Schrenk, H. H., Schreibeis, L., *Am. Ind. Hyg. Assoc. J.* **19**, 225 (1958).
Smith, A. E., *Analyst (London)* **100**, 300 (1975).
Stenhagen, E., Abrahamsson, S., McLafferty, F. W., "Registry of Mass Spectral Data", Vol. 1, Wiley, New York, 1974, p 34.
Talmi, Y., Bostick, D. T., *J. Chromatogr. Sci.* **13**, 231 (1975a).
Talmi, Y., Bostick, D. T., *Anal. Chem.* **47**, 2145 (1975b).
Tam, K. H., Charbonneau, S. M., Bryce, F., Lacroix, G., *Anal. Biochem.* **86**, 505 (1978).
Thompson, A. J., Thoresby, P. A., *Analyst (London)* **102**, 9 (1977).
Whitnack, G. C., Martens, H. H., *Science* **171**, 383 (1971).

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Comparative Study of Low-Temperature and Room-Temperature Phosphorescence Characteristics of Several Pesticides

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Room-temperature phosphorescence (RTP) and low-temperature phosphorescence (LTP) of 32 pesticides have been studied and compared. Low-temperature phosphorimetry has been shown to be a sensitive technique with the limits of detection ranging between 0.001 and 30 μg/mL according to the compound. The RTP method appears to be a very simple and specific technique of some pesticide standards with absolute limits of detection between 10 and 50 ng.

Because of their widespread use, especially to protect crops against various predators and to control plant growth, pesticides and herbicides have been studied extensively in recent years. Their presence in the environment (plants, water, soil) at the trace levels has been the subject of considerable concern since it is well known that animals which have been fed from pesticide-treated grains have the capability of concentrating pesticides or herbicides (Cheng, 1969). In order to study this concentrating effect and to determine which compounds showed long residual effects as compared to those which were biodegradable or photochemically decomposable, it was essential to identify and to evaluate quantitatively pesticide residues.

During the past few years, the number of analytical techniques and procedures developed for investigating pesticide residues and degradation products has increased considerably. Among these analytical methods, it is worthwhile to mention the use of colorimetry (Cheng, 1969; El Dib and Aly, 1972), conventional NMR, and Fourier-transform NMR spectrometry (Babad and Herber, 1968; Ross and Biros, 1970; Keith et al., 1969, 1972; Keith and Alford, 1970; Leyden and Cox, 1970), thin-layer chromatography (Zweig and Sherma, 1978), gas chromatography (Cram and Risby, 1978), and liquid chromatography (Lam and Grushka, 1977; Sparacino and Hines, 1976; Kitka et al., 1977; Carpenter et al., 1976; Olsson et al., 1976; Pietrzyk and Chu, 1977).

Several workers have demonstrated the usefulness of luminescence techniques for the determination of a number of pesticides (Adams and Anderson, 1966; Pease and Gardiner, 1969; Guilbault and Sadar, 1969; Jolliffe and Coggins, 1970; Brun and Mallet, 1973; Lawrence et al., 1976; Zakrevsky and Mallet, 1977; Volpe and Mallet, 1976; Cassie and Mallet, 1976; Prybil and Herzel, 1977; Francouer and Mallet, 1976; Moye and Wade, 1976; Moye and Winefordner, 1969; Chen, 1974; and Aaron and Winefordner, 1975). Originally, fluorometric methods were applied to the quantitative analysis of specific pesticide residues, after their identification, in plant or animal tissues (Adams and Anderson, 1966; Pease and Gardiner, 1969; Guilabult and Sadar, 1969; Jolliffe and Coggins, 1970; Brun and Mallet, 1973). More recently, fluorescence detection has been combined either with thin-layer chromatography for the qualitative or quantitative analysis of organophosphates (Lawrence et al., 1976; Zakrevsky and Mallet, 1977; Volpe and Mallet, 1976) for carbamate and organophosphate pesticides analyses. Phosphorescence characteristics of several pesticides have also been studied at low temperature (77 K), in EPA (diethyl ether–isopentane–absolute alcohol, 5:5:2, v/v), ethanol or ethanol–water solvent and their analytical utility has been shown in some cases (Moye and Winefordner, 1965; Chen, 1974).

