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Continuous membrane extraction coupled with chromatographic analysis for the determination of phenols in fuels

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Abstract

On-line coupling of devices for nonchromatographic separation to chromatographic analysis systems affords a substantial improvement in sample processing and facilitates the automation of the procedure, considerably decreasing the error of the analytical methods used. In this work, a silicone membrane device has been coupled to a high-performance liquid chromatograph with electrochemical and ultraviolet detection and the system has been used to determine phenols in complex organic matrices (gasolines and kerosene) with minimum sample handling. A microcomputer controls the set of operations required in the overall automatic process. Several quantification methods, internal standard, calibration in phenol-free matrices and standard addition, have been used, all of them providing similar results.

Keywords: Membrane extraction; Extraction methods; Phenols; Gasoline; Kerosene

1. Introduction

Knowledge of the types and quantities of polar compounds in fuels is important because they significantly affect both the refining and the stability behaviour of crudes and products [1]. Among such polar compounds are phenols, whose contribution to the formation of insoluble rubbers and sediments has been studied by different authors [2–4]. Rubbers are deposited in fuel lines and in motors and may damage them.

In a study of carbon-derived liquid fuels, White et al. [2] proposed a mechanism to account for the formation of insoluble particles. The mechanism is based on the oxidative coupling of phenols, leading to the formation of phenol polymers whose presence in such particles was checked by the authors using techniques such as X-ray diffraction and nuclear magnetic resonance. The authors also observed a decrease in the concentration of phenolic compounds in aged fuels. Hazlett and Power [3] proposed a similar mechanism and demonstrated that the phenolic extract of a catalytically cracked unstable fuel significantly increases the formation of sediments in another relatively stable fuel obtained by direct distillation of the crude. Later, Power and Mathys [4], characterizing the sediments of aged fuels, reported that these compounds contained a nucleus of polar materials, among which –OH phenolic and –NH indole groups were outstanding. This nucleus facilitates the later adsorption of other species and hence the formation of particles over time.

The phenols present in crudes of petroleum and its derivatives have been analysed by different methods,

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especially gas chromatography coupled with mass spectrometry (GC–MS) [3,5–7]. A frequent practice is to perform a prior chemical derivatisation to improve peak resolution and, sometimes, the response obtained in detection. This is the case of the formation of trifluoroacetate esters [8,9] or silyl ethers [10].

Phenols have also been determined in petroleum crudes and shale oils using liquid chromatography with electrochemical [11,12] and ultraviolet [5] detection and in combination with MS [13]. Another possible separation technique, although less used in these matrices, is capillary electrophoresis [14].

Other modes of detection used in the analysis of phenols in these matrices (with or without prior chromatographic separation) are infrared spectrophotometry [2,15], in which derivatisation has also been used [16], and NMR spectrometry, in which derivatisation is also possible [17,18].

In general, sample preparation is complicated and requires conventional liquid–liquid extraction or prior preparative chromatography to separate the different fractions of the matrices. In some cases, distillation has been used [1].

A simple alternative, involving minimum sample treatment, is the use of silicone membranes as a separation barrier before the sample is introduced into the analytical system. Only the components of the sample that are soluble in the acceptor and in the membrane are able to cross it, thus allowing direct introduction of complex samples into the analytical system. Using a membrane of this type, Rodríguez Gonzalo et al. [19] proposed a method for the determination of total phenols in kerosene and naphtha with a flow injection system. At our department [20], we have previously developed a method for the determination of phenols in petroleum crudes using high-performance liquid chromatography coupled with a separation device based on a silicone membrane.

In the present work we report the utilization of membrane extraction to separate the most abundant phenols in fuels, phenol, cresols and dimethylphenols from the matrix and the chromatographic determination of these compounds in kerosene and gasoline samples.

2. Experimental

2.1. Reagents and standards

Phenol (98.5% purity) was supplied by Panreac (Barcelona, Spain). *o*-Cresol, *m*-cresol and *p*-cresol (approx. 99% purity) were from Sigma (Madrid, Spain). α-Naphthol, 3,4-dimethylphenol, 3,5-dimethylphenol, 2,3-dimethylphenol, 2,4-dimethylphenol, 2,5-dimethylphenol and 2,6-dimethylphenol, (between 97 and 99% purity) were from Fluka (Madrid, Spain). Standard solutions of these compounds, with concentrations ranging from 502 to 549 mg/l, were prepared by dissolution of the commercial products in hexane (Carlo Erba, Barcelona, Spain). These stock solutions were stored at 4°C. Gasoline and kerosene samples were provided by official suppliers. Considering the changes in the volume of hexane with temperature, in all cases sample preparation was carried out at 4°C to ensure reproducibility. Kerosene and gasoline samples were introduced directly into the system by simply adding a given amount of hexane to them.

