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Determination of the Pesticide Napropamide in Soil, Pepper, and Tomato by Micelle-Stabilized Room-Temperature Phosphorescence

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A selective and sensitive method for determining napropamide by room-temperature phosphorescence in SDS micelles is proposed and applied to the determination of this substance in a technical formulation and in spiked soil, pepper, and tomato samples. The use of phosphorescence enhancers such as sodium dodecyl sulfate (micellar agent), thallium (I) nitrate (external heavy atom), and sodium sulfite (deoxygenation agent) was studied and optimized to obtain maximum sensitivity. The determination was performed in 66 mM SDS, 30 mM thallium (I) nitrate, and 8 mM sodium sulfite. Taking into account both maximum phosphorescence intensity and the time required to reach that, a pH value of 7.2 was selected. After the samples were left standing at room temperature for 10 min, the phosphorescence was totally developed. The intensity was then measured at $\lambda_{ex} = 282$ nm and $\lambda_{em} = 528$ nm. The calibration graph was linear for 50−600 ng mL^{-1} napropamide. The detection limit, according to the error propagation theory, was 16 ng mL^{-1}. The method has been demonstrated for the analysis of soils, peppers, and tomatoes, but, because of matrix interference, the method of standard additions was applied to determine napropamide in the vegetable samples. Recoveries from all these matrixes of added napropamide were near 100%.

KEYWORDS: Napropamide; phosphorimetry; room-temperature phosphorescence; soils; agricultural products; pepper; tomato

INTRODUCTION

Herbicides are chemicals often employed to kill weeds without causing injury to desirable vegetation. The agricultural use of herbicides has replaced human and mechanical weeding in developed countries. Herbicides have been the most widely used type of pesticide, and organic herbicides now dominate the market. Their high use on agrarian activity resulted in increasing need for sensitive analytical methods for herbicide determination in different matrixes, such as, soil, water, agricultural products, and biological fluids.

Phosphorimetry is characterized by high sensitivity, selectivity, a wide linear range, and small blank signals. Because at the triplet state it is readily deactivated by intermolecular vibrational relaxation, several methods have been used to minimize these deactivation mechanisms. One of these methods entails low-temperature rigid matrixes. Because of the difficulties associated with low-temperature phosphorescence (LTP), this technique has not been used extensively for the identification and determination of many compounds.

Room-temperature phosphorescence (RTP) allows various compounds to be measured, including substances of biological and pharmaceutical interest, pesticides, and polycyclic aromatic hydrocarbons (*1*−*4*). One of the methodologies employed is based on measuring the phosphorescence intensity emitted by the phosphor while fixed on an inert solid support such as filter paper (*5*−*8*), but this technique has the disadvantages of cumbersome sample preparation, critical drying requirements, and high phosphorescent background intensity from the filter paper substrate.

RTP can also be observed from many organic compounds in liquid solutions by incorporating the phosphors into organized media such as cyclodextrins, micellar systems, and microcrystalline media, or by using sensitized RTP. Micelle-stabilized room-temperature phosphorescence (MS−RTP), a type of RTP in solution first reported by Kalyanasundaram et al. (*9*), has been developed by several authors during the past decades (*10*−*13*). In a micellar solution the analytes included in the micellar assembly are apparently protected from the quenchers present in the solution. Observation of RTP in a micellar solution usually requires the presence of a heavy atom. It is placed as a counterion outside the micelle, thus being in proximity to the hydrophobic molecules associated with the micelle. The high local concentration of the heavy atoms produces an efficient spin−orbit coupling that can diminish the fluorescence and increase the phosphorescence. Furthermore, the micelles can effectively screen molecules in the excited triplet state from the action of potential quenchers present in the bulk water phase.

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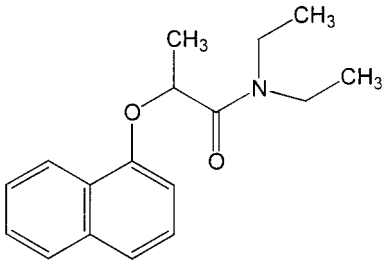

Figure 1. Chemical structure of napropamide.

