

THE INFLUENCE OF VARIOUS METALS ON THE ANODIC OXIDATION OF TRACES OF MERCURY FROM CARBON ELECTRODES IN THIOCYANATE MEDIA

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SUMMARY

The influence of traces of Cu(II), Pb(II), Sn(II), Cd(II), Ag(I), Fe(II), Ni(II), Te(IV) and Au(III) on the stripping process of mercury from graphite electrodes was investigated in thiocyanate media. The addition of Pb(II), Cd(II) or Cu(II) usually improves the detection limit for mercury, though copper(II) at certain concentrations has harmful effects. Iron(II) and nickel(II) can cause severe distortion of the mercury stripping peaks if the deposition potential or pH are not selected correctly. The stripping peaks of silver and mercury overlap at low thiocyanate concentration but are quite well separated at high thiocyanate concentrations. In the presence of gold(III) or tellurium(IV), the formation of intermetallic compounds may cause severe distortions of the mercury stripping peak. The nature of the multiple peaks sometimes observed during anodic oxidation of mercury is explained.

Many unexplained phenomena are described in the literature on the anodic oxidation of traces of mercury from graphite electrodes. In some earlier work [1], it was shown that the anodic oxidation was affected by the precipitation of sparingly soluble mercury(I) salts on the electrode surface, but these salts cannot explain the curious phenomena observed in thiocyanate medium, where during dissolution of mercury some authors obtained two [2–5] or even three [2, 3] stripping peaks. From the analytical point of view, the appearance of multiple peaks is harmful. It seemed possible that these multiple peaks could be caused, at least partially, by contaminants present at trace levels in the supporting electrolyte. The aim of the present work was, therefore, to investigate the influence of various substances deposited simultaneously with mercury on the mercury stripping peak.

EXPERIMENTAL

The voltammetric curves were recorded with a Radelkis OH-105 polarograph with a three-electrode arrangement. All potentials are reported relative to the saturated calomel reference electrode used. The counter electrode was a 2-cm² platinum foil. The indicator electrode was a paraffin wax-impregnated

graphite electrode [6] with surface area 3.14 mm^2 , or a glassy carbon electrode with surface area 6.15 mm^2 . In several tests, a HMDE [7] was used. The gold-plated graphite electrode was prepared by deposition of several monolayers of gold on the graphite electrode from a stirred solution 1 mol dm^{-3} in hydrochloric acid and $3 \times 10^{-3} \text{ mol dm}^{-3}$ in gold(III).

All solutions were prepared from reagent-grade chemicals and water purified as described earlier [8]. In some cases, the thiocyanate supporting electrolyte was purified at a large mercury cathode (surface area 20 cm^2) held at -1.0 V by means of a potentiostat (Radelkis OH-404/H). Solutions were deoxygenated with argon prior to measurements. All experiments were done at 25°C .

RESULTS

Preliminary experiments

Figure 1 illustrates the complexity of the processes connected with the occurrence of the multiple peaks. The blank test obtained after a lengthy preconcentration of impurities on the electrode surface (curve 1) shows no peak; such behaviour is usually interpreted as evidence of the high purity of the supporting electrolyte. However, curve 2, obtained after addition of a little mercury(II) to the same solution, has three peaks instead of the expected single peak. These peaks are designated a, b and c in Fig. 1. Peaks b and c were observed by Perone and Kretlov [2] and by Pniew et al. [3], who assumed that they correspond to oxidation of mercury. Both prolongation of the pre-electrolysis time as well as an increase of mercury(II) concentration led to a significant increase of peak b. The heights of peaks a and c increased more slowly under these conditions and at high mercury(II) concentrations they became insignificant compared with peak b. In solutions with lower thiocyanate concentration, all these peaks decreased but simultaneously peak c became better developed and peak b split.

