VOLTAMMETRIC AND POTENTIOMETRIC DETERMINATION OF GOLD IN GOLD-PLATED ELECTROTECHNICAL COMPONENTS

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Differential pulse voltammetry was used to determine gold in gold-plated electrotechnical components. Samples were dissolved to form tetrachloroaurate, which was determined on a carbon paste electrode containing tricresyl phosphate as pasting liquid. A characteristic cathodic peak for tetrachloroaurate, whose selective accumulation is based on extraction, is obtained during cathodic scan from +0.8 to −0.5 V vs Ag/AgCl electrode. The accompanying Fe(III) and Cu(II) ions from the matrix are masked by adding EDTA. Gold can be determined in the presence of their thousand-fold excess in the concentration range $1 . 10^{-5} - 1 . 10^{-7}$ mol l^{-1}. The results were confirmed by potentiometric titration with a solution of 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide (Septonex) by using a coated-wire indicator electrode with a softened plastic membrane.

Gold exists in aqueous solutions mostly in the form of complex anions, where typical ligands are halide or pseudohalide anions. Thus, dissolution in aqua regia yields tetrachloroauric acid. Many spectrophotometric methods of the determination of gold are based on the formation of ion associates between tetrachloroaurate and cationic dyes[1,2]. Extracts of ion pairs of tetrachloroaurate with lipophilic cations are used as liquid ion exchangers in ion-selective electrode membranes for the determination of gold(III) by direct potentiometry[3]. Lipophilic cationic reagents can also be used in potentiometric titrations, where the formation of ion pairs with the anions to be determined is followed by a suitable sensor[4]. Tetrachloroaurate ions can be determined by titration with hexadecyltrimethylammonium bromide[5], hexadecylpyridinium chloride[6], tetraphenylarsonium chloride[6] or crystal violet[7]. We have shown recently[8] that complex gold(III) anions can be determined by titration with 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide (Septonex) or benzyldimethyldodecylammonium bromide (Ajatin), indicated by simple potentiometric coated-wire sensors.

Gold(III) can be determined voltammetrically by using solid electrodes, usually carbon or platinum[9]. Often interfering heavy metal ions (Ag^+, Hg^{2+}, Cu^{2+}, Bi^{3+} and Sb^{3+}) can be masked by adding a suitable complexing agent. This is inevitable if the interfering ions are in a large excess against gold. So the success of the determination depends on the choice of the working electrode, basic electrolyte, and complexing agent. An enhanced selectivity can be achieved by using chemically modified electrodes.

For the determination of gold, the carbon paste (CP) electrodes, distinguished by a wide anodic potential range and very low residual currents, proved very suitable[10]. Chemically modified carbon paste (CMCP) electrodes contain a suitable modifying agent, their preparation being simpler than with modified solid electrodes[11]. CP electrodes modified by organophosphorus compounds, namely tributylphosphate or trioctylphosphine oxide, are used preferably in selective extraction of gold in the form of ion associates of the type $[(\text{trialkylphosphate})_2(H_2O)_nH]^+$, $[AuCl_4]^-$, and the reduction of Au(III) from this complex to the metal can be followed voltammetrically[12]. As shown recently[13], the mentioned organophosphorus compounds can even be used as the liquid phase in the carbon paste electrode. Carbon pastes obtained by mixing graphite powder with such a compound have better properties than the usual carbon pastes based on liquid hydrocarbons or their mixtures (e.g. Nujol). Voltammetric methods of determination of gold are listed in Table I. Possible use of voltammetric[13] and potentiometric[8] methods in analysis of gold-plated electrotechnical components was studied in the present work.

EXPERIMENTAL

Solutions and Instrumentation

All reagents were of reagent grade. Supporting electrolytes (1 M HCl, 1 M KBr, etc.) were prepared from demineralized water prepared in the apparatus Millipore Mill-Q Water System.

