SECTION 2

SUMMARY OF SAMPLING/ANALYTICAL METHODS FOR CLEAN AIR ACT LIST CHEMICALS

The primary sampling and analytical methods for the analytes listed in the Clean Air Act Amendments are shown in Table 1. The selection of a primary method for a given analyte was governed by the following considerations:

- Applicability of a given sampling and analytical methodology to a wide range of analytes;
- Availability of a sampling/analytical methodology which directly addresses stationary sources; and
- Availability of a validated methodology for a particular analyte.

Chemicals are listed alphabetically in Table 1, with primary sampling and analytical methods. If two validated methodologies are available for a given analyte, both are listed as primary methods. Many validated single-analyte methods are omitted to focus on broad coverage. A "Comments" section is provided to address validation status of methodology and to provide information on known problems which will be encountered with a given analyte. These comments describe problems such as "Decomposes upon heating", "Explosive", etc. More detailed information on a compound by compound basis is provided in Appendix C, where sampling and analytical problems are described for each analyte. An additional entry in Table 1 is "Target Compound for Method 8270". Method 8270 is an analytical methodology which incorporates the use of gas chromatography/mass spectrometry (GC/MS) as an analytical technique for semivolatile compounds. A semivolatile compound is any organic compound which boils above 100°C. The method includes a specific list of analytes for which the application of the analytical methodology has been validated, and these analytes are referred to as "Target

