63.   *The Quantitative Determination of Arsenic in Organic and Inorganic Compounds.*

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Volumetric and gravimetric methods for the estimation of arsenic in organic and in inorganic compounds are described.   The methods depend on the quantitative precipitation of the arsenic as uranyl ammonium arsenate, and in the gravimetric process, this compound is converted into black uranosic oxide, U_3O_8, which is weighed as such. Details of a modified Kjeldahl method for the rapid decomposition of organic arsenicals are given, the arsenic being then estimated as previously described.

THE commonest method for the determination of arsenic depends on its precipitation as magnesium ammonium arsenate and ignition to the pyroarsenate (see Messinger, *Ber.*, 1888, **21**, 2916; Warunis, *Chem.-Ztg.*, 1912, **36**, 1205; Palmer and Dehn, *Ber.*, 1901, **34**, 3596; Jacobs, Heidelberger, and Rolfe, *J. Amer. Chem. Soc.*, 1918, **40**, 1582); according to Puller (*Z. anal. Chem.*, 1871, **10**, 72), the temperature of ignition has to be carefully controlled to avoid volatilisation of arsenic.   The anhydrous arsenate itself cannot be weighed owing to the difficulty of obtaining it in a constant composition.

Volumetric methods for estimating arsenic generally depend on the titration of the arsenite solution obtained by the destruction of the arsenical organic compound under specified conditions (Gooch and Browning, *Amer. J. Sci.*, 1890, **66**, 11; Robertson, *J. Amer. Chem. Soc.*, 1921, **43**, 182; Morgan, J., 1909, **95**, 1478; Rogers, *Canadian J. Chem.*, 1919, **3**, 398.   Ewins's volumetric method (J., 1916, **109**, 1356) gives fairly consistent results after some experience of it, but otherwise, fading at the end-point of the titration causes difficulty.   In view of the foregoing disadvantages in existing methods, an arsenical compound was sought which could be readily precipitated and ignited to constant weight. These requirements were fulfilled by the slimy gelatinous ammonium uranyl acetate, $NH_4UO_2AsO_4,nH_2O$, which was shown by Puller (*loc. cit.*) to be quantitatively precipitated by addition of a uranyl salt solution to an arsenate solution containing excess of ammonium ions.   This precipitate is soluble in mineral acids but completely insoluble in acetic acid, and can be obtained in granular form by precipitation from a hot solution of the arsenate. Puller weighed this precipitate after controlled ignition to uranyl pyroarsenate, which, however, readily undergoes further decomposition.

The following volumetric and gravimetric methods are based on the quantitative formation of the ammonium uranyl arsenate precipitate.

EXPERIMENTAL.

Volumetric Method.—To 50 c.c. of the arsenate solution containing approximately 0·4 g. of arsenic per l., 10 c.c. of 4N-ammonium hydroxide are added, the solution is acidified with acetic acid until it smells faintly of the acid and is then heated to boiling, and 20 c.c. (excess) of 0·1N-uranyl acetate solution are added.   After several hours' standing, during which the precipitate becomes coarser, the solution is filtered through a fine, quantitative filter, the filtrate is acidified with sulphuric acid, and the excess uranium determined with 0·05N-permanganate as described by Lundell and Knowles (*J. Amer. Chem. Soc.*, 1925, **47**, 2637).   The volume of the titrated liquid should be about 300 c.c. and titration should be carried out in a large porcelain

dish, the liquid being kept well stirred; the masking of the end-point by the colour of the uranyl salt is thereby minimised, and, as Lundell and Knowles have shown, the uranous salt is not oxidised by the air, though the requisite oxidation of the over-reduced compound does occur.

Disodium hydrogen arsenate was twice recrystallised from water, and the efflorescent crystals so obtained were carefully dehydrated at 220° to prevent formation of pyroarsenate. Solutions of this salt were analysed (Found : As, 40·3, 40·4, 40·2, 40·2. Calc. : As, 40·3%).

The efflorescent crystals (H_2O, 44·28%) were also analysed, values of 22·61% and 22·7% being obtained, in good agreement with the calculated value, *i.e.*, As, 22·46%.

Gravimetric Method.—In the presence of nitrates, or of any other substances reduced by nascent hydrogen, the foregoing method of estimating the excess of uranium in the filtrate is inapplicable. An attempt was therefore made to determine the uranium in the precipitate, which is readily soluble in dilute sulphuric acid and may be reduced with zinc. Unfortunately the complete removal of the interfering arsenic as arsine was a long and tedious process, and the results obtained were not very concordant.

A study of the residue obtained by ignition of the precipitate (in a fume chamber) was there-fore made, and it was found that the arsenic was completely volatilised, leaving a moss-green residue consisting mainly of U_3O_8, which was probably reduced to some extent by the carbona-ceous matter present. This residue dissolves readily in a few drops of concentrated nitric acid, yielding a yellow solution of uranyl nitrate, which on cautious evaporation and subsequent ignition decomposes readily to give a coal-black residue consisting wholly of U_3O_8.

