CSIA OF CHALLENGING VOCS SAMPLE MATRICES USING 2D-GAS CHROMATOGRAPHY: PRINCIPLES AND APPLICATIONS OF THE METHOD

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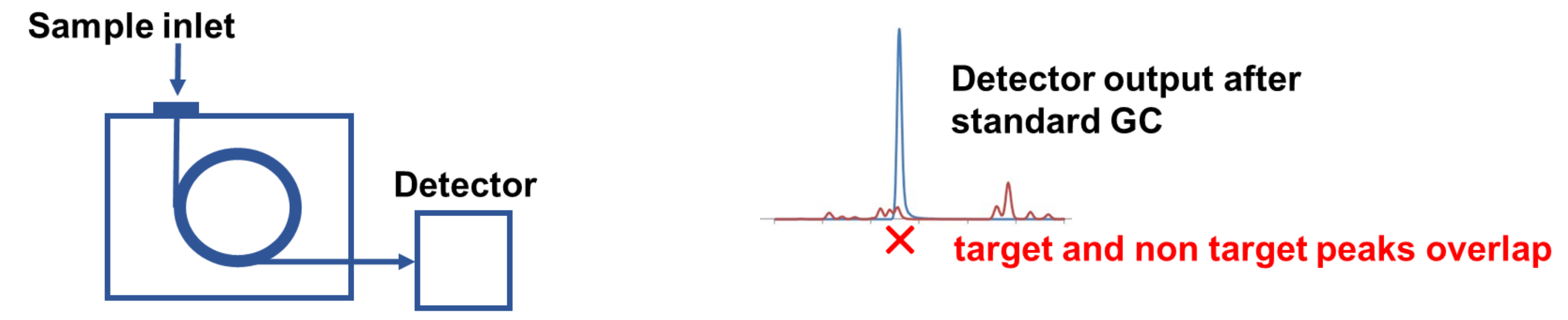
Background

- **Compound-specific Isotope Analysis (CSIA) uses gas chromatography (GC) to separate target compounds from environmental sample matrix.**
- **To obtain precise and accurate isotope ratio data, CSIA requires near-perfect chromatographic separation of the target compound from non-target compounds present in the sample.**
- **Due to GC separation problems for complex VOCs fingerprints, certain categories of samples cannot be analyzed by conventional GC.**
- **Even for those categories of samples that are most commonly subjected to CSIA, e.g., chlorinated ethenes in groundwater, chromatographic separation problems can occasionally limit the completeness of the data.**
- **We present CSIA combined with two-dimensional gas chromatography (2D-GC). This method permits analysis of samples that are not accessible to classic CSIA.**

