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K. Vytřas · E. Khaled · J. Ježková · H. N. A. Hassan B. N. Barsoum

Studies on the potentiometric thallium(III)-selective carbon paste electrode and its possible applications

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Abstract Construction, performance characteristics and applications of a carbon paste thallium(III) ion-selective electrode are described. The electrode, which is based on ion-associate compounds formed between cetylpyridinium and chlorothallate(III) complexes dissolved in tricresyl phosphate as pasting liquid, showed near-Nernstian response over the concentration range of $5.8 \times 10^{-6} - 2.9 \times 10^{-3}$ mol/L. Potentiometric titrations of thallium(III) with cetylpyridinium chloride were affected by higher concentrations of excess halides, probably due to the formation of higher halogenothallates.

K. Vytřas (✉) · E. Khaled · J. Ježková
Department of Analytical Chemistry,
Faculty of Chemical Technology, University of Pardubice,
532 10 Pardubice, Czech Republic

H. N. A. Hassan
Microanalytical Laboratory, National Research Centre,
Dokki, Cairo, Egypt

B. N. Barsoum
Department of Chemistry, Faculty of Science,
Cairo University, Giza, Egypt

1 Introduction

The high toxicity of thallium and its compounds has made their determination an important issue. Thallium is introduced into the environment mainly as a waste from the production of other metals (lead, zinc, and cadmium) and by coal combustion. Therefore, simple control methods allowing selective detection are often required.

Thallium(I) can be detected by means of potassium-selective liquid/polymeric membrane electrodes based on valinomycin [1]. Solutions of thallium (I) can selectively be titrated with sodium tetraphenylborate using PVC-based membrane electrodes [2–5].

Thallium(III) tends to form anionic halide complexes which are extractable into organic, water immiscible solvents in form of ion-pairs with lipophilic cations; these extracts can be used as electroactive ion–exchangers in liquid/polymeric membrane ion-selective electrodes [6–14]. Using a salt containing a lipophilic cation, titrations of thallium(III) halide complexes were possible [5, 11, 15–17]. Electrodes based on metallopophyrin derivatives were also examined [18].

Recently, we reported on the use of carbon paste-based ion-selective electrodes that, when compared with similar potentiometric sensors based on plasticized polymeric membranes, showed similar behavior but had the advantage of very low Ohmic resistance [19–22], probably due to the formation of a very thin film of the pasting liquid coated onto small particles of carbon powder [23]. Similarly, a thallium(III)-selective electrode was constructed and its analytical applications were examined.

2 Experimental

Reagents and solutions. Thallium(III) stock solution was prepared to contain 0.006 mol/L thallium(III) nitrate in either 0.1 mol/L hydrochloric acid or 0.6 mol/L nitric acid (freshly prepared).

For potentiometric titrations, aqueous solutions of cetylpyridinium chloride (CPC), sodium tetraphenylborate ($NaBPh_4$) and thallium(I) nitrate (all in concentrations of 0.01 mol/L) were prepared from corresponding salts of analytical grade purity. The exact concentration of the CPC titrant was determined by titration of $NaBPh_4$ solution standardized potentiometrically against standard thallium(I) nitrate solution. Stock 1 mol/L solutions of both KCl and KBr were also prepared. Deionized and distilled water was used throughout.

Preparation of the electrode. An electroactive ion-exchanger substance was prepared by slowly mixing thallium(III)-HCl stock solution (20 mL) with a slight excess of CPC solution (25 mL). The resulting precipitate (presumably cetylpyridinium tetrachlorothallate) was filtered, washed with water and air-dried for 24 h. Carbon paste was prepared by mixing the precipitate (0.1 g) with graphite powder CR5 (Tesla, Lanškroun, 0.9 g) and tricresyl phosphate (Fluka, 0.4 mL). This mixture was used for filling the electrode body as described earlier [24].

EMF measurements. Potentiometric measurements were carried out using either an OP-208/1 pH meter (Radelkis, Budapest) in case of manual mode, or an ATI Orion 960 Autochemistry System (Orion Research Inc, Boston) connected to an HW486 PX2 80 personal computer for automated mode. The Tl(III)-selective carbon paste electrode (CPISE) described was used in conjunction with an RCE-102 calomel electrode (Crytur, Turnov) of double-junction construction filled with saturated potassium chloride (inner compartment) and 0.1 mol/L sodium nitrate (outer compartment).