It seems unlikely that peak a corresponds to the oxidation of mercury, though it appeared only after the addition of mercury(II) to the solution. More probably it corresponds to the oxidation of another substance, deposition of which is activated by the simultaneous deposition of mercury. Cyclic voltammetric experiments with higher concentrations of various substances showed that in the potential range around peak a, peaks of lead and copper appeared. In the potential range around peak c, Te and HgTe were oxidized. Anodic stripping at the HMDE showed that the supporting electrolyte used ($0.1 \text{ mol dm}^{-3} \text{ NaSCN}$) contained traces of Cu(II) and Pb(II), but their exact determination was difficult under these conditions because the peaks overlapped. The total concentration of Cu(II) and Pb(II) in the $0.1 \text{ mol dm}^{-3} \text{ NaSCN}$ solution was estimated as $4 \times 10^{-8} \text{ mol dm}^{-3}$.

Strong evidence that peaks a and c on curves 2 and 3 (Fig. 1) do not correspond to oxidation of mercury but to codeposition of other metals

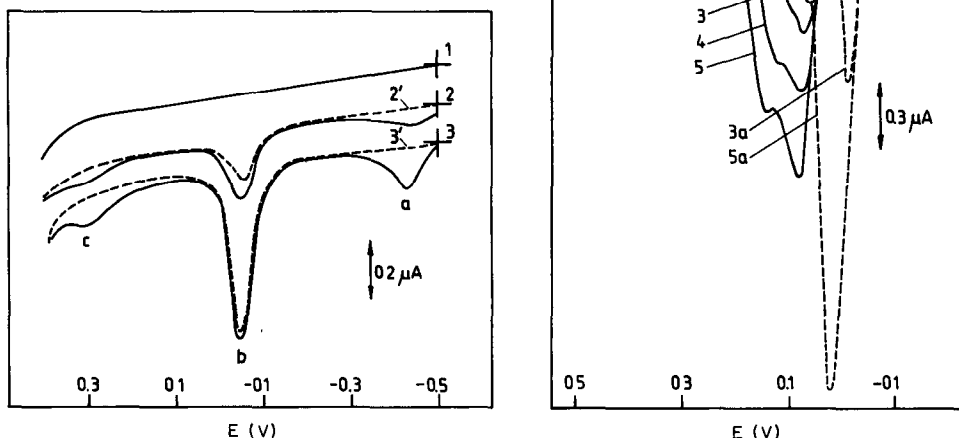


Fig. 1. Anodic stripping curves obtained for Hg(II) in 0.1 mol dm^{-3} sodium thiocyanate at pH 2 after a 20-min deposition at -0.9 V . Concentration of Hg(II): (1) 0; (2,2') 2×10^{-7} ; (3,3') $6 \times 10^{-7} \text{ mol dm}^{-3}$. (---) Purified, (—) unpurified supporting electrolyte.

Fig. 2. The influence of thiocyanate ion concentration and deposition time on the anodic stripping curves of mercury. Thiocyanate concentration: (—) 0.02 ; (---) 0.1 mol dm^{-3} . Concentration of Hg(II): $1 \times 10^{-6} \text{ mol dm}^{-3}$. Deposition potential -0.9 V . Deposition time: (1) 1; (2) 2; (3,3a) 3; (4) 6; (5,5a) 9 min.

with mercury is shown on curves 2' and 3', which were obtained in purified supporting electrolyte. The addition of a little Hg(II) to the purified thiocyanate solution gave peak b only. Under such conditions, the detection limit for Hg(II), after 30 min deposition, was $4 \times 10^{-8} \text{ mol dm}^{-3}$ at the impregnated graphite and the glassy carbon electrode.

A decrease in the thiocyanate ion concentration usually affected peak b, as shown in Fig. 2; the peaks obtained at the lower thiocyanate ion concentration were smaller, broader and often split. These effects were better seen on curves obtained for higher Hg(II) concentrations and for longer deposition times. Peak splitting of the type shown in Fig. 2 was observed by Perone and Kretlov [2] who, however, did not explain its origin. The appearance of the split at lower thiocyanate concentrations and longer deposition times suggests that it may be caused by formation of an additional thiocyanate compound of mercury.

The influence of copper(II)

Copper(II) is a common trace contaminant of thiocyanate solutions. It has also been added on purpose to enhance the height of the mercury stripping peak [9–11]. According to Luong and Vydra [12] a tenfold excess of

Cu(II), compared to Hg(II), was not harmful for the determination of traces of mercury by anodic stripping voltammetry in thiocyanate medium. According to Ulrich and Ruegsegger [9], copper is oxidized in thiocyanate medium in two well separated peaks. A comparison of the results of Ulrich and Ruegsegger with the results of Perone and Kretlov [2] and Pniew et al. [3] suggests that the second (more positive) peak of copper oxidation could have been assumed in the latter papers as an additional peak of oxidation of mercury.

