

Chlorophenols in Drinking Water Using GC/MS/MS

GC/MS

Varian Application Note

Number 61

I. Turnes, I Rodríguez, C.M. García, R. Cela
Departamento de Química Analítica, Universidad de Santiago de Compostela, Spain

Key Words: MS/MS, Water, Phenols, EPA, Environmental

Introduction

There is currently great environmental interest in chlorinated phenol derivatives due to their high toxicity and wide industrial use. In response, the Environmental Protection Agency (EPA) has compiled a list of eleven phenols that are considered to be priority pollutants. In 1982, the EEC issued its own pollutant list which includes a large number of polychlorophenols, and established a maximum allowable overall concentration of 0.5 µg/l for these compounds in drinking water. Few currently available analytical techniques allow the direct determination of chlorophenols at such low concentration levels. This has promoted the development of various procedures for their extraction from their matrices using liquid-liquid extraction, solid phase extraction or carbon cartridges. In every case, large volumes of sample have to be processed and then the final extracts must be concentrated. This solvent evaporation step has been shown to result in major losses of several chlorophenols¹.

Chlorophenols are usually determined by use of chromatographic techniques such as HPLC or GC. However, because of their high polarity, they give broad tailed peaks if separated directly (without prior derivatization) by GC. The effect worsens as the chromatographic column ages. It is therefore advisable to convert chlorophenols into less polar forms in order to improve peak shape, resolution and sensitivity². Acetylation is the most frequently used reaction for this purpose.

It is preferable to use a high selective and sensitive detection technique such as tandem mass spectrometry for this analysis. In fact, this technique is particularly useful for the analysis of very complex mixtures, as it allows the separation and identification of components with different structures that are eluted at similar retention times and with widely different concentration levels. Also, increased signal-to-noise ratios afford the sensitivity needed for low trace level analysis without having to process large volumes of sample.

The purpose of this work was to develop a method for the routine determination of chlorophenols at the parts-per-trillion and lower levels in drinking water by use of GC-ion trap tandem MS.

Results and Discussion

Figure 1 shows the total ion chromatogram for the chlorophenols studied at a concentration of 100 µg/l, acquired over a mass range of 50-300. The base peaks of these spectra were used as the parent ions for the MS/MS analysis. These parent ions are: monochlorophenols (128), dichlorophenols (162), trichlorophenols (198), tetrachlorophenols (232), pentachlorophenol (266), and 4-chloro-3-cresol (142). Dissociation conditions were optimized to achieve a balance between selectivity and sensitivity. To do this, parent ions were dissociated with the aim of obtaining one to three specific product ions of high relative intensity that afforded accurate quantitation and also different relative intensities of product ions for the different isomers. These different ion ratios for different isomers were used to ensure unequivocal identification of each compound. Both aims can be achieved by the appropriate selection of the non-resonant excitation amplitude and RF storage level.

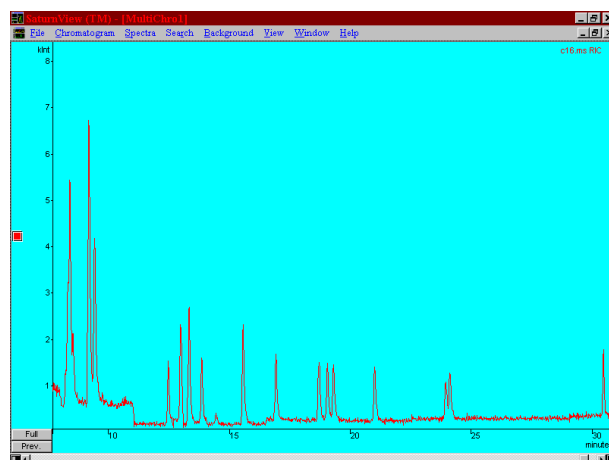


Figure 1: GC/MS/MS total ion chromatogram of 100 µg/L chlorophenol test mix.

NOTICE: Varian, Inc. was acquired by Agilent Technologies in May 2010. This document is provided as a courtesy but is no longer kept current and thus will contain historical references to Varian. For more information, go to www.agilent.com/chem.

