Consolidated GC-MS/MS Analysis of OCPs, PAHs, and PCBs in Environmental Samples

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Overview

Purpose: The goal of this analysis was to decrease the total work required for the analyses of Organochlorine pesticides (OCP), polyaromatic hydrocarbons (PAH), and polychlorinated biphenyls (PCB) compound classes using Triple quadrupole GC-MS/MS.

Methods: GC-MS/MS analysis of multiple compound classes in various sample matrices within EU regulatory guidance specifications for analytical performance.

Results: A consolidated method for the analysis of 60+ compounds from multiple compound classes was successfully developed that demonstrates excellent precision, maintained ion ration stability and linearity R2 values >0.995 with low concentration monitoring capabilities.

Introduction

Organochlorine pesticides (OCP), polyaromatic hydrocarbons (PAH), and polychlorinated biphenyls (PCB) are compound classes that are highly familiar to routine environmental or contract testing laboratories. Various approaches are taken to address these compound classes in the diverse matrix environment experienced by these laboratories. The use of triple-quadrupole GC-MS/MS provides a significant increase in selectivity when compared to single quadrupole GC-MS and other traditional detectors, such as ECD or FID and UV or fluorescence detectors in HPLC. The following methodology presents a high performance, highly productive analysis of OCPs, PAHs and PCBs in various environmental matrices through a consolidated GC-MS/MS methodology using the Thermo Scientific™ TRACE™ 1310 GC and the Thermo Scientific™ TSQ™ 8000 triple quadrupole GC-MS/MS.

Methods

Sample Preparation

Water samples

To 1 L of sample, n-hexane was added, and the mixture was shaken. After the separation of water and organic phases, the organic phase was removed and dried with anhydrous Na_2SO_4. An aliquot of the organic extract was evaporated to a volume of 3–4 mL and then evaporated under a gentle nitrogen stream to the final volume.

Solid samples

Into a glass jar, 10 g of the sample (soil, sediment, or building material) was weighed, then anhydrous Na_2SO_4 , and 40 mL of extraction solvent mixture (hexane and acetone) were added. The glass jar was sealed with a Teflon® seal and sonicated for 20 min. An aliquot of the sample extract was placed into a Kuderna - Danish apparatus, and another 40 mL of extraction solvent mixture was added to the sample and the extraction was repeated. An aliquot of second extraction was added to the first extraction aliquot. The extract was evaporated to a volume of 3–4 mL and then evaporated under a gentle nitrogen stream to the final volume.

Mass Spectrometry

A method was developed for the TRACE 1310 Gas Chromatograph and the TSQ 8000 Mass Spectrometer (Figure 1). Thermo Scientific Auto SRM software provided automated development of all SRM transitions.

FIGURE 1. Instrument parameters.

TRACE 1310 GC	
Injection Volume:	1 µL
Liner:	Siltec baffled liner (P/N 453T2120)
Carrier Gas:	He, constant flow, 1.15 mL/min
Column Type:	20 m, 18 mm ID, 0.18 µm df, TG-XLBMS (P/N 26079-5780)
Column Oven:	Initial 60 °C, hold 1 min. Ramp 30.0 °C min to 200 °C. Ramp 10.0 °C min to 320 °C. Hold 2.0 min.
Transfer Line:	320 °C

TRACE 1310 GC PTV program	
Injector Temperature:	80 °C, Splitless Injection 1 min
PTV Inject:	80 °C, 0.1 min. 600 °C/min to transfer step
PTV Transfer:	320 °C, 5 min, 870 °C/min to clean step
PTV Clean:	325 °C, 15 min, clean flow 25 mL/min

FIGURE 1. Instrument parameters, continued.

