ELSEVIER

Food Chemistry 64 (1999) 129–132

Food Chemistry

Analytical, Nutritional and Clinical Methods Section

Determination of trace tin in foods by single-sweep polarography

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Received 16 September 1997; received in revised form 25 November 1997; accepted 25 November 1997

Abstract

A new method for the determination of trace tin in a solution of oxalic acid–methylene blue by single-sweep polarography is developed. The mechanism for the polarographic waves and the conditions for determining tin are discussed in this report. The peak height is directly proportional to the concentration of tin (IV) over the range 2.0×10^{-8}–$1.0\times10^{-6}\,g\,ml^{-1}$. The detection limit and the recovery of the method are $1.0\times10^{-8}\,g\,ml^{-1}$ and 93–98%, respectively. The method was successfully employed for the determination of tin in juices of canned fruits. © 1998 Elsevier Science Ltd. All rights reserved.

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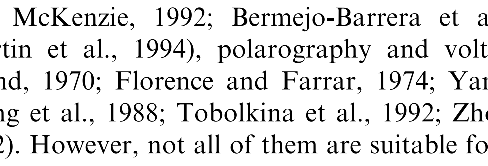
1. Introduction

Tin-plate is widely used in food industry as packings of canned foods. Tin is a heavy metal element which can do certain harm to human health (Zhang and Li, 1994). Many methods have been developed for the determination of tin. For example, spectrophotometry (Royal Society of Chemistry, 1967, 1968; Gutierrez et al., 1985; Chakraborty et al., 1991; Skurikhin, 1993), atomic absorption spectrometry (Royal Society of Chemistry, 1983; Pinnel et al., 1988; Chung and Tsai, 1992; Dabeka and McKenzie, 1992; Bermejo-Barrera et al., 1993; Martin et al., 1994), polarography and voltammetry (Bond, 1970; Florence and Farrar, 1974; Yang, 1983; Wang et al., 1988; Tobolkina et al., 1992; Zhou et al., 1992). However, not all of them are suitable for routine trace determinations. In this report, we have investigated the electrochemical behavior of tin (IV) in oxalic–methylene blue

( , R^+)

system by a DME electrode. Tin has a stable and well-defined cathodic peak in the presence of oxalic acid and methylene blue. Methylene blue as a spiked reagent added into the analytical system can increase the peak height of tin considerably. The method is characterized by sensitivity, cheapness and convenience. It was used for the determination of trace tin in juices of canned fruits with satisfactory results.

2. Experimental

2.1. Apparatus and reagents

A Model JP-2A oscillopolarograph (Chengdu Instrumental Factory, China) was used. A three-electrode system was used with a dropping mercury working electrode (DME). The reference and counter electrodes were saturated calomel and platinum wire electrodes respectively. A Model MF-1A voltammetric analyser (Jiangsu Electroanalysis Instrumental Factory, China) was used for cyclic voltammetric experiments. The electrolytic cell was a 10 ml beaker.

All reagents, unless otherwise stated, were of analytical grade and triple-distilled water was always used.

A $50\,\mu g\,ml^{-1}$ tin (IV) stock solution containing 20% concentrated hydrochloric acid was prepared by dissolving 0.0500 g metal tin (spectral purity) in a small amount of 6 M hydrochloric acid, transferring into a 1000 ml volumetric flask after cooling, adding an appropriate amount of concentrated hydrochloric acid and then diluting to 1000 ml with water. The standard solutions were obtained by diluting the stock solution.

A 0.5 M oxalic acid solution was prepared by dissolving 15.7588 g of oxalic acid in water and diluting to 250 ml.

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PII: S0308-8146(98)00023-5

A 0.02% methylene blue solution was prepared by weighing and dissolving 0.0200 g methylene blue in 100 ml water.

2.2. Sample preparation

A 10 ml sample (juice of canned pineapple, orange or pear) was transferred to a 100 ml conical flask, and 2.5 ml concentrated nitric acid was added. The sample was then carefully heated and evaporated to near dryness. After cooling, the digested sample was neutralized to weak acidic property (pH = 4) by sodium hydroxide solution. Then the solution was transferred and diluted to 10 ml with water.