 Agilent Technologies

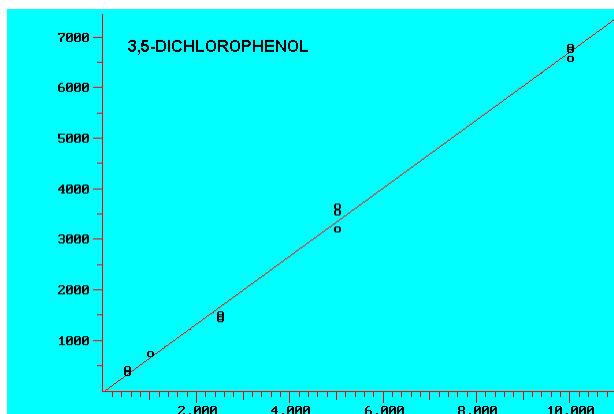


Figure 2: Typical external standard calibration curves for chlorophenols using GC/MS/MS.

Table 1 summarizes the results of this optimization process. A custom library was created by injecting the acetylated standards at a concentration level of 15 µg/l. This library was then used to identify the compounds in the samples. Even when analyzing very dilute samples (0.25 pg injected) the degree of fitting and purity obtained was quite satisfactory (70-90% purity in the worse case).

Table 1

Compound	Excitation Amplitude	RF Level	Product Ion
2-CP	68	60	65+100
3-CP	68	60	65+100
4-CP	68	60	65+100
2,6-DCP	81	75	99+126
2,5-DCP	81	75	99+126
2,4-DCP	81	75	99+126
3,5-DCP	81	75	99+126
2,3-DCP	81	75	99+126
3,4-DCP	81	75	99+126
2,4,6-TCP	74	70	97+135
2,3,6-TCP	74	70	97+135
2,3,5-TCP	74	70	97+135
2,4,5-TCP	74	70	97+135
2,3,4-TCP	74	70	97+135
2,3,5,6-TCP	82	80	131+133
2,3,4,6-TCP	82	80	131+133
PCP	92	90	167
4-Cl-3-Cresol	60	55	77

The limit of quantitation was calculated at a S/N ratio of 6 and these results are shown in Table 2. These limits are well below the legally established limits (0.5µg/l) in drinking water. This method affords detection levels between 24-60 ng/l for a 10 ml sample and 40-95 pg/l for a 1 liter sample.

Table 2

Compound	Limit of Quantitation (µg/l) (S/N=6)	Repeatability R.S.D. (%) (n=10)
2-CP	0.14	8.0
CP	0.12	5.5
4-CP	0.08	14.7
2,6-DCP	0.08	9.1
2,4+2,5-DCP	0.09	8.4
3,5-DCP	0.08	3.1
2,3-DCP	0.08	15.7
3,4-DCP	0.08	9.3
2,4,6-DCP	0.11	6.5
2,3,6-TCP	0.08	11.9
2,3,5-TCP	0.08	7.7
2,4,5-TCP	0.08	15.7
2,3,4-TCP	0.16	13.8
2,3,5,6-TCP	0.19	13.9
2,3,4,6-TCP	0.13	13.0
PCP	0.1	15.6
4-Cl-3-Cresol	0.11	7.6

Conclusion

Based on the results obtained in this work, GC/MS/MS allows the quantitation of chlorophenols in the pg/l range in drinking water by solid phase extraction from sample volumes of 1-5 liters. In the routine quality control analysis of drinking water, very low sample volumes (10 ml) have to be processed by derivatization and subsequent straight-forward extraction. In addition, the proposed method allows one to positively confirm the nature of each species and to distinguish between polychlorophenol isomers, a clear advantage over other techniques customarily used for the analysis of phenols. The low cost of benchtop instruments for implementation of the proposed method makes it a serious choice for the routine determination of chlorophenols in drinking water and other types of samples of environmental interest.

References

- M.I. Turnes, I. Rodriguez, M.C. Mejuto and R. Cela, *J. Chromatography A*, 683 (1994) 21.
- E. Ballesteros, M. Gallego and M. Valcarcel, *J. Chromatography* 518 (1990) 59.

This application note is an extract from the *Journal of Chromatography A*, 743 (1996) 283-292.