A MICROANALYTICAL.DETERMINATION OF SULPHUR IN ORGANIC COMPOUNDS BY TITRATION.

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Introduction. The determination of sulphur in a few milligrams of organic material may be carried out by the methods of F. Pregl.(2) Though the methods are quite excellent, they involve some inconveniences in the performance of experiments. For instance, the special apparatus "Micro-Neubauer crucible" must be used for carrying out the gravimetric determination and the material to be analysed must contain neither nitrogen nor halogen for the volumetric one.

One of the authors(3) had observed that the most active part of reduced nickel decomposes organic sulphur compounds (for instance thiophen) quantitatively in the hydrogen atmosphere and, while changing itself into nickel sulphide, it absorbes the sulphur completely.

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(1) P. P. von Weimarn, *Reports of the Imperial Industrial Research Institute of Osaka*, Vol. VIII, No. 6, 22–29, (June, 1927).

(2) F. Pregl "Die quantitative organische Mikroanalyse", 2 ed. (1923), 122.

(3) B. Kubota & K. Yoshikawa, *Japanese Journal of Chemistry*, 2 (1925), 45; *Scientific Papers of the Institute of Physical and Chemical Research*, No. 39 (1925), 223.

It seemed to us that this process might be carried out with all sorts of organic sulphur compounds and that it might make possible of microanalytical determination of sulphur in organic compounds by titration without any inconveniences above mentioned. Thus the studies of this process with several kinds of organic sulphur compounds were undertaken and the confirmation of the correctness of this view was obtained by the results, shown in the table on page 172, which gave complete satisfaction.

Experimental. In order to analyse by this method, a few milligrams of the material is weighed in an open small platinum boat just as for the Pregl's micro-determinations of carbon and hydrogen. It is then introduced into a small decomposition tube of an outer diameter of about 10 millimeters and of a length of about 400 millimeters which rests on F. Pregl's combustion stand, and is placed behind the reduced nickel previously prepared in this tube by the action of pure hydrogen at about 250°C. on 10–15 gr. of nickel oxide which was obtained by the calcination of pure nikel oxalate free from sulphur and allowed to cool in the current of hydrogen. Closing the one end of the decomposition tube with the rubber stopper provided with a tapered glass tube through which a current of purified hydrogen gas passes and drives the air out of the decomposition tube, the outlet of which is immersed into a water basin as shown in Fig. 1. The hydrogen is made from zinc and hydrochloric acid and passed through the tubes of sodium hydroxide solution, concentrated sulphuric acid, heated metallic copper and sodium hydroxide successively. The front portion of the decomposition tube is carefully heated with a tube burner and the temperature is raised to about 200°C. After the tube has been freed from air, the small roll of wire ganze and the burner being moved towards the boat, the material is rendered to volatilize and allowed to pass very slowly over the catalyst by means of cautiously regulated hydrogen current. When the whole of the material to be analysed has finally passed over the catalyst, the heating of the decomposition tube is ceased and the contents of the tube are left to cool.

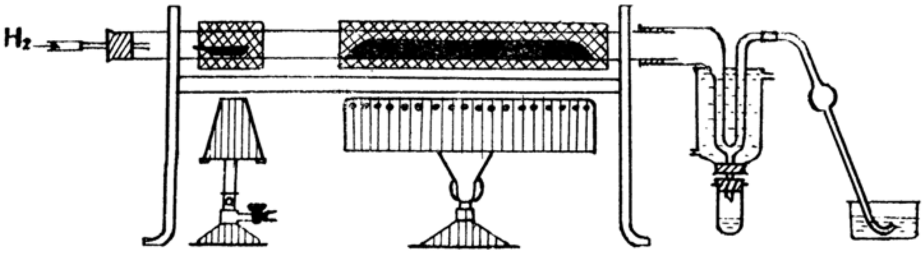


Fig. 1.

