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Automated on-line membrane extraction liquid chromatographic determination of phenols in crude oils, gasolines and diesel fuels

M[a] Esther Fernández Laespada, José Luis Pérez Pavón, Bernardo Moreno Cordero*

Departamento de Química Analítica, Nutrición y Bromatología, Facultad de Química, Universidad de Salamanca, 37008 Salamanca, Spain

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Abstract

Determination of phenols in crude oils and derived fuels requires a sample pretreatment step, usually performed by liquid–liquid extraction or preparative chromatography. In this work, sample preparation is accomplished using a silicone membrane separation unit coupled on-line to a high performance liquid chromatograph with amperometric and ultraviolet detection. The contents of phenol, cresols and dimethylphenols were determined in thirty three samples including three crude oils, twenty gasolines and ten diesel fuels. The whole set-up is fully automated through a feed-back system that allows the microcomputer controlling the process to examine the signals in real time and to make decisions while the experiment is running.

Keywords: Membrane extraction; Crude oils; Fuels; Phenols

1. Introduction

Together with naphthenic acids, phenols are found among the oxygenated compounds present in petroleum, although they may also be generated during its processing. Since commercial fuels are obtained via blending of straight run distillates, cracked products and others, their contents in phenolic compounds depend on the starting crude, the configuration of the refinery and the blending scheme [1].

The interest in the determination of phenols in crude oils and fuels lies in the fact that, upon storage, phenols and other polar compounds promote deposit formation, with deleterious effects for fuel quality and stability [2–4]. The analytical methods usually employed in these matrices are gas chromatography, usually coupled with mass spectrometry [5–8], and HPLC [8–11].

Until now, sample preparation has been accomplished via conventional liquid–liquid extraction [3,12], prior preparative chromatography [13,14] and, recently, by solid–liquid extraction [8]. The use of membranes as separation barriers for the extraction of compounds from complex matrices, is an alternative to liquid–liquid and solid–liquid extraction [15–18].

Coupling non-chromatographic separation units to analytical chromatographic systems [19] permits noteworthy improvements in the handling of samples, both organic and inorganic, whose physicochemical characteristics in terms of viscosity, density, toxicity, etc., hinder or prevent suitable manipulation.

*Corresponding author. Fax: + 34-923-294-574.
E-mail address: bmc@gugu.usal.es (B. Moreno Cordero)

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Separation devices based on membranes permit the enrichment or dilution of analytes, depending on the experimental working conditions and the transfer [20,21] of the species to be determined from a matrix that is not compatible with the mobile phases usually employed in HPLC to a compatible medium, such as methanol–water or acetonitrile–water.

Recently, we have studied the variables affecting the transfer of phenols through homogeneous silicone membranes and automatic coupling to high resolution chromatographic systems [10,11].

Here we report the results obtained in the determination of phenol, cresols and dimethylphenols in thirty three samples, including three petroleum crudes, twenty gasolines (both leaded and unleaded, and with different octane indices) and ten diesel fuels. This variety of samples shows the flexibility of the method with respect to the sample matrix. The standard addition method was chosen as the quantification method owing to the different natures of the matrices and their phenol contents.

We also propose a sequence of operations suitable for complete automation of the process, permitting reduced participation by the operator. To accomplish this, a microprocessor is used that has a feed-back system allowing it to ''decide'' whether a given sample fulfils the necessary specifications for it to be measured; if it does not, the microprocessor sends a signal ordering the sample to undergo the complete process under other experimental conditions.

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). 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 mg/l 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 diesel fuel samples were provided by official suppliers: Repsol, Campsa, Petronor, Cepsa, Galp, BP and Esso. Crude oil samples (Brass River Light, Iran Light and Maya) were supplied by Ertoil Refineries at La Rábida (Huelva, Spain).

HPLC grade acetonitrile, used in the preparation of the mobile phase and the acceptor solutions, was from Merck (Darmstadt, Germany). These 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 membrane separation module was coupled on-line to a chromatographic system. This module (Fig. 1) consisted of an aluminium unit, 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. The membrane employed for the extraction process was a Perthèse™ reinforced silicone layer 0.175 mm thick, provided by Laboratoire Perouse Implant. The donor and acceptor streams were conveyed using a Gilson Minipuls 3 MP4 peristaltic pump and a Gilson 401 dilutor used as piston pump. All connections in the separation module were 0.50 mm I.D. Teflon tubing and pump tubes were of 1 mm I.D. isoversinic.

A modular component liquid chromatographic system was used consisting of a Spectra Physics SP 8800 ternary pump, an SP 8450 UV detector and an

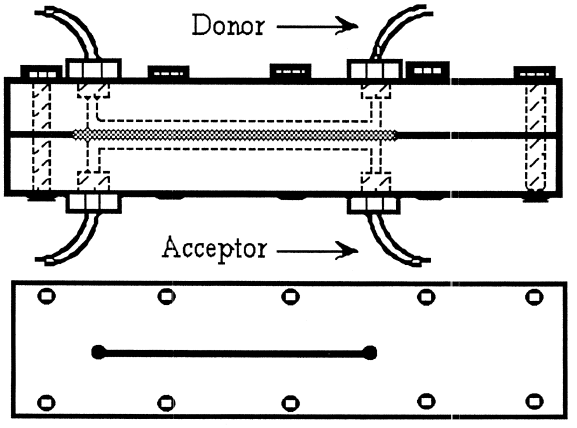

Fig. 1. Membrane separation unit.

