

Environmental

Screening workflow for priority and emerging pollutants in industrial stack particulate using Orbitrap Exploris GC

Authors

Nicholas A. Warner¹, Kjell Hope²,
Dominic Roberts³, Daniel Kutscher¹

¹Thermo Fisher Scientific, Bremen, Germany

²Pacific Rim Laboratories, Canada

³Thermo Fisher Scientific,
Hemel Hempstead, United Kingdom

Keywords

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Goal

The goal of this application note is to demonstrate the Thermo Scientific™ Orbitrap™ Exploris™ GC mass spectrometer to identify both priority and emerging pollutants in industrial stack particulate using a non-target analysis workflow.

Introduction

Stack sampling or monitoring is the collection of gases and particular matter discharged from industrial processes to the atmosphere via stacks or chimneys. This is a crucial activity towards environmental protection as it allows for air quality assessment of potential public health risk exposures and serves as a check from a regulatory standpoint to ensure industry is operating within safe environmental/health boundaries.

Stack emissions are produced from various industrial sectors including energy, waste management, and heavy manufacturing. Combustion of fuel to drive industrial processes can produce a variety of pollutants including volatile and semi-volatile organic compounds (VOCs and sVOCs). Under high temperature conditions, several known priority contaminants can be formed such as polycyclic hydrocarbons (PAHs) and polychlorinated dibenzodioxins/furans (PCDD/Fs), which are regulated in both national and international jurisdictions. In addition, chemical reactions/transformations can occur under such conditions, potentially resulting in toxic exposure from unknown chemical compounds.

In this study, we demonstrate the performance of the Orbitrap Exploris GC high resolution accurate mass (HRAM) spectrometer for the identification of priority contaminants and unknown chemical exposures in industrial stack particulate matter using a non-targeted workflow. High mass resolution combined with sub-ppm mass accuracy (<1 ppm, with internal lock mass) allows for selective and accurate identification with the help of Thermo Scientific™ Compound Discoverer™ software together with newest version of the Thermo Scientific™ Orbitrap™ GC-MS Contaminants Library. Confirmation of the molecular ion can be achieved using positive chemical ionization (PCI). Thermo Scientific™ NeverVent™ technology allows switching from the electron ionization (EI) source to the PCI source without venting the MS, minimizing instrument downtime while maximizing time available for compound identification.

Experimental

Standard and sample preparation

Two separate samples of particulate matter were collected from a waste incinerator stack on a 9 cm glass microfiber filter (VWR, USA) using a sampling train as described in U.S. EPA Method 23.¹ Samples were extracted for 12 hours with toluene using Soxhlet extraction followed by a semi-automated solid phase cleanup using a tandem acid silica-carbon column (Cape Technologies, USA). Extracts were evaporated close to dryness and reconstituted in 20 µL of iso-octane in a Thermo Scientific™ SureStart™ 0.7 mL micro GC vial (P/N 6ACV8-07C2)

For identification purposes, a 5 µg·mL⁻¹ C₇-C₄₀ alkane mixture (Sigma-Aldrich, Germany) was prepared in hexane and analyzed using the same method conditions as the samples to establish the retention time index. Injections and chromatographic conditions are outlined in Tables 1 and 2.

Instrument and method setup

A Thermo Scientific™ TRACE™ 1610 GC equipped with a Thermo Scientific™ TraceGOLD™ TG-PAH (30 m × 0.25 mm I.D. × 1.0 µm film) capillary column (P/N 26055-0470) was used to perform the chromatographic separation. A 1 µL injection was performed into a programmable temperature vaporization (PTV) inlet with a Thermo Scientific™ TriPlus™ RSH SMART autosampler. Injection and oven program conditions are described in Tables 1 and 2. Data acquisition was carried out in full scan analysis mode using both EI and PCI with the Orbitrap Exploris GC. Additional MS method parameters are summarized in Tables 3 and 4.

External mass calibration was performed prior to analysis, while characteristic ions representing column bleed were used as lock masses when scanning in EI to perform internal mass calibration. Sample acquisition and qualitative processing were performed using the Thermo Scientific™ Chromeleon™ version 7.3.2 Chromatography Data System (CDS). Unknown analysis and identification were performed using the Compound Discoverer version 3.3 software.