HPLC grade acetonitrile and methanol, used in the preparation of the mobile phase and the acceptor solutions, were from Merck (Darmstadt, Germany) and BDH (Poole, UK), respectively. All the mobile phases, mixtures of acetonitrile–water or methanol–water contained 1 g/l of KNO_3 and 0.025 g/l of H_2SO_4. 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. Instrumentation

The set-up 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 and a separation unit constructed in aluminium. This unit was formed of two blocks (0.85×3×8.5 cm), each of them with a 45-mm slit of approximately 1-mm depth and 2-mm width. These slits functioned as chambers for the acceptor and sample, respective-

ly, and the membrane employed for the liquid–liquid extraction process was a Perthèse reinforced silicone layer 0.175-mm thick, provided by Laboratoire Perouse Implant. In the working conditions used, membrane life exceeds 500 injections. All connections in the separation module were 0.50 mm I.D. PTFE tubing and pump tubes were of 1 mm I.D. isoversinic.

The chromatographic system comprised a Spectra Physics SP 8800 ternary pump, an SP 8450 UV detector and an EG&G PARC 400 electrochemical detector connected in series to an SP 4290 integrator: first the optical detector and then the electrochemical one. 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. In all experiments, a Rheodyne 7010 six-port injection valve with a 20-μl injection loop and a 220×4.6 mm Phenomenex LiChrospher 5 ODS stationary phase column were used.

The sample treatment module 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 microprocessor of a Gilson 213 automatic sampler controls the functioning of the whole system: the flow-rates of the sample and acceptor streams at the sample treatment module, the chromatographic pump, the position of the chromatographic injection valve, the time during which this remains in the charge or load positions and the integrator.

2.3. Chromatographic conditions

The optimal mobile phase composition was: acetonitrile–water (30:70, v/v) at 1.0 ml/min flow-rate. The chromatograms obtained with UV detection were recorded at 280 nm and the electrochemical ones at +1200 mV. The electrode was pretreated electrochemically every day by keeping the potential at +1350 mV for 10 min and then applying the working potential. Additionally, it was polished once every week.

In the case of fuel sample injection, a 5-min washing cycle with acetonitrile was performed at the end of each run in order to elute any strongly retained compounds. No electrode pretreatment was required between runs because electrode performance remained unaltered. The process is automatic since the microprocessor controls the chromatographic pump, ordering it to reinitiate the elution program with each new injection.

2.4. Membrane extraction

The functioning of the sample treatment module has been described previously in a work published by our Department [20]. For each sample it comprises a washing step of the acceptor and sample chambers, an enrichment step, during which acceptor flow is halted and the analytes crossing the membrane are concentrated in an acceptor portion, and finally, displacement of the most enriched acceptor portion to the loop of the chromatographic injection valve just before automatic injection into the chromatographic system.

3. Results and discussion

The composition of the acceptor for the separation of phenols through the membrane, the transfer of acceptor to the chromatographic system and the variables affecting chromatographic separation and detection were optimised.

The sample and acceptor volumes used, the transfer of acceptor to the valve loop and the coordination with the chromatographic separation were under automatic control of the autosampler, thus ensuring the reproducibility of the process. 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 (5 ml).

For the portion of acceptor enriched in analyte to be transferred to the loop of the injection valve of the

chromatograph, a volume of acceptor is displaced by the piston pump. The optimum volume that the piston must displace was 100 μl. For each set-up this value depends on the acceptor chamber volume (V_c), the valve loop volume (V_i) and the volume of the connection tubing between the separation unit and the injection valve (V_t). In this set-up V_c=45 μl, V_i=20 μl and V_t=25 μl.

3.1. Chromatographic separation and detection

The hydrodynamic voltammograms corresponding to the different phenols were obtained to determine the most appropriate oxidation potentials for their electrochemical detection. The oxidation intensities increased across the applied potential range whereas increases in potential did not lead to any significant increase in the background noise of the chromatograms. Accordingly, a potential of +1200 mV was chosen [mobile phase methanol–water (50:50, v/v)], which offered good sensitivity. This potential could be reduced slightly should there be interferences from other compounds at high oxidation potentials.

In order to determine the signal level at which electrode 'passivisation' owing to phenoxy radicals [21,22] occurs, solutions of phenol were prepared in hexane at different concentrations (0.20, 2.02, 10.1, 20.2, 30.2 and 40.3 mg/l, respectively) and ten consecutive aliquots of these solutions were subjected to the described overall process of separation and detection [mobile phase methanol–water (50:50, v/v)].

The 'passivisation' phenomenon was almost negligible up to phenol concentrations of 20.2 mg/l, affording signals of around 450 nA for the enrichment time used (2 min). The precision of the analytical responses for ten successive injections of phenol, expressed as its relative standard deviation (R.S.D.), was 2%. Instead, there was a signal decrease of 7 and 16% for the 30.2 and 40.3 mg/l phenol concentrations, respectively. In later studies, attempts were made to ensure that the electrochemical signals would remain below 450 nA in order to obtain good electrode performance. The signal corresponding to UV detection remained constant for all the phenol concentrations studied, indicating that the decrease in the electrochemical signals is indeed due to 'passivisation' of the electrode and not to saturation of the membrane or acceptor.