EG&G PARC 400 electrochemical detector connected to an SP 4290 integrator. The electrodes were as follows: an Ag/AgCl/0.1 *M* KCl reference electrode, a gold auxiliary electrode and a single glassy carbon electrode MP 1305. In all experiments, a Rheodyne 7010 six-port injection valve with a 20 μl injection loop and a 220×4.6 mm Phenomenex Lichrosphere 5 ODS stationary phase column were used.

The microprocessor of a Gilson 231 automatic sampler controls the functioning of the whole system: the flow-rates of the sample and acceptor streams at the sample treatment module, the transfer of acceptor to the chromatographic valve and the coordination with the chromatographic system. Additionally, the microprocessor is directly connected to the electrochemical detector, monitoring its signal in real time.

Multivariate statistical analysis – specifically, hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) – was performed with the programs included in the SPSS (6.1 version) software package.

2.3. Procedures

2.3.1. Sample preparation

Stock solutions of the three crude oil samples used in this study were obtained by weighing and later dissolving in 100 ml of hexane 24.0088 g of Brass River Light crude oil, 25.0078 g of Maya crude oil and 27.6806 g of Iran Light crude oil. The two last samples contained hexane-insoluble residues and were centrifuged for 10 min on a Kokusan H-103N centrifuge at 3500 rpm to eliminate the undissolved solid. Adsorption of phenols onto the insoluble residue was found to be less than 7% [10].

Gasoline and diesel fuel samples were introduced directly into the system by simply adding a given amount of hexane to them: between 10 and 25% for gasolines and 60% for diesel fuels. Hexane was used to dilute the samples and to add the phenols for the standard addition method. Considering the changes in the volume of hexane with temperature, in all cases sample preparation was carried out at 4°C to ensure reproducibility.

2.3.2. Functioning of the membrane separation module

As has already been described in our previous works [10,11], after a washing step of the donor and acceptor chambers analytes are transferred through the membrane from the sample to the acceptor solution, which is flowing (steady extraction) or kept halted for a preset enrichment time. Then, the piston pump displaces the optimum volume of acceptor (100 μl in this set-up) to fill the loop of the injection valve with the portion most enriched in analytes, which is automatically injected into the chromatograph.

When using the automated system, this cycle may be run several times for the same sample, until the system decides that the signals are adequate for measurement.

The acceptor solution used was a mixture of acetonitrile–water (60:40, v/v). Its flow-rate (0.7 ml/min) and that of the sample channel (0.3 ml/min) were chosen in order to avoid pressure decompensations which could damage the membrane.

2.3.3. Liquid chromatographic analysis

The mobile phase was a (30:70, v/v) mixture of acetonitrile–water (flow-rate=1.0 ml/min) to which 1 g/l of KNO_3 and 0.025 g/l of H_2SO_4 had been added as supporting electrolyte. The peak assignments for each analyte were as follows: (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. The compounds *p*-cresol and 2,4-dimethylphenol, respectively, were chosen as references for quantification of the two pairs of phenols that coelute (*m*- and *p*-cresol, and 2,4- and 2,5-dimethylphenol, respectively). A 5-min washing cycle with acetonitrile was automatically performed at the end of each run in order to elute any strongly retained compounds.

The UV wavelength and the oxidation potential used to record the chromatograms were 280 nm and +1200 mV, respectively. 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 a week.

