A Consolidated Approach for Routine Analysis of Soil Contaminants using GC-Orbitrap Mass Spectrometry

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ABSTRACT

The purpose of this study was to assess the quantitative performance and advantages of PAHs and PCBs analysis using the Thermo Scientific™ Orbitrap Exploris™ GC in addition to screening of other soil contaminants. Moreover, a large number of soil samples was injected to assess if Thermo Scientific™ Orbitrap Exploris™ GC can meet the demands of routine trace analysis in soil samples.

INTRODUCTION

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic compounds that can contaminate soils, air, sediments, and water as a result of natural and anthropogenic processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. Moreover, due to their lipophilicity these chemicals can undergo biomagnification and accumulation in the food chain and can pose significant health risks to humans. Their toxicity even at very low concentrations means that their presence in the environment needs to be monitored so that the risk of uptake of these compounds into to the food chain and subsequently into human populations is minimized. More recently it has become apparent that oxidized and substituted derivatives of PAHs (such as oxy and methyl PAHs) have similar or increased toxicities compared to non-substituted versions; therefore, governments have already began monitoring them in soil and particulate matter. The challenges for the analysis of PAHs and PCBs are the requirement for complicated and costly sample preparation such as Soxhlet extraction. Often long chromatographic separations (>40 min per sample) are required, which overall will result in low sample throughput and high cost of analysis. To comprehensively characterize an environmental sample, multiple methods are employed for both the sample preparation and GC-MS analysis of these compounds. Having multiple chromatographic methods for the same sample increases the requirement for both labor and instrumentation. Multiple methods and chemists to review the process and report the data add to the time and cost of analysis. In this study a consolidated approach for the rapid and cost-effective analysis of sixteen EPA PAHs, seven marker PCBs, three oxyPAHs, ten methylPAHs, and nine NSO-PAHs in soil samples using a sensitive HRMS instrument was employed. For this, a modified QuEChERS sample extraction and clean up was investigated. Chromatographic separation of target compounds was optimized for a 20 min/sample method and detection was achieved using the Orbitrap Exploris GC system. The evaluation of system robustness and method suitability for PAH and PCB GC-MS analysis was done.

MATERIALS AND METHODS

Sample Preparation

Calibration standards containing 45 native PCB, PAHs, methyl PAHs, oxyPAHs, PANHs, PASHs, and PAOHs at twelve concentration levels, and 14 (^{13}C-labeled) internal standards, were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada).

For the calculation of MDLs and LOQs QuEChERS soil extract was spiked at 0.5, 1.0, 1.5, 2.5, and 5.0 pg/µL. Soil was freeze dried, homogenized, and sieved prior to a modified QuEChERS extraction and clean up procedure.

Test Method(s)

An Orbitrap Exploris GC instrument equipped with the ExtractaBrite™ electron ionization source was used for this analysis. This configuration allows vent-free column changes and ionization source maintenance in under 2 minutes representing a 98% time saving versus traditional venting approaches, which take up to 4 hours. This is achieved using state of the art NeverVent technology, which increases laboratory productivity through the minimization of instrument downtime. Liquid injections of the sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH series autosampler and chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS 30 m × 0.25 mm i.d. × 0.25 µm film (P/N 26096-1420) capillary column. Additional details of instrument parameters are displayed in Tables 1 and 2.

Data Analysis

Data were processed and reported using Thermo Scientific™ Chromeleon™ 7.3 chromatography data system (CDS). The unknown screening was performed using Thermo Scientific™ Compound Discoverer™ software, version 3.2. Compound Discoverer software was also used for spectral deconvolution, NIST library searching, and compound identification using the EI and CI nodes.

