Spectrophotometric Determination of Acetone by the Salicylaldehyde Method

SVANTE BERNTSSON

AB Pripp & Lyckholm, Gothenburg, Sweden

A spectrophotometric method for determining acetone in aqueous solutions by means of salicylaldehyde is described. The color conforms to Beer's law in the range of 0.00015 to 0.0028 mmole and after the initial 2 hours it is stable for several hours.

CSONKA (*3*) proposed the salicylaldehyde method for determining acetone. The method of color development, which has been revised by several authors, involves the reaction of acetone with a solution of salicylaldehyde in ethyl alcohol in alkaline solution at an elevated temperature. The results are not reproducible and the color is not stable.

The present author, when studying the determination of pyruvic acid by the salicylaldehyde method (*1*), observed that the use of pure salicylaldehyde instead of an ethyl alcohol solution of this reagent gave much better results. The technique has been applied to the determination of acetone in aqueous solutions. The results are in agreement with Beer's law and the color intensity after the initial 2 hours remains constant for several hours.

Braunstein (*2*) reported that all compounds containing a CH_3CO group linked directly to a hydrogen or carbon atom give a positive salicylaldehyde reaction. Thomson (*4, 5*) reported that the specificity range of the reaction is not as narrow as reported by Braunstein. According to Thomson, the mechanism of the salicylaldehyde color reaction involves condensation of the salicylaldehyde with a methylene group in the α-position to an unsaturated group such as carbonyl (CO). Among substances that interfere with the determination of acetone by the salicylaldehyde method are acetaldehyde, diacetyl, acetophenone, benzoylacetone, pyruvic acid, levulinic acid, and acetoacetic acid. According to experiments by the present author, bisulfite ions and formaldehyde in large amounts prevent to some extent the development of color.

APPARATUS, REAGENTS, AND SOLUTIONS

Beckman Model DU spectrophotometer.
Acetone, "pour analyse, No. 1001," Union Chimique Belge.
Salicylaldehyde, from bisulfite compound, No. 225, Eastman organic chemicals.
Sodium hydroxide solution, 425 grams per liter.

RECOMMENDED PROCEDURE

In a 50-ml. volumetric flask 2 ml. of sodium hydroxide solution is added to the aqueous sample containing 0.00015 to 0.0028 mmole of acetone. The solution is diluted with water to about 25 ml. and 0.6 ml. of salicylaldehyde is added from a microburet. The flask is shaken, 20 ml. of sodium hydroxide solution is added, and the volume is adjusted to 50 ml. with water. The flask is allowed to stand for at least 2 hours before the extinction is read against a reagent blank at 474 mμ. The amount of acetone in the sample is then evaluated from a calibration curve.

EXPERIMENTAL

The conditions that affect the development of color were investigated systematically, using about 0.00065 mmole of acetone. The effects of time, sodium hydroxide concentration, and salicylaldehyde concentration on the color development were investigated (Table I). To determine the influence of temperature on color development, the reaction mixture was treated for half an hour at various temperatures (Table II). As can be seen, the best color development is obtained at room temperature with 2 + 20 ml. of sodium hydroxide solution and 0.6 ml. of salicylaldehyde. More than 2 + 20 ml. of sodium hydroxide solution cannot be used because of decreasing solubility of salicylaldehyde with increasing sodium hydroxide concentration. The color is stable for several hours after the initial 2 hours.

Table I. Effect of Time and Reagent Concentration

	Hours					
Added, Ml.	0.5	1	2	3	5	24
	Absorbance					
Sodium hydroxide						
2 + 5	0.015	0.019	0.032	0.048	0.066	0.148
2 + 10	0.097	0.090	0.120	0.155	0.188	0.208
2 + 15	0.149	0.172	0.231	0.240	0.235	0.223
2 + 20	0.230	0.241	0.253	0.249	0.250	0.240
Salicylaldehyde						
0.4	0.197	0.243	0.239	0.247	0.236	...
0.5	0.225	0.253	0.260	0.257	0.261	...
0.6	0.267	0.273	0.272	0.274	0.272	...
0.7	0.253	0.261	0.263	0.262	0.261	...

Table II. Effect of Temperature

Temp., ° C.	Absorbance
20	0.271
50	0.249
75	0.228
100	0.212

The curves of extinction *vs.* wave length at five different concentrations of acetone (0.0002 to 0.0020 mmole) were determined. The curves had a maximum at 474 mμ, independent of the acetone concentration. As the reagent blank had a considerable light absorption at 474 mμ, the readings were made against a reagent blank.

Experiments with 0.0001 to 0.0050 mmole of acetone were carried out to get a calibration curve. Beer's law was found to be valid up to an absorbance of 1.0, allowing a maximum amount of 0.0028 mmole of acetone to be determined according to the calibration curve. The relative error in the range of 0.00015 to 0.0028 mmole was less than 2%.

ACKNOWLEDGMENT

The managing director of AB Pripp & Lyckholm has kindly given permission for this work to be published.

LITERATURE CITED

(1) Berntsson, S., Anal. Chem. **27**, 1659 (1955).
(2) Braunstein, A. E., *Nature* **140**, 427 (1937).
(3) Csonka, F. A., *J. Biol. Chem.* **27**, 209 (1916).
(4) Thomson, T., *J. Soc. Chem. Ind.* **65**, 121 (1946).
(5) Thomson, T., *Nature* **141**, 917 (1938).

Received for review November 30, 1955. Accepted April 27, 1956.