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HERBICIDE RESIDUES

Determining Micro Amounts of Isopropyl *N*-Phenylcarbamate

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A new analytical method for determining microgram quantities of isopropyl *N*-phenylcarbamate is based upon alkaline hydrolysis and measurement of the resulting aniline, using the dye *N*-1-naphthylethylenediamine dihydrochloride. The method will determine concentrations of IPC as low as 0.1 p.p.m. in plant tissue. Direct hydrolysis of the plant tissue has been carried out with strawberries, thus eliminating extraction procedures. It is suggested that this method can also be used for the determination of isopropyl *N*-(3-chlorophenyl)-carbamates (CIPC).

A DIRECT and simplified analytical procedure has been found for microgram quantities of the selective herbicide isopropyl *N*-phenylcarbamate (IPC). Two methods are currently employed: The first (*3*) involves acid hydrolysis and measurement of the carbon dioxide liberated. The second (*1, 5*), which is more applicable to analyses of plant tissue, employs acid hydrolysis of the IPC. Either a phosphoric-hydrochloric-acetic acid mixture or a dilute (1 to 1) sulfuric acid mixture is used. Following the hydrolysis, the mixture is made basic and the aniline is removed from the mixture by steam distillation. It is then determined by hypochlorite-phenol-ammonia reagent. Determination of IPC in plant tissue requires that it be extracted prior to hydrolysis (*1*), because the aniline appears to combine with some product of hydrolyzed lettuce and cannot be recovered by steam distillation (*2*).

Although previous attempts to use basic hydrolysis failed because hydrolysis was incomplete (*1*), satisfactory hydrolysis was obtained using more concentrated basic solution and a longer hydrolysis period. In addition to this modification, aniline was determined by coupling with naphthylethylenediamine dihydrochloride (*2*).

Reagents

Sodium nitrite, 2%, prepared fresh daily
Sulfamic acid, 10%, prepared fresh every 3 days
N-1-Naphthylethylenediamine dihydrochloride, 2%, prepared fresh daily
Aniline, Eastman White Label redistilled
Isopropyl *N*-phenylcarbamate, recrystallized twice from Skellysolve B, 99.2% pure

Procedure

Preparation of Standard Curve. To prepare a standard solution of aniline, dissolve 0.1 gram in 100 ml. of 1*M* hydrochloric acid. Dilute this solution 100-fold with 1*M* hydrochloric acid (10 γ per ml.). Place 1-, 2-, and 3-ml. aliquots of this solution in 50-ml. volumetric flasks and add 1*M* hydrochloric acid until the volume is about 40 ml. Add 1 ml. of 2% sodium nitrite and allow 20 minutes for diazotization. Add 1 ml. of 10% sulfamic acid. Allow 15 minutes for complete destruction of excess nitrite; swirl flasks intermittently. After the decomposition of nitrite is complete, add 5 ml. of 2% *N*-1-naphthylethylenediamine dihydrochloride and make to volume with 1*M* hydrochloric acid. After 90 minutes determine the absorbance at 560 mμ. A plot of absorbance *vs.* aniline concentration data obeys Beer's law in the 0.1- to 0.8-p.p.m. range tested, representing 0.19 to 1.54 p.p.m. of IPC, respectively.

Method. Place 1 ml. of an acetone solution containing 20 to 200 γ in a 500-ml. round-bottomed boiling flask. Add 100 ml. of 20% aqueous sodium hydroxide and 30 to 40 ml. of water to simulate conditions encountered in analyzing plant tissue. Add 20 to 30 crystals of Norton 14X Alundum to prevent bumping. Connect a Liebig condenser to the flask and reflux 4 hours on a hot plate. After the hydrolysis period, set up a second Liebig condenser and join it to the first with connecting U-tubes. Stop the water flow in the first condenser and start the flow in the second condenser. Distill the aniline from the mixture with a Bunsen burner and use a 100-ml. beaker containing 20 ml. of 3*M* hydrochloric acid as the receiver. Raise the beaker to the tip of the condenser while the distillate is being received. Carry out the distillation at the rate of about 10 ml. per minute until 50 ml. of distillate has been received. When the distillation is complete, disconnect the second condenser and rinse the condenser tube into the distillate with a few milliliters of 1*M* hydrochloric acid. Transfer the distillate and washings to a 100-ml. volumetric flask and dilute to volume with 1*M* hydrochloric acid. Transfer a 40-ml. aliquot to a 50-ml. volumetric flask and determine aniline as previously described. Take smaller aliquots of the distillate when large amounts of IPC

