

Measurement of Acrylonitrile, Acetonitrile and Nitromethane in Ambient Air and Vehicle Exhaust by Gas Chromatography with Thermionic Specific Detector

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**Presented at 2008 EPA/AWMA Symposium on
Air Quality Measurement Methods and Technology,
Chapel Hill, NC,
November 5, 2008**

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Extended Abstract # 90

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INTRODUCTION

Nitrogen containing hydrocarbons are sometimes found as emissions from gasoline and diesel vehicle exhaust.¹ Generally, these compounds, if present, are very low in concentration, and require sophisticated analytical techniques to measure. The toxicity of organo-nitrogen compounds such as acetonitrile, acrylonitrile and nitromethane, is sufficient to cause concern, even at low concentrations.² With the evaluation of new vehicle technologies, such as diesel selective catalytic reduction (SCR) using urea, for example, the potential for emission of some nitrogen containing compounds may increase. This paper reports on the design of an instrument specifically dedicated to the measurement of very low levels of these nitrogen containing hydrocarbons.

Trace levels of organic compounds in ambient air and vehicle exhaust conventionally are measured by gas chromatography with flame ionization^{3,4} or mass spectrometric detectors.^{5,6} Although both of these detectors are sensitive enough for most organics, this particular family of organo-nitrogen compounds is typically found at levels below usual detection limits of these techniques or are not specific enough to pick them out from the rest of the huge number of other organics. These three targets typically elute between n-Pentane and n-Hexane, along with a multitude of possible C5- and C6-olefins and the target analytes cannot be readily distinguished from them. The low molecular weight of these (MW 41, 53, 61) preclude their positive identification from other possible coeluturs, especially hydrocarbons with common ions to these.

The thermionic specific detector (TSD) is specifically designed to detect organo-nitrogen and organo-phosphorus compounds and exclude hydrocarbon response.⁷ A rubidium-impregnated ceramic bead is mounted directly above a conventional flame tip and is heated to a red glow by applied current. The generated signal is then processed as other chromatographic detectors.

The design of the Organic Nitrogen Measurement System is intended to provide for the analysis of gas phase samples collected in conjunction with particulate measurements and exhaust monitoring programs at various government testing laboratories. Initial criteria were the following: 1) capability to analyze for very low concentration samples, 2) provision for two different analysis channels that can treat the sample with independent sample loading, trapping and chromatography, 3) provision for two different detectors to give analytical confirmation and/or to establish peak identification, 4) provision for enhancements to the instrument design based on past experience with the analytical principles involved.

EXPERIMENTAL

Acrylonitrile, acetonitrile and nitromethane are determined with a Varian 3800 Gas Chromatograph (Varian Inc., Walnut Creek, Ca) equipped with dual liquid-nitrogen concentrator traps, a thermionic specific detector with ceramic bead and a flame ionization detector. Instrument operating parameters are provided in Table I.

All valves are Valco Series 1/16" WE type. These valves are equipped with micro-electric actuators controlled through timed events in the chromatograph. Two valve ovens, holding all valves, are maintained at 120 °C and 150°C as appropriate for the valve location. A sixteen position automated sampler (Valco Multiposition Valve CSD Type with heated sample lines) is included to allow unattended operations with multiple samples. All data is collected, processed and reported with the Varian Star Workstation, with full control of most operating parameters and the automated sampler, including all Varian 3800 operations. Valving system is designed and assembled by Lotus Consulting (Long Beach, Ca).

A companion trap/column setup for the flame ionization detector is a duplicate design, with only the detector inserted in the setup. The two channels can be run simultaneously or singly.

Analytical column for each channel is Varian CP624, 60 m, 0.32 mm ID, 1.8 µ film. The stripper column for each channel is Varian CP CB, 0.53 mm ID, 25 m length, and both are housed in a third valve oven that has been hijacked as an isothermal column oven with separate control from the convention column oven. Column flows for both columns is controlled with separate electronic flow controllers (EFC Type 3). Varian EFC type 3 is a true flow controller where the flow rate is specified and the back pressure of the column seeks a setting to provide the requested flow. Flows are **not** computed from column dimensions with Poisselle's formula. Inter-trap transfer through stripper columns is controlled by a third electronic flow controller (EFC Type 3) for the thermionic specific detector and with a digital flow controller. Purge flows for the adsorbent traps are controlled with digital flow controllers.

The sample loading process is performed with dual mass flow controllers to allow large volumes to be loaded for thermionic specific detector and flame ionization detector independently.

Sensitivity of the thermionic specific detector is directly impacted by the current applied to the bead, but a high setting can shorten service life. A current is selected to give the same noise as inboard the flame ionization detector.

