reaction requires approximately 16 h for completion, and the derivatives are stable, in the absence of water, for 2–3 days. However, before chromatography, it is necessary to remove excess silyl reagent by the addition of water. After this, the derivatives remain stable for approximately 1 h. Therefore, chromatography of the sample must be accomplished in this period for optimum results.

Limited studies were conducted using the electron-capture detector but the possibility of making more stable derivatives with greater electron-capturing ability was not fully explored. If an alternate chromatographic approach ever becomes necessary, this will be an area worthy of further investigation. However, in our laboratory, we have found more general selectivity with the microcoulometric detector than with the EC detector. The Coulson conductivity detector was also tested and found to be less selective.

Due to the relatively large injection volumes (100 μl) necessary to obtain the required sensitivity, the use of small amounts of silylated glass wool in the glass inlet port of the chromatograph is recommended. This tends to retain nonvolatiles which would otherwise contaminate the inlet portion of the column. This material is changed daily, along with the septum, prior to initiation of chromatography.

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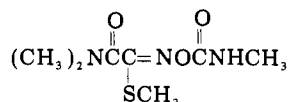
Spectrophotometric Determination of Oxamyl as Copper Dithiocarbamate

J. P. Singhal,* Samiullah Khan, and O. P. Bansal

A spectrophotometric method for the determination of oxamyl, a powerful nematocide, in aqueous solutions has been developed. Reaction variables for the formation of a characteristic colored system have been investigated. Average recoveries of oxamyl varied from 88.6 to 97.3% in different kinds of fortified samples in the 2–10-ppm range after a contact of 12 h. The method can be applied with practical utility in the field of soils, plant products, and water.

In view of its qualities, oxamyl (methyl N',N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-thiooxamimidate) (Biochemicals Department, Experimental Station, E. I. DuPont de Nemours & Co., Inc., Wilmington, Dela.), a newly formulated product, is finding wide application as a broad spectrum pesticide for the effective control of nematodes and other plant pests in soils, and as a foliar spray (Timmer, 1974). A gas chromatographic method for its estimation has recently been reported by Holt and Pease (1976). No published data are, however, available on its spectrophotometric analysis.

The structure of the compound

$$\underset{\underset{\overset{|}{\text{SCH}_3}}{}}{(\text{CH}_3)_2\,\text{N}\overset{\overset{\text{O}}{\|}}{\text{C}}=\text{NO}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NHCH}_3}$$

is indicative of the presence of carbamoyl and thiooxamimidate as functional groups. Because of the relative chemical inertness of its functional groups, quantitative analysis of this nematocide is difficult.

Our investigations revealed that when oxamyl was subjected to hydrolysis, its products gave a precipitate with CS_2 and Cu^{2+}, which produced an intense brownish yellow color in immiscible organic solvents.

The aim of this work was, therefore, to propose a sensitive, accurate, and reproducible method for the quantitative estimation of the chemical in aqueous solutions down to a few parts per million. Optimum conditions necessary for the spectrophotometric analysis have

been investigated through a study of the reaction variables involved. The method is expected to be especially useful for field use or in areas where more modern analytical instrumentation is not available.

EXPERIMENTAL SECTION

Apparatus. Spectrophotometric measurements were made with a Bausch and Lomb spectronic 20 spectrophotometer and pH was measured with an Elico pH meter, Model L1-10.

Reagents. The chemicals used in this study were of BDH analytical grade. Solutions used were prepared as follows.

Standard Oxamyl Solution. The solution was prepared by dissolving 25 mg of oxamyl in water and diluting to 1 l. with redistilled water.

Basic Copper Solution. A solution of 0.2 g of copper sulfate pentahydrate and 20 g of ammonium acetate in 30 ml of distilled water was mixed with 25 ml of 40% sodium hydroxide and 20 ml of ammonium hydroxide. The volume was made up to 100 ml with distilled water.

Carbon disulfide solution: 5% in benzene.

Potassium hydroxide: 10% in distilled water.