Table I. Recovery of IPC by Basic Hydrolysis

IPC Hydrolyzed, γ	IPC Recovered, γ	Recovery, %
60	54.9	91.5 ± 0.14
100	88.3	88.3 ± 4.7
200	187.4	93.7 ± 2.1
400	375.9	94.0 ± 2.2
		Av. 92.4 ± 3.9

are involved in the hydrolysis. Read the concentration of aniline from the standard curve and calculate the concentration of IPC from the following: p.p.m. of IPC = p.p.m. of aniline × 1.93 × K, where K = dilution factor = 100 ml./ml. distillate for analysis.

To test the validity of this method, a series of tests of recovery of IPC involving no crops was performed (Table I).

After this procedure was established, the applicability of the method to direct determination of IPC in plant tissue was determined. One hundred micrograms of IPC was added to 100 grams of strawberries and the recovery was determined by hydrolysis of the plant tissue. Untreated berries were hydrolyzed in the same manner to determine the control correction factor. Out of eight determinations, the average recovery was 97.5% with a standard deviation of 2.9%.

This compares favorably with recoveries of 95 and 89% reported by other methods (*1*, *4*). The distillate of untreated strawberries gives a small and uniform absorbance. This correction factor is equivalent to 0.05 p.p.m. of IPC.

The method was satisfactory for concentrations as low as 0.1 p.p.m. In using a 100-gram sample of plant tissue for hydrolysis and 40-ml. aliquot of the distillate, the method will determine a concentration of 0.1 p.p.m. in the plant tissue. If greater sensitivity is desired, larger samples can be used and extractions carried out by the method of Bissinger and Fredenberg (*1*). Determinations are then made after evaporation of the solvent.

The direct hydrolysis of plant tissue has been applied only to strawberries. Its applicability to other plant tissues can be ascertained only by experimental work.

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FERTILIZER TECHNOLOGY

Concentrated Fertilizer Material from Phosphorus, Air, and Ammonia

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A method was developed on a bench scale for producing a concentrated fertilizer containing phosphorus-nitrogen bonds by burning phosphorus with dry air and treating the fume with ammonia. The product, which contains about 17% nitrogen and 80% phosphoric oxide, is probably a mixture of ammonium metaphosphate, phosphoronitridic acid, and ammonium phosphoronitridate. It dissolves and hydrolyzes slowly in water. Greenhouse tests show that it is an effective source of nutrient phosphorus and nitrogen.

TWO PRINCIPAL PLANT-FOOD ELEMENTS, phosphorus and nitrogen, are directly bonded in phosphonitrilic compounds. Certain properties of these compounds, as reported by Stokes (*10–12*) and by Audrieth, Steinman, and Toy (*2*, *3*), suggested preliminary plant culture tests. Some of the compounds proved to be good sources of nutrient phosphorus and nitrogen.

Preparation of the phosphonitrilic compounds in essentially pure species has generally involved indirect methods (*2*, *3*) that are too costly for use in the production of fertilizers. A more direct method was sought.

Products that probably contained phosphonitrilic compounds were prepared by several investigators (*4–8*, *13*) through reaction of phosphorus pentoxide with ammonia under various conditions. In this approach, phosphorus vapor was burned in air, and the resultant phosphorus pentoxide was ammoniated immediately downstream from the burner. The primary factors affecting the process were evaluated, and the products were fairly well characterized.

The apparatus is shown in Figure 1. Molten phosphorus was water-pumped into a vaporizer which was held at 405° ± 5° C. The metal parts of the apparatus were Type 316 stainless steel. The collecting train comprised a 55-gallon drum, a 30-gallon drum, and a glass electrostatic precipitator.

Variables Studied

The variables that most affect the process are the temperature of the ammoniation reaction, and the ratio of ammonia to phosphoric oxide admitted to the system. In this study it was found also that the distance between the phosphorus flame and the ammonia sparger was important; best results were obtained when the sparger was about 7 inches below the top of the reaction chamber.

The temperature in the reaction chamber was controlled by regulating the amount and temperature of the combustion air, and in some tests, by external cooling of the combustion chamber with a water coil fitted snugly around it. The proportion of combustion air was varied in the range of three to four times that required to burn the phosphorus to phosphorus pentoxide. In tests in which water vapor was admitted to the reaction system,

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