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Continuous membrane extraction of phenols from crude oils followed by high-performance liquid chromatographic determination with electrochemical detection

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Abstract

On-line coupling of devices for non-chromatographic separation to chromatographic analysis systems affords a substantial improvement in the handling of organic samples whose physicochemical characteristics hinder their treatment. Here we report for the first time a simple and rapid automatic method for the determination of phenols in crude oil using high-performance liquid chromatography with electrochemical detection. The method involves minimum sample handling. Before the chromatographic process, phenols are separated from the matrix with a silicone membrane in a device coupled directly to the chromatographic system. The separation process across the membrane and later transfer of the analytes separated from the matrix to the chromatographic system are controlled automatically. The proposed procedure has been used successfully for the determination of phenols in real samples of crude oil without the need for complicated pretreatment steps.

Keywords: Oils; Sample preparation; Membranes; Phenols

1. Introduction

The analysis of phenols is of great interest both in the field of environmental protection and in the control of industrial processes. Phenols are applied as intermediates in the manufacture of plastics and pharmaceutical products. They also arise in the processing of carbon and the production of liquid fuels. In view of their importance, different methods have been developed for their quantification.

The reaction between phenols and 4-aminoantipyrene in the presence of an oxidizing agent furnishes an appropriate way for spectrophotometric determination in both natural and waste waters [1–4]. However, this method does not permit a distinction among different phenols and furthermore certain substituents in the *para* position reduce the extent of the reaction. Gas chromatography with flame ionization detection and mass spectrometry are widely used, generally by derivatization with halogen reagents to increase volatility and detectability [5,6]. The drawback in gas chromatography lies in the sample preparation time required and in the incomplete recovery of phenols.

Liquid chromatography, both in normal and reversed-phase, has also been used. The latter (reversed-phase) finds the widest applications. Both UV detection (these compounds show strong absorption

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in two bands centered at 230 and 280 nm) and electrochemical detection [7–9] have been used. Phenol determination by liquid chromatography followed by oxidative electrochemical detection improves selectivity and sensitivity. Moreover, sample preparation is simple and derivatization is not required. Glassy carbon electrodes are widely used although they may be rendered 'passive' owing to the formation of phenoxy radicals, which polymerize and are adsorbed onto the electrode surface. To avoid this, different alternatives have been proposed, such as anode polarization to reactivate the electrode surface [10] or electrode modification with polymers [11,12]. Enzymatic electrodes [13] are also used (those based on tyrosinase are the most used). Recently, supercritical fluid chromatography [14] and capillary electrophoresis have also been used [15,16]. However, the detection limits afforded by chromatographic methods are insufficient for the determination of phenols in environmental applications such that preconcentration steps are required; for this, liquid–liquid extraction and, more recently, solid-phase extraction [17] have been used.

Compounds such as alkyl phenols, thiophenols and organic acids are found at varying concentrations in crude oil and its different fractions. These compounds may act as precursors in the formation of rubbers, thus reducing fuel quality because they damage motors or even cause them to seize up. Additionally, in the oxidation step, phenols may couple together to form colored complexes that also affect product quality. In the light of the foregoing, most of these compounds should be eliminated in the processing of products such as gasoline and kerosene. The phenol compounds present in crude oil and similar matrices, have essentially been determined by chromatographic techniques [9,18], using different types of detectors, among them electrochemical detection [19]. However, sample preparation is complicated and in all the above cases a previous extraction process is mandatory.

As an alternative to liquid–liquid and solid–solid extraction, different research teams have used silicone membranes as a separation barrier prior to the introduction of the sample into the analysis system [20–24]. The three main goals when using membranes to introduce samples into the chromatographic system are: sample clean-up, concentration or dilution of the analytes and transfer of the analytes to an appropriate medium compatible with the mobile phase. Even though many examples can be found in the literature on the use of membrane-mediated introduction into chromatographic systems [25], only one paper [23] describes the use of a microporous barrier for the transfer of analytes from a non-aqueous medium.

