

Near-UV molar absorptivities of acetone, alachlor, metolachlor, diazinon and dichlorvos in aqueous solution

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Abstract

An experimental set-up consisting of two parallel absorption cells coupled to a CCD detector was used to determine absolute values of molar absorptivity coefficients ϵ of acetone and of several pesticides (alachlor, metolachlor, diazinon and dichlorvos) in water. The absorption spectra were measured using a deuterium lamp over the wavelength range of 240–320 nm at room temperature (298 ± 2 K).

Absorbance were also measured at 253.7 nm using an Hg-lamp in different concentrations range depending on the studied compound. The absolute values of molar absorptivity coefficients at this wavelength were determined according to the Beer–Lambert law: $\epsilon = 13.9 \pm 1.0$ for acetone, $\epsilon = 466 \pm 41$ for alachlor, $\epsilon = 615 \pm 63$ for metolachlor, $\epsilon = 3558 \pm 323$ for diazinon, $\epsilon = 5.5 \pm 0.5$ for dichlorvos (in units of $\text{M}^{-1} \text{cm}^{-1}$). The quoted errors correspond to 2σ obtained from the least square fit analysis and the estimated systematic error of 5% due to the uncertainties in aqueous concentrations. For all the studied compounds, the absorbances measured were lower than two and did not exhibit any deviation from the Beer–Lambert's law.

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1. Introduction

The amount of pesticides routinely applied, mainly for agricultural uses, has dramatically increased in recent years and consequently, there are serious concerns about the increasing risks to human health.

Once in the environment, pesticides can contaminate surface water and groundwater depending on their solubilities while the main input mechanisms of pesticides in the atmosphere are dispersion during spraying operations, volatilisation from ground or leaf surfaces and wind erosion [1].

This study will focus on four compounds, namely alachlor (herbicide), metolachlor (herbicide), diazinon (insecticide) and dichlorvos (insecticide) for which the molar absorptivity will be determined.

Chloroacetanilides, such as alachlor or metolachlor are widely used herbicides, applied as pre-planting, pre-emergent

or early post-emergent treatment to control annual grass weeds and broadleaf weeds in corn, cotton, peanuts, soybeans and beans. Estimated US annual uses of alachlor and metolachlor in 1997 were 6.8×10^6 and 30.3×10^6 kg, respectively [2]. Under exposition to short periods of time, alachlor leads to slight skin and eye irritations, while longer exposure times may lead to damage to liver, kidney, spleen, lining of nose and eyelids, cancer. Metolachlor is not very acutely toxic to humans. It is however more dangerous when inhaled than when ingested. Signs of human intoxication include abdominal cramps, anaemia, shortness of breath, dark urine, convulsions, diarrhoea, jaundice, etc.

Diazinon and dichlorvos are organophosphorus compounds used on lawns, around homes and in gardens to kill insects, such as fruit flies, earwigs, flies, mites, ants, spiders, fleas, etc. According to the EPA [3], over 13 million pounds of diazinon are used each year. About 80% of this pesticide is used on lawns and for residential control of insects. Organophosphorus compounds do not accumulate in organisms and they degrade easily in the environment. However,

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organophosphate pesticides are of great concern for the environment primarily because they are very toxic to mammals and birds [4]. Diazinon is known for its neurotoxins that target and poison the nervous system even for humans [5,6]. Dichlorvos has also a high acute toxicity and it is classified by the WHO as a ‘highly hazardous’ agent of the IB class [7]. Dichlorvos vaporizes quickly and its exposure by inhalation after its use in non-ventilated or poorly ventilated areas has been reported to be one of the principal causes of human poisoning [8].

Direct photolysis is a possible pathway for the elimination of pesticides in the environment. The photodissociation rate constants associated to these components depend either on their absorption cross sections $\sigma(\lambda)$ for the molecule in the gas phase or on their molar absorptivity coefficients $\epsilon(\lambda)$ for the molecule in the aqueous phase, on the primary quantum yield $\phi(\lambda)$ for photolysis and on the actinic flux of solar radiation $I(\lambda)$. Due to the low vapour pressures of pesticides, the direct measurements of their absorption cross sections in the gas phase cannot be performed using a classical absorbance cell [9,10]. Besides, the pesticides are generally poorly soluble in water so that direct measurements of ϵ using a classical path-length of 1 cm is rather limited, except if they exhibit high absorbance. We have then developed a new set-up based on a long path-length allowing the determination of the molar absorptivity coefficients. Such measurements provide useful information to estimate the potential fate of these pesticides by photolysis.