The medium concentration acrylonitrile/acetonitrile standard (7.8 and 12.2 ppbV/V, respectively) is NIST Standard Reference Material (NIST, Gaithersburg, Md); other standards (1 ppbV/V and 1 ppm V/V) are provided by Scott-Marrin, Inc. (Riverside, Ca); these standards are used for all calibrations. Multiple level calibrations are accomplished by adjusting the mass flow controller flow rate or sample loading interval or both.

Table 1. GC-TSD parameters for Trace Nitrogen System

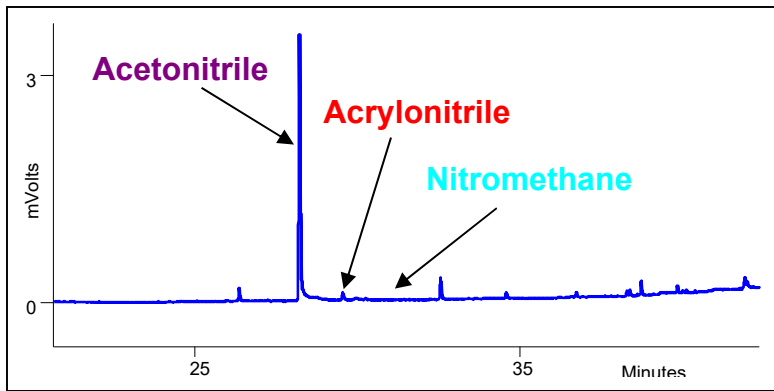
<u>Column Oven Program</u>	
Initial Temperature	10 °C for 6 min
Ramp 1	-100 °C/min to -20 °C, hold for 8.7 min
Ramp 2	5 °C/min to 80 °C
Ramp 3	10 °C/min to 150 °C, hold for 18 min
Carrier gas	Helium, 3 ml/min
<u>Adsorbent Trap Program</u>	
Initial Temperature	43 °C for 9.1 min
Ramp	200 °C/min to 202 °C, hold for 50.25 min
<u>Cryofocus Trap Program</u>	
Initial Temperature	79 °C for 3 min
Ramp 1	-200 °C/min to -179 °C, hold for 6.95 min
Ramp 2	200 °C/min to 202 °C, hold for 47.25 min
Adsorbent Trap Purge	Nitrogen, 47 ml/min
Inter-Trap Transfer through Stripper	Helium, 10 ml/min
Make-up gas to Detector	Nitrogen, 25 ml/min
Detectors Temperature	250 °C
Detectors Range	10 ⁻¹² amps/mv
Detectors Full Scale	1000 volts
Bead Current	3.150 amps
Typical Sample Loading	300 ml

RESULTS AND DISCUSSION

Typical Chromatograms

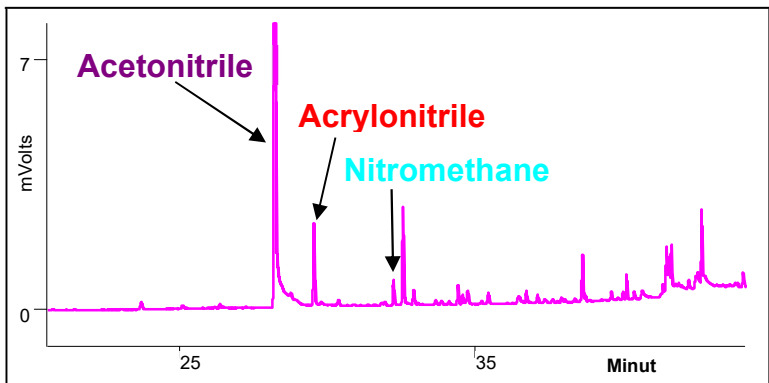
Ambient Air - An example of lab air is shown in Figure 2. Measured concentrations for target compounds are acetonitrile 0.285 ppbV, acrylonitrile 0.006 ppbV, and non-detect for nitromethane.

Figure 1. Chromatogram of Ambient Air



Vehicle Exhaust – A illustration of typical vehicle exhaust is shown in Figure 2. Measured concentrations for target compounds are acetonitrile 3.408 ppbV, acrylonitrile 0.225 ppbV, and nitromethane 1.528 ppbV.

