DETERMINATION OF GOLD IN RAW MATERIALS USING ANODIC STRIPPING VOLTAMMETRY

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A method for the determination of small amounts of gold in ores, using stripping voltammetry with a glassy carbon electrode, is described. For separation of gold, extraction into methyl tri-octylammonium chloride (TOMA) in chloroform was employed and the gold was preconcentrated on the electrode in the non-aqueous medium.

We used stripping voltammetry for the determination of low contents of gold in ores, where the fire-assay method, which has been used for decades, rarely yields reliable results with gold contents below 5 g/ton. The determination of gold by the present method has not been adequately investigated. Among older works, the paper by Jacobs[1] is most interesting; the author determined $5 \cdot 10^{-9}$M gold in a medium of hydrochloric and nitric acids. Also interesting is a paper by Japanese authors[2], who determined gold by stripping coulometry after its preconcentration on a glassy carbon electrode. Monien[3] determined gold by stripping voltammetry in a range from $25-500$ μg/ml and found that a precision of 5% can be obtained. The determination of gold in ores and ore concentrates has been described in several publications[4,5].

The authors agree that the chief difficulties are caused by the separation of gold from the original materials, since it is usually necessary to carry out preliminary extractions into organic solvents and back-extract the gold into an aqueous phase. In order to avoid these operations, we employed the extraction of gold by long-chain amines[6], followed by stripping voltammetry directly in the organic phase.

EXPERIMENTAL

An apparatus consisting of a rotating disk electrode and an OH-102 polarograph (Radelkis, Hungary) was employed. The potential sweep during the stripping of the deposit from the electrode was 16·7 mV/s. The disk electrode was made from a glassy carbon rod, 3 mm in diameter (Le Carbon Lorraine, France), fitted into a teflon holder, 15 mm in diameter. The measurements were performed against a saturated calomel electrode, placed close to the disk, rotating at 2 300 r.p.m. The carbon electrode was cleaned before each measurement by polishing with metallo-graphic paper (SIA, Switzerland) to a mirror-like finish. Polarization curves were measured with the same instrument in a three-electrode circuit, using a platinum auxiliary electrode.

All the chemicals used were of p.a. purity. A methyl trioctylammonium chloride (TOMA) solution was prepared by diluting Aliquat 336 (General Mills Chemicals, USA) with chloroform, to give a 5% solution.

RESULTS AND DISCUSSION

According to the literature data, chloro- and bromocomplexes are suitable forms for the extraction of gold. In contrast to photometry, chloro complexes of gold appear to be more advantageous for the stripping voltammetry on a graphite electrode, since the peak potential, $E_p = +0.9$ V, and the following current increase due to chloride oxidation occurs at potentials which are by about 200 mV more positive. In a bromide solution, bromide oxidation already takes place at the gold stripping potential. The recorded gold peak is smaller and in some cases difficult to separate and evaluate (Fig. 1). The peak height dependences on the pH of the solution were investigated in chloride and bromide media and it was found that pH 1·0 is best suited for the determination of gold (Fig. 2). In bromide media, a double peak is formed in too acid solutions.

In the determination of gold by direct electrolysis from the organic phase, the use of bromide is completely excluded since bromination of the amine, which was used as the extractant, occurs.

For practical application, when gold must be separated from interfering elements, extraction with methyl trioctylammonium chloride (TOMA) was found to be most suitable. After mixing with methyl alcohol, it can be used directly for the electrolysis.
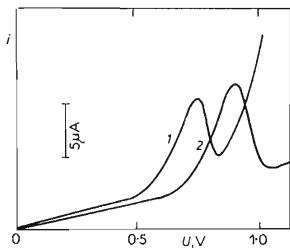

FIG. 1

The Stripping Curves of Gold on a Glassy Carbon Rotating Disk Electrode

2 0·1M-HCl; 1 0·5M-HCl + 0·2M KBr, $1 \cdot 10^{-6}$M-Au; $U_{el} = -1·0$ V, $t_{el} = 90$ s; 16·6 mVs^{-1}, 2 300 r.p.m.
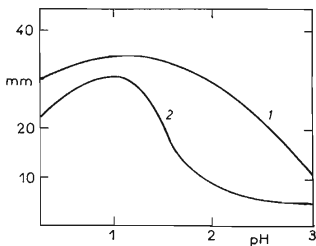
FIG. 2

The Dependence of the Peak Height on the Electrolyte Activity

1 HCl; 2 0·04M-KBr + HCl; $5 \cdot 10^{-7}$M-Au; $U_{el} = -1·0$ V, $t_{el} = 4$ min; 16·6 mV. . s^{-1}; 2 300 r.p.m.

On the other hand, it has the disadvantage that the stripping of the deposited film leads to the formation of broad unsymmetrical peaks, with a base width as great as 0·6 V, which are linearly dependent on concentration but have a different shape from that obtained for the stripping of deposited metal. For elucidation of the character of these peaks, logarithmic analysis of the gold polarization curves, obtained by d.c. voltammetry, was performed.

