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ABSTRACT

The California Air Resources Board (CARB) has been conducting through-the-probe (TTP) performance audits of continuous ambient air analyzers since 1981. TTP performance audits are conducted by presenting audit gases through the probe inlet of ambient air monitoring stations, as opposed to presenting audit gases to the back of the analyzers. This technique tests the integrity of the air monitoring station's entire sampling system. The CARB uses the TTP audit technique to audit criteria as well as non-criteria analyzers.

The CARB's Quality Assurance Section (QAS) uses a self-sufficient audit van to conduct TTP audits. The audit gas concentrations are generated in the van using a gas calibrator to dilute multi-blend gases with zero air. The audit gas is then delivered to the station through a presentation line. The gas calibrator is capable of generating ozone for ozone audits and gas phase titration of nitrogen oxide. The TTP audit technique and the use of multi-blend gas cylinders allow for simultaneous audits of multiple analyzers.

INTRODUCTION

The California Air Resources Board (CARB) has the responsibility of overseeing the implementation of the California Clean Air Act and the Federal Clean Air Act in California. An important component of the program requires quality assurance activities be conducted to ensure the validity of the ambient air quality monitoring data. The CARB's Quality Assurance Section (QAS) is responsible for assuring data quality in California through performance and system audits. The QAS has developed a method of performance audits for continuous ambient air analyzers that involves introducing the audit gas through-the-probe (TTP) inlet as opposed to the back of the analyzer. This paper addresses the TTP audit method developed by the QAS.

REQUIREMENTS FOR PERFORMANCE AUDITS

Performance audits are part of a comprehensive air monitoring quality assurance program. They validate and document the measurement system data accuracy. The Code of Federal Regulations (CFR) require that performance audits be conducted at least once a year for criteria pollutant analyzers operated at State and Local Air Monitoring Stations (SLAMS). In addition to annual SLAMS analyzers, the CARB conducts annual performance audits on special purpose monitoring and non-criteria analyzers.

THROUGH-THE-PROBE AUDITS

The typical air monitoring station in California is composed of a probe which directs

ambient air into the station, a distribution manifold, and analyzers which draw the ambient air from the manifold (Figure 1). When conducting an audit, the analyzers are operated in their normal sampling mode and the audit gas is passed through as much of the ambient air inlet system as practical. The United States Environmental Protection Agency's (U.S. EPA) Quality Assurance Handbook for Ambient Air Measurement Systems: Volume II recommends that each analyzer be audited separately by disconnecting an analyzer from the station manifold and connecting it to an audit manifold (Figure 2). This configuration works well for testing an analyzer's response to a pollutant concentration, but the ambient air sampling system from the probe inlet through the distribution manifold is bypassed. Contaminants which scavenge pollutants or leaks in the air sampling system will not be identified. The data quality from the air monitoring station may still be suspect using this audit method.

The TTP audit method is conducted by introducing the audit gas through the station's probe inlet (Figure 3). This method allows the audit gas to travel through the complete air sampling system with no modifications to the system. Problems such as contaminants or leaks will be identified by poor analyzer response. This method tests the station's response to a pollutant instead of just an analyzer's response.

The TTP audit method can also be used to assist with troubleshooting when a problem is identified during an audit. Any analyzer that failed an audit can be isolated from the air sampling system, and the audit gas can be introduced at the back of the analyzer. If the analyzer's response improves, the problem is in the air sampling system. If the analyzer's response does not improve, the analyzer is the source of the problem. QAS auditors use this technique to assist station operators to locate problems identified during an audit.

CARB'S AUDIT SYSTEM

The CARB audit system involves mixing high concentration pollutants in compressed gas cylinders with zero air using a gas calibrator. The audit gas is distributed to the air monitoring station's probe inlet through a presentation line. Figure 4 shows the gas flow diagram which includes the major components of the audit system. Each component is described below.