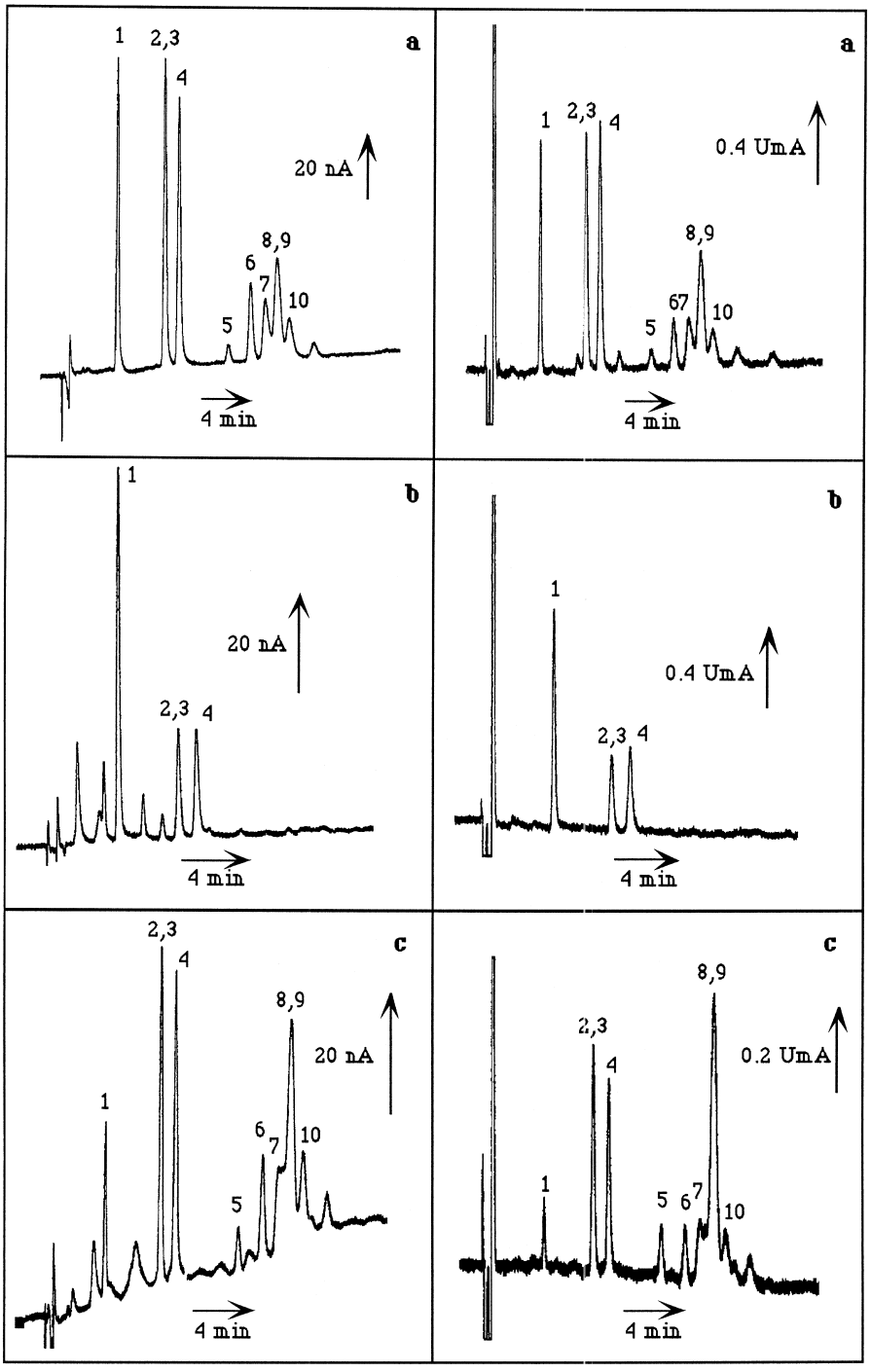

Fig. 2. Chromatograms obtained with electrochemical (left) and UV (right) detection for: (a) Brass River Light crude oil (b) unleaded 95 octane gasoline from Repsol; (c) diesel fuel for vehicles from Esso.

3. Results and discussion

We have previously reported [11] the analytical characteristics (detection limits, relative standard deviations, etc.) of the method and the possibility of using different quantification methods for the phenols present in kerosene and gasoline matrices that afford very similar results (standard addition, internal standard and calibration in phenol-free matrices). In this work, the standard addition method was chosen for quantification because we were dealing with thirty three samples – a fairly low number – with very diverse types of matrix and phenol contents.

Good linearities were always obtained, with regression correlation factors always greater than 0.990. Each point of the straight lines obtained was based on triple chromatographic runs.

3.1. Crude oil samples

The phenol contents of three samples of petroleum crude – Brass River Light, Maya and Iran Light – were determined. The samples of Brass River Light were prepared by weighing and later dissolving in hexane. The Maya and Iran Light samples contain hexane-insoluble residues and therefore, once the appropriate amount of solvent had been added, they were centrifuged to separate the undissolved solid. In this case, to accomplish the standard additions a single sample of each type was weighed and the additions were made to aliquots of the supernatant thus generated. This experimental procedure is feasible since we have earlier observed that the adsorption of phenols onto insoluble residue is not significant [10]. The enrichment times used in the separation unit were eight, ten and twelve minutes for the Brass River Light, Maya and Iran Light samples, respectively.

Fig. 2a shows the chromatograms obtained for the Brass River Light crude oil sample. The left side of the figure corresponds to electrochemical detection and the right side to UV detection. The three crude oil matrices afford few peaks corresponding to unidentified substances, although in the Maya and Iran Light samples a peak overlapping that of 3,4-dimethylphenol (peak 5) appears with electrochemical detection. In the Iran Light crude, the 3,4-dimethylphenol is almost completely masked such that its content was only evaluated with UV detection.

Table 1 shows the phenol contents of the three crudes, using both types of detection. It also includes the results obtained for the same samples in a study carried out previously at our laboratory [10] with a similar set-up but under different experimental conditions.

In all cases, the results can be seen to be similar. The greatest differences correspond to the content in 2,3-, 3,5-, and 2,6-dimethylphenol, which did not separate in the first study and hence their content is here referred to the content of one of them: 2,3-dimethylphenol.

3.2. Gasoline samples

Determination of phenols was carried out in seven leaded (octane index 97) and thirteen unleaded gasoline samples, seven of the latter with an octane index of 95 and the other six with an index of 98. The gasolines were introduced into the system with no further preparation than dilution in hexane (at a gasoline–hexane ratio between 90:10, v/v and 75:25, v/v). As well as for diluting the samples, this solvent was also used to add the phenols used in the standard additions.

Fig. 2b shows the chromatograms obtained with electrochemical and UV detection for the unleaded 95 octane gasoline from Repsol. The highest signals are seen to correspond to phenol and the cresols, the dimethylphenols affording weaker signals, close to the background noise.

The enrichment time used in the separation unit was chosen as a function of the signal intensity provided by the analytes present at the highest concentrations. This avoids ''passivization'' of the electrode during their passage through the electrochemical detector. In twelve of the gasoline samples studied, the time chosen only allowed quantification of the phenol and cresols; i.e. those determining the total content.