Table 1. Injection conditions

Conditions				
Injector	iConnect™ PTV			
Liner	Thermo Scientific™ PTV liner with concentric baffles (P/N 453T2845-UI)			
Injection volume (µL)	1			
Inlet temperature (°C)	90			
Carrier gas flow (mL·min ⁻¹)	1.2			
Injection type	Splitless			
Splitless time (min)	1.0			
Split flow (mL·min ⁻¹)	50			
Injection vial depth (mm)	40			
PTV ramp settings				
	Rate (°C·s ⁻¹)	Temp. (°C)	Time (min)	Flow (mL·min ⁻¹)
Injection phase	-	-	0.2	100
Transfer phase	2.5	300	1.0	-
Cleaning phase	14.5	330	5.0	100

Table 2. Oven temperature program

Parameter	Value
Initial temperature (°C)	80
Hold time (min)	1
Rate 1 (°C·min ⁻¹)	7
Temperature 1 (°C)	240
Rate 2 (°C·min ⁻¹)	1
Temperature 2 (°C)	245
Rate 3 (°C·min ⁻¹)	3
Temperature 3 (°C)	270
Rate 4 (°C·min ⁻¹)	12
Temperature 4 (°C)	335
Final temperature hold time (min)	5
Total analysis time (min)	47.6

Table 3. Orbitrap Exploris GC EI source and mass spectrometer parameters

Parameter	Value
Transfer line (°C)	300
Ion source temperature (°C)	320
Electron energy (eV)	70
Acquisition mode and scan range (<i>m/z</i>)	Full scan, 40 –830
Resolving power (at 200 <i>m/z</i>)	60,000
Emission current (μA)	50
C-Trap offset (V)	0
Mass accuracy on lock mass (ppm)	5
Internal lock mass calibration (column bleed, <i>m/z</i>)	207.02235, 281.05114, 355.06993

Results and discussion

Identification of priority pollutants with dedicated HRAM contaminant library

Mass spectrometric detection is a useful approach for environmental sample analysis as analytes of interest can be isolated from co-extracted sample matrix using their characteristic mass. In full scan acquisition on nominal mass instruments (GC-MS), sensitivity is compromised as less scanning time is spent on the ions of interest. Thus, single ion monitoring is often used to enhance sensitivity towards priority analytes, but at the cost of losing full spectral data for compound identification. However, the selectivity obtained using the Orbitrap Exploris GC avoids co-extracted interferences during full scan acquisition, allowing for priority analyte screening without compromising unknown pollutant identification.

An example of this can be seen in Figure 1, highlighting the identification of phenanthrene in waste incinerator stack particulate samples using a non-targeted workflow with HRAM. Performing spectral deconvolution with Compound Discoverer software, the sample spectra are cross referenced across both nominal (NIST 2023) and HRAM libraries. Comparison between the sample and library spectra found the top hit to be phenanthrene registered in the GC-Orbitraps Contaminants Library ver. 1.5, with a search index (SI) score of 939 (Figure 1). Comparison of the measured and theoretical molecular mass shows a mass error (Δ Mass) of 0.54 ppm. In addition to phenanthrene, several other PAHs were identified with the Orbitrap GC-MS Contaminants Library with sub-ppm mass

Table 4. Orbitrap Exploris GC PCI ion source and mass spectrometer conditions

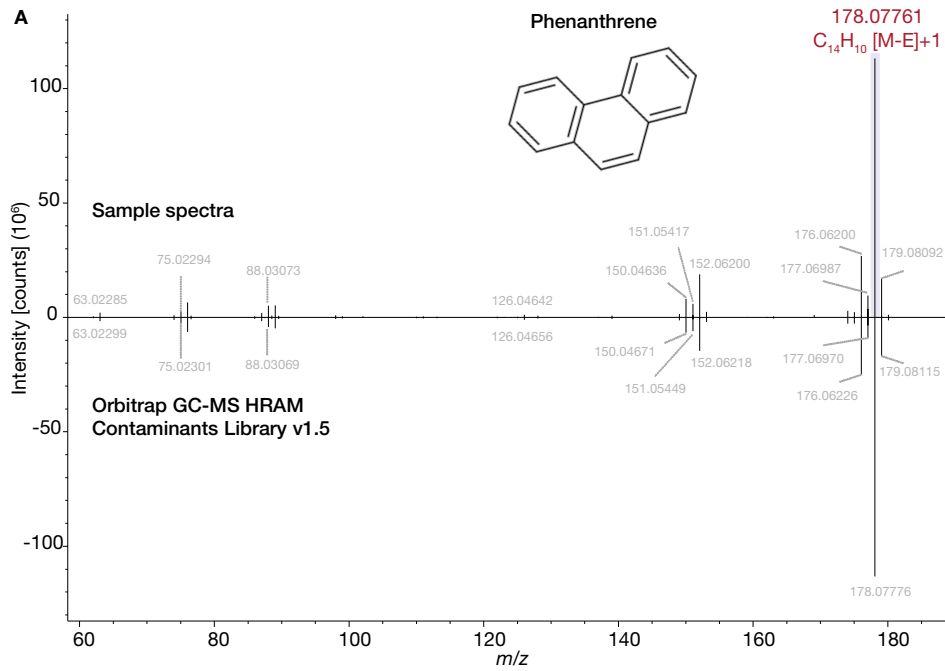
Parameter	Value
Transfer line (°C)	300
Thermo Scientific™ ExtractaBrite™ ion source temperature (°C)	180
Reagent gas and flow (mL·min ⁻¹)	Methane; 1.2
Ionization mode	Positive
Acquisition mode and scan range (<i>m/z</i>)	Full scan; 100–830
Resolving power (at 200 <i>m/z</i>)	60,000
Emission current (μA)	50

