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Analysis of Halogenated Polycyclic Aromatic Hydrocarbons in Atmosphere around Metallurgical Plants by 7250 High-resolution GC/Q-TOF

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Introduction

Metallurgical plants have been identified as dominant persistent organic pollutants (POPs) sources in China, with POPs such as polychlorinated dibenzo- p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) included. Toxicological studies have shown that halogenated polycyclic aromatic hydrocarbons (PAHs) have similar toxic effects to these well-known POPs[1,2].

Due to their typically trace-levels in environmental samples, gas chromatography coupled with sector high-resolution MS (GC-HRMS) systems are used widely for measurement of these compounds. However, GC-HRMS are usually run in selected ion monitoring (SIM) mode to achieve high sensitivity and selectivity.

In this study, a high-resolution GC quadrupole time-of-flight MS (GC/Q-TOF) was used in full-spectrum acquisition mode to investigate the target and non-target halogenated PAHs distribution in the atmosphere around metallurgical plants.

Experimental

Typical air samples were collected from an iron ore sintering plant by high-volume air samplers according to US EPA method TO-9A [1]. The gas phase of the air sample was gathered in polyurethane foam and then the foam was extracted by accelerated solvent extraction and cleaned up with silica columns and carbon columns [1].

Data were acquired using a 7250 GC/Q-TOF system equipped with a novel ion source (Figure 1). The full-spectrum mode of the GC/Q-TOF system enabled target and non-target acquisition using the same method. Instrument parameters are shown in Table 1.

8 polychlorinated naphthalenes (PCNs) congeners and 30 chlorinated and brominated PAH congeners were selected as target compounds and were quantitated by isotopic dilution. They were measured by calibration curves with ^{13}C-labelled compounds as internal standards.

Besides these target halogenated polycyclic aromatic hydrocarbons (PAHs), 19 priority PAHs were also collected in same acquisition method by virtue of the full spectrum data collection and quantitated by calibration curves with deuterated PAHs as internal standards.

The data were processed using MassHunter Qualitative Analysis and Quantitative Analysis software as well as Unknown Analysis.

Experimental

Figure 1. Agilent 7250 GC/Q-TOF

GC and MS Conditions:	
Column	DB-5ms UI 60m-0.25mm-0.25um
MMI Inlet Mode	Splitless
Injection Volume	1 µL
Inlet Temperature	60 °C (0.2 min)–700°C/min-300 °C
Oven Temperature Program	55 °C -25°C/min-160 °C-2.5°C/min-260°C -5°C/min-305 °C (16.8 min)
Column Flow	Helium, Constant mode, 1 mL/min
Transfer line temperature	300 °C
Source temperature	250 °C
Quadrupole temperature	150 °C
Mass range	m/z 50-600
Spectral acquisition rate	5 Hz

Table 1. GC/Q-TOF Conditions

Chlorinated and Brominated PAHs

13 Cl-PAHs and 17 Br-PAHs were quantitated with 6 labelled internal standards (Figure 2). The calibration curve range was set from 5 pg/µL to 500 pg/µL. The lowest level of calibration solution was sequentially injected eight times and the RSDs of almost all congeners were lower than 10% (Table 2).