In the case of the leaded and unleaded 95 octane gasoline samples, in general the enrichment times were a few seconds (from zero, i.e., continuous extraction, to twenty seconds). These times were increased to three or four minutes for four of the unleaded 98 octane gasoline samples (those corre-

Table 1
Contents of phenols in crude oil samples

Crude oil	Compound	EC detection (mg/kg)	UV detection (mg/kg)	Compound	EC detection[a] (mg/kg)
Brass	Ph	5.1	4.8	Ph	5.3
River	*m*-C and *p*-C	9.9	8.4	*m*-C and *p*-C	9.9
Light	*o*-C	10.1	9.7	*o*-C	8.5
	3,4-D	1.05	1.11	3,4-D	1.4
	3,5-D[b]	4.5	4.6	3,5; 2,3 and 2,6-D	10.2
	2,3-D	4.9	5.0		
	2,4 and 2,5-D	9.6	9.0	2,4 and 2,5-D	8.2
	2,6-D	4.6	5.3		
Iran	Ph	2.2	2.1	Ph	2.0
Light	*m*-C and *p*-C	4.1	2.9	*m*-C and *p*-C	3.4
	o-C	4.8	4.4	*o*-C	4.2
	3,4-D	ND	0.87	3,4-D	1.0
	3,5-D	1.8	2.0	3,5; 2,3 and 2,6-D	4.9
	2,3-D	1.7	1.9		
	2,4-D and 2,5-D	9.4	8.7	2,4 and 2,5-D	9.2
	2,6-D	4.4	4.6		
Maya	Ph	2.3	2.1	Ph	2.4
	m-C and *p*-C	5.1	4.6	*m*-C and *p*-C	4.7
	o-C	6.2	6.4	*o*-C	7.4
	3,4-D	0.69	0.72	3,4-D	1.2
	3,5-D	1.3	1.3	3,5; 2,3 and 2,6-D	5.8
	2,3-D	3.6	3.9		
	2,4-D and 2,5-D	5.4	5.7	2,4 and 2,5-D	6.6
	2,6-D	2.8	3.4		

[a] Data from [10].

(Ph) phenol, (*m*-C and *p*-C) *m*-cresol/*p*-cresol, (*o*-C) *o*-cresol, (3,4-D) 3,4-dimethylphenol, (3,5-D) 3,5-dimethylphenol, (2,3-D) 2,3-dimethylphenol, (2,4 and 2,5-D) 2,4-dimethylphenol/2,5-dimethylphenol, (2,6-D) 2,6-dimethylphenol.

ND: Not determined.

sponding to the Repsol, Campsa, Petronor and Galp distributors).

Table 2 shows the phenol contents of the leaded, unleaded 95 octane and unleaded 98 octane gasoline samples.

3.3. Diesel fuel samples

Phenol determination was carried out in ten samples of diesel fuel, seven of them for vehicles and three for tractors and farm machinery.

It was found that on injecting a single sample successively the chromatograms obtained underwent a progressive degradation, with an increasing broadening of the peaks and the consequent loss of resolution among them. To solve this, the samples were diluted in hexane up to percentages of at least 60% and the enrichment time in the separation unit was increased to compensate this dilution. With this, suitable signals for measuring the phenols were obtained while the other strongly retained compounds of the diesel fuels underwent a lower degree of enrichment, as seen from the good reproducibility within the samples.

Accordingly, the diesel fuel samples were introduced into the system with no further preparation than their dilution in hexane at a diesel fuel/hexane ratio of (40:60, v/v).

Fig. 2c shows the chromatograms corresponding to the diesel fuel sample for vehicles from Esso. The left part of the figure corresponds to electrochemical detection while the right part shows UV detection. More peaks corresponding to unidentified analytes are seen than in the crude or gasoline samples. One of those peaks overlaps that of 2,3-dimethylphenol in the samples of diesel fuel for vehicles such that its content was not determined in those samples.

