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Accurate and Precise Determination of 2–25 mg Amounts of Uranium by Means of a Special Automatic Potentiometric Titration

J. Slanina*, F. Bakker, A. J. P. Groen, and W. A. Lingerak

Netherlands Energy Research Foundation ECN, Petten (NH), The Netherlands

Genaue und reproduzierbare Bestimmung von 2–25 mg Uran durch automatische potentiometrische Titration

Zusammenfassung. Das Uran wird nach Eberle et al. [3] zu U(IV) reduziert und mit 0.05 N Kaliumdichromatlösung titriert, wobei der Endpunkt mittels einer Platinelektrode indiziert wird. Während der Probevorbereitung wird das Titrationsgefäß zentrifugiert, um die Wände zu reinigen. Eine Überschreitung des vorgewählten Endpunktes wird verhütet, indem ein spezieller Differentiator die Titration unterbricht, bis sich das Gleichgewicht eingestellt hat. Die Reproduzierbarkeit des Verfahrens beträgt 0,02% relativ, die Genauigkeit ist besser als 0,04% relativ. Die Zeitaufwand beträgt 5 min pro Titration.

Summary. A precise and accurate potentiometric titration of 2–25 mg of uranium is described. The uranium is reduced to U(IV) according to the method of Eberle et al. [3], and titrated with 0.05 N potassium dichromate, using a platinum indicator electrode. During the sample preparation the walls of the titration vessel are cleaned by centrifugation. To avoid overshoot of the set point a special differentiator is described, that interrupts the titration until equilibrium is reached. The precision of the method is 0.02%, the accuracy is better than 0.04% rel. Each titration takes 5 min.

Key words: Best. von Uran; Potentiometrische Titration; 2–25 mg, automatisch.

1. Introduction

For the determination of 60 – 200 mg amounts of uranium the potentiometric titrimetric procedure described by Davies and Gray [2] and Eberle et al. [3] gives good results. In this procedure phosphoric acid and sulphamic acid are added to the sample solution. The uranium is reduced to U(IV) with ferrous sulphate; the excess of Fe(II) ions is oxidized to Fe(III) by a mixture of nitric acid, sulphamic acid and ammonium molybdate. The titration of U(IV) with dichromate tends to be sluggish, so vanadyl sulphate is added to speed up the reaction.

For our purpose this procedure had to be adopted in such a way that amounts of 2–25 mg of uranium could be determined. Since it had to be used for nuclear safeguarding purposes the accuracy should be better than 0.05% relative.

2. Potentiometric Titration of 2–25 mg Amounts of Uranium

In this procedure the method mentioned above is applied on samples of about 1 ml containing 2–25 mg of uranium. The end-point of the titration is decteted potentiometrically by means of a Pt indicator electrode. The set-point of the titration is chosen close to the point of inflection of the titration curve (about 620 mV versus an Ag/AgCl electrode).

For the determination of 2–25 mg amounts of uranium with an accuracy better than 0.05% relative two difficulties had to be surmounted:

- When the titration was performed manually or by means of an ordinary set-point titrator the overshoot at the end-point of the titration was too high.
- During the reduction step of uranium and the oxidation of the Fe(II) little droplets could splash on the wall of the vessel, resulting in excessive errors.

2.1. Elimination of Overshoot

The overshoot of the set-point is caused by the long response time (> 20 s) of the platinum indicator electrode

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* Address for correspondence

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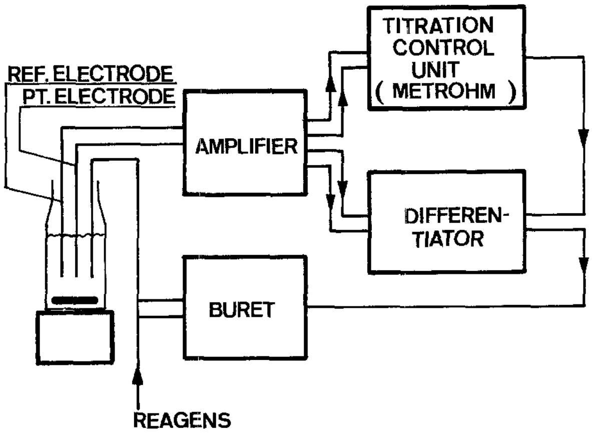

