

STATE OF CALIFORNIA
AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES
FOR
AIR QUALITY MONITORING

APPENDIX X

PERFORMANCE AUDIT PROCEDURES
FOR
LIGHT-END AND MID-RANGE NON-METHANE HYDROCARBON POLLUTANTS
IN AUTOMOTIVE EXHAUST - LABORATORY AUDITS

MONITORING AND LABORATORY DIVISION

MAY 2002

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LIGHT-END AND MID-RANGE NON-METHANE HYDROCARBON POLLUTANTS
IN AUTOMOTIVE EXHAUST - LABORATORY AUDITS

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X.1.0 INTRODUCTION

X.1.0.1 GENERAL INFORMATION

Performance audits of the analytical methods for light-end and midrange (C2 - C12) non-methane hydrocarbon (NMHC) pollutants in automotive exhaust are conducted by Quality Assurance (QA) Section staff to assess the accuracy of the methods used by the Southern Laboratory to measure pollutant concentrations in automotive exhaust.

Audits are conducted by supplying the laboratory with a cylinder that contains a mixture of standards prepared by the National Institute of Standards and Technology (NIST). The laboratory introduces a sample from the cylinder into the analyzer following calibration procedures (i.e., direct injection, Tedlar bags, stainless steel canisters, etc.) and reports the results of the analysis to the QA Section. The QA Section in turn reviews the analyzed data for completeness and compliance to standard laboratory procedures, calculates the percent difference of the results, and reports the final audit results to the laboratory.

X.1.1 AUDIT PROCEDURES

X.1.1.1 AUDIT MATERIALS

1. Light-end and mid-range non-methane hydrocarbon audit cylinder prepared by the National Institute of Standards and Technology (NIST).
2. Two-stage gas regulator.
3. Laboratory results form.

X.1.1.2 FIELD NOTIFICATION

One month prior to the tentative audit date, contact the participating laboratory to schedule the audit. Upon agreement of the date, mail an audit schedule and protocol along with a memorandum (see Figures X.1.1.1 and X.3.1.2) restating the audit period. If necessary, the package should also include completed carrier forms to facilitate the return of the audit materials (see Figures X.1.1.3 and X.1.1.4)

NOTE: Since an annual multipoint calibration of the analytical instruments is recommended, calibrations and audits should be scheduled at alternating six month intervals to provide a semi-annual performance check.

X.1.1.3 DELIVERY OF AUDIT MATERIALS

One working day before the audit, arrange for overnight delivery of the cylinder and the two-stage gas regulator. Prior to shipping, check the regulator for leaks following the procedure described below. Once the regulator is determined to be free of leaks, it should be packed with extra cushioning to minimize the risk of damage during shipping.

X.1.1.4 REGULATOR LEAK TEST

1. Securely install the regulator on a cylinder containing ultrapure air.
2. Close the pressure adjusting knob (full counterclockwise position) and the flow control valve. If the regulator is not equipped with a flow control valve, cap the gas delivery outlet.
3. Slowly, open the cylinder valve until the high pressure gauge indicates the full pressure of the cylinder.
4. Open the regulator pressure adjusting knob until the pressure on the delivery gauge reads 25 psi.

5. Close the cylinder valve and record the gauge readings.
6. Allow the system to sit for 15-30 minutes.
7. At the end of the testing period, check for pressure changes in both gauges. A decrease in the high pressure gauge indicates a leak in the cylinder valve inlet fitting or high pressure gauge. A decrease in the low pressure gauge indicates a leak in the outlet fitting or low pressure gauge. Tighten fittings and retest the regulator. If the fittings still leak, the regulator must be repaired. A decrease in the high pressure gauge concurrent with an increase in the low pressure gauge indicates a leak in the regulator seat, and the regulator must be repaired.

X.1.1.5 REGULATOR PURGE PROCESS

1. Attach the regulator to the audit cylinder.
2. Attach a vent line to the regulator outlet.
3. Turn the regulator adjustment counterclockwise to the fully closed position.
4. Open and quickly shut the cylinder valve. This will pressurize the inlet side of the regulator to the cylinder pressure. It is necessary to quickly close the valve after each cycle to eliminate downstream contaminants from entering the cylinder until the regulator is purged completely.
5. Turn the regulator adjustment clockwise to establish the appropriate delivery pressure and the gas will be released out the vent line.
6. Repeat steps 3 through 5 four more times.

X.1.1.6 SAMPLE ANALYSIS

The laboratory introduces a sample from the audit cylinder into the analyzer following calibration procedures (i.e., direct injection, Tedlar bags, stainless steel canisters, etc.). If the calibration procedures include humidification of the calibration standards, the audit samples must also be humidified using the same procedures.

The laboratory will attach an outline describing in detail the procedures used to introduce the audit sample to the instrument (see Figure X.1.1.2). For example, the regulator was attached to audit cylinder. The regulator was purged three times. A 1/8 inch teflon line, two feet in length, was attached to the regulator and purged three times. The teflon line was attached to the Tedlar bag and filled with

the audit gas. All Tedlar bags used in the program were cleaned and checked for contamination prior to use.

