



Casting Emission Reduction Program
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FY2004 Tasks
WBS # 2.1.1

HAP Method Validation 1

Ethyl Acrylate

Technikon # 1411-211 NA

January 2005
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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)
Ethyl Acrylate	99.8	0.92	100.12	0.3-370

3. DEFINITIONS

mg = milligram

L = liter

ml = milliliter

µg = microgram

m³ = cubic meter

°F = degrees Fahrenheit

4. APPARATUS AND REAGENTS

4.4 Gas chromatograph equipped with a Flame Ionization Detector or equivalent

4.4 Column - see instrument parameters

4.3 Syringes

4.4 Ethyl Acrylate - reagent (AR) grade

4.5 Carbon Disulfide – reagent (AR) grade

4.6 Vials - screw cap with Teflon™ cap liners

4.7 Assorted pipets and volumetric flasks

4.8 100/50 mg charcoal tubes treated with *tert*-butyl catechol

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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

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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.

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- 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:

$$V_a = 20 \times \frac{(TLV)(V_s)}{1000 \times d} \times V_{Sol} \quad 1$$

... 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:

$$\text{Area}_i = m_i * \text{Conc}_i + b_i \quad 2$$

where:

- Area_i is the area of the analyte peak "i" when the standard containing it is analyzed

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- 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:

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

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

$$Crt_d W_{t_i} = (W_{t_{Sf}} - W_{t_{Bf}}) + (W_{t_{Sb}} - W_{t_{Bb}}) * 2 \text{ (df)} \qquad 5$$

... where:

- W_{tBf} 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
- W_{tBb} 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
- W_{tSf} 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
- W_{tSb} 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

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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:

$$C_i \left(\frac{mg}{m^3} \right) = \frac{Crtd\ Wt_i \times 1000}{(V_s)(DE_i)} \quad 6$$

... where:

C_i is the concentration of analyte i in the sampled air, mg/m³
 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/m³
 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:

$$C_i (ppm) = \frac{C_i \left(\frac{mg}{m^3} \right) \times 24.45}{MW_i} \quad 7$$

... where:

C_i (ppm) is the concentration of analyte i in parts per million
 C_i (mg/m³) 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

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9. REFERENCES

9.1

Analyte

Literature

Reference

Ethyl Acrylate

Method OSHA 92

INSTRUMENT PARAMETERS

Capillary Columns

Analyte	Ethyl Acrylate
Column:	
Dimensions:	15 m x 0.53mm i.d. x 1 µm film thickness
Type:	ZB-5 or equivalent
Material:	Fused Silica
Temperature Profile	
Initial Temp:	50 °C
Final Temp.:	275 °C
Program Rate:	5°C/min to 100°C; 20°C/min to 275°C
Injector Profile:	
Temperature:	250°C
Mode:	Split
Split Flow:	21.2 mL/min
Pressure:	8.48
Detection:	
Type:	FID
Detector Temperature:	300 °C
Carrier Gas:	
Type:	He
Initial Flow Rate:	1.7 mL/min
Mode:	Constant Flow
Sample:	
Injection Volume:	1.0 µl
Solvent:	CS ₂

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Ethyl Acrylate Method Validation Average Recovery Results

Amount Recovered, ug	Standard Amount, ug	DE%
0.3	0.3	97%
2	2	97%
38	38	100%
355	376	94%

Ethyl Acrylate Method Validation Recovery Results

Sample Number	Amount Recovered, ug	Standard Amount, ug	DE%
DE-9F	0.3	0.3	97%
DE-7F	0.3	0.4	83%
DE-18F	2	2	95%
DE-16F	2	2	91%
DE-17F	2	2	105%
DE-12F	40	37	108%
DE-10F	33	37	91%
DE-11F	39	39	101%
DE-14F	332	371	90%
DE-13F	371	370	100%
DE-15F	361	388	93%

