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DETERMINATION OF TRACE AMOUNTS OF DIBUTYLTIN(IV) DICHLORIDE BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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Differential pulse anodic stripping voltammetry with a hanging mercury drop electrode was employed successfully for the determination of dibutyltin(IV) dichloride in the range of 3-50 μg dm^{-3} at the deposition time of 60 s in 50% (v/v) ethanol–water medium (pH 7.3).

In recent years, organotin compounds are finding increasing application as catalysts, stabilizers and biocides. Since most of these uses are dispersive, the possible entry of these toxic compounds into natural waters, sediments and biota must be assessed. Various methods have been proposed for the determination of organotin compounds, e.g., atomic absorption spectrophotometry,$^{1,2)}$ fluorometry,$^{3)}$ and voltammetry.$^{4-12)}$ Triphenyl-$^{4)}$ and tributyltin$^{5)}$ compounds when reduced at the mercury electrode are strongly adsorbed onto the electrode surface. The property has been utilized in the determination of trace amounts of triphenyl- and tributyltin compounds by anodic stripping voltammetry (ASV).$^{4,6,7)}$ Polarographic behavior of dialkyl- and diaryltin(IV) compounds (R_2SnX_2) (R=methyl, ethyl, butyl, phenyl and X= halogen) was investigated in acids, ethanol–water medium and so on.$^{7-12)}$ Fleet and Fouzder$^{10)}$ determined dibutyltin compounds over the concentration range 5 x 10^{-4} to 5 x 10^{-9} M (1 M=1 mol dm^{-3}) with differential pulse polarography (DPP) in 80% (v/v) ethanol–water medium (pH 7.0)

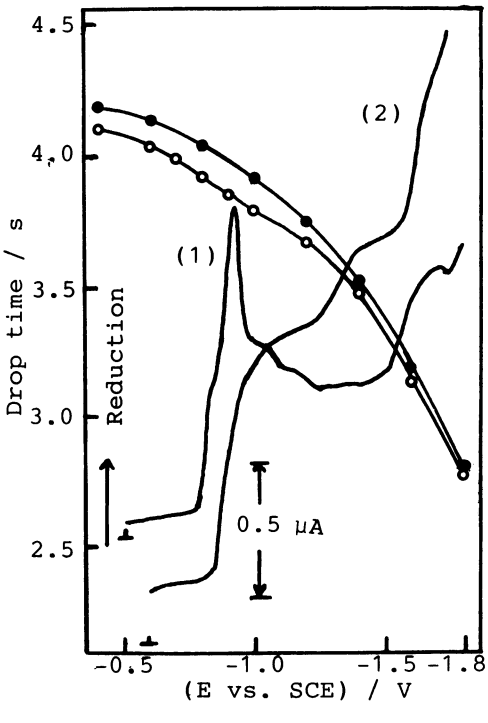

Fig. 1. Normal pulse polarograms (NPP) and electrocapillary curves (ECC) of Bu_2SnCl_2 in 0.1 M acetic acid–0.1 M ammonia buffer solution (pH 7.3) containing 0.002% Triton X-100. Conditions of NPP: Ethanol, (1) 50% (v/v) and (2) 80% (v/v); [Bu_2SnCl_2] = 1 x 10^{-4} M; (Initial potential vs. SCE) / V = (1) -0.5, (2) -0.6. Conditions of ECC: Ethanol, 50% (v/v); [Bu_2SnCl_2] = -●- 0 M, -○- 1 x 10^{-4} M.

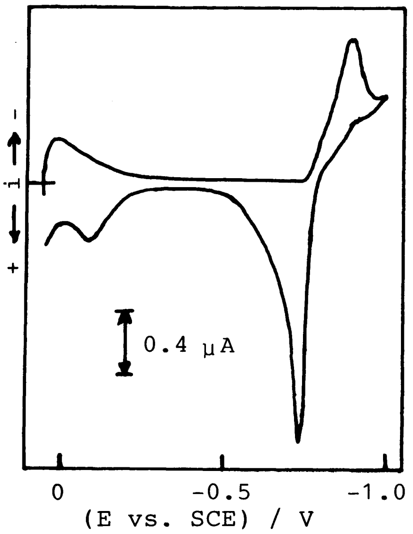

Fig. 2. Cyclic voltammogram of a 1 x 10^{-4} M Bu_2SnCl_2 solution in 50% (v/v) ethanol—water medium. Start potential, +0.05 V; scan rate, 200 mV s^{-1}.

