

Microdetermination of 2-(*p*-*tert*-Butylphenoxy)-1-methylethyl 2-Chloroethyl Sulfite (Aramite) Residues by Sulfur Dioxide Evolution

C. C. WATSON

Dominion Laboratory, Department of Scientific and Industrial Research, Wellington, New Zealand

A rapid and simple method for the determination of Aramite residues on fruit is based on the liberation of sulfur dioxide from the acaricide by acid. The amount of interference from some other sulfur-containing pesticides is given. As little as 2 γ of Aramite (or 0.38 γ of sulfur dioxide) can be detected with an error not greater than 2.5 γ over a range of 5 to 30 γ . Residues found on apples sprayed with Aramite are included.

THE ACARICIDE, ARAMITE, has been growing in importance in agriculture. Its increasing use has made desirable the development of a rapid micromethod for determining its residues on fruit.

Aramite, 2-(*p*-*tert*-butylphenoxy)-1-methylethyl-2-chloroethyl sulfite, an ester of sulfurous acid, is a slightly viscous amber liquid which decomposes slowly when concentrated. It is hydrolyzed by alkali to give ethylene oxide, and by acid to give sulfur dioxide.

Proposed micromethods for the analysis of Aramite residues include that of Gordon (5), in which the chlorine in the molecule is oxidized to gaseous chlorine and allowed to diffuse into and decolorize a green dye. A review by St. John (9) contains several additional methods for total chlorine, while Phillips and de Benedictis (8) have described a recent micromethod. The method of Gunther and others (6), uses alkaline hydrolysis to liberate ethylene oxide, which forms a blue dye on heating with diethylene glycol and lepidine. Although this last method has the advantage of being specific, it was found to give inconsistent results when tested with standard quantities of Aramite. For example, in a series of seven replicate tests, the results ranged from 0.6 to 2.4 p.p.m., and in others the dye decomposed during the incubation period.

Boedeker (1) discovered that sulfur dioxide gives a red complex with sodium nitroprusside in the presence of zinc sulfate and ammonia, and this reaction has been applied by Hernandez (7), Eegriwe (2), and Gandolfo (4) to the preparation of indicator papers.

This principle is applied to the determination of Aramite residues on apples. Gaseous sulfur dioxide liberated by acid is swept by a stream of inert gas on to the special indicator paper, which is then compared with standards. Gas-sweeping losses inherent in the methods

of Gunther and others (6) and Gandolfo (4) are avoided in the present method.

Reagents

Alumina. The absorption of chromatographic grade alumina is reduced slightly by adding 2% by weight of water and stirring vigorously until the mixture is of smooth consistency.

Aramite Standard. Commercial 15% Aramite dust (20 grams) is extracted with benzene, filtered, and passed through an alumina column. The eluted Aramite is made to volume with benzene to a concentration of approximately 1000 γ per milliliter. This solution is standardized by hydrolyzing aliquots with hydrochloric acid in isopropyl alcohol, absorbing the sulfur dioxide in standard 0.01*N* iodine solution and back-titrating with standard thiosulfate. Weak standard solutions (10 and 100 γ per milliliter) are then made from this solution.

Benzene. Technical grade is satisfactory.

Isopropyl Alcohol. Analytical grade is used; it must be kept in a brown bottle.

Inert Gas. Cylinder nitrogen, scrubbed oxygen-free with Fieser's solution (3) was used, but carbon dioxide is also satisfactory.

Indicator Papers. Indicator papers should be prepared weekly in the following manner: 1.1 grams of zinc sulfate heptahydrate is dissolved in 8 ml. of water, and sufficient concentrated ammonia solution is added to redissolve the initial precipitate. Ten milliliters of a freshly prepared 10% solution of sodium nitroprusside is then added and mixed. The papers are dipped quickly before the precipitate forms, so as to obtain even impregnation. They are then dried in a current of warm air not exceeding 40° C. Filter paper with a fine surface is suitable. The prepared paper is moderately sensitive to light, and should not be exposed to strong sunlight; the reagent is also destroyed by acid and alkali.