accuracy including naphthalene (Δ Mass: 0.19 ppm), fluorene (Δ Mass: 0.30 ppm), and pyrene (Δ Mass: 0.36 ppm), highlighting the accurate mass precision of the Orbitrap Exploris GC in providing confidence in identification of unknowns.

Identification of chlorinated-PAH analogs using hard and soft ionization

Findings of PAHs within particulate matter from waste incinerator stack emissions can be expected as these are produced through the combustion of organic material. However, under high temperature conditions within industrial furnaces, side reactions can occur with various chemical components present, forming unknown chemicals that may pose a severe environment/public health risk. In our analysis, chlorinated analogs of several PAHs were detected.

The presence of chlorinated PAHs has been previously reported in stack emissions due to burning of organic residues in the presence of halogens in combustion material.² One of the detected compounds in our analysis was identified as 9-chlorophenanthrene through the NIST 2023 spectral library (SI score of 848) (Figure 2B). Similarities in the extracted ion profile between phenanthrene (Figure 2A) and 9-chlorophenanthrene (Figure 2B) help support our library search findings that indicate the peak detected at 20.3 minutes is a transformation (i.e., chlorination) product of phenanthrene. In addition, the observed molecular mass 212.03864 showed a Δ Mass of 0.44 ppm compared to the theoretical mass of 9-chlorophenanthrene (212.03873), providing high confidence to our library search result.



B


Structure	Name	CAS Num	Formula	Total Score	HRF Score	RHRF Score	SI	RSI	Elements Found(%)	Molecular Weight	Theo. Mol. Mass	Observed Mol. Mass	Δ Mass [Da]	Δ Mass [ppm]	M+ found	Library
	Phenanthrene	85-01-8	C ₁₄ H ₁₀	97.8	97.4	98.0	939	941	100.0	178.07825	178.07770	178.07761	-0.00010	-0.54	Yes	gc-orbitrap contaminants library_v1.5

Figure 1. Sample mass spectra comparison with the Orbitrap GC-MS Contaminants Library phenanthrene spectra (A) with library search results table for phenanthrene (B)

