Prediction of the behaviour of organic pollutants using cloud point extraction

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Abstract

A preconcentration study based on the cloud point phenomenon was carried out for a set of triazine herbicides, three of them chloro-substituted and three of them methylthio-substituted. Concentration factors and recoveries were calculated as function of the percentage of the non-ionic surfactant Triton X-114 employed. From these values, obtained from a cloud point extraction (CPE) procedure, the distribution coefficient between the Triton X-114 micelles and water, K_c, prior to CPE was calculated for each triazine and related to the corresponding octanol–water partition coefficient, K_{ow}, In order to confirm the results obtained with the triazine herbicides, two sets of data from chemically different organic pollutants—organophosporous and chlorophenols—obtained from the literature were assessed, concluding that they display a similar behaviour to that of the triazine herbicides. This can be used to predict the CPE behaviour of other organic pollutants from their octanol–water partition coefficients. The K_c values were compared with the analyte concentration ratio in the surfactant-rich phase and aqueous phase (K_{sa}) with a view to obtaining a link between the analyte behaviour prior to and after cloud point extraction procedures.
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1. Introduction

Capillary electrophoresis (CE) is a technique widely used in both biochemical [1,2] and pharmaceutical analysis [3,4]. Over the past few years, CE has been successfully applied in the determination of

pollutants in samples of environmental interest [5,6] and appears to be a useful alternative technique in this field of analysis.

Owing to the low concentration levels permitted for organic pollutants in water samples and the low system loadability in CE, preconcentration steps are required to achieve success in this kind of analysis. Inorganic compounds can be satisfactorily determined in water samples using CE [7,8]. Organic pollutants, mainly phenolic derivatives, have recently been analysed in water samples using CE with on-

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line stacking [9,10] or solid-phase extraction (SPE) as preconcentration procedures [11,12].

The use of surfactant-mediated phase separations, also known as cloud point extraction (CPE), offers an alternative environmentally benign separation approach to more conventional extraction systems [13]. With this methodology, a fairly small volume of surfactant-rich phase is obtained and this permits the design of extraction procedures that are simpler and of lower toxicity than those employing organic solvents. During the past few years, this preconcentration methodology has been applied in the determination of inorganic pollutants in water samples, employing atomic absorption spectrometry [14,15] and atomic emission spectrometry [16,17]. Organic pollutants in environmental samples can also be preconcentrated with this methodology [18]; namely, polycyclic aromatic hydrocarbons (PAHs) [19], polychlorinated biphenyls (PCBs) [20] and fulvic and humic acids [21] in water samples, employing high-performance liquid chromatography (HPLC) for their later separation and analysis.

Recently, the application of CPE to CE has been described [22] and successfully applied for the determination of triazine herbicides in water samples. In the present paper, concentration factors and extraction recoveries for these analytes were studied as a function of the concentration of the surfactant employed in CPE. From the experimental values thus obtained, the distribution coefficients for the triazines and other organic pollutants in the Triton X-114 micelles–water system, K_c, were calculated. These distribution coefficients were correlated with the octanol–water partition coefficients of the analytes tested, K_{ow}, in order to predict the CPE behaviour of other analytes from only their K_{ow} values. Finally, the K_c value was related to the analyte concentration rate in the surfactant-rich phase and aqueous phase, K_{sa}, to obtain a link between the analyte behaviour before and after cloud point phenomenon.

2. Experimental

2.1. Apparatus

Capillary electrophoresis was performed with a P/ACE 2000 (Beckman Instruments, CA, USA)

apparatus equipped with a UV detector. Standard P/ACE capillaries were used: 57 cm (detection at 50 cm)×75 μm I.D.

A Kokusan H-103 N centrifuge was used for separation of the two phases obtained by the cloud point methodology. A Rotavapor (Buchs, Switzerland) was used for evaporating off the water in the surfactant-rich phase.
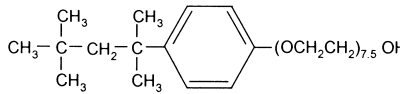
2.2. Reagents

All triazine herbicides were obtained from Riedel-de Häen (Seelze-Hannover, Germany) and were used without further purification (minimum percent purity greater than 98%). The chlorotriazines studied were as follows: atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine], simazine [2-chloro-4,6-bis(ethylamino)-1,3,5-triazine], and propazine [2-chloro-4,6-bis-(isopropylamino)-1,3,5-triazine]. The methylthiotriazines studied were ametryn [2-(methylthio)-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine], prometryn [2-(methylthio)-4,6-bis(isopropylamino)-1,3,5-triazine], and terbutryn [2-(methylthio)-4-(ethylamino)-6-(terbutylamino)-1,3,5-triazine]. Stock solutions of each triazine were prepared in methanol at 500 mg l^{-1}.

The surfactants Triton X-114 (Table 1) and sodium dodecyl sulphate (SDS) were obtained from Fluka (Buchs, Switzerland) and were used without further purification. The organic solvents, acetonitrile (ACN) and methanol (MeOH), were of HPLC grade (Carlo Erba, Milan, Italy) and were used as received. Ultra-high quality water obtained with an Elgastat UHQ water-purification system was used. All chemicals used for the preparation of buffer electrolytes were of analytical reagent grade.