When homogeneous silicone membranes are used donor and acceptor streams can be either aqueous or organic and a double extraction process (donor–membrane, membrane–acceptor) takes place, i.e., separation is governed by solubility (extraction) and diffusion in the membrane. Here we propose a method for the determination of phenols in crude oil by high-performance liquid chromatography with electrochemical detection using a previous separation system [20–22] based on a silicone membrane coupled directly to the chromatographic system, but now for non-miscible phases. The proposed procedure involves minimum sample treatment, thus considerably facilitating the experimental procedure.

2. Experimental

2.1. Reagents

Crude oil samples (Brass River light, Iran Light and Maya) were kindly supplied by Ertoil Refineries at La Rábida, (province of Huelva, Spain). Phenol (98.5% purity) was supplied by Panreac (Barcelona, Spain). Cresols (approx. 99% purity) were from Sigma and the dimethylphenols (between 97% and 99% purity) were from Fluka. Standard solutions of these compounds were prepared by dissolution of the commercial products in hexane (Merck).

HPLC-grade methanol, used in the preparation of the mobile phase and the acceptor solutions, was from BDH. Methanol–water (50:50, v/v) containing 1 g/l of KNO_3 and 0.025 g/l of H_2SO_4 was used as the mobile phase.

The mobile phase and acceptor solutions were filtered through nylon membrane filters of 0.45 μm pore size and ultra-high quality water obtained with an Elgastat UHQ water purification system was used.

2.2. Apparatus

The setup consisted of two parts: a module in which the analytes were separated from the matrix and a chromatographic system. The separation module comprised a Gilson Minipuls 3 MP4 peristaltic pump, a Gilson 401 dilutor used as a piston pump, a Gilson 213 automatic sampler with a Rheodyne 7010 six-port injection valve (injection loop 20 μl) and a separation unit constructed in plastic. This unit was formed of two blocks (1×2×10 cm), each of them with a slit of approximately 1 mm depth and 2 mm width. These slits functioned as chambers for the acceptor and sample, respectively, and the membrane employed for the liquid–liquid extraction process was a Dow-Corning Silastic silicone layer 0.005 in. thick (1 in.=2.54 cm).

The chromatographic system included a Spectra-Physics SP 8800 ternary pump, an SP 8450 UV detector and an EG&C PARC 400 electrochemical detector connected to an SP 4290 integrator. The system of electrodes for electrochemical detection consisted of a glassy carbon working electrode, an Ag/AgCl/0.1 *M* KCl reference electrode and a gold auxiliary electrode. The stationary-phase column was 150×3.2 mm LiChrospher 5 ODS from Phenomex.

Fig. 1 shows a simplified scheme of the overall extraction–separation system in which all connections were 0.50 mm I.D. PTFE tubing and pump tubes were of 1 mm I.D. isoversinic; the arrangement of the modules for sample treatment and chromatographic analysis is shown. The chromatographic detectors were connected in series: first the optical detector and then the electrochemical one. The system comprises two lines, one of them for the sample and the other for the acceptor. These are driven to the separation unit, each of them passing across one side of the membrane. The acceptor phase channel passes through the membrane cell to arrive at the injection valve of the chromatographic system. The flow-rates of the sample and acceptor streams as well as the position of the injection valve and the time during which this remains in the charge or load positions are controlled by the microprocessor of the automatic sampler.

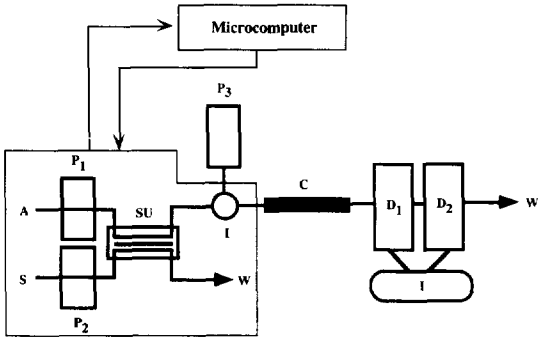

Fig. 1. Overall scheme of extraction–separation system and arrangement of different components. S: sample; A: acceptor; P_1: piston pump; P_2: peristaltic pump; SU: Separation unit; P_3: chromatograph pump; I: injection valve; C: chromatographic column; D_1: UV detector; D_2: electrochemical detector; W: waste; I: integrator.

