CSIA of VOCs in Water Samples, Using Purge and Trap Extraction: Method Description

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The outline of the methodology: Volatiles are extracted from water using a purge and trap apparatus (PT), with the PT transfer line interfaced to a gas chromatograph (GC) and a mass spectrometer appropriate for given element's isotope ratio analysis. For CSIA of low molecular weight compounds, including chlorinated ethenes, benzene and MtBE, the PT transfer line is extended to a polar-phase column used to separate water prior to the main stage of GC separation. Analytes eluting from the transfer line are trapped using a cryogenic focuser prior to being transferred to a main GC column, for target compound separation. The PT transfer line, the main GC column and the focuser are interfaced through a 6-port switching valve to allow splitless transfer of the analytes from the PT to the main GC column. In C and H CSIA, after GC separation, the analytes pass through a thermal conversion reactor and the analytes are converted individually to pulses of surrogate gas product (CO_2 or H_2) for isotope ratio determination by an isotope ratio-monitoring mass spectrometer (IRMS). In Cl CSIA, the $^{37}Cl/^{35}Cl$ is determined without thermal conversion, using a standard quadrupole mass spectrometer (qMS) operated in single ion mode.

Extraction from water: Instrument: OI Analytical model 4660; Adsorbent trap: Vocarb 3000 (Supelco) or custom Carbosieve-III (Supelco). The latter is used for VC, ethane and ethene analysis. The default PT program for chlorinated ethenes and ethanes is: sample temperature 45°C; purge with inert gas for 12 min at gas flow of 40 mL/min; dry purge for 3 min; trap desorption for 5 min at 250°C. The PT program for VC, ethane and ethene is: sample temperature 45°C; purge with inert gas for 8 min at gas flow of 12 mL/min; no dry purge; trap desorption for 2 min at 200°C.

Cryogenic focusing and water separation: PT effluent passes through DB-Wax column (30 m x 0.25 mm, film 0.50 µm) so that the fast-eluting VOCs are passed to the focuser (an automatic unit such as Optic-4 from GL Sciences) while slow-eluting water is delayed and separated from the target analytes. For DCE, TCE and PCE analysis, the focuser is cooled to at least -160°C, then warmed to 150°C. In VC, ethene and ethane analysis, the analytes are trapped on a coil of inert silica capillary immersed in liquid nitrogen, with passive heating in the GC oven after the focusing stage.

GC separation: Instruments: Agilent 6890 (C CSIA) or 7890 (C, H, Cl CSIA). For most target compounds, the default analytical column in C and H CSIA is DB-MtBE, 60 m x 0.32 mm. Gaseous compounds, including VC, ethene and ethane are analyzed using Q-PLOT column (25 m x 0.32 mm). The default analytical column in Cl CSIA is Q-PLOT column (25 m x 0.32 mm). Other GC columns may be used on project-specific basis. The temperature program is optimized to resolve the target analytes from each other and from interfering non-target compounds present in the sample matrix.

Thermal conversion and mass spectrometry: Instruments: IRMS units by Thermo-Finnigan (Carbon CSIA utilizes MAT 252 or MAT 253; H CSIA utilizes MAT 253); Cl CSIA utilizes qMS by Agilent (5975). The combustion reactor for the C isotope ratio determination is a ceramic tube packed with nickel and platinum wires held at 860°C and fed with an auxiliary oxygen trickle throughout analysis. The pyrolysis reactor used for the H isotope ratio determination is a ceramic tube packed with chromium granules (Goodfellow Corp.) held at 850°C. Mass spectrometers are operated at default manufacturer's settings for C and H isotope ratios determination. Cl isotope ratios are determined using a standard qMS operated in single ion monitoring mode. The ratio of $^{37}Cl/^{35}Cl$ is obtained by scanning two Cl-bearing mass fragments of identical structure: one containing ^{35}Cl only and no ^{37}Cl and the second containing a single ^{37}Cl.