

Essential Standards Used in California
for the Measurement of Toxics in Ambient Air,
Ozone Precursors from Automotive Emissions,
and Cleaner Burning Gasoline



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Air Resources Board



- Responsible for achieving federal and state health-based air quality standards through control measures for stationary and mobile sources
- Monitor ambient air, automotive emissions, fuels, and consumer products
- Protect the public from exposure to toxic air contaminants

Source of Standards

NIST / SRMP

Chemical Science and Technology Laboratory



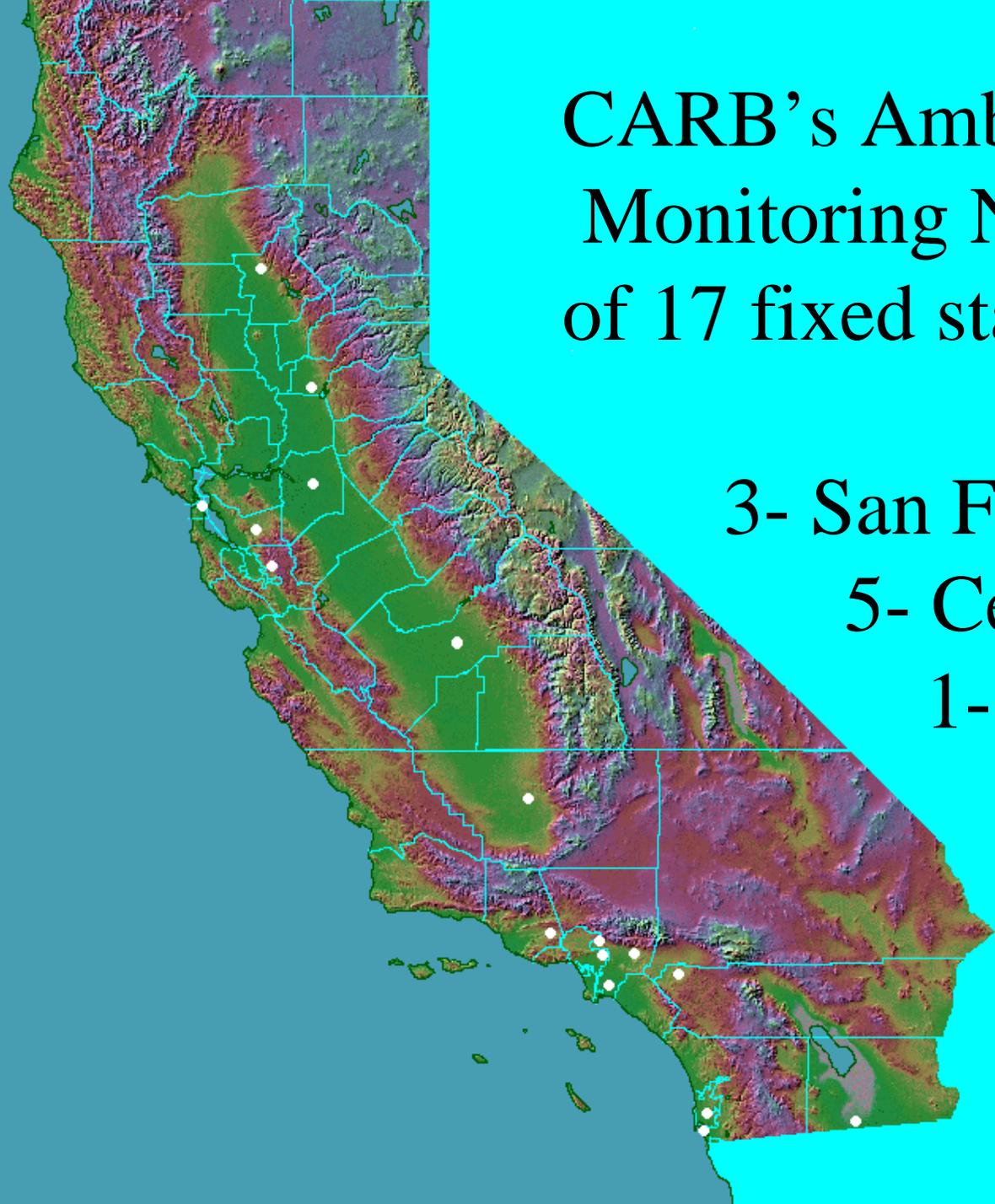
- *Standard Reference Materials
- *NIST Traceable Reference Materials NTRMs
- *Custom NIST Reference Material

