

California Environmental Protection Agency
 **Air Resources Board**

SOP MLD 104

**STANDARD OPERATING PROCEDURE FOR THE
DETERMINATION OF ALDEHYDE AND KETONE COMPOUNDS
IN AUTOMOTIVE SOURCE SAMPLES
BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY**

Southern Laboratory Branch
Monitoring and Laboratory Division

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Revision History for SOP MLD 104

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1 Introduction

- 1.1 This procedure describes a method of sampling and analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) in the range of 0.02 to 200 micrograms (μg) in 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges. Currently the target compounds analyzed and reported by this method are: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, methyl ethyl ketone (MEK), benzaldehyde, valeraldehyde, m-tolualdehyde, and hexanal.
- 1.2 This procedure is derived from a method used by the U.S.EPA (Riggin, 1984; Winberry et. al., 1999) and integrated into Method 1004 of the California Non-methane Organic Gas Test Procedures (ARB, 2002).

2 Method Summary

2.1 Sample Collection:

- 2.1.1 For routine motor vehicle testing, the vehicle is tested according to the Federal Test Procedure (FTP), using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust for sampling (see CFR in the reference section).
- 2.1.2 Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs), cartridge samples for round-robin testing and carbonyl-containing samples from other miscellaneous sources.
- 2.1.3 The automotive test personnel collect the carbonyl samples by flowing dilute exhaust (approximately 1.0 liter/min. flow rate) through cartridges (Tejada, 1986a). The samples are then brought to the laboratory for analysis.

2.2 Extraction and Analysis:

- 2.2.1 Each cartridge contains an absorbing compound (2,4-DNPH) which complexes with the carbonyl compounds to form their dinitrophenylhydrazone derivatives (called carbonyl-DNPH in this document). The cartridges are then extracted with 5.0 milliliters (mL) acetonitrile and analyzed (Tejada, 1986b).
- 2.2.2 Separation and analysis is performed using a High Performance Liquid Chromatograph (HPLC) with an ultraviolet (UV/VIS) detector.

3 Interferences and Limitations

- 3.1 As with any chromatographic method, this method is subject to interference by compounds in the acetonitrile extract having the same retention time as one of the

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thirteen target compounds and detectable by ultraviolet absorption. Periodic confirmations using an alternative method and/or instrumentation, e.g., alternative HPLC column or mobile phase, may be needed to minimize these interferences.

- 3.2 If samples are not analyzed the same day as received, they must be refrigerated at a temperature below 40°F. Refrigerated samples are stable for up to 30 days.
- 3.3 The extraction of cartridges with 5.0 mL acetonitrile performed in the laboratory established a statistical average eluted volume of 4.4 mL; the remaining 0.6 mL is retained in the cartridge.

4 Instruments and Apparatus

- 4.1 The Southern Laboratory Branch (SLB) currently utilize a modular Waters HPLC analytical system assembled from the components listed below. Equivalent HPLC systems that meet the requirements of this analytical procedure are also acceptable.
 - 4.1.1 Dual high pressure pumps (Waters Model 510). An equivalent HPLC system should consist of pump/pumps with a minimum of two channels and sufficient pulse dampening for meeting the limit of detection (LOD) requirement specified in section 8.7.6.
 - 4.1.2 Pump controller module (Water PCM/15xx). Typical modern HPLC systems do not require a separate pump controller module.
 - 4.1.3 Liquid autosampler with sample tray at 20°C (Waters Model 717 WISP). An equivalent HPLC system should consist of a sample handling module capable of maintaining 20°C.
 - 4.1.4 Temperature control module (Waters TCM). An equivalent HPLC system should consist of column holding module capable of maintaining 40°C.
 - 4.1.5 Chromatographic Columns: two Supelcosil columns (Supelco, Inc., 4.6 mm inside diameter x 25 cm long) in series and a guard column (2.0 cm long) packed with LC-18 beads of 5 µm particle size. Many vendors supply HPLC columns with similar stationary phase compositions (i.e. C-18). An equivalent column should be able to resolve the DNPH-derivatives of the 13 target compounds into 13 peaks.
 - 4.1.6 UV/VIS Detector (Waters Model 486 tunable absorbance detector). An equivalent HPLC system should consist of a detector able to measure absorbance in the 360-370 nm region and meet the LOD requirement specified in section 8.7.6

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4.1.7 Computer-based data system for peak integration (Millennium32). An equivalent software package should be able to control the HPLC system and to facilitate peak integration.

