DETERMINATION OF PHENOLS BY IONIC LIQUID CHROMATOGRAPHY AND MULTIVARIATE CALIBRATION

Pérez-Arribas, L.V., León-González, M.E., Polo-Díez, L.M.
Departamento de Química Analítica, Facultad de Ciencias Químicas. Universidad Complutense, 28040 Madrid, Spain

SUMMARY

Chromatographic separation and quantitation of seven phenols are possible using a cationic chromatographic column, a 60mM HNO_3 aqueous solution:methanol (5:95) mobile phase and an uv detector. Quantitation of components under partially overlapping chromatographic peaks is done by multivariate calibration. The detection limits were between 0.3 and 7.0 ng. A low level of interferences and easy regeneration of the column are the main advantages. Also, the need for an organic modifier (e.g. quaternary ammonium salts) is overcome.

INTRODUCTION

Phenolic compounds, especially chloro- and nitrophenols, are of concern in the environment because of their toxicity. They occur at ppm concentrations in waste water and sub-ppm in river water[1]. In order to quantify the individual phenols, chromatographic methods are needed. GC methods are used but, due to chloro and nitrophenols have high polarity and low vapour pressure, derivatization is required[2,3]. Disadvantages of the GC methods are sample preparation time and incomplete recoveries for most phenols. HPLC is suitable for the separation of chloro- and nitrophenols, but the differences in their chromatographic behavior are such that ionization suppression and gradient techniques are needed to achieve good resolution in short analysis times. To improve selectivity and sensitivity, several mobile phases and detection systems have been used to quantify priority pollutant phenols by HPLC[4-6]. Other separation improvements involve the use of ion pair reagents such as quaternary ammonium salts[7,8].

The aim of this work was to establish an alternative method for chlorophenols and nitrophenols at sub-ppm levels using a cationic choromatographic column based on polystyrene/divinylbenzene copolymer containing quaternary ammonium groups and uv detection. On the other hand, partial overlapping of the peaks could be overcome by multivariate calibration[9,10].

EXPERIMENTAL

Apparatus and column

A Perkin-Elmer isocratic LC pump 250 coupled with a Perkin-Elmer LC 290 uv-vis detector interfaced to an IBC

computer was used. Phenols quantitation was carried out by the Nelson software package and multivariate calibration. A Hamilton PRP-X100 IC cationic column (150x4.1 mm) was used.

Chemicals

Priority Pollutant Phenols: 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol and 4-chloro-3-methylphenol were analytical grade. Mobile phase was 60 mM HNO_3 aqueous solution:methanol (5:95).

Procedure

Phenol samples were injected into a 20 µl loop in a 60 mM HNO_3 aqueous solution:methanol (5:95) mobile phase at a flow rate of 2.0 ml/min. Uv detection took place at 286 nm. Calibration was made with 30 mixtures and using a least-squares method.

RESULTS AND DISCUSSION

Several mobile phases have been studied. The 60 mM HNO_3 aqueous solution:methanol (5:95) was chosen as a compromise between sensitivity, selectivity and analysis time. A higher amount of water in the mobile phase produces better selectivity but this means lower sensitivity mainly for pentachlorophenol. HNO_3 concentration in mobile phase between 10-80 mM produces slight changes in the retention times. Moreover, 60 mM HNO_3 produces self-regeneration of the column.

In the above experimental conditions, chromatograms are run in 6 min but a partial resolution of the peaks were obtained and the mixtures were resolved using least square multivariate calibration. Although the multivariate calibration process is long, this is balanced by the shorter chromatographic run when a high sample throughput is needed. Moreover, multivariate calibration takes into account the influence that chromatographic peaks have between each other and also the small variation in experimental conditions; this yields better accuracy and precision.

The column is unaffected by repeated injections of acids, bases or concentrated brine solutions. Interferences from inorganic ions can not be expected due to experimental conditions (mobile phase and detection system) and non polar compounds are not retained into the chromatographic column.

The detection limits for different phenols are shown in Table 1. These results are similar to or better than those obtained with C_{18} HPLC columns and uv detection[4], but the chromatogram is run in a shorter time and interferences from other similar organic compounds are prevented.

Table 2 shows the results obtained from several synthetic mixtures of the phenols.

TABLE 1

DETECTION LIMITS AND RESOLUTION FOR NITRO- AND CHLOROPHENOLS

phenol	DL, ng	Rs
2-chlorophenol (CP)	1.5	
		1.25
4-chloro-3-methylphenol (CMP)	3.0	
		0.86
2,4-dichlorophenol (DCP)	1.0	
		0.94
2,4-dinitrophenol (DNP)	0.3	
		0.57
2,4,6-trichlorophenol (TCP)	1.6	
		0.98
3-methyl-4,6-dinitrophenol (DNOC)	0.4	
		1.71
pentachlorophenol (PCP)	7.0	

DL=detection limit
Rs=resolution

TABLE 2

EVALUATION IN DIFFERENT MIXTURES

	A	F	E,%	A	F	E,%	A	F	E,%
CP	1.47	1.43	-2.7	0	0	-	1.47	1.50	2.0
CMP	0	0	-	1.53	1.68	9.8	8.04	7.95	-1.1
DCP	0.76	0.82	7.9	0.80	0.72	-10.0	0	0.02	
DNP	0	0	-	0.30	0.34	13.3	2.96	2.96	-
TCP	3.02	3.40	12.6	0	0.01		0.90	0.82	-8.9
DNOC	0	0	-	1.56	1.65	5.8	0	0.03	
PCP	8.48	9.02	6.4	0	0	-	1.77	1.69	-4.5

	A	F	E,%	A	F	E,%	A	F	E,%
CP	1.47	1.51	2.7	0.31	0.34	9.7	4.96	4.83	-2.6
CMP	1.53	1.57	2.6	8.04	8.18	1.7	4.98	4.97	-0.2
DCP	2.00	1.77	-11.5	0.88	0.78	-11.3	3.20	3.04	-5.0
DNP	1.18	1.26	6.8	2.96	3.08	4.1	0.74	0.68	-8.1
TCP	0.90	0.84	-6.7	0.45	0.50	11.1	5.04	5.57	10.5
DNOC	2.96	2.64	-10.8	2.96	2.93	-1.0	0	0.03	
PCP	3.71	3.44	-7.3	9.44	10.18	7.8	9.44	9.06	-4.0

	A	F	E,%	A	F	E,%	A	F	E,%
CP	0.31	0.35	12.9	0.92	0.96	4.3	1.47	1.52	3.4
CMP	4.98	4.71	-5.4	0	0.05		8.04	8.15	1.4
DCP	2.40	2.39	-0.4	3.60	3.27	-9.2	2.80	3.18	13.6
DNP	0.89	0.78	-12.3	1.18	1.30	9.2	0	0.05	
TCP	0.90	1.00	11.1	1.46	1.34	-8.2	0	0	
DNOC	0	0	-	2.96	2.92	-1.3	2.96	2.97	0.3
PCP	5.90	5.72	-3.1	5.90	5.87	-5.1	1.77	1.57	-11.3

A=ADDED F=FOUND E=ERROR

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