



Gas Chromatography

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PAMS: A Study of Performance in Low and High Humidity Environments

Introduction

The United States Environmental Protection Agency (USEPA) Photochemical Assessment Monitoring Stations (PAMS) are air quality monitoring locations that are used to

monitor pollutant compounds in air that contribute to ground level (bad) ozone. These nonpolar compounds are typically found in the 0.1 to tens ppbv, if not greater in some cases. Since these levels are too low to detect directly, a concentration technique such as cryotrapping or chemical adsorbent trapping needs to be used. One of the main issues with any sub-ambient temperature method is the negative effect of moisture in the air sample. Quantities up to tens of milligrams of water may be present and this can cause havoc with the chromatographic system, such as the water freezing with the formation of ice causing a flow restriction or blockage. Water can also cause poor peak shape/retention of analytes on certain columns such as Alumina PLOT. Several different techniques can be used for the effective removal of water from a gas sampling stream, prior to preconcentration, such as, drying agents, semipermeable membranes and reduced temperatures (used to condense out the water). One well accepted technique uses a Nafion® (TM, DuPont™) membrane to dry the incoming sample stream, and is very effective. The membrane permeability is very dependent on the analyte, generally speaking, and nonpolars are retained while water and certain polars are lost across the membrane.

This work is focused on humidity effects on low level sub-ppbv (0.3-1 ppbv) PAMS targets compared to the work done by G. Broadway et al¹ who studied humidity effects at a higher 10 ppbv.

Experimental

PAMS standard was purchased from Linde Canada at the USEPA recommended concentration of 3-10 ppbv and was used as the stock standard. The PAMS components dilutions were dynamically created in real time using a custom made on-line diluter, designed and built by the author, using UHP Nitrogen (LN2) as the diluent. The gas was purified using an advanced triple bed carrier gas purifier filter.

The on-line diluter utilized two 2000 mL/min. MKS Mass-Flo Mass flow controllers (MFC). One was used to control pure nitrogen diluent and the other was to control the flow to a 10 µm stainless steel frit, inserted into a 2L HPLC solvent bottle, ¾ filled with 18 megohm DI water. The bubbler MFC outlet was teed in to the pure nitrogen MFC output. To eliminate the possibility of trace level contaminants in the water and/or associated tubing/fittings/ MFC, since we are running at sub-ppbv levels, the total diluent flow (both Humid and Dry) was scrubbed of organics by the use of two Soil Vapour Intrusion tubes (SVI, thermal desorption) in series post blending of the diluent. The now clean diluent was blended with the PAMS standard (via a 200 mL/min. MKS MFC) into a ¼" SS tubing. To reduce the effects of laminar flow and promote mixing, the tubing was reduced to 1/8" SS (6 ft). This tubing was terminated into a SS 1/8" Tee with one arm going toward the on-line accessory approx. 1 ft. away with a 15 mL/min. flow. The remaining arm was plumbed with ¼" Bev-A-Line, as it was downstream of the sampling accessory, and at the end of this line a custom designed and manufactured humidity accessory was installed. A block diagram of the system is shown in Figure 1.

The custom designed humidity accessory utilized a Honeywell Humidcon™ H1H9130-021 with a 0-100% RH range, with +/-1.7 accuracy, +/-0.6 °C temperature reading communication via I2C. The I2C data was read via a customized Atmel® 328P microprocessor and the resulting data was displayed via I2C with a 16 x 2 LCD screen. The % RH and temperature was updated at 10 Hz. Similarly, the MFC were controlled by a custom programmed Atmel 328P, using SPI controlled MCP4821 12-bit DAC. Since the MCP4821 max output is 4096 mV and the MFC requires 0-5000