5 Reagents and Materials

5.1 For sample collection: DNPH impregnated cartridges (SEP-PAK DNPH Silica cartridges from Waters)

5.2 Acetonitrile (ACN), HPLC grade, VWR Scientific or equivalent

5.3 Purified water, HPLC grade, VWR Scientific or equivalent

5.4 Methanol, HPLC grade, VWR Scientific or equivalent

5.5 Stock solutions – Carbonyl-DNPH standard solution, by Cerilliant Corporation or equivalent, consisting of thirteen compounds (see Table 1), each having a concentration of 1.0 µg/mL, 3.0 µg/mL, or 15.0 µg/mL and 99% purity. The concentrations are the amount of carbonyl compound (NOT the carbonyl-DNPH derivative) per mL of solution.

5.6 Working Standard – A typical working standard is prepared as needed by diluting 2.0 mL of the 3.0 µg/mL stock solution to 10 mL (v/v) using ACN for dilution. Current working standard concentration is 0.6 µg/mL.

5.7 Control Standard – A quality control standard, containing all target carbonyl-DNPH derivatives within the typical concentration range of real samples, is analyzed to monitor the precision of the analysis of each target carbonyl. The control standard is prepared by batch mixing old samples and spiking with the stock carbonyl-DNPH standard solution, if needed, to obtain the desired concentration levels of the target analytes. All target compounds except acrolein have been found to be stable in the control standard.

5.8 Additional standards containing the target carbonyls listed in Table 1 are used in linearity and LOD (see section 8) determinations. These may be purchased or prepared by dilutions of an appropriate stock solution.

Derived From	Chemical Formula	Molecular Weight (g/mole)	Chemical Structure
Formaldehyde	C ₇ H ₆ N ₄ O ₄	210.15	

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Acetaldehyde	$C_8H_8N_4O_4$	224.18	
Acrolein	$C_9H_8N_4O_4$	236.19	
Acetone	$C_9H_{10}N_4O_4$	238.20	
Propionaldehyde	$C_9H_{10}N_4O_4$	238.20	
Crotonaldehyde	$C_{10}H_{10}N_4O_4$	250.21	
MEK (2-Butanone)	$C_{10}H_{12}N_4O_4$	252.23	
n-Butyraldehyde	$C_{10}H_{12}N_4O_4$	252.23	
Methacrolein	$C_{10}H_{10}N_4O_4$	250.21	
Benzaldehyde	$C_{13}H_{10}N_4O_4$	286.25	
Valeraldehyde	$C_{11}H_{14}N_4O_4$	266.26	
m-Tolualdehyde	$C_{14}H_{12}N_4O_4$	300.27	

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Hexanal	$C_{12}H_{16}N_4O_4$	280.28	
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Table 1: Dinitrophenylhydrazone derivatives of the thirteen target compounds listed in the order of elution from the Supelcosil column.

6 Procedure

- 6.1 DNPH-impregnated cartridges are used to collect carbonyl samples from automotive exhaust. Separate background samples are collected during each of the three test phases, although one composite background may be collected instead.
- 6.2 Each cartridge is extracted by connecting it to a syringe assembly and applying 5.0 mL of acetonitrile. The liquid containing the carbonyl-DNPH derivatives is allowed to flow by gravity into a glass storage container until the entire yellow color band has been eluted. The plunger is then pressed to expel the excess ACN from the cartridge. Although approximately 0.6 mL of ACN is retained in the cartridge, no carbonyls are retained.
- 6.3 Approximately 0.75 mL of the extract is transferred into a 1.0 mL autosampler glass vial and sealed with a plastic snap cap. For equivalent HPLCs sample vials of different volume and cap type are acceptable.
- 6.4 A typical sample run is comprised of:
- 6.4.1 Working standard, control standards, ACN blank, field blank, and samples.
- 6.4.2 A stock standard solution of an appropriate concentration is loaded within sequence if a sample that exceeds the working standard concentration (0.6 $\mu\text{g/mL}$) is expected.
- 6.5 Typical operating conditions for the HLPC system are:

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Columns	<u>Analytical column</u> - Supelcosil, 4.6 mm ID x 25 cm long, two columns in series <u>Guard column</u> - 4.6 mm ID x 2.0 cm long packed with LC-18, 5 µm pellicular beads
Column oven temperature	40°C
Detector	UV/VIS at 360 nanometers (nm)
Sample volume	10 µL
Solvent A	Acetonitrile (ACN)
Solvent B	10% (v/v) methanol in water
Flow	1.2 mL/minute (min)
Program	50% A, 50% B; 0 (initial condition) 60% A, 40% B; 0 to 10 min (linear gradient) 65% A, 35% B; 10 to 20 min (linear gradient) 100% A, 0% B; 20 to 30 min (linear gradient) 100% A, 0% B; 30 to 32 min (hold) 50% A, 50% B; 32 to 35 min (linear gradient) 50% A, 50% B; 35 to 45 min (equilibrating)
Data system	PC-controlled data acquisition system

Table 2: Operating Parameters for the HPLC Analysis.

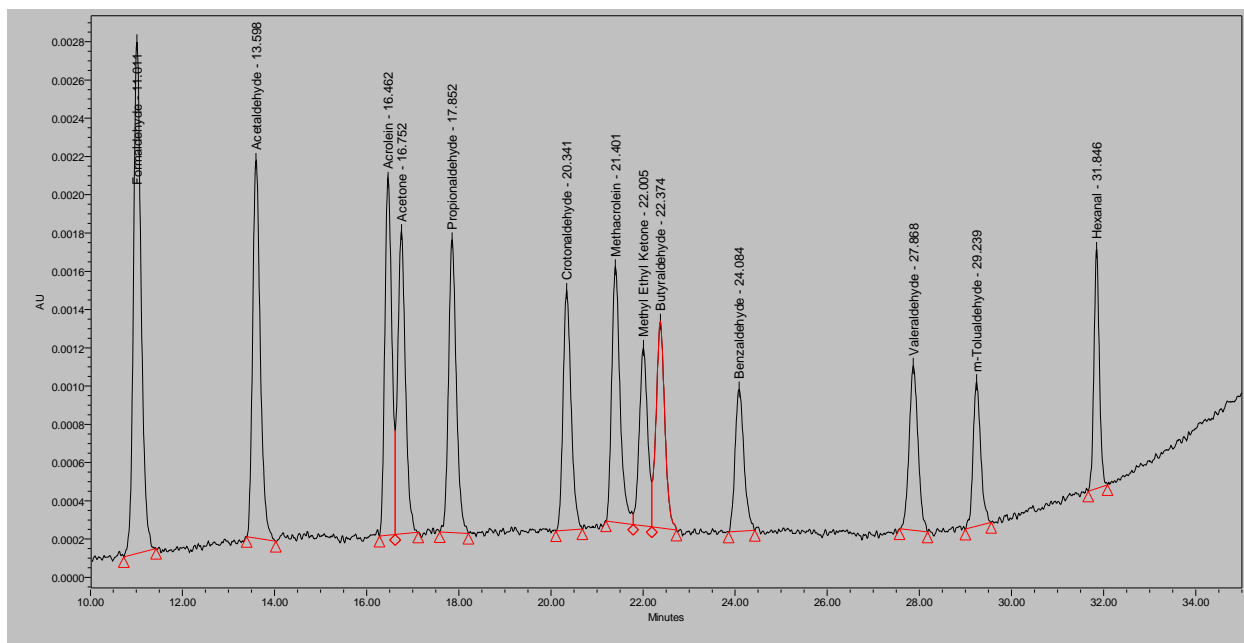


Figure 1: Elution profile of the target carbonyl-hydrazone from the Supelcosil HPLC column. This profile was captured from a dilution of the working solution where the concentration of each carbonyl-hydrazone was 0.1 µg/mL.

6.6 The peaks are identified and quantified by the data system. All chromatograms are checked for proper identification and baseline drift. Any misidentification and drifting in the baseline are manually corrected by the reintegration of the chromatograms.

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6.7 Only the target carbonyl peaks at or above the LOD are reported.

7 Calculations

7.1 The target carbonyl concentrations, in $\mu\text{g/mL}$, are calculated by the data system using each carbonyl-DNPH compound (Table 1) as an external standard.

7.2 The mass of each carbonyl compound per cartridge is determined using the following calculation:

$$\text{Mass}_{\text{sample}} (\mu\text{g}) = \text{Peak Area}_{\text{sample}} \times \text{RF} \times \text{Volume of Extract (mL)}$$

Where the RF is the response factor calculated from the daily calibration as follows:

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

And the Volume of Extract from the DNPH cartridge, as defined in section 3.3, is 4.4 mL.