2.3. Procedure

1.0 ml of 0.5 M oxalic acid and 1.0 ml of 0.02% methylene blue were transferred to a 10 ml volumetric flask and an appropriate amount of standard or sample solution (2.0×10^{-8} to 1.0×10^{-6} g ml^{-1} tin (IV)) was added. The solution was diluted to 10 ml with water and transferred to an electrolytic cell. The initial scanning potential was set at −0.50 V (vs. SCE) and a derivative scan was carried out in the negative direction. The peak height was recorded at −0.80 V (Fig. 1).

3. Results and discussion

Fig. 2 shows the effect of oxalic acid concentration on peak height of tin (IV). The peak maximum occurred by the addition of 1 ml 0.5 M oxalic acid to the analytical system (final volume, 10 ml). Therefore, 0.05 M oxalic acid was selected in all subsequent work.

Methylene blue was used as a spiked reagent in the system. It could enhance the peak height of tin (IV) above 15-fold. From Fig. 3, we can see that the peak height becomes constant when the amount of 0.02% methylene blue is over the range 0.6–1.5 ml, above which it starts to decline. Therefore, 0.002% methylene blue was chosen as an optimum.

The tolerance for various foreign ions was studied with 0.1 μg ml^{-1} tin (IV). The experimental results showed that 2-fold Cd (II), 100-fold Pb (II), Fe (II), Ag (I) had no effect. The other common cations, such as Zn (II), Ca (II), Mg (II) etc. did not interfere with the determination. 40-fold Ac$^-$, 60-fold HCO_3^-, 80-fold Br$^-$, CO_3^{2-} had little effect.

Under the optimum conditions described earlier, the peak height is directly proportional to the tin (IV) concentration over the range 2.0×10^{-8} to 1.0×10^{-6} g ml^{-1}. In this range, tin (IV) can be determined quantitatively

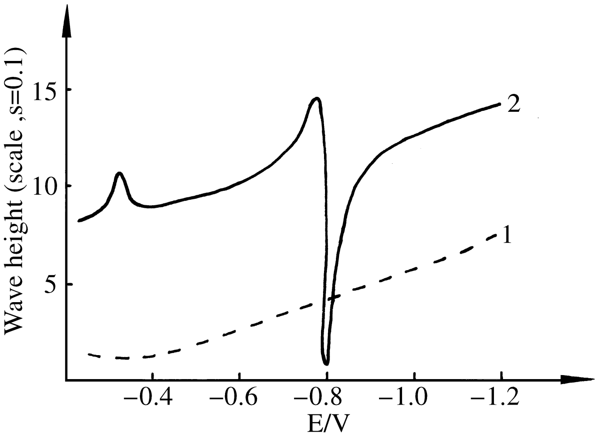

Fig. 1. Derivative single sweep polarograms, of tin (IV): (1) 0.05M oxalic acid + 0.002% methylene blue; (2) 0.05M oxalic acid + 0.002% methylene blue + 0. 1 μg·ml^{-1} tin(IV) (s, current sensitivity).

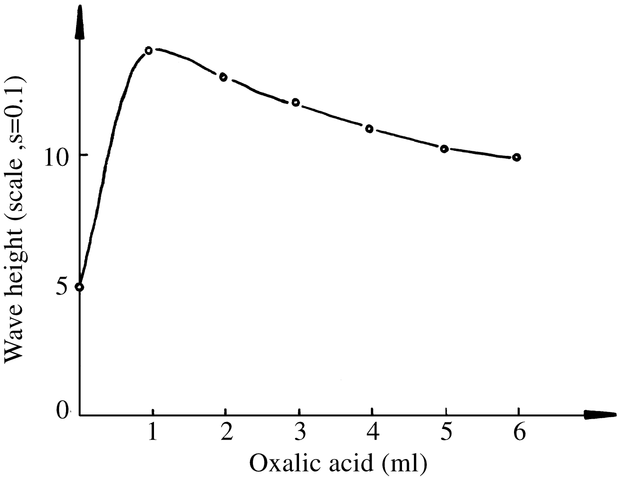

Fig. 2. Effect of the concentration of oxalic acid: 0.002% methylene blue + 0. 1 μg·ml^{-1} tin (IV) (s, current sensitivity).

