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Effects of Laboratory Lighting on the Stability of Analytical Grade Pesticides

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Analytical data generated from different laboratories using the same or similar methods has been known to differ significantly even form the same sample source. What these differences are attributed to is often difficult to determine. One factor that is generally overlooked but could cause differences in data between laboratories could be the laboratory lighting. The effect of sunlight and particulate ultraviolet light on pesticide degradation has been well documented under laboratory and field conditions. However, the effect of other sources of light in laboratory settings has not been well documented even though many researchers may have had personal experiences with degradation of some organic chemicals primarily due to certain types of fluorescent lighting. For example, several investigators, including the investigators of this study, have reported the relatively rapid degradation of furazolidone, a food additive and a nitrofuran known as N-5-nitro-2-furfurylidene-3-amino-2-oxazolidinone due to fluorescent lighting (Aufere, M.B. et al., 1977, Winterlin et al., 1981). The instability of alfatoxins under fluorescent lights has been well documented. However, these two examples are isolated instances and up to now most chemists have not considered laboratory lighting to be a problem, particularly with pesticides. The principle behind fluorescent lighting is based on excitation of mercury gas which when excited by electrons results in the emission of Ultra-violet radiation. The phosphor coating inside the glass tube prevents most of the ultra-violet light from passing through. However, small amounts do escape at wavelengths less than 400 nm (Table 1). Since there are so many different types of fluorescent lamps with different phosphors that are produced by various manufactures, it would be an overwhelming task to evaluate all pesticides and their various metabolites, degradation products, etc. Therefore, the purpose of this study was not to fulfill this latter function, but simply to verify the potential problem for those conducting experiments with unstable organic chemicals such as organophosphorus pesticides and to caution other laboratories that such photochemical reactions might be possible and that necessary precautions may be necessary.

Table 1. Fluorescent Lamp Characteristics

Lamp Description	Approximate Initial Lumens	Total Watts	Watts below 400 nm
Cool White	2350	9.2	.5728
Warm White	2850	9.1	.273
Daylight	2350	9.6	.528
Colortone 50	2200	9.3	.400*

*Estimate

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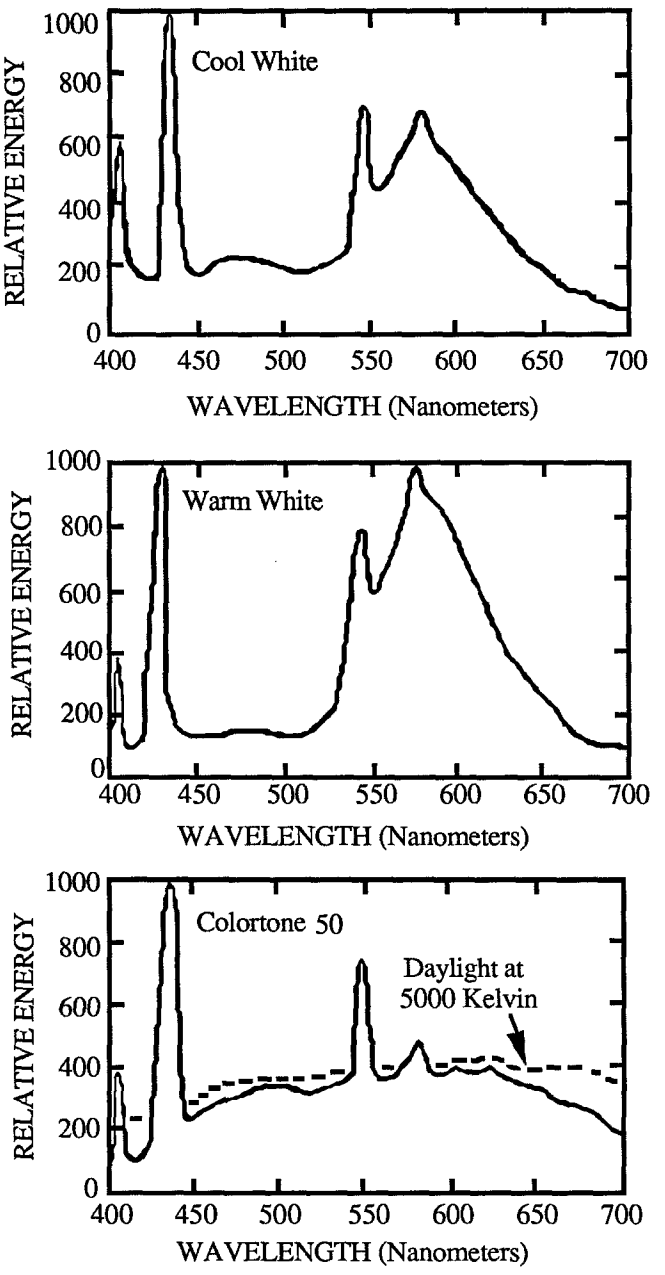

Figure 1. Spectral distribution of fluorscent lamps.