Fig. 1. Diagram of the titrator

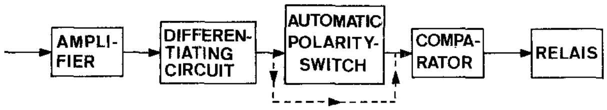

Fig. 2. Differentiator, described by Callicot and Carr [1]

Table 1. Results of titration with and without differentiator

mEq. of acid added	Response time electrode	mEq. found without differ-entiator	differ-ence in % rel.	mEq. found with differ-entiator	differ-ence in % rel.
0.917	0.5	0.917	0.0	0.917	0.0
0.917	3	0.917	0.0	0.917	0.0
0.917	12	0.928	1.2	0.916	− 0.1
0.917	15	0.930	1.4	0.916	− 0.1
0.917	26	0.940	2.5	0.917	0.0
0.917	30	0.944	3.0	0.917	0.0
0.1643	0.5	0.1643	0.0	0.1643	0.0
0.1643	3	0.1645	0.1	0.1643	0.0
0.1643	12	0.1649	0.4	0.1642	− 0.1
0.1643	15	0.1682	2.4	0.1642	− 0.1
0.1643	26	0.1754	6.8	0.1643	0.0
0.1643	30	0.1760	7.1	0.1643	0.0

near the end-point of the titration. For this reason a differentiator is applied to interrupt the titration if the signal of the indicator electrode changes more than 0.2 mV per second ($\mathrm{d}E/\mathrm{d}T > 0.2$ mV s^{-1}). A diagram of the titrator including the differentiator is given in Figure 1.

The differentiator is an adaptation of the apparatus described by Callicot and Carr [1] (see Fig. 2). An automatic polarity switch, a comparator and a relais are added to this differentiating circuit (Fig. 2).

The comparator circuit can detect either an increase or decrease of the signal; when the automatic polarity switch is used any change in the input signal can be detected. The time-constant of the differentiating circuit can be adjusted between 0.2 and 2.0 s. The apparatus can detect a $\mathrm{d}E/\mathrm{d}T$ of 0.03 mV s^{-1}.

We have tested the influence of a long response time of the indicator electrode in potentiometric acid-base set-point titrations. The assumption was made [4] that for our purposes the response of an electrode to a stepwise change in concentration could be approximated sufficiently as:

$$\Delta E_T = \Delta E_E\,(1 - e^{-t/T})$$

ΔE_T = change of the signal of the electrode at time T after the change in concentration,
ΔE_E = change of the signal of the electrode in equilibrium after the change in concentration,
t = time elapsed after the addition,
T = time constant (here defined as response time of the electrode)

T was varied between 0.5 and 30 s electronically. In Table 1 the results of titration with and without the differentiator are given. The parameters of the titrator (proportional band, set-point etc.) have been kept constant during all titrations.

The results of Table 1 make it very clear that no overshoot will occur if the differentiator is used, regardless of the response time of the electrode.

2.2. Elimination of Errors Caused by Splashing of Droplets on the Wall of the Titration Vessel

Droplets of sample Fe(II) splashed on to the wall of the titration vessel during pretreatment, will cause errors and should be avoided. To eliminate these errors we rotate the titration vessel, at least once during each pretreatment step, at such a speed that the liquid covers the wall completely. For this purpose the titration vessel is placed in a simple centrifuge, mounted directly on the motor shaft, shown in Figure 3. It allows intensive mixing of the solution by reversing the direction of rotation every 3 s, with a maximum speed of 400 rpm. Washing the wall is achieved by rotating it continuously at 2500 rpm for 15 s (see Fig. 3).

The automatic addition of reagents diminishes the number of outliers considerably. The addition of reagents used, the mixing and centrifugation periods are controlled by a programmable clock.

