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US Army Contract DAAE30-02-C-1095
FY2004 Tasks
WBS # 2.1.2

HAP Method Validation 2
Ethylene Glycol Monobutyl Ether
(butyl cellosolve)

Technikon # 1411-212

November 2005
Revised for public distribution.

United States Environmental Protection Agency

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Application Method

DOCUMENT NO.	
2.1.2	
DOCUMENT TITLE: HAP Method Validation 2	PAGE ii OF ii

DATE ISSUED	SUPERSEDES	PREPARED BY
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Application Method

DOCUMENT NO.	
2.1.2	
DOCUMENT TITLE: HAP Method Validation 2	PAGE 1 OF 10
DATE ISSUED: November 2005	SUPERSEDES: None
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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

	CAS #	Boiling Point (°C)	Density (g/mL)	MW (g/mole)	Range (ng)
2-Butoxyethanol (ethylene glycol Monobutyl ether, butyl cellosolve)	111-76-2	171.2	0.9022	118.7	0.2 - 500

3. DEFINITIONS

ng = nanogram
mg = milligram
L = liter
ml = milliliter
µg = microgram
m3 = cubic meter
°F = degrees Fahrenheit

4. APPARATUS AND REAGENTS

4.1 Gas chromatograph equipped with a Mass Selective Detector or equivalent
4.2 Column - see instrument parameters
4.3 Syringes
4.4 2-Butoxyethanol - ≥99.5% purity

4.5 Methylene Chloride – reagent grade
4.6 Methanol – reagent grade
4.7 Vials - screw cap with Teflon™ cap liners
4.8 Assorted pipets and volumetric flasks
4.9 100/50 mg coconut shell carbon adsorption tubes

5. CALIBRATION

5.1 Prepare, in a 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 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". "Va" then becomes the analyte weight in milligrams.

5.1.3 For "Vs" 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 Pipette 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.

6.5 Inject a known volume (same as used in part 5.2) of the solution, using solvent flush techniques or an automatic liquid sampler, 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 Record the weight for each analyte.

6.9 Analyze laboratory blanks, spikes, and sample duplicates 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. Instrument parameters contained in Table 2 have been used to successfully determine the analyte, and may be considered for use as a starting point for analysis of a different set of samples.

8. CALCULATIONS

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

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

. . . 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 (mi, bi) of the linear regression:

$$Area_i = {}_{mi} * Conc_i + b_i \qquad 2$$

. . . 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 linear regression must 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:

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

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

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

. . . 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:

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

. . . 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:

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

. . . 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
2-butoxyethanol	OSHA Method 83

Table 2

INSTRUMENT PARAMETERS

Analyte:	2-butoxyethanol
Chromatographic Column:	
Dimensions:	15 m x 0.25 mm i.d. x 0.25 μm film thickness
Type:	DB-5 or equivalent
Material:	Fused Silica
Chromatograph Temperature Program:	
Initial Temp:	30 °C
Final Temp.:	250 °C
Program Rate:	10°C/min to 150°C; 20°C/min to 250°C
Post Program:	250°C - 300 °C
Inlet Profile:	
Temperature:	250°C
Mode:	Split
Split Flow:	5:1
Pressure:	8.4 psi
Detection:	
Type:	Mass Spectrometer
Source Temperature:	230°C
Quadropole Temperature:	150°C
Carrier Gas:	
Type:	He
Column Flow Rate:	1.2 ml/min
Mode:	Constant Flow
Sample:	
Injection Volume:	1.0 μl
Desorbing Solvent:	95% Methylene Chloride, 5% Methanol