Various recent improvements of low-temperature phosphorimetry (LTP) have allowed this analytical method to be applied to the determination of a wide variety of organic molecules (Aaron and Winefordner, 1975). A novel technique, based on the observation of room-temperature phosphorescence (RTP) of ionic or polar compound absorbed on solid supports, has been developed into a simple, sensitive, and rapid method of analysis (Schulman and Walling, 1972, 1973; Wellons et al., 1974; Paynter et al., 1974; Vo Dinh et al., 1976; Von Wandruzka and Hurtubise, 1977; Vo Dinh et al., 1977; Schulman and Parker, 1977; Ford and Hurtubise, 1978; Bower and Winefordner, 1979).

In the present paper, we wish to report a detailed comparative study of the low-temperature and room-temperature phosphorescence properties of several pes-

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Table I. Pesticides[a] Studied by LTP and RTP

compounds	trade name
2,2[1]-methylenebis(4-chlorophenol)	dichlorophen
pentachlorophenol	
2,3,4,6-tetrachlorophenol	
2,4,5-trichlorophenol	
2,4,6-trichlorophenol	
2,3-dichloro-1,4-naphthaquinone	dichlone
phenylmercuric benzoate	
N[1]-(2-chloroallyl) diethyldithiocarbamate	CDEC
dimethyldithiocarbamic acid, ferric salt	ferbam
dimethyldithiocarbamic acid, zinc salt	ziram
ethylenebis(dithiocarbamic acid), manganese salt	maneb
ethylenebis(dithiocarbamic acid), zinc salt	zineb
tetramethylthiuram disulfide	thiram
N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide	captan
N-(trichloromethylthio)phthalimide	folpet
2-methylheptyl-4,6-dinitrophenyl crotonate	dinocap
1-naphthaleneacetamide	
1-naphthaleneacetic acid	planofix
methyl 1-naphthaleneacetate	
2-naphthoxyacetic acid	
disodium ethylenebis(dithiocarbamate)	nabam
sodium methyldithiocarbamate dihydrate	metham sodium
methyl 1-(butylcarbamoyl)-2-benzimidazole carbamate	benomyl
N-dodecylguanidine	dodine
1,4-dichloro-2,5-dimethoxybenzene	chloroneb
N-(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide	captafol
2-heptadecyl-2-imidazoline acetate	glyodin
p-dimethylaminobenzenediazosulfonic acid sodium salt	fenaminosul
4-amino-3,5,6-trichloropicolinic acid	picloram
2,6-dichloro-4-nitroaniline	dicloran
5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide	vitavax
2,3-dihydro-5-carboxanilide-6-methyl-1,4-oxathiin-4,4-dioxide	plantvax
phenylmercuric acetate	

[a] All pesticides listed were purchased from Chem-Service, Inc., Westchester, PA. The purity of all pesticides was 97-99+ %.

ticides and to show the analytical usefulness of LTP and RTP techniques for the quantitative determination of pesticides.

EXPERIMENTAL SECTION

Apparatus. The instrumental setup used in this study was previously described in detail (Wellons et al., 1974). Phosphorescence measurements were obtained using an Aminco-Bowman spectrophotofluorimeter with an Aminco-Keirs phosphoroscope attachment (American Instrument Co., Silver Springs, MD). Signals were detected with an IP21 photomultiplier tube (American Instrument Co., Silver Springs, MD) with S-4 spectral response and with PM voltage maintained at 750 V. Uncorrected phosphorescence spectra were recorded on an X-Y recorder (Photomatic, Bolt, Beranek and Newman Inc.).