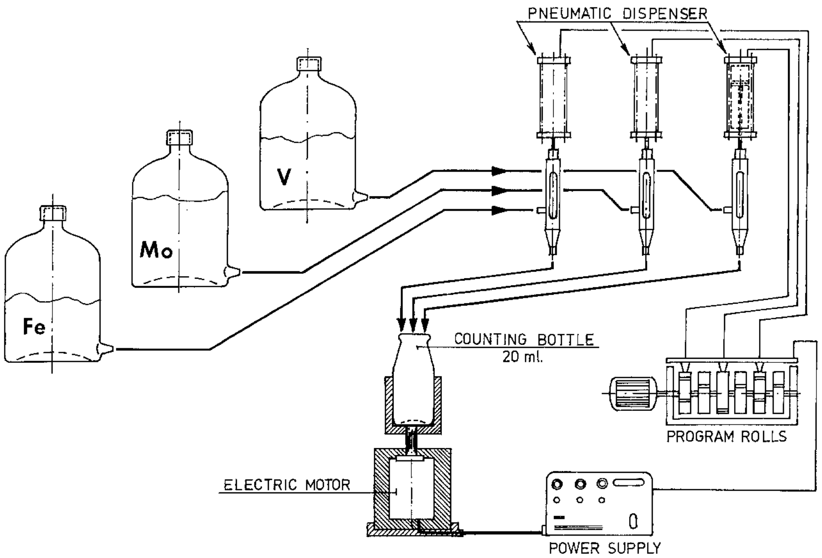

Fig. 3. Titration stand

3. Experimental

3.1. Apparatus

Electrode. Ingold platinum electrode equipped with an Ag/AgCl reference electrode and with an electrolytic bridge, type Pt-48059088. The electrolytic bridge (filled with 2 M H_2SO_4) is necessary to prevent the formation of silver phosphate which could plug the glass frit of the standard Ag/AgCl reference electrode.

Amplifier. E. C. N. design. Input impedance $> 2 \cdot 10^{13}$ Ω; adjustable gain and offset, equipped with an analog low-pass filter (for noise reduction).

Titrator. Metrohm E. 450, equipped with an adjustable proportional band, puls-length and puls-frequency.

Buret. Metrohm E. 538/4–5; 5 ml; the digital readout of the buret is modified to give a reading of 10000 instead of 5000 for 5 ml.

Differentiator. E.C.N.-design

Centrifuge. E.C.N.-design

Dispensor. E.C.N.-design

Titration vessel. A standard 20 ml vessel with screwcap, manufactured for liquid scintillation measurements.

All details about the amplifier, differentiator, centrifuge and dispensor will be sent on request.

3.2. Reagents

All reagents are p.a. unless stated otherwise.

Sulphamic Acid Solution. 150 g of sulphamic acid per litre.

Phosphoric Acid. 86.6% Baker No. 6024. 10 ml of 0.05 N potassium dichromate is added to 1 l of H_3PO_4 and the mixture is heated to 100°C. At this temperature all reducing substances in the phosphoric acid are oxidized. The potassium dichromate decomposes in a few minutes.

Ferrous Sulphate Solution. 280 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ and 200 ml of H_2SO_4, 1 : 1 per litre.

Nitric Acid, Sulphamic Acid and Ammonium Molybdate Mixture. 500 ml of HNO_3 conc., 4.0 g of $(NH_4)_6Mo_7O_{24}$ and 15 mg of sulphamic acid per litre.

Vanadyl Solution. 11.0 g of $VOSO_4$, Merck, and 110 ml of H_2SO_4, 1 : 1 per litre.

Dichromate Titrant. 0.05 m aeq. per gram of titrant.

Potassium dichromate (Primary Standard, N.B.S. 136 C) is dried at a temperature of 120°C during 1 h. 4.9 g is weighed to 0.00001 g accuracy and transferred into a 2 l flask, which has been weighed previously; 30 ml of conc. H_2SO_4 and water are added until the weight of the contents of the flask is 2000 g.

