Determination of Small Quantities of Acetone in Methyl Methacrylate Monomer

By Yuzi TAKAYAMA* and Fumikazu TOKIWA**

(Received May 24, 1957)

At the present time for the determination of acetone in methyl methacrylate monomer (simply M-MM), hydroxylamine hydrochloride method has been used, but the method is common to both ketones and aldehydes, so that it can not determine acetone only.

Many studies on the determination of acetone are reported and each of them has its own characteristics. Especially, salicylaldehyde method generally is not applicable to the determination of acetone in M-MM on account of coloration of M-MM itself. One of the best is J. Messinger's[1] iodo titration method by iodoform reaction and some of the reported modifications of Messinger's[1] technique indicate the widespread utility of this procedure. But iodometry has generally too low an accuracy for the determination of small quantities of acetone. Absorption method in the ultraviolet region has been well studied including the work of Barthauer[2], Nogare[3], Stolyarov[4], Andreev[5], Etienner[6] and Shchukarev[7]. Nogare's method may be considered as surpassing the others in easiness of obtaining the reagents, and in relative simplicity of the method; it seems also to be comparatively sensitive, but its application is, limited in determination of acetone in either aqueous solution or non-aqueous solvent which is miscible with water. In this report the application of Nogare's method was investigated for determination of small quantities of acetone in a medium which is immiscible with water to establish a method superior to those previously used.

Iodoform has a strong absorption in the ultraviolet region from 400 to 250 mμ. This is characterized by three defined maxima occurring at 274, 307 and 347 mμ, in chloroform as shown in Fig. 1. Therefore, acetone in sample M-MM is caused to react in an alkaline solution with sodium hypoiodite by vigorous shaking. The absorbancy of resulting iodoform is measured at 347 mμ.

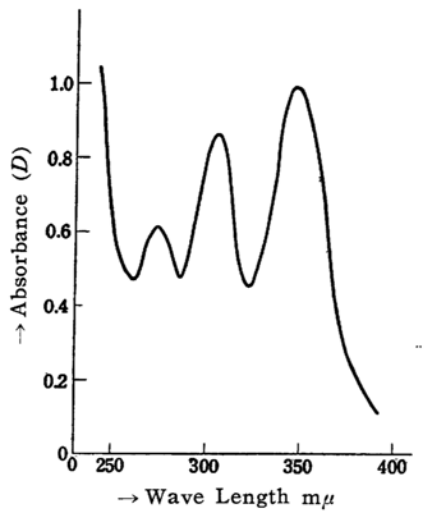

Fig. 1. Iodoform absorption spectrum.

Experimental

Apparatus.—Shimadzu's photoelectric spectrophotometer with glass cells of 10 mm. thickness and a tungsten lamp was used for absorbancy measurement.

Reagents.—Sodium hydroxide solution: 25% aqueous solution.

Iodine solution: 4 g. of potassium iodide and 20 g. of iodine in 80 ml. of water.

Sodium thiosulfate solution: 5% aqueous solution.

Anhydrous sodium sulfate: First grade reagent.

Chloroform: First grade reagent.

Procedure.—Place 7 ml. of 20% iodine solution in a 100 ml. separatory funnel and add 2 ml. of 25% sodium hydroxide solution. Mix by swirling. When the resulting solution is not distinctly orange-yellow, add iodine solution drop by drop. To this hypoiodite solution add 1 ml. of the sample containing no more than 400 γ acetone, and mix immediately. Shake for 5 minutes at

* Mitsubishi Rayon Co., Ltd., Kyobashi, Tokyo.
** Tokyo Scientific College, Shinjuku-ku, Tokyo.

1) J. Messinger, *Ber.*, **21**, 3366 (1888).
2) G. L. Barthauer, F. V. Jones and A. V. Metler, *Ind. Eng. Chem., Anal. Ed.*, **18**, 354 (1946).
3) S. D. Nogare, T. O. Narris and J. Mitchell, *Anal. Chem.*, **23**, 1473 (1951).
4) K. P. Stolyarov and I. A. Stolyarova, *Zhur. Anal. Khim.*, **8**, 33 (1953).
5) S. N. Andreev and R. I. Gindina, *Zhur. Priklad. Khim.*, **26**, 104 (1953).
6) H. Etienne, *Ind. Chem. Belge.*, **17**, 455 (1952).
7) S. A. Shchukarev, S. N. Andreev and O. V. Sapozhnikava, *Zhur. Anal. Khim.*, **9**, 193 (1954).

room temperature continuously to keep the mixture apparently homogeneous. When the orange-yellow color gradually fades, add more iodine solution dropwise until the color is restored.

