Non-Target Analysis of Electronic Waste Samples from China

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Background

The processing of electronic waste (e-waste) in developing countries has become an environmental problem because of a lack of regulation, and the increasing amount of e-waste generated as countries like China and India have increased demand for electronics. Most electronics contain environmental contaminants such as brominated flame retardants, which are a vector for environmental contamination. Potentially the most damaging environmental contaminants are produced by the improper processing of these components to form toxicants.[1,2] This study was aimed to chemically characterize new and emerging organic contaminants in environmental matrices surrounding an e-waste site using comprehensive two-dimensional gas chromatography high resolution time-of-flight mass spectrometry (GC×GC-HRT).

Methods

Samples

Map of sampling sites in Fengjiang, China. The red stars show sampling workshops in an e-waste recycling base, in and near Baifengao village, with a picture of e-waste dumped in an open air workspace.[1]

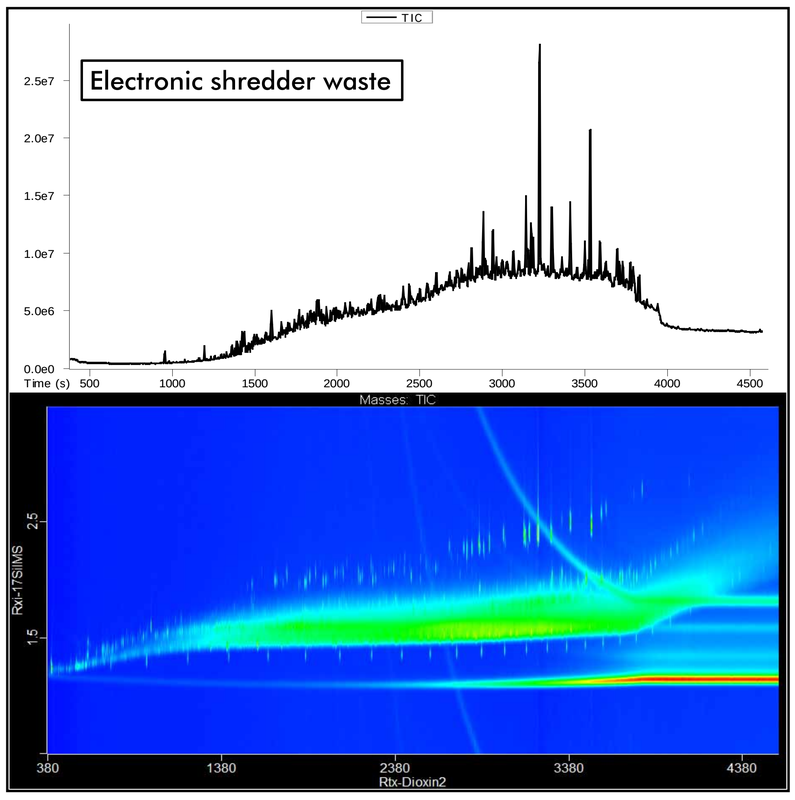
In this study, samples of workshop-floor dust (fine particles settled on the concrete floors of workshops), and electronic shredder waste (plastic materials discarded after the recovery of metals) were analyzed.

Instrumental Details

Gas Chromatograph	**Agilent 7890 with Dual Stage Quad Jet Modulator and Gerstel MPS2 Autosampler with CIS-4 inlet**
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)
Column Two	Rxi-17SilMS, 0.60 m x 0.25 mm x 0.25 µm coating (Restek)
Temperature Program	1.5 min at 80°C, ramped 10°C/min to 150°C, then 3.5°C/min to 340°C (20 min) Secondary oven maintained +10°C relative to primary oven
Modulation	3 s with temperature maintained +25°C relative to secondary oven
Transfer Line	340°C
Mass Spectrometer	**LECO Pegasus® HRT 4D**
Ion Source Temperature	250°C
Mass Range	15-1000 m/z
Acquisition Rate	5 spectra/s; 100 spectra/s