The enrichment time chosen for the analysis of the

Table 2
Contents of phenols (mg/l) in gasoline samples

Compound		Repsol		Campsa		Petronor		Cepsa		Galp		BP		Esso	
		EC	UV	EC	UV	EC	UV	EC	UV	EC	UV	EC	UV	EC	UV
Ph	a	91	85	57	56	61	62	48	45	8.8	8.3	57.8	53.9	80	76
	b	20.8	23.3	19.1	22.1	22.5	21	17.1	18.2	9.3	9.7	57	52	38	41
	c	4.7	5.1	8.4	8.7	10.9	11.0	38	36.8	1.5	1.4			37.9	36.6
m-C and *p*-C	a	34	30	23	22.0	28	26	18	15	8.4	7.3	78	55.6	106	91
	b	13.9	14.5	14.2	16.4	14.4	13.6	17.2	16.1	19.9	16.0	94.4	76	62	55
	c	2.2	2.1	4.30	3.83	5.6	4.94	42	44	1.9	1.8			41.4	36.2
o-C	a	48	47	35	33.9	40	0	26	24	7.4	7.4	53	48	86	84
	b	21.3	23.2	20.5	21.5	17.5	18	20.3	21.0	16.0	15.8	58	52	58	58
	c	3.3	3.4	4.91	4.97	7.1	7.39	41	43	1.8	1.8			51	50.7
3,4-D	a	ND	ND	ND	ND	ND	ND	ND	ND	1.17	1.19	10	9	11.8	12.6
	b	ND	ND	ND	ND	ND	ND	ND	ND	2.4	2.3	12.0	12.2	5.9	6.5
	c	ND	ND	ND	ND	ND	ND	4.80	5.6	ND	ND			4.8	5.4
3,5-D	a	ND	ND	ND	ND	ND	ND	ND	ND	1.6	1.78	12.6	12.0	13.8	13.6
	b	ND	ND	ND	ND	ND	ND	ND	ND	2.6	3.2	12.8	15.2	6.5	7.9
	c	ND	ND	ND	ND	ND	ND	5.5	5.8	ND	ND			5.40	6.1
2,3-D	a	ND	ND	ND	ND	ND	ND	ND	ND	5.0	5.0	18	17.6	24.6	24.2
	b	ND	ND	ND	ND	ND	ND	ND	ND	3.2	5.0	21	19	9.7	13
	c	ND	ND	ND	ND	ND	ND	7.5	7.8	ND	ND			8.6	8.9
2,4 and 2,5-D	a	ND	ND	ND	ND	ND	ND	ND	ND	4.5	4.4	42	34	58.4	55.4
	b	ND	ND	ND	ND	ND	ND	ND	ND	11.4	11.9	47	48	30	33
	c	ND	ND	ND	ND	ND	ND	23.9	27.5	ND	ND			20.4	19.9
2,6-D	a	ND	ND	ND	ND	ND	ND	ND	ND	1.8	2.8	14	15	14.9	18.7
	b	ND	ND	ND	ND	ND	ND	ND	ND	2.51	3.7	12.6	21	10.6	12.6
	c	ND	ND	ND	ND	ND	ND	5.4	8.5	ND	ND			4.60	10.5

EC: electrochemical detection; UV: ultraviolet detection.

a: 97 octane gasoline samples; b: 95 octane unleaded gasoline samples; c: 98 octane unleaded gasoline samples.

(Ph) phenol, (*m*-C and *p*-C) *m*-cresol/*p*-cresol, (*o*-C) o-cresol, (3,4-D) 3,4-dimethylphenol, (3,5-D) 3,5-dimethylphenol, (2,3-D) 2,3-dimethylphenol, (2,4 and 2,5-D) 2,4-dimethylphenol/2,5-dimethylphenol, (2,6-D) 2,6-dimethylphenol.

ND: Not determined.

different diesel fuels was six minutes, with the exception of the BP diesel fuel for vehicles for which a time of only two minutes was used (thus achieving suitable signals for analyte measurement), and the Esso diesel fuel for tractors and farm machinery for which an enrichment time of ten minutes was used.

The phenol contents corresponding to the samples of diesel fuel for vehicles and for tractors and farm machinery are shown in Table 3.

3.4. Comparison of phenol contents in the different types of samples

Although the number of samples was not very high, some general observations can be made regarding the contents in phenol, cresols and dimethylphenols in the different types of matrices studied.

In twelve of the thirty three samples analyzed the dimethylphenols were not quantified. All of these were gasolines in which the dimethylphenols were present at very low concentrations in comparison with those of phenol and cresols, which were much more important with regards to total contents.

Additionally, in the eight gasoline samples in which the dimethylphenol contents were determined, the relationship between their total contents and that of the sum of phenol plus cresols ranged between 0.3

Table 3
Contents of phenols (mg/l) in diesel fuel samples

Compound		Repsol		Campsa		Petronor		Cepsa		Galp		BP		Esso	
		EC	UV	EC	UV	EC	UV	EC	UV	EC	UV	EC	UV	EC	UV
Ph	a	1.16	0.97	0.88	0.64	0.66	0.50	0.81	0.93	0.13	0.13	3.53	3.13	0.83	0.58
	b					0.96	0.97	0.83	0.62					0.42	0.30
m-C and *p*-C	a	3.8	2.39	3.48	2.15	2.7	1.72	3.3	2.6	0.76	0.48	35.5	21.2	3.34	1.77
	b					4.06	3.03	3.82	2.03					1.28	0.70
o-C	a	3.8	3.6	3.09	3.07	2.4	2.6	3.4	3.5	0.82	0.79	29.8	28.5	3.52	2.74
	b					4.46	4.16	4.22	3.23					1.38	1.14
3,4-D	a	0.65	0.71	0.46	0.67	0.5	0.61	ND	1.0	0.47	0.40	8.8	9.12	0.69	0.64
	b					0.78	0.98	1.17	0.78					0.38	0.36
3,5-D	a	1.33	1.35	1.27	1.30	1.1	1.2	1.54	1.7	0.80	0.78	13.7	13.4	2.44	1.32
	b					1.81	1.82	2.16	1.34					0.87	0.74
2,3-D	b					3.06	2.42	3.6	1.66					1.33	1.27
2,4 and 2,5-D	a	5.52	5.37	5.39	5.24	5.2	4.9	6.4	6.4	3.3	3.3	40.1	28.2	5.85	4.53
	b					7.3	7.1	8.12	6.7					1.94	1.7
2,6-D	a	3.0	3.01	3.29	4.39	5.1	6.52	3.8	6.63	2.46	6.2	5.3	5.0	3.32	4.06
	b					5.16	7.8	5.5	4.4					1.94	2.58

