o-amino-N,N-dimethylbenzamide (VIII), and p-amino-N,N-dimethyl benzamide (X). The products are similar to those obtained from acetanilide (Elad et al., 1965; Rao and Lambreti, 1967), suggesting that the reaction takes place via a mechanism similar to that suggested for the photoanilide rearrangement (Figure 2). The initial formation of radical pair V would lead, via migration in a solvent cage, to VII and IX. Alternatively, hydrogen abstraction would account for aniline formation. Analysis of the gaseous product indicated that carbon monoxide was produced, in accord with expectations for the decomposition of an N,N-dimethylformyl radical.

An approximate comparison of the rates of photodegradation of I and II indicates that I reacts about four times as fast as II. Thus the photodegradation of II should not be an important process in irradiation of I.

Clearly then the initial process involved under these conditions is cleavage of a carbon–nitrogen bond in II to give the radical pair V. All stable photoproducts are due to subsequent reactions of these radicals.

In the case of I, by far the major process is cleavage of a carbon-chlorine bond followed by hydrogen abstraction from solvent to afford the reduced product fenuron (II). It has been shown in other cases (Kharasch and Sharma, 1966; Plimmer et al., 1970) that the presence of oxygen in photo-degradation reactions strongly influences the nature of the products formed. The differences between the results reported here and those of the previous investigators are most logically ascribed to the presence of oxygen in those studies.

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Semiautomated Analysis of Granular Organophosphorus Pesticide Formulations

Ted D. Talbott, Jerry C. Cavagnol,[1] C. Fred Smead, and R. Thomas Evans*

The determination of Dasanit [O,O-diethyl O-[4-(methylsulfinyl)phenyl] phosphorothioate] and Di-Syston [O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate] in 10 and 15% clay granular formulations is now carried out on a semiautomated basis. The procedure involves an extraction of the granular samples with an acetic acid bromine mixture and subsequent colorimetric phosphorus determination using an AutoAnalyzer. The method produced significant savings in analytical time and decreased the precision standard deviation by about 50% over previous manual methods.

Dasanit (Bay 25141 or fensulfothion) [O,O-diethyl O-[4-(methylsulfinyl)phenyl] phosphorothioate] is a product of Farbenfabriken Bayer AG, licensed in the U. S. and Canada to Chemagro Division of Baychem Corp. It exhibits both insecticidal and nematicidal activity and its formulations are used to control parasitic, sedentary, and free-living nematodes. The most commonly used formulations are impregnated granules and a spray concentrate.

Di-Syston (thiodemeton or disulfoton) [O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate] is also a product of Farbenfabriken Bayer AG, licensed to Chemagro in the U.S. and Canada. It is a systemic insecticide and its formulations are used for control of sucking insects and mites on plants. As with Dasanit, the most commonly used formulations are a spray concentrate and impregnated granules.

Granular formulations of both compounds are produced by a number of manufacturers under contract to Chemagro. This practice effects freight savings but produces severe demands on analytical control because of the many individual batches involved.

Prior to the 1968–1969 season, the active ingredient content of both Dasanit and Di-Syston granular production was monitored by use of conventional manual methods of analysis. These consisted of extracting the active ingredient, followed by acidimetric back-titration of hydrolyzed Di-Syston or reductimetric titration of Dasanit with titanous chloride. The thousands of samples resulting from a month's production imposed a severe burden on the analytical laboratory, since the analyst times required for Dasanit and Di-Syston were 45 and 40 min, respectively. Therefore a method more suitable for mass production of data was required.