Figure 3 presents the stripping curves obtained for small concentration of Cu(II) in the presence of increasing thiocyanate concentrations. As indicated by Ulrich and Ruegsegger [9], the anodic oxidation of copper in thiocyanate medium proceeds in two steps. Bilewicz et al. [13] showed recently that copper(I) thiocyanate is deposited on the electrode in the first step and this deposit is oxidized in the second step. With increasing thiocyanate concentration, the more negative peak shifts to more negative potentials but its height remains unchanged, whereas the more positive peak remains at the same potential but decreases in height. Similar effects were observed when the thiocyanate concentration was kept constant while the copper(II) concentration was increased. At very low Cu(II) concentration (5×10^{-8} mol dm⁻³), the CuSCN formed in the negative peak partly dissolves; the ratio of the quantity of electricity consumed in the positive and negative peaks, $Q_{\text{pos.}}/Q_{\text{neg.}}$, is therefore low (0.335). At 5×10^{-6} – 10^{-5} mol dm⁻³ Cu(II) concentrations, the deposit of CuSCN is quantitatively oxidized in the positive peak and the ratio $Q_{\text{pos.}}/Q_{\text{neg.}}$ is 0.99–0.994. At still larger Cu(II) concentrations (2 – 5×10^{-5} mol dm⁻³) the ratio $Q_{\text{pos.}}/Q_{\text{neg.}}$ is more than 1 (1.1–1.38 over the specified range); this can be explained by the occurrence of the chemical reaction



The height of the mercury stripping peak in thiocyanate medium depends in a complex way on the concentration of Cu(II) in solution. In the presence of low concentrations of Cu(II), the mercury stripping peak increases [12, 14] but at higher Cu(II) concentrations it begins to decrease. The increase was explained as a codeposition effect [12], probably correctly. In the presence of a little Cu(II), the detection limit for mercury improves markedly; some curves for very small Hg(II) concentrations in the presence of Cu(II) ions are shown in Fig. 4.

The causes of the decrease in the height of the mercury stripping peak at higher Cu(II) concentrations were not discussed by Luong and Vydra [12]. Two causes seem possible. First, in the presence of Cu(II), some CuSCN may be deposited over the mercury; as this deposit is stable in the potential range where mercury is oxidized, oxidation of the underlying mercury could be difficult. However, this influence cannot be strong because the general shape of the peak remains unchanged. Secondly, a side reaction may occur

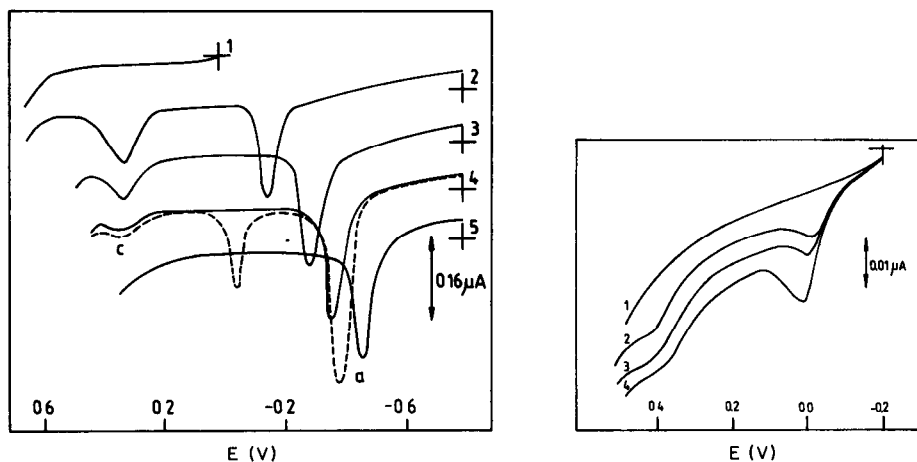
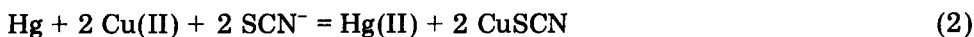