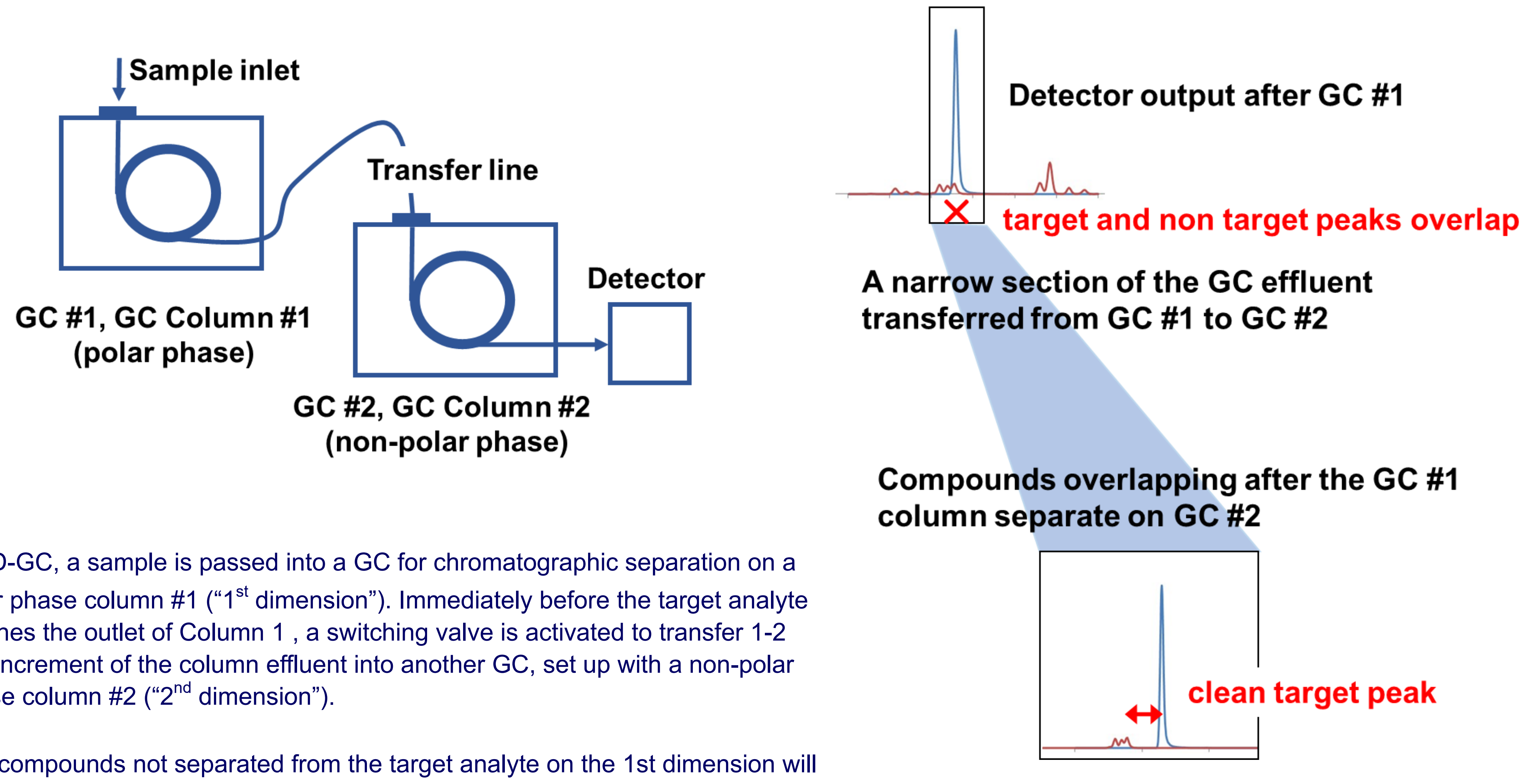
Examples of Common GC Separation Problems

Air VOCs, including indoor air samples from vapor intrusion sites.
Any samples collected in direct vicinity of gasoline or diesel LNAPL (see Case 3 below)
Chlorinated ethenes with commingled gasoline hydrocarbon plumes (see Case 2 below).
1,4-Dioxane in the presence of TCE.
Chlorinated ethenes commingled with halogenated alkanes in high-sulfide waters (due to interference of secondary alkyl sulfides such as DES, see Case 1 below).

The principle of operation of the 2D-GC method



- In standard GC, target compounds are resolved from the non-target compounds using a single GC column. Given the complexity of organic matrix of environmental samples, it is relatively common that more than one compound elute from the GC column at the same time (compound with similar volatility, polarity etc).

