

CHLOROPHENOL DETERMINATION IN WATER SAMPLES USING COMBINED GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

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Introduction

Chlorophenols in water are dangerous not only due to their own and metabolite's toxicity but also due to the possibility of their transformation to more toxic substances, for example, polychlorinated phenoxy-phenols, dibenzo-p-dioxins, dibenzofurans, etc.

Usually phenols are extracted with organic solvents and are analysed with GC and GC/MS. Now GC/MS is the main analytical tool for chlorophenols and related compounds (chloroanisols, chlorocatechols, chloroguaiacols, chloroveratrols etc.).

Usually chlorophenols are analysed as their derivatives - acetyl, trifluoroacetyl, pentafluorobenzoyl etc. Derivatisation is performed in extracts or directly in water sample before extraction.

We studied chlorophenol determination in surface, drinking and sewage water using GC/MS with and without derivatisation. Direct chlorophenol determination without derivatisation is often desirable when survey analysis or rapid screening is carried out. Chlorophenol derivatisation can be accompanied by volatile compounds loss and of the mixture change. Chlorophenols derivatives have lower polarity and reactivity and have thus better chromatographic and mass spectral characteristics than chlorophenols.

We analysed chlorophenol standard mixtures, their acetyl and trimethylsilyl derivatives to study chromatographic and mass spectral properties of these compounds, and we determined chlorophenols in a number of surface-, drinking- and sewage-water samples.

Experimental

To 1L water was added 1g internal standard 4-chloro-2-nitrophenol in acetone solution, we extracted with 50 ml methylene chloride at pH 11 and pH 2, combined extracts, dried with Na_2SO_4 and either cleaned the extract on an alumina column eluting by hexane-methylene-chloride (50:50), or analysed without cleaning.

For chlorophenol acetylation 50 ml glacial acetic acid was added to 50 ml chlorophenol solution and held 5-10 min at room temperature.

To prepare TMS 10 lI of Tri-Sil added to 5 lI chlorophenol mixture solution after solvent evaporation and held 3 - 5 min. at room temperature.

Standard mixture and extracts were analysed by Finnigan MAT ITD 700 ion trap detector coupled with a PH 5890A gas chromatograph with fused silica column HP-5 25m x 0.25 mm, or PONA 2.5 m x 0.2 mm or SPB-5 7.5m x 0.25 mm. For retention times and quantification 1 lg phenyldecane and 1 lg hexachlorobenzene were added to the sample before injection.

Results and discussion

For GC/MS chlorophenol quantification monoisotopic molecular peaks were used, their values are 15 - 30% on the base of total ion current. Taking into consideration all peaks getting in isotope cluster gives some advantages:

- 1) more peaks taking for calculation decrease background and interference effect and improve sensitivity and precision;
- 2) the possibility to check a correctness of isotope ratios and to correct peak values for interference effect;
- 3) it is possible to evaluate response factors when standards are not available.

Molecular peak values of chlorophenols acetates mass spectra are very small. $M\text{-AcO}^+$ -ions are usually the base peak, they have the same masses that correspond to molecular ion masses of the initial chlorophenols.

TMS derivatives of chlorophenols give comparatively large peaks of ions $(M\text{-CH}_3)^+$, that can be used for quantification.

Analysis was made by total mass spectra scanning and separate characteristic ion chromatograms were used for quantification. All peaks of these chromatograms were identified not only by their retention times and characteristic ions but also on the base's of total mass spectra.

Table 1 contains relative retention times and calibration factors of chlorophenols.

Table 2: Chlorophenols in sewage water before and after cleaning

NN	Substances	Before cleaning		After cleaning	
		Ret. time (s)	Content (lg/L)	Ret. time (s)	Content (lg/L)
1	2,4-Dichlorophenol	395	0.63	404	0.43
2	2,5-Dichlorophenol	415	0.22	323	0.01
3	2,4,6-Trichlorophenol	492	0.32	-	-
4	2,4,5-Trichlorophenol	509	0.07	-	-
5	2,3,4-Trichlorophenol	539	2.66	542	0.56
6	2,3,6-Trichlorophenol	555	0.08	567	0.05
7	Tetrachlorophenol	634	0.27	-	-
8	Tetrachloroguaiacol	887	0.29	-	-

Chlorophenols were determined in drinking water and a water sample from a water supply source of a big city. In both samples di- and trichlorophenol isomers were found. Chlorophenol content in drinking water was more than in water from the water supply source (0.53 and 0.18 lg/L respectively). Consequently chlorophenols must be produced during water chlorination.

Detection limit is about 0.1 ng. GC/MS even with short capillary columns can provide sufficient resolving and quantitation of chlorophenols without derivatisation. Chlorophenol derivatives can be used for more detailed and sensitive isomer differentiation.

Table 1 Relative retention times and calibration factors of chlorophenols for total ion current (TIC) and molecular ions (M)

NN	Chlorophenols	Retention time			Response factor	
		1	2	3	TIC	M
1	2-	0.13	0.23	0.12	0.16	0.12
2	3-	0.40	0.34	0.37	0.22	0.21
3	4-	0.40	0.34	0.37	0.29	0.27
4	2,6-	0.33	0.37	0.35	0.26	0.16
5	2,4-	0.34	0.45	0.31	0.30	0.17
6	2,3-	0.34	0.35	0.32	0.30	0.18
7	3,4-	0.37	0.37	0.35	0.35	0.20
8	3,5-	0.62	0.48	0.63	0.16	0.09
9	2,3,5-	0.52	0.49	0.53	0.17	0.08
10	2,4,6-	0.53	0.47	0.56	0.17	0.11
11	2,4,5-	0.54	0.48	0.57	0.17	0.08
12	2,3,4-	0.55	0.49	0.55	0.16	0.08
13	2,3,6-	0.56	0.50	0.59	0.16	0.10
14	3,4,5-	0.92	0.70	0.94	0.10	0.05
15	2,3,5,6-	0.78	0.70	0.94	0.10	0.05
16	2,3,4,5-	0.79	0.66	0.82	0.12	0.05
17	2,3,4,6-	0.79	0.66	0.82	0.12	0.05
18	2,3,4,5,6-	1.08	0.88	1.07	0.09	0.05
19	HCB	1.00	1.00	1.00	1.00	1.00

1- column 2.5 m x 0.2 mm; PONA (0.5 μ m); 40°C (2 min)--80°C (10°C/min)--240°C (5°C/min).

Retention time of hexachlorobenzene (HCB) - 12 min 40 s.

2- column 25 m x 0.25 mm; HP-5 (0.5 μ m); 80°C (2 min)--180°C (20°C/min)--240°C (3°C/min).

Retention time of HCB - 18 min 19 s.

3- column 7.5 m x 0.25 mm, SPB-5 (0.25 μ m); 60°C (1 min)--250°C (10°C/min).

Retention time of HCB - 11 min 19 s.

Columns with various stationary phases allow resolution of almost all chlorophenol isomers.

Using this method, chlorophenol in sewage water of cellulose mill before and after cleaning were determined (table 2).