Toxics Workgroup

Mobile Source Technical Review Subcommittee
Clean Air Act Advisory Committee

DRAFT Findings and Recommendations
June 2003

Table of Contents

Glossary of Terms

CARB – California Air Resource Board
CFR – Code of Federal Regulations
CV-AAS – Cold Vapor – Atomic Absorption Spectroscopy
CVS – Constant Volume Sampler
DA-AAS – Direct Aspiration – Atomic Absorption Spectroscopy
DNPH – 2,4-Dinitrophenylhydrazine
DEOG – Diesel Exhaust Organic Gases
FR – Federal Register
GC – Gas Chromatography
GF-AAS – Graphite Furnace – Atomic Absorption Spectroscopy
HPLC-FLD – High Performance Liquid Chromatography – with Fluorescence Detection
HPLC-UV – High Performance Liquid Chromatography-Ultraviolet
HRGC-HRMS – High Resolution Gas Chromatography – High Resolution Mass Spectroscopy
ICP-AES – Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS – Inductively Coupled Plasma – Mass Spectroscopy
LEV – Low-Emission Vehicle
LOD – Limit of Detection
MEK – Methyl Ethyl Ketone
MSAT FACA – Mobile Source Air Toxics Federal Advisory Committee Act
MSTRS – Mobile Sources Technical Review Subcommittee
MTBE – Methyl Tertiary-Butyl Ether
NMOG – Non-Methane Organic Gases
OC/EC – Organic Carbon/Elemental Carbon
PAH – Polycyclic Aromatic Hydrocarbon
PCDD/F – Polychlorinated Dibenzodioxins/Furans
PM – Particulate Matter
POM – Polycyclic Organic Matter
SOF – Soluble Organic Fraction
SULEV – Super-Ultra-Low-Emission Vehicle
TLEV – Transitional Low-Emission Vehicle
ULEV – Ultra-Low-Emission Vehicle
US EPA – United States Environmental Protection Agency
XRF – X-Ray Fluorescence Spectroscopy

I. Background

In March of 2001, the United States Environmental Protection Agency (US EPA) finalized the motor vehicle air toxics rule under Clean Air Act amendment 202(l).[1] The rule identified 21 mobile source air toxics that are known or suspected to cause cancer or other serious health effects. These toxics are listed in Table 1 below. The purpose of the list is to provide a screening tool that identifies those compounds emitted by motor vehicles or their fuels for which further evaluation of emissions controls is appropriate. Inclusion on the list is not itself a determination by EPA that emissions of the compound in fact present a risk to public health or welfare. The rule finalized gasoline toxic emissions baseline requirements, and established a Technical Analysis Plan, which will support the Agency's effort to more accurately characterize the potential risk posed by air toxics to public health and welfare. The technical analysis plan is intended to overcome data gaps and analytical limitations in the current inventory and exposure modeling of mobile source air toxics.

Table 1. List of 21 Mobile Source Air Toxics.

Acetaldehyde	Dioxin/Furans[b]	MTBE
Acrolein	Ethylbenzene	Naphthalene
Arsenic Compounds[a]	Formaldehyde	Nickel Compounds[a]
Benzene	n-Hexane	Polycyclic Organic Matter (POM) (sum of 7 PAHs)[c]
1,3-Butadiene	Lead Compounds[a]	Styrene
Chromium Compounds[a]	Manganese Compounds[a]	Toluene
Diesel Particulate Matter (PM) + Diesel Exhaust Organic Gases (DEOG)	Mercury Compounds[a]	Xylene

[a] Although the different species of the same metal differ in their toxicity, the on-road mobile source inventory contains emissions estimates for total compounds of the metal identified in particulate speciation profiles.

[b] This entry refers to two large groups of chlorinated compounds. In assessing their cancer risks, their quantitative potencies are usually derived from that of the most toxic, 2,3,7,8-tetrachlorodibenzodioxin.

[c] Benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, 7,12-dimethylbenzo(a)anthracene, and indeno(1,2,3-cd)pyrene.

In addition to EPA's efforts to better characterize toxics from mobile sources, states and private and public testing labs have worked to test light and heavy-duty vehicles for toxics. Approximately 150 light and heavy-duty vehicles (mostly heavy-duty vehicles) have been tested by states in the Northeast alone for carbonyls, polycyclic aromatic hydrocarbons (PAH), particulate matter (PM), and other toxics. Additionally, many state agencies and academic institutions are working to understand the mobile source contribution to toxic air pollution and the potential health effect risks associated with this pollution. The MSAT FACA workgroup was tasked with bringing together technical experts to assess how best to sample and analyze the mobile source air toxic compounds for the purpose of improving inventory estimates.