Under an isocratic regimen the two mobile phase compositions that gave the best results as regards peak resolution were methanol–water (50:50, v/v) and acetonitrile–water (30:70, v/v). The latter was chosen as the most appropriate for later studies. However, two pairs of compounds coeluted with the same retention times: *p*-cresol and *m*-cresol, and 2,4-dimethylphenol and 2,5-dimethylphenol. Mobile phase flow-rates between 0.5 and 1.5 ml/min provided similar values of peak resolution. As expected, analysis times were shorter at higher flow-rates, although 1 ml/min gave an adequate run time.

Calibration curves were obtained for enrichment times of 0 (steady extraction), 1 and 4 min. The parameters of the least squares fittings for a 1-min enrichment time are shown in Table 1, together with the calculated detection limits (twice the noise) and the R.S.D. for 10 samples. When a 4-min enrichment time was used, the slopes of the calibration graphs and the detection limits for the different compounds were improved by a mean factor of 3. The detection limits obtained with ultraviolet detection were between 2 and 3 times higher than the electrochemical ones.

3.2. Membrane extraction

Methanol–water and acetonitrile–water solutions were assayed at different proportions. A study was made of the transfer through the membrane of the different analytes for enrichment times of 0 (steady extraction) 1, 2, 4 and 8 min. When the acceptor was made up only of methanol or acetonitrile the peaks were broadened and also showed an asymmetry factor of less than one, such that peak resolution and height decreased. This effect can be attributed to the fact that the injection of a relatively high volume of a strong solvent in a reversed-phase C_{18} column could cause the analyte to prematurely move down the column, resulting in a loss of resolution [23].

Fig. 1 shows the variation in the electrochemical signal (measured as peak height) for different enrichment times and as a function of the acceptor content of methanol or acetonitrile. The variation in the UV signal was similar. For methanol–water mixtures, a continuous increase in the signals occurred parallel

Table 1
Analytical characteristics of the method

Compound	Range (mg/l)	Slope	Intercept	r^2	R.S.D.[a] (%)	LOD[b] (mg/l)
Phenol	0.26–19.2	(17.6±0.2)	(5±2)	0.9992	4.9 (0.88)	0.091
p-Cresol	0.43–31.9	(9.6±0.2)	(5±3)	0.9984	4.3 (1.63)	0.17
m-Cresol	0.20–30.7	(10.2±0.1)	(5±2)	0.9994	4.4 (0.75)	0.16
o-Cresol	0.25–37.6	(8.0±0.1)	(3±2)	0.9991	4.5 (1.93)	0.20
3,4-Dimethylphenol	0.50–75.6	(5.08±0.07)	(1±3)	0.9990	4.5 (3.64)	0.32
3,5-Dimethylphenol	0.51–75.9	(4.37±0.07)	(7±3)	0.9986	6.4 (3.74)	0.37
2,3-Dimethylphenol	0.51–75.9	(3.52±0.04)	(0±2)	0.9993	5.7 (3.90)	0.45
2,4-Dimethylphenol	1.05–78.4	(2.70±0.02)	(−0.7±0.9)	0.9996	4.9 (5.31)	0.59
2,5-Dimethylphenol	0.50–75.4	(3.07±0.03)	(0±1)	0.9995	4.8 (2.62)	0.52
2,6-Dimethylphenol	2.00–150	(1.80±0.02)	(−3±2)	0.9994	5.0 (7.25)	0.89

[a] Values in parentheses are the compound concentrations for which R.S.D. was obtained.
[b] LOD=limit of detection (calculated as twice the noise).
Enrichment time: 1 min.

to the increase in the proportion of methanol (with the exception of phenol, for which transfer through the membrane remained almost constant). In contrast, for acetonitrile–water mixtures bell-shaped curves were obtained, with a maximum at around 60% of acetonitrile in the acceptor (40% in the case of phenol). A possible explanation for this type of behaviour would involve a decrease in acceptor viscosity when the acetonitrile content is very high. Although the silicone membrane used here was reinforced, a very low degree of viscosity could decrease the pressure on the membrane on the acceptor side and hence the volume of the acceptor chamber would decrease.

Viscosity also affects the diffusion coefficient of the analytes; thus, the coefficient increases as viscosity decreases. Therefore, greater dispersion could occur in transport to the detector, with the consequent decrease in peak heights.

An acetonitrile–water (60:40, v/v) composition was chosen as optimum; in general this affords maximum signals for all the analytes studied.

3.3. Quantification

Since under the experimental conditions employed two pairs of phenols coeluted, it became necessary to choose one of the coeluting species as a reference for later quantification. The phenols chosen were: *p*-cresol for the *p*-cresol/*m*-cresol pair and 2,4-dimethylphenol for the 2,4-dimethylphenol/2,5-dimethylphenol pair.

The transfer of phenols through the membrane would be expected to be affected by the matrix since the value of the membrane-matrix distribution constant depends on this. In order to determine the effect of the matrix on the overall membrane– chromatographic separation–detection process, samples of a kerosene and a gasoline were taken and diluted with hexane at different proportions: 20, 40, 60 and 80% (v/v).