Low-temperature phosphorescence measurements were performed at 77 K using a capillary pure fused quartz tube, approximately 2 mm i.d. and 4 mm o.d. made of synthetic, high-purity grade optical grade quartz (Thermal American Fused Quartz Co., Montville, NJ) as the sample cell.

Room-temperature phosphorescence measurements were carried out at 298 K using individual replaceable sample holder tips as previously described (Bower and Winefordner, 1979).

Long phosphorescence lifetimes (≥1 s) were measured at 77 K by recording the ratio-photometer output as a function of time, after complete termination the exciting radiation by a guillotine-type shutter.

Shorter phosphorescence lifetimes (≤0.5 s) were measured at 77 K by means of a pulsed nitrogen-laser setup. Exponential-decay curves were determined and printed data were fed into a computer (PDP 11/20) to evaluate lifetime values (Boutilier and Winefordner, 1979).

Reagents. S and S 904 filter paper (Schleicher and Schuell, Keen, NH) was used as the sample support for all analytical investigations. Sodium hydroxide (Fisher Scientific, Fair Lawn, NJ), sodium iodide (Fisher Scientific, Fair Lawn, NJ), absolute ethanol (U.S. Industrial Chemicals Co., New York, NY), and deionized water were used to prepare the solvents.

The pesticides studied in this work are listed in Table I with their commercial source; they were used as received.

Procedure. For the RTP measurements, 0.25-in. diameter filter paper circles were spotted with 5 μL of the pesticide sample solution, then with 5 μL of any other solutions to be used, such as 1 M sodium hydroxide solutions. Sample holder tips were then placed under an infrared lamp and dried for about 10 min. As reported previously (Vo Dinh et al., 1976, 1977), drying was necessary because the RTP signals were very sensitive to moisture. The sample holder tips were then reproducibly replaced on the shaft of the sample holders. During all RTP measurements, the sample compartment was flushed with dry nitrogen. Since it was observed that the phosphorescence signal of the dried sample increased with time and then levelled off, all readings were taken 5 min after introduction of the sample holder in the sample compartment.

Stock solutions of pesticides (about 1000 ppm) were prepared in absolute ethanol. Several dilutions of stock solutions in deionized water or ethanol–water were made to determine analytical calibration curves and to estimate limits of detection.

RESULTS AND DISCUSSION

Spectral Characteristics. The LTP and RTP characteristics of 32 pesticides have been surveyed in ethanol–water solutions (10:90 v/v or 50:50 v/v). Twenty of those showed LTP spectra and 18 of those resulted in RTP spectra. Phosphorescence excitation and emission wavelengths of these pesticides are reported in Table II. Pesticides which gave no detectable phosphorescence signal for concentrations approximately 100 ppm in ethanol–water solutions either at low temperature or at room temperature, and are not listed in Table II, were CDEC, ferbam, ziram, maneb, zineb, thiram, captan, nabam, metham sodium, dodine, captafol, and glyodin. Most of these compounds had been shown previously to not be phosphorescent (at 77 K) in EPA or ethanol solvent (Moye and Winefordner, 1965; Chen, 1974).

Excitation and emission phosphorescence spectra of pesticides were generally similar at low and room temperature. In Figure 1, the RTP and LTP spectra of naphthalene acetic acid are compared. In general, RTP emission bands were red-shifted from their position at low temperature; they were also broadened and showed little vibrational fine structure, due to temperature-induced effects, as previously observed with other compounds (Schulman and Walling, 1972; Wellons et al., 1974; Bower and Winefordner, 1979). For most of the pesticides, the red-shift values were relatively small, except for several compounds like Folpet and Benomyl which presented, respectively, 50- and 90-nm red shifts.

