

Introduction

EPA methods for the analysis of volatiles include preconcentration on a sorbent followed by column separation and detection (typically by mass spectrometry). Interference is worst for the fast eluting volatiles that are gases at room temperature. Interferences can also be a problem for solvents which have strong attraction and similar masses to methanol and water. Furthermore, unwanted chemical derivitization and corrosion can be a problem when analyzing reactive species like nitric oxide, formaldehyde, and chlorine dioxide. Rotational spectroscopy is ideally suited for polar, "ultravolatiles" with masses below approximately 120 amu because the spectral signature is strong, the vapor abundance is high, and the high resolution nature makes it simple to analyze a mixture without chemical separation. In general, molecular spectroscopy is an ideal detection technique for its specificity by detection through unique spectral fingerprints rather than ambiguous detector responses which rely on filtration for chemical specificity.

Water and methanol, standard solvents in the EPA methods, are not significant sources of interference for MRR. Water has no spectral overlap with the 260-295 GHz range of BrightSpec's millimeter wave rotational spectrometer and methanol signals are well isolated from the rest of the sample matrix. This work introduces the concept of BrightSpec spectrometers as a detector for VOC analysis based on direct measurement of water headspace in vacuum without chemical separation or pre-concentration on a sorbent.

Experimental

The software controlled spectrometer consists of a millimeter wave light source which broadcasts an excitation pulse from 260-290 GHz, a heterodyne receiver which downconverts the molecular free induction decay for digitization on a PCI card, and a computer. The measurement cell is a 65cm steel tube approximately 5cm in diameter and 1L in volume. The glass sample holder is sealed by o-ring to a kovar glass/metal sealed tube which mates with the measurement cell by Swagelok.

The EPA VOC mix #6 standard of 2,000 $\mu\text{g/mL}$ each component in methanol was diluted in series with purified water (46871-U Supelco). The following concentrations were prepared: 100,000 $\mu\text{g/L}$, 10,000 $\mu\text{g/L}$, 1,000 $\mu\text{g/L}$, 100 $\mu\text{g/L}$, 10 $\mu\text{g/L}$, and 1 $\mu\text{g/L}$. Spectra for fullband analysis were acquired in fullband high dynamic range mode in order to determine the optimal set of spectral lines for a targeted analysis tailored for the each species sample matrix. Each individual component of the mixture is also available from Supelco as a standard solution in methanol. In order to generate reference spectra each of the standards were dissolved 1:10 in water to better match the matrix solvent of the mixture dilutions and retain the high concentration. Each sample is frozen, the air evacuated, warmed to room temperature, and the vapor is allowed to expand into vacuum up to 10mTorr of total pressure for direct measurement of the headspace without any chemical separation.

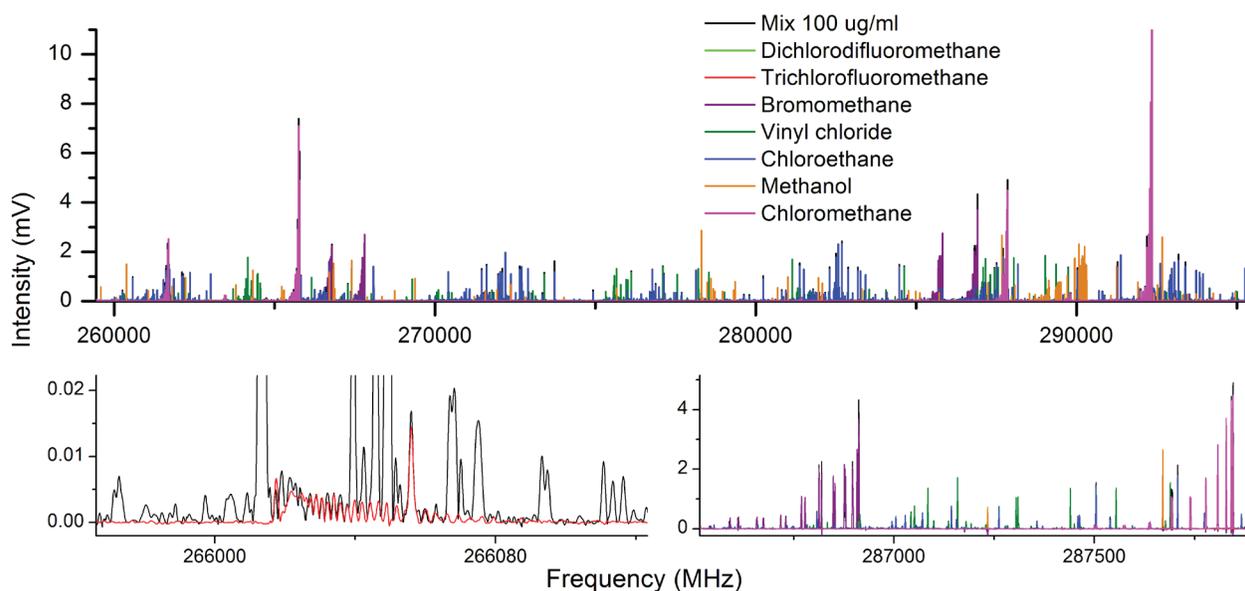


Fig 1: Broadband spectra of the 100 $\mu\text{g/mL}$ water VOC mixture. Reference spectra of each single component in water are scaled to comparable concentration and overlaid.

