

GC-MS/MS SCREENING OF DIOXIN-LIKE COMPOUNDS ON THE EXAMPLE OF POLYCHLORINATED DIBENZOTHIOPHENES - THIO-ANALOGUES OF POLYCHLORINATED DIBENZOFURANES

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Introduction

The determination of the presence of chlorinated dibenzothiophenes in the environment and foodstuffs has always been a great concern. Since there are no known safe levels of exposure to these substances the only way to minimize the risk is to minimize the exposure. Therefore, only the most sensitive and specific instruments, according to the Buser et al¹ and Sinkkonen² publication, are capable of achieving the required detection limits. These detection limits can be routinely achieved by using high-resolution magnetic sector instruments capable of detecting the dioxins, dibenzofurans and also dibenzothiophenes by their exact mass, usually after a very thorough, costly, and time-consuming sample cleanup. The typical sample cleanup may require up to six days. Purchasing automated sample preparation and cleanup equipment costing several tens of thousands of dollars can considerably reduce the cleanup time.

Methods and Materials

Ion trap mass spectrometers have long been known for their sensitivity and relatively low cost compared to other types of mass spectrometers. Applying ion trap MS/MS technology and splitless injections to the determination of polychlorinated dibenzothiophenes leads to a viable and robust analysis technique that can be used for screening, quantitation, and confirmation down to the low part-per-trillion range without an extensive sample cleanup.

The following solvents have been used: toluen, dichloromethane, hexan and iso-octan of the non-grade class (JT-Baker Germany). The standards of native PCDDs and 2,3,7,8-TCDD came from Promochem. The standards of other chlorinated dibenzothiophenes were obtained from prof. J.T. Andersson from the University of Muenster (Germany).

Chlorinated solvents were additionally kept over silver wool in order to avoid further chlorination of the analytes.

Lyophilisation: Alpha 1-4 Christ freezing dryer (Christ, Germany).

Evaporation/concentration of solutions: Büchi 310 rotary evaporator (Büchi, Germany)

GC-MS: *Finnigan GCQ* equipped with Excalibur data acquisition system and NIST spectra library (ThermoFinnigan, Austin Tx, USA).

Sample preparation:

Solid samples were freeze-dried for 8 hours, then they were extracted in Soxhlet apparatus with toluene for 16 hours. The extracts were evaporated and resolved in hexane. After that they were purified onto slightly acidic and neutral silica gel. In these conditions recoveries for 2,3,7,8-TCDD were about 76%.

The operation conditions of the chromatograph:

Injector – splitless @ 320°C,

Column – DB-5-MS (J&W) 30m x 0.32mm d_i=0.25µm

Oven temperature programming:

60°C (0.5 min hold) ramp 15°/min to 260°C then ramp 5°/min to 320°C, 5 min hold

The MS operating conditions:

The ion source temperature 250°C

The transfer line temperature 275°C

Scanning mode I: Full Scan

The beginning of scanning 50.0 amu

The end of scanning 550.0 amu

Scanning mode II: MS/MS

Ion-precursor for Cl₁-DCT 218.0 amu

The analysed derivative ions 148.0-158.0 amu

Ion-precursor for Cl₂-DCT 252.0 amu

The analysed derivative ions 183.0-193.0 amu

Ion-precursor for Cl₃-DCT 286.0 amu

The analysed derivative ions 218.0-228.0 amu

Ion-precursor for Cl₄-DCT 322.0 amu

The analysed derivative ions 253.0-263.0 amu

Ion-precursor for Cl₅-DCT 356.0 amu

The analysed derivative ions 288.0-298.0 amu

Ion-precursor for Cl₆-DCT 390.0 amu

The analysed derivative ions 322.0-332.0 amu

Ion-precursor for Cl₇-DCT 426.0 amu

The analysed derivative ions 357.0-367.0 amu

Ion-precursor for Cl₈-DCT 460.0 amu

The analysed derivative ions 391.0-401.0 amu

Results and discussion

In case of tetra-substituted thiophenes the m/z 322 ion is secondarily fragmented, which is also characteristic of dioxins, but it allows for a differentiation. It is also significant that the samples do not have to be as thoroughly purified as for the HRGC-HRMS systems. Figure 2 shows a sample polluted by a fraction of aromatic hydrocarbons of high boiling oils with an addition of 2,3,7,8-tetrachlorodibenzothiophene (about 7 ppb in an extract) and the TeCDT spectrum. It allows for an unequivocal differentiation from penta-substituted dioxins which may disturb determinations, and which eluate from the column in similar retention times.

