Application Method

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HAP Method Validation 1
Acetaldehyde

WBS # 2.1.1

Technikon # 1410-211

(revised for public distribution)

1. **PURPOSE**

This method may be used to determine the concentration(s) of the listed analytes (see Table 1) in ambient air, workplace air, and process/facility emissions.

2. **SCOPE**

This procedure applies to the compounds listed in Table 1.

TABLE 1
Analytes

	Boiling Point (°C)	Density (g/mL)	MW (g/mole)	Range (ug)
Acetaldehyde	20.4	0.78	44.05	1-77

3. **DEFINITIONS**

mg = milligram
L = liter
ml = milliliter
µg = microgram
m^3 = cubic meter
°F = degrees Fahrenheit

4. **APPARATUS AND REAGENTS**

4.4 Gas chromatograph equipped with a nitrogen-phosphorous ionization detector
4.4 Column - see instrument parameters
4.3 Syringes
4.4 Benzene - reagent (AR) grade
4.5 Acetonitrile (ACN) – reagent (AR) grade
4.6 Target Analyte(s) - reagent (AR) grade
4.7 Standard solution - ACN
4.8 Desorbing solution – 1:3 Benzene: ACN
4.9 Vials - screw cap with Teflon™ cap liners
4.10 Assorted pipets and volumetric flasks
4.11 100/50 mg silica gel tubes treated with 2,4-dinitrophenyl hydrazine

5. CALIBRATION

5.1 Prepare, in the standard solvent, a stock solution or solutions containing the target analyte(s), each at a concentration convenient for further dilution to levels approximating the levels expected in the field samples.

5.1.1 For liquids, the volume of pure analyte(s) needed for the stock solution(s) may be calculated using Equation 1 (see section 8.1).

5.1.2 For solids, use Equation 1 without "d". "V_a" then becomes the analyte weight in milligrams.

5.1.3 For "V_s" in Equation 1, use the mean air volume expected to be sampled in the field.

5.1.4 The following procedure has been found to provide accurate calibration standards, however, other procedures may be used at the discretion of the analyst.

5.1.4.1 Weigh the approximate calculated amount of each analyte into a volumetric flask of the appropriate volume and record the weight(s) to nearest 0.1 mg.

5.1.4.2 Fill the volumetric flask to the mark with the standard solvent and mix thoroughly.

5.1.4.3 Calculate the concentrations obtained with this stock solution and the dilutions necessary to achieve the target concentrations for each of the analytes. Use concentrations in units of mass/volume, e.g., mg/mL.

5.1.5 Perform dilutions, recording all volumes used, and clearly label both in a bound notebook and on the flasks containing the solutions. Each label should also include the solution disposal date and the analyst's initials. The labels should be made as indelible as possible, keeping in mind the environment in which the solutions will be stored.

5.2 Inject a known reproducible volume, using solvent flush techniques, of each standard into the gas chromatograph such that the lowest calibration standard response is greater than five (5) times the background noise level (see Section 7, Instrument Parameters).

5.2.1 When an autosampler is being used, its control parameters must be set to assure consistently accurate sample transfer and complete syringe rinsing between injected solutions.

5.3 Analyze each standard in triplicate, record and average the peak area(s).

5.4 Prepare a calibration curve by plotting the weight of analyte in each standard versus the mean peak area(s) for each standard.

5.5 The calibration curve shall have a correlation coefficient greater than 0.98 for the curve fit used. If the coefficient of variation is less than 0.98, the cause of the problem must be identified and corrected prior to sample analysis.

6. ANALYSIS OF SAMPLES

6.1 Remove samples from storage and allow warming to room temperature.

6.2 Transfer each section of solid sorbent to an appropriately labeled vial.

6.3 Pipet an appropriate volume (1.0 mL for 100 mg/50 mg tubes) of the desorbing solvent into each vial and cap immediately.

6.4 Allow to desorb for one (1) hour using an ultrasonic bath.

6.5 Inject a known volume (same as used in part 5.2) of the solution, using solvent flush techniques, into the gas chromatograph (see Section 7, Instrument Parameters).

6.6 Record the peak area(s) of the analyte(s) present.

6.7 Calculate the concentration of analyte in the sampled environment (equations 2-7).

6.8 Report the weight, in µg, for each analyte.

6.9 Laboratory blanks, spikes, and sample duplicates will be analyzed at a minimum frequency of 5% or one (1) each per batch for batches containing fewer than twenty (20) samples.

7. INSTRUMENT PARAMETERS

7.1 Instrument parameters may vary significantly with changes in sample matrix, instrument make and model, and column condition. Page nine (9) contains instrument parameters that have been used to successfully determine each analyte. These parameters should be considered a starting point only and optimized for each set of samples.

