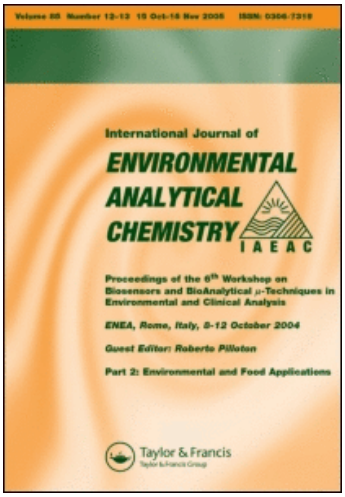

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Electron Donor-Acceptor Complexing Reagents in the Analysis of Pesticides

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Electron Donor-Acceptor Complexing Reagents in the Analysis of Pesticides

III. Quantitative *in situ* Analysis by Reflectance Spectroscopy on Thin-layer Chromatograms

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The quantitative *in situ* determination of pi-complexed pesticides by reflectance spectroscopy is discussed and quantitative results and stability studies obtained on cellulose and silica-gel thin-layer plates are presented. Detection limits are in the microgram region, with the linear working range for the Mobam-CNTNF complex chosen as an example being 1–10 mcg on cellulose and 3–10 mcg on silica gel. The complexed pesticide may be recovered following quantitative determination for mass spectral confirmation. The method shows particular utility in studying the degradation of pesticides.

INTRODUCTION

The detection of pesticides on thin-layer plates by the formation of coloured pi-complexes has been reported in several earlier papers and some qualitative indications of the possible use of *in situ* reflectance spectroscopy in the analysis of these pesticides have been given.[1,2] A thorough examination of the possible quantitative application of this method had not, however, been undertaken.

The use of *in situ* reflectance spectroscopy on thin-layer chromatograms has been the subject of a recent review.[3] One of the earliest studies of the utility of this method in pesticide analysis for sprayed plates was reported by Beroza *et al.*, who used a home-made fiber optics TLC scanner,[4] although the quantitative determination of triazines by u.v. reflectance on fluorescence indicator plates had previously been reported.[5] Another study published at about the same time reported the determination of several pesticides by reflectance on thin-layer chromatograms using also the u.v. absorption of these compounds.[6]

In this study, a donor (pesticide)-acceptor complex was chosen for complete study with the complexing agent 9-dicyanomethylene-2,4,7-trinitro-fluorene (CNTNF) which earlier experiments[1,2] had shown to give intense colours and to have optimum properties for mass spectral applications. The pesticide chosen for the study was 4-benzothienyl-*N*-methyl carbamate (Mobam), which formed stable, brightly coloured complexes.

EXPERIMENTAL

Reagents

An analytical-grade sample of Mobam was obtained from Mobil Chemical Co. (Metuchen, N.J., U.S.A.). Standard solutions (1 mg/ml, 3 mg/ml, 5 mg/ml, 10 mg/ml) were prepared in acetone and stored in the refrigerator when not in use. All other pesticides used were analytical grade, 5 mg/ml in acetone.

CNTNF was obtained from Eastman Organic Chemicals (Rochester, N.Y.). Freshly prepared 1% solutions of CNTNF in acetone were used to spray the sheets.

Chromatography

Pesticides were spotted on the sheets with a 1-mcl Drummond micropipette (Kensington Scientific, Oakland, Calif., U.S.A.).

Chromatography was carried out on Eastman Chromagram silica-gel sheets 6061 using an isopropyl ether-toluene (1:3)[2] solvent system and on Eastman Chromagram cellulose sheets 6064 using iso-octane-methylene chloride (5:1).

Chromatograms were developed at room temperature using an Eastman Chromagram Developing Apparatus 6071.

Instrumentation

The quantitative determinations were performed on a Farrand UV-VIS chromatogram analyzer (Farrand Optical Co., Inc., Mount Vernon, N.Y.).

Relative reflectance (spot to background) was measured in the double-beam mode at 500 nm on cellulose and at 490 nm on silica gel following chromatography and spraying with the complexing agent (CNTNF).

Measurements were made on a scale of 55–100% reflectance. A monochromator was used in the exciter side while a 3–73 auxiliary filter was used in the analyzer side. The 325–800 UV-VIS lens was used in the exciter drawer with 0.625 in aperture reducer with screen as recommended in the instrument manual. The 3/16–11/32 slit set was used. Suitable slit aperture reducers were chosen (0.062 in in the analyzer leg, 0.125 in in the reference leg). Two unused Chromagram sheets were placed on the stage beneath the sheet being scanned to approximate an infinite layer thickness.

