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RESIDUE DETERMINATION OF HYDRAZINE IN WATER BY DERIVATIZATION AND GAS CHROMATOGRAPHY

SAMI SELIM and CHARLES R. WARNER

Division of Chemistry and Physics, Food and Drug Administration, 200 C Street, S.W., Washington D.C. 20204 (U.S.A.)

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SUMMARY

A method is described for the determination of hydrazine residue in water. Hydrazine is converted to the acetone azine, which is extracted with methylene chloride and determined by gas chromatography using a nitrogen/phosphorus detector. The limit of detection is 0.1 part per billion (10^9), and the recoveries averaged 92% for water fortified with 0.1 to 10 parts per billion of hydrazine.

The derivatization of trace levels of hydrazine with a large excess of acetone was compared in a predominantly aqueous system and a methanolic system. The derivatization proceeds quantitatively in 53 min in the methanolic system and in less than 2 min in the aqueous system. Excellent yields of the azine were obtained at ppb levels.

INTRODUCTION

Hydrazine, hydrazine salts and simple organic derivatives are used as rocket fuel, in boiler water treatment, and in the manufacture of herbicides and medicinals. The parent substance, as well as its salts, has been shown to be carcinogenic in mice after oral and intraperitoneal administration and in rats after oral administration[1]. Hydrazine is at present regulated for use as a boiler water additive, provided it does not migrate to the steam which contacts foods. A zero tolerance for hydrazine in steam was placed on this use because of the carcinogenic properties of hydrazine.

A reliable method for the measurement of hydrazine at low levels in aqueous solution is needed to determine hydrazine in steam condensates. There are many tests for the detection of hydrazine based on its powerful reducing properties. Such methods are adequate if the sample is free of other reducing substances. A number of colorimetric methods have also been reported based on the reaction of hydrazine with an aldehyde or a ketone to give a colored derivative. Colored derivatives were formed with salicylaldehyde[2], indanedione[3–5], p-dimethylaminobenzaldehyde[6–10], 1,2-naphthoquinone-4-sulfonate[11–12], and 2,3-dichloro-1,4-naphthoquinone[13].

Colorimetric methods for hydrazine, although generally more specific than oxidation–reduction methods, still are subject to a number of interferences. Hydroxyl-

amine, urea, amino acids, and some amines are typical interferences that have been reported. The gas chromatographic analysis of the intact hydrazine[14] was difficult because of peak tailing due to the extremely polar nature of the compound and difficulty in separating it from commonly found impurities. Attempts to apply the gas chromatographic determination of aqueous traces (0.1 ppm) of hydrazine as its pyrazole[15] to tobacco and tobacco smoke were unsuccessful because of the instability of the derivative[16]. A polarographic method[17] and an electrochemical method[18] have also been described.

Since hydrazine is an animal carcinogen it cannot be permitted as either a direct or an indirect food additive. This paper presents a quantitative method for the determination of hydrazine in water at the parts per billion* (ppb) level to permit regulation of this highly toxic substance which may come in contact with food. This method involves the formation of the acetone azine, $[(CH_3)_2CN]_2$, which is determined by gas chromatography using the nitrogen/phosphorus detector.

EXPERIMENTAL

Materials and reagents

Hydrazine hydrate (85% in water), acetone, and monobasic potassium phosphate were obtained from Fisher Scientific (Fairlawn, N.J., U.S.A.). Distilled-in-glass methanol was obtained from Burdick & Jackson Labs. (Muskegon, Mich., U.S.A.).

Acetone azine was prepared by adding 5 ml of acetone to 1 ml of hydrazine hydrate in a 10-ml round-bottom flask and allowing the solution to stand at room temperature for 1 h. The solution was then distilled and acetone azine (b.p. 93°) was collected. A mass spectrum of the azine confirming the structure of the compound is shown in Fig. 1.

