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Spectrophotometric and Polarographic Determination of Ruthenium in Oxalic Acid

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A spectrophotometric and polarographic method is proposed for the determination of ruthenium tetroxide absorbed in oxalic acid.

Spectrophotometric measurements of ruthenium in 1 *N* oxalic acid were made at 375 mμ. In the concentration range from 2 to 36 micrograms of ruthenium per milliliter the relative standard error amounted 14% to 1%, respectively.

The polarographic determination was performed in a supporting electrolyte containing 1 *N* oxalic acid and 0.006% thymol (as a maximum suppressor). The determination is applicable in the concentration range from 4 to 120 micrograms ruthenium per milliliter with a relative standard error of 15 do 0.7%, respectively.

Hydrochloric, sulfuric and perchloric acid up to of 0.5 *N* does not interfere. In the presence of nitric acid spectrophotometric and polarographic determinations of ruthenium are impossible.

Ruthenium has always been a very difficult element to determine quantitatively. It exists in eight valency states from I to VIII and forms complex compounds. The complexes with nitrogen oxides interfere in many analytical methods.

Many methods are given for the separation of ruthenium from other metals. The macro method for the separation by volatilization of the tetroxide can be extended to the minute quantities as well.

Ruthenium is oxidized to the volatile ruthenium tetroxide by perchloric acid, sodium bromate-sulfuric acid, perchloric acid-sodium bismuthate-fuming nitric acid, sodium peroxydisulfate-sulfuric acid, potassium permanganate-sulfuric or phosphoric acid, chromium trioxide-sulfuric or phosphoric acid and sodium hypochlorit sodium hydroxide.[1-6] The volatile tetroxide is distilled into hydrochloric acid or alkaline hydroxides and is determined gravimetrically or spectrophotometrically.[1-7] Many sensitive colour reactions with organic reagents for the determination of ruthenium can be mentioned.[1,7,8,9]

The polarography of +4 ruthenium in perchloric acid (0.1 to 5 *M*) scrupulously freed from chloride was already studied[10] and three well-formed waves were obtained. In 1 *M* perchloric acid the first diffusion current is at zero e. m. f., and the half-wave potentials of the second and third waves are +0.21 and —0.34 V with respect to S. C. E. The sum of the first two waves corresponds to an irreversible (1-electron) reduction of two hydrolytic species of +4 ruthenium to the +3 ruthenium. The third wave is reversible reduction of the ruthenium +3 to the ruthenium +2. Willis[11] found that no reduction waves for +4 or +3 ruthenium are observed with solutions of the chloro complexes, neither from cyanide, thiocyanate, ammonia nor pyridine as supporting electrolytes. In contradictions with this investigation, R. B. Simpson and others[12] found a polarographic wave of ruthenium trichloride and compute from it a small diffusion current constant.

In this note spectrophotometric and polarographic determination of ruthenium in oxalic acid are given.

EXPERIMENTAL

Apparatus and reagents

Spektrophotometric measurements were made in silica cells of 10 mm light path with »Hilger«-Uvispek spectrophotometer operated at constant sensitivity.

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 satureted colomel electrode (or with a mercury pool anode) were used and kept in a constant temperature water bath at 25.0 ± 0.1°C. Oxygen was displaced by bubbling hydrogen through the solution for 15 minutes prior to the polarographic measurement. The reduction of Ru(VIII) to Ru(IV) probably occured simultaneously[5]. Hydrogen was purified by passing it through a saturated solution of pyrogallol in 20% sodium hydroxide. The capillary had $m = 1.87$ mg./sec. (at 0.0 V) and $t = 2.2$ sec. (at 0.2 V) in the respective 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.

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

Preparation and standardization of ruthenium solutions

Ruthenium trichloride was dissolved in 1 : 3 sulfuric acid and the solution evaporated under an infrared lamp until sulfuric acid fumes appeared to ensure removal of traces of chloride ions.