7.3 For tolualdehyde, the sum of all isomers present (m-, o- and p-) is reported as m-tolualdehyde.

8 Quality Control

8.1 Carbonyl- DNPH Purity – The carbonyl-DNPH stock solutions are checked and certified for purity by Cerilliant Corporation using chromatography and melting points. Analysis of the carbonyl-DNPH stock solutions must yield only the peaks of interest. No contaminant peaks above the LOD should be observed.

8.2 Blank Runs

8.2.1 Solvent Blank – The solvents used are of the highest HPLC grade and are tested for impurities when a new lot number is used. If this lot is found to be acceptable (no carbonyl compounds present at concentrations at or above the LOD), daily solvent blank analysis is not required.

8.2.2 Cartridge Blank – At least one cartridge per batch is analyzed as a batch blank. If the cartridge blank shows a peak greater than the LOD in the region of interest, the source of the contamination must be investigated and remedied. The SEP-PAK cartridges routinely yield significant concentrations of several aldehydes and ketones upon analysis, and concentrations detected in the field blank (see below) are routinely subtracted from results of the associated sample cartridges as remedy.

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- 8.2.3 Field Blank – One cartridge is analyzed as a field blank for each emission test. If the field blank shows a peak greater than the LOD in the region of interest, the source of the contamination must be investigated and remedied. The SEP-PAK cartridges routinely yielded significant concentrations of several aldehydes and ketones upon analysis, and as compensation the results from the field blank are routinely subtracted from vehicle exhaust samples. If a field blank (see below) for a particular experiment is found to be unsatisfactory, or if no field blank is provided by the client, either the cumulative average compiled from the cartridge blank runs of the same batch ID or another field blank from a recent analysis may be substituted.
- 8.3 Calibration Run – A single-point calibration is performed for each analysis day. The sample load frequently requires continuous instrument operation into the next calendar day. In these instances, the calibration factor of the first calendar day is used for all of the samples of such a sample load.
- 8.3.1 A running tabulation of the measured area of each carbonyl peak is established by entering the results of daily calibration standard analyses (Figure 2).
- 8.3.2 A running mean area and standard deviation for each of the 13 target carbonyls is calculated and used to establish the criteria for the latest response factor check (see section 8.3.3 below).
- 8.3.3 After twenty successful calibrations have been completed, control limits of ± 3 standard deviations (3s) or $\pm 10\%$ from the current mean area counts, whichever is greater, are established. A measurement with area counts outside this limit is considered to fail the quality control requirement with respect to calibration. The analysis in this situation is referred to as a “QC failure.”
- 8.3.4 Similarly, warning limits of $\pm 2s$ or $\pm 10\%$ from the current mean area, whichever is greater, are established. A measured area outside of this limit is considered a “warning”. When warnings occur on two consecutive analysis day, the second day is considered a QC failure.
- 8.3.5 A QC failure requires that the instrument and the conditions of analysis be investigated.
- 8.3.5.1 If major problems are discovered or the cause of the failure is unknown, results of sample analysis performed on the day of interest are invalid.
- 8.3.5.2 Instrument maintenance and repairs can affect the instrument response. If the response changes sufficiently that the subsequent calibration fails the control limits, a new QC chart should be started.

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8.3.6 In the event that twenty successful calibration analyses have not been performed before the need for running samples, the calibration is considered valid if the control standard run (Section 8.4) passes.