Procedures. The calibration dependences were first studied by measuring the EMF of the standard Tl(III) solutions (all in 0.1 mol/L HCl) with increasing concentration. The electrode was conditioned by soaking for 24 h in a solution containing 10^{-3} mol/L $Tl(NO_3)_3$ and 0.1 mol/L HCl. The effect of excess chloride on the electrode potential was investigated by adding chloride as either KCl to $Tl(NO_3)_3$ solutions in 0.6 mol/L HNO_3 or HCl to Tl(III) solutions in 0.1 M HCl. For potentiometric titrations, aliquots of the Tl(III) solutions in 0.1 M HCl corresponding to 0.5–5.1 mg Tl were pipetted into a 100 mL beaker; the volume was completed to 50 mL with 0.1 mol/L HCl, and the solutions were titrated with 0.01 mol/L CPC. Additionally, solutions of Tl(III) nitrate in 0.6 mol/L HNO_3 were investigated with different amounts of KCl or KBr. For automatic titrations, the rate was held constant at a potential stability of 10 mV/min.

3 Results and discussion

Response characteristics of the electrode. Figure 1 shows the dependence of the electrode potential on to the consecutive formation of chlorothallates. Calibration curves constructed in the concentration range of $5.0 \times 10^{-3} - 1.0 \times 10^{-6}$ mol/L for thallium(III) showed nearly Nernstian responses for decreasing concentration of $TlCl_4^-$; however, both the slope and linear range of the calibration graph varied with the total chloride present (Table 1). In particular the data given for higher Cl^- concentrations are interesting: if the electrode responds preferentially to singly-charged $TlCl_4^-$ or doubly-charged $TlCl_5^{2-}$, the slope should be close to 59.2 or 29.6 mV/decade, respectively. The decreasing response slope indicates that bivalent pentachlorothallate(III) is gradually formed with increasing chloride concentration. It should be noted that a similar electrode behavior was observed in case of chlorobismuthates(III) [25] . The best characteristics were obtained in the presence of 0.1 mol/L Cl^-. Detection limits evaluated by IUPAC recommendation [26] were closely around $(1–2) \times 10^{-6}$ mol/L.

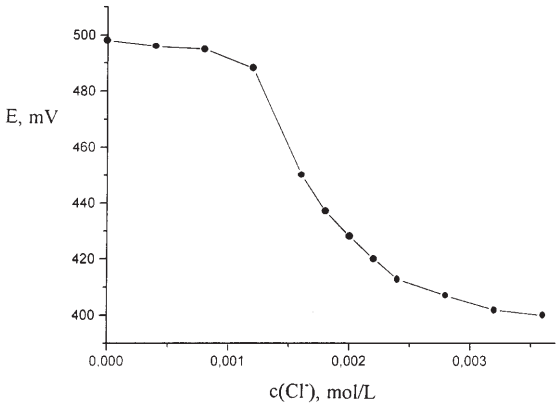

Fig. 1 Effect of chloride ion concentration on the electrode potential. Measured for 6.9×10^{-4} mol/L $Tl(NO_3)_3$ dissolved in 0.6 mol/L HNO_3, chloride added as KCl

Table 1 Response characteristics of the electrode at various chloride concentrations

$c(Cl^-)$, mol/L	Linear range, mol/L	Slope, mV/decade
Added as KCl		
0.00612	5.8×10^{-4}–5.8×10^{-6}	48.1 ± 0.9
0.0123	5.8×10^{-4}–5.8×10^{-6}	48.7 ± 1.8
0.0184	1.4×10^{-3}–5.8×10^{-6}	49.6 ± 1.9
0.025	2.9×10^{-3}–5.8×10^{-6}	61.7 ± 3.3
Added as HCl		
0.100	1.2×10^{-3}–1.2×10^{-5}	59.5 ± 0.9
0.300	2.3×10^{-3}–1.2×10^{-5}	57.5 ± 3.3
0.500	2.3×10^{-3}–1.2×10^{-5}	57.2 ± 2.3
0.700	2.3×10^{-3}–1.2×10^{-5}	55.1 ± 2.8
1.00	2.3×10^{-3}–1.2×10^{-5}	53.7 ± 2.4

