

Note on Polarographic Determination of +6 Uranium

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A polarographic method is proposed for determination of small amounts of +6 uranium. An aqueous solution of salicylic acid (1.6 g/l), sulphuric acid (0.4% v/v) and thymol (0.009%) is used as supporting electrolyte. This procedure is applicable in the concentration range from 5 to 50 μg of uranium per ml. of the solution used for polarographic measurement. Total amounts of 10 μg of uranium per sample can be determined with a standard error of $\pm 0.8 \mu\text{g}$.

Colorimetric and photometric methods for determination of uranium are not sensitive enough for determination of very small amounts of this metal. On the other hand, fluorometric methods in liquid or solid medium are suitable for detection and determination of minute amounts of uranium, but the smallest amounts of impurities interfere by quenching the fluorescence. Polarographic methods are both sensitive and specific enough, and if a suitable supporting electrolyte is used several other metal ions can be determined simultaneously with uranium.¹ Supporting electrolyte recommended by Lewis and Griffiths² seemed to be particularly suitable for this purpose. We tried to make use of this electrolyte in determination of very small amounts of uranium, but the results were not satisfactory. Therefore, an investigation was undertaken to find out the optimum concentrations of various constituents of this electrolyte, and to select the most suitable suppressor of polarographic maxima.

APPARATUS AND REAGENTS

A Cambridge Polarograph, Pen Recording Type, and a standard polarographic cell of the same firm with saturated calomel electrode were used. The cell was kept in a constant temperature water bath at $25.0 \pm 0.1^\circ\text{C}$. Dissolved oxygen was displaced by bubbling hydrogen through the solution for 10 minutes prior to the polarographic determination. The hydrogen was purified by passing it through a saturated solution of pyrogallol in sodium hydroxide.

The capillary had m and t values of 1.42 mg of mercury per second (at 0 V) and 3.08 seconds (at 0.2 V), respectively, at 54 cm mercury column height in the supporting electrolyte used in the analysis.

The wave heights were measured according to the point method, i. e. the increment in current between the extrapolation lines for the residual current and the diffusion current was measured at the half-wave potential.

Uranyl-nitrate, reagent grade (Schering-Kahlbaum, A. G. Berlin). Standard solution: A solution containing approximately 1 mg of uranium per ml. was first prepared and the exact concentration subsequently determined gravimetrically.³ The standard solution was kept in darkness.

Salicylic acid, reagent grade (Erba, Milano).

Sulphuric acid, reagent grade (»für forensische Zwecke«, Merck, Darmstadt).

Perchloric acid, reagent grade, 71% (Mallinckrodt, Saint Louis)

Thymol, recrystallised.

THE COMPOSITION OF THE SUPPORTING ELECTROLYTE

The supporting electrolyte used by Lewis and Griffiths² consisted of a half-saturated solution of salicylic acid which was at the same time saturated with alizarin and contained 10 per cent v/v of sulphuric acid. The salicylic acid is a complexing agent facilitating simultaneous determination of metal ions having similar half-wave potentials; sulphuric acid increases the acidity (pH value of the supporting electrolyte should be ~ 2) and the conductivity of the solution. When we tried to use this electrolyte for determination of very small amounts of uranium, and performed the polarographic measurements with the maximum sensitivity of the recording equipment (which is of the order of 10^{-9} A per mm.), we found that the relation between the wave height and the concentration of uranium was not linear. Further experiments showed that the lack of linearity was due to the deformation of the current-voltage curve of the supporting electrolyte. We decided, therefore, to investigate the influence of the concentration of salicylic acid and sulphuric acid on the form of the residual current of the supporting electrolyte. Experiments showed that an aqueous solution containing 1.6 g/l of salicylic acid and 0.4% v/v of sulphuric acid gave a residual current which increased linearly with the applied potential in the desired voltage range. This composition of the supporting electrolyte satisfied also the condition² that the pH value should be in the neighbourhood of 2. By applying the compensation arrangement it was possible to obtain a residual current curve that was almost parallel to the abscissa