Acetic acid: 30% in distilled water.

Diverse Interfering Ions. Aqueous solutions of Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cl^-, NO_3^-, SO_4^{2-}, acetic acid, benzoic acid, and dimecron, alcoholic solutions of pyridine, diphenylamine, methylamine, trimethylamine, nemagon, and telone, and carbon tetrachloride, acetaldehyde, and methyl alcohol as such were used for interference studies.

Procedure. For preparation of a calibration curve 0.1 to 2.0 ml of a 25 μg/ml solution of oxamyl were refluxed with 5 ml of 10% potassium hydroxide solution for 10 min

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Table I. Recovery of Oxamyl from Blanks and from That Added to 10 g of Different Samples

Nature of material	Amt of oxamyl added, µg	No. of determinations	Nature of sample	Av amt of oxamyl recovd, µg	Recovery, %	
					Av	Range
Red soil	0	3	Reagent blank	0.27		
	20	3	Fortified	18.40		
	40	3	Fortified	35.90	91.6	81.7-97.3
	100	3	Fortified	92.90		
Black cotton soil	0	3	Reagent blank	0.41		
	20	3	Fortified	18.70		
	40	3	Fortified	38.60	94.3	83.3-103.3
	100	3	Fortified	93.80		
Saline sodic soil	0	3	Reagent blank	0.27		
	20	3	Fortified	16.13		
	40	3	Fortified	36.75	88.6	75.0-96.7
	100	3	Fortified	93.00		
Potato	0	3	Reagent blank	1.00		
	20	3	Fortified	18.92		
	40	3	Fortified	37.20	93.9	85.0-99.2
	100	3	Fortified	94.22		
Tobacco	0	3	Reagent blank	2.67		
	20	3	Fortified	19.20		
	40	3	Fortified	39.11	97.3	83.0-106.6
	100	3	Fortified	98.00		
Water	0	3	Reagent blank	0.00		
	20	3	Fortified	18.50		
	40	3	Fortified	39.20	95.9	83.3-99.2
	100	3	Fortified	97.30		
Wheat	0	3	Reagent blank	0.41		
	20	3	Fortified	18.92		
	40	3	Fortified	38.93	94.3	84.7-99.2
	100	3	Fortified	91.30		

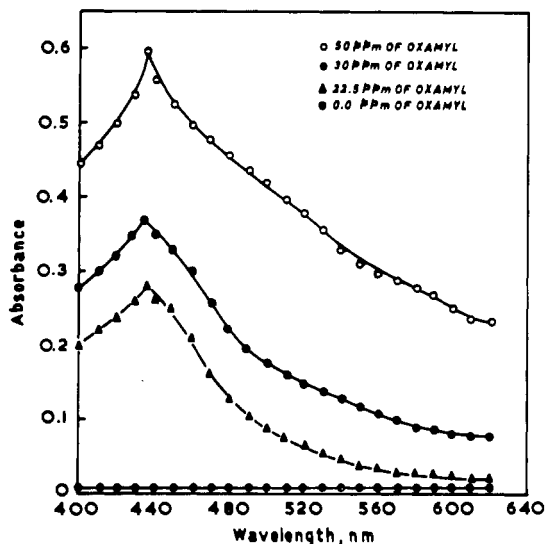
Figure 1. Absorption spectra of refluxed oxamyl with basic copper solution and carbon disulfide in benzene.

Figure 2. Effect of pH on color intensity.

in refluxing flasks fitted with a condenser over a water bath. The contents were allowed to cool, shaken with 1 ml of basic copper solution and 10 ml of 5% carbon disulfide solution in each case for 2 min, and then transferred to separating funnels. The refluxed liquids were then shaken with 1 ml of 30% acetic acid for 1 min and kept for 10 min to allow for full development of color, and the colored benzene layer eluted. Absorbance was recorded vs. a reagent blank at 435 nm over a range of 0-50 µg in the eluted layer.

