LVIII. THE MICRO-DETERMINATION OF METALS IN SALTS.

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THE practice of using salt formation as a means of purifying compounds of biological importance is one of the most commonly employed operations in biochemical studies, and it is therefore of the greatest importance to have an easy and certain method of analysing salts. The element which is generally selected for determination is the metal: and although the process of ashing or incinerating with sulphuric acid is so simple in theory the actual practical work is not only tedious but often leads to uncertain results. The cause of this must generally be ascribed to the persistent creeping of the sulphuric acid, and when, through lack or expense of material, it is necessary to do the analysis on a micro-scale, spitting or frothing also frequently adds to the difficulties.

Pregl has found it expedient to alter his original technique on several occasions [1924, 1]; and even with his present modification [1924, 2] the author and several others (private communications) have found it difficult or even impossible to obtain correct results with many salts, although others can be analysed with ease and accuracy. This uncertainty led the author to make some alterations in the method; and using the modifications described below he has been able to carry out many dozens of analyses on the most varied salts, always obtaining accurate results with certainty.

Fig. 1.

Fig. 2. (Full size.)

The chief modification consists in the use of a platinum cylinder¹ (Fig. 2) which surrounds the boat in which the combustion is done; any material which is generally lost by spitting or creeping is retained in the cylinder and finally weighed. The cylinder is about 40 mm. in length with a diameter of 8 mm. and is made of platinum foil 0.05 mm. in thickness. One part is flattened so that it can rest easily on a flat surface and the ends are strengthened with wire, one end also having a loop for ease of manipulation.

The cylinder and boat are boiled in dilute nitric acid (1 : 5), ignited, cooled on the block of the desiccator, placed side by side on the balance pan and weighed in the usual manner. Because of the comparatively large surface they should be allowed to remain five minutes on the pan so that they may assume a constant weight. 4 or 5 mg. of the substance to be analysed is weighed into the boat and is thoroughly moistened with two or three drops of sulphuric acid (1 : 5). It is of great advantage at this stage gently to evaporate off most of the water as this generally causes trouble in the incineration. For this purpose the boat is placed in the centre of the platinum cylinder which in turn is placed in a glass tube to protect it from dust. The whole is placed in a "regenerating" block at 120° for five minutes, a gentle current of air being drawn through the glass tube to remove the moisture.

The combustion is best carried out in a transparent silica tube (Fig. 1) about 45 cm. in length and 10 mm. internal diameter which is supported on an ordinary combustion stand *AB*. Pregl causes air to pass through the tube by using convection currents. This method has the obvious disabilities that the speed cannot be easily determined or controlled and therefore the author has found it much better to use an aspirator with a bubbler *C* to indicate the speed of the current. Moreover, when analysing salts with a high carbon content it is often difficult to burn all the carbon if only air is used and it is therefore advantageous also to have the tube connected with an aspirator containing oxygen.

After drying in the "regenerating" block the procedure of the combustion is to place the cylinder, which has the boat inside it, into the end of the silica tube, in the position shown in the figure. A fairly rapid stream of air is turned on and the flame slowly advanced from *D* to the centre of the cylinder *E*, using the wire gauze as shown to conduct the heat. This need not be done with the same great care as is necessary in the Pregl technique. After some time the gauze is removed and the full flame of the burner is allowed to play on the bare silica tube, the heat being also reflected by means of a semi-circular piece of coarse wire gauze placed over the silica tube. The air is gradually replaced by oxygen and after being heated strongly in this gas for three minutes the platinum cylinder may be removed to the desiccator, cooled and weighed as before. The course of the combustion can be watched quite well by looking through the end of the tube.

¹ The cylinder was made by Messrs Johnson, Matthey and Co., Ltd., Hatton Garden, London, for 28s., but the first experiments were done using a piece of foil rolled into a circular shape and this gave good results.

The author has never found any difficulty in obtaining the normal sulphates when using the above method and these give quite constant weights in air. It is obvious that if a deliquescent substance is obtained after incineration this can be weighed by placing the platinum cylinder in a suitable stoppered tube or weighing bottle after touching on the block of the desiccator. The author has also never found any reduction of the sulphates of the alkaline earths by carbon, but if there is any fear of this happening two or three drops of sulphuric acid can be distilled over the residue from small porcelain boats at *F* and *G*. In this way it is also possible to obtain excellent results from carbonates which have been obtained from ashing, etc. (cf. analyses of salt 4). Although the above experimental work has been given for incineration with sulphuric acid it is obvious that it can be used with great advantage for the generally simpler operation of ashing.

The accuracy of the method is shown by the analyses on the following pure substances (1-4). Dr H. W. Dudley was kind enough to send a few milligrams of the salts (5-8), the author only knowing the metal present. These were ordinary samples not specially purified.

No.	Salt and residue after ignition	Formula	Amount of salt taken mg.	Weight of residue mg.	Found %	Calc. %
1	Potassium tetroxalate (Potassium sulphate)	$\text{C}_4\text{H}_2\text{O}_8\text{K},$ $2\text{H}_2\text{O}$	3.748	1.286	15.40	15.38
			4.231	1.453	15.41	
2	Potassium nitrate (Potassium sulphate)	KNO_3	4.747	4.086	38.62	38.68
			4.434	3.821	38.67	
3	Copper sulphate (Copper oxide)	$\text{CuSO}_4,$ $5\text{H}_2\text{O}$	4.414	1.412	25.56	25.46
			4.747	1.521	25.60	
4	Lithium carbonate (Lithium sulphate)	Li_2CO_3	3.618	5.341	18.63	18.79
			4.521	6.679	18.65	
5	Potassium hydrogen phthalate (Potassium sulphate)	$\text{C}_8\text{H}_5\text{O}_4\text{K}$	4.625	1.973	19.14	19.15
			4.921	2.095	19.10	
6	Sodium succinate (Sodium sulphate)	$\text{C}_4\text{H}_4\text{O}_4\text{Na}_2,$ $6\text{H}_2\text{O}$	4.715	2.479	1.702	17.03
			4.296	2.252	16.97	
7	Calcium oxalate (Calcium sulphate)	$\text{CaC}_2\text{O}_4,$ H_2O	5.172	4.775	27.18	27.36
			4.424	4.104	27.30	
8	Barium benzenesulphonate (Barium sulphate)	$\text{C}_{12}\text{H}_{10}\text{O}_6\text{S}_2\text{Ba},$ H_2O	3.778	1.884	29.35	29.25
			3.487	1.733	29.25	

All the analyses on the above salts were carried out as unknowns for this communication by Mr A. Colwell of this laboratory and the author's best thanks are due to him.

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