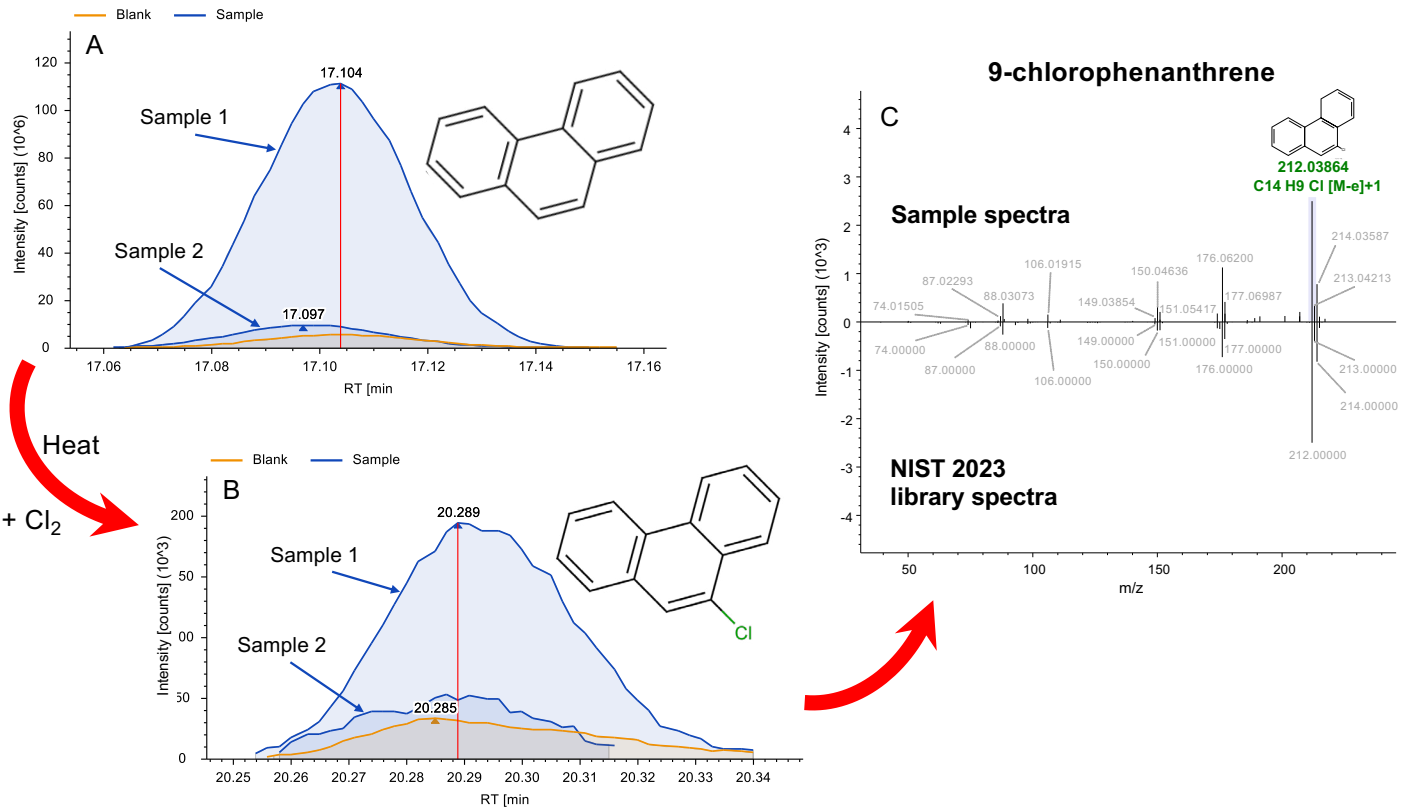


Figure 2. Extracted ion chromatogram of molecular ion for (A) phenanthrene and (B) 9-chlorophenanthrene, and (C) comparison of sample spectra to 9-chlorophenanthrene spectra in NIST 2023 spectral library

In addition to 9-chlorophenanthrene, 1-chloropyrene and several hits identified as monochlorinated-anthracene analogues were detected.

Continuing through our non-targeted workflow, the instrument configuration was quickly switched from the EI to the CI configuration by using the NeverVent technology. Performing PCI, molecular ion confirmation is possible due to its softer ionization. Detection of the molecular ($[M+H]^+ = 213.04666$, ΔMass of 0.5 ppm) and reagent adduct ions ($[M+C_2H_5]^+ = 241.07788$) of 9-chlorophenanthrene by Compound Discoverer software can be seen in Figure 3A.

As previously mentioned, several additional compounds were identified as monochlorinated analogues of anthracene (i.e., 1-chloroanthracene, 2-chloroanthracene) in our EI analysis. Chloroanthracene and chlorophenanthrene are structural isomers and thus share the same molecular ion ($m/z = 213.04666$). Extraction of the molecular ion shows four different compounds corresponding to the exact mass of chlorophenanthrene and/or chloroanthracene (Figure 3B). Information on the retention index helped provide tentative identification of 1-chloroanthracene. However, the remaining compounds represent structural isomers where chlorine substitution can occur at multiple positions around the phenanthrene or anthracene ring structure. Based on carbon electron density, positions 9 and 10 are considered the most favorable,¹ but confirmation with standards is needed.