However, deoxygenation is needed in all cases, as oxygen is a very efficient quencher that easily penetrates the micelles. The traditional MS−RTP method of using nitrogen purging to remove oxygen from solution, which is limited in application because of foam generation and other concomitant problems, has been replaced by a method proposed by Díaz-García and Sanz-Medel (*14*) based on a chemical deoxygenation with sodium sulfite, which represents a great technical advance in the use of MS−RTP. Because it is necessary to totally eliminate the oxygen in the micellar solution, sulfite ion can be used as an efficient oxygen scavenger in the micellar solution used for micelle-stabilized room-temperature phosphorescence. The method proposed for sample deoxygenation is based on the redox reaction of sulfite with molecular oxygen to product sulfate. In the presence of sulfite, however, the phosphorescence is not immediately observed. The oxygen in the bulk water phase is removed first, followed by that in the micelle pseudophases as it diffuses out. Equilibrium is achieved in a few minutes. The MS−RTP method, using sodium sulfite as oxygen scavenger, has been described to determine pesticides (*15*, *16*).

Napropamide [N, N-diethyl-2-(1-naphthalenyloxy) propanamide] is a residual herbicide appertaining to the amide series (**Figure 1**). It is quite polar and slightly soluble in water. Napropamide is used to regulate grasses and weeds in many agricultural cultivations. Only a few methods have been published on the determination of napropamide. Identification and quantification have been generally carried out by high-performance liquid chromatography (HPLC) (*17*−*20*) and HPLC with diode array detection (*21*, *22*) or gas chromatography (*23*, *24*). Moreover, there have been some reports in the literature describing liquid chromatography−mass spectrometry (*19*) for bioassay of napropamide enantiomers and the micellar extraction of napropamide combined with their quantification by fluorescence (*25*, *26*).

This paper demonstrates that the chemical deoxygenation micelle-stabilized room-temperature phosphorimetry may be successfully applied to the determination of napropamide in soil samples using a common spectrophotofluorometer. The various experimental conditions that contribute to the successful observation of phosphorescence in these systems for the determination of napropamide are discussed in detail, including micelle concentration, ratio of heavy atom/micelle, and sulfite concentration.

EXPERIMENTAL PROCEDURES

Caution. *Thallium salts are very toxic when inhaled, ingested, or absorbed through the skin.*

Apparatus. All phosphorimetric measurements were performed on an Aminco Bowman Series 2 luminescence spectrometer connected to OS2-based software. The instrument utilizes a 7 W integral pulsed Xenon lamp for phosphorescence measurements. Gated photomultiplier tube detection includes a unique masking method for detection with less than 200 μs after initiation of the flash lamp. Quartz glass cuvettes with a path length of 1.0 × 1.0 cm were used.

A Selecta ultrasonic bath, thermostatic equipment (Selecta 6000382), and a Crison model 2001 pH meter with a glass-saturated calomel combination electrode were also used.

Software. The AB2 program enabled the instrument to record excitation and emission spectra, total phosphorescence spectra, and time traces, such as decay curves and time-resolved curves. The Ftotal program (*27*) was used to generate fluorescence and phosphorescence contour spectra. Statistical analysis was performed by means of a program developed by us, which has an option menu that includes all the procedures mentioned in this paper.

Reagents. All experiments were performed with analytical reagent grade chemicals, pure solvents, and Milli-Q purified water. Napropamide (Riedel de Haën) is almost insoluble in water, so it was necessary to use an organic solvent. Sodium dodecyl sulfate (SDS) was obtained from Sigma, and thallium (I) nitrate and sodium sulfite were obtained from Merck. Sulfuric acid was supplied by Panreac.

A stock solution of napropamide (10.0 mg dissolved in 100 mL of 0.2 M SDS, using an ultrasonic bath to ensure complete dissolution) was diluted to prepare working standard solutions. This stock solution was stable for at least two weeks at room temperature. The working standard solutions of napropamide were stable for at least 2 days at room temperature.

Stock standard solutions of 0.2 M SDS, 0.25 M thallium (I) nitrate, and 0.02 M sulfuric acid solution were used. A 0.25 M sodium sulfite solution was prepared daily.

The herbicide technical formulation of Devrinol 45 LA, made by United Phosphorus Limited (Warrington, U.K.) and supplied by Agrimor (Agricultura Moderna S. A.) (Madrid, Spain), was labeled to contain 45% p/v of napropamide.

General Procedure. For the preparation of the calibration graph, an aliquot of napropamide standard solution was placed in a 25.0-mL volumetric flask at a final concentration of 50−600 ng mL^{-1}, then the following were added: SDS as required to give a 66 mM concentration; 3.0 mL of 0.25 M thallium (I) nitrate solution; 0.8 mL of 0.25 M sodium sulfite; 0.5 mL of 0.02 M sulfuric acid solution, and sufficient water to dilute to volume. Finally, the solution was shaken, a portion of the solution was transferred into a phosphorescence cuvette and kept for 10 min at 20 °C. Then, the intensity of RTP was measured at an excitation wavelength of 282 nm and an emission wavelength of 528 nm. Instrument settings were as follows: excitation monochromator 282 nm, both excitation and emission band-pass, 16 nm; detector voltage, 1100 V; flash lamp in phosphorescence, <200 μs with photomultiplier tube masked mode; delay after flash, 100 μs; gate width, 800 μs; and minimum flash period, 5 ms. The emission scan was applied from 450 to 700 nm with a 1-nm increment and a scan velocity of 5 nm s^{-1}.