Additionally, the laboratory will describe any special circumstances associated with the system. Once the sample has been introduced into the analyzer, the laboratory determines the concentration of the gases in the cylinder by following their standard operating procedures. The laboratory will perform two separate analyses on two different days for a total of four analyses.

X. 1.1.7 RETURN/TRANSFER OF AUDIT MATERIALS

At the completion of the audit period, the laboratory should immediately return the audit materials to the QA Section staff using the provided forms.



Winston H. Hickox
Agency Secretary

Air Resources Board

Alan C. Lloyd, Ph.D.
Chairman

1001 I Street • P.O. Box 2815 • Sacramento, California 95812 • www.arb.ca.gov



Gray Davis
Governor

TO: Mark Fuentes, Chief
Southern Laboratory Branch

THROUGH: Jeff Cook, Chief
Quality Management Branch

Michael Miguel, Manager
Quality Assurance Section

FROM: Merrin Bueto
Air Pollution Specialist

DATE: May 24, 2001

SUBJECT: MOTOR VEHICLE EXHAUST LABORATORY
PERFORMANCE AUDIT SCHEDULE AND PROTOCOL

Thank you for participating in the upcoming motor vehicle exhaust non-methane hydrocarbon (NMHC) laboratory performance audit. The audit is scheduled for the week of June 4, 2001. The Quality Assurance Section will provide the audit cylinder and regulator. The laboratory, however, will be responsible for supplying a Tedlar bag for each operational gas chromatograph (GC). The Tedlar bags must be verified to be free from contaminants.

The performance audit procedure is to be representative of your normal calibration and standard operating procedures (SOPs). Enclosed is the audit protocol. Audit samples will be introduced from the audit cylinder into the GCs using Tedlar bags. The laboratory will perform triplicate analyses on each operating GC. The GCs scheduled to be audited are #4, #5, #6, #7, and #8. If at the time of the audit additional GCs are operational, they will also be audited. After the samples have been introduced into the analyzer, the laboratory will determine the concentrations of the gases and report the results electronically. For your convenience, a diskette containing a reporting sheet is enclosed. Please return the diskette to the Quality Assurance Section by June 30, 2001.

Again, thank you for your participation in this performance audit. If you have any questions, please contact Merrin Bueto of my staff at (916) 323-0346, or via email at mbueto@arb.ca.gov.

Enclosures

cc: Leo Zafonte
Christine Maddox

The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.

California Environmental Protection Agency

Printed on Recycled Paper

PROTOCOL

Motor Vehicle Exhaust Laboratory Performance Audit June 2001

Objective: The purpose of the performance audit is to assess the accuracy of the analytical methods currently used by the Organic Analysis Section to measure concentrations of non-methane hydrocarbons in automotive exhaust.

Materials:

- 1) Gas regulator
- 2) National Institute of Standards and Technology (NIST) traceable gas cylinder

Schedule: MLD, Southern Laboratory Branch..... June 4-14, 2001

Delivery

Arrangements: The audit cylinder and regulator will be delivered priority 1 shipment by carrier.

Regulator

Leak Check: Attach the regulator to the audit cylinder and ensure the regulator valve is closed. Open the cylinder valve and record the pressure reading of the gauge. Adjust the regulator flow control until the pressure on the flow gauge reads 25 psi. Close the cylinder valve, and let the system sit for 15-30 minutes. Note the readings on both gauges for any pressure drop. If a substantial drop (5 psi or greater) has occurred, notify Merrin Bueto of the Quality Assurance Section at (916) 323-0346. Another regulator will be provided.

When returning the regulator after the audit, please pack it in the same protective carton in which it was originally shipped.

Regulator Purge Process:

1. Attach a vent line to the regulator outlet.
2. Turn the regulator adjustment counterclockwise to the fully closed position.
3. Open and quickly shut the cylinder valve. This will pressurize the inlet side of the regulator to the cylinder pressure. It is necessary to quickly close the valve after each cycle to eliminate downstream contaminants from entering the cylinder until the regulator is purged completely.

Figure X.1.1.2
Audit Schedule and Protocol

Regulator Purge Process (cont.):

4. Turn the regulator adjustment clockwise to establish the appropriate delivery pressure and the gas will be released through the vent line.
5. Repeat steps 2 through 4 four more times.

Sample Analysis:

The laboratory will follow their calibration and standard operating procedures in assaying the gases from the performance audit cylinder (methods 1002 and 1003). Following calibration procedures, the laboratory will introduce a sample from the audit cylinder into the analyzer (i.e., Tedlar bags). The laboratory will perform three separate analyses on each of the operating gas chromatographs (GCs). The GCs to be audited are #4, #5, #6, #7, and #8. If additional GCs are operational at the time of the audit, they will also be audited. Once the samples have been introduced into the analyzer, the laboratory determines the concentrations of the gases in the cylinder by following their standard operating procedures. To minimize instrument and analysis variability, please ensure that each instrument's limit of detection has been recently checked and that the amount of time an audit sample sits in a Tedlar bag is limited. The sample residence time should mimic an actual exhaust sample.

