

# Determination of Uranium in Natural Waters by Differential-pulse Polarography of a Trioctylphosphine Oxide Extract

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A method is described for the determination of trace amounts of uranium (down to  $10 \mu\text{g l}^{-1}$ ) in natural waters by differential-pulse polarography of a cyclohexane - trioctylphosphine oxide extract. Studies on the effect of possible interferences are included.

*Keywords:* Uranium determination; water analysis; differential-pulse polarography; trioctylphosphine oxide extraction

In connection with work on the geochemistry of uranium, an accurate and reasonably rapid method of determining trace amounts of uranium in waters is often required. Differential-pulse polarography is a sensitive technique for the determination of some trace elements but, when applied to uranium, the method is unsuitable without pre-concentration (and purification) for levels of less than about  $200 \mu\text{g l}^{-1}$ . Solvent-extraction techniques are generally more rapid than other processes such as ion exchange, particularly if the analysis can be run directly on the extract, thus avoiding the time and errors involved in back-extraction of the uranium into an aqueous phase or destruction of the extract.<sup>1-3</sup> The method reported here is based on that described by Belew *et al.*<sup>1</sup> in which uranium is determined in a cyclohexane - trioctylphosphine oxide (TOPO) extract.

Belew *et al.*<sup>1</sup> gave results that indicate that an accuracy of  $\pm 10\%$  should be obtainable for uranium at the  $10 \mu\text{g l}^{-1}$  level, and this level is near the lower limit for anomalous uranium in ground waters.<sup>4,5</sup> However, it is not clear if the stated accuracy was based on results obtained by repeated analysis using the full analytical procedure or if it was deduced from the reproducibility of the polarographic curves. In addition, although, as Belew *et al.* pointed out, interferences can be detected from the polarographic curve, they cannot in general be predicted, as the effect of TOPO complexation on reduction potentials is unknown. In this work, the effects of possible interfering elements in natural waters on uranium analyses were evaluated and a more realistic estimate of accuracy was obtained by applying the full procedure to samples of known uranium concentration.

## Experimental

### Apparatus

Polarograms were recorded with a PAR, Model 174, polarographic analyser and a Houston Instruments, Series 2000, X - Y recorder. The polarograph was used in the differential-pulse mode with a mercury drop time of 1 s, a modulation amplitude of 50 mV and a scan speed of  $2 \text{ mV s}^{-1}$ .

The polarographic cell is shown in Fig. 1. A platinum wire was used routinely as a reference electrode<sup>1</sup> but the potentials given in this paper were measured with a standard calomel electrode (S.C.E.) placed directly in contact with the cell solution. The potential of the platinum-wire reference electrode was  $-0.2 \pm 0.07 \text{ V}$  versus S.C.E. The cell solutions were de-oxygenated with solvent-saturated (1 + 1 cyclohexane - ethanol) high-purity nitrogen from which possible trace amounts of oxygen were removed with BASF R3-11 activated copper catalyst. A rapid stream of solvent-saturated nitrogen was passed over the cell solution during de-oxygenation and while the polarograms were being run. Oxygen must be rigorously excluded from the cell solution as variations in oxygen content were found to be the main cause of irreproducibility of the polarographic peak heights. Separating funnels were equipped with PTFE taps and polythene stoppers as trace amounts of grease

tended to decrease the polarographic peak of uranium. The polarographic solution was spiked with uranium in cyclohexane using an Excalibur Varipet micropipette. As the disposable plastic tip of this pipette is wetted by organic solvents, complete transfer of the spike was ensured by rinsing the tip in the cell solution.