After reaction, discharge the iodine color with a few drops of 5% sodium thiosulfate. Add 14 ml. of chloroform from a burette and extract the produced iodoform by shaking. Let stand until the phases are separated and transfer the chloroform layer to another 100 mm. separatory funnel containing approximately an equal volume of water. Shake vigorously, and transfer the chloroform layer to a 10 ml. glass cell, through a funnel containing a thin bed of anhydrous sodium sulfate supported on a glass wool as shown in Fig. 2. Measure the absorbancy of this chloroform extract against water in a 10 mm. glass cell. Calculate the amount of acetone using the calibration curve, shown in Fig. 3, obtained by the following procedure.

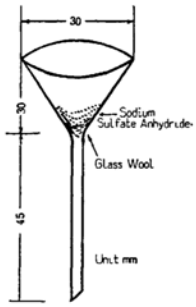

Fig. 2. Drying funnel

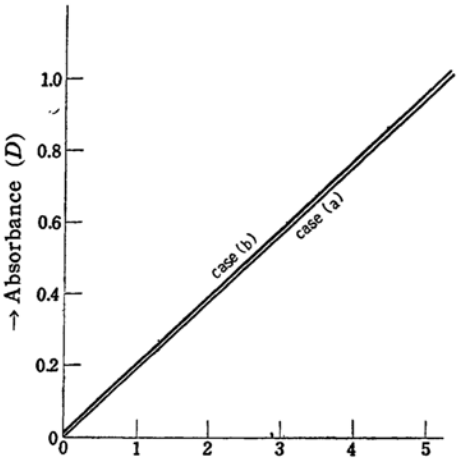

Fig. 3. Working curve for acetone.

Preparation of the calibration curve. Prepare the sodium hypoiodite solution similarly, to which less than 5 ml. of standard solution containing 79.6 γ of acetone in 1 ml. of water is added. Treat this similarly and extract the iodoform with 15 ml. of chloroform; wash the chloroform extract with water. The calibration curve obtained with pure acetone is shown in Fig. 3.

Discussion

(i) *On the calibration curve*:—On drawing the calibration curve employing 1 ml. of M-MM, the iodoform is extracted with 14 ml. of chloroform, as M-MM transfers to chloroform layer. When the M-MM is refined as shown in the following a), the calibration curve is in good agreement with that in Fig. 3; in the case of following b), it deviates higher than in the case of Fig. 3 by 0.1 in the absorbancy scale. This is due to the very small quantity of impurities, the presence of M-MM not affecting this analytical procedue.

(a) After washing M-MM with 10% sodium hydroxide, wash it with water five times, remove the water with calcium chloride, and collect the middle fraction 46°C, 100 mmHg, by vacuum distillation with cuprous chloride as stabilizer. Repeat this operation.

(b) After washing M-MM with 10% sodium hydroxide, wash it twice with water, remove the water with calcium chloride, and then collect the middle fraction similarly.

(ii) *Reaction conditions*:—The critical studies made by Hatcher and Mueller[8] and Nogare[3] showed that both the concentration and the order of addition of reagents determined the yield of the iodoform obtained. It was confirmed that the highest conversion from acetone into iodoform is effected by adding in the order iodine solution, sodium hydroxide solution, on the sample. Concerning the concentration of the reagents, the optimum condition is indicated by the orange-yellow color of the solution obtained by mixing 20% iodine solution and 25% sodium hydroxide. This experiment also exhibits that an insufficient or an excessive iodine relative to sodium hydroxide results in lower conversion into iodoform. Namely it is important to make the sample react in an orange-yellow solution and to maintain this orange-yellow by dropwise addition of iodine solution, when this color is discharged during reaction.

The effect of time on iodoform reaction under the optimum conditions is shown in Table I. Five minutes suffice; no marked change was observed with increasing reaction time up to 7 minutes. No significant difference was observed with the reaction temperature in this experiment but a low-temperature is desirable in order to avoid evaporation of M-MM. After reaction, the excess of iodine in the hypoiodite mixture can also be removed with sodium

8) W. H. Hatcher and W. H. Mueller, *Trans. Roy. Soc. Can.*, **23**, Sect. 3, 35 (1929).