The limit of the detection of the *Finnigan GCQ* for this screening methodology was estimated from a mass chromatogram of a 500 fg/µL injection of 2,3,7,8-TCDD. For others the chlorinated dibenzothiophenes equimolar response was assumed.

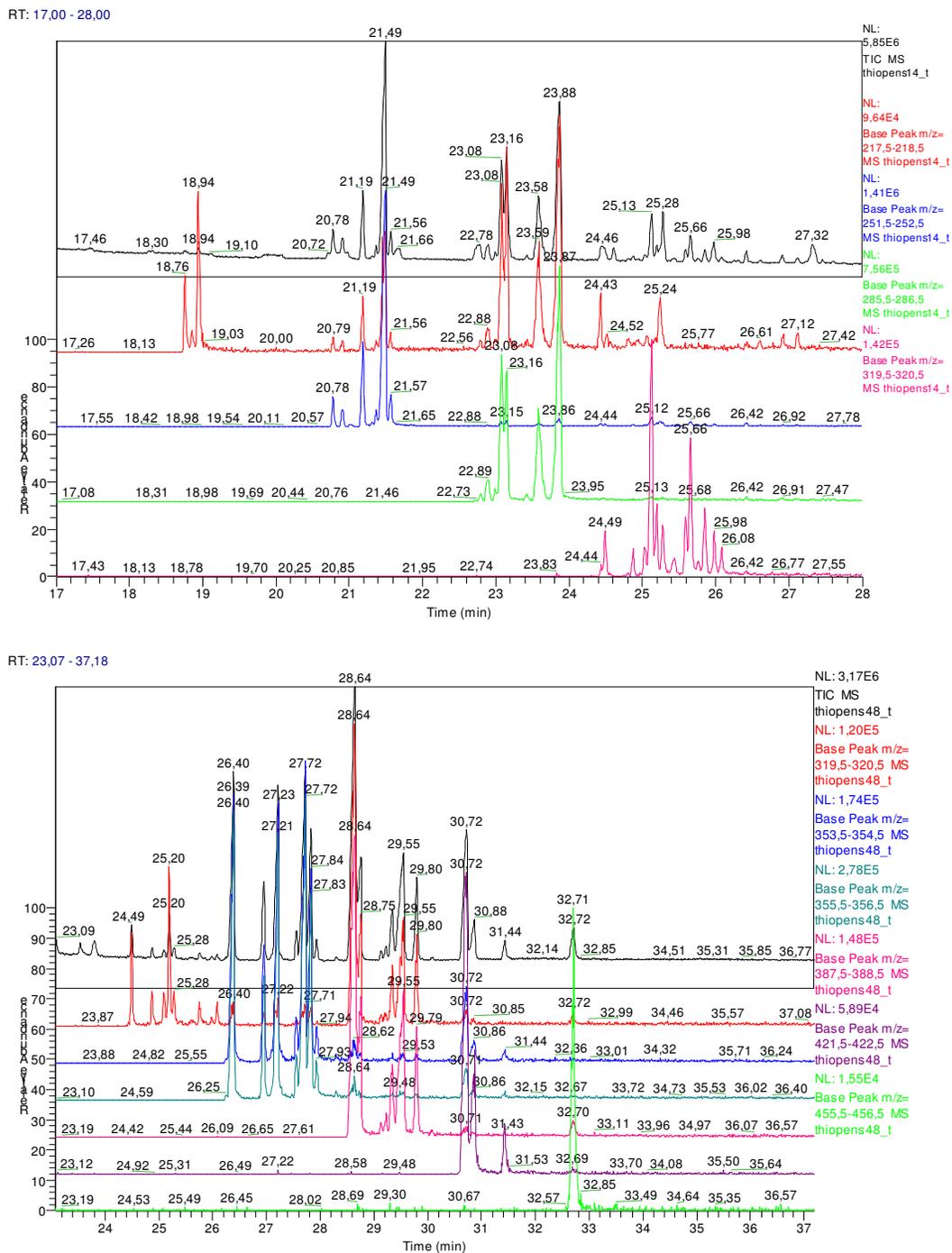


Figure 1. Chromatograms of the two standard mixtures of mono- to tetra- and tetra- to octachlorinated dibenzothiophenes at the total concentration about 0,1 mg/L

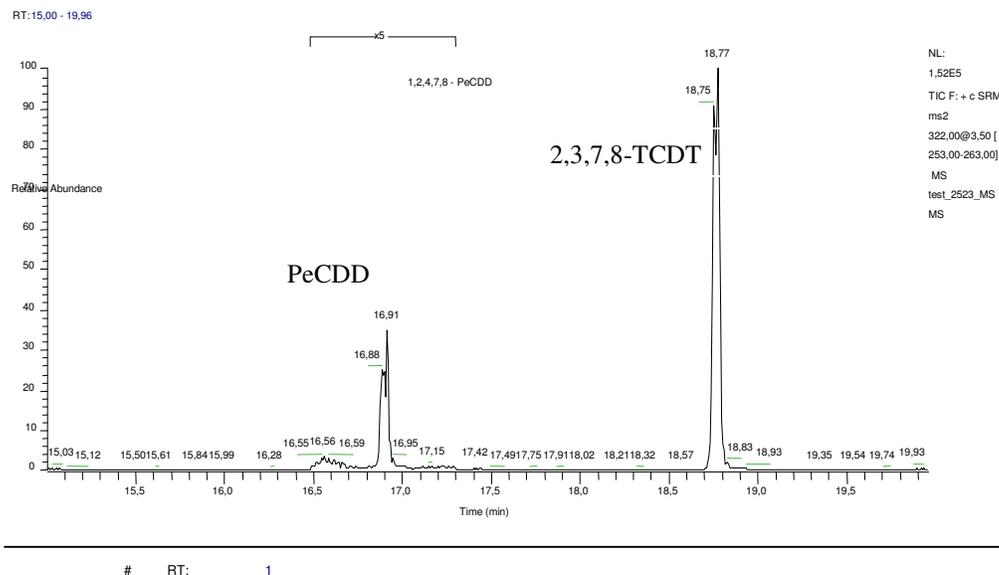


Figure 2. Chromatogram of the resonant ion for 2,3,7,8-TCDD and the nonresonant ion for 1,2,3,7,8-PeCDD Concentration of PeCDD 50 times higher in a sample polluted with aromatic hydrocarbons.

Figure 1 demonstrates quite clearly the gain in signal to noise that MS/MS can provide over the full scan or low-resolution SIM. Comparing the top two traces (TIC and MS/MS fragmentogram) indicates roughly a 10-fold increase in sensitivity in the MS/MS mode over the full scan data when analyzing a pure standard. Figure 2 shows the tremendous improvement that MS/MS provides when background matrix interferes with the full scan or low resolution SIM on example.

The selectivity of MS/MS for this method is performed by monitoring the transition of the molecular ion of each of the PCDDs to the loss of Cl. The use of the ion trap mass spectrometer and the reduced sample cleanup for the screening of dioxins, furans and dibenzothiophenes is both an economical and time saving alternative prior to the extensive traditional high-resolution sector GC-HRMS sample cleanup methodology.

This method was successfully applied to the determination of PCDD in solid environmental samples³.

References

1. Buser, H-R., Dolezal, I.S., Wolfensberger, M., Rappe, C.; (1991) *Environ. Sci. Technol.*, **25**, 1637
2. Sinkkonen, S.; (1997) *Chemosphere*, **34**, 2585
3. Czerwiński, J., Pawłowski, L., Rut, B., Pawłowska, M., Simplified method determination polychlorinated dibenzothiophenes in environmental samples., ESS, in print