

THE STRIPPING VOLTAMMETRIC DETERMINATION OF COPPER WITH A ROTATING RING-DISK ELECTRODE

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Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.

The use of a rotating ring-disk electrode in electrochemical stripping analysis was verified. The electrochemical deposition and stripping of copper was studied on an electrode with a glassy carbon disk and platinum ring or with a mercury-covered glassy carbon disk. Copper can be determined down to concentrations of about $10^{-9} \text{ mol l}^{-1}$ with an error not greater than 5% on a disk with a mercury film and 13% on the carbon electrode. The coverage of the glassy carbon by a monolayer of copper and the energy of interaction between the copper atoms and active sites on the surface of the glassy carbon were found from the areas and positions of the stripping peaks.

The use of a rotating ring-disk electrode (R.R.D.E.) for stripping analysis was proposed¹⁻³ primarily because, when the current is measured at the ring at constant potential, the charging current is zero, so that the substance deposited on the disk can be stripped at high polarization rates and thus the sensitivity and speed of the determination can be increased while retaining high precision. The determination of Cu, Pb, Cd and Zn on a glassy carbon R.R.D.E. with a mercury film deposited both on the disk and on the ring has been described⁴. In spite of the obvious advantages of the R.R.D.E., however, this method has not found wide use in analytical stripping practice, undoubtedly because construction of the R.R.D.E. is rather difficult. This work was carried out in order to verify the basic analytical potentialities of this method, both for a glassy carbon electrode and for a mercury film electrode on a glassy carbon support. We did not test the selectivity of the determination because this is known sufficiently well from the extensive literature dealing with stripping analysis⁵.

EXPERIMENTAL

Apparatus

The R.R.D.E. was constructed⁶ with a disk of glassy carbon (Tokay Electrode Mfg., Japan) and with a platinum ring. The electrode parameters were: disk radius $r_1 = 0.379 \text{ cm}$, inner ring radius $r_2 = 0.399 \text{ cm}$, outer ring radius $r_3 = 0.421 \text{ cm}$, disk surface area $A = 0.4510 \text{ cm}^2$.

The electrode surface was polished under water using Waterproof C 400 emery paper (Karbondum, Czechoslovakia) and polished to a mirror-like finish with an emulsion of metallographic aluminium oxide (Chemiewerke Greiz-Dörlau, GDR) with a grain size of 1 and 3 and on a damp metallographic wheel (Buehler Ltd., 40-7208, USA). After rinsing with distilled water, the electrode was cyclically polarized in 1M-HClO₄ at 10 rps (disk potentials $E_D +0.60$ and -0.70 V vs S.C.E., ring potentials, $E_R +0.70$ and -0.25 V (S.C.E.)), rinsed with distilled water and polarized in a base electrolyte solution until the residual current stabilized at a small constant value. Polishing on a damp wheel and cyclic polarization preceded each measurement.

The rate of electrode rotation was measured with a digital counter and could be adjusted in the range 5–40 rps with a precision of ± 0.1 rps. The glass electrolytic cell with a volume of 300 ml had an opening for the R.R.D.E., ground glass openings for the reference electrode (S.C.E, K 401, Radiometer, Denmark) and auxiliary electrode (a platinum wire immersed in the base electrolyte and separated from the working space by a frit) and tubes for introduction of nitrogen into the solution and above it.

The measurements were carried out using a bipotentiostat made of operational amplifiers and fitted with a control circuit⁷ which enabled simple adjustment of the operational parameters and their control during the measurement. The measured curves were recorded on an $x - y$ plotter (Bryans model 2100), Great Britain). The measurement was carried out at room temperature and the potential values are related to the S.C.E.

Chemicals

All the solutions were prepared from *p.a.* chemicals (Lachema, Czechoslovakia) and doubly distilled water. The nitrogen used for deaeration of the electrolyzed solutions was purified in traps containing amalgamated zinc, a 0.2% sodium anthraquinone-2-sulphonate solution in 1M-NaOH and a CrCl₂ solution prepared from 1.5 g K₂Cr₂O₇ in 500 ml of 1M-HCl.

The measurement was carried out in 0.5M-KCl as a base electrolyte. The concentration of the stock Cu(NO₃)₂ solution ($1.01 \cdot 10^{-2}$ mol l⁻¹) was determined chelometrically⁸. More dilute Cu²⁺ solutions were prepared before each measurement and small amounts were added with a microsyringe (Hamilton, USA). The mercury film on the disk electrode was deposited from 10^{-4} M-Hg(NO₃)₂.