Uses of Primary Standards at CARB

- Direct instrument calibration
- Development of working standards
- Laboratory audits (performance checks)
- Field audits of Air Monitoring Stations
- Round-robins (inter-laboratory comparison)

TOPICS

- ✓ **Toxics in Ambient Air**
- Ozone Precursors from Automotive Emissions
- Cleaner Burning Gasoline

A topographic map of California with 17 white dots indicating monitoring stations. The dots are distributed across the state: three in the San Francisco Bay area, five in the Central Valley, one in the Ventura County area, five in the Los Angeles Basin area, two in San Diego County, and one in the Southeast Desert.

**CARB's Ambient Toxics
Monitoring Network consists
of 17 fixed stations in the State**

3- San Francisco Bay

5- Central Valley

1- Ventura Co

5- L.A. Basin

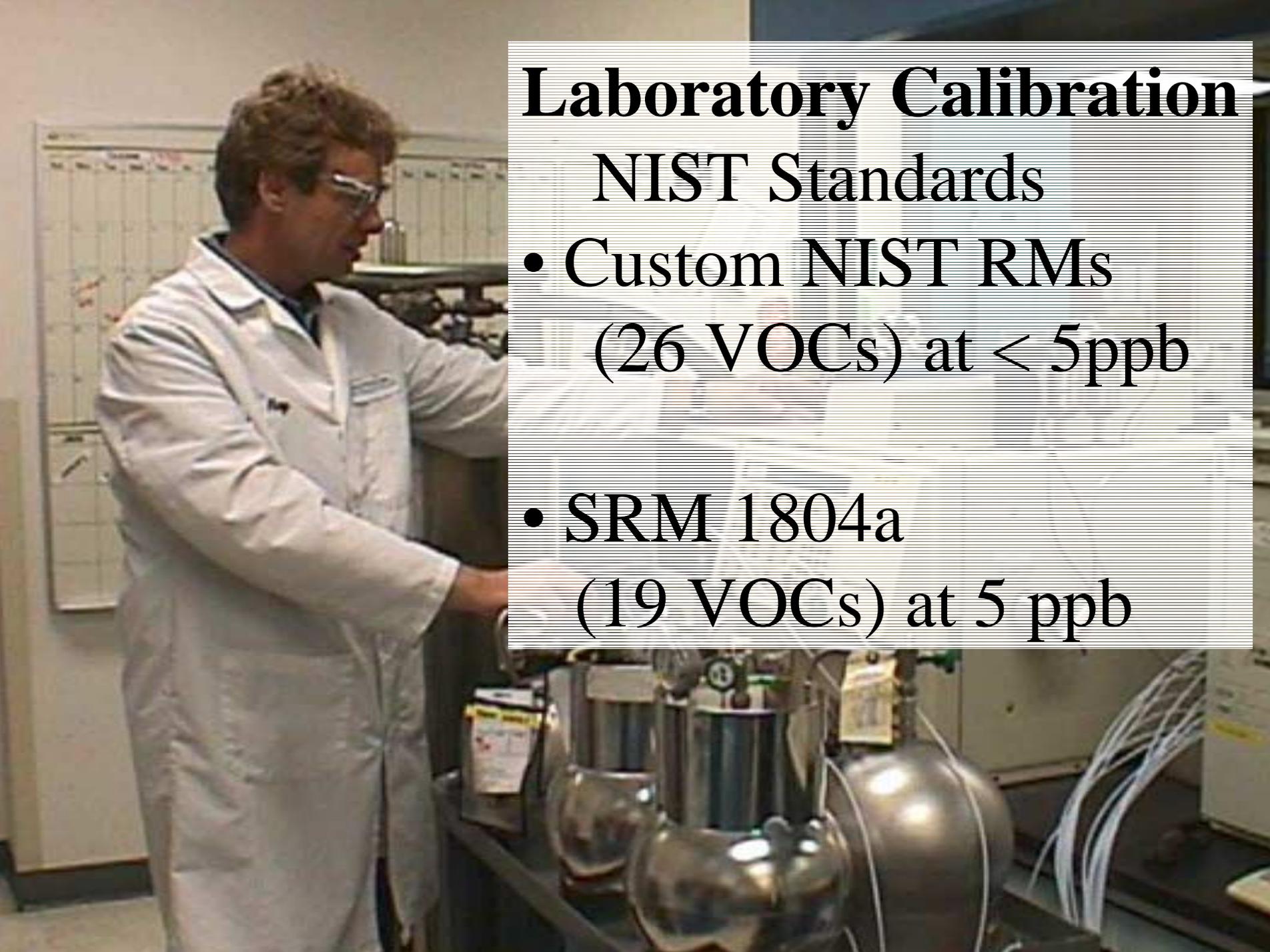
2- San Diego Co

1- S.E. Desert

Toxic VOCs Measured

- Benzene
- 1,3-Butadiene
- Tetrachloroethene
- Toluene, Xylenes
- Dichlorobenzenes
- Tetrachloromethane
- Trichloromethane
- Ethylbenzene
- Other halogenates





Laboratory Calibration

NIST Standards

- Custom NIST RMs
(26 VOCs) at < 5 ppb
- SRM 1804a
(19 VOCs) at 5 ppb

Quality Assurance Section audits air monitoring stations

- Custom NIST standards
- CARB working standards
assayed with SRMs



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Types of Vehicle Emissions Tests

- New vehicle emissions certification
- Compliance (verify emissions control is working for typically 2 or 3 year old cars-recall is issued for a failed engine family)
- Surveillance (random selection of vehicles-data used for emissions inventory and modeling)



**Dynamometer test for emissions:
Hydrocarbons, NO_x , and CO
CARB Laboratory in El Monte CA**

Hydrocarbon Evaporative Emissions testing

- 1-hour hot cycle soak
- Diurnal

Sealed
Housing
Evaporative
Determination



NON-METHANE ORGANIC GAS (NMOG)



**NMHC (Dyno) +
Carbonyls (Lab) +
Alcohols (Lab) =
NMOG**

Uses of NIST SRMs for Dynamometer test analyzers

- Accuracy check for instrument multi-point checks conducted quarterly or after repairs
- Assay working standards