Apparatus

The apparatus for the sulfur dioxide evolution is a modification of that of Gunther and others (6). Wider test tubes (21 mm. in outside diameter) are used, and in place of the capillary tip, a carrier for the absorbing paper is fitted to the apparatus by a ground-glass joint. The carrier is made from two pieces of 2-mm. capillary tubing, each widened at one end to a flat-ground flange with an aperture of 6 mm. The paper is placed between the flanges, which are held together with strong rubber bands. A graduated tube, fitted with an air lock to allow the addition of hydrochloric acid under slight pressure, is sealed into the side of the apparatus near the nitrogen inlet. Phosphoric acid is used to seal the large ground-glass joints, as silicone and rubber greases proved to be unsatisfactory.

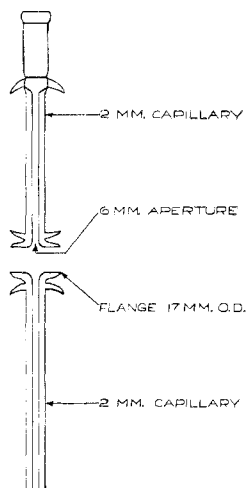


Figure 1. Carrier for absorbing paper

Nitrogen Flow Regulator. Two oil-filled aspirator bottles are used to control the slow rate of nitrogen flow (8 ml. per minute). The lower bottle is charged with nitrogen under pressure from a cylinder.

Experimental

Peelings from a known weight of apples (about 500 grams) are placed in a wide-necked flask with 50 ml. of benzene, and the flask is shaken for 30 minutes. The benzene is filtered and dried with sodium sulfate, and an aliquot (25 to 30 ml.) is passed through a dry-packed alumina column (40 mm. long, 15 mm. in outside diameter). The column is washed with benzene and the extract and washings are made to a standard volume of 50 ml. A small quantity of yellow material passes through the column, but causes no interference. If necessary the benzene extracts may be kept 1 week before the determination is made.

A suitable aliquot (10 ml.) from the standard flask is pipetted into the hydrolysis tube; 6 ml. of isopropyl alcohol is added together with a few small porcelain chips. The tube is attached to the apparatus and the ground-glass joints are sealed with phosphoric acid. The mixture is refluxed vigorously on a water bath so that the vapors reach the condenser. A small square of indicator paper dampened with aqueous ethyl alcohol (80% by volume) is placed between the flanges of the carrier, which is then attached to the apparatus, and the nitrogen is allowed to flow for 2 minutes to flush the apparatus. The nitrogen is then shut off and 1 ml. of concentrated hydrochloric acid is introduced slowly from the graduated tube. Nitrogen is then passed through and the sulfur dioxide evolved from the boiling homogeneous solution is swept on to the paper. After 5 minutes the paper is removed from the carrier, enclosed in cellophane tape, and compared with standards prepared from Aramite hydrolyzed in the same manner. Standards of 5, 10, 15, 20, 25, and 30 γ give a suitable color range.

Aramite can be estimated to within 2.5 γ of the standard color in a quantitative determination. The sensitivity is such that as little as 2 γ of Aramite or 0.38 γ of sulfur dioxide can be detected by this method.

Discussion

The colored complex formed by the action of sulfur dioxide on the indicator paper is rapidly decomposed by sunlight and atmospheric oxygen. The intensity of the colored spot can be maintained in the dark for several days by mounting the paper in cellophane

tape. Collodion and wax were found to be unsuitable.

In the preparation of the indicator paper, the amount of zinc sulfate was increased from 0.6 gram, used by Gandolfo (4), to 1.1 grams, because this improved the stability of the color. The sensitivity of the paper is reduced however, if a saturated solution of zinc sulfate is used.

Wetting the paper with ethyl alcohol (80% by volume) increases the intensity of the color, whereas water alone causes diffused and distorted spots.

