2D-GC-CSIA: Method Description

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Carbon CSIA and for hydrogen CSIA require a high quality of separation of the target compound peak 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.

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, 12DCA, 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 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.

Method outline: In summary, a sample is passed into a GC for chromatographic separation on a polar phase column ("1st 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 brief increment of the column effluent into another GC, where that sub-sample is separated on a non-polar phase column ("2nd GC dimension", item 14, Fig. 1). Any compounds not separated from the target analyte on the 1st GC dimension will usually separate on the 2nd GC dimension, due to the contrasting properties of the two GC columns. The organic compounds eluting from the second GC column are then converted to CO_2 in an in-line combustion reactor (converted to H_2 in a Cr reduction reactor for hydrogen CSIA) and then passed to the isotope ratio mass spectrometer (IRMS) for isotope ratio determination in individual chromatographic peaks. FID signal from the 1st GC (item 10, Fig. 1) allows verification of target compounds retention time and setting appropriate time program of activation of the switching valve (Item 9, Fig. 1) to transfer the analyte to the 2nd GC column.

Instrumentation: GC #1 model Agilent 6890 with a cryogenic focusing unit; GC #2 model Agilent 7890 with a cryogenic focusing unit; IRMS model Thermo-Finnigan MAT253. 1st dimension GC: DB-Wax column, 60 m x 0.53 mm, film 1 um. 2nd dimension GC: DB-MtBE column, 60 m x 0.32 mm, film 1.8 um.

VOCs were focused at the front end of Column #1 (item 6, Fig. 1) and then at the front end of Column #2 (not shown).

Data processing and QAQC: Identical to default CSIA procedures.

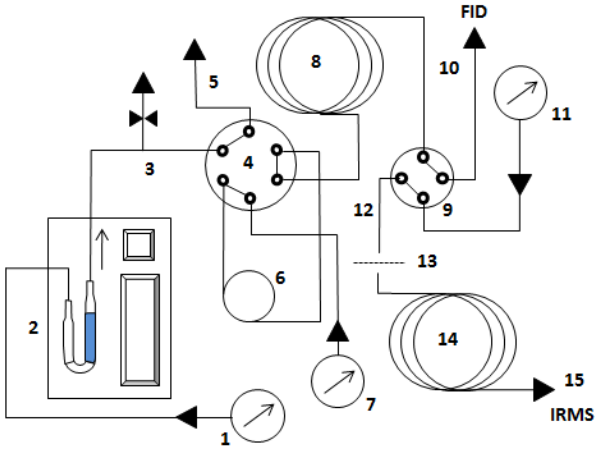

Fig. 1. Diagram of the 2D-GC CSIA instrument: 1) Purge & trap desorption and transfer line gas source; 2) Purge & trap unit; 3) Transfer line flow splitter; 4) Switching valve; 5) Vent with an optional capillary flow restrictor; 6) Cryogenic focuser; 7) GC column #1 carrier gas source; 8) GC column #1; 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.

Examples of applications: Refer to the presentation pdf (a modified poster from Fourth International Symposium on Bioremediation and Sustainable Environmental Technologies. Miami, Florida, 2017) available on the CSIA Laboratory website:

http://enviro-isotope.oucreate.com/CSIA/index.php/faqs/