During the 1968–1969 season, the present semiautomated

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To Sampler
side chamber

SAMPLER II

Tubing size,
inches
0.040* wash solution
0.035* sample

Rate
20/hr

0.073 air
0.100 water

DOUBLE MIXER

C3

To waste

0.110 water
0.110 water
0.045* sample
0.045 air
0.110* digestion mix

MIXER

A7

PC1

To vacuum waste bottle

DIGESTOR

MIXING CHAMBER

M
A
N
I
F
O
L
D

1

0.100 sample
0.081 air
0.110 0.02% Benax Al

DOUBLE MIXER

To waste

C3

0.100 sample
0.073 air
0.056 3N NaOH
0.035 3% molybdic acid
0.035 0.2% hydrazine
0.090

MIXER
JACKETED MIXER

MIXER

To waste

M
A
N
I
F
O
L
D

2

Tap water

90 °C

JACKETED MIXER

HEATING BATH

40' coil

COLORIMETER   RECORDER

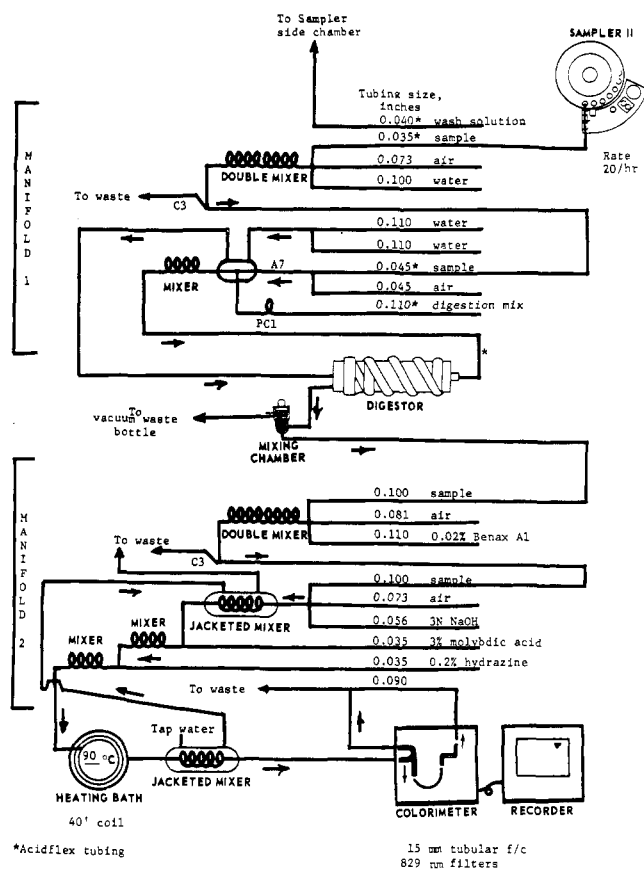*Acidflex tubing

15 mm tubular f/c
829 nm filters

Figure 1. Flow diagram for organophosphorus analysis

procedure was put into use at Chemagro. This involved a phosphorus determination based on the work of Whitley and Alburn (1965). The working time during the first year was reduced from 40 and 45 min to 14 and 28 min for Di-Syston and Dasanit, respectively. Subsequently, modifications in the method lowered this for each product to an average of less than 13 min per sample, including unpacking and similar handling, record keeping, reanalysis in doubtful cases, and all other ancillary operations.

EXPERIMENTAL

Apparatus. The AutoAnalyzer I system (Technicon Instruments Corp., Tarrytown, N. Y.) consisted of two proportioning pumps, a sampler II, a continuous digestor equipped with a 10-rpm motor, and a $^1/_4$-in. plexiglas shield over the exposed end of the helix, an oil bath containing a 1.6 mm i.d. $\times$ 40 ft glass coil, a colorimeter equipped with silicon detectors and 829-nm filters, and a recorder equipped with absorbance scale chart paper. Disposable plastic sample trays and 250-ml flasks (urine bottles) from Scientific Products were used.

Reagents. All chemicals were ACS grade unless otherwise noted and all aqueous dilutions were made in distilled water. Acetic acid, 80–82%, was purchased from Fisher Scientific. Benax 2A1 was obtained as a 45% solution from Dow Chemical Co., Midland Division, and diluted to 0.02% w/v in water. Bromine was prepared as 14% v/v solution in 80% acetic acid. Digestion mixture was prepared by adding 25 ml of a 1.1% vanadium solution to a mixture of 230 ml of 70% perchloric acid and 1.97 l. of sulfuric acid. Vanadium solution, 1.1% w/v, was prepared by dissolving 12.9 g of ammonium vanadate in 500 ml of 19.2% aqueous sulfuric acid.