Fig. 3. The influence of thiocyanate concentration on the anodic stripping curves obtained for 2×10^{-7} mol dm $^{-3}$ Cu(II). Deposition time 6 min. Deposition potentials: (1) 0.0 V; (2–5) -0.9 V. Solution: 0.1 mol dm $^{-3}$ NaClO $_4$ with increasing concentrations of thiocyanate: (1,2) 1×10^{-4} ; (3) 1×10^{-2} ; (4) 0.1; (5) 1 mol dm $^{-3}$. (---) As (4) but after addition of 1×10^{-7} mol dm $^{-3}$ Hg(II).

Fig. 4. Anodic stripping curves obtained for mercury in 0.1 mol dm $^{-3}$ thiocyanate solution in the presence of 5×10^{-8} mol dm $^{-3}$ Cu(II). Deposition time 20 min; deposition potential -1.0 V. Concentrations of Hg(II): (1) 0; (2) 2×10^{-9} ; (3) 4×10^{-9} ; (4) 8×10^{-9} mol dm $^{-3}$.

on the electrode surface:



This suggestion is supported by the following results. A graphite electrode covered by a mercury layer about 2 nm thick dipped into 0.1 mol dm $^{-3}$ solution of NaSCN gave voltammograms showing peak b only; when the same electrode was dipped first for 2 min in 0.1 mol dm $^{-3}$ NaSCN solution containing 1×10^{-4} mol dm $^{-3}$ Cu(II) and then transferred to pure NaSCN solution, the voltammograms showed peaks a and c. Evidently, in the presence of sufficient Cu(II), the mercury layer is completely replaced by a CuSCN deposit. At lower Cu(II) concentrations, reaction (2) is slow but its effect can be observed at 5-fold amounts of Cu(II) if the voltammograms are recorded slowly.

The influence of lead(II) and cadmium(II)

The presence of small concentrations of lead(II) [12, 15] and cadmium(II) [15] leads to an increase in the height of the mercury dissolution peak, i.e., these metals enhance the deposition of mercury on the graphite electrode. This was confirmed in the present work for solutions containing 0.1 mol dm $^{-3}$ NaSCN, 1×10^{-6} or 1×10^{-7} mol dm $^{-3}$ Hg(II) and Pb(II) or Cd(II) at concentrations in the range 3×10^{-8} – 5×10^{-6} mol dm $^{-3}$. Lead(II), however, was markedly less effective than cadmium(II). Mercury exerted a positive

effect on the behaviour of cadmium and lead. The width at half height of the peaks obtained for these metals was 38 mV, i.e., the value predicted theoretically [16] for the dissolution of lead or cadmium from homogeneous amalgams, even when the solubilities of lead and cadmium in mercury were markedly exceeded.

The influence of tin(II)

The influence of tin was studied for 0.1 mol dm^{-3} NaSCN at pH 2 containing 1×10^{-7} or $1 \times 10^{-6} \text{ mol dm}^{-3}$ Hg(II). The concentration of tin was varied in the range 1×10^{-7} – $5 \times 10^{-6} \text{ mol dm}^{-3}$. Special precautions were taken to minimize the reaction between Sn(II) and traces of dissolved oxygen [17]. Under the conditions used, tin(II) neither increased nor distorted the mercury stripping peak. The influence of mercury(II) on the tin stripping peak varied. At $1 \times 10^{-7} \text{ mol dm}^{-3}$ Hg(II) (i.e., under conditions where the electrode was not covered uniformly by mercury), the dissolution peak of tin was broad and low. At $1 \times 10^{-6} \text{ mol dm}^{-3}$ Hg(II), the tin peak became better developed; its width at half height was 38 mV, indicating a homogeneous amalgam [16], although a heterogeneous amalgam would be expected. At still higher Hg(II) concentrations, the height of the dissolution peak decreased, probably because Sn(II) and Hg(II) reacted in the bulk solution.