Procedure for Commercial Technical Formulations. For determination of napropamide in a commercial phytosanitary product, Devrinol 45 LA, an aliquot of the sample, previously homogenized, was dissolved in 0.2 M SDS. Suitable volumes of this micellar solution were placed in 25-mL volumetric flasks in order to obtain final concentrations within the calibration graph. The general procedure was applied to these solutions.

Procedure for Soil Samples. The proposed method has been applied to soil samples taken from sites within Ciudad Real province (Spain). These samples were scooped out from the surface to 5-cm depth of the farming soil and returned to the laboratory in polyethylene bags. The samples were air dried and sifted to separate the <2-mm size fraction. The samples were ground with an agate mortar and then these were retained for analysis.

A known quantity of napropamide (ethanolic solution) was added to 10 g of sample in such a way that the final concentration was included in the calibration graph. The sample was extracted twice with 30 mL of dichloromethane and filtered on vacuum, and the dry residue was washed with 10 mL of dichloromethane. All these extracts were mixed, and the solvent was removed under vacuum using standard Schlenk-tube techniques. The residue was diluted to 100 mL with 0.2 M SDS. Then, 8.25 mL of the aqueous micellar phase was transferred into a 25-mL volumetric flask, and 3.0 mL of 0.25 M thallium (I) nitrate solution, 0.8 mL of 0.25 M sodium sulfite, and 0.5 mL of 0.02 M sulfuric acid solution were added. The mixture was diluted with water

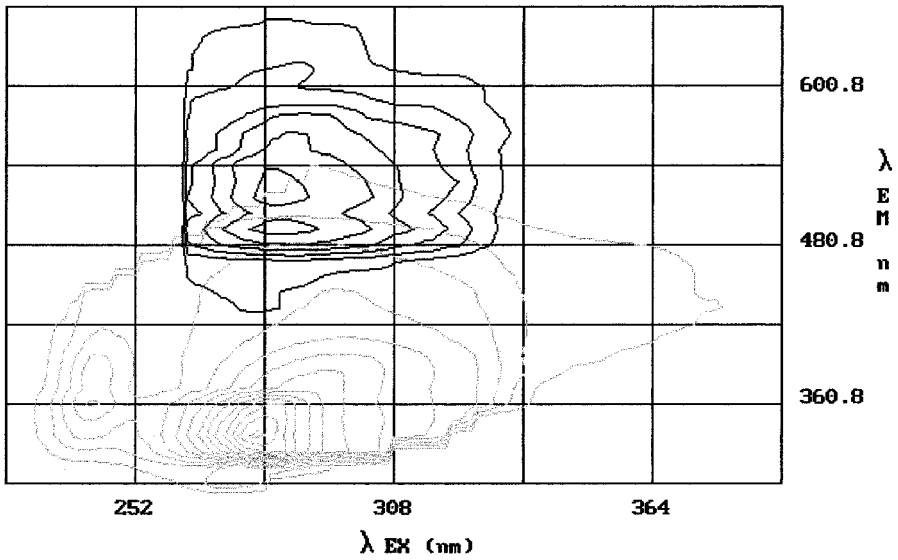

Figure 2. Total phosphorescence spectrum (black line) and total fluorescence spectrum (grey line) of napropamide. Photomultiplier voltage 1100 V in phosphorescence and 640 V in fluorescence.

to a final volume of 25 mL, and then the general procedure was followed.

Procedure for Pepper and Tomato Samples. Peppers (200−250 g) were chopped, blended, and triturated to form a homogeneous mixture. Approximately 10 g of the resulting aqueous slurry was transferred to four 250-mL conical flasks, each containing a known quantity of napropamide, and increasing quantities of the herbicide were added to three of them in such a way that the final concentration was included in the calibration graph. To each slurry was added 80 mL of dichloromethane, and the mixture was vigorously shaken for 10 min before being filtered on vacuum. Then 50 g of anhydrous sodium sulfate was added, and the extract was filtered through Albet No. 145 paper. The dichloromethane was removed by evaporation under vacuum using standard Schlenk-tube techniques. The residue was diluted to 100 mL with 0.2 M SDS. Then, 8.25 mL of the aqueous micellar phase was transferred into a 25-mL volumetric flask, and 3.0 mL of 0.25 M thallium (I) nitrate solution, 0.8 mL of 0.25 M sodium sulfite, and 0.5 mL of 0.02 M sulfuric acid solution were added. The mixture was diluted with water to a final volume of 25 mL. The intensity of RTP at 528 nm was measured in each of them with excitation wavelength of 282 nm. Least-squares adjustment was used on the straight line from the four points obtained when the phosphorescence intensity against the napropamide concentration added to the pepper solution was represented, and then the concentration of napropamide was calculated from the intercept point of the linear plot with the horizontal axis.

