



## 2D-GC-CSIA of VOCs: Methodology

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### When to use 2D-GC?

Carbon CSIA and for hydrogen CSIA require a high quality of separation of the target compound peaks to permit accurate determination of the target's isotope ratio. While conventional gas chromatography (using a single GC column) is appropriate for most environmental samples, there are several categories of samples (listed below) with predictable GC interferents that decrease the quality of CSIA results or even prevent obtaining meaningful results.

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1. Chlorinated ethene samples from sites with commingled hydrocarbon plumes (the interferents are the individual hydrocarbon compounds and volatile metabolites from fuel biodegradation).
2. Chlorinated ethene samples downgradient from biostimulation/bioaugmentation treatment areas (the interferents are volatile metabolites from degradation of EVO or similar substrates).
3. Samples from sites with alkyl halides, such as chloroform, 1,2-DCA, etc. in sulfide-rich groundwater (the interferents are volatile sulfides forming in reactions of the halides with sulfide ion).
4. In general, any samples where the target compound(s) occur at proportionally low concentration in a complex organic matrix, such as low ug/l of individual hydrocarbons in high-concentration gasoline matrix or individual VOCs in indoor air samples.

For such samples, improved GC separation can be achieved by 2D-GC (Fig. 1). While the 2D-GC-CSIA is more costly, it offers a near-100% success rate of obtaining good quality results from difficult matrix samples that are otherwise not accessible to CSIA. Moreover, 2D-GC-CSIA offers better detection limit than the conventional methods, due to eliminating baseline noise, which is the main source of decreased analytical precision of low-amplitude peaks.



## The outline of operation principles

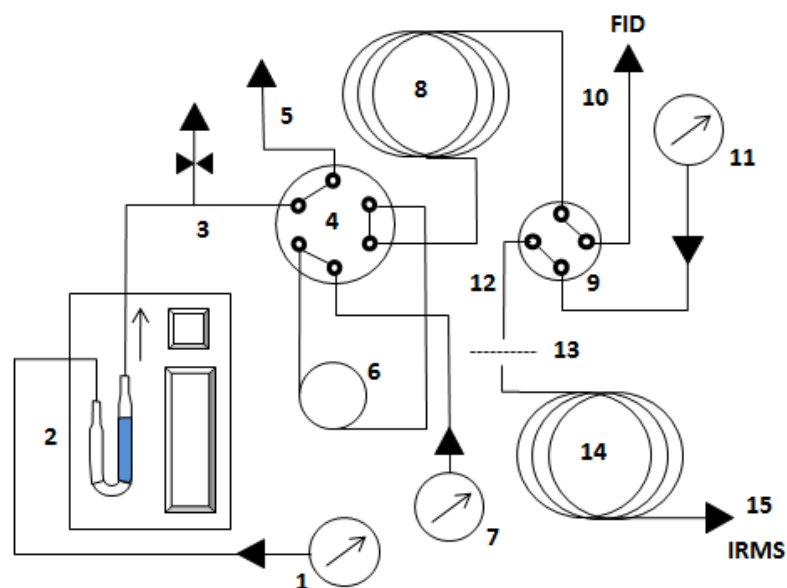
The concept of 2D-GC is not new, and several GC manufacturers offer similar solutions for compositional GC analysis, either using a single GC with two columns, with specialized pneumatic controllers such as Dean's Switch (Agilent) or two-oven configurations (Shimadzu). The present configuration utilizes the two-oven solution which is more versatile with respect to accepting different column dimensions and carrier gas flow rates.

2 VOCs are introduced into the 2D-GC system either from purge and trap (VOCs in water samples), or from a thermal desorber (gas phase samples after preconcentration on adsorbent media) or by syringe injection. In most cases, the sample requires cryofocusing before actual transfer onto the first GC column of the apparatus. Initially the sample undergoes chromatographic separation on a polar phase column ("1<sup>st</sup> GC dimension", item 8, Fig. 1). Immediately before the target analyte reaches the column outlet, a switching valve interface (item 9, Fig. 1) is activated to transfer a narrow increment of the column effluent into a heated transfer line and eventually trapped by the inlet cryofocuser of the second GC. The condensate from cryofocuser is separated on a non-polar phase column ("2<sup>nd</sup> GC dimension", item 14, Fig. 1). Compounds with similar retention times on 1<sup>st</sup> GC dimension will nearly always separate on the 2<sup>nd</sup> GC dimension, due to the contrasting properties of the two GC columns. The 2<sup>nd</sup> GC is part of the standard GC/IRMS configurations, with the thermal conversion of the analytes and the mass spectrometry occurring after the GC separation set up identically and in the conventional CSIA utilizing a single GC column separation.

FID signal from the 1<sup>st</sup> GC (item 10, Fig. 1) allows verification of the retention time of the target compounds and setting appropriate time program of activation of the switching valve (Item 9, Fig. 1) to transfer the analyte to the 2<sup>nd</sup> GC column. In most applications, 2D-GC permits analysis of isotope composition of a single compound only. While it is theoretically possible to program the instrument to collect several samples from the 1<sup>st</sup> column, this is not recommended for applications with unknown sample matrices due to unpredictable interferences from unknown components in the sample matrix.

## Instrumentation

GC #1 is Agilent 6890 with a cryogenic focusing unit. GC #2 is a Thermo Scientific Trace 1610 with a cryogenic focusing unit. IRMS is Thermo Scientific Delta Q, with Isolink 2 and Conflo IV interfaces. 1st dimension GC column is DB-Wax, 60 m x 0.53 mm, film 1  $\mu\text{m}$ . 2<sup>nd</sup> dimension column is DB-MtBE column, 60 m x 0.32 mm, film 1.8  $\mu\text{m}$ ., or DB-624 with similar dimensions.



**Figure 1.** Diagram of the 2D-GC CSIA instrument: 1) Purge & trap desorption and transfer line gas source; 2) Purge & trap unit; 3) Transfer line flow splitter; 4) Switching valve; 5) Vent with an optional capillary flow restrictor; 6) Cryogenic focuser; 7) GC column #1 carrier gas source; 8) GC column #1; 9) Switching valve; 10) Vent with capillary flow restrictor, leads to an FID detector; 11) Transfer line carrier gas source; 12) Heated transfer line; 13) Switching valve/cryogenic focuser interface between the transfer line and Column #2, configuration identical to items 5-7; 14) GC column #2; 15) Extension to the thermal conversion reactor and the IRMS.