

FUNGICIDE ANALYSIS

Direct Determination of Methyl Mercuric Dicyandiamide

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In an investigation of mercurial fungicides, an analytical procedure for methyl mercuric compounds was developed. The method may be used to determine methyl mercuric dicyandiamide or chloride in aqueous solution in the range of 1 to 100 γ . Common metallic ions, including mercury (II), do not interfere at the 1000 γ level. The expected accuracy is within $\pm 3\%$.

THE WIDESPREAD USE of methyl mercuric dicyandiamide (cyanoguanidine) in the seed treatment of cereal grains made the development of an analytical procedure for this organic mercury compound desirable. The determination is an adaptation of the procedure for ethyl and phenyl mercury compounds using diphenylthiocarbazone (dithizone) (7), and of a similar field test for methyl mercury compounds (2).

Reagents

1. Methyl mercuric dicyandiamide (supplied by Panogen, Inc.), dissolved at the rate of 100 γ per ml. of water, is used for preparing a standard curve. Methyl mercuric chloride, prepared by shaking hydrochloric acid and chloroform with the dicyandiamide compound, crystallizing from the chloroform, and recrystallizing from methanol, may also be used as a standard. The melting point is 170° C. (3).

2. To a solution 1N in respect to sodium chloride and 0.05N in hydrochloric acid is added 1 ml. of a 20% solution of hydroxylamine hydrochloride for each 400 ml. of solution. The sodium chloride and hydroxylamine used are dithizone extracted.

3. To 77 grams of ammonium acetate trihydrate per liter of water is added sufficient acetic acid to give a pH of 6.0. This buffer is purified by dithizone extraction.

4. Eastman white label dithizone is dissolved at the rate of 1 mg. per ml. in chloro-

Table II. Comparison of Absorbance of Equivalent CH_3Hg Dithizone from CH_3HgCl or $\text{CH}_3\text{HgC}_2\text{N}_4\text{H}_3$

Material, γ CH_3HgCl	Equivalent to γ CH_3Hg	Absorbance
17.4	15	0.652
29.0	25	0.537
40.7	35	0.417
52.3	45	0.299
$\text{CH}_3\text{HgC}_2\text{N}_4\text{H}_3$		
20.8	15	0.650
34.6	25	0.534
48.4	35	0.417
62.3	45	0.303

form. One milliliter of a 4 to 50 dilution of this stock solution gives a working range of 15 to 70 γ of methyl mercuric dicyandiamide. By further dilution of the dithizone, amounts down to 1 γ may be determined.

The water and chloroform are redistilled in a glass still.

Procedure

Exactly 15 ml. of chloroform and 20 ml. of reagent 2 are placed in a small separatory funnel. An aliquot of an aqueous solution of the sample, not larger than 2 ml. and containing 15 to 70 γ of the methyl compound, is added and the separator is shaken vigorously for 1

minute. The chloroform phase is transferred to a second funnel which contains 20 ml. of reagent 3. An additional 5.0 ml. of chloroform is measured into the first separator and the shaking and transfer are repeated. One milliliter of the diluted reagent 4 is measured into the second funnel and shaken for 30 seconds. The chloroform phase is transferred to a colorimeter tube. The percentage transmittance is determined using an Evelyn photoelectric colorimeter with a 620 filter.

The amount of methyl mercuric compound present is determined by comparing with a curve prepared by using the standard, reagent 1, in the above procedure.

Discussion

The solubility of methyl mercuric dicyandiamide in water is so great that it cannot be extracted into the chloroform phase (Table I). However, when shaken with the sodium chloride-hydrochloric acid reagent in the first separatory funnel, it is converted to methyl mercuric chloride, which has a solubility ratio of 14.9 in chloroform and water. The completeness of this conversion is shown by the identical standard curves prepared from the chloride and the dicyandiamide compounds (Table II). The extraction of the chloride into the chloroform phase is calculated to be 98.3% complete under conditions of the procedure. The solubilities given in Table I for methyl mercuric chloride are higher than previously reported (3). Repeated determinations gave solubilities of 88,750, 88,700, 84,330, and 86,610 γ of methyl mercuric chloride per ml. of chloroform and 5890, 5840, and 5790 γ per ml. of water. For the water solubility, the amount of chloride as well as methyl mercury was determined. The chloride was equivalent to 5670 and 5620 γ of

Table I. Approximate Solubilities of Two Methyl Mercuric Compounds at Room Temperature

Material	Solubility, γ /ml.			Solubility Ratio, Chloroform/Water
	Water	Chloroform	Reagent 2	
$\text{CH}_3\text{HgC}_2\text{N}_4\text{H}_3$	21,700	50	6,850 ^a	0.0023
CH_3HgCl	5,840 (1.4) ^b	86,850 (54,900) ^b	5,720	14.9

^a Dicyandiamide is converted to chloride in this reagent. Solubility calculated as chloride is 5770 γ per ml.