Zero Air Supply

The system's zero air supply is composed of an air compressor, pure air generator, methane reactor, and cooling coil. The air compressor provides ambient air to the pure air generator and methane reactor which remove pollutants from the air. A cooling coil is needed because the methane reactor heats the air to over 300 degrees Celsius. The output is a constant supply of zero air at up to 30 liters per minute (LPM). The zero air system is compared to an independent certified ultra pure air source to ensure that the system is operating properly before each audit.

Super Blend Cylinders

Three compressed gas cylinders the QAS calls super blends contain high concentration pollutants at specific ratios. When diluted with zero air, the pollutant ratios allow for simultaneous audits of several analyzers. Table 1 shows the pollutants in each super blend and their concentrations. The super blends are purchased certified to +/- 2 percent by the manufacturer, and the CARB's Standards Laboratory recertifies the cylinders each calendar quarter. All certifications are traceable to the National Institute of Standards and Technology (NIST). The super blends allow for audits of the following pollutants:

Carbon monoxide (CO)

Sulfur dioxide (SO₂)

Nitrogen dioxide (NO₂) through gas phase titration of nitric oxide (NO) with ozone (O₃)

Total hydrocarbons using methane (CH₄)

Non-methane hydrocarbons (NMHC) using hexane (C₆H₁₄)

Hydrogen sulfide (H₂S)

Gas Calibrator

A gas calibrator is used to dilute the high concentration pollutants from a super blend cylinder with zero air to target the desired audit concentration levels. The calibrator is capable of generating O₃ for audits and gas phase titration of NO to generate NO₂.

Audit Analyzers

The audit system uses O₃ and CO analyzers to accurately measure the system's audit gas concentrations. The O₃ analyzer is a transfer standard that is certified quarterly by the CARB's Standards Laboratory using a NIST standard reference photometer. The CO analyzer cannot be certified as a transfer standard, so it must be calibrated before each audit. Both the O₃ and CO analyzers have an accuracy of +/-3 percent.

Calibration Gases

To calibrate the CO analyzer, three compressed gas cylinders are used. A 40 parts per million (ppm) CO cylinder is used to span the analyzer, a 7 ppm CO cylinder is used for the low point, and an ultra pure gas is used for the zero point. The CO concentrations are critical for accurately calibrating the analyzer, so the cylinders are purchased certified to +/- 2 percent by the manufacturer. The CARB's Standards Laboratory recertifies the CO cylinders each calendar quarter. All certifications are traceable to the NIST.

Manifolds and Presentation Line

The system uses two manifolds to distribute gases. The output manifold receives the audit gas from the gas calibrator and distributes it to the van manifold and presentation line. The van manifold receives either audit gases or CO calibration gases and distributes them to the CO and O₃ analyzer. The type of gas the van manifold receives depends on a selector valve.

The system output is distributed by a 150 foot presentation line which connects the audit system to the air monitoring station. The presentation line is made of 1/2 inch Teflon enclosed in braided stainless steel. The line is mounted on a reel in the audit van for storage.

Audit Van

All the equipment is mounted and operated in a self-sufficient audit van. The latest audit van purchased by the CARB is a 30-foot long utility van. It contains a 17.5 kilowatt (kW) generator, heater and air conditioner for environmental control, computer with printer, rest room, microwave, refrigerator, and sink with running hot and cold water. Its large size accommodates the audit system and all the equipment necessary for conducting performance audits of various particulate samplers and meteorological sensors.

The audit van enables the auditors to drive to most air monitoring stations throughout California. Additionally, the equipment may be warmed-up en route to the station, so the audit may begin upon arrival.