8. CALCULATIONS

8.1 The volume of analyte needed to prepare appropriate standards may be calculated using the following equation:

$$V_a = 20 \; X \; \frac{(TLV) \;\; (V_s)}{1000 \; X \; d} \; X \; V_{Sol} \qquad 1$$

. . . where:

V_a is the volume of analyte needed to prepare the standard, μL

20 is a scaling factor to give a V_a that is conveniently measurable and a resulting stock solution concentration that is readily diluted to useful concentrations

TLV is the expected concentration of the analyte in the sampled gas, mg/m^3

V_s is the volume of air sampled in the field, L

d is the density of the analyte of interest, g/mL

V_{Sol} is the volume of the desorbing solvent used for the stock solution, mL

8.2 Using a computer application (e.g., a chromatography data system or Excel) or calculator, calculate the coefficients (m_i, b_i) of the linear regression:

$$Area_i = m_i * Conc_i + b_i \qquad 2$$

where:

$Area_i$	is the area of the analyte peak "i" when the standard containing it is analyzed
$Conc_i$	is the concentration of analyte "i" in the standard, e.g., mg/L
m_i	is the slope of the linear regression between the area and the concentration
b_i	is the y-intercept of the linear regression between the area and the concentration

If the y-intercept equals 0, then the slope is equivalent to the classical definition of the response factor. For EPA applications, the agency may require the linear regression to be calculated with the regression through the origin, i.e., the y-intercept (b_i) must be equal to 0.

8.3 Calculate the weight of analyte "i" in a sample as follows:

$$Wt_{Bf} = DV * (Area_{Bf} - b)/m \qquad Wt_{Bb} = DV * (Area_{Bb} - b)/m \qquad 3$$

$$Wt_{Sf} = DV * (Area_{Sf} - b)/m \qquad Wt_{Sb} = DV * (Area_{Sb} - b)/m \qquad 4$$

$$Crtd\ Wt_i = (Wt_{Sf} - Wt_{Bf}) + (Wt_{Sb} - Wt_{Bb}) * 2\ (df) \qquad 5$$

. . . where:

Wt_{Bf}	is the weight of the analyte of interest found on the front section of the blank solid sorbent tube, mg
$Area_{Bf}$	is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube front section, mV-sec
Wt_{Bb}	is the weight of the analyte of interest found on the back section of the blank solid sorbent tube, mg
$Area_{Bb}$	is the area of the analyte peak of interest from the chromatographic run of the blank solid sorbent tube back section, mV-sec
Wt_{Sf}	is the weight of the analyte of interest found on the front section of the solid sorbent tube on which the sample was collected, mg
$Area_{Sf}$	is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube front section, mV-sec

Wt_{Sb} is the weight of the analyte of interest found on the back section of the solid sorbent tube on which the sample was collected, mg

$Area_{Sb}$ is the area of the analyte peak of interest from the chromatographic run of the sample solid sorbent tube back section, mV-sec

DV is the volume of solvent use to desorb the sorbent media, mL

Crtd Wt_i is the total weight of analyte "i" corrected for any amounts found on the blank solid sorbent tube, mg

NOTE: If the corrected weight of analyte i found on the back section of the sample tube (Wt_{Sb}-Wt_{Bb}) is equal to or greater than 10% of the total amount of analyte present on the sample tube, then "breakthrough" has occurred. Breakthrough results should be reported, but clearly identified as such. These are to be considered ***minimum*** amounts present in the air sampled.

8.4 Calculate the concentration of analyte in the sampled air as follows:

$$C_i \ (\frac{mg}{m^3}) = \frac{Crtd\ Wt_i\ X\ 1000}{(V_S)\ (DE_i)} \qquad 6$$

. . . where:

C_i is the concentration of analyte i in the sampled air, mg/m^3

Crtd Wt_i is the corrected weight of analyte i in the sample, mg

1000 is the number of liters in a cubic meter, L/m^3

V_s is the volume of air sampled, L

DE_i is the desorption efficiency of the analyte

8.5 Calculate the concentration of analyte(s) in the sampled air in parts per million (ppm) using the following equation:

$$C_i\ (ppm) = \frac{C_i\ (\frac{mg}{m^3})\ X\ 24.45}{MW_i} \qquad 7$$

. . . where:

C_i (ppm) is the concentration of analyte i in parts per million

C_i (mg/m^3) is the concentration of analyte i in milligrams per cubic meter
24.45 is the molar volume of a gas at 70°F and standard pressure, mL/mmole
MW_i is the molecular weight of analyte i, mg/mmole