RESULTS AND DISCUSSION

The measurement was carried out with copper(II) ions whose electrode reaction is quite rapid both on mercury and on carbon and platinum electrodes. The reduction and oxidation processes, however, mostly consist of two single-electron steps and are complicated by disproportionation of Cu(I). It has been demonstrated⁹ that Cu²⁺ is reduced in 1M-KCl medium on a glassy carbon electrode at approximately +0.15 V to Cu⁺ and at -0.475 V Cu⁺ is reduced to Cu⁰. Reoxidation of Cu⁰ to Cu⁺ occurs at about -0.25 V. In 0.5M-KCl medium, used in this work, the reduction Cu²⁺ → Cu⁺ occurs at +0.25 V and Cu⁺ → Cu⁰ at -0.30 V. The reoxidation Cu⁰ → Cu⁺ occurs at a potential of about -0.2 V. The oxidation Cu⁺ → Cu²⁺ could be followed on the platinum ring at a potential of +0.4 V and the reduction Cu⁺ → Cu⁰ at a potential of -0.25 V.

Determination of the collection efficiency of the R.R.D.E. The theoretical value of the collection efficiency $N_{\text{theor}} = 0.3932$ was calculated¹⁰. The experimental value N_{exp} was determined using a solution with $c(\text{Cu}^{2+}) = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ in 0.5M-KCl by a procedure which has already been described¹¹ (initial potential $E_D = +0.30 \text{ V}$, polarization rate $v = 0.08 \text{ V s}^{-1}$, $E_R = +0.40 \text{ V}$, rotation rate 34 rps). The experimental value $N_{\text{exp}} = 0.3892$ obtained for the uncovered disk is in good agreement with the theoretical value.

It was observed in the determination of N_{exp} for a disk covered with a mercury film that the collection efficiency decreases with increasing thickness of the mercury film (Fig. 1). The determination was carried out under the same conditions as for the uncovered disk, except for the initial potential ($E_D = -0.05 \text{ V}$ to prevent stripping of the mercury film). The mercury film was deposited from a 0.5M-KCl solution containing $10^{-4} \text{ mol l}^{-1} \text{ Hg}(\text{NO}_3)_2$ at $E_D = -1.00 \text{ V}$ and rotation rate of 30 rps. This decrease is apparently a result of disproportionation of Cu(I). With increasing thickness of the mercury film, the disproportionation equilibrium is shifted to the right as a result of rapid formation of the Cu^0 amalgam and thus the concentration of Cu^+ oxidized at the ring decreases.

Stripping determination of copper on a mercury film electrode. The mercury film was deposited on the disk electrode from a 0.5M-KCl + $10^{-4} \text{ M-Hg}(\text{NO}_3)_2$ solution at $E_D = -1.00 \text{ V}$ for a period of 5 min and at an electrode rotation rate of 30 rps. The actual determination was carried out in 0.5M-KCl. The pre-electrolysis time at $E_D = -1.00 \text{ V}$ was 10 min, electrode rotation rate 34 rps, rate of polarization of the disk electrode during the electrochemical stripping was $v = 0.160 \text{ V s}^{-1}$ and $E_R = -0.25 \text{ V}$. After the determination, the potentials were changed to $E_D = -0.10 \text{ V}$ and $E_R = +0.40 \text{ V}$ for a period of 5 min to remove traces of copper and the electrode was prepared for the next measurement.

The stripping curve contains a single peak at a potential of $E_p = -0.225 \text{ V}$. The calibration curve (peak height) was linear from $c(\text{Cu}^{2+}) \cdot 10^{-9}$ to $1.7 \cdot 10^{-8} \text{ mol l}^{-1}$. It was not possible to measure lower concentrations because the Cu^{2+} concentration in the reagents had a value of about $3 \cdot 10^{-9} \text{ mol l}^{-1}$. The reproducibility of the determination is good (Table I).

Stripping of copper on a glassy carbon electrode. The measuring conditions were the same as those given above, except for the pre-electrolysis potential which was $E_D = -0.70 \text{ V}$ and polarization rate of the disk electrode, which was $v = 0.08 \text{ V s}^{-1}$. Residual metallic copper was removed from the electrode at potentials of $E_D = +0.30 \text{ V}$ and $E_R = +0.40 \text{ V}$. In contrast to the mercury electrode, the stripping is more complicated. At copper concentrations lower than $10^{-7} \text{ mol l}^{-1}$, the stripping curve contains a single peak at $E_{p1} = +0.25 \text{ V}$. The height of this peak is directly proportional to the Cu^{2+} concentration to a value of $6 \cdot 10^{-8} \text{ mol l}^{-1}$, then the dependence becomes curved and at values greater than $10^{-7} \text{ mol l}^{-1}$ the

TABLE I
Reproducibility of the determination of copper

$c(\text{Cu}^{2+})$ mol l^{-1}	Average peak current μA	Relative standard deviation ^a %
Mercury film electrode		
$5 \cdot 10^{-9}$	0.171	4.8
$1.2 \cdot 10^{-8}$	0.340	2.5
Glassy carbon electrode		
$5 \cdot 10^{-9}$	0.31	12.8
$1 \cdot 10^{-7}$	0.61	7.8