Granular Control Standards. Both Dasanit and Di-Syston

standards were prepared by solution coating to contain known amounts of active ingredient (AI). For the nominal 15% granular, 392.7 g of presieved clay (passed through USS No. 20 and retained on USS No. 60) was weighed into a tared 2-l. ST 24/40 boiling flask. Twenty-five grams of diethyleneglycol and 500 ml of methylene chloride were added. The contents were mixed; then the solvent was evaporated at 40–45° on a rotary evaporator. Technical grade Dasanit or Di-Syston, 82.5 $\pm$ 0.01 g of known AI, was dissolved in 200 ml of methylene chloride and quantitatively transferred onto the diethyleneglycol-coated granules with another 300 ml of methylene chloride. The solvent was evaporated as above to constant weight (no more than 0.0002 g lost from a 2-g sample exposed to the atmosphere for 1 min). It was found that a variable amount of water initially contained in the clay was lost as an azeotrope with methylene chloride during the solvent removal steps. Hence the final AI content could not be calculated from the weights of materials initially added, but instead was calculated on the basis of the exact weight of technical grade pesticide added, its known purity, and the final formulation weight.

The finished granular control standard was riffled into four portions and stored in 8-oz clear glass jars at room temperature away from direct sunlight. Retention periods were 2 and 6 months for Dasanit and Di-Syston, respectively; fresh standards were prepared after these storage periods to avoid possible effects of aging on the extractability of the AI.

Sample Materials. Clay granules discussed in this paper and used to formulate granular control standards were as follows: Attapulgite 25/50 ALVM (attapulgite clay), Minerals and Chemicals Div. of Engelhard Mineral and Chemicals Co., Edison, N.J.; Excel 24/48 (serecite clay), Excel-Mineral Co., Los Angeles, Calif.; Creek-O-Nite 24/48 calcined (montmorillonite clay), Lowe's, Inc., Cassopolis, Mich.; Oil-Dri 24/48 LVM (montmorillonite clay), Oil-Dri Corp., Chicago, Ill.; Pikes Peak H6 (montmorillonite clay), Pikes Peak Clay, Inc., Subsidiary of Lowes', Inc., Cassopolis, Mich.

PROCEDURE

The experimental samples and control standards were prepared in the same manner by weighing 1.75 $\pm$ 0.0001 g of Dasanit 15% granules or 1.65 $\pm$ 0.0001 g of Di-Syston 15% granules into separate 250-ml disposable flasks after the bulk sample or standard was mixed with a wide spatula in a beaker of appropriate size to ensure homogeneity. Five milliliters of 14% bromine reagent was added into each flask and allowed to stand for 10 min, 100 ml of 80% acetic acid was added from an automatic pipet, and the flasks were capped and shaken mechanically for 1 hr.

The flow diagram required for our method is shown in Figure 1. Portions of extracts of the standard and sample were placed sequentially on the sampler tray. Standard was placed in the first three and last two cups of the tray. A single cup was used for each sample extract. If a full tray of samples was to be run, an additional standard was placed in the middle. The sampler was operated with a standard 20 sample/hr cam having a 2:1 sample to wash ratio. The sample probe was a 1.4 mm o.d. $\times$ 75 mm glass capillary attached to a length of 0.035-in. i.d. polyethylene tubing. The sample extract from the cups and the wash solution (50 v/v% acetic acid) in the side chamber were sampled alternately with the sample probe. Except where noted in Figure 1, the pump tubing and transfer lines were standard Tygon. The sample extract from the tray was diluted 1:8 with distilled water, and a portion of this solution was further

