The use of Kendrick mass defect plots, a new feature in GC Image™ software for GCXGC/high resolution mass spectrometric data analysis: an application on the identification of halogenated contaminants in electronic waste

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Introduction

The combination of GC x GC with high resolution mass spectrometry (HRMS) is a powerful tool for the analysis of complex mixtures. Hundreds/thousands of components can be separated and detected. However, interpreting the data sets generated by a GC x GC/high resolution time-of-flight mass spectrometry system can be challenging due to the unprecedented amount of information the data offers.

In 1963, Edward Kendrick realized that by converting the International Union of Pure and Applied Chemistry (IUPAC) mass scale (C = 12.000 Da) to one in which CH_2 = 14.000 Da (equation 1), organic ions belonging to a homologous series have identical Kendrick mass defect (equation 2). An example of Kendrick mass and Kendrick mass defect for methyl, ethyl, and propyl naphthalene is listed in Table 1. This approach greatly simplifies the high resolution mass spectrometric data analysis [1].

$$\text{Kendrick mass} = \text{IUPAC mass} \times (14/14.01565) \quad (1)$$

$$\text{Kendrick mass defect} = \text{nominal Kendrick mass} - \text{exact Kendrick mass} \quad (2)$$

Table 1. Kendrick Mass Defect for Naphthalenes

Compound	Kendrick Mass	Kendrick Mass Defect
Methyl naphthalene ($C_{11}H_{10}$)	141.9195	0.0805
Ethyl naphthalene ($C_{12}H_{12}$)	155.9195	0.0805
Propyl naphthalene ($C_{13}H_{14}$)	169.9195	0.0805

In this study, nontraditional Kendrick mass defect by the substitution of a hydrogen with a chlorine atom was used to facilitate the identification of halogenated components in an electronic waste sample [2]. The capability of constructing Kendrick mass defect plots has been implemented into GC Image™ software version 2.5.

Method

Sample analysis

A dust sample collected from an electronic recycling facility was analyzed by using GC x GC (Zoex ZX2 thermal modulator) in combination with a new high-resolution time-of-flight (TOF) mass spectrometer (JEOL *AccuTOF GCv 4G*). The instrument parameters are listed in Table 2.

Table 2. Instrument Parameters

Conditions	GC x GC/EI
Sample	Dust collected from an electronic recycling facility
GC x GC system	Zoex ZX2 thermal modulator
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 s
Modulation duration	400 ms
Inlet mode	Splitless, constant flow
Oven temp.	50 °C (1 min) -> 5 °C/min -> 320 °C (5 min)
GC-TOFMS system	AccuTOF GCv 4G (JEOL)
Ionization mode	EI+, 70 eV
Ionization current	300 µA
Ion source temp.	250 °C
MS transfer line temp.	280 °C
m/z range	m/z 45-800
Acquisition time	20 ms (50 Hz)
Software	GC Image™ Version™ 2.5

