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MADISON SQUARE AREA
Report A-2903
ANALYTICAL INFORMATION REPORT
For the Period
1 June --- 30 June 1945

CH. WALKER

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MADISON SQUARE AREA
MANHATTAN DISTRICT
CORPS OF ENGINEERS

1 July 1945

1. The following report has been received from the Princeton Analytical Group, Princeton, N.J. N.H. Furman, Leader.

CONDUCTANCE OF URANYL NITRATE IN DIETHYL ETHER

by

R. J. Mundy

Conductivity measurements of uranyl nitrate hexahydrate and uranyl nitrate dihydrate in diethyl ether have been made with the aim of obtaining fundamental information that would be of value in defining the mechanism of ether extraction.

The uranyl nitrate used was a C.P. product of Mallinckrodt Chemical Works (Lot M-4264YD01). Calculations from an assay indicated 5.78 moles of water per mole of uranyl nitrate. This decrease in water content was undoubtedly brought about by partial efflorescence of the salt. The uranyl nitrate dihydrate was prepared from the above hexahydrate by drying to constant weight at 65 to 90°C. Exactly two moles of water per mole of uranyl nitrate was found from calculations of an assay. The ether used in these determinations was prepared by treating C.P. diethyl ether with sodium to remove the water, and distilling over lime in a system protected from atmospheric moisture.

The conductance measurements were made with a dip cell having a cell constant of 0.102, a conductivity bridge with a range of 0.2 to 250,000 ohms, and a resistance box covering a range of 0.1 to 10,000 ohms. Measurements were made by obtaining a balance with the conductivity bridge and then replacing the cell with the standard resistance box which was adjusted to the balance point of the conductivity bridge. The values indicated by the resistance box were considered more reliable than the values given by the conductivity bridge, and were the ones used to calculate the conductance. In most cases the difference between the values of the resistance box and the conductivity bridge were substantially less than 1 per cent. The temperature at which the measurements were made was within a few degrees of 25°C, and a temperature correction curve was determined for each system and applied to the measured values.

Conductivity measurements were made on the hexahydrate in two different ways. A nearly saturated solution of uranyl nitrate hexahydrate was prepared by dissolving the salt in absolute ether. During the dissolving, part of the water of crystallization is left behind and produces a water phase.

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In one case the ether was separated from the water phase, and measurements made on the ether at different uranyl nitrate concentrations by diluting with absolute ether. In the other case, the water was left in contact with the ether phase, and measurements at different concentrations were made by adding absolute ether, shaking, and allowing the water to settle completely before taking a reading. The conductance of the dihydrate was made in the same manner as that of the hexahydrate except no water phase was obtained on preparing a nearly saturated solution in ether.

The values of the equivalent conductance of these systems are given in Table I and Figure 1. The concentration of uranyl nitrate in the cases where no aqueous phase was present was obtained from calculations of the initial concentration and the volume of ether used in diluting. The concentration of uranyl nitrate in the system in which a water phase was present was obtained by analysis of the ether each time a reading was taken.

The equivalent conductance increases with increasing concentration of uranyl nitrate. This is the reverse of the normal trend in aqueous solutions. However, numerous cases are listed in the literature where this reverse direction takes place in organic solvents. A few such cases are, silver nitrate, cadmium nitrate, and ferric chloride in amyl amine (2), hydrochloric acid in ether (1,4) and in amyl alcohol (1), and arsenic bromide in methyl ethyl ether (5). Many cases of organic solutes in inorganic low dielectric solvents also produce this effect. Qualitative tests in this laboratory revealed that nitric acid and ferric chloride in diethyl ether, and uranyl nitrate in dibutyl cellosolve likewise bring about an increase in equivalent conductance as the concentration increases. Both the uranyl nitrate and the ferric chloride used in these tests were hexahydrate salts. Concentrated solutions of these salts were prepared, and conductivity measurements were made at different stages of dilution after removing the water phase that formed in both cases.

