

# AccuTOF-GC Series

## Analysis of Electronics Waste by GCxGC Combined with High-resolution Mass Spectrometry: Using Accurate Mass Information and Mass Defect Analysis to Explore the Data <sup>[1]</sup>

### Introduction

Comprehensive two-dimensional gas chromatography (GCxGC) in combination with high-resolution mass spectrometry (HRMS) is a powerful tool for the analysis of complex mixtures. However, new software tools are required to facilitate the interpretation of the rich information content in GCxGC/HRMS data sets. In this work, we analyzed a dust sample collected from an electronics recycling facility by using GCxGC in combination with a new high-resolution time-of-flight (TOF) mass spectrometer. Nontraditional Kendrick Mass Defect (KMD) plots were used to identify halogenated contaminants in an electronics waste sample. Database search results combined with elemental composition determinations from exact-mass data were used to identify (potential) persistent organic pollutants (POPs).

### Sample and Instrument

A dust sample was collected from an electronics recycling facility. Then, 1 gram of this sample was used for extraction into hexane. Afterwards, the hexane solution was analyzed with the JEOL JMS-T100GCV “AccuTOF GCv 4G” equipped with a Zoex ZX2 thermal modulator (Figure 1) and a high-resolution version of the GC Image software (version 2.5.0a2). Table 1 shows the measurement conditions used for the analysis.

### Result and Discussion

Figure 2a shows the GCxGC/EI TIC for the sample. Afterwards, a composite mass spectrum was created by summing the mass spectra for all components in the GC x GC/HRMS analysis (Figure 2b). Halogenated contaminants are readily recognized by their mass defects <sup>[2]</sup>. The next step then was to then create nontraditional KMD plots by converting the measured IUPAC  $m/z$  to H/Cl mass scales corresponding to the mass of a chlorine atom minus the mass of a hydrogen atom. Afterwards, the nominal mass was plotted vs. the corresponding mass defect for each peak (Figure 2c).

$$H/Cl \text{ mass} = IUPAC \text{ mass} \times (34/33.96102)$$

The resulting mass defect plot facilitated the rapid identification of families of compounds that differ by the number of chlorine substituents. The KMD plots for H/Cl and H/Br are nearly identical, allowing us to view both Cl and Br substitutions in one plot.

1. We found chlorinated and brominated compounds immediately, easily and visually by using H/Cl KMD plots. We then used this information to make the 2D mass chromatograms (Figure 3).
2. Additionally, we obtained NIST library search results and accurate mass measurement results from the data acquired in EI mode (Figure 3).
3. We showed a good example for the analysis of a complex sample using GCxGC, high-resolution MS and the KMD method. The combination of these techniques is a very powerful and useful tool for detailed qualitative analysis.
4. We also performed NICI measurements with GCxGC and KMD analysis (Figure 4). We observed similar results to the EI data for several compounds. However, some compounds showed abundant Cl<sup>-</sup> and Br<sup>-</sup> peaks instead of molecular ions so their 2D mass chromatograms were plotted as well (Figure 5). The NICI method is a good ionization technique for low-concentration samples and quantitative analysis.



Figure 1. JMS-T100GCV AccuTOF GCv 4G GCxGC/HR-TOFMS system

Condition	GC x GC/EI	GC x GC/NICI
Sample	Dust sample collected from an electronics recycling facility	
GC x GC system	ZX2 thermal modulator (ZOEX)	
1st column	Rxi-5SilMS, 30 m x 0.25 mm, 0.25 μm	
2nd column	Rxi-17SilMS, 2 m x 0.15 mm, 0.15 μm	
Modulation loop	Deactivated fused silica, 1.5 m x 0.15 mm	
Modulation period	8 sec	
Modulation duration	400 msec	
Inlet pressure	200 kPa at Oven temp. 50 °C (Constant flow mode)	
Inlet mode	Splitless	
Oven temp.	50 °C (1 min) → 5 °C/min → 320 °C (5 min)	
GC-TOFMS system	AccuTOF GCv 4G (JEOL)	
Ionization mode	EI+	CI-
Ionization voltage	70 V	150 V
Ionization current	300 μA	300 μA
CI gas		Ammonia/Methane 0.5 mL/min
Ion source temp.	250 °C	200 °C
GC-ITF temp.	280 °C	
$m/z$ range	$m/z$ 45-800	$m/z$ 30-800
Acquisition time	20 msec (50 Hz)	
Sampling time	0.25 nsec (4 GHz)	
External calibrant	$m/z$ 207.0329 (C <sub>5</sub> H <sub>13</sub> O <sub>3</sub> Si <sub>3</sub> )	$m/z$ 234.9405 (ReO <sub>3</sub> )
Software	GC Image™ Version 2.5.0a2	

