



# On-site analysis of gold, palladium, or platinum in acidic aqueous matrix using liquid electrode plasma-optical emission spectrometry combined with ion-selective preconcentration

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## ABSTRACT

A technique for the concurrent on-site 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 SPE-retention or recovery behavior towards Au, Pd, or Pt has been optimized for solution pH, sample-loading flow-rates, eluent-type or eluent-volume, and matrix components. 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 preconcentration factor was 250 for Au, Pd, or Pt. The LEP-OES operating variables such as applied voltage, on-time, off-time, and pulse count for applied voltage have been optimized to obtain distinct peaks in spectra for Au ( $\lambda_{\text{max}}$ , 274.826 nm), Pd ( $\lambda_{\text{max}}$ , 267.958 nm), and Pt ( $\lambda_{\text{max}}$ , 270.240 nm). The limit of detection ( $3\sigma$ ) for Au, Pd, Pt determination using the technique were found, respectively, as 0.8, 3.1, 57.3 ng mL<sup>-1</sup>. 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.

## 1. Introduction

Gold (Au), palladium (Pd), or platinum (Pt) has been regarded as 'precious metal (PM)' and recognized as investment commodity via ISO 4217 code that delineates those metals as currency [1]. Furthermore, the specific physical and chemical properties of Au, Pd, or Pt promoted their consumptions as binary (Au-Pt, Au-Pd) or ternary (Au-Pd-Pt) alloys in biomedicine, aerospace construction, catalysts in chemical processes, development of fuel cells, conductor material in electronic systems, and so forth [2–4]. The Au, Pd, or Pt is collected primarily through mining, while the corresponding low abundance in the earth crust and high economic values [5] created a difference in the supply-demand ratio [6,7]. Therefore, recycling of PMs from the metallurgical

waste spills is receiving increased attention in recent days [8,9].

The analyses of PMs in geological, metallurgical, or environmental samples are often challenging because of trace or ultra-trace content, including the complexity of sample matrices [10]. Hence, an analyte separation and enrichment step are often included even with the highly sensitive laboratory-based analytical processes, such as graphite furnace atomic absorption spectrometry (GF-AAS) [11,12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13,14], or inductively coupled plasma mass spectrometry (ICP-MS) [15,16]. Biosorption [9,17], ion-exchange [18], coprecipitation [19], membrane filtration [20], liquid-liquid extraction [21], solid-phase extraction (SPE) [22], and so forth [23,24] are examined for separation and enrichment of PMs from aqueous matrices. Column-packed SPEs often

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preferred among the variety of separation and preconcentration options due to faster operation, less-possibility of emulsion formation, reduced solvent consumption, cleaner extract, and high reproducibility [25].

The recent trends in analytical chemistry are focused on the simplified and miniaturized sample treatment assembly including the minimum consumptions of reagents during the analysis [26]. The analytical instruments, such as GF-AAS, ICP-OES, or ICP-MS are incompatible for on-field rapid analysis of samples due to the large-sized assembly, sophisticated instrumentation, and requirement of AC voltage or flow of inert gases for operation [27]. The recycling activities of metallurgical wastes are principally well-established considering those as a potential secondary source of PMs [28]. The end-of-life metallurgical scraps are often processed in developing countries [29], while the recycling entities are eventually unable to conduct quick-analysis of waste leachates even though it is a strategically important factor for recycling or managing waste. Hence, compact, low-cost instruments are desirable for facilitating the task of on-site monitoring of PMs, e.g., Au, Pd, or Pt in waste leachates. The operating principle of optical emission spectrometry (OES) has been adopted to develop techniques for on-site analysis of elements in aqueous matrices combining with electro-cathode discharge [30–32], dielectric capillary barrier discharge [33,34], liquid-electrode spectral emission chip [35], liquid-electrode discharge plasma [36], and liquid-electrode plasma (LEP) [36–38] systems. A comprehensive list of analytical merits for some representative metal ion detection techniques using liquid electrode discharge microplasma in combination with OES is available from He, et al. [31]. The liquid-electrode plasma-optical emission spectrometry (LEP-OES), as introduced by Iiduka, et al. [37], has attracted attention due to the simplicity, high-sensitivity, and capability to complete analysis with as low as 0.1 mL sample [27,39,40]. Moreover, in LEP-OES, the LEP is created from the vapor-bubble of an electro-conductive aqueous sample using high-voltage DC pulse power, while the emission spectra from the discharged plasma are recorded and used for the quantification of metal ions [38]. It facilitated the on-site application due to the portability of the LEP-OES instrument, while the cost of analysis per sample is much lower than the GF-AAS, ICP-OES, or ICP-MS as the operation does not require any inert-gas supply [41,42].

