variety is more important. Thus, the wine samples were separated into two groups: red wines and white wines. For each group, the above set of 10 variables was used in deriving discriminant functions for group classification according to grape variety. The white wines (Figure 7) are classified according to two main groups, respectively Tamarez–Manteûdo and Roupeiro–Rabo de Ovelha. The function was tested by the leave-one-out method. The red wines behave identically (Figure 8). The function distinguishes in 80% of the cases between Aragonez–Moreto and Trincadeira–Periquita. This confirms the observations drawn from principal component analysis and hierarchical clustering.

The results of this study of pattern recognition of amino acid profiles in elementary wines show that there is a clear correlation between wine free amino acid content and the original grape variety. The use of elementary wines obtained under the same fermentation procedures from well-known Portuguese *V. vinifera* varieties, grown under the same soil and climatic conditions, eliminates the influence of these factors. Under this conditions, a direct correlation between grape variety and wine free amino acid content in the absence of extraneous factors was established for the 42 wines studied.

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A Direct Spectrofluorimetric Determination of the Herbicide Flurecol in Cultivated Soils

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A method for determining residues of the herbicide and plant growth regulator flurecol in soil is described. Soil is extracted with methanol. The organic extracts were evaporated to dryness and redissolved in *N,N*-dimethylformamide. The compound is determined with a spectrofluorimetric detector. A concentration range from 0.13 to 6.8 μg/mL with a detection limit of 40.90 ng/mL could be determined by normal, first, or second synchronous derivative spectrofluorimetric technique with a maximum relative standard deviation of 4.58%. Recoveries of spiked soil samples varied from 88.23 to 105.64%.

Since the advent of organic pesticides (insecticides, herbicides, fungicides) in the 1930s, numerous compounds have been developed for the control of different pests. During the past 15 years, there has been a trend toward the use of pesticides that would degrade more readily and thus be less detrimental to the environment.

This is the case of flurecol (9-hydroxyfluorene-9-carboxylic acid), introduced by Schneider (1964), which acts via leaves and roots as a growth-retarding and -suppressing agent with an effect limited to dicotyledoneous plants. The general symptoms are inhibition of natural growth together with dwarfing, inhibition of elongation of internodes, and breaking of apical dominances.

Because flurecol and its derivatives differ in their action from other plant growth regulators, the term morphactin has been proposed for them (Schneider et al., 1965). They are nontoxic to honey bees and are quickly and completely degraded in soil.

Trace analysis methods for the determination of pesticide residues in crops, animal tissues, soil, and water need to have both high sensitivity and selectivity (Roberts, 1985). As can be seen in the literature, most organic pesticides would be observed with a UV detector. Selective detection techniques are beginning to be used for improving the determination of these compounds. One of these detection techniques, fluorescence, is well regarded as an analytical tool because of its excellent sensitivity and added selectivity, as compared to classical colorimetric methods. Nevertheless, its application to organic residue analysis has been somewhat limited due to the fact that not too many pollutants are very fluorescent and that many naturally occurring compounds interfere. A number of pesticides have been reported to fluoresce naturally (Argauer, 1977; Addison et al., 1977). Recently, several

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Table I. Spectral Characteristics of Flurecol in Different Solvents

solvent	dielectric const (25 °C)	λ_{abs}, nm	λ_f, nm	$\Delta\lambda$,[a] nm	RFI	RE × 10^{-3}	log ϵ
dioxane	2.21	285	310	25	27.0	120.4	4.71
acetone	20.70	325	400	75	0.3		
ethanol	24.55	265	306	41	49.6	163.4	4.48
methanol	32.70	265	305	40	34.8	52.7	4.82
acetonitrile	35.50	235	500	265	4.9	7.7	4.80
dimethylformamide	36.71	270	495	225	5.1	54.9	3.96

[a] Stokes shift ($\lambda_{em} - \lambda_{ex}$).

authors have used fluorescence detectors to selectively determine pesticide residues (Argauer, 1980; Isshiki et al., 1980; Krause and August, 1983; Cruces-Blanco and García-Sánchez, 1986; García-Sánchez and Cruces-Blanco, 1986, 1988).