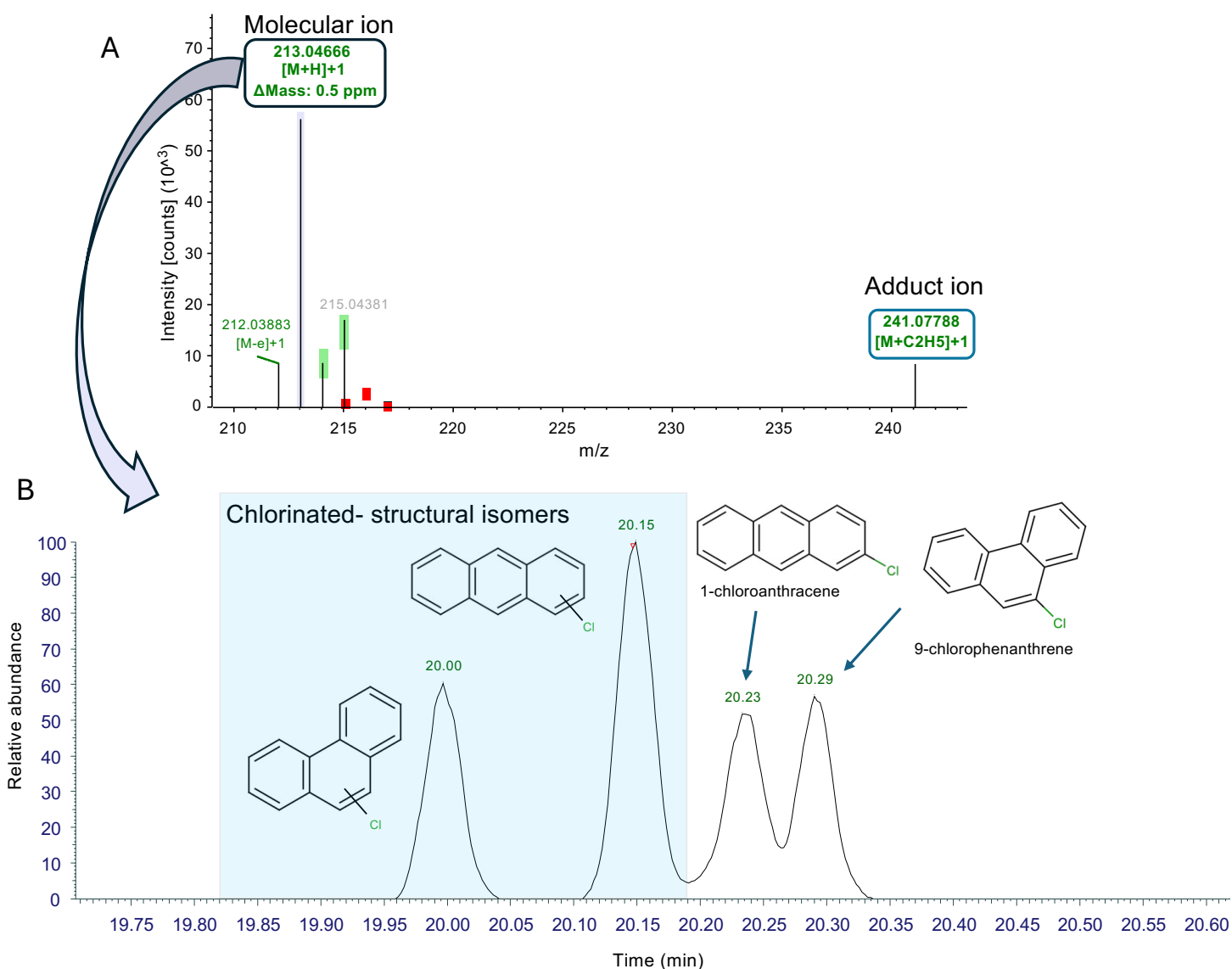


Figure 3. (A) PCI mass spectra of molecular and reagent adduct ions of 9-chlorophenanthrene and (B) extracted ion chromatogram of molecular ion mass of 9-chloroanthracene ($m/z = 213.04666$)

Identification of halogenated persistent organic pollutants (POPs) in industrial stack particulate

In addition to PAHs and chlorinated PAHs, several polychlorinated biphenyls (PCBs) were identified by the Orbitrap GC-MS Contaminants Library. Several matches to 2,8-dichlorodibenzofuran within the NIST 2023 spectral library were also observed with ΔMass less than 0.2 pm, indicating the presence of multiple congeners of dichlorodibenzofuran with differing chlorine substitution (Figure 4).