Because the presence of air in the apparatus is sufficient to cause bleaching of the colored spot, the apparatus is flushed with nitrogen before introducing the concentrated acid.

A rate of nitrogen flow of 8 ml. per minute is satisfactory. Slower rates are permissible if the heating time is extended, but faster rates cause a diffusion of the color through the paper.

The evolution of sulfur dioxide is found to be suppressed by an apple extractive; therefore, chromatography of the apple extract is necessary. If the alumina contains at least 2% of water, Aramite is less strongly absorbed than the interfering substances, and may be completely eluted by washing the column with 20 ml. of benzene.

Isopropyl alcohol in correct proportion with benzene and concentrated hydrochloric acid produces a homogeneous solution from which sulfur dioxide is more rapidly evolved than from a mixture of benzene and hydrochloric acid. Fumes from the concentrated acid, which could be swept on to and destroy the reagent, are absorbed by the refluxing solution. Phosphoric acid as a hydrolyzing agent is unsuitable for low concentrations of Aramite, because the rate of evolution of sulfur dioxide is very slow.

Recoveries. Samples of apples were peeled and standard amounts of Aramite added to the 50 ml. of benzene used for extraction. The samples were then processed as detailed in the experimental section. The recoveries obtained are given in Table I.

Table I. Recovery of Known Amounts of Aramite

Aramite in 10-ml. Aliquot, γ		Recovery, %
Present	Recovered	
0	0	...
5.7	5.7	100
5.7	5.7	100
8.0	8.0	100
8.0	9.2	115
13.8	13.8	100
13.8	11.5	88
20.7	23.0	110
22.5	23.0	102
23.0	21.8	95
23.0	23.0	100
23.0	21.8	95
26.8	26.8	100
27.5	23.0	84
27.5	26.0	94
27.5	28.5	103
34.5	34.5	100
34.5	32.2	93
34.5	31.0	90
34.5	33.0	95
34.5	34.5	100
35.0	34.5	99

Table II. Interference of Pesticides

Pesticide	Amount Equivalent to 10 γ of Aramite
Bis(dimethylthiocarbamoyl) disulfide (TMTD)	200 γ
Ferric dimethyldithiocarbamate (Ferbam)	1200 γ
Colloidal sulfur	50 mg.
<i>p</i> -Chlorophenylbenzene sulfonate (Ovotran)	>1 g.

Interference of Pesticides

The interference of some sulfur-containing pesticides and the quantity necessary to produce a colored spot equivalent to that from 10 γ of Aramite are presented in Table II.

Any substance capable of liberating sulfur dioxide under the conditions of hydrolysis will interfere with this method.

Residues

Residues found at harvest time on apples sprayed with varying amounts of Aramite 15W (15% wettable powder) throughout the season are given in

Table III. Aramite Residues on Apples

Apple Variety	Aramite Applied, Lb./100 Gal.	No. of Applications	Days between Last Spraying and Harvest	Aramite Residues ^a	
				γ	P.p.m.
Delicious	2	4	54	390, 370	0.85, 0.82
	1/2	6	54	115, 115	0.20, 0.22
	1 1/2	4	48	215	0.42
Ballarat	1 1/2	4	59	315, 385	0.62, 0.75
	Dunns	1	4	8	185, 195
1/2		5			
Granny Smith	2	3	69	160, 150	0.30, 0.30

^a Weight of apples taken, 450 to 550 grams.

Table III. Each determination was made in duplicate and several aliquots of each benzene extract were analyzed. The residues are calculated on the weight of the whole fruit.

Acknowledgment

The author wishes to thank H. Jacks, Plant Diseases Division, Department of Scientific and Industrial Research, for providing the treated apples.

Literature Cited

- (1) Boedeker, C., *Ann.* **117**, 193 (1861).
- (2) Eegriwe, E., *Z. anal. Chem.* **65**, 182 (1924).
- (3) Fieser, L. F., "Experiments in Organic Chemistry," 2nd ed., pp. 395-6, D. C. Heath, Boston, 1941.
- (4) Gandolfo, N., *Ann. chim. appl.* **38**, 649 (1948).
- (5) Gordon, H. T., *Anal. Chem.* **24**, 857 (1952).