[1] EPA "Control of Emissions of Hazardous Air Pollutants from Mobile Sources; Final Rule" 66 FR 17230 (March 29, 2001).

II. Charter for the Toxics Workgroup

The MSTRS Air Toxics Workgroup charter is as follows:

> The mission of this workgroup is to define a single suite of mobile source air toxic emissions sampling and analysis methods for each of the 21 mobile source air toxics identified in the March 2001 rule (see Table 1). These measurements are intended to be taken from the source (engine or vehicle) using a constant volume sampler or similar laboratory setup. This effort will include air toxics emissions sampling and analysis protocols for light-duty vehicles, heavy-duty vehicles, and non-road engines. The Agency intends to use these updated and standardized emissions testing protocols to improve our air toxic inventories for mobile sources.

III. Overview of Current Toxics Testing Methods

This section provides a summary of current existing methods to sample for and analyze mobile source toxics and provides an overview of testing methods used. The methods outlined in this section were used as a basis for development of the workgroup's recommendations to the MSTRS.

A. Existing Environmental Protection Agency Methods

EPA currently has a recommended procedure for the measurement of formaldehyde from mobile sources as prescribed in 40 CFR Part 86.109-94. This method outlines sampling and analytical procedures and is similar in scope to California Air Resources Board (CARB) Method 1004 (specifying use of 2,4 dinitrophenylhydrazine [DNPH] cartridge or impinger system with HPLC-UV analysis), but is not as detailed as the CARB method.

B. Existing California Air Resources Board Methods

CARB has established methods for testing some of the 21 MSATs. CARB has procedures for automobile manufacturers to submit data on $C_2 - C_{12}$ paraffins, isoparaffins, aromatics, naphthenes, olefins, aldehydes, and ketones for 1993 and subsequent model year transitional low-emission vehicles (TLEV), low-emission vehicles (LEV), ultra-low-emission vehicles (ULEV), and super-ultra-low-emission vehicles (SULEV) certifying to non-methane organic gas (NMOG) emission standards.[2] The sampling and analytical method for testing hydrocarbons (C_2 to C_{12}) in automotive

[2] California Non-Methane Organic Gas Test Procedures, Part D (Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method 1002), Part E (Determination of C_6 to C_{12} Hydrocarbons in Automotive Source Samples by Gas Chromatography (Method 1003), Part F (Determination of Aldehyde and Ketone in Automotive Source Samples by High Performance Liquid Chromotography (Method 1004)), amended July 30, 2002.
http://www.arb.ca.gov/msprog/levprog/cleandoc/clean_nmogtps_final.pdf

exhaust gases is described in Method 1002/1003.[3] These procedures are updated periodically. The latest available version was published in 2002. Method 1002/1003 describes a method of analyzing by gas chromotography (GC) light (C_2 to C_5) and mid-range (C_6 to C_{12}) hydrocarbons in the range of 20 to 10,000 parts per billion carbon from automotive source samples.

In addition to method 1002/1003, CARB has established a method to sample aldehydes and ketones, called Method 1004.[4] Method 1004 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 in DNPH impregnated cartridges. The targeted compounds analyzed and reported by the method are: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, hexanal, benzaldehyde, methyl ethyl ketone (MEK), methacrolein, crotonaldehyde, valeraldehyde, and m-tolualdehyde.

C. Methods Developed by Testing Laboratories

Testing laboratories have established internal procedures for sampling and analysis of mobile source air toxics. For $C_2 - C_{12}$ paraffins, isoparaffins, aromatics, naphthenes, olefins, aldehyde, and ketones these laboratories use CARB Methods 1002, 1003, and 1004. For measurement of MSATs where mobile source sampling and analysis methods are not well established (metals, POM, and dioxin/furans), these labs use modified stationary source sampling and analytical methods.

IV. Recommendations of Toxics Workgroup

A. 1,3-Butadiene, n-Hexane, Benzene, Ethyl Benzene, Xylenes, Methyl Tertiary-Butyl Ether (MTBE), Naphthalene, Styrene, Toluene, Acetaldehyde, Acrolein, and Formaldehyde

EPA and the workgroup agreed that 1,3-butadiene, n-hexane, benzene, ethyl benzene, xylenes, methyl tertiary-butyl ether (MTBE), naphthalene, styrene, toluene, acetaldehyde, acrolein, and formaldehyde can be successfully sampled and analyzed using CARB methods 1002/1003, "Procedure for the Determination of C_2-C_{12} Hydrocarbons in Automotive Exhaust Samples by Gas Chromatography" and Method 1004, "Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography".