Phosphorescence lifetimes were measured at low temperature and were found to be greater than 1 s for Dinocap,

Table II. Low-Temperature and Room-Temperature Phosphorescence Spectral Characteristics of Pesticides[a]

compound	LTP λex,[b] nm	LTP λem,[b] nm	LTP lifetimes,[c] s	RTP λex,[b] nm	RTP λem,[b] nm
dichlorophen	234, *290*	*487*	0.028	*309*	*489*
pentachlorophenol	264, *310*	*454*	0.05	267, *311*	*492*
2,3,4,6-tetrachlorophenol	262, *306*	464, *484*		(278), *310*	*494*
2,4,5-trichlorophenol	245, *306*	480	0.068	(275), *308*	489
2,4,6-trichlorophenol	238, *297*	482	0.06	274, *310*	*494*
dichlone	240, (264), *308*	*446*	0.03	*310*	*489*
phenylmercuric benzoate	240, *275*	*404*	0.007_6	*244*, 275	*439*
folpet[d]	(245), *305*	*440*		*306*	*489*
dinocap	244, 275, *308*	442			
1-naphthaleneacetanide	234, *308*	*485*, 514, (555)	2.2	228, *300*	*490*, (509)
1-naphthaleneacetic acid	(230), *297*	*484*, 514, (550)	2.7	233, *299*	*494*, 516, (554)
methyl 1-naphthaleneacetate	(275), *310*	*487*, 518, (550)	2.6	240, *306*	*494*, (514), (559)
2-naphthoxyacetic acid	(238), 274, *313*	476, *503*, (530)	2.8	235, (284), *310*	*504*
benomyl[d]	(240), 286	*386*	2.6	(264), *308*	*480*
chloroneb[d]	240, *303*	*487*	0.009_6	*307*	*490*
fenaminosulf[e]	275, *310*	*468*	2.3_6	280, *310*	*498*
fenaminosulf (with 1 M NaI)	(280), *310*	*430*			
4-amino-3,5,6-trichloropicolinic acid	(270), *308*, 370	*462*	0.07_2	(280), *310*	*490*
dicloran	268, 322, *368*	*504*, 524		*310*, 368	*494*
vitavax	(250), *311*	462			
plantvax	236, *305*	*433*		280, *309*	*487*

[a] Concentrations about 100 ppm in 10:90 v/v ethanol-water solution, except otherwise noted. Spectra uncorrected for instrumental response. [b] Wavelengths of the main peaks are italicized; wavelengths of shoulders are given in parentheses. [c] Lifetime values were measured as described in the experimental part. Precision of the lifetime values: ±5%. [d] Ethanol-water solutions (50:50, v/v) were used, because of the difficult solubility of these compounds in water. [e] Fifty parts per million in 10:90 v/v ethanol-water solution.