Interference of thallium(I) with direct potentiometric measurements. Interference of Tl(I) with the determination of Tl(III) using the calibration graph procedures was studied from the viewpoint of possible speciation. When the Tl(III) concentration was fixed at 10^{-4} mol/L and the Tl(I) concentration was changed from 2.3×10^{-6} to 1.0×10^{-2} mol/L, the electrode potential remained stable with a slight deviation of ± 2 mV up to a 50-fold excess of Tl(I).

Selectivity measurements. The interference of various ions studied by the mixed solution method showed that the selectivity coefficients of the CPISE were very similar to those described for polymeric membrane-based Tl(III)-selective electrodes [11, 14]. No detailed studies were performed taking into account the known fact that for many electrodes, especially liquid-membrane systems, selectivity coefficients are not highly reproducible because they are time dependent.

Potentiometric titrations. In constrast to direct potentiometry, the potentiometric titration technique usually offers the advantage of high accuracy and precision, although at the cost of increased time and increased consumption of titrants (which is, of course, not so serious in automated titrations). A further advantage is that the potential break at the titration end-point must be well defined, but the slope of the sensing electrode response need be neither reproducible nor Nernstian, and the actual potential value at the end point is of secondary interest.

The method for thallium(III) is based on the decrease of the $TlCl_4^-$ concentration by precipitation with cetylpyridinium salt. The titration process was carried out either manually or automatically in solutions acidified with HCl (0.05–0.1 mol/L) and containing 0.5–5 mg Tl. The results corresponded to the given amount with slight differences. For 2.0 mg of the metal, the recovery in manual and automated mode was 98.9% with standard deviation of 1.7% for 8 measurements, or 103.5% with standard deviation of 1.1% for 10 determinations, respectively. Corresponding titration curves showed a well-developed titration peak of about 180 mV (Fig. 2). Analogous results were obtained when samples of drinking water spiked with a known amount of thallium(III) were titrated.

Possible interferences of Tl(I) with the potentiometric titration of Tl(III) with CPC were also studied by adding $TlNO_3$. Up to 30-fold excess, Tl(I) salt did not interfere with the recovery of Tl(III). Therefore, the method could be applied to speciation in solutions containing metal concentration levels detectable by potentiometric titration.

Effect of excess halide and titration stoichiometry. Precipitation of cetylpyridinium tetrachlorothallate was supposed to be the only reaction influencing the titration stoichiometry. Potentiometric titrations of tetrachlorothallate based on such ion-pair formation with oppositely charged univalent cationic titrants have been described [11, 15–17], and stoichiometric composition of the product formed between cetyltrimethylammonium

