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Polarographic Determination of Ruthenium in Citrates and Tartrates Solutions

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Polarographic methods are proposed for the determination of small amounts of ruthenium in two new supporting electrolytes: a. citric acid (0.3 M) and sodium hydroxide (0.15 M); b. tartaric acid (0.2 M), sodium hydroxide (0.1 M) and thymol (0.009%).

Determination of ruthenium is applicable in the concentration range from 4 to 120 micrograms of ruthenium per milliliter with a relative standard errors from 15 to 0.8% in both electrolytes. Hydrochloric, sulfuric and perchloric acids (up to 0.5 N) do not interfere, but in the presence of nitric acid (any traces of nitrites) polarographic determinations are impossible.

The polarographic characteristics of ruthenium in described electrolytes¹⁻³ were not satisfactory for quantitative determinations. In an earlier⁴ paper, we described a supporting electrolyte (1 N oxalic acid and 0.006% thymol) for the quantitative determination of ruthenium. Our further investigations of interactions between ruthenium-ions and organic acids show the existence of ruthenium complexes in citrate and tartrate solutions. These complexes were most satisfactory for the quantitative polarographic determination of ruthenium.

The colour of such complexes was not persistent enough and faded in almost no time, giving no possibility for spectrophotometric determination of ruthenium.

EXPERIMENTAL

A Cambridge Polarograph, Pen recording type with a maximum sensitivity of 2.47×10^{-9} A/mm has been used. Polarographic cells of the same Company with a saturated calomel electrode (or with a mercury pool anode) were used and kept in a water bath at $25.0 \pm 0.1^\circ\text{C}$. Oxygen was displaced by bubbling hydrogen through the solution for 15 minutes prior to the polarographic measurement and probably the reduction of Ru(VIII) to Ru(IV) occurred simultaneously⁵. Hydrogen was purified by passing through a saturated solution of pyrogallol in 20% sodium hydroxide. The capillary had $m = 1.95$ mg/sec (at 0.0 V) and $t = 2.32$ sec (at 0.2 V) in the citrate and $m = 1.98$ mg/sec and $t = 2.23$ sec in the tartrate supporting electrolyte.

The wave heights were measured in the points of intersection of the extrapolation lines for the residual and the diffusion current and the polarographic wave slope as well.

The apparatus for distillation of ruthenium tetroxide was a distillation flask with three traps in series. Reagents used were: ruthenium trichloride, purissimum (Fluka, A. G. Buchs); ruthenium tetroxide, reagent grade (Hopkin & Williams, London); thymol, recrystallised. All other reagents were analytical grade (Pliva, Zagreb).

We described preparations and standardisations of ruthenium solutions in an earlier paper⁴.

RESULTS

Experiments showed that 0.3 M citric acid and 0.15 M sodium hydroxide as supporting electrolyte gave a residual current which increased linearly with the potential in the voltage range where ruthenium gives a polarographic wave.

The solution of 0.2 M tartaric acid and 0.1 M sodium hydroxide gives the same effect. By applying the compensation current it was possible to obtain the residual current curves which were parallel to the abscissa (Fig. 1, curve 1, and Fig. 2, curve 1). The counter current was found necessary to be exactly $-0.30 \mu\text{A/V}$ for citrate electrolyte and $-0.10 \mu\text{A/V}$ for tartrate solution.

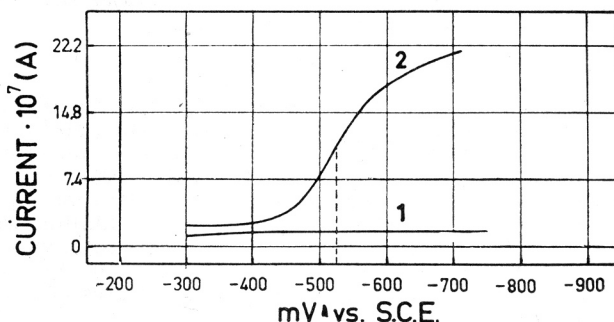


Fig. 1. Curve 1: Residual current (counter current $-0.30 \mu\text{A/V}$) of the supporting electrolyte (0.3 M citric acid and 0.15 M sodium hydroxide, without any maximum suppressor). Curve 2: Current-voltage curve of ruthenium in the same electrolyte. Sensitivity of the recorder 0.37×10^{-7} A/mm. (sen. switch 1/15); damping 5; rate of recording 3.78 mm/min. Potential are given with respect to the saturated calomel electrode and the position of the half-wave potential is marked (-530 mV).

Fig. 1 (curve 2) shows also the polarographic wave of ruthenium in 0.3 M citric acid and 0.15 M sodium hydroxide as the supporting electrolyte and the position of the half-wave potential (-530 mV) with respect to the saturated calomel electrode.

