The Measurement of Acrylonitrile in Ambient Air Using Solid Sorbent Tubes and Thermal Desorption.

Extended Abstract #42

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INTRODUCTION

The State of California Air Resources Board (ARB) Monitoring and Laboratory Division (MLD) maintains a number of monitoring sites for toxic organic compounds in ambient air throughout the State and two border sites in Mexico. A discrepancy in results from one of these sites which contained two samplers each monitored by a different government laboratory indicated that acrylonitrile results were dependent on the sampler's condition. The sampler either retained or released acrylonitrile which affected the concentrations measured. Further investigation indicated that time in service between sampler cleaning and possibly sampler temperature played a major role in the laboratory results.

Acrylonitrile is considered a Group B-1 'possible' carcinogen by EPA and is given a lifetime inhalation potential of one cancer per million at 1.0×10^{-2} ug/m^3 (micrograms per cubic meter). ARB's reporting limit with canister sampling was 6.5×10^{-1} ug/m^3 which corresponds to a potential cancer rate of 65 cancers per million. Therefore a method which was not affected by a sampler and had a lower reporting limit needed to be developed. Two alternate techniques were considered for the trapping and measurement of low levels of acrylonitrile that do not require a sampling device ahead of the trap. Both methods involve drawing air over a solid sorbent; however one method desorbs the acrylonitrile from the sorbent using solvent while the other uses heat. Since thermal desorption avoids the large dilution which occurs with solvent extraction, it was chosen as the best analytical option.

Initial experimentation involved determining the best solid sorbent and thermal desorption parameters. Several solid sorbents appeared to retain acrylonitrile under controlled conditions; however when those sorbents were used in ambient air their effectiveness degraded severely. The majority of these sorbents were hydrophilic which can cause problems in a refocusing thermal desorption apparatus and the solid sorbents tested showed some variance in tube-to-tube response when spiked with the same concentration of acrylonitrile.

Initial in-lab conditioned ambient air studies gave recoveries in the 60% to 90% range. When the sorbent tubes were deployed for outside ambient air sampling, recoveries were less than 10%. This indicated that something in the unconditioned ambient air was interfering with the trapping, stability or desorption of the acrylonitrile. The laboratory conducted several studies to determine what could be done to increase the recovery.

STUDY

Equipment and Materials

The following equipment and materials were used during this study: Perkin Elmer TurboMatrix 650 thermal desorption unit, Varian 3800 GC connected to a Varian Saturn 4000 MS controlled by a Varian dataStation, Markes International tube conditioning unit , and an in-house constructed heated

tube loader for spiking the sample collection tubes. The column used for analysis is a DB-VRX (60m x .32mm x 1.8um). Markes International pre-packed sorbent tubes and Perkin Elmer empty tubes packed with Sigma Aldrich Carboxen 1000 and Porapak N™ were used for compound trapping. Fisher Scientific purge and trap methanol was used to prepare standards which were obtained from ChemService.

Experimental

Sorbents

Several solid sorbent materials were evaluated in this study. The evaluation consisted of injecting approximately 2nanograms (ng) of acrylonitrile dissolved in 1uL of methanol into a 100sccm zero-air stream that was connected to a standard size stainless steel thermal desorption tube packed with the sorbent. The sorbents investigated were Tenax GR (porous polymer with graphite), Carbopack B (graphitized carbon black), Carbosieve S111 (carbonized molecular sieve), Porapak N™ (a porous polymer), and Carboxen 1000 (carbonized molecular sieve). Of the sorbents tested the Porapak N™ and Carboxen 1000 proved to be more suitable than the others. However, under very low flows or short sampling times using Porapak N™ trapping acrylonitrile from ambient air was very inefficient. The Carboxen 1000 did retain small amounts of acrylonitrile when subjected to ambient air, but recovery of tube spikes varied from 5% to 15%.