RESULTS AND DISCUSSION

Spectral Curve. Absorption spectra were recorded in the pH range 10.0-10.5 and are shown in Figure 1. The absorbance maximum occurred at 435 nm.
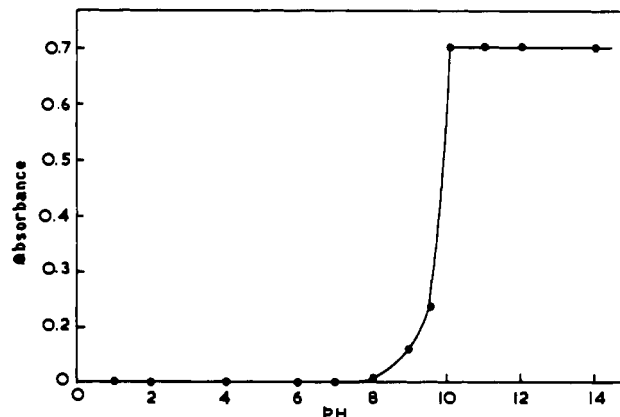
Effect of Variables. Effect of pH. The effect of pH on absorbance is given in Figure 2. Maximum absorbance occurred at pH 10. Thereafter the color intensity became independent of pH. A pH in the range 10.0-10.5 was, therefore, chosen for all further work.

Reagent Concentration. A series of tests showed that the maximum color development occurred at 0.4 ml of carbon disulfide per 50 µg of oxamyl and further concentrations of carbon disulfide had no effect on color intensity as shown in Figure 3. A similar study on the effect of other reagents concentration showed an optimum requirement of 0.3 ml of 1 × 10^{-3} M Cu^{2+} and 1 ml of 25% ammonium hydroxide, respectively, for maximum color development.

Sequence of Reagent Addition. The order of addition of reagents was without effect on color intensity.

Effect of Time. Maximum development and stability of color were attained in 10 min. Absorbance remained
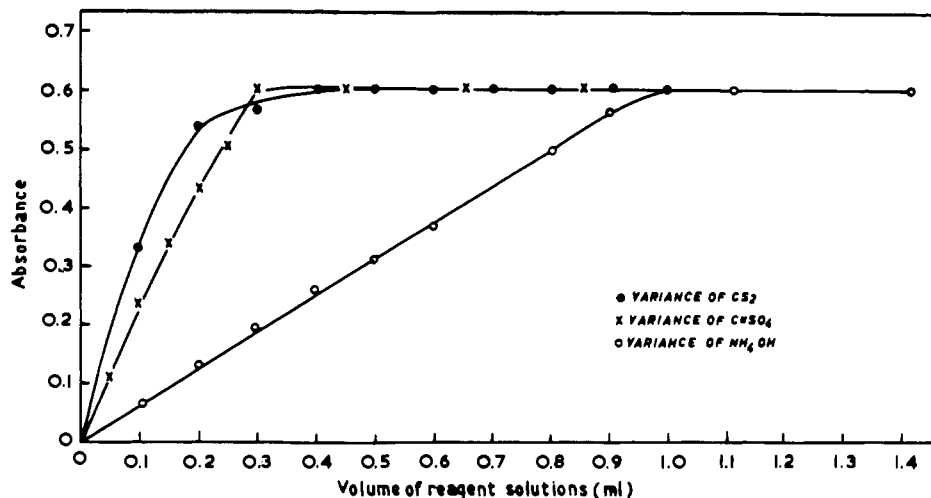
Figure 3. Variance of absorbance with reagent concentrations.