The method actually recommended for the analysis of residues of flurecol is based on measuring the UV absorbance at 273 nm (Amadori, 1969). At this wavelength, all known impurities do not render the results unacceptable because of their much lower molar absorptivities.

The method for the analysis of technical flurecol must be specific with respect to acidic byproducts. Therefore, alkalimetric titration cannot be used alone because of the presence of other carboxylic acids. A suitable method consists of the combination of alklimetric titration and GLC following the procedure of Röder and Laas (1976). This method, initially designed for the analysis of phenoxy acids, can be used for flurecol with slight modifications.

There are also methods for the determination of flurecol in commercial formulations using separatory techniques such as thin-layer chromatography with different detectors: densitometric (Amadori, 1978) or photometric (Amadori and Hempt, 1980). As has been indicated for the method of Amadori (1969), the direct spectrophotometric detection at a low wavelength (λ_{abs} = 273 nm) gives numerous interferences in this zone. But this can be avoided by the conversion of flurecol to fluorenone and then to (*p*-nitrophenyl)hydrazone, measuring the absorbance at 597 nm (Sieper, 1971). Recently, amadori and Hempt (1980) have utilized gas chromatography with electron capture detector for the determination of flurecol in cereals, soil, and water with a detection limit of 0.01 mg/kg.

The purpose of the work reported here is to determine the herbicide flurecol in soil samples by a simple spectrofluorimetric technique to give an alternative to the classical spectrophotometric methods that are the only ones actually in use for its determination. As demonstrated in previous works (Ramos-Rubio et al., 1986; García Sánchez et al., 1985), the application of the synchronous derivative technique markedly increases both sensitivity and selectivity of the analytical procedure.

The technique was first suggested by John and Soutar (1976) and applied by different authors (Miller et al., 1982; Cruces-Blanco and García-Sánchez, 1984). The main advantages they offer are the simplification of the spectral profile and the band-narrowing effect that coupled with the derivative technique makes feasible both identification of weak bands and magnification of the overall signal that leads to increase sensitivity and selectivity (Vo-Dinh, 1978; Rubio et al., 1985).

EXPERIMENTAL SECTION

Solvents and Reagents. Flurecol (≥99% purity) was purchased from Serva, Feinbiochemica. Carbaryl, 1-naphthol, and guthion (minimum 99% purity, quality Pestanal) were obtained from Riedel-de Haën, AG Seelze (Hannover). Colchicine, kinetin, 2,4-D, and 2,4,5-T were obtained from Sigma Chemical Co. All solvents used were of analytical reagent grade (Merck). The water was both distilled and demineralized. Hydrochloric acid and sodium hydroxide (0.1 M and 0.5 M solutions) were also analytical reagent grade (Merck). A stock solution of flurecol (1×10^{-3} M) was prepared in *N,N*-dimethylformamide (DMF). Stock solutions (100 μg/mL) of the other pesticides were also prepared in 100% DMF.

Apparatus. Spectral photometric measurements were made with a Shimadzu UV-240 Graphicord recording spectrophotometer using quartz cells of 1-cm path length. Fluorescence measurements were made with a Perkin-Elmer MPF-43A spectrofluorometer equipped with a 150-W Osram XBO xenon lamp, excitation and emission monochromators, 1 × 1 cm quartz cells, and a Perkin-Elmer 023 recorder. Instrument sensitivity was adjusted daily with a Rhodamine B bar as a reference standard. An ultrasonic water bath Ultrasons Selecta was used to homogenize soil samples.

Analytical Procedure. Different aliquots of flurecol standard solution (1×10^{-3} M) in DMF were placed in 10-mL standard flasks and diluted to the mark with DMF to obtain a final concentration between 0.2 and 6.80 μg/mL. The fluorescence intensity was measured immediately after the preparation of the samples using 495 nm with excitation at 310 nm, against a solvent blank.

