

THE SELECTIVE EXTRACTION AND DETERMINATION OF URANIUM USING DIPHENYL ACETIC ACID

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It has been found that a benzene solution of diphenyl acetic acid is suitable for the extraction of uranyl ions from alkaline aqueous solutions. Addition of nitrilotriacetic acid to the aqueous phase renders the extraction selective for uranium in the presence of iron(III), nickel(II), lead(II), zinc(II), cobalt(II), cadmium(II), manganese(II), copper(II), chromium(IV), and molybdenum(VI) by selective masking of these ions. Gold(III) and platinum(IV) were found to interfere slightly. Transfer of the uranium into the organic phase is virtually quantitative after two extractions. Polarographic and spectrophotometric determinations were studied; in the latter case, dibenzoylmethane is added to the organic extraction phase as a colorimetric reagent. The polarographic determination is preferably performed after re-extraction of the uranium into aqueous solution (0.5M-KCl-0.5M-HCl). The former method provides a wider useful concentration range (10^{-5} to $5 \cdot 10^{-3}$ M-U(VI) in the extract) than the latter (10^{-5} to $2 \cdot 10^{-4}$ M-U(VI) in the extract); however, the latter has greater accuracy ($\pm 3\%$) than the former ($\pm 5\%$) as well as being more simple.

In a number of recent works¹⁻⁴, the use of phenyl acetic acid and its derivatives as extracting agents for the selective determination of various metals has been discussed. These reagents seem to have broad usefulness and problems of selectivity can generally be solved by judicious choice of complexing agents. In a recent study⁵, we discussed the extraction and polarographic determination of uranium using a chloroform solution of methyltrioctylammonium chloride for the extraction, followed by re-extraction into aqueous solution for the determination. This procedure greatly improved the selectivity of the determination over that previously reported⁵, but a number of elements (notably Mo, Au and the platinum metals) still interfered.

In this work it was decided to undertake a study of the selective extraction and determination of uranium using a benzene solution of diphenyl acetic acid as extractant. It was also felt to be of interest to compare the polarographic determination, performed similarly as in the previous case⁵, with the spectrophotometric determination carried out on the organic phase to which dibenzoylmethane^{6,7} had been added prior to the determination as a colorimetric reagent.

EXPERIMENTAL

Chemicals and solutions. 0.005 and 0.05M uranyl sulphate solutions were prepared as described previously⁵. 0.5M diphenyl acetic acid solutions in pure benzene were employed. For spectrophotometric determinations, dibenzoylmethane was added to this solution to give a final concentration of 0.09M. Nitrilotriacetic acid was used as a 0.5M solution in 1M-NaOH. A saturated solution of hexamethylenetetraamine (hexamine) was employed for pH adjustment. The remaining metal ion solutions were prepared from analytical grade chemicals and were standardized complexometrically.

Apparatus. Polarographic measurements were carried out using a Kalousek cell and the OH-102 polarograph (Radelkis, Hungary). Spectrophotometric measurements were made on the spectrophotometer „Specord UV-VIS“ (Zeiss, Jena).

RESULTS

The Polarographic Determination of Uranium

In hydrochloric acid solutions, UO_2^{2+} is reduced in two steps, giving polarographic waves at -0.18 V (s.c.e.) and about -1.0 V (s.c.e.) (the half-wave potential of the latter depending on the acidity of the solution), corresponding to one electron and to a maximum of two electrons, respectively⁸⁻¹⁰. The use of the second wave for analytical purposes has not been recommended, due to its dependence on the pH,

TABLE I

The Determination of Uranium in the Presence of Various Metals

0.270 mg of uranium taken. Results obtained by spectrophotometric method.

Ion added	Amount mg	Molar excess over UO_2^{2+}	UO_2^{2-}	
			amount found mg	error %
Fe(III)	5.6	100	0.27	0
Ni(II)	5.9	100	0.26	- 2.1
Pb(II)	20.7	100	0.26	- 2.1
Zn(II)	6.5	100	0.26	- 2.1
Co(II)	6.0	100	0.28	+ 2.2
Cd(II)	11.2	100	0.27	0
Mn(II)	5.5	100	0.27	0
Cu(II)	6.4	100	0.26	- 2.1
Cr(VI)	5.2	100	0.28	+ 2.2
Mo(VI)	9.6	100	0.28	+ 2.2
Au(III)	4.9	25	0.30	+ 11
Pt(IV)	1.95	10	0.31	+ 13

presence of maximum suppressors, *etc.* and most applications have concentrated on use of the first wave^{9,11}. As has been pointed out in a previous work⁵, even use of the first wave does not provide very great selectivity, and a number of methods have been devised for avoiding interferences, particularly from iron(III), molybdenum(VI), cerium(IV), chromium(VI), vanadium(V), gold and the platinum metals⁵.