In this work, the absolute values of molar absorptivity coefficients ϵ of acetone (for calibration purposes), alachlor, metolachlor, diazinon and of dichlorvos have been measured at room temperature (298 ± 2 K), over a wavelength range of 240–320 nm using an absorbance cell coupled to a CCD detector. The chemical formulas of the four studied pesticides are given in Fig. 1. Acetone measurements were performed in order to validate our new experimental set-up by comparison with data available in the literature [11–13]. To our knowledge, we report the first absolute UV spectra for the four studied pesticides.

2. Experimental

The set-up consists of two parallel absorption cells, made out of Pyrex, and equipped with quartz windows at both ends (see Fig. 2). They are 105 cm long and have a 3.4 cm internal diameter. The two cells are installed on a sliding system so that they can be exposed alternatively to the output of a deuterium lamp (Ocean Optic, D-2000) equipped with an optical fibre or of a Hg(Ne) lamp (Oriol Instruments, 6034). After passing through the cell, the UV light, is focused onto another optical fibre connected to the entrance slit of a spectrometer (Jobin Yvon, TRIAX 320) equipped with a 1200 grooves/mm grating, which disperses the radiations onto a CCD (Andor Technology, DV420-OE). Experiments were conducted using a 100 μm entrance slit, provid-

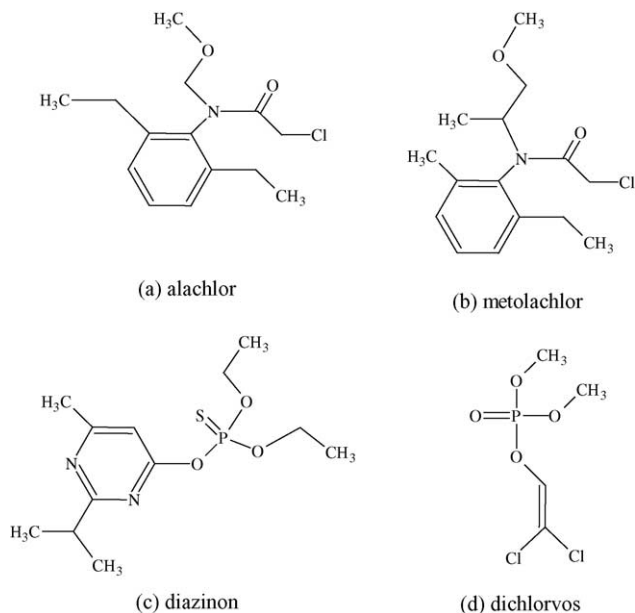


Fig. 1. Chemical formula of the four pesticides: (a) alachlor, (b) metolachlor, (c) diazinon and (d) dichlorvos.

ing a spectral resolution of about 0.066 nm. With this configuration, the spectrometer recorded spectra over two 67.6 nm intervals and the measurements covered two wavelength regions: 236–304 and 276–344 nm. Thus, there was a 28 nm overlap segment, which made easy to construct the entire spectrum. Since the light produced by the deuterium lamp is temperature dependent, the wavelength scale of the spectrometer was first calibrated with the Hg-lamp using two spectral lines: 253.7 and 296.7 nm for the 236–304 nm range, and 312.6 and 313.2 nm for 276–344 nm range.