For concentrations between 200 and 1000 ng/mL, the first- and second-derivative synchronous spectra were recorded with the following fixed instrumental parameters: $\Delta\lambda$ = 200 nm, scan speed 120 nm/min, response time 1.5 s, scale expansion 5. The first- and second-derivative values were measured as the vertical distance on the dIf or d2If scale in centimeters as indicated in Figure 3b. The concentration of flurecol is determined from the conversion of relative fluorescence intensity (RFI) units or centimeters by the corresponding calibration graph obtained for each case.

Extraction of Soil Samples. Soil samples were obtained from a cultivated field in Motril (Granada, Spain) with use of a V-shaped shovel introduced in the ground to a depth of 20 cm. Twenty subsamples were taken from different sites of the same field and combined, obtaining a final amount of 2 kg approximately. The sample was spread in a dish, and large pieces and pebbles were removed. The sample was mixed thoroughly and reduced by quartering to obtain portions of 300 g. This soil sample was air-dried at room temperature and passed through a 2-mm sieve. Different volumes of the stock solution of flurecol in DMF were added to an aliquot of 10 g of soil sample. After thorough mixing, the sample was extracted with methanol in a proportion of 2:1 solvent to sample (v/w). For a rapid homogenization of the sample with the extracting solvent, the glass vase was introduced on an ultrasonic bath for 1 min after which the sample is left to stand. The supernatant was filtered through a 30-mL medium-porosity glass Buchner funnel, and vacuum was applied. The procedure was repeated three times. The contents of the filter flask were quantitatively transferred to a round-bottom flask and taken to near dryness on a rotary evaporator at 45 °C. The residue was taken to a final volume of 10 mL with DMF. This solution was used for the analytical determination.

RESULTS AND DISCUSSION

Due to the weak intrinsic fluorescence intensity shown by the flurecol, a detailed study of the solvent effect on its absorption and fluorescence spectra has been very valuable for its analytical determination.

The spectral characteristics obtained from a solution of flurecol (5×10^{-5} M) in solvents of different polarity are indicated in Table I. Absorption wavelengths suffer a bathochromic shift of 35 nm with solvent change from acetonitrile (λ_{abs} = 235 nm) to DMF (λ_{abs} = 270 nm). The same phenomenon is observed with the emission wavelengths when increasing solvent polarity from dioxane (λ_{em}

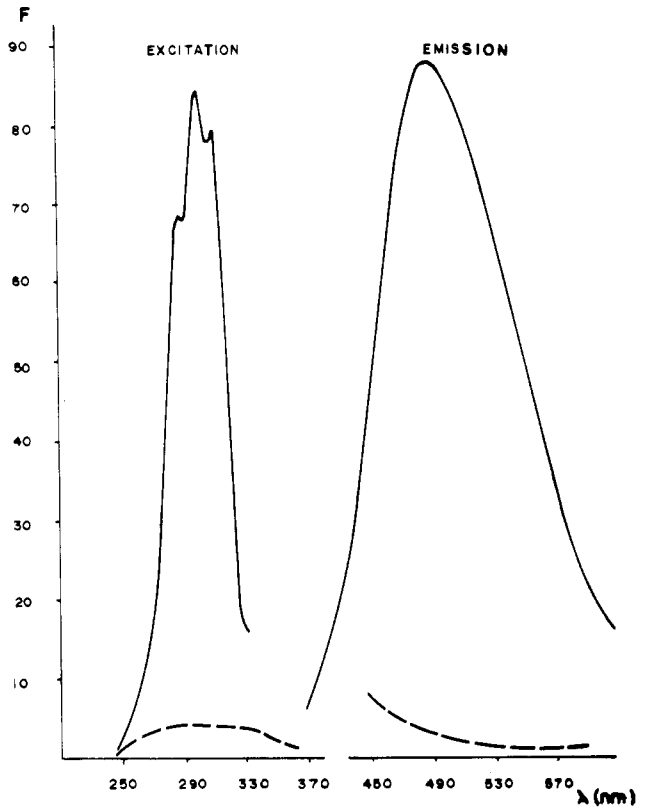

Figure 1. Fluorescence excitation and emission spectra of 0.2 μM flurecol solution in 100% dimethylformamide (—) and a blank of solvent (- - -) in the same conditions.

