Instrument: Pegasus® GC-HRT 4D

Discovery of Environmental Pollutants at an Electronic Waste Recycling Facility by Pegasus GC-HRT 4D

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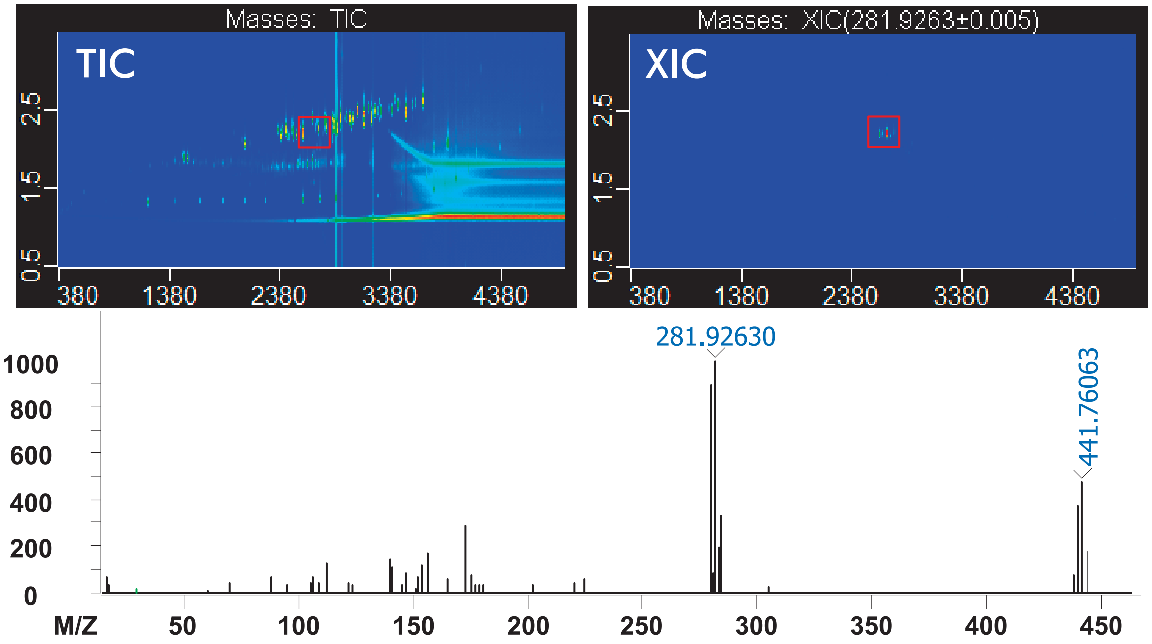
Key Words: GCxGC-HRT, Persistent Organic Pollutants, E-Waste, Non-Target Analysis, Compound Discovery, Screening

Introduction

The global production of electronic waste (e-waste) was estimated to have risen from 20 million tons per year in 2009 to more than 41 million in 2014, with Europe, North America, and Australasia producing the majority of the waste.[1] As countries like China and India have increased demand for electronics, the processing of e-waste in developing countries has become an environmental problem because of a lack of regulation and the increasing amount of e-waste generated. Most electronics contain environmental contaminants such as brominated flame retardants, which are a vector for environmental contamination. Though, potentially the most damaging environmental contaminants are produced by the improper processing of these components to form toxicants.[2,3] This study aimed to discover new and emerging organic contaminants in the environment of an e-waste recycling facility using comprehensive two-dimensional gas chromatography high resolution time-of-flight mass spectrometry (GCxGC-HRT).



Formula	Species	Observed m/z	Calculated m/z	MA (ppm)
$C_{12}H_6Br_3ClO$	$M^{+\bullet}$	437.76480	437.76518	-0.87
	$[M+2]^+$	439.76313	439.76307	0.14
	$[M+4]^+$	441.76063	441.76093	-0.68
	$[M+6]^+$	443.75897	443.75876	0.47
$C_{12}H_6BrClO$	$[M-2Br]^+$	279.92866	279.92851	0.55
	$[M-2Br+2]^+$	281.92630	281.92630	-0.00
	$[M-2Br+4]^+$	283.92321	283.92386	-2.3