D. C. Voltammetry

The shape of the peaks obtained in the stripping voltammetry of gold in the organic phase clearly indicates that this is not simple metal dissolution. Therefore an attempt has been made to explain the nature of the electrode processes by the application of D.C. voltammetry. On the glassy carbon rotating disk electrode the dependence of the gold wave height on its concentration in TOMA medium is linear in the range from $1 . 10^{-5}$ to $1·5 . 10^{-4}$M. With polarization from positive to negative values, the wave height limits to a certain value at higher concentrations and above 2.0^{-4}M Au only a drawn-out current increase occurs but no wave is formed. The shape of the polarization curves of an aqueous solution of gold chloro complexes differs considerably from that of a gold − TOMA solution during polarization from negative to positive potentials. With an aqueous solution of gold chloro complexes, the deposited product is liberated from the electrode during the formation of the voltammetric wave, which is manifested in the form of a peak, while in the case of reduc-
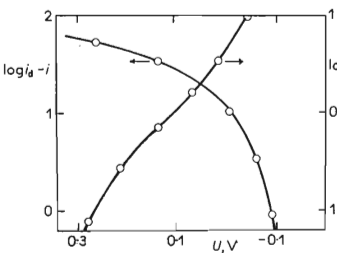

FIG. 3

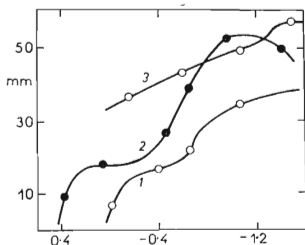Logarithmic Analysis of Voltammetric Curves of Au in TOMA

FIG. 4

The Dependence of the Peak Height on the Voltage During the Electrolysis
1 0·1M-HCl; 1 . 10^{-6}M-Au; 2 0·5M-HCl + + 0·2M-KBr; 1 . 10^{-6}M-Au; 3 TOMA + + CH_3OH saturated with KNO_3; 7 . 10^{-6}M- -Au.

tion from TOMA, only a drawn-out voltammetric wave is formed. This also indicates the different character of the electrode reaction.

For logarithmic analysis of the voltammetric curves of gold in the organic phase, gold was extracted from a $1 . 10^{-4}$M solution in 0.1M hydrochloric acid into 5% TOMA. Methanol saturated with potassium nitrate was added to the separated organic phase to improve the solution conductivity. Polarization was performed from $+0.9$ V to negative potentials. The values obtained by the logarithmic analysis of the polarization curve are shown in Fig. 3. In the case of a reversible system, the E vs log $i/(i_d - i)$ dependence followed would have to be a straight line with a slope of $0.058/n$ volts, where n is the number of electrons exchanged in the electrode reaction[7]. The linear dependence of the potential E on log $(i_d - i)$ would then mean that a solid phase, in our case gold, is formed on the electrode. Since neither dependence is linear, it can be assumed that a more complex process takes place, most probably adsorption of the Au — TOMA associate on the electrode. This assumption is also supported by the fact that the voltammetric wave is formed only in a limited concentration range. Adsorption of quaternary ammonium ions on a mercury electrode was proven by Hayter and Hunter[8].

Stripping Voltammetry

In a hydrochloric acid medium in water, the electrolysis can be performed at potentials as positive as $+0.2$ V. However, the yield of the deposition on the electrode is very low. As is shown in Fig. 4, an applied voltage of about -1.0 V is most suitable for electrolysis in chloride solutions, since at higher voltages a complexing reaction on the electrode, *i.e.* hydrogen evolution, appears, leading to a decrease in the gold peak height.