2.3. Cloud point preconcentration procedure

Deionised aqueous solutions (100 ml) of Triton X-114 were prepared in the range 0.25–6% (w/v). Ten-ml aliquots were placed in a graduated centrifuge tube and heated for 10 min in a thermostatted bath at 40 °C, triggering the cloud point effect and the appearance of two phases. These two phases—the aqueous phase and the surfactant-rich phase—

Table 1
Structure and micellar characteristics of the non-ionic surfactant Triton X-114

Structure	Name	Abbreviation	CMC ($\times 10^{-3}$ mol l^{-1})	M_r	CPT (°C)
	t-Octylphenoxy polyoxyethylene ether	OPE$_{7.5}$ Triton X-114	0.27$_5$	536.72	22–25

CMC, critical micellar concentration [13]; M_r, average molecular mass; CPT, cloud point temperature for solutions in which the Triton X-114 concentration was in the 0.2–6% (w/v) range [24].

were separated by centrifugation for 15 min at 3500 rpm (2195 g).

2.4. Nonaqueous capillary zone electrophoresis separation of triazines

Uncoated capillaries were used throughout the study. Before use, all new capillaries were pretreated as described elsewhere [23]. Before each injection, the capillaries were rinsed for 2 min with methanol and 3 min with the separation buffer, applying a voltage of 22 kV. Electrokinetic injection at 5 kV over 15 s was employed to introduce the samples into the capillary. Analyses were performed with an applied voltage of 22 kV with the capillary thermostatted at 25±1 °C and with UV detection at 214 nm. The separation medium was ACN–MeOH (50:50, v/v), 0.010 mol l^{-1} perchloric acid and 0.020 mol l^{-1} SDS. Electrolyte solutions of perchloric acid in ACN–MeOH (50:50, v/v) were prepared. These solutions must be used freshly since SDS run buffers may undergo acid-catalysed hydrolysis after long storage.

2.5. Preparation of sample for injection

To obtain samples for injection, a 100-μl aliquot of the surfactant-rich phase obtained after CPE was collected with a Hamilton syringe and placed in a rotavapor at 70 °C for 10 min to remove all water present in the surfactant-rich phase aliquot. The dry residue containing Triton X-114 and the analytes thus obtained (if present in the initial sample) was diluted with an appropriate volume of a solution containing ACN–MeOH (70:30, v/v), 0.002 mol l^{-1} perchloric acid to achieve a final percentage of

Triton X-114 of 10% (w/v) (solution A). Then 70 μl of this latter solution was placed in a microvial for injection in the CE system. With this protocol, it is possible to achieve maximum sensitivity in the nonaqueous capillary zone electrophoresis separation of triazines [22].

2.6. Procedure for the determination of concentration factors and recoveries

The concentration factor, F_c (Eq. (1)), is the ratio between the concentration of the analyte in the sample injected (C_{fin}) and the concentration of the analyte in the initial sample before preconcentration (C_{ini}):

$$F_c = \frac{C_{fin}}{C_{ini}} \tag{1}$$

Recovery, R (%) (Eq. (2)), is the ratio (expressed in %) between the mass of an analyte in the injection sample (m_{fin}) and the maximum theoretical possible mass of the analyte in the injection sample if no loss of this occurs along the whole preconcentration procedure (m_{theor}):

$$R\,(\%) = \frac{m_{fin}}{m_{theor}} \cdot 100 \tag{2}$$

Experiments were carried out as follows: two 100-ml deionised water samples were prepared for each percentage of Triton X-114 studied (0.25–6.0%, w/v, range), one of them free of triazine and the other spiked with different triazine stock solutions at concentrations of: ametryn, 1.00 μg l^{-1}, terbutryn, 1.02 μg l^{-1}, prometryn, 1.04 μg l^{-1}, simazine, 4.36 μg l^{-1}, atrazine, 2.62 μg l^{-1}, propazine, 2.04 μg

l^{-1}. These concentrations were designated C_{ini}. Three 10-ml aliquots were obtained from the spiked water sample and two from the non-spiked one, and the CPE procedure was applied to the five aliquots at the same time.

Following that, the surfactant-rich phase volume was recorded, and a 100-µl fraction of the surfactant-rich phase present in each of the five centrifuge tubes was collected and successively prepared for CE injection, as explained in Section 2.5. The two fractions coming from the non-spiked water sample were dissolved with a suitable volume of solution to obtain a final Triton X-114 percentage of 10% (w/v). The composition of this solution (solution B) was ACN–MeOH (70:30, v/v), 0.002 mol l^{-1} perchloric acid and triazines at concentrations of: ametryn, 15.1 µg l^{-1}, terbutryn, 14.8 µg l^{-1}, prometryn, 14.8 µg l^{-1}, simazine, 14.8 µg l^{-1}, atrazine, 14.2 µg l^{-1}, propazine, 14.8 µg l^{-1}. These concentrations were designated C_{std}. These two dissolved fractions spiked after the CPE procedure were used as standards to obtain—by comparison with the other three dissolved fractions—the F_c and R (%) of the triazines in the whole CPE procedure.