Table 1

Primary Sampling and Analytical Methods for Clean Air Act Chemicals

Chemical/Compound	Sampling	Analysis	Comments
Acetaldehyde	Draft 0011	Draft 8315	Requires validation.
Acetamide	0010	8270	Requires validation.
Acetonitrile	18	18	Specific GC detector required.
Acetophenone	0010	8270	Method 8270 target.
2-Acetylaminofluorene	0010	8270	Requires validation.
Acrolein	Draft 0011	Draft 8315	Requires validation.
Acrylamide	0010	8270	Requires validation.
Acrylic acid	0010	8270	Requires validation. Methodology optimized with control of pH during extraction and derivatization.
Acrylonitrile	0030	5040, Draft 5041[a]	Analysis of condensate suggested. Analytical methodology validated for modified 5040.
Allyl chloride	0030	5040, Draft 5041	Requires validation.
4-Aminobiphenyl	0010	8270	Requires validation. Samples unstable at ambient temperatures. Requires control of pH during extraction.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Aniline	0010	8270	Method 8270 target.
o-Anisidine	0010	8270	Requires validation.
Benzene	0030	5040, Draft 5041	Validated methodology.
Benzidine	0010	8270	Target compound for Method 8270. Compound decomposes readily and chromatographs poorly.
Benzyl chloride	0010	8270	Requires validation.
Biphenyl	0010	8270	Target compound for Method 8270.
Bis (2-ethylhexyl) phthalate	0010	8270	Target compound for Method 8270.
Bis (chloromethyl) ether	18	18	Compound is very reactive and decomposes in water. Method development required.
Bromoform	0010	8270	Volatile compound; easily lost in concentration of extract.
1,3-Butadiene	18	18	Methodology has been validated.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Caprolactam	0010	8270/632	Requires validation. Amenability to gas chromatographic techniques (8270) not established; may require use of high performance liquid chromatography (632).
Captan	0010	8270	Requires validation.
Carbaryl	0010	8318	Requires validation.
Carbon disulfide	0030	5040, Draft 5041	Requires validation. Compound decomposes on standing.
Carbon tetrachloride	0030	5040, Draft 5041	Methodology validated.
Carbonyl sulfide	15	15	Requires validation.
Catechol	0010	8270	Requires validation. Control of pH during extraction is required for optimal recovery.
Chloramben	0010	515/615	Requires validation.
Chlordane	0010	8270	Target compound for Method 8270.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Chloroacetic acid	0010	8270	Control of pH during extraction is required for optimal recovery. Must be derivatized for successful gas chromatographic analysis.
2-Chloroacetophenone	0010	8270	Requires validation.
Chlorobenzene	0010 0030	8270 5040, Draft 5041	Compound is on the border of volatility for applicability of either of the two methods. Special precautions must be taken with either method. Validated for both methods.
Chlorobenzilate	0010	8270	Requires validation.
Chloroform	0030	5040, Draft 5041	Methodology validated.
Chloromethyl methyl ether	0030	5040, Draft 5041[a]	Compound is water-soluble; method 5040 methodology must be modified for optimum recovery.
Chloroprene	0030	5040, Draft 5041	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
o-Cresol	0010	8270	Method 8270 target compound.
m-Cresol	0010	8270	Method 8270 target compound.
p-Cresol	0010	8270	Method 8270 target compound.
Cresylic acid	0010	8270	Cresylic acid is a mixture of cresols, which are all target compounds for Method 8270.
Cumene	0010	8270	Requires validation; sufficiently volatile to be lost in extract concentration.
2,4-D salts and esters	0010	515/615	Requires validation.
DDE	0010	8270	Method 8270 target.
Diazomethane			Extremely explosive; reactive; existence in stacks and ambient air atmospheres questionable. Method development required.
Dibenzofurans	Method 23	Method 23	
1,2-Dibromo-3-chloropropane	0010	8270	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Dibutyl phthalate	0010	8270	Method 8270
1,4-Dichlorobenzene	0010	8270	Method 8270 target; may be lost in extract concentration.
3,3'-Dichlorobenzidene	0010	8270	Careful control of pH during extraction required for optimum recovery; chromatographs poorly. Validation required.
Dichloroethyl ether	0010	8270	Requires validation.
1,3-Dichloropropene	0030	5040/Draft 5041	Requires validation.
Dichlorvos	0010	8270	Requires validation.
Diethanolamine	0010	8270	Requires validation; chromatography may be very poor.
N,N-Diethylaniline	0010	8270	Requires validation; requires control of pH during extraction for optimum recovery.
Diethyl sulfate	0010	8270	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
3,3'-Dimethoxybenzidine	0010	8270	Requires validation; requires careful control of pH during extraction for optimum recovery. Chromatographs poorly.
Dimethylaminoazobenzene	0010	8270	Method 8270 target.
3,3'-Dimethylbenzidine	0010	8270	Requires validation; requires careful control of pH during extraction for optimum recovery. Chromatographs poorly.
Dimethyl carbamoyl chloride	0010	531	Requires validation; compound decomposes in water and is very reactive.
Dimethyl formamide	0010	8270	Requires validation.
1,1-Dimethylhydrazine	0030	5040/Draft 5041[a]	Compound unstable and water-soluble. Analysis of condensate suggested.
Dimethyl phthalate	0010	8270	Method 8270 target; common laboratory contaminant.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Dimethyl sulfate	0010	8270	Requires validation. Compound decomposes at 188°C.
4,6-Dinitro-o-cresol and salts	0010	8270, 515/615	Requires validation. Method 8270 applies to 4,6-Dinitro-o-cresol only. Compounds are very reactive.
2,4-Dinitrophenol	0010	8270	Method 8270 target.
2,4-Dinitrotoluene	0010	8270	Method 8270 target.
1,4-Dioxane	0010	8270	Method has been validated. Compound is sufficiently volatile to be lost in extract concentration.
