



## Project Summary

# Analysis of Ambient Polar Volatile Organic Compounds Using Chemical Ionization-Ion Trap Detector

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The current approach to measuring trace levels of volatile organic compounds (VOCs) in ambient air requires cryogenic trapping of the analytes, followed by thermal desorption and low-temperature refocussing onto a column for analysis by capillary gas chromatography/mass spectrometry (GC/MS). This approach has been successfully applied to nonpolar VOCs, but its use for more polar species has been complicated by the problems associated with the ambient water vapor collected with the VOCs.

A promising technique for measuring polar VOCs is chemical ionization GC/MS (CI-GC/MS) in the quadrupole ion trap. This approach allows whole air samples to be taken since the water present in the air is used as the CI reagent gas. Water CI leads to appreciable intensities for the proton transfer agent  $H_3O^+$ , which produces intense pseudomolecular ions and class-specific fragmentation patterns for various low molecular weight polar compounds. Using water CI enhances sensitivity by a factor of about 5, as is apparent from a comparison of CI and electron impact intensities obtained with the Finnigan MAT 800 Ion Trap Detector™ (ITD) in full scan mode.

Standard mixtures of polar species at low concentrations in humidified zero air were analyzed without a membrane dryer, using a cryogenic trap and GC/CI-ITD with the ion trap detector in the full scan mode. Water appears to be an effective CI reagent

gas in the ion trap, and the GC/CI-ITD system can exploit the water vapor normally present in ambient air to circumvent the problems usually encountered when analyzing humid ambient air for these compounds. The water vapor present in the samples does, however, have a deleterious effect on the quality of the chromatography achieved. Future work will focus on optimizing the analytical technique and evaluating its suitability for various polar compound classes.

*This Project Summary was developed by EPA's Atmospheric Research Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Increasing public concern over polar volatile organic compounds (VOCs) of low molecular weight has spurred the current interest in developing better measurement techniques for these compounds. Some polar VOCs are often the subject of nuisance complaints from the public (e.g., alkylthiols, amines, aldehydes, etc.), while others are cited as potentially toxic compounds from industrial emissions (e.g., ethylene oxide, propylene oxide, acrolein, etc.). Analysis of trace levels of polar VOCs in air, however, poses many problems, and at present, the nature and distribution of these compounds in the atmosphere cannot be adequately characterized.

By contrast, the method for determining a large number of nonpolar VOCs in air is well established. Stainless steel polished sampling canisters are used with a combination of cryogenic trapping and high resolution gas chromatography (GC) coupled to a suitable detector, such as flame ionization, electron capture, or mass spectrometry (GC/MS). Cryogenic trapping preconcentrates the analytes by first passing the gaseous sample through a cold tube in which the organic components condense on the cold surface; the condensate is then desorbed and analyzed.

In general, attempts to sample polar VOCs at trace levels have been ineffective due to their chemical reactivity, affinity for surfaces, and tendency to undergo polymerization. The analytical problem has been exacerbated, especially for GC/MS measurements, by co-collected water vapor, which occurs at concentrations that are several orders of magnitude greater than that of the analytes.

The moisture problem has been overcome for many nonpolar compounds by incorporating a drying step before GC analysis. The air sample passes through a Nafion membrane dryer tube before being cryogenically concentrated; water vapor in the air stream permeates the dryer walls while most of the air pollutants of interest pass through the tube. This technique is limited, however, to relatively nonpolar compounds since small polar molecules also permeate the walls of the drying tube.

A promising technique for measuring volatile polar compounds in whole air samples is chemical ionization GC/MS (GC/CI-MS) in the quadrupole ion trap, using the water present in the air as the chemical ionization reagent gas. Water CI has been shown to produce intense pseudomolecular ions and class-specific fragmentation patterns for several polar compound classes in a conventional quadrupole GC/MS system. To date, the chemical ionization capabilities of the Finnigan MAT Ion Trap Detector have been investigated in detail for the reagent gases ammonia, methane, and isobutane. A recent study has shown that chemical ionization in the trap can improve the lower detection limit for some compounds by as much as a factor of 10 over that for electron impact (EI) ionization. The relatively low cost and exceptional sensitivity of the ITD make it an ideal candidate detector for the analysis of polar VOCs of environmental interest.

The objectives of this study were to evaluate the conditions under which

water chemical ionization can be used for the analysis of selected polar VOCs in whole air samples, using GC/CI-ITD in the full cyclic scan mode. The study consisted of generating and comparing electron impact and water CI mass spectra for several representative polar compounds, and evaluating the effects of humidified air and dry air on the CI-ITD analysis of these compounds.