Figure 1
2-Butoxyethanol Calibration Curve

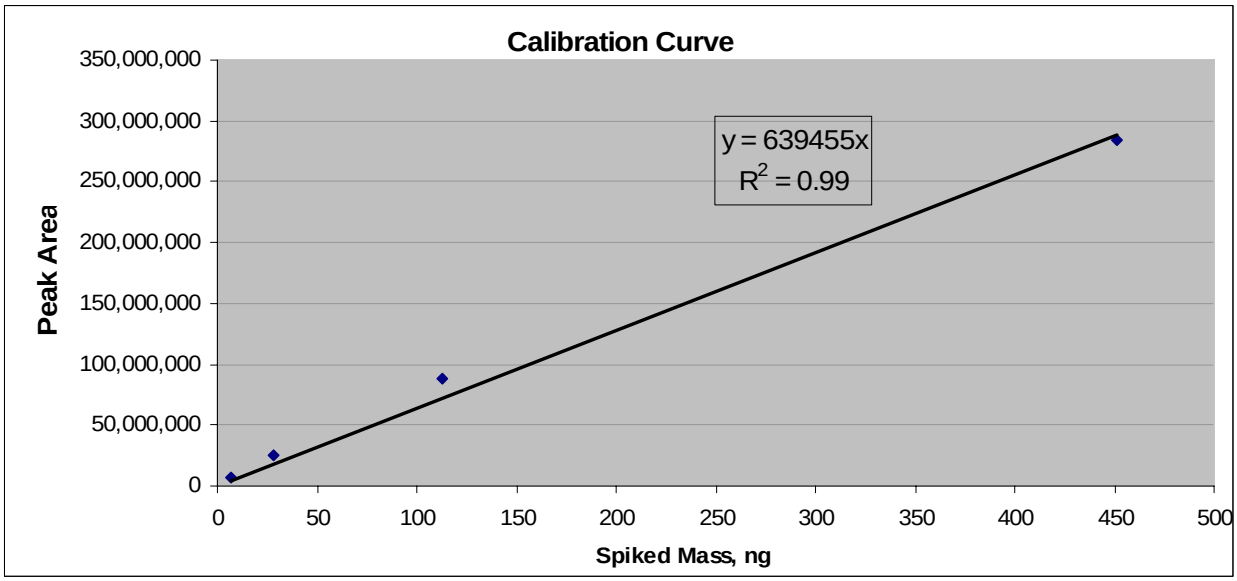


Table 3
2-Butoxyethanol Validation Average Recovery Results

Standard Amount Spiked ng	Amount Recovered, ng	% Recovery
442	451	98
103	113	115
39	28	137
10	7	137
2	2	79

Table 4
2-Butoxyethanol Method Validation Storage Results

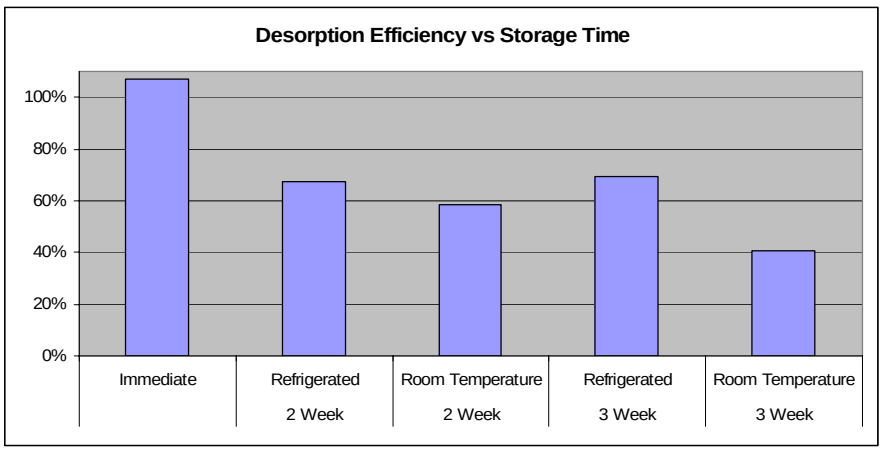
Sample Name	Storage Type	Spiked Amount, ng	Recovered Amount, ng	Desorption Efficiency, percent
1-1	Immediate	18	29	161
20-3		361	331	90
5-3		90	91	101
10-1		180	182	99
			Average	113
1-3	2 Week Refrigerator	18	14	71
20-1		361	203	57
5-1		90	69	74
10-2		180	121	65
			Average	67
1-4	2 Week Room Temperature	18	11	57
20-4		361	191	52
5-2		90	60	62
			Average	58
1-2	3 Week Refrigerator	18	11	61
5-4		90	66	76
10-4		180	126	67
			Average	68
1-5	3 Week Room Temperature	18	10	54
20-5		361	152	42
5-5		90	32	15
10-3		180	90	51
			Average	40
			Overall Average	79

10. Discussion

10.1 Procedures from OSHA Method 83 for butyl cellosolve were followed for this validation study. This particular method specifies the collection of 2-butoxyethanol on coconut shell charcoal tubes, followed by desorption with a 95/5 (volume/volume) methylene chloride/methanol solution and subsequent analysis using a gas chromatograph equipped with a flame ionization detector. Positive identification of the analyte of interest in the current study was determined by the use of a mass spectrometer instead of an FID. This is suggested as a means of confirmation of analyte identification in the OSHA method. Both desorption efficiency and storage stability studies were performed.

10.2 Desorption efficiency was determined by injecting micro liter amounts of the stock 2-butoxyethanol standard onto the front section of the charcoal tubes. Storage stability was determined by analyzing spiked samples after three time periods under both refrigerated and room temperature conditions. Desorption was accomplished by adding 1 ml of the desorbing solvent to the front and back sections of the charcoal tube after the allotted storage time had elapsed. The average desorption efficiency percentage overall for 2-butoxyethanol was found to be 79%. In general, desorption efficiencies were found to be low except for those samples which were analyzed immediately after spiking. Refrigerated samples were more stable and had higher recoveries than did the samples held at room temperature.

Figure 2
2-Butoxyethanol Calibration Curve



Breakthrough was not detected for any of the analyses.