Table VIII. Release of Dimilin from 0.5 and 1.0% Granules

Formulation + rate	h after treatment					
	1	8	24	48	96	144
1.0% granules at 0.1 ppm	0.023[a]	0.020	0.025	0.032	0.037	0.037
	0.021	0.023	0.032	0.032	0.041	0.035
	0.022[b]	0.022	0.029	0.032	0.039	0.036
0.5% granules at 0.1 ppm	0.034	0.033	0.028	0.030	0.039	0.027
	0.036	0.032	0.028	0.039	0.050	0.035
	0.035	0.032	0.028	0.035	0.045	0.031

[a] Concentration in parts per million. [b] Averages.

parison to only 22% from the 1.0% granules and this difference may account for differences in the field results. Thus, when granular formulations are used, it is very important when attempting to correlate control and residues to measure the actual release rate of the granules applied.

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Role of Water in the Hydrolysis of Parathion and Methylparathion on Kaolinite

Sarina Saltzman,* Uri Mingelgrin,[1] and Bruno Yaron

Oven-dried kaolinite has a catalytic effect upon parathion and methylparathion hydrolysis. Addition of water to kaolinite, in the limits of sorbed water, affected the degradation kinetics of both insecticides and increased the degradation rate. A slight increase in the moisture content above that corresponding to sorbed water results in a steep decrease in the degradation rate. Following hydrolysis, part of the organophosphate hydrolysis product is fixed at the clay surface. The data obtained suggest that water molecules associated with the exchangeable cations participate in the hydrolysis.

The sorption of organic molecules by clay surfaces is one of the most studied aspects of the clay–organic interactions. Almost all the studies of the sorption of organics by clays point out the decisive role of the hydration level of the system on the sorption process (e.g., see Yariv et al., 1966; Mortland and Meggit, 1966). The sorbed organic molecules may undergo several kinds of reactions as a result of the catalytic effect of the clay surfaces.

Catalytic reactions on clay surfaces have received considerable attention, but information on the role of water in these reactions is scarce (Rosenfield and Van Valkenburg, 1965; Solomon and Murray, 1972). Most of the older studies were undertaken on dehydrated systems and at high temperatures, and only recently was it observed that catalytic reactions could also occur at low temperatures and at relatively high hydration levels (Mortland, 1970).

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In a previous work (Saltzman et al., 1974) it was shown that kaolinite has a catalytic effect upon parathion degradation at room temperature. The degradation products were p-nitrophenol and an alkyl thiophosphate. The same hydrolysis occurred with methylparathion. The degradation rate was dependent on the nature of the saturating cation, and the process was hindered by the presence of free water. As the degradation rate on oven-dried clays was much slower with Na- than with Ca-kaolinite, it was suggested that the determining factor could be the presence of cation hydration water on clays, that is, the capacity of the different cations to retain their hydration shell, when dried at 105 °C.

In a recent study of pirimiphos ethyl, another bioactive phosphate thioester (Mingelgrin et al., 1975), catalytic activity of kaolinite at room temperature was also noted. Additional sorbed water in Na-kaolinite enhanced the catalytic effect of the clay, as compared with that of the oven-dried clay. The presence of free water, on the other hand, drastically reduced the chemical conversion of parathion on kaolinitic soils (Yaron, 1975).

Knowledge concerning the effect of water content on the degradation of organic molecules in an adsorbed state is important, as it may shed light on the mechanism of the process. From a practical point of view, it may clarify some

Table I. Water Content of Kaolinite at Different Relative Humidities (%)[a]

Cation	Rel humidity, %		
	15	51	98
Na	0.84	1.64	11.54
Ca	0.64	1.39	11.04
Al	0.75	2.33	9.14

[a] The water content is defined as the quantity of water lost upon drying at 105 °C, for 24 h.

aspects of the nonbiological degradation of organic substances in soils, in which some sorbed water is always present. The use of clays as carriers for pesticides may also be influenced by knowledge of that effect of water.

The present work was carried out to study the effect of water on the degradation of organophosphorus pesticides on kaolinite.

MATERIALS AND METHODS

Homoionic kaolinites were prepared from Peerless No. 2 kaolinite as described previously (Saltzman et al., 1974). The CEC was 10 mequiv/100 g and the surface area was 48 m²/g. In order to obtain a range of different water contents, the homoionic kaolinites were equilibrated in desiccators over saturated salt solutions, at different relative humidities prior to the addition of the pesticide. The water content obtained (determined by drying at 105 °C) is shown in Table I.