= 310 nm) to DMF and acetonitrile (λ_{em} = 495 and 500 nm, respectively).

Taking into account the different parameters of Table I, ethanol, methanol, and dioxane should be chosen because of their highest RFI and relative efficiency (RE), but greater selectivity and possible light scattering are avoided choosing DMF as solvent. A 2×10^{-4} M solution of flurecol in a 100% (v/v) DMF has its emission maximum at 495 nm, with an excitation at 310 nm (Figure 1).

Due to the fact that flurecol molecule has an acid and phenolic group, the fluorescence intensity could be affected by changes in the pH of the medium. A fluorometric titration was carried out with a solution of flurecol (5×10^{-5} M) in a 40% (v/v) DMF–water. The results in Figure 2 showed that the reagent is fluorescent in strong acid (pH <4) and basic (pH >12) media, having a minimum between pH 6.5 and 8.5.

If the proton transfer in the excited state takes place to some extent and the RFI is measured at the maximum wavelength of acidic or basic form, the dissociation constants can be calculated from the expressions of Rosenberg et al. (1979). The values obtained were

$$pk_1 = 5.29 \pm 0.27 \quad (n = 4) \tag{1}$$

$$pk_2 = 10.70 \pm 0.13 \quad (n = 5) \tag{2}$$

These values have been attributed to the deprotonation of the acid group (–H) and phenolic group (–OH), respectively.

The influence of DMF percentage on the RFI of flurenol solutions (5×10^{-6} M) indicated that a rectilinear increase is observed when increasing the DMF percentage from 10 to 100%.

The fluorescence intensity obtained when a solution of the same concentration is at the optimum pH (see Figure 2) with a 40% DMF–water percentage is lower that the

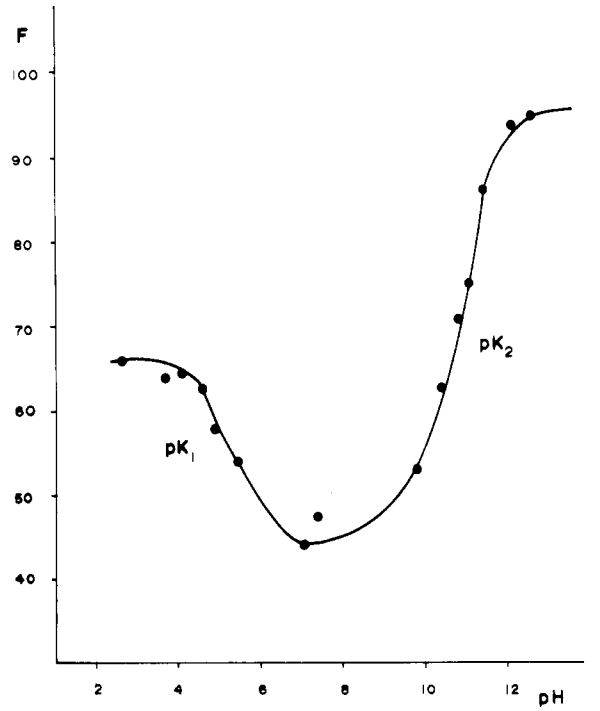

Figure 2. Effect of pH on fluorescence intensity of 5×10^{-5} M flurecol solution in a 40% DMF–water (v/v) mixture: λ_{ex} = 310 nm; λ_{em} = 495 nm.

one obtained with a 100% DMF percentage. For such a reason, the last conditions have been used for the experimental work.