Tomato samples were extracted and pretreated by the same procedure as that used for pepper samples.

RESULTS AND DISCUSSION

Spectral Characteristics. The total luminescence spectrum can be transformed to a plot in the form of level curves or as a contour map where the *X* and *Y* axes constitute the excitation and emission wavelengths, while intensities are shown by lines joining the points of equal luminescence. This contour representation has generally been found to be more useful than the isometric projection for observing spectral characteristics because it indicates the presence of hidden emission peaks.

Figure 2 shows the total phosphorescence spectrum (black line) and the total fluorescence spectrum (grey line) of napropamide. The transition from ground singlet state to second singlet excited state (excitation fluorescence located at $\lambda_{ex} = 243$ nm) disappeared in phosphorescence, whereas the transition from the ground singlet state to the first singlet excited state (excitation fluorescence located at $\lambda_{ex} = 282$ nm) was retained

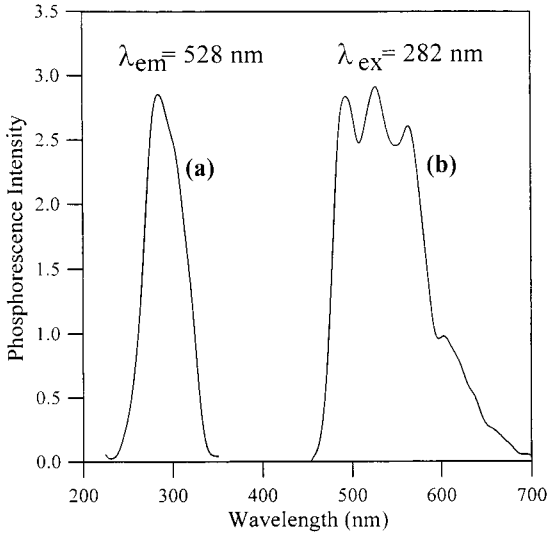

Figure 3. Room-temperature phosphorescence spectra of napropamide (600 ng mL^{-1}). Photomultiplier voltage 1100 V. (a) Excitation spectra; (b) emission spectra.

in phosphorescence. The emission corresponding to the transition from the first triplet excited state to the singlet ground state was unfolded into three maxima (phosphorescence excitation located at $\lambda_{ex} = 282$ nm, emission at $\lambda_{em1} = 492$, $\lambda_{em2} = 528$, $\lambda_{em3} = 564$ nm). In **Figure 3** the phosphorescence excitation spectrum at the emission wavelength of maximum intensity, i.e., $\lambda_{em} = 528$ nm, and the phosphorescence emission spectrum at 282 nm of excitation wavelength are shown. The fluorescence and phosphorescence spectra show different characteristic emission wavelengths. This difference of 164 nm gives an idea of the nonradiant energy that is lost in the intersystem crossing and the subsequent vibrational relaxation to the lowest vibrational level of the excited triplet.

The phosphorescence lifetime is the time required for the population of the excited triplet state to decrease to $^1/_e$ of its original value after the excitation source has been off. The lifetime is a means of considering the luminescence process in terms of rates. The phosphorescence lifetime of napropamide is approximately 234 μs. Fluorescence lifetimes are typically on the order of 1−20 ns. As phosphorescence is a spin forbidden

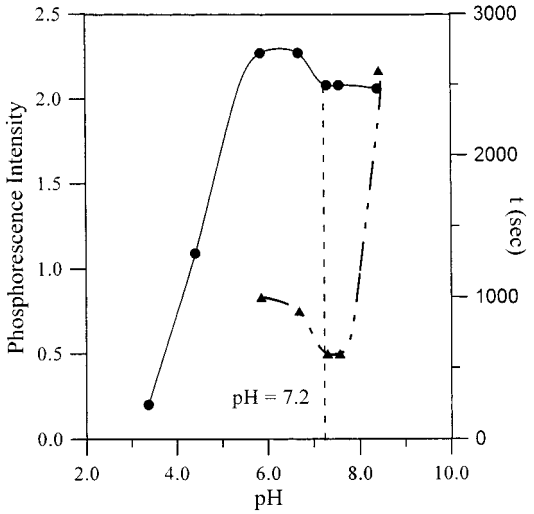

Figure 4. Effect of pH. ●, Room-temperature phosphorescence intensities. ▲ Time required to obtain a stable room-temperature phosphorescence signal (*t*).

process, phosphorescence lifetimes are considerably longer, generally ranging from milliseconds to seconds. Consequently, the phosphorescence lifetime is a measure of the forbiddenness of singlet−triplet transitions in a given molecule.

