

United States
Environmental Protection Agency
Office of Transportation and Air Quality
National Vehicle and Fuel Emissions Laboratory
2565 Plymouth Road
Ann Arbor, MI 48105

Determination of Benzene, Toluene and
Total Aromatics in Finished Gasoline by Gas
Chromatography / Mass Spectrometry Method

This method is written for the Environmental Protection Agency, National Vehicle and Fuel Emissions Laboratory (NVFEL) internal use. The use of specific brand names by NVFEL in this method are for reference only and are not an endorsement of those products. This document may be used for guidance by other laboratories.

NVFEL Reference Number

130

Implementation Approval

Original Procedure Authorized by EPCN # 325 on 06-11-2003

Revision Description

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1. Scope

This procedure measures the concentrations of benzene, toluene and other specified aromatic compounds in gasoline.

2. Summary of Method

Gasoline samples are infused with an internal standard gravimetrically. They are then introduced into a gas chromatograph with a mass selective detector that separates their components to identify and quantify them.

3. Significance

The identities and concentrations of aromatic compounds in a sample of gasoline can be determined.

4. Applicable Documents

4.1 ASTM Standard D5769-98

4.2 40 CFR 80.46 (f)(1)

Agilent ChemStation for GC/MSD 6890/5973 Network

NVFEL 120, Chain of Custody Procedure for Fuel analysis Requested by OECA

5. Definitions

5.1 Internal Standard (ISTD) :

Deuterated analogs of benzene, toluene, ethylbenzene and naphthalene are used as internal standards because of their similar chromatographic characteristics and the ability of the mass selective detector to resolve them.

5.2 Control Fluid:

Test fuel drawn from the National Vehicle Fuel Emissions Laboratory underground storage tank is used as a control fluid. The large and stable supply of fuel is used as a reference for the consistency of calibration curves used by the instrument.

5.3 Quality Control Standard (QCSTD) :

A mixture of alkanes and aromatics prepared per ASTM D5769. This mixture is analyzed prior to samples to ensure the performance of the instrument. This analysis must meet the criteria detailed in ASTM D5769.

6. Interferences and/or Limitations

The concentrations of results should lie between the concentrations of the standards. If the concentrations of the results lie outside the range of the standards, then the range of the standards needs to be extended or the sample should be diluted to fall into that range.

7. Safety

Gasoline and its components are extremely volatile and flammable. They are carcinogenic, mutagenic and toxic. Persons performing this procedure must be familiar with the chemicals and hazards they represent; read the Material Safety Data Sheets available for them.

All handling should be performed under an approved fume hood.

8. Apparatus

8.1 Gas chromatograph with a mass selective detector.

Equipment used: Agilent 6890Network with 5973MSD configured as in appendix A (many different configurations are equally acceptable) and Chemstation Analytical software on a computer.

8.2 Analytical Balance: Mettler AG 204

9. Reagents and Materials

Use the highest purity compounds available for calibrations. Impurities must be accounted for when standards are made and used.

10. Sampling

Sampling is done by agents in the field.

11. Calibration

Determine if an instrument calibration is required. The following are criteria for calibration:

- 11.1 If the instrument has not previously been calibrated for this analysis.
- 11.2 If the current calibration is lost or damaged.
- 11.3 If the instrument has been reconfigured or repaired.
- 11.4 If the standards or control fluids are outside the acceptance criteria and it is determined that the instrument calibration is at fault.
- 11.5 If a calibration is needed, calibration curves are generated by analyzing the compounds of interest over five levels of concentrations covering the range of interest. Each compound is measured discretely by weight and its concentration in each level is calculated.

A typical calibration set is shown in appendix B.

12. Analytical Procedure

- 12.1 Tare a sealable 5ml bottle. Add approximately 4ml of sample to the bottle and record the weight to the nearest 0.1mg. Add 0.5ml of ISTD to the bottle and record the weight to the nearest 0.1mg. Repeat for all samples, control fluids and QC check standards.
- 12.2 Dispense an appropriate amount of analyte into a uniquely marked autosampler compatible vial for introduction into the instrument.
- 12.3 Arrange items to be analyzed on the autosampler tray in accordance to the sequence to be followed by the instrument.
- 12.4 Build the sequence (Appendix C) to run a QC check standard first, then a control fluid, then the samples followed by another control fluid.
- 12.5 The Chemstation sequence file contains the identity of the analyte, the position of the sample vial, the method used to analyze it, the weight of the sample, the weight of the ISTD and the specific gravity of the sample being quantified.
- 12.6 Running the sequence causes the instrument to inject a portion of the analyte into the gas chromatograph. The gas chromatograph separates the various compounds, which are identified in turn by the mass selective detector.