The analytical signals corresponding to the phenol and cresols in these samples are shown in Fig. 2. The signals do not increase linearly with the concentration of the samples, whereas in the calibrations performed with hexane linearity is maintained for signals of the same magnitude. This shows that a matrix effect is involved. This effect can be attributed to the different acceptor–sample distribution ratios for the different matrices studied.

Accordingly, the possibility of performing quantification by different methods was studied: internal standard addition, calibration in the matrix itself, prior extraction of the phenols present in it (with two variants, depending on whether an internal standard was added or not, to improve reproducibility) and standard addition.

Three samples were chosen for the study: one of kerosene and two of gasoline (one 97 octane and the other unleaded). The top parts of Figs. 3 and 4 show the chromatograms corresponding to the kerosene

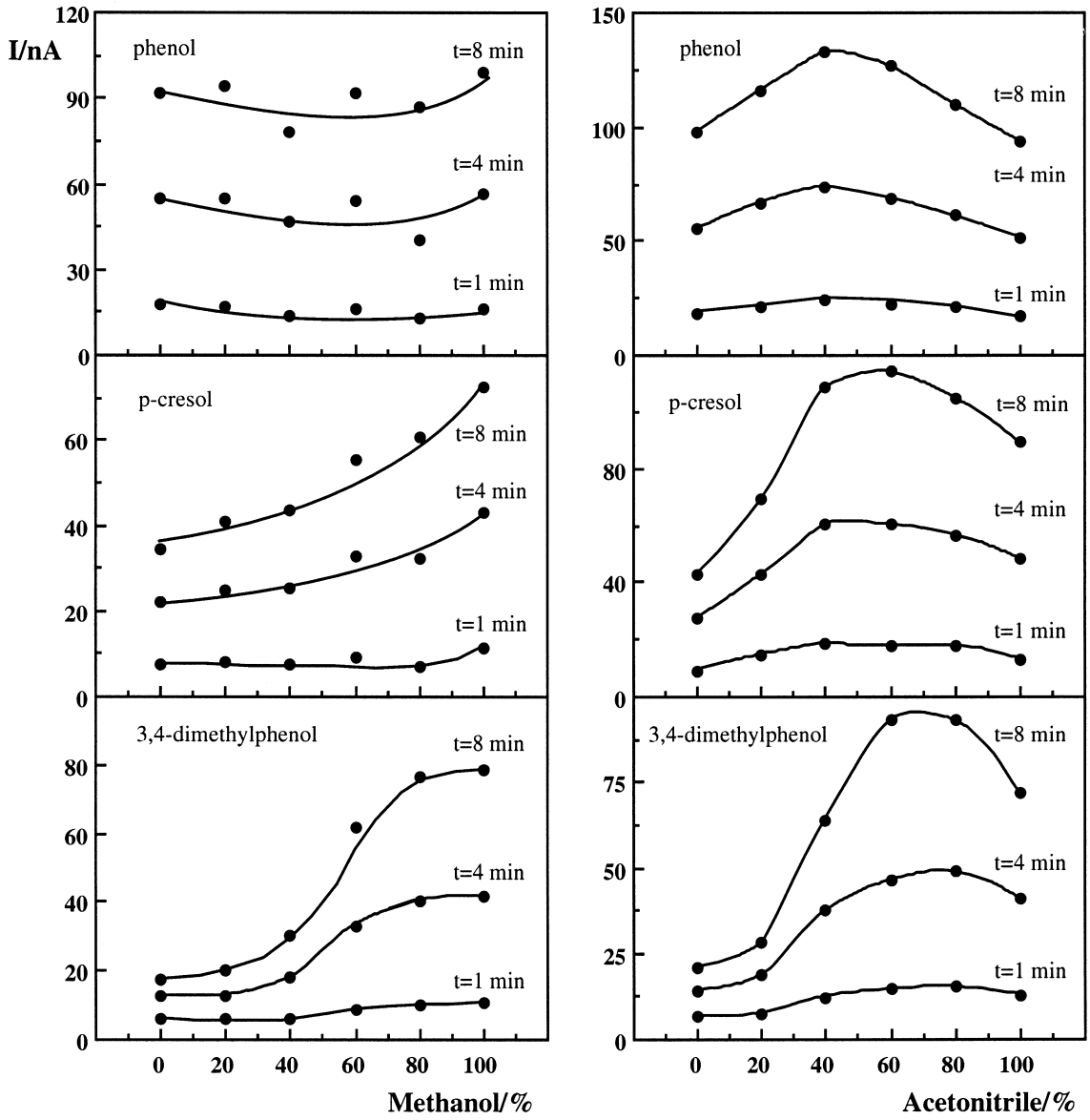

Fig. 1. Variation in analytical signal as a function of the composition of the acceptor phase. Left: methanol–water mixtures. Right: acetonitrile–water mixtures. Concentrations of compounds, in mg/l: (0.81) phenol; (1.23) *m*-cresol; (1.21) *p*-cresol; (1.23) *o*-cresol; (1.22) 3,4-dimethylphenol; (2.56) 3,5-dimethylphenol; (2.64) 2,3-dimethylphenol; (2.56) 2,4-dimethylphenol; (2.41) 2,5-dimethylphenol; (3.64) 2,6-dimethylphenol. Chromatographic conditions as described in Section 2.