2.3. Procedures

2.3.1. Sample preparation

Samples of Brass River Light crude oil were prepared by dissolution of a weighed amount of crude oil in hexane. Samples of Iran Light and Maya, containing hexane-insoluble residues were prepared by dissolving a weighed amount in hexane followed by centrifugation for 10 min on a Kokusan H-103N centrifuge at 3500 rpm to eliminate the undissolved solid. To ensure reproducibility in the preparation of the samples due to changes in the density of hexane with temperature, in all cases sample preparation was carried out at 5°C.

2.3.2. Functioning of the system

The functioning of the extraction-enrichment system comprises four successive steps:

(1) With the injection valve in the load position, the acceptor and sample chambers are washed by pumping acceptor (0.7 ml/min) and sample (9.3 ml/min) across both sides of the membrane.

(2) Acceptor flow is halted and during a preset enrichment time analytes are transferred from the sample, which continues to flow, to the acceptor solution.

(3) Following this, the piston pump displaces a small volume of acceptor until the portion most enriched in analyte fills the loop of the injection valve.

(4) Finally, the acceptor and sample flows are

halted and the enriched portion of acceptor is injected into the chromatographic system.

2.3.3. Chromatographic separation

In the chromatographic separation, a mobile flow-rate of 0.4 ml/min was used, recording the chromatogram at 280 nm at the UV detector and at +1200 mV at the electrochemical detector. Electrode pretreatment was carried out daily by maintaining the electrode for 10 min at a potential of +1300 mV and then applying the working potential.

3. Results and discussion

In the analytical system described here, the portion of acceptor enriched in analyte is introduced into the loop of the injection valve of the chromatographic system by displacement of a volume of acceptor by a piston pump. The acceptor chamber volume ranges between 200 and 300 μl while the volume of the valve loop is only 20 μl; it is, therefore, necessary to optimize the volume used to drive the piston so that the part richest in analyte will be loaded into the injection valve, thus obtaining the maximum signal.

Fig. 2 shows the variation in the normalized analytical signal (H: signal/maximum signal) as a function of the volume displaced by the piston pump for a sample containing 1.8 ppm of phenol and an enrichment time of 2 min. The optimum volume (125 μl) is a function of the length of the teflon tube connecting the separation device to the injection valve (12 cm in this case). Fig. 3 shows the chromatograms obtained with UV detection (Fig. 3A) and electrochemical detection (Fig. 3B) when a sample of Maya crude oil was subjected to the overall analytical procedure.

The determination of phenols in this type of sample can be accomplished with both UV detection and electrochemical detection, although the latter is more sensitive and selective. However, on performing successive injections of the same sample, the chromatograms obtained with electrochemical detection are seen to have better reproducibility than those obtained with UV detection because the latter decay progressively owing to the overlap of peaks from previous injections that elute over long times and must correspond to non-electroactive species.

3.1. Automatization of the chromatographic separation–determination system

The set of operations necessary to accomplish the different steps in the overall separation–determination process automatically requires control over pump function for the sample and acceptor and

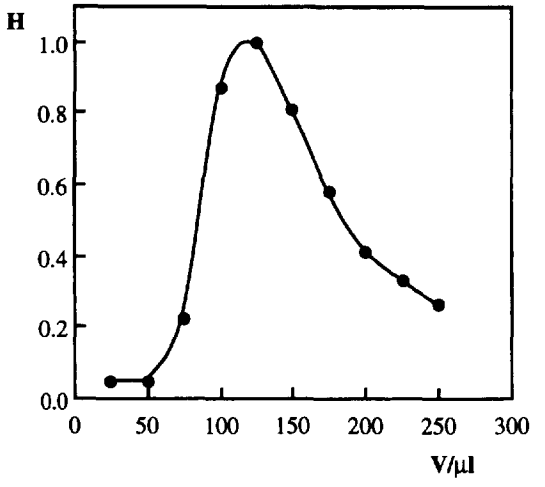

Fig. 2. Variation in signal normalized with the volume displaced by the piston pump. Sample: 1.8 ppm phenol; enrichment time: 2 min. Chromatographic conditions as described in Section 2.

