

Identifying organic contaminants in an e-waste recycling facility in China

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The global production of electronic waste (e-waste) was estimated at 41.8 million tons 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.

Many electronic items contain high amounts of precious metals like gold or silver, and the recovery of these precious metals for profit is the aim of e-waste recycling facilities. However, there are environmental concerns as all electronics also contain known contaminants such as flame retardants. Although, the most damaging environmental contaminants are produced by the improper processing of these electronic components [2, 3]. The first step in understanding the environmental effect of e-waste recycling is to characterize the chemical components in e-waste using non-targeted analysis, since many of the contaminants present initially and produced during processing are not known. This study aimed to discover new and emerging organic contaminants in the environment of an e-waste recycling facility in China using comprehensive two-dimensional gas chromatography high resolution time-of-flight mass spectrometry (GC×GC-HRToFMS).



Figure 1. E-waste dumped in an open air workspace in Fengjiang, China. Reprinted with permission from [2] Copyright 2008 American Chemical Society.

Experimental Section

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) [2]. The fraction of these extracts previously analyzed for flame retardants were analyzed using LECO's Pegasus GC×GC-HRT 4D. 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 quad jet thermal modulator utilizing LN₂ as cryogen. Complete method conditions are shown in Table 1. Perfluorotributylamine was infused throughout the chromatographic run and used as a post-acquisition mass calibration to ensure sub ppm mass accuracies. Data processing was completed using ChromaTOF-HRT.

Table 1. GC×GC-High Resolution TOFMS (Pegasus® HRT 4D) Conditions

| Agilent 7890 with Dual Stage Quad Jet Modulator and MPS2 Autosampler | |
|--|---|
| Injection | 1 µL cold splitless, 80°C (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 df |
| Column Two | Rxi-17SiIMS, 0.6 m x 0.25 mm i.d. x 0.25 µm df |
| Temperature Program | 80°C (1.5 min), 10°C/min to 150°C, then 3.5°C/min to 340° (20 min); secondary oven +10°C relative to primary oven |
| Modulation | 3 s with temperature maintained +15°C relative to secondary oven |
| LECO Pegasus HRT 4D | |
| Transfer Line | 340 °C |
| Source Temp. | 250 °C |
| Acq. Mode | R = 25,000 (FWHM) |
| Ion. Mode | EI |
| m/z range | 15-1000 |
| Acq. Rate | 5 spectra/s (1D); 100 spectra/s (2D) |



Figure 2. Map of sampling sites in Fengjiang, China. Reprinted with permission from [2] Copyright 2008 American Chemical Society.

Results and Discussion

Data were collected and mass calibrated as described in the methods section, where the root mean square of the coefficients was less than 1 ppm. Thousands of peaks were determined in each sample by GC×GC-HRTofMS, 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-HRT). The complexity of the e-waste samples is demonstrated in Figure 3, which also illustrates the need for GC×GC-HRTofMS analysis.

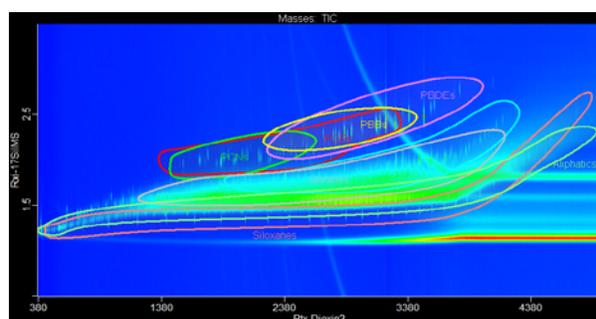


Figure 3. A total ion chromatogram (TIC) contour plot of an electronic shredder waste sample analysed by comprehensive GC×GC-HRTofMS. Due to the structured nature of GC×GC separations, analytes of the same compound class elute in similar regions of the chromatogram that can be defined with classification regions, indicated by colored circles. The regions were drawn based on results of the automatic Peak Find in ChromaTOF-HRT, and by plotting extracted ion chromatograms (XIC) of characteristic masses of known compounds.

For chemical characterization, deconvoluted mass 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. Additionally, a scaled mass defect plot (C1-H) was also employed to identify unique peaks [5].

