A Colorimetric Method for the Determination of Arsenite, Arsenate, Monomethylarsonic Acid, and Dimethylarsinic Acid in Biological and Environmental Samples

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A spectrophotometric method is described for the determination of arsenite, arsenate, monomethylarsonic acid, and dimethylarsinic acid in biological and environmental samples. The arsenic species are volatilized to their corresponding arsines after reduction by sodium borohydride. The arsine and methylarsines form two different color complexes with silver diethyldithiocarbamate. By use of simultaneous spectrophotometric equations, the amount of each arsine can be determined. The quantitative limit is 1.0 μg of elemental As for all four arsenic species. Recoveries of 90–100% of all four arsenic species from albumin, plant extracts, plasma, urine, and water are reported.

Spectrophotometry has become the standard method for arsenic determination because of its simplicity, accuracy, precision, and low cost (AOAC, 1975; APHA, 1971; Talmi and Bostick, 1975a). The total arsenic content in a great variety of biological and environmental samples has been determined using the silver diethyldithiocarbamate–pyridine (AgDDC) spectrophotometric reagent (AOAC, 1975). However, recent reports in the literature indicate an increasing need to measure the various forms of arsenic, particularly the herbicide forms monomethylarsonic acid (MA) and dimethylarsinic acid (DMA), in such diverse materials as irrigation runoff, plant and animal tissues, blood, and urine (Committee, 1977). The method reported here describes a quantitative spectrophotometric method for measuring microgram amounts of inorganic arsenite (As(III)), inorganic arsenate (As(V)), MA, and DMA in a sample. Recoveries of 90–100% of all four arsenic species from bovine serum albumin, plant extracts, plasma, urine, and water are also reported.

EXPERIMENTAL SECTION

Theory. The four species of arsenic (As(III), As(V), MA, and DMA) are separated out of a sample by a two-step reduction to their corresponding arsines using a modification of the differential volatilization method of Aggett and Aspell (1976). During step 1, As(III) and DMA are reduced to arsine and dimethylarsine when sodium tetrahydridoborate ($NaBH_4$) is added to an oxygen-free pH 4.0 solution of the sample to be analyzed. During step 2, As(V) and MA are reduced to arsine and methylarsine by $NaBH_4$ in a pH 1 solution of the sample. The various arsines are bubbled through a pyridine solution of AgDDC. The arsine reacts with the AgDDC to give a chromophore which absorbs maximally at 540 nm. The methyl- and dimethylarsines produce a chromophore which absorbs maximally at 440 nm (see Figures 1 and 2). The molar absorptivity for all three arsine species is shown in Table I. By reading the colored AgDDC reagent from each step, at both wavelengths, and using simultaneous equations the concentration of all four species in a sample can be determined. This new method is an improvement of the Peoples et al. (1971) and Lakso et al. (1973) arsenic determination methods.

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Table I. Molar Absorptivity Coefficient (Am) for Some Arsenic Compounds (AsX-AGDDC Chromophore)[a]

compound	nm	pH[b]	Am[c]
arsenite	440	4.0	1.95×10^{-4}
	540	4.0	1.11×10^{-4}
arsenate	440	1.0	1.38×10^{-4}
	540	1.0	1.13×10^{-4}
monomethylarsonic acid	440	1.0	6.38×10^{-5}
	540	1.0	2.59×10^{-4}
dimethylarsinic acid	440	4.0	8.42×10^{-5}
	540	4.0	1.00×10^{-3}

[a] Calculations based upon 1 gmw As per molecule of compound. [b] pH of reaction mixture from which the arsine was generated. [c] Because the chromophore is generated in 4 mL of pyridine, the molarity was calculated as moles of arsenic/liter of pyridine.