Another problem noted with these sorbent tubes was the variability of response, particularly when a new series of tubes was used. With low concentrations of acrylonitrile spiked into the tubes recovery would start at about 50% compared to older used tubes. After a number of conditionings and uses the tubes recovery would be within 15% of the used tubes. There also appeared to be a slight amount of acrylonitrile degradation over time on the spiked tubes. Approximately 15% of a 2ng spike would be lost over a 24 hour period with a maximum of 20% after five days. Because of this variable response the use of a standard additions technique was employed. Using standard additions not only addressed the acrylonitrile contamination in the methanol used for making standards, it also handled the compound variable recovery problem. Regardless of the recovery, the correlation coefficient of the standard addition line generally had a value of 0.99 or better.

Carboxen 1000 is very hydrophilic which presented a problem for the thermal desorption device. If too much water collected on the focusing trap when the tube was desorbed, it would plug the trap and the analysis would fail. To lessen the water problem, but still maintain adequate sensitivity, the desorbing gas was split by a factor of 2 on the tube outlet. Additionally a long dry purge of the tube was used to partially dry the sorbent material. Even if half the water in the sample was removed prior to the trap and not too much was concentrated on the trap, water making its way to the column caused peak tailing of the acrylonitrile. Therefore, the desorbing gas was split by a factor of 2 prior to introducing the sample into the gas chromatograph.

Observation

Several sampling parameters were adjusted to overcome the low recoveries of acrylonitrile from ambient air . Lower flow rates and shorter sampling time combinations were attempted with no success. Noting that the conditioned air samples gave better recoveries than outside ambient air, it was surmised that water was interfering with acrylonitrile recovery. Any attempt to remove or lessen the water entering the sorbent tube removed the acrylonitrile. Since the sample tube could be dry purged at 100°C without loss of acrylonitrile from the Carboxen 1000 the sorbent tubes were heated while sampling. Heating the sample tubes appeared to alleviate a large amount of the water interference. A short study indicated that heating the tubes while sampling improved recovery to at least 50% or better. Varying the tube temperature between 30°C to 50°C did not seem to degrade

recovery of acrylonitrile. At these temperatures Carboxen 1000 is still absorbing water but by heating the tube the temperature drop caused by the pressure drop across the tube prevents the air from falling below its dew point. It is hypothesized that when the temperature falls below the air's dew point liquid water is formed which washes the sorbent and removes the acrylonitrile. It is possible this liquid water which contains dissolved acrylonitrile is then carried out by the air flow through the tube.

Method

A set of four conditioned tubes is prepared by injecting three with different concentrations of acrylonitrile in 1uL of methanol. The sample tube is loaded with 1uL of the methanol used in the standards. Two additional tubes are prepared with a standard and kept within the laboratory. The initial four sorbent tubes are attached to a flow adjustable four port manifold that is connected to a low flow air pump. The tubes are heated to approximately 40°C and the air flow through the tubes is adjusted to 100sccm. Ambient air is drawn through the tubes for a period of 24 hours, after which the tubes are capped and taken to the laboratory for analysis by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS). The concentration of the acrylonitrile is then calculated using the four tubes exposed to ambient air by the standard additions technique. This technique involves plotting a line through the points and the x-intercept is the concentration of the acrylonitrile in the sample tube. Benzene and carbon tetrachloride response is also monitored during the analysis and can be used as pseudo internal standards to adjust for flow variations. Additionally, these results monitor the efficiency of the tubes. The spiked tube responses are compared against the laboratory standard tubes to determine recovery. After analysis the tubes are conditioned and capped for further sampling. Table 1 lists the thermal desorption and GC/MS parameters.

