MSCi GCxGC webinar

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Abstract

Comprehensive two-dimensional gas chromatography (GCxGC) is a powerful analytical method for the separation of complex samples containing volatile chemicals.

The GCxGC setup most often consists of two capillary columns of different stationary phases (selectivity) to enhance separation power.

The two columns are interfaced with the modulator that performs two important tasks, one is the transfer of the chemicals to the second column, the other one is the thermal or pneumatic re-focusing of the introduced effluent fractions.

Due to this re-focusing and the relatively short second dimension columns the resulting chromatographic peaks are quite narrow. In order to achieve a desirable peak definition for quality data analysis, detectors with high data acquisition rates are used (FID, ECD or TOF-MS).

The more challenging parts of GCxGC method development are setting up the modulation process and to understand the effect of each of its parameters within the framework of chromatographic system as a whole.

Also, practical work with connections and developing a practice to operate such a system may prove to be challenging even for some experienced GC users. In the last 5 – 10 years GCxGC has been becoming more widespread and suppliers have been following this process by providing more user-friendly consumables (e.g., the substitution of press-fits with leak-tight column connectors using Vespel and SilTite ferrules and assemblies).

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The other more challenging aspect of GCxGC is data processing which requires the use of specialized software packages optimized for the visualization of 2D chromatographic data.

Single sample processing has come a long way since the inception of GCxGC but post-processing of sample batches is still a complicated task which requires supervision. This step still is probably the biggest bottleneck in the data mining process.

In this webinar, the basic concepts of GCxGC, modulation types and basic data treatment is going to be covered along with some examples in diverse application fields.

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Introduction to GCxGC

Multidimensional gas chromatography (*Figure 1*) is an ideal tool for the volatile chemical analysis of complex samples. It consists of a dual column setup coated with stationary phases of different selectivity (e.g., the first column is apolar and the second column is polar/aromatic).

There are several concepts and instrumentation available for performing two-dimensional GC separation.

One is known as heart-cutting (GC-GC), where the effluent during a complex part of the chromatogram is trapped either in a sample loop or in a cryotrap for a specified duration. However, using this setup the first-dimension separation is completely lost for the selected part of the chromatogram. After the first chromatographic run is completed, the previously trapped fraction is re-introduced into the second column and the separation is performed.