^b Calculated from literature data (3).

methyl mercuric chloride per ml. of water. The spectrophotometric curve for the methyl mercury dithizonate has a minimum at 480 m μ , which is 10 m μ shorter than the mercury dithizonate.

The commercial formulation in common use, Panogen, is 2.2% methyl mercuric dicyandiamide and contains a red dye. This dye interferes by masking the color reaction at the pH used in the ethyl and phenyl determination. At a pH above 5.5, the red dye becomes colorless and therefore does not interfere in the procedure described.

One thousand micrograms of copper, cobalt, cadmium, iron, lead, nickel, silver, zinc, bismuth, and mercury (II) do not interfere in the determination. However, when large amounts of these

Table III. Accuracy of Procedure

CH ₃ HgC ₂ N ₄ H ₃ . γ /Ml.	
Calcd.	Found
28	28
44	42
55	54
88	88
110	110
133	133
176	177
220	225
264	263
308	312
440	439

ions are present, one drop of the chloroform phase should be held back in trans-

ferring to the second separatory funnel, so that none of the interphase will slip through. The accuracy of the procedure is within 3% or 2 γ , whichever is the larger (Table III).

Literature Cited

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FUNGICIDE DETERMINATION

Quantitative Determination of Biphenyl in Citrus Fruits And Fruit Products by Means of Chromatostrips

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Biphenyl-treated collars, liners, and pads are currently being used by the citrus industry to prevent molding during shipping and storage of citrus fruits. The possibility that the biphenyl vapors will be absorbed by the fruit has created a need for an analytical method for determining the amounts of biphenyl in the fruit and in processed citrus products. A procedure has been developed to separate the biphenyl from interfering citrus oils by chromatographing on chromatostrips. Two methods of quantitatively measuring the amount of biphenyl on the strips are presented. A visual method makes use of the point of minimum detection of the biphenyl spot under ultraviolet light. In the second method, the biphenyl spot is removed from the strip and eluted with alcohol. The concentration of biphenyl is then measured in an ultraviolet spectrophotometer at 248 m μ . Added biphenyl has been determined in citrus juices in as low a concentration as 0.1 p.p.m. and in citrus peel as high as 600 p.p.m. These methods are well suited to determine the amounts of biphenyl absorbed by citrus fruits during storage or shipment in a biphenyl atmosphere, and amounts occurring in processed citrus products.

THE USE OF BIPHENYL-TREATED COLLARS, liners, and pads for the prevention of molding during shipping and storage of citrus fruits in fiberboard cartons has created a need for an analytical method for the determination of this compound in juice, peel, whole fruit, and processed citrus products.

Tomkins and Isherwood's (9) colorimetric method does not have the accuracy required, because of the partial destruction of biphenyl by the sulfuric

acid treatment. Steyn and Rosselet (8) used an ultraviolet absorption method by applying a correction factor for the absorption caused by the citrus oils. The correction factor was obtained from biphenyl-free fruit, but the accuracy of this method is open to question, as the ultraviolet absorption of orange oil varies with individual fruits (2). Knodel and Elvin (5) have developed an infrared method for the determination of biphenyl in treated fiberboard cartons where citrus oil is not a factor.

A rapid method is needed capable of detecting biphenyl in as small an amount as 1 p.p.m. in juice, peel, or whole fruit of all varieties of citrus fruits. To achieve

this purpose, a chromatographic method was developed for separating the biphenyl from interfering citrus oils by using the chromatostrips of Kirchner, Miller, and Keller (4).

These are glass strips coated with an ultraviolet fluorescing adsorbent which is held in place by a suitable binder. The coated strips are used as a microchromatographic column in a manner analogous to paper chromatography, and after development of the chromatogram and removal of excess solvent the strips are examined under ultraviolet light to locate the biphenyl spot.

Two methods of measuring the amount of biphenyl in the spot are presented.

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