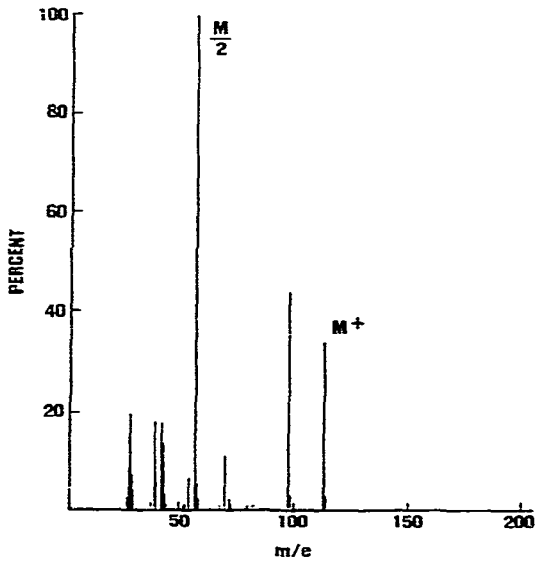

Fig. 1. Mass spectrum of acetone azine.

* Throughout this article the American billion (10^9) is meant.

Apparatus

A Tracor Model 560 gas chromatograph equipped with a Tracor 702 nitrogen/phosphorus detector was used. The glass chromatographic column (9 ft. × 2 mm I.D.) was packed with 10% EGA on 80–100 mesh Chromosorb W AW DMCS (commercially available from Supelco, Bellefonte, Pa., U.S.A.). The carrier gas flow was set at 30 ml/min, the hydrogen flow at 5.0 ml/min, and the air flow at 150 ml/min. The oven, detector and injector temperatures were set at 80°, 200° and 200°, respectively.

The gas chromatograph–mass spectrometer used was a Hewlett-Packard 5992 system. The 6-ft. glass gas chromatographic column was packed with 5% OV-17 on 80–100 mesh Chromosorb W HP. The oven and injector temperatures were set at 100° and 150°, respectively.

Procedure

One gram of monobasic potassium phosphate was dissolved in 100 ml of water. Twenty milliliters of methanol and 10 ml of acetone were added and the sample was left at room temperature for about 1 h. The sample was then extracted three times with 100 ml of methylene chloride. The methylene chloride extract was dried over sodium sulfate and collected in a 500-ml round-bottom flask. The sample was concentrated on a rotary evaporator to about 3 ml and transferred to a graduated test tube. The solvent was further concentrated, using a gentle stream of nitrogen. The solution should not be permitted to evaporate to dryness. The solvent volume was adjusted and an aliquot injected into the gas chromatograph.

RESULTS AND DISCUSSION

The reaction between hydrazine and acetone was studied at room temperature in methanol and water. An excess of acetone (1 ml) was added to 10 ml of methanol containing hydrazine, and at different time intervals, an aliquot was injected onto the gas chromatograph. Hydrazine was quantitatively converted to its acetone azine in 53 min (Table I, Fig. 2). The reaction was repeated in water (buffered at pH 5)–methanol (4:1). Aliquots were taken at the same time interval and extracted with methylene chloride, and the methylene chloride was injected into the gas chromatograph. Hydrazine was quantitatively converted to the azine at the first sampling time of 2 min. The reaction between acetone and hydrazine is much faster in the aqueous medium than in methanol.

Although a number of carbonyl compounds could be used to derivatize hydrazine, acetone offers many advantages. It is very water-soluble, and an excess of it can be used to insure a quantitative conversion of all the hydrazine to the azine. After the derivatization, the excess acetone is eliminated in the extraction and the concentration process. The reaction of acetone, a symmetrical ketone, and hydrazine will give only one compound, which chromatographs as a single peak. The reaction of aldehydes or unsymmetrical ketones with hydrazine will yield the *syn*- and *anti*-isomers of the corresponding azine. These compounds could give two peaks on the gas chromatogram. The acetone azine contains two nitrogen atoms and can be analyzed by gas chromatography using a nitrogen-specific detector. As little as 200 pg of the derivative could be detected.

