Acetic Anhydride

Related Information: Chemical Sampling - Acetic Anhydride

Method no.:	102
Matrix:	Air
Target concentration: OSHA PEL: ACGIH TLV:	5 ppm (20 mg/m^3) 5 ppm (20 mg/m^3) TWA 5 ppm (20 mg/m^3) ceiling
Procedure:	Samples are collected open face on glass fiber filters coated with veratrylamine and di-n-octyl phthalate. Samples are extracted with 50/50 (v/v) 2-propanol/toluene and analyzed by GC using a nitrogen-phosphorus detector (NPD).
Recommended air volume and sampling rate:	7.5 L at 0.5 L/min ceiling 7.5 L at 0.05 L/min TWA
Reliable quantitation limit:	0.094 ppm (0.39 mg/m^3)
Standard error of estimate at the target concentration:	6.4%
Special caution:	Ketene and acetyl chloride produce the same derivative as acetic anhydride. Coated filters should be used within a month of preparation.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

October 1993

Yihlin Chan

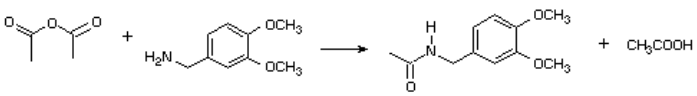
Methods Development Team
Industrial Hygiene Chemistry Division
OSHA Salt Lake Technical Center
Sandy UT 84070-6406

1. General Discussion

1.1 Background

1.1.1 History

In OSHA Method 82, acetic anhydride is collected on a glass fiber filter impregnated with 1-(2-pyridyl)piperazine, which reacts with the anhydride to form a derivative (Ref. 5.1). Attempts at using 1-(2-pyridyl)piperazine for the derivatization of maleic, phthalic, and trimellitic anhydrides failed, however, because the resulting derivatives of these anhydrides were found to be unstable. These anhydrides were derivatized with veratrylamine instead (Refs. 5.2-5.4). Di-n-octyl phthalate was added to the filter to improve collection efficiency. In an effort to have a common sampler for all four anhydrides, the use of veratrylamine as the derivatizing agent for acetic anhydride was evaluated. The equation for the derivatization reaction is shown below:



The acetic anhydride-veratrylamine derivative (AcVA) can be analyzed either by HPLC or GC; GC was selected for this evaluation. The method was evaluated at the then current OSHA PEL of 5 ppm (20 mg/m^3) ceiling. But after the evaluation work had been completed and the method was being written, the PEL was reverted back to 5 ppm (20 mg/m^3) TWA (Ref. 5.5). The validity of the sampling capacity at a slower flow rate was reevaluated in order to accommodate a longer sampling time.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

The following is quoted from the ACGIH Documentation of TLV:

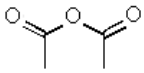
Smyth et al reported an oral LD_{50} in rats as 1.78 g/kg. Henderson and Haggard mentioned eye, nose and throat irritation and suggested that bronchial and lung injury were likely to occur from inhalation of acetic [an]hydride vapor. Fairhall considered acetic anhydride a marked lachrymator and found systemic effects unlikely. McLaughlin discussed serious corneal injury from the liquid in industry. Smyth found rats inhaling 1000 ppm for four hours survived, but 2000 ppm was fatal. The liquid causes skin burns. No cumulative effects are known. The value of 5 ppm, as a ceiling limit, is recommended by analogy with acetic acid and to prevent undue irritation. (Ref. 5.6)

The OSHA PEL for acetic anhydride is 5 ppm (20 mg/m^3) TWA. (Ref. 5.5)