For Na-kaolinite an intermediate moisture content (4%) was also obtained. For higher moisture contents (15, 25, and 100% water, w:w) the required amount of water was added to the clays, and the samples were allowed to equilibrate for 24 h at 5 °C. The moisture content of oven-dried kaolinites (overnight, at 105 °C) was taken as "zero".

The insecticides used were parathion [O,O-diethyl O-p-nitrophenyl phosphorothioate] and its methyl analogue. The parathion was ¹⁴C labeled on an alkyl chain (Amersham Radiochemical Centre). Hexane solutions of these insecticides were shaken with kaolinite samples for 30 min, and the supernatant was evaporated in an air stream. The concentrations used were: parathion, 500 and 100 μg/g for Na- and Ca-kaolinites and 500 μg/g for Al-kaolinite; and methylparathion, 500 μg/g for all the clays used in the experiment. A minor concentration effect in this range was found and results are all for the 500 μg/g samples. The samples were incubated in the dark at room temperature (22 °C) in the appropriate desiccators.

Parathion and methylparathion were extracted from clays by shaking 0.2 g of the samples for 60 min with a 4-cm³ hexane and 6-cm³ water mixture. A previous check (Saltzman et al., 1974) showed that the insecticides are 100% distributed in the organic phase, and the hydrolysis products are totally in the water phase. Parathion was determined as ¹⁴C in hexane and the labeled organophosphate degradation product as ¹⁴C in water. This extraction procedure gave complete recovery with samples before degradation occurred. As the recovery of parathion plus the water-soluble organophosphate products decreased with the aging of the samples, another extraction procedure was utilized. The purpose of this procedure was to determine whether the decrease in recovery was caused by the loss of parathion or of its organophosphate degradation product. This second procedure enables the separate determination of p-nitrophenol and the water-soluble organophosphate degradation product by eliminating the interferences which occur in the analysis of p-nitrophenol in the aqueous clay extract.

Table II. Degradation of Parathion and Methylparathion on Oven-Dried Kaolinites after 40 Days of Incubation

Cation	Degradation, %	
	Parathion	Methylparathion
Na	16	9
Ca	92	64
Al	16	15

In this procedure, a 0.2-g clay sample was extracted with 6 cm³ of benzene and the amount of parathion in benzene was determined by ¹⁴C counting. Four cubic centimeters of the benzene extract was shaken with 6 cm³ of water acidified with HCl and the water extract was checked colorimetrically for p-nitrophenol in the presence of a pH 10 borate buffer. The partition coefficient of p-nitrophenol between benzene and water at the appropriate pH values has been established for the purpose of this extraction procedure. The same sample, which was extracted with benzene, was further extracted with a 4-cm³ hexane and 6-cm³ water mixture. No ¹⁴C was detected in the hexane; ¹⁴C in the water extract was counted for the soluble organophosphate hydrolysis product. It was ascertained that no water-soluble organophosphate hydrolysis product was extracted by the initial benzene extraction.

At all moisture contents between oven dryness and that in equilibrium with 98% relative humidity the total amount of parathion applied was recovered as parathion plus p-nitrophenol. At higher moisture contents (when free water was present) not all the applied parathion was accounted for by the above procedures. At these higher moisture contents evaporation losses were also demonstrated by analyzing the parafilm covers of the vessels. Accordingly, in the case of parathion at equilibrium with 98% relative humidity or less, degradation was calculated from the difference between the initial amount of labeled parathion and the amount of ¹⁴C recovered in the hexane extract. Fixation of the labeled organophosphate degradation product was calculated from the difference between the degradation as defined above, and the amount of the labeled water-soluble organophosphate recovered. In the case of the unlabeled methylparathion degradation was defined as the amount of p-nitrophenol recovered.

RESULTS AND DISCUSSION

The catalytic effect of oven-dried kaolinite on the hydrolysis of parathion at room temperature was described elsewhere (Saltzman et al., 1974). A similar behavior of methylparathion in kaolinite complexes was observed. As pointed out before, the total quantity of parathion lost was recovered as p-nitrophenol from samples with moisture contents at equilibrium with 98% relative humidity or less, indicating that hydrolysis was practically the only mode of parathion loss on the clay surface, and that the nonhydrolyzed parathion was completely recovered by the procedure used. This demonstrates the equivalency of both quantities, defining the degradation of parathion and methylparathion.

