

California Environmental Protection Agency
 **Air Resources Board**

**PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST
FOR METHANOL AND ETHANOL**

**Standard Operating Procedure No. MLD 101
Revision 2**

September 1996

Organic Analysis Section
Southern Laboratory Branch
Monitoring and Laboratory Division
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1 Introduction

- 1.1 This document describes a method of analyzing automotive exhaust for methanol and ethanol in the range of 4 to 1200 micrograms (μg) per 15 milliliter (mL) of solution.
- 1.2 This procedure is based on a method developed by the U.S. Environmental Protection Agency (EPA, Ref. 9.1) which involves flowing diluted engine exhaust through deionized water contained in glass impingers and analyzing this solution by gas chromatography.
- 1.3 This SOP is based on Method 1001 of the California Non-methane Organic Gas Test Procedures (Ref. 2, Part C).
- 1.3 Lower alcohol concentrations may be analyzed by increasing the volume of exhaust sampled.
- 1.4 Higher concentrations may be determined by quantitatively diluting the aqueous impinger solution with deionized water or extending the calibration curve to include higher standard concentrations.

2 Method Summary

- 2.1 For routine motor vehicle exhaust testing, the vehicle is tested according to the Federal Test Procedure (FTP, Ref. 9.3), using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust for sampling.
- 2.2 Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs, Ref. 9.3), gas standard cylinders or canisters, and hydrocarbon-containing samples from other miscellaneous sources.
- 2.3 Two impingers, each containing 15 mL deionized water, are used to collect samples for each phase of the CVS test.
 - 2.3.1 For each phase, the two impingers are connected in series; the one closest to the source is designated as the primary impinger and the one farthest from the source the back-up impinger.
- 2.4 Upon completion of the CVS test, the impinger solutions are analyzed by gas chromatography.

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3 Interferences and Limitations

- 3.1 An interferent is any component present in the sample with a retention time similar to that of any target alcohols described in this method. To reduce interference error, proof of chemical identity may require periodic confirmations using an alternate method or instrumentation, e.g., (GC/MS).

4 Instrumentation and Apparatus

- 4.1 The analytical system is comprised of the following:
 - 4.1.1 Varian model 3400 or 3600 gas chromatograph (GC), equipped with DB-Wax Megabore [30 meters, 0.53 millimeters (mm) internal diameter (ID), 1 micron (u) film thickness] column and flame ionization detector (FID).
 - 4.1.2 Varian model 8000 autosampler.
 - 4.1.3 Varian Star version 4.5 (or similar) data system.

5 Reagents and Materials

- 5.1 Methanol, 99.9%, HPLC grade, EM Science or equivalent.
- 5.2 Ethanol, absolute.
- 5.3 ASTM Type I purified water, or Type II deionized water, HPLC grade, Burdick and Jackson or equivalent.
- 5.4 Stock solutions are prepared by diluting 1 g each of methanol and ethanol to 100 mL with high purity water. This standard is prepared gravimetrically and the concentration expressed in ug/mL.
 - 5.4.1 Working standards of 3 ug/mL are prepared by successive dilutions (v/v) of the stock solution(s). Figures 1 illustrates typical chromatograms of methanol and ethanol standards.
 - 5.4.2 A control standard is also prepared by successive dilutions of a different stock solution. The concentration should be approximately that of the samples, typically 25 to 35 ppm.
 - 5.4.3 Calibration and control standards are prepared at least every six months
 - 5.4.4 All standards should be refrigerated at a temperature below 40°F during storage.

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5.5 If other alcohols are found in the exhaust, standards containing these additional compounds are prepared, as above.

6 Procedure

6.1 Each of nine graduated fritted midget impingers (Ref. 9.2) is filled with 15 mL of deionized water.

6.2 For a normal FTP test, eight impingers are divided into four sets of two; a ninth is used as a traveling blank; a tenth is used as a trap. Each set is connected in series and placed in an ice bath. Dilute exhaust is drawn from the CVS through each of the four pairs of impingers during phase 1, 2, 3 and background, respectively.

6.3 The impingers are refrigerated at a temperature below 40°F until the solution contained in each impinger is transferred to a vial and sealed.

6.3.1 Samples shall be refrigerated (at a temperature below 40°F) if immediate analysis is not feasible or if reanalysis at a later date may be required.

6.4 Prior to analysis, an aliquot of 1 to 2 mL of each sample is transferred to a 2-mL autosampler vial.

6.5 A 1.0 microliter aliquot of each unmodified sample is injected via autosampler into a gas chromatograph, configured as follows:

Column	DB-wax, 30 m, 0.53 mm ID, 1.0 u film thickness
Carrier gas	helium at 5 mL/minute (mL/min)
Make-up gas	helium at 25 mL/min
Detector	FID, hydrogen at 30 mL/min, air at 300 mL/min; 250°C
Injector	packed column injector with megabore adapter insert; on-column injection; 175°C
Temperature	50°C(hold 1min), 50°C to 75°C (5°C/min), 70°C to 110°C (15°C/min), 100°C (hold 4 min)
Data System	Varian Star 4.5 or later

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- 6.6 One calibration standard, one control standard and one water blank are analyzed daily at the beginning of each set of samples.
- 6.7 A replicate analysis is performed on one of every ten samples, or at least once per day.
- 6.8 The control standard is repeated every ten samples and again at the end.
- 6.9 The above procedure may be modified for analysis of higher alcohols by increasing the final temperature and adjusting the temperature ramping to achieve good separation of the desired components. In addition, a less polar impinger solution would be required to capture alcohols above C₅.