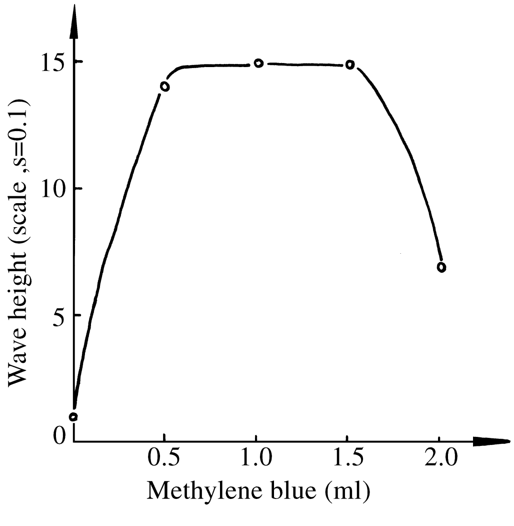

Fig. 3. Effect of the concentration of methylene blue: 0. 05M oxalic acid + 0. 1 μg·ml^{-1} tin (IV) (s, current sensitivity).

in juices of canned fruits by using standard curve. Three different samples were analysed. The results agree well with those obtained by the spectrophotometric method developed by Gutierrez et al. (1985) (Table 1).

4. Mechanism

The experiments showed that tin oxalate and methylene blue could form an adsorptive ionic complex at DME electrode surface. Accordingly, a sensitive polarographic peak resulted from the reduction of tin (IV) to tin (II) at −0.30 V (vs. SCE) and further reduction of tin (II) to tin (0). Cyclic voltammograms recorded from 0 to −1.0 V showed that the polarographic wave appeared at −0.80 V (vs. SCE) was reversible (Fig. 4). Since methylene blue (R^+) has adsorption (Yang, 1983; Lu and Cai, 1987), the ionic complex of methylene blue and tin oxalate can be absorbed on the surface of the DME and changes the surface tension of the mercury drop. Thus, its electrocapillary curve was much lower than that of the supporting electrolyte solution. The effect of temperature showed that when the temperature was in the range of 5 to 30°C, the peak height was basically unchangeable, but when the temperature was at 35°C, the peak height fell. All these phenomena give evidence of the adsorption character of the wave. The possible electrode reaction mechanism is:

$$\mathrm{R^+ - Sn(IV) \rightleftharpoons R^+Sn(IV)ads}$$

$$\mathrm{R^+ - Sn(IV)ads + 2e \rightleftharpoons R^+Sn(II)}$$

$$\mathrm{R^+ - Sn(II) \rightleftharpoons R^+Sn(II)ads}$$

$$\mathrm{R^+ - Sn(II)ads + 2e \rightleftharpoons R^+Sn}$$

Table 1
Results for determination of tin in samples of juices of canned fruits

Sample	Proposed method (μg ml^{-1})	Recovery (%)	Spectrophotometric method (μg ml^{-1})
pineapple	2.30 ± 0.23*	93	2.40 ± 0.21
orange	8.50 ± 0.41	93	8.20 ± 0.52
pear	0.50 ± 0.05	98	0.48 ± 0.06

* Values are expressed as mean ± standard deviation ($n = 4$).

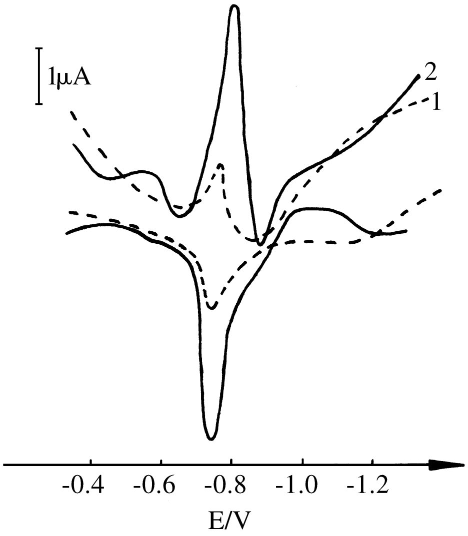

Fig. 4. Cyclic voltammgrams. (1)0.05M oxalic acid + 0.002% methylene blue; (2)0.05M oxalic acid + 0.002% methylene blue + 1 μg·ml^{-1} tin(IV) Scan rate, 50 mV·s^{-1}; Y,50 mV·cm^{-1}; Current sensitivity, 20 μA.

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