Standard solution of Au(III) was prepared by dissolving 1.050 g of pure powdered gold (Safina, Vestec, The Czech Republic) in a porcelain dish in 50 ml of aqua regia (a 3 : 1 mixture of concentrated HCl and HNO_3), evaporating to dryness, dissolving in 0.1 M HCl, and making up to the desired volume. The resulting concentration was 0.0106 M Au^{3+}. Solutions of heavy metal ions had a concentration of 0.01 mol l^{-1}. A solution of 0.1 M EDTA was prepared by dissolving disodium ethylenediaminetetraacetate (Chelaton III) in warm water. Dilute solutions were freshly prepared every day.

Gold was determined in nine samples of gold-plated electrotechnical components (wires, contacts, parts of diodes and transistors) made of copper, tin, iron, and ceramic materials. The content of gold, specified by the manufacturer (Kovohutě, Příbram, The Czech Republic) in terms of mass fractions, was expressed in weight per cent; it varied from 0.01 to 5 wt.%. The tenth sample was ordinary brass for comparison.

The samples were degreased in hexane, weighed, and dissolved in aqua regia as in the case of pure gold. The final concentration of gold was adjusted to about (5 – 10) . 10^{-4} mol l^{-1} to facilitate potentiometric titrations. The solutions were evaporated to dryness, dissolved in 0.1 M HCl, the undissolved residue (ceramics, stannic acid) was separated on a filter, and the solutions were made up to 250 ml.

Voltammetric measurements were carried out with a PA-3 type polarographic analyzer (Laboratorní přístroje, Praha, The Czech Republic) connected with an XY recorder of the same manufacturer. The electrolytic cell contained, in addition to the CP electrode, an Ag/AgCl reference and an auxiliary Pt electrode. The indicator electrode was prepared by thorough mixing of 1.0 g of powdered graphite (CR-2, Tesla Lanškroun, The Czech Republic) with 0.4 ml of tricresyl phosphate (Lachema, Brno, The Czech Republic) for 10 min. The paste was placed into a piston type electrode holder[10]. The electrode surface was renewed by wiping with a wet filter paper after every experiment. After accumulation performed under open-circuit conditions, the differential pulse voltammetric curves were recorded by imposing a cathodic scan.

The titrant solution of about 0.01 mol l^{-1} 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide was prepared from the commercial product Septonex (Slovakofarma, Hlohovec, Slovakia). Its concentration was determined by potentiometric titration of a standard solution of chloroauric acid. The coated-wire indicator electrode was prepared from an ordinary insulated aluminium wire (Kablo, Vrchlabí, The Czech Republic). The membrane was deposited from a solution of 0.09 g polyvinylchloride and 0.2 ml of 2,4-dinitrophenyl octyl ether in 3 ml of tetrahydrofuran. The electrolytic

TABLE I
Voltammetric determination of gold on solid electrodes[a]

Method	Electrode	Modifier of the electrode	Treatment, electrolyte	Detection limit mol l^{-1}	Ref.
CSV	graphite	polyacrylamide-dithiocyanate	0.1 M KCl + buffer	$5 . 10^{-5}$	14
FCCSA	carbon or Pt fibre	–	HCl	$5 . 10^{-9}$	15
ASV	glassy carbon	–	extraction into ether	$3 . 10^{-8}$	16
SdASV	glassy carbon	–	preseparation in 6 M HNO_3	$1 . 10^{-8}$	17
CSV	glassy carbon	TOPO	1 M HCl	$3 . 10^{-9}$	18
ASV	CPE	–	0.5 M HCl	$5 . 10^{-9}$	19
ASV	CPE	–	0.2 M HCl, 0.2 M KBr	$1 . 10^{-7}$	20
AdSV	CPE	–	0.1 M HCl	$1 . 10^{-8}$	21
CSV	CMCPE	alga of tribe chlorella	HCl	–	22
CSV	CMCPE	*tert*-alkylamine	HCl	$4 . 10^{-9}$	23
CSV	CMCPE	alkylthiol resin	0.2 M KCl, 0.2 M HCl	$1 . 10^{-8}$	24
CSV	CMCPE	Dowex, Amberlite LA-2 or R-IRA	KCl, HCl	$5 . 10^{-7}$	25
AdSV	CMCPE	dithizone	0.01 M HCl	$5 . 10^{-8}$	26
CSV	CMCPE	Rhodamine B	HCl	$3 . 10^{-8}$	27
CSV	CMCPE	TBP, TOPO	0.1 M KCl, KBr	$1 . 10^{-8}$	12

[a] ASV anodic, CSV cathodic, AdSV adsorptive stripping voltammetry, SdASV semidifferential ASV, FCCSA flow-constant current stripping analysis, TBP tributyl phosphate, TOPO trioctyl phosphinoxide, CPE carbon paste electrode, CMCPE chemically modified carbon paste electrode.

cell was supplemented with an RCE-102 type calomel electrode (Crytur, Turnov, The Czech Republic). An apparatus of type OP-208/1 (Radelkis, Budapest, Hungary) served for potentiometric measurements.