7 Calculations

- 7.1 The concentration of each alcohol is determined by comparing the sample peak area with that of an external standard:

$$\text{Concentration } (\mu\text{g/mL})_{\text{sample}} = \text{Peak Area}_{\text{sample}} \times \text{Response Factor}$$

where the response factor (RF) is calculated during the calibration by:

$$\text{RF} = \frac{\text{Concentration}_{\text{standard}} (\mu\text{g/mL})}{\text{Peak Area}_{\text{standard}}}$$

- 7.1.1 This concentration is then used to calculate the total amount of methanol and ethanol in each impinger:

$$\text{Mass } (\mu\text{g}) = \text{Concentration } (\mu\text{g/mL}) \times 15 \text{ mL}$$

8 Quality Control

- 8.1 A deionized water blank is analyzed daily to check the analytical system for contamination.
 - 8.1.1 If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the blank is repeated.
 - 8.1.2 If the peak area is consistent, the blank is subtracted from the standards and samples.
 - 8.1.3 If the peak area is not consistent, the source of the contamination must be investigated.
- 8.2 One run of the calibration standard(s) is performed per day to generate the response factors needed for quantifying sample analyses.

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- 8.3 The quality control standard is analyzed at the beginning of each set of samples, and repeated every ten samples and again at the end.
- 8.3.1 A quality control chart is maintained for each alcohol in the control standard. The control charts, used on a daily basis, establish that the method is "in-control". The following describes how a typical control chart is constructed:
- (1) Obtain at least 20 daily control standard results;
 - (2) Calculate the control standard mean concentration and standard deviation for the monitored hydrocarbon; and
 - (3) Create a control chart for the monitored hydrocarbon by placing the dates on the x-axis and the concentrations on the y-axis. Establish an upper and lower warning limit at two standard deviations (2σ) above and below the average concentration. Establish an upper and lower control limit at three standard deviations (3σ) above and below the average concentration.
- 8.3.2 Measurements of both methanol and ethanol must be within the control limits ("in-control") before sample analysis may proceed. Values which exceed three standard deviations above or below the mean are considered to be "out of control". If all measurements on two consecutive days exceed two standard deviations above or below the mean, the second day's analysis is also considered to be out of control. If either methanol or ethanol is out of control, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards until the control standard criteria are met; when the QC criteria are met, sample analysis can continue. Figures 2a and 2b demonstrate a typical QC chart.
- 8.4 A duplicate analysis of one sample bag is performed at least once a day. The relative percent difference (RPD) is calculated for each duplicate run:

$$\text{RPD (\%)} = \frac{\text{Difference between duplicate and original measurements} \times 100}{\text{Average of duplicate and original measurements}}$$

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For each monitored hydrocarbon compound in the control standard, the allowable RPD depends on the average concentration of the duplicate runs, as shown in the following table (Ref. 9.1):

<u>Average Measurement for Duplicate</u>		<u>Allowable RPD (%)</u>
1 to 10	times LOD	100
10 to 20	" "	30
20 to 50	" "	20
Greater than 50	" "	15

The results from duplicate analysis must meet the criteria above for all monitored hydrocarbon compounds in the control standard for Methods 1002 and 1003 (Ref.9.1). If the criteria are not met, the sample must be rerun. If the criteria are still not met, all sample results for the day from this instrument must be deleted and the samples reanalyzed. Figure 3 shows a typical duplicate sample report.

- 8.6 A multipoint calibration to confirm instrument linearity is performed for methanol and ethanol. It is done for new instruments, after making instrument modifications which can affect linearity, and at least once per year. The multipoint consists of at least five concentrations, each above the maximum allowable LOD (0.50 ug/mL), about evenly distributed over the range of expected sample concentration. Each concentration is measured at least twice. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The r must be greater than 0.995 to be considered sufficiently linear to ensure the accuracy of the daily one-point calibration. Figure 4 illustrates a typical multipoint calibration.
- 8.7 The LOD for methanol and ethanol must be determined for new instruments, after making modifications which can affect linearity and/or sensitivity and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration consisting of at least four "low" concentration levels, each above the LOD. The LOD is calculated using the following equation:

$$\text{LOD (ppbC)} = \frac{|b| + (t \times \sigma)}{m}$$

where

- |b| = the absolute value of the y-intercept, area counts
- m = the slope of the linear regression, area counts/ppbC
- σ = the standard deviation of at least five measurements of the lowest concentration standard, area counts
- t = the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution, dimensionless

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The number of degrees of freedom is equal to the number of runs (n) of the lowest concentration standard, minus one. An abbreviated t-table is (Ref.9.1):

Degrees of Freedom (n-1)	t-values
4	3.7
5	3.4
6	3.1
7	3.0

- 8.7.1 The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the estimated LOD. The maximum allowable LOD for each compound is 0.50 ug/mL ppbC. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD.
- 8.7.2 All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported.
- 8.7.3 If the calculated laboratory LOD is less than the maximum allowable LOD, the Southern Laboratory Branch (SLB) may set its reporting limit at either the maximum allowable LOD or the calculated laboratory LOD. The current reporting limit is 0.50 ug/mL. Figure 5 shows a typical LOD determination.
- 8.7 Additional compounds may be identified by GC/Fourier Transform Infrared Spectroscopy (GC/FTIR).
- 8.7.1 The presence of alcohol in samples which show an interference or an unidentified peak may be confirmed by GC/MS, GC/FTIR, or by a second GC method.
- 8.8 Recovery tests have been limited, due to the instability and resulting unavailability of gas phase methanol standards.
- 8.9 Quality control of the sampling procedure is overseen by MSD.