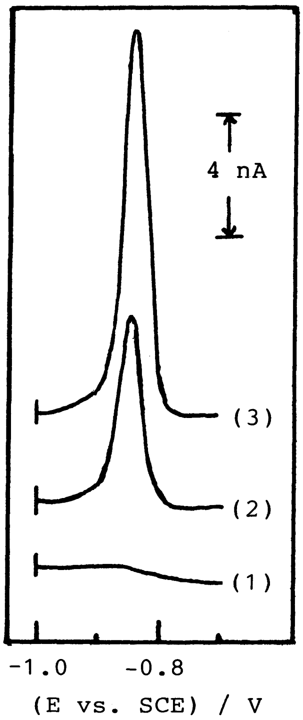

Fig. 3. Typical differential pulse anodic stripping voltammograms of Bu_2SnCl_2 in 50% (v/v) ethanol—water of the same composition in Fig. 1. Pulse interval time, 0.1 s; modulation amplitude, 50 mV; scan rate, 20 mV s^{-1}; deposition potential, -1.0 V vs. SCE; deposition time, 60 s (stirred); equilibration period, 10 s (unstirred); $[Bu_2SnCl_2]$ / μg dm^{-3} = (1) 0 (blank), (2) 4.2, (3) 8.4.

containing 0.1 M acetic acid—0.1 M ammonia buffer solution.

In this paper, we studied the characteristics of adsorption of dibutyltin dichloride (Bu_2SnCl_2) and its reduction product(s) and reoxidation of the reduction product(s) at the mercury electrode, primarily with the aim of the determination of Bu_2SnCl_2 by DPASV.

Normal pulse polarograms (NPP) for Bu_2SnCl_2 in 50% (v/v) and 80% (v/v) ethanol—water media (apparent pH 7.3) containing 0.1 M acetic acid—0.1 M ammonia buffer and 0.002% Triton X-100[4,8,10] are shown in Fig. 1. In 80% ethanol, Bu_2SnCl_2 showed three reduction steps. In 50% ethanol, the first step was accompanied a maximum at -0.8 V vs. SCE, which is attributed to the specific adsorption of Bu_2SnCl_2 on the mercury surface.[13] A maximium is also observed at the same potential in the reverse pulse polarogram. The electrocapillary curve (Fig. 1) showed the depression on both sides of the maximum, and the cyclic voltammogram (Fig. 2) showed a pair of steep peaks. These results indicate that both Bu_2SnCl_2 and its reduction product or products are significantly adsorbed in 50% ethanol—water medium and that the adsorbed reduction product(s) is readily reoxidized. The reoxidation peak in this medium can be utilized for the determination of traces of Bu_2SnCl_2 by means of DPASV.

DPASV of Bu_2SnCl_2 was investigated under the conditions presented in Fig. 3 by using a three-electrode cell with a hanging mercury drop electrode (HMDE). Typical anodic stripping voltammograms of Bu_2SnCl_2 are shown in Fig. 3, where the stripping peak with a peak half-width of 30 mV appears at -0.85 V vs. SCE. The peak current increased linearly with depolarizer mass concentration in the range

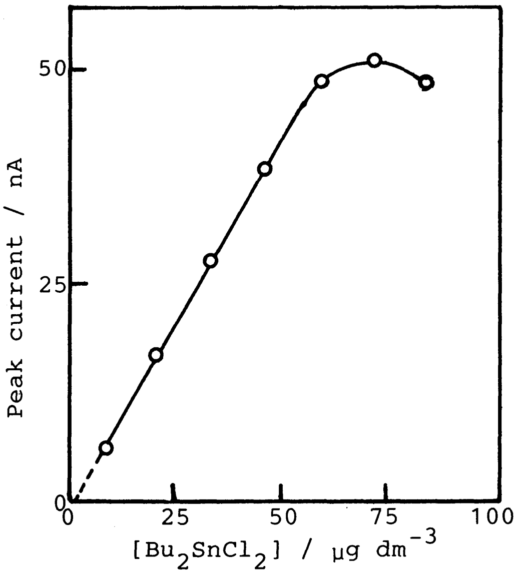

Fig. 4. Effect of concentration of Bu_2SnCl_2 on peak height. Measurement conditions are the same as for Fig. 3.