^a Values calculated from 7 measurements

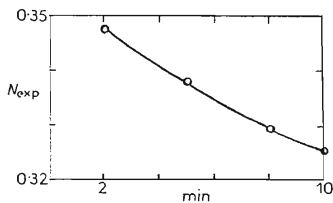


FIG. 1

Dependence of the experimental collection efficiency N_{exp} on the time of deposition of the mercury film t . $E_R = +0.40\text{V}$, $c_{\text{Cu}^{2+}} = 10^{-3} \text{ mol l}^{-1}$, $v = 0.08 \text{ V s}^{-1}$, 34.7 rps, 0.5M-KCl

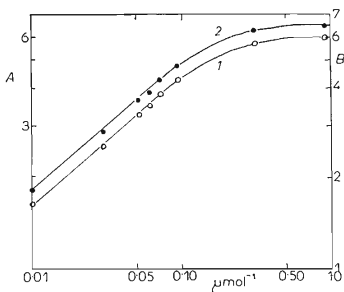


FIG. 2

Dependences of the number of Cu atoms forming a monolayer (A) and the relative electrode coverage (B) on the Cu^{2+} concentration in solution. $E_D = -0.70 \text{ V}$, $E_R = -0.25 \text{ V}$, $v = 0.08 \text{ V s}^{-1}$, 34.0 rps, $t_{\text{el}} = 10 \text{ min}$, 0.5M-KCl. A = number of atoms $\cdot 10^{13}$; B = relative coverage, %

peak height is constant. Simultaneously, another peak appears at a potential of $E_{p2} = -0.20$ V. While the potential of this first peak is independent of the Cu^{2+} concentration, potential E_{p2} shifts slightly to more positive values with increasing Cu^{2+} concentration and is constant from a concentration of $3 \cdot 10^{-7} \text{ mol l}^{-1}$. The height of the more negative peak is proportional to the Cu^{2+} concentration in the range 10^{-7} , to $1.1 \cdot 10^{-6} \text{ mol l}^{-1}$. As follows from Table I, the reproducibility of the determination is worse than for a mercury film electrode.

It is apparent that the more positive peak corresponds to electrochemical stripping of a copper monolayer from the electrode, while the more negative peak corresponds to stripping of further layers of metallic copper. The number of copper atoms forming a monolayer was calculated from the area of the more positive peak and the collection efficiency values in dependence on the concentration of Cu^{2+} in solution and coverage of the electrode by a monolayer (assuming close packing of spherical Cu atoms with a radius of $1.27 \cdot 10^{-10} \text{ m}$ (ref.¹²). These dependences are given in Fig. 2. It is apparent that the maximal coverage of the electrode by a monolayer is roughly 7% of the geometric surface area.

The interaction energy between the Cu monolayer and the active sites on the surface of the carbon electrode can be estimated from the difference between potential E_{p1} and E_{p2} . It holds for the equilibrium potential E that

$$-\Delta G = nFE, \quad (1)$$

where ΔG is the affinity of the reaction, n is the number of electrons exchanged and F is the Faraday constant. As the electrode reactions of Cu are relatively rapid, it can be assumed without great loss of precision that the difference in peak potentials E_{p1} and E_{p2} corresponds to the difference in the interaction energies for copper-carbon and copper-copper. The sublimation energy for copper¹³ is $339.6 \text{ kJ mol}^{-1}$, so that for a difference $E_{p1} - E_{p2} = 0.45 \text{ V}$, an interaction energy for copper-carbon of $424.4 \text{ kJ mol}^{-1}$ is obtained.

The results obtained indicate that the use of the R.R.D.E. leads to a considerable increase in the sensitivity of the stripping determination while maintaining high precision. The value of the detection limit, $10^{-9} \text{ mol l}^{-1}$, found here, is a result primarily of the high copper content in the reagents, which were not specially purified and thus this value could be considerably decreased. Measurement with the mercury film electrode is much more precise than determination using a glassy carbon electrode. The latter electrode must also be polished after each measurement; otherwise passivation occurs and the measuring sensitivity gradually decreases. A certain disadvantage is the impossibility of preparing mercury film electrodes *in situ*, as the Hg^{2+} ions present would produce electrochemical interference on the ring. In practical use, however, the selectivity problem will have to be considered, as discussed in a number of works^{1-3,5}.

The behaviour of copper on a glassy carbon electrode found here is in agreement with the qualitative results obtained in earlier works^{4,14-16}. The values of the electrode coverage are much lower than the values obtained for a monolayer of Hg (ref.¹⁷) and for adsorbed Cu^+ (ref.⁹), on glassy carbon (about 36%); however, these values certainly depend strongly on the type of glassy carbon, on its history and on the composition of the base electrolyte.

The interaction energy between copper atoms and the electrode surface estimated in this work cannot be compared as similar values are not available in the literature. Nonetheless, this procedure can be used quite generally for semiquantitative determination of the electrode coverage and of the energy of the active sites on the electrode surface.

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