All dissolved fractions were injected in the electrophoretic system as described in Section 2, and peak areas (NPAs) normalized against migration time were evaluated. The NPAs of the three injected samples coming from the sample spiked *before* CPE were designated NPA_{SB} and those two that were spiked *after* the CPE procedure were named NPA_{SA}.

It has been reported above that a suitable volume was used to dissolve the dry residue in order to obtain an injection sample with 10% (w/v) of Triton X-114. This added volume, V_{ad}, was calculated as follows: when CPE is applied with Triton X-114 and centrifugation is carried out, two phases are present. The upper is an aqueous solution that contains the Triton X-114 at a concentration close to its critical micelle concentration (cmc). The lower one is the surfactant rich phase that contains all the rest of the Triton X-114 and water. Eq. (3) gives the amount of Triton X-114 in the dry residue; i.e. when all the water of the surfactant-rich phase is removed, taking into account that the initial volume to be preconcentrated, V_{ini}, is the sum of the surfactant-rich phase volume, V_{sp}, and the aqueous phase volume, V_{aq}, after the centrifugation step, as observed experimentally:

$$m_{TX} = \left[\% \, T_{ini} \cdot \frac{V_{ini}}{100} - \% \, cmc \cdot \frac{(V_{ini} - V_{sp})}{100} \right] \cdot \frac{0.1}{V_{sp}} \tag{3}$$

m_{TX} is the mass in grams of the dry residue of Triton X-114, % T_{ini} and % cmc are the concentration and critical micelle concentration of Triton X-114 expressed as percentages (w/v) in the initial volume of preconcentrated solution, respectively. All the volumes are expressed in millilitres, been V_{ini} 10 ml.

Once the amount of Triton X-114 present in the surfactant-rich phase has been calculated, it is possible to add a suitable volume of solution A or solution B (depending on whether the fraction comes from the spiked water sample or non-spiked water sample, respectively), to reach the final percentage of 10% (w/v) of Triton X-114. It was experimentally concluded that to obtain a 10% (w/v) of Triton X-114 it is necessary to add 11.7 ml of solution A per gram of Triton X-114 to reach that percentage. Accordingly, the added volume, V_{ad}, in millilitres, was calculated in each case from Eq. (4):

$$V_{ad} = 11.7 m_{TX} \tag{4}$$

The injected sample volume, V_{fin}, in millilitres, can be calculated, Eq. (5), recalling that the concentration of Triton X-114 in the injected sample is 10% (w/v):

$$V_{fin} = 10 m_{TX} \tag{5}$$

For the experimental determination of F_c, Eq. (6) was employed, which was obtained from Eqs. (1), (4) and (5). Likewise, the experimental determination of R (%) was accomplished from Eq. (7), which was obtained from Eqs. (2), (1), (5) and (3):

$$F_c = \frac{NPA_{SB}}{NPA_{SA}} \cdot \frac{C_{std}}{C_{ini}} \cdot 1.17 \tag{6}$$

$$R \, (\%) = F_c \cdot \left[\% \, T_{ini} - \% \, cmc \cdot \left(1 - \frac{V_{sp}}{V_{ini}} \right) \right] \cdot 10 \tag{7}$$

The NPA_{SA} used was the average value of the two injected samples spiked after the CPE procedure.

3. Results and discussion

3.1. Concentration factor and recovery of each triazine as a function of the Triton X-114 concentration employed in the CPE procedure

The experimental values of R (%) and F_c for the triazines are depicted in Figs. 1 and 2, respectively, plotted versus the initial aqueous concentration of Triton X-114 employed in the CPE procedure. The variability observed in the figures is acceptable bearing in mind that the whole procedure involves complex sample handling together with non-aqueous CZE injection and separation.

The maximum concentration factor for all the triazines was reached when the lowest percentage of Triton X-114 was used, as expected. This is why the proposed CPE preconcentration procedure [22] employs 0.25% (w/v) of Triton X-114. By contrast, the use of high percentages of Triton X-114 afforded the best recoveries for all analytes, as was also expected.

3.2. Determination of the distribution coefficients, K_c, for the triazines

The origin of the cloud point phenomenon is currently a mater of debate. Theoretical thermodynamic models have been developed and the kinetic features of such phase-separation processes have been studied [13]. Recently, correlations between the structure of non-ionic surfactants (of the poly(oxyethylene)-alkyl-ether type) and their physicochemical properties, such as the cmc, partial molar volume, density and cloud point temperature, have been proposed and discussed [25].

Different approaches to CPE can be made (Fig. 3). One of them is direct study of analyte partitioning between the two phases that appears after cloud point extraction: the surfactant-rich phase and the aqueous phase [26,27], K_{sa}. Another way is to start from the distribution coefficient between the surfactant micelles and water in the initial solution, K_c (Eq. (8)). $C_{analyte,mc}$ is the concentration of the analyte in the micellar system and $C_{analyte,aq}$ is the concentration of the analyte in the aqueous system before cloud point phenomenon has occurred:

$$K_{c,analyte} = \frac{C_{analyte,mc}}{C_{analyte,aq}} \tag{8}$$

In this work the relationship between this coefficient, which is well known to be a thermodynamic constant [28,29], and CPE was obtained for groups of chemically different compounds. Finally, the K_c coefficient is related with K_{sa}, showing when K_{sa} coefficient works as a real constant parameter.