Chemicals, Materials, and Apparatus. The chemicals used include those purchased from: (1) Aldrich Chemical Company, potassium arsenate (KH_2AsO_4, 99+%) and silver diethyldithiocarbamic acid ($(C_2H_5)_2NCSSAg$, 99%); (2) Alfa (Ventron) Chemical Company, potassium *m*-arsenite ($KH(AsO_2)_2$, 99%) and sodium tetrahydridoborate ($NaBH_4$, 98%); (3) Eastman Kodak, silver diethyldithiocarbamic acid; (4) Mallincrodt (analytical reagent grade), citric acid, hydrochloric acid, sodium citrate, sodium hydroxide, and pyridine (spectra grade); (5) Sigma Chemical Company, antifoam A (No. A-5633) and dimethylarsinic acid (cacodylic acid, $(CH_3)_2AsO_2{\cdot}Na$, 99%); (6) Vineland Chemical Sales Corporation, monomethylarsonic acid ($CH_3AsO(OH)_2$, 99.95%); (7) local suppliers, 95% ethanol (for extracting plants and washing pyridine contaminated glassware) and nitrogen gas (N_2). The arsine–methylated arsine generating and trapping apparatus used is shown in Figure 3. The generator (F in Figure 3) can be made any size that will accommodate the sample and reagents, but the aerator (G) must be submerged. An air flowmeter for controlling and measuring the N_2 flow rate between 0–60 mL/min is also needed. Reagent volumes effectively used for sample volumes of 1–50 mL are given in the procedure section. Analytical sample volumes should be selected so the resulting elemental As values will be between 5 and 15 μg for any one arsenic species. A Beckman 24 spectrophotometer with a cell width of 1.0 cm was used.

Analytical Procedure. Step 1 of the analytical procedure was begun by putting the sample to be analyzed in the generator (F) with enough 2% antifoam solution (approximately 1 mL or less) to reduce any foaming which may occur if surface-active materials are present. Add 15

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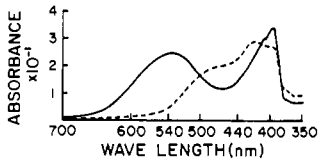

Figure 1. Spectral curves for 4 mL of AgDDC following step 1: (--) DMA (20.0 μg of elemental As); (—) As(III) (15.0 μg of elemental As). Beckman Acta C II spectrophotometer, scan speed 100 nm/min, Omniscribe Recorder, Houston Instrument, chart speed 2.5 cm/min, full scale 0.1 V.

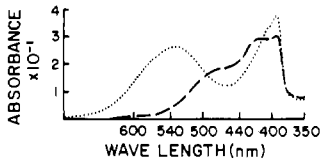

Figure 2. Spectral curves for 4 mL of AgDDC following step 2: (--) MA (10.0 μg of elemental As); (···) As(V) (15.0 μg of elemental As). Beckman Acta C II spectrophotometer, scan speed 100 nm/min, Omniscribe Recorder, Houston Instrument, chart speed 2.5 cm/min, full scale 0.1 V.

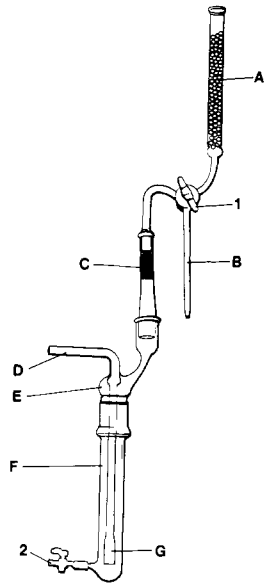

Figure 3. Diagram of arsine–methylated arsine generating and trapping apparatus: A, AgDDC bubbler with 3-mm beads; B, exit-downspout; C, dental cottonroll in scrubber tube; D, N_2 inlet; E, head; F, generator; G, aerator; 1, glass stopcock 1; 2, plastic stopcock 2.

mL of 0.5 M sodium citrate–citric acid pH 4 buffer. Since the reduction reaction releases NaOH, the solution must be strongly buffered. Experience has shown that the pH never exceeded 5.5 during step 1 nor pH 1 for step 2 following $NaBH_4$ addition. Insert the generator in the head (E) of the apparatus. Put a cotton roll in the scrubber (C) and thoroughly moisten it with a saturated lead acetate solution. Any hydrogen sulfide generated will be taken out as the gases pass through the moist scrubber roll. All tubes leading to the bubbler (A) should be dry of any visible moisture. Fill the bubbler with beads and 4 mL of 0.5% AgDDC (we used a Repipet) and place it in the scrubber (see Figure 3). Turn on a 50 mL/min flow of N_2. Turn stopcock 1 to allow the N_2 to flow through the sample and AgDDC for a 4-min deoxygenation period. Place the 6-mL syringe containing 4 mL of 5% $NaBH_4$ in stopcock 2 which is turned to connect it to the generator. The $NaBH_4$ solution was made fresh daily in 0.1 N NaOH. Now start the 1–2-min $NaBH_4$ injection and concurrently lower the N_2 flow to 10 mL/min. When the syringe is empty, immediately increase the N_2 flow to 50 mL/min. After 3 min more bubbling, gas a spectrophotometric cuvette with N_2 via the exit-downspout (B), fill the cuvette with AgDDC from the bubbler and cover the cuvette. Take a reading immediately and after 6–10 min at both 440 and 540 nm using the AgDDC as the reagent blank.

