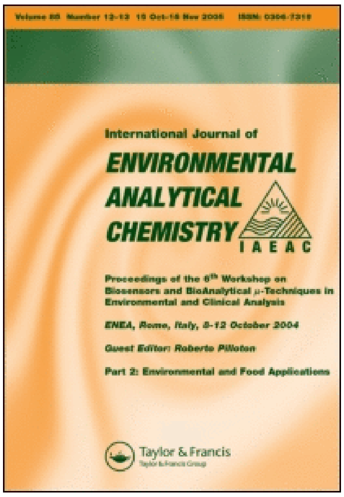

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Simple and Rapid Screening of Total Aromatic Hydrocarbons in Polluted WaterSamples By the Flow Reversal Liquid-Liquid Extraction Technique

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SIMPLE AND RAPID SCREENING OF TOTAL AROMATIC HYDROCARBONS IN POLLUTED WATER SAMPLES BY THE FLOW REVERSAL LIQUID-LIQUID EXTRACTION TECHNIQUE

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The iterative flow reversal approach was used for the liquid/liquid extraction of hydrocarbons from water samples. The proposed mamifold offered the possibility of studying the extraction process continuously and with a single measurement several kinds of analytically useful information could be obtained. Aromatic hydrocarbons were separated effectively from *more* polar compounds and fifteen different compounds were grouped according to their extraction properties. Synthetic samples were classified using the extraction efficiency at various UV-wavelengths. Natural water samples were also analysed with satisfactory results.

Keywords: Continuous flow; liquid-liquid extration; rapid screening; aromatic hydrocarbons; water samples.

INTRODUCTION

Liquid/liquid extraction is an important tool for solving major selectivity and sensitivity problems for many kinds of determinations. The main drawback of the technique is the labour intensive nature of the conventional manual batch extraction and the relatively high consumption of organic solvents. Implementation of liquid-liquid extraction in automatic methods of analysis such as segmented flow analysis or flow injection analysis can help to solve these problems. Especially, liquid/liquid extraction based on flow injection analysis has become a

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useful tool in sample preparation and preconcentration since its first application in 1978 [1,2]. The great advantage of this approach compared to the manual procedure is that the liquid/liquid extraction unit can form an integral part of a more complex FIA system. Automation and on-line measurements are easily implemented as well as the use of unconventional techniques like a partition between partially miscible phases [3] or the exploitation of kinetic differences of extraction processes [4] (the manual "shaking funnel"-technique relates normally on thermodynamic equilibriums). Technically, three main problems must be solved in the construction of a flow extraction system, namely segmentation of the two immiscible phases, selection of suitable dimensions and material of the extraction coil and separation of the two phases, all these steps being critical for the performance of the system. Several designs have been proposed, simplifying the original design [1,2] or adapting it to special applications. Simplifications can be obtained by direct monitoring in the extraction coil, avoiding a phase separation step but involving computerised signal processing [5]. Instrumental modifications include replacing of the segmenter and the extraction coil by a membrane module similar to a dialysis unit [3,6] or using the formation of a thin film of organic phase on the wall of the extraction coil, allowing a kind of partition chromatography with two mobile phases [7].

Two other unconventional approaches for liquid/liquid extraction with flow systems have been recently introduced [8,9]. By the continuous liquid/liquid extraction method with on-line monitoring [8,10] the three basic components of the extraction system are replaced combining them into one unit, a normal cuvette. This design simplifies the solvent extraction-flow injection manifolds considerably and was successfully applied to the determination of mercury [8] and anionic surfactants [10] in water. The other methodology is the iterative flow reversal approach [4, 9, 11, 12], which is based on monitoring a single plug of one phase inserted into the carrier phase. The flow direction is changed periodically and the concentration change of the analyte at the interface of the two phases is recorded. The contact area between the two phases is significantly increased by the formation of a film of one phase at the tube wall. Both methods have been investigated in this work for the extraction of hydrocarbons from water. In the standard method [8] of analysis oil and grease are defined by extractibility from water with organic solvents like hexane or Freon 113. A flow method would offer the advantage of reducing the organic phase consumption and providing an easily automated extraction process.

EXPERIMENTAL

Reagents

As organic phase hexane was used, for the continuous liquid/liquid extraction carbon tetrachloride was applied (both p.A., Panreac).