In these conditions, the stability of the working solution 3×10^{-5} M) was studied by measuring the fluorescence intensity when exposed to light and storage in the dark. The same RFI with no changes was observed during the 2 h of the experiment. No extra precautions should be needed to carry out the measurements for the rest of the experimental work.

A linear increase in RFI with increasing flurecol concentration from 10^{-6} to 10^{-4} M was observed, with no fluorescence inversion occurring in this wide concentration range.

The application of synchronous derivatives to the normal spectrum of flurecol (Figure 1) could modify the analytical characteristics of the spectrofluorimetric method. For such a reason, the selection of the main instrumental parameters affecting both (wavelength increment $\Delta\lambda$; response time t_r; scanning speed V_{scan}) was carefully done. A solution of flurecol (11.30 μg/mL), prepared as indicated under analytical procedure, was chosen for this study. An increase in the RFI from 42 to 85 was observed when the scanning interval was increased from 160 to 200 nm, the latter corresponding to the Stokes shift.

Despite a good signal to noise ratio obtained with $\Delta\lambda$ = 200 nm, one maximum and two shoulders were observed in this spectrum, making the synchronous derivative measurements difficult (Figure 3a). This is avoided with the monochromators maximum scanning speed (120 nm/min), a slow response time (1.5 s), maximum wavelength increment (10 nm), and a slow chart recording speed (10 cm/min). The improvement obtained, indicating the analytical measurements for both first (DS1) and second (DS2) synchronous derivatives, is shown in Figure 3b.

Quantitative Analysis. The calibration curves were obtained by plotting the relative fluorescence intensity or relative intensity of the derivatives in centimeters against flurecol concentrations. The statistical treatment of the

Table II. Analytical Characteristics of the Methods Proposed for Flurecol

method	s_a, cm	s_A, μg/mL	c_L, ng/mL	linear dynamic range, μg/mL	$\bar{x}$, μg/mL	error, %	RSD, %
direct	0.1[a]	0.01	54.0	0.2–6.8	2.2	3.6	4.6
1st syn deriv	6.6	0.82	127.5	0.4–1.0	0.6	3.6	4.6
2nd syn deriv	5.1	0.46	40.9	0.1–1.0	0.7	2.3	2.9

[a] Value in relative fluorescence intensity.

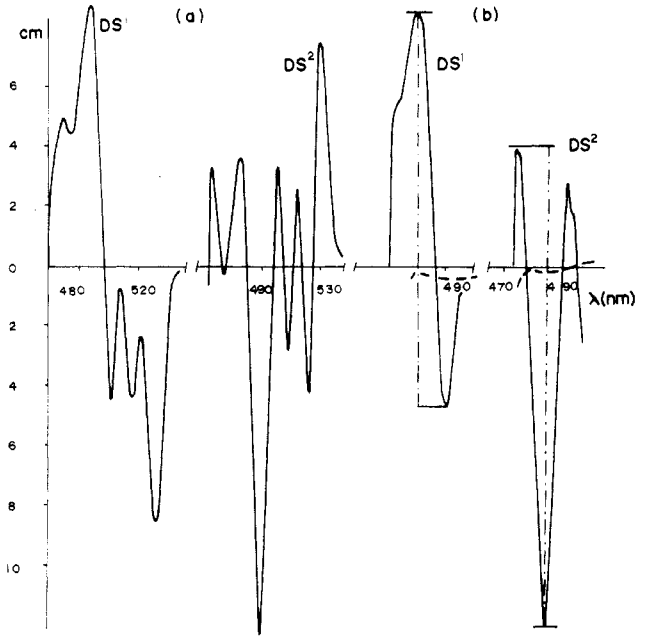

Figure 3. (a) Influence of monochromator scanning speed on the first (DS1) and second (DS2) synchronous derivatives and (b) analytical measurements for the quantitative determination of flurecol.

analytical data gave the following equations. From 0.56 to 6.80 μg/mL:

$$I_f = 9.44[\text{flurecol}] + 3.45 \qquad r = 0.9962 \qquad (3)$$

From 200 to 1000 ng/mL:

$$\text{DS1} = 0.008[\text{flurecol}] - 0.057 \qquad r = 0.9947 \qquad (4)$$

$$\text{DS2} = 0.011[\text{flurecol}] - 0.500 \qquad r = 0.9863 \qquad (5)$$

From these analytical data, it is deduced that the direct spectrofluorimetric method can be recommended for flurecol concentrations in the microgram per milliliter range while first and second synchronous derivatives would be preferred for lower concentrations (nanogram per milliliter levels).