Results

1D to 2D Chromatographic Comparison



Results

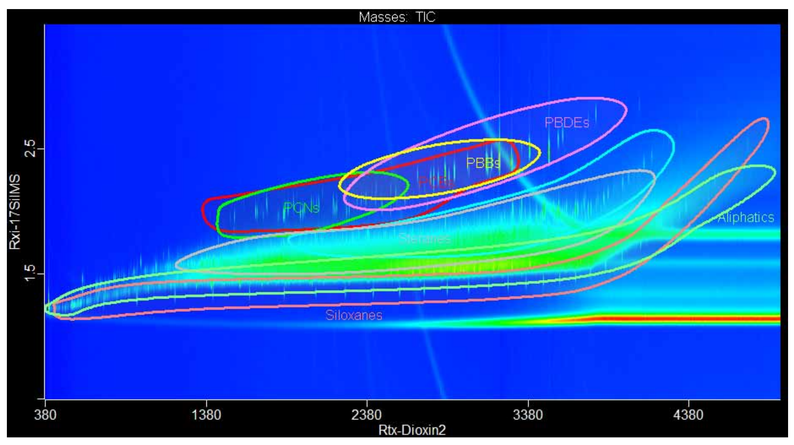
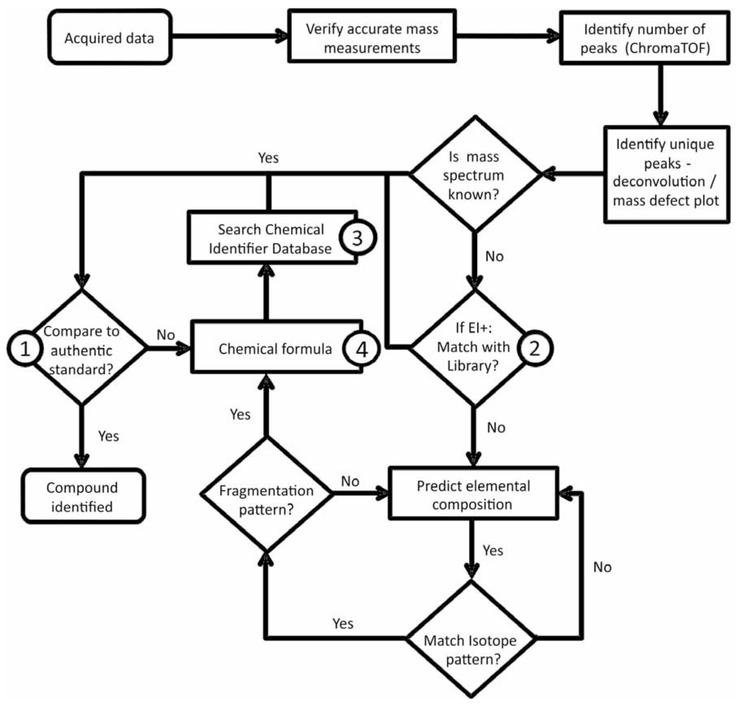


Figure 1. A total ion chromatogram (TIC) contour plot of an electronic shredder waste sample analyzed by GC×GC-HRT. The classification regions, indicated by the colored circles, were drawn based on results of the automatic Peak Find in ChromaTOF-HRT, and plotting extracted ion chromatograms of characteristic masses of known compounds.

Compound Identification Workflow



Confidence Level of Identification

1. Mass spectrum, with less than 1.5 ppm mass accuracy, and retention time matched to an authentic standard.
2. Mass spectrum matched to a commercial library with less than 1.5 ppm mass accuracy to the monoisotopic mass.
3. Chemical formula predicted based on mass accuracy and EI fragmentation pattern used to predict a structure present in a commercially available chemical database (i.e. ChemSpider).
4. Chemical formula predicted based on mass accuracy, but the structure is unknown.

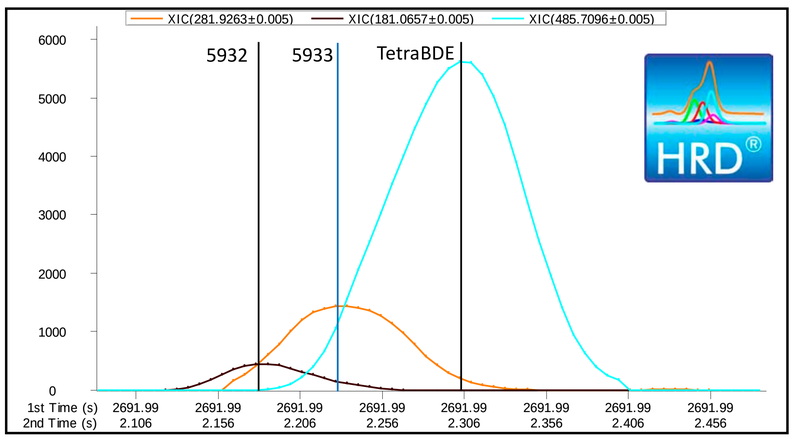


Figure 2. Extracted ion chromatograms (XIC) of three deconvoluted peaks in the comprehensive GC×GC analysis of an electronic shredder waste sample using ChromaTOF-HRT® brand software. The unknown Peak 5933 is tentatively identified in the subsequent figures.