Moissan (*Ann. Chim. Phys.*, 1896, **9**, 264) prepared this oxide in a pure state by igniting the nitrate, though it is well known that it is formed from most uranyl salts on strong ignition (cf. Berzelius, *Ann. Phil.*, 1895, **9**, 266; de Coninck, " Recherches de l'Uranium," Paris, 1911) : this fact renders this oxide a suitable form in which to weigh uranium. Jolibois and Bousset (*Compt. rend.*, 1922, **174**, 388) have shown that only a small fraction of the oxygen is lost even when this oxide is maintained for 3 hours in a vacuum at 1000°, and Lebeau (*ibid.*, p. 338) confirmed its stability in air at high temperatures. We, too, found that the nitrate could readily be ignited to constant weight by a good Bunsen burner.

Anhydrous disodium hydrogen arsenate and resublimed arsenious oxide were used as stan-dards in the following work. Considerable difficulty was experienced in oxidising arsenite to arsenate, even by boiling nitric acid, but a solution of potassium bromate added dropwise to the acidified arsenite solution at 70° rapidly effected oxidation. The arsenic trichloride used was decomposed with dilute potassium hydroxide, and similarly oxidised in acid solution. Excess ammonia was added to the arsenate solutions (sufficient ammonium ion is essential), followed by acetic acid, and precipitation was carried out as described above. The results were as follows (1 g. U_3O_8 = 0·02668 g. As) :

Sub-stance.	Wt. used, g.	U_3O_8, g.	As, %, found.	As, %, calc.	Sub-stance.	Wt. used, g.	U_3O_8, g.	As, %, found.	As, %, calc.
As_2O_3	0·1342	0·3800	75·54	75·72	Na_2HAsO_4	0·1110	0·1688	40·58	40·30
	0·2618	0·7435	75·98	,,		0·09759	0·1472	40·27	,,
$AsCl_3$	0·2842	0·4392	41·24	41·32					

Should the solution to be analysed contain both arsenite and arsenate, the simplest procedure is to titrate a known volume, acidified with hydrochloric acid, with 0·1N-potassium bromate in the usual way. The total arsenate in the resulting liquid may then be determined by precipi-ation as the uranium salt. An interesting qualitative distinction between arsenite and arsenate is that the former will not yield a precipitate with uranyl acetate in the presence of excess ammonium ion, whereas the latter is quantitatively precipitated.

Gravimetric Determination of Organic Arsenicals.—The organic compound may be decom-posed by the Carius method to arsenic acid, the tube washed out with ammonia, and the arsenic precipitated from acetic acid solution. Some of the organic arsenicals listed in the following table decompose spontaneously and explosively in contact with fuming nitric acid, and great care must be exercised during their introduction into the Carius tube and subsequent sealing. The following alternative method has yielded consistently good results with various arsenic derivatives and is more rapid and less dangerous than the Carius method.

About 0·1—0·3 g. of the organic compound contained in an open tube is dropped into a Kjeldahl flask containing a cold mixture of 20 c.c. of concentrated sulphuric acid, 10 g. of potassium nitrate, and 0·25 g. of pure starch. The mixture is then gently warmed, and dense brown fumes soon fill the flask. The temperature is gradually increased, and boiling continued

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until all the oxides of nitrogen have been evolved and no trace of organic matter is seen in the flask. In the case of organic arsenical halides, the halogen is also volatilised during this process and assists in oxidation to the arsenate. The contents of the flask are then allowed to cool, about 40 c.c. of cold water are slowly added, and to the hot solution thus obtained a concentrated solution of potassium bromate is added dropwise until the solution acquires the tinge of free bromine. The contents of the flask are then neutralised with concentrated ammonium hydroxide and filtered free from particles of glass, the filter-paper being well washed. The filtrate is acidified with acetic acid, heated to boiling, and excess of approximately 0.1N-uranium acetate solution added. A light yellow precipitate is formed after 3—4 minutes, and precipitation is completed by standing overnight. The precipitate is washed free from soluble salts, and the filter-paper containing it is pressed into a compact wad, placed in the bottom of a silica crucible, and strongly ignited over a Meker burner until all the carbonaceous matter has disappeared, the arsenic volatilising simultaneously. The residue is then moistened with a few drops of strong nitric acid and ignited to constant weight over an ordinary Bunsen flame for a few minutes : identical results were obtained whether this ignition was carried out in air or in a current of oxygen.

Some typical results are given below :

Substance.	Wt., g.	U_3O_8, g.	As, %, found.	As, %, calc.
Cacodyl iodide	$\begin{cases}0.2116\\0.3342\end{cases}$	0.2546 / 0.4018	32.10 / 32.07	32.30 / ,,
p-Arsanilic acid	$\begin{cases}0.0965\\0.0776\end{cases}$	0.1238 / 0.1000	34.23 / 34.38	34.52 / ,,
*Phenyldiallylarsine	0.1232	0.1447	31.36	31.99
Phenyldi-iodoarsine	$\begin{cases}0.2394\\0.5132\end{cases}$	0.1676 / 0.3502	18.67 / 18.21	18.45 / ,,
*Tri-β-methylallylarsine	0.1125	0.1323	31.38	31.22
*Phenyldi-β-methylallylarsine	0.0778	0.0838	28.74	28.58