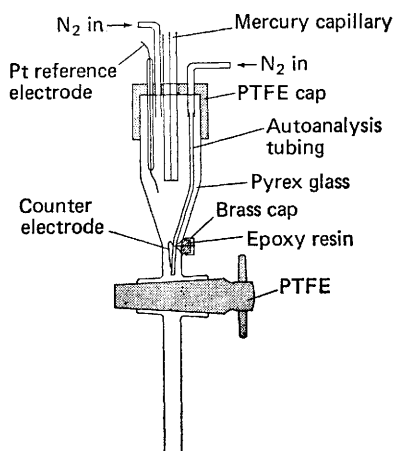


Fig. 1. Polarographic cell (capacity 3–12 ml).

### Reagents

All reagents were of analytical-reagent grade unless otherwise specified.

*Trioctylphosphine oxide.* Eastman TOPO was used as supplied.

*Cyclohexane.* One brand of cyclohexane was found to be unsuitable as it gave a strong polarographic peak at approximately  $-0.9$  V *versus* the platinum-wire reference electrode. Merck cyclohexane (GR grade) and Univar "cyclohexane for UV spectroscopy" were satisfactory.

*Standard solution of uranium in cyclohexane.* This solution was prepared by extracting 5.00 ml of  $240 \mu\text{g l}^{-1}$  of uranium as uranyl nitrate in 0.5 M nitric acid with 5.00 ml of 0.1 M TOPO in cyclohexane. The solution was stored in a stoppered glass tube and did not deteriorate with time, but fresh solutions were prepared weekly in order to minimise the effect of solvent evaporation.

### Procedure

Pipette 50–100 ml of sample into a separating funnel, make it 0.5 M in acid with concentrated nitric acid, add 0.1 g of ascorbic acid, add by pipette 3 or 5 ml of 0.1 M TOPO in cyclohexane and shake the mixture for 5 min. Transfer the organic layer into a centrifuge tube, centrifuge for 1–2 min and remove trace amounts of the aqueous layer with a capillary dropper. Pipette a 2-ml volume of the organic phase into the polarographic cell, add 2 ml of 0.2 M ethanolic lithium perchlorate solution, de-oxygenate for at least 10 min and run a polarogram from about  $-0.2$  to  $-0.9$  V *versus* the platinum-wire reference electrode two or three times. Spike the cell solution with a suitable volume of uranium in cyclohexane (sufficient to increase the peak height by 50–100%), de-oxygenate for 5 min and re-run the polarogram at least twice. Determine a blank daily by following the above procedure with an equal volume of distilled water substituted for the sample.

Calibration graphs were obtained by adding spikes of the standard solution of uranium in cyclohexane to 4 ml of 0.1 M lithium perchlorate solution in 1 + 1 cyclohexane - ethanol that was 0.05 M in TOPO, and recording the polarograms as described above.

### Results and Discussion

The extraction of small amounts of uranium(VI) into 0.1 M TOPO in cyclohexane from dilute nitric acid (0.5–1 M) is quantitative.<sup>1,6,7</sup> For the polarographic determination the

extract is diluted with a solution of lithium perchlorate in ethanol to decrease the cell resistance.<sup>1</sup>

**Caution**—Perchlorates in the presence of organic materials are liable to explode violently and unpredictably.<sup>7</sup>

Lithium chloride is unsuitable as an additive as the chloride ion produces an anodic peak that interferes in the uranium determination.<sup>1</sup> This interference precludes the use of a halide-coated silver wire as a reference electrode. The platinum-wire reference electrode<sup>1</sup> gave sufficiently constant peak potentials for analytical purposes.

A linear calibration graph is obtained for uranium concentrations from  $60 \mu\text{g l}^{-1}$  to  $10 \text{ mg l}^{-1}$  in the polarographic solution ( $0.05 \text{ M}$  TOPO and  $0.1 \text{ M}$  lithium perchlorate in  $1 + 1$  ethanol - cyclohexane; note that the TOPO concentration in the cell solution is halved by dilution of the extract with ethanolic lithium perchlorate). The calibration graph obtained using one brand of TOPO was not linear, but bent towards the concentration axis at concentrations of uranium less than  $3.6 \text{ mg l}^{-1}$  (the peak heights being reduced by up to 80%). The differential-pulse peak for this TOPO was also broader and at lower potentials for the lower uranium concentrations. The potential of the differential-pulse peak for uranium was  $-0.3 \text{ V}$  versus S.C.E. (see Fig. 2).

