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論文の内容の要旨

#### Part 1: Research Content

**Background:** Liquid electrode plasma (LEP) driven by alternating current (AC) is used as an excitation source for elemental analysis. LEP forms in a vapor bubble generated inside a narrow-center microchannel by using high-voltage power. This technique can detect metals with high sensitivity and high selectivity. More recently, we found the better conditions to generate LEP by alternating current with higher stability and significantly low damages on microchannel, called the new method as AC-LEP. In this plasma, an air bubble remained in the LEP channel during plasma generation by AC power source. The bubble is expected to affect plasma generation strongly. In order to investigate in detail the effect of the bubbles, we fabricated a microfluidic system to introduce different kinds of gas bubbles intentionally into the LEP channel. In AC-LEP, significantly less channel damage (1/3000) was reported compared to direct current LEP (DC-LEP) [1]. The plasma was continuously generated in a poly(dimethylsiloxane) (PDMS) chip for about 10 min without severe channel damage or expansion. These observations indicated that AC-LEP showed great potential for reducing channel damage, although the mechanism of this improvement was not clear. In order to increase detection efficiency, electrochemistry is one of an attractive method for preconcentration of heavy metal. Depending on the nature of analytes and sample matrix, electrochemical detection (ECD) is very sensitive and can be detected in the femtomole  $L^{-1}$ (10<sup>-15</sup> M) range. A more chemical-specific detection condition can be acquired by selecting the suitable applied voltage for the oxidation and reduction potential and working electrode materials. Target compounds (analytes) are separated using a specific voltage in reduction reaction process. After separation, the compounds present at working electrode will be directly desorption and detection by using LEP.

**Aim:** In this study, various types of gases were introduced intentionally from outside into the AC- and DC- LEP and their effects on plasma generation and channel damage were investigated. For that purpose, a new chip design for the introducing gas into the channel was developed. Channel damage was compared in both DC-LEP and AC-LEP with and without gas introduction. Moreover, the combination of two techniques for heavy metal detection was studied. With the aid of deciding on the excellent utilized voltage for the oxidation/reduction potential and properties of the working electrode, an extra selectivity of detecting condition can be acquired.

#### **Experimental:**

#### 1. Development of the liquid electrode plasma (LEP) chip with gas introduction

The PDMS layer is attached onto a glass slide that is a substrate for the chip. The channel is carved on the PDMS sheet by a photolithographic technique. There are two inlets, liquid inlet and gas inlet, and one outlet on the chip. The width and depth of the channel on PDMS sheet is determined by the height of photoresist patterned on silicon wafer. Two 2-mm diameter holes were punched at each end of the LEP channel. Finally, the PDMS layer and the substrate are bound together by oxygen plasma. Both liquid and gas were pushed by syringe pumps with same flow rate and then observed with microscope. Types of selected gases in this work are Ar gas, nitrogen gas, oxygen gas and air.

# 2. Study on effect of introduced gas bubbles for the low channel damage in direct and alternating current liquid electrode plasma atomic emission spectrometry

For LEP determination, chip was fixed in the experimental setup shown in Fig. 1. Both platinum electrodes were connected to either a DC or AC power source. Syringe pumps were used to introduce sample solutions and gas. AC-LEP was generated using a specially designed power-controllable AC power source. A DC power supply was used for DC-LEP. The plasma was observed with an optical microscope and a UV-VIS spectrophotometer. The chip dimension was observed using a digital microscope. For fair comparison of channel damage, both AC-LEP and DC-LEP conditions were optimized to give the same signal intensity (limit of detection, LOD) for Pb in 0.1 M nitric acid. To obtain same LOD in all cases, the optimized conditions were used, and channel damage was evaluated as a function of plasma duration. Microscopy images were obtained from after first applied voltage for 10 measurements (interval time of 10 s) and then the channel width was measured and compared.