In electrolysis from a TOMA + CH_3OH organic phase, the effect of the voltage is unimportant and a good deposition yield is achieved even at very low voltages, which increases the selectivity of the determination, since less noble metals, which may be co-extracted into the organic phase, are not deposited on the electrode. A linear dependence of the peak height on the Au^{3+} concentration in aqueous solutions of chloro and bromo complexes was found in the range from $2 . 10^{-7}$ to $5 . 10^{-6}$M. Lower concentrations could not be determined because of the high charging current at higher instrument sensitivities. With gold solutions in TOMA + CH_3OH, the concentration dependence is linear within the range from $1 . 10^{-6}$ to $2 . 10^{-5}$M Au^{3+}. When electrolyte exchange was performed, *i.e.* electrolysis from the organic phase and product stripping from the electrode into 0.1M-HCl, which was successful in the determination of silver[9], low, broad, symmetrical peaks appeared, which were not proportional to the gold concentration. Their width indicates slow stripping of the adsorbed associate into the aqueous medium.

For separation of gold for subsequent stripping determination, three procedures

appear to be useful: *1.* extraction with ethylacetate[10]; *2.* extraction with dithizone at lower pH values than 1·0 (ref.[11]); *3.* extraction with TOMA (ref.[6]). The first two extractions are very tedious and analytically demanding. We have found extraction with TOMA in chloroform satisfactory; only Cr, Pt, U and Pd interfere. Molybdenum which interferes in the photometric determination, does not affect the electroanalytical determination. The extraction of gold is carried out from a medium of diluted HCl (1 : 4). To the solution in a separatory funnel is added a 5% TOMA solution in chloroform and the extraction is performed for 1 minute. All the gold is then in the organic phase and it is unneccessary to extract with further portions of TOMA. If a larger amount of iron is present, it is better to extract from a medium of 5M--H_2SO_4 in the presence of phosphoric acid.

DETERMINATION OF GOLD IN ORES

A sample amount of 15—25 g is dissolved in 300 ml of nitric acid (1·40), added in several portions, in a 800 ml beaker. The beaker is covered with a watch-glass. The decomposition is first carried out at normal temperature and later the beaker content is heated on a sand bath with frequent stirring. When decomposition is complete, the watch glass is removed and the solution is evaporated to a volume of about 150 ml. Then the solution is diluted with 150 ml of distilled water and filtered through a dense filter while still warm. It is decanted with distilled water and slightly acidified with nitric acid. The filter with the washed insoluble residue is burnt in a new porcelain crucible, briefly ignited and added to the insoluble material in the original beaker. The entire insoluble residue is then covered with 300 ml of aqua regia and decomposed first at room temperature and later on a sand bath with frequent stirring, After completion of decomposition, the beaker contents are evaporated to a volume of 100 ml, diluted with the same amount of distilled water, and filtered through a dense filter while still warm. The filter is washed with distilled water slightly acidified with HCl. To the filtrate obtained, 20 ml of dilute sulphuric acid (1 : 1) is added and the solution is evaporated to the formation of white fumes of sulphur trioxide. Then 50 ml of 5M sulphuric acid are added, the solution is heated until the salts are dissolved, and is transferred to a 100 ml volumetric flask, which is then cooled, filled to the mark and the contents stirred. An aliquot portion of this solution, containing 5—100 µg gold, is pipetted into a 200 ml separatory funnel and phosphoric acid is added dropwise until the solution becomes pale in colour. Then 5 ml of a 5% TOMA solution in chloroform is added and extraction is performed for 1 minute. After phase separation, the lower, organic phase is collected in a 100 ml beaker and 20 ml of methanol, saturated with potassium nitrate, are added. The electrodes are immersed in the beaker and the electrolysis is performed with an applied voltage of −1·0 V for a pre-set time. After completion of the electrolysis, the potential is shifted to 0·0 V by the switch on the polarograph without opening the electric circuit, the potential sweep towards positive potentials is commenced and the stripping peak of gold is recorded. After the film stripping, the electrode is cleaned using metallographic paper. The results are evaluated by the calibration curve method, using values obtained in a 5M sulphuric acid medium.

Practical application was verified on a sample of an antimony ore, in which the gold content, determined by the fire assay method, was 0·37 g Au/ton. By stripping voltammetry, employing the above procedure, a value of 0·32 g Au/ton was found;

however, this value is not fully comparable to the fire assay method value, since only the so-called extractable, technologically treatable gold was determined by stripping voltammetry. The relative error of parallel determinations amounted to $\pm 12\cdot5\%$.

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