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FOR
ACETONITRILE EMISSIONS FROM STATIONARY SOURCES**

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Presented At
EPA/A&WMA International Symposium
Measurement of Toxic and Related Air Pollutants
Research Triangle Park, NC
April 1997

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ABSTRACT

A method for measurement of acetonitrile emissions from stationary sources of air pollution has been badly needed. Acetonitrile is a widely used industrial solvent and reaction medium, and appears in numerous hazardous waste streams. Acetonitrile is one of the most difficult non-halogenated compounds to incinerate, and has been suggested as an excellent compound for use as a hazardous constituent spike during trial burn tests of hazardous waste combustors. Lack of an effective sampling and analysis method has prevented its utilization.

This paper describes successful laboratory development and field evaluation of an effective method for sampling acetonitrile from stationary sources. The acetonitrile sampling train uses Modified Method 5 sampling procedures and hardware nearly identical to those described in US EPA Method 0010, but employs Carboxen-1000 sorbent rather than Amberlite XAD-2. A field evaluation conducted according to US EPA Method 301 demonstrated RSDs of 17% and 13% for the 20 unspiked and dynamically spiked samples, respectively. The bias was statistically insignificant, so no bias correction factor was required. The estimated detection limit for the method is 60 ppbv ($100 \mu\text{g}/\text{m}^3$), using quantitation by flame ionization detector.

INTRODUCTION

A method for measurement of acetonitrile emissions from stationary sources of air pollution has been badly needed for a number of years. Acetonitrile is a component of many industrial hazardous waste streams, especially from fiberglass and synthetic fiber manufacturing. Acetonitrile is one of the most difficult non-halogenated compounds to incinerate, and has been suggested as an excellent compound for use as a hazardous constituent spike during Resource Conservation and Recovery Act (RCRA) Subpart-B trial burn tests of hazardous waste combustors. It is important to have a difficult-to-burn spike compound which doesn't produce halogens or halogen acids upon combustion, in order to test combustors not equipped with scrubber systems. Lack of an effective sampling and analysis method for acetonitrile has prevented its utilization as a principal organic hazardous constituent (POHC) indicator compound. In addition to its importance in the field of hazardous waste combustion, acetonitrile is one of the 189 hazardous air pollutants listed in the Clean Air Act Amendments of 1990. Acetonitrile is a widely used solvent and reaction medium, and is employed in production of synthetic fibers, pharmaceuticals, petroleum products, perfumes, and fiberglass.

The 82°C boiling point of acetonitrile along with its high polarity and high water-solubility, all make the compound difficult to sample from stationary sources and to recover and analyze quantitatively. Unconfirmed reports have been received that the compound has been successfully sampled from low moisture emission or process streams, using a midjet impinger train with water as the

collection medium. In theory, a modified Method 0030/ 5041a (VOST) procedure¹ should also work for sources dry enough that no moisture drops are present in the stack, and no condensate is formed during sample collection. The sample would be collected as usual, using Method 0030, but would be analyzed by a modified 5041a where the water filled purge-and-trap chamber would be omitted. This modification would avoid problems caused by the poor efficiency and precision of purging of acetonitrile. No written reports of application of either of these approaches have been identified. In any case, many of the emissions from sources of interest contain moderate to high moisture levels, which greatly complicate the process of collecting and analyzing a representative sample for acetonitrile. The first complication occurs very early in the sampling process. If water droplets larger than 2 µm are present in the emission stream, then isokinetic sampling is necessary in order to avoid non-representative sampling of dissolved acetonitrile. This immediately rules out the use of most methods usually used for volatile organics, including Method 0030, Method 0031¹, Method 0040¹, and Method 18². Each of these methods also contains the potential for serious acetonitrile recovery problems during analysis, caused by the combination of high water-solubility and volatility. Method 0010, a.k.a. MM5 or SemiVOST, samples isokinetically but is designed for collection of compounds with boiling points above 100°C. Lower boiling compounds bind less strongly to the XAD-2 sorbent, and are swept off the end of the column before sampling is completed.

Considerable time and effort was expended trying to turn the high water solubility of acetonitrile into a sampling asset rather than a liability.³ A project was carried out to evaluate collection of acetonitrile in water-filled impingers using standard Method 5 hardware². The intent was to demonstrate a train similar in principle to the reported midget impinger train, but capable of isokinetic sampling. The project was abandoned after a condensate collector followed by 6 sequential water impingers only collected 72% of the acetonitrile. Apparently the relatively higher gas flow rates through the isokinetic train make quantitative trapping of acetonitrile in water impractical. Attempts to increase the collection efficiency by cooling the impingers and by placing oily barrier layers on the water were unsuccessful.