Figure 1 Experimental setup

### 3. Design of microchip for metal detection by electrodeposition coupled with LEP-OES

The reaction chamber was fabricated by PDMS and glass substrate. After PDMS sheet fabrication, 3-mm diameter hole was punched on 1 cm<sup>2</sup> PDMS sheet. Glass substrate was cleaned prior bonding with PDMS. Then, oxygen plasma treatment was used for bonding PDMS onto substrate and covered with other PDMS layer. Working electrode and counter electrode are platinum wire with 0.3 mm diameter. For working electrode, PDMS was coated except for the area that will use for analyte deposition. For efficiency comparison, Au wire was selected to be working electrode with same fabrication and usage. The reaction chamber is shown in Fig. 2. Below the chamber, fiber optic was applied to obtain the detection signal after electrodeposition. In the LEP detection step, DC-LEP with 200-1500 V of applied voltage with 0.5 msec on-time and 2 msec off-time was applied for 20 cycles. Analyte model in this study is 50 ppm Pb in nitric acid and HMImBr. For the characterization

of electrodeposition of target heavy mental, Energy Dispersive Spectrometer (EDS) attachment for scanning electron microscope for chemical analysis was performed. Electrodeposition was achieved by using Potentiostat.



*Figure 2* Reaction chamber and experimental setup for heavy metal detection by electrodeposition coupled with LEP-OES

#### Part 2: Research Purpose

#### **Results and Discussion:**

#### 1. Development of the liquid electrode plasma (LEP) chip with gas introduction

The bubble was formed after passing through the intersection, which was matched with previous studied. For smaller gas channel size, the gas was hard to divide into small bubbles. On the other hand, when gas channel size was bigger, it became quite hard to push out the gas especially with small liquid channel size. Because of the pressure of gas and liquid inside of channel was different, the flow rate of gas and liquid must be optimized to achieve the suitable pressure condition for reproducible bubble generation. To compare the effect of type of introduced gas, Ar gas, nitrogen gas, oxygen gas, and air were selected. At the same analyte concentration, Air introduction system shown the relatively high peak area with low standard deviation. While, without gas introduction shown lower peak area with relatively satisfy standard deviation. This is one of benefits of AC–LEP usually provide stable and reproducible signal intensity.

# 2. Study on effect of introduced gas bubbles for the low channel damage in direct and alternating current liquid electrode plasma atomic emission spectrometry

Figure 3 compares channel damage when different gases were introduced during DC-LEP and AC-LEP. The DC-LEP samples (Fig. 3A and B) showed less channel damage when gas was introduced. As before, the AC-LEP (Fig. 3C and D) samples showed much less channel damage than the DC-LEP ones, where the least damage was observed when argon gas was introduced. Figure 3E summarizes the volume percentage of channel expansion with and without gas introduction. There was an obvious difference between the huge channel expansion of the DC-LEP sample and small channel expansion of the AC-LEP sample, with Ar gas introduced. In the case of DC-LEP, the plasma generated after Joule heating creates vapor bubbles and some time is required to remove remaining products from previous plasma generation; the pulses of the applied DC power may not correspond with the times when the introduced bubbles are present. Synchronization of applied voltage and bubble generation will allow lower power (lower applied voltage) to generate plasma than in case of bubble generation from Joule heating. Therefore, the channel damage did not reduce significantly in the case of DC-LEP with gas introduction. In contrast, the AC power source can be applied continuously for a longer period compared to the DC source; hence, the generated bubbles are expected to remain inside the narrow channel for a longer period, stabilizing the plasma. Hence, introduction of bubbles could greatly facilitate plasma generation.



**Figure 3** Optical microscopy images of chips used under different condition. (A) DC-LEP with air, (B) DC-LEP with Ar, (C) AC-LEP with air, and (D) AC-LEP with Ar. (E) Comparison of channel expansion in DC-LEP and AC-LEP during the different experiments.

## 3. Design of microchip for metal detection by electrodeposition coupled with LEP-OES

Longer deposition time will provide higher time of reduction of analyte on the working electrode. From Fig. 4, the amount of deposited Pb was increase when deposition time is increase. At 30 minutes of deposition time showed the highest amount of deposited Pb. After that, LEP was performed to observe the dissolution of Pb from electrode. The result showed the consistent tendency with the found Pb on electrode. The highest peak area came from the electrode that found highest Pb. We can conclude that the optimum condition for these couple technique are Au wire as working electrode and solution was prepared from 0.1 M HMImBr. The linear dynamic range from this calibration curve is 0 - 10 ppm of lead concentration. Within linear range, peak area is directly proportional to the lead concentration and illustrates satisfied linear regression ( $R^2 = 0.9992$ ). The detection limit (LOD) of this system is 0.0279 ppm of lead.