and one of the gasolines obtained at enrichment times of 8 min and 0.5 min, respectively. In the case of the gasoline sample, the signals of the phenol and of the cresols are much higher than those of the dimethylphenols (this behaviour was also found for the other gasoline studied); hence, to calculate the content in dimethylphenols it would be necessary to increase the enrichment time in the separation unit. However, since the consequent increase in the phenol and cresol concentrations could lead to electrode 'passivisation' and since the total content is determined by these major analytes, an enrichment

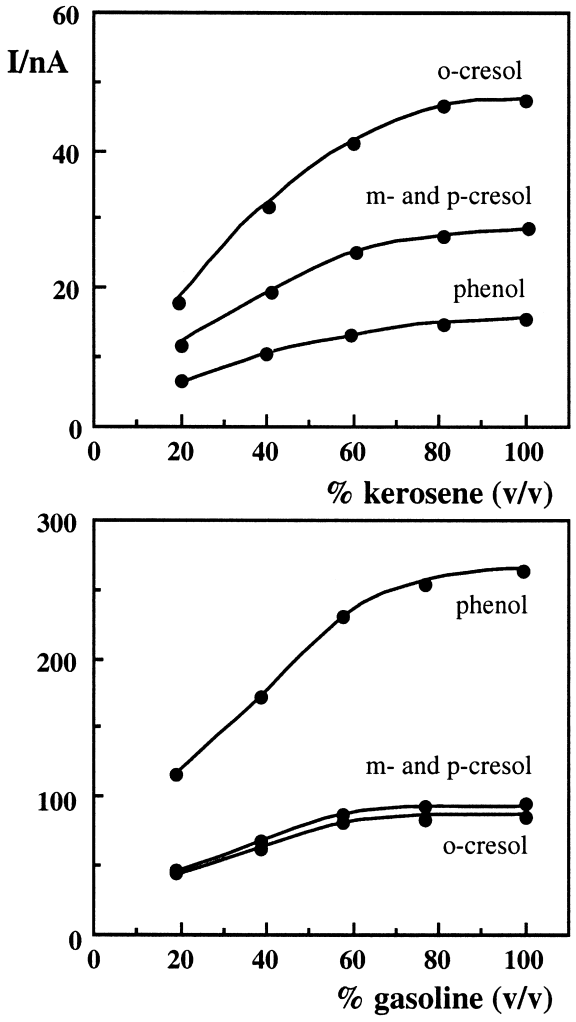

Fig. 2. Matrix effect on analytical signal. Enrichment time: 8 min for kerosene and 1.5 min for gasoline. Chromatographic conditions as described in Section 2.

time of 0.5 min was chosen to quantify phenol and cresols in later studies.

3.4. Internal standard

The possibility of using α-naphthol as internal standard was also studied. Under the experimental conditions used, this compound has a retention time of 25 min and therefore does not interfere in chromatographic determination. If α-naphthol is a suitable internal standard, the relationship between its analytical signal and that of the analytes in a given matrix should remain constant with dilution. From this it may be induced that the relationship will be the same in hexane and hence it should be possible to obtain calibrations of the analytes in it using internal standard.

Samples of kerosene and gasoline were spiked with known amounts of α-naphthol, diluting aliquots of them with different proportions of hexane. As from a hexane dilution of 50%, the relationships did not vary significantly, suggesting that transfer of the analytes and internal standard through the membrane is affected similarly in the diluted matrices, thus compensating for the matrix effect.

From the above results it may be concluded that it would be possible to carry out quantification using calibration curves in hexane. Samples should be previously diluted with hexane at least 50%.

3.5. Calibration curves in phenol-free matrices

Phenol was removed from the samples by successive extractions of 200 ml of sample with four 50-ml aliquots of 0.5 *M* sodium hydroxide.

Figs. 3 and 4 (bottom) show the chromatograms of the samples of kerosene and unleaded gasoline obtained with electrochemical and ultraviolet detection after the phenols had been removed. In this case, the signals of the phenols are almost negligible, which means that these matrices can be used to prepare calibration standards. The peaks persisting after the extraction do not correspond to any of the analytes.

Calibrations of the phenols were carried out in the matrices obtained after the extraction, both directly and after the addition of α-naphthol as internal standard, in this case not to compensate the matrix effect but to improve the precision of the method. In the case of the gasoline samples, assuming that the matrix of both must be similar, the possibility of using the calibrations obtained in one of them to calculate the phenol content of the other one and vice versa was studied. If this were feasible, it would be possible to quantify phenols in different matrices of the same type, performing extraction on only one of them.