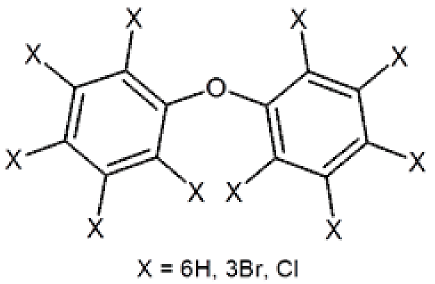


Figure 1. Putative identification of a mixed bromo-chloro diphenyl ether compound class in an electronic shredder waste sample by GCxGC-HRT. The extracted ion chromatogram (XIC) of the base peak (m/z = 281.9263) from the deconvoluted mass spectrum indicated the occurrence of at least five congeners with the chemical formula $C_{12}H_6Br_3ClO$ in this sample. The sub ppm mass accuracy values for the proposed molecular ion cluster and the $[M-2Br]^+$ ion cluster, along with isotope ratio pattern matching were used for the tentative identification.

Experimental

Chemical extracts were prepared from workshop-floor dust (fine particles settled on the concrete floors of workshops) and electronic shredder waste (plastic materials discarded after the recovery of metals).[4] The fraction of these extracts previously analyzed for flame retardants were analyzed using LECO's *Pegasus* GCxGC-HRT. Extracts were injected using a Gerstel MPS2 Autosampler into a CIS-4 inlet with a septumless head, operated in cold splitless mode. The autosampler was coupled to an Agilent 7890B GC fitted with a secondary oven and dual-stage LN_2 thermal modulator. Complete method conditions are shown in Table 1. In addition to real-time drift correction, perfluorotributylamine was infused throughout the chromatographic run and used as a post-acquisition mass calibrant to ensure sub ppm mass accuracies. Data processing was completed using ChromaTOF® brand software.

Table 1. GCxGC-High Resolution TOFMS *(Pegasus* HRT 4D) Conditions

Gas Chromatograph	**LECO GCxGC Quad Jet Thermal Modulator & MPS2 Autosampler**
Injection	1 μL cold splitless, 80 °C held for 0.1 min, then ramped at 12 °C/s to 300 °C
Carrier Gas	He @ 1.2 ml/min
Column One	Rtx-Dioxin2, 60 m x 0.25 mm i.d. x 0.25 μm coating (Restek, Bellefonte, PA, USA)
Column Two	Rxi-17SilMS, 0.6 m x 0.25 mm x 0.25 μm coating (Restek, Bellefonte, PA, USA)
Temperature Program	1.5 min at 80 °C, ramped 10 °C/min to 150 °C, then 3.5 °C/min to 340 °C held 20 min; Secondary oven maintained +10 °C relative to primary oven
Modulation	3 s with temperature maintained +15 °C relative to secondary oven
Mass Spectrometer	**LECO (*Pegasus* GC-HRT 4D)**
Transfer Line	340 °C
Ion Source Temperature	250 °C
Acquisition Mode	High Resolution, R = 25,000 (FWHM)
Ionization Mode	EI
Mass Range (m/z)	15-1000
Acquisition Rate	5 spectra/s (1D); 100 spectra/s (2D)

Results and Discussion

Data was collected and mass calibrated as described in the methods section, where the RMS of the coefficients was less than 1 ppm. Thousands of peaks were determined in each sample by GCxGC-HRT, which provides unsurpassed analyte resolving power by leveraging multiple degrees of orthogonality. Chromatographic peaks were separated first using two orthogonal chromatographic dimensions (non-polar then polar), and then deconvolved mass spectrometrically using accurate mass, high resolution mass spectrometry *(ChromaTOF)*. Peak True (Deconvoluted) Spectra were searched against commercially available library databases such as NIST 14 and Wiley 10 for tentative identification. Hits with a similarity greater than 800 (out of 1000) and a mass accuracy less than 1.5 ppm were considered to be correct in the absence of an authentic standard. Accurate mass was used to determine chemical formulae for peaks with a library hit less than 800. The mass spectrum was used to elucidate a structure where possible, and combined with information from online chemical databases like ChemSpider. In some cases, identifications were confirmed with authentic standards.

The complexity of the e-waste samples is demonstrated in Figure 2, which also illustrates the need for GCxGC-HRT analysis. Many classes of legacy contaminants such as polychlorinated biphenyls were readily identified, as well as several other classes of chemical contaminants (Table 2), aided by the chromatographic separation in the second dimension which distinguished the halogenated compounds from the complex unresolved chromatographic region. An example of an unknown identification is highlighted in Figure 1.