**Figure 4** (Left) EDS images of Au-WE before and after Pb deposition and elemental mapping of Au (as WE) and Pb. Graph shown percentage of deposited Pb on electrode surface. (Right) Analytical performance of electrodeposition coupled with LEP-OES of 0 - 100 ppm of lead in 0.1 M HMImBr.

**Conclusion:** In this study, an elemental analyzer based on LEP-OES for long time environmental monitoring has been successfully investigated. The effects of external gas introduction into AC-LEP and DC-LEP were studied. In both case of AC-LEP and DC-LEP, the external gas bubbles facilitated

stable and high sensitive plasma generation with lower power, which result in reducing channel damage and increasing the lifetime of the analysis chip. These effects are significant in Ar introduction and AC-LEP case. The power for homogeneous nucleation of bubble in conventional DC-LEP is higher than that required for plasma generation, resulting in high channel damage. To overcome of drawbacks of both methods, an elemental analysis based on electrodeposition integration with LEP-OES has been realized. We investigated suitable deposition potential, solution system and WE materials could maintain high stable plasma and improve intensity of deposited heavy metal ions. This system is allowed to monitoring heavy metal for a long time and continuously.

**References:** [1] K. Do Van, M. Hidekazu, Y. Tamotsu, T. Phan Trong, O. Akitoshi, T. Yuzuru, Development of AC-driven liquid electrode plasma for sensitive detection of metals, Jap J Appl Phys, 55 (**2016**) 02BC23.

Keywords: Liquid electrode plasma, Electrodeposition, Elemental analysis

#### 論文審査の結果の要旨

本論文は、液体電極プラズマ原子発光分析法において、直流電源と交流電源の違いや、液中に 様々な気体を導入する効果等を調べ、性能上の大きな課題であるプラズマ発光容器に対するプラ ズマのダメージを軽減させる具体的な方法を2種類見出し、長期間の連続計測や検出限界の向 上を可能としたものである。

液体電極プラズマは、本学で発案された新しい元素分析法で、小型ながら、幾つかの元素にお いては従来の誘導結合型プラズマ原子発光分析法に匹敵する検出限界を有し、工場における工程 管理や、廃水中の重金属のモニター等への応用が期待されている。しかし低い検出限界や高い精 度の測定には多くの積算を要し、特に長時間の連続測定ではプラズマによる発光容器へのダメー ジが深刻な問題であった。本論文では、様々な気体の導入がダメージを軽減することを明らかに し、交流電源利用時の内在的な気泡の導入が低ダメージ化する機構を明らかにした。また、電気 化学と液体電極プラズマ法を結合することにより、長期間の高感度な測定が可能になることを示 した。

第1章では、液体電極プラズマ発光分析法に関連するこれまでの研究と、その問題点をまとめ、本論文の課題を明確にした。

第2章では、液体電極プラズマにおいて様々な気体の導入の効果を調べるために、液体電極 プラズマ中に外部より気体を導入しつつ液体電極プラズマを発生させる機構を開発した。十字流 路を用いて外部気体の微小な気泡を発生させ、これを液体に混入させることで、気体導入液体電 極プラズマを安定に発生させることに成功した。

第3章では、第2章で作成した機構を用いて、直流および交流で駆動される液体電極プラズ

マにおいて、発光強度およびダメージに及ぼす様々な気体の導入効果を調べた。その結果 Ar 導入の交流駆動液体電極プラズマが最も安定かつ高輝度で、ダメージを劇的に軽減できることが分かった。また直流駆動液体電極プラズマにおいても気体導入でダメージが軽減され、従来の交流駆動における低ダメージは、電極で水の電気分解により発生した気泡が内在的な気体導入効果をもたらしたと推察された。

第4章では、液体電極プラズマを電気化学と結合し、通常は電気化学で金属をモニターし、 異常を認めたときのみ電極上に測定対象金属を濃縮し、液体電極プラズマで測定することで、電 気化学の高感度区、プラズマ発光法の高信頼性を両立できる方法が提案された。また効果的に測 定対象金属を濃縮し発光させるには、電極材料が重要なことが示された。

以上、本論文は、液体電極プラズマ元素発光分析法において、気体の導入効果や容器ダメージの主因を明らかにし、また電気化学濃縮を併用するための基礎を確立したものであり、学術的 に貢献するところが大きい。よって博士(マテリアルサイエンス)の学位論文として十分価値あ るものと認めた。