Mass calibration

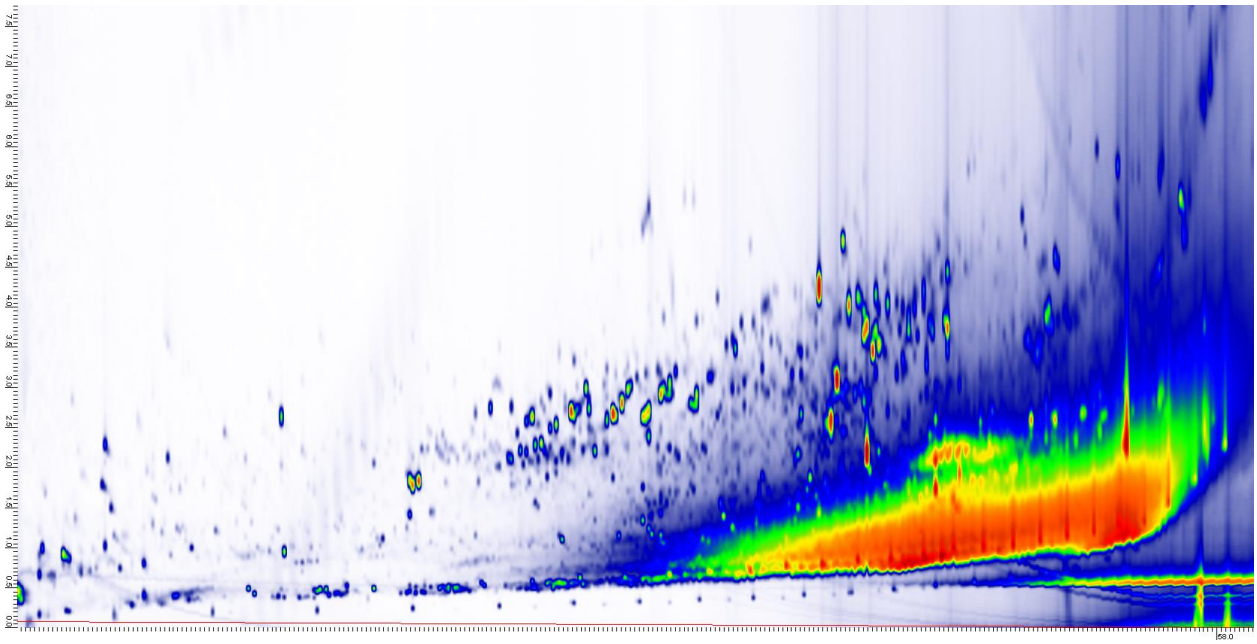
A single point external mass calibration with one column bleed ion $C_5H_{15}O_3Si_3^+$, m/z 207.0329 was performed after data acquisition.

Kendrick mass defect plot

An average mass spectrum for the entire retention time region was created by summing the mass spectra for all data points in a GC x GC/HRMS data set. Nontraditional Kendrick mass defect (H/Cl mass defect) was calculated. Kendrick mass defect plot was constructed with the nominal mass vs. the corresponding mass defect for each peak in the average mass spectrum.

Results and Discussion

Figure 1 shows the GC x GC total ion chromatogram for an electronic waste sample. An average mass spectrum for the entire retention time region was generated and showed in Figure 2. The exact mass for each ion was converted to H/Cl mass (equation 3) and an H/Cl mass defect plot for the average mass



spectrum was constructed and showed in Figure 3 automatically with GC Image™ software version 2.5.

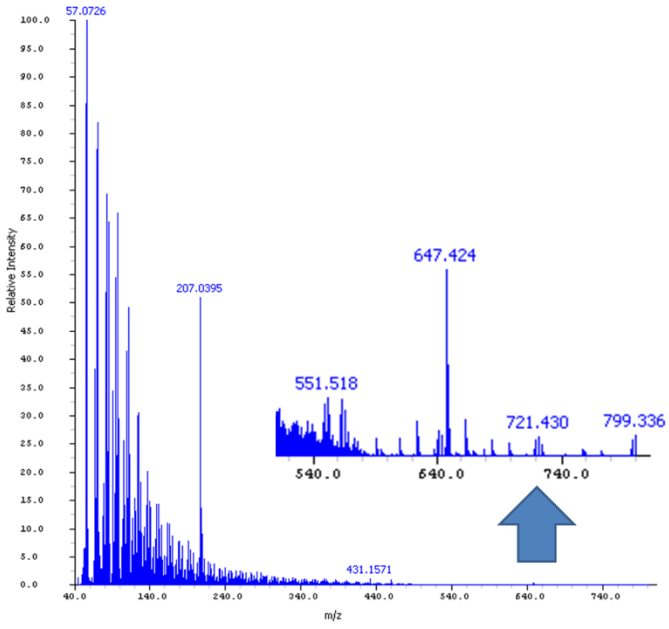


Fig.2 Average mass spectrum for the entire retention time region

H/Cl mass =

IUPAC mass x (34/33.96102) (3)

Figure 3 shows that ions in each class of halogenated compounds differing by H/Cl substitution align with the horizontal axis since they have the same H/Cl mass defect. Those compounds can be easily, immediately recognized visually in the H/Cl mass defect plot. This greatly simplified halogenated compounds identification in a complex GC x GC chromatogram. By drawing a polygon around each class of halogenated compounds, mass chromatograms can be generated automatically. Figure 4 shows the high resolution GC x GC mass chromatograms for the most abundant