TSQ 8000 Mass Spectrometer in EI mode	
Source Temperature:	350 °C
Ionization:	EI, 70 eV
Emission Current:	50 µA
Resolution:	Q1 normal
Collision Gas:	Argon

Data Analysis

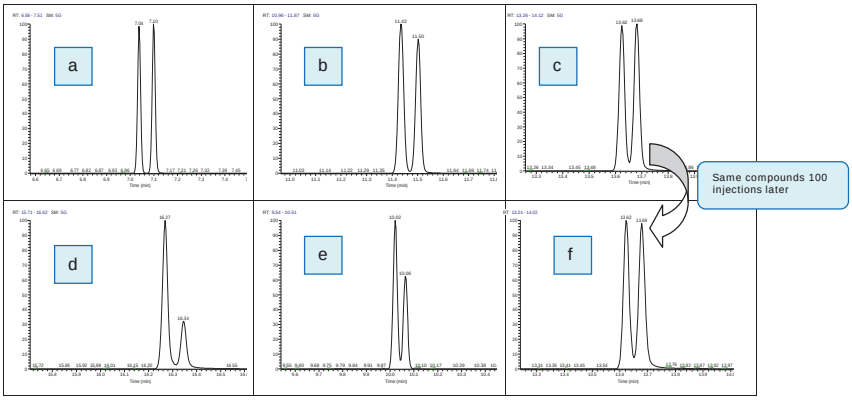
All precursor product ion pairs for over 126 compound SRM transitions, were developed in Auto SRM and directly imported into Thermo Scientific™ TraceFinder™ software instrument and processing methods for peak detection and compound quantitation.

Results

Method Productivity & Performance

All 62 compounds representing the various compound classes eluted within 17 minutes. Use of the TRACE 1310 GC and a 20 m, 18 mm ID, 0.18 µm df, TG-XLBMS analytical column optimized the chromatographic separation of critical isomer pairs (Figure 2).

FIGURE 2. Chromatograms A-E demonstrate critical separations in a standard at 2000 pg absolute injection – a.) phenanthrene and anthracene, b.) chrysene and benzo(a)anthracene, c.) benzo(b) and benzo(k)fluroanthene, d.) indeno (1,2,3,c,d)pyrene and dibenzo(a,h) anthracene, e.) o,p DDD and p,p DDT. Chromatogram F depicts isomeric separation of sample extract from building material at 400 pg after 100 injections of sample, and f.) benzo(b) and benzo(k)fluoranthene.

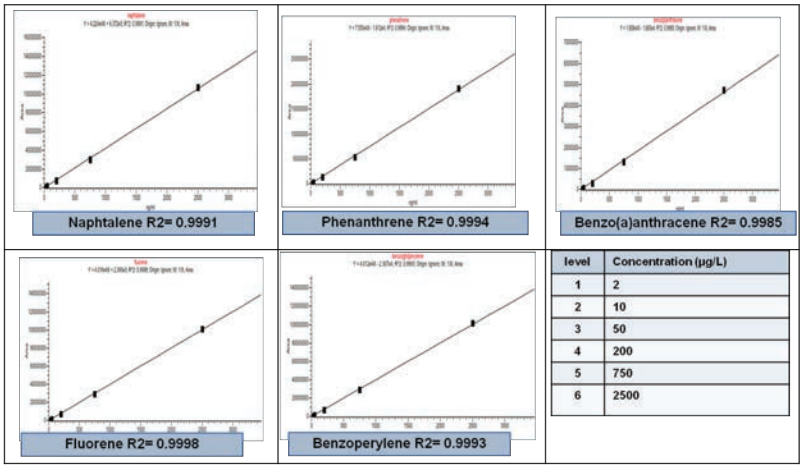


The separation of critical isomeric components was maintained over more than 100 injections of water, soil, and building material sample extracts.