The influence of silver(I)

At low thiocyanate ion concentrations, the dissolution peak of silver showed distortions similar to those in Fig. 2 for oxidation of mercury. For more than $1 \times 10^{-6} \text{ mol dm}^{-3}$ silver(I) and for deposition times longer than 9 min, these effects, probably caused by deposition of AgSCN, were observed even in 0.1 mol dm^{-3} thiocyanate.

Figure 5 shows the stripping curves obtained for mercury and silver at varying concentrations of thiocyanate, in 0.1 mol dm^{-3} NaSCN the stripping peaks of silver (curve 1) and mercury (curve 2) occur at nearly the same potential, as reported earlier [18]. The single peak obtained after simultaneous deposition of both metals is higher than the sum of the peaks obtained separately for the same concentrations of Ag(I) and Hg(II), which means that the deposition of one metal is enhanced by the presence of the other. At a thiocyanate concentration of 1 mol dm^{-3} , the stripping peaks of silver and mercury were well separated when the concentrations of Hg(II) and Ag(I) were similar. In 3 mol dm^{-3} thiocyanate, separation was good even at a 100:1 ratio of Hg(II) to Ag(I), in accordance with earlier results [18, 19]. Under the conditions used, silver deposited simultaneously with mercury formed the heterogeneous amalgam only; instead of 75 mV predicted by theory [16] for the width of the silver dissolution peak at half height, a value of 50 mV was observed.

The influence of iron(II)

The voltammetric behaviour of iron(II) at the HMDE in thiocyanate medium has been described [20–22], but the influence of iron on the

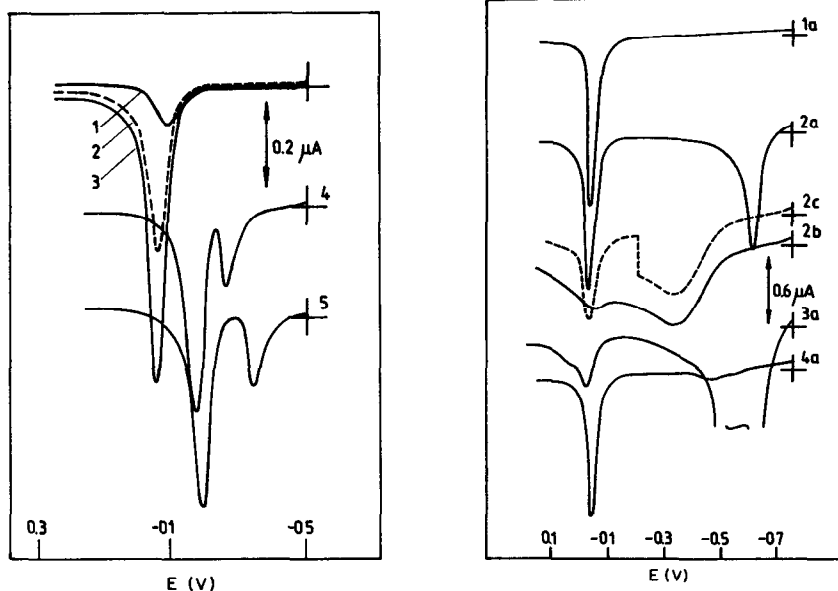


Fig. 5. Mercury stripping curves obtained in the presence of 4×10^{-7} mol dm $^{-3}$ silver(I). Concentration of Hg(II): (1) 0; (2–5) 1×10^{-6} mol dm $^{-3}$. Concentration of NaSCN: (1–3) 0.1; (4) 1; (5) 3 mol dm $^{-3}$. Deposition potential -1.0 V; deposition time 3 min; scan rate 1 V min $^{-1}$.

Fig. 6. Mercury stripping curves obtained in the presence of iron(II) from 0.1 mol dm $^{-3}$ NaSCN at pH 4 containing 3×10^{-6} mol dm $^{-3}$ Hg(II). Concentration of Fe(II): (1) 0; (2) 1×10^{-5} ; (3) 3×10^{-5} mol dm $^{-3}$; (4) as (3) but at pH 2. Deposition time 3 min. Deposition potential: (a) -1.1 V; (b) -1.5 V; (c) at 0.0 V, the scan rate was stopped for 1 min.

mercury stripping peak has not been considered. After deposition on the HMDE at less negative potentials, iron remains on the electrode surface and can easily be re-oxidized during the anodic scan, whereas on deposition at more negative potentials, iron penetrates into the drop and is re-oxidized only with difficulty [20–22].

