

On-site Analysis of Trace Elements Using Liquid Electrode Plasma-Optical Emission Spectrometry Combined with Solid-Phase Extraction

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Dissertation Abstract

On-site Analysis of Trace Elements Using Liquid Electrode Plasma-Optical
Emission Spectrometry Combined with Solid-Phase Extraction

Graduate School of Natural Science & Technology

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ABSTRACT

Liquid electrode plasma-optical emission spectrometry (LEP-OES) is a novel approach for the analysis of trace elements in the aqueous matrix, which does not require an inert gas for operation while simple, highly-sensitive, and capable of complete analysis with as low as 0.1 mL sample. A high-voltage DC pulse power creates the LEP in LEP-OES form the vapor-bubble of an electro-conductive aqueous sample, and the emission spectra from the discharged plasma are interpreted into the quantitative content of ions in solution. The portability of LEP-OES not only facilitates on-site application but also reduces the analysis cost per sample as compared to the laboratory-based techniques, such as GF-AAS, ICP-OES, or ICP-MS. However, the analytical sensitivities of LEP-OES for some analytes are limited or interfered due to the coexisting ions. In the current work, rapid and precise on-site methodologies are presented for the determination of toxic (Pb, Se) and precious (Au, Pd, Pt) elements in the waste matrices using LEP-OES preceded by the selective separation or pre-concentration of the target analytes. The solid-phase extraction (SPE) materials, containing macrocycles designed for precise selectivity towards target ions based on the host-guest type interaction, were used for the separation and preconcentration step. The impact of SPE performance variables, e.g., solution pH, flow-rates at loading and elution step, type or volume of eluents, the effect of matrix ions, enrichment factor, sustainability duration regarding loading-elution cycles, and so forth were investigated. The LEP-OES operating parameters, such as solution conductivity, applied-voltage, duration of the voltage pulse, pulse-count for applied-voltage, number of measurements, matrix effects, and so forth have also been optimized to obtain a distinct peak for the target analytes (Au, Pd, Pt, Pb, or Se) at designated wavelengths. The following protocols have been designed and reported: (a) selective recovery of precious metals from the acidic wastewater; (b) on-field determination of Au, Pd, or Pt contents in the acidic wastewater; (c) on-site quantification of Pb in wastewater; and (d) on-site analysis of inorganic Se-species in wastewater. The accuracy of methodologies was verified using certified reference material and real samples. The results from the proposed methods were compared with those from ICP-OES to observe a good agreement.

EXTENDED DESCRIPTION

Toxic elements in industrial wastewater are one of the most severe angst in respect of environmental protection. Monitoring and recovery of the toxic ions from waste solution before discharge in the environment are significant from the viewpoints of reduction of environmental burden and recovery of valuable components. Moreover, efficient recovery mitigates the ecological health-related impacts. Accurate determination of even in trace level elements in waste solution provides useful information for recovery strategy and about geochemical processes that occur in the environment. Inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) are frequently performed to routine analysis of trace metal ions in the sample. However, these techniques are not suitable for on-site analysis due to the use of more extensive and sophisticated instruments and requirement of nebulizer gas and AC voltage for operation. For on-site analysis of elements using a portable system, liquid electrode plasma-optical emission spectrometry (LEP-OES) operated by micro-plasma source could be a solution. The LEP-OES system is small, portable, user-friendly, and battery-operated and not require nebulizing gas. In this work, the method was developed for analysis of trace level Au, Pd, Pt, Se and Pb in solution using an LEP-OES system couple with solid phase extraction (SPE) and preconcentration. The system is portable enough, and technique is simple, rapid and suitable for field analysis.

Selective separation of different ions from the liquid matrix was attained using supramolecular type molecular recognition technology (MRT) gel containing SPE columns. In MRT, macrocycles covalently attached to the inert silica or polymeric support materials are used as the SPE material, and separation of the target analyte is performed based on the combination of size, configuration, electronic interaction, charge, wetting, and other factors. The MRT-SPE materials are commercially available and offer non-destructive, precisely

selective, and fast separation of the analyte of interest. The dissertation includes the discussion on following findings accomplished with the use of LEP-OES and SPEs systems:

(a) On-site analysis of gold, palladium, or platinum in acidic aqueous matrix

A technique for the concurrent onsite quantitative analysis of gold (Au), palladium (Pd), or platinum (Pt) in the aqueous acidic matrix has been proposed. The Au, Pd, or Pt in the matrix was selectively concentrated in macrocycle-equipped solid-phase extraction (SPE) system, followed by analysis of the concentrates in a portable liquid electrode plasma-optical emission spectrometer (LEP-OES). The selectivity of two macrocycle-equipped SPEs, Pd-03 and PM-09, towards Au, Pd, or Pt was evaluated regarding retention and recovery ratios. A quantitative separation behavior was confirmed with PM-09 (SPE-mass, 500 mg) at the following optimized conditions: SPE-conditioning pH, ≤ 2 (1 mol L⁻¹ HCl); sample loading flow-rates, 40 mL min⁻¹; washing liquid, ultrapure water; eluent, acidic thiourea (1 mol L⁻¹ thiourea in 0.5 mol L⁻¹ HCl, 2.0 mL, 1 mL min⁻¹). The optimum preconcentration factor was 250 for Au, Pd, or Pt at an RSD of $< 5\%$. The preconcentrated sample (40 μ L) was then analyzed in LEP-OES to generate distinct peaks in the spectra at the λ_{\max} (nm) of 274.826 (Au), 267.958 (Pd), and 270.240 (Pt) using pre-optimized operating variables (applied voltage, 800 V; on-time, 6 ms; off-time, 50 ms; pulse count, 40; number of measurements per spectra, 10). The SPE-assisted pre-treatment minimized interfering impacts due to the competing ions in solution and limitations in LEP-OES sensitivity at low Au, Pd, or Pt content in the matrix. The limit of detection (3σ) for Au, Pd, Pt determination using the technique were found as 0.8, 3.1, 57.3 ng mL⁻¹. The proposed method was applied to the analysis of Au, Pd, or Pt contents in the European Commission Joint Research Center certified reference material of wastewaters (ERM-CA713; recovery by the standard addition method, $> 96\%$), and real aqueous waste from the plating process (recovery, $> 95\%$). A relative standard deviation of $\leq 5\%$ indicated a good precision in Au, Pd, or Pt analysis

using the technique. The LEP-OES data-sets were also comparable with those obtained from the inductively coupled plasma optical emission spectrometric measurements for the same matrix.

(b) On-site analysis of lead from aqueous matrix

A relatively rapid and precise method is presented for the determination of lead in an aqueous matrix. The procedure involves analyzing quantitation using liquid electrode plasma-optical emission spectrometry (LEP-OES), with solid phase extraction (SPE) separation / preconcentration. The impact of operating variables such as pH, the flow rate of the sample solution; type, volume, the flow rate of the eluent; and matrix effects on the retention of lead in SPEs was investigated. Three MRT-SPE columns (AnaLig Pb-01, Pb-02, and AnaLig Pb-04) were evaluated for the separation/ preconcentration of Pb from high matrix metal-waste solutions followed by ICP-OES analysis. Quantitative collection of Pb was achieved using the following optimized conditions: a) pH 1; b) washing solution: 0.01 M HNO₃; c) sample loading and elution flow rate: 0.5 mL min⁻¹; and c) eluent: 0.03 M EDTA. Of the three SPE-MRT cartridges available for Pb separation, Pb-02 showed enhanced Pb-selectivity in the presence of competing ions and preconcentration factor 187. Therefore, Pb-02 is a better candidate for the selective separation of Pb from solutions. Selective SPE-separation/preconcentration minimized the interfering effect due to manganese in solution and limitations in lead-detection in low-concentration samples by LEP-OES. The LEP-OES operating parameters such as acid concentration, applied voltage; on-time, off-time, pulse count for applied voltage; number of measurements; and matrix effects have also been optimized to obtain a distinct peak for the lead at $\lambda_{\max} = 405.8$ nm. The optimized operating parameters were; a) acid concentration, 0.1 mol L⁻¹ HNO₃; b) applied voltage, 950 V; c) on-time, 5 ms; d) off-time, 60 ms; e) pulse count for applied voltage, 90; f) number of measurements per spectra, 10. The limit of detection (3σ) was 1.9 ng mL⁻¹, and the limit of

quantification (10σ) for lead determination was found 6.5 ng mL^{-1} . The precision, as relative standard deviation, was lower than 5% at $0.1 \text{ } \mu\text{g mL}^{-1}$ Pb. The proposed method was applied in the analysis of lead content in natural aquatic matrices (recovery rate: > 95%). The method accuracy was verified using certified reference material of wastewaters: SPS-WW1 and ERM-CA713. The results from LEP-OES were in good agreement with inductively coupled plasma optical emission spectrometry measurements on the same samples. The application of the proposed method is fast (≤ 5 minutes, without preconcentration) with a reliable detection limit on trace level.

(c) On-site quantification of inorganic selenium in wastewater

A novel technique has been proposed for the concurrent on-site inorganic selenium species analysis in waste solution using LEP-OES combined with an ion-selective SPE-assisted sample pre-treatment step. Se (VI) reduction was examined by hydrochloric acid or UV irradiation as a pretreatment for solid phase extraction. For the Se (VI) reduction, the reduction ratio was 97.7% in 6 M hydrochloric acid at $120 \text{ } ^\circ\text{C}$ for 20 minutes. The solid phase extraction using the mini-cartridge packed with supramolecular SPE sorbent As-01 was useful for LEP-OES determination of selenium. The supramolecular SPE sorbent As-01 is excellent in selenium (IV) selectivity and adsorption capacity compared with other resins. Good regeneration, easy elution condition and higher enrichment factor and most of the common coexisting anions do not interfere with analyzed ions are other advantages. A quantitative separation behavior was confirmed with As-01 (SPE-mass, 250 mg) at the following optimized conditions: SPE-conditioning pH, 2 (0.01 mol L^{-1} HCl); sample loading flow-rates, 0.5 mL min^{-1} ; washing liquid, ultrapure water; eluent, NaOH (1 mol L^{-1} , $\leq 3 \text{ mL min}^{-1}$). The optimum preconcentration factor was >50 for selenium (IV) at an RSD of < 5%. The preconcentrated sample was then analyzed in LEP-OES to generate distinct peaks in the spectra at the λ_{max} of 196.026 nm using pre-optimized operating variables (applied voltage,