1,2-Diphenylhydrazine	0010	8270	Method 8270 target.
Epichlorohydrin	0010	8270	Requires validation.
1,2-Epoxybutane	0030	5040/Draft 5041[a]	Requires validation. Reactive compound. Analysis of condensate suggested.
Ethyl Acrylate	0030	5040/Draft 5041[a]	Requires validation. Analysis of condensate suggested.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Ethylbenzene	0010	8270	Requires validation. Compound is sufficiently volatile to be lost in extract concentration.
Ethyl carbamate	0010	8270	Requires validation. Compound is very reactive and polymerizes readily.
Ethyl chloride	0030	5040/Draft 5041	Very volatile compound; special precautions required to avoid sorbent breakthrough.
Ethylene dibromide	0010	8270	Requires validation. Compound is sufficiently volatile to be lost in extract concentration.
Ethylene dichloride	0030	5040/Draft 5041	Requires validation.
Ethylene glycol	0010	8270	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Ethylene imine	0030	5040/Draft 5041[a]	Requires validation. Hydrocarbons will interfere with analysis. Compound is reactive and polymerizes easily. Compound will probably be present in the condensate in the sampling train.
Ethylene oxide	18 CARB 431	18 CARB 431	Compound is explosive and water-soluble.
Ethylene thiourea	0010	632	Requires validation.
Ethylidene dichloride	0030	5040/Draft 5041	Requires validation.
Formaldehyde	Draft 0011	Draft 8315	Requires validation.
Glycol ethers	0010	8270	Category too broad for a single method. Non-volatile or polar glycol ethers will require HPLC analysis.
Heptachlor	0010	8270	Method 8270 target.
Hexachlorobenzene	0010	8270	Method 8270 target.
Hexachlorobutadiene	0010	8270	Method 8270 target.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Hexachlorocyclopentadiene	0010	8270	Method 8270 target.
Hexachloroethane	0010	8270	Method 8270 target. Laboratory validation of the methodology.
Hexamethylene-1,6-diisocyanate	0010	8270	Compound is very reactive; reacts with water. Present in gas and particulate phases.
Hexamethylphosphoramide	0010	632	Requires validation; very reactive compound.
Hexane	0030	5040/Draft 5041	Requires validation.
Hydrazine	18	18	Compound is unstable, reactive, and water-soluble. Method development required.
Hydroquinone	0010	8270	Requires validation. Compound is very reactive and oxidizes readily.
Isophorone	0010	8270	Method 8270 target.
Lindane	0010	8270	Method 8270 target.
Maleic anhydride	0010	8270	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Methanol	18	18	Mass spectrometric analysis difficult because mass of methanol (32) is the same as the mass of oxygen. GC analysis preferred.
Methoxychlor	0010	8270	Method 8270 target.
Methyl bromide	0030	5040/Draft 5041	Special precautions are required to avoid sorbent breakthrough.
Methyl chloride	0030	5040/Draft 5041	Special precautions are required to avoid sorbent breakthrough.
Methyl chloroform	0030	5040/Draft 5041	Validated methodology.
Methyl ethyl ketone	Draft 0011	Draft 8315	Requires validation.
Methyl hydrazine	0030	5040/Draft 5041[a]	Requires validation; analysis of condensate required.
Methyl iodide	0030	5040/Draft 5041	Requires validation; decomposes at elevated temperatures.
Methyl isobutyl ketone	Draft 0011	Draft 8315	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Methyl isocyanate	0030	5040/Draft 5041[a]	Compound is polar, water-soluble, and reactive. May require development of a new method. Analysis of condensate suggested.
Methyl methacrylate	0030	5040/Draft 5041[a]	Requires validation. Compound may polymerize upon heating. Analysis of condensate suggested.
Methyl tert-butyl ether	0010	8270	Requires validation.
4,4'-Methylene bis (2-chloroaniline)	0010	8270	Requires validation.
Methylene chloride	0030	5040/Draft 5041	Methodology requires validation; common laboratory contaminant.
Methylene diphenyl diisocyanate	0010	8270	Requires validation.
4,4'-Methylenedianiline	0010	8270	Requires validation; compound is very reactive.
Naphthalene	0010	8270	Method 8270 target.
Nitrobenzene	0010	8270	Method 8270 target; methodology validated.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
4-Nitrobiphenyl	0010	8270	Requires validation; may decompose on heating.
4-Nitrophenol	0010	8270	Method 8270 target.
2-Nitropropane	0010	8270	Requires validation; compound is reactive and explosive, and may decompose upon heating.
N-Nitroso-N-methylurea	0010	8270	Requires validation. Compound is very reactive, and is near the limits of volatility for gas chromatography.
N-Nitrosodimethylamine	0010	8270	Method 8270 target; very reactive compound.
N-Nitrosomorpholine	0010	8270	Requires validation; compound is very reactive.
Parathion	0010	8270	Requires validation.
Pentachloronitrobenzene	0010	8270	Method 8270 target.
Pentachlorophenol	0010	8270	Method 8270 target.
Phenol	0010	8270	Method 8270 target; methodology validated.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
p-Phenylenediamine	0010	8270	Requires validation. Requires control of pH during extraction for optimum recovery.
Phosgene			No stationary source sampling/analytical methodology presently available.
Phthalic anhydride	0010	8270	Requires validation. Compound reacts with water.
Polychlorinated biphenyls	0010	680	Method 8080 not applicable to stack samples since Aroclor pattern will be disrupted.
1,3-Propane sultone	0010	8270	Requires validation.
beta-Propiolactone	0010	8270	Requires validation. Compound may decompose upon heating.
Propionaldehyde	Draft 0011	Draft 8315	Requires validation.
Propoxur	0010	8318	Requires validation. Compound is reactive and may decompose upon heating.
