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Polarographic determination of selenium in tea leaves using a dropping mercury electrode

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A new polarographic method is described for the estimation of selenium in tea leaves. Copper with selenium can produce intermetallic Cu–Se compound in acetic acid–EDTA solution. The intermetallic Cu–Se compound yields a well-defined high sensitivity polarographic wave at a potential of about −0.7 V (vs SCE). Under optimum conditions, the wave height is proportional to the concentration of selenium (IV) in the range of 0.04–0.4 μg/ml. The method has been used to determine selenium in tea leaves and results obtained agreed favourably with an atomic absorption method. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

The role of selenium as an important biological trace element in the human body has been investigated and close correlations between various cancers and the selenium content of waters, soils, foods, animals and plants found in certain areas have been reported (Cheng *et al.*, 1993). In proper amounts, selenium can enhance immunity and protect against certain cancers and heart diseases, but is toxic in excess causing diseases of neurosystem, skin and others (Hang *et al.*, 1992). Accordingly, a sensitive and rapid method for the determination of selenium is desirable.

A large number of methods have been reported for the determination of selenium, such as atomic absorption spectrometry (Strugeon *et al.*, 1985; Zheng, 1991; Kumpulainen & Saarela, 1992; Yang & Qian, 1992; Zhang *et al.*, 1994), gas and liquid chromatography (Kengo *et al.*, 1980; Lan *et al.*, 1992), cathodic stripping voltammetry (Dennis *et al.*, 1976), anodic stripping voltammetry (Hamilton & Ellis, 1979; Roberts & Richard, 1981; Hasan & Abdul, 1992; Hrehocik *et al.*, 1993) and polarography (Batley, 1986; Wu *et al.*, 1988; Ferri *et al.*, 1989; Wu *et al.*, 1989). In the polarographic determination of selenium, copper was the most serious interfering element, owing to its very similar half-wave potential. Although there are many studies in which polarography has been used for the determination of selenium, no direct method has yet been reported for when copper is also present.

This paper describes a simple polarographic method for the determination of selenium (IV) in the presence of copper (II) without any separation. The method has been applied to selenium determination in tea leaves.

EXPERIMENTAL

Apparatus and reagents

A JP-2A oscillopolarograph (Chengdu Instrumental Factory, China) was used. The triple electrode system comprised a dropping mercury electrode, platinum counter electrode, and saturated calomel electrode (SCE) as reference. The electrolytic cell was a 10 ml beaker.

The conditions for derivative polarography were: drop-time, 7 s; scan rate 250 mV/s; scan range −0.4 to −0.9 V.

Analytical reagent grade chemicals were used and all solutions were prepared from triply distilled water. 9 M sulphuric acid (H_2SO_4), 12 M hydrochloric acid (HCl), concentrated perchloric acid ($HClO_4$) and concentrated ammonia (NH_3) were used in sample preparation. 0.1% EDTA solution, 2 M acetic acid (HOAC) solution and a 6.3×10^{-3} M copper (II) solution, prepared from copper sulphate crystals, were used.

A 1000 μg/ml selenium (IV) stock solution was prepared by dissolving 140.5 mg of selenium dioxide (SeO_2, 99.999%) in 0.1 M HCl and made up to a volume of 100 ml. A working standard solution of certain concentration of selenium (IV) was obtained as required by diluting the stock solution with triply distilled water.

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Sample preparation

A propriate amount of Chinese tea (10–20 g) was ground and sieved through a 20-mesh sieve. A 2.0 g portion was impregnated with 5 ml concentrated $HClO_4$ and 1.0 ml 9 M H_2SO_4 in a conical flask (50 ml) for 24 h. The sample solution was heated on a hot plate until it turned primrose or colourless. After cooling, 0.1 ml of 12 M HCl was added to reduce selenium (VI) to selenium (IV), and the liquid was evaporated on a boiling water-bath until the volume was about 0.5 ml (about 15 min). The conical flask was removed from the water-bath and allowed to cool to room temperature. Each sample digest was transferred into a 50 ml volumetric flask. The pH was adjusted to 6–7 with concentrated ammonia solution and then diluted to volume with water.

Method

Standard selenium (IV) solution was mixed with 3 ml of 2 M HOAC solution, 0.1 ml of 6.3×10^{-3} M copper (II) solution and 1.2 ml 0.1% EDTA solution, and then diluted to 10 ml with water. The prepared solution was left to stand for 5 min, then the derivative polarogram was recorded from −0.4 to −0.9 V to find where the peak appears, and the peak heights were also measured.