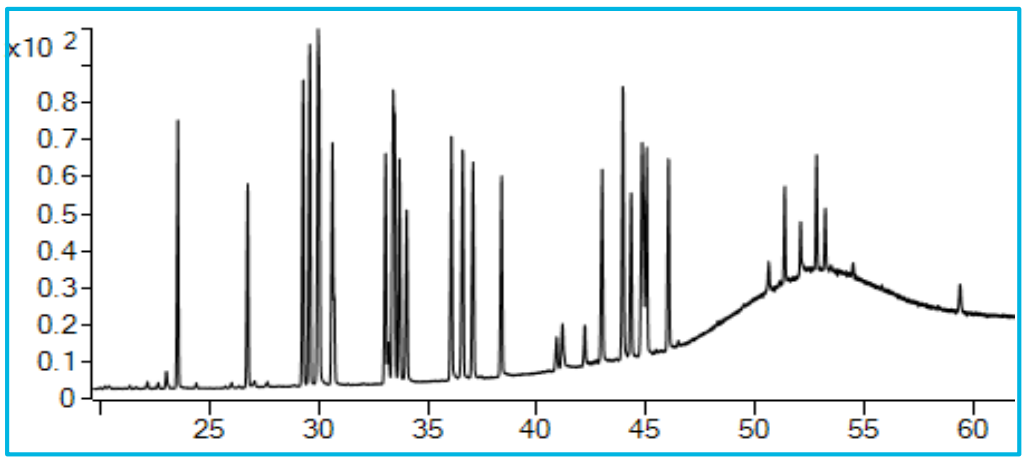

Figure 2. TIC of Chlorinated and Brominated PAHs

Compound Name	RT/min	Quant Ion	Qual Ion	CF R2	ISTD	5ppb RSD/%
5-Br-Ana	23.54	231.9882	233.9862	0.994	ISTD 1	4.2
2-Br-Fle	26.74	243.9882	245.9862	0.995	ISTD 1	5.8
3-Cl-Phe	29.29	212.0389	214.0358	0.997	ISTD 1	3.1
2/9-Cl-Phe	29.59	212.0389	214.0358	0.998	ISTD 1	2
1-Cl-Ant	29.59	212.0389	214.0358	0.998	ISTD 2	2.9
2-Cl-Ant	30.01	212.0389	214.0358	0.998	ISTD 2	6.5
2,7-2Cl-Fle	30.62	233.9998	235.9968	0.998	ISTD 2	4.5
1,2-2Br-Any	30.70	309.8811	307.8831	0.996	ISTD 2	8.4
3-Br-Phe	33.06	257.9867	255.9883	0.994	ISTD 3	5.3
9-Br-Phe	33.47	257.9867	255.9883	0.996	ISTD 3	6.5
2-Br-Phe	33.47	257.9867	255.9883	0.996	ISTD 3	9.4
1-Br-Ant	33.70	257.9867	255.9883	0.992	ISTD 3	7.5
9-Br-Ant	34.02	257.9867	255.9883	0.994	ISTD 3	7.7
1,4-2Cl-Ant	36.08	245.9998	247.9968	0.991	ISTD 3	2.9
1,5/9,10-2Cl-Ant	36.59	245.9998	247.9968	0.994	ISTD 3	5.2
9,10-2Cl-Phe	37.07	245.9998	247.9968	0.997	ISTD 3	5.5
2,7-2Br-Fle	38.37	323.8967	325.8947	0.992	ISTD 3	5.7
3-Br-Flu	42.99	279.9883	281.9862	0.989	ISTD 4	5.3
1,8/1,5-2Br-Ant	43.94	335.8967	337.8947	0.980	ISTD 4	7.2
9,10-2Br-Ant	44.31	335.8967	337.8947	0.988	ISTD 4	6.4
4-Br-Pyr	44.80	279.9883	281.9862	0.992	ISTD 4	7.7
9,10-2Br-Phe	44.87	335.8967	337.8947	0.982	ISTD 4	5.8
1-Br-Pyr	45.02	279.9883	281.9862	0.994	ISTD 4	4.6
3,8-2Cl-Flu	46.03	269.9998	271.9969	0.994	ISTD 4	9
1,5,9,10-4Cl-Ant	51.35	315.9189	313.9218	0.980	ISTD 5	9
2-Br-Triph	52.81	306.0039	308.0019	0.997	ISTD 6	8
1,6-2Br-Pyr	53.21	359.8967	361.8947	0.997	ISTD 6	8.9
6-Cl-BaP	59.39	286.0544	288.0515	0.996	ISTD 6	14.4
ISTD 1_9-Cl-Phe-^{13}C	29.56	218.0589	220.0559			
ISTD 2_2-Cl-Ant-^{13}C	30.01	218.0589	220.0559			
ISTD 3_9-Br-Phe-D_9	33.20	265.0447	267.0427			
ISTD 4_1-Cl-Pyr-^{13}C	41.16	242.0589	244.0559			
ISTD 5_7-Cl-BaA-^{13}C	50.63	268.0745	270.0716			
ISTD 6_7-Br-BaA-^{13}C	53.23	312.0240	314.0220			

Table 2. Chlorinated and Brominated PAHs Quantitative Method Performance

As shown in Figure 3, the matrix in the chlorinated and brominated PAHs fraction of the air sample was very complex. An accurate mass extraction window ± 15 ppm was used to eliminate the matrix noise effectively.