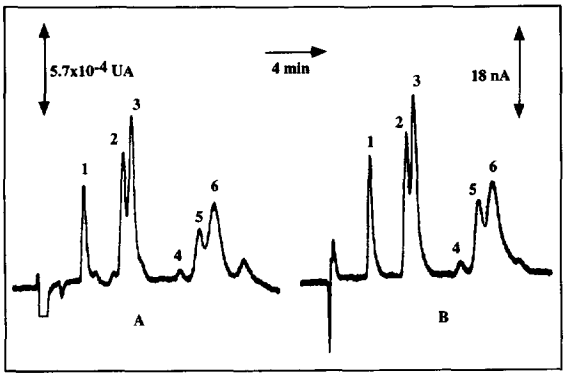

Fig. 3. Chromatograms obtained with UV (λ=280 nm) (A) and electrochemical (E=+1200 mV) (B) detection. Sample: 3.3597 g/50 ml hexane of Maya crude oil. Chromatographic conditions as described in text. Peak assignment: 1: phenol; 2: *m*-cresol and *p*-cresol; 3: *o*-cresol; 4: 3,4-dimethylphenol; 5: 2,3-dimethylphenol, 3,5-dimethylphenol and 2,6-dimethylphenol, and 6: 2,4-dimethylphenol and 2,5-dimethylphenol.

control over the injection valve of the chromatographic system. The flow-rates of the piston and peristaltic pumps were chosen in such a way that no pressure decompensations sufficiently strong to damage the membrane would occur. The volume used to clean the separation cell before each cycle was held at the minimum value necessary to avoid contamination among samples, i.e., 2.5 ml. After successively subjecting a sample containing 1 ppm of the compounds phenol, *o*-cresol and 3,4-dimethylphenol dissolved in hexane and hexane alone, no cross-contamination was observed. Only phenol gave a signal in the second injection close to 1% of the first signal while no signal at all was detected in the case of the other two analytes.

3.2. Acceptor solution

Two different acceptor solutions were assayed: different methanol–water mixtures and aqueous solutions of NaOH at different concentrations. All experiments were carried out for four different enrichment times of 1, 2, 3 and 4 min, respectively, using solutions of Maya crude oil in hexane as samples. Fig. 4 shows the variation in the electrochemical signal for different acceptor phases formed of methanol–water mixtures for four of the analytes studied.

All cases showed bell-shaped curves, with a maximum situated around 60% methanol. These curves differ from the expected shape for this type of sample; once the maximum has been reached, the decrease observed in the signal could be due, among other factors, to the variation in the viscosity of the methanol–water mixtures and the corresponding alteration in the pressure to which both sides of the membrane are subject. Since the viscosity of the sample remains constant throughout all the experiments, the pressure differences on both sides of the membrane must be attributed to modifications in viscosity when the acceptor composition is varied. Because the methanol–water mixtures show a maximum viscosity at values close to 60% methanol, this mixture will exert the greatest pressure on the membrane and will thus provide the greatest acceptor chamber volume and hence the strongest signal.

When aqueous solutions of NaOH are used as acceptor solutions (Fig. 5) the signal increases steadily with the rise in the NaOH concentration