Different ions were also added to 0.06 μg/ml selenium (IV) solution to find whether they would interfere with the determination of selenium (IV).

0.1 millilitres of the sample solution was transferred into a cell (10 ml). Three millilitres of 2 M HOAC, 1.2 ml 0.1% EDTA and 5.7 ml water were then added and the peak height was recorded by the procedure described above.

RESULTS AND DISCUSSION

In 0.6 M HOAC and 0.012% EDTA (pH 2.5) solution, no peak was observed for a solution of copper (II) (6.3×10^{-5} M) at the peak potential of −0.70 V in absence of selenium (IV) (Fig. 1). Similarly in 0.6 M HOAC and 0.012% EDTA (pH 2.5), no selenium (IV) peak was observed at 0.08 μg/ml selenium (IV) when copper was absent. When the copper (II) and selenium (IV) solutions were both added in 0.6 M acetic acid (HOAC) and 0.012% EDTA solution, a polarographic wave appears at −0.70 V (vs SCE) (Fig. 1). Therefore, this result suggest that the polarographic wave is the reduction peak (cathodic peak) of the intermetallic Cu–Se compound.

In 0.6 M HOAC and 0.012% EDTA (pH 2.5) solution, neither reduction peak (cathodic peak) nor oxidation peak (anodic peak) was observed for a solution of copper (6.3×10^{-5} M) in the scan range (−0.4 to −0.9 V) (Fig. 2). When 2.0 μg/ml selenium (IV) was present in the solution both the reduction peak (−0.7 V) and the oxidation peak (−0.63 V) appeared (Fig. 2). It is obvious that the former and the latter respectively correspond to the reduction and oxidation of intermetallic Cu–Se compound. The electrode reaction is apparently reversible, as there is only a small difference between the reduction and the oxidation potentials when the scan direction is reversed.

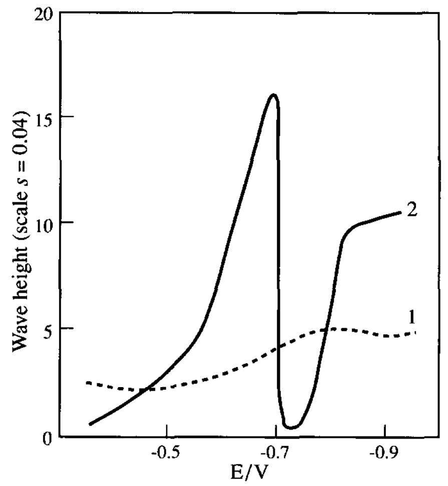

Fig. 1. Derivative polarogram of Se–Cu compound: (1) 0.6 M HOAC + 6.3×10^{-5} M Cu^{2+} + 0.012% EDTA (blank); (2) 0.6 M HOAC + 6.3×10^{-5} M Cu^{2+} + 0.012% EDTA + 0.08 μg/ml Se (IV) (*s*, current sensitivity).

Figure 3 shows the effect of HOAC concentration on peak height of selenium (IV). The peak maximum occurred with the addition of 3 ml 2 M HOAC to the analytical system (final volume, 10 ml). If the final HOAC concentration is higher than 0.6 M the peak shape deteriorates. At low acidity, the peak height decreases as a result of copper (II) hydrolysis. Thus, 0.6 M HOAC was chosen.

Copper (II) is a key factor for the polarographic wave of selenium (IV), so the concentration of copper (II) will