The synthetic samples were prepared by adding a stock solution of the analyte in methanol to distilled water, which was adjusted pH = 2 with hydrochloric acid and 5 gl^{-1} sodium chloride. The final methanol concentration was kept at 500 $\mu l\ l^{-1}$. Analytical grade reagents supplied by Panreac or Merck were used throughout. It was found that it was necessary to prepare the samples without a gaseous phase in the flask to avoid losses through evaporation or enrichment at the air/water interface. These samples were sonicated before use during 5 minutes.

Apparatus

A Unicam 8625 single-beam spectrophotometer was equipped with a Hellma 178.12QS flow-through cuvette (10 mm light path, inner volume 18 μl). The detector was connected via a RS 232 interface to a personal computer (IBM ThinkPad 701CS). The data acquisition was performed using a laboratory-written program (MS QuickBASIC 4.50), which wrote the data to an ASCII-file. These data could be easily imported into other programs and were processed using the spreadsheet functions of MS EXCEL 5.0. Statistical calculations were performed with STATGRAPH V 5.0.

The programmable pump was a Gilson Minipuls–3 peristaltic pump controlled via a laboratory made interface by a Commodore 64 microcomputer. The controlling software was written in BASIC and allowed the programming of cycle time, pump speed, cycle number and starting direction of the pump.

A Schauer HP4 peristaltic pump served as auxiliary pump for the delivery of the organic phase and for washing the cell after sample extraction. A Rheodyne 5041 injection valve and a Rheodyne 5031 selection valve were also employed.

Teflon tubing of 0.5 and 0.8 mm inner diameter were applied as indicated in the manifold scheme.

The same apparatus, but equipped with a Hellma QS cuvette (10 mm light path) with a laboratory-made cap, was used to investigate the continuous liquid/liquid extraction with on-line monitoring.

Manifold and basis of the method

Figure 1 shows the manifold used, as well as the type of recording obtained. Each experiment was performed using the following procedure: (1) the system was washed with methanol and hexane, until a stable baseline was achieved, special care was given to the total absence of air bubbles; (2) the pumps were stopped, the tube was placed in the sample flask (test tube with 5 ml sample) and the injection valve IV was switched; (3) the measurement program was started on the microcomputer. In the first cycle the interface was directed to the detector cell, then the flow direction was reversed and all the aqueous phase and a small amount of the organic phase were pumped back to the sample tube. All air bubbles were collected by the moving interface and expelled out of the system in form of one big bubble. Afterwards six measurement cycles were recorded, to equalise the different flow rates of the cycles to and from the cell the latter ones were 5 % shorter.

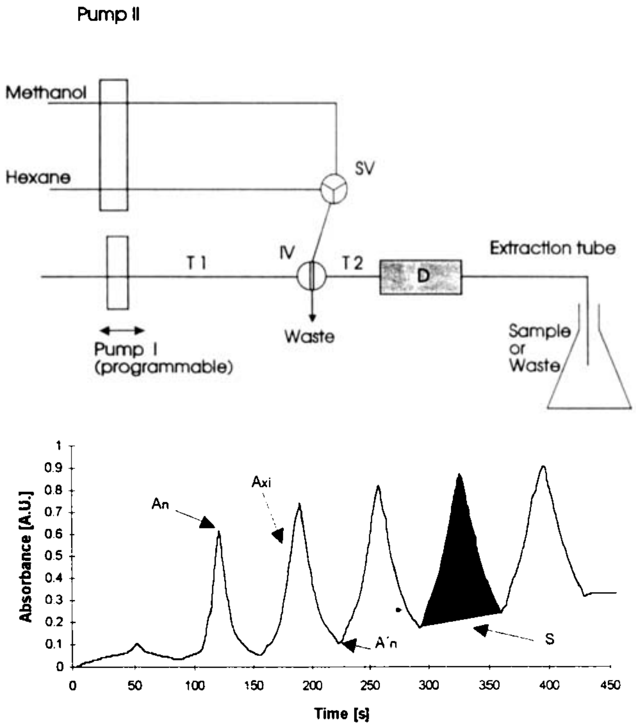

FIGURE 1 Manifold for the iterative flow reversal technique (IV = injection valve; SV = selecting valve: D = detector; T1 = Teflon tube 130 cm. 0.8 mm i.d.: T2 = Teflon tube 45 cm, 0.8 mm i.d.) (a). Multipeak recording for the iterative flow reversal method, in which the small signal at 50 s resulted from the washing step (A'_n = absorbance at minimum between the peaks; A_{x_i}= absorbance at certain point of the organic plug; S = area of the peak) (b)

RESULTS AND DISCUSSION

The continuous liquid/liquid extraction with on-line monitoring [9] was investigated because of its simplicity and very low consumption of organic phase (approx. 200 µl). The extraction efficiency found was very low due a small contact area and a short contact time, therefore this approach was not further investigated.