13. Calculations and Reporting

The chemstation calculates the quantity of each compound by measuring the area response against that of the internal standard.

14 Performance Criteria

- 14.1 The linearity of the calibration curves must be 0.995 or higher.
- 14.2 The Quality Control sample values must be within +/- 5% of the theoretical values except for 1,2,4,5-tetramethylbenzene and naphthalene, which must be within +/- 10%.
- 14.3 The Control Fluid must be within +/- 3 sigma of the mean value of at least ten previous analyses.
- 14.4 The balance should measure check weights within 0.1% of theoretical value.

Appendix A Continued

Gas type: Helium

COLUMN 1

Capillary Column
Model Number: J&W 121-1023
DB1
Max temperature: 325 'C
Nominal length: 20.0 m
Nominal diameter: 180.00 um
Nominal film thickness: 0.40 um
Mode: constant flow
Initial flow: 0.4 mL/min
Nominal init pressure: 8.85 psi
Average velocity: 30 cm/sec
Inlet: Front Inlet
Outlet: MSD
Outlet pressure: vacuum

COLUMN 2

(not installed)

FRONT DETECTOR (NO DET)

BACK DETECTOR (NO DET)

SIGNAL 1

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

SIGNAL 2

Data rate: 20 Hz
Type: test plot
Save Data: Off
Zero: 0.0 (Off)
Range: 0
Fast Peaks: Off
Attenuation: 0

COLUMN COMP 1

(No Detectors Installed)

COLUMN COMP 2

(No Detectors Installed)

THERMAL AUX 2

Use: MSD Transfer Line Heater
Description: MSD Transfer Line
Initial temp: 280 'C (On)
Initial time: 0.00 min
Rate Final temp Final time
1 0.0(Off)

POST RUN

Post Time: 0.00 min

TIME TABLE

Time	Specifier	Parameter & Setpoint
------	-----------	----------------------

7673 Injector

Front Injector:

Sample Washes	2
Sample Pumps	2
Injection Volume	0.1 microliters
Syringe Size	0.5 microliters
PostInj Solvent A Washes	2
PostInj Solvent B Washes	2
Viscosity Delay	2 seconds
Plunger Speed	Fast
PreInjection Dwell	0.00 minutes

Appendix A Continued

PostInjection Dwell 0.00 minutes

Back Injector:
 No parameters specified

MS ACQUISITION PARAMETERS

General Information

Tune File : atune.u
 Acquisition Mode : Scan

MS Information
 -- -----

Solvent Delay : 1.50 min
 EM Absolute : False
 EM Offset : 0
 Resulting EM Voltage : 1423.5

[Scan Parameters]

Low Mass : 50.0
 High Mass : 170.0
 Threshold : 25
 Sample # : 3 A/D Samples 8

[MSZones]

MS Quad : 150 C maximum 200 C
 MS Source : 230 C maximum 250 C

END OF MS ACQUISITION PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\MSDCHEM\1\METHODS\A3R0506.M

Percent Report Settings

Sort By: Retention Time

Appendix A Continued

Output Destination

Screen: No
Printer: Yes
File: No

Integration Events: Meth Default

Generate Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

Library to Search	Minimum Quality
C:\Database\Nist98.1	70
C:\Database\Wiley275.L	0

Integration Events: libsrch.e

Report Type: Summary

Output Destination

Screen: No
Printer: Yes
File: No

Generate Report During Run Method: No

Quantitative Report Settings

Report Type: Summary

Output Destination

Screen: Yes
Printer: Yes
File: No

Generate Report During Run Method: Yes

accustdcal

Calibration Last Updated: Tue May 06 17:27:33 2003

Reference Window: 5.00 Percent
Non-Reference Window: 10.00 Percent
Correlation Window: 0.20 minutes
Default Multiplier: 1.00
Default Sample Concentration: 0.00

Compound Information

Method: A3R0506.M

Wed May 14 12:35:37 2003

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Determination of Benzene, Toluene and Total Aromatics in Finished Gasoline by Gas Chromatography / Mass Spectrometry Method