1.1.3 Workplace exposure

Exposure to acetic anhydride may occur in the following operations: manufacture of cellulose esters, fibers, plastics, lacquers, protective coating solution, photographic films, cigarette filters, magnetic tape, and thermoplastic molding compositions; manufacture of pharmaceuticals and pharmaceutical intermediates; use in organic synthesis as an acetylating agent, bleaching agent, and dehydrating agent; synthesis of perfume chemicals, explosives, and weed killers; use in acetylation of animal and vegetable oils; use as an acetylating and dehydrating agent in textile dyeing, chemical treatment of paper, and chemical analysis. (Ref. 5.7) Of these, by far the greatest single application for acetic anhydride is in the manufacture of cellulose esters. It is estimated that 95% of the total U.S. production is used for this purpose. (Ref. 5.8)

1.1.4 Physical properties and other descriptive information (Ref. 5.9)

CAS no.:	108-24-7
synonyms:	acetic acid, anhydride; acetic oxide; acetyl anhydride; acetyl ether; acetyl oxide; ethanoic anhydrate
structural formula:	
molecular wt:	102.10
boiling point:	139°C
melting point:	-73°C
appearance:	colorless liquid
odor:	strong acetic odor
vapor pressure:	0.67 kPa (5 mmHg) at 25°C
flash point:	49°C (closed-cup)
solubility:	slowly soluble in water, forming acetic acid; forms ethyl acetate with ethyl alcohol; soluble in chloroform, ether.

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg). The analyte amounts and concentrations are listed as those of acetic anhydride even though the derivative is the actual species analyzed.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 6.1 pg. This is the amount of analyte that will give a response that is significantly different from the background response of a reagent blank. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.88 µg per sample (0.028 ppm or 0.12 mg/m^3). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 2.94 µg per sample (0.094 ppm or 0.39 mg/m^3). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precision of the analytical procedure, measured as the pooled relative standard deviation over a concentration range equivalent to 0.5 to 2 times the target concentration, is 0.53%. (Section 4.5)

1.2.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage test (at the target concentration) is ±12.5% (Section 4.6). This includes an additional 5% for sampling error.

1.2.6 Recovery

The recovery of AcVA from samples used in a 15-day storage test remained above 96.1% when the samples were stored at ambient temperature. (Section 4.7)

1.2.7 Reproducibility

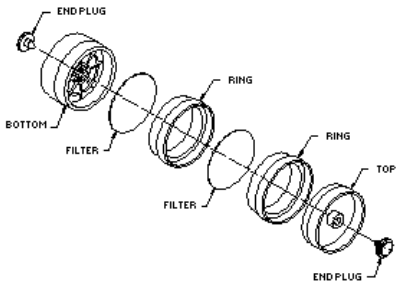
Six samples collected from a controlled test atmosphere, with a draft copy of this procedure, were submitted to an SLTC service branch for analysis. The samples were analyzed after 2 days of storage at 5°C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.8)

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to ±5% of the recommended flow rate.

2.1.2 Samples are collected with a four-piece polystyrene cassette containing two coated glass fiber filters assembled as shown. Each treated filter is coated with 10 mg of veratrylamine (3,4-dimethoxybenzylamine) and 10 mg of di-n-octyl phthalate. Di-n-octyl phthalate is added to improve the collection efficiency.



2.1.3 The treated filters are prepared as follows: To make 40 coated filters, weigh 0.4 g of veratrylamine and 0.4 g of di-n-octyl phthalate in a scintillation vial. Add 16 mL of methanol and shake well. Place glass fiber filters on a clean glass plate. Apply 0.4 mL of the methanol solution to each filter. Air dry for 5 minutes. Place filters in a wide-mouth jar. Dry under vacuum at room temperature overnight. Store the coated filters in a refrigerator and use within a month. Filters stored longer than this period developed several small interfering peaks (believed to be decomposition products of veratrylamine) in the chromatogram.

2.2 Reagents

None required.

2.3 Technique

2.3.1 Prepare the sampler for open-face sampling by removing the top piece and the end plug from the bottom piece. Attach the sampler to the sampling pump with a piece of flexible tubing and place it in the worker's breathing zone with the open face of the cassette facing down.