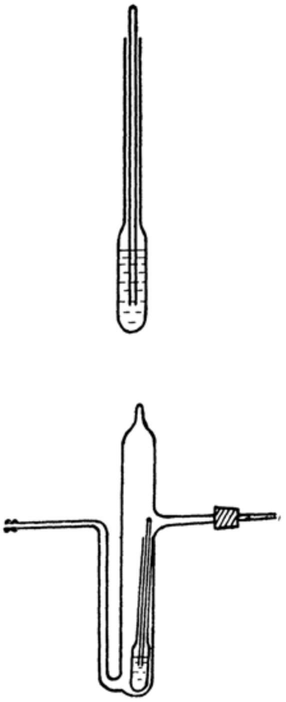


Fig. 2.

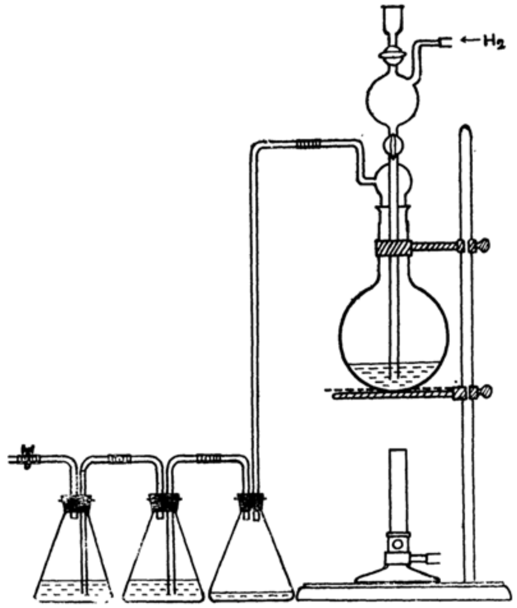


Fig. 3.

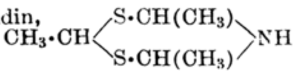
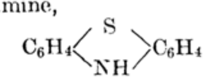
They are now subjected to the determination of sulphur by means of ordinary method of determination of sulphur in metallic sulphides: when the whole contents of the decomposition tube is dissolved, in a flask shown in Fig. 3, into a concentrated hydrochloric acid solution in the hydrogen atmosphere, the hydrogen sulphide gas is evolved at the same time that the hydrogen is produced. Being swept out by the current of pure hydrogen delivered from reservoir, this gas mixture passes though an ammoniacal cadmium solution (20 gr. $CdCl_2 + 400$ c.c. $H_2O + 600$ c.c. ammonia water, sp. gr. 0.96) and produces the precipitation of cadmium sulphide. This is filtered off and the residue is oxidised by an excess of an iodine solution which is obtained by the action of the potassium permanganate solution (approximately 0.08 N.) on the solution of potassium iodide (30 gr. $KI + 10$ gr. $NaHCO_3 + 1000$ c.c. H_2O). The amount of potassium permanganate used is estimated by the titration with sodium oxalate solution. The volumetric analysis of iodine employed in the oxidation of cadmium sulphide is then carried out by means of a 0.02 N. solution of sodium thiosulphate in the presence of starch solution. The percentage of sulphur in the material can then be calculated as follows,

$$\frac{\mathrm{S}}{\mathrm{Na_2C_2O_4}} \times a \times \frac{T_1-T_2}{T_1} \times \frac{100}{P} = 23.\dot{9}3 \times a \times \frac{T_1-T_2}{T_1 P} = \%\ \text{of S}.$$

where P represents the weight of the material to be analysed, a the weight of $Na_2C_2O_4$ just oxidised by 10 c. c. of potassium permanganate solution, T_1 the volume (c.c.) of the $Na_2S_2O_3$ solution used for the oxidation of the iodine produce by the action of 10 c.c. of the $KMnO_4$ solution on KI, T_2 the volume (c. c.) of the $Na_2S_2O_3$ solution used for the oxidation of the iodine which is produced by the action of 10 c.c. of $KMnO_4$ solution on KI and is remained unchanged, not being used for the oxidation of the cadmium sulphide.