Appendix B

			1	1	1	mass std	2	2	2	mass std	3	3	3
			vol	mg	mass%		vol	mg	mass%		vol	mg	mass%
BOTTLE													
benzene	71-43-2	1	3	2.5603	3.124714	0.268314	1	1.5	1.2856	1.653596	0.132776	1	0.75
toluene	108-88-3	2	19	16.3904	20.00364	1.717678	2	9.5	8.0288	10.327	0.829208	2	4.75
ethylbenzene	100-41-4	3	5	4.3315	5.286372	0.453932	3	2.5	2.1357	2.747033	0.220573	3	1.25
m-xylene	108-38-3	4	6	5.0383	6.148985	0.528003	4	3	2.5356	3.261402	0.261875	4	1.5
p-xylene	106-42-3	5	6	5.0543	6.168512	0.529668	5	3	2.5248	3.247511	0.260759	5	1.5
o-xylene	95-47-6	6	6	5.1703	6.310084	0.541836	6	3	2.5764	3.313881	0.266088	6	1.5
isopropylbenzene	98-82-8	7	3	2.537	3.096278	0.265872	7	1.5	1.2615	1.622598	0.130287	7	0.75
propylbenzene	103-65-1	8	3	2.5551	3.118368	0.267769	8	1.5	1.2712	1.635074	0.131288	8	0.75
3-ethyltoluene	620-14-4	9	3	2.5642	3.129474	0.268723	9	1.5	1.2734	1.637904	0.131516	9	0.75
4-ethyltoluene	622-96-8	10	3	2.5788	3.147292	0.270253	10	1.5	1.2603	1.621054	0.130163	10	0.75
1,3,5-trimethylbenzene	108-67-8	11	3	2.5683	3.134478	0.269152	11	1.5	1.2737	1.63829	0.131547	11	0.75
2-ethyltoluene	611-14-3	12	3	2.6254	3.204165	0.275136	12	1.5	1.3174	1.694499	0.13606	12	0.75
1,2,4-trimethylbenzene	95-63-6	13	5	2.5858	3.155835	0.270986	13	2.5	2.1776	2.800927	0.224901	13	1.25
1,2,3-trimethylbenzene	526-73-8	14	3	2.6647	3.252129	0.279255	14	1.5	1.3283	1.708519	0.137186	14	0.75
indan	496-11-7	15	3	2.8428	3.469491	0.297919	15	1.5	1.443	1.856051	0.149032	15	0.75
1,4-dietlylbenzene	105-05-5	16	3	2.5073	3.06003	0.26276	16	1.5	1.2755	1.640605	0.131733	16	0.75
n-butylbenzene	104-51-8	17	3	2.5383	3.097864	0.266008	17	1.5	1.2788	1.64485	0.132073	17	0.75
1,2-diethylbenzene	135-03-1	18	3	2.6037	3.177681	0.272862	18	1.5	1.3248	1.704017	0.136824	18	0.75
1,2,4,5-tetramethylbenzene	95-93-2	19	2	2.0818	2.540729	0.218168	19	1	1.1116	1.42979	0.114805	19	0.5
1,2,3,5-tetramethylbenzene	527-53-7	20	2	1.7422	2.126265	0.182579	20	1	0.8828	1.135497	0.091175	20	0.5
naphthalene	91-20-3	21	2	1.942	2.370111	0.203517	21	1	1.0384	1.335637	0.107245	21	0.5
permethylnaphthalene	700-12-9	22	2	2.1358	2.606634	0.223827	22	1	1.0702	1.376539	0.110529	22	0.5
1-methylnaphthalene	90-12-0	23	2	2.0378	2.48703	0.213557	23	1	1.0189	1.310555	0.105231	23	0.5
2-methylnaphthalene	91-57-6	24	2	2.281	2.783643	0.239044	24	1	1.0252	1.318658	0.105882	24	0.5
			95	81.9371	100			47.5	41.7195			23.75	
2,2,4-trimethylpentane	540-84-1							-140.899				-120.4	
								36.0262				52.333	
								77.7457				73.2727	
benzene-d6	1076-43-3		%	mass									
ethylbenzene-d10	5837-05-2		0.1644	9.4223	0.156788							0.154355	
naphthalene-d8	1146-65-2		0.1632	9.3495	0.155644							0.153228	
toluene-d8	2037-26-5		0.0901	5.1612	0.085928							0.084595	
			0.5824	33.3723	0.555435							0.546815	

Determination of Benzene, Toluene and Total Aromatics in Finished Gasoline by Gas Chromatography / Mass Spectrometry Method

