

## THE STRIPPING VOLTAMMETRIC DETERMINATION OF SILVER IN NON-AQUEOUS MEDIUM AFTER EXTRACTION WITH DITHIZONE

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A stripping voltammetric determination of trace amounts of silver has been studied in a non-aqueous (chloroform) medium after extraction with dithizone. In order to increase the conductivity and optimize the properties of the medium an alcoholic solution of ammonium thiocyanate was added to the chloroform solution. Silver concentrations down to  $10^{-8}$  M can be determined (photometry is reliable to  $10^{-6}$  M). When the extraction conditions are selected suitably, silver can be separated from many metals (including copper and mercury) and hence trace amounts of silver can be determined with high selectivity.

By combining electrochemical stripping analysis with separation methods, the selectivity of the former method is improved "non-electrochemically". Extraction is a separation and preconcentration method marked in chemical analysis by efficiency, simplicity, rapidity and versatility<sup>1-4</sup>.

In this paper, anodic stripping voltammetry on a carbon disk electrode in a non-aqueous medium was employed for the selective determination of silver after extraction with dithizone, so that under suitable conditions silver can be separated from virtually all other metals.

### EXPERIMENTAL

#### Instruments and Chemicals

Stripping polarization curves were studied using an apparatus consisting of a rotating disk electrode ( $d = 3$  and  $5$  mm) made from GC 20 glassy carbon (Tokay Electrode Mfg.Co., Japan) in the Institute workshops and an OH-102 three-electrode polarograph (Radelkis, Hungary). An electrolytic vessel with a universal top and saturated calomel reference and platinum auxiliary electrodes were employed. Prior to each measurement, the surface of the disk electrode was polished to a mirror-like finish using SIA No 6 metallographic paper (Switzerland). The pH values of aqueous solutions were measured on a Radiometer PHM 26 pH-meter (Denmark).

All chemicals employed were of *p.a.* purity. Aqueous solutions of the ions studied were prepared from doubly-distilled water. Dithizone solutions were prepared daily by dissolving the accurately weighed substance in chloroform. Solutions of silver dithizonate and of dithizonates

of the other metals were prepared by extraction from aqueous solutions with suitable pH values<sup>1,2,4</sup>. For increasing the conductivity of the non-aqueous phase, 1M solutions of  $\text{NH}_4\text{SCN}$  in ethanol or methanol were used.

**Preparation of the test solution:** The pH value of the solution analyzed was adjusted to the optimum value with a strong acid or with ammonia. For extraction of silver dithizonate a chloroform solution of  $8 \cdot 10^{-5}$  or  $2 \cdot 10^{-4}$  M dithizonate was employed, depending on the silver concentration in the aqueous solution. After the extraction, 15 ml of the organic phase were separated into a 50 ml volumetric flask, 30 ml of an alcoholic solution of the base electrolyte were added and the volume was made up with chloroform. The  $\text{NH}_4\text{SCN}$  concentration amounted to 0.2 to 0.3M. The test solution in the electrolytic vessel was deaerated with nitrogen for 10–15 min; nitrogen was passed through a solution with composition identical to that of the test solution before it was led into the vessel.

The pre-electrolysis was carried out at a constant potential on the rotating electrode (2200 r.p.m.). After a certain time the electrolysis was terminated and, if the stripping was carried out from a stationary electrode, after a pause the potential was linearly scanned toward positive

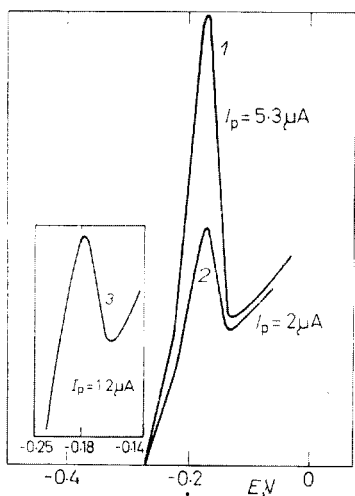


FIG. 1

Anodic Stripping Curves for Silver in a Non-Aqueous Medium

Media: Methanol-chloroform (curves 1, 3) and ethanol-chloroform (curve 2).  $V_{\text{ROH}} : V_{\text{CHCl}_3} = 3 : 2$ .