The spectra were measured using the following method. First, the Hg(Ne) lamp was used to calibrate the experimental set-up. For each of the four spectral lines, the light intensities $I_{0,A1}$ and $I_{0,B1}$ transmitted through the two cells A and B were determined when both cells were filled up with pure water in order to determine the ratio $I_{0,B1}/I_{0,A1}$. Cell B was then purged and filled with a diluted aqueous solution of either acetone or pesticide (light intensity I_{B2}) while water was maintained in cell A. This allowed the determination of $I_{B2}/I_{0,A2}$. Since during these operations, light intensity from the lamp may have been subject to small variations, the reference intensity $I_{0,B2}$ was calculated from $I_{0,B1}$ according to:

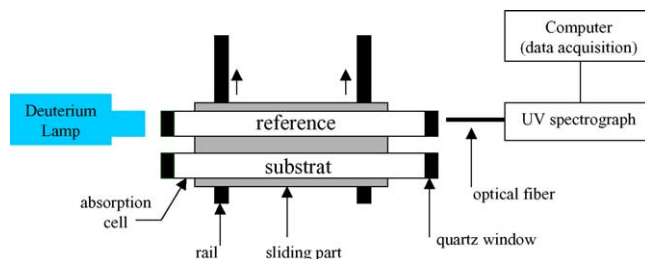


Fig. 2. Scheme of the experimental set-up.