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9 References

- 9.1 "Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles", EPA 460/3-82-004.
- 9.2 California Environmental Protection Agency, California Air Resources Board, "California Non-methane Organic Gas Test Procedures", May 31, 1996.
- 9.3 Code of Federal Regulations, Title 40, Part 86.

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Title : Alcohols by MLD method 1001
Run File : c:\star\module16\module16\alc#6725.run
Method File : C:\STAR\ALC#3ER1.MTH
Sample ID : A3.0PPM

Injection Date: 22-JAN-99 11:57 AM Calculation Date: 25-JAN-99 9:17 AM

Operator : ESR Detector Type: ADCB (10 Volts)
Workstation: ALCOHOL Bus Address : 16
Instrument : REC ALCOHOL Sample Rate : 10.00 Hz
Channel : A = FID Run Time : 4.002 min

***** Star Chromatography Workstation ***** Version 4.51 *****

Chart Speed = 4.95 cm/min Attenuation = 16 Zero Offset = 2%
Start Time = 0.000 min End Time = 4.000 min Min / Tick = 1.00

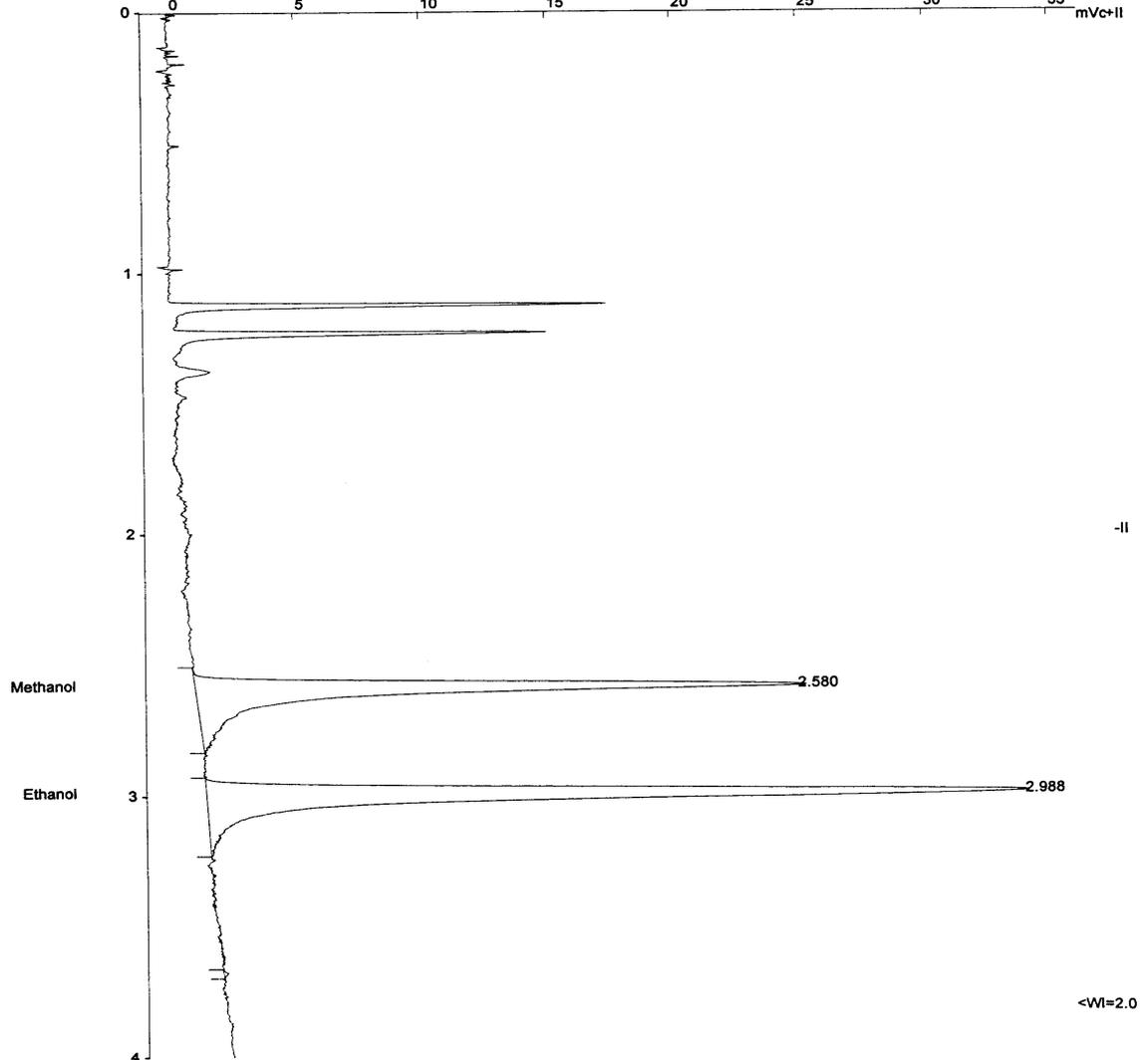


Figure 1

SOP No. 101 - PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR METHANOL AND ETHANOL

