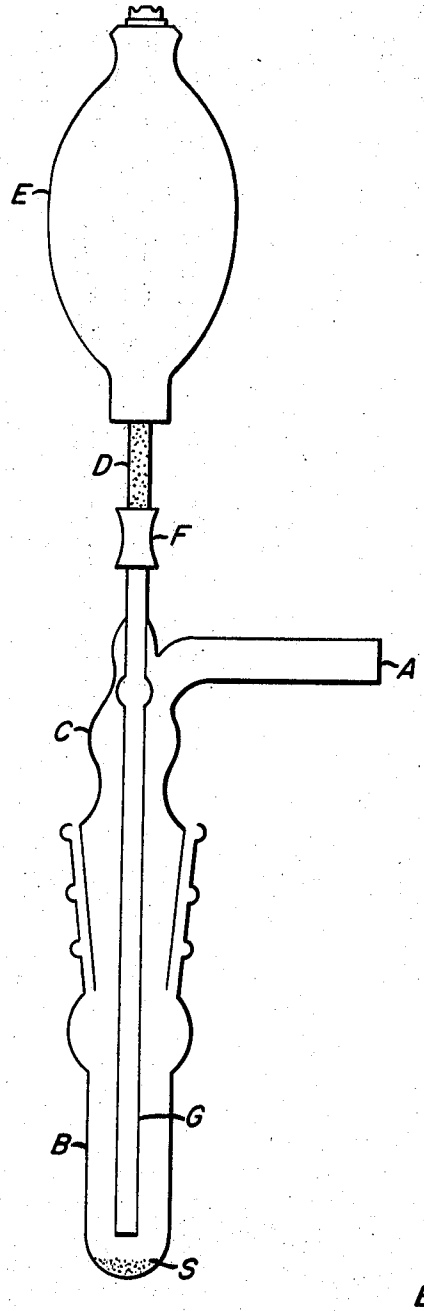
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ISOCYANIDE INDICATOR

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ISOCYANIDE INDICATOR

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ABSTRACT OF THE DISCLOSURE

The colorimetric method of detecting the presence of microgram amounts of isocyanide groups in the various chemical compounds or mixtures comprising the steps of placing the chemical compound or mixture upon an inert support medium and then contacting with the detector a benzidine reagent or tetra base reagent producing a blue color indicating the presence of the isocyanide group.

DEDICATORY CLAUSE

The invention described herein may be manufactured, used, and licensed by or for the Government for governmental purposes without the payment to us of any royalty thereon.

SPECIFICATIONS

This invention is directed to the detection of isocyanides.

The object of this invention is the microchemical detection of isocyanides.

The further object of this invention is the colorimetric detection of isocyanides.

The independent discovery of isocyanides by Hofmann and Gautier was about 100 years ago. During this period of time only one chemical-detection method for isocyanides has been mentioned in the literature by Smith et al. J. Org. Chem., 23, 1599 (1958). The coauthors mentioned the work of Pertusi and Gastaldi stating that the test is not specific for isocyanides and then are silent as to the various experimental details such as proportions and conditions for this non-specific method.

The detection of hydrogen cyanide has been reported by several investigators. Fritz Feigel, Spot Test in Organic Analysis, 4th ed., p. 258, Elsevier Publishing Company, New York (1954) describes the reagent palladium-di-methylglyoximate and Ni^{++} for detecting the presence of cyanide (—CN). This same reagent does not show the presence of isocyanide (—NC). Similarly, Brooke, Anal. Chem., 24, p. 583, 1952, teaches the use of the reagent palladium-α-furildioxime and Ni^{++} for detecting cyanide. This reagent does not indicate the presence of isocyanide.

In view that there are no reported chemical detection methods for isocyanides, an investigation was instituted for detecting isocyanides which are known toxic compounds.

As a result of our investigation, it is now possible to detect at least 0.06 μg. of an aliphatic or aromatic isocyanide with benzidine acetate or tetra base reagent.

The benzidine reagent is mixed just prior to use, comprises equal volumes of (a) aqueous cupric acetate solutions, 2.29–3.43 g./l. and (b) 675 ml. of benzidine acetate solution, saturated at room temperature, mixed with 525 ml. of water. The solutions (a) and (b) are best stored separately and in dark bottles. The preferred range for the aqueous cupric acetate is 2.86 g./l.