To start step 2 of the analytical procedure, inject 4 mL of 6 N HCl into the top of the generator via the head (E). Put a new bubbler (A), filled with beads and 4 mL of AgDDC, in place and connect it to the generator by turning stopcock 1. Allow N_2 to bubble through the sample and reagents for 4 min at 50 mL/min. Concurrently reduce the N_2 flow to 10 mL/min and inject 4 mL of 5% $NaBH_4$ into the generator via stopcock 2 in 1–2 min. When finished, immediately raise the N_2 flow to 50 mL/min for 3 more min. Repeat cuvette gassing, filling, and reading steps described in step 1.

This method has worked at room temperatures ranging from 19 to 32 °C. The gas generating steps must be done in a ventilating hood to protect the operator from breathing pyridine. The cuvette is covered to prevent oxygen from reacting with the methylated arsines and to reduce the amount of escaping pyridine. We found that peak 440-nm absorption occurred between 6 and 10 min after terminating step 1 generation. AgDDC from different commercial sources had different peak response times, so the exact optimum response time will have to be determined for each batch of AgDDC purchased. Recrystallizing the AgDDC (AOAC, 1975) aids in standardizing the time to peak absorption and increases the sensitivity of the AgDDC to dimethylarsine. The standard curves were linear over the range of arsenic concentrations tested (0.05 μg of elemental arsenic/mL to 2.0 μg of elemental arsenic/mL from 20-mL samples).

Calculations. Our studies indicate none of the arsenic species significantly crosses over from steps 1 or 2; therefore, a standard spectrophotometric analysis of mixtures may be used (Kolthoff et al., 1969). The concentrations of each arsenic species in a sample may be determined by using the following equations:

$$\text{As(III)} = \frac{(A540S1)b_2 - (A440S1)a_2}{a_1b_2 - b_1a_2} \quad (1)$$

$$\text{DMA} = \frac{(A440S1)a_1 - (A540S1)b_1}{a_1b_2 - b_1a_2} \quad (2)$$

$$\text{As(V)} = \frac{(A540S2)d_2 - (A440S2)c_2}{c_1d_2 - d_1c_2} \quad (3)$$

$$\text{MA} = \frac{(A440S2)c_1 - (A540S2)d_1}{c_1d_2 - d_1c_2} \quad (4)$$

where A is the absorbance at either 440 or 540 nm, S1 is step 1, S2 is step 2, a_1 = slope of the standard curve (SSC) from $A540S1$ using As(III), a_2 = SSC from $A540S1$ using DMA, b_1 = SSC from $A440S1$ using As(III), b_2 = SSC from $A440S1$ using DMA, c_1 = SSC from $A540S_2$ using As(V), c_2 = SSC from $A540S2$ using MA, d_1 = SSC from $A440S_2$ using As(V), d_2 = SSC from $A440S_2$ using MA.

Sample Sources and Treatment. The fresh water samples were dipped from land edge or taken from a running tap and concentrated by evaporation. The plant samples were collected approximately 20 m from the nearest road and then air-dried and milled. The milled plant tissue was then processed following the method of Lakso et al. (1973), which consists of an ethanol extraction, followed by ether cleanup. The human urine samples were

Table II. Background Arsenic in Plants

samples[a]			mean ppm dry wt background arsenic[b]				
plant type	collection location	stage of growth	As(III)	As(V)	MA	DMA	total
alfalfa	Arpan, SD	second cutting	0.00	0.02	0.00	0.08	0.10
alfalfa	Rogerson, ID	first cutting	0.00	0.03	0.00	0.03	0.06
alfalfa	Burley, ID	first cutting	0.03	0.04	0.00	0.04	0.11
alfalfa	Lovelock, NV	first cutting	0.00	0.00	0.00	0.38	0.38
alfalfa	Palisades, ID	second cutting	0.03	0.03	0.14	0.15	0.35
oats	Petaluma, CA	headed out	0.00	0.05	0.00	0.04	0.09
grape leaves	Sacramento, CA[d]	young	0.06	0.00	0.03	0.13	0.22
grape leaves	Lodi, CA[d]	young	0.09	0.03	0.09	0.18	0.39
grape leaves	Lodi, CA[d]	mature	0.06	0.09	0.13	0.42	0.70

[a] Three hundred grams of dry material was used for extraction; then the extract was concentrated to 100 mL with a 20-mL aliquot being used for analysis. [b] The average parts per million (dry weight basis) of background arsenic species (as elemental As) found in three different aliquots per sample. [c] These grape leaves taken from a home garden in May. [d] These grape leaves taken from commercial vineyard in May or September.