Note: Extreme care must be taken when filling a Tedlar bag as to prevent the cylinder from being drained. Under **NO** circumstances should the cylinder valve remain open for extended periods of time without direct supervision.

Analysis Reporting:

The laboratory will report the results of each analyses and the average results for each GC. A diskette containing a reporting sheet is provided. Please use the diskette to record the results of the analyses. Also, if able to email the results, send them to mbueto@arb.ca.gov. Then return the results (diskette) within two weeks of the analyses. Please mail the disk to:

California Air Resources Board, Monitoring and Laboratory Division
Attn: Michael Miguel, 1927 13th Street, Sacramento, CA 95812

Note: Please report the data to the appropriate number of significant figures.

Quality Assurance staff will report the performance audit results to the laboratory with a summary comparing the laboratory's reported test results and the true concentrations.

AIRBILL
 INCLAS
 TRACKING NUMBER

2401801124

42298
 2401801124

1136-9231-4

1523

5463

25

FEDEX COPY

157

SIGNATURE RELEASE UNAVAILABLE

2401801124

Two completed and signed copies of this Declaration must be handed to the operator.

WARNING
 Failure to comply in all respects with the applicable Dangerous Goods Regulations may be in breach of the applicable law, subject to legal penalties. This Declaration must not, in any circumstances, be completed and/or signed by a consolidator, a forwarder or an IATA cargo agent.

TRANSPORT DETAILS

Shipper's Name: AIR RESOURCES BOARD
 Shipper's Address: 1309 7TH STREET, SACRAMENTO, CA 95814

Receiver's Name: AIR RESOURCES BOARD
 Receiver's Address: 1309 7TH STREET, SACRAMENTO, CA 95814

Service: AIR SERVICE

Delivery and Special Handling: HOLD AT FEDEX LOCATION WEDNESDAY

Service Conditions, Declared Value and Limit of Liability: \$157

MATURE AND QUANTITY OF DANGEROUS GOODS

Proper Shipping Name	Class or Division	Lit or ID No.	Special Handling	Quantity and Type of packing	Packing Inst.	Authorization
FOR SHIPMENTS WITHIN USA, AK, AND HI ONLY						

Additional Handling Information:

I hereby declare that the contents of this consignment are fully and accurately described above by proper shipping name and are classified, packed, marked, and labeled, and are in all respects in the proper condition for transport by air according to the applicable International and National Government Regulations.

Signature: [Signature]

Emergency Telephone Number (Required for ICAO Origin or Destination Shipments):

IF ACCEPTABLE FOR PASSENGER AIRCRAFT, THIS SHIPMENT CONTAINS RADIOACTIVE MATERIAL INTENDED FOR USE IN, OR INCIDENT TO, RESEARCH, MEDICAL DIAGNOSIS, OR TREATMENT.

Figure X.1.1.3
 Example Carrier Form for Gas Cylinders

GENERAL **AIRBILL**
 PACKAGE TRACKING NUMBER **6476086912**

USE THIS AIRBILL FOR SHIPMENTS WITHIN THE CONTINENTAL U.S., ALASKA AND HAWAII.
 USE THE INTERNATIONAL AIR AIRBILL FOR SHIPMENTS TO PORTS AHEAD AND ALL OTHER U.S. LOCATIONS.
 QUESTIONS? CALL 300-229-5555 TOLL FREE.

3008M **6476086912**

3008M **6476086912**

1136-9231-6
 FROM (YOUR NAME) PLEASE PRINT
 AIR RESOURCES BOARD
 1309 T STREET
 SACRAMENTO CA 95814

TO (RECIPIENT'S NAME) PLEASE PRINT
 DEPARTMENT/FLOOR NO. COMPANY DEPARTMENT/FLOOR NO.
 STREET ADDRESS LOCAL STREET ADDRESS (IN CASE OF A U.S. AIR FORCE OFFICE ONLY)
 CITY STATE ZIP+4

YOUR INTERNAL BILLING REFERENCE INFORMATION (optional) (Print if shippers will appear on invoice)

FOR SHIPMENTS WITHIN USA, AK, HI ONLY

FEDEX COPY

21690919 6476086912

21690919 6476086912

227
0114
125
200

Figure X.1.1.4
 Example Carrier Form for Regulators

X.1.2 **POST AUDIT PROCEDURES**

X.1.2.1 LABORATORY REPORTS

Upon completion of the analysis, the laboratory reports the results and procedural summaries to the QA Section using the laboratory results forms (see Figure X.1.1.2). The report includes the following:

1. Date of analysis.
2. Number of runs.
3. Average measured concentration.
4. Standard deviation.

X. 1.2.2 CALCULATIONS

Calculate the percent bias for each compound analyzed in the audit by comparing the reported concentrations against the NIST assigned concentrations.

$$\text{Percent Difference} = \frac{\text{Measured Conc.} - \text{Assigned Conc.}}{\text{Assigned Concentration}} \times 100$$

X.1.2.3 AUDIT REPORTS

Prepare a table showing NIST assigned concentrations, laboratory measured concentrations and the percent bias for each compound analyzed (see Figure X.1.2.1).