Propylene dichloride	0030	5040/Draft 5041	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Propylene oxide	0030	5040/Draft 5041[a]	Requires validation. Compound is reactive and water-soluble. Analysis of condensate suggested.
1,2-Propylenimine	0030	5040/Draft 5041[a]	Requires validation. Compound is reactive and may decompose when heated. Analysis of condensate suggested.
Quinoline	0010	8270	Requires validation. Control of pH during extraction required for optimum recovery.
Quinone	Draft 0011	Draft 8315	Requires validation.
Styrene	0010	8270	Requires validation. Compound is sufficiently volatile to be lost in extract concentration.
Styrene oxide	0010	8270	Requires validation. Compound is reactive.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	23	23	The spiking scheme for Method 23 may cause concern in some regulatory areas.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
1,1,2,2-Tetrachloroethane	0010	8270	Validated methodology.
Tetrachloroethylene	0030	5040/Draft 5041	Validated methodology.
Toluene	0030	5040/Draft 5041	Validated methodology.
	0010	8270	Validated methodology. Compound is sufficiently volatile to encounter losses in extract concentration.
2,4-Toluene diamine	0010	8270	Requires validation. Control of pH essential for optimum extraction recovery.
2,4-Toluene diisocyanate	0010	8270	Requires validation. Compound is very reactive.
o-Toluidine	0010	8270	Requires validation. Control of pH essential for optimum recovery during extraction.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Toxaphene	0010	8270	Method 8270 target. Toxaphene is a multicomponent group of chlorinated camphenes which may decompose upon heating.
1,2,4-Trichlorobenzene	0010	8270	Method 8270 target.
1,1,2-Trichloroethane	0030	5040/Draft 5041	Methodology validated.
Trichloroethylene	0030	5040/Draft 5041	Methodology validated.
2,4,5-Trichlorophenol	0010	8270	Methodology 8270 target.
2,4,6-Trichlorophenol	0010	8270	Method 8270 target.
Triethylamine	0030	5040/Draft 5041[a]	Requires validation. Compound is reactive and water-soluble.
Trifluralin	0010	8270	Requires validation. Compound is very reactive.
2,2,4-Trimethylpentane	0030	5040/Draft 5041	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Vinyl acetate	0030	5040/Draft 5041[a]	Requires validation. Compound is reactive, water-soluble, and polymerizes upon exposure to light. Analysis of condensate suggested.
Vinyl bromide	0030	5040/Draft 5041	Requires validation. Special precautions required in sampling to avoid sorbent breakthrough.
Vinyl chloride	0030	5040/Draft 5041	Methodology validated. Special precautions required in sampling to avoid sorbent breakthrough.
Vinylidene chloride	0030	5040/Draft 5041	Special precautions required in sampling to avoid sorbent breakthrough. Requires validation.
Xylenes (isomers and mixture)	0010	8270	Requires validation. Special care must be taken in extract concentration to avoid compound loss.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
o-Xylene	0010	8270	Requires validation. Special care must be taken in extract concentration to avoid compound loss.
m-Xylene	0010	8270	Requires validation. Special care must be taken in extract concentration to avoid compound loss.
p-Xylene	0010	8270	Requires validation. Special care must be taken in extract concentration to avoid compound loss.
Antimony compounds	Draft 0012	Draft 0012	Requires validation.
Arsenic compounds	Draft 0012	Draft 0012	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Asbestos	CARB 427	CARB 427	Methodology will not differentiate between asbestos and other mineral fibers. A fiber emission may have a wide range in particle size. Side-by-side measurements by visual observation, PCM, and TEM are required to characterize particle size in order to choose an appropriate analytical method.
Beryllium compounds	Draft 0012	Draft 0012	Requires validation.
Cadmium compounds	Draft 0012	Draft 0012	Requires validation.
Calcium cyanamide			Decomposes in cold water; reacts with acid; may polymerize in water/alkali. Method development required.
Chlorine	0050, 0051	9057	Choice between 0050 and 0051 determined by presence of water droplets.
Chromium compounds	Draft 0012	Draft 0012	Requires validation.
Cobalt compounds	Draft 0012	Draft 0012	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Coke oven emissions	0010	8310	Coke oven emissions constitute a complex family of compounds, not totally addressed by one methodology. Methodology listed addresses polynuclear aromatic hydrocarbons, a major constituent of coke oven emissions and may be modified to address functionalized compounds.
Cyanide compounds	6 (modified)	NIOSH 7904	Method 6 impinger solution modified to 0.1N KOH; analysis is performed for HCN and cyanide salts.
Hydrochloric acid	0050, 0051	9057	Choice between 0050 and 0051 determined by presence of water droplets.
Hydrogen fluoride	13 A or B	13 A or B	
Lead compounds	Draft 0012[b]	Draft 0012	Requires validation.
Manganese compounds	Draft 0012	Draft 0012	Requires validation.
Mercury compounds	Draft 0012	Draft 0012	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Mineral fibers	CARB 427[c]	CARB 427[c]	Methodology will not differentiate between mineral fibers and asbestos.
Nickel compounds	Draft 0012	Draft 0012	Requires validation.
Phosphine	Draft 0012	Draft 00112	Requires validation; methodology cannot differentiate among forms of phosphorus.
Phosphorus	Draft 0012	Draft 0012	Requires validation. Phosphorus is reactive and explosive, and undergoes spontaneous combustion upon contact with air.
Polycyclic organic matter	CARB 429	CARB 429	Complex group of compounds; not all adequately addressed by the methodology.
Radionuclides	114	114	Methodology will detect gaseous and particulate forms.
Selenium compounds	Draft 0012	Draft 0012	Requires validation.