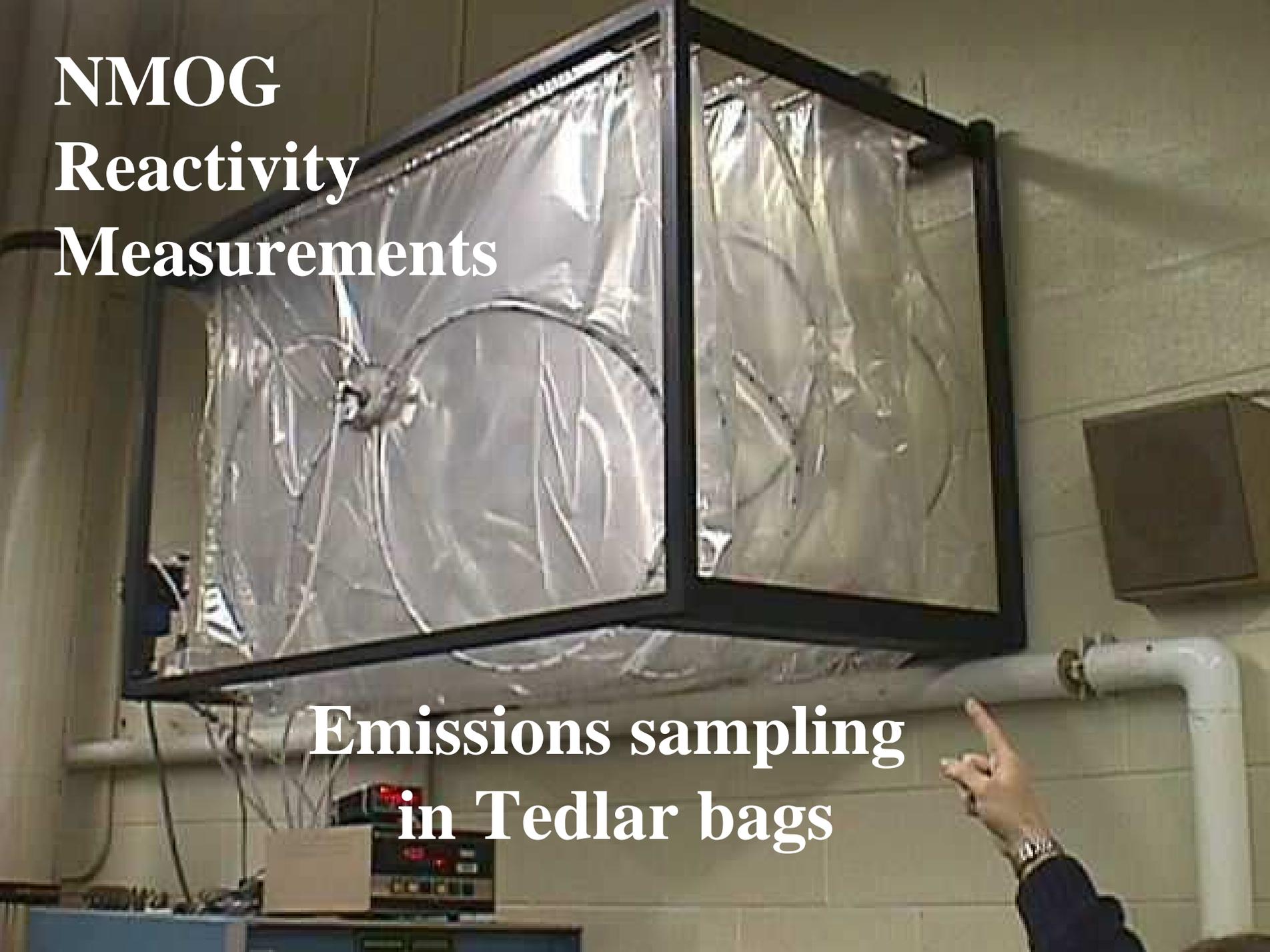


33 SRMs in use at CARB

- **Propane** (0.25, 3, 50, 100, and 500 PPM)
- **Methane** (1, 10, 50, 100)
- **NO_x, NO** (5, 10, 100, 250, 500, 1500, and 3000 PPM)- need lower SRM, new analyzer can go down to 0.1 PPM
- **CO** (10, 50, 100, 250, 500, 1000, 2500, 5000, 10000, 40000, and 80000 PPM)
- **CO₂** (2, 2.5, 3.5, 4, 7, and 14 mol %)

NMOG Reactivity Measurements

Emissions sampling
in Tedlar bags



Uses of Custom NIST Hydrocarbon standards for laboratory (GC/FID)

- Direct instrument calibration
- Limit of detection
and linearity checks
- Diagnostics

