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Quinetric Titration Of Uranium (Quantitative stanovení uranu). by Otakar Kubin. Chemické listy 19, No. 1, p. 1-3, 1925. (In Czechoslovakian)

A need for a titration method, as against a gravimetric method, arises especially in cases where it is necessary to perform as many tests as possible in a short time in order that the control of manufacture is actually efficient. Up to date we have no such fast and reliable methods for the uranium states. For a long time already, especially in America, experiments have been performed to find such a method; however, up to date a simple and reliable method has not been found.

In 1857, Belohoubek proposed reduction of uranyl salts with zinc and sulfuric acid into uranic sulfate but later it was found that this method is very unreliable. The reduction of uranyl salts with hydrogen does not usually produce a singular lower compound but permits production of two compounds.

Thus, in previous experiments, reduction of the uranyl sulfate with zinc and sulfuric acid gave an added picture. On axis Y there is drawn the quantity of the produced uranic sulfate in percent, on X, the time of reduction in minutes. Point A indicates the speed of reduction of uranyl sulfate into uranic sulfate (1/2 gram U_3O_7 reduced with zinc and 50 cm^3 (also) H_2SO_4 (1:4)). This reduction is finished in about 21 minutes from the start of the boiling; after that, however, continues further to point B. (The liquid turns brown and separates as a lower oxide.) From this it is seen that the results of Belohoubek cannot be exact.

Therefore, many analysts like Kern (Journal of the American Chemical Society 23, p. 702, 1901), Pulman (American Journal of Science 166, p. 229, 1903), and Pierce (Journal of Industrial and Engineering Chemistry 12, No. 1, p. 60-63) and others attempted to perfect a method here and to prevent further argument of the reduction, or to state its step. However, after many vain experiments, they stopped modifying this method. In repeating their experiments I have confirmed that similar conditions exist in the reduction in HCl medium. Namely, in the moment when the uranyl chloride is completely reduced to uranic chloride, we can separate a brown sediment (very quickly with zinc, slower with Cd).

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However, it was not possible to perform this analysis exactly. After various attempts I have found that in the analysis of the uranyl group (UO_2), it is possible to make use of lead in HCl medium as Stolba has already observed (Z.A.C. 1887, 225).

With this method uranyl compounds may be completely reduced to uranic chloride without further reduction to some lower compound of U. Sodium uranate was used for the experiment, and it is possible to distinguish the processes of the reaction in this way:

Analysis:

$Na_2U_2O_7 + 6HCl = 2UO_2Cl_2 + 2NaCl + 3H_2O$ or

$U_2O_7^{=} + 6H^{+} = 2UO_2 + 3H_2O$

Reduction

$UO_2Cl_2 + 2I^{-} + 2HCl = UCl_4 + 2H_2O$ or

$UO_2^{++} + 4H^{+} + 2(-) = U^{++++} + 2H_2O$

U^{IV} is then again oxidized with potassium permanganate to U^{VI} or U^{2} to U^{III}, for which 2 electropositive charges are necessary and then 1cc n/10 manganese solution corresponds to U/2000 = $\frac{238.2}{2} \times 2.10^{-4}$ g U = 0.01191 g U (or 0.01404 g U_3O_8 or 0.01586 g $Na_2U_2O_7$).

Method of procedure

About 0.5 grams of the substance is introduced into a 500 cc flask, 2 g of lead and 25 cc of diluted H_2SO_4 (1:1) are added and heated in a small current of CO_2 for approximately one half hour (at the same time driving out as much as possible of the HCl).

In the meantime we heat in a vessel approximately 300 cc distilled water to which 50 cc dilute H_2SO_4 (1:4) and 15 cc $MnSO_4$ (1:10) is added. After sufficient reduction we allow the content of the flask to cool somewhat in a stream of CO_2, add to it directly the hot content of the vessel, and immediately titrate with the $KMnO_4$ solution (N/10) to red color. We must titrate while warm (appr. 70°C) in order not to free the chlorine. During titration, the solution becomes cloudy with the $PbSO_4$, which however does not in the slightest degree hinder recognition of the end of the reaction.

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Results

The method yields the following results. Sodium uranate was used, which contains 98.5% $Na_2U_2O_7$.

(Remainder was sodium carbonate)

Quantities of $Na_2U_2O_7$ (g)	cc n/10 HNO_3 consumed I.	II.	III.	average	Theoretical amounts n/10 HNO_3 (cc)
0.1000	6.20	6.25	6.20	6.23	6.21
0.2500	15.47	15.52	15.50	15.50	15.50
0.5000	31.00	30.96	31.05	31.00	31.00
0.7500	46.55	46.50	46.52	46.52	46.52
1.0000	61.88	61.95	61.98	61.94	61.94

Kind of Uranium product of the Jachymov plant	U_3O_8 content in % by Patera's gravimetric method	U_3O_8 content by described method
Yellow U 1	80.2%	80.25%
Yellow U 2	73.6%	73.66%
Orange U 3	80.9%	80.35%
Dark Orange U	83.9%	83.95%

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(Czechoslovakia)

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