The present experiments were done with slightly acidic solutions (pH 4 or 2) containing 0.1 mol dm $^{-3}$ thiocyanate, 3×10^{-6} mol dm $^{-3}$ mercury(II) and increasing concentrations of iron(II). For 1×10^{-6} mol dm $^{-3}$ Fe(II), deposition at -1.1 V provided a sharp anodic peak corresponding to oxidation of iron, and the mercury stripping peak was in no way affected; yet, after deposition at -1.5 V, the mercury stripping peak was diminished by about 20%. Figure 6 illustrates the influence of slightly higher concentrations of iron(II). At 1×10^{-5} mol dm $^{-3}$, iron(II) deposition at -1.1 V provided complete oxidation of iron before the mercury stripping peak started but the mercury peak was slightly lowered (curve 2a). In the same solution but after deposition at -1.5 V, re-oxidation of iron started at less negative potentials, the peak was elongated, and the mercury stripping peak appeared only as a

small hump on the iron dissolution current (curve 2b). The shape of the mercury peak could be improved by stopping the voltage scan to allow most of the iron to re-oxidize before mercury was stripped, but the mercury peak thus obtained was quite small (curve 2c). At $3 \times 10^{-5} \text{ mol dm}^{-3} \text{ Fe(II)}$ (curve 3a), the mercury stripping peak was affected markedly even after deposition at -1.1 V .

The distortions caused by iron(II) could be easily eliminated by appropriate variations of deposition potential or pH. A deposition potential of -0.8 V was convenient because iron(II) is not then reduced, whereas Hg(II) is reduced effectively. The influence of decreased pH is shown by curve 4a.

The influence of nickel(II)

The deposition of nickel on mercury electrodes proceeds in a very complex way. Depending on the conditions used, a homogeneous or heterogeneous nickel amalgam, a surface nickel deposit or an intermetallic compound may be formed. According to Krogulec et al. [23, 24], the deposition of nickel on the mercury surface is a secondary process, preceded by electroreduction of thiocyanate and formation of a nickel sulphide deposit. According to Luong and Vydra [12], the mercury stripping peak is markedly affected by the addition of nickel(II) to the solution.

In the present experiments, the slightly acidic (pH 4 or 2) 0.1 mol dm^{-3} thiocyanate solutions contained $3 \times 10^{-6} \text{ mol dm}^{-3} \text{ Hg(II)}$ and 1×10^{-7} – $1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Ni(II)}$. In principle, the effect of Ni(II) was similar to that of Fe(II), i.e., deposition at -1.5 V led to severe distortion of the mercury stripping peak, whereas after deposition at -1.1 V the mercury was affected only slightly or not at all. Similarly, any effect of nickel could be easily eliminated by proper choice of deposition potential or pH.

The influence of gold

Contamination of solutions by gold compounds is unlikely, but thin gold layers may be deposited on graphite electrodes to improve the determination of mercury by anodic stripping [4, 10, 25]. In the present experiment, 0.1 or 0.01 mol dm^{-3} thiocyanate solutions at pH 2 were used with a graphite electrode covered by a layer of gold (0.45 – 1.2 nm thick). In the supporting electrolyte used, the gold deposit was not dissolved prior to oxidation of thiocyanate. As the curves presented in Fig. 7 show, gold affects the mercury stripping peak significantly. At low Hg(II) concentrations there is only a single diffuse peak, which occurs at markedly more positive potential than the peak obtained at a pure graphite electrode (curve 6). At higher Hg(II) concentrations, an additional peak b appears on the stripping curve; its position is close to that of the peak obtained at a pure graphite electrode. Increasing Hg(II) concentrations affect the height of peak a in a complex manner. Under conditions where the second peak is absent, the height of peak a increases proportionally to increasing Hg(II) concentration. However, after the appearance of peak b, the increase in

height of peak a is no longer proportional. It is evident that peak a represents mercury oxidized from the intermetallic Au—Hg compound whereas peak b corresponds to mercury not bound with gold. For the determination of the higher concentrations of Hg(II), where two stripping peaks appear, the gold-plated electrode is less convenient than the pure graphite electrode, whereas for very low concentrations the gold-plated electrode is advantageous. The detection limit attained at this electrode after a deposition time of 20 min is 2×10^{-8} mol dm⁻³; this concentration gave no stripping peak at the pure graphite electrode.

