343. *Microvolumetric Determination of Methoxyl.*

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Viebock and Schwappach (*Ber.*, 1930, **63**, 2818) have shown that Pregl's methoxyl estimation can be effected volumetrically by absorbing the alkyl iodide in a solution of bromine, destroying excess of bromine, adding potassium iodide, and titrating the iodine liberated, according to the scheme $CH_3I \longrightarrow CH_3IBr_2 \longrightarrow IBr \longrightarrow HIO_3 \longrightarrow 3I_2$. Arndt and Martius (*Annalen*, 1932, **499**, 269), who used this method with a series of sulphur and nitrogen alkoxy-derivatives, found it very satisfactory with 25—50 mg. of material.

Vieböck and Brecher (*Ber.*, 1930, **63**, 3207) also described a procedure for 1—5 mg.

substance, but, in disagreement with them, we find that with such quantities the blank given by the absorbing solution is significant and is seriously increased by time, temperature, dilution with water, and even by illumination.

After the decomposition, Vieböck washes the absorbing solution into a conical flask containing ½—1 g. of dissolved sodium acetate, destroys the excess of bromine with 4 or 5 drops of formic acid, adds 0·1—0·2 g. of potassium iodide, acidifies the solution with sulphuric acid, and titrates it with thiosulphate. He suggests that the presence of undissolved sodium acetate gives rise to bromate formation; but we consider it more likely that the discrepancy arises from deficiency of dissolved acetate. Further, we found it necessary to use excess of sulphuric acid for the liberation of total iodine.

We find that a solution of bromine in potassium bromide obviates these difficulties and recommend the following modifications.

An amount of material corresponding to 3—10 c.c. of *N*/50-thiosulphate should be taken. The " Verschlussstäbchen " should fit tube A as tightly as possible without seizing (cf. Pregl, 3rd German Edition, p. 199).

A very small flame within 1 cm. of the flask gives better control of the heating than does a glycerol-bath (Vieböck). Heating should be continued for 40 minutes, *i.e.*, 5 minutes after bumping begins.

As little washing solution as possible should be used. A saturated solution of sodium bicarbonate is efficient.

The absorbing solution should be freshly prepared by adding 6 drops (0·05 c.c.) of bromine to 18 c.c. of 20% aqueous potassium bromide. Half of this serves as a blank, and is kept beside the absorption tubes during the estimation, being titrated under the same conditions at the end. The remaining absorption solution is filled into two absorption tubes (cf. Pregl, *op. cit.*, p. 207, Fig. 36), 7·5 c.c. into the first, 1·5 c.c. into the second. The absorption tubes and the blank are immersed in ice-water during the estimation.

When the decomposition is complete, the two absorbing solutions are washed into a conical flask with 45 c.c. of 25% potassium acetate, and decolorised with 1 c.c. of 85% formic acid. 2 C.c. of 10% potassium iodide and 25 c.c. of 5*N*-sulphuric acid are added, and the iodine titrated with *N*/50-sodium thiosulphate. The blank, similarly treated, does not exceed 0·10 c.c.

The following results were obtained :

Substance.	Wt., mg.	OMe, %. Found.	Calc.
Vanillin	0·544	20·5	20·4
	0·802	20·2	—
	1·318	20·2	—
	2·017	20·3	—
	2·498	20·4	—
	3·100	20·4	—
	3·216	20·3	—
	3·592	20·2	—
	4·198	20·3	—
	4·603	20·2	—
	4·693	20·1	—
α-Methyl-glucoside	3·472	16·2	16·0
	3·771	16·1	—
	3·890	16·1	—
p-Methoxybenzaldoxime	2·349	20·2	20·5
	2·845	20·6	—
Papaverinol	3·854	34·6	34·9
p-Methoxybenzylideneaceto-phenone	3·294	12·9	13·0
Dibenzoyl *p*-toluenesulphonyl methylglucoside	4·241	5·61	5·57
	3·849	5·61	—
Iododibenzoyl *p*-toluene-sulphonyl methylglucoside	4·610	5·02	4·55
	4·613	5·02	—
Tetramethyl α-methyl-glucoside	1·741	60·9	62·0

Low results were obtained if (i) only one receiver was used; (ii) the heating lasted less than 40 minutes; (iii) the titration was too large.

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