$c_{\text{NH}_4\text{SCN}} = 0.2\text{M}$ ,  $c_{\text{H}_2\text{Dz}} = 3 \cdot 10^{-5}\text{M}$ ,  
 $c_{\text{AgHDz}} : 1, 2 \cdot 5 \cdot 10^{-7}\text{M}, 3 \cdot 2 \cdot 10^{-8}\text{M}$ .  $E_e = -1.2\text{V}$ ,  $\omega = 2200\text{ r.p.m.}$ ,  $v = 0.025\text{Vs}^{-1}$   
 (1, 2),  $0.05\text{Vs}^{-1}$  (3);  $t_e = 5\text{ min}$  (1, 2),  
 18 min (3);  $d = 5\text{ mm}$ .

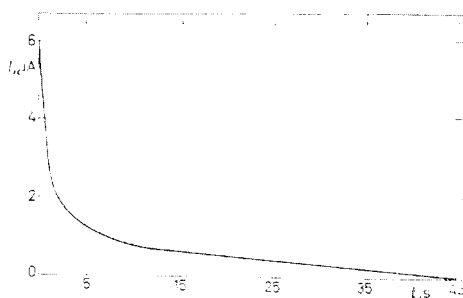


FIG. 2

The Dependence of the Stripping Current on Time at a Potential of  $-0.175\text{V}$

$c_{\text{AgHDz}} = 6 \cdot 10^{-7}\text{M}$ ,  $E_e = -1.2\text{V}$ ,  $t_e = 5\text{ min}$ ,  $v = 0.025\text{Vs}^{-1}$ ,  $d = 5\text{ mm}$ .

values. After recording the curve, the surface of the disk electrode was renewed by polishing with metallographic paper.

## RESULTS

Anodic stripping polarization curves for silver in media of chloroform and ethanol or chloroform and methanol in the presence of dithizone and ammonium thiocyanate are given in Fig. 1. Silver can be determined down to a concentration of  $10^{-8}$  (curve 3) in these media. Under identical conditions and with identical concentrations of silver dithizonate, the peak is higher in the chloroform-methanol medium than in chloroform-ethanol. This phenomenon can be explained by the higher relative permittivity of methanol than of ethanol.

The stripping current-time curves at a constant electrode potential are exponential with a negative exponent (Fig. 2), indicating that the electrode process of stripping of silver from the graphite disk electrode is reversible in the given medium<sup>5</sup>. The peak

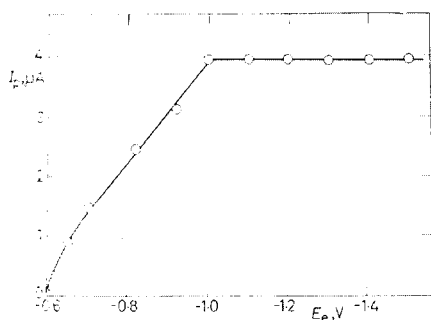


FIG. 3

The Peak Current Dependence on the Pre-electrolysis Potential

$c_{\text{AgHDz}} = 10^{-6} \text{ M}$ ,  $c_{\text{NH}_4\text{SCN}} = 0.2 \text{ M}$ ,  
 $V_{\text{CH}_3\text{OH}} : V_{\text{CHCl}_3} = 3 : 2$ ,  $t_e = 2 \text{ min}$ ,  $v =$   
 $= 0.25 \text{ Vs}^{-1}$ ,  $t_e = 5 \text{ min}$ .

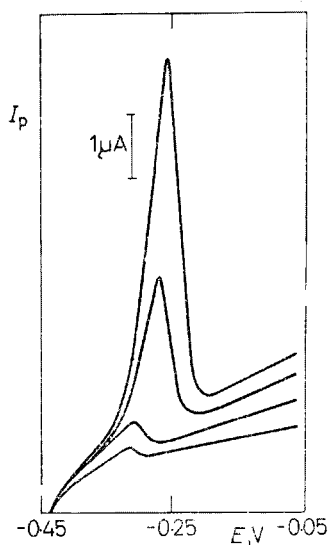


FIG. 4

The Anodic Stripping Curves at Various Potential Scan Rates

$c_{\text{AgHDz}} = 10^{-6} \text{ M}$ ,  $c_{\text{NH}_4\text{SCN}} = 0.2 \text{ M}$ ,  
 $c_{\text{H}_2\text{Dz}} = 3 \cdot 10^{-5} \text{ M}$ ,  $V_{\text{C}_2\text{H}_5\text{OH}} : V_{\text{CHCl}_3} = 3 : 2$ ,  
 $t_e = 2 \text{ min}$ ,  $E_e = -1.2 \text{ V}$ ,  $d = 5 \text{ mm}$ ,  $v (\text{Vs}^{-1})$ :  
 $: 1.0 \cdot 05, 2.0 \cdot 025, 3.0 \cdot 0042, 4.0 \cdot 0021$ .

potential depends on the concentration of ammonium thiocyanate in the solution, due to the formation of thiocyanate complexes with silver ions. The higher the thiocyanate concentration is, the more positive the peak potential becomes. The dependence of the peak potential on the log of the thiocyanate concentration is linear from  $5 \cdot 10^{-1}$  to  $5 \cdot 10^{-2} \text{M-NH}_4\text{CNS}$ .