The data of Kraus and Fuoss (3) show that the conductance of isoamylammonium nitrate and other solutes, in a mixture of dioxane and water is dependent upon the dielectric constant of the solvent. When the dielectric constant of the solution is less than 12, the equivalent conductance decreases at first with decreasing concentration, and then increases on further dilution at about 0.01 normal. When the solvent contains a larger amount of water, the dielectric constant increases and the abnormal effect disappears. The equivalent conductance under these conditions assumes the normal form of decreasing continuously with increasing concentration of solute.

Apparently the abnormal conductance of uranyl nitrate in diethyl ether results from the low dielectric constant of the solvent. Conductivity

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measurements at lower concentrations could not be obtained with the apparatus available for these determinations. It is quite possible that the equivalent conductance might have been found to increase with further dilution in extremely dilute solutions. The equivalent conductivities of other systems previously mentioned, show an increase with increasing concentration in moderately strong solutions, while at higher concentrations the conductance decreases with increasing concentration. The two curves in Figure 1 for the hexahydrate show this trend.

A comparison of the curves for the dihydrate and the hexahydrate in Figure 1, appears to indicate that the increased conductance at higher concentrations is due to the increased amount of water which accompanies the uranyl nitrate and which changes the nature of the solvent in a manner such that it more nearly approaches that of water. There is no satisfactory means of determining the degree of dissociation of uranyl nitrate in the ether from the figures in Table I. However, comparison of the highest equivalent conductance obtained in ether with that in water at infinite dilution reveals a ratio of about 1:1000. Although this cannot be considered as the true degree of dissociation, it does indicate that the dissociation of uranyl nitrate in diethyl ether is slight.

Table I

Conductance Of Uranyl Nitrate In Diethyl Ether

<u>Grams of Anhyd. Uranyl Nitrate per liter</u>	<u>Volume in cc containing an eq. weight of uranyl nitrate</u>	<u>Equivalent Conductance at 25°C</u>
Hexahydrate - Water phase left in contact with ether		
632	312	0.221
453	435	0.286
340	579	0.231
268	736	0.159
217	907	0.109
182	1081	0.0721
156	1261	0.0532
120	1642	0.0325
97.4	2025	0.0232
81.6	2418	0.0182
65.0	3036	0.0110
45.9	4293	0.00555

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Table I (Cont'd)

<u>Grams of anhyd. Uranyl Nitrate per liter</u>	<u>Volume in cc containing an equal weight of uranyl nitrate</u>	<u>Equivalent Conductance at 25°C</u>
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Hexahydrate - Water phase separated from ether

602	327	0.217
526	375	0.240
468	421	0.244
421	468	0.231
383	514	0.208
351	562	0.182
324	608	0.149
300	657	0.131
281	702	0.109
263	750	0.0908
236	835	0.0598
206	956	0.0401
183	1080	0.0280
150	1310	0.0156

Dihydrate

650	303	0.160
578	341	0.132
520	379	0.0839
473	417	0.0527
433	455	0.0336
400	493	0.0220
371	531	0.0153
347	568	0.0113
306	648	0.00707
274	719	0.00505
217	908	0.00294

Ether containing dihydrate was saturated with water

157	1250	0.0608
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FIGURE I

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2. The following report has been received from the Princeton Analytical Group, Princeton, N.J., N.H. Furman, Leader.

THE DETERMINATION OF BORON IN SODIUM HYDROXIDE
AND SODIUM CARBONATE

by

John A. Nyitrai

In the routine determination of boron in uranium by the distillation procedure, one gram of the sample is dissolved in ten ml of phosphoric acid (low in boron) in a quartz reaction flask. Two successive 50 ml portions of methyl alcohol are then distilled through the reaction mixture and the distillate collected in a No. 728 Corning receiving flask. Since the presence of even small amounts of water in the reaction mixture lowers the values obtained by this method, it is essential that all apparatus be thoroughly dry and that other precautions be taken to exclude moisture.