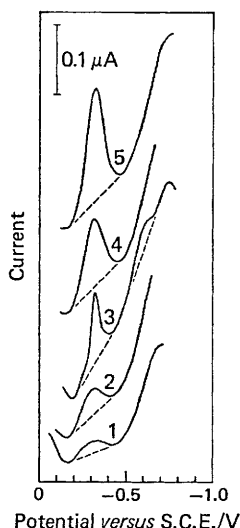


Fig. 2. Polarographic traces obtained by extracting 50 ml (trace 1) or 100 ml (traces 2-5) of sample with 3 ml of TOPO solution. 1, Blank for 50 ml of solution; 2, blank for 100 ml of solution; 3, blank for 100 ml of solution with  $134 \mu\text{g l}^{-1}$  of molybdenum; 4, ground water containing  $53 \mu\text{g l}^{-1}$  of uranium; and 5, ground water containing  $92 \mu\text{g l}^{-1}$  of uranium.

Uranium concentrations were measured by the standard additions method.<sup>8</sup> When the analytical procedure was applied to  $0.5 \text{ M}$  nitric acid a small blank was obtained, as noted by Belew *et al.*<sup>1</sup> These workers reported that the blank could be made insignificant by adding sulphamic acid to the nitric acid before extraction. However, in this work no effect on the blank was observed when the aqueous solution was made  $0.1 \text{ M}$  in sulphamic acid.

The blank was not affected by ascorbic acid or by the presence of sodium chloride at concentrations of 0.1–0.5 M in the aqueous solution. When 0.5 M hydrochloric acid was used instead of nitric acid in the extraction step a blank was not obtained, but the extraction was not quantitative and the cyclohexane solution appeared to lose uranium rapidly, as judged from the polarographic peak heights obtained. Blanks were determined by extracting 50- or 100-ml samples of 0.5 M nitric acid with 3 ml of 0.1 M TOPO in cyclohexane (see Table I).

TABLE I  
DETERMINATION OF BLANKS

Volume of 0.5 M HNO <sub>3</sub> /ml	No. of determinations	Blank in cell solution (U)/ $\mu\text{g l}^{-1}$		Blank in sample (U)/ $\mu\text{g l}^{-1}$	
		Mean	Standard deviation	Mean	Standard deviation
50	4	367	45	44	5
100	5	647	35	39	2

The standard deviation of 5% in the blank for 100 ml of 0.5 M nitric acid can be attributed mainly to the variability in pipetting 2 or 3 ml of organic solvent and in the addition of the standard spike (a total of 3–4%) with a further 1% due to irreproducibility in the two measurements of peak heights. The larger standard deviation obtained for the 50-ml samples indicates some real variation in the blanks. The blank appears to increase slightly with time after the extraction step, and increases rapidly (more than 50% per hour) when the organic and aqueous layers are left in contact. In practice, the detection limit (standard deviation of 50%) was found to be approximately  $6 \mu\text{g l}^{-1}$  in the original sample if 100 ml of sample were extracted with 3 ml of 0.1 M TOPO in cyclohexane. Table II gives measured values for some solutions made up with uranyl nitrate in 0.5 M sodium chloride solution.