Procedures

The stock solutions of the samples were diluted, usually in the ratio 1 : 50, before the measurements; 10 ml of the resulting solution was added to the base solution of 2 ml of 1 M HCl + 0.5 ml of 0.1 M EDTA + 7.5 ml of water. Oxygen was removed from the solution by bubbling argon for 10 min. The standard solution of 0.0106 M Au^{3+} was diluted 10 times. The concentration of gold(III) was determined by the method of two standard additions. Small volume additions were dosed by a micropipette (Varipipette, Poland). The surface of the CP electrode was renewed before each measurement. Optimum conditions of voltammetric analyses were as follows: The accumulation step performed during open circuit, potential limits of cathodic scan +0.8 to −0.5 V vs Ag/AgCl, scan rate 20 mV s^{-1}, pulse amplitude 50 mV, and time of accumulation 40 or 80 s according to the Au content.

For potentiometric titrations, 50 ml of the sample solution was placed in a 100 ml laboratory vessel. The titrant solution of 0.01 M Septonex was added dropwise from a 10 ml burette during stirring. The end-point was determined graphically by the method of concentric circles.

RESULTS AND DISCUSSION

Accumulation of tetrachloroaurate in the CP electrode with tricresyl phosphate is based on the extraction mechanism[13]; it proceeds best in the currentless state. An excessively long time of accumulation is not advantageous from the analytical point of view, since the associate can penetrate in depth of the electrode. The reduction process is thus complicated by slow diffusion in the carbon paste, manifested in peak broadening and worse reproducibility of the results[13]. The same phenomena were observed in analyses of solutions prepared from the electrotechnical components. Therefore, the time of accumulation was limited to at most 80 s regardless of the Au content. When the surface of the CP electrode was not renewed, the current response gradually increased. This is typical for redeposition of extracted substances[12,28]. To obtain reproducible results, the surface was renewed after each measurement. Since the fresh surface of the CP electrode has a complicated microstructure[29], it is somewhat surprising that the results obtained on the renewed surface were reproducible to within 5%. The peak potential corresponding to reduction of Au(III) from the extracted associate was +0.35 V vs Ag/AgCl electrode.

In testing the influence of halide or pseudohalide anions, it was preferable to accumulate gold in the form of $[AuCl_4]^-$ in the medium of dilute HCl. This resembled the practical sample solutions. The highest reduction peak of Au was obtained in the medium of acidified 0.1 M KBr solution, however this was not suitable for analytical purposes, since the cathodic peak obtained after accumulation of tetrabromoaurate was not well reproducible. Moreover, with samples with very low Au contents doubling of the peaks occurred.

Figure 1 shows a typical calibration curve, obtained during accumulation of tetrachloroaurate in the concentration range from 1.5 . 10^{-6} to 1.5 . 10^{-7} mol l^{-1}. It can be seen that the dependence of the peak height on the concentration of Au is nonlinear in the region of higher concentrations. A similar nonlinearity is often observed in redeposition of substances extracted into the carbon paste[28]. Similar calibration curves were obtained for higher Au concentration ranges. The CP electrode with tricresylphosphate can be used for the determination of Au(III) in the concentration range from 1 . 10^{-5} to 1 . 10^{-7} mol l^{-1}.

Although the determination with the mentioned electrode is very selective[13], Fe^{3+} and Cu^{2+} ions originating from the dissolved electrotechnical components may interfere since they are in a large excess (100-fold or more). Concurrent accumulation of Fe or overlapping of the peak of Au by the large peak of Cu was observed (Fig. 2*b*). These undesirable effects can be suppressed by the addition of a complexing agent (EDTA) into the solution. Thus, the peaks of Fe and Cu are shifted to more negative potentials as can be seen from Fig. 2 (curves *4*) and are separated from the peak of Au. With Fe^{3+} ions, a similar effect was achieved by adding a KF solution.