Method Calibration

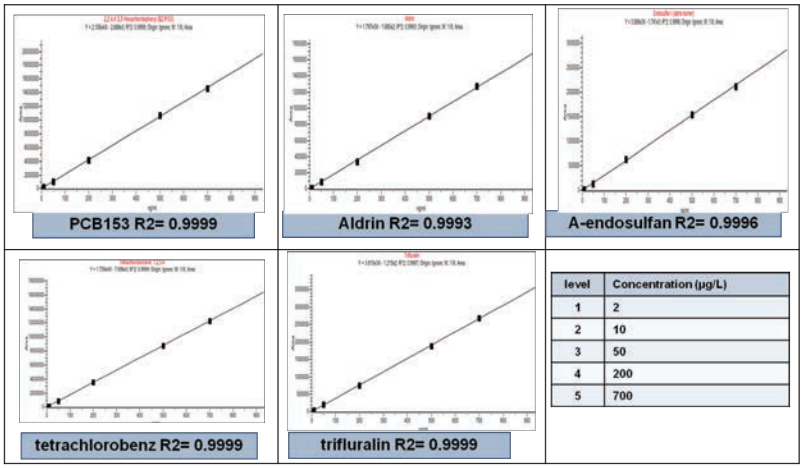
Calibration curves were produced in the range of 2 µg/L to 700 µg/L for the OCPs and PCBs. A higher range, 2 µg/L to 2,500 µg/L, was necessary for the PAHs. The curves were not corrected for internal standard calibration. All curves had a regression coefficient higher than 0.995. Curves for a selection of target compounds are plotted in Figures 3 & 4.

FIGURE 3. Calibration curves of selected PAH compounds and their respective regression coefficients.



level	Concentration (µg/L)
1	2
2	10
3	50
4	200
5	750
6	2500

FIGURE 4. Calibration curves of various pesticides compounds and their respective regression coefficients.

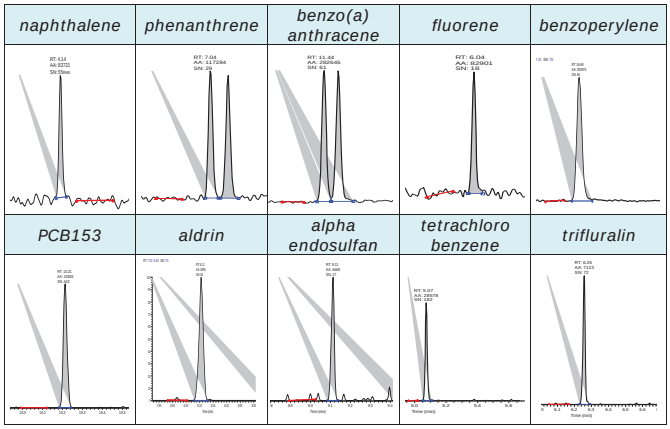


level	Concentration (µg/L)
1	2
2	10
3	50
4	200
5	700

Compounds at 2 µg/L level

At the lowest calibrated level (2 µg/L or 2 pg on column), all compounds displayed excellent responses and high signal-to-noise values. A selection of extracted SRM chromatograms at this level are depicted in Figure 5.

FIGURE 5. Resulting peaks from 2 µg/L calibration standards; 2 pg absolute amount injected on column.



Precision in Spiked Matrix Samples

The repeatability of the analysis was assessed by performing repeat injections of 3 different sample matrices including spiked soil extracts, spiked water extracts, and spiked building material extracts. Seven replicates of each sample matrix type were analyzed. The resulting RSD was calculated using an external calibration (Table 1). Repeatability for all compounds was demonstrated below 10% RSD. TraceFinder software performed all integrations without manual intervention.

TABLE 1. Relative standard deviation of seven injected samples in various matrices.