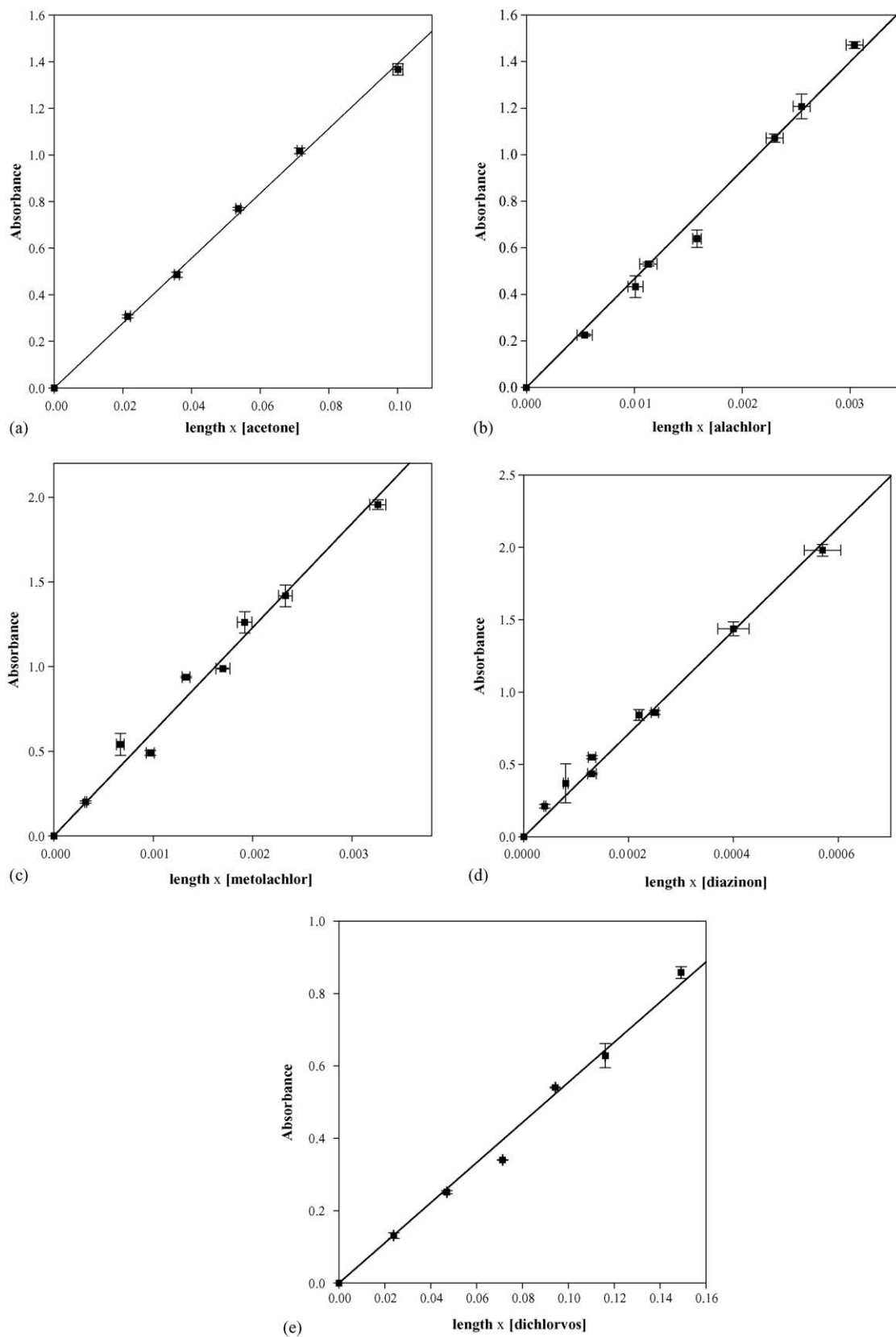


Fig. 3. $\ln(I_0/I)$ vs. LC at 253.7 nm for (a) acetone, (b) alachlor, (c) metolachlor, (d) diazinon and (e) dichlorvos. The slopes of these plots are the corresponding molar extinction coefficients ϵ (in units of $M^{-1} \text{ cm}^{-1}$) according to the Beer–Lambert's law (see Eq. (1)).

$I_{0,B2} = I_{0,B1}(I_{0,A2}/I_{0,A1})$. This operation was repeated several times.

The wavelength-dependent molar absorptivity coefficient ε ($M^{-1} \text{ cm}^{-1}$) was obtained using the Beer–Lambert's law:

$$A = \log \frac{I_{0,B2}}{I_{B2}} = \varepsilon LC \quad (1)$$

where A is absorbance (dimensionless), L the path length of the cell filled with the sample (cm), and C the concentration of the compound in solution (in mol L^{-1}).

The same operation was repeated by replacing the Hg(Ne) lamp with the deuterium lamp in order to explore the entire spectrum from 240 to 320 nm. Each measurement of I consisted of 50 scans, which required a maximum 10 s to be completed.

Acetone (99.8%) was from Prolabo, alachlor (99.9%), metolachlor (98.4%), diazinon (98.4%) were from Riedel de Haën and dichlorvos (98%) was provided free of charge by Sipcam-Phyteurop. They were used without any additional purification.

3. Results and discussion

Absorbances were measured at 253.7 nm with the Hg(Ne) lamp for different concentration ranges depending on the compound: 11.8–55.3 mg L^{-1} for acetone, 1.4–7.8 mg L^{-1} for alachlor, 0.9–8.8 mg L^{-1} for metolachlor, 0.10–1.65 mg L^{-1} for diazinon and 50–314 mg L^{-1} for dichlorvos. The absolute values of molar absorptivity coefficients at this wavelength were determined from the plot of $\log(I_{0,B2}/I_{B2})$ versus LC , where the slope is equal to ε (see Fig. 3a–e). The following values have been found: $\varepsilon = 13.9 \pm 1.0$ for acetone, $\varepsilon = 466 \pm 41$ for alachlor, $\varepsilon = 615 \pm 63$ for metolachlor, $\varepsilon = 3558 \pm 323$ for diazinon, $\varepsilon = 5.5 \pm 0.5$ for dichlorvos (in units of $M^{-1} \text{ cm}^{-1}$). The quoted errors correspond to 2σ obtained from the least square fit analysis and the estimated systematic error of 5% due to the uncertainties in concentrations. For all the studied compounds, the absorbances were smaller than two and did not exhibit any deviation from the Beer–Lambert's law as shown in Fig. 3a–e.

Table 1

Molar absorptivities ε of acetone, alachlor, metolachlor, diazinon and dichlorvos measured between 240 and 320 nm using a deuterium lamp and normalized with the value determined at 253.7 nm with a Hg-lamp