The solution was transfered into a 500 ml. washing bottle which served as distilling flask[6] and diluted to give a 30 to 50% sulfuric acid solution. Ruthenium tetroxide was prepared by oxidising the sulfate solutions with a twofold excess of sodium peroxydisulfate and traces of silver sulfate. The sodium peroxydisulfate was added in portions during the course of the distillation. The solution was heated to boiling. A slow current of air carried the tetroxide into ice-cold 1 *N* oxalic acid. The absorption solution was transferred in a volumetric flask and adjusted with oxalic acid to 1 *N*.

From this stock solution various solutions of ruthenium for spectrophotometric and polarographic measurements were prepared. Ruthenium in the stock solution, was determined by precipitation with magnesium or with hydrogen sulfide gas, ignated in a current of hydrogen and weighed as metal.[7]

Spectrophotometric determination

The yellow colour produced when ruthenium tetroxide is absorbed in oxalic acid has been studied spectrophotometrically. The colour showed measurable change with the time, the temperature and the concentration of oxalic acid. The stable maximum is reached by 0.05 *N* and 0.1 *N* oxalic acid after five hours and by 1 *N* oxalic acid after three hours at room temperature. At elevated temperature the stable colour developed rapidly. When heated to 80°C the mixture developed an intense and stable colour within ten minutes. The absorption did not change over a period of five hours.

All solutions for the spectrophotometric measurements were made in the same way.

Appropriate aliquots of the standard solution to give a final concentration of 2 to 36 microgram of ruthenium per milliliter were heated on a water bath at 80°C for ten minutes, and were cooled to room temperature and made up to 10, 25, 50 or 100 milliliters with oxalic acid. The final solution was 1 *N* oxalic acid.

The measurements were made after the solution has been cooled (about 30 min.).

Fig. 1 curve 1 shows the absorption of ruthenium tetroxide in 1 *N* oxalic acid and curve 2 represents the absorption of 1 *N* oxalic acid.

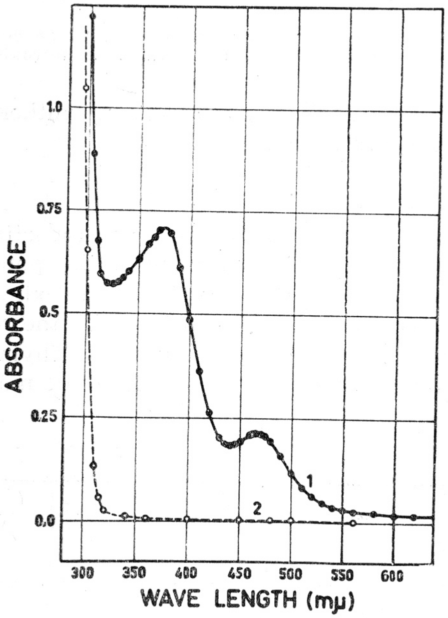
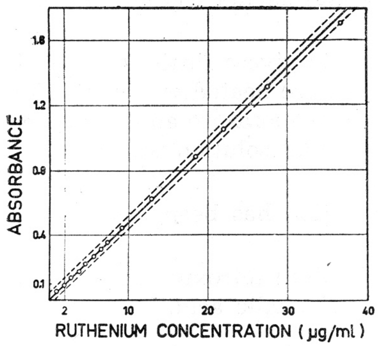


Fig. 1. Absorption spectra (1) of ruthenium tetroxide in 1 *N* oxalic acid (after three hours at room temperature or after heating on water bath to 80°C during 10 minutes), (2) of 1 *N* oxalic acid. Silica cell, 10 mm.

The system has a sharp absorption band at 375 mμ and a broad absorption band at 475 mμ. The regression of ruthenium concentration upon absorbance (at 375 mμ) and the 99% confidence limits for predictions of concentration of ruthenium from measured values of absorbance are shown in Fig. 2.

The absorbance (at 375 mμ) against concentration of ruthenium showed good agreement with Beer's law over the range investigated.

The standard errors (curve 1) and relative standard errors (curve 2) of spectrophotometric determination of ruthenium in 1 *N* oxalic aced are given in Fig. 3.