2.3.2 Replace the top piece and the end plug after sampling. Wrap each sample with a Form OSHA-21 seal.

2.3.3 Submit at least one blank with each set of samples. Blanks should be handled in the same manner as samples, except no air is drawn through them.

2.3.4 Record sample air volume for each sample.

2.3.5 List any compounds that could be considered potential interferences.

2.4 Sampler capacity

Sampling capacity is determined by measuring how much air can be sampled before breakthrough of analyte through the sampler occurs. Breakthrough is considered to occur when the effluent from the sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). The sampler capacity was determined to be over 30 L at a sampling rate of 0.5 L/min with an acetic anhydride concentration of 40 mg/m^3 (2 times the target concentration). At a sampling rate of 0.05 L/min, 5% breakthrough point was not reached in 18 L. (Section 4.9)

2.5 Extraction efficiency

2.5.1 The average extraction efficiency for AcVA from the treated glass fiber filter over the range of 0.5 to 2.0 times the target concentration was 99.8%. (Section 4.10.1)

2.5.2 The extraction efficiency at 0.2, 0.1, and 0.05 times the target concentration was found to be 100.9%, 107.8%, and 108.0% respectively. (Section 4.10.1)

2.5.3 Extracted samples remain stable for at least 24 h. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1. For TWA samples the recommended air volume is 7.5 L at 0.05 L/min.

2.6.2. For short-term samples the recommended air volume is 7.5 L at 0.5 L/min.

2.7 Interferences (sampling)

2.7.1 Acetyl chloride and ketene react with veratrylamine to form AcVA, causing positive interference. But in most industrial applications they are rarely used together with acetic anhydride. Other compounds that react with veratrylamine, such as isocyanates, acyl halides, and other anhydrides, may interfere by consuming part of the derivatizing agent.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 All safety practices that apply to the work area being sampled should be followed.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with an NPD. A Hewlett-Packard 5890 GC equipped with an NPD and a 7673 autosampler were used in this evaluation.

3.1.2 A GC column capable of separating AcVA, benzalazine, and any interferences. A 5-m HP-1 (0.53-mm i.d., 2.65-µm film) column was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Scintillation vials, 20-mL glass, with poly(tetrafluoroethylene)-lined caps.

3.1.5 A dispenser capable of delivering 5.0 mL of extraction solvent.

3.2 Reagents

3.2.1 Acetic anhydride. Acetic anhydride, ACS reagent grade, was obtained from Aldrich Chemical.

3.2.2 Veratrylamine. Veratrylamine, 97%, was obtained from Aldrich.

3.2.3 Benzalazine. Benzalazine (95-99%) from ICN was used in this evaluation.

3.2.4 Toluene. Toluene, Optima grade, was obtained from Fisher.

3.2.5 2-Propanol. 2-Propanol, Optima grade, was obtained from Fisher.

3.2.6 Extraction solvent with internal standard. Dissolve 30 mg of benzalazine in 1 L of 2-propanol/toluene (50/50).

3.3 Standard preparation

3.3.1 Synthesis of AcVA:

With constant stirring, slowly add a solution of 5.18 g of veratrylamine in 25 mL of toluene to a solution of 3.23 g of acetic anhydride in 25 mL of toluene. Continue stirring for 10 more minutes. Isolate the product by distillation; b.p. 175-178°C at 0.67 kPa (2 mmHg); m.p. 87.0-88.5°C.

3.3.2 Prepare stock standards by weighing about 10 mg of AcVA in 10-mL volumetric flasks and diluting to volume with the extraction solution. Apply a factor of 0.4880 to the weight of AcVA to convert it to that of acetic anhydride. For example, 10 mg of AcVA dissolved in 10 mL will give a standard stock solution representing 488.0 µg/mL of acetic anhydride.

(MW acetic anhydride) / (MW AcVA) = 102.09 / 209.2 = 0.4880

3.3.3 Prepare analytical standards by diluting the stock standards with extraction solvent. A 30 µg/mL standard solution corresponds to the target concentration.