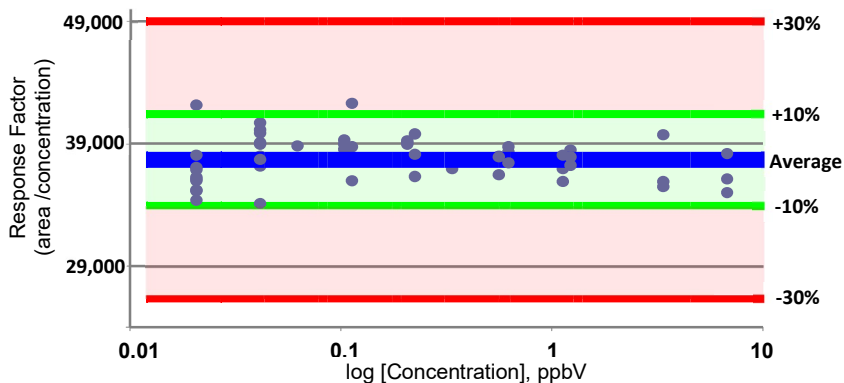
Figure 2. Typical Chromatogram of Vehicle Exhaust



Detector Linearity

Acrylonitrile - Multi-point calibration is performed with NIST Standard Reference Material oxygenate standard and with 1 ppbV acrylonitrile/acetonitrile mix calibrated against the NIST mixture and is shown in Figure 3. The average response factor is 37,231 area/ppbV, with an RSD of 0.6% and r^2 of 0.998.

Figure 3. Plot of Acrylonitrile Response Factors versus log[Concentration] over the range of 0.020 to 6.78 ppb V, with 14 levels and 56 data points.



Acetonitrile - Multi-point calibration is performed with NIST Standard Reference Material oxygenate standard and with 1 ppbV acrylonitrile/acetonitrile mix calibrated against the NIST mixture. The calibration range is 0.03 to 10.8 ppbV, with 14 levels and 56 data points. The average response factor is 43,707 area/ppbV, with an RSD of 3.4% and r^2 of 0.998.

Nitromethane - Multi-point calibration is performed with 1 ppmV nitromethane standard. The calibration range is 3.33 to 200 ppb V, with 6 levels and 18 data points. The average response factor is 1,503 area/ppbV, with an RSD of 7.3% and r^2 of 0.9995.

Detection Limits

Acrylonitrile - Detection limit is determined from 12 consecutive runs of the lowest standard used in the multi-point calibration (0.020 ppbV) and is calculated following protocols given in California Air Resources Board Method 1002.⁹ Table 2 lists the raw areas for the series and computations to yield a preliminary detection limit of 3.3 ppt V (0.0033 ppb V) for acrylonitrile.

Table 2. Detection Limit Calculation for Acrylonitrile

<u>Area Counts</u>	<u>Area Counts</u>
748	730
773	792
732	876
753	766
751	714
774	770

$$LOD = \frac{t * s}{m} = \frac{3 * 41}{37,231} = 0.0033 \text{ ppbV}$$

where m = average response factor

t = t-factor for 99% confidence level; 3 for >7 replicates

s = standard deviation of at least five replicates

Acetonitrile - Detection limit is determined from 12 consecutive runs of the lowest standard used in the multi-point calibration (0.020 ppbV). This calculation yields a detection limit of 0.0038 ppbV

Nitromethane - Detection limit is determined from 9 consecutive runs of the lowest standard used in the multi-point calibration (3.33 ppbV). This calculation yields a detection limit of 0.13 ppbV.

Nitrogen-Carbon Selectivity

Samples from both ambient air and vehicle exhaust can have significant amounts of hydrocarbons. Potentially these can respond with the thermionic specific detector. The design of the detector minimizes its response to such hydrocarbons. To validate the selectivity, a mixture of hydrocarbons is run on both detectors and compared with the equivalent response of acrylonitrile. Selectivity is calculated by:

$$N : C \text{ Selectivity} = \frac{\text{Peak Area of Nitrogen Compound}}{\text{Peak Area of Hydrocarbon}} \times \frac{[\text{Hydrocarbon}] \times n}{[\text{Nitrogen Compound}]}$$

where n is number of carbon atoms in the hydrocarbon, and concentrations are ppbV. For example, propane selectivity calculates as:

$$N : C \text{ Selectivity} = \frac{244,846}{8,134} \times \frac{955 \times 3}{6.78} = 13,741$$

Results for representative hydrocarbons are given in Table 3.

Table 3. Nitrogen/Carbon Selectivity for several hydrocarbons.

<u>Component</u>	<u>N:C</u>
Propane	13,741
2Methylpropene	17,969
n-Butane	16,469
1,3-Butadiene	25,796

Stability of Acrylonitrile in Tedlar Bag

Acrylonitrile is inherently very reactive and could either degrade chemically with Tedlar or permeate through the polymer. Both high (1 ppmV/V) and low levels (6.78 ppb V/V) of acrylonitrile were filled into clean Tedlar bags and then repeatedly run approximately every hour for over 14 hours. To test of photochemical changes in the bag from ambient light, one Tedlar bag is enclosed in three layers of black plastic bags. Typical results for this test with darken black bags are shown in Figures 4 and 5.