B. Diesel PM and Diesel Exhaust Organic Gases

[3] California Air Resources Board "Procedure for the Determination of C_2 to C_{12} Hydrocarbons in Automotive Exhaust Samples by Gas Chromatography Standard Operating Procedure No. MLD 1002/1003 Revision 5.0" July 30, 2002.

[4] California Air Resources Board "Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography Standard Operating Procedure No. 1004," July 30, 2002.

Characterization of particulate matter from mobile sources should be completed using established definitions and procedures in 40 CFR Part 86.1310-2007. This method characterizes particulate matter on a mass basis.

Additional method development may be necessary for a more thorough characterization of particle bound diesel exhaust organic gases. This development may include investigation into organic carbon/elemental carbon (OC/EC) and the soluble organic fraction (SOF) analysis.[5]

C. Metals, Dioxins, Furans, and Polycyclic Organic Matter (POM)

The workgroup investigated methods for sampling and analysis of metals, dioxins, furans, and polycyclic organic matter and determined that there are a variety of methods used, which are based mainly on stationary source testing methods. Because there are no established methods for sampling these compounds for mobile sources, the workgroup believes it is beyond the scope and technical ability of the Workgroup to guide the development of additional or alternative analytical methods with respect to POM, metals, and dioxin/furans. A description of methods investigated for measurement of these compounds and the reasoning behind the non-recommendation can be found in the Technical Appendix.

A summary of the protocol recommendations for specific compounds is given in Table 2.

Table 2. Recommendation for Air Toxic Test protocols.

	MSATs	Recommended Procedure		MSATs	Recommended Procedure
1	Acetaldehyde	CARB 1004	12	Lead compounds	*
2	Acrolein	CARB 1004	13	Manganese compounds	*
3	Arsenic compounds	*	14	Mercury compounds	*
4	Benzene	CARB 1002/1003	15	MTBE	CARB 1002/1003
5	1,3-Butadiene	CARB 1002/1003	16	Naphthalene	CARB 1002/1003
6	Chromium compounds	*	17	Nickel compounds	*
7	Dioxin/Furans	*	18	POM (Sum of 7 PAHs)	*
8	Diesel Particulate Matter + Diesel Exhaust Organic Gases	40 CFR Part 86.1310-2007	19	Styrene	CARB 1002/1003
9	Ethylbenzene	CARB 1002/1003	20	Toluene	CARB 1002/1003
10	Formaldehyde	CARB 1004	21	Xylenes	CARB 1002/1003
11	n-Hexane	CARB 1002/1003			
*It is beyond the scope and technical ability of the Workgroup to guide the development of additional or alternative analytical methods for these species.					

[5] The terms elemental carbon (EC) and organic carbon (OC) as used in this report are operational, not chemical, definitions of analytical measurements made on particulate carbon. Considerable research is being performed to better identify and quantify chemical species found in exhaust particulate carbon.

V. Conclusion

The MSTRS Air Toxics Workgroup has investigated the methods available for sampling and analysis of mobile source air toxics and has made recommendations for sampling and analysis of 12 of the 21 toxics listed in the 2001 MSAT rule. The members believe that the Workgroup has successfully used the combined expertise of its members to the greatest extent possible. Our conclusions are listed below:

- C_2 - C_{12} hydrocarbons, aldehydes, and ketones can be successfully sampled and analyzed using existing CARB procedures. It is important that EPA harmonize with these methods through the use of scientifically sound equivalence procedures that have been developed by independent testing laboratories and the regulated community.

- Where it is determined that new analytical methods are needed for the MSAT toxics not addressed by this workgroup, their development should be completed in cooperation with the California Air Resources Board and private sector labs having expertise in this area and should result in a method that will be used by both regulatory agencies. Technical collaborations between industry, the Agencies, academia and private sector labs, have been successful in developing such methodologies when needed.

- Current and future emissions control technology is expected to result in near zero levels of mobile source air toxics. Considering that any characterization of these near zero levels will require highly scientific and state-of-the-art procedures for their measurement, EPA should first determine the cost, extent, and practical usefulness of any proposed analytical methods prior to embarking on the development of new methods.

- The need to develop any new methods, as well as the determination of appropriate detection limits to measure the near zero emissions, should be based on an analysis of the probable emissions levels needed to create significant health effects from ambient air.

- Poorly maintained vehicles are known to contribute disproportionately to the atmospheric inventory. The resulting high concentration of exhaust contaminants will require continued study.