Table I. Precision Comparison of Manual and AutoAnalyzer
Procedures for Dasanit and Di-Syston 10% Granular Formulations

| Sample no. | Dasanit AI, % | | | | | | | | Di-Syston AI, % | | | | | | | |
| | Titanous chloride | | | | AutoAnalyzer | | | | Manual hydrolysis | | | | AutoAnalyzer | | | |
	Observation		Mean	σ^2	Observation		Mean	σ^2	Observation		Mean	σ^2	Observation		Mean	σ^2
1	10.1	11.7	10.9	1.28	11.1	11.1	11.1	0.00	10.9	11.6	11.3	0.28	12.3	12.4	12.4	0.01
2	11.7	12.9	12.3	0.72	11.7	12.0	11.9	0.05	11.7	11.4	11.6	0.05	12.0	11.7	11.9	0.05
3	11.8	11.9	11.9	0.01	11.8	11.3	11.6	0.13	11.2	10.7	11.0	0.13	11.3	11.6	11.5	0.05
4	10.6	11.3	11.0	0.25	12.2	11.3	11.8	0.41	11.0	11.4	11.2	0.08	11.5	11.7	11.6	0.02
5	10.8	9.1	10.0	1.45	11.0	10.6	10.8	0.08	9.8	9.9	9.9	0.01	9.6	9.7	9.7	0.01
6	12.3	11.0	11.7	0.85	11.9	11.1	11.5	0.32	11.4	11.0	11.2	0.08	11.3	11.4	11.4	0.01
7	10.2	9.2	9.7	0.50	10.6	10.2	10.4	0.08	10.8	11.2	11.0	0.08	11.2	11.4	11.3	0.02
8	11.6	11.7	11.7	0.01	12.2	11.9	12.0	0.08	11.4	11.4	11.4	0.00	11.6	11.5	11.6	0.01
9	11.2	11.6	11.4	0.08	12.1	11.7	11.9	0.08	10.8	10.9	10.9	0.00	11.1	10.8	11.0	0.05
10	12.1	11.0	11.6	0.41	11.9	11.7	11.8	0.02	11.1	10.9	11.0	0.05	11.3	11.5	11.4	0.02
	Average		11.2	0.556	Average		11.5	0.125	Average		11.1	0.076	Average		11.4	0.025
			$\sigma = \pm 0.8$				$\sigma = \pm 0.4$				$\sigma = \pm 0.3$				$\sigma = \pm 0.2$	
		95% C.L. $= \pm 1.6$				95% C.L. $= \pm 0.8$				95% C.L. $= \pm 0.6$				95% C.L. $= \pm 0.4$		

diluted 1:6 with digestion acid and dumped into the digestor helix. The digestor was operated with a helix speed of 7 rpm and a current of 3.5 and 4.5 A on Sections 1 and 2, respectively, to give a solution temperature just below the boiling point. The digestate was diluted about 1:2 with water and transferred from the helix to the mixing chamber by vacuum from a polypropylene water aspirator connected to a 9-l. glass bottle, which also served as the waste container for the digestor.

After leaving the mixing chamber, the digestate was further diluted with 0.02% Benax A1. A portion of this solution was partially neutralized with 3 N sodium hydroxide and the remainder was sent to waste. As the manifold tube for the digestion acid began to fatigue, the sodium hydroxide concentration was increased to maintain a stable base line and smooth peaks. The molybdenum blue complex was developed by mixing the solution sequentially with 3% molybdic acid and 0.2% hydrazine hydrochloride and passing it through the 40-ft coil in the heating bath maintained at 90–91°. The absorbance of the complex was measured in a 15-mm flow cell at 829 nm in the colorimeter.

When interpreting the chart, the first two and last standard peaks were discarded to avoid effects of diffusion interference. Net absorbances were obtained by subtracting the base line from the standard and sample peak maxima. If the absorbances of the two standards bracketing the samples differed by more than 3.0% of their average, the run was discarded and the analysis was repeated using fresh portions of the extracts. The AI of the sample was calculated by comparison of the sample absorbance with the average standard absorbance.

RESULTS AND DISCUSSION

Early in the investigations of the automated method for Dasanit and Di-Syston, primary attention was devoted to sample preparation. The initial extraction solvent had to have three characteristics other than being a good solvent for Dasanit and Di-Syston: water solubility, low volatility, and compatibility with the digestion mixture. One attempt to use methanol resulted in an explosion which shattered the helix at the point where dilution water was added to the digestate. An excessive solvent concentration in the digestion mixture may have been a contributing factor, but methanol was abandoned as the solvent and an explosion shield was installed over the exposed portion of the helix.

