

Minoru Fukuda : Studies on Organic Microanalysis. IX.<sup>1)</sup>

## Sensitive Detection of Alkoxy Groups.

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A method for detection of alkoxy groups has already been reported by Tobie.<sup>2)</sup> In his method, alkyl iodide formed by the reaction between a sample and hydriodic acid is applied on a piece of filter paper soaked in mercuric nitrate solution. The presence of alkoxy groups is recognized by the red color of mercuric iodide which appears on the filter paper. The procedure of his method and preparation of the reagent are not simple. In addition, it is on semimicro-scale. Pregl method<sup>3)</sup> for alkoxy determination may also be used for this detection, but recognition of the precipitation is difficult when the amount of sample is too small.

By the application of the present combustion method<sup>4~6)</sup> for alkoxy determination, a trace of alkoxy group in the sample can be detected simply without any special reagent. In this method, alkyl iodide formed by the reaction between a sample and hydriodic acid is burnt to iodine, which is detected by starch solution.

## Experimental

**Reagent**—Starch solution : A small amount of powdered HgI is added to 0.05% starch solution, the mixture is boiled, and the solution is filtered when cooled.

Reaction mixture : A mixture of 100 g. of HI (sp. gr.=1.7), 60 g. of phenol, 5~10 g. of propionic

TABLE I.

Compd.	Taken (γ)	CH <sub>3</sub> O (γ)	C <sub>2</sub> H <sub>5</sub> O (γ)	Iodine-starch reaction
Vanillin	95	19.0		+
	40	8.0		+
	34	6.8		+
	32	6.4		+
	15	3.0		+
	15	3.0		+
	10	2.0		—
	10	2.0		—
	10	2.0		—
Phenacetin	32		8.0	+
	25		6.3	+
	23		5.8	+
	21		5.3	+
	15		3.8	±
	15		3.8	—
Sucrose	15		3.8	—
	210			—
Acetanilide	3083			—
	290			—
	850			—

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1) Part VIII. Yakugaku Zasshi, **80**, 1160(1960).

2) W.C. Tobie : Ind. Eng. Chem., Anal. Ed., **15**, 433(1943).

3) F. Pregl, H. Roth : "Quantitative organische Mikroanalyse," **6**, 215(1949). Springer-Verlag, Wien.

4) M. Fukuda : Yakugaku Zasshi, **78**, 83(1958).

5) *Idem* : Bunseki Kagaku, **8**, 390(1959).

6) *Idem* : Yakugaku Zasshi, **80**, 25(1960).

acid, and some red phosphorus is refluxed in a stream of carbon dioxide for 1~1.5 hr. in a flask provided with an air condenser. The flask is stoppered and left to stand over night to settle the red phosphorus. Supernatant solution is transferred into a bottle with a ground glass stopper. This reaction mixture is the same as in the alkoxy determination.<sup>5)</sup>

**Apparatus**—The apparatus is the same as in the alkoxy determination reported previously.<sup>5,6)</sup> The gas testing tube is the same as shown (Fig. 2 in a previous paper).<sup>4)</sup>

**Procedure**—A gas testing tube with 4 drops of starch solution is connected to the end of the combustion tube.<sup>5,6)</sup> A very minute quantity of the sample and 1 cc. of the reaction mixture are introduced into the reaction flask, the flask is connected to the apparatus, and heated as in the determination for 10 min. In the presence of alkoxy groups, alkyl iodide is formed and burned to iodine, by which the starch solution turns blue.

**Limit of Detection**—Using an ultramicro amount of vanillin and phenacetin, the detection limit of methoxy and ethoxy groups was examined, and the results obtained are shown in Table I. The detection limit of methoxy group is 3  $\gamma$  and that of ethoxy group, 5  $\gamma$ .

The feature of this method is that it can be carried out by the same apparatus and under the same condition as in the determination during routine analysis, and that it is so sensitive that the detection can be carried out with about 50  $\gamma$  of a sample. The method can also be applied to the detection of alcohols such as methanol and ethanol.

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### Summary

By the application of the present combustion method for alkoxy determination, a trace of alkoxy group in a sample can be detected simply without any special reagent. Alkyl iodide formed by the reaction between a sample and hydriodic acid is burned to iodine, which is detected by starch solution. The detection limit of methoxy group is 3  $\gamma$  and that of ethoxy group, 5  $\gamma$ . The method can also be applied to the detection of alcohols such as methanol and ethanol.

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