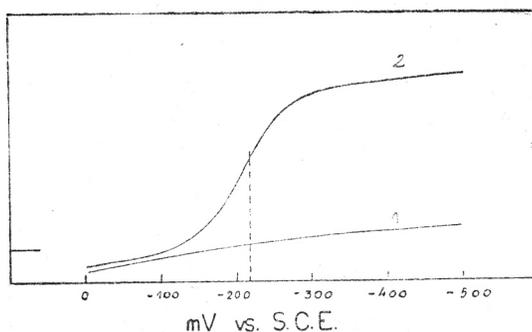


Fig. 1. Curve 1: Residual current of the supporting electrolyte (1.60 g salicylic acid, 4 ml sulphuric acid [$d = 1.84$] and 0.090 g thymol per liter of solution). Curve 2: Current-voltage curve of +6 uranium (39.4 $\mu\text{g/ml.}$) in the same supporting electrolyte. Potentials are given with respect to the saturated calomel electrode; sensitivity of the recorder: 7.90×10^{-9} A/mm.; damping 6; rate of recording: 3.75 mm. per min.

(Fig. 1). The necessary counter current amounted to $-0.12 \mu\text{A}$ per volt. Figure 1 shows also a typical polarographic wave of +6 uranium in this electrolyte and the position of the half-wave potential with respect to the saturated calomel electrode.

Thymol in a concentration of 0.009% was chosen as suppressor of polarographic maxima, because it had no influence on the height of the waves in a wide concentration range.

PROCEDURE

The solution to be analysed (containing at least 10 μg of uranium) is evaporated to dryness with addition of 1 ml. of perchloric acid. (Small amounts of perchloric acid which may remain after evaporation have no influence on the height and form of the polarographic wave.) The residue, containing +6 uranium, is dissolved in the supporting electrolyte. The electrolyte should be added in small amounts and the mixture gently heated. When a clear solution is obtained, it is transferred quantitatively to a volumetric flask and, after addition of the necessary amount of thymol solution, diluted to the mark with supporting electrolyte. The concentration of uranium in the solution prepared for polarographic measurement should be between 5 and 50 $\mu\text{g}/\text{ml}$. If necessary, the volume of this solution can be limited to 2 ml.

It is essential that the dissolved oxygen is completely removed from the solution prior to the polarographic measurement as the half-wave potentials of oxygen and +6 uranium have very similar values. Besides, even traces of oxygen tend to distort the residual current curve of the supporting electrolyte. With regard to the interfering metal ions our experiences are in agreement with data given by other authors.²

ANALYSIS OF THE CALIBRATION CURVE

As it is well known that the diffusion current is proportional to the concentration of the electroreducible or electrooxidizable substances^{4, 5, 6}, a linear regression analysis was performed for the calibration data presented in Table 1,

TABLE 1

Sample No.	Concentration C ($\mu\text{g}/\text{ml}$)	Wave height h^* (mm)	Mean wave height h (mm)
1		4.3	
2	1.97	4.5	4.4
3		11.6	
4	3.94	12.0	11.8
5		17.8	
6	5.92	16.8	17.3
7		27.8	
8	9.86	27.8	27.8
9		40.0	
10	13.8	41.2	40.6
11		40.8	
12	13.8	41.4	41.1
13		60.0	
14	19.7	58.8	59.4
15		88.5	
16	29.6	90.0	89.4
17		116.4	
18	39.4	117.0	116.7
19		149.4	
20	49.3	150.0	149.7

* h -values for samples No. 1 to 10 were obtained using maximum sensitivity of the recorder; the sensitivity was reduced to $1/3$ for samples No. 11 to 20.

subject to the condition that the straight line passes through the origin. The following regression equations were obtained:

$$h = 3.003 C \quad \text{and} \quad C = 0.333 h,$$

where h is the height of the polarographic wave in mm. and C is the concentration of uranium in the solution prepared for polarographic measurement. The standard errors of the slopes in the above equations were ± 0.015 and