Tetra base reagent comprises mixing solutions of equal volumes of (a) 80–120 mg. of p,p'-tetramethyldiaminodiphenylmethane and 400–600 mg. of salicylic acid in 100 ml. of acetone and (b) 1.2–1.8 g. of cupric sulfate in 100 ml. of water. The preferred range is 100 mg. p,p'-tetramethyldiaminodiphenylmethane, 500 mg. salicylic acid and 1.5 g. cupric sulfate.

Our invention comprises the method utilizing two different reagents for detecting isocyanides colorimetrically on various support media such as filter paper, synthetic resin treated filter paper, or silica gel.

A satisfactory colorimetric reaction must (1) give sharp, clear, color change; (2) preferably upon a white background; and (3) extremely sensitive. Filter paper and silica gel being white are therefore considered as the desired support media.

The filter papers such as S&S 589W, 597, 604 (available from Carl Schleicher & Schuell Co.) and Whatman 3, 531, 120 (available from W. and R. Bolson, Ltd.) used in our invention have low speed that is a long time required to pass a given amount of water, high retention being the ability to retain fine precipitates and the paper is unwashed that is no available residual acid remaining upon the paper to react with the isocyanide. A modified filter paper such as described in Military Specification, Detector Paper, U.S. Government Printing Office, MIL–P–51181 (MU), Mar. 6, 1964, being a high α-cellulose filter paper impregnated with about an 0.8% of a powdered melamine-formaldehyde resin such as commercially available or as Parez Resin 607, available from American Cyanamid Company. Other various support media which proved to be unsatisfactory are, for example, Whatman paper No. 40, 41 are washed with hydrochloric and hydrofluoric acids and the double washed grades of S and S 589 Blue and Black Ribbon.

The use of silica gel tubes and the detecting apparatus are well established in the open literature that may be employed according to our colorimetric method, Shepherd, Anal. Chem., 19, 77, 1947; Williams et al., Anal. Chem. 34, 225, 1962.

In general the silica gel tube is constructed as follows: a glass tube about 4 inches in length (3 mm. I.D.)containing the untreated silica gel or treated silica gel and then sealing off both ends ofglass tubing. The filling operation are those conventional in the art such as tamping the silica gel into the tube. Prior to use of the silica gel filled tube each end of the tube is broken off a fraction of an inch from each end and inserted in the various commercially available sampling apparatus.

When an unimpregnated silica gel detector tube is used, the isocyanide vapor is collected on the silica gel, the detector tube is removed from the apparatus, and the silica gel is moistened with a drop of either the benzidine or the tetra base reagent. The appearance of a blue color is a positive test for isocyanide. Those detector tubes prepared with the tetra base reagent impregnating the silica gel are read directly while on the testing apparatus.

The figure represents the apparatus we employed in our studies and that can be assembled from equipment readily available in the laboratory. A—air inlet; B—2 x 9 cm. test tube with 19/38 standard taper joint fitted with a length of glass tubing G that extends to within about 5–10 mm. of the bottom; C—adapter; D—silica gel detector tube; E—rubber aspirator bulb with a one-way valve; F—a short length of rubber tubing connecting the detector tube and length of glass tubing; S—sample.

The only requirement imposed on the sample when using the silica gel detector tubes is that the isocyanide compound be readily vaporizable. There are no physical characteristics placed upon the sample when utilizing the filter paper support.

Sample S is placed in bottom of test tube B and upon compressing the rubber aspirator bulb E air is available thru A striking the sample, thus permitting the volatilizables to pass up through the glass tubing into the detector

silica gel D which is removed for detecting the presence of isocyanides according to the present invention.

EXAMPLE 1

(a) A sample of about 0.06 μg. of n-butyl isocyanide was placed in the test tube B of the apparatus of the figure and the vaporizable isocyanide is collected on the silica gel which is subsequently treated with about 1 drop (0.05 ml.) of the benzidine reagent turning blue indicating an isocyanide.

(b) The above procedure was followed substituting a sample of about 0.05 μg. which did not give the characteristic blue color for isocyanides indicating the sensitivity to be about 0.06 μg.

(c) The procedure in (a) supra was repeated utilizing up to 0.15 μg. of isocyanide, all giving positive tests.