System Operation

Ozone Audits - The O₃ audit concentrations are controlled by the gas calibrator and measured by the audit O₃ analyzer. The calibrator generates O₃ and mixes it with zero air to target the desired audit concentration levels. The audit gas is directed to the output manifold where the majority of the gas is distributed to the air monitoring station through the presentation line. A portion of the audit gas is distributed to the van manifold which directs it to the audit O₃ analyzer. The audit O₃ analyzer measures the audit concentrations. The air monitoring station's O₃ analyzer is allowed to stabilize and its responses are compared to the audit concentrations. The audit concentration levels are listed in Table 2. Figure 5 shows a report of an O₃ audit conducted by the QAS.

Super Blend Based Audits - The pollutant audit concentrations are controlled by the gas calibrator. The calibrator dilutes pollutants from the selected super blend cylinder with zero air to target the desired audit concentration levels. The audit gas is directed to the output manifold where the majority of the gas is distributed to the air monitoring station through the presentation line. A portion of the audit gas is distributed to the van manifold which directs it to the audit CO analyzer. The audit CO analyzer measures the audit gas CO concentration. The audit concentrations of the other pollutants are not directly measured, but are calculated based on the amount of CO dilution. The dilution is expressed as a ratio (dilution ratio) by comparing the CO concentration after dilution (audit concentration) to the CO concentration before dilution (super blend concentration) using Equation 1:

$$\text{Dilution Ratio} = \text{Audit Concentration} \div \text{Super Blend Concentration} \quad (1)$$

The dilution ratio is then applied to each pollutant in the super blend cylinder to calculate

it's audit concentration using.

Equation 2:

$$\text{Super Blend Concentration} \times \text{Dilution Ratio} = \text{Audit Concentration} \quad (2)$$

For example:

If the CO audit concentration = 40.0ppm then,

$$\text{Dilution Ratio} = \text{Audit Concentration} \div \text{Super Blend Concentration}$$

$$\text{Dilution Ratio} = 40.0 \text{ ppm CO} \div 15,000 \text{ ppm CO}$$

$$\text{Dilution Ratio} = 0.002667$$

Apply the Dilution Ratio to the other pollutants,

$$\text{Super Blend Concentration} \times \text{Dilution Ratio} = \text{Audit Concentration}$$

$$325 \text{ ppm NO} \times 0.002667 = 0.867 \text{ ppm NO}$$

$$140 \text{ ppm SO}_2 \times 0.002667 = 0.373 \text{ ppm SO}_2$$

$$6,600 \text{ ppm CH}_4 \times 0.002667 = 17.60 \text{ ppm CH}_4$$

NO₂ performance audits are conducted by gas phase titration of the NO. Equation 3 below shows how NO reacts with O₃:



Excess NO is utilized to force the complete reaction of O₃. The resulting NO₂ concentration is nearly equal to the O₃ concentration. The audit NO₂ concentrations are calculated based on the method described in the U.S. EPA's Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, Section 2.0.12.7.

The audit concentration levels for each criteria pollutant are listed in Table 2. The station analyzers are allowed to stabilize at each audit level and their responses are compared to the audit concentrations. Figure 5 shows a report of a CO and NO₂ audit conducted by the QAS.

SYSTEM ACCURACY

The system has an accuracy of +/-3 percent. This is based on the accuracy of the audit analyzers and the certifications of the gas cylinders. The accuracy is confirmed by checks of the system against the CARB Standards Laboratory each calendar quarter.

EQUIPMENT EXPENSES

A complete audit system can be purchased for between \$150,000 and \$175,000. Table 3 shows a cost break-down for the components. These components are expected to be used for at least seven years before replacement. Yearly maintenance and repair costs run between \$5,000 and \$7,000. Maintenance and certifications of the instruments are

performed by CARB staff at no expense to the QAS.

SYSTEM ADVANTAGES

The CARB TTP audit system has advantages such as flexibility and time savings. The van mounted system offers the flexibility required to conduct audits over a large territory and at a variety of site locations. During 1996, the QAS conducted 371 TTP performance audits of ambient air analyzers at 228 air monitoring stations throughout California and Northern Mexico. The site locations ranged from three story office buildings in metropolitan areas to small trailers in open deserts.