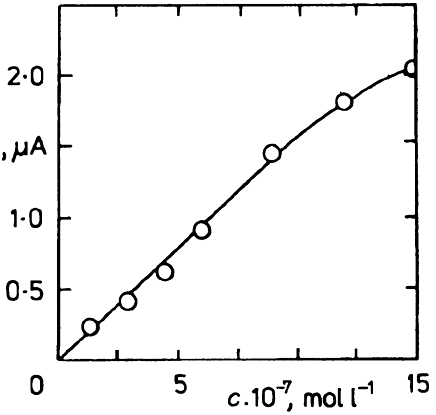

Fig. 1

Calibration curve for gold(III) in the concentration range from 1.5 . 10^{-6} to 1.5 . 10^{-7} mol l^{-1}

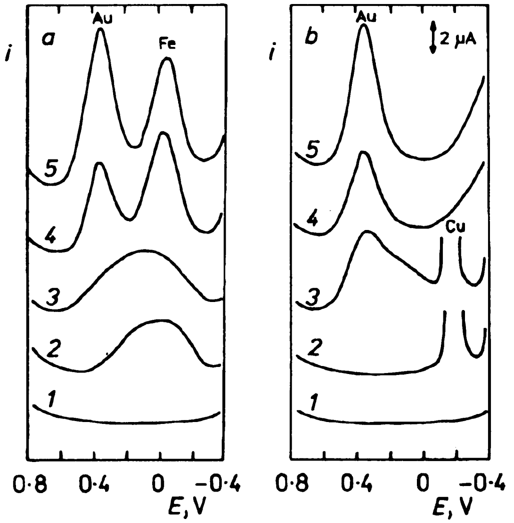

Fig. 2

Influence of *a* Fe^{3+} and *b* Cu^{2+} ions on the cathodic peak for gold(III) and its suppression by the addition of EDTA. *1* residual current; *2* addition of 100 μl of 0.01 M Fe^{3+} or Cu^{2+}; *3* addition of 100 μl of 1 . 10^{-4} M Au^{3+}; *4* addition of 500 μl of 0.1 M EDTA; *5* further addition of 100 μl of 1 . 10^{-4} M Au^{3+}

The results of determination of the Au content are summarized in Table II. Each sample was analyzed at least three times. The relative standard deviation was around ±20% for samples with a very low Au content (e.g. No. 4 and 8). This is probably caused by the interference of Cu and Fe ions, which were in some cases present in a more than 1 000-fold excess, as compared to gold. The relative standard deviation for other samples was around ±10%; the results were possibly affected by strong dilution of the sample solutions. In comparison with the results of potentiometric analyses and with the Au contents given by the manufacturer, the results seem satisfactory. In the analysis of sample No. 7 (Fig. 3), it can be seen that the current response was well reproducible and that its dependence on the concentration of Au (based on the method of two standard additions) was linear.

Most samples were diluted so that the Au content was in the concentration range where the current response was a linear function of the concentration ($5 \cdot 10^{-6}$ to $5 \cdot 10^{-7}$ mol l^{-1}), hence the method of (a single) standard addition could be used. The method of evaluation of the records is shown in Fig. 3. It is also possible to add the non-diluted sample solution by a micropipette into the cell with the base electrolyte.

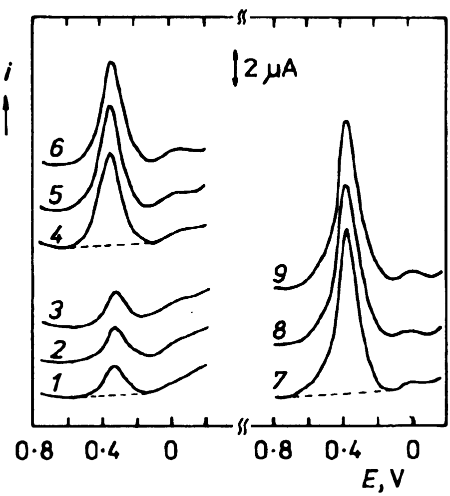

FIG. 3

Voltammetric determination of the gold content in sample 7. *1* – *3* base electrolyte with sample; standard addition of $1.06 \cdot 10^{-3}$ M Au^{3+}: *4* – *6* first, 200 µl; *7* – *9* second, 200 µl. Experimental conditions are given in the text