EXAMPLE 2

(a) Other alkyl isocyanides such as sec-butyl and tertiary butyl were similarly tested as in Example 1, but substituting the tetra base reagent for the benzidine reagent giving the blue color with the isocyanides in the proportion of 0.06 μg. to 0.09 μg.

(b) Other aliphatic (e.g., C_1 to C_{15} carbon atoms), aromatic (e.g., phenyl), or heterocyclic (e.g., pyridyl) isocyanides gave the colorimetric test with a sample containing at least 0.06 μg. of isocyanide in accordance with the procedure (a) supra.

The stability of the color formed by the benzidine or tetra base reagent on the silica gel as in Examples 1 and 2 was found to vary considerably. Utilizing about 0.1 μg. of butyl isocyanide, for example, the color formed in the benzidine test faded after about 1 to 5 minutes. The color formed as a result of the use of the tetra base reagent was stable for about 1 hour. All the silica gel support media impregnated with aliphatic, aromatic or heterocyclic isocyanides and the blank controls utilizing tetra base reagent turned deep blue on prolonged standing of about 2 hours.

EXAMPLE 3

(a) Benzidine reagent of about 10 μl. was placed on filter paper, Whatman 3, and a solution containing 0.18 μg. of n-butyl isocyanide placed on the benzidine reagent producing the blue color.

(b) The procedure in (a) supra was repeated substituting the tetra base reagent for the benzidine giving a positive test for the n-butyl isocyanide.

(c) Other aliphatic or aromatic isocyanides such as methyl isocyanide in the proportion of 0.2 μg. to 5 μg. were tested indicating the presence of isocyanide with either the benzidine or tetra base reagent in accordance to procedure of (a) or (b) supra on other unwashed, high retention and low speed filter paper as support media such as S&S 589W, 597 or 604; Whatman 120, 31, 5; filter paper covered with about 0.8% of melamine-formaldehyde resin.

EXAMPLE 4

(a) Tetra base reagent of about 10 μl. placed on filter paper covered with about 0.8% of melamine-formaldehyde resin and a sample containing about 5 μg. of n-butyl isocyanide gave a positive test.

(b) Benzidine reagent of about 10 μl. was placed in the filter paper treated with resin as in (a) supra and a sample containing about 0.5 μg. of n-butyl isocyanide also gave a positive test.

(c) Similar results were obtained under (a) and (b) supra when substituting unwashed, high retention, and low speed filter paper as support media such as Whatman 120 as the support media.

(d) The blue color with the tetra base reagent was stable, whereas that with the benzidine reagent faded within a few minutes.

We claim:

1. The colorimetric method of detecting the presence of isocyanide groups in a mixture of components comprising the steps of placing the said mixture comprising small amounts of organic isocyanide compounds upon an inert support medium and then contacting with the detector a benzidine reagent comprising equal volumes of (a) 2.29–3.49 grams cupric acetate per liter of water and (b) 675 ml. saturated solution benzidine acetate and 525 ml. of water, and producing a visible blue color indicating the presence of isocyanide groups.

2. A method according to claim 1 wherein the organic isocyanides are aliphatic compounds containing from C_1 to C_{15} carbon atoms, aromatic compounds or heterocyclic compounds.

3. A method according to claim 1 wherein the detector is the benzidine reagent.

4. A method according to claim 1 wherein the detector is impregnated upon the silica gel prior to contact with the components comprising the organic isocyanides.

5. A method according to claim 1, wherein the inert support medium is filter paper of low speed, high retention and unwashed, synthetic resin treated filter paper or silica gel.

6. A method according to claim 5 wherein the synthetic resin treated filter paper is a high α-cellulose filter paper impregnated with about 0.8% of powdered melamine-formaldehyde resin.

7. The colorimetric method of detecting the presence of the isocyanide groups in a mixture of components comprising the steps of placing the said mixture comprising isocyanide groups upon an inert support medium and then contacting with the detector a tetra base reagent comprising equal volumes of (a) 100 ml. of acetone containing 80–120 mg. of p,p'-tetramethyldiaminodiphenylmethane and 400–600 mg. salicylic acid and (b) 1.2–1.8 grams of cupric sulfate in 100 ml. water, and producing a visible blue color indicating the presence of isocyanide groups.

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