3.3.4 Prepare a sufficient number of analytical standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations.

3.4 Sample preparation

3.4.1 Transfer the two filters to separate scintillation vials.

3.4.2 Add 5.0 mL of the extraction solvent to each vial.

3.4.3 Cap the vials and shake them on a mechanical shaker for 30 min.

3.5 Analysis

3.5.1 GC conditions

column:	HP-1 (5-m, 0.53-mm i.d., 2.65-µm film)	
zone temp:	column	150°C to 270°C at 10°C/min
	injector	270°C
	detector	300°C
gas flow:	column (He)	1.83 mL/min
	hydrogen	3.84 mL/min
	auxiliary (N_2)	27.4 mL/min
	air	110.5 mL/min
	split vent	68 mL/min (split ratio 37:1)
ret. times:	AcVA	3.8 min
	benzalazine	4.5 min (ISTD)

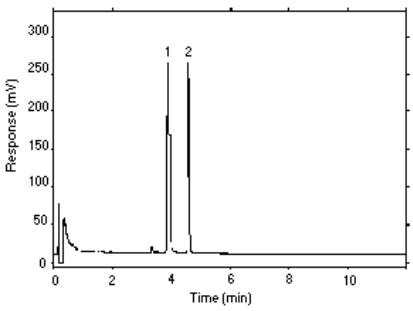


Figure 3.5.1.1. Chromatogram of a standard at the target concentration.
Key: 1 = AcVA, 2 = benzalazine (internal standard).

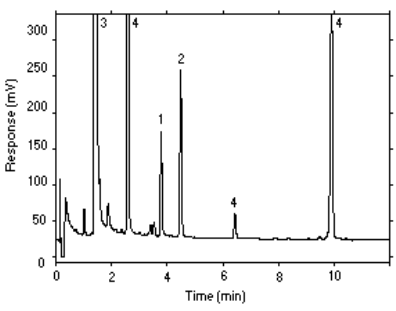


Figure 3.5.1.2. Chromatogram of an extracted sample at 0.75 times target concentration.
Key: 1 = AcVA, 2 = benzalazine, 3 = veratrylamine, 4 = impurities.

3.5.2 Peak areas are measured by an electronic integrator or other suitable means.

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve is prepared by plotting micrograms per milliliter

versus ISTD-corrected response of standards. Bracket the samples with analytical standards.

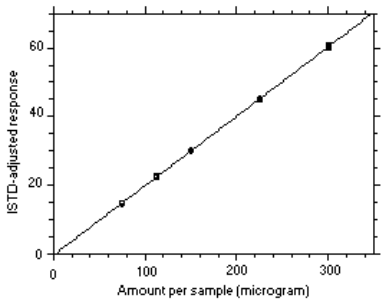


Figure 3.5.3. Calibration curve constructed from the data in Table 4.5.
Equation for the line is Y = 0.203X - 0.574.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an NPD response and has a similar retention time as benzalazine or AcVA is a potential interference. If any potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data (Section 4.11).

3.7 Calculations

The amount of acetic anhydride per sample is obtained from the appropriate calibration curve in terms of micrograms uncorrected for extraction efficiency. The back filter is analyzed primarily to determine the extent of breakthrough. If any analyte is found on the back filter, it is added to the amount on the front filter. This total amount is then corrected by subtracting the total amount (if any) found on the blank. The air concentration is calculated using the following formulae.

$$mg/m^3 = \frac{\text{micrograms of acetic anydride per sample}}{\text{liters of air sampled} \times \text{extraction efficiency}}$$

$$ppm = \frac{24.46 \times mg/m^3}{\text{molecular weight of acetic anhydride}} = (0.2396)\ (mg/m^3)$$

3.8 Safety precautions (analytical)

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1 Determination of detection limits

Detection limits (DL), in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total number of data points
k = 2 for linear regression curve

At point Y_{DL} on the regression curve
$Y_{DL} = A(DL) + Y_{BR}$ A = analytical sensitivity (slope)
therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DL}gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte actually introduced into the chromatographic column. Ten analytical standards whose concentrations were equally spaced from 0 to 1.202 µg/mL were prepared. The standard containing 1.202 µg/mL represented approximately 10 times the baseline noise. The data obtained from analyzing these standards were used to determine the required parameters (A and SEE) for the calculation of the DLAP. Values of 0.0368 and

0.0751 were obtained for A and SEE respectively. DLAP was calculated to be 6.1 pg.