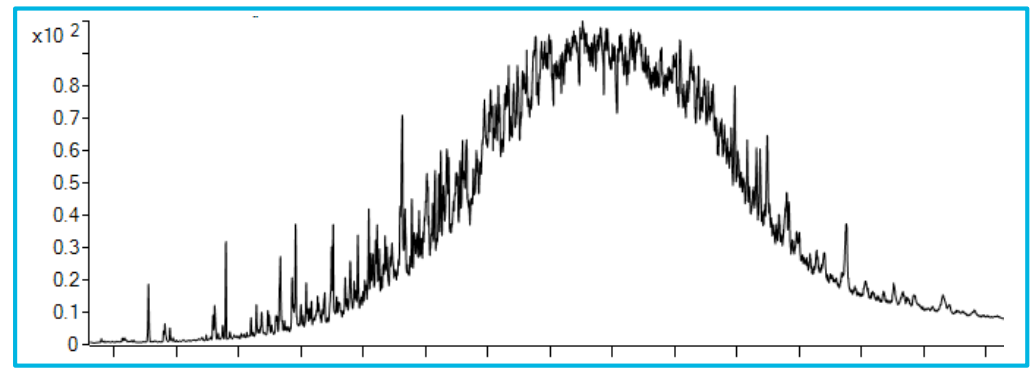

Figure 3. TIC of Chlorinated and Brominated PAHs Fraction in Air Sample

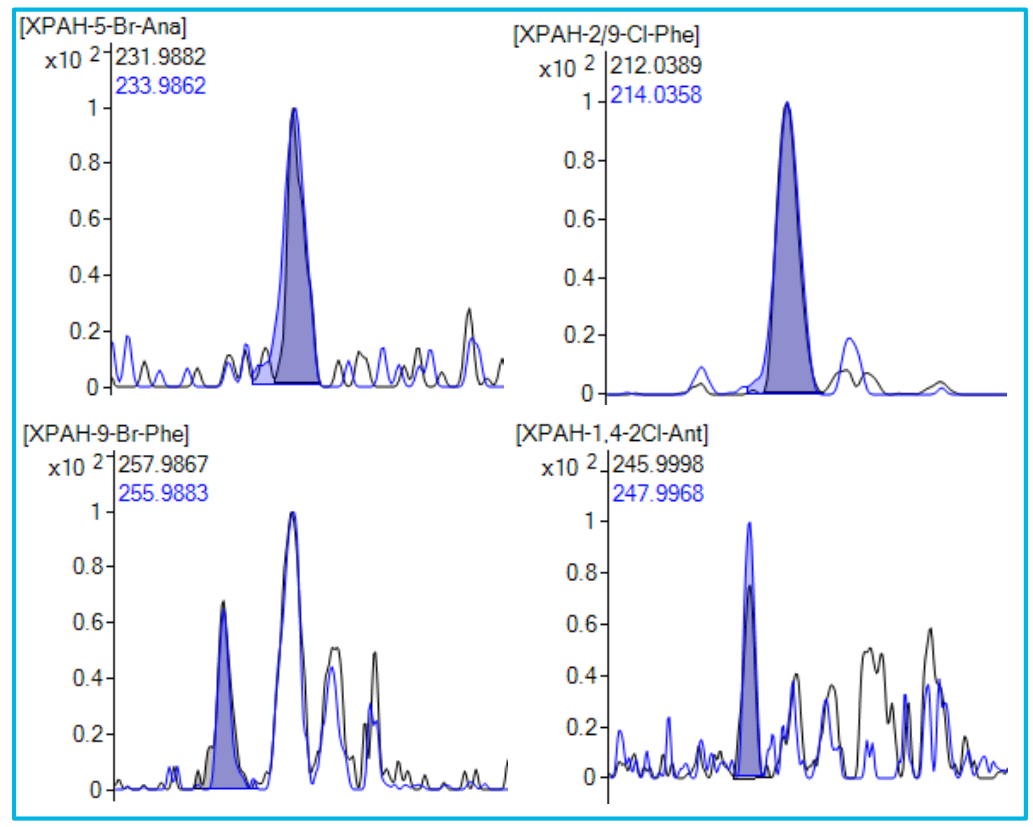

Figure 4. EIC of Chlorinated and Brominated PAHs in Air sample

Polychlorinated Naphthalenes (PCNs)

8 PCNs congers were quantitated with 6 labelled internal standards (Table 3). The relative response factors (RRFs) were calculated at concentrations of 1-400 pg/µL and the RSDs of these RRFs were below 15%.

The TIC of the PCN fraction in the air sample from the iron ore sintering plant is shown in Figure 5. The target PCNs in this complicated sample ranged between 0.01-0.23 pg/m^3. As shown in EICs of some specific PCN homologues (Figure 6), more PCNs congeners could be easily found and semi-quantitated by RRFs due to the full spectrum acquisition mode in GC/Q-TOF.