Table II. Interference Effect of Inorganic Ions and Organic Compounds in Solutions Containing 50 µg of Oxamyl

Ions	Added as	Amt of ion or compd, µg	Oxamyl found, µg	Deviation from arith. mean of 50.3, µg
Na$^+$	NaNO$_3$	15 000	50.0	-0.3
K$^+$	KNO$_3$	15 000	50.0	-0.3
Ca^{2+}	Ca(NO$_3$)$_2$	5 000	50.0	-0.3
Mg^{2+}	Mg(NO$_3$)$_2$	5 000	50.0	-0.3
Ni^{2+}	NiCl$_2$·7H$_2$O	150	45.3	-5.0
Co^{2+}	CoCl$_2$·6H$_2$O	100	46.3	-4.0
Zn^{2+}	ZnSO$_4$·7H$_2$O	2 000	46.3	-4.0
Fe^{3+}	FeCl$_3$	3 000	46.3	-4.0
Al^{3+}	Al$_2$(SO$_4$)$_3$	2 000	46.3	-4.0
Cl$^-$	NaCl	5 000	50.0	-0.3
NO$_3^-$	NaNO$_3$	5 000	50.0	-0.3
SO$_4^{2-}$	K$_2$SO$_4$	5 000	50.0	-0.3
	Nemagon	5 000	50.4	0.1
	Telone	5 000	50.4	0.1
	Dimercon	5	54.0	3.7
	CH$_3$COOH	100	44.3	-6.0
	C$_6$H$_5$COOH	200	44.3	-6.0
	CH$_3$COONa	5 000	50.0	-0.3
	C$_5$H$_5$N	10 000	50.0	-0.3
	(C$_6$H$_5$)$_2$NH	10 000	50.0	-0.3
	CH$_3$NH$_2$	200	53.7	3.4
	(CH$_3$)$_3$N	10 000	50.0	-0.3
	CH$_3$OH	75 000	46.3	-4.0
	CCl$_4$	15 000	46.3	-4.0
	CH$_3$CHO	40 000	46.3	-4.0

constant for at least 1 h as shown in Figure 4. Thereafter, turbidity appeared.

Oxamyl Concentrations. The calibration curve obeyed Beer's law in the range 0–50 µg of oxamyl per 10 ml of benzene. The molar absorptivity of the color was 2.7 × 10^6 at 435 nm.

Precision. A reproducibility study of a series of ten solutions, with each series containing 25 and 50 µg of oxamyl, respectively, using a 1-cm cell, gave arithmetic mean, standard deviation, and relative standard deviation equal to 24.85, 0.82, and 3.35%, respectively, and 50.3, 0.58, and 1.18%, respectively.

Recovery Experiments. The efficiency or applicability of the procedure for the determination of oxamyl residues in a variety of samples was tested by adding known amounts of the nematocide to 10 g of powdered or meshed untreated samples. A blank was also run at the same time.

The recoveries were conducted by extraction of the fortified samples. Before extraction 10-g samples of soils, wheat, potato, and water were fortified with 0 to 100 µg of oxamyl and allowed to be in contact for 12 h. At the end of this period, the nematocide was extracted from the samples with ethyl acetate and water. The filtrate was
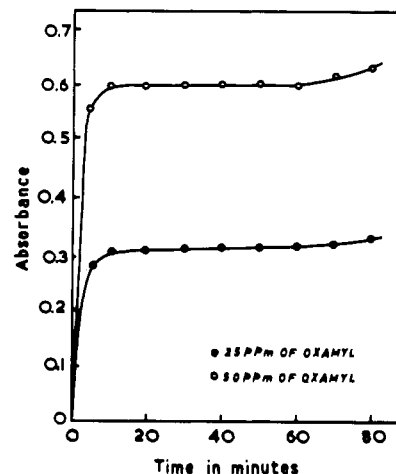

Figure 4. Effect of reaction time on color intensity.

heated on a water bath to evaporate ethyl acetate and the aqueous layer extracted with n-hexane and chloroform to remove organic and other impurities. The residual aqueous

layer was then refluxed with 10% KOH and oxamyl estimated as already described.

The recovery study results obtained at different levels of fortification on replicate analyses are given in Table I. Except in saline sodic soil the recovery yields were over 80% for fortifications of 2 to 10 ppm after a contact of 12 h. A greater loss in the case of sodic soil was due to alkalinity which had a tendency to decompose oxamyl. Even in this case the recovery was 75% and above. These results indicated essentially satisfactory recoveries and the applicability of the method for estimation of oxamyl residues in various types of soils, water, and plant materials.

