

# **HAP Method Validation 2**

**FY 2002 Tasks**

**WBS # 2.1.2**

**31 July 2003**

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Casting Emission Reduction Program

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**FY 2002 Tasks**

## **HAP Method Validation 2**

**Technikon # 1409-212**

**31 July 2003**



# Application Method

DOCUMENT NO. 01
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PREPARED BY Martin Wilt, Ph.D.
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DOCUMENT TITLE NAPHTHALENE IN AIR	
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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**

	Boiling Point (°C)	Density (g/mL)	MW (g/mole)	Range (mg/m <sup>3</sup> )
Naphthalene	218	0.997	128.17	40.0-1,000

## 3. DEFINITIONS

mg = milligram

L = liter

ml = milliliter

µg = microgram

m<sup>3</sup> = cubic meter

°F = degrees Fahrenheit

## 4. APPARATUS AND REAGENTS

4.4 Gas chromatograph equipped with a flame ionization detector

4.4 Column - see instrument parameters

4.3 Syringe - 10 µL

4.4 Target Analyte(s) – Aldrich 147141-25G, Supelco, 5,000ug/ml in methanol

4.5 Carbon disulfide - interference free

4.6 Desorbing solvent – Carbon disulfide (100%)

4.7 Glass vials - screw cap with Teflon™ cap liners

4.8 Assorted pipets and volumetric flasks

4.9 Analytical balance (readability to 0.1 mg , linearity = ± 0.2 mg)

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## 5. CALIBRATION

- 5.1 Prepare, in the desorbing 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 The volume of pure analyte(s) needed for the stock solution(s) may be calculated using Equation 1 (see section 9.1).
- 5.1.2 For " $V_s$ " in Equation 1, use the mean air volume sampled in the field for the set of samples currently being processed.
- 5.1.3 The following procedure has been found to provide accurate calibration standards, however, other procedures may be used at the discretion of the analyst.
- 5.1.3.1 Weigh the approximate calculated volume of each analyte into a volumetric flask of the appropriate volume and record the weight(s) to nearest 0.1 mg.
- 5.1.3.2 Fill the volumetric flask to the mark with the desorbing solvent and mix thoroughly.
- 5.1.3.3 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/L.
- 5.1.4 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 8, Instrument Parameters).

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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 and field blanks from storage and allow to warm 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 forty-five (45) minutes with occasional shaking.

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 8, 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  $\mu\text{g}$ , 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. Appendix A 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,  $\mu\text{L}$
- 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,  $\text{mg}/\text{m}^3$
- $V_s$  is the volume of air sampled in the field, L
- d is the density of the analyte of interest,  $\text{g}/\text{mL}$
- $V_{Sol}$  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:

$\text{Area}_i$  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:

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

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

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

... 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

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DV is the volume of solvent use to desorb the sorbent media, mL  
 Crtd Wt<sub>i</sub> 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 (W<sub>tSb</sub>-W<sub>tBb</sub>) 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<sub>i</sub> is the concentration of analyte i in the sampled air, mg/m<sup>3</sup>  
 Crtd Wt<sub>i</sub> is the corrected weight of analyte i in the sample, mg  
 1000 is the number of liters in a cubic meter, L/m<sup>3</sup>  
 V<sub>s</sub> is the volume of air sampled, L  
 DE<sub>i</sub> 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<sub>i</sub> (ppm) is the concentration of analyte i in parts per million  
 C<sub>i</sub> (mg/m<sup>3</sup>) 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

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$MW_i$  is the molecular weight of analyte i, mg/mole

## 9. REFERENCES

9.1

Analyte

Naphthalene

Literature

Reference

NIOSH 1500

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## INSTRUMENT PARAMETERS

### Capillary Columns

<b>Analyte</b>	Naphthalene		
<b>Column:</b>			
Dimensions:	30m x 0.32mm i.d. x 0.25um film thickness		
Type:	HP-5, RTX-5, DB-5; or equivalent.		
Material:	Fused Silica		
<b>Temperature Profile</b>			
Initial Temp.:	40 °C		
Initial Hold:	0 min		
Final Temp.:	225 °C		
Final Hold:	0 min		
Post Run Temp.:	225 °C		
Post Run Hold:	0 min		
Program Rate:	20°C/min to 225°C		
<b>Injector Profile:</b>			
Temperature:	300°C		
Mode:	Splitless		
Purge Flow:	60 ml/min		
Purge Time:	1.00 min		
<b>Detection:</b>			
Type:	FID		
Detector Temperature:	300 °C		
<b>Carrier Gas:</b>			
Type:	He		
Initial Flow Rate:	2.5 mL/min		
Initial Hold:	0 min		
Program Rate:	Constant flow		
Post Run Flowrate:	2.5 mL/min		
<b>Sample:</b>			
Injection Volume:	1.0 µl		
Solvent:	CS <sub>2</sub> (100% v/v)		

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## Sample Chromatogram