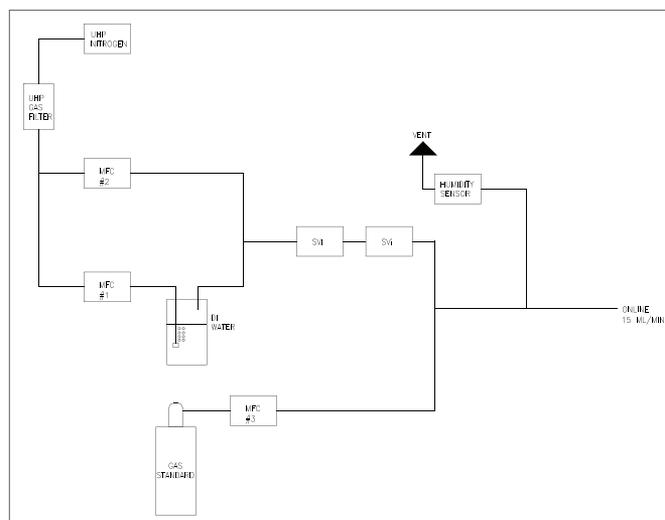


Figure 1. Diagram of a dynamic diluter.

mV, a TLC2272 Rail to Rail Op Amp was used to scale the DAC 0-4096 mV output by 1.25. A rotary encoder with momentary push buttons was used for the setpoint and MFC selection. The MFC readback was read by the ATmega328P 10-bit internal ADC directly without buffering. The readbacks/setpoints were displayed on a 16 x 2 LCD via I2C. An electronic block diagram showing the basic components of the MFC control is shown in Figure 2.

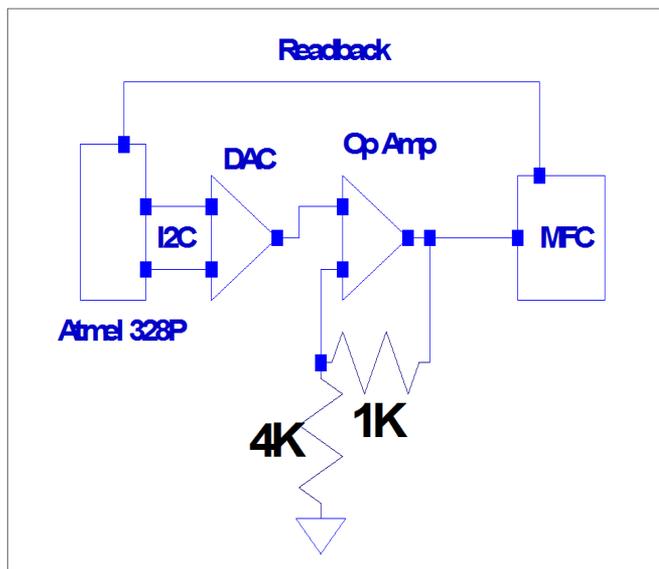


Figure 2. Schematic of MFC control electronics.

Table 1. System Conditions for Ozone Precursor Analysis.

GC	Clarus® 580 GC with heartcut option
Column Ozone Precursor Column Set	50 m x 0.22 mm x 1 µm dimethyl siloxane column Part number 04978179
	50 m x 0.32 mm alumina/Na2SO4 PLOT column Part number N6301107
Oven Conditions	46 °C for 15 min., then 5 °C/min. to 170 °C, then 15 °C/minute to 200 °C and hold for 6 min. (48-min. chromatogram)
Detector	Dual FID at 250 °C
Carrier Gas	42 psig helium at the ATD
	16 psig helium at the midpoint
ATD	Thermal Desorber TurboMatrix™ TD with online sampling accessory
Trap	Air Toxics trap packed with carbonaceous adsorbents
	Low -30 °C High 325 °C
Transfer Line	200 °C
Operating Mode	On-Line at 15 mL/min. for 40 min.
Split	Inlet Off
	Outlet 2 mL/min.
Data Handling	TotalChrom™

MFC Settings and Flows

MFC settings were 10 bit (0-1023) for the 0-5 V analog input for the MFC via the 12 bit DAC. The MFC flows were calibrated using a NIST traceable PE1000 electronic flow meter. The MFCs used were identified as MFC#1 (for Humid Flow), MFC#2 (Dry Flow) and MFC#3 (Gas Standard). Unless otherwise noted the MFC were set as follows:

MFC#1, set to 100, produced a measured flow of 228 mL/min. direct at MFC output, and 263 mL/min. of humid flow at 77% RH after humidification. Since the extra volume of the water vapor at RT contributes, it is believed the difference in flow with the humidifier attached is a result of the extra backpressure due to humidifier.