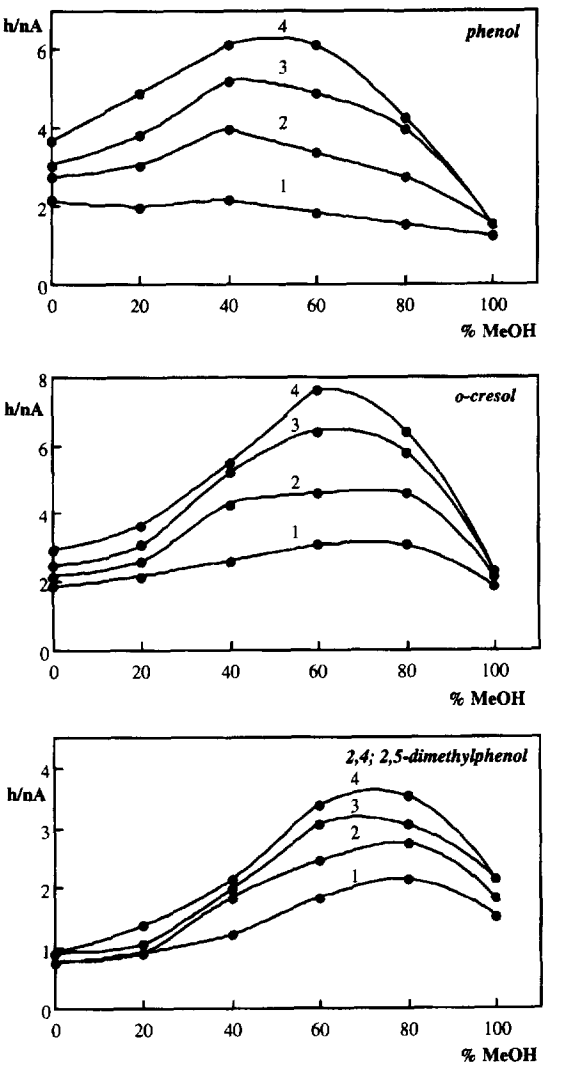

Fig. 4. Variation of electrochemical signal as a function of the composition of the acceptor phase. Methanol–water mixtures. The numbers over the curve indicate the enrichment time in min. Maya crude oil sample 2.0140 g/100 ml hexane.

because within the concentration range studied the viscosity of the acceptor phase remains practically unaltered. Similar experiments carried out with methanol–water (60:40, v/v) in the presence of NaOH did not afford significantly improved results with respect to those obtained in the absence of NaOH.

Fig. 6 shows the effect of the enrichment time on the electrochemical signal for two different amounts

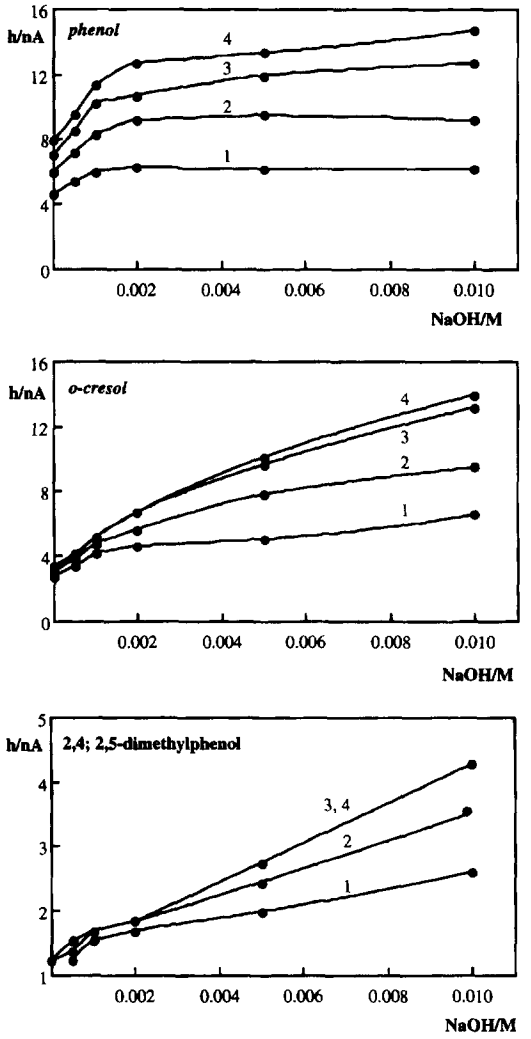

Fig. 5. Variation in the electrochemical signal as a function of the composition of the acceptor solution. NaOH solutions. The numbers over the curve indicate the enrichment time in min. Maya crude oil sample (5.5495 g/100 ml hexane). Acceptor: methanol–water (60:40, v/v). Other conditions are described in the text.

