

## APPENDIX H-1

### Summary of Proposed Modifications to California Non-methane Organic Gas Test Procedures

Staff is proposing the following modifications to Methods 1001 to 1004 (Parts C through F) of the California Non-Methane Organic Gas (NMOG) Test Procedures:

#### 1. METHODS 1001, 1002, 1003 AND 1004

The limit of detection (LOD) language is being clarified to allow reporting limits of the experimentally determined LOD, the maximum allowable LOD or any value in between. This will allow laboratories to have more flexibility and consistency in their reporting limits.

For example, the maximum allowable LOD for Method 1001 is 0.50  $\mu\text{g}/\text{mL}$  for both compounds measured, methanol and ethanol. A laboratory performs its LOD analysis by analyzing several analytical standards at different concentration levels and using a mathematical formula to determine the point at which measurements are statistically different from zero. When a laboratory performs its LOD analysis, it will generate slightly different values for the two compounds, e.g. 0.10 and 0.15  $\mu\text{g}/\text{mL}$ . The current language would allow the laboratory to set the reporting limit at either 0.50  $\mu\text{g}/\text{mL}$  or the actual values of 0.10  $\mu\text{g}/\text{mL}$  for methanol and 0.15  $\mu\text{g}/\text{mL}$  for ethanol. The current language, however, does not permit setting both reporting limits at the higher of the two, 0.15  $\mu\text{g}/\text{mL}$ , to simplify data processing. It also does not allow setting the reporting limit slightly above the laboratory determined LOD, to allow for small deviations each time the LOD is performed. The proposed changes would allow this additional flexibility and consistency.

The proposed change also provides a guideline for Methods 1002 and 1003, which measure approximately 200 compounds, only 10 of which are in the standards used to perform the LOD analyses. Currently the methods do not address determining the level at which to set the reporting limit for the remaining 190 compounds. The proposed language would explicitly allow a third option of setting a reporting limit somewhere between the laboratory determined LOD and the maximum allowable LOD. Therefore, a laboratory could choose to set one reporting limit for all 200 compounds, vastly simplifying its data processing and ensuring a consistent LOD throughout the course of a project.

#### 2. METHODS 1001, 1002 AND 1003

One aspect of the quality control (QC) requirements is being revised for instruments with extremely low day-to-day variability. Currently, the pass/fail criteria for the daily quality control standard analysis depends only on how much, or how little, the measurements have varied (standard deviations) in the past. The more an instrument varies, the more leeway it is allowed;

conversely, the less it varies the less leeway is allowed. This can lead to a situation where a very precise instrument fails the QC criteria even though the control standard measurement differs from the mean by a small amount. This can cause standard analyses to be repeated, functioning instrument to be taken out of service for maintenance and/or exhaust tests to be repeated. Staff considers these control actions to be unnecessary; the same value obtained by an instrument with a history of greater variability would have passed the QC requirement.

Staff believes that the data quality objectives can be achieved by using alternative criteria for instruments that operate with very little variability. Staff is proposing that analyses be considered valid for instruments that vary by five percent or less from the mean measurement of the daily control standard. The current two standard deviation warning and three standard deviation failure will still apply where the results are greater than five percent from the mean. An alternate criteria is already in Method 1004 for the reasons stated above. These changes to the other three methods will provide more flexibility to laboratories while still providing good quality analytical data.

### **3. METHOD 1002**

Two chromatographic columns, a packed column and a porous layer open tubular column (PLOT), are allowed in the current method. Since the packed column is no longer manufactured, it is being stricken from the method. The PLOT column remains in the method.

### **4. METHOD 1003**

Two changes to the suggested operating conditions are proposed. First, the gas chromatograph detector range has been changed to a more sensitive range to more accurately measure lower emission vehicles. Second, the injector temperature, which was not previously included in the method, has been added to the parameters. Suggested operating conditions are given as guidelines for laboratories setting up analytical methods, and are adjusted to optimize individual instrument performance. Conditions will vary slightly from instrument to instrument, laboratory to laboratory and among different instrument manufacturers. Therefore the proposed changes will not affect other laboratories.

### **5. METHOD 1004**

The column, standards, and suggested instrument conditions are updated to reflect current operating parameters. The alternate column added is simply a different brand; the column material is identical. This option is provided to give laboratories more flexibility.