VI. Workgroup Members – See Appendix A.

VII. Technical Appendix

CARB test methods 1002/1003/1004 can be found at:
http://www.arb.ca.gov/msprog/levprog/cleandoc/clean_nmogtps_final.pdf.

While analytical and sampling methods developed in conjunction with stationary source measurement methods do exist for the analysis of benzo(a)anthracene,

benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, 7,12-dimethylbenzo(a)anthracene, and indeno(1,2,3-cd)pyrene (polycyclic organic matter); arsenic, chromium, lead, manganese, mercury, and nickel compounds (metals); and dioxin/furans (PCDD/Fs, 75 dioxin and 135 furan congeners), published sampling methods have been developed only for stationary sources. The workgroup is uncertain of the applicability of these stationary source methods to mobile source applications at this time. The listed methods were developed to determine the concentration of metals, POM, or PCDD/Fs in stack emissions from hazardous waste incinerators and similar combustion processes (stationary sources). This is not directly applicable to sampling mobile source air toxics from a constant volume sampler (CVS) or modal exhaust stream due to the different natures of the sample stream. It is also not known if the concentrations of the toxic compounds of interest in mobile source applications are above or below the limits of detection (LOD) of the current stationary source analytical methods. A list of analytical and sampling methods for measurement of these compounds from stationary sources can be found in Table 3.

Table 3. List of MSATs and Stationary Source Sampling and Analytical Techniques.

MSAT	Stationary Source Sample Collection Method	Analytical Method
As	EPA Method 60, ARB Method 436	ICP-AES, ICP-MS, GF-AAS, DA-AAS, XRF
Cr	EPA Method 60, ARB Method 436	ICP-AES, ICP-MS, GF-AAS, DA-AAS, XRF
Pb	EPA Method 60, ARB Method 436	ICP-AES, ICP-MS, GF-AAS, DA-AAS, XRF
Mn	EPA Method 60, ARB Method 436	ICP-AES, ICP-MS, GF-AAS, DA-AAS, XRF
Hg	EPA Method 60, ARB Method 436	CV-AAS
Ni	EPA Method 60, ARB Method 436	ICP-AES, ICP-MS, GF-AAS, DA-AAS, XRF
POM	EPA Modified Method 10 or 23A, ARB Method 429	HPLC-UV, HPLC-FLD, HRGC-HRMS
PCDD/Fs	EPA Method 23A, ARB Method 428	HRGC-HRMS

Appendix B			
Name	**Organization**	**Email**	**Phone**
Coralie Cooper, co-chair	NESCAUM	ccooper@nescaum.org	617-367-8540
Chris Laroo, co-chair	EPA	laroo.chris@epa.gov	734-214-4937
Jeanette Clute	Ford	jclute@ford.com	313-322-9213
Susan Collet	Toyota Tech Center	scollet@ttc-usa.com	734-995-2086
Doug Lawson	NREL	doug_lawson@nrel.gov	303-275-4429
Jeff Loo	General Motors	jeffery.loo@gm.com	248-685-5025
Rick Middleton	DaimlerChrysler	ram12@dcx.com	248-576-6966
Antonio Santos	MECA	asantos@meca.org	
Lawrence Smith	Southwest Research Institute	lsmith@swri.org	210-522-2977
Joe Suchecki	EMA	jsuchecki@enginemanufacturers.org	312-827-8734
Steve Swarin	General Motors	steve.swarin@gm.com	586-986-0808
Mike Vaillancourt	Ford	mvaillan@ford.com	313-322-5228
John Cabaniss	Association of International Automobile Manufacturers (AIAM)	jcabaniss@aiam.org	703-247-2107
Matt Maricq	Ford	mmaricq@ford.com	313-594-7527
Donald Nagy	General Motors Powertrain	donald.nagy@gm.com	248-685-6385
Joe Norbeck	CE-CERT at University of California, Riverside	joe@cert.ucr.edu	909-781-5778
David Lax	American Petroleum Institute (API)	lax@api.org	202-682-8479
Ted Jensen	Ford	tjensen2@ford.com	313-322-4598
Barbara Warren	Clean Air Task Force	warrenba@email.msn.com	
Tom Hesterberg	International Truck and Engine Corporation	tom.hesterberg@nav-international.com	312-927-2697
Michael Reale	DaimlerChrysler	mjr2@daimlerchrysler.com	248-576-5505
Shida Tang	NYS Dept. of Environmental Conservation	sdtang@gw.dec.state.ny.us	518-782-7248