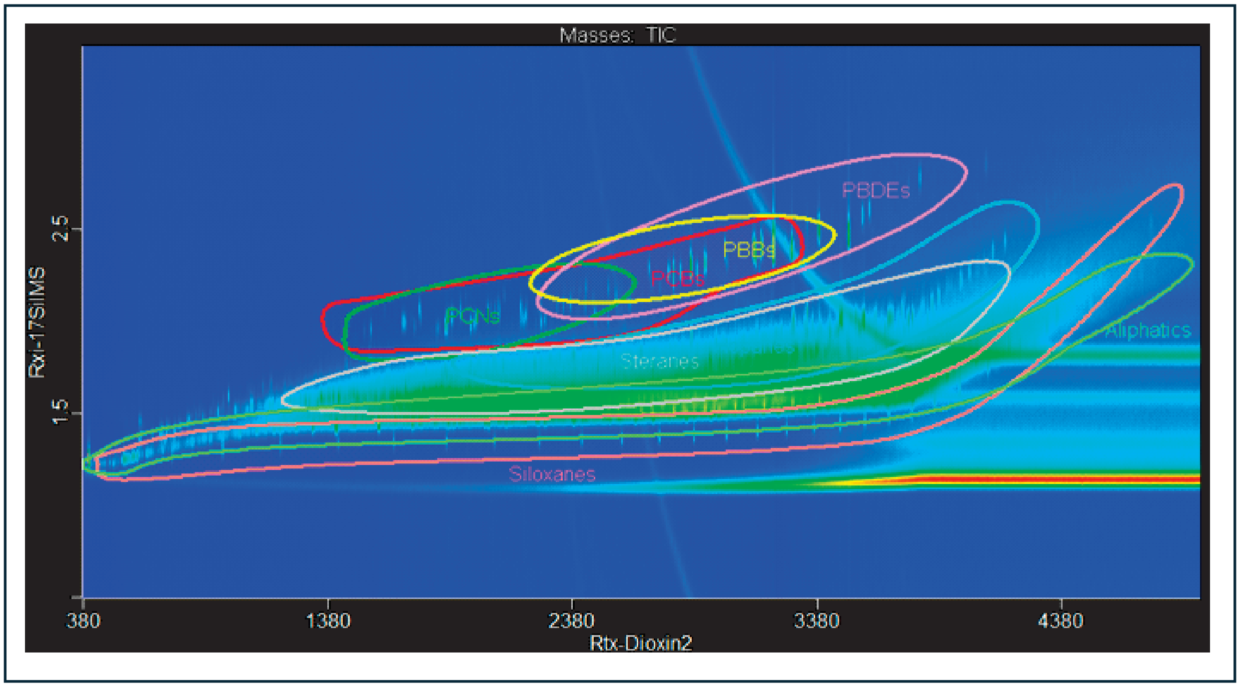


Figure 2. A total ion chromatogram (TIC) contour plot of a dust sample from an e-waste facility analysed by comprehensive GCxGC-HRT. The classification regions, encompassed by colored lines, were drawn based on results of the automatic Peak Find in ChromaTOF-HRT, and plotting extracted ion chromatograms (XIC) of characteristic masses of known compounds.

Table 2. Select list of compounds detected in electronic shredder waste (ESW) and dust samples collected from an e-waste facility in China and their relative intensities.

Name	Formula	ESW	ESW	Dust	Dust	Dust	Dust
Polychlorinated biphenyls	$C_{12}H_{10-n}Cl_n$	*****	***	*****	*****	*****	*****
Polychlorinated naphthalenes	$C_{10}H_{8-n}Cl_n$	*	-	**	***	***	**
Polybrominated diphenyl ethers	$C_{12}H_{10-n}Br_nO$	*****	*****	*	*	*	-
Polybrominated biphenyls	$C_{12}H_{10-n}Br_n$	*	-	-	-	-	-
Tris(2,4-di-tert-butylphenyl) phosphate	$C_{42}H_{63}O_4P$	-	****	-	-	-	-
Pentabromotoluene	$C_7H_3Br_5$	*	-	**	**	**	***
Hexabromobenzene	C_6Br_6	*	-	***	****	*****	***
Dechlorane Plus	$C_{18}H_{12}Cl_{12}$	**	*****	*	*	*	*
Mixed bromo-chloro diphenyl ether	$C_{12}H_6Br_3ClO$	-	*	-	-	-	-
Tetrabromo-methoxy-biphenyl	$C_{13}H_8Br_4O$	*	*	-	-	-	-
1-ethoxy-dibromobenzene	$C_8H_8Br_2O$	-	*	-	-	-	-
1-ethoxy-tribromobenzene	$C_8H_7Br_3O$	-	*****	-	-	-	-

Note: The relative intensities are reflected by the number of asterisks.