Table 1. TD/GC/MS Parameters

Thermal Desorption Parameters						
Temperatures	**^{o}C**	**Times Min.**	**Options**	**Set**	**Pneumatics**	**mL/min**
Tube Desorb	275	5.0	Tube Split	On	Tube Split	2.0
Transfer Line	140		Trap Split	On	Trap Split	2.0
Valve	200		Split Mode	Ratio	Tube Desorb	20.0
Trap Collect	5				Column	1.5
Trap Desorb	220	5.0			Column/Trap Desorb	1.5
Trap Heating Rate (^{o}C/s)	40				Dry Heated/Purge	50.0
Heated Purge	100	30.0				
GC Settings Parameters			**MS Settings Parameters**			
Column			Scan Full: 45-400			
Initial	40		Scan Delay: 5 min.			
Initial Hold		5	Ionization Type: EI			
Rate (^{o}C/min.)	10		Emission Current: 20uAmps			
Final	220		Target TIC: 20000 counts			
Final Hold		3	Maximum Ion Time: 25000uAmps			
			Data Rate 1.82 Hz			

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Results

Use of this sampling technique and analytical method has reduced the reporting limit by more than a 100 fold. A sampling device was placed on MLD's roof top monitoring platform starting in March 2010. The average and median value obtained for 46 twenty-four hour ambient air samples for acrylonitrile through July 2010 was 2.4ppt (0.0052ug/m^3) and a median value of 2.5ppt (0.0054ug/m3) with a maximum of 8.2ppt (0.0176ug/m^3) and a minimum of 0.7ppt (0.0015ug/m^3). Recovery for acrylonitrile averaged 66% with a median value of 70% and a maximum recovery of 102% and a minimum recovery of 21%. Correlation coefficients for the standard addition curves during this sampling period averaged 0.9973 with a median value of 0.9988 and a maximum of 1.000 and a minimum of 0.9816. Figure 1 displays the results over time, Figure 2 illustrates a total ion chromatograph (TIC) from an ambient sample and Figure 3 shows typical ion extracted chromatograms showing the 52amu ion used for quantification.