Table 1. Measurement Conditions

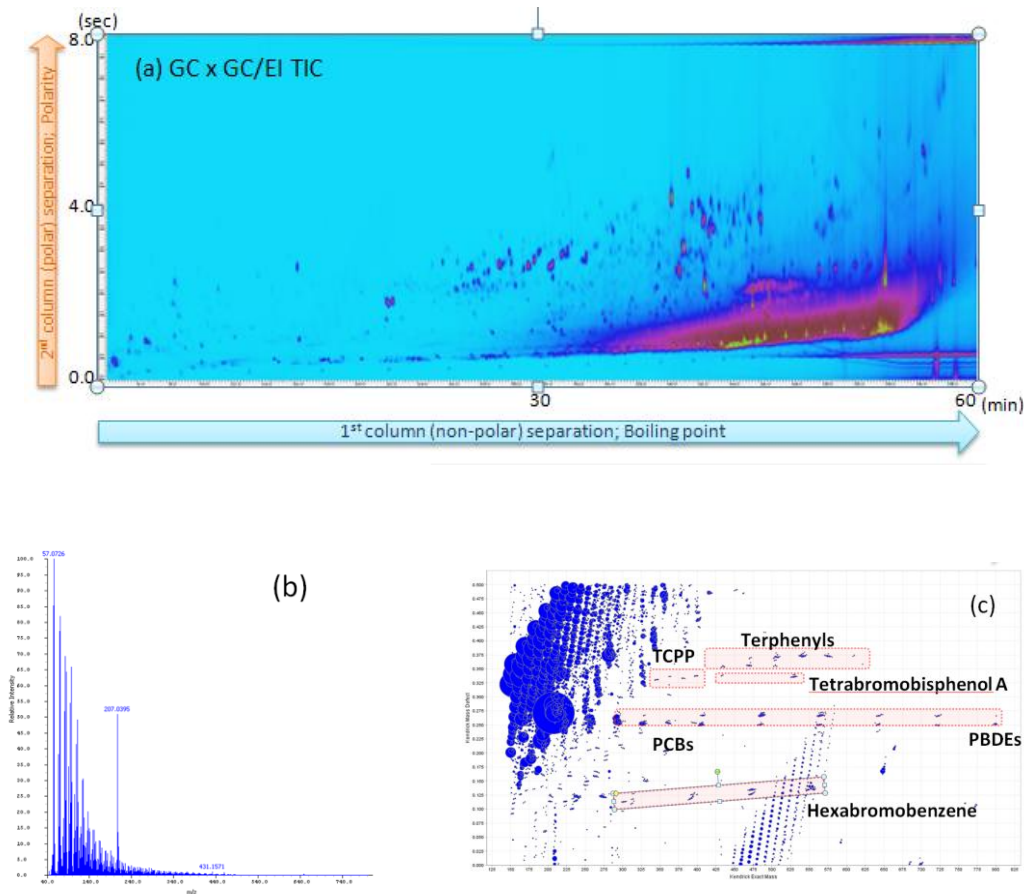
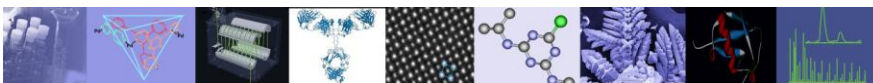


Figure 2. (a) GCxGC/EI TIC chromatogram of the dust sample, (b) Averaged mass spectrum for the whole retention time region, (c) H/Cl mass defect plot for the averaged mass spectrum.

