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BT-8Solubility of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in Ethyl Acetate. In the Sep-

tember report, the solubility of uranyl nitrate in ethyl acetate was given as 400 grams in 100 grams of pure solvent. The determination was repeated. A supersaturated solution was seeded and allowed to come to equilibrium at 26°. Samples of the solution were analyzed by converting the solute to U_3O_8 . The solution was found to contain 66.74% $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ or 200.7 grams per 100 g. solvent. The anhydrous ethyl acetate used was obtained from Carbide and Carbon Chemical Corporation with the following specifications: 99% pure, not denatured, B.P. range 75°-85°C.

Preparation of Pure $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$. Commercial $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was found to contain considerable UO_3 . It was recrystallized by dissolving it in water, adding excess nitric acid and filtering. After two recrystallizations from water, it still contains some excess HNO_3 .

Distribution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ between CH_3NO_2 and H_2O . 10 grams of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (Baker and Adamson, C.P.) were dissolved in 5 ml. of CH_3NO_2 , which had been dried and redistilled, and a total of 2.25 ml. of water was added. Upon addition of the first milliliter of water, the system separated into two liquid phases. After the addition of the remaining 1.25 ml. of water, the two liquid phases were about equal in volume and in equilibrium with the excess solute. The aqueous phase was the more dense. The concentration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ in the two layers was determined approximately by evaporating the solvent and weighing the residue:

CH_3NO_2 phase	48% $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$
H_2O phase	79% "

Photostat Price \$ 1.80

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More accurate results were obtained by analyzing samples of the solutions gravimetrically, by converting the salt to U_3O_8 :

CH_3NO_3 phase	38.23%	$UO_2(NO_3)_2 \cdot 6 H_2O$
H_2O phase	71.01%	"

It is apparent that the rough method of estimating the concentration of the solution may at times lead to very large errors.

Thermal Decomposition of $UO_4 \cdot 2 H_2O$. Upon adding hydrogen peroxide to a solution of uranyl nitrate, uranium tetroxide separates with a considerable amount of water of hydration. When the product is heated in vacuo at $50^\circ C$, water is readily lost until the composition corresponds to the dihydrate, $UO_4 \cdot 2 H_2O$. This compound loses oxygen extremely slowly up to $125^\circ C$. Above this temperature it decomposes, losing both water and oxygen, and if heated just above 325° it ultimately yields the trioxide, UO_3 . However, the manner in which the decomposition proceeds is dependent upon the rate of heating; if the dihydrate is maintained at around $125^\circ C$ for a period of 24 hours, the water can be nearly completely removed while over half of the excess oxygen remains combined. An anhydrous oxide, containing oxygen beyond that corresponding to UO_3 and capable of existence up to at least 325° , may thus be prepared. The nature of this new oxide is not apparent from the data available. A comparison of the properties of hydrated uranium tetroxide and the new oxide show striking dissimilarities. $UO_4 \cdot 2 H_2O$ is only slightly soluble in $4 N H_2SO_4$, with no loss of oxygen, and the resulting solution shows the characteristic reaction of peroxy-compounds in that it reduces $KMnO_4$. When the new oxide is put into acid or water, all of the excess oxygen is evolved immediately; the UO_3 left behind dissolves, if the solution is acid, or remains suspended if pure water is used. The solution produced when the

new oxide is decomposed by contact with dilute sulfuric acid does not reduce KMnO_4 .

Comparison of Methods of Analyzing Solutions of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$.

The methods which were used for the analysis of solutions of uranyl nitrate were (1) the gravimetric, in which U_3O_8 is weighed; (2) the volumetric, in which the uranium is reduced in solution and titrated with standardized $\text{K}_2\text{Cr}_2\text{O}_7$; and (3) the conductance method, in which the concentration of uranyl nitrate is determined by measuring the conductivity of the solution under carefully controlled conditions. These methods give concordant results, when carried out on aliquot parts of a solution of pure $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$.

1. Gravimetric Method

The solution is heated nearly to boiling and made alkaline with carbon dioxide-free ammonium hydroxide*. The precipitated

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* Distilled water was freed from dissolved gases by displacement with purified nitrogen; the water was then saturated with ammonia and diluted.

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ammonium di-uranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, was caught on ashless filter paper, ashed and ignited in a platinum crucible to U_3O_8 .

2. Volumetric Method (Kolthoff and Sandell, page 579)

The sample is evaporated on a steam bath, treated with concentrated H_2SO_4 and heated in a 500 ml Erlenmeyer flask, in an oil bath with the temperature increasing from 135° to 175°C in 15 minutes, with a stream of clean air directed at the surface of the liquid. This effectively removes the nitrates. The concentration is adjusted to give 100 ml of dilute H_2SO_4 (1 pt. H_2SO_4 : 20 pts. H_2O), the solution is reduced in an amalgamated zinc (Jones) reductor, clean air is bubbled through it for a few minutes to oxidize U^{III} to U^{IV} and the sample is titrated, using a weight burette,

with 0.1 N $K_2Cr_2O_7$, using barium diphenylamine sulfonate as an indicator.