Table 4.2.
Detection Limit of the Analytical Procedure

concentration (µg/mL)	mass on column (pg)	ISTD-adjusted response
0	0	0.030
0.120	3.2	0.063
0.240	6.5	0.379
0.361	9.7	0.383
0.481	13.0	0.347
0.601	16.2	0.594
0.721	19.5	0.724
0.842	22.7	0.850
0.967	26.0	0.942
1.082	29.2	1.034
1.202	32.5	1.283

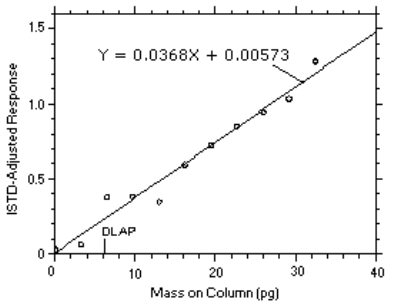


Figure 4.2. Plot of data to determine the DLAP.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten treated filters were spiked with amounts of AcVA equally spaced from 0 to 6.01 µg/sample. The latter amount, when spiked on a sampler, would produce a peak approximately 10 times the baseline noise for a sample blank. These spiked filters were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 1.35 and 0.3975 were obtained for A and SEE respectively. DLOP was calculated to be 0.88 µg/sample (0.028 ppm, 0.12 mg/m^3).

Table 4.3
Detection Limit of the Overall Procedure

mass per sample (µg)	ISTD-adjusted response
0	0.88
0.60	1.70
1.20	2.71
1.80	3.19
2.40	3.31
3.01	3.98
3.61	5.62
4.21	6.36
4.81	7.09
5.41	8.36
6.01	9.04

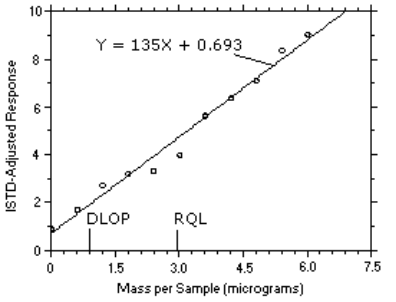


Figure 4.3. Plot of data used to determine the DLOP/RQL.

4.4 Reliable quantitation limit

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 4.3), providing at least 75% of the analyte is recovered. The RQL is defined as the amount of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

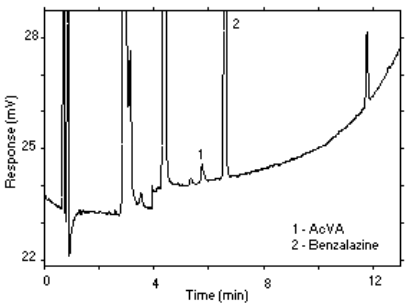


Figure 4.4. Chromatogram of the RQL.

The RQL was calculated to be 2.94 µg per sample (0.094 ppm, 0.39 mg/m^3). Recovery at this concentration is 103.0%.

4.5 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled relative standard deviation (RSD_P). Relative standard deviations were determined from six replicate injections of analytical standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, RSD_P was calculated to be 0.53%.