EC: electrochemical detection; UV: ultraviolet detection.
a: vehicles; b: tractors and farm machinery.
(Ph) phenol, (*m*-C and *p*-C) *m*-cresol/*p*-cresol, (*o*-C) o-cresol, (3,4-D) 3,4-dimethylphenol, (3,5-D) 3,5-dimethylphenol, (2,3-D) 2,3-dimethylphenol, (2,4 and 2,5-D) 2,4-dimethylphenol/2,5-dimethylphenol, (2,6-D) 2,6-dimethylphenol.
ND: Not determined.

and 0.6; i.e. the proportion of dimethylphenols was always lower. In this the gasolines differed from all the rest of the samples for which, on comparing the content in dimethylphenols and phenol plus cresols, the relationship was equal to or greater than one.

Moreover, cluster analysis (complete linkage based on Euclidean distance) of the obtained analyte contents (with the exception of crude oils) shows two clear groups of samples, gasolines and diesel fuels, as can be observed in the dendrogram of Fig. 3.

Similarly, on applying LDA gasoline and diesel fuel samples constitute two clear groups because they are too different. Fig. 4 shows the plot of the discriminant scores for the same samples, the gasolines are placed on left side of the figure and the diesel fuels on the right side. Besides, a distinction can be observed between the three types of gasolines: leaded (octane index 97), unleaded (octane index 95) and unleaded (octane index 98).

On the other hand, the gasolines were the matrices in which the highest phenol contents were found; this could be related to the complex processing undergone by these fuels, during which phenols may be generated. By contrast, diesel fuels are mainly obtained by straight run distillation of crudes. However, no definite conclusions can be drawn because this would require having available the starting crudes.

4. Automation

The proposed procedure allows the separation of the matrix analytes and their later automatic determination by chromatography since the functioning of the whole system is controlled by a microprocessor. However, external operator participation is required to decide whether the signals are suitable for measurement or not.