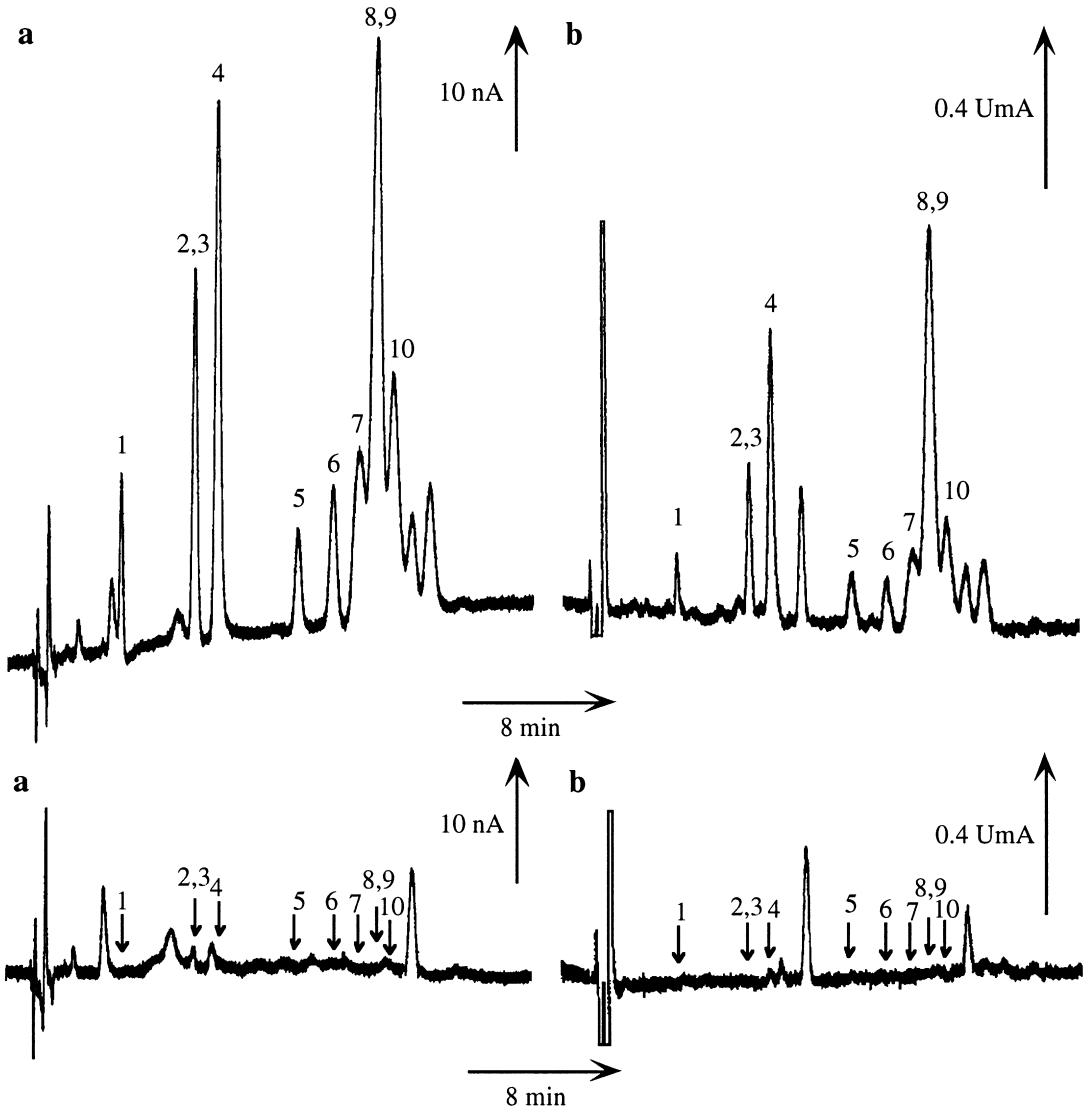

Fig. 3. Upper chromatograms: electrochemical (left) and UV (right) detection of phenols in a kerosene sample. Lower chromatograms: electrochemical (left) and UV (right) detection in the same kerosene sample after the extraction of phenols with 0.5 *M* NaOH. Enrichment time: 8 min. Chromatographic conditions as described in text. Peak assignment: (1) phenol; (2) *m*-cresol; (3) *p*-cresol; (4) *o*-cresol; (5) 3,4-dimethylphenol; (6) 3,5-dimethylphenol; (7) 2,3-dimethylphenol; (8) 2,4-dimethylphenol; (9) 2,5-dimethylphenol; (10) 2,6-dimethylphenol.

3.6. Standard addition

Standard additions were made by direct addition of standards to the samples. In this way, they would be affected by the sample in the same way as the phenols already present in it. Since the analytes were added dissolved in hexane, in all cases the final kerosene–hexane and gasoline–hexane ratios were adjusted, even in the unspiked samples, to 90:10, (v/v) and 85:15, (v/v).