Table 4 shows a comparison of the time required to conduct audits using the CARB TTP audit system verses a system that audits analyzers individually. Time is saved by auditing multiple analyzers simultaneously. Additional time is saved by using van mounted equipment which eliminates the audit equipment set-up and breakdown time, and allows the equipment to warm-up en route to the station. The actual time saved by using the CARB system depends on the type of system to which it is compared.

EXPECTED IMPROVEMENTS

The QAS has developed and will soon begin field testing an automated audit system. The automated system uses a computer program to control the gas calibrator, and gather information from the van's instruments and station's data acquisition system. The computer program stores the audit information in databases and generates a report when the audit is complete.

CONCLUSIONS

The CARB's QAS uses a unique system to audit continuous ambient air analyzers at air monitoring stations throughout California and Northern Mexico. The method of introducing the audit gas through the probe inlet tests the complete air sampling system. It identifies problems that would not have been identified using audit methods that bypass sections of the air sampling system. The CARB system can target and accurately measure the true concentrations of multiple pollutants in the audit gas. It saves time by allowing the audit instruments to warm-up en route to a station and auditing multiple analyzers simultaneously.

The QAS has found this system to be very useful for annually auditing a large number of air monitoring stations and would recommend it to organizations with similar responsibilities. The costs may be prohibitive for some organizations; however, regions with common interests may want to consider working together to purchase and operate a similar system.

ACKNOWLEDGMENTS

The concept of the TTP audit system was developed at the CARB in 1979 by

Bob Fletcher. The audit system was designed and implemented in 1981 by Kevin Kalthoff, Ron Lewis, and Rudy Abangan with the support of the section manager, Bill Oslund and Branch Chief, Don Crowe.

REFERENCES

1. 40 CFR, Part 58, Ambient Air Quality Surveillance; Office of the Federal Register, National Archives and Records Administration, July 1996; Appendix A, Section 3.2, pp 168-169.
2. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition); EPA/600/R-94/038b; U.S. Environmental Protection Agency: Research Triangle Park, April 1994; Section 1.0.12; pp 2-30.
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Table 1. Super Blend Contents And Concentrations.

Super Blend 1: Criteria and Total Hydrocarbon Analyzers.

Pollutant	Concentration
Carbon Monoxide (CO)	15,000 ppm
Nitric Oxide (NO)	325 ppm
Sulfur Dioxide (SO ₂)	140 ppm
Methane (CH ₄)	6,600 ppm

Super Blend 2: Hydrogen Sulfide Analyzers.

Pollutant	Concentration
Carbon Monoxide (CO)	14,000 ppm
Hydrogen Sulfide (H ₂ S)	320 ppm

Super Blend 3: Non-Methane Hydrocarbon (NMHC) Analyzers.

Pollutant	Concentration
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Carbon Monoxide (CO)	15,000 ppm
Methane (CH4)	680 ppm
Hexane (C6H14)	540 ppm

Table 2. Audit Concentration Levels (in ppm).

Audit Level	O3/SO2	NO2	CO
1	0.03-0.08	0.03-0.08	3-8
2	0.15-0.20	0.15-0.20	15-20
3	0.35-0.45	0.35-0.45	35-45
4	0.08-0.90	-----	80-90

* Note: CARB does not conduct audits at level 4-received waiver from U.S. EPA Region IX.

Table 3. Equipment Costs.

Audit System	Cost	Miscellaneous Equipment	Cost
Chart Recorder	\$3,800	Audit Van	\$99,000
Compressor	\$6,400	17.5 kW Generator	\$7,100
Pure Air Generator	\$6,400	Line Conditioner	\$5,300
Methane Reactor	\$1,540	Computer w/Printer	\$4,100
Calibration Gases (3)	\$270		
Super Blends (3)	\$600		
Gas Calibrator	\$15,000		
CO Analyzer	\$11,000		
O3 Analyzer	\$6,500		

TOTAL COST: \$161,110

Table 4. Estimate Of Time Using CARB Audit System vs A System That Audits Analyzers Individually.