Inasmuch as the reaction of sodium hydroxide and sodium carbonate with phosphoric acid produces water, a slight modification of the usual procedure is necessary. A one-gram sample of the alkali is first dissolved in about five ml of water in a quartz flask, and the solution is neutralized with phosphoric acid. To this solution is added five ml of a 0.1 N boron-free calcium hydroxide suspension to render it alkaline, and it is then evaporated to dryness in an oven at a temperature of 100°C.

After allowing the dry sample to cool, ten ml of phosphoric acid are added and the distillation is carried out in the usual manner. The distillate is diluted to 100 ml in a volumetric flask, a suitable aliquot is taken, depending upon the amount of boron present in the sample, and the determination is completed as described in Report A-133.

Three distillations are run simultaneously. Two are regular samples and the third is a blank. The blank contains five ml of 0.10 N calcium hydroxide suspension, previously evaporated to dryness in a quartz flask, plus an amount of phosphoric acid in excess of ten ml which was required to neutralize the sodium hydroxide and the sodium carbonate samples. After each distillation, the apparatus is flushed clean by distilling 25 ml of methyl alcohol through it and then allowing it to dry. Flasks are rinsed in tap water, then three times with distilled water, and finally dried in an oven.

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Rough, preliminary estimations on the recent samples of sodium hydroxide indicated fairly large amounts (12-16 ppm) of boron and so half-gram samples were taken, the color being developed on a 1/5 aliquot (20 ml) of the distillate. However, since the sodium carbonate samples were found to be very low in boron (0.0-0.5 ppm), larger samples are needed to obtain accurate results.

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3. The following report has been received from the laboratory of the Linde Air Products Company, Tonawanda, N.Y.

THE DETERMINATION OF URANIUM AND VANADIUM IN
PLANT DIGESTION LIQUORS

by

W.N. Moore
E.L. Morehouse

There has constantly been a need for a method for the determination of uranium in the vanadium-containing plant liquors, which is simpler and faster than the standard cupferron method.

The lead acetate-sodium fluoride method herein described proves to be as precise and accurate as the cupferron method, and at the same time is simple and fast. It presents no particular hazards in its operation, as is the case with the cupferron method.

In the new method the vanadium is separated from uranium as lead vanadate in a buffered acetic acid-sodium acetate solution. The uranium is held up by the use of sodium fluoride.

This method is not suitable for solutions containing iron, but, as iron is usually removed with the ore tailings during the primary soda ash treatment, plant liquors are generally iron-free.

The standard cupferron procedure and the new lead acetate-sodium fluoride procedure for the determination of uranium are described. The present procedure for the determination of vanadium is also described along with a new method suitable for use with the lead vanadate separation.

A comparison of analyses of Ceramic Plant liquors for uranium and vanadium obtained using both methods is listed.

Determination of Uranium in Plant Digestion Liquors

Cupferron Method

Pipette 100 ml liquor into a 400 ml beaker and carefully acidify with dilute sulfuric acid (1:1) using litmus paper as indicator. Add 10 ml excess dilute sulfuric acid for each 100 ml solution. Heat to boiling and add potassium permanganate solution (2.5 per cent) dropwise until a permanent

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pink color persists. Pass hydrogen sulfide through the hot solution for 15 minutes. Boil out the excess hydrogen sulfide, add 1 gram ammonium persulfate and continue boiling the solution for ten minutes to destroy the excess persulfate. Again pass hydrogen sulfide into the hot solution for 15 minutes. Let settle and filter through a No. 30 paper containing a little pulp and wash with five per cent sulfuric acid saturated with hydrogen sulfide. Discard the residue.