3.7. Comparison of results

The R.S.D. of the analytical responses for ten

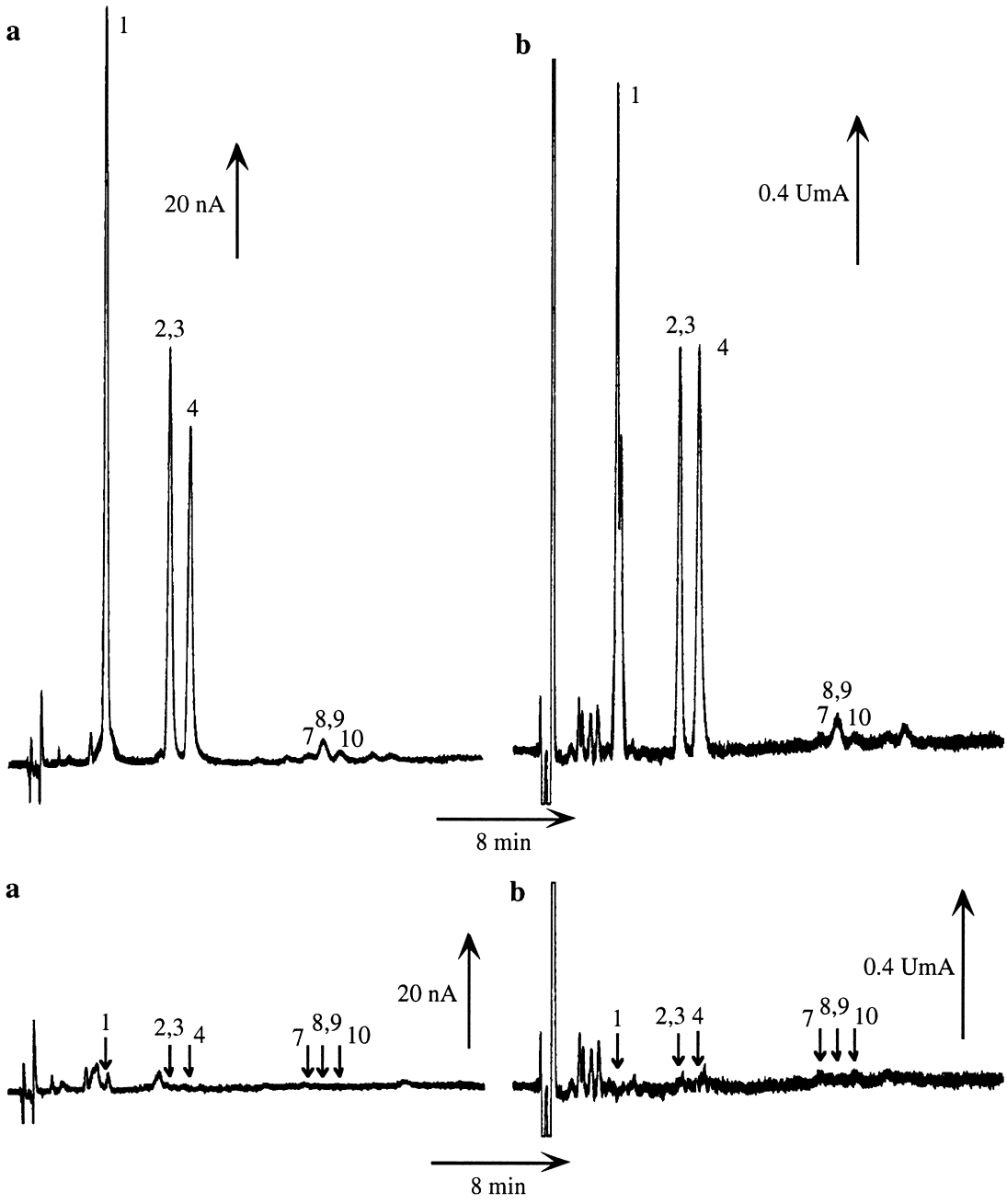

Fig. 4. Upper chromatograms: electrochemical (left) and UV (right) detection of phenols in a gasoline sample. Lower chromatograms: electrochemical (left) and UV (right) detection in the same gasoline sample after the extraction of phenols with 0.5 *M* NaOH. Enrichment time: 0.5 min. Chromatographic conditions as described in text. Peaks as in Fig. 3.

successive injections of a gasoline sample was not higher than 8% for the phenols analyzed by all the different methods. Table 2 shows the calculated concentration values of the analytes in the kerosene sample, using different methods of quantification, and both types of detection — electrochemical and

Table 2
Contents of phenols (mg/l) in a kerosene sample by different quantification methods

Compound	Electrochemical detection				Ultraviolet detection			
	a	b	c	d	a′	b′	c′	d′
Phenol	0.11	0.12	0.10	0.10	0.12	0.11	0.11	0.08
p-Cresol	0.52	0.46	0.44	0.55	0.45	0.42	0.42	0.53
o-Cresol	1.9	2.1	1.9	1.8	2.0	2.0	1.9	1.8
3,4-Dimethylphenol	0.59	0.54	0.48	0.52	0.59	0.56	0.53	0.58
3,5-Dimethylphenol	0.69	0.75	0.70	0.75	0.71	0.81	0.77	0.66
2,3-Dimethylphenol	1.0	1.0	0.90	0.92	0.96	1.1	1.0	1.0
2,4-Dimethylphenol	5.5	5.7	5.2	5.3	5.5	5.6	5.2	5.0
2,6-Dimethylphenol	2.9	3.1	2.8	2.1	2.7	2.9	2.6	2.2

a and a′: standard addition.
b and b′: calibration in phenol-free matrices.
c and c′: calibration in phenol-free matrices with internal standard.
d and d′: calibration in hexane with internal standard.
Enrichment time: 8 min.