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ALCOHOL GC CALIBRATION DATA

METHANOL 3.0 UG/ML

ETHANOL 3.0 UG/ML

NO. OF RUNS	DATE OF ANAL.	DATA FILE	AREA COUNT	CALIBRATION FACTOR	DATE OF ANAL.	DATA FILE	AREA COUNT	CALIBRATION FACTOR	
1	07/17/1998	4701	6295	210	07/17/1998	4701	9090	303	prepd 7/17/98
2	07/17/1998	4723	6705	224	07/17/1998	4723	9625	321	
3	07/18/1998	4755	6868	230	07/18/1998	4755	9691	330	
4	07/18/1998	4756	6799	227	07/18/1998	4756	9778	326	
5	07/18/1998	4757	6635	221	07/18/1998	4757	9512	317	
6	07/18/1998	4758	6863	229	07/18/1998	4758	9877	329	
7	07/18/1998	4759	6854	228	07/18/1998	4759	9810	327	
8	07/18/1998	4760	6873	229	07/18/1998	4760	9889	330	
9	07/21/1998	4770	6470	216	07/21/1998	4770	9199	307	
10	07/21/1998	4783	6792	226	07/21/1998	4783	9811	327	
11	07/22/1998	4834	6758	225	07/22/1998	4834	9617	321	
12	07/22/1998	4856	6934	231	07/22/1998	4856	9734	324	
13	07/23/1998	4886	6759	225	07/23/1998	4886	9648	322	
14	07/23/1998	4907	6910	230	07/23/1998	4907	9824	327	
15	07/24/1998	4931	6737	225	07/24/1998	4931	9693	323	
16	07/24/1998	4957	7127	238	07/24/1998	4957	10076	336	
17	07/27/1998	4997	6938	231	07/27/1998	4997	9931	331	
18	07/27/1998	5018	7070	236	07/27/1998	5018	10027	334	
19	07/28/1998	5033	6907	230	07/28/1998	5033	9787	326	
20	07/28/1998	5052	6827	228	07/28/1998	5052	9736	325	
21	07/29/1998	5066	6740	225	07/29/1998	5066	9651	322	prepd 7/29/98
22	07/29/1998	5087	6821	227	07/29/1998	5087	9651	322	
23	07/31/1998	5097	6743	225	07/31/1998	5097	9617	321	
24	08/06/1998	5126	6560	219	08/06/1998	5126	9182	306	
25	08/06/1998	5147	6680	223	08/06/1998	5147	9462	315	
26	08/07/1998	5159	6771	226	08/07/1998	5159	9554	318	
27	08/07/1998	5180	7025	234	08/07/1998	5180	9694	323	
28	08/10/1998	5204	6800	227	08/10/1998	5204	9709	324	prepd 8/10/98
29	08/10/1998	5225	6642	221	08/10/1998	5225	9372	312	
30	08/13/1998	5241	6715	224	08/13/1998	5241	9601	320	
31	08/13/1998	5262	6271	209	08/13/1998	5262	9028	301	
32	08/14/1998	5292	6354	212	08/14/1998	5292	8984	299	
33	08/14/1998	5309	6394	213	08/14/1998	5309	8992	300	
34	08/14/1998	5330	6657	222	08/14/1998	5330	9473	316	
35	08/14/1998	5331	6708	224	08/14/1998	5331	9419	314	
36	08/18/1998	5355	6676	223	08/18/1998	5355	9454	315	prepd 8/18/98
37	08/18/1998	5379	6665	222	08/18/1998	5379	9480	316	
38	08/18/1998	5399	6467	216	08/18/1998	5399	9216	307	
39	08/18/1998	5400	6523	217	08/18/1998	5400	9206	307	
40	08/20/1998	5427	6596	220	08/20/1998	5427	9392	313	prepd 8/20/98
41	08/20/1998	5448	6827	228	08/20/1998	5448	9614	320	
42	08/20/1998	5470	6716	224	08/20/1998	5470	9473	316	
43	08/21/1998	5478	6611	220	08/21/1998	5478	9551	318	"
44	08/21/1998	5479	6660	222	08/21/1998	5479	9457	315	
45	08/21/1998	5498	6540	218	08/21/1998	5498	9318	311	
46	08/25/1998	5502	6511	217	08/25/1998	5502	9284	309	"
47	08/25/1998	5503	6543	218	08/25/1998	5503	9269	309	
48	08/26/1998	5525	6588	220	08/26/1998	5525	9196	307	"
49	08/28/1998	5551	6729	224	08/28/1998	5551	9432	314	prepd 8/28
50	08/28/1998	5573	6730	224	08/28/1998	5573	9494	316	"
51	09/03/1998	5580	6811	227	09/03/1998	5580	9683	323	"
52	09/04/1998	5605	7091	236	09/04/1998	5605	10064	335	"
53	09/04/1998	5629	7227	241	09/04/1998	5629	10181	339	
54	09/08/1998	6004	6947	232	09/08/1998	6004	9960	332	stdprep9/8fromstock prepd 9/8
55	09/08/1998	6011	6854	228	09/08/1998	6011	9807	327	"
56	09/08/1998	6012	6838	228	09/08/1998	6012	9761	325	stdprep 8/28from stock prep7/2
57	09/08/1998	6016	6908	230	09/08/1998	6016	9753	325	stdprep9/8 fromstockprepd7/2
58	09/09/1998	6650	7076	236	09/09/1998	6650	10125	338	stdprep 9/8fromstockprepd9/8
59	09/10/1998	6676	7162	239	09/10/1998	6676	10258	342	"
60	09/14/1998	6701	6735	225	09/14/1998	6701	9719	324	"
61	09/14/1998	6702	6789	226	09/14/1998	6702	9832	328	"
62	09/14/1998	6706	6679	223	09/14/1998	6706	9671	322	stdprep9/14fromstockprepd9/8
63	09/14/1998	6707	6763	225	09/14/1998	6707	9808	327	"
64	09/18/1998	6736	7052	235	09/18/1998	6736	10136	338	
65	09/21/1998	6763	6968	232	09/21/1998	6763	10011	334	std prep 9/21
66	09/22/1998	6787	6897	230	09/22/1998	6787	9923	331	"
67	09/23/1998	6793	6990	233	09/23/1998	6793	10038	335	stdprep9/23
68	09/24/1998	6804	6954	232	09/24/1998	6804	9960	332	"
69	09/24/1998	6821	6994	233	09/24/1998	6821	10026	334	"
70	09/25/1998	6844	6880	229	09/25/1998	6844	9898	330	"
71	09/29/1998	6849	7010	234	09/29/1998	6849	9854	328	"
72	09/29/1998	6870	6912	230	09/29/1998	6870	9913	330	stdprep9/29