Working Standard, 0.6 µg/ml for HPLC										
		Final Mean Area Count		177172				131657		
		Final Standard Deviation		5658				4271		
		Final RSD		3.19%				3.24%		
		Current Quarter's Mean Conc.		178070				133390		
		Current Quarter's Std. Dev.		1463				1365		
		Current Quarter's RSD		0.82%				1.02%		
			<i>Formaldehyde</i>						<i>HPLC SYS2</i>	
			<i>Acetaldehyde</i>					<i>HPLC SYS2</i>		
#	Date	File	area cts.	r_mean	r_avg		area cts.	r_mean	r_avg	
1	3/22/2005	STD_322	182859	182859	#DIV/0!		133895	133895	#DIV/0!	
2	3/23/2005	STD_323	161068	182859	#DIV/0!		118078	133895	#DIV/0!	
3	3/24/2005	STD_324	175570	171964	15409		133362	125987	11184	
4	3/25/2005	STD_325	181148	173166	11093		132933	128445	8982	
5	3/28/2005	STD_328	183319	175161	9898		135024	129567	7669	
6	3/29/2005	STD_329	179022	176793	9316		131257	130658	7076	
7	3/30/2005	STD_330	180264	177164	8382		133088	130758	6334	
8	5/12/2005	STD_512	183825	177607	7741		135742	131091	5849	
9	6/8/2005	STD_608	176176	178384	7496		129897	131672	5659	
10	6/10/2005	STD_610	188296	178139	7050		138802	131475	5326	
11	7/21/2005	STD_721	182036	179155	7382		135032	132208	5531	
12	7/22/2005	STD_722	172037	179417	7057		128244	132465	5315	
13	8/1/2005	STD_801	174224	178802	7058		129039	132113	5212	
14	8/3/2005	STD_803	171854	178450	6876		127820	131876	5063	
15	8/18/2005	STD_818	162147	177978	6837		120216	131587	4984	
16	8/18/2005	STD_818_2	172288	176923	7754		128311	130829	5629	
17	8/19/2005	STD_819	175262	176633	7580		130083	130671	5474	
18	8/22/2005	STD_822	178083	176553	7347		132633	130637	5302	
19	8/23/2005	STD_823	178070	176638	7136		131950	130748	5165	
20	9/14/2005	STD_914	177817	176713	6943		132139	130811	5027	
21	10/13/2005	STD_A13	178342	176768	6762	OK	133172	130877	4902	OK
22	10/25/2005	STD_A25	178009	176843	6600	OK	133301	130987	4804	OK
23	11/3/2005	STD_B03	174628	176896	6446	OK	130147	131092	4714	OK
24	11/9/2005	STD_B09	179016	176798	6315	OK	133661	131051	4610	OK
25	11/17/2005	STD_B17	177259	176890	6193	OK	133073	131159	4540	OK
26	11/30/2005	STD_B30	179193	176905	6063	OK	134014	131236	4461	OK
27	12/5/2005	STD_C05	178252	176993	5958	OK	133636	131343	4405	OK
28	12/7/2005	STD_C07	179578	177039	5847	OK	134785	131428	4342	OK
29	12/13/2005	STD_C13	178349	177130	5758	OK	134718	131548	4308	OK

Figure 2: A sample tabulation of calibration run results. Application of “pass/fail” criteria begins with data point number 21.

8.4 Control Standard Run: The quality control standard is analyzed each analysis day and the concentrations of the target carbonyls, except acrolein which has been shown to degrade, are checked to see if the day-to-day variability meets specified criteria. The procedure for this quality control check is described below:

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8.4.1 A running control chart containing the measured concentrations of the 13 target compounds is established by entering the results of daily control standard analyses (Figure 3).