Figure 1: Acrylonitrile Concentration Measured from MLD Roof Platform

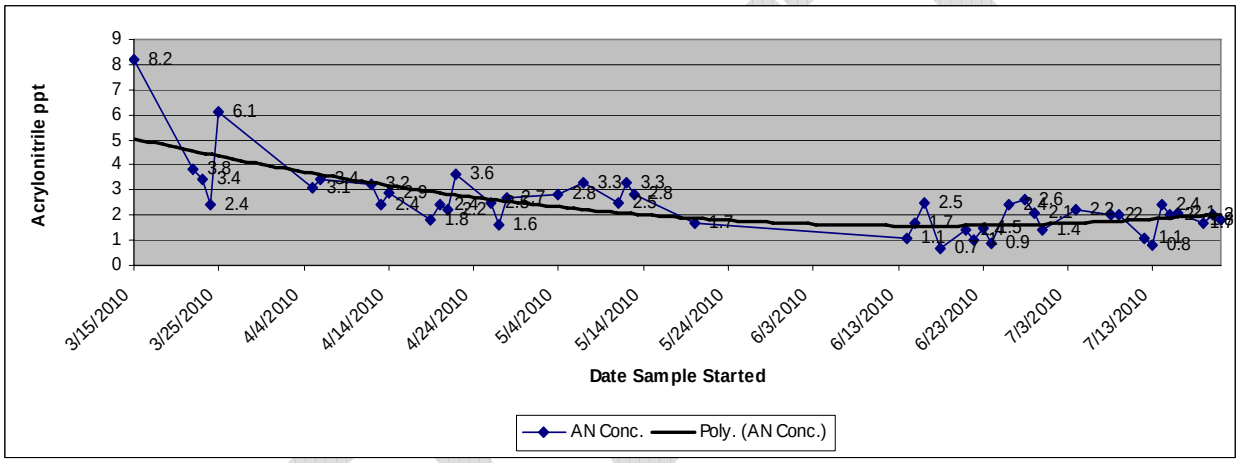


Figure 2: TIC of Ambient Air Thermal Desorbed from Carboxen 1000

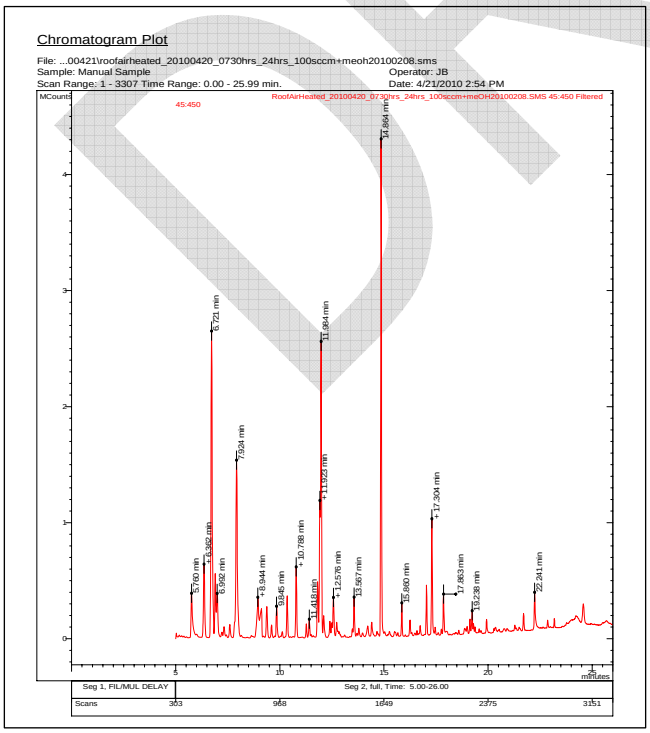
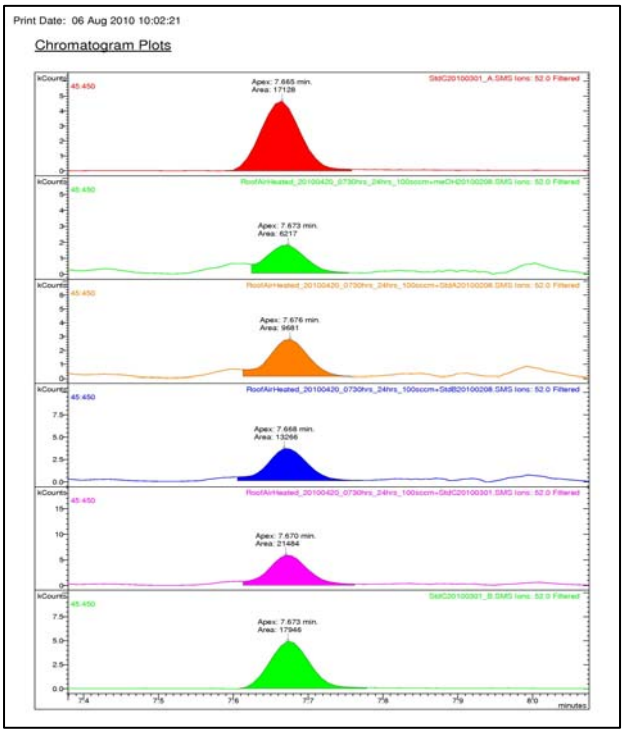


Figure 3: Extracted Ion Chromatogram of Standards, Ambient Air, Spikes



Summary

Acrylonitrile can be measured in ambient air through the use of solid sorbent collection followed by TD/GC/MS analysis. The method does not exhibit the problems encountered with samplers that are used to fill canisters. This technique can produce results within the toxic levels estimated by EPA for a one-in-a-million cancer risk and shows that for one location ambient acrylonitrile levels are below the calculated guidelines. The use of standard additions combined with TD/GC/MS analysis produces sensitive, selective, precise, and accurate results.

Acknowledgements

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References

1. *Turbomatrix Series Thermal Desorbers User's Guide*; PerkinElmer, Inc.: Shelton, CT, 2007

2. *Integrated Risk Information System*; U.S. EPA; last updated 12/01/1991

3. *Unity Thermal Desorber Users Manual*; Markes Int'l.; Sept. 2006

4. *TC Sample Tube Conditioner, Dry Purge Rig Operators Manual*; ver. 6.1; Markes Int'l.; July, 2006

5. Brown, J.; Shirey, B; *A Tool for Selecting and Adsorbent for Thermal Desorption Applications*; Supelco, Bellefonte, PA; 2001

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