It was found that the first uranium reduction wave in 0.5M-KCl-0.5M-HCl medium has a half-wave potential of -0.200 V (S.C.E.) and that the diffusion-controlled current is linearly dependent on the uranium(VI) concentration, as theoretically predicted⁹, in the concentration range 10^{-5} M to $5 \cdot 10^{-3}$ M. The determination in freshly diluted solutions was accurate to $\pm 2\%$. The reproducibility of the measured values was $\pm 1\%$.

When this determination method was combined with prior extraction using a 0.5M benzene solution of diphenyl acetic acid (DPA) (discussed in detail below), followed by re-extraction into the base electrolyte solution (0.5M-KCl-0.5M-HCl), the accuracy of the method decreased to $\pm 5\%$; the precision was similar. However, the useful concentration range, applying to the re-extracted aqueous phase was identical to the determination in the absence of extraction.

The Spectrophotometric Determination of Uranium

Přibil and Jelinek⁶ and Joe, Will and Black⁷ have pointed out that reaction of uranium(VI) with dibenzoylmethane (DBM) provides a rapid and accurate method for the quantitative determination of uranium. A number of papers have been published describing the extraction of uranium with various reagents and subsequent determination of the uranium in the organic phase using DBM (refs¹³⁻¹⁵). However, cations and especially anions were frequently found to interfere¹⁵ and it was felt of interest to find an extraction method with improved selectivity.

The DBM - uranium(VI) complex in benzene exhibits two absorption maxima, a sharp peak at 417 nm and a broader shoulder at 446 nm. The absorbance decreases sharply at about 410 nm and again below 400 nm. The absorbance at 417 nm, measured against the appropriate blank, was found to depend linearly on the uranium(VI) concentration in the range 10^{-5} M to $2 \cdot 10^{-4}$ M-U(VI) in the extract. Prior extraction of the uranium from alkaline aqueous solution into an organic phase, using DPA as extractant and containing DBM as colour forming reagent, is without effect on the determination and results in an accuracy of $\pm 2\%$ (the precision also equalled $\pm 2\%$).

Thus the polarographic method is useful for a broader range of uranium concentrations, while the spectrophotometric method is somewhat simpler, involving only one extraction step, and is more accurate and precise.

Characteristics of the Extraction of Uranium(VI) with DPA-Benzene

The extraction of uranium(VI) from alkaline aqueous media using a diphenylacetic acid-benzene solution was found to be more efficient than the identical extraction using chloroform as the organic medium. In the former case, virtually complete extraction occurred using only two 5 ml benzene-DPA aliquots, whereas using identical amounts of chloroform-DPA led to negative errors. These errors could be eliminated by increasing the number of extractions to three or more; similar arguments apply to the re-extraction of uranium into the aqueous phase, employed during the polarographic determination of uranium(VI).

Because of the difficulties encountered previously in determining uranium(VI) in the presence of various metal ions using the two described methods^{5,6}, a number of cations were tested for their effect on the extraction procedure. The results obtained were identical irrespective of the determination procedure employed, being given by the extraction characteristics. It was found that addition of 5 ml of nitrilotriacetic acid (0.5M) to the extracted aqueous solution prevents simultaneous extraction of a 100 times excess (molar) of iron(III), cadmium(II), nickel(II), lead(II), zinc(II), cobalt(II), manganese(II), copper(II), chromium(VI), and molybdenum(VI) by preferential complexation of these ions (Table I). Gold(III) is reduced by NTA and interferes only slightly. It was found that the calculated uranium(VI) concentration was about 10% higher in the presence of a 25 times molar excess of gold(III), provided that the metal solution mixture with NTA was left to stand one hour prior to extraction. Platinum(IV) causes a greater interference, the uranium concentration appearing to increase by more than 10% in the presence of a ten times molar excess of platinum(IV). Both these interferences can be eliminated by the use of standard solutions containing the same amount of the interfering metal. The results obtained using polarographic determination did not differ substantially from those given in the table, except that the error of determination was slightly higher (as has already been discussed). The interference from various elements is identical, being given by the extraction procedure rather than by the final determination step.

Procedure for the Analysis

The uranium sample solution is transferred to a 250 ml separating funnel and, if necessary, 10–20 ml of water are added. Then 2 ml of hexamine solution and 5 ml of nitrilotriacetic acid are added (the latter amount may be increased if larger amounts of interfering elements are present). The mixed solution is then extracted twice with 5 ml portions of DPA-benzene solution. (For spectrophotometric measurements, DPA-benzene containing dibenzoylmethane is employed. This ensures an identical concentration of colorimetric reagent in all determinations and provides a „ready-made“ blank for the optical measurement.) The benzene extracts are combined and, in the case of spectrophotometric determination, their absorbance at 417 nm is measured against a blank benzene-DPA-DBM solution (the extractant solution). For the polarographic determination, the combined extracts are re-extracted twice with 5 ml portions of the 0.5M-KCl-

-0.5M-HCl base electrolyte solution. The combined solutions are then polarographed in the usual manner, measuring the current between 0 and -0.500 V, or the diffusion current at -0.500 V. For both determinations, the uranium concentration is then calculated by referring to the appropriate calibration curve.

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