Trace silver concentrations are often extracted with  $10^{-5}$ – $10^{-4} \text{M}$  dithizone solutions. Within this concentration range the peak potential and height are practically independent of the dithizone concentration.

The peak height (the maximum current,  $I_p$ ) depends on the preelectrolysis potential,  $E_e$ . An  $I_p$ – $E_e$  curve is given in Fig. 3. The maximum current is constant at potentials more negative than  $-1 \text{ V}$ ; no deposition takes place at potentials more positive than  $-0.6 \text{ V}$ . The optimum pre-electrolysis potential is  $-1.2 \text{ V}$ .

The scanning rate affects the peak potential and height. With decreasing scanning rate, the peak potential shifts to more negative values and the peak current decreases (Fig. 4). The dependences of the peak potential and height on the scanning rate are linear from  $4 \cdot 10^{-3}$  to  $5 \cdot 10^{-2} \text{ Vs}^{-1}$ . The optimum pre-electrolysis times ( $t_e$ ) for various silver concentration ranges are:

$c_{\text{Ag}}, \text{M}$ :	$10^{-8}$ – $5 \cdot 10^{-8}$	$5 \cdot 10^{-8}$ – $10^{-7}$	$10^{-7}$ – $5 \cdot 10^{-7}$	$5 \cdot 10^{-7}$ – $10^{-6}$	$10^{-6}$ – $10^{-5}$
$t_e, \text{min}$ :	15–18	12–15	8–10	5–8	1–2

In these concentration ranges the peak current is directly proportional to the silver concentration both in non-aqueous and aqueous media (before the extraction) and is proportional to the amount of silver deposited on the electrode surface, which is expressed in terms of the electric charge passed during stripping.

### Analytical Application

In acidic media, silver, copper and mercury are extracted simultaneously; hence, the effect of copper and mercury on the silver peak must be considered. In a medium containing chloroform, alcohol, dithizone and ammonium thiocyanate, copper and mercury do not yield peaks, provided their concentrations are less than  $5 \cdot 10^{-6} \text{M}$ ; however, the peak of silver increases. For example, at  $c_{\text{AgHDz}} = 5 \cdot 10^{-7} \text{M}$ ,  $E_e = -1.2 \text{ V}$ ,  $t_e = 4 \text{ min}$ ,  $v = 0.025 \text{ Vs}^{-1}$ ,  $d = 5 \text{ mm}$ ,  $V_{\text{C}_2\text{H}_5\text{OH}} : V_{\text{CHCl}_3} = 3 : 2$  and  $c_{\text{NH}_4\text{SCN}} = 0.3 \text{M}$ , the following values were obtained in the presence of mercury ( $c_{\text{Hg}}, \text{M} : I_p, \mu\text{A}$ ):  $0 : 1.82$ ,  $5 \cdot 10^{-7} : 3.26$ ,  $10^{-6} : 4.00$ ,  $6 \cdot 10^{-6} : 5.30$ . For reliable determination of silver it must be first separated from mercury and copper<sup>1,6</sup>. Up to several milligrams of mercury are extracted by a solution of  $5 \cdot 10^{-4} \text{M}$  dithizone, if the aqueous phase contains 10% sodium chloride and  $0.02 \text{M-HCl}$ . Silver is then extracted from the aqueous phase by a dilute dithizone solution after pH adjustment to 5 (refs<sup>1,6</sup>). In this way we determined traces of silver in the presence of a two thousand-fold (molar) excess of mercury. For extraction of silver in the

presence of large amounts of copper, bismuth, zinc, lead, cadmium *etc.*, 2 moles of EDTA are added per mol of these metals. Silver can then be selectively extracted with dithizone at pH 3–5. In this way we determined a trace amount of silver in the presence of these metals at concentrations of  $10^{-3}$ M. The error of the determination of silver does not exceed  $\pm 5\%$ .

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