Factors Affecting Phosphorescence. Chemical variables were studied and optimized to obtain the best measurement conditions, which include the maximum and stable phosphorescent signal and adequate selectivity.

SDS was used to dissolve napropamide because its micellar properties, in addition to the semirigid structure of the solution, favor the development of phosphorescence. Besides SDS in this determination of napropamide, RTP required the use of thallium nitrate, which provides the heavy metal effect necessary to enhance the rate of intersystem crossing, and sodium sulfite for the total sample deoxygenation, thus avoiding the problem of extreme sensitivity of the triplet state to quenching by oxygen.

The concentration of sulfite in the system is an important factor that affected RTP intensity. Thus, the effect of Na_2SO_3 concentration was investigated by preparing samples in which Na_2SO_3 concentration was varied. It was observed that a concentration of Na_2SO_3 of 8 mM was required to eliminate oxygen completely from the solution, which was evident from the intensity of the phosphorescence signal. This signal decreased at higher concentrations of Na_2SO_3, which has been interpreted as the displacement of thallium(I) from the micelle because of the high concentration of sodium in the solution (*14*). On the other hand, it was observed that the time for phosphorescence signal to reach stability was shortened as Na_2SO_3 concentration increased. A Na_2SO_3 concentration of 8 mM was chosen for determination.

The pH is an important factor that affects RTP intensity of napropamide in this method. Thus, the influence of pH on phosphorescence intensity was studied by adding different amounts of H_2SO_4 and NaOH to a napropamide solution. In **Figure 4** phosphorescence intensity is plotted versus the pH of the solution, and, as can be readily observed, napropamide has maximum intensity in the range of pH 5.8−6.9, and in this experiment a slight decrease was observed under more basic conditions. The phosphorescence is not significant, and almost unobserved, at pH values up to 4.0 because in this case SO_3^{2-} exists mainly as HSO_3^- which has a lower deoxygenation efficiency. With increase in Na_2SO_3, the RTP intensity of the system increased gradually and finally stabilized. This period of time necessary for RTP to reach maximum intensity and stabilization is called *t*. As can be see in **Figure 4**, the *t* was obviously affected by pH, showing a *t* extremely large at pH values higher than 8.0. Thus, approximately 45 min was necessary to reach a phosphorescent signal maximum and stable at pH 8.5; and the higher the pH, the longer the *t*. Taking into account both maximum phosphorescence intensity and time required to reach that, a pH value of 7.2 was selected as best suited for the determination. Phosphate buffer was first used to adjust this pH value, but the phosphorescence intensity diminished. This is a quenching situation due to the formation of excipletes. The explanation for this behavior is that an excited napropamide molecule associates with the phosphate in the ground state. Consequently, the phosphorescence intensity of excited napropamide diminishes. This pH was subsequently adjusted by adding 0.5 mL of 0.02 M H_2SO_4.

Following the procedure described in the experimental section, it was determined how the phosphorescence intensity varies with changes in thallium concentration. **Figure 5a** illustrates this relationship for heavy metal concentrations between 5 and 35 mM. It is seen that the phosphorescence intensity increases with increase in thallium concentration. When the concentration of thallium was above 35 mM, the system precipitated, which may interfere with RTP measurement. For lower concentrations of thallium, the heavy atom effect is very sensitive. When the thallium salt is not present the phosphorescence intensity disappears. A thallium concentration of 30 mM was selected for the determination because it provides high intensity without problems of precipitation.

The effect of surfactant concentration was investigated by preparing samples with SDS concentrations ranging from 40 to 96 mM. The protection of micelle is the key to obtaining, and so to determining, napropamide by chemical deoxygenation micelle-stabilized room-temperature phosphorescence. Therefore, the RTP can be observed only when the surfactant concentration is suitable in the system. As **Figure 5b** shows, phosphorescence intensity of napropamide diminished as SDS concentration increased. For SDS concentrations lower than 40 mM precipitation occurred. A 66 mM concentration of SDS was chosen, giving good sensitivity while being sufficient to dissolve the napropamide, besides bringing a sufficiently high percentage to develop the micellar system.

