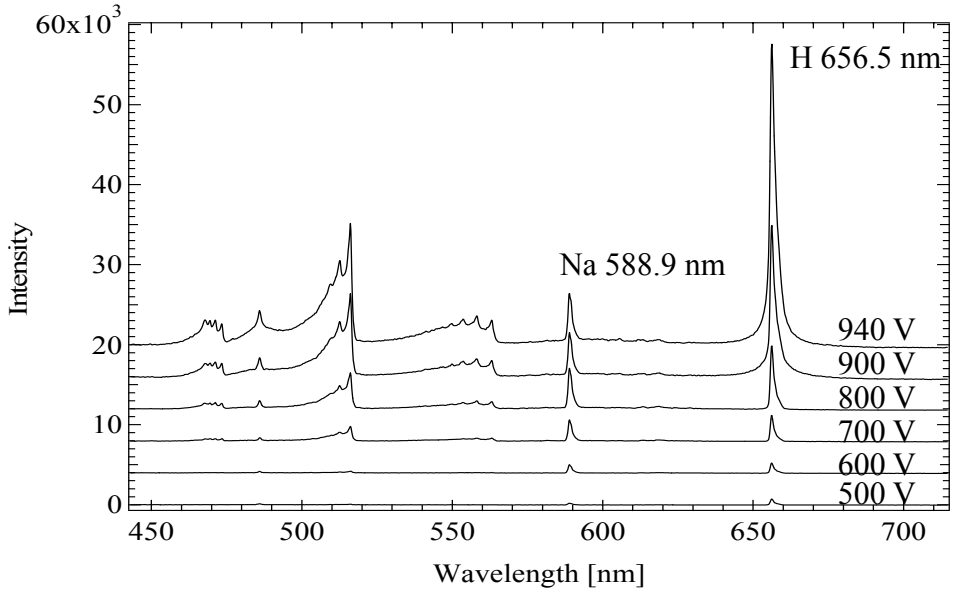

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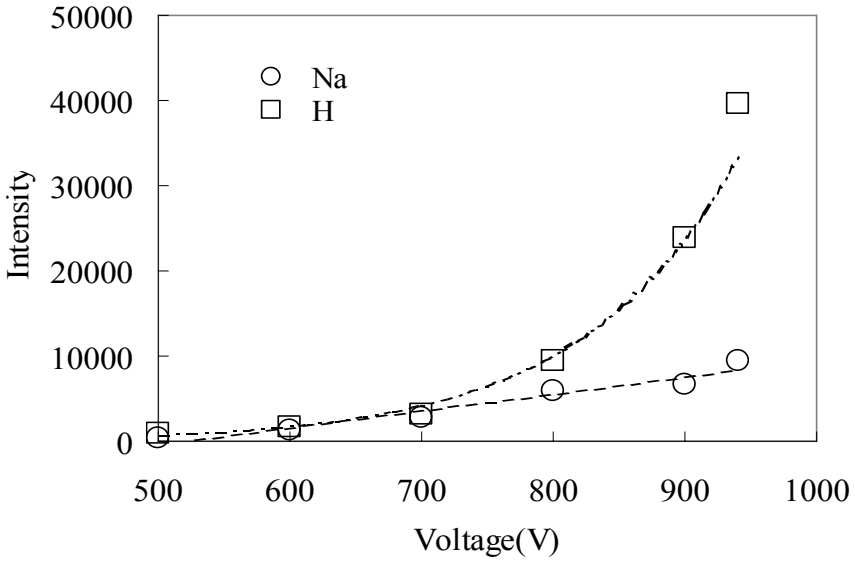