Table II shows the degradation of parathion and methylparathion after a 40-day incubation period, on different oven-dried homoionic kaolinites. It is generally known that dimethyl derivatives of phosphates are less stable than diethyl ones in aqueous solutions. For example, the half-life of methylparathion at pH 1–5 and 20 °C is 175 days, while for parathion it is 690 days (Melnikov, 1971). The results in Table II indicate that, adsorbed on kaolinite surfaces, methylparathion seems more stable than parathion. The degradation of methylparathion in an aqueous solution at pH 7 was about 4% after a 40-day incubation
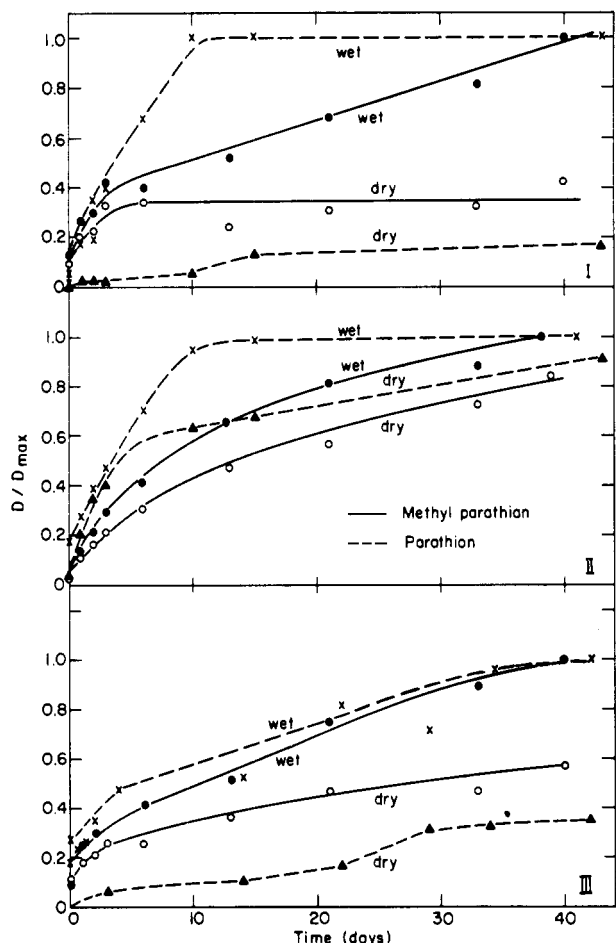
Figure 1. The effect of bound water on parathion and methylparathion degradation on kaolinite: (I) Na-kaolinite; (II) Ca-kaolinite; (III) Al-kaolinite; (dry) clay oven-dried at 105 °C for 24 h; (wet) clay equilibrated at 98% relative humidity; (D/D_{max}) the ratio between the degradation at each sampling time and the degradation on the wet clay after 40 days.

Figure 2. Parathion degradation as affected by the clay water content (incubation period 15 days).

period. This clearly shows the catalytic effect of the clay.

Additions of relatively small amounts of water to kaolinite (in the limits of sorbed water) increased the degradation rate of both insecticides. Figure 1 shows the degradation of parathion and methylparathion on Na-, Ca-, and Al-kaolinites both oven-dried and equilibrated at 98% relative humidity. The results were expressed for each pesticide as the ratio between the degradation on the wet clay after 40 days and the degradation at each sampling time $(D_{max}:D)$. The curves obtained show that the greater degradation rate on the wet as compared with the oven-dried kaolinites is common to the degradation of both the organophosphorus insecticides adsorbed on all the examined kaolinites. At the higher moisture contents, degradation of methylparathion was slower than that of parathion. The differences between dry and wet clays are relatively small for the Ca-saturated kaolinite (Figure 1-II), because of the already significant decomposition on oven-dried Ca-kaolinite, but striking for the Al-kaolinite (Figure 1-III) and Na-kaolinite (Figure 1-I).