λ (nm)	ε ($M^{-1} \text{ cm}^{-1}$) ^a				
	Acetone	Alachlor	Metolachlor	Diazinon	Dichlorvos
240	7.88	872	1203	3670	20.0
242	8.81	765	1130	4175	20.3
244	9.80	672	1015	4560	19.9
246	10.7	592	902	4779	17.8
248	11.7	535	797	4759	14.2
250	12.6	492	717	4536	10.6
252	13.4	471	657	4086	7.57
253.7 ^b	13.9 ± 0.3	466 ± 18	615 ± 32	3558 ± 146	5.54 ± 0.24
254	14.0	467	617	3448	5.29
256	14.7	472	599	2689	3.63
258	15.1	484	594	1866	2.47
260	15.4	503	602	1153	1.70
262	15.4	522	616	677	1.16
264	15.4	545	633	404	0.85
266	15.2	548	646	244	0.61
268	15.0	520	632	138	0.47
270	14.6	488	591	99	0.36
272	14.2	461	568	71	0.31
274	13.7	405	537	62	0.27
276	13.1	284	426	63	0.22
278	12.2	162	278	70	0.19
280	11.1	82	157	78	0.16
282	10.0	39	86	87	0.14
284	8.95	20	51	95	0.13
286	7.85	13	36	110	0.12
288	6.79	9	29	115	0.10
290	5.74	5	24	136	0.08
295	3.50	3	18	138	0.03
300	1.88	2	13	131	0.00
305	0.90	0	5	93	0.00
310	0.38	0	2	87	0.00
315	0.12	0	1	38	0.00
320	0.02	0	4	0	0.00

^a The reported values are averaged over 2 nm intervals in the range of 240–290 nm and over 5 nm intervals in the range of 290–320 nm.

^b The values are obtained using an Hg-lamp. The quoted errors correspond to 2σ obtained from the least square fit analysis.

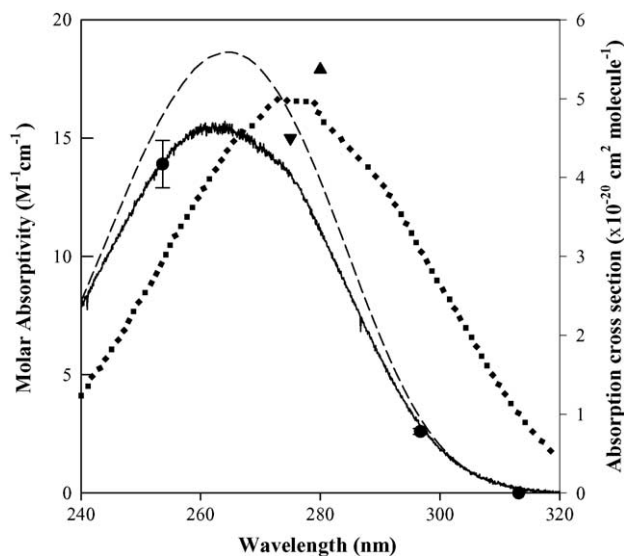


Fig. 4. Comparison of molar extinction coefficients ϵ (in units of $\text{M}^{-1} \text{cm}^{-1}$) of acetone between 240 and 320 nm measured in this work at $298 \pm 2 \text{ K}$ and in previous studies [11–13]: (—) this work using a deuterium lamp, (●) this work using a Hg lamp, (---) [13], (▼) [11], (▲) [12]. Absorption cross sections of acetone measured by [9] correspond to the dotted line.

Absorbance were also measured between 240 and 320 nm using the deuterium lamp for the same concentrations ranges. The agreement between ϵ values obtained for the two lamps at 253.7 nm was always better than 15% for all compounds and the entire spectra obtained in the wavelength range of 240–320 nm (Figs. 4–7) have been normalized with our determinations of ϵ at 253.7 nm made with the Hg(Ne) lamp since these latter are much more accurate. Absolute values of molar absorptivity coefficients, with either 2 nm intervals in the 240–290 nm range or 5 nm intervals in the 290–320 nm range, are listed in Table 1.

Our acetone spectrum is shown in Fig. 4 together with those obtained in previous studies either in the aqueous phase [11–13] or in the gas phase [9]. The absorption band centred at about 260 nm results from a dipole forbidden $\pi\text{--}\pi^*$ electronic transition of the $\text{C}=\text{O}$ group. Our ϵ values are in reasonably good agreement with those determined by Stefan et al. [13] and Dudik et al. [12] in the aqueous phase. The older measurement made by Bayliss and McRae in 1954 [11] at 280 nm is about 1.6 times higher than our value. Fig. 4 shows also that the data are slightly shifted towards higher wavelengths when acetone spectrum is recorded in the gas phase [9]. Consequently, the UV spectrum of a given substance recorded in the aqueous phase can provide some information about its potential photolysis rate in the gas phase.