Results and Discussion

Compound Name	RT/min	Quant Ion	Qual Ion	Ave. RRF	RRF RSD/%	ISTD
2-Cl_Nap	11.66	162.0231	164.0202	1.65	13.04	ISTD 1
1,5-diCl-Nap	15.96	195.9841	197.9812	1.50	13.92	ISTD 1
1,2,3-TriCl-Nap	22.38	229.9451	231.9422	1.21	13.28	ISTD 1
1,2,3,5-TetraCl-Nap	27.81	265.9033	263.9062	1.25	13.51	ISTD 2
1,2,3,5,7-PentaCl-Nap	32.47	299.8643	301.8614	1.32	14.64	ISTD 3
1,2,3,4,6,7-HexaCl-Nap	39.94	333.8253	335.8224	1.25	10.22	ISTD 4
1,2,3,4,5,6,7-HeptaCl-Nap	47.91	367.7863	365.7892	1.37	8.69	ISTD 5
OctaCl-Nap	52.92	403.7444	401.7473	1.46	8.29	ISTD 6
ISTD 1_1,3,5,7-TetraCl-Nap-^{13}C	24.92	275.9368	273.9397			
ISTD 2_1,2,3,4-TetraCl-Nap-^{13}C	28.39	275.9368	273.9397			
ISTD 3_1,2,3,5,7-PentaCl-Nap-^{13}C	32.45	309.8978	311.8948			
ISTD 4_ 1,2,3,5,6,7-HexaCl-Nap-^{13}C	39.98	343.8588	345.8559			
ISTD 5_ 1,2,3,4,5,6,7-HeptaCl-Nap-^{13}C	47.90	377.8199	379.8169			
ISTD 6_ OctaCl-Nap-^{13}C	52.92	413.7779	411.7809			