In order to emphasize the relationship between the degradation rate and the moisture content, the percent parathion remaining on the kaolinite after a 15-day incubation period was plotted against the kaolinite water content (Figure 2). The functional dependence of degradation on moisture content on the various homoionic clays is very similar. As the water content of oven-dried Na-kaolinite is the lowest of the homoionic clays inves-
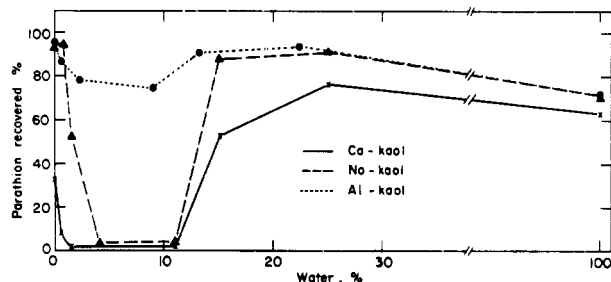
tigated, this kaolinite displays the widest range of hydration states and was chosen for a detailed examination.

The curve obtained for Na-kaolinite shows the existence of four points of discontinuity corresponding, probably, to a qualitative change in the state of water on the clay surface. Up to a water content of about 0.8%, the degradation rate is very low. Increasing the moisture content further, up to less than 2% water, results in a very sharp increase in the degradation rate. A second point of discontinuity occurs at about 2% moisture content (determined by extrapolating the 0.8% to 1.6% and the 4% to 10% lines in Figure 2). Relatively little change in the degradation rate occurs between 2 and 11.2% moisture. Since the hydration energy of the cations is much higher than that of the other various sites on the surface (Fripiat and Dondeyne, 1960), it is suggested that the cations' first hydration shells became fully saturated at the second point of discontinuity (approximately 2%). About 1.2% moisture content is needed to obtain 6 mol of $H_2O/1$ mol of Na^+. The third discontinuity point (11% water) is the upper limit of bound water, as this moisture content was obtained by equilibrating the kaolinite at 98% relative humidity. A slight increase in the moisture content above that corresponding to bound water at about 11% moisture content resulted in a steep decrease in the degradation rate. The presence of free water hindered almost completely the catalytic effect of the clay surface.

A similar relationship between parathion degradation and the water content of the system was also obtained for Ca- and Al-kaolinites (Figure 2) in spite of the quantitative differences observed. The lack of the first point of discontinuity may be explained by the amounts of water that Ca- and Al-kaolinites retain, when dried at 105 °C. Another difference is that the second point of discontinuity (marking the beginning of the range with the highest degradation rate) appears at a lower moisture content as compared with Na; again, probably for the same reason. Over a wide range of moisture contents, the rate of parathion degradation is rather similar for Na- and Ca-kaolinites, showing that in some cases the effect of water may be stronger than that of the cation. For Al-kaolinite the contrary is true: the cation seems to be the determining factor of the degradation rate.

At far different concentrations the degradation kinetics of parathion on kaolinite may be different. The effect of parathion concentration on the degradation kinetics of parathion on Ca-kaolinite has already been reported (Mingelgrin et al., 1976). It is suggested that the high degradation percent obtained in this experiment is due to the relatively low parathion:cation ratio (Mingelgrin et al., 1976).

It has already been shown that parathion degradation on oven-dried kaolinites proceeds in two first-order stages (Saltzman et al., 1974). The effect of water on the degradation kinetics of parathion on Na- and Ca-kaolinite is shown in Table III. As the degradation rate on Al-

Table III. Effect of Water on the Kinetics of
Parathion Degradation

Cat-ion	Water con-tent,[a] %	Two evident stages	Half-life, days	Rate constant (days⁻¹) × 10² First stage	Rate constant (days⁻¹) × 10² Second stage	Para-thion hydro-lyzed in the first stage, %
Ca	0	Yes	4	17	3.5	60
	0.64	Yes	~1	69	3.2	84
	1.39	Yes	~1	69		~100
	11.04	Yes	~3	23		~100
Na	0	No	~280		0.25	
	0.84	No	~280		0.25	
	1.67	No	17		4.1	
	4.16[b]	Yes	~2	~34	~6.0	~70
	11.54	Yes	~4	17		~100

[a] The water content is defined as the quantity of water lost upon drying at 105 °C, for 24 h.   [b] Only four incubation times were checked in this case. All other samples were checked at eight incubation times at least.