In the supporting electrolyte 0.2 M tartaric acid and 0.1 M sodium hydroxide, the polarographic wave of ruthenium has a maximum which could be suppressed with thymol (gelatine reacts with ruthenium). Investigations have

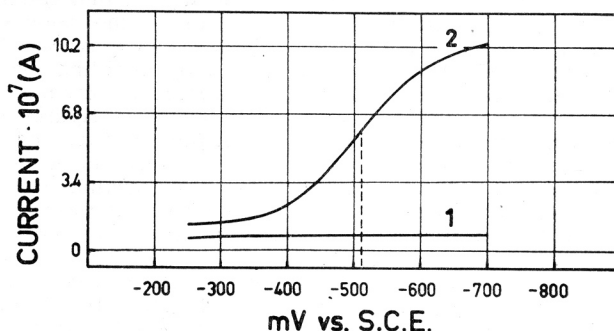


Fig. 2. Curve 1: Residual current (counter current $-0.10 \mu\text{A/V}$) of the supporting electrolyte (0.2 M tartaric acid, 0.1 N sodium hydroxide and 0.009% thymol). Curve 2: Current-voltage curve of ruthenium in the same electrolyte. Sensitivity of the recorder 0.17×10^{-7} A/mm. (switch 1/7); damping 5; rate of recording 3.78 mm./min. Position of the half-wave potential (-510 mV) is marked and potentials are given with respect to the S. C. E.

shown that 0.009% of thymol is satisfactory for suppressing polarographic maxima. In Fig. 2 (curve 2) the polarographic wave of ruthenium in 0.2 *M* tartaric acid, 0.1 *N* sodium hydroxide and 0.009% thymol and the position of the half-wave potential (—510 mV) *vs.* S. C. E. are shown. The slope of the polarographic wave is too small compared with a theoretical one. Probably the reduction of ruthenium in tartrate solution is not a reversible process or it is a poor resolution of two polarographic waves (this is a matter of our future investigations).

Distilled ruthenium tetroxide was absorbed in citric or tartaric acid solution and ruthenium was gravimetrically or colorimetrically determined as previously described.⁴

From this standard solution a series of solutions with various concentration of ruthenium were prepared being:

- a. 0.3 *M* in citric acid and 0.15 *M* in sodium hydroxide,
- b. 0.2 *M* in tartaric acid, 0.1 *M* in sodium hydroxide and 0.009% in thymol.

The concentration of ruthenium in the solution so prepared for polarographic measurements should be between 2 and 120 $\mu\text{g Ru/ml}$.

Traces of oxygen tend to distort the residual current curve and dissolved oxygen must be completely removed from the solution by passing hydrogen through the solution for 15 minutes. In this operation all ruthenium was probably converted to Ru(IV).⁵

A linear regression analysis was performed for the diffusion current (*mm*, or in 10^{-7} A) against the concentration of ruthenium ($\mu\text{g. Ru/ml}$). The calibration curve in the described conditions was a straight line which passes through the origin. The following regression equations were obtained:

$$c = 3.09 h$$

(for 0.3 *M* citric acid and 0.15 *M* sodium hydroxide as a supporting electrolyte), and

$$c = 2.22 h$$

(for 0.2 *M* tartaric acid, 0.1 *M* sodium hydroxide and 0.009% thymol), where *h* is the height of the polarographic wave in *mm*. (at sensitivity $S = 1/3$; 7.4×10^{-9} A/*mm*) and *c* is the concentration of ruthenium ($\mu\text{g./ml.}$) in the solutions.

The regression of ruthenium concentration *c* ($\mu\text{g. Ru/ml.}$) upon polarographic wave height *h* (*mm*, or in 10^{-7} A) and the 99% — confidence limit for predictions of *c* from a measured value of *h* (*h* is the arithmetic mean of two repeated determinations) are shown in Fig. 3. Curve 1 represents the calibration curve for the determination of ruthenium in 0.3 *M* citric acid and 0.15 *M* sodium hydroxide as supporting electrolyte and curve 2 represents the calibration curve for the determination of ruthenium in 0.2 *M* tartaric acid, 0.1 *M* sodium hydroxide and 0.009% thymol.

The standard errors and the relative standard errors of the polarographic determinations of ruthenium (from 4 to 120 $\mu\text{g. Ru/ml.}$) are given in Fig. 4. Curves 1 (standard errors) and 3 (relative standard errors) are for determinations in 0.3 *M* citric and 0.15 *M* sodium hydroxide as the supporting electrolyte; and curves 2 (standard errors) and 3 (relative standard errors) for deter-

minations of ruthenium in 0.3 M tartaric acid, 0.1 M sodium hydroxide and 0.009% thymol.