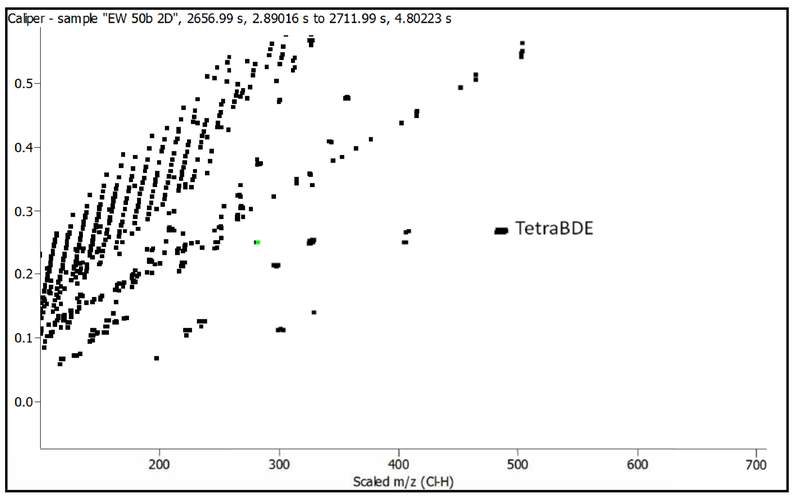


Figure 3. Scaled mass defect plot (Cl-H) of an electronic shredder waste sample. The highlighted point corresponds to m/z = 281.9263, the base peak for the compound identified in Figures 4 and 5.

Results

Mixed Bromo-Chloro Diphenyl Ethers

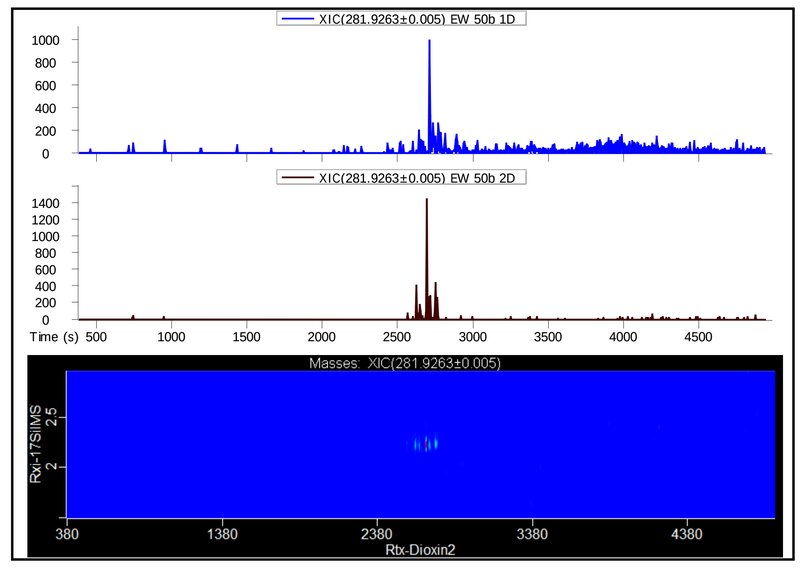
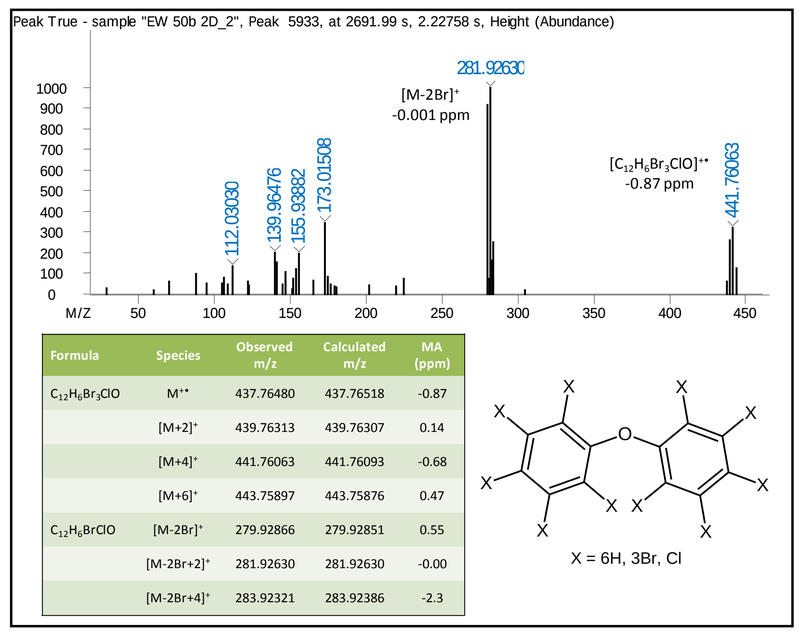


