

A Spectrophotometric Determination of 2-(*p*-*tert*-Butylphenoxy)-1-methylethyl 2-Chloroethyl Sulfite (Aramite) Residues

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Aramite residues as low as 0.1 p.p.m. on 100-gram samples can be determined by a method which depends on the breakdown of Aramite to ethylene oxide. The ethylene oxide is trapped and converted to formaldehyde which is determined colorimetrically. Interferences are negligible and recoveries are good.

THE INSECTICIDE, Aramite, 2-(*p*-*tert*-butylphenoxy)-1-methylethyl 2-chloroethyl sulfite, has gained considerable use on agricultural crops. Its determination in micro quantities is necessary in residue control work to ensure its further development as a pesticide. The analytical problems encountered in residue work require that the method of detection be sensitive, specific, and reliable. The method presented meets these specifications for the quantitative determination of Aramite.

Several techniques have been described for the determination of Aramite residues. In addition to the total chlorine method proposed by Gordon (1), an indicator paper method, depending upon the evolution of sulfur dioxide, has been described (5). Prior to that, Gunther (3) described a colorimetric method which depended upon the evolution of ethylene oxide when Aramite was refluxed with sodium isopropoxide. This reaction has been used as a basis for the development of the present method.

In acid solution, ethylene oxide is converted to ethylene glycol which can be cleaved with periodic acid to produce formaldehyde. The formaldehyde, when conjugated with phenylhydrazine and treated with sulfuric acid in the presence of periodic acid, forms a brilliant red color.

The determination is simple and rapid. One individual can make eight to 10 analyses daily with one set of apparatus. No interfering plant materials have been encountered during the study of nine different crops. Other insecticides commonly used with Aramite do not interfere in the determination.

Reagents

Aramite, analytical grade, furnished by Naugatuck Chemical Division, U. S. Rubber Co.

Benzene, technical grade.

Acetone, technical grade.

Sodium isopropoxide, 0.25*N*, prepared by dissolving 6.75 grams of clean metallic sodium in 1 liter of reagent grade isopropyl alcohol.

Potassium periodate, 0.5%, reagent grade.

Sulfuric acid, 0.1*N* and 10*N*, made from C.P. reagent.

Phenylhydrazine hydrochloride, 1%, prepared by dissolving 1 ml. of phenylhydrazine, reagent grade, and 0.68 ml. of concentrated hydrochloric acid, C.P., in water to make a total of 100 ml. of solution. Prepare fresh daily.

Apparatus

The apparatus used to hydrolyze the Aramite sample and collect the ethylene oxide is illustrated in Figure 1. This is an adaptation of an apparatus recently described by Rosenthal, Frisone, and Gunther (4) for the determination of Kelthane residues. A perforated disk made from porcelain or Teflon is sealed into the scrubber at the bottom of the receiving chamber. The scrubber is provided with a ball and socket joint and is connected to a three-way stopcock. This simplifies recovery of the scrubbing solution and allows a quick change-over from one sample to the next.

Procedure

Extraction. Because of the variety of problems encountered with different types of samples, definite procedures for sample extraction are difficult to outline. The primary consideration is to achieve complete removal of the pesticide from the sample. Benzene is the usual solvent for Aramite residues, although *n*-hexane has been found suitable in some cases. Solvents which are attacked by periodic acid cannot be used. The solvent to sample ratio can be varied from 1 to 1 for leafy or soft samples, such as alfalfa or strawberries, and to 1 to 4 for smooth-skinned samples, such as apples or pears. Depending upon the nature of the sample, chopping or macerating before extraction may be necessary. Extracts should be dried with anhydrous sodium sulfate prior to storage or analysis. Such extracts can be stored for several weeks without loss of Aramite. Gunther and Blinn (2) give further suggestions

Table I. Recovery of Aramite Added to Various Crop Extracts

Crop Extract	Equivalent Sample Size, G.	Aramite		
		Added, p.p.m.	Found, p.p.m.	Recovery, %
Lemon	200	0.0	0.0	—
	200	0.30	0.27	90
	200	0.30	0.33	110
Orange	200	0.0	0.06	—
	200	0.30	0.36	100
Apple	200	0.0	0.0	—
	200	0.26	0.24	93
Alfalfa	200	0.0	0.0	—
	200	0.21	0.23	109
	200	0.11	0.14	127
Clover	100	0.0	0.0	—
	100	0.63	0.63	100
Pear	40	0.0	0.0	—
	40	1.0	0.95	95
	40	0.50	0.48	96

on the extraction of samples for residue determinations.

For maximum sensitivity, extracts should be concentrated to a small volume before analysis. Otherwise the extract can be analyzed directly by transferring an aliquot to the evolution apparatus. A convenient volume for the concentrate or the direct aliquot is 10 to 15 ml. contained in a 100-ml. round-bottomed flask. Larger aliquots can be taken, in which case, larger amounts of hydrolyzing solution must be used.