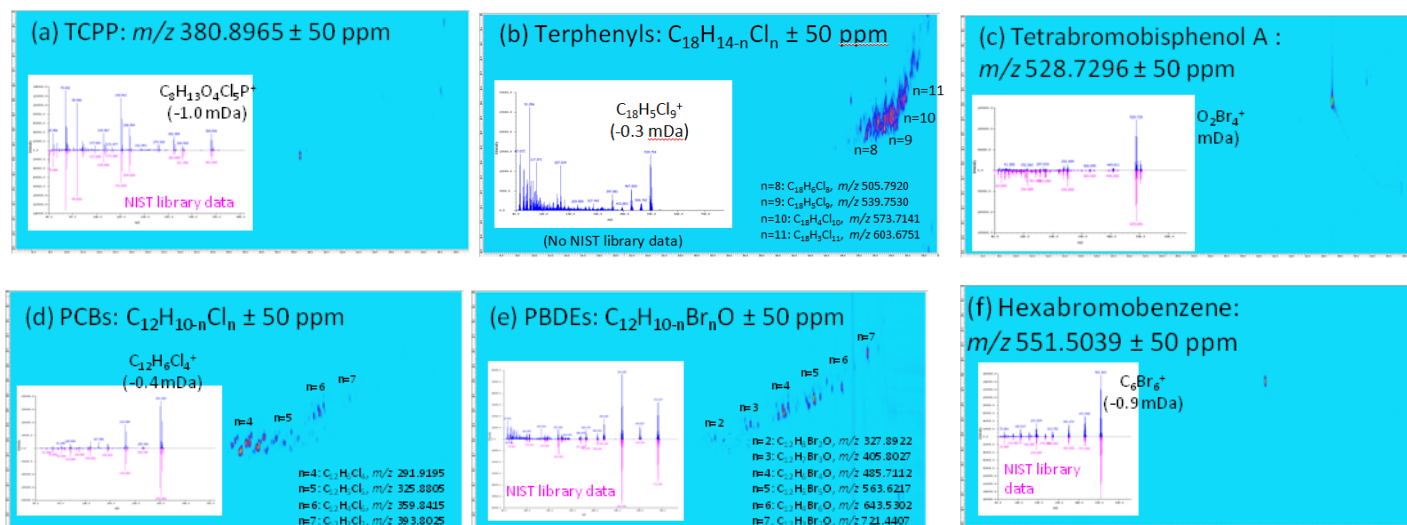


Figure 3. 2D mass chromatogram using mass of the most abundant isotope ion  $\pm$  50 ppm (a) TCPP, (b) Terphenyls, (c) Tetrabromobisphenol A, (d) PCBs, (e) PBDEs, (f) Hexabromobenzene

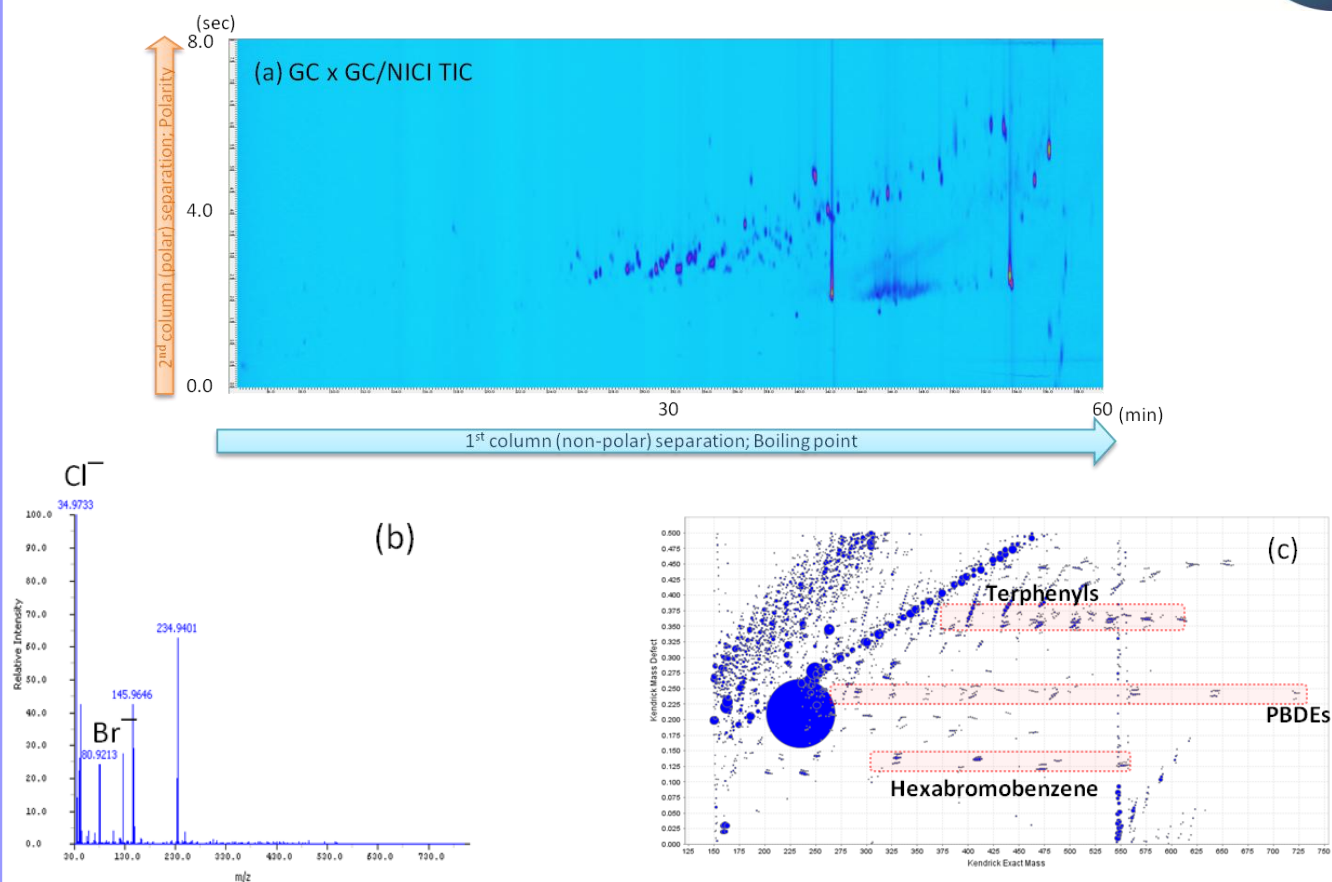
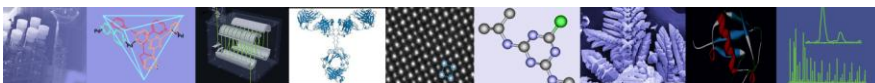