The influence of tellurium(IV)

The influence of tellurium(IV) on the mercury stripping peak has not been studied in thiocyanate solutions. In hydrochloric acid solutions, the behaviour of mercury was significantly affected by tellurium(IV) [26]. In the present work, cyclic voltammetry of 0.1 mol dm⁻³ thiocyanate at pH 2 containing 1×10^{-4} mol dm⁻³ Te(IV) showed that the reduction of Te(IV) to tellurium began at -0.35 V and reduction to H₂Te at -0.75 V. Tellurium deposited on the graphite electrode was oxidized at 0.35 V. In stripping experiments done with the same electrolyte, the concentrations of Hg(II) and Te(IV) were varied from 5×10^{-7} to 5×10^{-6} mol dm⁻³ and from 5×10^{-8} to 5×10^{-6} mol dm⁻³, respectively. Figure 8 shows the influence of increasing concentrations of Te(IV) on the mercury stripping peak. At low Te(IV) concentrations, the peak decreases and when the concentrations of Hg(II) and Te(IV) are equal, the peak disappears completely; the intermetallic compound HgTe must be formed. Further increase of the Te(IV) concentration gives an increase in the positive peak, which corresponds to simultaneous oxidation of tellurium and HgTe. In order to eliminate the effect of Te(IV) on the mercury peak, the deposition potential was changed from -0.7 V to -0.3 V. At the latter potential, Te(IV) was not reduced, but the efficiency of mercury deposition was decreased significantly.

DISCUSSION

Numerous effects must be considered in discussing the influence of substances on the anodic stripping peak of mercury from graphite electrodes in thiocyanate solutions: (1) enhancement of the peak by co-deposition of another metal; (2) formation of heterogeneous amalgams; (3) formation of intermetallic compounds; (4) deposition of the metal or a sparingly soluble salt on the mercury surface; (5) electroreduction of thiocyanate or reactions between Hg(0) and Cu(II).

An essential defect of pure graphite or glassy carbon electrodes, compared with mercury electrodes, is the possible electrodeposition of very small amounts of metals on the electrode surface. Co-deposition of mercury in situ, as in mercury film electrodes, enhances significantly the possibility of deposition of traces of many metals. Conversely, electrodeposition of traces of mercury should be enhanced by the codeposition of other