Optimisation and performance of the iterative flow reversal technique

All preliminary measurements and optimisation steps were carried out with naphthalene as a test compound. At first, the influence of the methanol concentration, which was used for preparing the solutions was investigated. The methanol concentration had no significant effect of the signal in the range of 50 - 1000 µl l^{-1}. Nevertheless, the methanol concentration was kept at a constant 500 µl l^{-1}. The optimum pH and the optimum ionic strength were also determined. No influence for the determination of naphthalene was found, but because of an expected influence on other compounds like phenols or amines the same standard matrix was used as suggested for the manual batch method (pH = 2 with hydrochloric acid and a salt concentration of 5 gl^{-1} sodium chloride).

Measurements with a steel tube as an extraction coil were performed in order to determine if the extraction occurs directly between the organic and aqueous phase. The other possibility was an extraction from the aqueous phase to the tube wall followed by a transfer from the tube wall to the organic phase. The steel tube acted as an inert material thus the extraction of hydrocarbons to the tube wall could not occur. The extraction tube consisted of a short (8 cm) Teflon tube (0.5 mm i.d.) connected with a steel tube (123 cm, 0.5 mm i.d.) using a steel HPLC-connection (calculated total volume 242 µl). The aqueous/organic interface had never contact with Teflon, hence an extraction process could only occur between the liquid phases. In comparison with a Teflon tube of similar length and diameter the resulting signal was about two times smaller, but an extraction was monitored as well. The differences could be easily explained by the differences in the interface area, which was much higher in the case of the Teflon tube.

The flow rate and the exchanged aqueous volume were investigated in the range 0.3 - 0.8 ml $min^{-1}$and 75 to 175 µl using a 45 cm 0.8 mm inner diameter teflon tube. Other teflon tubes were used as well, but one with an inner diameter of 0.8 mm was finally chosen because of its better stability against small perturbations of the pump rate. The optimal conditions regarding sensitivity and reproducibility were found to be a flow rate of 0.28 ml min^{-1} and a cycle time of 34 seconds. Series of experiments were conducted changing the time increment of the first cycle from 1 to 11 seconds, the extracted sample plug was thus exchanged to a different extent with fresh sample solution. The cycle time of the other cycles was reduced proportionally. If the interface was far away from the sample flask (short cycle time), the peak height did not increase during the analysis. A near approach of the interface to the sample flask (= long cycle time) resulted in an increase in peak height for successive peaks, thus allowing a preconcentration in the organic phase (Figure 2).

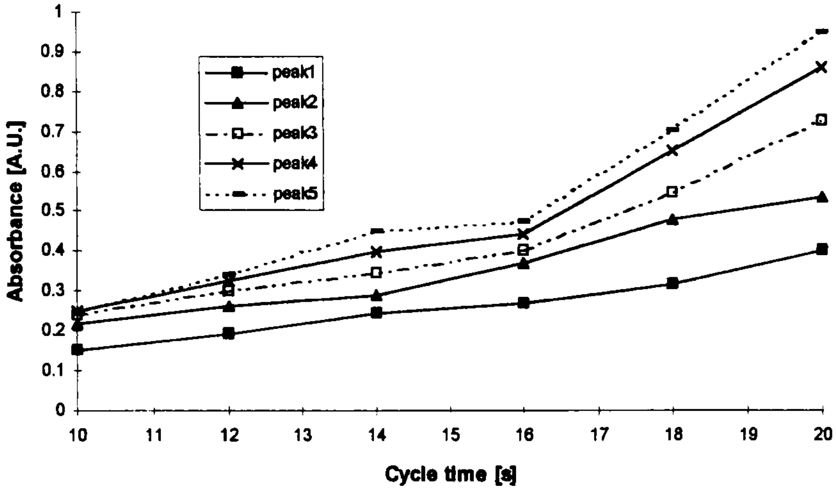

FIGURE 2 Influence of cycle time on the measurements of 2 µg $ml^{-1}$of naphthalene (flow-rate = 0.3 ml min^{-1}; volume of the tube 85 µl)