Rapid and complete extraction of the toxicant from the granules required an oxidative pretreatment. Bromine was

chosen as the reagent because of its high oxidative ability, volatility, and relative ease of handling. Acetic acid proved to be the most desirable solvent tried, and it was soon determined that at least 10% water must be present to prevent swelling of the acid-flex primary sampling tube. Further investigation showed that both Dasanit and Di-Syston required a minimum acetic acid concentration of 50% for solubility, with an optimum concentration of 75–85%.

Maximum extraction of Di-Syston and Dasanit was obtained by adding bromine dissolved in 80–100% acetic acid to the granules, allowing it to stand 5 min, diluting it with 80% acetic acid, and then shaking for 30–60 min. A solution of 14% bromine in 80% acetic acid proved optimum for the pretreatment and the reaction time was extended to 10 min to ensure complete oxidation. After the oxidative pretreatment, 10% granular samples could be completely extracted in 0.5 hr on a mechanical shaker; the 15% formulations required a full hour.

In the Whitley and Alburn method, the diluted digestate passed directly into the second manifold from the mixing chamber, where it was partially neutralized with 30% sodium hydroxide. These conditions proved unsuitable for our material, resulting in a very noisy signal from the colorimeter. Satisfactory peaks were obtained by further diluting the solution 1:2 with 0.02% Benax 2A1 in water, followed by partially neutralizing it with 3 N sodium hydroxide.

Benax 2A1 emulsifier in the diluting water improved the bubble pattern throughout the second manifold. This anionic emulsifier was reported to be quite stable under acidic, basic, or oxidative conditions (Detergents and Emulsifiers Annual, 1963). However, it could not be used in the first manifold because it could not be completely digested and therefore caused undesirable turbidity.

Table I shows comparative precision data for the previously used manual procedures and an early version of the automated methods for Dasanit and Di-Syston 10% granulars, both formulated on Pikes Peak clay. These data represent a random sampling of 30 replicate analyses of different manufacturing batches of Dasanit and Di-Syston. For both toxicants, the σ values of the automated method were about half those of the corresponding manual methods. (These data do not reflect the benefit of subsequent refinements discussed later.)

During the development and early use of the automated method, Pikes Peak clay was the carrier in most of the samples analyzed. Technical grade material of known AI was used as

Table II. Effect of Clay Type of the Analysis of Dasanit 15% Granular using Technical Standard

Clay type	AI, % Found[a]	AI, % Difference
Pikes Peak H6	17.4	+0.6
Oil-Dri	16.8	0.0
Creek-O-Nite	17.0	+0.2
Excel	17.3	+0.5

[a] The theory for each clay type was 16.8%.

Table III. Effect of 2-Ethylthioethanol on Clay Granule Interference

Clay type	Apparent % Dasanit Without 2-ethyl-thioethanol	Apparent % Dasanit With 2-ethyl-thioethanol
Pikes Peak H-6	0.1	0.4
Oil-Dri	0.1	0.1
Creek-O-Nite	0.1	0.2
Excel	0.1	0.5
Attapulgite	0.7	3.7

the standard during this period. Subsequently, the AI levels of the granular formulations were increased from 10 to 15%, additional clays began to be used for the formulations, and dubiously high values began to appear in the analyses. Examination of previous data such as the means in Table I indicated that the automated method gave a slightly high bias compared with the manual methods for both Dasanit and Di-Syston. These facts implied the presence of a previously unsuspected interference.