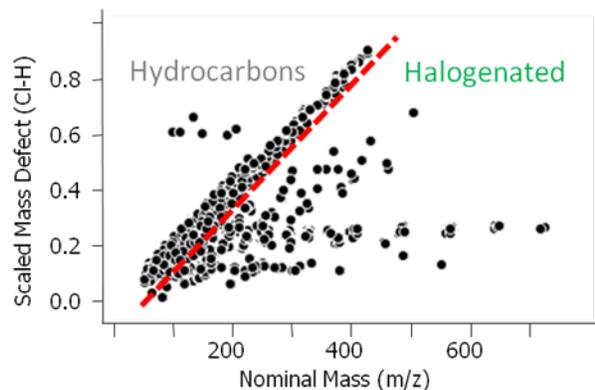
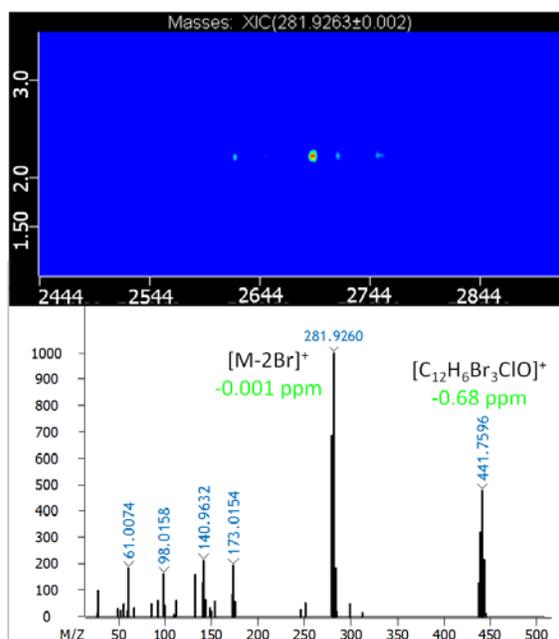
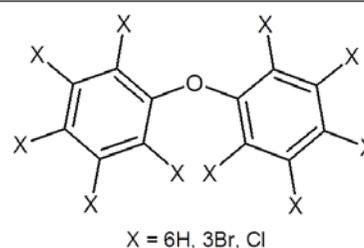


Figure 4. Scaled Mass Defect Plot (C1-H) of an electronic shredder waste sample. The masses left of the dotted red line represent mainly hydrocarbons, and the masses right of the line represent mainly halogenated compounds.

Accurate mass was also used to determine chemical formulae for peaks with a library hit less than 800. In some cases, the mass spectrum was used to elucidate a structure where possible, in combination with information from online chemical databases like ChemSpider. An example of an unknown identification is highlighted in Figure 5. When available, identifications were confirmed with authentic standards. Many classes of legacy contaminants such as polychlorinated biphenyls were readily identified, as well as several other classes of chemical contaminants (Table 2). Six dimensions of separation, comprehensive 2D gas chromatography, spectral deconvolution, accurate mass, mass defect and intensity were utilised to distinguish an unprecedented number of features in e-waste samples, all within a single data acquisition.



| Formula | Species | Observed m/z | Calculated m/z | MA (ppm) |
|--------------------|---------------|--------------|----------------|----------|
| $C_{12}H_6Br_3ClO$ | M^{++} | 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 | -2.30 |



Mixed bromo-chloro diphenyl ether

Figure 5. Putative identification of a mixed bromo-chloro diphenyl ether compound class ($C_{12}H_6Br_3ClO$) in an electronic shredder waste sample by GC×GC-HRToFMS, using the mass accuracy values for the proposed molecular ion cluster and the $[M-2Br]^+$ ion cluster, along with isotope ratio pattern matching. Analytes in this compound class are potential toxicants.

Table 1. Select list of compounds detected in samples collected from an e-waste facility in China and their relative intensities.

| Name | Formula | ESW1 | ESW2 | Dust1 | Dust2 | Dust3 | Dust4 |
|---|-----------------------|-------|-------|-------|-------|-------|-------|
| 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.

Conclusions

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



Pegasus GC-HRT 4D

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