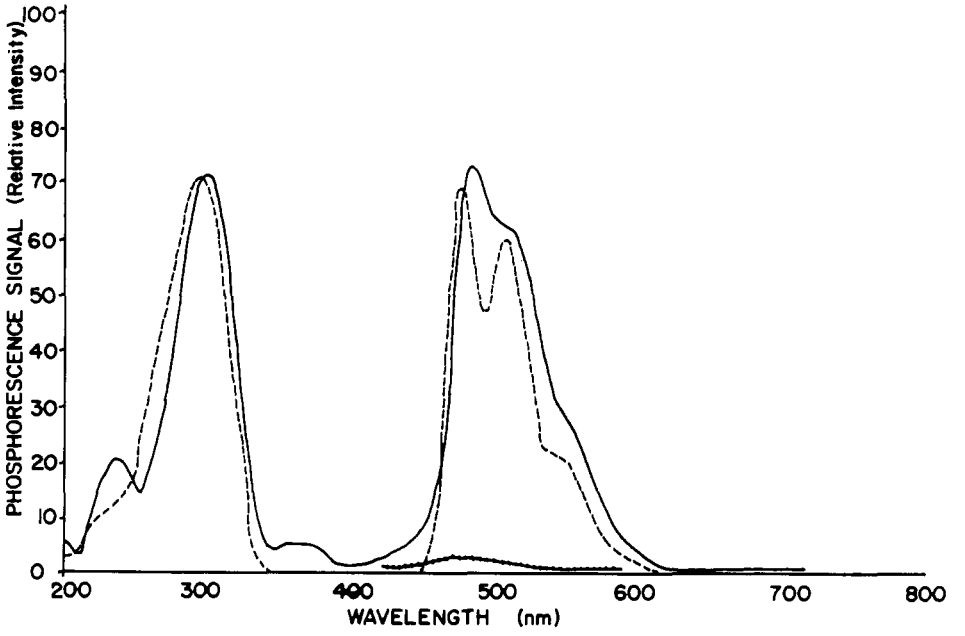

Figure 1. Room-temperature phosphorescence and low-temperature phosphorescence spectra of 1-naphthaleneacetic acid: (---) excitation and emission spectra at 77 K, (—) excitation and emission spectra at 298 K, (←) emission spectrum of the blank (paper with ethanol–water, 10:90, v/v) at 298 K. Relative intensities were arbitrarily adjusted.

1-naphthaleneacetamide, 1-naphthaleneacetic acid, methyl-1-naphthalene acetate, 2-naphtoxyacetic acid, benomyl, *p*-dimethylaminobenzenediazosulfonic acid sodium salt, and plantvax; for the other pesticides, however, lifetimes are much shorter (see Table II). For the former compounds, lifetimes longer than 1 s indicated that phosphorescence originated from the π, π^* triplet state (Becker, 1969). Since the structures of the latter pesticides include one or several chlorine or mercury atoms, it is very probable that their phosphorescence lifetimes decreased due to the internal heavy atom effect of chlorine or mercury, known to increase the probability of the singlet to triplet intersystem crossing transition. Although RTP lifetimes of pesticides were not measured in the present study, it is expected that they should be shorter than those observed at 77 K.

RTP vs. LTP Signal. Table III reports the low-temperature enhancement factor I_p^{77K}/I_p^{298K} defined as the ratio of the phosphorescence signals of pesticides at low temperature to that obtained at room temperature. The low-temperature enhancement factors are greater than unity for all compounds studied, which indicates the low-temperature phosphorescence signals of pesticides increased compared to the signals measured at room temperature, as observed for other polar or ionic compounds (Wellons et al., 1974; Bower and Winefordner, 1978). It can be seen that the values of the low-temperature enhancement factors vary considerably with the molecular structure of the pesticides. Values greater than 14 were obtained for monoaromatic pesticides containing chlorine or mercury atoms, while values in the range between 10.9 and 2.2 were found for polyaromatic pes-