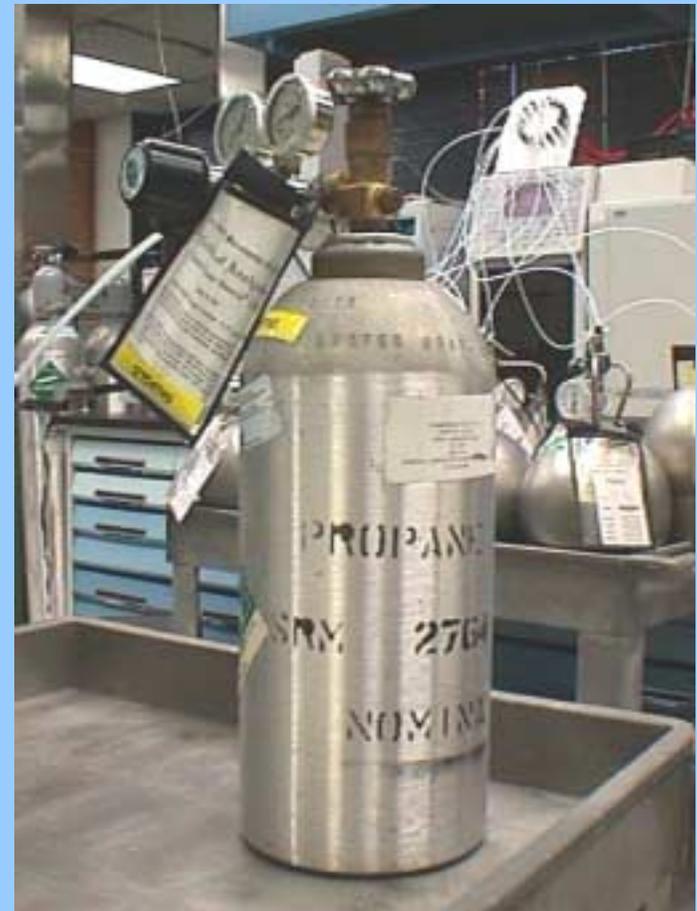


Reference Material Working Group:

- California ARB
- General Motors Corp
- Ford Motor Company
- Chrysler Corp
- Navistar
- U.S. EPA (Ann Arbor, and RTP)

AIGER / NIST Products

- SRM 2764
Propane in Air
(0.25 $\mu\text{mol/mol}$)
- Zero Air
(< 9 ppbc, < 10 ppb
CO, < 1 ppb NO_x)
- Ethanol in Air
(40 $\mu\text{mol/mol}$)