Table 1: VOC mix #6 Components and Properties

Standard Solution	Formula	Mass (amu)	Vapor Pressure (Torr)	Net Dipole Moment (Debye)	Henry's Law Constant (atm m ³ /mol)
Chloromethane (200 ug/ml)	ClCH ₃	50	3795	1.9	0.0088
Bromomethane (200 ug/ml)	BrCH ₃	95	1420	1.8	0.0062
Chloroethane (200 ug/ml)	ClCH ₂ CH ₃	64	993	2.06	0.0085
Vinyl Chloride (2000 ug/ml)	ClCHCH ₂	62	2600	1.45	0.027
Dichlorodifluoromethane (5000 ug/ml)	Cl ₂ F ₂ C	121	4260	0.51	0.225
Trichlorofluoromethane (5000 ug/ml)	Cl ₃ FC	137	668	0.45	0.097

Results and Discussion

The broadband spectrum in Fig. 1 illustrates full composition analysis by library matching. An expansion of the horizontal scale illustrates the highly resolved spectrum, despite the complexity of the mixture. For normal operation, an automated matching algorithm produces a quantitative composition list. The illustrated spectrum was acquired in approximately 1 min, however the spectrum can be acquired in seconds using fast scan mode with some tradeoff in sensitivity for real-time monitoring of the mixture.

In targeted mode, the spectrometer measurement protocol is optimized to measure the presence of each species individually. The chloromethane, and chloroethane plots in Fig. 2,3 illustrate the performance of dynamic range across six orders of magnitude. Since no column is used for separation, band broadening and overloading are not an issue. The detection limits for some of these chemicals are comparable to established EPA methods using purge and trap preconcentration followed by GC/MS quantitation. The BrightSpec concept introduces a simple procedure that is a direct measurement of the headspace. Liquid samples can be injected directly into vacuum, and then heated to enhance the detection limits further. The measurement time for analyzing the mixture in target mode is less than 10 minutes (which includes a background subtraction measurement).

Table 2: Detection Limits in Water

	Broadband (5min)	Targeted (40sec)
Chloromethane	0.005 µg/mL	0.1 µg/L
Bromomethane	0.022 µg/mL	0.8 µg/L
Chloroethane	0.026 µg/mL	0.5 µg/L
Vinyl Chloride	0.042 µg/mL	0.5 µg/L
Dichlorodifluoromethane	100 µg/mL	100 µg/L
Trifluorochloromethane	100 µg/mL	1000 µg/L

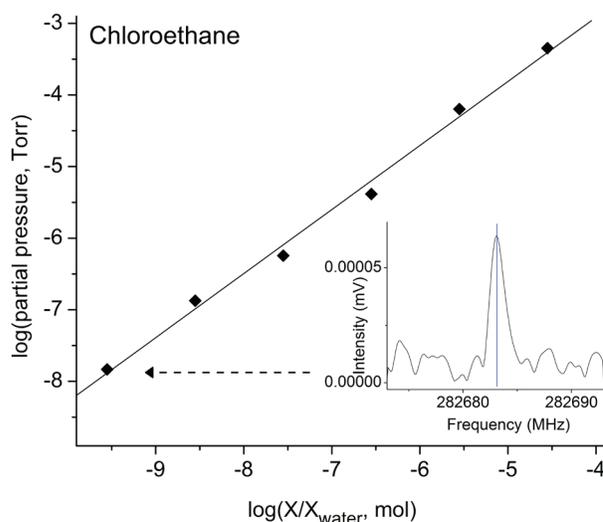
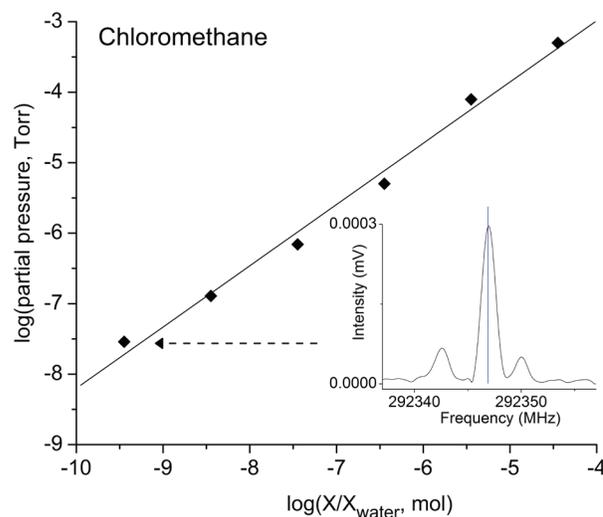


Fig 2,3: Log plots of signal linearity in partial pressure. The inset represents the signal at lowest concentration of the standard mixture.