We therefore studied the possibility of completely

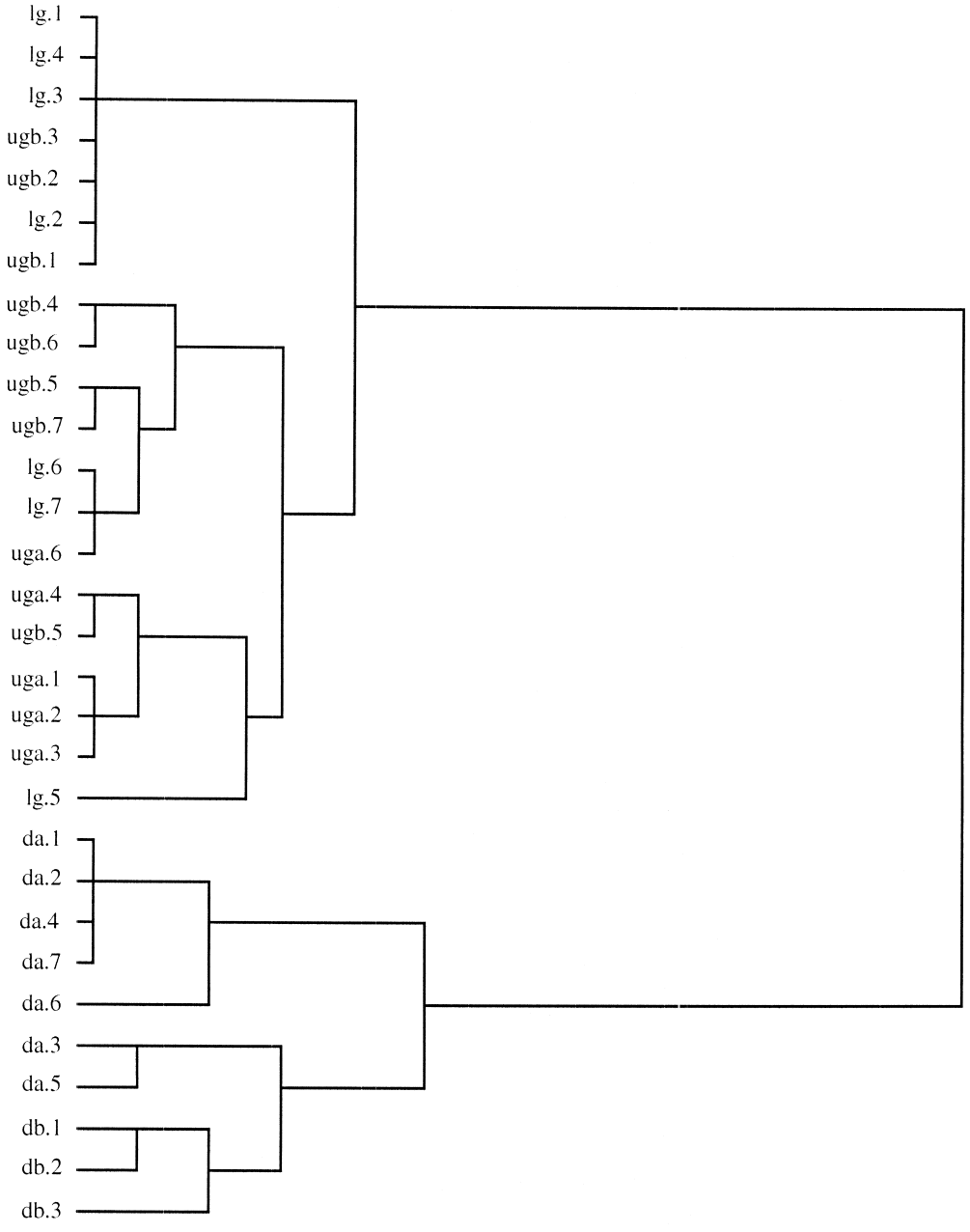

Fig. 3. Dendrogram showing the results of cluster analysis. *lg*, leaded 97 octane gasolines; *uga*, unleaded 95 octane gasolines; *ugb*, unleaded 98 octane gasolines; *da*, diesel fuels for vehicles; *db*, diesel fuels for tractors and farm machinery.

automating the system so that it could function independently. The microprocessor controlling the functioning of the system was connected to one of the detectors, being continuously supplied with the measurement data. This feedback capacity allows the system to control itself and make decisions about the

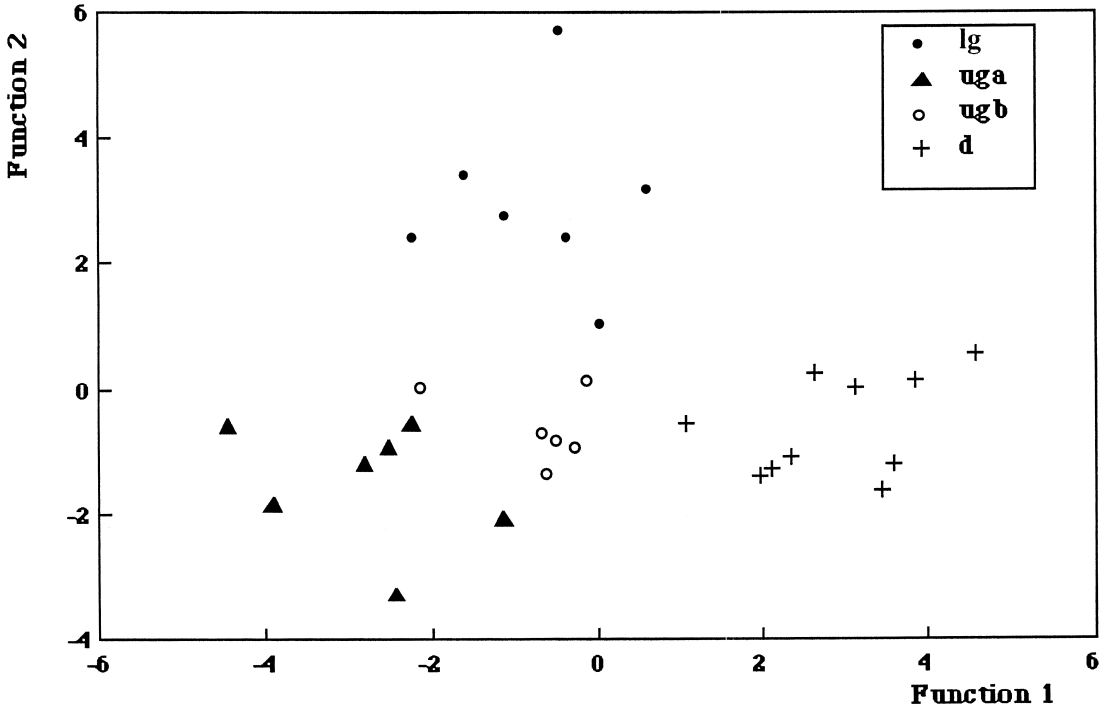

Fig. 4. Results of linear discriminant analysis with the first two discriminant scores. *lg*, leaded 97 octane gasolines; *uga*, unleaded 95 octane gasolines; *ugb*, unleaded 98 octane gasolines; *d*, diesel fuels.

most appropriate procedure for each sample. This requires prior programming to determine the range of signals that can be considered acceptable for the samples being studied.

With the system employed here, the variable on which such programming can act is the enrichment time. If the microprocessor is connected to the electrochemical detector one needs a program that begins with low enrichment times, fixing a minimum signal limit that will allow suitable quantification. The aim of this is to avoid the passage of very concentrated solutions of the analytes past the electrode, which could lead to its passivization.

Fig. 5 shows the flow diagram of the program. The inputs of the program are the number of samples to be measured (n), the maximum number of cycles per sample (m), the initial enrichment time at the separation unit (t_o), and the limit signal (s). According to this scheme, the first sample flows across the membrane and extraction takes place for the preset time: t_o. Then, the portion of acceptor enriched is injected into the chromatograph and the analytes are detected. The microprocessor receives the signals in real time and compares them with the preset minimum signal limit. If this is surpassed, the microprocessor allows the system to continue with the next sample; however, if this condition is not met, another aliquot of the sample being analyzed is automatically introduced into the system, using a longer enrichment time at the separation unit ($t = jt_o$). This process may be performed several times. Nevertheless, in order to prevent the system from introducing the same sample indefinitely, in the event of the sample not containing the analytes or having them at very low concentrations the system incorporates a counter to detect the number of cycles performed per sample. When this surpasses the limit, m, set by the operator, the system passes on to the next sample.