The light source was a xenon lamp. 1P28 Photomultiplier tubes were used as detectors in the analyzer and reference legs.

Mass spectra were obtained with a DuPont/CEC 21-110B instrument using standard probes for direct introduction into the ion source as previously described.[2]

Solution spectra were measured using a Beckmann DK-2 A.

RESULTS AND DISCUSSION

Chromatography and Complexation

The Mobam-CNTNF complex formed immediately when the chromatographed pesticide was sprayed with CNTNF. This complex is bright red, with absorption maxima at about 500 nm on cellulose and approximately 490 nm on silica gel.[2] Detection limits are less than 1 mcg on cellulose and $\sim$ 1 mcg on silica gel. In solution (0.1 M Mobam in 10^{-3} M CNTNF), the absorption maximum of the complex is at $\sim$ 475 nm.

The isopropyl ether-toluene solvent system for silica gel has been discussed previously[2] and is still superior to any of the solvent systems developed for use with cellulose sheets. The iso-octane-methylene chloride system used for this work is, however, more satisfactory than others described previously.[2] Spots were uniform with little tailing and R_f values were reproducible. R_f values of a number of carbamates in this solvent system are given in Table I.

Spectra

The shifts in absorption maxima observed for the complex in this experiment on different adsorbents are quite common.[3] Measurements in solution have shown that even inert solvents can affect the formation constants of pi-complexes.[7] Thus, the variations in intensity between complexes on cellulose and silica gel and in acetone solution are not surprising.

TABLE I

R_f values of selected representative carbamates on Eastman Chromagram cellulose 6064 sheets, eluant iso-octane-methylene dichloride (5:1)

Compound[15]	R_f†	S.D.
Banol (3,4-xylenol-6-chloromethylcarbamate) (carbanolate)	0.76	0.03
Barban (4-chloro-2-butynyl-N-(3-chlorophenyl)carbamate) (carbyne)	0.57	0.04
Baygon (N-methyl-2-isopropoxyphenyl carbamate) (propoxur)	0.74	0.05
Carbaryl (1-naphthyl N-methylcarbamate) (sevin)	0.67	0.04
Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl N-methylcarbamate) (Furadan)	0.72	0.04
IPC (isopropyl N-phenyl-carbamate) (propham)	0.87	0.03
Matacil (4-dimethylamino-3-tolyl N-methylcarbamate) (aminocarb)	0.71	0.04
Mesurol (3,5-dimethyl-4-methylthiophenyl N-methylcarbamate)	0.75	0.03
Mobam (4-benzothienyl N-methylcarbamate)	0.62	0.05
Swep (3,4-dichlorophenyl N-methylcarbamate)	0.04	0.00
Zectran (4-dimethylamino-3,5-xylyl N-methylcarbamate)	0.79	0.03

† Average of four determinations.

Quantitative Analysis

To determine the reproducibility of the method, four plates containing nine spots of pesticide of the same concentration were developed and scanned. The results are shown in Table II. Better reproducibilities were obtained on cellulose sheets than on silica-gel sheets. It was also possible to work with a 1-mcg sample on cellulose, whereas 5 mcg proved to be the working limit on silica gel. In both cases, best results were obtained when 5 mcg of Mobam was determined as the complex. On silica gel, the results obtained below 5 mcg were only semi-quantitative, due to an unfavourable signal-to-noise ratio.

Visual observation had shown that the complexes remained stable on cellulose with little apparent change over several days, whereas a more rapid fading occurred on silica gel within a few hours after spraying.

TABLE II

Reproducibility of *in situ* analysis of Mobam-CNTNF complex

	Conc. (mcg)	Av. rel. % S.D.†
Cellulose	10	8.1
	5	7.1
	1	12.1
Silica gel	10	10.7
	5	7.6
	3	21.2

† Average of four plates, nine spots per plate.

Instrumental measurements verified these observations (Figure 1). Considerable variations in intensity may be observed for a complex on silica-gel thin-layer plates, unless the plates are dried for approx. 30 min.