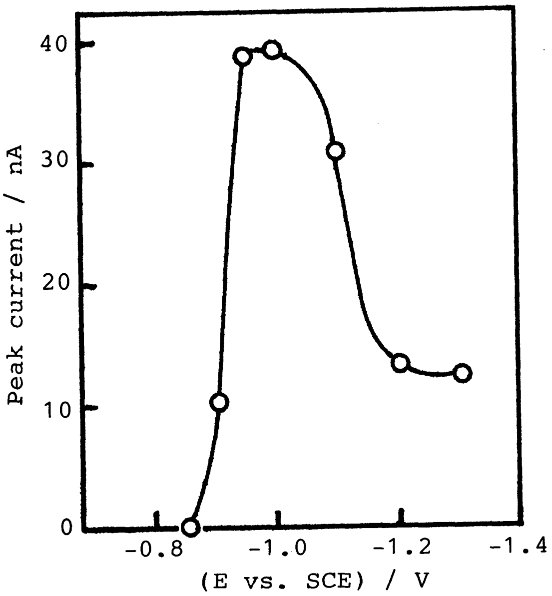

Fig. 5. Effect of deposition potential on peak current. [Bu_2SnCl_2] = 25.2 μg dm^{-3}.

of 3-50 μg dm^{-3} as Bu_2SnCl_2 at the deposition time of 60 s (Fig. 4). The deviation from the linearity is observed above 50 μg dm^{-3}, at which HMDE is completely covered with the film of insulating material of the reduction product(s). The lower limit of detection is 3 μg dm^{-3} of Bu_2SnCl_2, and the relative standard deviation at 8.4 μg dm^{-3} of Bu_2SnCl_2 (eight runs) was 3.1%.

The effect of the deposition potential on the peak current is shown in Fig. 5. The maximum peak current is observed in the range of -0.95 to -1.0 V vs. SCE. The effects of the modulation amplitude (ΔE) on the peak current and the peak half-width are shown in Fig. 6. The peak current was proportional to ΔE up to 25 mV and the deviation from linearity was particularly marked for ΔE above 25 mV. The peak half-width increased with an increase in ΔE, as is generally observed in DPASV. The peak current was also proportional to the deposition time (t_{dep}) up to 2 min, beyond which it negatively deviated from the proportionality. The peak current reached a maximum at the t_{dep} of 5 min and decreased gradually above 5 min. This relationship between the peak current and the t_{dep} was similar to that of the peak current and the mass concentration of

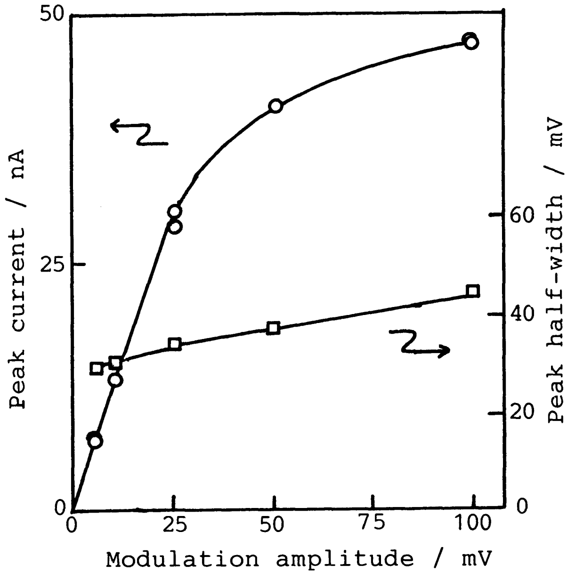

Fig. 6. Effects of modulation amplitude on peak current and peak half-width.

[Bu_2SnCl_2] = 25.2 μg dm^{-3}.

Bu_2SnCl_2. The effect of the scan rate on the peak current was examined over the scan rate of 5 to 100 mV s^{-1}. The peak current steeply increased with increasing the scan rate in the range of 5-50 mV s^{-1} and remained almost constant above 50 mV s^{-1}. From these results, the experimental conditions of DPASV determination of Bu_2SnCl_2 were chosen to that described in Fig. 3. The stripping peak current of Bu_2SnCl_2 was constant over the standing time up to 180 min under the stream of nitrogen gas.

The presence of triphenyltin chloride above 4 μg dm^{-3}, of which stripping peak potential was -0.72 V vs. SCE, depressed the stripping peak current of Bu_2SnCl_2 (25.2 μg dm^{-3}). The presence of tributyltin chloride at ca. 30 μg dm^{-3}, which was little deposited on HMDE when reduced at -1.0 V vs. SCE, scarcely affected the stripping peak current of Bu_2SnCl_2.

DPASV was adopted to the determination of Bu_2SnCl_2 in natural waters. The proposed method involves extraction and cleaning up by chromatography on cation-exchange resin in order to avoid interferences from heavy metals and organic materials in the measurement of DPASV:[15,16] Bu_2SnCl_2 in natural water (250 ml) was extracted twice with 50% ethyl acetate–hexane (25 ml); The extract was dehydrated, evaporated to near dryness, and then dissolved in ethanol followed by cleaning up; After buffer and Triton X-100 were added to the solution, Bu_2SnCl_2 was determined by DPASV by use of the method of standard addition.

The recoveries of Bu_2SnCl_2 (1 μg) obtained from river water and sea water were 67% and 91%, respectively.

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