TABLE I

EFFECT OF TIME ON IODOFORM REACTION

Sample	Acetone, mg.	Reaction time, min.	Absorbancy
A	0.232	2	0.465
	0.232	3	0.505
	0.232	4	0.540
	0.232	5	0.550
	0.232	6	0.550
	0.232	7	0.550
B	0.256	2	0.530
	0.256	3	0.590
	0.256	4	0.605
	0.256	5	0.610
	0.256	6	0.610
	0.256	7	0.610

sulfite or additional sodium hydroxide without sodium thiosulfate.

(iii) *On the volume of the sample*:—When more than one ml. of the sample is taken, the absorbancy becomes lower than that calculated or the results are not reproducible, as shown in Table II. The

TABLE II

RELATION BETWEEN THE VOLUME OF THE SAMPLE M-MM AND ABSORBANCY

Sample	Volume		
	1 ml.	2 ml.	3 ml.
D	0.095	0.169 obs.	0.210 obs.
		0.190 calcd.	0.285 calcd.
E	0.286	0.535 obs.	0.810 obs.
		0.572 calcd.	0.845 calcd.
F	0.317	0.555 obs.	0.835 obs.
		0.630 calcd.	0.940 calcd.

calcd.: Absorbance at sampling volume 1 ml. × sampling volume.

reason may be considered as follows. The M-MM layer and the aqueous layer should be mixed well by shaking and acetone in the M-MM layer should be transfered to the aqueous layer, since acetone reacts with sodium hypoiodite in the aqueous layer. On taking more than 1 ml. of the sample, the M-MM and the aqueous layer do not mix perfectly, as M-MM is very easily separated from water.

(iv) *On iodoform*:—The intensity of the absorption in chloroform-M-MM layer was not affected by temperature from 15°C to 30°C. It was observed that iodoform slowly decomposed to liberate iodine in chloroform to decrease the absorbancy; it did not decompose, however when M-MM was present in the chloroform and maintained the absorbancy unchanged for more than one hour.

Ultraviolet absorption spectrum of the chloroform extract, using commercial M-MM as a sample showed complete agreement with that by the use of a mixture of aqueous acetone solution and refined M-MM. It can be ascertained that the product of the reaction is iodoform.

(v) *Effect of coexisting substance*:—Interference will be encountered from compounds which give iodoform by reaction with sodium hypoiodite. Possible interfering compounds are acetaldehyde, ethanol and methyl ethyl ketone, but in this method conversion of acetaldehyde and ethanol into iodoform is, respectively, 58 and 0.3%[3]. In many cases carbonyl compounds which interfere with the absorption at 347 mμ can be washed away from the chloroform extract with aqueous hydroxylamine hydrochloride.

Effect of methanol, formaldehyde, hydroquinone and peroxides which possibly coexist with M-MM is shown in Table III. Small quantities of methanol and formaldehyde do not affect this method.

TABLE III

EFFECT OF COEXISTING SUBSTANCE

Acetone mg.	Coexisting substance	(%)	Absorbancy
0.256	M-M only		0.610
0.256	Methanol*	(0.5)	0.615
	〃	(0.2)	0.610
0.256	Formaldehyde	(0.1)	0.610
	〃	(0.05)	0.610
0.256	Hydroquinone	(0.04)	0.520
	〃	(0.02)	
0.256	Hydrogen Peroxide	(0.06)	0.505
	〃	(0.04)	0.610

* Large quantities of methanol cause white precipitate.

(vi) *Example of analysis*:—A commercial M-MM (90 ml.) was used as the sample of unknown concentration of acetone; this was submitted to single distillation and 5 ml. fractions were collected from forerun fraction in order. These fractions were, respectively named sample No. A_1,

TABLE IV

EXAMPLE OF ANALYSIS OF ACETONE IN M-MM FRACTION

Sample No.	Acetone content mg./ml.
A_1*	0.656
A_2*	0.608
A_3*	0.504
A_4	0.364
A_5	0.268

* Measured after twice dilution.

A_2,……, A_5 and the acetone in these fraction determined by the procedure mentioned above. Table IV shows an example of the results.

Summary

The method described here is based on the utilization of the iodoform reaction. The essential point of this method consists in the complete shaking of the methyl methacrylate monomer with sodium hypoiodate solution. The methyl methacrylate monomer is water-insoluble and iodoform reaction proceeds in an aqueous medium. As a result, it was confirmed that methyl methacrylate monomer does not affect this reaction substantially and one ml. sample makes it possible to determine small quantities (0.001%) of acetone in the sample monomer. This method is more sensitive than the hydroxylamine hydrochloride method previously used.

Institute of Techno-Analytical Chemistry
Faculty of Engineering, Tokyo
University, Hongo, Tokyo