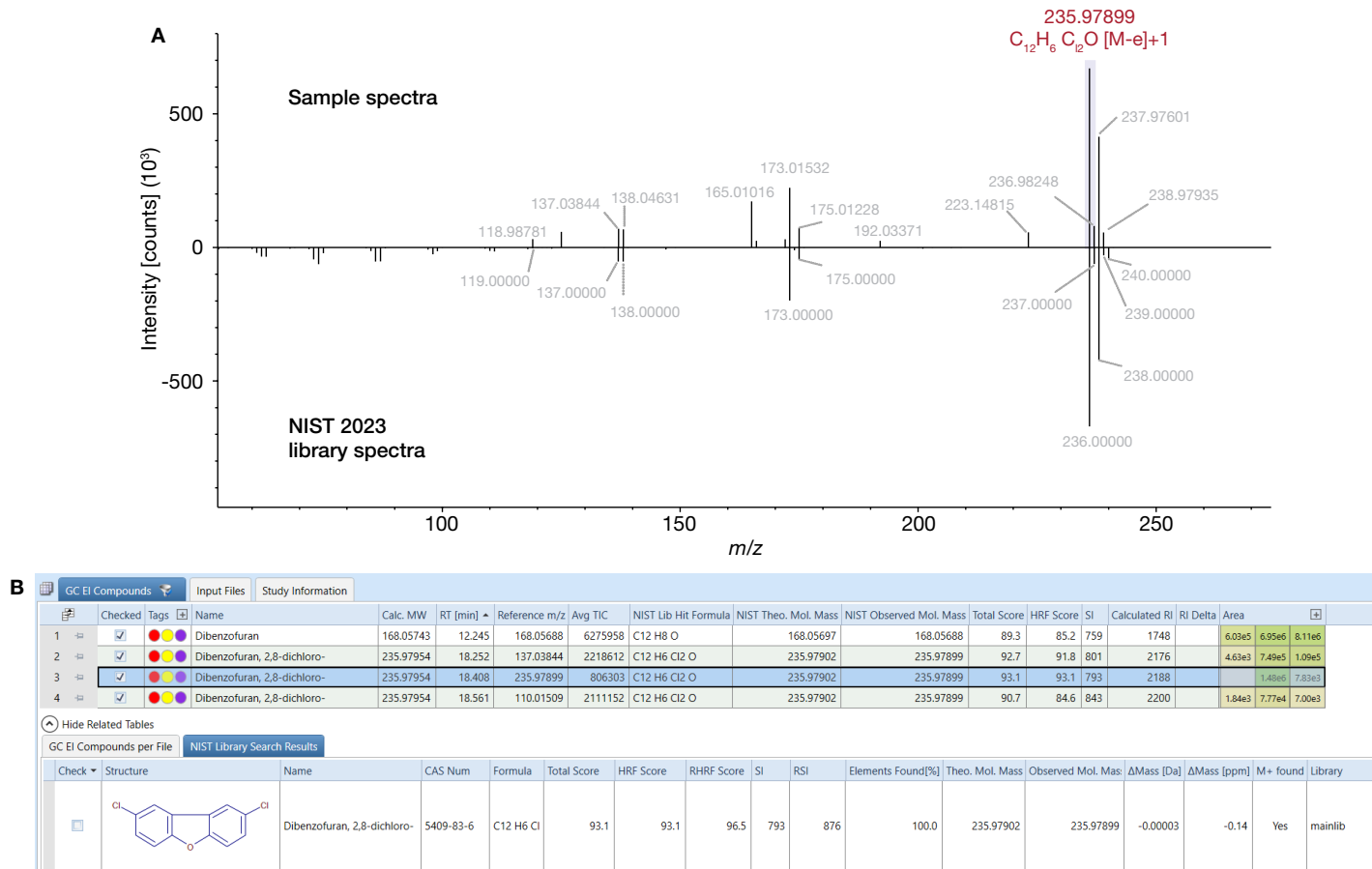
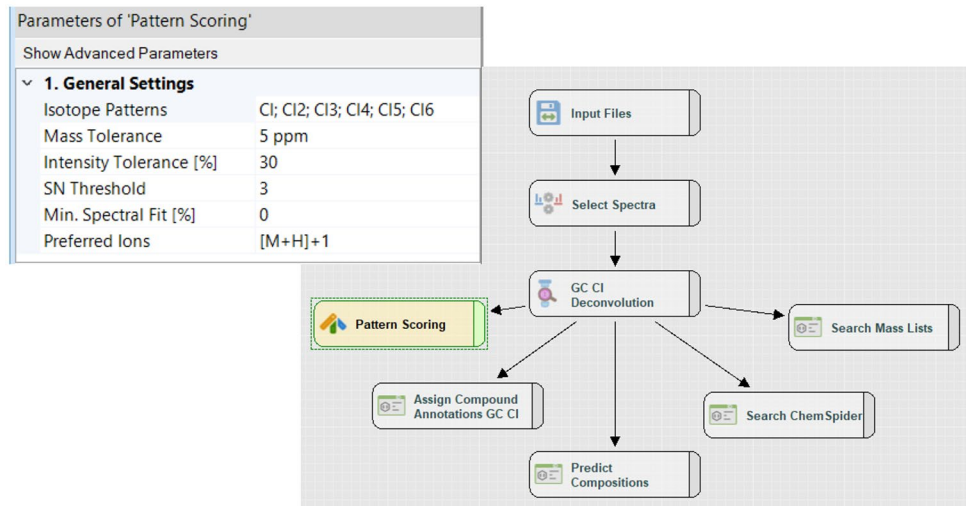


Figure 4. (A) EI mass spectra comparison between sample and 2,8-dichlorodibenzofuran NIST library mass spectra and (B) Compound and NIST library search result table of identified of halogenated dibenzofuran NIST 2023 library hits

Analysis in PCI confirmed the presence of the molecular ion and predicted the correct elemental composition for the dichlorinated dibenzofurans initially identified in EI. Using the pattern scoring node in the Compound Discover workflow (Figure 5), confirmation of several other halogenated contaminants can also be made.

Figure 5. Workflow tree for PCI analysis with Pattern Scoring node in Compound Discoverer software



In the pattern scoring node, the isotopic pattern of halogens present in unknown spectra can be compared to theoretical isotopic patterns. This information combined with information on the molecular ion provides additional confidence for identification. An example of this can be shown in Figure 6, where the PCI spectra for the peak at 18.26 min that was identified as 2,8 dichloro-dibenzofuran in our initial EI analysis. Not only do we have confirmation of the molecular ion with high mass accuracy ($m/z = 236.9868$, $\Delta\text{Mass} = -0.13$ ppm), we also have the presence of the reagent adduct ions ($[\text{M}+\text{C}_2\text{H}_5]+1$, $[\text{M}+\text{C}_3\text{H}_5]+1$) as well as the isotopic pattern match (Figure 6B).