Calibration curves (peak area versus concentration) obtained for this complex are shown in Figure 2. Plots of peak area versus the square root of concentration were also made, but did not yield a linear plot in the range 1–10 mcg. This type of plot approximates the Kubelka-Munk functions of diffuse reflectance spectroscopy, so the results indicate that within the

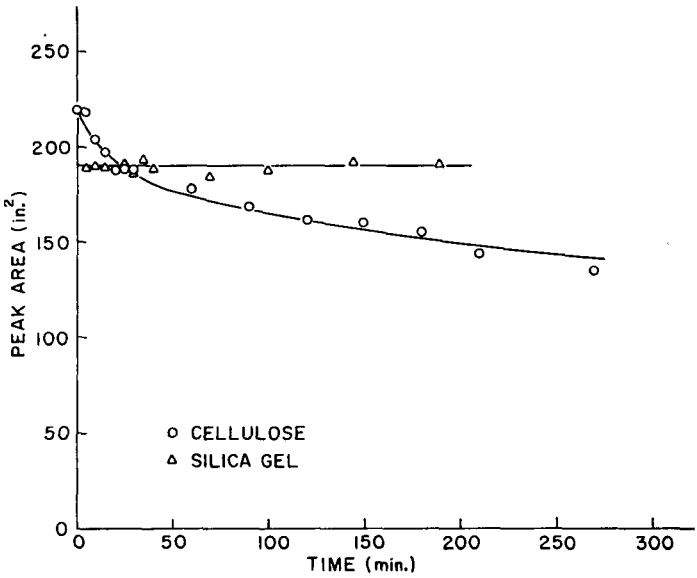

FIGURE 1 Change in intensity of absorption of Mobam-CNTNF complex with time on cellulose and silica-gel thin-layer plates.

working range chosen, the conditions for diffuse reflectance spectroscopy are not met. A similar linear relationship in the 1–10 mcg range has been found to exist for plots of peak area versus concentration for other pi-complexes.[8]

A single spot of complexed pesticide was also scanned repeatedly on a cellulose plate after chromatography and spraying to reveal the actual error in measurement. A relative standard deviation of 1.6% was obtained, which represents the instrumental error, planimetric error and the error introduced by the fading of the spot due to repeated scanning. From these results, it may be judged that the main source of error lies not in the instrumental measurement, but rather in the chromatography and spraying. Similar results have been described by other authors.[4]

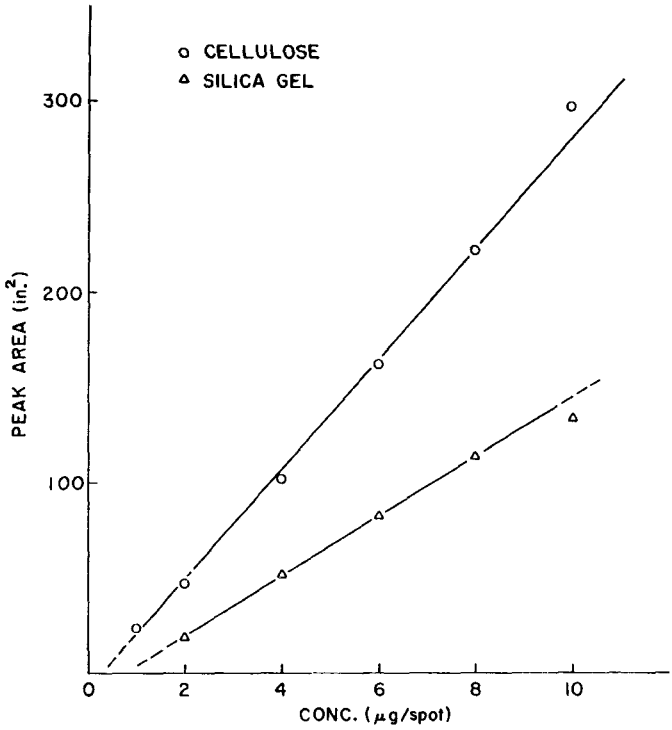

FIGURE 2 Calibration plots for Mobam-CNTNF complex on cellulose and silica-gel thin-layer plates.

Mass Spectra

The mass spectra obtained for a pure sample of Mobam and for a sample of Mobam determined on cellulose as the CNTNF complex had identical fragmentation patterns (Figure 3). The mass spectral fragmentation pattern of Mobam is analogous to that of carbaryl reported earlier.[9] The $M^{+\cdot}$ peak appears at m/e 207, with the base peak being m/e 150 ($M^{+\cdot} - 57$). The other major peaks in the spectrum are due to the loss of CO and NCO, again as found for carbaryl.