Table IV. Correlation between Fixation of the Organophosphate Degradation Product and Some Other Factors[a]

Cation	X	Y	a	b	r	SD	N
Al			2.42	0.394	0.795	5.65	36
Ca	D	F	0.911	0.169	0.669	6.15	90
Na			2.46	0.152	0.669	5.70	37
Al			0.550	-0.0021	-0.170	0.250	
Ca	t	F/D	0.189	0.00028	0.033	0.165	
Na			0.203	0.0016	0.170	0.230	
Al			0.560	-0.0010	-0.230	0.250	
Ca	W	F/D	0.177	0.00035	0.079	0.164	
Na			0.468	-0.0041	-0.629	0.182	

[a] The linear regressions tested were of the form $Y = a + bX$ where r is the correlation coefficient, SD is the standard deviation from the regression, and N is the number of points; t refers to the incubation time in days, up to 72 days; W is the percent relative humidity, up to 98%, with which the clays were in equilibrium; D is the percent decomposition and F is the percent fixation.

kaolinite is relatively low (Figure 2), it was omitted from this analysis.

The results show a dramatic effect of water on the degradation kinetics, in the case of Na-kaolinite (Table III). The addition of 1.7% water to the dry kaolinite brought about a 16-fold decrease in the half-life of parathion. In the presence of only bound water (after the second point of discontinuity), the kinetics is similar to that of Ca-kaolinite.

As oven-dried Ca-kaolinite has a strong catalytic effect, the degradation kinetics seems to be less affected by the increase in the clay water content. The half-life is very short at all water contents investigated up to 11% (Table III). If we consider the amount of parathion hydrolyzed in the first stage, a dependence on the moisture content is evident. An increase in the water content up to 1.4% resulted in a 40% increase in the amount of parathion decomposed at the end of the first stage.

As the radioactivity recovered in the solvent system used to extract parathion and its degradation products was in some cases less than 100%, it was supposed that a fixation process may occur. The results obtained by comparing the amount of ¹⁴C in the aqueous phase with the amount of p-nitrophenol obtained indicated that in samples in equilibrium with 98% relative humidity or at lower moisture contents it is the organophosphate hydrolysis product and not parathion which is not totally extractable. Fixation of orthophosphates on kaolinite has been noted in the past (Kafkafi et al., 1967). Table IV summarizes the relationship of the fixation of the organophosphate hydrolysis product to degradation and some additional factors. The linear regressions indicate that fixation is positively correlated with parathion degradation with all of the cations tested. Incubation time on the other hand, did not correlate with the ratio of the quantity fixed to quantity degraded. This means that the rate of fixation directly correlates to the rate of the hydrolysis. The degradation is thus the rate-limiting step in the degradation–fixation sequence. Examination of the correlations given in Table IV shows that the fraction of the degradation product fixed is correlated with the exchangeable cation, Al-kaolinite having a fixation to degradation ratio significantly larger than the Ca- and Na-kaolinites. Namely, independently of affecting the degradation rate, the cations will also determine the fraction of the hydrolysis product fixed from any given quantity decomposed. The linear regression of the residuals of fixation (from the regression on degradation) against moisture

content as well as against incubation time (up to 72 days) was also computed. All the above analyses indicated that the rate of degradation is the dominant factor which correlates with the rate of fixation and that the ratio of degradation to fixation is strongly correlated with the nature of the cation. There is, in addition, a relatively high negative correlation between moisture content and fixation to degradation ratio on the Na-kaolinite.

At moisture contents above these at equilibrium with 100% relative humidity there is a substantial decrease in parathion recovery with time. Yet, relatively small quantities of either p-nitrophenol or the ¹⁴C-labeled hydrolysis product were detected indicating a low degradation rate. On the other hand, large amounts of parathion were extracted from the vessels' cover indicating that evaporation of parathion was a major cause in the decrease in recovery. Such evaporation was not detected in samples with lower moisture contents. The existence of evaporation loss only in samples with a moisture content above that in equilibrium with 100% relative humidity (namely only in those where free water is present) suggests that free water hinders the adsorption of parathion on the kaolinite surface.