Both C_L and C_Q (determination limit and lower limit of the linear dynamic range) and the sensitivity of the analytical determination were calculated from the definitions of the International Union of Pure and Applied Chemistry (IUPAC, 1980) and García-Sánchez and Cruces-Blanco (1986), respectively.

The results of these parameters together with those of the reproducibility assays (relative standard deviation, mean value, relative error) are indicated in Table II. Similar values of relative standard deviation and error are obtained for the different method tested, despite the 3 times smaller concentration used in the derivative measurements (2 and 0.6 μg/mL, respectively).

The synchronous second-derivative technique resulted in the lowest detection limit (40.90 ng/mL flurecol with an error of 2.28%).

Table III. Interference Study (Flurecol Concentrations 2.26 and 0.60 μg/mL)

interferent	flurecol to interferent molar ratio	recovery, % 2.26 μg/mL direct	0.60 μg/mL 1st deriv	0.60 μg/mL 2nd deriv
guthion	1:3	91.6		
	1:5		85.7	127.2
carbaryl	1:10	152.2		
	1:12		86.9	106.6
2,4,5-T	1:4	98.2		
	1:5		85.7	95.3
2,4-D	1:5	96.0	76.7	95.3
1-naphthol	1:12	139.8		
	1:20		128.7	114.1
colchicine	1:3	82.0		
	1:5		72.2	95.3
kinetin	1:5	77.4	81.2	99.1

Table IV. Recoveries of Flurecol from Soil Fortified at 6.80 mg/kg

solvent system	recovery, % direct	1st deriv	2nd deriv
methanol	109.0	95.7	90.0
acetone	39.7	60.1	137.0
benzene	301.7	108.0	46.6

Interference Study. Although the first- and second-derivative measurements provide only slight gains in sensitivity, they do provide greater selectivity in the presence of interferring compounds. The effects of various pesticides in the determination of 2.26 μg/mL and 600 ng/mL of flurecol by means of the different methods tested have been demonstrated.

Several insecticides (guthion, carbaryl, 1-naphthol), plant growth regulators (colchicine, kinetin), and phenoxy derivative herbicides ((2,4-dichlorophenoxy)acetic acid (2,4-D) and (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T)) that can occur with flurecol in real samples or commercial formulations have been tested. Different ratios of flurecol to interferent were tried at the concentration levels indicated above. These values together with the percentage recoveries obtained are indicated in Table III.

The tolerance criterion (Sommer et al., 1956) is defined as a function of the standard deviation for each particular method: $\bar{x} \pm ts$, where $\bar{x}$ is the mean flurecol concentration value for the reproducibility assay at 2.26 μg/mL and 600 ng/mL (see Table II), t is Student's t-test for nine values with a 99% confidence, and s is the standard deviation of the analytical signal.

Guthion, 2,4-D, and 2,4,5-T do not interfere when measured by the direct spectrofluorimetric method at molar tolerance ratios of 1:3, 1:4, and 1:5, respectively, but these ratios are amplified to 1:5 in all cases when using the synchronous derivative approach. From Table III, it is concluded that the best results are obtained by first and second synchronous derivative methods, especially the latter with recoveries between 95 and 127%.