Alachlor and metolachlor show similar UV spectrum, which is expected since their chemical formulae are very close (see Fig. 5). Their spectra exhibit two peaks corresponding to $\pi\text{--}\pi^*$ bands characteristic of aromatic compounds. One of them is rather weak ($\epsilon \sim 500\text{--}700 \text{ M}^{-1} \text{cm}^{-1}$), centred at 265 nm and corresponds to the 1L_b band while the maximum of the second peak (not reached in this study)

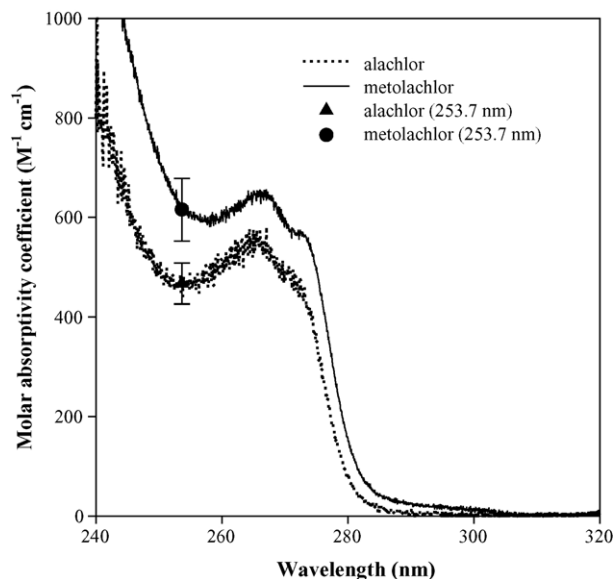


Fig. 5. Molar extinction coefficients ϵ (in units of $\text{M}^{-1} \text{cm}^{-1}$) of alachlor and metolachlor measured in this work between 240 and 320 nm at $298 \pm 2 \text{ K}$. The solid and dotted lines correspond respectively to the UV spectra of alachlor and metolachlor obtained with a deuterium lamp while the values of ϵ determined at 253.7 nm with an Hg-lamp are symbolized by (●) and (▲) for alachlor and metolachlor, respectively.

is below 240 nm and corresponds to the 1L_a band. The replacement of the $\text{--N--CH}_2\text{--O--CH}_3$ or $\text{--CH}_2\text{--CH}_3$ groups in the alachlor molecule by the $\text{--N--CH(CH}_3\text{)--CH}_2\text{--O--CH}_3$ and --CH_3 groups, respectively, in the metolachlor molecule, causes a small bathochromic shift: metolachlor spectrum appears as shifted towards the higher wavelengths by comparison with alachlor. Absorption of alachlor and metolachlor above 290 and 305 nm respectively can be considered as negligible since $\epsilon \leq 5 \text{ M}^{-1} \text{cm}^{-1}$ as shown in Table 1.

Below 260 nm, diazinon absorbs up to five times more than alachlor and metolachlor as shown in Fig. 6. Its UV spectrum exhibits two peaks, which maxima are located at 245 nm ($\epsilon \sim 4800 \text{ M}^{-1} \text{cm}^{-1}$) and 295 nm ($\epsilon \sim 150 \text{ M}^{-1} \text{cm}^{-1}$) and its spectrum is quite similar to that obtained for 1,3-diazine [14], from which this pesticide is derived. The different substituent groups added on the diazine ring, to obtain the diazinon molecule, lead only to a small bathochromic shift of about 15 nm.

Dichlorvos absorbs very weakly in the studied wavelength range (see Fig. 7) in comparison to the above compounds since it does not contain any aromatic or diazine rings. Alkenes absorb only for $\lambda < 200 \text{ nm}$ that corresponds to $\pi\text{--}\pi^*$ band but the presence of both chlorine and of oxygen atoms linked to the carbon atoms of the double bond causes an important bathochromic shift of more than 50 nm by comparison with ethylene [14]: the unshared pairs of electrons on either Cl or O atoms are conjugated with the double bond >C=C< in the dichlorvos molecule. Its UV spectrum exhibits only one peak which has an absorbance maximum around 242 nm ($\epsilon \sim 20 \text{ M}^{-1} \text{cm}^{-1}$). The molar absorptivity coefficient is less than $1 \text{ M}^{-1} \text{cm}^{-1}$ for wavelength above 265 nm.