Appendix B Continued

mass std	4	4	4	4	5	5	5	5	5	total	total		
	vol	mg	mass%	mass std	vol	mg	mass%	mass std			mg		
0.06992	1	0.375	0.323	0.464113	0.037813	1	0.1875	0.1605	0.230861	0.019225	1	5.8125	4.9694
0.440288	2	0.375	0.3202	0.46009	0.037485	2	1.1875	1.0099	1.452625	0.12097	2	34.8125	29.7794
0.117105	3	0.625	0.5276	0.758099	0.061764	3	0.3125	0.2655	0.381891	0.031803	3	9.6875	8.3322
0.139927	4	0.75	0.6278	0.902075	0.073494	4	0.375	0.3192	0.459133	0.038235	4	11.625	9.8017
0.13961	5	0.75	0.6285	0.903081	0.073576	5	0.375	0.3176	0.456831	0.038043	5	11.625	9.8031
0.142647	6	0.75	0.6461	0.92837	0.075637	6	0.375	0.3268	0.470064	0.039145	6	11.625	10.0253
0.070007	7	0.375	0.3203	0.460234	0.037496	7	0.1875	0.16	0.230142	0.019165	7	5.8125	4.9196
0.070171	8	0.375	0.3184	0.457503	0.037274	8	0.1875	0.1591	0.228847	0.019058	8	5.8125	4.9461
0.070346	9	0.375	0.3231	0.464257	0.037824	9	0.1875	0.1794	0.258046	0.021489	9	5.8125	4.984
0.070346	10	0.375	0.3285	0.472016	0.038456	10	0.1875	0.161	0.23158	0.019285	10	5.8125	4.9725
0.070171	11	0.375	0.3202	0.46009	0.037485	11	0.1875	0.1598	0.229854	0.019141	11	5.8125	4.9643
0.072575	12	0.375	0.3406	0.489402	0.039873	12	0.1875	0.1632	0.234744	0.019549	12	5.8125	5.1109
0.118361	13	0.625	0.5303	0.761979	0.06208	13	0.3125	0.2679	0.385343	0.03209	13	9.6875	6.645
0.072662	14	0.375	0.3317	0.476614	0.038831	14	0.1875	0.165	0.237334	0.019764	14	5.8125	5.1548
0.07819	15	0.375	0.3572	0.513255	0.041816	15	0.1875	0.1841	0.264807	0.022052	15	5.8125	5.5428
0.069942	16	0.375	0.3202	0.46009	0.037485	16	0.1875	0.1589	0.228559	0.019034	16	5.8125	4.9021
0.071854	17	0.375	0.3191	0.458509	0.037356	17	0.1875	0.1594	0.229279	0.019094	17	5.8125	4.9533
0.072531	18	0.375	0.3335	0.4792	0.039042	18	0.1875	0.1622	0.233306	0.019429	18	5.8125	5.0881
0.066249	19	0.25	0.2332	0.335081	0.0273	19	0.125	0.1906	0.274156	0.022831	19	3.875	4.2236
0.048037	20	0.25	0.2189	0.314534	0.025626	20	0.125	0.1096	0.157647	0.013128	20	3.875	3.3932
0.053259	21	0.25	0.3571	0.513111	0.041805	21	0.125	0.1395	0.200655	0.01671	21	3.875	3.9645
0.055892	22	0.25	0.2808	0.403477	0.032872	22	0.125	0.1296	0.186415	0.015524	22	3.875	4.128
0.0548	23	0.25	0.2505	0.359939	0.029325	23	0.125	0.1069	0.153763	0.012805	23	3.875	3.9157
0.052768	24	0.25	0.4054	0.582512	0.047459	24	0.125	0.1388	0.199648	0.016626	24	3.875	4.3334
		9.875	8.9622	12.87763			5.9375	5.2945	7.615531			158.853	
			-108.44					-104.469					
			60.6329					34.4551					
mass std			69.5951	mass std				29.7728	dodecane			mass std	
0.9534				0.945				69.5224				0.9565	
0.156739				0.155358								0.157249	
0.155595				0.154224								0.156101	
0.085901				0.085145								0.086181	
0.55526				0.550368								0.557066	

Appendix C

Sample Log Table for A3R0512.S (on line 1 of 19)

Line	Type	Vial	Data File	Method	Sample Name
1)	Sample	1	-----	A3R0506	QC
2)	Sample	2	-----	A3R0506	12182
3)	Sample	3	-----	A3R0506	12183
4)	Sample	4	-----	A3R0506	12184
5)	Sample	5	-----	A3R0506	12185
6)	Sample	6	-----	A3R0506	12186
7)	Sample	7	-----	A3R0506	12187

Type: Vial: Data File: Method: Sample Name:

Miscellaneous Information: Expected Barcode:

Sample Amt: Multiplier:

Gas Smpl Wt: Gas Density: Gas ISTD Wt:

Use the arrow keys to select entry