The standard concentrations and preparations have been revised to reflect current ARB standards. For the stock calibration standard, the current method contains a typographical error. It gives the concentration as “approximately 5 to 15 mg/mL of each target carbonyl/DNPH complex.” However, that should read “ $\mu\text{g/mL}$ ” instead. The proposed change is due to the fact

that ARB now purchases its standards, and they are 3.0  $\mu\text{g}/\text{mL}$  of each carbonyl. The current method gives the concentration in terms of carbonyl/DNPH complex. When the concentration of the actual carbonyl is calculated the new standard falls within the approximate concentration range currently in the method. Therefore, this proposed change will not require any procedure changes of other laboratories. Staff is also proposing adding a sentence allowing stock calibration standards of other concentrations to be used, to allow laboratories more flexibility.

The working standard has also been updated to reflect ARB's current practices. The example given in the current language was due to the former practice of pipetting both the stock calibration standard and the reagent with which it is diluted. Staff has changed that practice to use a volumetric flask to make the dilution easier. The dilution was changed from four times to five simply because of the glassware available. Again, this is just an example of diluting the stock calibration standard so a minor change in our procedure has no affect on other laboratories.

The control standard preparation procedure is also being updated to reflect current practices. The example given of mixing old samples has been modified to spike the mixture with the stock solution to ensure that all target carbonyls are present in the control standard. The proposed changes reduce the minimum stirring time from 24 hours to 2 hours. Staff believes that 24 hours is excessive and potentially hazardous if left unsupervised; 2 hours is believed to be sufficient. It also states that precipitates may result and, in that event, the solution should be filtered. This is something which would fall into the category of good laboratory practices and should not affect any other laboratories. The current method states that commercial standards may be purchased instead and this option will remain unchanged.

The changes to the instrument conditions involve the eluents, which are used to separate the target carbonyls. There are two reservoirs, A and B, which contain different compounds. These are mixed in certain proportions and used to propel (elute) the sample through the chromatographic column. It is the combination of the column material and the eluent composition which separate the individual carbonyl compounds from each other. The current method lists one eluent as pure water and the other as pure acetonitrile. The pure water sample would then have the potential for growing bacteria, which can adversely affect the instrument performance. The pure water reservoir was then changed to 35% acetonitrile in water. The mixing program was changed to compensate for this. The resulting eluent mixing program is mathematically equivalent to the old procedure. Therefore, this change does not affect the separation of the carbonyl compounds. This separation is necessary not only for speciation of all exhaust components, but for determination of reactivity. This is because the ultraviolet detector responds differently to each of the carbonyls and because these compounds have vastly different MIRs (-0.55 to +7.15). As explained above, these suggested standard operating conditions must be optimized and vary from instrument to instrument. These proposed changes will not require any procedural changes at other laboratories.

The following is the regulatory text of the proposed modifications:

### **Proposed Changes to Method No. 1001 (Part C)**

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#### 8.5 Control Charts....

3. Create a control chart for the target analyte by placing the concentration on the Y-axis and the date on the X-axis. Establish ~~an~~ upper and lower warning limits ~~and a lower warning limit~~ at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish ~~an~~ upper and lower control limits ~~and a lower control limit~~ at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.

The measured concentrations of all target analytes contained in the control standard must be within the control limits (“in-control”) for the sample results to be considered acceptable. A control standard measurement is considered to be “out-of-control” when the analyzed value exceeds the ~~3s~~ control limit, or two successive control standard measurements of the same analyte exceed the ~~2s~~ warning limit.

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8.8.1. The maximum allowable LOD...must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at ~~either~~ the maximum allowable LOD, ~~or~~ the calculated laboratory LOD or any level in between.

### **Proposed Changes to Method No. 1002 (Part D)**

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- 2.3 The gas chromatographic analysis is performed on ~~a packed column isothermally at 35 C;~~ ~~or~~ an Alumina (AL<sub>2</sub>O<sub>3</sub>) ( PLOT column ...

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- 4.4 ~~A stainless steel column [6 ft x 1/8 in] packed with phenylisocyanate Durapak 80/100 mesh is used. An Alumina PLOT column (50 m x 0.32 mm) may also be is used. A wax precolumn.....~~

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6.2.1 ~~Packed Column:~~

Helium carrier gas flow: 50 mL/min)  
Hydrogen gas flow: 32 mL/min  
Air flow: 300 mL/min  
Sample valve temperature: ambient  
Heating bath temperature: 60°-80°C  
Injector temperature: 35°C  
Column temperature: 35°C (isothermal)  
(temperature program) (AI PLOT Column)  
Detector temperature: 200°C

6.2.21 PLOT Column:

Helium carrier.....  
Detector temperature: 250°C  
Injector temperature: 150°C

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6.12 ~~After each run the packed column is back flushed with helium while the oven temperature is raised and maintained at 60 C for 15 mins, or as required to flush the column.~~

6.132 The Alumina...

6.1.43 Before the next run.....

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8.4 Control Charts...