3.3. Procedure

The samples are prepared and interfering species are removed according to the N.B.L. procedure [3]. The addition of reagents is either done manually or by means of our automatic dispenser. A 0.8–1.2 ml portion of the sample containing 2–25 g of uranium is weighed in the titration vessel, 0.1 ml of the sulphamic acid solution and 4.5 ml of conc. phosphoric acid are added. The titration vessel is placed into the centrifuge and the contents are mixed during a few seconds. 0.5 ml of the ferrous sulphate solution is added and after centrifugation at high speed mixing is continued for 60 s, then 1 ml of the HNO_3-molybdate mixture is added. A dark colour appears that vanishes within 20 s. The contents of the vessel mixed during 30 s, centrifugation is applied for 15 s, again followed by mixing during 30 s and centrifugation. After 2 additional min of mixing 4.5 ml of the vanadyl sulphate solution is added and the sample is ready for titration.

The titration is performed in an air-conditioned room where the temperature is kept constant within ± 1°C. This is necessary because the volume of a buret will change for approximately 0.02% per degree Celsius temperature variation. The buret is calibrated by weighing. The Metrohm buret we use has an accuracy of 0.01%. The inflection point of the titration curve is determined by manual titration of a few uranium solutions. The set-point of the titrator is ad-

Table 2. Titrimetric results

Number of determinations	Blank found in µg of U	Titre found/ titre make-up	Correlation coefficient
6	9.6	0.9997	0.99999993
6	9.4	1.0000	0.99999998
12	7.3	0.9997	0.9999995
12	6.0	0.9997	0.99999995

Table 3. Analytical results for NBS-standard 960

	% Uranium found	Mean	NBS value
Batch 1	99.93		
	99.96	99.95^3	99.97^5
	99.97		
Batch 2	99.98		
	99.93	99.95^3	99.97^5
	99.95		

Table 4. U-determination in SALE-samples

	% Uranium found	Mean	Standard dev. in %	Make-up value	% Bias
Batch 1	87.37				
	87.38	87.37^7	0.01^1	87.35^7	0.02^5
	87.38				
	87.39				
	87.37				
	87.36				
	87.39				
Batch 2	87.36				
	87.35				
	87.35	87.34^9	0.00^8	87.35^5	0.00^6
	87.34				
	87.34				
	87.34				
	87.46				
	87.34				

justed to the inflection point, which does not vary much (620 mV ± 10 mV versus Ag/AgCl electrode).

The proportional band and the cycle time of the titrator are adjusted to 120 mV and 1 s respectively. The differentiator is set to interrupt the titration if dE/dT exceeds 0.2 mV s^{-1}.

Six to twelve samples of a standard solution, containing 2–25 mg of uranium are titrated to determine the blank and to check the titrant. The blank corresponds to 5–10 µg of U, the found and make-up value of the titrant should not differ more than 0.04%. This check is repeated at least once a week. Titration must be completed within 6 min, a systematic bias appears otherwise.

4. Results and Discussion

Table 2 gives the results of some determinations of the blank and the titres of the dichromate of some batches of titrant. The range of the titrations was from 2–26 mg of uranium.

Table 3 gives the results of the determination of the uranium content of N.B.S. standard 960. 2 pieces were dissolved in nitric acid and 3 titrations were performed with each solution.

The ECN participates in an inter-laboratory comparison and qualification program for uranium analyses (SALE). Some results of analysis of uranium in UO_2 are given in Table 4.

The last 2 years all sorts of samples, such as uranium dioxide, uranium-carbonitrides, uranium alloys, uranium-zirconium alloys etc., have been analysed by means of our micromethod. We find typically a precision of 0.02% and an accuracy of 0.04% or better.

The precision and accuracy of our micromethod are fully comparable with the results of the original N.B.L.-method, that needs samples, which must contain 60–200 mg of uranium.

Micromethods are very attractive for radioactive samples and presently we are investigating the possibilities to determine amounts of 100–2000 µg of uranium by means of a computer controlled titrator.

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