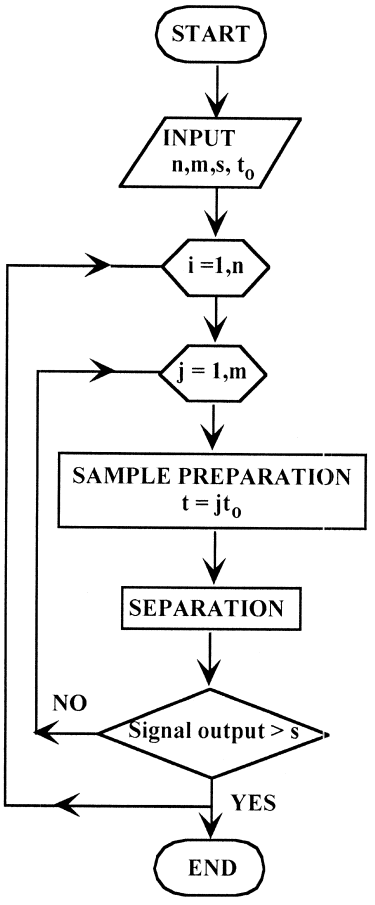

Fig. 5. Flow diagram of the program used to automate the process. *n*, number of samples to be measured; *m*, maximum number of cycles per sample; t_o, initial enrichment time at the separation unit; *s*, limit signal.

If the detector used is of the UV type, the amount of analytes that can be injected is high, although this does not affect the reproducibility of the measurements. In this case, it may be appropriate for the initial enrichment time to be high and to set a maximum limit to the signals, in order to ensure a good linearity.

The program used would be the same, only replacing $t = jt_o$ by $t = t_o/j$ in the sample preparation step. If the signals of the sample reaching the microprocessor surpass the maximum preset limit, the sample is introduced into the system again, with a lower enrichment time, until the signals fall below that limit.

As an example of the functioning of the automated system, Fig. 6 shows the chromatograms obtained with electrochemical detection when a sample of leaded gasoline is introduced into the system, setting 250 nA as the maximum signal limit. In the first injection, for an enrichment time of 30 s the signals do not surpass this limit, such that the system gives the order to process the sample with an enrichment time of 60 s. Since the signals continue to fail to reach 250 nA, the system performs a third injection, this time with an enrichment time of 90 s. In this case, the signals do meet the preset condition and the system considers sample analysis to have been completed.

5. Conclusions

The contents of phenol, cresols and dimethylphenols has been determined in thirty three samples of crude oils and derived fuels using an automatic chromatographic method coupled to a membrane separation unit that minimizes sample pretreatment. Multivariate discriminant analysis of the results allows to differentiate between groups of samples.

The whole procedure may be fully automated through a feedback system that allows the microprocessor controlling the system to decide whether the signals it receives are suitable for measurement and to vary the procedure used with a view to ensuring that this condition is met throughout the analysis.

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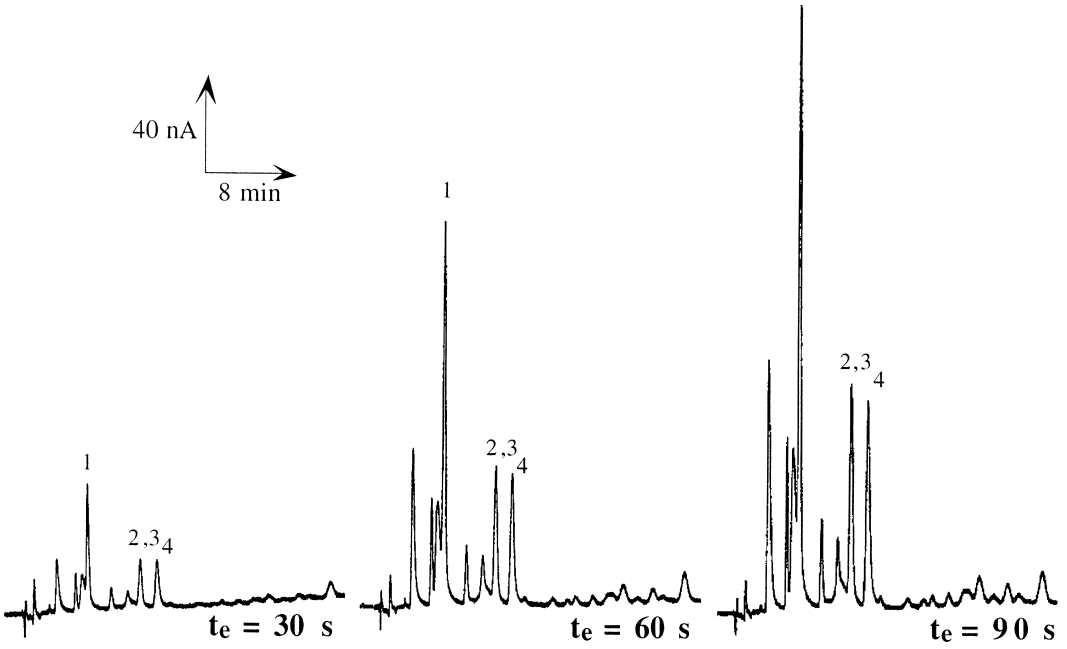

Fig. 6. Example of the functioning of the automated system for the determination of phenols. Chromatograms corresponding to a sample of leaded gasoline with electrochemical detection.

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