Extraction efficiency for various aromatic hydrocarbons and their classification

To characterise the extraction process as well as the dispersion process in the organic phase a classification value was introduced. The absorbancies in the aqueous phase were calculated for the standard solutions of the analytes in water. Dividing the measured signal by this number gave the extraction efficiency:

$$\text{Extraction efficiency, EE (\%)} = \frac{\text{Absorbance}_{\text{organic phase}}}{\text{Absorbance}_{\text{aqueous phase}}} \times 100$$

The extraction efficiency for the various compounds is shown graphically in Figure 3 and allowed the compounds to be grouped.

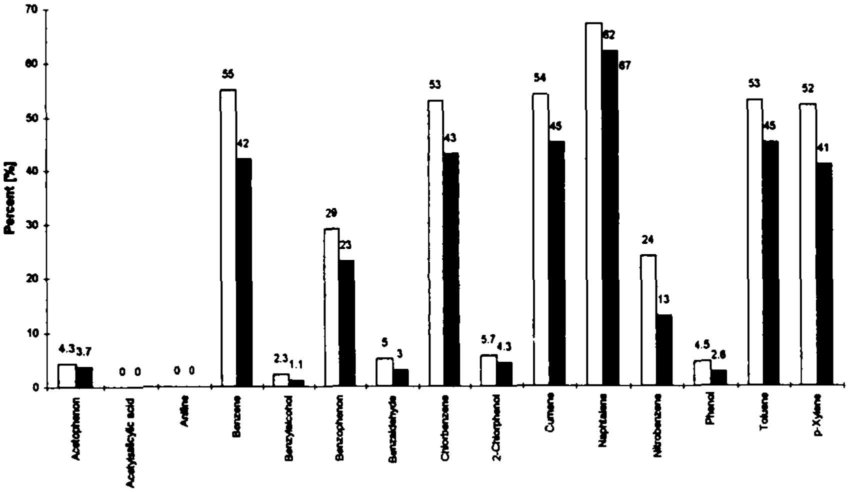

FIGURE 3 Extraction efficiency of the two first peaks for several hydrocarbons [left (white): peak 2; right (black): peak 1]

Naphthalene

This compound exhibited the highest extraction efficiency of all the compounds investigated. One reason may be the concentration range, which was an order of magnitude smaller than for the other compounds.

Benzene, chlorobenzene, cumene, toluene, p-xylene

All these compounds were extracted with similar efficiencies (around 50 % for the second peak). They all belong to the same homologous series of compounds (chlorobenzene being an exception, but it is also quite similar regarding acidity or polarity properties).

Benzophenone, nitrobenzene

The extraction efficiency was in the range of 30 % – 40 % of the extraction efficiency of naphthalene. Because of their high UV-absorption they could be determined with a low limit of detection.

Acetophenone, benzaldehyde, benzylalcohol, 2-chlorophenol, phenol

All these compound were only extracted to a small extent. They were quite polar compounds, especially phenol and 2-chlorophenol which have acidic properties.

Aniline, 2-acetylsalicylic acid

No signal at all was obtained for these compounds. For aniline this could be explained by salt formation and for 2-acetylsalicylic acid by its high polarity and acidity which prevented the compound being extracted to any reasonably extent.

After this classification for single compounds, synthetic samples containing two or three hydrocarbons were prepared and measured at three different wavelengths (208 nm, 220 nm and 250 nm). The measured extraction efficiencies for synthetic samples were used to carry out a classification according to the content of easily extracted substances. All hydrocarbons without functional groups had almost the same extraction efficiency, which was remarkably higher than that for the more polar compounds. The extraction efficiency at the three wavelengths was used to plot a three-dimensional graph of the thirty samples, the projections of which on two-dimensional planes are shown in Figure 4. The fifteen pure compounds are also included.