9. REFERENCES

9.1

Analyte	Literature Reference
Acetaldehyde - DNPH	Method TO-11

INSTRUMENT PARAMETERS

Capillary Columns

Analyte	Acetaldehyde - DNPH
Column:	
Dimensions:	15 m x 0.53mm i.d. x 1 μm film thickness
Type:	DB-17 or equivalent
Material:	Fused Silica
Temperature Profile	
Initial Temp:	180 °C
Final Temp.:	240 °C
Post Run Hold:	8 min
Program Rate:	20°C/min to 240°C
Injector Profile:	
Temperature:	180°C
Mode:	Split
Split Flow:	87.4 mL/min
Pressure:	1.76
Detection:	
Type:	NPD
Detector Temperature:	325 °C
Carrier Gas:	
Type:	He
Initial Flow Rate:	2.5 mL/min
Mode:	Constant Flow
Sample:	
Injection Volume:	1.0 μl
Solvent:	ACN/Benzene

Acetaldehyde Method Validation Average Results

Desorption Efficiency

Average Mass, ug	Spike Mass, ug	DE %
1	1	95%
2	2	100%
25	26	97%
52	51	102%

Acetaldehyde Recovery Results

Sample Number	Mass, ug	Mass Spiked, ug	Concentration, ug/mL	Sample % Recovery
1001	71	26	0.0011	72
1002	51	NA	0.00082	NA
1101	69	26	0.0011	68
1102	47	NA	0.00076	NA
1201	62	23	0.0010	71
1202	44	NA	0.00071	NA
1401	78	26	0.0013	69
1402	54	NA	0.00087	NA
1501	84	26	0.0013	79
1502	66	NA	0.0011	NA
1701	71	26	0.0011	81
1702	57	NA	0.00092	NA
1801	73	26	0.0012	72
1802	53	NA	0.00085	NA
			Average % Recovery	**73**

Discussion

Aldehydes and ketones are commonly analyzed in their derivative form with 2,4-dinitrophenyl hydrazine (DNPH) using HPLC with a UV-vis detector. For this study, the derivative of acetaldehyde was analyzed using gas chromatography and a nitrogen-phosphorous selective detector. Acetaldehyde may form two isomers with the derivative and both isomers were detected and quantified in the recovery samples. Due to handling issues, acetaldehyde (neat) was not used for these analyses.

The target analyte method verified with acetaldehyde-dnph included analyte analysis and recovery. A series of seven pairs of samples were collected during pouring, cooling, shakeout testing at the Technikon facility. One from each pair of samples was spiked with acetaldehyde-dnph prior to testing and the percent (%) recovery was found to be 73% overall.

Samples were also analyzed to determine the desorption efficiency of acetaldehyde-dnph. The average percent (%) desorption efficiency for acetaldehyde-dnph was found to be 97%.

Breakthrough was not detected for any analyses.

Detailed results are shown in the following tables. The results are shown for reference purposes only.

Acetaldehyde Method Validation Detailed Results – Sample Recovery

Sample Number	Mass, ug	Mass DE 0.98, ug	Total Volume, mL	ug/mL	Mass Spiked, ug	Mass Difference, ug	Sample % Recovery	Standard % Difference
1001F	71	72	61894	0.0011	26	46	72	NA
1002F	51	52	62254	0.0008	NA	NA	NA	NA
1101F	69	70	61939	0.0011	26	44	68	NA
1102F	47	48	62250	0.0008	NA	NA	NA	NA
1201F	62	63	62171	0.0010	23	40	71	NA
1202F	44	45	62303	0.0007	NA	NA	NA	NA
1401F	78	80	61868	0.0013	26	54	69	NA
1402F	54	55	62145	0.0009	NA	NA	NA	NA
1501F	84	85	62100	0.0013	26	59	79	NA
1502F	66	66	62235	0.0011	NA	NA	NA	NA
1701F	71	72	61883	0.0011	26	46	81	NA
1702F	57	58	62175	0.0009	NA	NA	NA	NA
1801F	73	74	62055	0.0012	26	48	72	NA
1802F	53	54	62325	0.0009	NA	NA	NA	NA

Acetaldehyde Method Validation Detailed Results – Desorption Efficiency

Sample	Calculated Mass, ug	Standard Amount, ug	DE %
210-01	1	1	110%
210-02	1	1	90%
210-09	1	1	90%
210-10	1	1	100%
210-03	2	2	80%
210-11	2	2	90%
210-05	28	26	106%
210-06	26	26	101%
210-12	22	26	86%
210-14	25	26	97%
210-07	55	49	112%
210-08	59	51	116%
210-15	45	51	89%
210-16	47	51	93%
		Total Avg.	**98%**