Figure 2a

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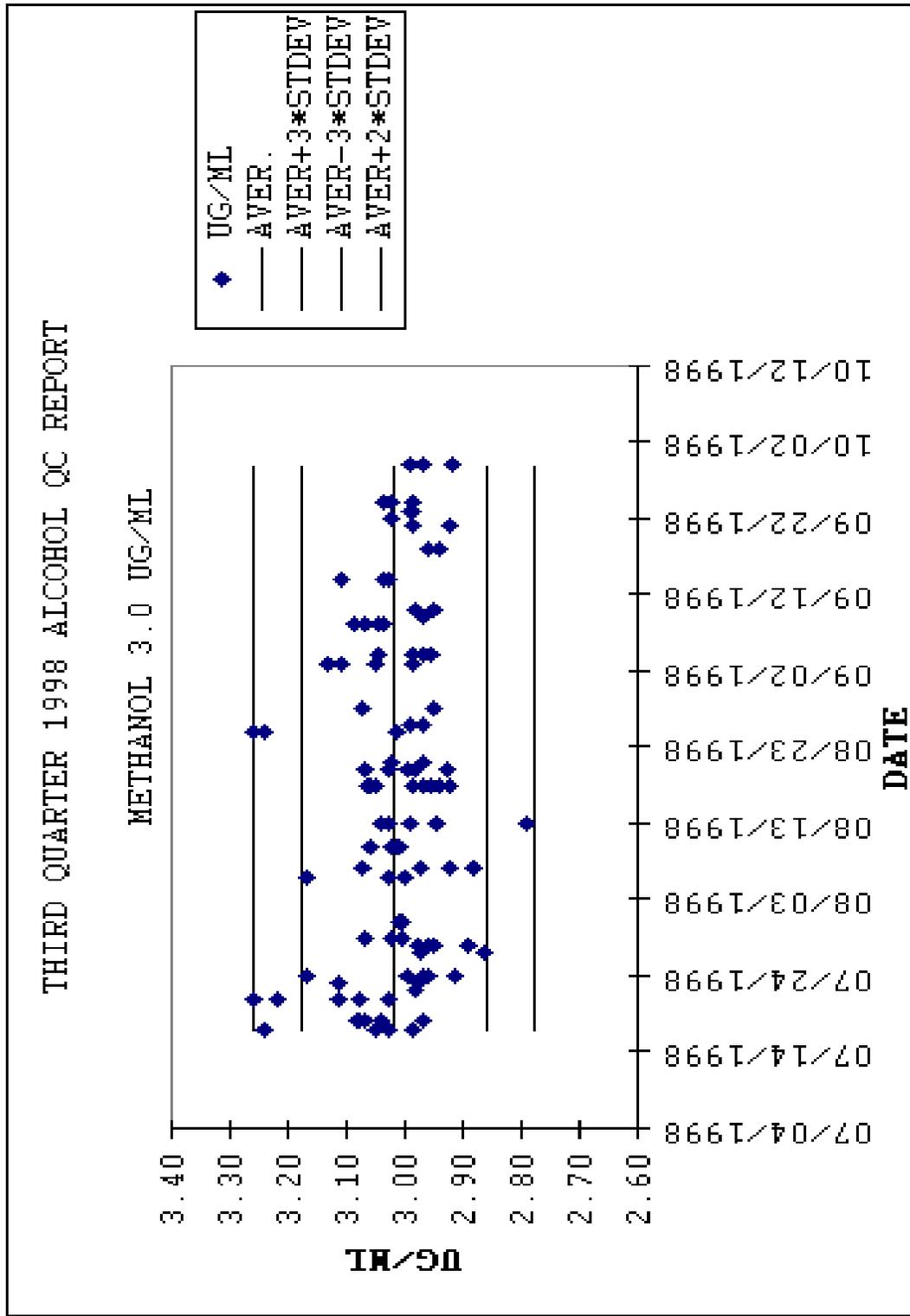


Figure 2b

SOP No. 101 - PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR METHANOL AND ETHANOL