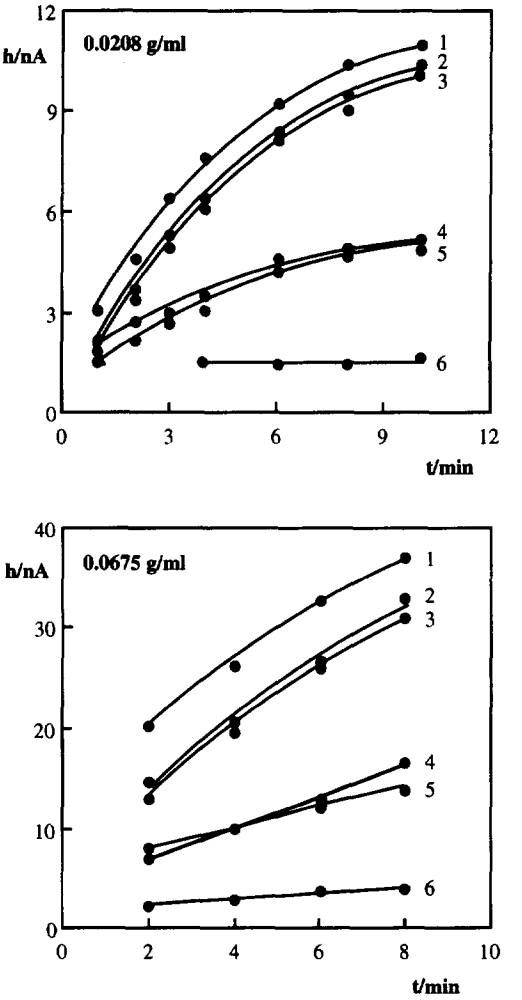

Fig. 6. Variation in the electrochemical signal as a function of the enrichment time. Maya crude oil sample (1) *m*-cresol and *p*-cresol; (2) *o*-cresol; (3) phenol; (4) 3,4-dimethylphenol; (5) 2,4-dimethylphenol; (6) 2,5-dimethylphenol, 2,3-dimethylphenol, 3,5-dimethylphenol and 2,6-dimethylphenol.

of Maya crude oil. The signals are seen to increase with the increase in the enrichment time. However, when a smaller amount of crude oil is used, the signals tend towards a constant value because equilibrium is reached.

3.3. Stability of the analytical signal

Glassy carbon electrodes may be rendered 'passive' or may age due to the adsorption of both analytes and of the products of the electrodic reaction onto the electrode surface. Over time, this phenomenon leads to a progressive decrease in the electrochemical signal. Since the loss in activity on the electrode surface depends on the medium in which oxidation or reduction takes place and on its concentration, the stability of the signal was studied with two samples of crude oil (Maya and Brass River Light) at two different concentrations (1.3025 and 4.5244 g dissolved in 50 ml of hexane, respectively). In both cases, the signal remains constant

over time and hence the 'passivization' phenomenon can be considered negligible. This is because the mobile phase contains 60% methanol and the surface of the electrode is thus continually renewed.

3.4. Matrix effect

Fig. 7 shows the effect of the concentration of crude oil on the analytical signal in the overall chromatographic-detection enrichment–separation process. It may be seen that the signal does not increase linearly with the concentration of crude oil, indicating that the samples have a matrix effect that causes the analytical signal to decrease. In order to determine the effect of the matrix, and, hence, quantification of this effect, the signals obtained for phenol in hexane were compared with those obtained when each of the samples of crude oil was spiked with the same amount of analyte. The results obtained (Table 1) clearly show that the three samples of crude oil produce an important matrix effect and it is, therefore, not possible to quantify the different phenols by the corresponding calibration curves in hexane.