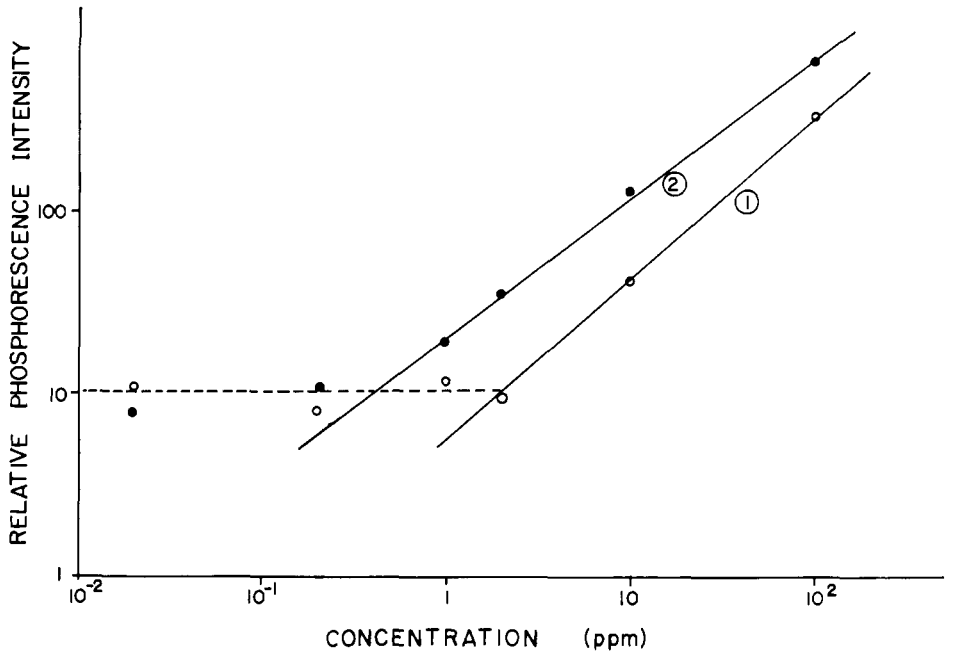

Figure 2. Phosphorescence analytical curves for 1-naphthaleneacetic acid in ethanol–water (10:90, v/v) solution: (curve 1) obtained at room temperature, (curve 2) obtained at low temperature.

Table III. Comparison of Phosphorescence Signals of Pesticides at Room Temperature and at 77 K[a]

pesticide	I_p^{77K}/I_p^{298K}
dichlorophen	16
2,4,5-trichlorophenol	14
2,4,6-trichlorophenol	38
phenylmercuric acetate	367
folpet	380
1-naphthaleneacetamide	3.5
1-naphthaleneacetic acid	2.2
methyl 1-naphthaleneacetate	8.4
2-naphthoxyacetic acid	4.0
benomyl	10.9
chloroneb	34.4
4-amino-3,5,6-trichloropicolinic acid	109
dicloran	130

[a] Phosphorescence signals measured at 77 K (I_p^{77K}) or at 298 K (I_p^{298K}) at the wavelength maximum emission in ethanol-water solution. Concentration approximately 100 ppm.

ticides. These results indicate that the latter compounds, which are characterized by a greater molecular rigidity, exhibit relatively high RTP signals compared to their low-temperature phosphorescence signals. This is in agreement with the concept of strong interactions between rigid phosphor molecules and the support—in our case, filter paper—which has been proposed by several authors (Schulman and Parker, 1977; Ford and Hurtubise, 1978). These interactions would minimize collisional radiationless deactivation of the excited triplet state at room temperature.

Effect of Sodium Hydroxide. Although the actual mechanism of the matrix effect on RTP emission is not fully understood, it is of interest, from an analytical standpoint, to study the effect of sodium hydroxide on the phosphorescence signals of pesticides at room temperature. The RTP signals of most of the pesticides were quenched when a 1 M NaOH aqueous solution was added to the paper, the sample being carefully dried and maintained under dry nitrogen. For example, under these conditions, the phosphorescence signal of 1-naphthaleneacetic acid at room temperature was decreased ten times in the presence of 1 M NaOH. Although the quenching effect of NaOH

Table IV. Phosphorimetric Limits of Detection (L.O.D.) of Pesticides with LTP and RTP

compound	limits of detection,[a] ppm		absolute L.O.D.,[b] ng	
	LTP	RTP	LTP	RTP
dichlorophen	0.1		5.	
pentachlorophenol	30		1500.	
2,3,4,6-tetrachlorophenol	2.0		100.	
2,4,5-trichlorophenol	0.3		15.	
2,4,6-trichlorophenol	0.15		7.5	
dichlone	8.		400.	
phenylmercuric benzoate	0.01	10.	0.5	50.
folpet	0.001		0.05	
1-naphthaleneacetamide	0.02	8.	1.	40.
1-naphthaleneacetic acid	0.2	2.	10.	10.
methyl 1-naphtaleneacetate	0.1	10.	5.	50.
2-naphthoxyacetic acid	0.3	8.	15.	40.
benomyl	0.7	10.	35.	50.
chloroneb	0.4		20.	
fenaminosulf[c]	0.6		30.	
4-amino-3,5,6-trichloropicolinic acid	0.04		2.	
dicloran	0.001		0.05	