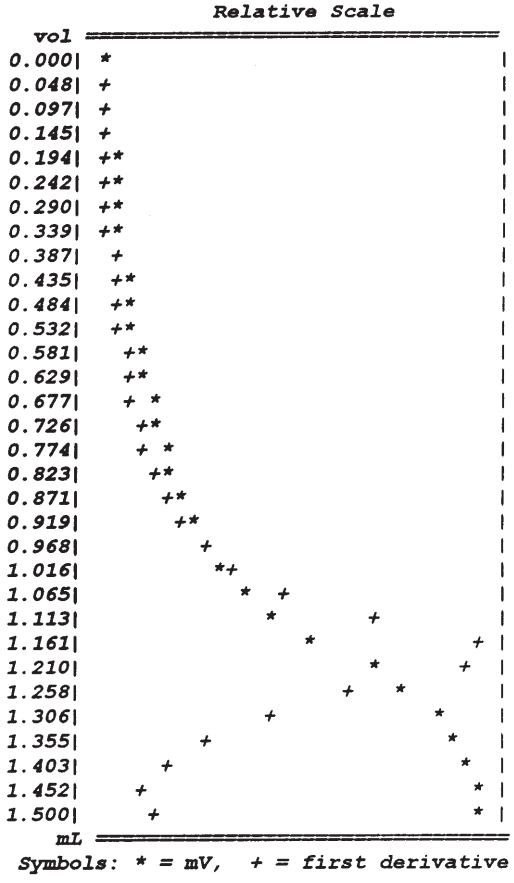

Fig. 2 Automatic potentiometric titration of thallium(III) in the presence of excess chloride. Monitored with a thallium(III) CPISE. Sample volume, 2.000 mL; titrant, 0.008843 mol/L CPC; constant increment, 0.100 mL; titrant volume, 1.500 mL; stability criterion, 10.0 mV/min; prestirring, 5.0 s; continuous stirring. Output of the ATI Orion Autochemistry system

Table 2 Stability constants for thallium(III) halide complexes

X^-	log $\beta(TlX_i^{(i-3)-})$ for given i					Ref	
	1	2	3	4	5	6	
Cl^-	6.25	11.4	14.5	17	19.15	–	[34]
	8.8	13.6	15.8	18.0	17.47	–	[35]
Br^-	8.3	14.6	19.2	22.3	25.8	26.5	[34]

and tetrachlorothallate was confirmed by elemental analysis [15]. Similarly, our previous results obtained for samples in which Tl(III) was determined after oxidation of Tl(I) by chlorine and using 1-(ethoxycarbonyl)pentadecyltrimethylammonium titrant, did not indicate significant differences [5]. Various spectrophotometric, gravimetric and voltammetric determinations [27–31] based on presumptive tetrahalogenothallates(III) were also investigated.

Concerning potentiometric titrations based on ion-pair formation of tetrahalogenothallates(III) against univalent cationic titrants, some discrepancy was first observed by Selig [17] when the titrant of $TlBr_4^-$ was CPC, however the isolated precipitates were not related to the calculated values. Experiments of this study indicated from the start that the recoveries were usually higher than expected, especially at higher excess of HCl present in the solution (the recoveries reached repeatedly up to 125% and thus too far to be explained by experimental faults). It seemed very probable that tetrachlorothallate(III) was not the final step of the complex formation. In fact, evidence of such species as $TlCl_5^{2-}$, $TlCl_6^{3-}$, $Tl_2Cl_9^{3-}$ has been reported [32] and chloride, bromide and cyanide complexes of Tl(III) have been investigated more recently [33]; an evidence of higher chloride complexes as $TlCl_5(OH_2)^{2-}$ and $TlCl_6^{3-}$ has been confirmed. According to the data characterizing these equilibria (Table 2), distribution coefficients for both chloro- and bromocomplexes were calculated and corresponding distribution diagrams constructed (Figs. 3, 4). Evidently, there is no region of the exclu-

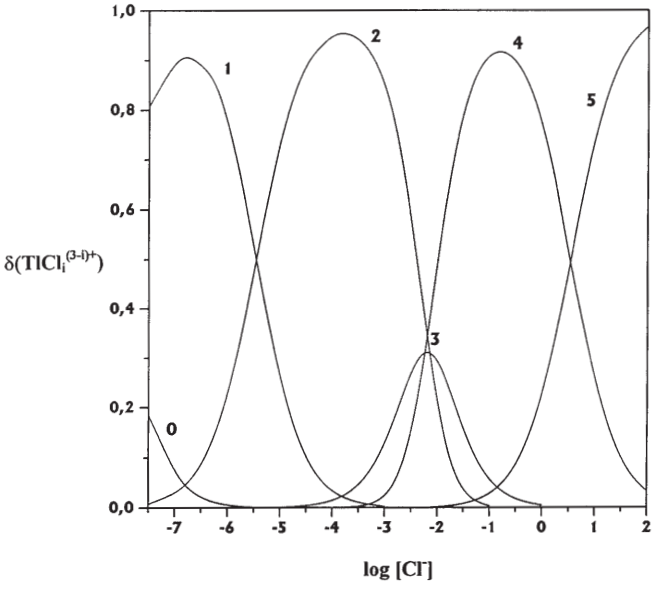

Fig. 3 Distribution diagram for thallium(III) chlorocomplexes. Distribution coefficients δ for individual species are denoted by the following numbers: *0* – $\delta(Tl^{3+})$, *1* – $\delta(TlCl^{2+})$, *2* – $\delta(TlCl_2^+)$, *3* – $\delta(TlCl_3)$, *4* – $\delta(TlCl_4^-)$, and *5* – $\delta(TlCl_5^{2-})$. Calculated from the stability constants given in [35]