Table 4.5
Instrument Response to AcVA

× target concn µg/mL	0.5× 15.03	0.75× 22.55	1× 30.06	1.5× 45.09	2× 60.12
ISTD-adjusted	14.541	22.342	30.142	45.009	59.990

response	14.546	22.188	30.109	44.842	60.253
	14.553	22.316	30.066	44.994	60.396
	14.657	22.431	30.149	44.909	60.917
	14.686	22.320	29.908	45.081	60.519
	14.679	22.673	29.850	45.163	60.976
$\bar{x}$	14.610	22.378	30.037	45.000	60.509
SD	0.0705	0.1640	0.1274	0.1153	0.3827
RSD (%)	0.483	0.733	0.424	0.256	0.632

The Cochran test for homogeneity:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5x}^2 + RSD_{0.75x}^2 + RSD_{1x}^2 + RSD_{1.5x}^2 + RSD_{2x}^2} = 0.3796$$

Since the g statistic does not exceed the critical value of 0.5065, the RSDs can be considered equal and they can be pooled (RSD_P) to give an estimated RSD for the concentration range studied.

$$RSD_P = \sqrt{\frac{5(RSD_{0.5x}^2 + RSD_{0.75x}^2 + RSD_{1x}^2 + RSD_{1.5x}^2 + RSD_{2x}^2)}{5+5+5+5+5}} = 0.53\%$$

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE_R is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery form the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1 and 4.7.2. The precision of the overall procedure of ±12.5% was obtained from Figure 4.7.1.

4.7 Storage test

Storage samples for AcVA were prepared from a controlled test atmosphere of acetic anhydride. Thirty-six samples were collected. Six samples were analyzed on the day of preparation. The rest of the samples were divided into two groups: 15 were stored at 5°C, and the other 15 were stored in a closed drawer at ambient temperature (about 22°C). At 2-4 day intervals, three samples were selected from each of the two storage sets and analyzed.

Table 4.7
Storage Test for AcVA

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	102.2	103.4	93.2	102.2	103.4	93.2
0	98.8	98.0	104.3	98.8	98.0	104.3
3	95.0	91.8	101.6	111.0	96.7	98.8
7	103.0	106.5	99.9	90.9	107.0	109.7
10	97.8	99.2	97.9	111.4	104.1	111.1
13	92.3	96.5	98.3	105.9	100.8	102.4
15	94.2	93.0	97.6	96.5	98.1	94.5

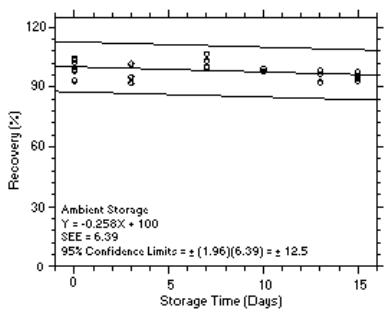


Figure 4.7.1. Ambient storage test for AcVA.

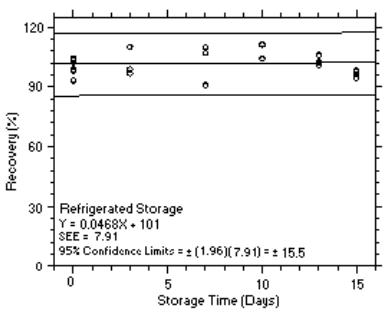


Figure 4.7.2. Refrigerated storage test for AcVA.

4.8 Reproducibility

Six samples were prepared by collecting them from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to an SLTC service branch for analysis. The samples were analyzed after being stored for 2 days at 5°C. No sample result had a deviation greater than the precision of the overall procedure determined in Section 4.7, which is ±12.5%

Table 4.8
Reproducibility Data

mg/m^3 expected	mg/m^3 found	percent found	percent deviation
33.58	32.20	95.9	-4.1
33.58	32.63	97.2	-2.8
33.58	32.14	95.7	-4.3
33.58	30.11	89.7	-10.3
33.58	29.71	88.5	-11.5
33.58	31.31	93.2	-6.8