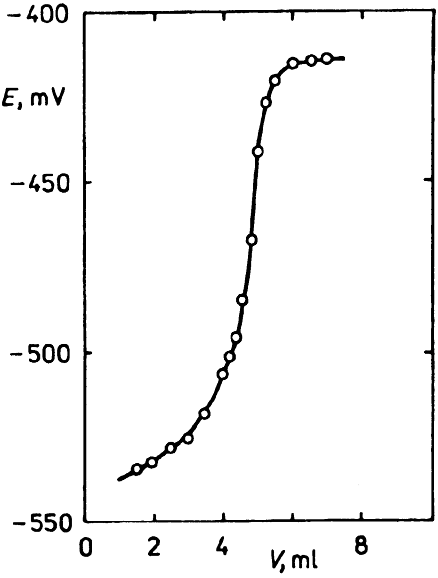

FIG. 4

Potentiometric titration curve for sample 1 solution titrated with 0.01 M Septonex

After accumulation and recording the cathodic curve, a standard addition was pipetted and again the cathodic curve was recorded. Thus, the analysis was speeded up. Although the high value of the dilution factor may cause errors, the results were in some cases in a good agreement with those of the slower method described above. For example, analysis of sample 2 in dilute solution revealed 1.51 wt.% of Au (Table II), whereas the more rapid, simpler method gave 1.63 wt.%.

Potentiometric titration, which proved well in pure solutions of Au(III) complexes[8], gave good results in our case as well. The method is sufficiently selective; the presence of the matrix components causes a decrease of the height of the potential jump, but it has no influence on the end-point reading. A certain drawback consists in the fact that relatively large amounts of the samples had to be taken in order that the concentration of Au in the titrated solutions be in the desired range from 5 to 10 . 10^{-4} mol l^{-1}. For this reason, only two parallel determinations were made with most samples, their arithmetic means being given in Table II. A typical potentiometric titration curve is shown in Fig. 4. For comparison with the data of the manufacturer, the gold content was recalculated in wt.%.

It can be concluded that both the methods used can be recommended for the determination of gold in gold-plated electrotechnical components and similar objects.

TABLE II
Voltammetric and potentiometric determination of gold in gold-plated electrotechnical components

Sample	Matrix[a]	Quantity g per 250 ml	Declared content wt.%	Voltammetry[b]		Potentiometry[c]	
				n	L, wt.%	n	$\bar{x}$, wt.%
1	Cu + Sn	10.00	0.2 – 0.6	3	0.25 ± 0.13	2	0.39
2	Cu	4.81	1.0 – 1.7	4	1.51 ± 0.09	2	1.36
3	Fe + cer.	5.04	1.7 – 2.4	4	2.55 ± 0.16	2	2.24
4	Cu	10.04	0.1 – 0.4	3	0.03 ± 0.01	2	0.19
5	Cu + Sn	2.54	2.0 – 3.0	4	2.43 ± 0.13	2	2.61
6	Cu	9.34	0.3 – 0.6	3	0.64 ± 0.26	2	0.69
7	Fe + cer.	2.49	3.0 – 4.0	4	3.48 ± 0.19	2	3.14
8	unknown	20.04	0 – 0.1	3	0.07 ± 0.05	–	–
9	Cu	2.50	2.8 – 3.5	4	2.35 ± 0.22	2	2.62
10	brass	20.00	–	3	0	–	–

[a] Cer. denotes ceramics; [b] reliability interval $L = \bar{x} \pm u_0 R$, where $\bar{x}$ denotes arithmetic mean of the gold content (excluding extreme values), u_0 critical value of the coefficient of Lord's test for the number of determinations n and significance level $\alpha = 0.05$, and R denotes range; [c] arithmetic mean of two parallel determinations.

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