The Right Badge for Acetic Acid Monitoring
A Comparison Between the Popular PTFE Encased Charcoal and Loose Carbon

When sampling for acetic acid vapor using a diffusive monitor, two different types of media are readily available: loose carbon sorbent and carbon pads/wafers that generally utilize a polytetrafluorethylene (PTFE) binder. NIOSH and OSHA approved methods mention analysis can be done by gas chromatography (GC) or ion chromatography (IC). During initial validation studies under taken by Assay Technology, an interesting phenomenon was observed where liquid spikes of acetic acid (AA) did not appear to be absorbed into the PTFE based carbon media. Because of this, we decided to investigate it a little further and here, we present a small study looking into the desorption efficiencies (DE's) of various readily available diffusive monitor media, specifically for acetic acid sampling. The spikes were done in both the liquid phase and in the vapor phase. The PTFE-based media was found to lead to false high DE's when done in the traditional method of using a liquid standard that which could not be verified when a vapor spike was done. Only media that did not use a binder showed agreeable DE values for studies done in both the liquid and vapor phase.

NIOSH/OSHA Approved Methods for Sampling of Acetic Acid using Diffusive Monitors

The two major methods for AA analysis is either by IC or GC. OSHA methods PV2119 and 186SG both call for IC analysis with the former using 0.01 N NaOH and the latter using a 0.0015 M borate solution as the extraction solvent.[1,2] PV2119 method is an updated 186SG method stating a change in the extraction solvent was needed due to a non-linear extraction efficiency when using 0.0015 M borate across varying AA concentrations. Sodium hydroxide was found to have a linear extraction efficiency in PV2119. The NIOSH 1603 method uses high purity formic acid as the extraction solvent and is then analyzed via GC.[3] Because formic acid is known to contain background acetic acid, it is recommended to purchase a high purity formic acid to reduce the AA background. Even with this, it may be difficult to find a source of formic acid with a low enough AA background to result in acceptable detection limits. IC methods do not require the addition of formic acid; due to this and the hazards of working with pure formic acid, the IC methods are generally more popular for AA analysis.

Commercially Available Diffusive Monitors for Acetic Acid Sampling

Of the four most popular and commercially available diffusive monitors advertised for acetic acid monitoring, only two explicitly state the media used. Assay Technology's 543 monitor uses GBAC; a bead shaped activated carbon that is more of a loose carbon sorbent inside the badge.[4] 3M's 3500 monitor uses charcoal adsorbent pads, more of a carbon wafer with a polytetrafluoroethylene (PTFE) binder while SKC and ACS state their badges use activated carbon but do not explicitly say if it is a loose carbon sorbent or a wafer/pad like that of 3M's.[5]

Desorption Analysis using Liquid Spikes

We undertook a small study to try and verify the use of an acetic acid badge with a loose carbon sorbent (Assay Technology's 543 badge) versus a carbon-PTFE based badge like that of 3M's 3200 and Assay Technology's 566, organic vapor badge. Analysis was done by following OSHA methods 186SG and PV2119. The OSHA and NIOSH methods for acetic acid sampling mentioned above all use active sampling for validation, specifically activated coconut shell charcoal tubes. We wanted to make sure the IC based methods were transferrable to a different kind of carbon based sorbent (GBAC) and to carbon-PTFE based media.

A total of four different types of media were used for this small study:

- GBAC, loose carbon sorbent (GBAC)
- GBAC with a PTFE binder (GBAC-PTFE)
- In-house manufactured carbon wafer with PTFE binder, (AT-PTFE)
- Commercially available charcoal adsorbent pad (C-Pad)

When performing liquid spikes for a DE study, we noticed the AA standard would form a bead, with a high contact angle, on all the PTFE containing media. The only media where the AA standard appeared to absorb into the media was the GBAC sorbent. This was concerning as it inferred little to no interaction was occurring between the AA standard and the PTFE bound carbon. A DE study normally uses liquid spikes and serves the purpose of mimicking the interaction between the chemical of interest and the absorbing media. It is meant to experimentally determine the amount of analyte released from the media by the extraction solution. If the AA stock solution is just beading up and sitting on top of the carbon-PTFE based media, no interaction may be occurring.

Continuing with the DE study, the results are summarized in the table below, table 1.