Taking into account the two previous experiments, it can been concluded that phosphorescence intensity was at a maximum with SDS and thallium concentrations in a proportion of 2.2. **Figure 5c** shows phosphorescence intensity versus SDS concentration with SDS and thallium concentration in this same proportion. As can be observed, the phosphorescence intensity increases as the concentration of SDS increases, and this variation is small for SDS values higher than 44 mM. Concentrations of 66 mM SDS and 30 mM of thallium were selected as adequate. At concentrations of SDS above 77 mM, insolubility processes were observed in the samples.

The effect of temperature on RTP is a topic of great theoretical significance and of practical benefit in application (*4*). On increasing temperature, molecular thermomotion will be aggravated and the probability of radiationless transition will be increased. Meanwhile, the phosphorescence quantum yield will be decreased. Consequently, the influence of the temperature on the phosphorescence intensity was studied. It was observed that if the temperature is lower than 20 °C, precipitate appears in the system. Phosphorescence intensity decreased when the temperature increased from 20 to 70 °C. For temperature higher than 40 °C the phosphorescence signal

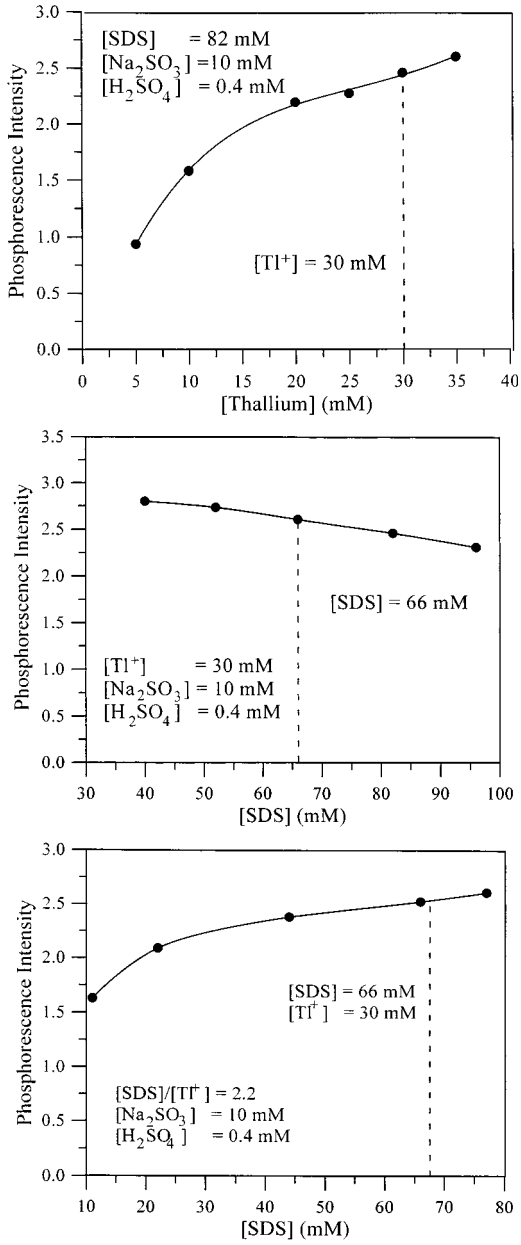

Figure 5. (a) Effect of thallium (I) concentration on phosphorescence intensity at an SDS concentration of 82 mM; (b) effect of SDS concentration phosphorescence intensity at a thallium (I) concentration of 30 mM; and (c) effect of SDS and thallium (I) on phosphorescence intensity at an SDS to thallium (I) ratio of 2.2.

disappeared (**Figure 6**). This decrease is measured by plotting the relative signal decrease (i.e., intensity at each temperature minus intensity at the highest temperature, divided by intensity at the lowest temperature and multiplied by 100) versus temperature. This relationship was linear and the slope (which is the temperature coefficient of napropamide) was 4.74% $°C^{-1}$. A temperature of 20 °C was selected for phosphorescence development and determination of napropamide. This temperature was controlled with a thermostatic bath.

The phosphorescence signal of the system can reach stability in 10 min under the condition of chemical deoxygenation, and it can remain stable at least 3 h.