Analysis of Soil Samples. As indicated above, flurecol and its main derivative flurecol-butyl are used in combination with phenoxyalkanoic acid herbicides for weed control in different crops at rates of 2–4 L/ha, which

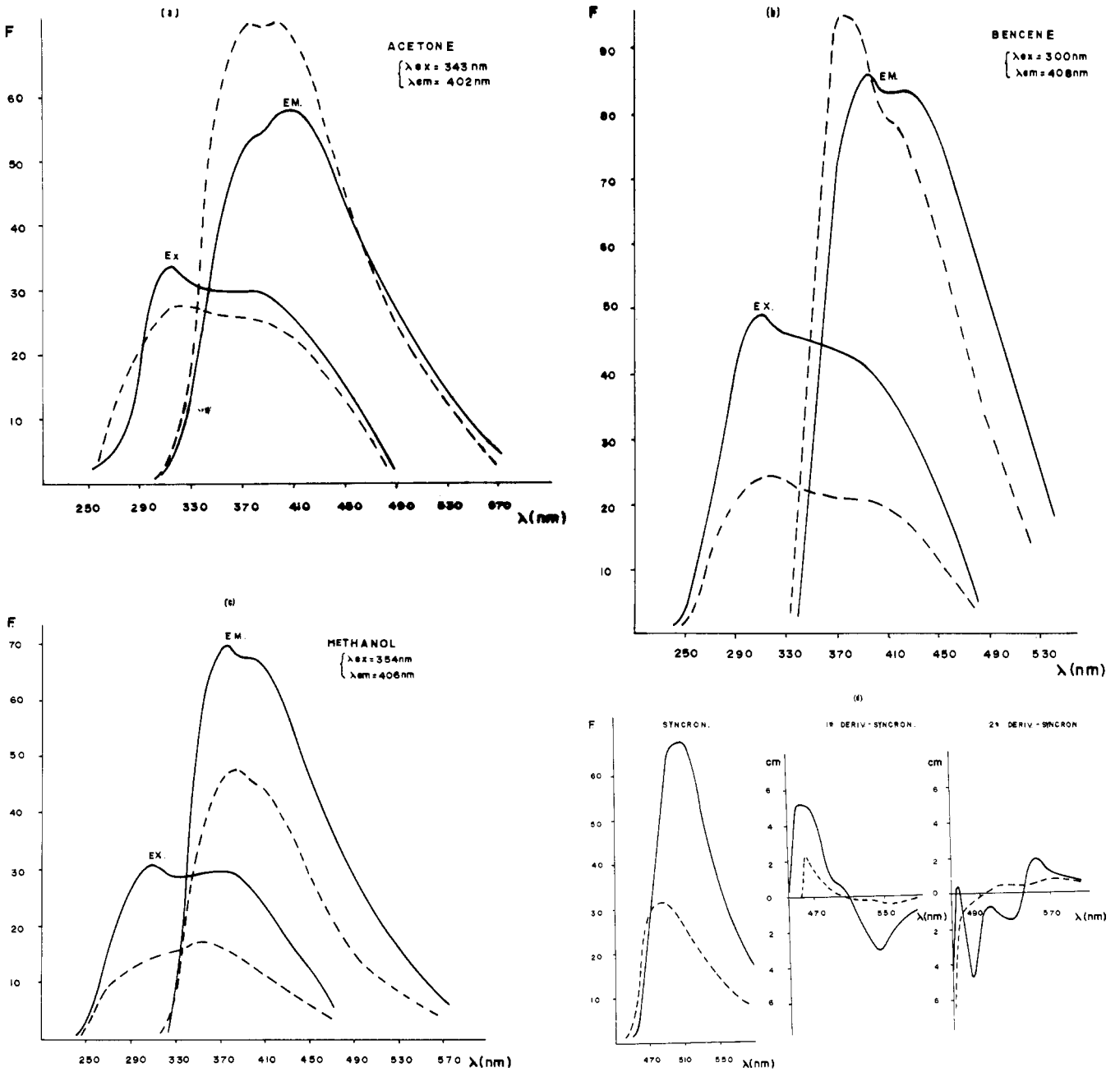

Figure 4. Fluorescence excitation and emission spectra of fortified at the 6.80 mg/kg level (—) and unfortified soil samples (- - -) extracted with acetone (a), benzene (b), and methanol (c) and the corresponding first and second synchronous derivatives with methanol extraction (d).