In this section, calculation of distribution coefficients in the Triton X-114 micelles–water system for the triazines studied, K_c, was performed using their experimental data of R (%) and on the basis of what might occur during CPE.

According to Terabe et al. [30], the distribution of an analyte in an aqueous micellar system can be described as in Eq. (9), where $n_{analyte,mc}$ and $n_{analyte,aq}$ refer to the number of moles of the analyte in the micelles and water, respectively; K_c is defined as in Eq. (8); v_{mc} is the partial molar volume of surfactant in the micellar states, and $C_{surfactant}$ is the analytical concentration of the surfactant and cmc its critical micelle concentration:

$$\frac{n_{analyte,mc}}{n_{analyte,aq}} = K_c \cdot \frac{v_{mc}(C_{surfactant} - cmc)}{1 - v_{mc}(C_{surfactant} - cmc)} \tag{9}$$

Thus, before the formation of the two phases, the distribution of a triazine between Triton X-114 and water can be described as in Eq. (9), or—changing units—as in Eq. (10), where $n_{triazine,TXmc}$ and $n_{triazine,aq}$ refer to the number of moles of triazine in the micelles of Triton X-114 and water, respectively; v_{TXmc} is the partial molar volume of Triton X-114 in the micellar states expressed in millilitres per mol; $M_{r,TX}$ is the molecular mass of the Triton X-114. The Triton X-114 concentration and its critical micellar concentration are expressed as percentages (w/v):

$$\frac{n_{triazine,TXmc}}{n_{triazine,aq}} = K_c \cdot \frac{v_{TXmc}(\% \, T_{ini} - \% \, cmc) \cdot \dfrac{10^{-2}}{M_{r,TX}}}{1 - v_{TXmc}(\% \, T_{ini} - \% \, cmc) \cdot \dfrac{10^{-2}}{M_{r,TX}}} \tag{10}$$

An experimental study was carried out to determine the partial molar volume of Triton X-114 in the micellar states. A value of 502 ml mol^{-1} was found, using a Triton X-114 molecular mass of 536.72. It
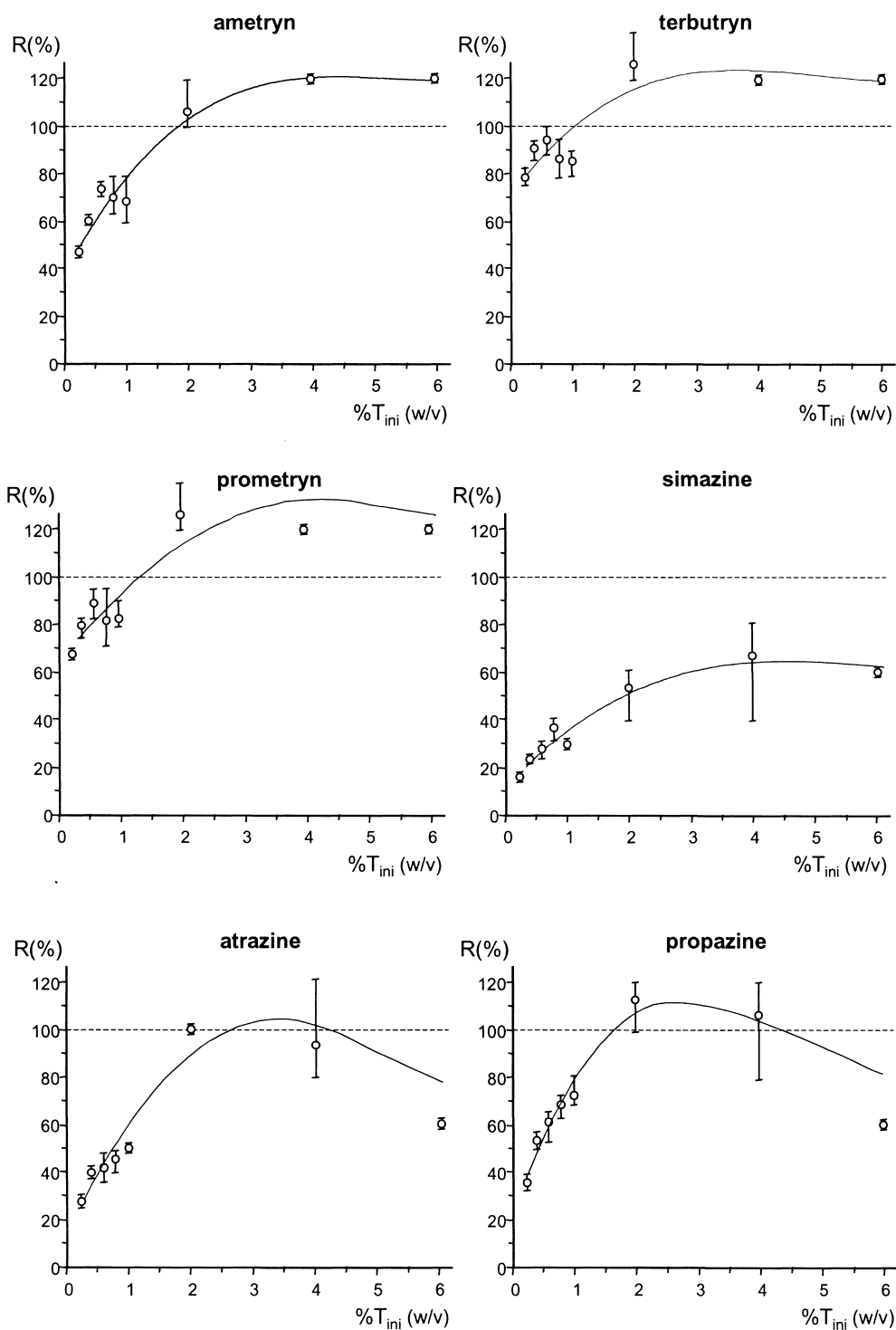
Fig. 1. Recovery, *R* (%), of each triazine for the entire CPE procedure against the initial aqueous concentration of Triton X-114. Dotted line corresponds to the maximum possible value. Three replicates of each point.