As shown in Table II, the recovery of hydrazine from water fortified with

TABLE I

CONVERSION OF HYDRAZINE TO THE ACETONE AZINE AT ROOM TEMPERATURE IN METHANOL

Time (min)	*Added (μg)*	*Found (μg)*	*Recovery (%)*
2	100	20.0	20.0
8	100	52.5	52.5
15	100	67.5	67.5
21	100	77.5	77.5
27	100	90.0	90.0
34	100	92.5	92.5
40	100	95.0	95.0
46	100	97.0	97.0
53	100	100.0	100.0
59	100	100.0	100.0

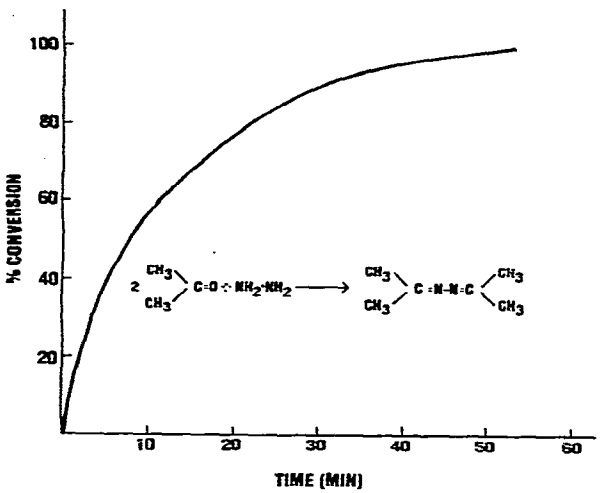

Fig. 2. Rate of conversion of hydrazine to acetone azine in methanol.

TABLE II

RECOVERY OF HYDRAZINE FROM WATER

Fortification level (ppb)	*Recovery (%)*
0.1	82.1
	92.4
	87.3
1.0	93.0
	89.6
	109.0
6.0	99.4
	98.8
	104.8
10.0	88.0
	78.2
	81.0
Av.	92

0.1–10 ppb hydrazine averaged 92%. The method can detect as little as 0.1 ppb. Fig. 3 shows a chromatogram of a standard of acetone azine obtained by the procedure described.

Representative chromatograms obtained from a water blank, water fortified with 0.1 ppb and a steam condensate sample collected from boiler water containing hydrazine are shown in Fig. 3. Check samples of boiler water and steam condensate, tap water and distilled deionized water were found to contain no GC interferences in the acetone azine area.

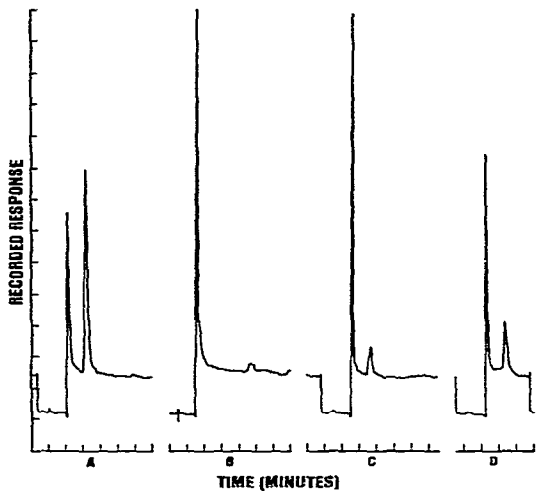

Fig. 3. (A) chromatogram of 1.76 ng of acetone azine on a 9 ft. × 2 mm I.D. glass column packed with 10% EGA on 80–100 mesh Chromosorb W AW DMCS. Column temperature 80°. (B) Water blank. (C) Water fortified with 0.1 ppb of hydrazine. (D) Water containing 0.2 ppb of hydrazine.

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