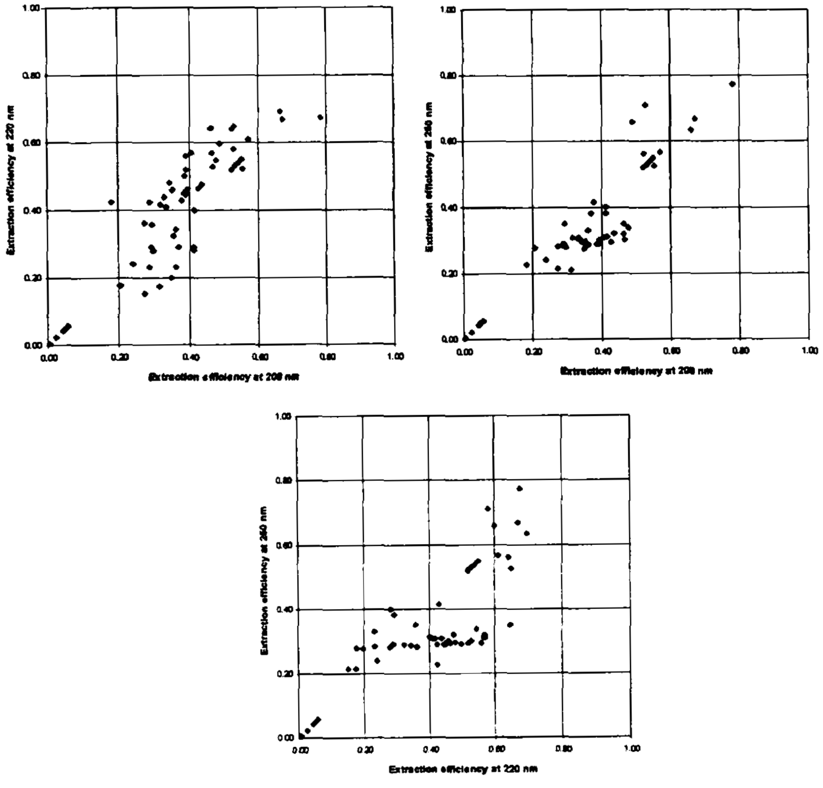

FIGURE 4 Plots of extraction efficiencies at various wavelengths for samples containing differents hydrocarbons (for details, see text)

If the absorption before the extraction process is originated mainly from hydrocarbons, the extraction efficiencies were high. If it was mainly caused by compounds like phenol or benzophenone, the efficiencies were relatively small. Another information about the composition of the sample was also provided. Samples which consisted only of a single compound were supposed to have the same extraction efficiency at all wavelengths. These were situated along the main diagonal of the diagrams. Multicomponent mixtures had different extraction efficiencies at each wavelength, they were more scattered over the diagrams.

Calibration for various aromatic hydrocarbons

The multipeak recording provided by the iterative flow reversal technique allowed the application of different methods for signal processing (for further discussion see Cañete et al. [4]), such as the use of peak heights, gradients of the peaks or differences between subsequent peaks. These different methods were applied on the calibration curve of naphthalene. Calculations using the peak heights of the first two peaks provided the most reliable results. The exploitation of the peak heights after several cycles gave a better sensitivity but the reproducibility was considerably lower due to the accumulation of small instabilities in pumping rates and flow conditions. Fifteen different compounds covering a great range of chemically different compounds were tested. The results for a calibration using the second peak are given in Table I.

Aplication of the method to water samples

Using the linear calibration curves of the single compounds the expected signal for mixed samples was calculated and compared to the obtained signal. This calculation was a linear combination of the signals for the single compounds. The agreement between the two values was high, indicating no mutual influence of the compounds on their extraction process. Even for those signals at 250 nm, which were in absolute terms sometimes very small, a very good agreement was achieved. No tendencies or significant deviations were found, the sometimes higher deviations at 250 nm resulted from the smaller absorbencies (Table II).

The method was applied to real water samples. Because of the low concentrations of extractable compounds in these natural samples some have been spiked with different amounts of toluene. The results are given in Table III. The recoveries are quite satisfactory. It is worth to note that no other sample treatment except adjusting the pH and adding the sodium chloride was performed.