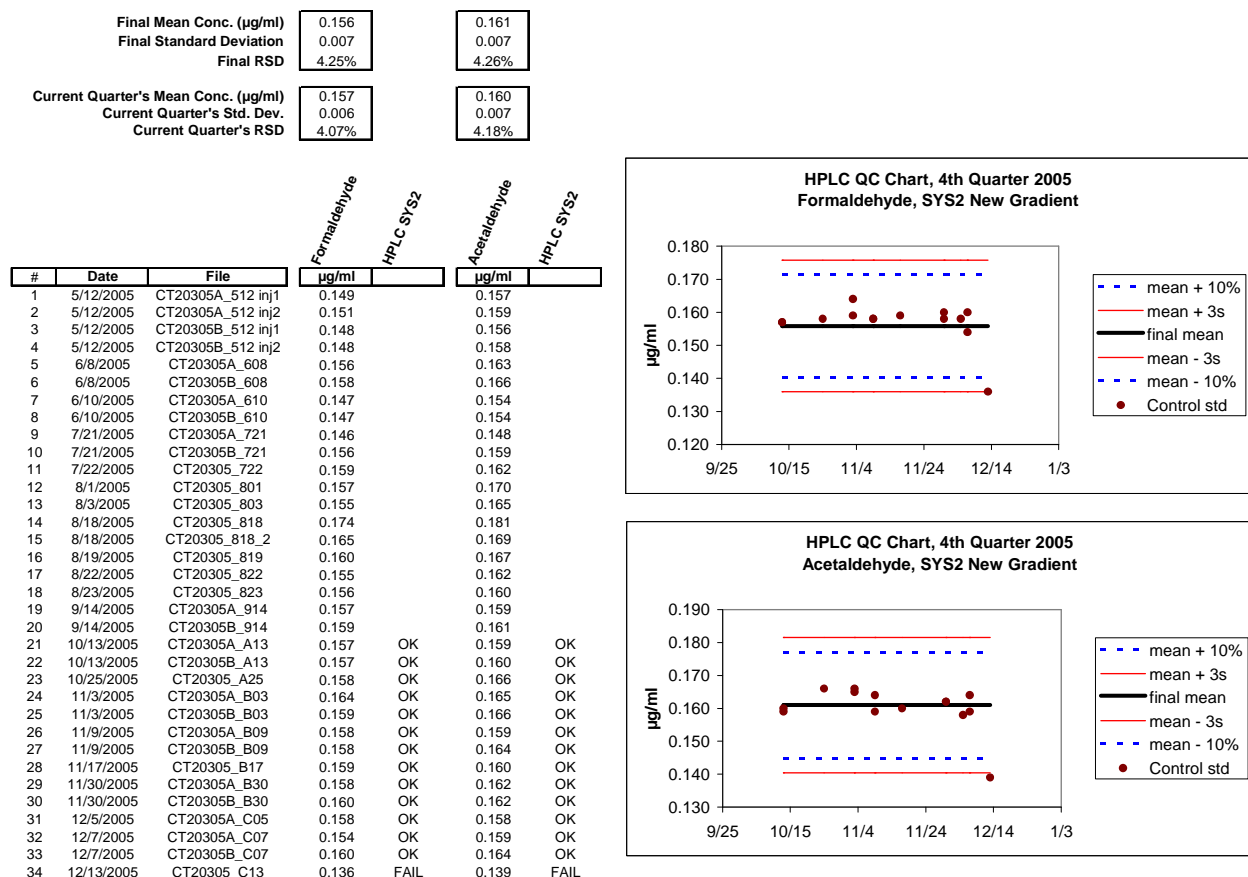


Figure 3 A sample QC chart. Application of “pass/fail” criteria begins with data point number 21.

8.4.2 A running mean concentration and standard deviation for each carbonyl compound is calculated and used to establish the criteria for the latest control standard check (see section 8.4.3 below).

8.4.3 After twenty successful analyses have been completed, control limits of ± 3 standard deviations (3s) or $\pm 10\%$ from the current mean concentration, whichever is greater, are established. A measured concentration outside of this limit is considered a QC failure.

8.4.4 Similarly, warning limits of $\pm 2s$ or $\pm 10\%$ from the current mean concentration, whichever is greater, are established. A measured concentration outside of this limit is considered a QC warning. When warnings occur on two consecutive analysis day, the second day is considered a QC failure.

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- 8.4.5 A QC failure requires that the instrument and the conditions of analysis be investigated, and sample analyses performed on that analysis day are considered invalid.
- 8.4.6 In the event that twenty successful control standard analyses have not been performed before the need for running samples, an alternative QC criterion will be used. In this case, a measurement not within 10% of an independently certified standard (i.e. independent from the working standard) is considered a QC failure.
- 8.4.7 No control requirements have been established for acrolein because it has been shown to degrade over time.
- 8.5 Replicate Run: A replicate analysis of one sample cartridge is performed once per analysis day. The relative percent difference (RPD) in concentration between the pair of analyses is calculated for each of the 13 target compounds and inputted to a replicate chart (Figure 4).
- 8.5.1 The RPD is calculated as follows:

$$RPD = \frac{|\text{Sample Conc.} - \text{Replicate Conc.}|}{\text{Average Conc. of Both Analyses}} \times 100$$