[a] Defined as the concentration giving a signal-to-noise ratio of 3. [b] Absolute limit of optical detection, calculated for 50-μL (at room temperature) sample solutions. [c] L.O.D. determined in 1 M NaI solution.

on the RTP signal was not mentioned previously by other authors, it was noted that the presence of sodium hydroxide was not necessary to observe phosphorescence at room temperature (Schulman and Walling, 1972, 1973; Wellons et al., 1974; Paynter et al., 1974; Schulman and Parker, 1977). This alkaline media quenching effect of phosphorescence might result from a process of competition of the hydroxide ions with the phosphor molecules for adsorption on the support. Recent work which showed the importance of hydrogen-bonding interactions phosphor-support during the adsorption process (Schullman and Parker, 1977; Ford and Hurtubise, 1978) is in agreement with our hypothesis.

Analytical Calibration Curves. The analytical calibration curves of 1-naphthaleneacetic acid at low tem-

perature and room temperature are reported in Figure 2. The slopes of the log–log analytical calibration curves are close to unity, and the ranges of linearity are fairly large, but smaller at room temperature ($\approx 10^2$) than at low temperature ($\approx 10^3$). This difference in the analytical linearity ranges results from the poorer detection limits at room temperature ($\approx$2 ppm) than at low temperatures ($\approx$0.4 ppm). It can be explained by the relatively large background phosphorescence emission and noise of the filter paper at room temperature and by the weaker phosphorescence signal at room temperature compared to low temperature.

Limits of Phosphorimetric Detection. The limits of phosphorimetric detection of pesticides at room temperature and at low temperature are given in Table IV. Limits of detection were determined only for those pesticides which gave a signal-to-background ratio of at least three and where the phosphorescence signals were expected to be analytically useful. Obviously, phosphorimetric limits of detection are better (lower) at low temperature than at room temperature.

Advantages of RTP for Pesticide Analysis Compared to LTP. In the case of polyaromatic pesticides, absolute detection limits in nanograms are comparable at low and room temperatures because of the small amount ($\approx$5 μL) of sample required for the RTP techniques; however, in LTP, approximately 50 μL is needed to prepare a sample (refer to Table IV for a comparison of absolute detection limits).

Besides its simplicity, another advantage of the use of the RTP technique for the analysis of pesticides is its specificity; it would be possible to determine for example planofix (1-naphthaleneacetic acid) or benomyl residue at the nanogram level in the presence of organochlorinated pesticide residue without interference of the latter compounds which are not detectable by RTP at these quantities.

This study has shown that RTP of several pesticides is analytically useful, although LTP is a more sensitive technique of analysis for most of these compounds. The RTP technique is more suitable than conventional phosphorimetry (LTP) if the purpose of the analysis is to determine *specifically* a given phosphorescent pesticide in the presence of large amounts of other pesticides only weakly phosphorescent at room temperature. A study is being undertaken in order to investigate the improved sensitivity of the RTP method applied to pesticide analysis by the presence of external heavy atom perturbers.