In the case of materials which volatilize with difficulty and by being heated in the hydrogen atmosphere decompose and leave some residue in the boat (for example ammonium bromocamphor-sulphonate and barium benzene-sulphonate in the table on page 172), it is necessary, after weighing the material in the boat, to cover it with reduced nickel which is prepared at the same time with the catalyst from pure nickel oxide in a porcelain boat placed behind the filled portion of the catalyst in the decomposition tube and, being taken out cautiously from the latter before entering into the analysis, is placed on the material in the boat. When the decomposition of the material is completed, the boat and the catalyst are introduced to-gether into the decomposition flask and the process of the analysis is conducted as mentioned above.

In the case of analysing volatile liquids (for example carbon bisulphide and thiophen in the following table) a small tube of about 5 mm. wide and of about 20 mm. long provided with a comparatively long neck of about 2 mm. wide and of about 30 mm. long is prepared and, in order to introduce a small drop of the material to be analysed into the bottom of the tube, a capillary is used, of about 1 mm. diameter, which is drawn out at one end for some millimeters to the thickness of a hair. By this means one can avoid putting the material on the wall of the weighing tube. After weighing the material in this tube, some benzene is added by means of another capillary, and a small capillary (Fig. 2), sealed at the upper end, which prevents superheating by producing a slow stream of air bubbles though the liquid, is immersed in it. The benzene freezes when cooled by ice and enables one to avoid the loss by vaporization and easily to charge the tube into the apparatus which is sealed afterwards and, being heated in a bath at a suitable temperature, serves to control the desired vapour velocity of the material (Fig. 2). In the same way it is able to determine even a trace of sulphur compound in a very large quantities of organic liquids, only by using a larger weighing tube and the suitable outer apparatus (Fig. 2).

Materials	P (mg.)	a (gr.)	T_1 (c.c.)	T_2 (c.c.)	% of S. calc.	% of S. found
Carbon bisulphide,* CS_2	4.62	0.03375	25.66	13.20	84.24	84.64
Thiophen, C_4H_4S	15.98	0.05027	36.50	18.00	38.14	38.13
Thioacetic acid, CH_3COSH	8.55	0.03375	5.09	2.83	42.14	41.93
Phenyl thiocyanate, C_6H_5NCS	10.65	0.03745	24.90	17.95	23.73	23.49
Ethyl benzene sulphonate, $C_6H_5SO_3C_2H_5$	10.31	0.03894	23.95	19.39	17.23	17.20
Ammonium bromocamphor sulphonate, $C_{10}H_{18}O_4NBrS$	12.30	0.03837	22.62	19.47	10.08	10.40
Barium benzene sulphonate, $(C_6H_5SO_3)Ba+H_2O$	13.95	0.03837	22.92	18.40	12.66	12.98
Quinine sulphate $(C_{20}H_{24}N_2O_2)_2SO_4H_2+8H_2O$	6.43	0.03745	22 64	22.03	3.60	3.75
Thialdin,  $CH_3\cdot CH\left\langle\begin{matrix}S\cdot CH(CH_3)\\S\cdot CH(CH_3)\end{matrix}\right\rangle NH$	6.73	0.03745	22.51	15.80	39.29	39.57
Thiodiphenylamine,  $C_6H_4\left\langle\begin{matrix}S\\NH\end{matrix}\right\rangle C_6H_4$	9.59	0.03837	22.76	18.97	16.10	15.95

* It was informed by Prof. P. Sabatier (*Bull. Soc. Chim.*, [4], 15 (1914), 228) that the carbon bisulphide was reduced by means of hydrogen on nickel catalyst and gave rise to the formation of $CH_2\,SH)_2$, but in our experiment it was not observed while the most active part of the catalyst existed.

Summary.

A microanalytical determination of sulphur in organic compounds is carried out by decomposing cautiously the material to be analysed in the hydrogen atmosphere on reduced nickel, which absorbs the sulphur completely and changes itself into sulphide, and by determining iodometrically the hydrogen sulphide which is evolved from the reduced nickel when it is dissolved in hydrochloric acid. It was found thus that the nickel catalyst is able to be applied to the organic microanalysis of sulphur.

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