Table 1

Continued

Chemical/Compound	Sampling	Analysis	Comments
Titanium tetrachloride	Draft 0012	Draft 0012	Requires validation. Methodology cannot differentiate forms of titanium. Compound decomposes at ambient moisture levels.

[a] Method 5040 or Draft 5041 modified to optimize recovery of water-soluble compounds (EPA 600/8-877-008).

[b] Draft Method 0012 does not speciate inorganic compounds.

[c] See Comments for Asbestos.

compound for Method 8270." For these target compounds, the precision and bias of an overall sampling and analytical methodology have not been established: the combined sampling and analytical methodology is not validated. However, the analytical methodology has at least been tested and operating parameters for the analysis have been established.

Table 1 is not comprehensive. Every available methodology which might possibly be applicable is not listed. A major consideration for the selection of methodology was the broadest possible coverage: a single-analyte method has been used as a primary method only in those situations where no multiple analyte method could be considered applicable.

Several methods in Table 1 are labeled "Draft." A Draft Method is in a review process prior to inclusion in a compendium of methods or promulgation in the Federal Register. For Draft EPA Methods, the text of the Method may be obtained through the Emission Measurements Technical Information Center (EMTIC), which can be reached by telephone at (919) 541-1059. The availability of a text of the Draft Methods is determined by the EPA laboratory responsible for the development of the Method. Some of the EPA laboratories are willing to release the text of a Draft Method as soon as the Method is written, while other EPA laboratories will release no Method until all of the review process is complete. If a Draft Method is available, the text can be obtained from EMTIC.

Some of the Methods listed in Table 1 are specifically written to address gaseous emissions from stationary sources. Other methods are written to address liquid or solid hazardous waste, soil, leachates, or water of various types. When a sorbent is used in the sampling methodology, the solution obtained from the extraction of the sorbent can be treated similarly to the extract of water or the extract of a hazardous waste or other media. Some adaptation of the sample preparation methodology will be required to address air as a sampling matrix and, in general, the adaptations or modifications required to make the analytical methodology directly

applicable to gaseous emissions as a sampling matrix have not been appended to the methodology. Some of the analytes listed in Table 1 explode at elevated temperatures or react with ambient levels of moisture. However, occurrence of such an analyte at levels of parts per million in a stationary source may mean that a significant portion of that analyte may survive intact to be sampled and analyzed. Appropriate laboratory and field experiments are required to establish the loss or survival of certain analytes under the conditions encountered at a stationary source.

