CERP

Casting Emission Reduction Program

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HAP Method Validation 1 - Phenol

Technikon # 1409- 2.1.1

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EPA United States Environmental Protection Agency

CISA

AFS American Foundry Society, Inc.

USCAR United States Council for Automotive Research — DaimlerChrysler, Ford Motor Company, General Motors

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HAP Method Validation 1 – Phenol

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^3)
Phenol	181.7	1.07	94.1	0.32-200

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 flame ionization detector
4.4 Column - see instrument parameters
4.3 Syringes
4.4 Methanol - reagent (AR) grade
4.5 Target Analyte(s) - reagent (AR) grade
4.6 Desorbing solvent – Methanol
4.7 Vials - screw cap with Teflon™ cap liners
4.8 Assorted pipets and volumetric flasks
4.9 Balance, sensitive to 0.1 mg

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 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 desorbing 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 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 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. 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:

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

. . . 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:

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

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

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

. . . 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
Phenol	NIOSH 2002

INSTRUMENT PARAMETERS

Capillary Columns

Analyte	Phenol
Column:	
Dimensions:	60 m x 0.32mm i.d. x 1um film thickness
Type:	RTX-1 or equivalent.
Material:	Fused Silica
Temperature Profile	
Initial Temp.:	100 °C
Initial Hold:	3 min
Final Temp.:	170 °C
Post Run Temp.:	225 °C
Post Run Hold:	1 min
Program Rate:	11°C/min to 170°C
Injector Profile:	
Temperature:	250°C
Mode:	Split
Split Flow:	14.3 mL/min
Pressure:	33.62
Detection:	
Type:	FID
Detector Temperature:	280 °C
Carrier Gas:	
Type:	He
Initial Flow Rate:	4.4 mL/min
Mode:	Constant Flow
Post Run Flowrate:	3 mL/min
Sample:	
Injection Volume:	1.0 µl
Solvent:	CH_3OH

Phenol Method Development Average Results

Desorption Efficiency

Mass, ug	Spike Amount, ug	DE (%)
30.2	25	121
503	455	111
1520	1350	113
1040	880	118
4910	4140	119

Storage Stability

	Sample Average, ug/L	Spike Average, ug/L	% Recovery Spike
Immediate	235.7	312.8	73
One Week	242.3	328.1	72
Two Weeks	234.6	339.7	70
Four Weeks	228.0	318.8	72

Discussion

The target analyte method verified with phenol included analyte collection, analyte analysis, storage of the collected samples, and analyte recovery. A series of twenty-four (24) samples were collected from the mixing process during core making at the Technikon facility. The samples were divided into groups to be analyzed immediately after collection, and after one (1), two (2), and four (4) weeks. Storage was evaluated at both room temperature and freezer temperature. Duplicate spike samples were also analyzed for each storage group, and the percent (%) recovery was determined and found to be approximately 72% overall.

Samples were also analyzed to determine the desorption efficiency of phenol. The average percent (%) desorption efficiency for phenol was found to be 116%.

Detailed results for all analyses are shown in the following tables.

Phenol Method Development Detailed Results

Sample Results - Storage Stability

	Sample Number	Total, ug/L	Back Section ug/L	% BT
Immediate	21013	216.8	23.2	10.7%
	21014	238.5	21.8	9.1%
	21016	250.3	22.8	9.1%
	21017	237.2	20.4	8.6%
Week One	21019	233.0	32.1	13.8%
	21020	240.5	22.9	9.5%
	21022	239.7	24.5	10.2%
	21015	255.9	23.5	9.2%
Week Two	21025	218.5	51.3	23.5%
	21026	220.5	54.4	24.7%
	21028	252.2	57.9	22.9%
	21018	247.1	23.4	9.5%
Week Four	21031	235	61.3	26.1%
	21032	226.8	59.9	26.4%
	21034	218.4	56.4	25.8%
	21035	231.9	62.9	27.1%

Note: Results >10% BT are reported as a minimum.

Spike Results Storage Stability

	Sample Number	Total ug/L	Back Section ug/L	% BT	% Recovery
	21023	300.2	48.8	16.3%	73
Immediate	21029	325.5	56.7	17.4%	73
	21021	314.5	54.6	17.4%	75
Week One	21024	341.6	57.2	16.7%	70
	21027	328.2	61.0	18.6%	72
Week Two	21030	351.1	60.2	17.1%	68
	21033	321.0	55.1	17.2%	71
Week Four	21036	316.5	57.2	18.1%	72

Note: Results reported as a mimimum due to apparent breakthrough.

Desorption Efficiency

Sample Number	Mass, ug	Spike Amount, ug	DE (%)
DE-1	32.8	25	131.2
DE-2	28.9	25	115.6
DE-3	28.9	25	115.6
DE-4	497	455	109.2
DE-5	511	455	112.3
DE-6	501	455	110.1
DE-7	1490	1365	109.2
DE-8	1550	1365	113.6
DE-9	1520	1320	115.2
DE-10	1050	910	115.4
DE-11	1020	865	117.9
DE-12	1040	865	120.2
DE-13	4680	4066	115.1
DE-14	5030	4173	120.5
DE-15	5030	4173	120.5
		Average	**116.1**