4.9 Sampler capacity

The sampler capacity was assessed by sampling from a dynamically generated test atmosphere of acetic anhydride at 2 times the target concentration and at 25°C and 80% RH. The test atmosphere of acetic anhydride was generated by pumping an ethyl acetate solution of acetic anhydride at a rate of 9.9 mg/min (11 mg/mL × 0.9 mL/min) through a TSI Model 3076 atomizer where it was dispersed with an air stream of 3.5 L/min. The aerosol passed through an electrostatic charge neutralizer and was mixed with a dilution air stream of 47 L/min. The test atmosphere was drawn through a sampler consisting of two filters in series (separated by a spacer ring) at 0.5 L/min. Three samplers were used in each of the two experiments. At 15-min intervals, the flow was stopped and the back filters were replaced with new ones. This was repeated six times. At the end of the experiment, all the back filters as well as the front filters were analyzed for AcVA. The downstream air concentration was obtained by dividing the amount found on the back filter by the air volume. The upstream concentration was obtained by dividing the sum of amounts found on the front as well as all the back filters by the total air volume. The breakthrough is defined as the downstream concentration divided by the upstream concentration. The average breakthrough for each sampling period versus the air volume was plotted in Figure 4.9.1. No clear indication of exceeding the 5% breakthrough limit was observed in 45 L.

Additionally, two experiments with four samplers were conducted with vapor generator system where acetic anhydride in ethyl acetate was simply evaporated directly into an air stream. The breakthrough data obtained with acetic anhydride vapor were plotted in Figure 4.9.2. The data obtained from the two experiments were not very consistent but both showed that the 5% breakthrough point is over 30 L. The recommended air volume of 7.5 L provides an ample margin of safety against exceeding sampler capacity.

When the OSHA PEL was changed from 20 mg/m^3 ceiling to 20 mg/m^3 TWA, a breakthrough curve was also determined at a flow rate of 0.05 L/min. First, it was determined that sampling at flow rates of 0.5, 0.1, and 0.05 L/min resulted in the same concentration of acetic anhydride in the test atmosphere. This indicated that all three flow rates were suitable for collecting acetic anhydride atmosphere. The flow rate of 0.05 L/min was selected in order to accommodate a longer sampling time for TWA sampling. The breakthrough data with 0.05 L/min were plotted in Figure 4.9.3. The 5% breakthrough point was not reached in 18 L.

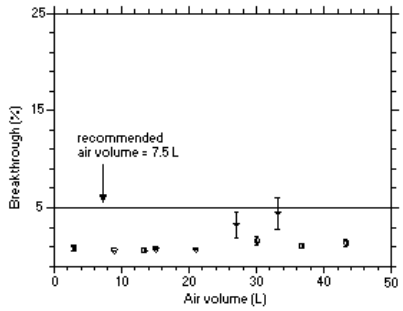


Figure 4.9.1. Capacity test for acetic anhydride at a flow rate of 0.5 L/min (aerosol).

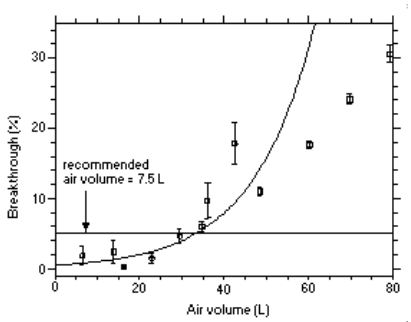


Figure 4.9.2. Breakthrough curve for acetic anhydride at a flow rate of 0.5 L/min (vapor).

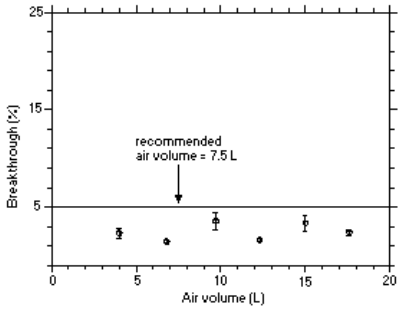


Figure 4.9.3. Capacity test for acetic anhydride at a flow rate of 0.05 L/min (aerosol).