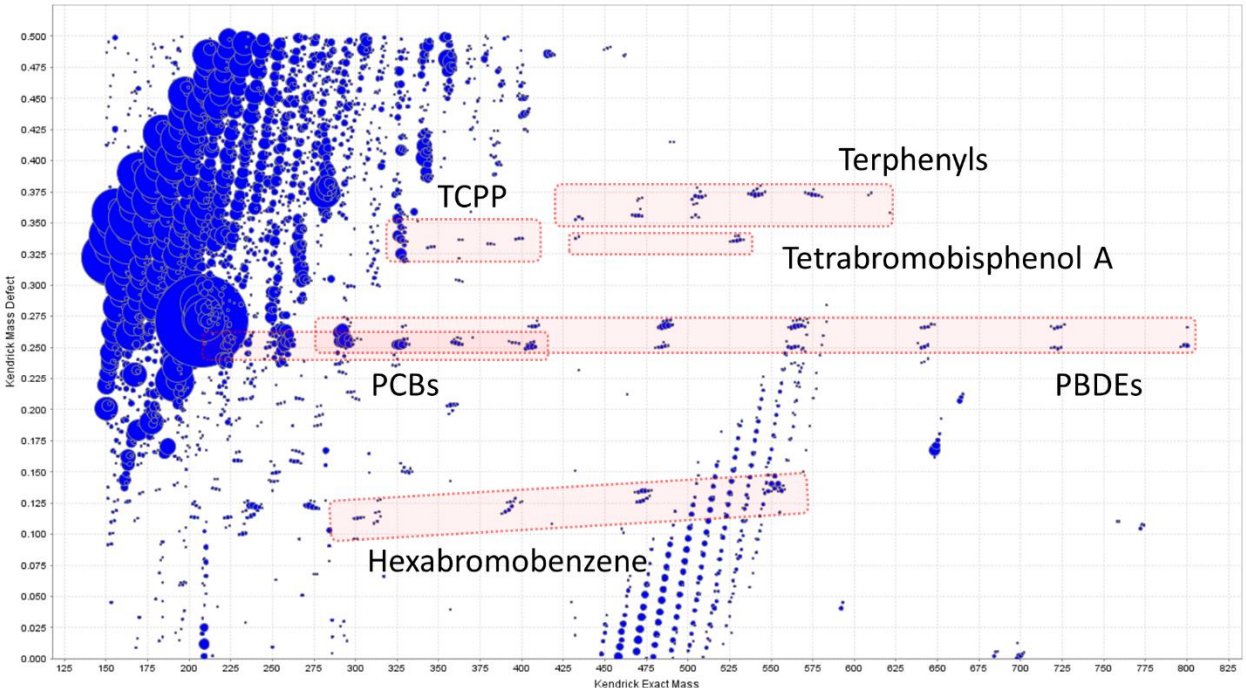


Fig. 3 H/Cl mass defect plot for the average mass spectrum

isotope ions for each class of halogenated compounds. The NIST library search and exact mass measurement were used to confirm the identification. The exact mass measurement results are listed in Table 4.

