

# GCxGC-TOFMS Analysis of Aerosol Samples Collected on Quartz Filters

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## 1. Introduction

Ambient aerosol plays an important role in the radiation budget and climate for the earth-atmosphere system. More recently it has been concluded that there is a causal relationship between particulate matter exposure and health effects, but the mechanics of this relationship are still unresolved. As analysis methods have improved over the years, health scientists have turned their attention to the chemical composition of the aerosol particles.

Organic compounds are a significant fraction of the fine aerosol mass (less than  $2.5 \mu\text{m}$ ). Their concentration in atmospheric aerosol is very low and requires analytical methods with high sensitivity to be used for detection. Current analysis for these types of samples is done by either solvent extraction or thermal desorption followed by GCMS analysis. The thermal desorption method eliminates the use of solvents, is less labor intensive, and removes the time-consuming sample preparation step. To increase the separation power of the chromatographic system and to lower detection limits, comprehensive two-dimensional gas chromatography (GCxGC) coupled with TOFMS detection was selected as the method of choice for this study.

## 2. Instruments and Methods

GCxGC: Agilent 6890 GC equipped with a LECO Thermal Modulator

Column 1: Rtx-5, 30 m x 0.25 mm x 0.25  $\mu\text{m}$

Main Oven: 35°C (9 min hold) to 110°C at 40°C/min and then to 300°C at 4°C/min

Column 2: DB-17, 1.4 m x 0.1 mm x 0.1  $\mu\text{m}$

Secondary Oven: +10°C offset from main oven

Inlet Temperature: 275°C

Carrier Gas: He at a constant flow of 1.5 ml/min

Modulator Temperature: 100°C offset from main oven

Modulation Frequency: 5 s with a 2 s hot pulse time

MS: LECO Pegasus® 4D GCxGC-TOFMS

Mass Range (u): 35 to 650

Acquisition Rate: 200 spectra/s

Source Temperature: 300°C

## 3. Samples

The quartz filter paper used for the aerosol collection was cut into small square pieces (about 1 x 1 cm and 10 mg in weight) and directly placed in the GC inlet insert. The insert was then introduced in the cooled inlet (40°C) and the inlet was rapidly heated to 275°C.

## 4. Results

Over 1500 peaks were found in each of the quartz filter samples when the data was processed at an S/N ratio of 500. This is more than a two-fold increase in the peak number when compared to the results obtained from one-dimensional analysis (processing of data done at an S/N ratio of only 200 in the one-dimensional case).

The two-dimensional chromatogram for one of the samples is presented in Figure 1 as a contour plot. Retention time on the first and second column are shown on the X and Y axis respectively. The intensity of the peaks is presented on a color scale with blue showing the baseline, and red showing the most intense peak. The black dots on the figure represent peak markers. It is easy to see even for an untrained eye that some of the peaks form nice elution patterns in the two-dimensional display of the chromatogram. The presence of a pattern allows for better peak identification when the data is used in conjunction with the mass spectral information. Display of unique masses for chemical classes present in the sample allows even better visualization of these chemical class patterns.

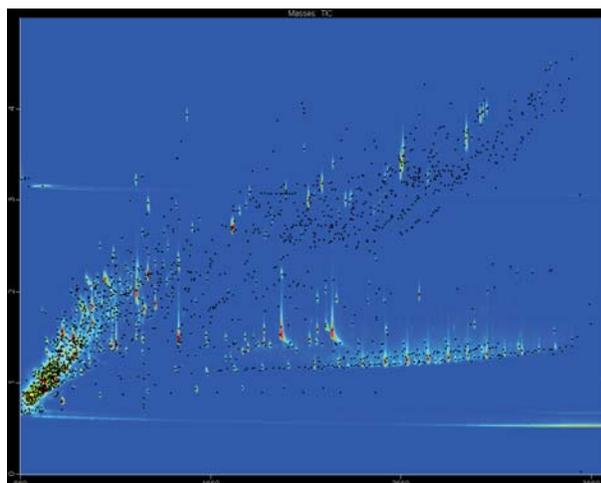


Figure 1. TIC chromatogram of one sample displayed in a contour plot view.

To take advantage of the structured chromatogram, the ChromaTOF® software allows the analyst to create (draw) classes of compounds based on their retention time characteristics using a feature called Classifications. After a class is created using the Classifications feature, both the chromatogram display and the peak table can be filtered to selectively display only the peaks present in one or more of the created classes. Using the ability to display one characteristic mass (or sum of masses) at a time,

together with the ChromaTOF's Classification feature, the analyst can completely characterize the entire sample both in a qualitative and a semi-quantitative way (% Area for each of the classes).