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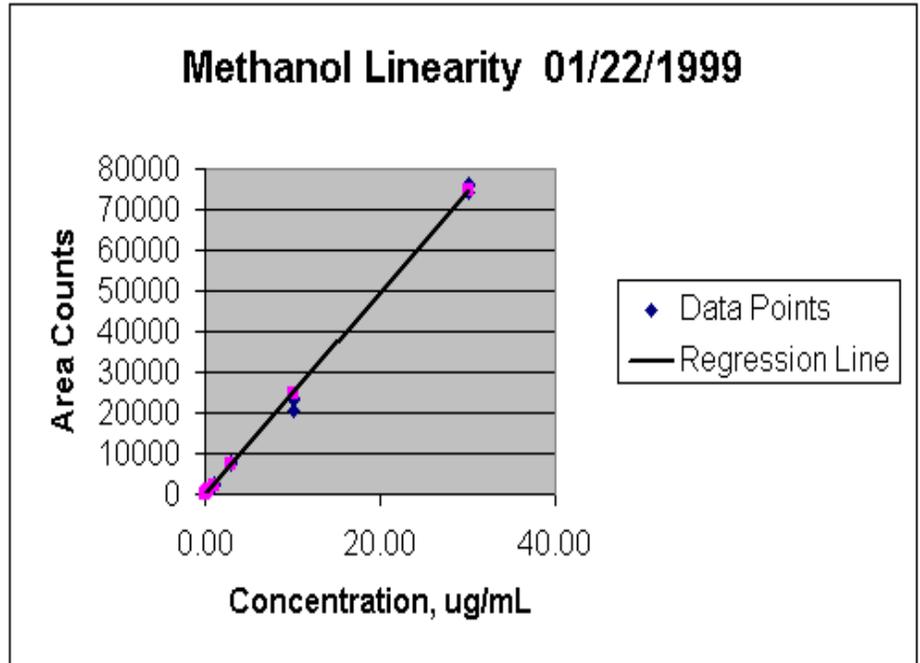
ALCOHOL REPLICATES