The on-site analysis of Au, Pd, or Pt in metallurgical waste leachates using LEP-OES has been limited by the insufficient sensitivity of the instrument at trace-analyte concentrations [43], and reduced accuracy in determination due to the competing ions in the matrices. In the current work, ion-selective SPEs equipped with a supramolecular sorbent that utilizes ‘host-guest’ chemistry [44–46] were evaluated for the separation and enrichment of Au, Pd, or Pt from complex matrices. Furthermore, the operating variables of LEP-OES, such as applied voltage, voltage application duration, pulse count, and so forth were optimized to maximize the emission peaks for Au, Pd, or Pt in the spectra. In brief, a new technique is developed for the simultaneous high-precision field-scale analysis of Au, Pd, or Pt in the complex waste matrices combining SPE-assisted selective enrichment step with the LEP-OES analysis, which has not been reported before.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Instrumentation

The S-2043 MH-5000 ultra-compact elemental analyzer from Micro Emission (Nomi, Japan) was used for the LEP-OES analysis, which is portable in size ( $10.5 \times 20.4 \times 11.4 \text{ cm}^3$ ) with a total weight of 1400 g. The LEP-OES require a 40  $\mu\text{L}$  of the sample to complete the analysis, and it can analyze elements within a wavelength range of 200–430 nm. A quartz-made LepiCuve-C (Fig. 1) was used as a sample holder, and the measured spectra were interpreted with LepiSuite LEP-Analyzer software. The operating mechanism of LEP-OES is described with illustration by Kitano, et al. [39]. The optimization of the LEP-OES operating

parameters, e.g., applied-voltage, on-time, off-time, and pulse-count for the simultaneous analysis of Au, Pd, or Pt is described in the current work.

The iCAP 6300 ICP-OES from Thermo Scientific (Waltham, MA) was used to verify the measurements from LEP-OES or primary elemental analysis, and optimization of SPE operating parameters. The ICP-OES used 1.15 KW frequency at the EMT duo quartz torch. The gas flows in plasma, auxiliary and nebulizer were maintained, respectively, at 12, 1 and 0.5  $\text{L min}^{-1}$ . Three-replicates of measurement was considered with an integration time of 30 s for each.

The GL-SPE vacuum manifold kit from GL Sciences (Tokyo, Japan) combined with a CAS-1 air pump from AS ONE (Osaka, Japan), and the Q-CON-IHTC8PF25 speed controller unit from Japan Servo Co. (Tokyo, Japan) was used for SPE operations. The solution pH measurement was performed with a Navi F-52 digital pH meter from Horiba Instruments (Kyoto, Japan). An Arium Pro water purification system from Sartorius Biotech GmbH (Göttingen, Germany) was used to obtain ultrapure water of  $> 18.2 \text{ M}\Omega \text{ cm}^{-1}$  resistivities.

#### 2.1.2. Reagents

Analytical reagent grade chemicals have been used throughout without further purification. The Au, Pd, Pt, Na, Mg, K, Ca, Sr, Co, Ni, and Ba standards ( $1000 \text{ mg L}^{-1}$ ) from Kanto Chemicals (Tokyo, Japan) were used as the stock source for simulated matrix preparation or elemental analysis. The stock solutions were diluted with ultrapure water to prepare working solutions in the range of  $\text{mg L}^{-1}$  to  $\mu\text{g L}^{-1}$ .

The solution pH at  $\leq 2$  was achieved using 1 to 6  $\text{mol L}^{-1}$  HCl, while the pH above that range for other working solutions was using 0.1  $\text{mol L}^{-1}$  solution of buffer reagents adjusted by  $\text{HNO}_3$  or NaOH ( $1 \text{ mol L}^{-1}$ ). The MES (2-(*N*-morpholino)ethanesulfonic acid) from Sigma-Aldrich (St. Louis, MO), HEPES (2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid) from Nacalai Tesque (Kyoto, Japan), and TAPS (*N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid) from MP Biomedicals (Solon, OH) are the buffer reagents used to maintain solution pH, respectively, in the range of 3–5, 6–8 and 9–10. The Aurum-101 etchant, HCl,  $\text{HNO}_3$ , NaOH,  $\text{NH}_3$  from Kanto Chemicals (Tokyo, Japan), and Scat 20X-PF alkaline detergent, ethanol, thiourea from Nacalai Tesque (Kyoto, Japan) were the multipurpose reagents used during the experiments as additives, extractant or washing agents.

#### 2.1.3. Laboratory wares

Low-density polyethylene containers from Nalgene Nunc (Rochester, NY), screw-capped polyethylene tubes and polypropylene jars from AS ONE (Osaka, Japan), and micropipette tips from Nichiryo (Tokyo, Japan) were used in experiments. All the laboratory wares were pre-cleaned by overnight soaking in each of the alkaline detergents (5%) and HCl ( $4 \text{ mol L}^{-1}$ ), followed by rinsing with ultrapure water after each step.

#### 2.1.4. Ion-selective SPEs

MetaSep Analig<sup>®</sup> PM-09 and Pd-03 (500 mg particles packed in 3 mL mini-columns) from GL Sciences (Tokyo, Japan) were the SPE-systems evaluated for the separation of Au, Pd, or Pt from complex matrices. The SPE materials are attached to the silica gel base support and equipped with crown ether functional groups (mesh size, 60–100; density,  $0.4 \text{ g mL}^{-1}$ ).

#### 2.1.5. Reference or real samples

Certified reference material (CRM) of wastewater: ERM-CA713 from European Commission Joint Research Center, Institute of Reference Materials and Measurements (Geel, Belgium) was used to check the method accuracy. The certified concentration of elements ( $\mu\text{g L}^{-1}$ ) in ERM-CA713 are follows: As,  $10.8 \pm 0.3$ ; Cd,  $5.09 \pm 0.20$ ; Cr,  $20.9 \pm 1.3$ ; Cu,  $101 \pm 7$ ; Fe,  $445 \pm 27$ ; Hg,  $1.84 \pm 0.11$ ; Mn,  $95 \pm 4$ ; Ni,  $50.3 \pm 1.4$ ; Pb,  $49.7 \pm 1.7$ ; Se,  $4.9 \pm 1.1$  [47].

Real metal plating waste solution from Sasaki Chemical (Tokyo,

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