Figure 2 shows an example of some of the classes created for the same sample presented in Figure 1. The classes displayed in this figure were created using the  $m/z$ -chemical class correlations shown in Table 1.

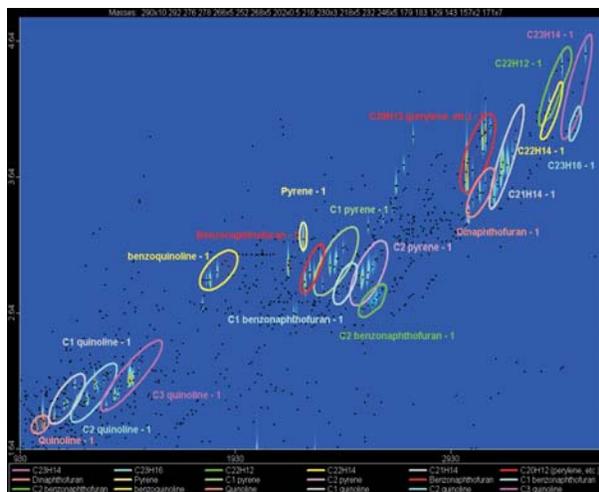


Figure 2. TIC chromatogram of one sample with a few of the chemical classes present shown.

Table 1. Characteristic  $m/z$  values for some selected chemical classes.

Class name	$m/z$	Class name	$m/z$
C23H14 (C1 benzophenylene and isomers)	290	Pyrene	202
C23H16 (C1 dizeoanthracene and isomers)	292	C1 Pyrene	216
C22H12(benzoperylene and isomers)	276	C2 Pyrene	230
C22H14(dizeoanthracene and isomers)	278	Benzenaphthofuran	218
C21H14 (C1 perylene and isomers)	266	C1 Benzenaphthofuran	232
C20H12 (perylene and isomers)	252	C2 Benzenaphthofuran	246
Dinaphthofurans	262	Benzoquinoline	179
		C1 Benzoquinoline	183
		Quinoline	129
		C1 Quinoline	143
		C2 Quinoline	157
		C3 Quinoline	171

Even with the tremendous increase in peak capacity obtained by the use of GCxGC technology, some overlap of the chemical classes can occur. Drawing perfect free shapes around the overlapped classes can become a challenge even for a skilled analyst. ChromaTOF gives you the ability to use the mass spectral information to a higher level and design second pass filters to better define the chemical class composition of your sample. Scripts are mass spectral filters created using Visual Basic scripting language that use mathematical and logistical operators in conjunction with mass spectral criteria to create the additional constraints (first constraint being elution region defined by the drawing of free shapes) needed

for an improved chemical class definition in a two-dimensional chromatogram.

A simple example of class coelution is presented in Figure 3. Part A of the figure shows a region of the chromatogram where class coelutions are present. The chromatograms shown in this figure only show the unique  $m/z$  for the classes displayed. ChromaTOF allows the user to display the found peaks as bubbles with the radius of the bubble being directly proportional with the peak intensity. When the peaks are represented as bubbles, the color of the bubble is taken from the class they belong to. Due to the class overlap, some of the peaks are represented as striped bubbles (part B of the figure) showing that those peaks belong to multiple classes. When Scripts functions are applied together with the Classifications method, all the peaks are now represented by a single color (part C of the figure).

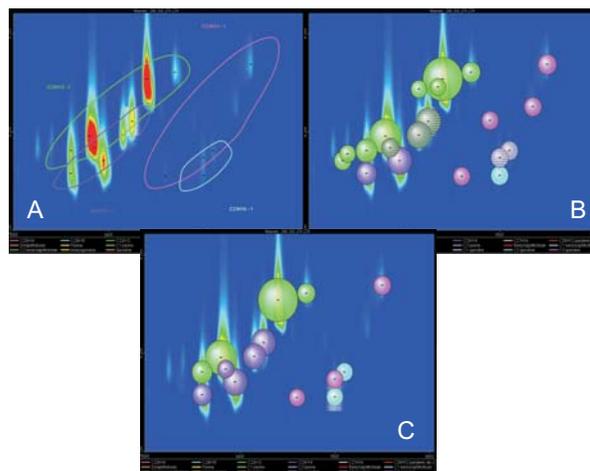


Figure 3. Classifications with Scripts applied for four of the classes present in one of the samples.

## 5. Conclusions

The use of GCxGC technology combined with TOFMS detection increased the number of peaks detected by more than a factor of four when compared to the results obtained from one-dimensional GC-TOFMS data. In addition to the increase in peak capacity, the structure of the chromatogram based on chemical classes used in conjunction with ChromaTOF's Scripts and Classifications function gives the ability to fully characterize the samples both in a qualitative and a semi-quantitative way.

