

SPECTROPHOTOMETRIC DETERMINATION OF URANIUM(VI)  
BY EXTRACTION OF ITS THIOCYANATE ANION  
WITH CATIONOGENIC TENSIDES

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The method is described of a spectrophotometric determination of U(VI) based on the extraction of its complex thiocyanate anion with a chloroform solution of 1-ethoxycarbonylpentadecyltrimethylammonium. The method is rapid and affords reliable results; 0.2 to 5  $\mu$ g of uranium can be determined in 1 ml of organic phase. Combination with a preliminary separation treatment is feasible.

Cationogenic tensides have recently been so employed for a spectrophotometric determination of U(VI) that they constituted the third component in the ternary complex of a binary mixture of  $\text{UO}_2^{2+}$  with, *e.g.*, chromazurol S (refs<sup>1-4</sup>) or eriochromcyanine R (refs<sup>5,6</sup>); the tensides used were cetylpyridinium bromide<sup>1-3,5</sup>, cetyltrimethylammonium bromide<sup>3,6</sup>, 1-ethoxycarbonylpentadecyltrimethylammonium bromide<sup>4</sup>, and others<sup>3</sup>. Cationogenic tensides can also be utilized in extraction photometric determinations of some metals in such a manner that the complex thiocyanate anions of the latter are extracted with a chloroform solution of 1-ethoxycarbonylpentadecyltrimethylammonium or other tensides soluble in chloroform<sup>7</sup>. The present work is a brief contribution to the problem of determination of U(VI) by this extraction method.

## EXPERIMENTAL

### Chemicals and Apparatus

Uranyl nitrate solution ( $c = 10^{-2} \text{ mol l}^{-1}$ ) was prepared by dissolution of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ ; the uranium content was checked by determination with oxine. 1-Ethoxycarbonylpentadecyltrimethylammonium bromide (CPTB, Septonex) solution in chloroform,  $c = 6 \cdot 10^{-3} \text{ mol l}^{-1}$ , was prepared by dissolving 0.6340 g of the chemical in the solvent and diluting to 250 ml. The buffer solution (pH 1.2) was prepared by mixing 260 ml of 1 M-HCl with 200 ml of 1M-CH<sub>3</sub>.COONa. Used were also 2.5M-KSCN, 0.1M Chelaton 3, 2M-KCl, Amberlite IRA 400 ion exchanger (grain size 100–200 mesh); salts of the cations used were also reagent grade chemicals.

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The spectrophotometric measurements were performed on Specord UV VIS (Zeiss, Jena) and SP 8-100 (Pye-Unicam, Cambridge) spectrophotometers using cells of the optical path length 1 cm. The pH measurements were carried out on a PHM 62 instrument (Radiometer, Copenhagen).

## RESULTS

The complex uranyl thiocyanate anion is extracted with chloroform solution of 1-ethoxy carbonylpentadecyltrimethylammonium bromide (CPTB). The extract of the presumed ionic associate exhibits the maximum absorbance at 300 nm, where the absorbance of the blank extract is virtually zero. The measurements were therefore carried out at this wavelength. The conditions suiting best to the extraction of uranium, *i.e.* the pH of the aqueous phase, the thiocyanate concentration, *etc.*, were also sought. No extraction was observed to occur from phosphoric acid solutions. Extracts from nitric acid solutions displayed a variable absorbance at 333 nm and those obtained from blank experiments were of yellow colour. The extraction can be performed from dilute sulphuric or hydrochloric acid, pH 1 to 2, the extracts from the latter acid exhibiting a higher absorbance. The subsequent experiments were therefore carried out using buffers containing hydrochloric acid combined with sodium acetate, or glycine, and potassium chloride. As identical results were obtained, combination with sodium acetate giving pH 1.2 was used in the further study.