3. Conductance Method

The sample of known volume is washed into a calibrated conductivity cell and diluted with equilibrium conductivity water (specific conductance = 1.0×10^{-6} mhos) until the total volume of the solution is 100 ml. The cell is brought to temperature in an oil thermostat at $25.000 \pm 0.004^\circ C$, and the specific conductivity determined at frequencies of 1000 and 4000 cycles. The concentration is read from a plot of conductance values of solutions of $UO_2(NO_3)_2 \cdot 6 H_2O$ of known concentrations. Such a series of conductances is given in Table 1.

TABLE 1

Specific Conductance of Solutions of Uranyl Nitrate

Concentration of $UO_2(NO_3)_2 \cdot 6 H_2O$	Specific Conductances $K_{25^\circ C}$
2.499%	0.01788 Mhos
2.151	.01566
1.653	.01236
1.363	.01043
1.085	.008504
0.8165	.006584
.5898	.004910
.4387	.003758
.3300	.002903
.2486	.002244
.1795	.001668
.1114	.001078
.07072	.0007111
.03934	.0004113

Solutions of uranyl nitrate in pure water are quite stable, the conductivity remaining constant over a period of several days. The amount of uranium in the solutions, determined by measurement of the specific conductance, agrees very well (within a percentage error of 0.2%) with the analyses carried out by standard gravimetric and volumetric procedures.

4. Reliability of the Three Methods

Checks on the methods were run by three operators, each one using one of the methods. The results are tabulated in Table 2.

TABLE 2

Comparison of Results on the Analysis of Solutions of Uranyl Nitrate by the Gravimetric, Volumetric and Conductance Methods

<u>Series No.</u>	<u>Gravimetric Method</u>	<u>Volumetric Method</u>	<u>Conductance Method</u>
1	23.82 %U 24.01	23.93 %U 24.02	- -
2	17.42 %U 17.42	17.49 %U 17.42	- -
3	31.76 %U 31.76 31.75 31.76	31.81 %U 31.84 31.80	31.77 %U 31.81 31.81 31.78
	av. 31.757	av. 31.816	av. 31.792

Effect of Ether on the Conductance of Aqueous Solutions of Uranyl Nitrate. Since there was a possibility that in the distribution experiments (see below) the aqueous solutions of uranyl nitrate might be contaminated with ethyl ether, the effect of ether on the conductance of a solution of uranyl nitrate was investigated. After dilution in the conductance cell, the concentration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was 0.5250% and the specific conductance was 0.004425 mhos. Addition of small quantities of ether produced a linear decrease in the conductivity. The decrease in conductance is much greater than would be predicted by dilution effect, and may be due to some interaction, such as complex formation or actual chemical reaction. The results are given in Table 3 and shown graphically in Figure 1.

TABLE 3

	<u>% ether</u>	<u>K</u>	<u>% decrease in K</u>
A	0	0.004425	0
B	0.075	0.004411	0.316
C	0.135	0.004400	0.564
D	0.193	0.004384	0.814
E	0.247	0.004378	1.062
F	0.923	0.004228	4.4452

Analysis for Uranium in the Presence of Ether. An aqueous solution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was shaken with peroxide-free ether over a period of 1-1/2 hours and allowed to settle for 9 hours. The layers were separated and collected in clean, brown, glass-stoppered bottles. Samples of both the ether-rich phase and the water-rich phase were weighed out and analyzed by the three methods - gravimetric, volumetric and conductance. With Series No. 4, an attempt was made to detect the action of light; one bottle was exposed to a bright light for several hours, and a duplicate sample was kept in the dark. In analyzing the solutions by the conductance method, the ether was first removed at room temperature, after addition of water, by blowing air over the surface of the solution for 1-1/2 hours, or until the odor of ether could no longer be detected. The results are given in Table 4.

TABLE 4

Distribution of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ between Water and Ether - Comparison of Analyses by Gravimetric, Volumetric, and Conductance Methods

Series No.	Layer	Concentration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ - %		
		Gravimetric	Volumetric	Conductance
1	water	26.07	26.18	-
		26.09	26.26	-
	ether	21.11	20.97	-
		20.98	20.66	-
2	water	23.96	-	23.42
		23.98	-	22.83
			-	22.82
	ether	16.37	-	16.50
		16.33	-	16.32
			-	
3	water	27.03	27.20	26.91
		27.06	27.00	26.90
			26.98	
	ether	22.90	22.67	23.21
			22.88	23.31
			22.98	23.11

4 Influence of light

a. Exposed to strong light

water	-	27.25	27.03
		27.21	27.05
ether	-	23.34	23.61
		23.36	23.68

b. Not exposed to light

ether	-	-	23.80
			23.80

It will be recalled that the results of analysis of the pure aqueous solutions of uranyl nitrate by each of the three methods are in reasonable agreement; the conductance method of analysis is just as reliable for aqueous solutions of uranyl nitrate as the gravimetric and volumetric techniques. In the distribution experiments, the analyses by the gravimetric and volumetric techniques are in reasonably good agreement, but the conductance method fails to

give concordant results. In the water layer, the percentage of uranyl nitrate computed to be present from the results of conductance measurements is too low, and in the ether layer it is too high. Exposure of the ether layer to light for several hours has the effect of lowering the conductance somewhat. The amount of ether remaining in the solution is too small to have an appreciable depressing effect on the conductance. We may conclude that effects of the type observed must be due to reaction rather than to the presence of small amounts of ether, and that the conductance method of analysis is not suitable for this system. The gravimetric and titration methods are, however, both satisfactory, and the titration method has the advantage of being much more rapid.

Charles A. Kraus

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