The spectral similarity between the defined and measured isotope pattern can be evaluated using the SFit score, where values closest to 100% represent greater similarity (Figure 6C). The isotope intensity between measured and theoretical pattern is evaluated using the Pattern Coverage Score (i.e., Pattern Cov. (%)). The 100% coverage combined with the high SFit score provides confidence towards our identification for dichloro-dibenzofuran.

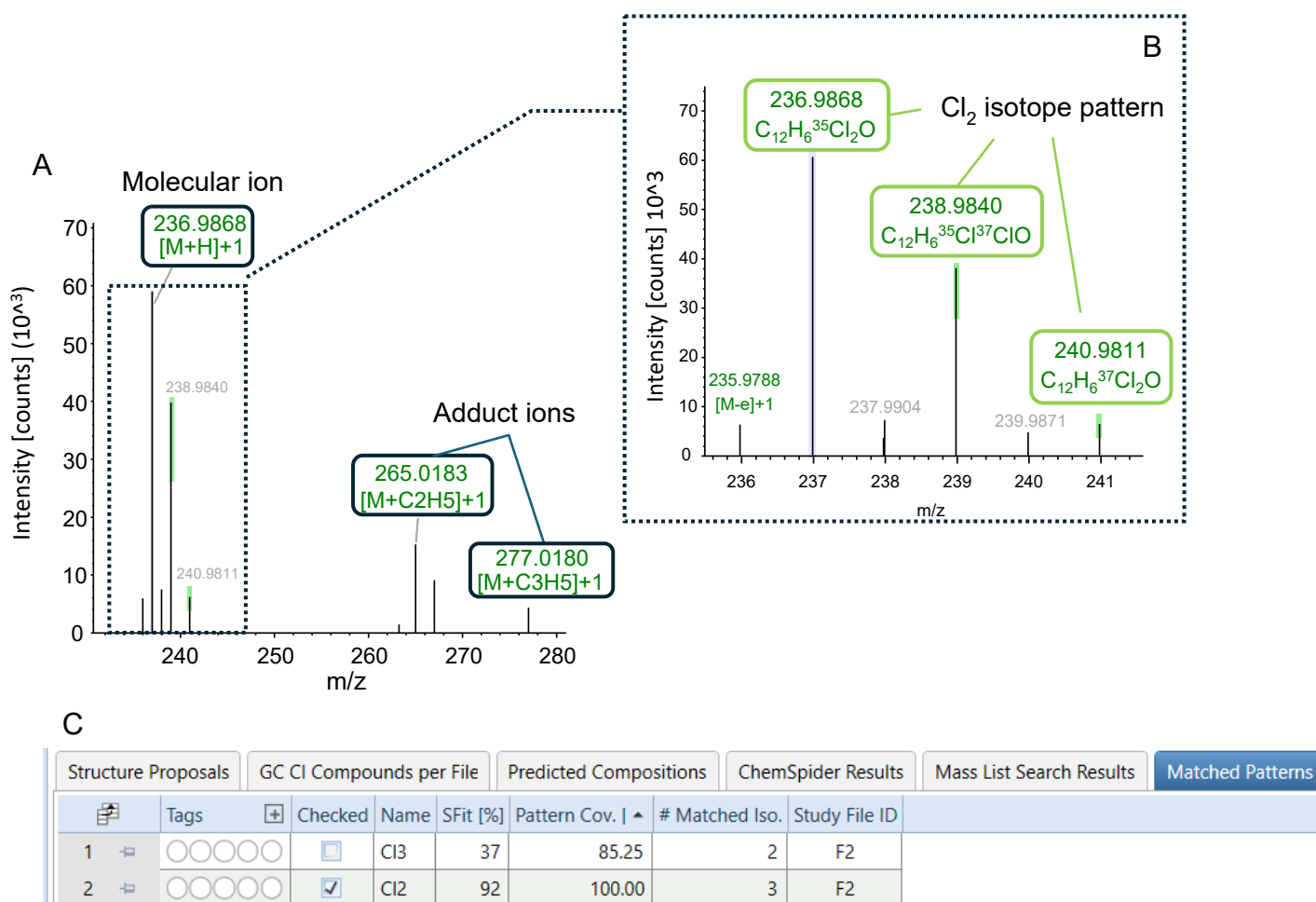


Figure 6. (A) PCI mass spectra for peak at 18.26 min, (B) isotope pattern match to Cl_2 theoretical isotope pattern, and (C) isotope pattern match results table showing detected isotope pattern with similarity (SFit) and pattern coverage (Pattern Cov.) scores

Results from the pattern scoring node can also be easily visualized in the compound result table. Several matches to both molecular ion and chlorine isotope pattern can be observed for other chlorinated PAHs, dibenzofurans, and several PCBs (Figure 7). Expanding our analysis to investigate other halogens such as bromine, we identified 2-bromodibenzofuran with a $\Delta\text{Mass} = 0.96$ ppm and SFit and Pattern Coverage scores of 93% and 100%, respectively.