Compound	% RSD	% RSD	% RSD
	Building Material	Soil	Water
PCB180	2.5	6.4	5.3
PCB118	2.8	5.7	4.3
Benzo[a]anthracene	2.7	1.6	6.7
Benzo[a]pyrene	2.5	2.4	7.2
Benzo[b]fluoranthene	2.2	3.2	7.5
BHC-gamma (Lindane, gamma HCH)	2.9	7.3	7.8
Dieldrin	4.2	3.5	6.9
Endosulfan I (alpha isomer)	2.9	7.2	7.2
Endosulfan II (beta isomer)	3.4	7.7	7.3

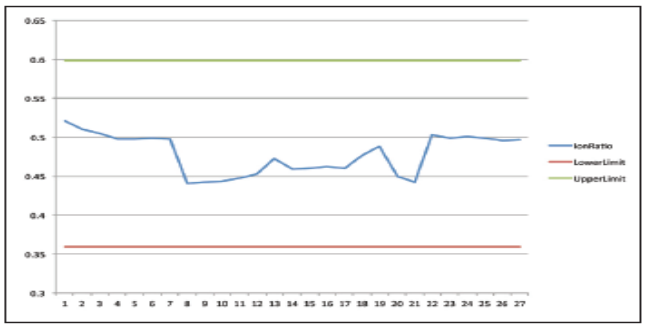
Ion Ratio Stability

At least two transitions were monitored for each compound. The ion ratios were calculated from the selected ions which were monitored throughout the duration of the analysis including the complete series of calibration curves, water samples, soil samples, and building materials. The observed ion ratio precision demonstrated accurate confirmation in both samples and standard injections across the concentration range throughout the analysis (Table 2 and Figure 6).

Table 2. The observed ion ratio stability throughout the analysis for hexachloroethane and benzoperylene compounds.

Hexachloroethane	Ratio	Benzoperylene	Ratio
Average	0.479	Average	2.910
Standard deviation	0.025	Standard deviation	0.124
RSD	5.3%	RSD	4.3%

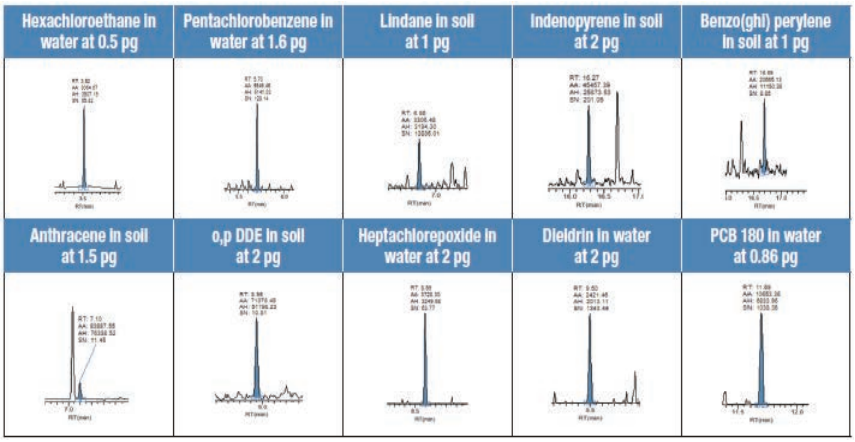
FIGURE 6. Ion ratio of hexachloroethane, plotted with the upper and lower allowed limit according to the EU guidelines for performance of analytical methods(4).



Low Concentration Sample Analysis

The developed method successfully identified and quantitated low concentrations of multiple target compound classes in their associated matrices. Figure 7 demonstrates the sensitivity and selectivity of the analytical method at low concentration levels.

FIGURE 7. Compound peaks in various sample matrices at low levels.



Conclusion

The goal of the developed method was to decrease the total work required by laboratories when analyzing various compound classes in various sample matrices.

- The TSQ 8000 GC-MS/MS enabled simple method consolidation with greater specificity for targeted compounds across a broad range of sample and compound types.
- Validation of the method performance attributes indicates excellent applicability to environmental labs interested in monitoring multiple compound classes with a single methodology.
- Combining separate analysis methods through the use of integrated software and hardware tools demonstrated the potential for increased productivity in the laboratory.
- Quantitative performance of the system and methodology was excellent with a good level of linearity, excellent sensitivity, and high precision in a variety of environmental sample types.

References

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