HPLC Replicate Analyses, 4th Quarter 2005												
Limit of Detection:			0.007 µg/mL					0.007 µg/mL				
#	Anal. Date	Vehicle Test	Formaldehyde					Acetaldehyde				
			Run #1	Run #2	RD	Max RD	Status	Run #1	Run #2	RD	Max RD	Status
			µg/mL	µg/mL				µg/mL	µg/mL			
1	10/13/2005	1014765_S1A_242UC2_914	0.365	0.368	0.8%	15%	Pass	0.296	0.297	0.3%	20%	Pass
2	10/13/2005	1014898_S1A_247UC2_A04	0.296	0.295	0.3%	20%	Pass	0.226	0.223	1.3%	20%	Pass
3	11/3/2005	1014891_S1A_248UC1_A05	0.236	0.235	0.4%	20%	Pass	0.187	0.189	1.1%	20%	Pass
4	11/3/2005	1014998_S1A_251UC1_A14	0.648	0.649	0.2%	15%	Pass	0.429	0.428	0.2%	15%	Pass
5	11/9/2005	1014997_S1B_246UC4_A21	0.126	0.126	0.0%	30%	Pass	0.191	0.191	0.0%	20%	Pass
6	11/9/2005	1015089_S1A_254UC1_A26	0.127	0.127	0.0%	30%	Pass	0.191	0.191	0.0%	20%	Pass
7	11/30/2005	1014997_S1B_246UC4_A21	0.020	0.020	0.0%	100%	Pass	0.035	0.039	10.8%	100%	Pass
8	11/30/2005	1015228_S1A_257UC1_B04	0.093	0.096	3.2%	30%	Pass	0.159	0.158	0.6%	20%	Pass
9	12/7/2005	1015339_S1A_259UC1_B10	0.051	0.051	0.0%	100%	Pass	0.098	0.099	1.0%	30%	Pass
10	12/7/2005	1015366_S1A_260UC1_B16	0.073	0.074	1.4%	30%	Pass	0.141	0.143	1.4%	20%	Pass

Figure 4: A sample replicate chart.

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8.5.2 A limit on the allowable RPD is established based on the average concentration of the replicate runs, as shown in the following table:

Average Measurement for Replicate Runs	Allowable RPD
1 to 10 times LOD	100
10 to 20 times LOD	30
20 to 50 times LOD	20
Greater than 50 times LOD	15

8.5.3 If the measured RPD of any of the 13 target compounds is greater than the allowable limit, the sample should be analyzed again. If reanalysis is not feasible or if the RPD criteria are still not met on reanalysis, all of the sample results for that analysis day from the instrument are considered invalid.

8.6 Linearity Determination – A multipoint calibration to confirm instrument linearity is performed for all target analytes for new instruments, after making instrument modifications that can affect linearity, and at least once every year. The multipoint calibration consists of at least five concentration levels, each above the LOD and distributed over the range of expected sample concentration. Each concentration level 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 for one-point calibrations. An example of a multipoint calibration determination is shown in Figure 5.

8.7 LOD Determination: A limit of detection determination for each of the 13 target carbonyls is performed for new instruments, after making modifications which can affect the sensitivity of an instrument, and at least once per year. To make the calculations, it is necessary to perform a multipoint calibration of at least four low concentration levels, each above the expected LOD. The two lowest concentrations is measured a minimum of five times while the other concentrations are measured a minimum of four times. The LOD determination can be performed concurrently with the linearity determination (Section 8.6) if the requirements listed above are satisfied. Figure 5 shows a typical LOD determination.

8.7.1 A linear regression analysis is performed on this data set to identify slopes, m_i , for each of the i th target compounds.

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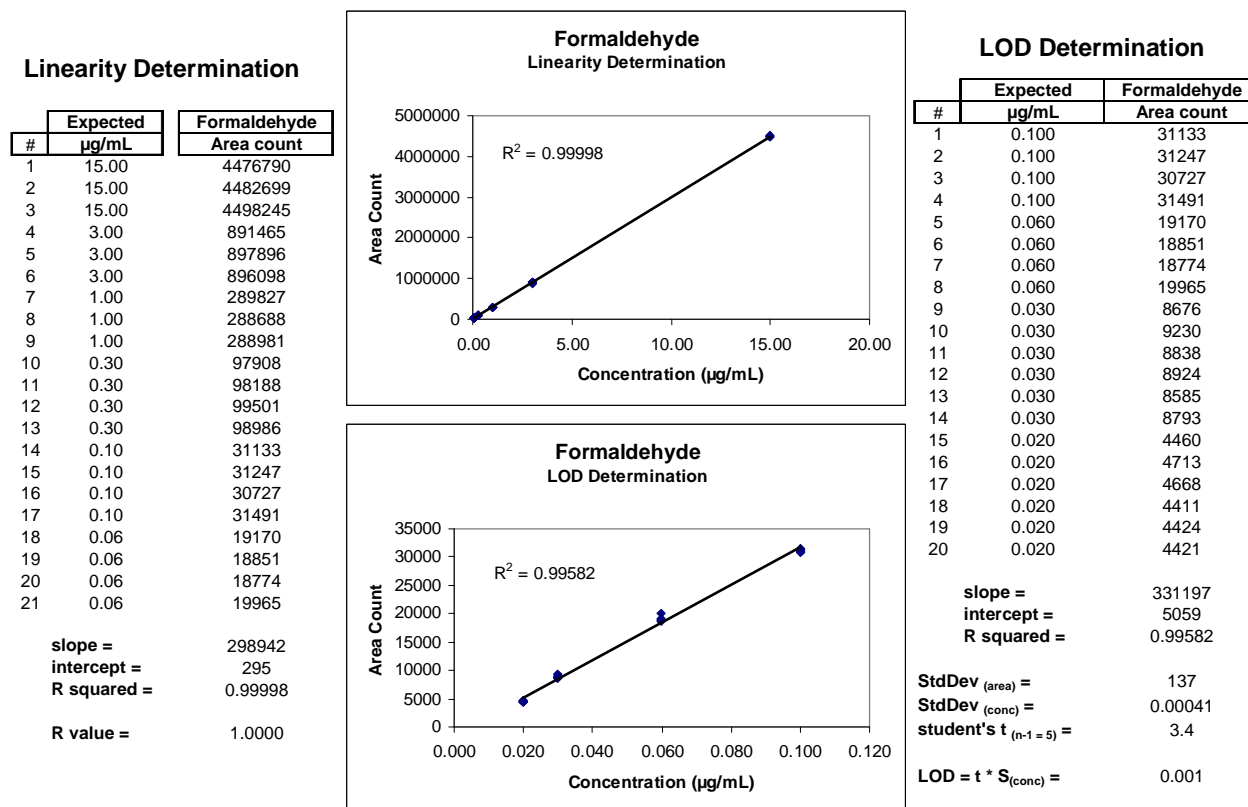


