LOW LEVEL ANALYSIS OF PHENOLS BY GC/MSMS AFTER ON-LINE ACETYLATION WITH A ROBOTIC SAMPLE HANDLER

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Phenols comprise a class of chemical components consisting of a hydroxyl moiety, which is directly bound to an aromatic ring, and a range of alkyl, chlorine and nitro-substituents. Phenols are applied in various chemical processes and their presence in the environment needs to be monitored carefully. Analysis is generally carried out by means of GC/MS after acetylation to prevent severe peak tailing that compromises chromatographic separation from occurring. Unfortunately, sample preparation is tedious and time-consuming and highly prone to user-induced variability.

In this report we present the performance of a fully automated method in which phenols are acetylated according to standard reference procedures and analyzed using GC/MSMS after in-vial liquid/liquid extraction (LLE) and large volume PTV injection.

MATERIALS AND METHODS

Target components:

Table 1. Overview of target components.

Component	Component
2-methylfenol	4-chloro-3-methylfenol
3-methylfenol	2,5-dichlorofenol
4-methylfenol	2,4-dichlorofenol
2-chlorofenol	3,5-dichlorofenol
2,6-dimethylfenol	2,3,5-trimethylfenol
2-ethylfenol	2,3-dichlorofenol
3-chlorofenol	3,4-dichlorofenol
2,5-dimethylfenol	2,4,6-trichlorofenol
4-chlorofenol	2,3,6-trichlorofenol
2,4-dimethylfenol	2,3,5-trichlorofenol
3-ethylfenol	2,4,5-trichlorofenol
2-isopropylfenol	2,3,4-trichlorofenol
2,3-dimethylfenol	3,4,5-trichlorofenol
4-ethylfenol	2,3,5,6-tetrachloofenol
3,5-dimethylfenol	2,3,4,6-tetrachlorofenol
3,4-dimethylfenol	2,3,4,5-tetrachlorofenol
4-chloro-2-methylfenol	pentachlorofenol
2,6-dichlorofenol	bisfenol-A

Standards:

Stock solutions of native and labeled components were provided by the customer. Standards were prepared by adding the native components to drinking water before extraction/derivatization. An overview of standard concentrations is given in Table 2. Please note that at this stage only one labeled component was applied, i.e. 3,4-dichlorophenol-D3.

Table 2. Overview of standards and concentrations.

Reference	Concentration (µg/L)
Standard 1	0.01
Standard 2	0.02
Standard 3	0.05
Standard 4	0.10
Standard 5	0.20
Standard 6	0.50
Standard 7	1.00
Drinking water addition 1	0.10
Drinking water addition 2	0.10
Drinking water addition 3	0.10
Drinking water addition 4	0.10
Drinking water addition 5	0.10
Surface water addition	0.10
Ground water addition	0.10

Autosampler settings:

In-vial extraction and derivatization was carried out by means of a Thermo TriPlus RSH robotic sampler, which is placed on top of the GC/MSMS instrument (Thermo Trace 1300 GC and TSQ 8000 Evo, see Figure 1).

The device is equipped with the following (modular) tools:

- Tool stations for 10 mL, 1 mL and 100 µL tools
- Vortex option
- Fast Wash Station
- Solvent reservoirs for 100 mL vials
- Solvent reservoir for 10 mL vials
- Trays for 20 mL and 2 mL vials

The software control is completely embedded in the Xcalibur/TraceFinder instrument method. Method overlapping is enabled; the next sample is prepared during the analysis of the previous. Instrumental settings are described in Table 3.

RESULTS AND DISCUSSION

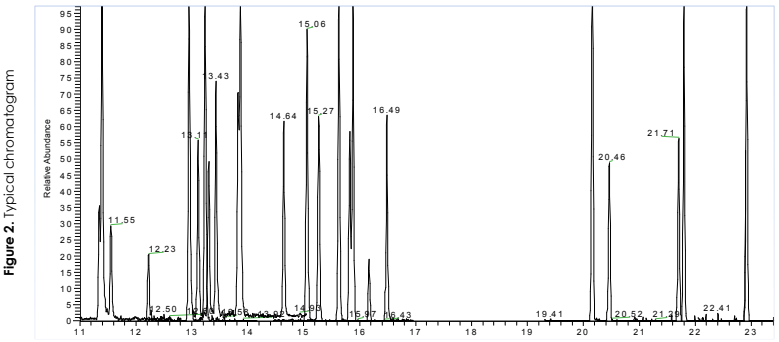

Figure 2. Typical chromatogram

Table 3, Validation results.

Compound	%RSD (n=5)	R²	Surface water, spike @ 0,1 µg/L
2-methylphenol	11.4	0.9999	0,11
3-methylphenol	12.9	0.9987	0,10
4-methylphenol	9.5	0.9998	0,11
2-chlorophenol	7.4	0.9998	0,11
2,6-dimethylphenol	7.1	0.9990	0,12
2-ethylphenol	6.7	0.9998	0,11
3-chlorofenol	8.4	0.9999	0,11
2,5-dimethylfenol	7.3	0.9994	0,11
4-chlorofenol	9.3	0.9998	0,11
2,4-dimethylfenol	6.3	0.9997	0,12
3-ethylfenol	7.1	0.9999	0,11
2,3-dimethylfenol	7.0	0.9997	0,11
3,5-dimethylfenol	8.1	0.9986	0,11
4-ethylfenol	8.1	0.9986	0,11
3,4-dimethylfenol	7.6	0.9997	0,11
4-chloro-2-methylphenol	7.2	0.9997	0,11
2,6-dichlorophenol	6.5	0.9999	0,11
4-chloro-3-methylphenol	6.9	0.9998	0,11
2,5-dichlorophenol	7.0	0.9999	0,11
2,4-dichlorophenol	6.5	1.0000	0,10
3,5-dichlorophenol	6.7	1.0000	0,11
2,3-dichlorophenol	7.8	0.9999	0,10
3,4-dichlorophenol	7.2	0.9997	0,10
2,4,6-trichlorophenol	6.6	1.0000	0,11
2,3,6-trichlorophenol	6.1	0.9999	0,11
2,3,5-trichlorophenol	6.4	0.9999	0,10
2,4,5-trichlorophenol	6.4	1.0000	0,09
2,3,4-trichlorophenol	7.2	0.9999	0,10
3,4,5-trichlorophenol	7.2	1.0000	0,10
2,3,5,6-tetrachloophenol	7.1	0.9999	0,11
2,3,4,6-tetrachlorophenol	7.3	1.0000	0,10
2,3,4,5-tetrachlorophenol	8.5	0.9999	0,10
Pentachlorophenol	9.1	0.9997	0,11

Figure 1. Instrumental set-up.

CONCLUSIONS

A fully automated large volume GC/MSMS method was developed for the analysis of residual phenols in water after on-line derivatization with acetic anhydride. The method was fully validated with linearity coefficients > 0.998 for all components by using only one labelled internal standard. Method precision was < 10% for all components with minor deviation for the most volatile phenols in the target list. An additional, volatile, ISTD will act as a more effective control and reduce this phenomenon. Recovery was tested for two matrices with results fulfilling typical laboratory requirements.