LITERATURE CITED

Aaron, J. J., Winefordner, J. D., *Talanta* **22**, 707 (1975).
Adams, J. M., Anderson, C. A., *J. Agric. Food Chem.* **14**, 53 (1966).
Babad, K., Herber, W., *Anal. Chim. Acta* **41**, 259 (1968).
Becker, R. S., "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley, New York, 1969, p 155.
Boutilier, G., Winefordner, J. D., *Anal. Chem.*, in press (1979).
Bower, E. L. Y., Winefordner, J. D., *Anal. Chim. Acta* **1–13**, 102 (1978).
Brun, G. L., Mallet, V. N., Bower, J. N., Winefordner, J. D., *J. Chromatogr.* **80**(1), 119 (1973).
Caissie, G. E., Mallet, V. N., *J. Chromatogr.*, **117**(1), 129 (1976).
Carpenter, A., Siggia, S., Carter, S., *Anal. Chem.* **48**, 225 (1976).
Chen, J., Dissertation, Memphis State University, Memphis, TN, 1974.
Cheng, H. H., *J. Agric. Food Chem.* 17, 1174 (1969).
Cram, S. P., Risby, T. H., *Anal. Chem.* **50**(5), 213R (1978).
El Dib, M. A., Aly, O. A., *J. Assoc. Off. Anal. Chem.* **53**, 1276 (1972).
Ford, C. D., Hurtubise, R. J., *Anal. Chem.* **50**(4), 610 (1978).
Francouer, Y., Mallet, V., *J. Assoc. Off. Anal. Chem.* **59**, 172 (1976).
Guilbault, G. G., Sadar, M. H., *Anal. Chem.* **41**, 366 (1969).
Jolliffe, V. A., Coggins, C. W., *J. Agric. Food Chem.* **18**, 394 (1970).
Keith, L. M., Alford, A. L., Garrison, A. L., *J. Assoc. Off. Anal. Chem.* **52**, 1074 (1969).
Keith, L. M., Alford, A. L., *J. Assoc. Off. Anal. Chem.* **53**, 157 (1970).
Keith, L. M., Alford, A. L., McKinney, J. D., *Anal. Chim. Acta* **60**, 1 (1972).
Kitka, E. J., Stange, A. E., Lam, S., *J. Chromatogr.* **138**, 41, 321 (1977).
Lam, S., Grushka, E., *J. Chromatogr. Sci.* **15**, 234 (1977).
Lawrence, J. F., Renault, C., Frei, R. W., *J. Chromatogr.* **121**(2), 343 (1976).
Leyden, D. H., Cox, R. H., in "Analytical Applications of NMR", Wiley, New York, 1977, pp 344–354.
Moye, H. A., Wade, T. E., *Anal. Lett.* **9**(10), 891 (1976).
Moye, H. A., Winefordner, J. D., *J. Agric. Food Chem.* **13**, 516 (1965).
Olsson, L., Renne, N., Samuelson, O., *J. Chromatogr.* **123**, 355 (1976).
Paynter, R. A., Wellons, S. L., Winefordner, J. D., *Anal. Chem.* **46**, 736 (1974).
Pease, H. L., Gardiner, J. A., *J. Agric. Food Chem.* 17, 267 (1969).
Pietrzyk, D. J., Chu, C. H., *Anal. Chem.* **49**, 860 (1977).
Prybil, J., Herzel, F., *Fresenius', Z. Anal. Chem.* **286**(1-2), 95 (1977).
Ross, R. T., Biros, F. J., *Anal. Chim. Acta* **52**, 139 (1970).
Schulman, E. M., Walling, C., *Science* **178**, 53 (1972).
Shulman, E. M., Walling, C., *J. Phys. Chem.* **77**, 902 (1973).
Schulman, E. M., Parker, R. T., *J. Phys. Chem.* **81**, 1932 (1977).
Sparacino, C. M., Hines, J. W., *J. Chromatogr. Sci.* **14**, 549 (1976).
Vo Dinh, T., Bower, E. L. Y., Winefordner, J. D., *Anal. Chem.*, **48**, 1186 (1976).
Vo Dinh, T., Walden, G. L., Winefordner, J. D., *Anal. Chem.* **49**, 1126 (1977).
Volpe, Y., Mallet, V. N., *Anal. Chim. Acta* **81**(1), 111 (1976).
Von Wandruszka, A. M. A., Hurtubise, R. J., *Anal. Chim. Acta* **93**, 331 (1977).
Wellons, S. L., Paynter, R. A., Winefordner, J. D., *Spectrochim. Acta* **30A**, 1123 (1974).
Zakrevsky, J. G., Mallet, V. N., *J. Chromatogr.* **132**(2), 315 (1977).
Zweig, G., Sherma, J., *Anal. Chem.* **50**(5), 50R (1978).

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