Figure 5: Sample linearity and LOD determinations in which the r-value is 1.000 and the LOD is 0.001 µg/mL for formaldehyde.

8.7.2 For each of the i th target compounds, the standard deviations, s_i , in units of peak area are determined using the five (or more) replicate measurements of the lowest concentration standard. These are then converted to units of concentration using the slopes determined in Section 8.7.1.

$$s_i^{conc} = \frac{s_i^{area}}{m_i}$$

8.7.3 The LOD for each of the i th target compounds can now be calculated using the following equation:

$$LOD_i = t * s_i^{conc}$$

where t is the Student's t value associated with a 98% confidence interval.

8.7.4 The Student's t value is dependent upon the degrees of freedom associated with the analysis. This "degrees of freedom" is equal to the number of replicate measurements for the lowest concentration standard, n , minus one. An

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abbreviated table of values of t associated with a 98% confidence interval is shown below (Ref. 9.7):

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

- 8.7.5 The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the maximum allowable LOD (see below).
- 8.7.6 The maximum allowable LOD is 0.0075 µg/mL for each carbonyl (not the carbonyl- DNPH derivative). The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD for sample analyses to be considered valid.
- 8.7.7 For sample analysis, all peaks identified as target compounds that are equal to or greater than the maximum allowable LOD must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, SLB may set its reporting limit at the maximum allowable LOD, the calculated laboratory LOD, or any level in between.
- 8.7.8 For the purpose of calculating the total mass of all species, the concentrations of all compounds below the LOD are considered to be zero.
- 8.8 Quality control of the sampling procedure is outside the scope of this standard operating procedure and is the responsibility of the client.

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9 References

- 9.1 Air Resources Board (ARB), "California Non-methane Organic Gas Test Procedures", Part F. Latest revision in 2002.
- 9.2 Code of Federal Regulations (CFR), Title 40, Part 86. Updated yearly at frwebgate.access.gpo.gov.
- 9.3 Riggin, R. M., "Determination of Aldehydes and Ketones in Ambient Air: Method TO-5" in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-84-041, Research Triangle Park, NC, April 1984
- 9.4 Tejada, S. B., "*Standard Operating Procedure for DNPH-coated Silica Cartridge For Sampling Carbonyl Compounds in Air and Analysis by High-performance Liquid Chromatography*," Unpublished, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1986
- 9.5 Tejada, S. B., "Evaluation of Silica Gel Cartridges Coated in situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air," *Intern. J. Environ. Anal. Chem.*, Vol. 26: 167-185, 1986.
- 9.6 Winberry, W. T., Tejada, S. B., Lonneman, B., and Kleindienst, T., "Determination of Aldehydes and Ketones in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography: Method TO-11A" in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-625/R-96/010b, Center for Environmental Research Information, OH, January 1999.