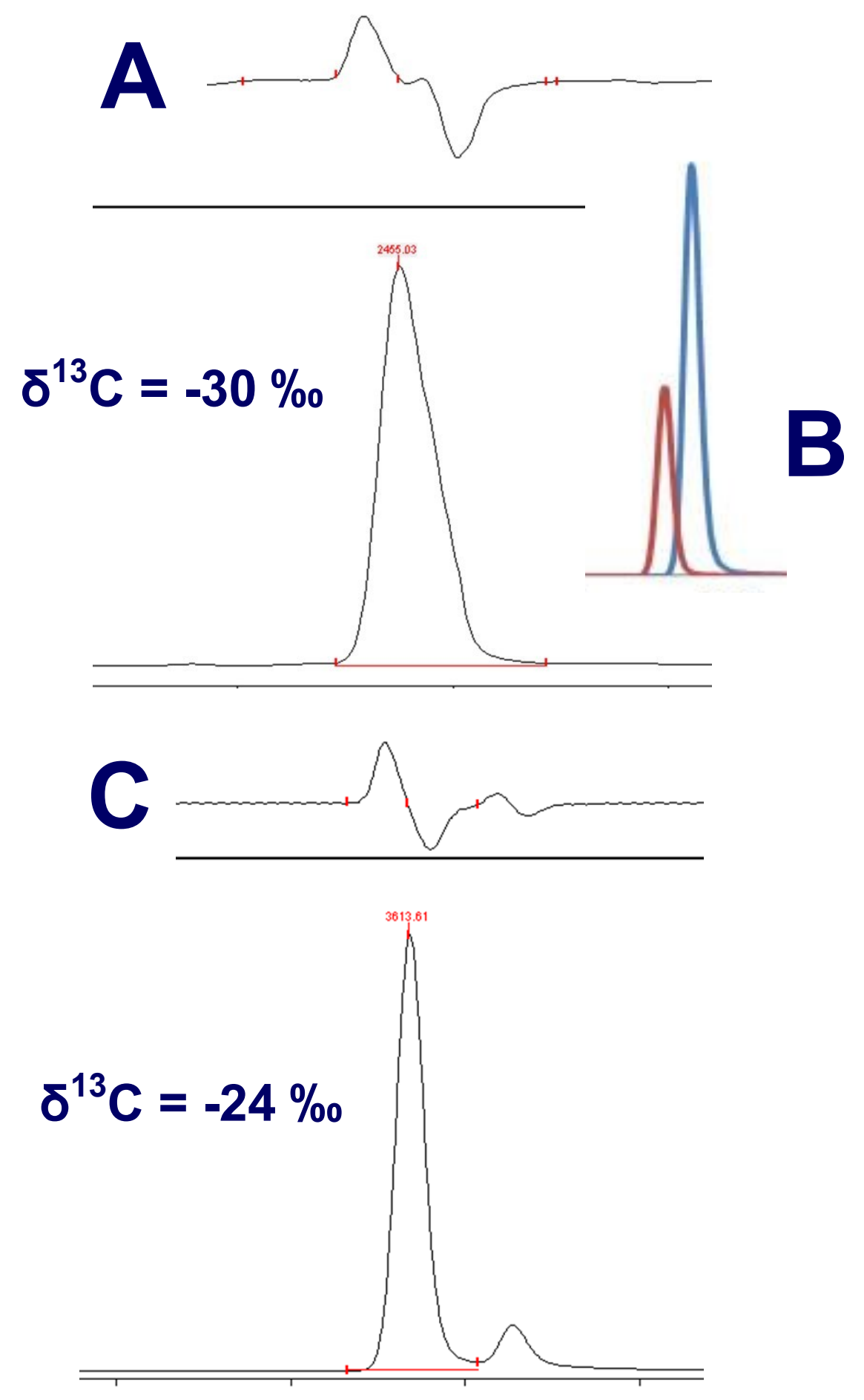


- In 2D-GC, a sample is passed into a GC for chromatographic separation on a polar phase column #1 ("1st dimension"). Immediately before the target analyte reaches the outlet of Column 1 , a switching valve is activated to transfer 1-2 min increment of the column effluent into another GC, set up with a non-polar phase column #2 ("2nd dimension").
- Any compounds not separated from the target analyte on the 1st dimension will usually separate on the 2nd dimension, due to the contrasting properties of the two GC columns.
- Currently, due to the limitation of the transfer line temperature, only VOC-class compounds can be analyzed.

Examples of 2D-GC CSIA Applications

Case 1: Separation of TCE from Diethyl Sulfide (DES)

CSIA utilizing a standard GC configuration produced a peak at the retention time of TCE. The peak geometry was slightly deformed (apparent for the 45/44 ratio trace in particular). Verification by GCMS confirmed that the observed peak represents two overlapping compounds, TCE and DES . DES was probably formed by degradation of co-occurring chlorinated ethanes, under sulfate reduction environment. After 2D-GC, the TCE peak is completely free from the DES interference.