Distillation of Ethylene Oxide. The procedure for the hydrolysis of Aramite and the collection of ethylene oxide is as follows:

Fill the scrubber tube with glass beads to a depth of 4 inches, and add 1 ml. of 0.5% periodate solution and 3.5 ml. of 0.1*N* sulfuric acid. Add 6 ml. of 0.25*N* sodium isopropoxide to the sample in the round-bottomed flask, and attach the flask to the distillation apparatus. Start the nitrogen flow at a slow rate, just enough to counteract the back pressure in the system, and turn the three-way stopcock so as to admit gas to the scrubber. Heat the sample with a heating mantle—begin at a low heat, gradually increase it. The sample should be brought to reflux in approximately 5 minutes. Increase the gas flow as needed to sweep the apparatus. An ideal rate is about 2 bubbles of sweeping gas per second. This phase of the determination requires constant attention because of the erratic nature of the gas flow as the temperature increases. Reflux for 30 minutes at a slow rate of boiling. At the end of this time, transfer the scrubbing solution to a test tube and let it stand for 20 minutes to allow completion of the periodate cleavage.

Color Development. Add to a 3-ml. aliquot of the scrubbing solution 1 ml. of 1% phenylhydrazine hydrochloride. Let stand for 10 minutes, then add 2 ml. of 10*N* sulfuric acid and 2 ml. of acetone. Mix well and read within 20 minutes in a colorimeter or spectrophotometer at 520 $m\mu$. Prepare a standard curve by refluxing benzene solutions of Aramite and developing the color in the same way as above.

Discussion

The method has been used successfully for two seasons in the determination of Aramite on field-treated apples and pears. It has been tested also on extracts of wheat, alfalfa, clover, corn, sorghum, lemons, and oranges. Recovery studies (Table I) show the method to be satisfactory for residue determinations of these crops.

Tests were run to determine whether Aramite could be recovered quantitatively from mixtures with other pesticides commonly used in combination sprays. Although the data shown in Table II

Table II. Interference by Other Pesticides

Pesticide	Amount Present, γ	Aramite		
		Added, γ	Found, γ	Recovery, %
Parathion	600	63	74	117
Malathion	600	63	56	89
DDT	600	63	50	79
Ziram	600	63	53	84

Table III. Precision of Aramite Method Using Beckman Model B Spectrophotometer

Date of Analysis	Aramite, γ				
	0	21	42	62	84
2/14/57		0.14	0.21	0.30	0.26
2/15/57	0.11 0.06				0.39
2/18/57	0.06		0.20	0.28	0.40
2/20/57	0.07 0.06			0.27	
2/28/57	0.09	0.15 0.12	0.20		0.39
3/1/57	0.05	0.14	0.19	0.17 0.27	0.42
Average	0.08	0.14	0.20	0.26	0.37
Standard deviation,	± 0.04				

indicate slightly poorer recoveries, any interferences, if real, are minor and would not prevent the determination of Aramite under such conditions.

Several types of gas evolution and gas scrubbing devices were tested during the development of the method and were found to be satisfactory. The apparatus shown in Figure 1 was chosen because of its simplicity. The scrubbers are efficient in trapping ethylene oxide and are easy to remove and clean. In addition to nitrogen, carbon dioxide or compressed air can be used as sweeping gases.

The reproducibility of results by the method is shown in Table III. No explanation can be offered for the occasional stray values encountered. Most of the points on a concentration-absorbance curve show a straight-line relationship.

The sensitivity is such that residues of 0.1 p.p.m. can be determined with samples of 100 grams. Greater sensitivity is possible by increasing the sample size or by taking a larger proportion of the scrubbing solution for color development.

The recommended 30-minute hydrolysis time is a minimum as indicated by time-color studies. Too rapid sweeping of the apparatus during a determination may lead to poor recoveries, probably because of incomplete absorption of ethylene oxide.

Literature Cited

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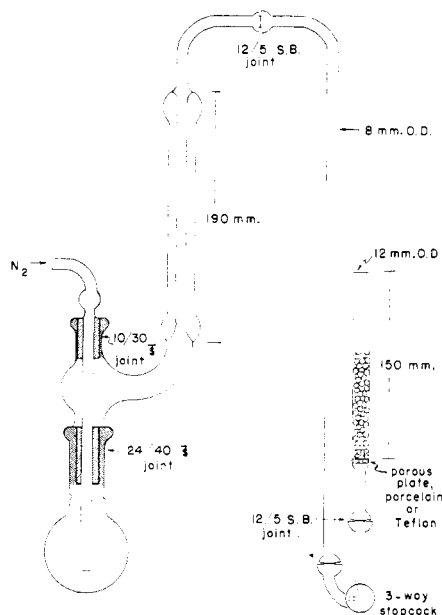


Figure 1. Apparatus for determination of Aramite