Boil the filtrate ten minutes to remove the hydrogen sulfide, adjust to ten per cent acidity with sulfuric acid (1:1), cool, and add potassium permanganate solution (2.5 per cent) dropwise until a pink color persists. Cool to 10 to 20°C. Add some paper pulp and while stirring vigorously, add a slight excess of aqueous six per cent cupferron solution. Let stand in the cooler until the precipitate settles (about five minutes) and filter through a No. 30 paper containing a little paper pulp. Wash 10 to 15 times with cupferron wash (10 per cent sulfuric acid with 25 ml 6 per cent cupferron solution per liter).

Test filtrate for complete precipitation by adding one ml cupferron solution. Add 25 ml concentrated nitric acid solution and evaporate to fumes. (Place a small piece of filter paper at the end of the stirring rod and use a cover which does not extend beyond the rim of the beaker.) Carefully add concentrated nitric acid dropwise from a dropping bottle until all organic matter is destroyed. Cool, wash down the sides of the beaker, the full length of the rod, and the cover with water. Add five ml concentrated nitric acid and two ml 60 per cent perchloric acid, and again evaporate to copious fumes and let fume 15 minutes. Cool, wash down cover and sides, add one gram ammonium persulfate, and again evaporate to fumes.

Cool, rinse down cover and sides, and dilute to five per cent acidity of sulfuric acid. Heat to solution, add potassium permanganate solution (2.5 per cent) dropwise until a permanent pink persists (no more than one or two drops should be required) and cool to room temperature.

Reduce in the Jones Reductor as follows: Pass 30 ml dilute (five per cent) sulfuric acid through the reductor. Next pass the sample. Then pass 120 ml dilute sulfuric acid (five per cent) in 30 ml portions. Finally pass 150 ml water through the reductor. Never let the reductor run dry. Blow filtered air through the reduced solution for 15 minutes, add 25 ml ferric alum solution (twelve per cent), 5 ml phosphoric acid (85 per cent) and five drops barium diphenylamine sulphonate indicator. Titrate to a purple end point with 0.1 N potassium dichromate. Deduct a titration blank of 0.1 ml.

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Calculation

Grams uranium per 100 ml liquor

$$= \frac{(\text{ml} - 0.1) \text{K}_2\text{Cr}_2\text{O}_7 \times N \times 0.1404 \times 100}{V}$$

N = normality $\text{K}_2\text{Cr}_2\text{O}_7$

V = volume of sample taken in ml

Determination of Uranium in Plant Digestion Liquors (Iron-Free)

Lead Acetate - Sodium Fluoride Method

Reagents

Sodium Acetate - Ten per cent aqueous solution.

Sodium Fluoride - Solid C.P. reagent.

Lead Acetate - Two per cent aqueous solution of the trihydrate salt.

Boric Acid - Four per cent aqueous solution.

Barium Diphenylamine Sulphonate 0.005 M Indicator

- Dissolve 0.317 g barium diphenylamine sulphonate in 100 ml water and add 0.5 g sodium sulfate. Filter to remove barium sulfate

Procedure

Transfer a suitable aliquot to a 400 ml beaker and dilute to 100 ml volume. Add two drops methyl orange indicator and concentrated hydrochloric acid dropwise until the indicator changes. Add exactly eight drops concentrated hydrochloric acid in excess. Add potassium permanganate solution (2.5 per cent) dropwise to the cold solution until a pink color persists for two minutes. Add two g solid sodium fluoride and ten ml sodium-acetate solution (ten per cent). Heat to boiling and slowly add while stirring 50 ml lead acetate solution (two per cent). Boil a few minutes, stir in some paper pulp and filter through a No. 30 paper containing a little paper pulp (save the precipitate for vanadium determination). Catch the filtrate in a beaker

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containing 50 ml boric acid solution (four per cent) and 40 ml dilute sulfuric acid (1:1). Wash well with hot water. Cool the solution and reduce in the Jones Reductor as follows:

Pass 30 ml dilute sulfuric acid (five per cent) through the reductor. Next pass the sample. Then pass 120 ml dilute sulfuric acid (five per cent) in 30 ml portions. Finally pass 150 ml water through the reductor. Never let the reductor run dry.