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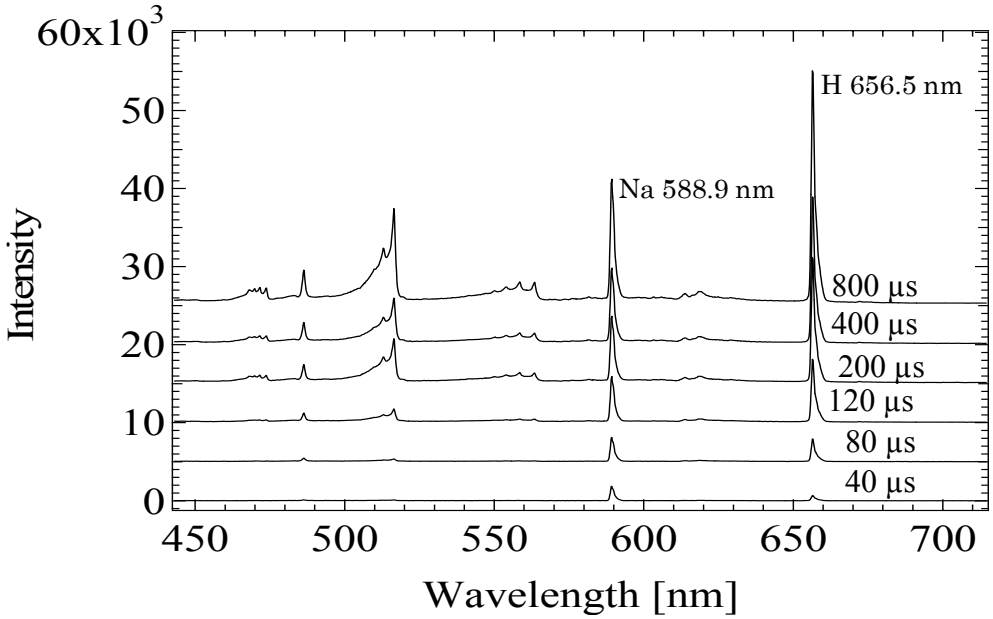
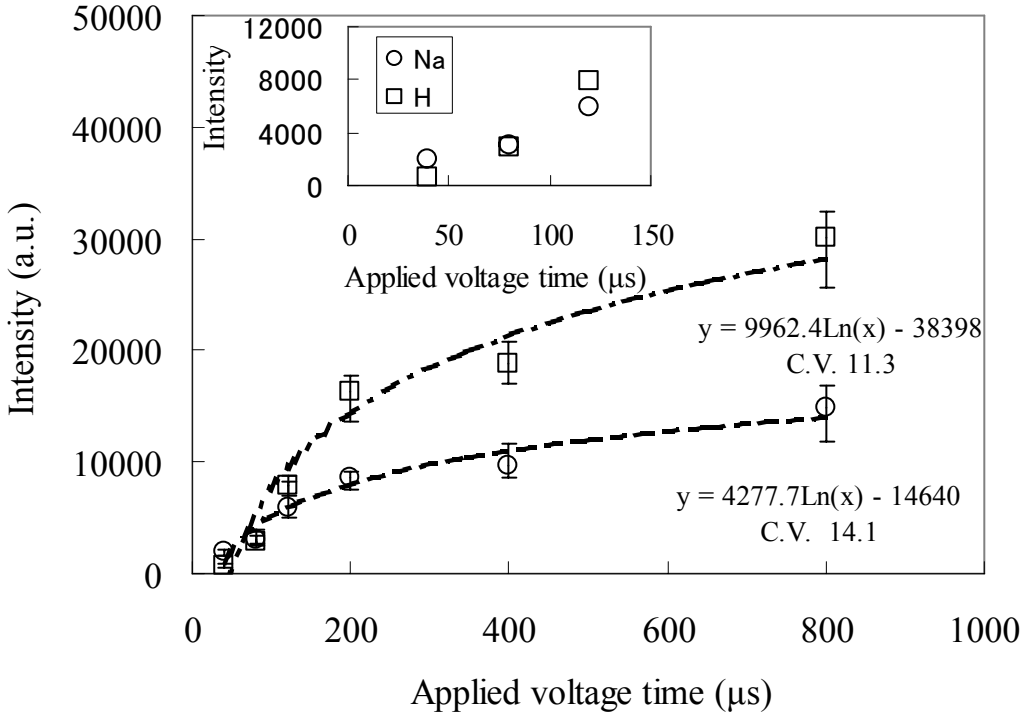


Fig.5 The voltage application time dependence for the spectrum, The solution conditions are Na 10 μg g^{-1}, sulfuric acid 1.8M, ZrO_2 4000 μg g^{-1}. Voltage is 600 V, and Voltage is applied as three pulses. Period between pulses is 2ms.