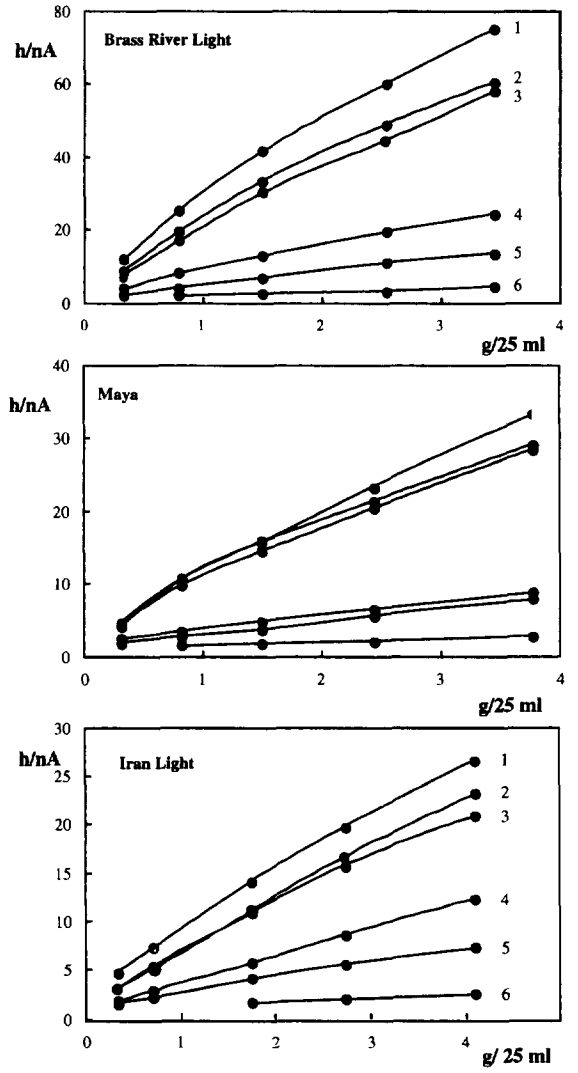

Fig. 7. Effect of sample amount on the electrochemical signal. (1) *m*-cresol and *p*-cresol; (2) *o*-cresol; (3) phenol; (4) 3,4-dimethylphenol; (5) 2,4-dimethylphenol; (6) 2,5-dimethylphenol, 2,3-dimethylphenol, 3,5-dimethylphenol and 2,6-dimethylphenol. Experimental conditions as described in text.

Since under the experimental conditions employed several phenols coelute, it is necessary to choose one of the coeluting species as a reference for later quantification of each of the groups obtained. Table 2 shows the values obtained in the signal normalized for solutions of phenol in hexane and spiked and unspiked samples, also dissolved in hexane. The phenols chosen were: phenol, *m*-cresol, *o*-cresol, 3,4-dimethylphenol, 2,3-dimethylphenol and 2,4-dimethylphenol.

3.5. Quantification

Quantification of the phenols in crude oil samples was done by the standard additions method. For samples in which a centrifugation process is required after hexane addition (Maya and Iran Light crude oil) direct addition of phenols to the sample would involve weighing as many aliquots as points neces-

Table 1
Matrix effect

Crude oil	Phenol (mg/l)	Peak height (nA)		*R*
		Hexane	Crude oil	
	–		20.7	
Brass River Light	0.25	28.7	43.9	0.81
(0.50 g)	0.50	60.4	64.0	0.72
	–		11.3	
Iran Light	0.15	16.5	20.7	0.57
(1.0 g)	0.30	32.6	33.2	0.67
	–		13.4	
Maya	0.20	22.1	24.4	0.50
(0.50 g)	0.40	42.1	37.2	0.56

R: signal in crude oil/signal in hexane. Enrichment time: 4 min.

Table 2
Normalized signal

Compound	Signal A	Signal B
Phenol	1.00	1.00
m-Cresol	0.37	0.40
p-Cresol	0.39	0.38
o-Cresol	0.31	0.30
3,4-Dimethylphenol	0.28	0.24
2,3-Dimethylphenol	0.19	0.16
3,5-Dimethylphenol	0.24	0.21
2,6-Dimethylphenol	0.10	0.07
2,4-Dimethylphenol	0.16	0.13
2,5-Dimethylphenol	0.14	0.12

Signal A: Relative peak height in hexane; Signal B: Relative peak height in crude oil.
1.5 g Brass River Light in 50 ml hexane.

sary for the determination. The experimentation becomes much simpler if a single sample is weighed and additions are performed on aliquots of supernatant after centrifugation. However, this mode may lead to false results because the phenols added do not enter into contact with the hexane-insoluble residues.

In order to determine whether the degree of adsorption of phenols onto insoluble residue is significant, an experiment was carried out in which two almost identical samples of Maya crude oil (≈1.9 g in 15 ml hexane) were used. One of them (sample A) was centrifuged and the supernatant was spiked with a mixture of phenols dissolved in hexane. The other sample (B) was spiked with the mixture of phenols before it was diluted and centrifuged. The ratio of the peak heights of the chromatograms of both samples (R=signal B/signal A) showed that on adding the phenols after the centrifugation step the greatest difference observed was only 7%. Accordingly, it was decided to carry out the standard additions using aliquots from a single weighing subjected to dilution and centrifugation.