Fig. 2. Concentration factor, F_c, of each triazine for the entire CPE procedure against the initial aqueous concentration of Triton X-114. Dotted line corresponds to the maximum possible value. Three replicates of each point.
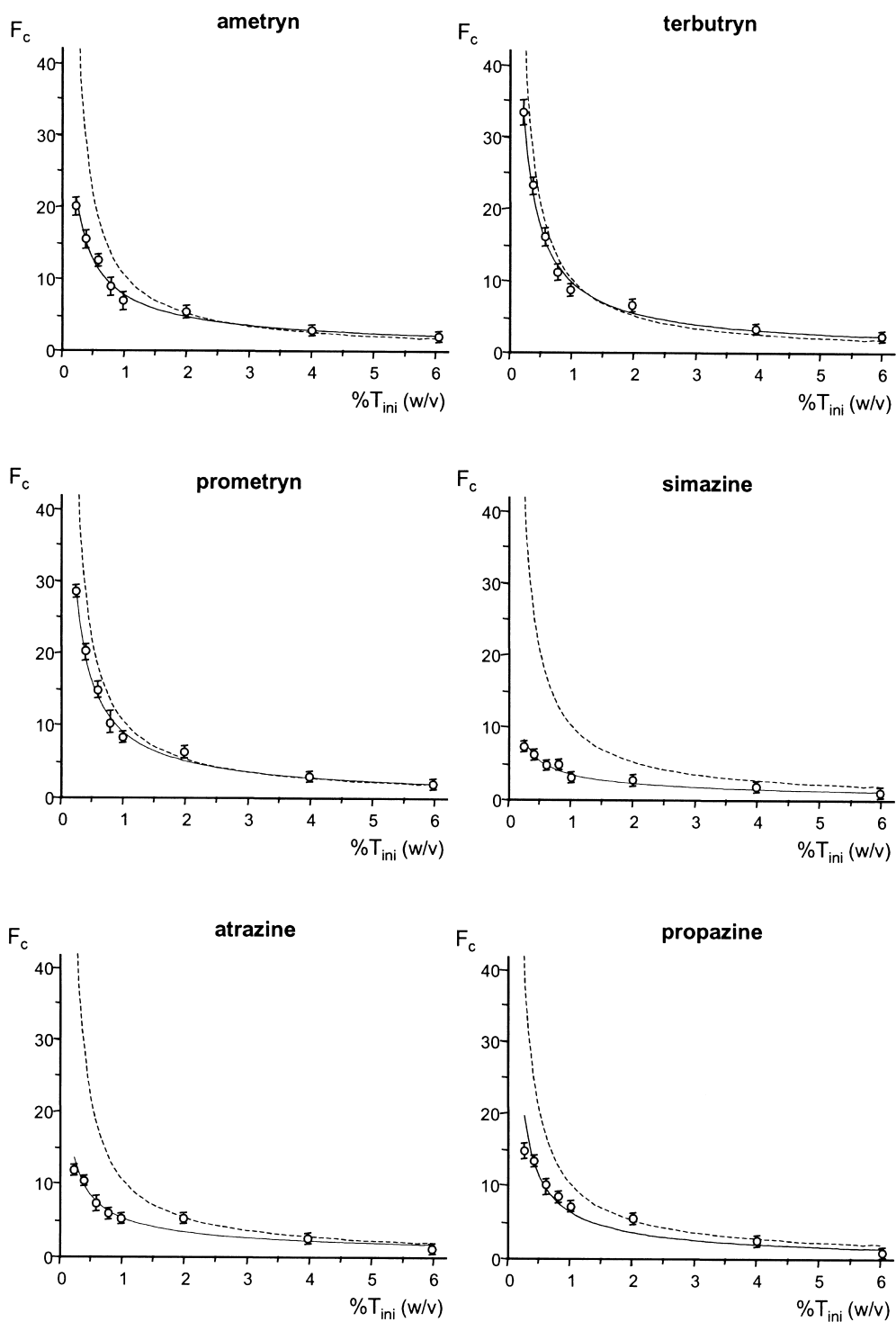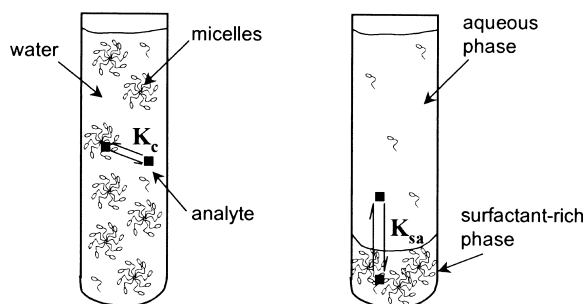
Fig. 3. Two different kinds of distribution coefficients.