EXPERIMENTAL

It was decided that an experimental train configuration with a back-up sorbent trap after water impingers would be inherently inferior to one with the sorbent ahead of the impingers. Assuming the sorbent had adequate "stopping power," the latter design would concentrate most of the acetonitrile on the sorbent, while the former configuration would result in the compound of interest being distributed through a series of impingers and a sorbent bed.

Final Method

Investigation of revisions to the Method 0010 technology^{4,5,6} produced a method capable of isokinetic sampling and analysis of acetonitrile, which performed better than needed to meet Method 301 acceptance criteria.⁷ The sampling train configuration for the Acetonitrile Sampling Method is shown in Figure 1. Readers familiar with Method 0010 will recognize that the only change in the equipment is the substitution of Carboxen 1000 sorbent for the XAD-2 that is usually used in Method 0010. The analytical recovery method employs a reverse gravity or "backflush" extraction with dichloromethane rather than the usual Soxhlet extraction. Determinative analysis, for this study, was by Gas Chromatography with Flame Ionization Detection (GC/FID). Other detector systems, such as the Nitrogen Phosphorus Detector (NPD) could be used with this method, but Mass Spectrometry (MS) usually performs poorly for acetonitrile.

Laboratory Phase

Sorbent Selection. The first step in modifying Method 0010 for acetonitrile collection was to identify and evaluate a sorbent with a sufficiently high volumetric breakthrough capacity for acetonitrile

that collection would be quantitative after two hours of sampling. It was further reasoned that the extremely high water solubility of acetonitrile might result in a tendency for liquid condensate to strip the compound from the sorbent bed during sampling. The initial screening tests for sorbent performance measured the ability of the sorbent to remove acetonitrile from water and to release the acetonitrile upon extraction.

Selection of the eight sorbents for initial screening was based on a literature survey, discussions with sorbent suppliers, and previous experience of the investigators. Table 1 shows the eight sorbents, suppliers of each sorbent, and the results of initial screening tests. "%ACN Retained" is the portion of the acetonitrile retained on a sorbent column when an aqueous solution of 250 ppm concentration was passed through it. The percentage retained was acquired by analysis of the eluant for acetonitrile, followed by subtraction of the amount of acetonitrile in the eluant from the amount introduced to the column and reduction to a percentage. No attempt to recover the acetonitrile from the resin was made during this phase of the test. The negative retention figure for Amberlite XAD-7 was a result of sorbent contamination. The eluant contained more acetonitrile, or another interfering compound, than was contained in the original solution passed through the column. The test was repeated with similar results. Since several other compounds showed excellent retention, it was not worthwhile developing a cleaning procedure for the XAD-7. Amberlite 200 and Porapak N both exhibited unacceptable retention for acetonitrile, and were eliminated from further consideration along with XAD-7.

The remaining five sorbents were tested to determine recovery of sorbed acetonitrile after extraction with several solvents. A small column, containing 4-6 g of each sorbent was spiked with 25 mg of acetonitrile in 100 mL of water and then extracted by simple column elution. The column in Table 1 labeled "%ACN Recovered" lists the recoveries from each sorbent with dichloromethane elution. Similar recoveries were obtained by elution with mixed carbon disulfide/dimethylformamide and with mixed dichloromethane/butanol. Ease of handling and simplicity of dealing with a single solvent rather than a mixture dictated that the solvent of choice be dichloromethane. Porapak T was dropped from further consideration because of its extremely poor recovery performance. It can easily be seen that Carboxen 1000 was far superior to the other sorbents in these initial screening tests, and could have been chosen as the sole sorbent for further evaluation based on the results in Table 1. Because of the high cost and questionable availability in bulk of Carboxen 1000, the other three top sorbents in Table 1 were carried throughout the further extraction experiments, described below, in hope that one of them would exhibit acceptable behavior as the extraction process was optimized. All three did show improved results, but never reached performance levels of Carboxen 1000.