The influence of napropamide concentration on phosphorescence intensity was studied under the above conditions. Phosphorescence intensity increased with napropamide concentration, until a constant value for napropamide concentration

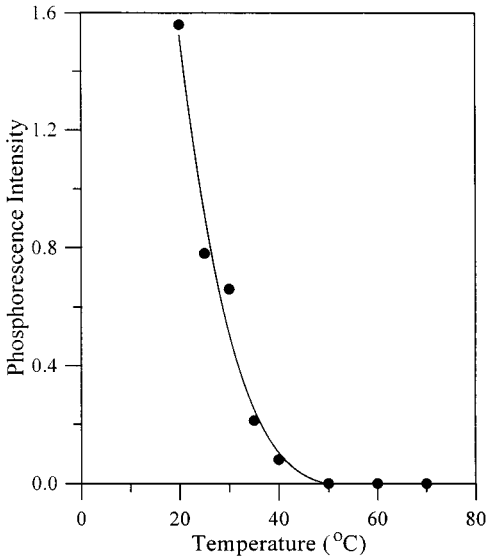

Figure 6. Effect of temperature on phosphorescence intensity of napropamide.

above 1000 ng mL^{-1} was reached. For higher levels, phosphorescence diminished. The napropamide concentration range for a linear relationship between phosphorescence intensity and concentration was found to be up to 600 ng mL^{-1}. Inner filter quenching due to high phosphorophor concentration, that is, deviation from the linear relationship between the concentration of napropamide to be assayed and the observed phosphorescence, becomes significant when the napropamide concentration exceeds 600 ng mL^{-1}. Consequently, calibration was performed for napropamide concentration up to 600 ng mL^{-1} with three replicates per point.

Calibration Curve and Analytical Parameters. Under the operating conditions previously specified, we propose a method to determine napropamide by direct measurement of phosphorescence intensity at 528 nm of emission wavelength and 282 nm of excitation wavelength in a concentration range 50−600 ng mL^{-1}. The delay time required was 100 μs. The best gate time and time between flashes to this delay were 800 μs and 5 ms, respectively. Other parameters selected for instrumental setup were excitation and emission band-pass of 16 nm, a photomultiplier tube voltage of 1100 V, and a scan rate of 5 nm s^{-1}.

A calibration graph was constructed with three replicates per point. **Figure 7** shows the average emission spectra of the calibration concentrations. A linear regression equation ($y = a + mx$) for napropamide was obtained. Statistical parameters of the calibration graph are summarized in **Table 1**. The linearity of standard curve in the usable concentration range and the negligible scatter of the experimental points is clearly evidenced by the high value of the determination coefficient.

A detection limit of 12 ng mL^{-1} was obtained by applying the IUPAC definition (*28*), in which only the standard deviation of the blank is considered. If the theory of error propagation is considered, the value of detection limit is consistent with the reliability of the blank measurements and the signal measurements of the standards (*29*, *30*). In this case, a detection limit of 16 ng mL^{-1} was obtained.

To study the repeatability of the method, a series of 10 solutions was prepared containing 300 ng mL^{-1} of napropamide. Their phosphorescence spectra were acquired and the intensity measurements were made according to the proposed method. By applying the IUPAC definition, a mean standard deviation

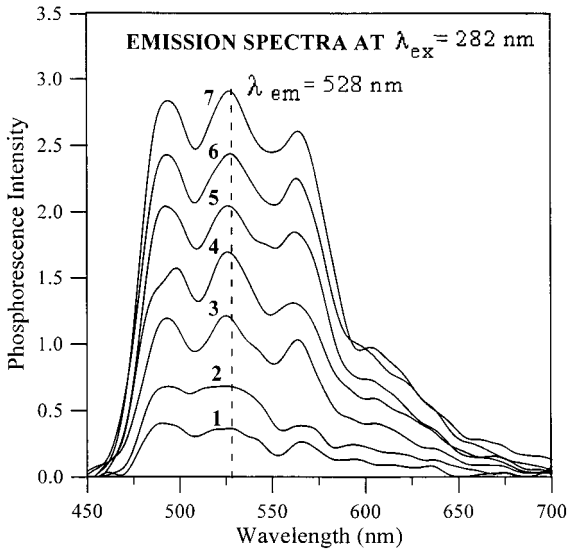

Figure 7. Set of room-temperature phosphorescence spectra. Napropamide concentrations: (1) 50; (2) 100; (3) 200; (4) 300; (5) 400; (6) 500; (7) 600 ng mL^{-1}.

Table 1. Analytical Characteristics for the Room-Temperature Phosphorimetric Determination of Napropamide

linear range (ng mL^{-1})	50–600
intercept on the *y*-axis (*a*)	0.231
standard deviation of intercept	0.052
slope (*m*)	4.51
standard deviation of slope	0.14
determination coefficient (r^2)	0.995
detection limit (ng mL^{-1})	16

value of replicates of 3.9 ng mL^{-1} and a relative error of 2.7% for napropamide were found at the 95% confidence level.