MATERIALS AND METHODS

Table 1 lists the light characteristics for each of the four different types of fluorescent lamps used in this study and Figure 1 shows the spectrum distribution (Phillips Lighting Co., Sumerset, N.J.).

The four pesticides utilized in this study were malathion, fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone. Analytical grade malathion was supplied by the USEPA Pesticide and Industrial Chemical Repository, Research Triangle Park, NC 27709. Fenamiphos, its sulfoxide and sulfone metabolites, were supplied complimentary by Mobay Corp., K.C., MO 64120. Ethyl acetate, benzene, chloroform, and acetone were 'Baker Resi-Analyzed' JT Baker, Inc., Phillipsburg, NJ 08865.

Ten mL of either acetone, ethyl acetate, benzene, or chloroform was transferred to 50 ml round bottom boiling flasks containing 100 µg of each pesticide. One additional flask contained only the pesticide void of any solvent. Each flask was sealed and placed under a pair of 4 foot long fluorescent lamps suspended in a hood 10 cm above the flasks and sealed off to avoid any possible outside light source. In order for the light radiation to be at its maximum penetration, the flasks were placed on their side. Another set of flasks containing the same mixtures and conditions were placed under a 75 watt incandescent lamp with the light source placed approximately 50 cm above the sample with a fan blowing ambient air across the flasks to minimize the heat effect from the incandescent lamp. All samples were exposed for 72 hours except the Daylight 144 hour samples. Additional samples used as control void of solvent and in ethyl acetate were also prepared and stored under "no light" conditions.

Following exposure, samples were prepared for analysis by evaporating the solvent just to dryness on a rotary evaporator. The residue in the flask was then dissolved in ethyl acetate and brought to a final volume of 2 mL. Samples were kept in 4 mL stoppered amber vials and stored under refrigeration until analyzed by gas chromatography.

Analyses were conducted on a Varian 3500 gas chromatograph (glc) equipped with a nitrogen-phosphorus detector and a 6 m x 0.25 mm id DB 1701 capillary column with a 25 micron film thickness. The split ratio for the column was 9.3. The column, injector, and detector temperatures were maintained at 210°, 250°, and 300°C, respectively. Helium was the carrier gas with a flow rate of 2.7 mL/min. The limit of detection for each pesticide was 1 ng.

RESULTS AND DISCUSSION

Table 2 is a summary of the results obtained from the pesticides exposed to no light, incandescent and fluorescent light, with and without organic solvents. All experiments were repeated 4 to 16 times (N). It should be noted that all solutions were contained in sealed Pyrex® glass flasks such as would be found in a normal laboratory setting. The results are reported as the arithmetic means with appropriate standard deviations and are expressed as percentages of their initial concentration.

The pesticides placed under no light and under incandescent lighting were for all practical purposes near 100% recovery. Heat generated in the enclosed area from the incandescent light reached temperatures > 30°C and it was a concern that some of the solvent might evaporate from the flask even though the flasks were sealed with standard tapered ground joint stoppers. However, loss of solvent from the heat generated in the chamber was negligible. Temperatures in the fluorescent lamp chamber were about the same as in the room where the experiment was conducted which was 25 ± 1°C.

Table 2. Recovery of pesticides dissolved in organic solvents or neat.