Table III. Background Arsenic in Human Urine

			mean ppm[a] arsenic found				
sex	type of dinner[b]	number[c]	As(III)	As(V)	MA	DMA	total
M	chicken	4	0.00	0.00	0.03	0.03	0.06
M	seafood	3	0.00	0.03	0.05	0.24	0.32
F	chicken	3	0.00	0.00	0.00	0.05	0.05
F	seafood	2	0.00	0.00	0.08	0.18	0.26

[a] Average parts per million of various arsenic species (as elemental As) found in 35-mL urine samples. [b] Urine samples are upon-rising sample following either a chicken or seafood dinner. [c] The number of individuals supplying a sample. Duplicate aliquots were analyzed from each sample.

aliquots of upon-rising urine. Normally urine samples can be put directly into the generator. However, if the subject has been eating seafood, NaOH hydrolysis increases methylated arsenic recovery. Digestion was done by adding enough NaOH pellets to a sample to make a 30% NaOH–urine solution. The sample was digested at room temperature for 15 min, then neutralized with HCl to pH 4. The blood was drawn using a Vacutainer containing Li-Heparin. After 24 h of refrigeration, the plasma was drawn off and analyzed. No differences were noted in recovery values from background and fortification experiments between whole blood and plasma; however, with plasma there was less foaming.

Interferences. Various metal ions have been reported to interfere with borate reduction of arsenic, but such interference occurs at concentrations far exceeding that found in most natural water and biological samples (Aggett and Aspell, 1976; Andreae, 1977; Braman et al., 1977; Fiorino et al., 1976; Goulden and Brooksbank, 1974; Pierce and Brown, 1977; Smith, 1975). However, if a particular sample, such as desert or sulfur spring water (Whitnack and Martens, 1971) were to contain potentially interfering ion(s), then the sample should be treated to eliminate or reduce their concentrations. Belcher et al. (1975) recommends using 0.01 M EDTA in the sample generator to reduce interference of cobalt, nickel, zinc, iron, bismuth, cadmium, and copper ions. Haywood and Riley (1976) suggest preliminary extraction with dithizone in chloroform or ion-exchange treatment to remove selenium, silver, copper if they exceed 0.5 mg/L and nickel, cadmium, tin, and bismuth ions if they exceed 2.5 mg/L.

Under the experimental conditions described here, the hydrides of sulfur, selenium, antimony, and tin are the only nonarsenic compounds which would be volatile enough to reach the AgDDC (Metal Hydrides, 1958; Smith, 1975). The hydrogen sulfide is eliminated by the lead acetate scrubber (C in Figure 3). Selenium hydride does not form a chromophore with AgDDC. However, stibine and tin hydrides do, but in most environmental samples these compounds are present at concentrations (Analytical Methods Committee, 1975; Gladney and Owens, 1976) below the detection limits of this method; which were 2.7 μg for antimony potassium tartrate, 3.7 μg for dimethyltin dichloride, 4.0 μg for methyltin trichloride, and 26.9 μg for stannous chloride.

RESULTS AND DISCUSSION

Although there are now methods which determine the concentrations of various arsenic species in nanogram amounts (Andreae, 1977; Braman et al., 1977; Daughtrey et al., 1975; Talmi and Bostick, 1975b; Tam et al., 1978), these methods require more expensive equipment and elaborate methodology than the one described in this paper. The qualitative detection limit for As(III), As(V), or DMA is 0.5 μg elemental As and for MA is 0.25 μg elemental As per sample. The method is quantitative at 1.0 μg elemental As for all four species. Analyses of two well water samples from Nevada, which the Nevada Division of Health, Bureau of Laboratories and Research analyzed as having a total arsenic content of 0.099 and 0.095 ppm, gave total arsenic values of 0.107 and 0.101 ppm, respectively, by the method described.

As shown on Tables II–V all of the biological and environmental samples tested contained some background arsenic. The total arsenic content ranged from 0.004 to 0.70 ppm, with the major portion being methylated arsenic compounds, except for two well water samples (Table IV). The human urine samples demonstrated an increase in arsenic content, particularly DMA, following a dinner of shrimp or marine fish. This is in agreement with previous reports of increased urine–arsenic, following seafood dinners (Schrenk and Schreibeis, 1958). Base hydrolysis may cause the MA or DMA to break off from larger arseno-organic compounds which may be present in the urine.