Figure 4. (a) GCxGC/NICI TIC chromatogram of the dust sample, (b) Averaged mass spectrum for the whole retention time region, (c) H/Cl mass defect plot for the averaged mass spectrum.

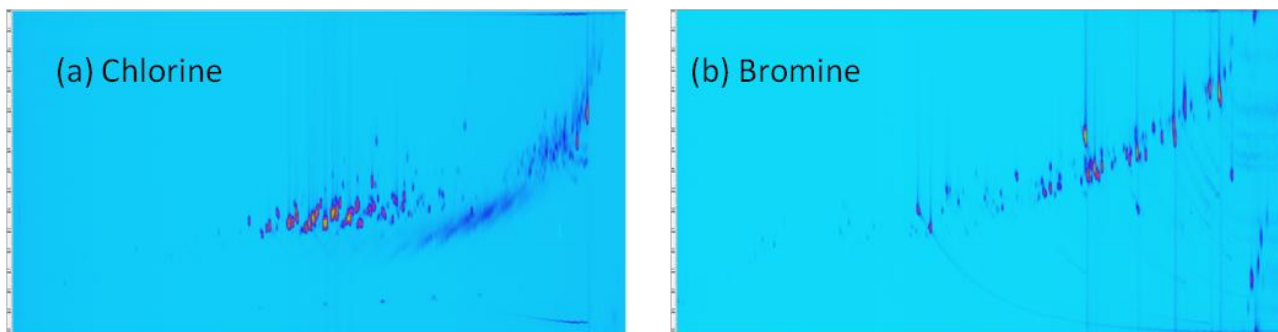


Figure 5. 2D mass chromatogram using mass of the most abundant isotope ion  $\pm 0.02$  u for (a) Chlorine ( $m/z$  34.9689), and (b) Bromine ( $m/z$  78.9183)

### Reference

[1] M. Ubukata, K. J. Jobst, E. J. Reiner, S. E. Reichenbach, Q. Tao, J. Hang, Z. Wu, A. J. Dane, R. B. Cody. Non-targeted analysis of electronics waste by comprehensive two-dimensional gas chromatography combined with high-resolution mass spectrometry: using accurate mass information and mass defect analysis to explore the

data. *Journal of Chromatography A*, **2015**.

[doi:10.1016/j.chroma.2015.03.050](https://doi.org/10.1016/j.chroma.2015.03.050)

[2] K. J. Jobst, L. Shen, E. J. Reiner, V. Y. Taguchi, P. A. Helm, R. McCrindle, S. Backus. The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment, *Anal Bioanal Chem* (2013) 405:3289–3297