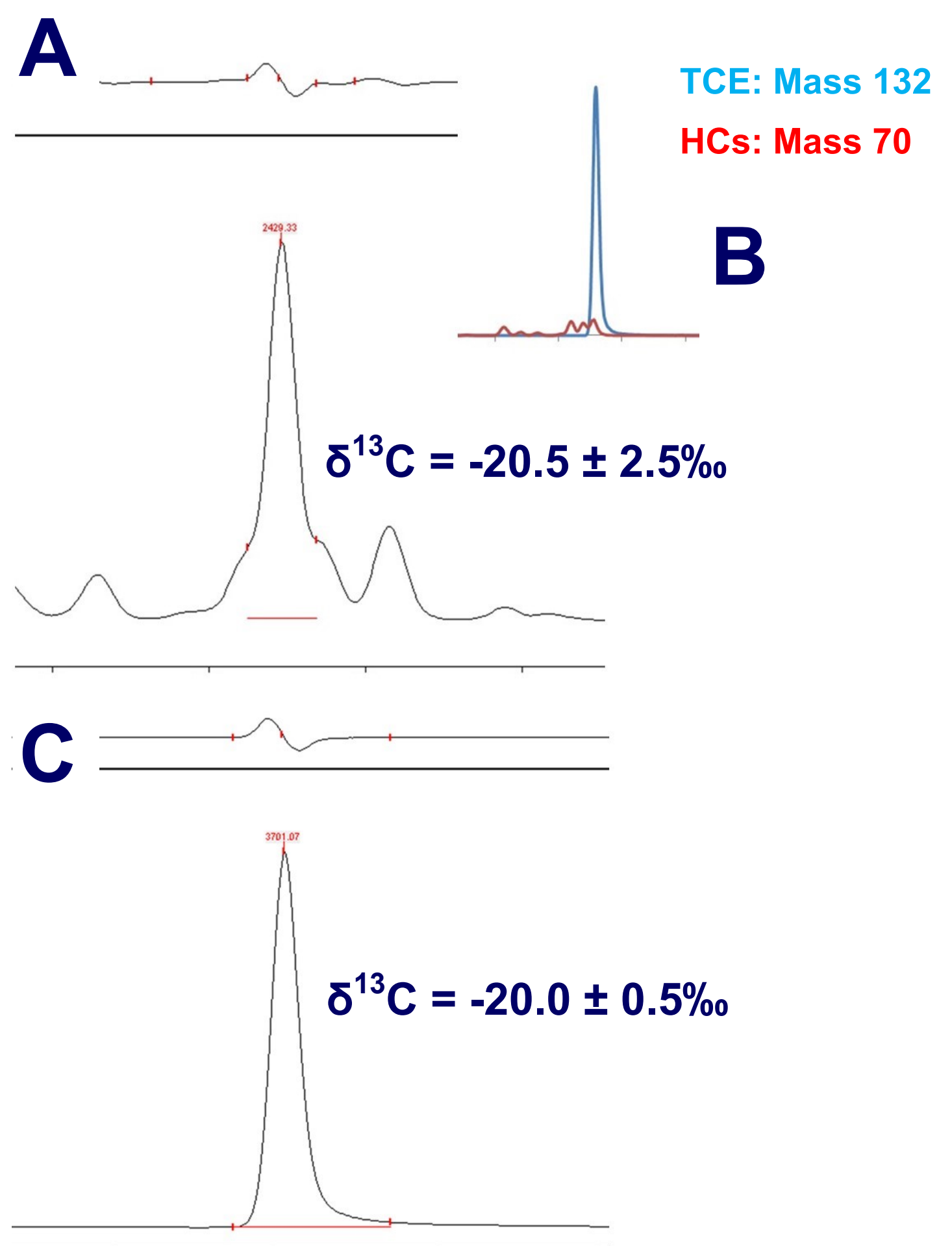
TCE: Mass 132
DMS: Mass 90

Chromatograms and mass 45/44 ratio traces of a sample containing Trichloroethene (the target analyte) and Diethyl Sulfide. A) CSIA, standard GC; B) GCMS, SIM mode; C) CSIA, 2D-GC

Case 2: Separation of TCE from Dilute Hydrocarbon Matrix

CSIA utilizing a standard GC configuration produced a peak of TCE , with a relatively significant baseline noise. The noise resulted with an increased uncertainty of the isotope ratio of TCE. Verification by GCMS identified a number of hydrocarbon compounds overlapping with TCE. The hydrocarbons (alkylated cyclopentanes) are likely sourced from a dilute gasoline plume commingled with TCE.

- After 2D-GC, the TCE peak is completely free from the hydrocarbon interferences.
- Note that after 2D-GC, the uncertainty of the TCE result is greatly decreased.