Interference Effects. The results of an investigation of the effect of inorganic and organic compounds in solutions containing an average of 50.3 μg of oxamyl are shown in Table II. Analyses of aqueous solutions of oxamyl containing diverse inorganic ions and organic compounds showed that Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-,

SO_4^{2-}, nemagon, telone, pyridine, diphenylamine, and trimethylamine did not interfere. Other ions such as Ni^{2+}, Co^{2+}, Zn^{2+}, Fe^{3+}, and Al^{3+} and organic compounds such as dimercon, acetic acid, benzoic acid, methyl alcohol, carbon tetrachloride, and acetaldehyde in the amounts added did interfere. The tolerance limit was considered as that giving a deviation less than three standard deviations.

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Gas Chromatographic Determination of Sencor and Metabolites in Crops and Soil

John S. Thornton* and Charles W. Stanley

A gas chromatographic procedure is described for the analysis of residues of Sencor herbicide and its metabolites in a variety of crops. Conjugated residues are released by refluxing the sample as a part of the initial extraction. Following this, Sencor and metabolites are separated by liquid–liquid partition and the two fractions cleaned up individually for electron-capture gas chromatographic analysis. A separate extraction scheme is described for analysis of soil. Considerable effort was made to ensure maximum recovery of residue from field-weathered samples. Recovery of Sencor is generally in the 80–100% range with metabolite recoveries averaging somewhat less. The sensitivity limit of the method is 0.01 ppm for Sencor and all metabolites.

Sencor [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one], also known as metribuzin and Bay 94337, is an as-triazinone herbicide (Eue et al., 1969) which has shown effective control of a large number of grass and broadleaf weeds infesting agricultural crops such as potatoes, soybeans, sugarcane, and tomatoes.

Metabolism studies have been conducted by a number of workers (Gronberg et al., 1971; Church and Flint, 1972; Hargroder and Rogers, 1974; Hilton et al., 1974). In all cases, the metabolism in plants follows a stepwise pathway as shown in Figure 1, resulting in three identified metabolites: deaminated Sencor (DA), deaminated diketo-Sencor (DADK), and diketo-Sencor (DK). Any of these metabolites could conceivably be found as residues in crops. However, the metabolism studies show it is unlikely that the DK or DA metabolite would ever be present in mature crops grown above the ground. Residues which have been found have been mainly Sencor with minor amounts of DADK. This is in contrast to root crops which have shown residues of Sencor and the DK metabolite and, to a limited extent, DA. The DA metabolite was also shown to be the major photodegradation product in water solutions (Pape and Zabik, 1972).

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Residues of Sencor were first analyzed by Stanley and Schumann (1969). The method employed a single blender extraction, followed by Florisil column cleanup and electron-capture gas chromatographic analysis using a 5% OV-101 column. A modification of that method, reported by von Stryk (1971), employed flame photometric detection in the sulfur mode. Thornton and Schumann (1971) reported an electron-capture gas chromatographic method for Sencor and its DADK metabolite in soybeans. Later, Thornton et al. (1972) reported a procedure for the analysis of Sencor and all three metabolites in sugarcane with electron-capture detection of the compounds after separation on a column of 5% OV-225 on Gas-Chrom Q. Webster et al. (1975) also reported separation of Sencor and metabolites on 5% OV-225 on Chromosorb W (HP).

The method of Thornton et al. (1972) has been refined and extended to additional crops and soil and is reported in detail in this paper. Briefly, the crop procedure involves a refluxing step to release Sencor and any metabolite that may be conjugated. Sencor and metabolite residues are separated from the solids by filtration and the filtrate solution evaporated until only water remains. Following this, Sencor and metabolites are separated from each other by liquid–liquid partition and cleaned up on liquid chromatography columns prior to individual gas chromatographic analysis on a 5% OV-225 column with electron-capture detection. A summary of the analysis