Table 3. PCNs Quantitative Method Performance

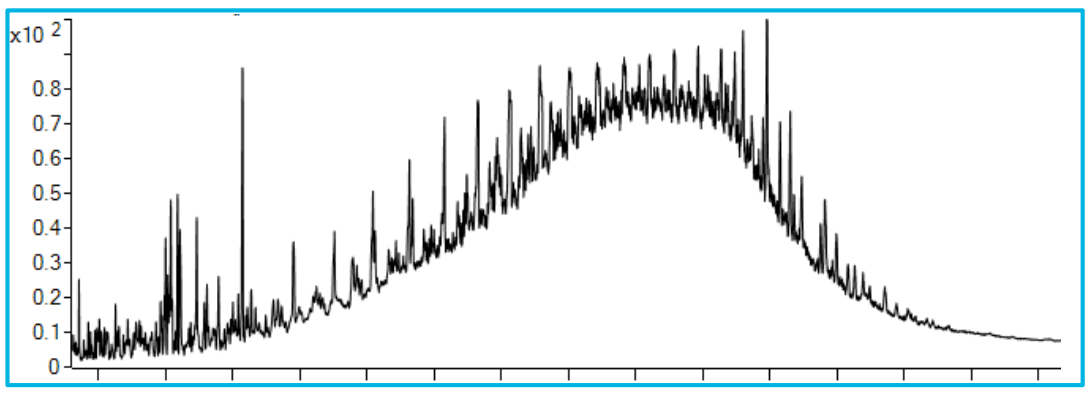

Figure 5. TIC of PCN Fraction in Air sample

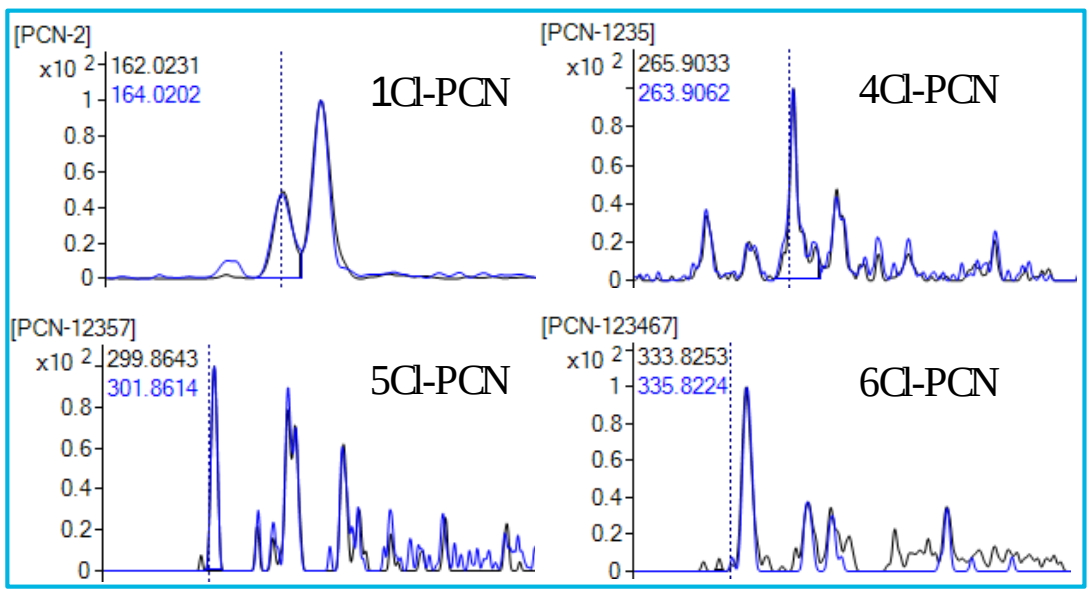

Figure 6. EIC of Specific homologue PCN Fraction in Air sample

PAHs

Target priority PAHs were quantitated by calibration curve with labeled ISTDs. The concentrations ranged from 0.12-101.2 pg/m^3. To identify more PAHs, an untargeted study was performed using MassHunter Unknowns Analysis software (Figure 7). SureMass signal processing was used for GC/Q-TOF data to deconvolute components and NIST 2017 library was used for identification.

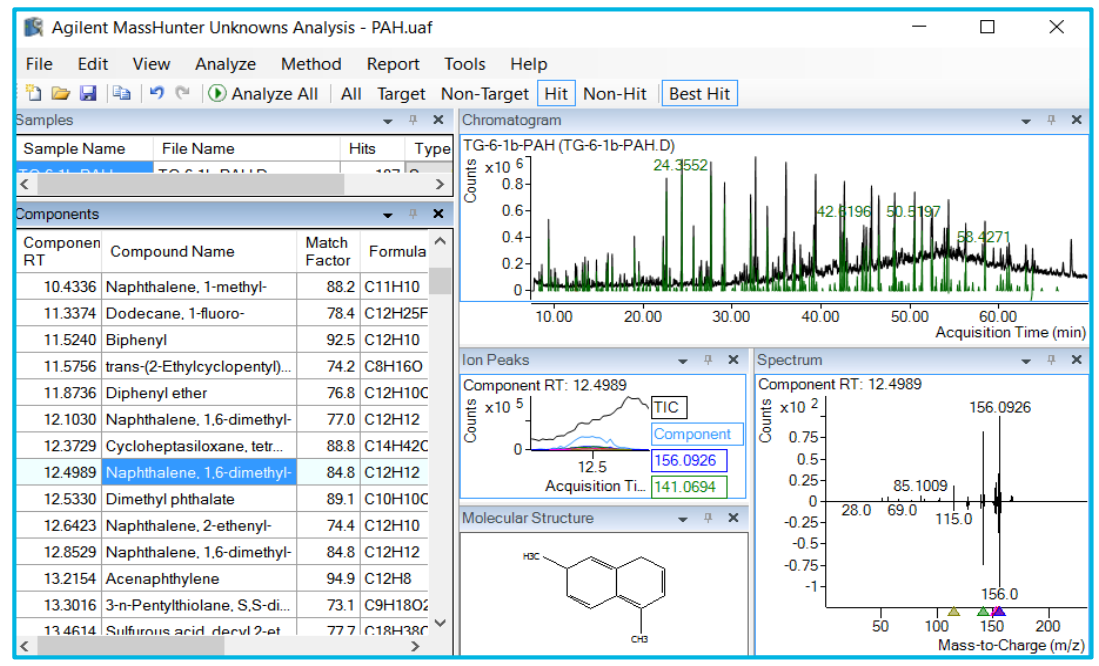

Figure 7. Non-target Study in Unknown Analysis

Conclusions

It is demonstrated that the Agilent 7250 GC/Q-TOF can measure trace levels of halogenated PAHs in complex samples.

Beyond target quantitation, the 7250 GC/Q-TOF can capture full spectrum data to extend analytical scope. Non-target study as well as retrospective analysis can be processed without the need to repeat injections.

Innovative data mining tools are provided by MassHunter software to improve data analysis efficiency.

References

[1]Lili Yang, Guorui Liu, Minghui Zheng et al., Sci. Total Environ., 2017, 580, 1146-1154

[2]Rong Jin, Guorui Liu, Minghui Zheng et al., J. Chromatogr. A, 2017, 1509, 114-122

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Trusted Answers