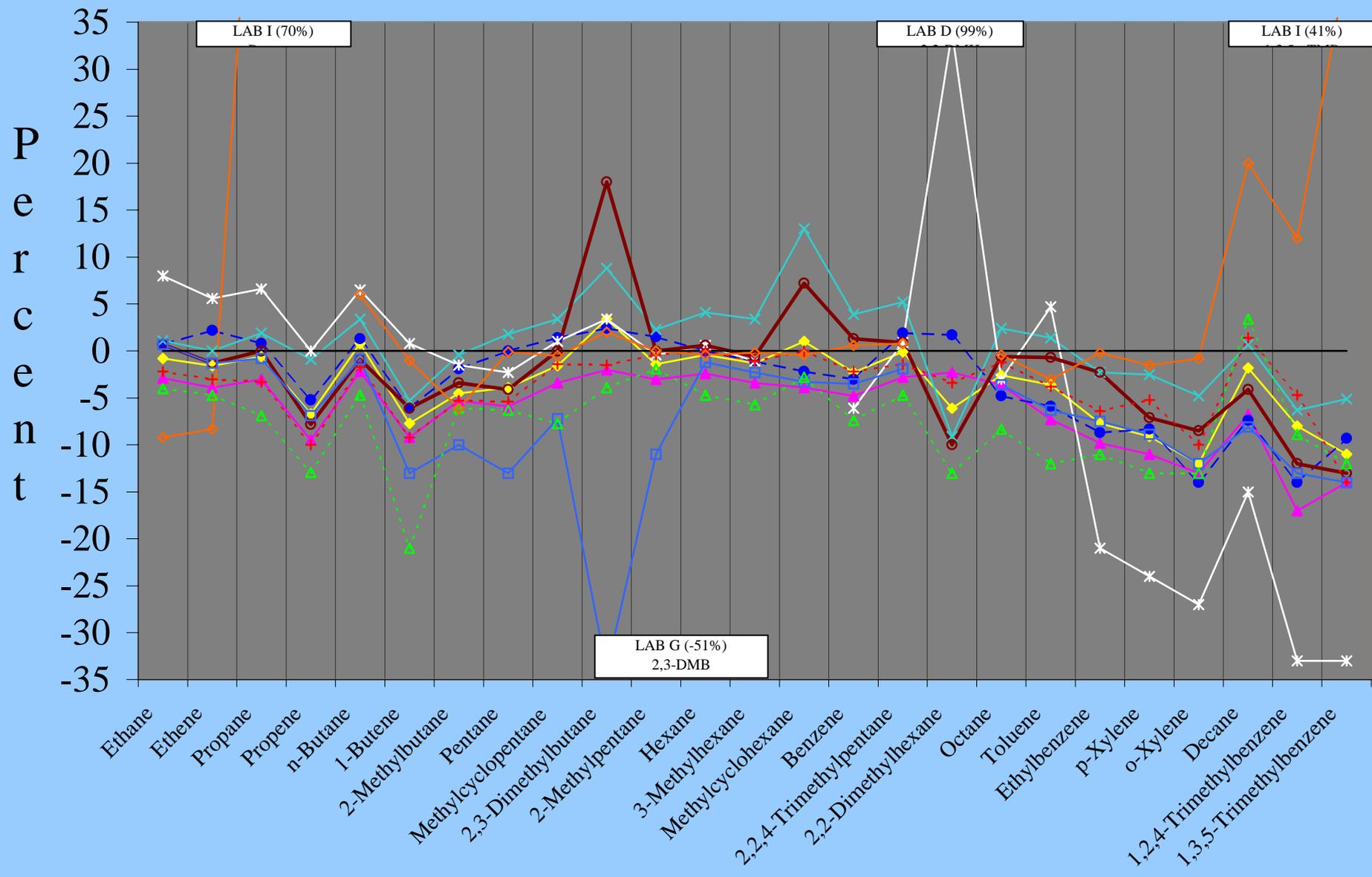


Laboratory Round-Robins with a Custom NIST Speciated Hydrocarbon Standard

Advantages of using a NIST standard

- High accuracy and stability
- Certified values for each component
- Independent source
- Propane traceability required

25 Hydrocarbon Round Robin with Custom NIST Standard



TOPICS

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- ✓ **Cleaner Burning Gasoline**

Cleaner Burning Gasoline in California

- Started Statewide in April 1996
- Lower toxics (benzene and aromatics)
- Contain oxygenates year-round, refiners typically use methyl tert-butyl ether (MTBE)
- Lower Sulfur
- Lower Reid Vapor Pressure and boiling points

CARB / Western States Petroleum Association (WSPA) Test Procedure Working Group



- CARB / WSPA develop analytical methods for publication in American Society For Testing and Materials (ASTM)



Mobile Laboratory Analysis

- Screening Instrument (FTIR)
- Benzene & Total Aromatics
- Distillation (T50 & T90)
- Oxygen
- Sulfur
- RVP



In-House Analysis at El Monte

- Olefins
- Low Sulfur
- Diesel Aromatics & PAHs

SRMs Used to Check Accuracy

- CARB / WSPA Petitioned NIST to produce four SRMs for gasoline
- Synthetic gasoline contains: 10-aromatics, 3-olefins, 8-saturates, organic sulfur, and one of three oxygenates (i.e. MTBE, ethyl tert-butyl ether ETBE, and ethanol)
- SRM (2294-97) vials released in 1998
- SRMs used to check accuracy for benzene, oxygenates, total aromatics, and total sulfur

Future Efforts / New Standards

- Government Agencies have a growing interest in expanding the ambient toxics network and increasing the number of VOCs measured (1,3-butadiene is vital)
- New SRMs for NO_x at lower concentrations are essential to measure low emission vehicle exhaust emissions
- The need for replacement fuel SRMs should be investigated

Conclusions

- Highly accurate and traceable standards are required for compliance purposes
- NIST needs to continue working with Federal and State Air Quality Agencies to assist with standards development
- Custom NIST standards are essential for quality assurance and can be used to aid the development of SRMs
- NIST should maintain resources for SRMs, and Custom RMs.