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Sonoelectrochemical analysis of trace metals

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Abstract

Ultrasonically-enhanced mass transport was exploited to increase preconcentration efficiency in anodic stripping voltammetry. We developed a Nafion-coated mercury thin-film working electrode which is stable under ultrasonic irradiation, making it possible to achieve very low limits of detection for relatively short preconcentration times. This allows the investigation of a variety of biological and environmental samples. © 1997 Elsevier Science B.V.

Keywords: Ultrasound; Sonoelectroanalysis; Trace metals; Anodic stripping voltammetry; Lead; Cadmium

Anodic stripping voltammetry (ASV) is a powerful method for trace analysis of heavy metal ions in solution. The metal to be quantified is preconcentrated by reduction of the corresponding cation onto an electrode, usually a mercury film or a solid substrate, followed by a reoxidation (stripping) step. Convective mass transport in the preconcentration step in well-defined hydrodynamic systems results in high sensitivity and low detection limits, previously demonstrated in flowing solution, e.g. Ref. [1].

The aim was to exploit ultrasonically-enhanced mass transport to increase preconcentration efficiency in ASV and to develop a modified mercury thin-film electrode which is stable under ultrasonic irradiation.

For all work described in this paper we used a recently developed small volume sonovoltammetric cell [2] which is particularly suitable for analytically oriented studies. A high intensity ultrasonic processor capable of delivering up to 500 W at 20 kHz frequency was employed. The horn was connected to a tapered microtip, 3 mm in diameter. A horn tip–electrode separation of 6 mm and a power intensity of 30 W cm^{-2} were selected for ultrasound-enhanced ASV measurements.

A Nafion-coated mercury thin film working electrode was prepared by spin coating through application of 0.5% Nafion solution followed by a casting solvent (DMF), curing in a hot air stream and carrying out mercury deposition through the Nafion film.

The characterization of the Nafion-coated mercury thin film electrodes was done electrochemically and by optical microscopy. It was found that small closely-spaced mercury droplets are formed on the glassy carbon substrate beneath the Nafion film, with similar behaviour to a continuous film. The Nafion film acts as protective layer which prevents the destruction of the mercury thin film in the ultrasonic field.

The analytical procedure consists of preconcentration in the presence of ultrasound and stripping determination in silent solution whilst applying a square wave potential–time waveform scan. Due to the significantly greater mass transport in the presence of ultrasound the preconcentration efficiency increased by a factor of about five in ultrasound-enhanced ASV compared to conventional ASV with stirring during accumulation. As a consequence, very low limits of detection of 3×10^{-11} M for lead and cadmium were achieved for relatively short preconcentration times of 30 s. This allows the investigation of a variety of biological and environmental samples, where low (sub-ppm) concentrations of trace metals are encountered. From the practical point of view, the Nafion coating has the additional and important advantage of reducing interferences from complex matrices, since it prevents adsorption of organic compounds which would otherwise block the electrode surface.

More details of the performance characteristics of ultrasound-enhanced ASV are given in Ref. [3].

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