UV — for each of them. In all cases, the contents were similar.

Each method was also compared with the others using a *t*-test for paired data. In each case the level of significance was determined; when this value was greater than 0.05 (chosen as minimum level of significance) the null hypothesis that there were no significant differences among the different results was accepted. Table 3 shows the levels of significance corresponding to this test applied to the analyte contents obtained for the kerosene sample with the different methods. In most cases, the level of significance obtained was greater than 0.05. Three of the values were below 0.05 but above 0.01 and may hence be considered acceptable. It is thus concluded that any of the quantification methods studied could be used in this type of matrix.

Table 3
Paired *t*-test for different quantification methods in a kerosene sample

	Level of significance						
	b	c	d	a′	b′	c′	d′
a	0.12	0.05	0.18	0.50	0.22	0.14	0.12
b		0.04	0.13	0.11	0.36	0.09	0.11
c			0.04	0.54	0.16	0.03	0.97
d				0.15	0.11	0.40	0.62
a′					0.10	0.16	0.12
b′						0.05	0.08
c′							0.18

a and a′: standard addition.
b and b′: calibration in phenol-free matrices.
c and c′: calibration in phenol-free matrices with internal standard.
d and d′: calibration in hexane with internal standard.
a, b, c and d: electrochemical detection; a′, b′, c′ and d′: ultraviolet detection.

Regarding the gasoline samples, for which the phenol and cresol contents were determined, the results obtained for each of them with the different methods were also analogous, as shown in Tables 4 and 5, corresponding to the 97 octane and unleaded gasolines, respectively. Application of the *t*-test for paired data also showed that there were no significant differences among the results since levels of significance higher than 0.05 were obtained in almost all cases.

In the light of these observations, it is concluded that the different quantification methods afford comparable results.

4. Conclusions

An automatic method, which requires minimum sample treatment thanks to the coupling of a membrane-based separation unit to a chromatographic system, is proposed for the determination of phenol, cresols and dimethylphenols in petroleum-derived fuels. The content of phenols has been determined in samples of kerosene and gasoline. The results show that, using different methods, analyte quantification can be achieved with very similar results. Thus, when many samples are to be measured, it is useful

Table 4
Content of phenols (mg/l) in a 97 octane gasoline sample by different quantification methods

Method	Electrochemical detection			Ultraviolet detection		
	F	*p*-C	*o*-C	F	*p*-C	*o*-C
Calibration 1	26.6	10.3	26.6	24.2	9.65	26.8
Internal standard 1	24.0	9.34	23.9	22.2	8.89	24.5
Calibration 2	28.8	11.0	28.3	27.0	10.7	26.8
Internal standard 2	26.2	10.1	25.5	24.7	9.69	24.0
Standard addition	22.8	9.33	27.4	24.5	7.95	25.1

Calibration 1: calibration in 97 octane gasoline matrix.
Calibration 2: calibration in unleaded gasoline matrix.
Internal standard 1: calibration in 97 octane gasoline matrix with internal standard.
Internal standard 2: calibration in unleaded gasoline matrix with internal standard.
Enrichment time: 0.5 min.

Table 5
Contents of phenols (mg/l) in an unleaded gasoline sample by different quantification methods

Method	Electrochemical detection			Ultraviolet detection		
	F	*p*-C	*o*-C	F	*p*-C	*o*-C
Calibration 1	35.7	18.5	42.8	32.2	16.9	39.9
Internal standard 1	33.5	17.3	39.9	30.9	16.1	37.8
Calibration 2	31.9	17.3	40.2	28.9	15.3	39.9
Internal standard 2	30.6	16.1	37.3	27.9	14.7	38.5
Standard addition	31.7	16.8	41.7	32.6	15.2	41.6

Calibration 1: calibration in unleaded gasoline matrix.
Calibration 2: calibration in 97 octane gasoline matrix.
Internal standard 1: calibration in unleaded gasoline matrix with internal standard.
Internal standard 2: calibration in 97 octane gasoline matrix with internal standard.
Enrichment time: 0.5 min.

to perform extraction of only one and then quantify the phenols present in the rest, comparing their analytical signals obtained with those provided by the calibration curve of the initial sample.

In contrast, when the samples are of different types, it would be more appropriate to use standard addition, thus avoiding the previous extraction step — which prolongs analysis time —, or to dilute the samples in hexane by at least 50% and compare the signals with calibration curves obtained in hexane, using an internal standard. If it is not present in the samples, α-naphthol could be used.

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