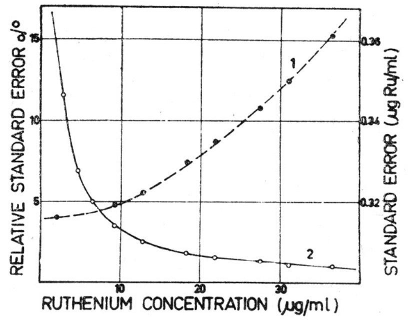


Fig. 2. The regression of ruthenium concentration upon absorbance at 375 mµ and the 99% confidence limits.

Fig. 3. Curve 1 shows the change of the standard error and the curve 2 the change of the relative standard error of the concentration of ruthenium tetroxide in 1 *N* oxalic acid.

In the concentration range from 2 to 36 p. p. m. ruthenium was determined with relative standard error from 14% to 1%.

Polarographic determination

Experiments showed that 1 *N* oxalic acid as supporting electrolyte gave a residual current which linearly increased with the potential applied to the electrodes in the voltage range where ruthenium exhibits a polarographic wave. By applying the counter current —0.30 µ A/V, the residual current curve was almost parallel to the abcissa (Fig. 4, curve 1). Thymol in a concentration of 0.006% was used for suppressing the polarographic maximum of ruthenium in 1 *N* oxalic acid.

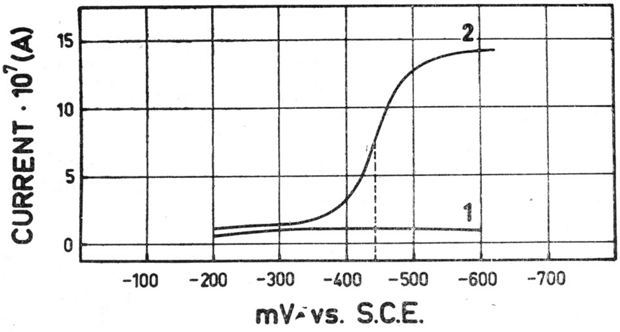


Fig. 4. Curve 1: Residual current of the supporting electrolyte (applied counter current —0.30 µA/V) consists of 1 *N* oxalic acid and 0.006% thymol. Curve 2: Current — voltage curve of ruthenium in the same supporting electrolyte. Sensitivity of the recorder 0.25×10^{-7} A/mm. (switch 1/10); damping 5; rate of recording 3.78 mm/min; potentials are given with respect to the saturated calomel electrode and the position of half-wave potential is marked (—440 mV).

Fig. 4 (curve 2) shows also a typical polarographic wave of ruthenium in 1 N oxalic acid and 0.006% thymol as a supporting electrolyte and the position of the half-wave potential (—440 mV) with respect to the saturated calomel electrode.

Distilled ruthenium tetroxide was absorbed in oxalic acid (as previously described). From this solution a series of solutions with various concentrations of ruthenium were prepared and adjusted to 1 N with respect to oxalic acid (0.006% in thymol). The concentration of ruthenium in the solution so prepared should be between 2 and 120 μg. 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 about 15 minutes. With this operation all ruthenium was probably converted to Ru(IV).[3]

A linear regression analysis was performed for the diffusion current (mm at S = 1/3, or in 10^{-7}A) against the concentration of ruthenium (μg/ml.). The calibration curve in the described conditions was a straight line which passed through the origin. The following regression equation was obtained:

$$c = 3.19\, h$$

where h is the height of the polarographic wave (S = 1/3) in mm. and C is the concentration of ruthenium (μg. Ru/ml.) in the solution. The regression of ruthenium concentration C upon polarographic wave height and the 99%-confidence limits for predictions of C from the measured value of h (h is the mean of two repeated determinations) are shown in Fig. 5.