Extraction Studies. Initial attempts to scale up the extraction procedure for use with full size Method 0010 sorbent modules produced highly variable recoveries. A reverse gravity elution procedure as shown in Figure 2 was considerably more successful. Reverse gravity elution of 70 mL of dichloromethane through the sorbent module resulted in better than 90% recovery of acetonitrile from Ambersorb XEN-563, Carboxen 1000, and Anasorb 747. The acetonitrile recovery from Carboxen 569 was less than 40% with dichloromethane. Recovery of acetonitrile from this sorbent was improved to 80% by use of 1:1 carbon disulfide/dimethylformamide as the extraction solvent. This level of performance was adequate for use in full scale sampling train tests.

Full Scale Sampling Train Tests. The ability of the four sorbents to remove acetonitrile from simulated stack gas containing high levels of moisture was evaluated using sampling trains containing multiple sorbent modules in series. Because a limited supply of Carboxen 1000 was available, only two Carboxen 1000 traps were used in series. Three sequential modules were used in testing the other three sorbents. The trains were dynamically spiked with an aqueous solution of acetonitrile. Each train was rinsed with 1:1 methanol/dichloromethane for the front half and methanol for the condenser and

condensate collector. The results in Table 2 were obtained using simulated stack gas containing 20-30% moisture and dynamic spike levels of 32-45 ppmv of acetonitrile. Each entry represents a single experimental run. Although all four sorbents performed well from an overall recovery standpoint, the ability of the Carboxen 1000 to collect virtually all of the acetonitrile on the first sorbent module made it a clear winner and the sorbent selected for field evaluation. Carboxen 1000 is a carbon molecular sieve sorbent available from Supelco Inc. in 60/80 mesh size. It is slightly hydrophobic, which tends to be helpful in sampling high moisture stack gas. Approximately 48 g of the sorbent is needed to fill a typical Method 0010 sorbent module. At the time of testing, the cost of a module full of the sorbent was approximately \$400.

Field Test

The newly developed acetonitrile sampling and analysis procedures were field tested using an experimental design consistent with guidance outlined in EPA Method 301, "Protocol for the Field Validation of Emission Concentrations from Stationary Sources." The field test included ten "quad train" runs at a single hazardous waste incinerator emission source. For each quadruple run, four independent flue gas samples were collected. Two of the sampled gas streams for each quad run were dynamically spiked with known concentrations of acetonitrile equivalent to approximately 45 ppmv in the stack gas. The dynamic spiking procedure and equipment have been described in previous publications.^{8,9} The precision of the test method was estimated from the variation in results obtained for pairs of spiked and unspiked samples. Accuracy (bias) was determined from the differences between the spiked and measured quantities of acetonitrile.

Ten quad runs (40 sample trains) were scheduled during the testing program. All 40 independent trains were completed and accepted during the test period. This completion rate exceeded the minimum requirement of at least six quad runs (24 independent trains) for statistical analysis by Method 301. This number of runs provided a sample population large enough to produce credible data quality assessments as described in the project report.⁶ The static pressure in the stack was positive, and remained constant at approximately 6.35 mm (0.25 inches) of water during all test runs. The average sample volume collected was 0.959 ± 0.041 dry standard cubic meters (33.9 ± 1.5 dry standard cubic feet). The sampling time was 60 minutes. Moisture values ranged from 15 to 28% by volume. Moisture values were low (15 %) for one run because the process was interrupted during the run. The process interruption did not affect the test data. The source did not contain acetonitrile so acetonitrile levels in the unspiked trains were not reduced by the interruption.

The samples were collected in seven fractions: the probe rinse, the rinse of the front half of the filter housing, the filter, the rinse of the back half of the filter and the condenser rinse, the sorbent, the condensate, and the impinger contents. The probe rinse was collected at the end of each day. The other fractions were collected for each train. Runs 4 and 5 had two sequential sorbent modules, which were collected and analyzed separately in order to gain additional information about breakthrough. The high cost and limited bulk availability of the Carboxen 1000 prevented equipping all ten of the quad runs with two sorbent modules. All of the fractions for Runs 4 and 5, except for the impinger fraction, were analyzed. Runs 1 through 3 and Runs 6 through 10, had one sorbent fraction. Only the sorbent and condensate fractions were analyzed for these runs. The impinger components of the trains were not analyzed and were archived. No acetonitrile was detected in any of the sample fractions except the sorbent and some of the condensates.