Average
% Recovery **96%**

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Storage Stability

Storage Type	Recovered Mass, ug	Mass Spiked, ug	Mass, ug 96% DE Applied	% Change Column E
immediate	0.7	0.7	0.7	7%
immediate	2	2	2	-8%
immediate	19	18	20	10%
immediate	41	39	43	11%
immediate	388	370	404	9%
immediate				6%
one week	0.6	0.7	1	-14%
one week	2	2.2	2	-6%
one week	21	20	22	11%
one week	42	38	44	16%
one week	343	370	357	-3%
one week				1%
two weeks	0.6	0.7	1	-8%
two weeks	2	2	2	-12%
two weeks	24	20	25	26%
two weeks	43	38	45	19%
two weeks	424	370	442	19%
two weeks				9%
four weeks	0.5	0.7	1	-21%
four weeks	2	2	2	-15%
four weeks	21	20	22	8%
four weeks	34	38	36	-6%
four weeks	331	360	345	-4%
four weeks				-8%

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Discussion

NIOSH Methods 1450 and S-38 specify that ethyl acrylate is collected on coconut shell charcoal tubes, desorption with carbon disulfide (CS₂), and analysis using GC with a flame ionization detector. Desorption efficiencies were found to be low and a function of sampler loading with these methods. For this study, OSHA Method 92 was utilized for analysis. In this method, the coconut charcoal tubes are coated with *tert*-butyl catechol to stabilize the ethyl acrylate and increase desorption efficiencies and also aid in handling issues. Desorption is with CS₂ and analysis by GC FID. Desorption efficiency and storage stability studies were performed.

Samples were analyzed to determine the desorption efficiency of ethyl acrylate. The average percent (%) desorption efficiency for ethyl acrylate was found to be 96%.

Breakthrough was not detected for any analyses.

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

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Ethyl Acrylate Method Validation Detailed Results – Storage

Sample Number	Recovered Mass, ug	Mass Spiked, ug	Mass, ug 96% DE Applied	% Change Column E	Storage Type	Storage Conditions
SS-17	0.7	0.7	1	3%	immediate	NA
SS-13	2	2.2	2	-6%	immediate	NA
SS-1	20	20.3	21	4%	immediate	NA
SS-5	43	40.7	45	11%	immediate	NA
SS-9	388	369.6	404	9%	immediate	NA
SS-37	388	369.6	404	9%	immediate	NA
SS-25	2	2.2	2	-10%	immediate	NA
SS-33	39	37	41	11%	immediate	NA
SS-29	18	16.6	19	16%	immediate	NA
SS-21	0.7	0.67	0.8	12%	immediate	NA
SS-18F	0.6	0.7	1	-12%	one week	R.T.
SS-14F	2	2.2	2	-14%	one week	R.T.
SS-2F	20	22.3	20	-9%	one week	R.T.
SS-6F	40	38.8	42	8%	one week	R.T.
SS-10F	313	369.6	326	-12%	one week	R.T.
SS-22F	0.6	0.7	1	-16%	one week	FREEZER
SS-26F	2	2.2	2	2%	one week	FREEZER
SS-30F	23	18.5	24	31%	one week	FREEZER
SS-34F	44	37	46	24%	one week	FREEZER
SS-38F	373	369.6	389	5%	one week	FREEZER
SS-3F	24	22.2	25	13%	two weeks	R.T.
SS-7F	43	38.8	45	15%	two weeks	R.T.
SS-11F	370	369.6	385	4%	two weeks	R.T.
SS-19F	0.6	0.7	1	-9%	two weeks	R.T.
SS-15F	2	2.2	2	-15%	two weeks	R.T.
SS-23F	0.7	0.74	1	-8%	two weeks	FREEZER
SS-27F	2	2.2	2	-8%	two weeks	FREEZER
SS-31F	25	18.5	26	38%	two weeks	FREEZER
SS-35F	43	37	45	22%	two weeks	FREEZER
SS-39F	478	369.6	498	35%	two weeks	FREEZER
SS-4F	23	20.3	24	17%	four weeks	RT
SS-8F	32	38.8	33	-15%	four weeks	RT
SS-12F	260	369.6	270	-27%	four weeks	RT
SS-16F	2	2.2	2	-13%	four weeks	RT
SS-20F	0.5	0.74	1	-25%	four weeks	RT
SS-24F	0.5	0.67	1	-18%	four weeks	FREEZER
SS-28F	2	2.2	2	-16%	four weeks	FREEZER
SS-32F	19	20.3	20	0%	four weeks	FREEZER
SS-36F	37	37	38	3%	four weeks	FREEZER
SS-40F	402	351.1	419	19%	four weeks	FREEZER