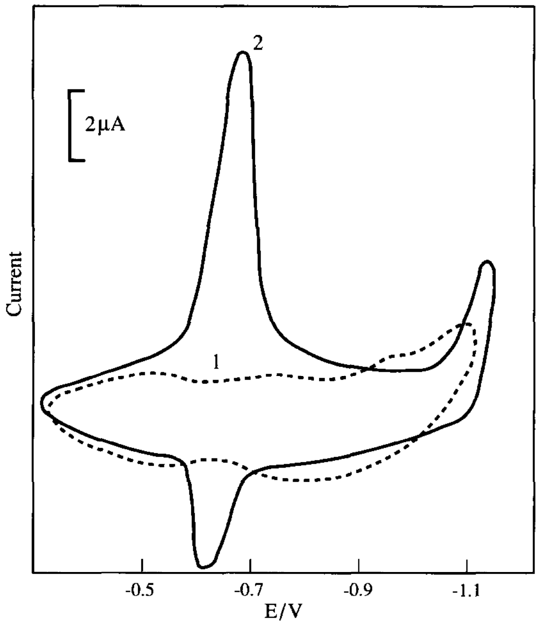

Fig. 2. Cyclic voltammograms: (1) 0.6 M HOAC + 6.3×10^{-5} M Cu^{2+} + 0.012% EDTA (blank); (2) 0.6 M HOAC + 6.3×10^{-5} M Cu^{2+} + 0.012% EDTA + 2.0 μg/ml Se (IV).

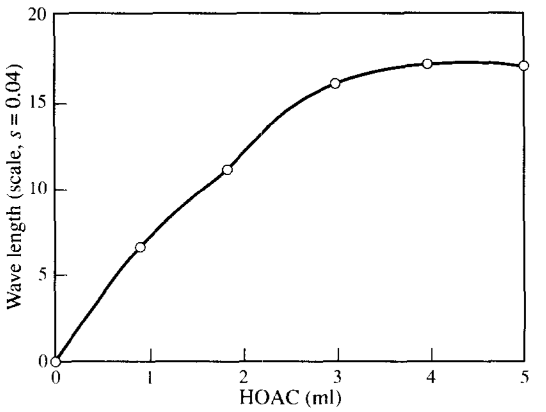

Fig. 3. Effect of the concentration of HOAC: 6.3×10^{-5} M Cu^{2+} + 0.012% EDTA + 0.08 μg/ml Se (IV) (*s*, current sensitivity).

Table 1. Results for determination of selenium in samples of tea leaves

Sample	Present method (μg/g) Mean ± SD (*n* = 4)	AAS (μg/g) Mean ± SD (*n* = 3)
1	1.23 ± 0.31	1.00 ± 0.29
2	0.98 ± 0.12	0.93 ± 0.28
3	3.20 ± 0.25	3.40 ± 0.25
4	4.58 ± 0.32	4.76 ± 0.30
5	4.30 ± 0.30	4.10 ± 0.35

influence the sensitivity of the selenium (IV) peak height. No selenium (IV) peak appeared in the HOAC–EDTA solution alone. After adding copper (II) (6.3×10^{-5} M), the selenium (IV) peak occurred at a potential of −0.70 V (vs SCE), which increased in sensitivity with increasing amounts of copper (II). The peak height varied with selenium (IV) concentration only when the volume of copper (II) solution was at least 0.1 ml in a 10 ml solution. The optimum volume of copper (II) was therefore 0.1 ml.

EDTA acts not only the supporting electrolyte, and as stabilizer of selenium (IV) (Cai & Shi, 1988), but also as a masking reagent. For example, Pb (II) interferes with the determination of selenium (IV) in the absence of EDTA. The interferences can be eliminated with EDTA. When the concentration of EDTA was 0.012%, the recovery values of selenium (IV) were 85–105%. Moreover, if the final EDTA concentration is >0.012%, the peak shape deteriorates, and thus influences the measurement of peak height. Therefore, its concentration was chosen to be 0.012% (w/v) in all subsequent work.

In the presence of 0.012% EDTA, the experimental results show that a 1000-fold excess of Al (III), Ca (II), Mg (II), Sr (II), K (I), Na (I), 500-fold excess of Fe (III), Mn (II), Zn (II), Co (II); 100-fold excess of Sb (III), Ni (II); 80-fold excess of Pb (II), Cd (II) and 50-fold excess of Te (IV) do not interfere with the determination of selenium (IV) (6×10^{-8} g/ml).

Under the optimum conditions described above, the peak height is directly proportional to the selenium (IV) concentration over the range 0.04–0.4 μg/ml. In this range, by using the calibration curve or the standard addition technique, selenium (IV) can be determined quantitatively in tea leaves. Five different kinds of samples of tea leaves, which were obtained from EnShi district of HuBei province, were analysed using the proposed method and atomic absorption spectroscopy (Hong, 1987). The results are given in Table 1. In order to evaluate the validity of the proposed method to determine selenium (IV) in tea leaves, recovery studies were carried out on samples, and the values were 85–105%. Good agreement on the amount of selenium obtained by atomic absorption spectroscopy and by the proposed method were obtained (Table 1).

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