Solvent	N	--Malathion-- Mean*	S.D.	-- Fenamiphos -- Mean*	S.D.	-- F. Sulfoxide -- Mean*	S.D.	-- F. Sulfone -- Mean*	S.D.
				No Light 72 HOURS					
no solvent	8	100.5	7.2	102.5	9.7	106.4	7.0	104.4	6.1
ethyl acetate	10	106.6	7.1	95.6	5.8	113.1	8.0	105.8	6.3
				Incandescent 72 HOURS					
no solvent	6	99.5	5.4	101.5	5.3	101.5	10.5	99.9	9.6
ethyl acetate	11	106.5	6.6	85.1	9.1	115.4	5.7	104.3	6.8
benzene	8	98.7	6.2	95.5	6.5	104.5	5.8	100.0	5.8
chloroform	14	107.6	13.2	97.4	8.2	116.4	9.5	106.5	7.7
acetone	14	99.0	17.2	76.1	17.6	125.6	28.3	100.7	13.3
				Colortone 50 72 HOURS					
no solvent	6	102.2	7.4	97.4	10.3	99.2	9.5	100.7	10.1
ethyl acetate	8	107.0	8.4	71.6	14.4	123.4	11.6	101.1	9.6
benzene	7	107.2	4.5	91.9	6.8	101.9	4.4	97.3	3.8
chloroform	8	104.5	15.4	79.8	14.6	113.4	17.7	98.1	12.5
acetone	13	99.0	12.3	65.7	12.3	130.6	18.9	100.0	10.3
				Daylight 72 HOURS					
no solvent	12	83.3	22.9	82.4	19.7	84.0	18.9	81.4	18.7
ethyl acetate	6	98.1	11.9	67.2	10.7	117.6	22.9	95.7	12.0
benzene	6	91.2	13.1	81.4	9.9	96.5	16.7	91.4	15.6
chloroform	12	150.3	44.3	95.4	17.4	125.3	23.4	104.6	19.6
acetone	8	91.8	21.4	51.7	12.0	152.9	65.0	105.8	46.0
				Daylight 144 HOURS					
no solvent	4	113.4	6.2	110.6	4.8	114.0	5.3	114.4	4.9
ethyl acetate	4	101.7	14.3	48.2	20.2	141.5	22.0	98.7	13.9
benzene	4	84.4	12.9	74.7	11.8	91.4	10.6	85.2	11.8
chloroform	4	135.5	37.6	47.2	47.7	153.9	24.3	106.9	19.4
acetone	4	126.5	9.6	0.0	3.3	251.1	19.7	131.2	10.2
				Warm White 72 HOURS					
no solvent	6	99.8	7.1	99.2	9.0	100.2	7.2	100.5	7.4
ethyl acetate	8	93.1	13.5	70.9	15.1	111.2	18.1	96.9	14.3
benzene	6	98.1	8.7	90.3	5.7	99.8	12.3	96.8	11.8
chloroform	6	100.2	10.9	79.9	7.8	117.9	8.3	101.4	7.4
acetone	8	90.1	13.9	62.3	17.0	124.1	26.5	93.1	17.5
				Cool White 72 HOURS					
no solvent	4	103.5	6.6	104.6	7.4	106.6	5.7	106.6	6.3
ethyl acetate	4	117.2	4.3	98.5	4.7	117.0	13.2	106.9	11.9
benzene	6	109.6	7.5	94.9	7.7	104.9	9.9	98.9	8.5
chloroform	12	102.1	19.8	77.0	12.1	110.8	13.0	96.2	11.7
acetone	16	92.5	16.9	36.9	33.2	146.5	37.2	94.7	13.9

* Percent of initial concentration by lamp type

The data generated from the four fluorescent lamps clearly shows that some pesticides have the potential for degradation. In this study, the route of degradation appeared to be oxidation as noted with fenamiphos which was oxidized to the sulfoxide. Further oxidation to the sulfone did not occur as the sulfone levels remained quite stable through the exposure period. The one exception was the 144

hour exposure in acetone where the sulfone was 131.2%. However, it was not certain whether this increase was due to oxidation and further studies would need to be conducted to verify these findings.

Results varied according to the different light source and as might be expected, not all pesticide reacted the same. The reactions were not only specific for the particular pesticide but were solvent dependent. As noted from Table 2, malathion was also stable during the exposure period. Fenamiphos on the other hand was quite unstable particularly in the presence of acetone. Light from the Cool White lamps in the presence of acetone was particularly noteworthy as only 36.9% of the fenamiphos remained after 72 hours while the sulfoxide had increased to 146.5%. The Daylight lamps also had a remarkable effect on fenamiphos in acetone. After 72 hours only 51.7% remained and after 144 hours there was no detectable residue while the sulfoxide increased proportionately. This may not be too surprising when one observes that these two light sources radiate the most energy below 400 nm (Table 1). The Warm White and the Colortone 50 lamps had the lowest radiation below 400 nm and consequently the recovery values were higher and were almost identical to the levels found in all of the respective solvents following the 72 hour exposure. However, some of the other solvents also had some effect on degradation but in different proportion to the other lamps. Ethyl acetate was particularly noteworthy, while as fenamiphos was quite stable under the Cool White lamps, it was degraded to approximately 70% with the Colortone 50, the Daylight and the Warm White lamps after 72 hours. Therefore, such an oxidation reaction might be hard to predict for a particular type of lamp and any combination of fluorescent light and solvent could potentially result in an oxidation reaction. Figure 2a-c compares by bar graphs the results from the various exposures to fenamiphos, fenamiphos sulfoxide, and fenamiphos sulfone. The solvent effect can be readily noted with acetone generally being more reactive than ethyl acetate followed by chloroform and benzene.