TABLE II  
DETERMINATION OF URANIUM IN STANDARD SOLUTIONS

Sample volume/ml	U present/ $\mu\text{g l}^{-1}$	U found/ $\mu\text{g l}^{-1}$	Error, %
50	428	421	–1.6
50	428	431	+0.7
100	119	116	–2.5
100	119	110	–7.5
100	60	63	+5.0
100	60	65	+8.3
100	10	9	–10
100	10	7	–30
100	10	7	–30
100	10	12	+20

Metal species tested for interference in the analytical method were vanadium(V), copper(II), iron(III), nickel(II), molybdenum(VI), cerium(IV) and lead(IV). They were tested by observing the effect that their presence at a concentration of  $60 \mu\text{g l}^{-1}$  for the first five or  $200 \mu\text{g l}^{-1}$  for the last two had on the size of the blank obtained. Only molybdenum(VI) interfered; most of the other metals were not extracted under the experimental conditions used.<sup>6,9</sup> The ascorbic acid reduces cerium(IV), iron(III) and vanadium(V) to non-extractable valence states.<sup>2</sup> Molybdenum(VI) gave a sharp peak at  $-0.33 \text{ V}$  versus S.C.E., which overlapped with the uranium peak, causing a positive error in the peak height (it also gave a peak at  $-0.60 \text{ V}$ ; see Fig. 2). A 100-ml solution containing  $134 \mu\text{g l}^{-1}$  of molybdenum(VI) gave a blank due to the molybdenum equivalent to  $45 \mu\text{g l}^{-1}$  of uranium in the aqueous solution when extracted with 3 ml of TOPO solution. It has been reported that molybdenum is extracted less when the concentration of nitric acid in the aqueous layer is increased.<sup>6</sup> However, the blank due to nitric acid increased rapidly with an increase in the concentration of the acid.

Of the natural waters analysed (ground waters from the Murchison District of Western Australia), significant amounts of molybdenum occurred, in general, only with higher uranium concentrations (greater than  $120 \mu\text{g l}^{-1}$ ). The highest concentration of molybdenum found

in the cell solution when analysing natural waters was about  $190 \mu\text{g l}^{-1}$  for a 50-ml sample containing  $190 \mu\text{g l}^{-1}$  of uranium. The molybdenum can be determined by spiking aqueous molybdenum into the cell solution and measuring the height of the molybdenum peak at  $-0.6 \text{ V}$ , but the uncertainty is high (about 30%) owing to the steepness of the base line and its greater variability (probably due to trace amounts of oxygen) at the more negative potentials (see Fig. 2, trace 3). The resultant error in the blank introduces a large error into the determination of uranium in natural waters that contain molybdenum (approximately 10% in the instance cited). Two typical polarographic traces of solutions derived from natural waters are included in Fig. 2. Results of duplicate determinations of uranium in some natural ground waters are given in Table III.

TABLE III  
DUPLICATE DETERMINATIONS OF URANIUM IN SOME NATURAL WATERS

Sample No.	Uranium/ $\mu\text{g l}^{-1}$	
	Analysis 1	Analysis 2
1	208	223
2	80	92
3	46	56
4	40	44

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### References

1. Belew, W. L., Fisher, D. J., Kelley, M. J., and Dean, J. A., *Microchem. J.*, 1966, **10**, 301.
2. Florence, T. M., in Florence, T. M., *Editor*, "Proceedings of a Symposium on the Analytical Chemistry of Uranium and Thorium," Australian Atomic Energy Commission, Sydney, TM552, 1970, p. 50.
3. Milner, G. W. C., Wilson, J. D., Barnett, G. A., and Smales, A. A., *J. Electroanalyt. Chem.*, 1961, **2**, 25.
4. Denson, N. M., Zelber, H. D., and Stephens, J. E., *Prof. Pap. U.S. Geol. Surv.*, No. 300, 1956, p. 673.
5. Fix, P. J., *Prof. Pap. U.S. Geol. Surv.*, No. 300, 1956, p. 667.
6. Schults, W. D., and Dunlop, L. B., *Analytica Chim. Acta*, 1963, **29**, 254.
7. Wolsey, W. C., *J. Chem. Educ.*, 1973, **50**, A335.
8. Meites, L., "Polarographic Techniques," John Wiley, New York, 1965, p. 398.
9. Horton, C. A., and White, J. C., *Analyt. Chem.*, 1958, **30**, 1779.

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