GC Cl Compounds												ChemSpider Results		Input Files		Study Information	
	Check	Tags	Name	Formula	Annot. Source	Annot. ΔMass (ppm)	Calc. MW	# ChemSpider Results	Reference m/z	Avg TIC	Mass List Matches	# Adducts	Pattern Matches				
1	<input checked="" type="checkbox"/>	○○○●	2,8-Dichlorodibenzofuran	C12 H6 Cl2 O	■ ■ ■	-0.13	235.97954	18	265.01834	53645	■ ■	3	■ ■ ■ ■ ■				
2	<input checked="" type="checkbox"/>	○●○○○	1-Chloropyrene	C16 H9 Cl	■ ■ ■	0.52	236.03940	10	239.04358	40412	■ ■	3	■ ■ ■ ■ ■				
3	<input checked="" type="checkbox"/>	○○○●○	3,3',4,4'-Tetrachlorobiphenyl	C12 H6 Cl4	■ ■ ■ ■	0.38	289.92247	45	129.06990	18613	■ ■	1	■ ■ ■ ■ ■				
4	<input checked="" type="checkbox"/>	○○○●○	4,4'-PCB	C12 H8 Cl2	■ ■ ■ ■	0.42	222.00040	29	223.00768	30607	■ ■	2	■ ■ ■ ■ ■				
5	<input checked="" type="checkbox"/>	○○○●○	2,8-Dichlorodibenzofuran	C12 H6 Cl2 O	■ ■ ■	-0.13	235.97954	18	199.05754	32728	■ ■	2	■ ■ ■ ■ ■				
6	<input checked="" type="checkbox"/>	○○○●○	2-BROMODIBENZOFURAN	C12 H7 Br O	■ ■ ■	0.96	245.96826	7	246.97554	38640	■ ■	2	■ ■ ■ ■ ■				
7	<input checked="" type="checkbox"/>	○○○●○	3,3',4,4'-Tetrachlorobiphenyl	C12 H6 Cl4	■ ■ ■ ■	0.38	289.92247	45	290.92975	58513	■ ■	2	■ ■ ■ ■ ■				
8	<input checked="" type="checkbox"/>	○○○●○	2,8-Dichlorodibenzofuran	C12 H6 Cl2 O	■ ■ ■	0.39	235.97966	18	138.05495	82302	■ ■	3	■ ■ ■ ■ ■				
9	<input checked="" type="checkbox"/>	○○○●○	2,8-Dichlorodibenzofuran	C12 H6 Cl2 O	■ ■ ■	-0.13	235.97954	18	265.01834	53663	■ ■	4	■ ■ ■ ■ ■				
10	<input checked="" type="checkbox"/>	○○○●○	2-chlorodibenzofuran	C12 H7 Cl O	■ ■ ■	-0.38	202.01846	7	435.39862	51119	■ ■	3	■ ■ ■ ■ ■				

Figure 7. Compound result table for PCI analysis using pattern scoring node in Compound Discover software

Conclusions

Priority pollutants at trace levels can be monitored in stack emissions through targeted analysis approaches. However, such approaches are confined to target analyte lists, while compounds formed through chemical reactions and/or thermal breakdown will not be captured. This highlights the need for untargeted analysis workflows to provide information on unknown chemical exposures to help safeguard environment and public health. Analysis using the Orbitrap Exploris GC with its high mass resolution and accuracy provides:

- Dedicated Orbitrap GC-MS Contaminants HRAM Library for accurate identification of priority pollutants (PAHs, POPs).
- Full scan acquisition with rapid switching between hard (EI) and soft (CI) ionization with NeverVent technology.
- Accurate identification of reaction/thermal breakdown products and their isomers using the NIST nominal mass library at sub-ppm mass accuracy.
- Molecular ion identification and isotope pattern matching for confirmation of halogenated pollutants.

References

1. U.S. EPA Method 23 – Determination of Polychlorinated Dibenzo-*p*-Dioxins, Polychlorinated Dibenzofurans, Polychlorinated Bipheyls and Polycyclic Aromatic Hydrocarbons from Stationary Sources. <https://www.epa.gov/emc/method-23-dioxins-and-furans>
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