was concluded that this value remains constant throughout the 0.22–10% range (w/v) of aqueous Triton X-114 solutions. With this value, an approximation can be made in Eq. (10) (i.e. Eq. (11)) due to the fact that the denominator term "$v_{\text{TXmc}}(\% \, T_{\text{ini}} - \% \, \text{cmc})(10^{-2}/M_{\text{r,TX}})$" can be rejected against unity for any value of Triton X-114 concentration in the whole range (0.25–6.0%, w/v):

$$\frac{n_{\text{triazine,TXmc}}}{n_{\text{triazine,aq}}} = K_c v_{\text{TXmc}} \cdot (\% \, T_{\text{ini}} - \% \, \text{cmc}) \cdot \frac{10^{-2}}{M_{\text{r,TX}}}$$

$$(11)$$

After the appearance of the cloud point phenomenon

and centrifugation, the distribution of the triazine between the surfactant-rich phase and the aqueous phase is not known, although the following hypothesis can be made: the same amount of triazine that before cloud point phenomenon was associated with Triton X-114 micelles remains entrapped in the surfactant-rich phase after extraction and centrifugation (Eq. (12), where $n_{\text{triazine,sp}}$ and $n_{\text{triazine,ap}}$ refer to the number of moles of triazine in the surfactant-rich phase and aqueous phase, respectively, after the CPE procedure):

$$\begin{aligned} n_{\text{triazine,TXmc}} &= n_{\text{triazine,sp}} \\ n_{\text{triazine,aq}} &= n_{\text{triazine,ap}} \end{aligned} \qquad (12)$$

With this assumption, it is possible to obtain a hypothetically linear relationship between the experimental values of R (%) of the triazine and the initial Triton X-114 percentage employed in the CPE procedure (Eq. (13)):

$$\frac{100}{R \, (\%)} = \frac{A}{K_c} \cdot \frac{1}{(\% \, T_{\text{ini}} - \% \, \text{cmc})} + 1$$

where $A = \dfrac{10^2 M_{\text{r,TX}}}{v_{\text{TXmc}}}$

$$(13)$$

Table 2 shows the linear correlation parameters when

Table 2
Linear regression parameters and calculated K_c [a] values for each triazine

	$\dfrac{100}{R \, (\%)}$ $vs.$ $\dfrac{1}{(\% \, T_{\text{ini}} - \% \, \text{cmc})}$			log K_c	Log K_{ow} [b]
	Slope	Intercept	r^2		
Ametryn	0.23±0.20	1.01±0.36	0.924	2.66±0.38	2.63 [31]
					2.83 [33]
Terbutryn	0.07±0.02	0.98±0.05	0.993	3.18±0.11	3.48 [31]
					3.74 [32]
					3.65 [33]
Prometryn	0.14±0.02	0.88±0.05	0.998	2.87±0.06	3.1 [31]
					2.99 [33]
Simazine	1.22±0.13	1.11±0.29	0.994	1.94±0.05	2.10 [31]
					2.10 [32]
					2.03 [33]
Atrazine	0.60±0.17	1.13±0.44	0.992	2.25±0.12	2.5 [31]
					2.66 [32]
					2.47 [33]
Propazine	0.38±0.09	0.90±0.16	0.994	2.45±0.10	2.89 [33]

[a] Calculated from slope and Eq. (10). Confidence intervals for 95% significance. Three to four replicates each point.
[b] Octanol–water partition coefficients for triazine herbicides reported in the literature.

the first term of Eq. (13) is plotted against the variable part of the second term of Eq. (13).

If the assumption represented in Eq. (12) is possible, Eq. (13) must be fulfilled. Thus, a linear relationship of positive slope and with the intercept close to unity must be found. The parameters shown in Table 2 describe an acceptable linear regression coefficient for all triazines, with an intercept value close to unity, as expected. Table 2 shows the K_c values calculated from Eq. (13) for all the triazines, using the experimental partial molar volume for Triton X-114 in the micellar states and the mean molecular mass for Triton X-114 from Table 1.

The distribution coefficients observed in Table 2 show that the hydrophobicity order of the triazine herbicides studied is terbutryn>prometryn>ametryn>propazine>atrazine>simazine. The log K_{ow} coefficients for these analytes, shown in Table 2, follow almost exactly the same hydrophobicity order.

3.3. Determination of the distribution coefficients, K_c, for other organic pollutants in CPE

In order to confirm that Eq. (12) can be extrapolated to analytes other than the triazine herbicides studied, data sets found in literature concerning CPE

for organophosphorus pesticides [34] (paraoxon, methylparathion, phenitrothion, ethylparathion) and chlorophenol pollutants [35] (2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol) were tested.