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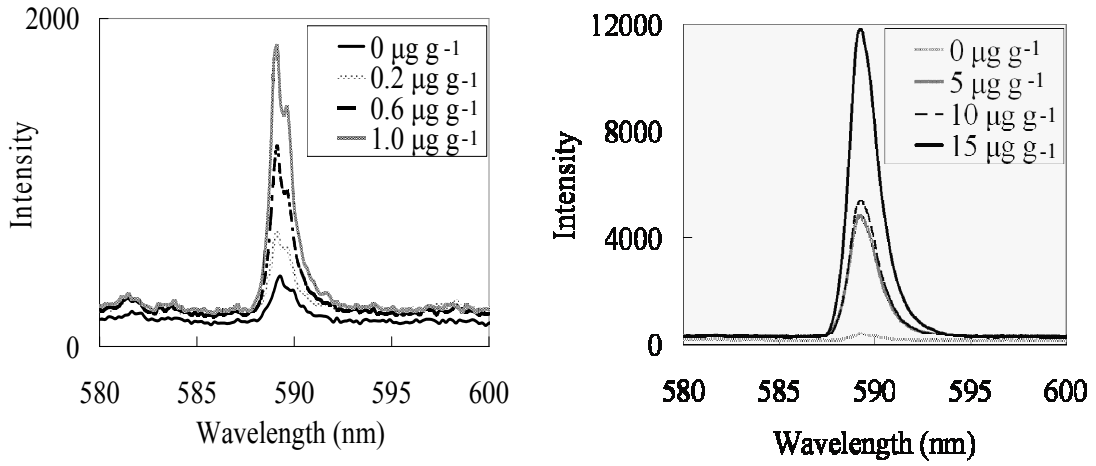

Fig. 7 Trace sodium element (a) 0-1 μg g^{-1}, (b) 0-15 μg g^{-1} spectrum in 4000μg g^{-1} zirconium dioxide. The solution condition is sulfuric acid 1.8M. The applied voltage condition is voltage 600V, the number of pulse, 10, the pulse width, 80 μsec, the period between pulse, 2msec.

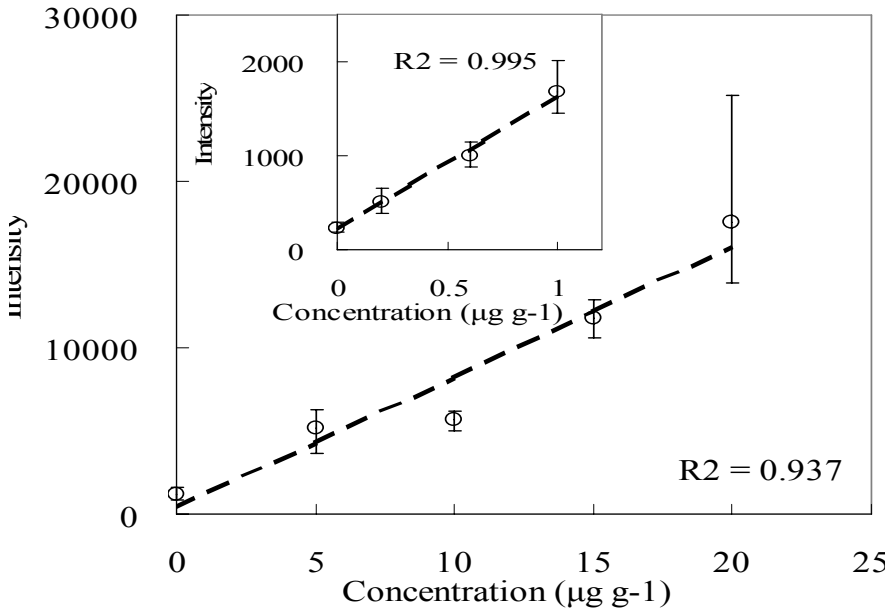

Fig. 8 The calibration curve of sodium optical intensity.