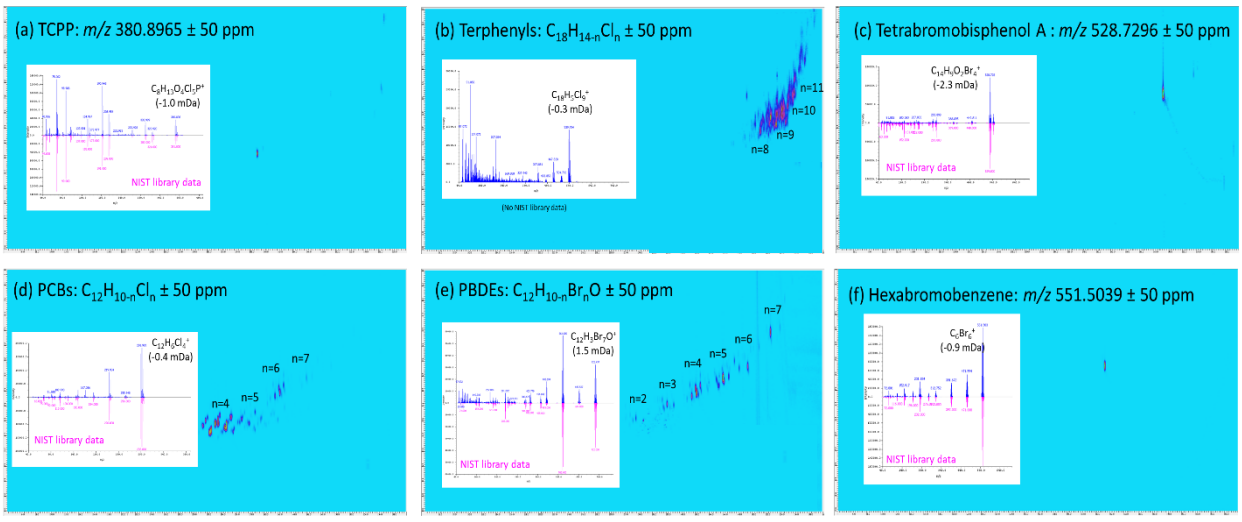


Fig. 4 GC x GC mass chromatograms for the most abundant isotope ions ± 50 ppm (a) TCPP, (b) polychlorinated terphenyl, (c) tetrabromobisphenol A, (d) PCBs, (e) PBDEs, and (f) hexabromobenzene

Table 4. Exact mass measurement results					
Compound		Elemental Composition	Theoretical Mass	Measured Mass	Difference (mmu)
TCPP		$C_8H_{13}Cl_5O_4P^+$	380.895910	380.896356	-0.446
Terphenyls	Cl 8	$C_{18}H_6Cl_8^+$	505.791323	505.791346	-0.023
	Cl9	$C_{18}H_5Cl_9^+$	539.752351	539.752675	-0.324
	Cl10	$C_{18}H_4Cl_{10}^+$	573.713378	573.714726	-1.348
	Cl11	$C_{18}H_3Cl_{11}^+$	607.674406	607.675086	-0.68
Tetrabromobisphenol A		$C_{14}H_9Br_4O_2^+$	528.728964	528.728857	0.107
PCBs	Cl4	$C_{12}H_6Cl_4^+$	291.918862	291.918259	0.603
	Cl5	$C_{12}H_5Cl_5^+$	325.879890	325.879644	0.246
	Cl6	$C_{12}H_4Cl_6^+$	359.840918	359.840915	0.003
	Cl7	$C_{12}H_3Cl_7^+$	393.801945	393.802354	-0.409
	Cl8	$C_{12}H_2Cl_8^+$	429.760023	429.760063	-0.04
PBDEs	Br2	$C_{12}H_8Br_2O^+$	327.891595	327.891217	0.378
	Br3	$C_{12}H_7Br_3O^+$	405.802108	405.801461	0.647
	Br4	$C_{12}H_6Br_4O^+$	485.710574	485.709147	1.427
	Br5	$C_{12}H_5Br_5O^+$	563.621087	563.620149	0.938
	Br6	$C_{12}H_4Br_6O^+$	643.529553	643.529852	-0.299
	Br7	$C_{12}H_3Br_7O^+$	721.440066	721.439888	0.178
Hexabromobenzene		$C_6Br_6^+$	551.503338	551.502866	0.472

Conclusion

The combination of GC x GC with high resolution time-of-flight mass spectrometry is a powerful tool for analysis of complex mixtures. The halogenated compounds can be easily, immediately, and visually distinguished in a very complicated GC x GC chromatogram by using H/Cl mass defect plots – a new feature in GC Image software™ version 2.5. The identification is further confirmed by NIST library search and the exact mass measurement results.

References

[1] Edward Kendrick, A mass scale based on CH2 = 14.000 for high resolution mass spectrometry of organic compounds, Anal. Chem (1963) 35:2146 – 2154

[2] Karl J. Jobst, Li Shen, Eric J. Reiner, Vince Y. Taguchi, Paul A. Helm, Robert McCrindle, Sean Backus, The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment, Anal Bioanal Chem (2013) 405:3289–3297