Figure 4. Extracted ion chromatograms (XIC) of the mass base peak for mixed bromo-chloro diphenyl ethers (m/z = 281.9263) with the molecular formula $C_{12}H_6Br_3ClO$, collected in 1D and 2D modes. The chemical noise is significantly reduced in the 2D chromatogram .



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

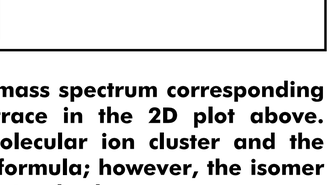


Figure 5. The Peak True (Deconvoluted) mass spectrum corresponding to the most intense chromatographic trace in the 2D plot above. Accurate mass measurements of the molecular ion cluster and the $[M-2Br]^+$ fragment confirm the chemical formula; however, the isomer cannot be identified without an authentic standard.

Select Compounds Identified in E-Waste

Name	Formula	Level	ESW	ESW	Dust	Dust	Dust	Dust
Polychlorinated biphenyls	$C_{12}H_{10-n}Cl_n$	1	*****	***	*****	*****	*****	*****
Polychlorinated naphthalenes	$C_{10}H_{8-n}Cl_n$	1	*	-	**	***	***	**
Polybrominated diphenyl ethers	$C_{12}H_{10-n}Br_nO$	1	*****	*****		*		-
Polybrominated biphenyls	$C_{12}H_{10-n}Br_n$	2	*	-	-	-	-	-
Tris(2,4-di-tert-butylphenyl) phosphate	$C_{42}H_{63}O_4P$	2	-	****	-	-	-	-
Pentabromotoluene	$C_7H_3Br_5$	1	*	-	**	**	**	***
Hexabromobenzene	C_6Br_6	1	*	-	***	****	*****	***
Dechlorane Plus [3]	$C_{18}H_{12}Cl_{12}$	1	**	*****		*	*	
Mixed bromo-chloro diphenyl ether	$C_{12}H_6Br_3ClO$	3	-	*	-	-	-	-
Tetrabromo-methoxy-biphenyl	$C_{13}H_8Br_4O$	3	*	*	-	-	-	-
1-ethoxy-dibromobenzene	$C_8H_8Br_2O$	3	-	*	-	-	-	-
1-ethoxy-tribromobenzene	$C_8H_7Br_3O$	2	-	*****	-	-	-	-
Unknown	$C_{20}H_{15}Br_3O$	4	-	*	-	-	-	-

Conclusions

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

References

1. Ma, J., et al. Concentrations, profiles, and estimated human exposures for polychlorinated dibenzo-*p*-dioxins and dibenzofurans from electronic waste recycling facilities and a chemical industrial complex in Eastern China. *Environ Sci Technol.* **2008**, 42, 8252-8259.
2. Wen, S., et al. Elevated levels of urinary 8-hydroxy-2′-deoxyguanosine in male electrical and electronic equipment dismantling workers exposed to high concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, polybrominated diphenyl ethers, and polychlorinated biphenyls. *Environ Sci Technol.* **2008**, 42, 4202-4207.
3. Sverko, E., et al. Dechlorane plus and related compounds in the environment: a review. *Environ Sci Technol.* **2011**, 45, 5088-5098.

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