Hydrochloric, sulfuric and perchloric acid up to 0.5 N in both electrolytes exhibit no effect upon the height of the polarographic wave of ruthenium. In the presence of nitric acid (or even any traces of nitrites) the polarographic determination of ruthenium in the described electrolytes is impossible.

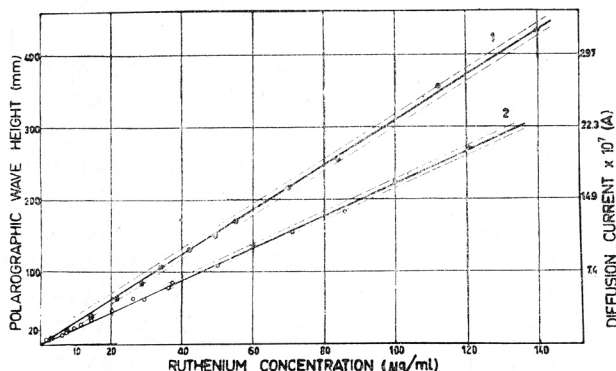


Fig. 3 Regression of ruthenium concentration c ($\mu\text{g./ml.}$) upon polarographic wave height h (mm, or i in 10^{-7} A) and the 99%-confidence limits for predictions of c . The plotted points h are the mean values of polarographic wave heights of two repeated measurements.

Curve 1. 0.3 M citric acid and 0.15 M sodium hydroxide as a supporting electrolyte.
Curve 2. 0.2 M tartaric acid, 0.1 M hydroxide sodium and 0.009% thymol as supporting electrolyte.

The polarographic determinations of ruthenium in the presence of hydrochloric, sulphuric and perchloric acid up to 0.5 N, show that the proposed methods are reliable and precise in a very wide range of ruthenium concentrations (4–120 $\mu\text{g./ml.}$) with relative standard errors of 15 to 0.8%.

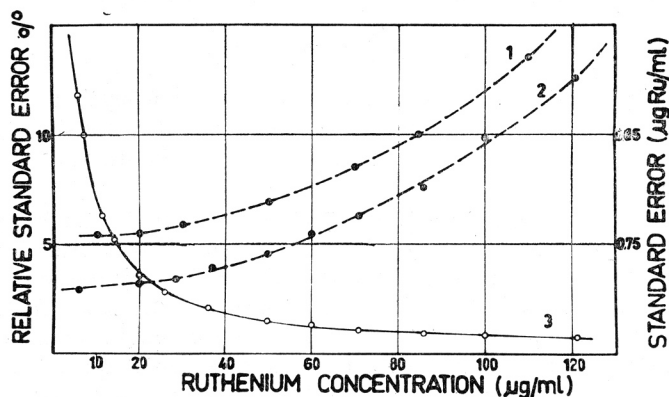


Fig. 4. Curves 1 and 2 are the standard errors ($\mu\text{g. Ru/ml.}$) and curve 3 is the relative standard error (in %) of the determinations of ruthenium plotted against ruthenium concentration in the solutions used for polarographic measurements. Polarographic wave-heights h are arithmetic means of two repeated measurements.

Curve 1: 0.3 M citric acid and 0.15 M sodium hydroxide as a supporting electrolyte.
Curve 2: 0.2 M tartaric acid, 0.1 M sodium hydroxide and 0.009% thymol as a supporting electrolyte.

Curve 3 presents relative standard errors for both electrolytes (differences are very small)

It appears that the form of the polarographic waves obtained in citrate solutions enables the determination of ruthenium with greater accuracy and in broader range of concentrations than in tartrate solutions.

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IZVOD

Polarografsko određivanje rutenija u otopinama citrata i tartarata

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Prikazane su polarografske metode za određivanje niskih koncentracija rutenija u dva osnovna elektrolita:

- a) limunska kiselina (0.3 M) i natrijev hidroksid (0.15 M),
- b) vinska kiselina (0.2 M), natrijev hidroksid (0.1 M) i timol (0.009%).

Opisane polarografske metode osjetljive su i precizne u koncentracijskom području od 4 do 120 μg Ru/ml s relativnim standardnim pogreškama od 15 do 0.8%. Na osnovu dobivenih rezultata možemo reći da je za polarografsko određivanje rutenija citratni elektrolit bolji od tartaratnog.

Solna, sumporna i perklorna kiselina (do 0.5 N) ne smetaju, a dušična (najmanji tragovi nitrita) kiselina onemogućuje polarografsko određivanje rutenija.

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