The percentage of acetonitrile recovered in all of the analyzed components of each spiked sampling train ranged from 74 to 119% for the 20 spiked trains. The average recovery was 100%. The relative standard deviation was 13%. Recovery results for individual spiked runs are shown in Table 3. Data for unspiked runs are in the field report,⁶ but show no significant acetonitrile content.

The second sorbent module in Runs 4 and 5 were analyzed, in order that breakthrough of acetonitrile into the second sorbent could be examined. Any amount of compound detected in the second

sorbent was classified as having broken through the first sorbent module. For the four spiked double sorbent module trains, breakthrough ranged from 2 to 8 percent. The average breakthrough was 4 percent. The relative standard deviation was 90 percent. Breakthrough of acetonitrile was inconsistent. Three of the trains exhibited 2% breakthrough, while one train exhibited 8% breakthrough. No reason was identified to explain why breakthrough was higher in the one train.

The condensate fraction was analyzed for Runs 1 through 3 and Runs 6 through 10, in order that breakthrough of acetonitrile into the condensate could be estimated. Since acetonitrile is not quantitatively collected in water, some of the acetonitrile that broke through the sorbent may not have been collected, thus causing low bias in the breakthrough estimates for the single sorbent trains. Any amount of acetonitrile detected in the condensate was classified as having broken through the sorbent module. No acetonitrile was detected in the condensate for the unspiked single sorbent module trains. Thus, no breakthrough analysis was possible using these samples. For the 16 spiked double sorbent module trains, breakthrough ranged from 0 to 11 percent. The average breakthrough was 5 percent. The relative standard deviation was 73 percent. Two of the trains exhibited 0% breakthrough. These were the two spiked trains collected when the process went down. Less moisture was collected during this run than during the other runs, so it may be speculated that the amount of moisture in the source may contribute to the amount of acetonitrile that breaks through the sorbent. One train exhibited 11% breakthrough. Calculated breakthrough for all of the other trains was less than 10 percent. Again, breakthrough of acetonitrile was inconsistent. No explanation of why breakthrough was higher in some trains was identified. Breakthrough was <10% for 95% of the spiked trains. For 50% of the spiked trains, breakthrough was <5%. Use of two sorbent modules in series may be necessary when sampling sources containing higher levels of moisture.

CONCLUSIONS

Based on laboratory studies and one field test, the acetonitrile train consisting of a Method 0010 train with 48 g of Carboxen 1000 in the sorbent module, is adequate for sampling and collection of acetonitrile from hazardous waste incinerators, and probably other combustion sources. Extraction using a reverse gravity elution with dichloromethane, followed by analysis with GC/FID was effective.

- The bias for acetonitrile (0.07 mg of acetonitrile at the 74 mg level) was calculated and shown to be insignificant using Method 301 statistical procedures. Thus, no bias correction factor is needed.
- The relative standard deviations were 13% for spiked trains and 17% for unspiked trains. These standard deviations are within the Method 301 criteria of < 50%.
- The mean recovery of 100% and relative standard deviation of 13% for the spiked trains is within the EPA's Quality Assurance Handbook⁹ requirements of 50 to 150% recovery and less than 50% relative standard deviation.
- The detection limit, estimated according to Method 301, for the method is 60 ppbv (100 $\mu\text{g}/\text{m}^3$), using quantitation by flame ionization detector.
- Greater than 90% of the recovered acetonitrile was collected on the Carboxen-1000. Essentially no acetonitrile was collected in the probe rinses, in the rinse of the front half of the filter holder, or on the filters.
- For the four spiked trains containing dual sorbent modules, less than 2% of the acetonitrile broke through to the second module for three of the trains and less than 8% broke through in the fourth train.

- For the 16 spiked trains containing single sorbent modules, less than 5% of the acetonitrile broke through to the condensate for eight of the trains and less than 9% broke through for 15 trains.

STATUS

A draft method and report are currently under review, and are expected to be available by July 1997. The draft acetonitrile method will be transmitted to EPA's Office of Solid Waste (OSW) and to EPA's Office of Air Quality Planning and Standards (OAQPS). It is expected that OSW will eventually publish the method as part of a future update to the SW-846 Methods Manual, and that OAQPS will likely include it in their collection of Provisional Test Methods.

ACKNOWLEDGEMENTS

The following people contributed to one or more phases of the work reported here: Merrill Jackson, EPA (retired), Ray Merrill, David Epperson, Amy Bederka, Danny Harrison, Steve Hoskinson, Cheryl Klassa, Jim Howes and Mark Owens, all with Radian Corp./Eastern Research Group at the time of their contributions. Because of the long time span involved in the multiphase project, it is inevitable that others who deserve recognition have been left off this list. To them, we apologize.

