Casting Emission Reduction Program

Prepared by:

TECHNIKON LLC

5301 Price Avenue ▼ McClellan, CA, 95652 ▼ (916) 929-8001

www.technikonllc.com

US Army Task N256

Methodology Validation
Determination of Aromatic Amines in Air

Technikon # 322

This document was revised for unlimited public distribution and published on
16 April 2003

EPA United States Environmental Protection Agency

CISA

AFS AMERICAN FOUNDRY SOCIETY, INC.

UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH

USCAR

DAIMLERCHRYSLER Ford Motor Company General Motors

THIS PAGE INTENTIONALLY BLANK

Methodology Validation

WBS # 3.2.2

Application Method

Determination of Aromatic Amines in Air

June 26, 2001

Prepared by
Scott Forbes

Approved by
Cliff R. Glowacki, CIH
Measurement Technologies

THIS PAGE INTENTIONALLY BLANK

Table of Contents

Table of Figures

Table of Tables

THIS PAGE INTENTIONALLY BLANK

1. Purpose

This method may be used to determine the concentration(s) of the listed analytes (see Table 1) in ambient air, workplace air, or to monitor foundry emissions by adjusting the sorbent tube size, desorbing solvent volume, and sampling rate and total volume.

2. Scope

This procedure applies to the aromatic amines as vapors in air listed below in Table 1.

Table 1 Analytes

	Boiling Point (?C)	Density (g/mL)	MW (g/mole)	Range (mg/m^3)
Aniline	184	1.02	93.1	1.0-50.0

3. Definitions

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

4. Apparatus and Reagents

4.1 Gas chromatograph equipped with a flame ionization detector
4.2 Column - see instrument parameters for specific analyte
4.3 Syringe - 10 ?L
4.4 Silica gel adsorption tubes
4.5 Pump - personal sampling
4.6 Analyte - reagent (AR) grade
* 4.7 Methanol - interference free desorbing solvent
4.8 Vials - screw cap with Teflon? cap liners
4.9 Assorted pipets and volumetric flasks
* 4.10 Balance, sensitive to 0.1 mg

Table 2 Recommended Maximum Sampling Rates and Volumes (100 mg/50 mg tubes)

	Rate (ml/min)		Volume (liters)	
	Minimum	**Maximum**	**Minimum**	**Maximum**
Aniline	25	1000	1.5	15

5. Calibration

5.1 Prepare in an appropriate volume, *e.g.*, 10.0 mL or 25.0 mL of the desorbing solvent a stock solution containing all of the analytes of interest, each at a concentration convenient for further dilution to five (5) levels encompassing the concentrations expected in the samples.

5.1.1 Calculate the volume of pure analyte needed for the stock solution by 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 target concentrations for each of the analytes. Use concentrations in units of mass/volume, e.g., mg/L.

5.2 Prepare dilutions and 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).

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. Desorption Efficiency

6.1 The desorption efficiency of each analyte must be determined for each lot of solid sorbent in use.

7. Analysis of Samples

7.1 Remove samples and field blanks from storage and allow to warm to room temperature.

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

NOTE: Labeling of the separate sections is facilitated by splitting a label on which the sample identification number has been written twice and transferring the two portions to the two separate vials.

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

7.4 Allow to desorb for forty-five (45) minutes with occasional shaking.

7.5 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).

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

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

7.8 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.

8. Instrument Parameters

8.1 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.

9. Calculations

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

$$V_a = 20 \; X \; \frac{(TLV)\;(V_s)}{1000 \; X \; d} \; X \; V_{Sol} \quad \textbf{11}$$

. . . where:

V_a	is the volume of analyte needed to prepare the standard, ?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 threshold limit value or fraction thereof, 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 desorbing solvent used for the stock solution, mL

9.2 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:

$$Area_i = m_i * Conc_i + b_i$$

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.

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

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

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

$$Crtd\ Wt_i = (Wt_{Sf} - Wt_{Bf}) + (Wt_{Sb} - Wt_{Bb}) \qquad 55$$

. . . 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

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

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

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

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.

