Stripping Voltammetry of Trace Metals at Gold Electrode in the Presence of Ultrasound Irradiation

超音波照射下における微量金属イオンの金電極上のストリッピングボルタメトリー

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<Introduction>

Anodic stripping voltammetry (ASV) with a hanging mercury-drop (or mercury film) electrode has been regarded as well established as a powerful method for trace metal analysis. However, the toxicity of mercury and the potential risks of it during disposal make it undesirable to use. Recently, mercury-free solid electrodes like gold electrodes have been gained much attention and several applications for determination of trace copper (Cu²⁺) with gold electrodes have been reported. However, it is common to encounter the problems due to the lower preconcentration efficiency and the formation of intermetallic species at the gold electrode surface, which would lead to lower broader peaks, and shifts in the peak potential. Hence, the development of reliable ASV with solid electrodes is considered a major challenge in recent year. The combination of ultrasound with ASV has shown the advantages such as increase of mass transport with respect to improvement of electrolysis efficiency in the preconcentration step[1]. In addition, the activation the electrode surface by ultrasound might alter the electrochemical deposition process, and therefore is expected to improve the problem caused by the intermetallic formation. The main purpose of this work is to investigate the effects of ultrasound on ASV of trace Cu²⁺ with a view to examining the effect of ultrasound on the process of trace metal electrodeposition at a gold electrode.

<Experimental>

An ultrasonic cell homogenizer (SONICS) operating at 20 kHz at power levels of up to 130 W was used as a source of ultrasound. The electrochemical measurements were performed in a home-made H-type electrochemical cell with a three-electrode arrangement. A gold disk electrode (0.5 mm in diameter) served as a working electrode, with the Ag/AgCl (3 M NaCl) and platinum wire acting as the reference and counter electrodes, respectively. The working electrode was set at the bottom in one component of the H type cell, facing a titanium-tipped horn (2 mm in diameter) as is shown in Fig. 1.

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Abstract: Anodic stripping voltammetry (ASV) with a hanging mercury-drop (or mercury film) electrode has been regarded as a versatile and sensitive analytical technique for monitoring environmental and clinical trace metals. However, the toxicity of mercury and the potential risks of it during disposal make it undesirable to use. Recently, mercury-free electrodes have been gained much attention. With solid electrodes, it is common to encounter the problems due to the lower preconcentration efficiency and the formation of intermetallic species at the electrode surface. Our previous studies have shown the advantages of using ultrasound in stripping analysis because acoustic streaming increases the mass transport of the system resulting in shorter deposition times, greater sensitivity and a corresponding lowered detection limit. The main purpose of this work is to further investigate the effects of ultrasound on ASV of trace Cu²⁺ at a gold electrode with a view to developing sono-ASV as an electroanalytical procedure.
ASV measurements consist of 2 operation steps. At the preconcentration step, the target metal was deposited at the electrode under a certain deposition potential in the presence of ultrasound irradiation. Following the preconcentration, the ultrasound irradiation was stopped and the voltammograms were recorded by applying an anodic square-wave potential scan with a frequency of 30 Hz, amplitude of 25 mV and potential step of 5 mV.

<Results and Discussions>

Electrochemical behavior of 0.5 mM Cu²⁺ was first examined by cyclic voltammetry at a gold electrode in 10 mM HClO₄ supporting electrolyte in a potential range between -0.6 and +0.8 V vs. Ag/AgCl. Under quiescent condition, the voltamogram displayed three distorted oxidation peaks at +0.15 V, +0.4 V and 0.55 V which were attributed to the oxidation of bulk layer, underpotential deposition (UPD) layer of Cu and the formation of Au-Cu intermetallic compound on the gold electrode surface, respectively. Upon the ultrasound irradiation, however, the oxidation peak at +0.4 V predominately increased, in the meanwhile, the peak height at +0.55 V was decreased significantly. It is thus suggested that the sonication of electrode surface was in favor of UPD for Cu, probably due to the continuously renewed gold surface under ultrasound irradiation.

Figure 2 shows the ASV curves of Cu²⁺ with concentration range from 0 to 10 ppb (ng ml⁻¹). Fig.2 (a) is the results obtained with per-electrolysis time of 120 s and deposition potential of -0.4 V vs. Ag/AgCl in the presence of ultrasound irradiation. Fig.2 (b) are the results obtained by conventional ASV procedure using magnetic stirrer in preconcentration steps. There are two peaks corresponding Cu-UPD layer (peak I) and Cu-Au intermetallic compound (peak II) are observed in Fig.2(b).

![Square wave ASV results of trace Cu²⁺ at gold electrode 0.01 M HClO₄.](image)

Fig.2 Square wave ASV results of trace Cu²⁺ at gold electrode 0.01 M HClO₄. (A) The preconcentration step was conducted in the presence of ultrasound irradiation; (B) The preconcentration step was conducted with mechanic stirrer.

Since the stripping current arisen from Au-Cu intermetallic compound was very low, determination of Cu²⁺ in low concentration levels are facilitated by Sono-ASV (Fig2(a)). The ASV peak height at +0.4 V was proportional to the concentration of Cu²⁺ in the range 0 – 10 ppb. At much higher concentrations, the stripping peak was not symmetrical, and a shoulder near to +0.15 V vs. Ag/AgCl which is attributed to the bulk Cu oxidation, became evident. Sono-ASV was applied to the direct measurement of trace Cu²⁺ in tap water samples, with the results being excellent agreement with those determined by ICP-MS.

Reference