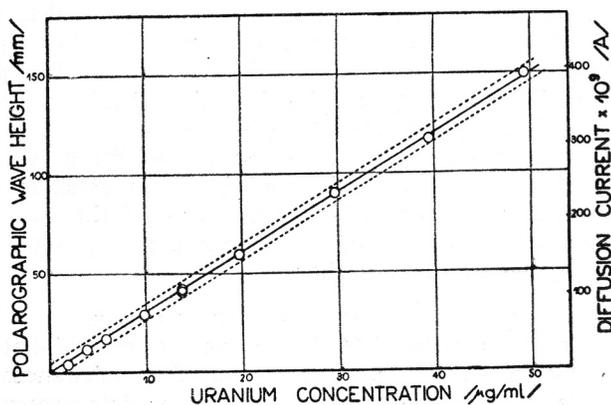


Fig. 2. Regression of C upon h and 95% confidence limits for predictions of C from measured values of h . Uranium concentration in $\mu\text{g/ml}$ of the solution used in polarographic measurements. Wave-heights in mm. and $A \times 10^{-9}$. The plotted points are mean values of h of two repeated measurements.

± 0.002 , respectively. The regression of C upon h and the 95% confidence limits (i. e. the limits of error for $P = 0.05$) for predictions of C from the measured value of h (h is the mean of two repeat determinations) are shown in Fig. 2.

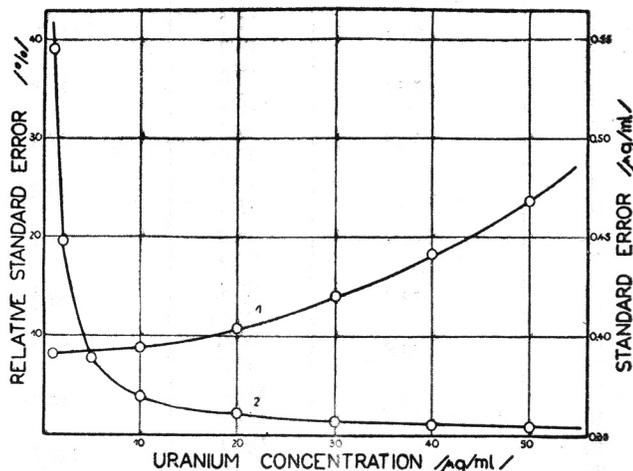


Fig. 3. Standard error (1) and relative standard error (2) of concentration v. uranium concentration in the solution used for polarographic measurements, h -values used for predicting concentration are arithmetic means of two repeated measurements.

The standard errors and the relative standard errors of the concentration are given in Fig. 3 for the concentration range from 0—50 μg of uranium per ml. of the solution used for polarographic measurements.

This analysis of the calibration curve shows that the proposed method is reliable and precise even when very small amounts of uranium are involved. Thus, for instance, if the final volume of the solution is 2 ml., and the concentration of uranium is 5 $\mu\text{g/ml}$., the total amount of 10 μg uranium per sample can be determined with a standard error of $\pm 0.8 \mu\text{g}$.

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IZVOD

Prilog polarografskom određivanju $+6$ urana

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Opisana je polarografska metoda za određivanje malih količina urana u osnovnom elektrolitu, koji sadržava sumpornu i salicilnu kiselinu. Utvrđen je najpovoljniji odnos tih komponenata u osnovnom elektrolitu, a kao kriterij je uzet najpravilniji tok rezidualne struje. Za potiskivanje polarografskih maksimuma upotrebljen je timol. Rezultati pokazuju, da je u koncentracijskom području do 50 $\mu\text{g/ml}$ predložena metoda pouzdana, osjetljiva i precizna. Vršiti se određivanje s dva paralelna uzorka, standardna pogreška određivanja koncentracije iznosi manje od 0.5 $\mu\text{g/ml}$. Ukupne količine od 10 μg mogu se odrediti s pogreškom od $\pm 0.8 \mu\text{g}$.

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