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

$$C_i \left(\frac{mg}{m^3}\right) = \frac{Crtd\ Wt_i\ X\ 1000}{(V_s)\ (DE_i)} \quad \textbf{66}$$

. . . 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

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

$$C_i\ (ppm) = \frac{C_i \left(\frac{mg}{m^3}\right)\ X\ 24.45}{MW_i} \quad \textbf{77}$$

. . . 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/mole

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

10. References

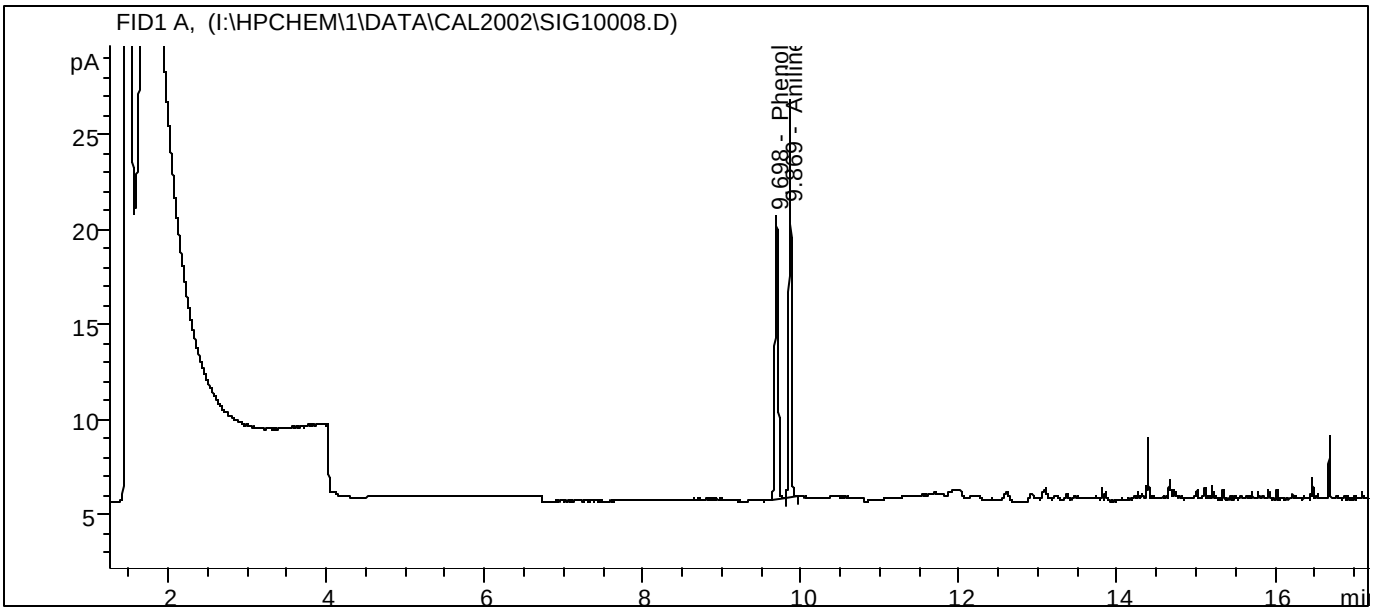
10.1 Literature

Analyte	Reference
aniline	NIOSH 2002

Instrument Parameters: Capillary Columns

Analyte:	**Aniline**		
Column:			
Dimensions:	30 m x 0.32mm i.d. x 0.25 um film thickness		
Type:	HP-5, RTX-5, DB-5; or equivalent.		
Material:	Fused Silica		
Temperature Profile			
Initial Temp.:	50 °C		
Initial Hold:	5 min		
Final Temp.:	280 °C		
Final Hold:	0 min		
Post Run Temp:	300 °C		
Post Run Hold:	5 min		
Program Rate:	4 °C/min to 66 °C, then 20 °C/min to 130 °C, then 30 °C/min to 280 °C		
Injector Profile			
Temperature:	300 °C		
Mode:	Splitless		
Purge Flow:	250 mL/min		
Purge Time:	2.50 min		
Detection:			
Type:	FID		
Detector Temperature:	315 °C		
Carrier Gas:			
Type:	He		
**Flow Rate:	2.0 mL/min (constant)		
Sample:			
Injection Volume:	3.0 uL		
Solvent:	CH_3OH		

Phenol and Aniline Standard (50 ug)



Sample Chromatogram