NO. OF RUNS	DATE OF ANAL.	SAMPLE NO.	METHANOL				STATUS	ETHANOL				
			RUN #1	RUN #2	% RPD	MAX %RPD		RUN #1	RUN #2	%RPD	MAX %RPD	
1	07/03/1998	142UC1A	0.72	0.75	4	100	OK	<L	<L	<L	<L	OK
2	07/06/1998	142C2 1A	0.621	0.694	11	100	OK	<L	<L	<L	<L	OK
3	07/06/1998	142C2 2A	0.078	0.078	8	100	OK	<L	<L	<L	<L	OK
4	07/06/1998	142C2 3A	0.168	0.115	5	100	OK	<L	<L	<L	<L	OK
5	07/06/1998	151C1 1A	0.377	0.378	0	100	OK	<L	<L	<L	<L	OK
6	07/06/1998	151C1 2A	0.545	0.545	3	100	OK	<L	<L	<L	<L	OK
7	07/06/1998	151C1 3A	0.442	0.467	6	100	OK	<L	<L	<L	<L	OK
8	07/07/1998	151UC1 1A	0.341	0.36	6	100	OK	<L	<L	<L	<L	OK
9	07/07/1998	151UC1 2A	0.557	0.565	2	100	OK	<L	<L	<L	<L	OK
10	07/07/1998	151UC1 3A	0.358	0.357	0	100	OK	<L	<L	<L	<L	OK
11	07/08/1998	156C1 1A	0.882	0.809	9	100	OK	<L	<L	<L	<L	OK
12	07/08/1998	156C1 2A	0.393	0.427	8	100	OK	<L	<L	<L	<L	OK
13	07/08/1998	156C1 3A	0.496	0.506	2	100	OK	<L	<L	<L	<L	OK
14	07/08/1998	142UC1 1A	0.777	0.712	9	100	OK	<L	<L	<L	<L	OK
15	07/08/1998	142UC1 1B	<L	<L	<L	<L	OK	<L	<L	<L	<L	OK
16	07/08/1998	142UC1 2A	0.127	0.137	6	100	OK	<L	<L	<L	<L	OK
17	07/08/1998	142UC1 2B	<L	<L	<L	<L	OK	<L	<L	<L	<L	OK
18	07/08/1998	142UC1 3A	0.119	0.153	25	100	OK	<L	<L	<L	<L	OK
19	07/09/1998	156UC11A	0.411	0.514	22	100	OK	<L	<L	<L	<L	OK
20	07/09/1998	156UC12A	1.341	1.354	1	30	OK	0.051	0.30	<L	<L	100
21	07/09/1998	156UC13A	0.366	0.349	5	100	OK	<L	<L	<L	<L	OK
22	07/09/1998	151C1 1A	0.406	0.359	12	100	OK	<L	<L	<L	<L	OK
23	07/09/1998	151C1 2A	0.694	0.648	10	100	OK	<L	<L	<L	<L	OK
24	07/09/1998	151C1 3A	0.481	0.494	3	100	OK	<L	<L	<L	<L	OK
25	07/09/1998	142C2 1A	0.697	0.66	2	100	OK	<L	<L	<L	<L	OK
26	07/09/1998	142C2 2A	0.068	0.07	23	<	OK	<L	<L	<L	<L	OK
27	07/09/1998	142C2 3A	0.194	0.164	17	100	OK	<L	<L	<L	<L	OK
28	07/17/1998	164C1 1A	0.21	0.23	3	100	OK	<L	<L	<L	<L	OK
29	07/17/1998	164C1 2A	0.075	0.063	34	<	OK	0.054	0.051	<L	<L	100
30	07/17/1998	164C1 3A	0.102	0.073	33	<	OK	<L	<L	<L	<L	OK
31	07/22/1998	166C1 1A	0.506	0.509	4	100	OK	<L	<L	<L	<L	OK
32	07/22/1998	166C1 2A	0.115	0.082	34	<	OK	<L	<L	<L	<L	OK
33	07/22/1998	166C1 3A	0.222	0.298	29	100	OK	<L	<L	<L	<L	OK
34	07/23/1998	169C1 1A	2.27	2.923	4	20	OK	<L	<L	<L	<L	OK
35	07/23/1998	169C1 2A	2.281	2.33	2	20	OK	<L	<L	<L	<L	OK
36	07/23/1998	169C1 3A	2.018	1.835	9	30	OK	<L	<L	<L	<L	OK
37	07/24/1998	169UC1 1A	0.055	2.14	3	20	OK	<L	<L	<L	<L	OK
38	07/24/1998	169UC1 2A	6.662	6.605	1	15	OK	0.058	<L	<L	<L	100
39	07/24/1998	169UC1 3A	1.104	1.141	3	30	OK	<L	<L	<L	<L	OK
40	07/27/1998	173C1 1A	1.361	1.363	1	30	OK	0.054	0.051	<L	<L	100
41	07/27/1998	173C1 2A	1.4	1.387	1	30	OK	0.056	0.053	6	100	OK
42	07/27/1998	173C1 3A	0.952	1	1	30	OK	<L	<L	<L	<L	OK
43	07/28/1998	173UC1 1A	0.696	0.684	10	100	OK	0.054	<L	<L	<L	100
44	07/28/1998	173UC1 2A	2.631	2.609	1	20	OK	0.078	0.065	18	100	OK
45	07/28/1998	173UC1 3A	0.487	0.516	4	100	OK	<L	<L	<L	<L	OK
46	07/29/1998	175C1 1A	0.665	0.692	4	100	OK	<L	<L	<L	<L	OK
47	07/29/1998	175C1 2A	0.149	0.158	6	100	OK	<L	<L	<L	<L	OK
48	07/29/1998	175C1 3A	0.268	0.261	2	100	OK	<L	<L	<L	<L	OK
49	07/31/1998	176UC1 1A	0.601	0.611	2	100	OK	<L	<L	<L	<L	OK
50	07/31/1998	176UC1 2A	0.416	0.432	4	100	OK	<L	<L	<L	<L	OK
51	07/31/1998	176UC1 3A	0.117	0.134	14	4	OK	<L	<L	<L	<L	OK
52	08/06/1998	182C1 1A	0.527	0.511	3	100	OK	<L	<L	<L	<L	OK
53	08/06/1998	182C1 2A	0.22	0.206	7	100	OK	<L	<L	<L	<L	OK
54	08/06/1998	182C1 3A	0.263	0.245	3	100	OK	<L	<L	<L	<L	OK
55	08/06/1998	AF NEUV	0.428	0.455	6	100	OK	<L	<L	<L	<L	OK
56	08/06/1998	AF CLD	0.227	0.222	2	100	OK	<L	<L	<L	<L	OK
57	08/07/1998	185C1 1A	1.504	1.493	2	100	OK	0.108	0.107	1	100	OK
58	08/07/1998	185C1 2A	1.703	1.727	1	30	OK	0.088	0.091	3	100	OK
59	08/07/1998	185C1 3A	0.079	0.087	8	30	OK	0.065	0.063	2	100	OK
60	08/07/1998	B2UC1BKG	0.121	0.101	18	100	OK	0.057	0.053	7	100	OK
61	08/10/1998	182UC1 1A	0.406	0.41	1	100	OK	<L	<L	<L	<L	OK
62	08/10/1998	182UC1 2A	0.625	0.635	2	100	OK	<L	<L	<L	<L	OK
63	08/10/1998	182UC1 3A	0.168	0.149	12	100	OK	<L	<L	<L	<L	OK
64	08/13/1998	186UC1 1A	0.387	0.425	9	100	OK	<L	<L	<L	<L	OK
65	08/13/1998	186UC1 2A	0.242	0.23	4	100	OK	<L	<L	<L	<L	OK
66	08/13/1998	186UC1 3A	0.201	0.244	19	100	OK	<L	<L	<L	<L	OK
67	08/13/1998	186C1 1A	0.312	0.323	3	100	OK	<L	<L	<L	<L	OK
68	08/13/1998	186C1 2A	0.106	0.084	11	23	OK	<L	<L	<L	<L	OK
69	08/13/1998	186C1 3A	0.177	0.197	11	100	OK	<L	<L	<L	<L	OK
70	08/14/1998	189C1 1A	2.553	2.689	5	20	OK	<L	<L	<L	<L	OK
71	08/14/1998	189C1 2A	2.48	2.502	1	20	OK	0.072	0.073	1	100	OK
72	08/14/1998	189C1 3A	1.813	1.805	0	30	OK	0.061	0.074	19	100	OK
73	08/18/1998	189UC1 1A	0.579	0.579	4	100	OK	<L	<L	<L	<L	OK
74	08/18/1998	189UC1 2A	0.55	0.567	3	100	OK	<L	<L	<L	<L	OK
75	08/18/1998	189UC1 3A	0.265	0.253	5	100	OK	<L	<L	<L	<L	OK
76	08/18/1998	189C1 1A	0.618	0.642	4	100	OK	<L	<L	<L	<L	OK
77	08/18/1998	189UC1 2A	5.831	5.738	2	15	OK	0.091	0.104	13	100	OK
78	08/18/1998	189UC1 3A	0.536	0.584	9	100	OK	<L	<L	<L	<L	OK
79	08/20/1998	191C1 1A	0.675	0.693	2	100	OK	<L	<L	<L	<L	OK
80	08/20/1998	191C1 2A	<L	<L	<L	<L	OK	<L	<L	<L	<L	OK
81	08/20/1998	191C1 3A	0.793	0.801	1	100	OK	<L	<L	<L	<L	OK
82	08/20/1998	191UC1 1A	0.462	0.539	15	100	OK	<L	<L	<L	<L	OK
83	08/20/1998	191UC1 2A	0.698	0.737	5	100	OK	<L	<L	<L	<L	OK
84	08/20/1998	191UC1 3A	0.347	0.407	16	100	OK	<L	<L	<L	<L	OK
85	08/21/1998	197C1 1A	1.447	1.433	1	30	OK	<L	<L	<L	<L	OK
86	08/21/1998	197C1 2A	1.116	1.03	8	30	OK	<L	<L	<L	<L	OK
87	08/21/1998	197C1 3A	1.113	1.088	2	30	OK	<L	<L	<L	<L	OK
88	08/25/1998	197UC1 1A	0.959	0.958	0	100	OK	<L	<L	<L	<L	OK
89	08/25/1998	197UC1 2A	2.23	2.254	1	20	OK	0.062	0.077	6	100	OK
90	08/25/1998	197UC1 3A	0.914	0.916	0	100	OK	<L	<L	<L	<L	OK
91	08/26/1998	199UC1 1A	0.918	0.839	9	100	OK	<L	<L	<L	<L	OK
92	08/26/1998	199UC1 2A	0.496	0.486	2	100	OK	<L	<L	<L	<L	OK
93	08/26/1998	199UC1 3A	0.403	0.388	4	100	OK	<L	<L	<L	<L	OK
94	08/28/1998	199C1 1A	0.833	0.853	2	100	OK	<L	<L	<L	<L	OK
95	08/28/1998	199C1 2A	1.018	1.015	0	30	OK	<L	<L	<L	<L	OK
96	08/28/1998	199C1 3A	0.36	0.37	3	100	OK	<L	<L	<L	<L	OK
97	09/03/1998	207C1 1A	1.318	1.326	1	30	OK	<L	<L	<L	<L	OK
98	09/03/1998	207C1 2A	0.312	0.302	3	100	OK	<L	<L	<L	<L	OK
99	09/03/1998	207C1 3A	0.373	0.376	1	100	OK	<L	<L	<L	<L	OK
100	09/04/1998	208C1 1A	0.29	0.276	5	100	OK	<L	<L	<L	<L	OK
101	09/04/1998	208C1 2A	<L	<L	<L	<L	OK	<L	<L	<L	<L	OK
102	09/04/1998	208C1 3A	<L	<L	<L	<L	OK	<L	<L	<L	<L	OK
103	09/04/1998	207UC1 1A	1.121									