Table V displays the results of recovery experiments when the four species of arsenic were added to alfalfa hay, bovine albumin, human plasma, and urine. The recovery was 90% or better for all of the arsenic species added to these samples.

Table IV. Background Arsenic in Water

sample			mean ppb arsenic found[a]				
type	collection area	source	As(III)	As(V)	MA	DMA	total
fresh[b]	Shelter Cove, CA,	spigot	0.00	0.00	1.23	2.93	4.16
fresh[b]	Lake Alpine, CA	river	0.00	0.80	2.06	5.89	8.75
fresh[b]	Angles Camp, CA	river	0.00	0.00	1.54	4.89	6.43
fresh[c]	Lake Titicaca, Bolivia	lake	2.81	0.00	1.83	2.23	6.87
fresh[d]	Fallon, NV	well	5.00	102.00	0.00	0.00	107.00
fresh[d]	Fallon, NV	well	0.00	101.00	0.00	0.00	101.00

[a] The average parts per billion of background As species (as elemental As) from triplicate aliquots per sample. [b] A 5-L sample was evaporated to 50.0 mL and 15.0-mL aliquots were analyzed. [c] A 2-L sample was evaporated to 50.0 mL and 15.0-mL aliquots were analyzed. [d] A 30-mL sample was placed directly into the generator.

Table V. Recovery of Arsenic Added to Various Substances

		ppm arsenic added				ppm arsenic recovered[a]			
sample	condition	As(III)	As(V)	MA	DMA	As(III)	As(V)	MA	DMA
alfalfa	background[b]	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.08
hay[c]	spiked	0.50	0.50	0.50	0.50	0.50	0.53	0.59	0.56
bovine	background	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00
albumin[d]	spiked	0.15	0.15	0.15	0.15	0.14	0.16	0.18	0.14
human	background	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
plasma[e]	spiked	0.10	0.10	0.10	0.10	0.10	0.09	0.09	0.15
human	background	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.05
urine[f]	spiked	0.10	0.10	0.10	0.10	0.09	0.10	0.14	0.14

[a] Mean values of each arsenic species (as elemental As) for three or more samples. [b] Unspiked sample analyzed to determine background levels of arsenic present. [c] The arsenic was added to 300 g of dry, milled alfalfa powder and allowed to dry before extraction. [d] The bovine albumin was dissolved (1.0 mg/mL) in distilled water and 5 mL was used for analysis. [e] Twenty millilters of plasma was used per sample. [f] Thirty-five milliliters of urine was used per sample.

The measurement of total arsenic based on its reduction to arsine in acidic solutions of $NaBH_4$ has been published by several investigators (Committee, 1977). Haywood and Riley (1976) and Pierce and Brown (1977) discuss the advantages of using $NaBH_4$ over the previously employed Zn–HCl reducing system. Andreae (1977), Braman et al. (1977), and Talmi and Bostick (1975a) have shown that various alkylarsenic acids, including MA and DMA, can be reduced to their corresponding arsines by $NaBH_4$ reduction. Mass spectrograms of the methylated arsines produced in our system matched those published by Talmi and Bostick (1975b); the arsine spectrogram matched that of Stenhagen et al. (1974). We confirm the Kang and Valentine (1977) report that H_2SO_4 in a sample will reduce recovery. Although, Thompson and Thoresby (1977) have recommended its use for hydride generation of arsines from soil samples. Andreae (1977) used differing buffer pH in a double-step reduction to separate As(III) from As(V). However, he used a pH 6 buffer in the first step. In agreement with Aggett and Aspell (1976), our experience has shown that, for the quantitative conversion of As(III) and DMA into the corresponding arsines, the pH of the first step cannot be above 5.5. If all of the As(III) or DMA is not evolved during step 1, it will appear in step 2. If the buffered solution used in step 1 is less than pH 3.9, then small amounts (<1 μg) of As(V) and MA can be reduced during the first step. Like Talmi and Bostick (1975b) and Thompson and Thoresby (1977), we found that all oxygen must be eliminated from the system and $NaBH_4$ addition must be as consistent as possible to obtain quantitative reduction.

Sodium hydroxide digestion of urine increased the recovery of background methylated arsenics, but not of directly added methylated arsenics. This is in agreement with Edmonds and Francesconi (1977) who found NaOH digestion improved recovery of arsenic from methanol extracts of marine fauna muscle tissue. However, background arsenic recovery from bovine serum albumin, human blood, and plant extracts was not increased following NaOH digestion.

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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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