Table 1. GC conditions

TRACE 1310 GC parameters	
Injection volume (µL)	1.0
Liner	Single gooseneck with glass wool LinerGOLD™
Inlet (˚C)	300
Inlet module and mode	SSL, Splitless
Splitless time (min)	1.0
Split flow (mL/min)	50.0
Septum purge flow (mL/min)	5.0
Carrier gas, flow rate (mL/min)	He, 1.2
Oven temperature program	
Temperature 1 (˚C)	40
Hold time (min)	1.0
Temperature 2 (˚C)	285
Rate (˚C/min)	28
Hold time (min)	0
Temperature 3 (˚C)	305
Rate (˚C/min)	3
Hold time (min)	0
Temperature 4 (˚C)	350
Rate (˚C/min)	30
Hold time (min)	5
Total GC run time (min)	20

Table 2. Mass spectrometer conditions

Orbitrap Exploris GC EI GC-MS parameters	
Transfer line (˚C)	320
Ion source (ionization type)	ExtractaBrite (EI)
Ion source (˚C)	350
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	Full scan (FS)
Mass range (m/z)	50–550
Mass resolution	60,000 (FWHM @ m/z 200, scan speed 7.4 Hz)
Lock mass (m/z)	207.03235

Orbitrap Exploris GC CI GC-MS parameters	
Transfer line (˚C)	320
Ion source (ionization type)	ExtractaBrite (PCI)
Reagent gas type	10% ammonia in methane
Flow rate (mL/min)	0.6
Ion source (˚C)	190
Electron energy (eV)	70
Emission current (µA)	100
Acquisition mode	Full scan (FS)
Mass range (m/z)	65–690
Mass resolution	60,000 (FWHM @ m/z 200, scan speed 7.4 Hz)
Lock mass	None

RESULTS

PAHs snd PCBs – target analysis

Figure 1. Example chromatograms showing overlaid native PAHs and PCBs FS XICs for a 50 pg/µL (50 pg on column (OC)) solvent standard in n-hexane with excellent chromatographic peak shapes for all compounds in <20 min. A) Peak shape for nitrogen containing polyaromatic heterocycle quinoline with peak asymmetry of 1.0; (B) Resolution of critical components phenanthrene and anthracene with EP resolution of 1.5; (C) Resolution of critical components benzo(a)anthracene and chrysene with chromatographic resolution of 1.3; (D) Resolution of critical components benzo(b)fluoranthene and benzo(k)fluoranthene with EP resolution of 1.0.

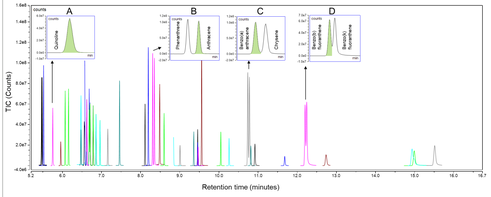


Figure 2. Graph showing individual MDLs (as detectable fg on column) for 45 native PCB, PAH, methyl PAH, oxyPAH, and NSO-PAHs calculated from n=18 replicate injections of the lowest serially diluted matrix-matched standards. *1,8-Dimethyl naphthalene 1.0 pg OC had a peak area % RSD >15% so the nearest standard 2.5 pg OC was used giving a higher MDL; however, by using a lower amount OC ~1.5 pg the true MDL value would be expected to be lower.

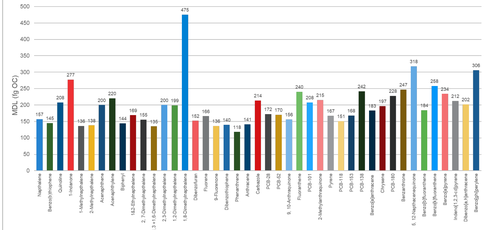


Figure 3. Linearity of example PAHs and PCBs as demonstrated using solvent-based calibration curves ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample). Average calibration factor function (AvCF) was used in Thermo Scientific™ Chromeleon™ CDS software and three replicate injections at each concentration with internal standard adjustment were performed. Coefficient of determination (R2) and average calibration factor values (AvCF %RSD) are displayed.