CPE was applied to the organophosphorus pesticides studied by the above author [34] as follows: a 10-ml aqueous solution containing the pesticides was heated in a water bath at 40 °C to induce the cloud point phenomenon. On comparing the HPLC–UV signal from the aqueous solution after the centrifugation step and the signal from the aqueous solution prior to CPE for each pesticide, that author obtained the F_c values for the analytes for each initial Triton X-114 percentage employed. R (%) values were calculated from these F_c data and the V_{ini}/V_{sp} experimental relation.

In the case of chlorophenol pollutants the CPE procedure was accomplished by the above authors [35] as follows: a 10-ml aqueous solution containing the analytes plus 0.6 mol l^{-1} sodium chloride was heated to 65 °C to induce the cloud point phenomenon. Following this, the tubes were centrifuged and chilled in an ice bath to increase the viscosity of the surfactant-rich phase. Thus, upon inverting the tubes, the aqueous phase was could be discarded, the surfactant-rich phase remaining at the bottom of the tube. This surfactant-rich phase was diluted with 250

Table 3
Linear regression parameters and calculated K_c [a] values for some organophosphorus and chlorophenol pollutants[b]

	$\dfrac{100}{R\ (\%)}$ vs $\dfrac{1}{(\%\ T_{ini} - \%\ cmc)}$			Log K_c	Log K_{ow} [d]
	Slope	Intercept	r^2		
Paraoxon	0.41±0.04	1.11±0.14	0.987	2.41±0.04	1.98 [32]
Methylparathion	0.04±0.03	1.03±0.12	0.958	3.43±0.28	3.0 [31]
Fenitrotion[c]	0.032	0.964	1.000	3.53	3.5 [31]
Ethylparathion[c]	0.025	0.985	1.000	3.62	3.83 [31]
					3.83 [32]
2-Chlorophenol	0.37±0.11	1.06±0.69	0.973	2.46±0.13	2.15 [36]
4-Chloro-3-methylphenol	0.08±0.02	1.03±0.12	0.981	3.13±0.11	3.10 [36]
2,4-Dichlorophenol	0.05±0.03	1.04±0.17	0.968	3.33±0.24	3.23 [36]
2,4,6-Trichlorophenol	0.02±0.02	1.07±0.12	0.780	3.74±0.42	3.72 [36]
Pentachlorophenol	0.04±0.04	1.00±0.14	0.992	3.46±0.48	3.81 [37]

[a] Calculated from slope and Eq. (10). Confidence intervals for 95% significance.

[b] Experimental R (%) values from quotations [34] (one replicate each point) and [35] (three replicates each point).

[c] Number of regression points=2.

[d] Octanol–water partition coefficients for some organophosphorus and chlorophenol pollutants reported in the literature.

µl of MeOH and injected into the HPLC–UV system. Comparing the signal before and after the CPE procedure, and with the initial volume and final measured volume known, R (%) was calculated for each chlorophenol pollutant as a function of the initial Triton X-114 percentage employed.

Table 3 shows the linear regression parameters and calculated K_c values for each organophosphorus pesticide and chlorophenol pollutant from the corresponding plot of Eq. (13).

As in the case of the triazine herbicides, if the assumption of Eq. (12) is accepted, Eq. (13) must be fulfilled. Thus, a linear relationship of positive slope and an intercept of unity must be found. The parameters shown in Table 3 describe acceptable linear regression coefficients for those herbicides with a number of points greater than two, with a positive slope, and intercept close to unity, as was expected. Table 3 shows the calculated K_c values for all these pesticides obtained from the slope value, using the experimental partial molar volume for Triton X-114 in the micellar states and the mean molecular mass for Triton X-114 from Table 1.

The distribution coefficients seen in Table 3 show that the hydrophobicity order of the organophosphorus pesticides is ethylparathion > fenitrothion > methylparathion > paraoxon. The octanol–water partition coefficients for these analytes, depicted in Table 3, follow the same hydrophobicity order.

As also seen in Table 3, prediction of the hydrophobicity order for the chlorophenol pollutants is 2,4,6-trichlorophenol > pentachlorophenol > 2,4-dichlorophenol > 4-chloro-3-methylphenol > 2-chlorophenol. The octanol–water partition coefficients for these analytes, shown in Table 3, follow the same order, except for the pair 2,4,6-trichlorophenol–pentachlorophenol.