## Procedures

### Sampling System

The system used for sampling and analyzing volatile organic compounds in zero-grade air streams consisted of a semi-automated cryogenic trapping and desorption unit (Nutech Model 3538-02) and a Finnigan MAT 800 Ion Trap Detector. Normally, whole air samples collected in stainless steel canisters are preconcentrated by passing them through the cryogenic trapping system prior to analysis. To investigate the effects of ambient water vapor on the analysis of polar VOCs, a special sample delivery system was constructed. This system, which was used in lieu of canisters for whole-air samples, allowed us to generate sample mixtures of polar compounds in dry zero air or humidified zero air. Samples were injected into a dry zero-grade air stream through a septum. Humidified samples were prepared by first passing the air through a flask partially filled with water, while dry samples were generated by bypassing the humidifier. Experiments were also carried out, using a Nafion membrane dryer tube, to demonstrate the effects of removing water from a humidified gas stream on the analysis of polar VOCs.

### Instrumentation

A Varian 3400 GC, equipped with a 60 m x 0.32 mm id fused silica capillary column (J&W DB-1701) with a film thickness of 0.2  $\mu$ m, was attached directly via a heated transfer line to a Finnigan MAT 800 Ion Trap Detector (ITD). The column was temperature programmed from -10°C at 10°C/min to 250°C. To avoid problems with humidified samples that caused ice to form in the column and block it, a 1m x 0.53 i.d. fused silica pre-column was connected to the analytical column inlet.

The Finnigan MAT 800 ITD is a fully integrated benchtop mass spectrometer with high sensitivity in both the electron impact (EI) and the chemical ionization (CI) mode. It is also capable of full cyclic

scanning and selected ion monitoring. As opposed to CI in a conventional mass spectrometer ion source, CI in the ITD requires only  $10^{-6}$  to  $10^{-4}$  torr of reagent gas. This low pressure is sufficient to convert sample molecules to ions with high efficiency because of the long reaction times (milliseconds) in the trap. The ion trap operates in a pulsed mode; a special sequence of rf voltages and time intervals are used to select the reagent ions, then react them with the sample to form analyte ions before the rf voltage is scanned for mass analysis.

### EI/CI Mass Spectra Study

For the water CI experiments, an externally mounted water source was used to maintain a constant reagent gas pressure in the ion trap. The water was introduced into the ion trap from a vial attached to the reagent gas inlet port. Several representative polar compounds were injected into the instrument to obtain their EI and water CI mass spectra.

### Trapping and Recovery Studies

Cryogenic trapping and recovery studies of several polar VOCs of interest (and some nonpolar compounds, for comparison) were carried out using the sample delivery system and the cryogenic trapping unit described above. Using a gas-tight syringe, a fixed volume of a standard mixture was injected into the humidified zero-grade air stream in the sample delivery system. The VOCs were concentrated in the cryogenically cooled trap. To desorb the trapped sample, the temperature of the trap was raised rapidly and the contents of the trap were flushed onto the capillary column for GC-ITD analysis. Several experiments were carried out under dry conditions (i.e., no water in the humidifier), and some runs were performed using humidified air with the Perma-Pure dryer between the sample delivery system and the trapping unit.

## Results and Discussion

### Comparison of EI and Water CI Mass Spectra

Some of the water CI and EI mass spectra obtained for selected polar VOCs using fixed operating conditions in the ion trap are summarized in Table 1. The reduction in molecular ion fragmentation achieved by using water CI instead of EI is striking. All of the water CI spectra, except for amyl acetate, have the  $(M+H)^+$  pseudomolecular ion as one of

**Table 1.** Ion Trap CI and EI Mass Spectra of Selected Polar VOCs

Compound	m/z	% Rel. Abundance	
		Water CI	EI
3-Octanone (MW 128)	129	100	
	99		35
	73		16
	72		34
	71		65
	57	10	100
	55		16
Benzophenone (MW 182)	184	13	
	183	100	
	182		41
	181		10
	105	47	100
	77		86
	51		67
	50		29
Acrolein (MW 56)	57	100	
	55		100
	56		32
Amyl Acetate (MW 130)	71	15	
	70		11
	61	100	15
	55		14
	43	35	100
	42		20
	41		20
	40		12
Heptanal (MW 114)	39		15
	115	23	
	97	100	97
	81		36
	71		18
	70	25	62
	69	17	17
	68		20
	67		18
	57	15	50
	55	46	100
	53		10
	45		22

the major ions. Heptanal is the only compound listed in which the (M+H)<sup>+</sup> ion does not occur as the base peak.