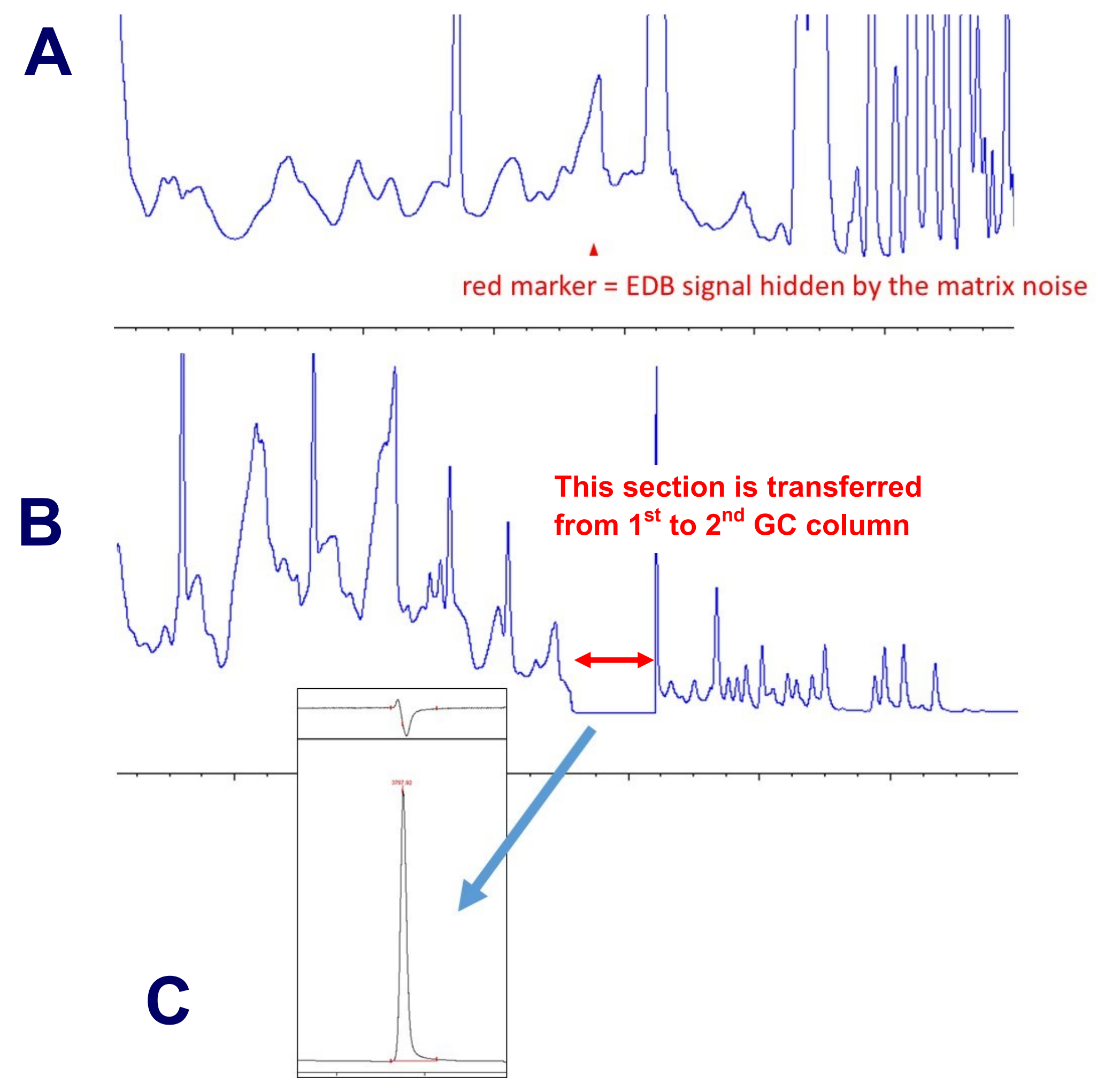


Chromatograms and 45/44 traces of a sample containing Trichloroethene (the target analyte) and a mix of cyclopentane isomers. A) CSIA, standard GC, signal integration uncertainty represents different ; B) GCMS, SIM mode; C) CSIA, 2D-GC

Case 3: Separation of EDB from Concentrated Hydrocarbon Matrix

In groundwater, ethylene dibromide (EDB) often occurs together with significant concentrations of gasoline-range hydrocarbons. Standard GC is unable to separate EDB from the hydrocarbon matrix (Fig. A). 2D-GC is necessary for CSIA of such type of samples.

- After 2D-GC, the complex mixture of hydrocarbons is completely separated EDB.



Chromatograms of a sample containing ~ 200 ng of EDB (the target analyte) and several mg of gasoline-range hydrocarbons. A) Standard GC, with EDB marker drawn to represent the amount of EDB-attributable signal hidden by the sample matrix (FID detector, 1st column); B) 2D-GC (FID detector, 1st column) GCMS; C) 2D-GC (IRMS detector, 2nd column).