The stock solutions of crude oil from which aliquots for the standard additions were obtained by weighing and later bringing volume up to 100 ml with hexane. 3.3974 g of Brass River Light, 6.7066 g of Maya crude oil and 6.7294 g of Iran Light were used. Table 3 shows the parameters of the equations, fitted by least squares, the regression coefficients and the contents of the different phenols in the three samples of crude oil studied. The peaks corresponding to more than one species are given as

Table 3
Analytical characteristics and contents of different phenols

Crude oil	Compound	Slope	Intercept	r^2	Found (mg/g)
Brass	P	$(2.38\pm0.06)\times10^2$	$(4.3\pm0.2)\times10$	0.9987	5.3
River	*m*-C and *p*-C	$(8.6\pm0.3)\times10$	$(2.9\pm0.2)\times10$	0.998	9.9
Light	*o*-C	$(7.3\pm0.1)\times10$	$(2.1\pm0.1)\times10$	0.9993	8.5
	3,4-D	$(5.6\pm0.3)\times10$	(2.7 ± 0.3)	0.993	1.4
	2,3; 3,5 and 2,6-D	$(3.82\pm0.07)\times10$	$(1.33\pm0.05)\times10$	0.9993	10.2
	2,4; 2,5-D	$(3.0\pm0.1)\times10$	(8.4 ± 0.6)	0.998	8.2
Iran	P	$(1.88\pm0.04)\times10^2$	$(2.50\pm0.07)\times10$	0.9993	2.0
Light	*m*-C and *p*-C	$(7.1\pm0.2)\times10$	$(1.64\pm0.08)\times10$	0.9991	3.4
	o-C	$(5.8\pm0.1)\times10$	$(1.66\pm0.07)\times10$	0.9991	4.2
	3,4-D	$(4.5\pm0.4)\times10$	3.0 ± 0.4	0.985	1.0
	2,3; 3,5 and 2,6-D	$(2.99\pm0.07)\times10$	(9.8 ± 0.4)	0.9988	4.9
	2,4 and 2,5-D	$(2.45\pm0.09)\times10$	$(1.51\pm0.07)\times10$	0.997	9.2
Maya	P	$(1.75\pm0.05)\times10^2$	$(2.8\pm0.1)\times10$	0.9985	2.4
	m-C and *p*-C	$(7.0\pm0.2)\times10$	$(2.19\pm0.09)\times10$	0.9990	4.7
	o-C	$(5.4\pm0.1)\times10$	$(2.69\pm0.08)\times10$	0.9993	7.4
	3, 4-D	$(4.1\pm0.2)\times10$	(3.4 ± 0.2)	0.995	1.2
	2,3; 3,5 and 2,6-D	$(2.77\pm0.06)\times10$	$(1.07\pm0.04)\times10$	0.9991	5.8
	2,4; 2, 5-D	$(2.31\pm0.06)\times10$	$(1.03\pm0.04)\times10$	0.9985	6.6

P: phenol; *m*-C, *p*-C: *m*-cresol and *p*-cresol; *o*-C: *o*-cresol; 3,4-D: 3,4-dimethylphenol.
2,3; 3,5 and 2,6-D: 2,3-dimethylphenol, 3,5-dimethylphenol and 2,6-dimethylphenol.
2,4 and 2,5-D: 2,4-dimethylphenol and 2,5-dimethylphenol.

contents with respect to *m*-cresol; 2,3-dimethylphenol and 2,4-dimethylphenol, respectively.

The R.S.D. for the different phenols in nine replicates of the Maya crude oil sample was between 3.0% (2,4-dimethylphenol and 2,5-dimethylphenol) and 6.7% (3,4-dimethylphenol).

4. Conclusions

A method for the determination of phenols in samples of crude oil is proposed in which separation is carried out with a silicone membrane separation module coupled on-line to a chromatographic system. Even though the standard additions method is used for quantification, the procedure is simpler, cheaper and less toxic than liquid–liquid extraction. Sample treatment consists simply of dissolution in hexane and centrifugation (where necessary). The proposed chromatographic extraction–separation system can be used for the separation of other analytes found in organic matrices that are difficult to handle.

Acknowledgments

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