Determination of Napropamide in a Technical Formulation and Soil, Pepper and Tomato Samples. The above procedure has been applied to the analysis of napropamide in a commercial phytosanitary product, Devrinol 45 LA. Three determinations were carried out in three different packings of this technical preparation. The recovery percentages of napropamide, computed from the regression equation discussed above, were 97.6, 98.1, and 98.4% for a concentration level of 300 ng mL^{-1}. Recoveries achieved by means of the method proposed are in accordance with the real content of napropamide in commercial preparations.

Moreover, the proposed method has been applied to soil samples taken from sites within Ciudad Real province (Spain), and also to determine napropamide in Spanish agricultural products such as pepper and tomato. All these samples analyzed were either free of napropamide contamination or perhaps at lower concentration than the detection limit. Therefore, a recovery study was carried out with standard solutions of napropamide.

Initially, soil samples (10 g) spiked with napropamide were shaken for 30 min with 60 mL of 0.2 M SDS. The suspensions were filtered to remove the particles of soil. A portion of the separated micellar phases was analyzed following the phosphorimetric method described. A strong quenching effect due to the matrix was observed, which probably was caused by the presence of ionic compounds in the soil samples. So, a strategy based on the prior extraction of napropamide was developed to avoid the matrix interference. The high solubility of napropamide in dichloromethane permits the solvent extraction of this compound, as it is described in the section on soil samples procedures. The recovery ratios of known amounts of napropamide added to the soil were obtained by using the calibration graph (phosphorescence intensity vs concentration). The percentages of recovery, from the average of three determinations of three different samples, obtained for concentration levels of 200, 350, and 500 ng mL^{-1} were 98.6, 97.4, and 99.1%.

Finally, to determine napropamide in pepper and tomato samples spiked with the herbicide, the first procedure applied was similar to that realized in soil samples with a prior extraction of the herbicide in dichloromethane. Using the calibration graph obtained for micellar standard solution (described above), recoveries on the order of 70% were obtained. It was observed that pepper and tomato sample solutions containing napropamide gave phosphorescence intensities different from those obtained with micellar standard solution. For this reason, the method of standard additions (*31*), widely used as a powerful tool for the analysis of real-world samples when the analyses are inaccurate because of matrix effects in the system, was applied. Standard additions is performed by adding a small amount of standard solution to a portion of a previously analyzed sample and repeating the analysis using the same reagents, instrument, and technique. The amount of increase in the test result should exactly equal the amount of standard added to the sample. For maximum effectiveness, standard additions requires that the substance added be the same as the analyte, and, if possible, the same species. A shortcut method of a single addition is not advisable. Higher precision will be obtained if multiple additions of increasing concentrations are added to the sample rather than replicates of a single addition. Thus, the phosphorescence spectra of napropamide were obtained in different pepper and tomato samples, which were prepared as described in the procedures for pepper and tomato samples , to construct a calibration graph for each one of these two matrixes. Using the standard addition method, the recovery percentages in the pepper and tomato samples were 94.2 and 93.5%, respectively.

The selectivity of method has been studied. The proposed method has been applied in the presence of other pesticides. Compounds such as chlorfenac, 2,4-dicholorophenoxyacetic acid, 2-(2,4-dicholorophenoxy) propionic acid, isoproturon, propham, diuron, neburon, and linuron did not show interference. Naptalam, with a chemical structure similar to that of napropamide, did not interfere because it is not soluble in micellar medium. Only 2-naphthylacetic acid, 2-naphthoxyacetic acid, and carbaryl interfered in the proposed determination when these were present in a proportion of 1:1.

CONCLUSIONS

A sensitive and selective room-temperature phosphorimetric method using micellar medium is proposed, allowing the determination of napropamide in concentrations in the range 50−600 ng mL^{-1}. The determination of this herbicide was performed by measuring phosphorescence intensity within an emission wavelength of 528 nm after excitation at 282 nm with excellent repeatability and sensitivity. The proposed method is fairly sensitive, as can be seen by its application concentration range, showing a low detection limit.

Owing to the high selectivity of the phosphorimetric methods, the determination of napropamide by RTP shows no significant interferences and is suitable for its determination in commercial phytosanitary products. Other components of these technical formulations do not interfere in the phosphorescence spectra of napropamide. Moreover, adequate recovery values were obtained when the proposed method was applied to soil and

agricultural product samples which had been subjected to a previous extraction of napropamide in dichloromethane to avoid the matrix interference.

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