3.4. Relationship between K_c and K_{ow} and prediction of the CPE behaviour from K_{ow} data

In many cases it is interesting to know the behaviour of analyte extraction before experiments are carried out. It may be concluded from previous sections (see above) that there is an intimate relationship between the K_c value of an analyte and its CPE concentration factor, such that knowing the CPE procedure to be carried out and the K_c value of the analyte it is possible to estimate its F_c value.
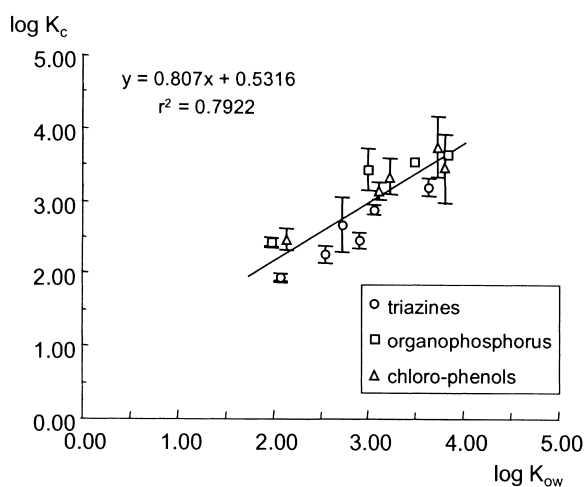

Fig. 4. Relationship between calculated K_c values and K_{ow} values from the literature.

Regarding the calculation of K_c values for an analyte, Fig. 4 depicts the relationship between the K_c values of the organic pollutants previously studied and their literature K_{ow} values. An acceptable linear correlation between their logarithms can be found.

This supports the assumption adopted (Eq. (12)), because three different sets of organic compounds exhibit the same behaviour when they are preconcentrated with the CPE procedure.

Edwards et al. [38] studied the solubilization of five hydrophobic compounds, including three different polycyclic aromatic hydrocarbons, in Triton X-100 solutions and reported a linear relationship between the logarithms of K_m and K_{ow} which indicated a slope of about 0.81 and an intercept of 1.85 on the $\log K_m - \log K_{ow}$ curve, where K_m is the distribution coefficient between the Triton X-100 micelles and water, expressed in (molar fraction/ molar fraction) units instead of (molar/molar) units, as K_c is expressed in this paper.

In order to compare the regression line obtained by those authors for the Triton X-100 surfactant with the regression line obtained for Triton X-114 surfactant in this paper, it is necessary change units to K_c to be transformed to K_m. Bearing in mind that "$K_m = K_c(v_{mc}/v_w)$" for diluted analyte solutions, where v_w is the partial molar volume of water, Eq. (14) is obtained from the Triton X-114 regression of Fig. 4:

$$\log K_m = 0.807 \log K_{ow} + 1.98 \qquad (14)$$

It can be concluded that the slope and intercept for Triton X-114 regression are close to those obtained for the non-ionic surfactant Triton X-100, as would be expected from the similarity between these two non-ionic surfactants. This adds support to the assumption in Eq. (12).

Thus, the regression parameters can be used to estimate K_c values, and hence the CPE behaviour for other analytes for which only their K_{ow} values are known as is shown in the next section.

3.5. Relationship between K_c and K_{sa}

Once the assumption of Eq. (12) supposition has been proved, it can be used to obtain the relationship between the distribution coefficient for an analyte in the micelle–water system prior to CPE, K_c, and the partition coefficient in the surfactant-rich phase-aqueous phase system, K_{sa}, after CPE, Eq. (15):

$$K_{sa} = K_c \cdot \frac{V_{ap}}{V_{sp}}$$
$$\cdot \frac{(\% \text{ Surfactant} - \% \text{ cmc})}{\dfrac{M_{r,Surfactant}}{10^{-2}v_{mc}} - (\% \text{ Surfactant} - \% \text{ cmc})} \qquad (15)$$

In Eq. (15), ''%Surfactant'' and ''$M_{r,Surfactant}$'' are the concentrations expressed in percentage (w/v) and molecular mass for the non-ionic surfactant employed and other notations have been defined previously in the text.

This equation acts as a nexus between studies based on distribution coefficients between the micellar–water system for an analyte, K_c, and the partition coefficients in CPE, K_{sa}. This relationship can also be used to calculate the CPE behaviour for an analyte if its K_c value is known, and, in turn, K_c can be estimated from regressions such as that shown in Eq. (14) or similar ones.

It can be concluded, in general, that the K_{sa} coefficient acts as a surfactant concentration-dependent coefficient and would only be a constant parameter under certain ranges of the non-ionic surfactant employed, in which the surfactant concentration-dependent factor of the equation remains constant or almost constant. By contrast, the K_c factor acts as a thermodynamic constant.

4. Conclusions

The concentration factor of triazine herbicides decreases as the concentration of the cloud point extractant Triton X-114 increases, while extraction recovery is higher for solutions with a high concentration of Triton X-114. In order to obtain the best increase in the analytical signal, the lowest possible concentration of Triton X-114 should be employed. By contrast, for remediation purposes the highest concentration of Triton X-114 would be the most appropriate.

The experimentally proven assumption—that the same amount of analyte associated with Triton X-114 micelles remains entrapped in the surfactant-rich phase after the extraction and centrifugation steps— allows one to link the behaviour of an analyte prior to CPE with its behaviour once CPE has been achieved.

The linear relationship between the K_c and K_{ow} found, or other similar ones from the literature, can be used to estimate the K_c value and, once this parameter is known, the CPE behaviour for this analyte can be predicted via K_{sa} calculation. Thus, knowing the steps of sample manipulation after CPE and before injection into the system it is possible to predict, as a first estimation, the Triton X-114 concentration to obtain the maximum concentration factor before the experiments are done.

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