When a Table 1 method is described as "Validated," precision and bias for the sampling and analysis of that analyte have been established for a single stationary source.

2.1 Alternative Methods

Table 2 provides a listing of alternative sampling and analytical methods. These methods are a secondary choice to the methods shown in Table 1 as the primary methods. In many cases, the methodology cited as Alternative Methodology is a more specific or more focused methodology than the methodology listed in Table 1, even though the method may be validated. Broad applicability for screening was the main criterion in the selection of primary methodology. For example, Method 18 is cited frequently as an alternative method for volatile organic compounds. Method 18 is used for single analytes or, perhaps, for a small number of analytes. Method 0030 combined with Method 5040 or Draft Method 5041 would have a broader application to a wide range of analytes (all volatile organic compounds with a boiling point less than 100°C), and would therefore be the choice as the primary method. In some instances, it is

Table 2

Alternative Sampling and Analytical Methodology

Compound/Chemical	Sampling	Analysis	Comments
Acetaldehyde	0030	5040, Draft 5041[a]	Requires modification of analytical conditions. Analysis of condensate suggested.
Acetophenone	Draft 0011	Draft 8315	Requires validation.
Acrolein	18	18	
Allyl chloride	18	18	
Biphenyl	0010	8310	
Bromoform	0030	5040, Draft 5041	Non-quantitative; boiling point outside directly applicable range of methodology.
Carbon disulfide	15	15	Compound may decompose upon standing.
Carbonyl sulfide	0030	5040, Draft 5041	Non-quantitative methodology; boiling point outside directly applicable range of methodology. Analysis of condensate suggested.
2-Chloroacetophenone	Draft 0011	Draft 8315	Requires validation.
Chloroform	18	18	
Chloromethyl methyl ether	18	18	

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Chloroprene	18	18	
2,4-D salts and esters	0010	8270	Applies to esters only.
1,4-Dichlorobenzene	0030	5040, Draft 5041	Qualitative only; boiling point outside directly applicable range of methodology.
1,3-Dichloropropene	18	18	
1,1-Dimethylhydrazine	18	18	
1,4-Dioxane	0030 18	5040, Draft 5041[a] 18	Analysis of VOST condensate suggested.
1,2-Epoxybutane	18	18	
Ethyl acrylate	18	18	
Ethylbenzene	0030	5040, Draft 5041	Qualitative only; boiling point outside directly applicable range of methodology.
Ethyl chloride	18	18	
Ethylene dibromide	0030	5040, Draft 5041	Qualitative only; boiling point outside directly applicable range of methodology.
Ethylene dichloride	18	18	

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Ethylene imine	18	18	
Ethylene oxide	18	18	
Ethylidene dichloride	18	18	
Formaldehyde	18	18	
Glycol ethers	0010	632	Some members of the class may require HPLC analytical method because of low volatility.
Hexane	18	18	
Hydroquinone	Draft 0011	Draft 8315	
Isophorone	Draft 0011	Draft 8315	
Methyl bromide	18	18	
Methyl chloride	18	18	
Methyl ethyl ketone	0030	5040, Draft 5041[a]	Analysis of condensate suggested.
Methyl hydrazine	18	18	
Methyl iodide	18	18	
Methyl isocyanate	18	18	
Methyl methacrylate	18	18	
Methyl tert-butyl ether	18	18	
Methylene chloride	18	18	

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Methylene diphenyl diisocyanate	0010	632	HPLC analysis may be required.
Naphthalene	0010	8310	
4-Nitrobiphenyl	0010	8310	
N-Nitroso-N-methylurea	0010	632	HPLC analysis may be required.
N-Nitrosomorpholine	0010	632	HPLC analysis may be required.
Polychlorinated biphenyls	0010	8270	Detection limits much poorer than primary method.
Propionaldehyde	18	18	
Propylene dichloride	18	18	
Propylene oxide	18	18	
1,2-Propyleneimine	18	18	
Quinone	0010	8270	