The constituents of the complex region of the 2D chromatogram represent a variety of petroleum hydrocarbons, a number of which are considered to be biomarkers such as steroids and hopanoids.[5] Two examples are shown in Figure 3, a C30 hopane and a C29 monoaromatic 8,14-secohopanoid. The deconvoluted mass spectrum was used to determine a chemical formula, and the EI mass spectrum was in turn interpreted to establish a tentative identification. Hundreds of hopanes, steranes, hopanoic acids, benzohopanes, mono-, di-, tri-aromatic hopanes and secohopanoids were identified in the electronic shedder waste. The detection of these compounds in these samples present an interesting environmental question as to the reason for their occurrence.

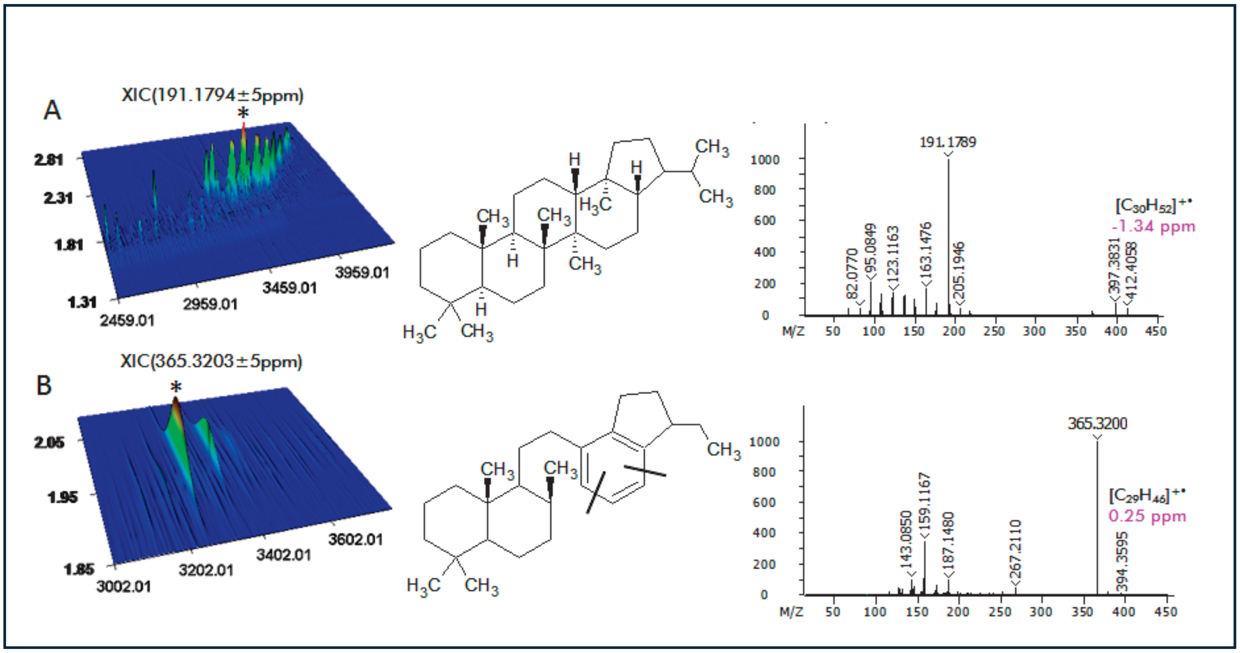


***Figure 3.** Three dimensional chromatogram of the characteristic mass fragment for (A) hopanes (m/z 191.1794) and (B) monoaromatic 8,14-secohopanoids (m/z 365.3203) for an electronic shredder waste sample analysed by comprehensive GCxGC-HRT. The peaks with asterisks were tentatively identified based on the interpretation of the accurate mass deconvoluted mass spectrum shown.*

Conclusion

The combination of high resolution front-end separation with high resolution time-of-flight mass spectrometry lead to the identification of compounds previously unknown in these samples. GCxGC-HRT is a powerful tool for the comprehensive analysis and chemical characterization of analytes in complex matrices.

References

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