3. Create a control chart for the target hydrocarbon by placing the concentration on the Y -axis and the date on the X-axis. Establish ~~an upper and lower warning limits and a lower warning limit~~ at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish ~~an upper and lower control limits and a lower control limit~~ at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (“in-control”) for the sample results to be considered acceptable. A control standard measurement is considered to be “out-of-control” when the analyzed value exceeds the 3s control limit, or two successive control standard

measurements of the same analyte exceed the ~~2s~~ warning limit.

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8.7.1. The maximum allowable LOD...must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at ~~either~~ the maximum allowable LOD, ~~or~~ the calculated laboratory LOD or any level in between.

### **Proposed Changes to Method No. 1003 (Part E)**

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6.1.2 Suggested operating.....  
Range ~~1+2~~ ...  
Detector temperature: 300°C  
Injector temperature 150°C  
Column ~~T~~temperature.....

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8.4 Control Charts.....

3. Create a control chart for the target hydrocarbon by placing the concentration on the Y -axis and the date on the X-axis. Establish ~~an upper and lower warning limits and a lower warning limit~~ at either two standard deviations (2s) or 5 percent, whichever is greater, above and below the average concentration. Establish ~~an upper and lower control limits and a lower control limit~~ at either three standard deviations (3s) or 5 percent, whichever is greater, above and below the average concentration.

The measured concentrations of all target hydrocarbons contained in the control standard must be within the control limits (“in-control”) for the sample results to be considered acceptable. A control standard measurement is considered to be “out-of-control” when the analyzed value exceeds the ~~3s~~ control limit, or two successive control standard measurements of the same analyte exceed the ~~2s~~ warning limit.

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8.7.1. The maximum allowable LOD...must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at ~~either~~ the maximum allowable LOD, ~~or~~ the

calculated laboratory LOD or any level in between.

**Proposed Changes to Method No. 1004 (Part F)**

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3.3 When using the DuPont Zorbax or Supelco's Supelcosil column.....

3.4 When using the Delta Bond column....tend to coelute. The guard column for the Delta Bond column must be changed frequently in order to prevent the coelution of butyraldehyde and methacrolein and to prolong the life of the column.

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4.1.5 The primary system incorporates two DuPont Zorbax ODS or Supelco's Supelcosil columns in tandem. Other columns may be used, provided the alternate(s) can be demonstrated to be equivalent.....

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5.6 Stock Calibration.....with acetonitrile. A typical stock calibration standard contains ~~approximately 5 to 15 mg/mL~~ 3.0 µg/mL of each target carbonyl/~~DNPH complex~~ compound. Stock calibration standards of other concentrations may also be used.

5.7 Working Standard - A working standard is prepared when required by diluting the stock calibration solution, making sure that the highest concentration of the standard is above the expected test level; ~~e.g., 5 mL of stock calibration solution is diluted to 20 mL.~~ Typically, the 3.0 µg/mL stock is diluted five times with acetonitrile in a volumetric flask to yield a 0.6 µg/mL solution.

5.8 Control Standard .....target carbonyl. The control standard may be prepared by batch mixing old samples, spiking it with a stock solution of target compounds, and stirring for ~~24 hours~~ a minimum of 2 hours. If necessary, the solution is filtered using filter paper to remove precipitation. All target.....

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6.6 Place the vials.....

Primary System:

Columns: 4.6 mm ID x 250 mm x 1/4 inches OD Dupont Zorbax ODS or Supelco Supelcosil - two columns in series, Guard column....

Column temperature.....

Secondary System:

Columns.....

Solvent A: ~~purified water~~ acetonitrile

Solvent B: acetonitrile in water, 35 percent (v/v)

Flow: 1.5 mL/min

Program - ~~65 percent A, 35 percent B (initial time)~~  
~~65 percent A, 35 percent B 0 - 5.5 min~~  
~~50 percent A, 50 percent B 5.5 - 8.0 min~~  
~~35 percent A, 65 percent B 8.0 - 11.1 min~~  
~~65 percent A, 35 percent B 11.0 - 13.0 min~~

0 percent A, 100 percent B 0 (initial time)  
23 percent A, 77 percent B 0 to 5.5 min  
46 percent A, 54 percent B 5.5 to 13 min  
0 percent A, 100 percent B 13 to 30 min

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8.10.1 The maximum allowable LOD...must be reported. If the calculated laboratory LOD is less than the maximum allowable LOD, the laboratory may choose to set its reporting limit at ~~either~~ either the maximum allowable LOD, or the calculated laboratory LOD or any level in between.