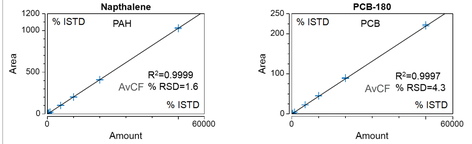
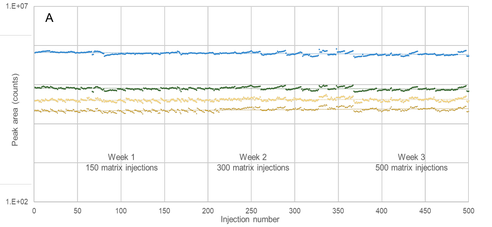


Figure 4. (A) Repeatability %RSD of absolute peak area response (no internal standard correction), for example PAHs and PCBs from n=500 injections of a QuEChERS soil extract post-spiked at 10 pg/µL (ppb); (B) Absolute peak area %RSDs (no internal standard adjustment) for all PAHs and PCBs from n=500 injections of a QuEChERS soil extract.



*Inlet septa were replaced every 100 injections. Apart from this no other inlet maintenance was undertaken.

Screening for additional soil contaminants

Figure 5. Example NIST SI match scores for compounds detected in the deconvoluted EI spectra QuEChERS soil extract spiked at 100 pg/µL.

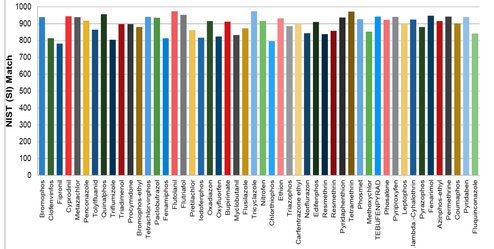


Figure 6. (A) Overlaid FS (m/z = 50–550) TIC for a soil QuEChERS extract spiked with pesticides at 100 pg/µL. (B) Compound Discoverer 3.2 software deconvoluted EI spectrum showing closely eluting compounds extracted from the complex TIC FS data.

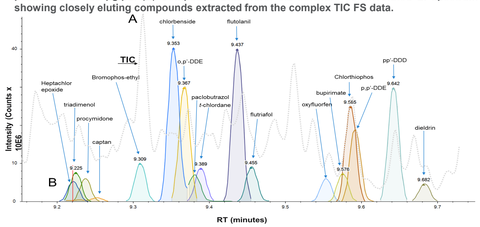
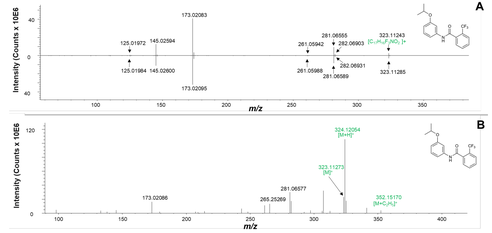


Figure 7. (A) Compound Discoverer software EI spectrum of a spiked QuEChERS soil extract – deconvoluted versus NIST library of the peak eluting at 9.437 min (m/z 323.11243), with the structure from the top SI match flutolanil from the result table. (B) PCI mass spectrum for flutolanil displaying adducts [M+H]+ and [M+C2H5]+ used for confirmation of this compound in conjunction with the EI data.



CONCLUSIONS

- Comprehensive method consolidation with chromatographic separation and overall analytical performance was achieved for the analysis of PAHs and PCBs in soil in 20 min
- Femtogram level sensitivity was achieved using the Orbitrap Exploris GC instrument, with the MDLs values calculated for 45 native compounds ranging from 115 to 475 fg OC (0.1–0.5 µg/kg in sample)
- Linearity was achieved across a calibration range of 0.1–500 pg/µL (0.1–500 µg/kg in soil) showed coefficient of determination values of R2 ≥0.995, and residuals <13%
- Excellent system repeatability in routine use.The peak area repeatabilities for the incurred residues were <20% RSD over the 500 complex soil sample injections and three weeks of continuous analysis with an average of 10.5% across all compounds
- Rapid change-over from EI (for spectral library search) to softer ionization such as PCI (for molecular ion confirmation using adduct information) is possible
- The streamlined GC-EI data processing workflow with Compound Discoverer software allows for quick extraction, deconvolution, and identification of unknown compounds

TRADEMARKS/LICENSING

PO66079 EN0921S