MFC#2, set to 100, produced a flow of 193 mL/min.

MFC#3, set to 100, produced a flow of 34.7 mL/min.

Dilution of standard with dry nitrogen =
 $(193+34.7)/34.7 = 1:6.56$

Dilution of standard with humidified nitrogen =
 $(263+34.7)/34.7 = 1:8.58$

Humidity Notes

Since the generated humidity is passed through two SVI tubes in series, the humidity needs time to stabilize as each tube has a moisture capacity of approx. 35 mg each. This effect is described in detail by Snow et al². In this study, typically one hour stabilization time was used prior to sampling.

Results

Both the 77% RH and dry dilutions of the PAMS standard give similar chromatograms in both the PLOT and BP-1 separations as shown in Figures 3 and 4 respectively. Figure 5 is an overlay of four sequential chromatographic runs highlighting excellent repeatability at low levels.

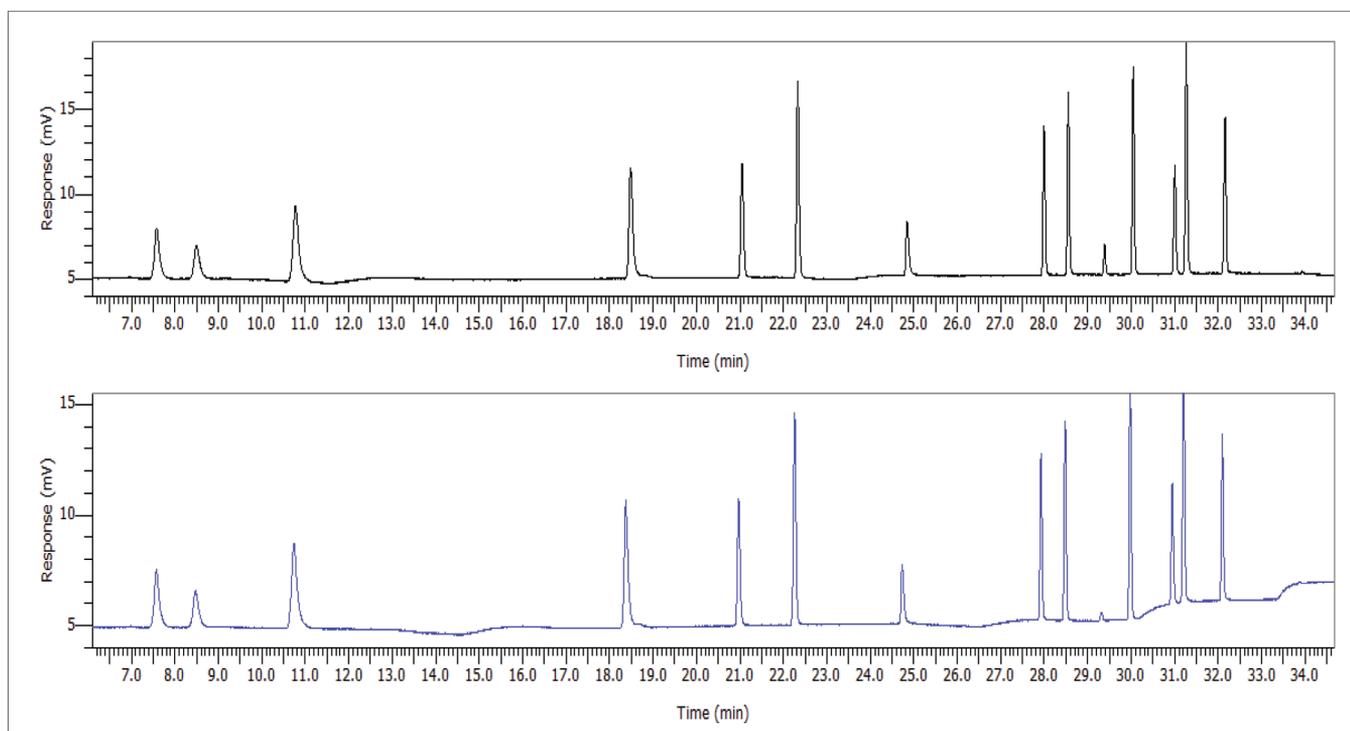


Figure 3. PLOT chromatogram of PAMS standard at approx. 0.3-1 ppbv. Top chromatogram is 77% RH and bottom is approximately 0% RH.

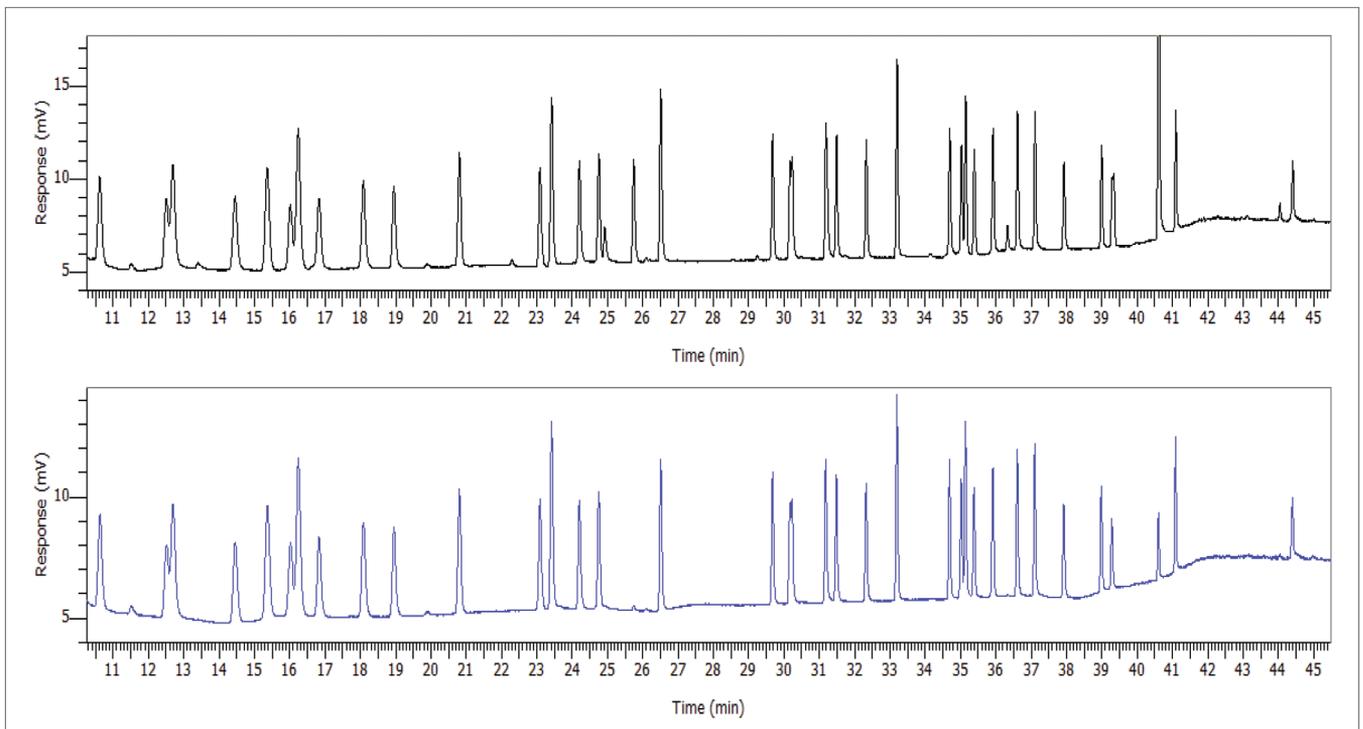


Figure 4. BP-1 chromatogram of PAMS standard at approx. 0.3-1 ppbv. Top chromatogram is 77% RH and bottom is approximately 0% RH.