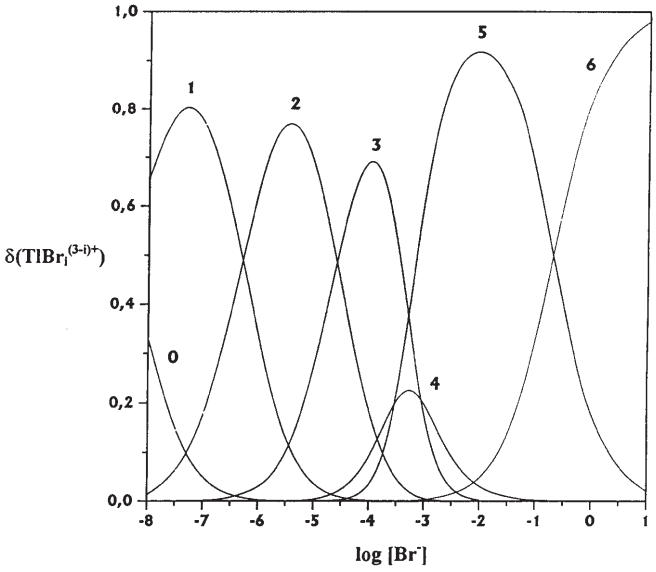

Fig. 4 Distribution diagram for thallium(III) bromocomplexes. Distribution coefficients δ for individual species are denoted by the following numbers: *0* – $\delta(Tl^{3+})$, *1* – $\delta(TlBr^{2+})$, *2* – $\delta(TlBr_2^{+})$, *3* – $\delta(TlBr_3)$, *4* – $\delta(TlBr_4^{-})$, *5* – $\delta(TlBr_5^{2-})$, and *6* – $\delta(TlBr_6^{3-})$. Calculated from the stability constants given in [34]

Table 3 Recoveries of potentiometric titrations of thallium(III) nitrate with cetylpyridinium chloride at different halide concentrations

c(halide), mol/L	Effect of chloride, %		Effect of bromide, %	
	predicted[A]	found	predicted[B]	found
0.0002	0	0	0	0
0.0005	0	0	0	0
0.0010	0	0	69	89
0.0050	20	91	194	117
0.0100	46	103	201	144
0.0500	89	104	219	196
0.100	97	105	233	215
0.200	103	108	249	234
0.300	106	110	260	246
0.500	112	115	271	267
0.700	116	116	278	297
0.900	121	119	283	⊗

2.5 mL of 5.125×10^{-3} mol/L $Tl(NO_3)_3$ acidified with HNO_3 and after addition of potassium halide completed to 50 mL and titrated with 0.01 mol/L CPC. Theoretically predicted recoveries calculated according to [A]) Ref. [35], or [B]) Ref. [34] as $[\delta(TlCl_4^{-}) + 2\,\delta(TlCl_5^{2-})] \times 100$ for chloride, or as $[\delta(TlBr_4^{-}) + 2\,\delta(TlBr_5^{2-}) + 3\,\delta(TlBr_6^{3-})] \times 100$ for bromide, respectively. ⊗ not determined

sive presence of either tetrachloro- or tetrabromothallate(III). It seems probable that when stoichiometric portions of thallium (III) and a halide are mixed (1:4), the tetrahalogeno complex expected undergoes a reaction according to $2\,TlX_4^{-} = TlX_3 + TlX_5^{2-}$. If neutral ion-associates with lipophilic cations are formed with both the charged species (1:1 with the first, 1:2 with the second one), then the overall consumption of a cationic titrant imitates the 1:1 stoichiometry because TlX_3 is not charged. For higher halide concentrations, however, the recoveries based on the presumption of the 1:1 stoichiometry must be higher as well. To confirm these considerations, new solutions of $Tl(NO_3)_3$ in HNO_3 were freshly prepared and titrated with changing additions of either KCl or KBr. Some discrepancies between predicted and found values (Table 3) may follow either from incorrect equilibrium data for stability constants or, which also seems probable, from the influence of precipitation reactions on the conditional values of these constants. Concerning recoveries for higher excess of halides, the data in Table 3 are intermittently in surprising agreement.