Blow filtered air through the reduced solution for 15 minutes, add 25 ml ferric alum solution (12 per cent) and five drops barium diphenylamine sulphonate indicator. Titrate to a purple end point with 0.1 N potassium dichromate. Deduct a titration blank of 0.1 ml (0.1 N potassium dichromate).

Calculation

Grams uranium per 100 ml liquor

$$= \frac{(\text{ml} - 0.1) \text{K}_2\text{Cr}_2\text{O}_7 \times N \times 0.1404 \times 100}{V}$$

N = normality of $\text{K}_2\text{Cr}_2\text{O}_7$
V = volume of sample in ml

Determination of Vanadium Pentoxide in Plant Digestion Liquors

Lang and Kurtz Method

Transfer a 50 ml aliquot of the liquor to a 400 ml beaker. Place a strip of litmus on the side of the beaker just dipping in the solution and neutralize by slow addition of dilute sulfuric acid (1:1). Add exactly five ml dilute sulfuric acid (1:1) in excess. Heat to boiling and add potassium permanganate solution (2.5 per cent) dropwise until a pink color just persists. Cool to room temperature and add a slight excess of 0.1 N ferrous ammonium sulfate solution. Again add potassium permanganate solution (2.5 per cent) dropwise to the cold solution until a slight excess is present which persists at least two minutes. Add 0.5 M sodium nitrite solution dropwise until the permanganate color disappears. Avoid unnecessary excess. Immediately add five g urea, followed by 120 ml dilute sulfuric acid (1:1). Dilute to at least 200 ml volume, add one drop ortho-phenanthroline ferrous complex indicator and titrate to the red end point with standard 0.1 N ferrous ammonium sulphate solution.

Calculation

Grams vanadium pentoxide per 100 ml liquor

$$= \frac{\text{ml FeSO}_4(\text{NH}_4)_2\text{SO}_4 \times N \times 0.09095 \times 100}{V}$$

N = normality of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$

V = volume of sample taken in ml

Determination of Vanadium Pentoxide in Plant Digestion LiquorsLead Vanadate MethodProcedure

Transfer the paper and lead vanadate precipitate to a beaker containing a cold solution of 100 ml hydrochloric acid (20 per cent), 15 g sodium chloride, and 25 ml boric acid solution (4 per cent). Stir to dissolve. (Be sure no manganese dioxide is present.) Add five ml phosphoric acid and five drops barium diphenylamine sulphonate indicator, and titrate with 0.1 N ferrous ammonium sulfate solution.

Calculation

Grams vanadium pentoxide per 100 ml liquor

$$= \frac{\text{ml FeSO}_4(\text{NH}_4)_2\text{SO}_4 \times N \times 0.09095 \times 100}{V}$$

N = normality of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$

V = volume of sample taken in ml

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A Comparison of Results of the Analysis of Plant Digestion Liquors
Using the Standard Method of Analysis and the New Lead Acetate Sodium
Fluoride Method

<u>U</u>	<u>Grams U per 100 ml</u>							
	<u>Standard Cupferron Method</u>				<u>New Lead Acetate-Sodium Fluoride Method</u>			
A	0.536	0.535	0.536	0.531	0.534	0.535	0.535	0.540
					0.536	0.534		
B	0.518	0.523	0.529	0.529	0.527	0.527	0.524	0.521
C		1.005				1.012		
D		0.954				0.968		
E		0.244				0.243		
F		0.123				0.119		
G		0.066				0.067		
H		0.026				0.027		

<u>V₂O₅</u>	<u>Grams V₂O₅ per 100 ml</u>							
	<u>Standard Lang-Kurtz Method</u>				<u>New Lead Acetate-Sodium Fluoride Method</u>			
A		0.038	0.038			0.0370	0.0375	
B		0.036	0.036		0.036	0.038	0.037	0.039

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