Action	CARB System	Individual Analyzer System
Equipment Set-up	-----	1.0
Equipment Warm-up	0.0 (if warmed-up en route)	1.0
O3 Audit	2.0	2.0

Criteria Audits	4.5 (using Super Blend 1)	-----
-Pre Calibration	0.5	-----
-CO	-----	2.5
-NO2	-----	4.0
-SO2	-----	2.5
-THC	-----	2.5
-Post Calibration	0.5	-----
H2S Audit	3.0	3.0
NMHC Audit	2.5	2.5
Equipment Break Down	-----	1.0
TOTAL	11.5 Hours	22.0 Hours

* Actual time may vary depending on the response time of the analyzers and audit method used.

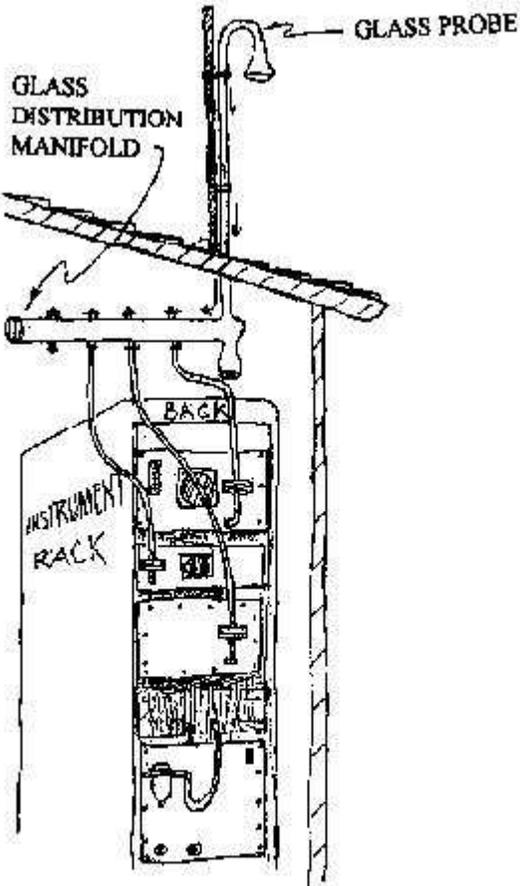


