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

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1 The outline of the methodology

The content below is representative to CSIA of the common VOCs, including chlorinated ethenes, benzene and MtBE. Significant modification of the instrumentation or protocols may be involved for specific applications and for specific VOCs not explicitly listed.

KEI uses purge and trap (PT) for VOCs extraction and preconcentration. Thanks to the large capacity of the PT adsorbent trap, PT is relatively resistant to saturation of the adsorbent capacity or to permanent damage of the adsorbent by VOCs present in groundwater and less prone to extraction artifacts than microextraction methods such as SPME. PT permits high extraction yields for the commonly analyzed VOCs, which translates to state-of-the-art reporting limits.

KEI uses a custom switching valve PT/GC interface with an integrated cryogenic trap to permit 100% transfer of the sample mass from PT to the GC column of the instrument. The setup mitigates the main disadvantage of using PT in CSIA applications, which is the excessive transfer of water into the chromatographic column of the instrument, without the need to sacrifice effective detection limits by splitting the PT gas effluent. After GC separation, isotope ratios of the target peaks are determined using a relevant variant of mass spectrometry, IRMS for carbon and hydrogen, and qMS for chlorine CSIA.

2 Extraction from water

Extraction and preconcentration of VOCs is performed using OI Analytical model 4660, with Vocarb 3000 (Supelco) adsorbent trap. The default PT program for chlorinated ethenes is to warm the sample to 45°C, activate purge gas for 12 min at flow rate of 40 mL/min, followed by a dry purge for 3 min, followed by trap desorption for 5 min at 250°C, followed by trap bake-out and autosampler wash. Alternatively, PT is set up with a Tenax A trap (Supelco) with a similar program except for lower desorption temperature.

3 PT/GC interface

The PT transfer line is interfaced to a gas chromatograph (GC). The PT transfer line is initially extended to a polar-phase GC column (DB-Wax, 30 m x 0.25 mm, film 0.50 µm). The polar column retains a portion of water transferred from the GC which simplifies the follow up steps. VOCs eluting from the transfer line are trapped using a cryogenic focuser (an automatic unit such as Optic-4 from GL Sciences) prior to being transferred to a main GC column. The PT transfer line, the main GC column and the focuser are interfaced through a 6-port switching valve to allow toggling the carrier gas flow from the high PT effluent flow to low GC column flow. Cryogenic trapping permits retention of the analytes from the PT desorption gas stream without sacrificing a portion of sample.

4 GC separation

KEI uses either Thermo Scientific Trace 1610 (C, H CSIA) or Agilent 7890 (Cl CSIA). For most target compounds, the analytical columns are either DB-MtBE and DB-624, 60 m x 0.32 mm. Other GC columns may be used on project-specific basis. The temperature programs are optimized to resolve the target analytes from each other and from interfering non-target compounds present in the sample matrix.

5 Thermal conversion and mass spectrometry

For carbon and hydrogen CSIA, KEI uses a Thermo Scientific Delta Q IRMS detector, with Conflo IV and Isolink 2 interfaces. The combustion reactor setup of the Isolink interface has been modified to feed a Ni-Pt reactor continuously with auxiliary O_2 stream to regenerate the oxidation capacity in real time. For hydrogen CSIA, KEI uses a standard high-temperature hollow tube pyrolysis setup for non-chlorinated target compounds. For halogenated compounds, KEI utilizes an in-house variant of a chromium-packed reactor tube. The IRMS is operated at default manufacturer’s settings for C and H isotope ratios determination.

Cl isotope ratios are determined using an Agilent 5975C MSD 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 one ^{35}Cl and the other containing only ^{35}Cl.