900 V; on-time, 9 ms; off-time, 300 ms; pulse count, 50; the number of measurements per spectra, 10). The sensitivity, accuracy, and precision in LEP-OES were significantly improved by combination with a simple separation/preconcentration method based on the solid phase extraction. The combined method with the solid phase extraction using the mini-cartridge packed with As-01 SPE material and LEP-OES will be applicable to the determination of selenium in wastewater and can be applied on field analysis because of the portability of the total system.

(d) Selective recovery of gold, palladium, or platinum from acidic waste solution

End-of-life electrical and electronic equipment is the secondary resource for economically-viable precious metals (PMs), e.g., gold (Au), palladium (Pd), or platinum (Pt). The hydrometallurgical processes produce acidic leachates during the recovery of PMs from waste sources, while the selective recovery of Au, Pd, or Pt from such a matrix is challenging either due to the chemical similarities of elements or complexities in the sources and matrices. A total of nine solid-phase extraction (SPE) systems, all claimed to be designed for separation of PMs from complex matrices, was evaluated at varying solution pH (≤ 2 to 10) based on the selectivity towards Au, Pd, or Pt. Among them, AnaLig PM-05 was evaluated for the selective recovery of Au, Pd, or Pt from the metal-rich wastewater matrix at strong acidic pH. A negligible influence of feed solution flow-rates ($\leq 50 \text{ mL min}^{-1}$) and coexisting matrix ions was observed. A quantitative back extraction of Au or Pd, retained in the PM-05, was possible using an eluent mix of thiourea in HCl (1: 0.5). The enrichment factor of the protocol for the selective separation of PMs was ≥ 500 , and the SPE-system successfully sustained 100-cycle of a complete SPE-operation. The relative affinity in solid-phase of the macrocycles toward the precious metal ions (Pd > Au > Pt) is the main phenomenon of the proposed method, and it is expected that the host-guest type interaction to be more stable than the resin-based separation processes. Furthermore, application of the macrocycle-equipped

SPE system is advantageous regarding economics as it minimizes the impact of coexisting ions in the matrix and provides unaltered separation performance for several loading-elution cycles.

学位論文審査報告書（甲）

1. 学位論文題目（外国語の場合は和訳を付けること。）

On-site Analysis of Trace Elements Using Liquid Electrode Plasma-Optical
Emission Spectrometry Combined with Solid-Phase Extraction（固相抽出法と液体
発光プラズマ法を組み合わせた環境中微量元素の on site 分析法）

2. 論文提出者 (1) 所 属 物質化学 専攻
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Barua Suman

3. 審査結果の要旨（600～650 字）

提出学位論文について、各審査委員が個別に審査した後、平成 30 年 7 月 17 日に予備審査会を実施した。平成 30 年 7 月 31 日に行われた口頭発表会に引き続き、審査員による審査委員会を開催し、以下のとおり判定した。

液体発光プラズマ法(LEP-OES)は、可搬型小型装置でも実験室クラスの測定機器に準じたプラズマ発光分析ができる優れた方法であるが、微量成分分析の際には定量感度とマトリクス成分の干渉が課題になる。本論文では、超分子型固相抽出材の金属イオンに対する新しい分離挙動を検討するとともに、その成果を LEP-OES の前処理法に活用して新しい on site 定量分析法を開発した。環境水中の有害金属については、本抽出材を前濃縮や化学種分離、妨害元素の分離除去に利用して、自然水中における鉛の高感度分析法や工場排水中セレンの酸化状態別定量法を確立した。さらに有用金属について、多量の妨害成分が存在しても Au、Pt、Pd をそれぞれ定量的に抽出分離できる固相抽出法を見い出し、金属メッキ廃液等の実試料にも適用可能な、白金族元素の分離回収法や現場分析法を開発した。

以上、本研究は、超分子型固相抽出材の新しい機能を開拓して LEP-OES による on site 分析法の高度化を達成したものであり、環境化学分野における有害元素の動態解明や排水中有害元素の資源化に貢献することが期待される。従って、本論文は博士（学術）の学位に値するものと判断する。

4. 審査結果 (1) 判 定（いずれかに○印） ○合 格 ・ 不合格
(2) 授与学位 博 士（学 術）