Benzophenone and naphthalene were used to compare the sensitivity of the ITD in the full cyclic scan mode under both EI and water CI conditions. For naphthalene, which undergoes very little fragmentation by either EI or water CI, the estimated limit of detection was about 0.05 ng. For benzophenone, which fragments to a much larger extent by EI, the smallest amount of sample required to give good quality full scan mass spectra (mass range m/z 45-300) was about 0.03 ng by water CI and 0.15 ng by EI. This enhancement in sensitivity using CI arises because the ion current is usually concentrated in only a few fragments in

CI, as opposed to the large number of fragments involved in the EI case. Furthermore, the increased reaction time in the CI-ITD mode results in a greater accumulation of sample ions for detection.

### Water CI-ITD Analysis of Humidified and Dry Air Samples

A standard mixture containing selected polar and nonpolar VOCs was analyzed by water CI in the ion trap, to evaluate the effects of humidified zero-grade air, dry zero-grade air, and Nafion dried air on simulated whole-air samples. The chromatographic behavior of the compounds listed was generally quite poor. This was largely due to the fact that the

water vapor had a significant effect upon the chromatography of the compounds, and that neither the GC column nor the operating conditions were optimized for this work. Nevertheless, the experiments carried out were able to demonstrate the value of the water CI technique for the analysis of polar VOCs.

Despite the effects of the water vapor on the chromatography, relatively little retention time variability was observed in these experiments. Table 2 shows the average retention times obtained for the test mixture that was analyzed under humidified, dry and Perma-Pure dried conditions. The increased fluctuations noted with shorter retention times in the table has been observed before for non-polar compounds, and occurs when cryogenically trapped compounds including water are transferred from the trap to a capillary column held initially at a reduced temperature. Despite the use of a precolumn and a slow initial temperature program, the column is probably blocked temporarily by ice until the column temperature rises above the freezing point of the water. Since this condition is difficult to control due to the erratic character of the blocking process, the retention time fluctuations for the early eluting compounds are not unexpected.

The effect of the Perma-Pure dryer on some of the compounds in Table 2 is striking. All of the polar compounds, with three exceptions, are removed from the gas stream along with the water vapor. The exceptions are acetone (very small peak), acrylonitrile, and 1-methyl-2-propanethiol. Both acetone and acrylonitrile are soluble in water. Thus, the small amount of acetone detected is most likely due to the fact that acetone was present at a very high level in the original mixture. The disappearance of limonene from this sample is equally surprising, since it is insoluble in water and should have passed through the dryer into the GC column, in much the same way as styrene or m-dichloro-benzene. The reasons for this aberrant behavior in the case of acrylonitrile and limonene are not understood at this time.

### Conclusions and Recommendations

The laboratory tests that have been conducted to evaluate the effects of humid air matrixes on the analysis of polar VOCs using water CI with the Finnigan MAT Ion Trap Detector, indicate the following:

**Table 2.** Retention Times for Several Polar and Nonpolar Compounds Cryogenically Collected and Analyzed by Water CI-ITD

Compound	Retention Time, minutes		
	Humidified <sup>a</sup>	Dry	Perma-Pure Dried
Acetone	8.66	8.22	9.05
Acetonitrile	10.11	9.68	ND <sup>b</sup>
Acrylonitrile	10.73	10.55	10.83
Tetrahydrofuran	12.89	12.68	ND
Ethyl acetate	12.97	12.83	ND
2-Butanone	13.20	13.00	ND
1-Methyl-2-propanethiol	16.68	16.57	16.70
Acrolein	18.39	18.15	ND
Styrene	23.49	23.45	23.22
Amyl acetate	24.12	24.10	ND
Limonene	25.77	25.75	ND
m-Dichlorobenzene	26.21	26.18	26.25
Nitrobenzene	29.43	29.38	29.50

<sup>a</sup>Average of two runs

<sup>b</sup>ND = not detected

- Water appears to be an effective CI reagent gas in the ion trap. Its proton affinity is low enough to allow it to react with a wide range of polar VOCs.
- The ITD permits the use of the very long reaction times necessary to detect low sample concentrations with high sensitivity.
- The GC/CI-ITD system can exploit the water vapor present in the air, thus circumventing the problems normally encountered when analyzing humid air. However, the presence of water vapor in the air has a deleterious effect on the quality of the chromatography achieved. The exceptional sensitivity of the Ion Trap Detector, together with water chemical ionization, may lead to the use of significantly smaller whole air samples to further reduce the deleterious effects of humidified air on the trace-level analysis of polar VOCs.

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Joachim Pfeil is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Ambient Polar Volatile Organic Compounds Using Chemical Ionization-Ion Trap Detector," (Order No. PB 90-106 451 /AS; Cost: \$15.00, subject to change) will be available only from:

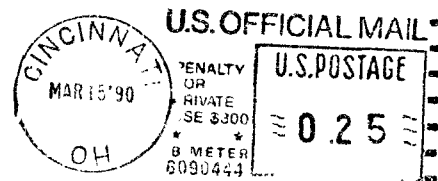
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