TABLE I Calibration curves for various hydrocarbon compounds

Compound (Measurement wavelength)	*Investigated range ($\mu g\ ml^{-1}$)*	*Equation $y = a + b*x$*	*Limit of detection ($\mu g\ ml^{-1}$)*	*Regression coefficient r*	*Extraction efficiency EE*	*Standard deviation of the method s_{xo}*
Acetophenone (246 nm)	0 - 40	$b = 3.81*10^{-3}$ $a = 4.4*10^{-3}$	4	0.9958	4.5 %	1.3
o-Acetylsalicylic acid (228 nm)	0 - 40		-	-	-	
Aniline (208 nm)	0 - 40	-	-	-	-	
Benzene (208 nm)	0 - 10	$b = 4.44*10^{-2}$ $a = 3.1*10^{-3}$	0.45	0.9945	55 %	0,1
Benzaldehyde (250 nm)	0 - 25	$b = 3.83*10^{-3}$ $a = 2.1*10^{-3}$	2.7	0.9895	5 %	1.4
Benzophenone (258 nm)	0 - 20	$b = 2.5*10^{-2}$ $a = 6.1*10^{-3}$	0.27	0.9967	29 %	0.3
Benzylalcohol (210 nm)	0 - 40	$b = 1.94*10^{-3}$ $a = -3.1*10^{-3}$	8	0.9769	2.5 %	3.1
Chlorobenzene (214 nm)	0 - 25	$b = 2.61*10^{-2}$ $a = 6.9*10^{-3}$	0.31	0.9985	53 %	0.3
2-Chlorophenol (216 nm)	0 - 40	$b = 2.51*10^{-3}$ $a = 8.1*10^{-3}$	2.5	0.9887	5.7 %	2.6
Cumene (210 nm)	0 - 20	$b = 2.18*10^{-2}$ $a = 2.4*10^{-3}$	0.5	0.9941	54 %	0.8
Naphthalene (220 nm)	0 - 1.5	$b = 0.330$ $a = 1.1*10^{-2}$	0.030	0.9959	67 %	0.1
Nitrobenzene (268 nm)	0 - 30	$b = 1.66*10^{-3}$ $a = 10.4*10^{-3}$	0.51	0.9932	24 %	0.7
Phenol (212 nm)	0 - 40	$b = 2.41*10^{-3}$ $a = -9.4*10^{-3}$	10	0.9678	4.5 %	6.3
Toluene (208 nm)	0 - 20	$b = 3.35*10^{-2}$ $a = -3.3*10^{-2}$	0.36	0.9900	53 %	0.1
p-Xylene (212 nm)	0 - 20	$b = 2.77*10^{-3}$ $a = 7.4*10^{-3}$	0.4	0.9981	52 %	0.4

TABLE II Sample composition and deviation of the measured and calculated signal (in percent)

Sample	*Toluene*	*Naphthalene*	*Benzophenone*	*Phenol*	*Cumene*	*Deviation in %*	*Deviation in %*	*Deviation in %*
1	5	0.5	5	0	0	12.0	8.2	12.3
2	5	0	0	0	0	–0.7	9.5	9.6
3	5	1	10	0	0	–1.2	3.4	–1.3
4	0	0.5	10	0	0	–9.2	–2.6	–0.9
5	0	0	5	0	0	2.3	–3.8	–3.2
6	10	0.5	10	0	0	–6.2	–2.7	–3.3
7	5	1	0	0	0	16.9	7.6	12.3
8	5	0.5	5	0	0	9.8	4.5	0.6
9	10	1	5	0	0	–0.9	2.9	2.6
10	10	0	5	0	0	–7.0	–3.7	2.2
11	5	0	10	0	0	–3.0	–5.5	–2.2
12	10	0.5	0	0	0	–10.1	–0.9	21.9
13	0	1	5	0	0	2.7	–0.1	0.0
14	0	0.5	0	0	0	16.8	0.7	15.6
15	5	0.5	5	0	0	2.3	–5.8	6.7
16	0	0	0	10	10	7.1	0.9	–8.8
17	10	1	0	10	0	–1.2	0.3	9.0
18	10	1	0	0	10	–3.5	5.6	–3.8
19	0	1	10	0	10	–4.2	–0.9	–1.3
20	0	0	10	10	10	–1.3	2.9	–1.3
21	10	0	0	10	10	2.5	–0.4	4.2
22	0	1	10	10	0	9.6	–1.3	–1.8
23	0	1	0	10	10	–6.8	–0.7	3.1 1
24	0	0	10	0	10	–4.3	–2.3	–2.1 1
25	0	1	0	0	10	–0.2	–5.2	–2.4
26	10	0	0	0	10	3.5	–2.1	–1.4
27	0	0	10	10	0	–0.6	2.5	–2.4
28	0	1	0	10	0	–2.4	5.2	23.0
29	10	1	0	0	10	–4.7	4.2	2.6
30	0	1	0	10	10	–2.2	–2.3	3.4