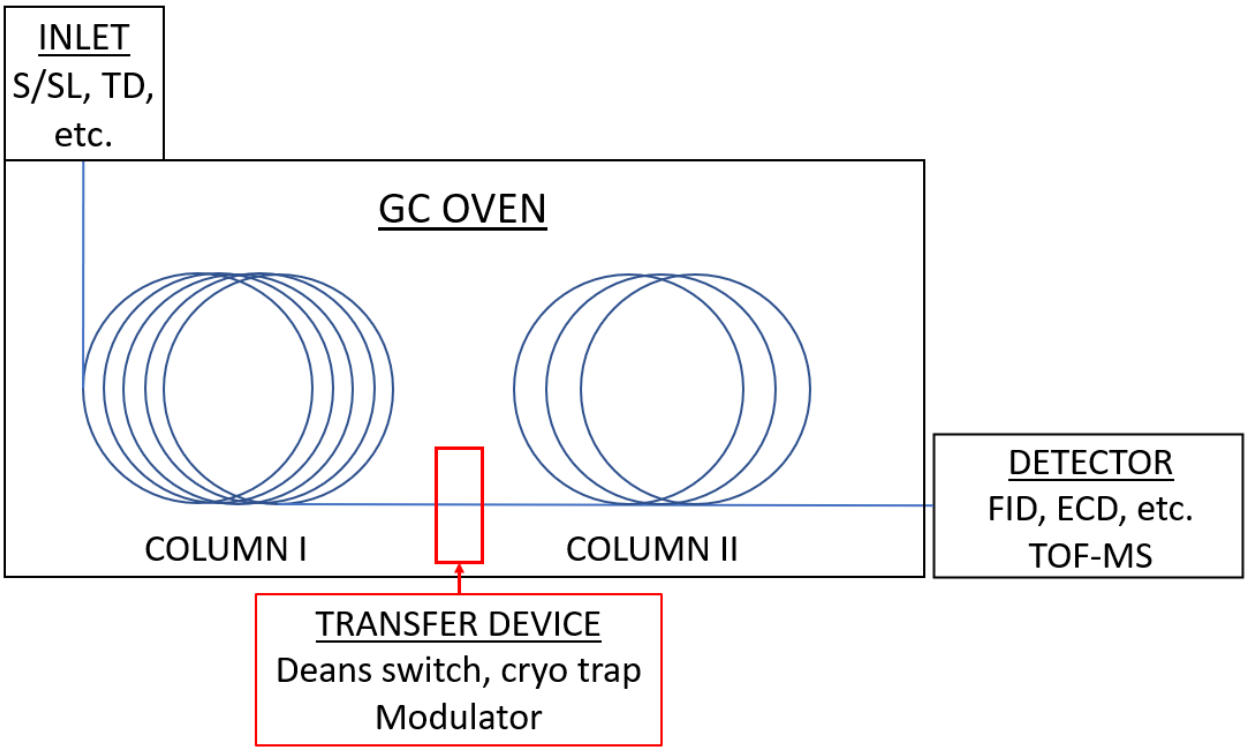

Figure 1: The conceptual instrument configuration of a two-dimensional gas chromatograph. The sample is introduced through some kind of injection method (split/splitless, thermal desorption, etc...). The two columns are located in the GC oven compartment they can be in the same or two separate ovens. Usually, the secondary oven in contained inside the GC oven. The transfer device facilitates the transfer of the effluent from the first column onto the second. This device can

be a Deans switch, a cryo-trap (GC-GC) or a modulator (GCxGC). The second column is then connected to a suitable detector.

With comprehensive two-dimensional gas chromatography (GC**x**GC), the first-dimension chromatogram is chopped up into slices usually a few seconds long with by a continuous purge-and-trap process called modulation.

The length of this process is called the modulation period. The heart and soul of a comprehensive GCxGC system is the modulator. This device facilitates not only the transfer of the effluent between the two columns but it also re-focuses the sample "packages" eluting from the first column. As a rule of thumb, a chromatographic peak in the first column should be modulated in a way that its "sliced" peaks show up in at least 3 consecutive modulation periods - in practice better to have 4-5 slices (*Figure 2.a*.).

The column dimensions, flows and modulation periods should be carefully considered accordingly during method development. If all of these variables are correctly selected and defined, the resulting peaks should appear on the second-dimension chromatogram whose length matches the length of the modulation period (*Figure 2.b*.).

If the second-dimension retention time (t_{R2}) of a peak exceeds the length of the modulation period and shows up in the consecutive one, it is called a wrap-around. Having wraparound is not a life-altering tragedy but it may cause difficulties if one tries to deduce physico-chemical properties of the analytes using t_{R2} data.