After finding the optimum acidity, some other conditions were also investigated. Satisfactory results of extraction were obtained when the thiocyanate concentration in the aqueous phase was at least  $0.3 \text{ mol l}^{-1}$  and  $6 \cdot 10^{-3} \text{ M}$ -CPTB solution in chloroform was employed. The extraction procedure is comparatively fast, the aqueous

TABLE I  
Results of determination of uranium by five replicate experiments

Sample No	Uranium added $\mu\text{g}$	Uranium found $\mu\text{g}$	Relative standard deviation, %
1	1.20	$1.29 \pm 0.06$	3.8
2	3.60	$3.76 \pm 0.17$	3.9
3	6.00	$5.50 \pm 0.24$	3.4
4	9.00	$9.14 \pm 0.30$	2.6
5	12.00	$12.00 \pm 0.17$	1.2
6	15.00	$15.22 \pm 0.36$	1.9
7	21.00	$20.88 \pm 0.41$	1.6

phase being extractable after as little as one minute's standing and a one-minute extraction being also sufficient. The organic phase then contains 95.2% of the uranium initially present in the aqueous phase, and the extract is steady for a minimum of 24 h. The ionic strength of the aqueous phase is about 0.5; it was raised to 1.2 by adding potassium chloride, whereupon the absorbance of the extract showed a 3% increase.

Beer's law is obeyed over the concentration region of  $0.2-5.0 \mu\text{g ml}^{-1}$  U in the organic phase; the calibration straight line equation obtained was  $y = (0.0540 \pm 0.0010)x + (0.0440 \pm 0.0086)$ , where  $y$  stands for the absorbance and  $x$  for the uranium concentration in the organic phase in  $\mu\text{g ml}^{-1}$ , the standard deviation characterizing the scatter of the points around the regression straight line was 0.0196. The data are given in Table I.

The effect of some elements on the extraction determination of uranium was also examined. Of those elements that are extracted as complex thiocyanate anions, the following interfere in amounts lower than the present amount of uranium: Hg(II), Ti(IV), Mo(VI), W(VI), Co, Fe(III), Bi, Ta, Pd, Ru(III), Pt(IV), and Au(III). On the other hand, five-fold excess of Zr(IV), ten-fold excess of Ni, Pb, Al, or Mg, and fifty-fold excess of Ca do not interfere. Of anions, phosphate does interfere, whereas ten-fold excess of fluoride and, naturally, excess of sulphate or chloride do not, nor does Chelaton 3 in concentration  $3 \cdot 10^{-2} \text{ mol l}^{-1}$ . In view of the fact that the studied determination of U(VI) is affected by a number of elements, the selectivity of determination being not appreciably improved by Chelaton 3, separation of uranium on Amberlite IRA 400 ion exchanger was tested for this method, similarly as in the previous work<sup>1</sup>. In this case, the calibration plot was constructed after the uranium separation; the equation  $y = (0.050 \pm 0.004)x + (0.020 \pm 0.001)$  was obtained. The separation was carried out on a synthetic sample in which 9.0  $\mu\text{g}$  of uranium was accompanied by (in  $\text{mg ml}^{-1}$ ): Fe(III) 0.2, NaF 0.1, Al(III) 0.2,  $\text{NH}_4\text{NO}_3$  0.5,  $\text{Na}_2\text{SiO}_3$  20, and  $\text{H}_2\text{SO}_4$  20. After separation on the anion exchanger,  $8.7 \pm 0.5 \mu\text{g}$  U was found by 8 replicate determinations; the relative standard deviation was  $s_r = 6.8\%$ .

Extraction was also investigated of tetravalent uranium prepared by reduction with zinc metal and ascorbic acid<sup>8</sup>; it was found to be extracted as well, affording the same absorbance values as hexavalent uranium.

In the same conditions, U(VI) was extracted also by  $5 \cdot 10^{-3} \text{ M}$  chloroform solutions of dimethylallylbenzylammonium bromide (Ajatin) or tetradecyldimethylbenzylammonium bromide (Zephiramine); the same results were obtained as with CPTB.

*Working procedure:* To a solution containing 1–25  $\mu\text{g}$  of U(VI) are added 2 ml of buffer and 1.2 ml of 2.5M-KSCN. The system is diluted to 10 ml with redistilled water and after 1 min, extracted with 5 ml of  $6 \cdot 10^{-3} \text{ M}$ -CPTB for 1 min. The extract is made clear by filtration over a cotton wool plug, and its absorbance is measured at 300 nm using the CPTB solution in chloroform as the reference system.

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