**SOP No. 101 - PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR
METHANOL AND ETHANOL**

**METHANOL LINEARITY
01/22/1999**

Concentration, ug/mL	Area Counts
0.10	281
0.10	246
0.10	283
0.10	269
0.10	272
0.30	706
0.30	700
0.30	719
0.30	690
0.30	751
0.50	1228
0.50	1161
0.50	1237
0.50	1283
0.50	1086
0.50	1169
0.50	1122
0.50	1315
1.00	2183
1.00	2571
1.00	2420
1.00	2216
3.00	7574
3.00	7784
3.00	7665
3.00	7409
3.00	7276
3.00	7591
3.00	7737
3.00	7584
10.00	20622
10.00	23482
10.00	22982
30.00	74354
30.00	75670
30.00	76072



Regression Output:

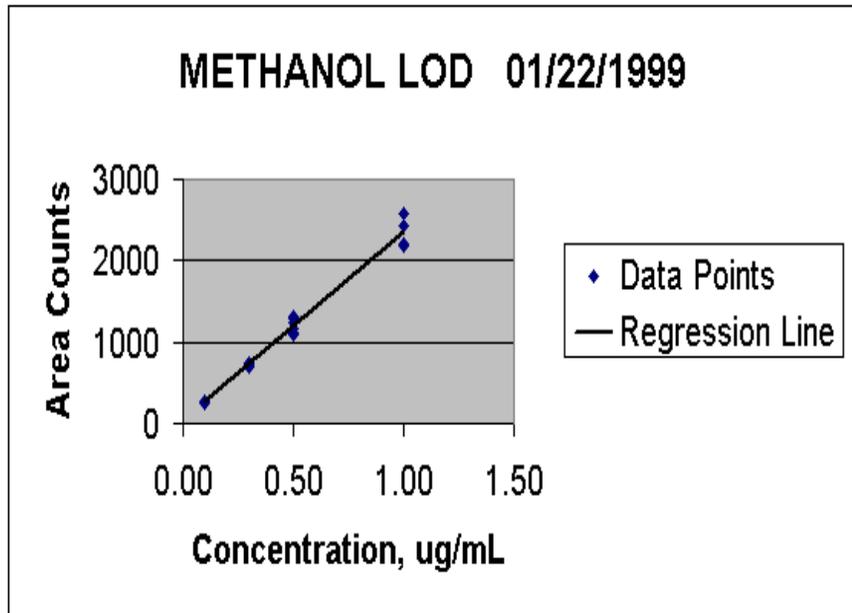
Slope	2494	
Intercept	-178	
Correlation Coefficient	0.9991	(Passing Requirement (<0.995)

Figure 4

**SOP No. 101 - PROCEDURE FOR THE ANALYSIS OF AUTOMOTIVE EXHAUST FOR
METHANOL AND ETHANOL**

METHANOL LOD
01/22/1999

Concentration, ug/mL	Area Counts
0.10	281
0.10	246
0.10	283
0.10	269
0.10	272
0.30	706
0.30	700
0.30	719
0.30	690
0.30	751
0.50	1228
0.50	1161
0.50	1237
0.50	1283
0.50	1086
0.50	1169
0.50	1122
0.50	1315
1.00	2183
1.00	2571
1.00	2420
1.00	2216



Regression Output:

Slope 2316.716
Intercept 33.67442
Correlation Coefficient 0.993003

σ 14.75466 for five measurements of the lowest concentration standard

LOD 0.0381 ug/mL

Figure 5