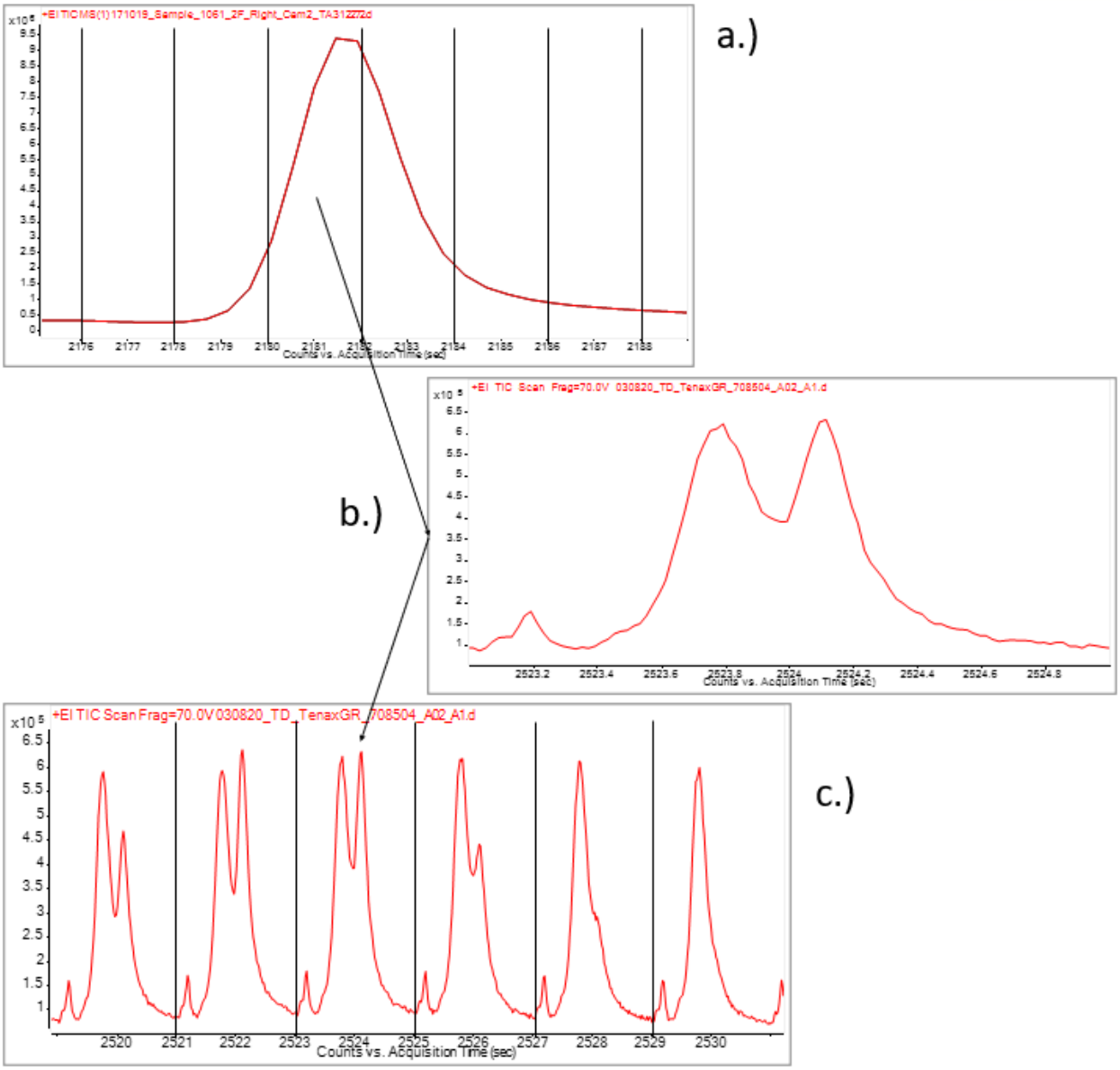

Figure 2: The modulation process illustrated in concept. 2.a. An illustration of a usual chromatographic peak that is achieved by a typical single-dimension setup. IMPORTANT: this chromatogram is never seen during GCxGC analysis. This peaks baseline width is 6-7 s long, to get at least 3 modulated peaks it is reasonable to choose a 2s modulation period in this case. 2.b., This 2 s long chromatogram presents the second-dimension separation of a single modulation period. These 2s long chromatograms consecutively make up the raw 2D chromatogram 2.c., The resulting raw 2D chromatogram. By defining the modulation periods, the data processing software can create the 3D map based on this chromatogram.

The raw data that is recorded by the detector is a series of these 2^{nd} dimension chromatograms (*Figure 2.c.*). Based on this chromatogram and information about the modulation periods, the

GCxGC software generates the 3D plot where the first-dimension retention time (t_{R1}) is shown on the *x*-axis, the t_{R2} is on the *y*-axis - which also is the raw data "sliced up" according to the modulation period length (Figure 2.b.). The intensity values are then converted to a heatmap, usually using an RGB (red – green - blue) color scale (*Figure 3*).