The blank (toxicant-free) clays had, of course, been run through the procedure and the results had indicated that the clays alone would contribute only negligible interference. In view of the apparent bias, however, 15% Dasanit formulations were prepared in the laboratory from Dasanit technical standard and four different clays. These were analyzed against the same technical standard and the results showed that interference from the clays did occur when Dasanit was present (Table II). This indicated that some type of interaction occurred between the organic material and the clay and produced absorbances greater than the sum of the separately analyzed components. To confirm the existence of such interaction and to determine its extent by clay type without

the obscuring effect of the organic phosphorus moiety, five different types of blank clay granules were extracted alone and in the presence of 2-ethylthioethanol, added in an amount equal to about one-third of the weight of clay. (This material exemplified the phosphorus-free side chain in both Di-Syston and Dasanit and was available in pure form.) The data in Table III, calculated as equivalent amounts of Dasanit, confirm the existence of an interaction effect, as 2-ethylthioethanol produced an increase in the blank interference. The least effect was found with Oil-Dri and Creek-O-Nite clays. These are more highly calcined than the other clays, implying that their physical properties may play a role at least as important as chemical composition. It is postulated that the interaction consists of extraction of inorganic phosphorus naturally occurring in the clay by the oxidized toxicant under the conditions of the analysis, and that this effect is diminished by severe calcining of the clay before formulation.

Merely adding blank clay granules to solutions of the technical grade toxicant standard failed to compensate fully for the interference and eliminate all the bias, particularly with Attapulgite clay. Experimentation showed that the toxicant must be impregnated into the granules in order to cancel the interference completely. Therefore, granular control standards for both Dasanit and Di-Syston were prepared for each clay type in the manner previously described. These have since been used in lieu of the technical grade standard. Proper utilization of such granular control standards obviously required knowledge of the type of clay in the sample being tested, but this posed no problem for manufacturing control purposes.

The appearance of an operator bias in the analysis of Dasanit 15G led to an examination of subsampling techniques. Observation of the analysts showed that certain types of sample handling caused demixing (segregation by particle size). To ascertain whether this could introduce a bias, samples of Dasanit 15G and Di-Syston 15G were sieved to produce a number of fractions according to particle size. Analyses of the individual fractions showed little variation of AI with particle size for Di-Syston, but a large one for Dasanit. Fractions passing USS #100 and USS #60 showed high Dasanit contents, and throughout the sample AI decreased as the particle size increased. Hence stirring and subsampling techniques were standardized for both Dasanit and Di-Syston samples, as well as all granular control standards, to minimize errors from this source and maintain consistency.

Table IV. Accuracy and Precision for Dasanit 15% Granular

			AI, % Found Day 1	AI, % Found Day 2	AI, % Found Day 3		Standard deviation, % Precision σ	Standard deviation, % Accuracy σ
Sample	Theory	Fraction	1	2	3	Average	Precision σ	Accuracy σ
1	13.9	A	13.9	14.5	14.5	14.1	±0.3	±0.3
		B	14.0	13.7	13.7			
		C	14.0	14.0	14.0			
		Average	14.0	14.1	14.1			
2	15.6	A	15.6	15.5	14.7[a]	15.6	±0.2	±0.2
		B	15.4	15.6	15.6			
		C	15.3	15.7	15.7			
		Average	15.4	15.6	15.7			
3	15.6	A	15.3	15.7	15.7	15.6	±0.2	±0.2
		B	15.3	15.8	15.8			
		C	15.4	15.8	15.8			
		Average	15.3	15.8	15.8			
						Average	±0.2	±0.2

[a] Statistically rejected by the technique of Dixon (1953). 95% C.L. for both accuracy and precision = ±0.4%.

Following these modifications, a new accuracy and precision study was carried out on Dasanit 15% granular formulations which were quantitatively prepared in the laboratory by a spray coating technique, simulating commercial production. Three riffler fractions of each preparation were analyzed on three different days. As shown in Table IV, the mean value for each preparation was in very good agreement with the theory and the σ values for accuracy and precision were identical. All of these samples as well as the secondary standard were stirred prior to sampling, while the samples shown in Table I were not. A comparison of the σ values for

Dasanit granules showed that utilizing a secondary standard and introducing the standardized stirring step halved the confidence limits.

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Residue Study of Phenoxy Herbicides in Milk and Cream

E. LeRoy Bjerke,* James L. Herman, Paul W. Miller, and James H. Wetters

Cows were fed a complete ration containing 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, 2-(2,4,5-trichlorophenoxy)propionic acid, or 2-methyl-4-chlorophenoxyacetic acid at six levels from 10 to 1000 ppm for 2 or 3 weeks at each level. Milk and cream samples were collected at predetermined intervals during the feeding of these chemicals and for 7 days following withdrawal of the highest level. Residues of the acids and their phenol moieties were extracted with diethyl ether, separated by liquid chromatography on alumina, and determined as esters and phenols by electron capture or microcoulometric gas chromatography.