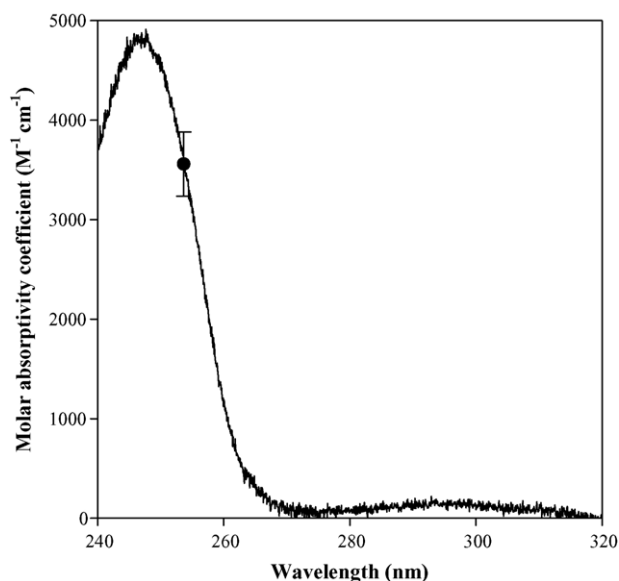


Fig. 6. Molar extinction coefficients ϵ (in units of $M^{-1} \text{ cm}^{-1}$) of diazinon measured in this work between 240 and 320 nm at 298 ± 2 K. The solid line corresponds to its UV spectrum obtained with a deuterium lamp while the value of ϵ determined at 253.7 nm with an Hg-lamp is symbolized by (●).

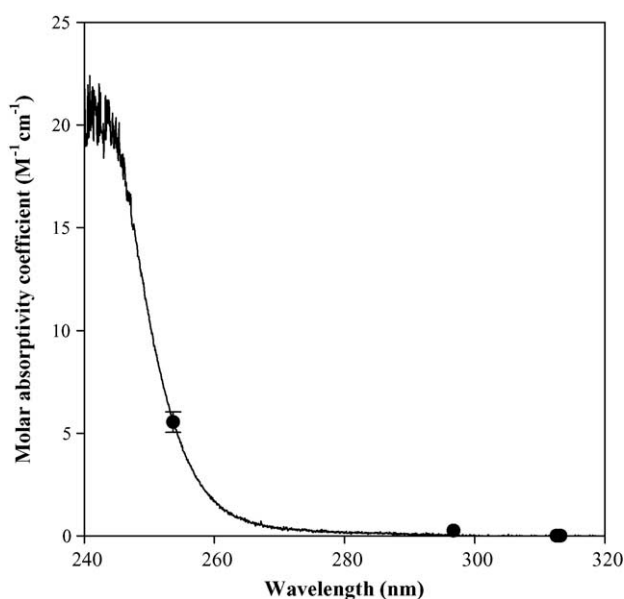


Fig. 7. Molar extinction coefficients ϵ (in units of $M^{-1} \text{ cm}^{-1}$) of dichlorvos measured in this work between 240 and 320 nm at 298 ± 2 K. The solid line corresponds to its UV spectrum obtained with a deuterium lamp while the value of ϵ determined at 253.7 nm with an Hg-lamp is symbolized by (●).

For all the studied pesticides, the uncertainties on ϵ values between 240 and 320 nm are estimated to be less than 20%.

4. Conclusion

We have developed a new set-up based on a long path-length (~ 1 m) allowing the determination of the molar ab-

sorptivity coefficients ϵ , especially for poorly soluble compounds such as pesticides. The new set-up was validated by measuring the UV spectrum of acetone in the aqueous phase in the 240–320 nm range. Afterwards, the UV spectra of alachlor, metolachlor, diazinon and dichlorvos have been determined in the same experimental conditions.

Such data have many interesting applications. Our experimental determinations provide useful information to estimate the potential fate of these pesticides by sunlight photolysis in both aqueous and gas phases. They can also be considered for chemical remediation of wastewaters to eliminate such pesticides or for analytical measurements by HPLC coupled to UV detection.

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