Figure 4. Stability of low level Acrylonitrile (6.78 ppbV/V) in darken Tedlar Bag over 14 hours

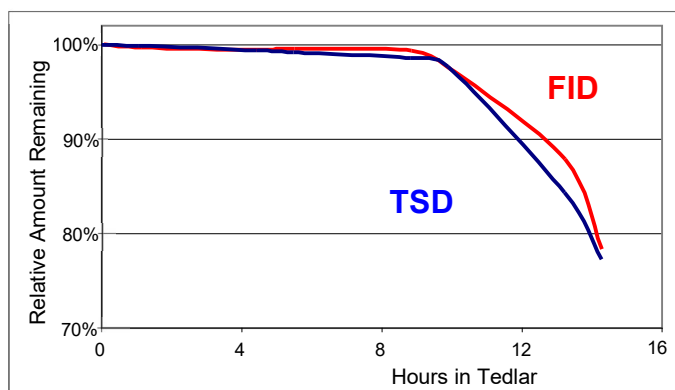
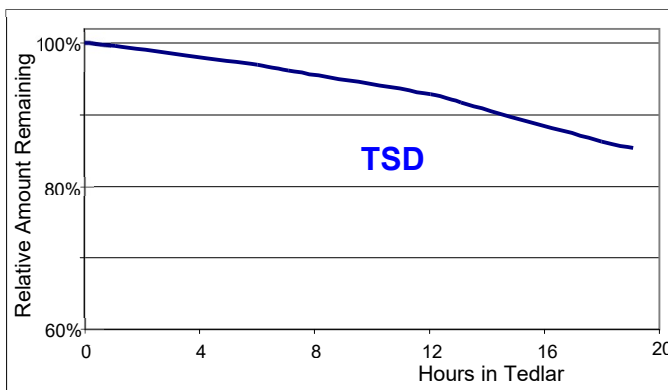


Figure 5. Stability of high level Acrylonitrile (1 ppm V/V) in darken Tedlar Bag over 19 hours



SUMMARY

The Organic Nitrogen Measurement System is very sensitive to the measurement of acrylonitrile, acetonitrile and nitromethane with the Varian thermionic specific detector (TSD) and the concentration steps involved in focusing large volumes into focused loadings in the separation column. Detection limits are demonstrated for levels down to low part per trillion volume. Hydrocarbon concentrations expected in ambient air and vehicle exhaust samples are adequately rejected with the selectivity available with the thermionic specific detector.

Acetonitrile is difficult to properly quantitate due to its ubiquitous presence in the modern laboratory, due to common use of this chemical as a reagent or liquid chromatography mobile phase. Blank runs frequently have detectable levels of acetonitrile. The other two target analytes are typically absent or close to their detection limits in ambient air and blanks.

Acrylonitrile is a common reactant in many polymer reactions and is often detected in sampling systems involving plastics, commonly employed in sample collection apparatus, especially vehicle

test stations. Its concentration assessment becomes suspect with many surfaces possibly releasing acrylonitrile not detected by normal analytical tools, such as flame ionization or mass spectrometry, with their higher detection limits than possible with the thermionic specific detector. More importantly, both acrylonitrile and acetonitrile degrade readily over a few hours in clear Tedlar bags, a common sample container in vehicle emission testing. To reduce congestion in the organic analysis laboratory, samples are likely to be required to be collected in Summa™ canisters to lengthen their holding times.

References

1. Australian Department of the Environment, Water, Heritage and the Arts, Acrylonitrile (2-propenenitrile) Fact Sheet; www.npi.gov.au/database/substance-info/profiles/7.html#environmentaleffects.
2. Agency for Toxic Substances and Disease Registry, "Tox FAQ", 2008, www.atsdr.cdc.gov/tfacts125.html.
3. California Non-Methane Organic Gas Test Procedures, 2002, www.arb.ca.gov/msprog/levprog/cleandoc/clean_nmogtps_final.pdf.
4. California Air Resources Board SOP No. MLD 032, 2002, www.arb.ca.gov/aaqm/sop/sop032.pdf.
5. USEPA, Compendium Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GCMS)", 1999, www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf
6. California Air Resources Board SOP No. MLD 066, 2002, www.arb.ca.gov/aaqm/sop/sop066.pdf.
7. Burgett, C.A., Smith, D.H., Bente, F.B., *J. Chrom.* **1977**, 134; pp 57-64.

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