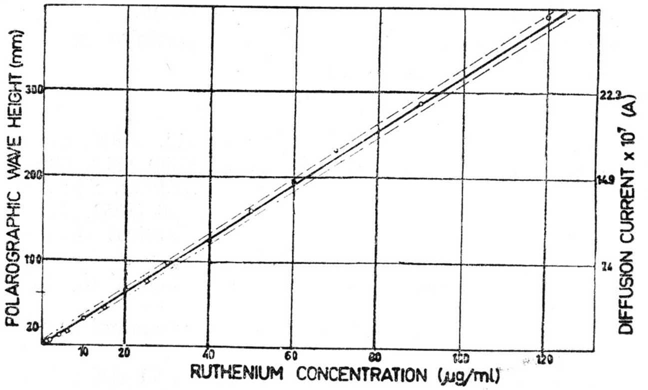


Fig. 5. Regression of ruthenium concentration c (μg. Ru/ml.) upon polarographic wave height h (mm., or in 10^{-7} A) and the 99%-confidence limits for predictions of c. The plotted points h are the mean values of polarographic wave heights of two repeated measurements.

The standard errors (curve 1) and the relative standard errors (curve 2) of the polarographic determinations of ruthenium are given in Fig. 6, for the concentration range from 3 to 120 μg. Ru/ml.

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

The polarographic determination of ruthenium in presence of hydrochloric, sulfuric and perchloric acid, shows that the proposed method is reliable and precise in a very wide range of ruthenium concentration (4—120 μg./ml.) with relative standard errors of 15 to 0.7%.

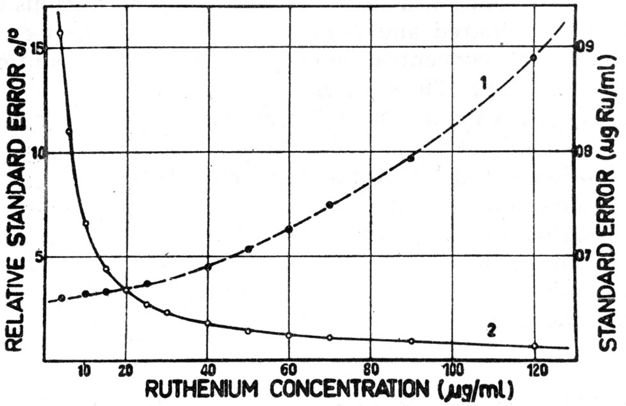


Fig. 6. Curve 1 is the standard error and curve 2 is the relative standard error of ruthenium concentration plotted against ruthenium concentration in the solutions used for polarographic measurements. Polarographic wave-heights h used in determinations are arithmetic means of two repeate dmeasurements.

Spectrophotometric determinations of smaller concentrations of ruthenium are more accurate than polarographic determinations.

The polarographic determination has an advantage because it is useful in a greater concentration range of ruthenium.

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IZVOD

Spektrofotometrijsko i polarografsko određivanje rutenija u oksalnoj kiselini

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Prikazana je spektrofotometrijska i polarografska metoda određivanja malih koncentracija rutenijeva tetroksida absorbiranog u oksalnoj kiselini. Žuta boja rutenijeva tetraoksida absorbiranog u 1 *N* oksalnoj kiselini poslužila je za fotometrijsko određivanje rutenija. Mjerenja su vršena kod valne dužine od 375 mμ za koncentracijsko područje od 2 do 36 μg Ru/ml, uz relativne standardne pogreške od 14% do 1%.

Opisana je polarografska metoda za određivanje niskih koncentracija rutenija u osnovnom elektrolitu, koji sadrži oksalnu kiselinu (1 *N*) i timol (0.006%). Rezultati pokazuju da je predložena metoda osjetljiva i precizna u koncenracijskom području od 4 do 120 μg Ru/ml. Relativne standardne pogreške kreću se u granicama od 15 do 0.7%, ako se određivanja vrše s dva paralelna uzorka.

Solna, sumporna i perklorna kiselina (do 0.5 *N*) kod fotometrijskog i polarografskog određivanja ne smetaju. Određivanja se ne mogu vršiti, ako je nazočna dušična kiselina (najmanji tragovi *nitrita*).

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