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contracts 68-D1-0010 and 68-D4-0022 to Radian Corp. and Eastern Research Group. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 1. Results of initial sorbent retention and recovery tests.

Sorbent	Supplier	% ACN Retained	% ACN Recovered
Ambersorb XEN-563	Supelco	95	66
Anasorb 747	SKC	85	53
Carboxen 569	Supelco	88	33
Carboxen 1000	Supelco	99	94
Porapak T	Supelco	92	6
Porapak N	Supelco	16	Not tested
Amberlite 200	ICN	8	Not tested
Amberlite XAD-7	Supelco	-17	Not tested

Table 2. Laboratory train recoveries.

Sorbent	Tube 1	Tube 2	Tube 3	Liquid	Total, %
Ambersorb XEN-563	85	15	4	1	105
	76	11	5	1	93
Carboxen 1000	89	1	0	0	90
	99	1	0	0	100
Carboxen 569	75	18	7	1	101
	88	7	2	1	98
Anasorb 747	75	17	4	1	97
	81	14	5	1	101

Table 3. Field test recoveries.

Run	Acetonitrile Recovery ^a (%)	
	Train A	Train B
1	105	111
2	89.3	100
3	95.6	114
4	99.2	97.2
5	101	104
6	73.8	108
7	83.9	114
8	109	87.6
9	103	74.9
10	109	119

^aSpike Recovery = (100)(Amount Recovered in Train)/(Amount Spiked)

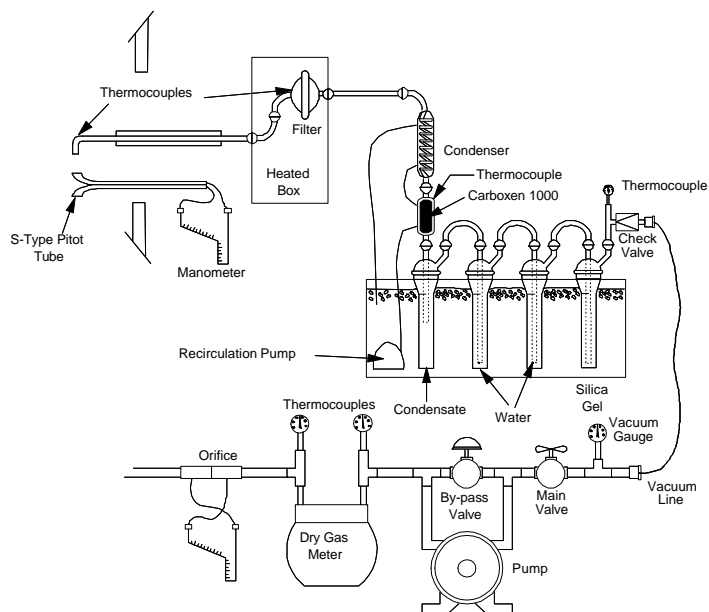


Figure 1. Acetonitrile sampling train.

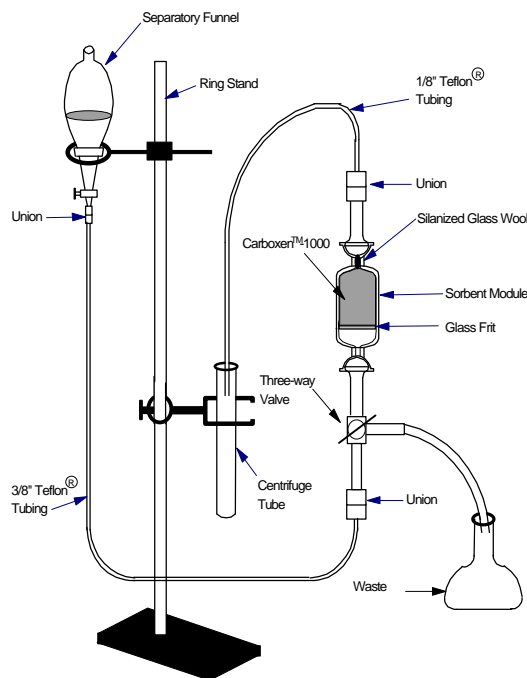


Figure 2. Reverse gravity sorbent extraction.