The 144 hour exposure to the Daylight fluorescent lamps as shown in Table 2, verifies the relative effect the solvent has as described previously. Acetone had a most dramatic effect with fenamiphos as the percentage dropped from approximately 50% after a 72 hour exposure to nondetectable levels in 144 hours while the sulfoxide increased proportionately resulting from an oxidation reaction. Under these same lighting conditions, chloroform compared well with ethyl acetate as both solvents contained about 50% fenamiphos under the Daylight lamps and about 80% and 71% respectively, under the Colortone 50 and Warm White lamps.

Although it was not the purpose of this study to determine the photochemical reactions responsible for this oxidation reaction, the point to be made is that some organic chemicals under fluorescent lighting in conjunction with organic solvents can cause a photochemical reaction and the chemist might be advised to take precautions when working with these chemicals such as storing under no light and refrigerated conditions and avoid certain polar solvents, such as acetone for any prolonged period. When in doubt, a solution containing the standard (s) with the same solvents should be analyzed (along with other recovery studies as prescribed by good laboratory practices) during an experiment in order to verify the stability, or lack of, the chemicals being investigated.

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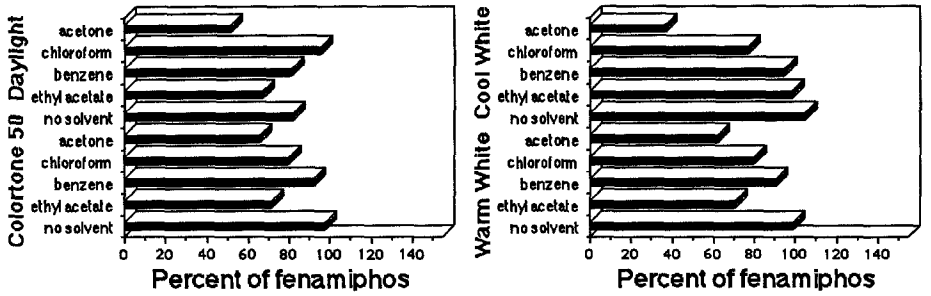

Figure 2a. Effect of Daylight, Colortone 50, Cool White, and Warm White fluorescent lamps on the degradation of fenamiphos in 4 laboratory solvents after 72 hours of exposure.

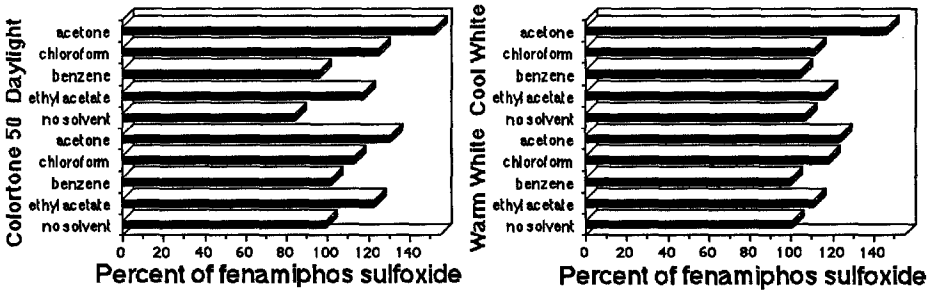

Figure 2b. Effect of Daylight, Colortone 50, Cool White, and Warm White fluorescent lamps on the degradation of fenamiphos sulfoxide in 4 laboratory solvents after 72 hours of exposure.

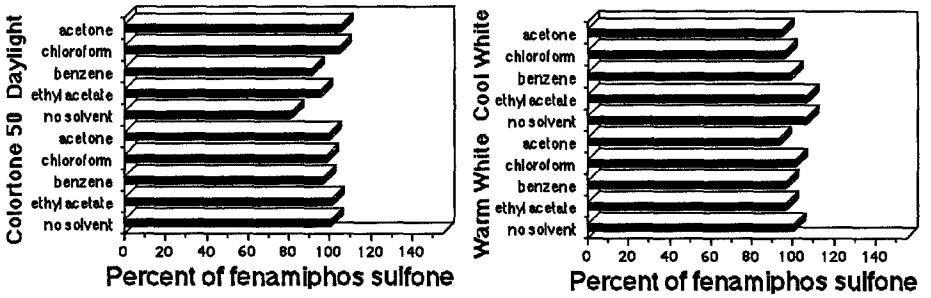

Figure 2c. Effect of Daylight, Colortone 50, Cool White, and Warm White fluorescent lamps on the degradation of fenamiphos sulfone in 4 laboratory solvents after 72 hours of exposure.

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