Table V. Analysis of Flurecol Residues in Ground Soil

flurecol added, μg/mL	extraction no.	direct		1st deriv		2nd deriv	
		a	*b*	*a*	*b*	*a*	*b*
6.8	1	6.2		5.6		6.1	
	2	6.1	92 ± 2	6.4	91 ± 7	6.1	88 ± 5
	3	6.4		6.7		5.5	
	4	6.4		6.2		6.3	
4.5	1	4.0		4.4		4.3	
	2	4.2	97 ± 7	4.2	95 ± 2	4.0	102 ± 11
	3	4.7		4.2		4.9	
	4	4.5		4.3		5.1	
2.3	1	2.5		2.5		2.3	
	2	2.4	103 ± 9	2.7	105 ± 15	1.9	92 ± 9
	3	2.0		2.3		2.1	
	4	2.4		2.0		2.1	

[a] Concentration found in micrograms per milliliter. [b] Percentage recovery.

persists in the soil for about 42 days.

Soil samples from a cultivated sugar cane field in south Spain (Motril, Granada) were used to demonstrate the applicability of the proposed spectrofluorimetric methods.

The first step in the analysis of pesticide residues is usually its separation from the material by solvent ex-

traction. For efficiency, the solvent must remove the pesticide in a reproducible manner without removing large amounts of interfering compounds from the substrate.

One of the most complicated procedures is the extraction of pesticides from soil (Klisenko, 1980), because the extraction efficiency is affected by the type of soil, the extracting properties, extracting method, etc. Klisenko (1980) has proposed the use of ultrasonic techniques to avoid the effect of soil water or organic matter content type of soil (Johnson and Starr, 1972) on the extraction efficiency. This can be due to the breakdown of soil structure allowing the extractant to work on a greater surface area. For such a reason, the ultrasonic technique was selected for the extraction procedure.

Some preliminary experiments were carried out to choose the best extracting solvent from those where flurecol presents maximum solubility (methanol, acetone, benzene). Sample aliquots were extracted with the three solvents according to the general method described above, and the results were compared for efficiency of extraction. These results and the corresponding excitation and emission spectra are indicated in Table IV and Figure 4, respectively.

Different recoveries were obtained in the three systems. With benzene and acetone, high RFI of the blank signals are observed, which implies that most interfering soil substances appear as coextractives. Methanol was chosen because it is the one that gives the better signal to noise ratio.

This is in accordance with other authors (McKone, 1969; Kahn et al., 1975; Cotterill, 1980; Peña-Heras and Sánchez-Rasero, 1986) that also found that methanol was the most efficient solvent. Systems using acetone and benzene (Johnson and Starr, 1972) are not recommended because the first one usually produce extracts containing high levels of extraneous soil constituents and the second one causes health hazards.

Comparing the three solvents tested, a bathochromic shift in the excitation wavelength is observed with increasing solvent polarity. No appreciable changes were observed in the emission maxima.

Due to the fact that broad excitation and emission spectra are obtained for the blank extracts, the application of the derivative technique clearly diminishes the corresponding blank signal and, consequently, increases the signal to noise ratio (see Figure 4d).

Having taken into account the above experiences, the direct and first and second synchronous derivative spectrofluorimetric methods proposed can be applied to the analysis of soil samples fortified with different concentrations of flurecol standard solution, following the extraction procedure indicated above.

In Table V, the results of concentration found and the corresponding percentage recoveries are indicated for the three methods proposed. The percentage data are accomplished with the relative standard deviation obtained after four individual extractions and three determinations. Blank signals corresponding to four individual extractions of untreated soil samples were subtracted from the recovery data. The percentage data are very similar for the different methods tested, and an increase with decreasing the analysis concentration is observed. This is due to the positive interference caused by soil coextractives.

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Registry No. Flurecol, 467-69-6.

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