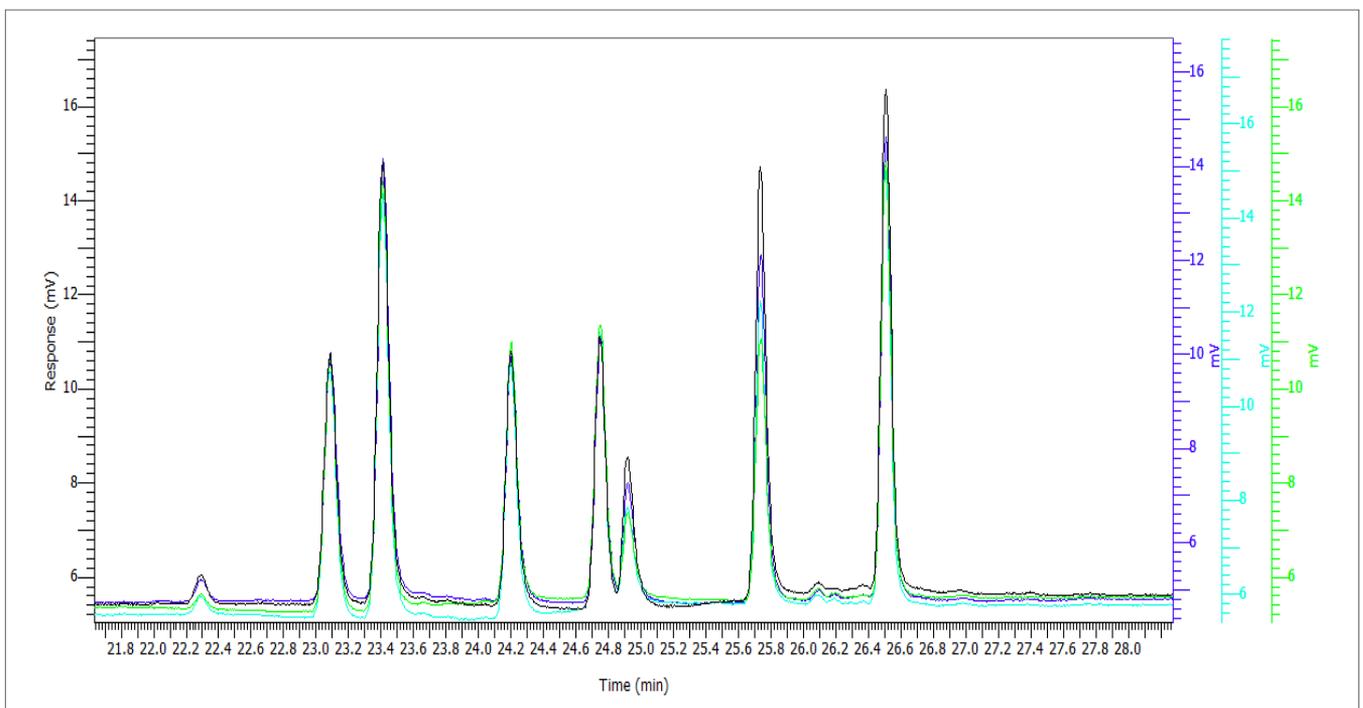


Figure 5. Expanded section of BP-1 column separation with four overlaid 77% RH samples.

Conclusion

The ozone precursor system performance at the 0.3 ppbv-1 ppbv, with a PAMS standard under high humidity conditions, are virtually identical to that under low/zero humidity. The chromatographic peak shapes and intensities show that high humidity has little/no negative effect on the analysis of PAMS target compounds at low levels. This enables the use of dry gaseous standards to be used without the laborious preparation of humidified standards.

References

1. "Ozone Precursor Analysis Using a Thermal Desorption-GC System" by G. Broadway and A. Tipler available for download at www.perkinelmer.com.
2. Patient Application US 20130180315 A1 Devices, systems and methods for purging and loading sorbent tubes by Snow et al.