TABLE III Analysis of real water samples (n = 2)

Type of sample and amount of toluene added	*Absorbance of the water sample before extraction at 208 nm*	*Absorbance of the organic phase after extraction at 208 nm*	*Concentration of extractable substances - calculated as toluene*	*Toluene found (background substracted)*
μg ml^{-1}	*A.U.*	*A.U.*	*μg ml^{-1}*	*μg ml^{-1}*
Guadalquivir river	1.745	0.017	0.6	
+ 5	2.098	0.193	5.8	5.2
+ 10	2.456	0.372	11.1	10.6
+ 15	2.839	0.540	16.2	15.6
Córdoba tap water	0.230	0.004	0.2	
+ 5	0.585	0.184	5.5	5.4
+ 10	0.924	0.367	11.0	10.8
+ 15	1.263	0.555	16.6	16.4
Canal near the townwall of Córdoba	- (1:10 diluted: 0.280)	0.297	8.9	
+ 5	- (1:10 diluted: 0.314)	0.502	15.3	6.2
+ 10	- (1:10 diluted : 0.348)	0.625	18.7	9.8
+ 15	- (1:10 diluted: 0.373)	0.768	22.9	14.0
Pool near	- (1:10 diluted: 0.323)	0.346	10.3	
+ 5	- (1:10 diluted: 0.358)	0.522	15.6	5.3
+ 10	- (1:10 diluted: 0.392)	0.713	21.3	11.0
+ 15	- (1:10 diluted: 0.423)	0.878	26.2	16.0
Street puddle I	1.995	0.233	6.2	
+ 5	2.339	0.398	11.9	5.7
+ 10	- (1:10 diluted: 0.276)	0.585	17.5	11.3
+ 15	- (1:10 diluted: 0.303)	0.752	22.5	16.3
Street puddle II	2.128	0.278	7.6	
Reservoir of power plant	1.641	0.015	0.5	

CONCLUSIONS

In this work the liquid/liquid extraction has been proven to be an important tool for the screening of aromatic hydrocarbons in polluted waters, improving the selectivity of the rather unspecific UV-detection. The method can be implemented into more complex flow systems and substitutes the tedious manual batch procedure, with a high degree of automation an in a miniaturised way. Organic solvent consumption is reduced and the hazards for laboratory staff and environment are minimised. With the reported iterative tlow reversal approach a multi-peak recording offers substantial information about the extraction process. A continuous monitoring of the process is provided, including useful kinetic information.

Acknowledgements

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References

[1] B. Karlberg and S. Thelander, *Anal. Chim. Acta,* **98,** 1–7 (1978).

[2] F.H. Bergamin, J.X. Medeiros, B.F. Reis and E.A.G. Zagatto, *Anal. Chim. Acta,* **101,** 9–16 (1978).

[3] Y. Sahleström and B. Karlberg, *Anal. Chim. Acta,* **179,** 315–323 (1986).

[4] F. Cañete, A. Ríos, M.D. Luque de Castro and M. Valcárcel, *Anal. Chim. Acta,* **224,** 127–132 (1989).

[5] F. Ortiz-Boyer, J.A. Garcia-Mesa and M.D. Luque de Castro, *Anal. Chem.,* **66**, 2794–2798 (1994).

[6] R. G. Melcher, *Anal. Chim. Acta,* **214,** 299–313 (1988).

[7] C.A. Lucy and K. Yeung, *Anal. Chem.,* **66,** 2220–2225 (1994).

[8] M. Agudo, A. Ríos and M. Valcárcel, *Anal. Chem.,* **65,** 2941–2943 (1993).

[9] F. Cañete, A. Ríos, M.D. Luque de Castro and M. Valcárcel, *Anal. Chem.,* **60,** 2354–2357 (1988).

[10] M. Agudo, A. Ríos and M. Valcárcel, *Analyst,* **119,** 2097–2100 (1994).

[11] J. A. García-Mesa, P. Linares, M.D. Luque de Castro and M. Valcárcel, *Anal. Chim. Acta,* **235,** 441–444 (1990).

[12] Z. Zhi, A. Ríos and M. Valcárcel, *Anal. Chem.,* **67,** 871–877 (1995).

[13] C. Watson (Ed.), *Official and standarized methods of analysis* (The Royal Society of Chemistry, London, 1994), p. 569.