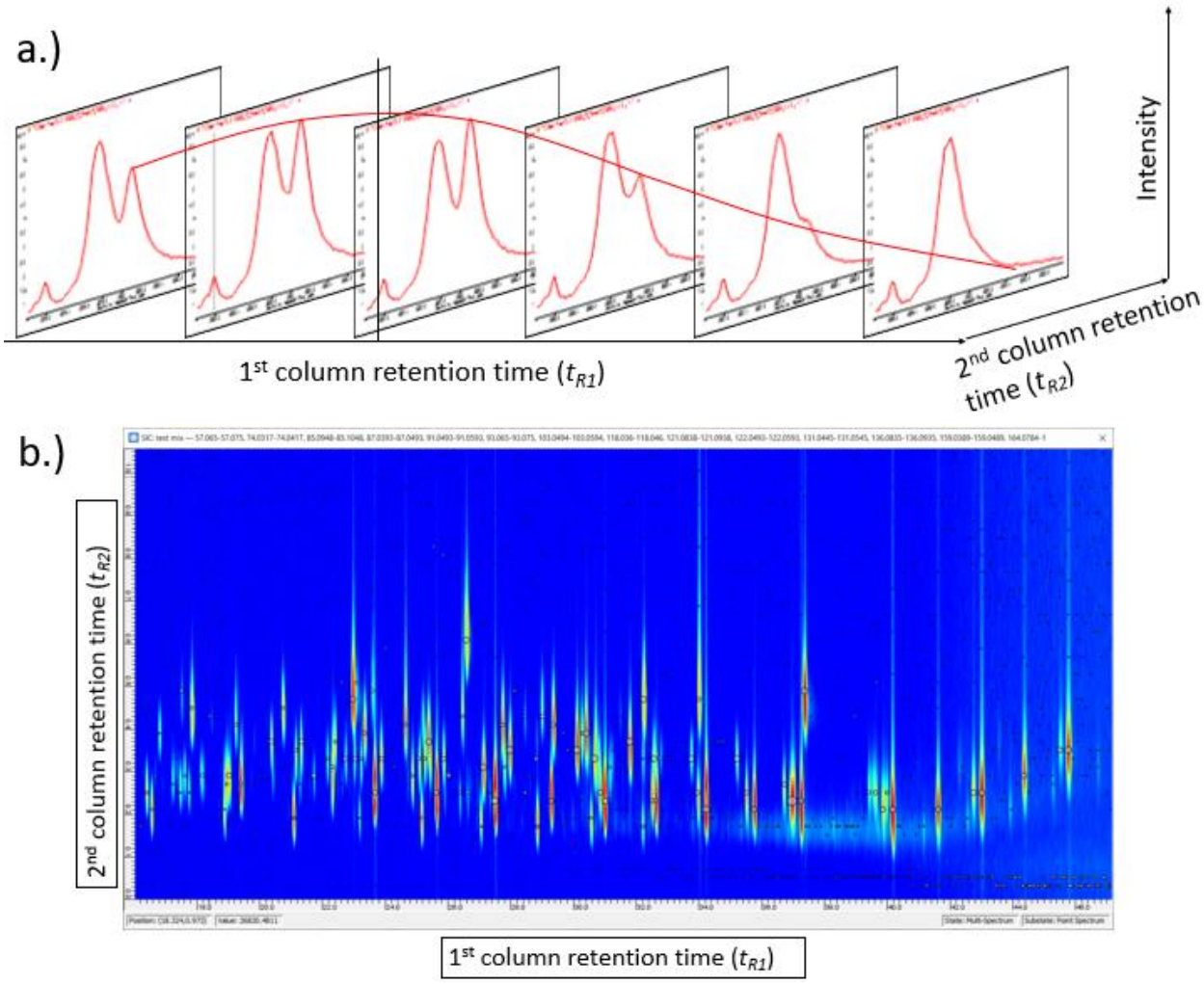

Figure 3: The generation of the 3D chromatogram. 3.a.: The 2nd dimension chromatograms (raw signal) are "sliced up" according to the modulation periods and are presented on the y-axis. The 1st dimension chromatograms are reconstructed. This reconstruction is done by fitting a Gaussian-curve based on the intensities of the peaks that appear at the same t_{R2}. 3.b.: The intensity values are than translated into an RGB color scale to form the 3D chromatogram.

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