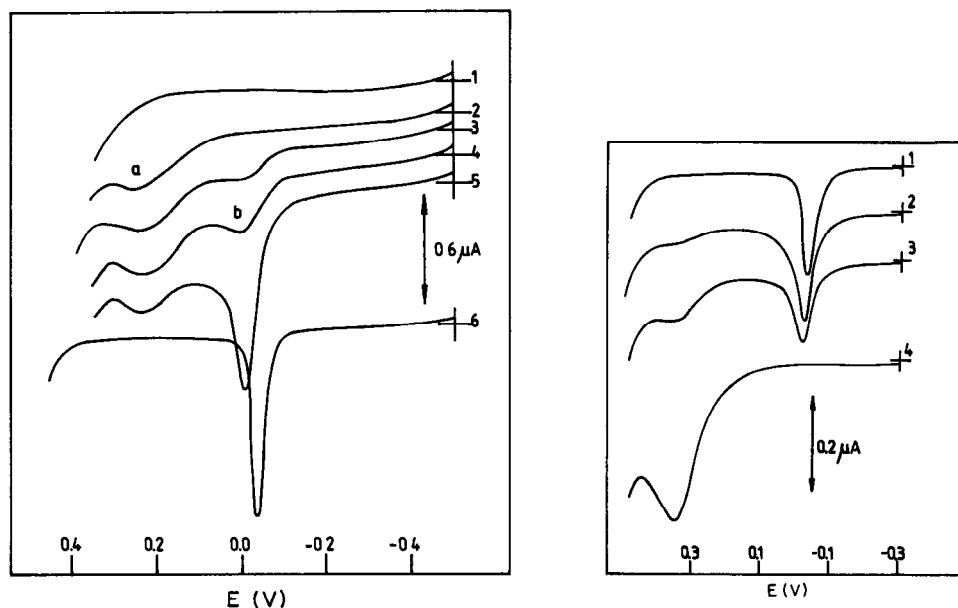


Fig. 7. Mercury stripping curves obtained in the presence of gold in 0.1 mol dm^{-3} NaSCN at pH 2. Hg(II) concentration: (1) 0; (2) 2×10^{-6} ; (3) 3×10^{-6} ; (4) 5×10^{-6} ; (5, 6) $1 \times 10^{-5} \text{ mol dm}^{-3}$. Electrodes: (1–5) graphite electrode with 0.9-nm gold layer; (6) graphite electrode. Deposition for 3 min at -0.9 V .

Fig. 8. Influence of tellurium on stripping curves for $1 \times 10^{-6} \text{ mol dm}^{-3} \text{ Hg(II)}$ in 0.1 mol dm^{-3} NaSCN at pH 2. Concentration of Te(IV) : (1) 0; (2) 1×10^{-7} ; (3) 3×10^{-7} ; (4) $1 \times 10^{-6} \text{ mol dm}^{-3}$. Deposition for 6 min at -0.7 V .

metals. It appears from the above results that the significant discrepancies observed in the literature for the mercury detection limit at graphite electrodes can be satisfactorily explained in terms of codeposition effects exerted by fortuitous contaminants of the solution. The results also show that the codeposition effect can also be responsible for the additional stripping peaks described previously [2, 3] as the second and third peaks of mercury oxidation.

Under the conditions used here (i.e., when similar amounts of mercury and another metal are deposited on the graphite electrode), the solubility of the second metal in mercury is easily exceeded even for metals readily soluble in mercury. The oxidation of heterogeneous amalgams usually proceeds in a complex way [27] and this can cause difficulties in explaining the stripping curves. The above experiments showed that cadmium, lead and tin do not distort the mercury peaks; this may mean that these metals easily form supersaturated amalgams. In contrast, the stripping peaks in presence of silver were distinctly distorted, probably because of the formation of a heterogeneous amalgam. Iron deposited at sufficiently negative potentials easily forms the heterogeneous amalgam, and the mercury stripping peak then obtained is significantly distorted.

During the deposition of several metals on a graphite electrode, the possibility of the formation of intermetallic compounds is significant. The above experiments show that the formation of such compounds does not yield uniform results. When the second constituent of the mercury-metal system is oxidized at a potential more positive than that of mercury, the mercury stripping peak will be affected; such effects were observed for the Au-Hg and Te-Hg systems. When the oxidation potential of the second constituent is more negative than that of mercury, the formation of an intermetallic compound may or may not affect the mercury peak. This effect will depend on the rate of dissociation of the intermetallic compound. In the case of cadmium, the mercury peak was not distorted, possibly because CdHg_3 dissociates easily [28]. Severe distortions were caused by nickel, which forms several intermetallic compounds with mercury, but intermetallic compound formation cannot really be blamed because similar effects were observed for iron which does not form intermetallic compounds with mercury. Iron and nickel deposited with mercury could be oxidized completely prior to the mercury stripping peak, which was then affected only slightly or not at all. In contrast, when enough CuSCN was deposited, the mercury stripping peak was affected because the CuSCN deposit remained on the mercury surface during stripping.

According to some authors [23, 24, 29], thiocyanate can be electro-reduced in solutions containing certain transition metal ions. Sulphides formed in the electroreduction process may cause additional peaks. Yet, although the stripping curves obtained above for iron and nickel were complex, the observed effects could not be attributed to the reactions of electro-reduction products of thiocyanate.

The presence of copper(II) can lead to enhancement of the mercury stripping peaks [9-11]. However, in thiocyanate medium in the presence of excess of copper(II), the opposite effect can be observed, i.e., the mercury stripping peak is decreased owing to oxidation of mercury by copper(II) in forming copper(I) thiocyanate.

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