Figure 1. Air Monitoring Station

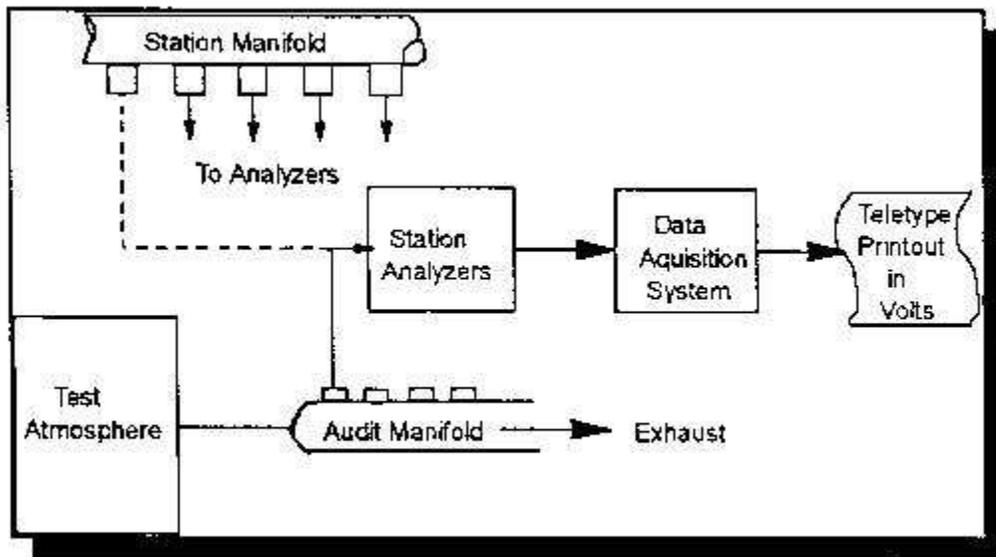


Figure 2. U.S. EPA Recommended Audit Configuration

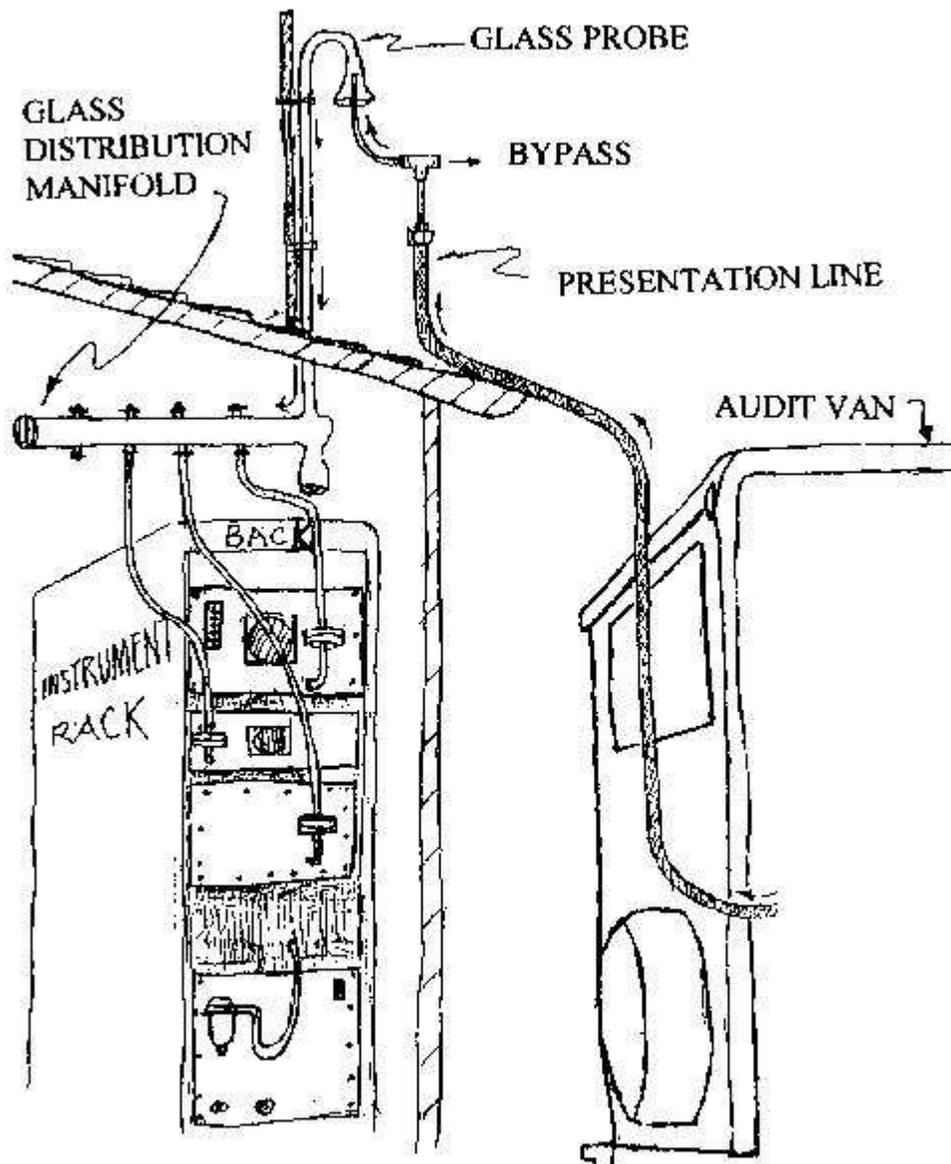


Figure 3. CARB TTP Audit Configuration

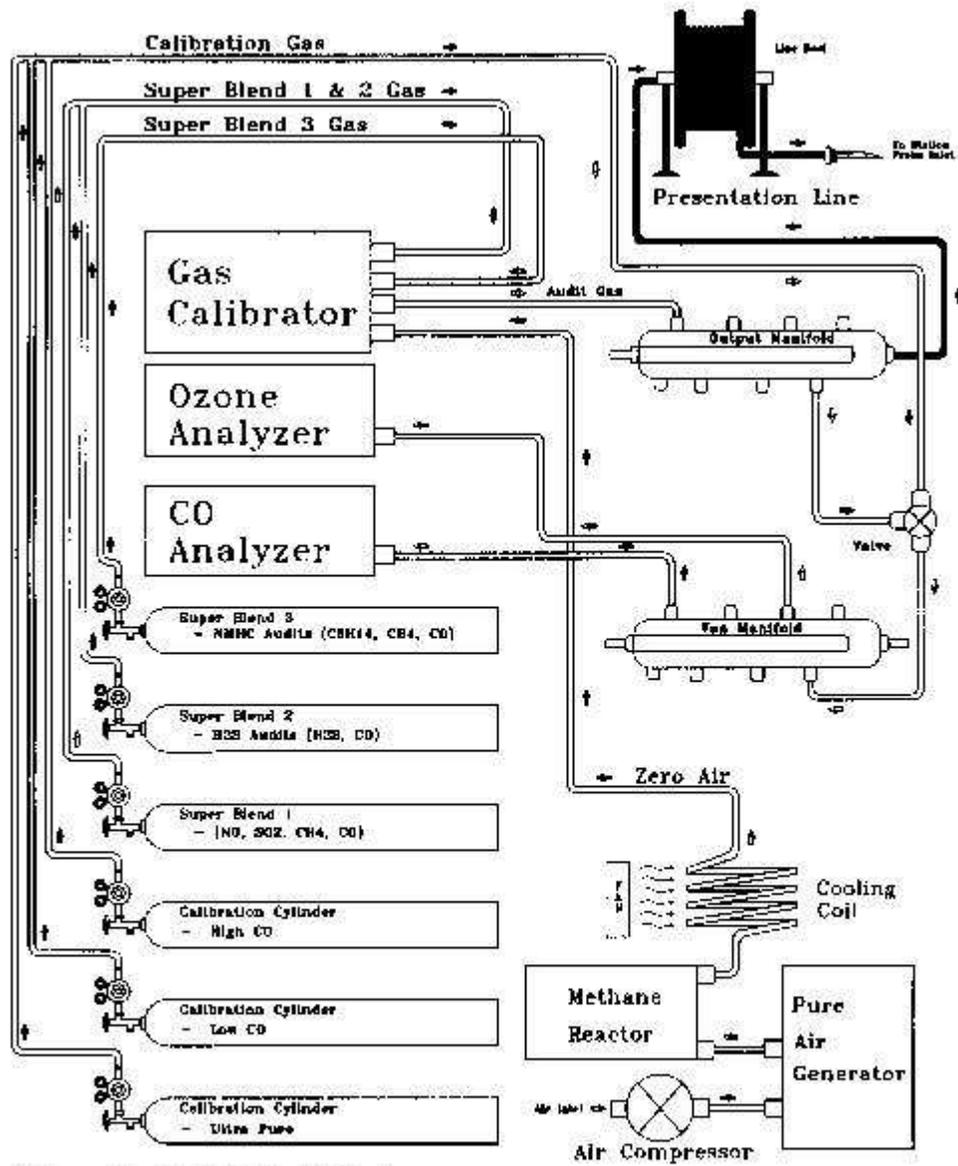


Figure 4. CARB Audit System