CONCLUSIONS

The investigation revealed that a chromatographed pesticide on a thin-layer chromatogram may be determined quantitatively by measuring its absorption as a pi-complex for quantities of 1 mcg and greater. Although there are more sensitive TLC spray reagents available for *in situ* residue analysis of particular

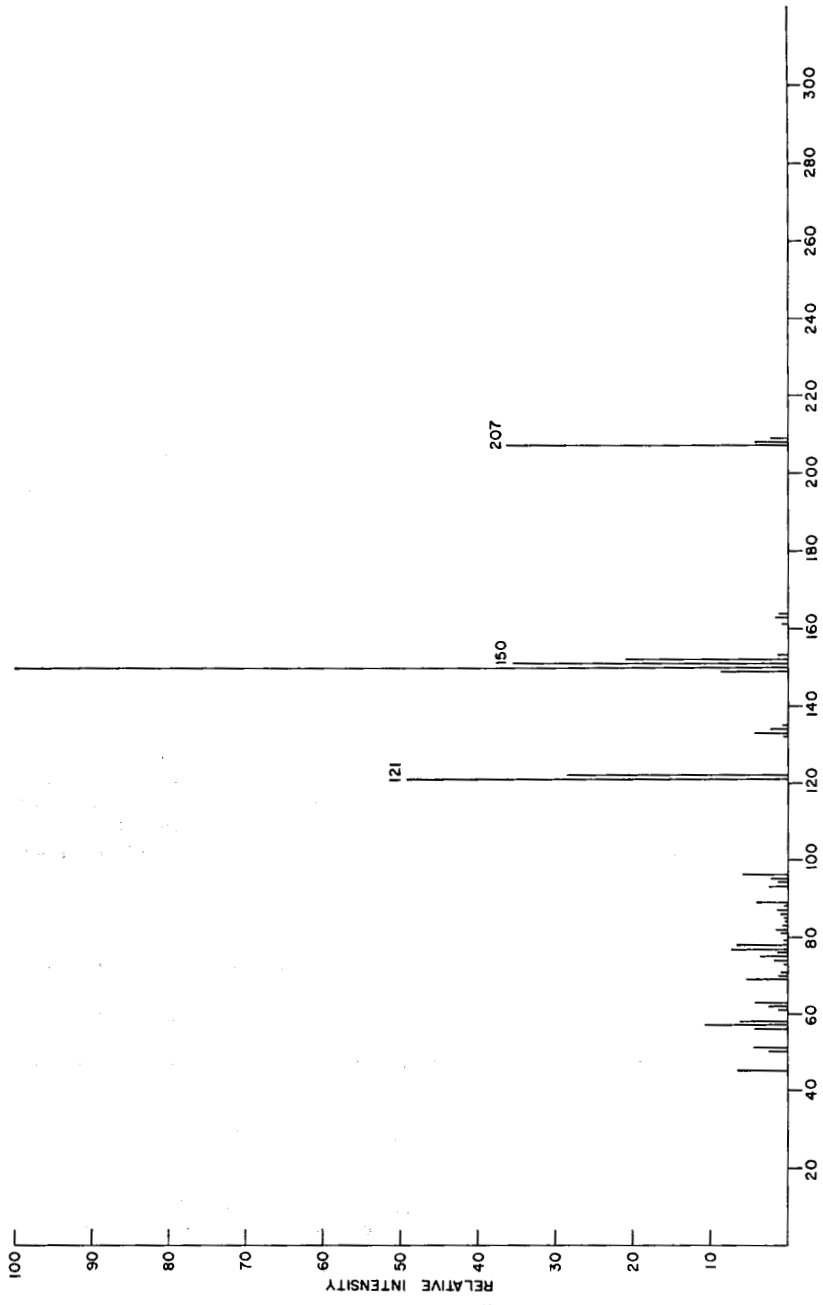

FIGURE 3 Mass spectrum of Mobam from Mobam-CNTNF complex on cellulose.

pesticides or groups of pesticides,[10-12] there are certain features of these reagents which can be useful. As described previously,[1,2] these reagents are non-destructive and the chromatographed pesticide may be recovered from the complex for further mass spectrometric study after a quantitative analysis by reflectance. The wavelengths in the visible region where these complexes absorb do not have sufficient energy to cause photochemical activity, but the same is not necessarily true for determinations on fluorescent indicator plates at 254 nm.[5] An added advantage is that several pesticides, as well as model breakdown products which have similar R_f values, may be differentiated by the colour of the complex they form.

Thus, although the method will probably be of limited practicality for residue analysis, it could prove quite useful for other applications, such as breakdown studies or formulation analysis, where recovery of the unchanged material for positive identification by mass spectrometric or other methods could prove advantageous and quantitative results are desirable. The simplicity of the technique is also in its favour, as there is no time lost heating plates to obtain a reaction[13,14] or in prior chemical treatment of the sample.[12] The results obtained in this study further more suggest that the possibility of using *in situ* reflectance methods for other chromatographic colour reagents for pesticides should be more fully investigated.

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