Desorption Efficiency – Liquid Spikes

	GBAC	**GBAC-PTFE**	**AT-PTFE**	**C-Pad**
DE	71.7 %	82.9 %	90.2 %	98.5 %
	70.2 %	88.9 %	89 %	98.4 %
Average	70.9 %	85.9 %	89.6 %	94.5 %

Table 1. Summary of desorption efficiency values when done using liquid spikes of an acetic acid standard

All PTFE based media had DE's greater than 85% while the GBAC carbon sorbent had the lowest at 70.9%. A modified OSHA 186SG method (IC analysis) was followed using a desorption solution of 0.02 N NaOH instead of the sodium borate. Although the DE's were relatively high for the carbon-PTFE media, we were not convinced they were true DE's due to the liquid spikes not being readily absorbed. At this point, we decided to perform a vapor spike on the media. This is a much truer version of what would be expected to occur during real time monitoring of acetic acid vapor.

Vapor Spikes using a Chamber Study

All the media was placed in appropriate badge housing and put inside a non-reactive chamber. Acetic acid vapor was generated by heating a high purity acetic acid solution and passed through the chamber using a Miller-Nelson atmosphere generator to control the flow rate, temperature and relative humidity. Vapor concentration was verified using both a fourier transfer infrared (FTIR) instrument for real-time detection and charcoal tubes so as to more closely follow the OSHA 186SG and PV2119 methods. According to the FTIR, a 40 ppm acetic acid vapor environment was generated and according to the charcoal tubes, 39 ppm acetic acid was generated; in good agreement with one another.

Comparing the micrograms (µg) of acetic acid recovered from the various media to the µg recovered from the charcoal tubes and taking into consideration total volume sampled and time sampled, a percent recovered for each media can be calculated. Again, this is compared to µg found on the charcoal tubes which serve as the reference. A table with the values of percent recovered is highlighted below, table 2.

	GBAC	**GBAC-PTFE**	**AT-PTFE**	**C-Pad**
Percent Recovered	70.9%	30.9%	42.2%	25.2%
	77.3%	29.5%	74.0%	24.2%
	77.0%	8.7%	37.6%	21.7%
	79.6%	21.3%	32.3%	25.8%
	75.6%			
	75.4%			
Average:	76.0%	22.6%	46.5%	24.2%

Table 2. Micrograms of acetic acid recovered from various media using 0.02 N NaOH desorption solution and IC analysis. Amounts have been converted into percent recovered compared to charcoal tubes serving as a reference.

The percent recovered from the PTFE based wafers is drastically low with the GBAC-PTFE and C-Pad media being in the 20% range. The in-house C-PTFE did slightly better at an average recovery of 46% but still significantly below the high DE's seen previously with liquid spiking. The GBAC material was the best in the vapor spikes with an average percent recovery of 76%. Comparing this value to the DE obtained with liquid spikes of 70.9%, they are in relatively good agreement with each other further proving the liquid spike DE of ~70% is in fact true.

If a 70% DE is applied to the µg of acetic acid recovered from the GBAC media for the vapor spike and the percent recovered is re-analyzed with the DE correction, the values are much closer to 100% recovery. The DE adjusted values for percent recovered can be seen in table 3.

	GBAC
Percent Recovered	101.3%
	110.4%
	109.9%
	113.7%
	108.0%
	107.8%
Average:	108.5%

Table 3. DE corrected percent recovery of the GBAC media when vapor spiked

This small study readily highlights the simple fact that PTFE based carbon media should not be used for acetic acid vapor monitoring if analysis is to be done via the IC method. The standard method of performing DE studies with liquid spikes leads to false high DE's that are not verified when a vapor spike is performed. If the IC based OSHA methods are to be performed, it is best to use a carbon sorbent not containing PTFE as a binder, like that of the GBAC media.

References

1. "Acetic and Formic Acids in Workplace Atmospheres" OSHA Method no: ID-186SG. April 8, 1993.
2. "Sampling and Analytical Methods: Acetic Acid, PV2119" OSHA Method no: PV2119. Mary E. Eide, February 2003.
3. "Acetic Acid" NIOSH Method: 1603, Issue 2. August 15, 1994.
4. "ChemDisk™ Monitor for Acetic Acid" Technical Insert. Assay Technology. August 10, 2018 edition. https://www.assaytech.com/product/543-acetic-acid-monitor/
5. "Organic Vapor Monitor Sampling and Analysis Guide Technical Bulletin" 3M Occupational Health and Environmental Safety Division. https://multimedia.3m.com/mws/media/110731O/organic-vapor-monitor-sampling-and-analysis.pdf