The results in the present work suggest that the catalytic effect of kaolinite on the hydrolysis of parathion and methylparathion is highly moisture dependent. A considerable catalytic activity of kaolinites in nonaqueous media on various other reactions has already been observed. In a number of cases (Hawthorne and Solomon, 1972; Solomon and Murray, 1972), it was observed that moisture content is very important in the interactions at the kaolinite surface: even small amounts of water hindered those reactions. On the other hand, the present results show that adding water in the range of sorbed water may enhance the catalytic decomposition of parathion on the clay surface. Subsequently, it may be that sorbed water molecules serve as adsorption and degradation sites for the neutral, polar molecules of the organophosphates used in our experiment. Sorbed water on kaolinite may be associated with the surface oxygen atoms or hydroxyl groups, the broken edges of the lattice, or alternatively with the exchangeable cations (e.g., as ligand water). There arises the question, which of these forms of water promotes the degradation of the organophosphates?

By summing up many studies of the adsorption of a large number of organic molecules by clays, Mortland (1970) showed that, contrary to older concepts, the exchangeable cations with their associated water are very

important in the adsorption of neutral, polar molecules. Adsorption on the hydrated cations was considered one of the main adsorption mechanisms of parathion, *p*-nitrophenol, and phenol by montmorillonite (Saltzman and Yariv, 1975; Saltzman and Yariv, 1976). Fripiat and Dondeyne (1960) demonstrated that the bonding energy of water on the kaolinite surface proper is much lower than the hydration energy of the ions. Namely, at the lower moisture contents where the largest increase in the rate of hydrolysis was observed upon a small addition of water, this water probably is sorbed mostly as ligand water of the cations. These ligand water molecules associated with the exchangeable cations may be the hydrolysis sites for the organophosphates studied. The dependence of the hydrolysis kinetics on the cation (Figure 2 and Table III) further supports this suggestion. In the solid systems used, the catalytic site could also be the fixation site of the phosphate decomposition product. This appears so because the movement of the hydrolysis products for any distance on the dry surface would be extremely slow, whereas the fixation to degradation ratio being independent of time suggests that the fixation step is rapid and not limiting. The nature of the alkyl thiophosphate and the fact that fixation occurs only after hydrolysis suggests that fixation and decomposition occur also at locations in the adsorbed organophosphate that are close to each other or even identical. This identity or proximity of the degradation and fixation sites together with the direct effect of the exchangeable cation on the fixation discussed above (aside from its effect on the degradation rate) supports again the proposal that the cation and its hydration shell may be the hydrolysis site. Infrared studies are being conducted in an attempt to obtain direct evidence for this assumption.

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Field Desorption Mass Spectrometry of Commercial Pesticides and Mixtures of Pesticides

Hans-Rolf Schulten

Highly polar pesticides that are used as insecticides, acaricides, fungicides, and herbicides have been investigated with low- and high-resolution field desorption mass spectrometry. By use of defined sample amounts, standard field desorption emitters, a controlled time/temperature program for desorption, and photographic detection, the potential of the method for qualitative and semiquantitative analyses of commercial pesticides and mixtures of pesticides has been demonstrated. The high molecular ion intensities displayed, the strongly reduced fragmentation, and the sensitivity and analytical resolution obtained indicate that field desorption is particularly well suited for the investigation of mixtures. Furthermore, desorption of a synthetic combination of a parent pesticide, *p,p'*-DDT, and five of its metabolites yielded almost exclusively molecular ions of the different constituents of the mixture. Interaction of the various components of the mixtures in field desorption was remarkably small and did not prevent the identification of the individual components.

The utility of field desorption mass spectrometry (FDMS) for the analyses of compounds of low volatility has been demonstrated for a wide variety of substances (Beckey and Schulten, 1975a,b). The first application of the method to environmental chemicals showed that bridged polycyclic chlorinated pesticides and some of their metabolites yield high molecular ion intensities and little or no fragmentation as compared to other ionization

methods in mass spectrometry such as electron impact (EI) and chemical ionization (CI) (Schulten and Beckey, 1973a). The basic advantages of the FD technique, namely small sample consumption, high sensitivity, and strongly reduced thermal degradation (no evaporation is required in FDMS), make it particularly applicable to the detection and identification of metabolites and/or nonmetabolic decomposition products (Schulten et al., 1973). In addition to pesticides and pesticide metabolites mutagenic, cocarcinogenic, and antiseptic substances have been the subject of preliminary FD investigations (Schulten, 1973). The results obtained underline the utility of the technique

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