- (6) Gunther, F. A., Blinn, R. C., Kolbezen, M. J., Barkley, J. H., Harris, W. D., Simon, H. S., *Ibid.*, **23**, 1835 (1951).
- (7) Hernandez, J. F., *Anales soc. españ. fis. quim.* **9**, 16 (1911), *J. Chem. Soc.* **100**, **AII**, 226 (1911).
- (8) Phillips, W. F., de Benedictis, M. E., *J. Agr. Food Chem.* **2**, 1226 (1954).
- (9) St. John, J. L., *Anal. Chem.* **27**, 654 (1955).

Received for review May 13, 1955. Accepted January 31, 1956.

PESTICIDES LITERATURE

Literature of Chemical Weed Control

C. J. WILLARD and E. K. ALBAN

Ohio State University and Ohio Agricultural Experiment Station, Columbus, Ohio

Weed control literature is scattered through the publications of chemists, agronomists, horticulturists, foresters, public health specialists, agricultural engineers, plant physiologists, ecologists, agricultural aviators, wildlife specialists, right-of-way maintenance engineers, and the technical weed control organizations. These last mentioned are the first source of practical information, and special serial weed control bibliographies are the first choice for making searching studies of the field.

CHEMICAL WEED CONTROL presents a literature that is extremely scattered and hard to find. This is more or less true of all fields, but it is probably more completely true with chemical weed control than with most others.

One of the fundamental reasons for this difficulty is that although weed control itself is not new, as a separate discipline it is new, dating basically from the announcement in 1944 of the value of 2,4-D for weed control. The control of unwanted plant growth has been a part of agriculture since the time of Adam; consequently writings on the subject can be found in every field concerned in any way with plant production.

In the United States, the best sources of immediate information on new developments in the practical business of controlling weeds are the meeting and publications of the Weed Society of America and the regional weed control conferences, four of which are well established.

Weed Society of America
W. C. Shaw, Secretary
U. S. Department of Agriculture, Beltsville, Md.

Weeds

W. C. Jacob, Business Manager
Department of Agronomy
University of Illinois, Urbana, Ill.

Western Weed Control Conference
W. C. Robocker, Secretary-Treasurer
Nevada Agricultural Experiment Station,
Reno, Nev.

North Central Weed Control Conference
Fred W. Slife, Secretary
Department of Agronomy
University of Illinois, Urbana, Ill.

Northeastern Weed Control Conference
R. J. Aldrich, Secretary
Department of Farm Crops
Rutgers University, New Brunswick, N. J.

Southern Weed Control Conference
E. G. Rodgers, Secretary-Treasurer
Department of Agronomy
University of Florida, Gainesville, Fla.

Other important similar conferences are the Western Canadian Weed Control Conference; the Canadian National Weed Committee, Eastern Section; and the British Weed Control Conference.

An important source of announcements of new materials and techniques in recent years has been the magazine

Science. This organ of the AAAS made the original announcement of the effectiveness of 2,4-D, and has also made many other short announcements of important weed control items.

Longer publications of the integrated results of experiments are found in many journals. Work of fundamental importance in chemical weed control involves plant physiology, and these papers are found in *Plant Physiology*, *Botanical Gazette*, and other botanical publications. No fundamental consideration of weed control can omit an account of the ecology of weeds. Consequently, *Ecology* and other similar journals have had items relating to weed control.

Control of weeds is a vital factor in the culture of most crops, and is also concerned with many features of soil management, so that *Agronomy Journal*, the *Proceedings of the Soil Science Society of America*, *What's New in Crops and Soils*, the *Journal of Range Management*, and other agronomic publications have many articles on weed control. Many such articles have also appeared in the *Proceedings of the American Society for Horticultural Science*.