The procedure was used to quantitate the chemicals down to 0.05 ppm, with overall average recoveries of greater than 80%. The average residues found in milk at the highest feeding level were: 0.06 ppm, 2,4-dichlorophenoxyacetic acid; <0.05 ppm, 2,4-dichlorophenol; 0.42 ppm, 2,4,5-trichlorophenoxyacetic acid; 0.23 ppm, 2,4,5-trichlorophenol; 0.12 ppm, silvex; <0.05 ppm, 2,4,5-trichlorophenol; and <0.05 ppm, 2-methyl-4-chlorophenoxyacetic acid; 0.06 ppm, 2-methyl-4-chlorophenol. Residues of all chemicals decreased rapidly upon removal of the chemicals from the feed.

Work at Cornell University (Gutenmann *et al.*, 1963a,b; Bache *et al.*, 1964; St John *et al.*, 1964) indicated that ingested phenoxy compounds are not readily transferred to milk. Doses of various compounds administered daily to individual cows at rates equivalent to 5 ppm in 50 lb of feed per day for up to 5 days produced no detectable residues in milk.

Residues up to 0.06 ppm of 2,4-D (2,4-dichlorophenoxyacetic acid) were found in milk from cows grazed on pastures sprayed with isopropyl or isooctyl esters of 2,4-D at 2 lb of acid equivalent per acre (Klingman *et al.*, 1966).

This study was designed to determine the residue levels of 2,4-D, 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), silvex [2-(2,4,5-trichlorophenoxy)propionic acid], or MCPA (2-methyl-4-chlorophenoxyacetic acid) and their corresponding phenol moieties which might occur in milk and cream when cows were fed very high levels of phenoxy herbicides for prolonged periods of time.

APPARATUS

Barber-Colman Models 10 and 5000 gas chromatographs equipped with Sr[90] electron capture detectors were used for determining 2,4-D, 2,4,5-T, and silvex and their corresponding phenols. The Infotronics GTS-20 system for microcoulometric determination of halogen was used for MCPA and 2-methyl-4-chlorophenol.

Residue Research, Ag-Organics Department, Dow Chemical U.S.A., Midland, Michigan 48640.

REAGENTS

Analytical grade 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2-methyl-4-chlorophenol, 2,4-D, 2,4,5-T, silvex, MCPA, and the methyl esters of the four phenoxy acids used in this study are obtainable from the Sampling Coordinator, Ag-Organics Department, Dow Chemical U.S.A.

GAS CHROMATOGRAPHIC OPERATING CONDITIONS

The electron capture systems consisted of 185-cm × 3-mm i.d., U-shaped borosilicate glass columns packed with 4% LAC-446 + 0.55% H_3PO_4 on 80–100 mesh Chromosorb W-HP. Chromatograph oven temperatures adjusted to give a retention time of 2.5 to 3.5 min for all chemicals were: 150°C for 2,4-dichlorophenol; 180°C for 2,4,5-trichlorophenol and the methyl ester of silvex; and 190°C for the methyl esters of 2,4-D and 2,4,5-T. Detector and injector block temperatures were 220°C. The carrier gas was prepurified nitrogen with a flow rate of approximately 100 cm^3/min. Injection volume was 2 µl.

The microcoulometric system included a quartz pyrolysis furnace, C-200-AR microcoulometer, T-300-S titration cell, and R-100-I strip chart recorder. A capillary stainless steel line wrapped with heater tape was used to connect the furnace to the gas chromatographic column in a Barber-Colman Model 5000 oven. The 185-cm × 6-mm i.d., U-shaped borosilicate glass column was packed with 6% DC-200 on Gas Chrom Q, 80–100 mesh. A "T" joint was fabricated on the outlet end of the column with one side connected to the vent and the other to the furnace. The column was operated at