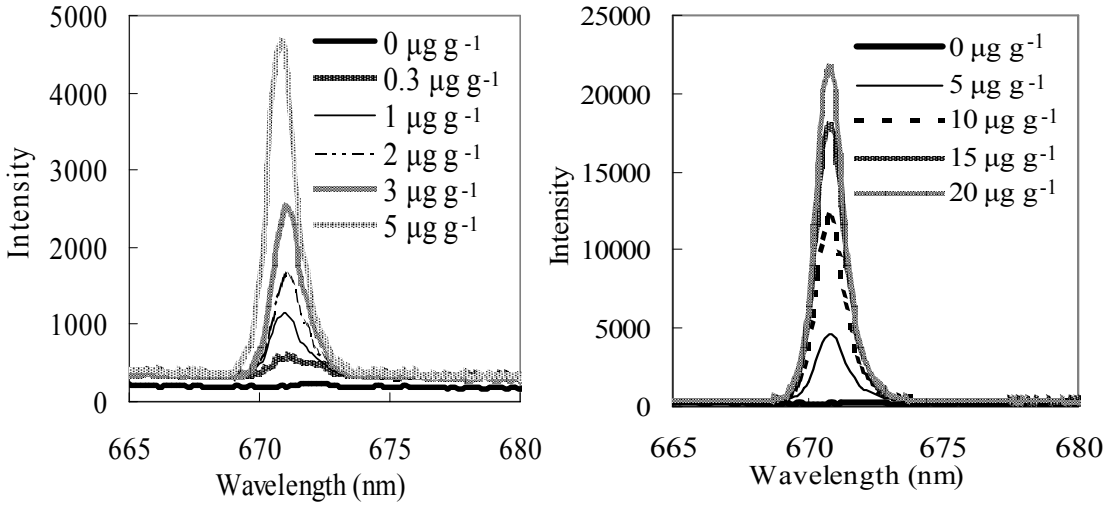

Fig. 9 Spectra of trace element of lithium (Wave length value is 670.784 nm) (a) 0-5 μg g^{-1}, (b) 0-20 μg g^{-1} in 4000 μg g^{-1} zirconium dioxide solution. The solution condition is sulfuric acid 1.8M. The applied voltage condition is voltage 600V, the number of pulses,10, the width of pulse, 80μsec, the period between pulse, 2 msec, the number of measurement, 8.

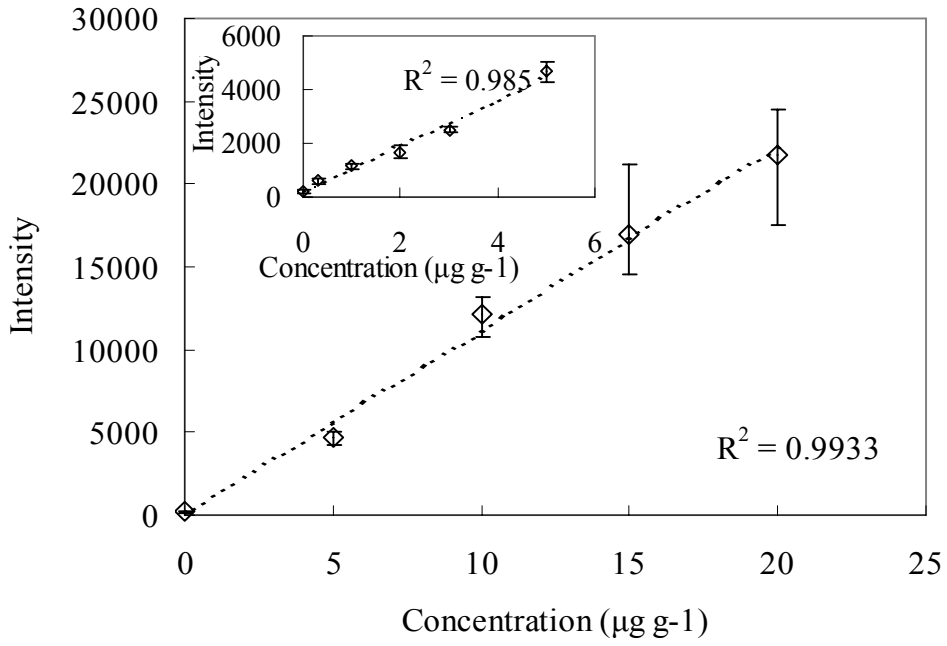

Fig. 10 The calibration curve of lithium optical intensity.