4.10 Extraction efficiency and stability of extracted samples

4.10.1 Extraction efficiency

The extraction efficiencies (EE) of AcVA were determined by liquid-spiking the treated glass fiber filters with AcVA at 0.05 to 2 times the target concentrations. These samples were stored overnight at ambient temperature and then extracted and analyzed. The average extraction efficiency over the working range of 0.5 to 2 times the target concentration was 99.8%.

Table 4.10.1

Extraction Efficiency

× target conc (µg)	0.05× 7.46	0.1× 14.92	0.2× 29.83	0.5× 74.58	1.0× 149.2	2.0× 298.3
EE (%)	113.0	102.3	100.4	98.2	100.6	96.9
	87.4	98.1	98.7	95.4	102.5	98.1
	109.3	103.6	101.9	104.3	99.2	98.4
	106.5	106.0	102.5	98.0	101.0	101.3
	120.4	132.6	104.4	96.8	104.4	99.2
	111.5	104.0	97.3	101.6	101.7	97.4
$\bar{x}$	108.0	107.8	100.9	99.1	101.6	98.6

4.10.2 Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed three vials were recapped with new septa while the remaining three retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -4.8% for samples that were resealed with new septa, and -2.0% for those that retained their punctured septa.

Table 4.10.2
Stability of extracted samples

punctured septa replaced			**punctured septa retained**		
initial EE (%)	EE after one day (%)	difference	initial EE (%)	EE after one day (%)	difference
100.6	94.3	-6.3	101.0	98.9	-2.1
102.5	98.2	-4.3	104.4	103.5	-0.9
99.2	95.5	-3.7	101.7	98.8	-2.9
	(averages)			(averages)	
100.8	96.0	-4.8	102.4	100.4	-2.0

4.11 Qualitative analysis

The GC/MS of AcVA can easily be obtained by using GC conditions similar to those given in Section 3.5. A Perkin-Elmer Ion Trap Detector interfaced to a Hewlett-Packard Series II GC was used to obtain the mass spectra shown at right.

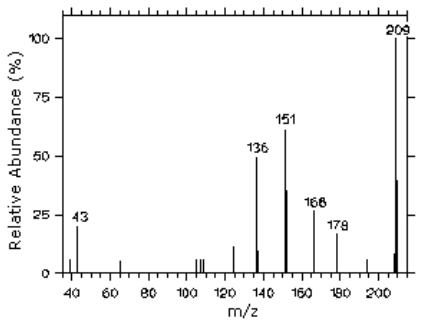


Figure 4.11. Mass spectrum of AcVA.

5. References

5.1 Chan, Y. "OSHA Method No. 82; Acetic Anhydride", OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165, April 1990.

5.2 Chan, Y. "OSHA Method No. 86; Maleic Anhydride", OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165, December 1990.

5.3 Chan, Y. "OSHA Method No. 90; Phthalic Anhydride", OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165, October 1991.

5.4 Chan, Y. "OSHA Method No. 98; Trimellitic Anhydride", OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165, November 1992.

5.5 Code of Federal Regulations, Title 29, 1910.1000, Table Z-1, U.S. Office of the Federal Register National Archives and Records Administration, Washington, DC, 1993.

5.6 Documentation of the Threshold Limit Values and Biological Exposure Indices, 5th ed., American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986.

5.7 "NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards", U.S. Department of Health and Human Services, Government Printing Office, DHHS(NIOSH) Publication No. 81-123.

5.8 Grayson, M., Ed., "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd edition, Volume 1, p. 151, Interscience Publishers, New York, NY, 1984.

5.9 Sweet, D.V., Ed., "Registry of Toxic Effects of Chemical Substances", 1985-86 edition, U.S. Department of Health and Human Services, Government Printing Office, DHHS(NIOSH) Publication No. 87-114.

U.S. Department of Labor | Occupational Safety & Health Administration | 200 Constitution Ave., NW, Washington, DC 20210
Telephone: 800-321-OSHA (6742) | TTY

www.OSHA.gov