4 Conclusions

Although the equilibria of thallium(III) halide complexes seem more complicated than usually considered, this fact did not seriously influence the analytical applications of procedures in which direct measurement of the signal is utilized. Such procedures usually prescribe the use of some constant conditions which must be applied to both the calibration solutions and the samples. Thus, analogously to spectrophotometric or stripping voltammetric methods for the Tl(III) determination, the procedures based on direct potentiometric measurements with a CPISE described here can be recommended. To avoid the matrix effect on the slope of the calibration graph, the well-known standard multi-addition method, in which the slope factor is determined simultaneously with the concentration by iterative calculation, is especially suitable. On the contrary, the titration method based on precipitation of Tl(III) halide anionic complexes with cationic titrants is more sensitive to the overall content of halide present the sample and the interfering effect of bromide is higher than of chloride.

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S. Arpadjan · I. Karadjova · L. Jordanova

Electrothermal atomic absorption spectrometric determination of trace elements in high-purity silver after total and partial reductive separation of the matrix

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Abstract A sensitive and reliable ETAAS determination of metal traces in high purity silver after total (Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb) and partial (As, Hg, Sb, Se) separation of the matrix with ascorbic acid is described. The temperature program is optimized for analyte determination in ascorbic acid media and in 1% silver solution.

Introduction

The determination of trace impurities in high-purity silver is important due to its application in microelectronics and pharmacy. Due to the insufficient sensitivity of the flame atomic absorption spectroscopy (AAS) and the relative strong silver matrix interference effect in the graphite furnace AAS [1] separation and preconcentration procedures are generally required prior to the determination [1–6]. The applied methods include mainly separation of the matrix either by precipitation as AgCl [2–5], or by extraction of the macrocomponent silver with selectively complexing agents [1, 6]. After precipitation as AgCl, the liquid aqueous phase contains relative high concentration of chlorides, undesired for electrothermal AAS. The extraction separation of the matrix does not allow the achievement of high preconcentration factors.

The present paper describes a simple preconcentration technique for determination of traces of As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se after reductive precipitation of the matrix with ascorbic acid. Ascorbic acid as organic modifier ensures appropriate conditions for AAS measurements in the graphite furnace. Silver as matrix media acts as physical modifier [7] in the case of the determination of As, Hg, Sb and Se.

S. Arpadjan (✉) · I. Karadjova · L. Jordanova
Faculty of Chemistry, University of Sofia,
1126 Sofia, Bulgaria

Experimental

Apparatus and reagents. The measurements were performed with a Zeeman Perkin Elmer 3030 atomic absorption spectrometer and HGA-600 atomizer. A high-purity silver metal in granular form, produced by electrolytic deposition (Institute for high-purity substances, University of Sofia), was used for the investigations. Standard solutions for AAS of 1 g/L (BDH) were applied for preparation of working standard solutions by appropriate dilution. Nitric acid (p.a. Merck) was additionally purified by distillation and the ascorbic acid (p.a. Merck) – by recrystallization. Doubly distilled water was used throughout.

Procedure. In two small beakers (50 mL) two parallel silver samples (0.500 ± 0.001) g each were weighed. To one sample 1.00 mL of mixed standard solution was added and then the samples were dissolved in 5 mL HNO_3 (1:1), covered by watch glasses, by gentle heating. After the dissolution, the watch glasses were rinsed above the beakers and removed. The samples were placed on a sand bath (120 °C) and the nitric acid evaporated till moisture salts were obtained. The samples were quantitatively replaced into glass centrifuge tubes (10 mL) with water (3.0 mL). Then the preconcentration procedure was carried out in two different modes:

a) Procedure for separation after total reductive matrix precipitation: To the centrifuge tubes with the sample solutions, 2.0 mL 10% ascorbic acid were added and heated in a water bath for 15 min. After cooling to room temperature the samples were centrifuged at 4500 rpm for 2 min. The supernatant solution above