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Styrene	0030	5040, Draft 5041	Qualitative only; boiling point outside directly applicable range of methodology. Also, styrene is a common decomposition product of Tenax®; blanks may be a problem.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	0010	8280, Draft 8290	
Tetrachloroethylene	0010	8270	Compound is sufficiently volatile to be lost in an extract concentration step.
2,4-Toluenediamine	0010	632	HPLC analysis may be required.
2,4-Toluene diisocyanate	0010	632	HPLC analysis may be required.
1,1,2-Trichloroethane	0010	8270	Compound is sufficiently volatile to be lost in an extract concentration step.
2,2,4-Trimethylpentane	18	18	
Vinyl acetate	18	18	

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Vinyl bromide	18	18	
Vinyl chloride	18 106	18 106	
Vinylidene chloride	18	18	
Xylenes (isomers and mixture)	0030	5040, Draft 5041	Qualitative only; boiling point outside the directly applicable range of the methodology.
o-Xylene	0030	5040, Draft 5041	Qualitative only; boiling point outside the directly applicable range of the methodology.
m-Xylene	0030	5040, Draft 5041	Qualitative only; boiling point outside the directly applicable range of the methodology.
p-Xylene	0030	5040, Draft 5041	Qualitative only; boiling point outside the directly applicable range of the methodology.

Table 2

Continued

Compound/Chemical	Sampling	Analysis	Comments
Asbestos	NIOSH 7400	NIOSH 7400	Methodology not directly applicable to stationary sources. Methodology cannot differentiate between asbestos and other mineral fibers.
Arsenic compounds	18	18	Some of the compounds in this category are sufficiently volatile for application of Method 18.
Chlorine	18	18	
Cyanide compounds	9010,9012	9010,9012	
Mineral fibers	NIOSH 7400	NIOSH 7400	Method cannot differentiate between asbestos and other mineral fibers.
Phosphine	18	18	
Lead compounds	12	12	Validated method.
Beryllium compounds	103, 104	103, 104	Validated method.
Mercury compounds	101, 101A, 102	101, 101A, 102	Validated method.

Table 2

Continued

[a] Method 5040 or Draft 5041 modified to optimize recovery of water-soluble compounds (EPA-600/8-87-008).

[b] See Comments, Table 1.

possible to perform quantitative sampling and analysis of a particular analyte with a certain methodology. However, this same analyte may also be observed when a different methodology is applied, although not quantitatively analyzed. There may be circumstances in which the qualitative information still has value: recognizing that the data are not quantitative, the user can still obtain some indication of the presence or absence of a given analyte.

The alternative methodology is not necessarily validated, since complete validation of a multi-analyte sampling and analytical methodology would cause the methodology to be selected as a primary methodology. Method 18, for example, is a methodology which has been published in the Federal Register. However, the applicability of this methodology to many Clean Air Act analytes must be established.

2.2 Stationary Source non-Point Emissions

The vast majority of the Methods listed in Tables 1 and 2 are directly applicable to stacks. However, a stationary source is any emission source which does not move. There can be stationary sources which are not stacks, such as vents or ducts. In the sampling and analysis of non-stack stationary sources, the primary methodologies listed in Table 1 can frequently be applied. However, methods developed for the sampling and analysis of ambient air samples may also be applicable with some adaptation or modification. If ambient methodology is applied, appropriate precautions must be taken to ensure that the capacity of the methodology is not exceeded so that results will be quantitative. Table 3 summarizes the methods developed for ambient air sampling which would be applicable to a non-stack stationary source. Care must be taken with all of these methods to avoid saturation: typical ambient concentration levels are low ppbv, whereas some stationary sources can have concentrations at ppmv levels. Ambient methods which require the use of sorbents (see Section 3.0) are susceptible to saturation of the sorbent if

concentration levels are high. If the capacity of the sorbent is saturated, breakthrough will occur and quantitative sampling/analysis cannot be performed.

2.3 Making Use of Collected Information

There are many options for using the information compiled in this report. The two major methodologies in performing stationary source testing for organic compounds are the Volatile Organic Sampling Train (VOST) which is a combination of SW-846 Method 0030 for sampling and SW-846 Method 5040 or SW-846 Draft Method 5041 for analysis and the SemiVolatile Organic Sampling Train (SemiVOST), which is a combination of SW-846 Method 0010 for sampling and SW-846 Method 8270 for analysis. The methods divide according to boiling point: a volatile organic compound for the VOST is any compound with a boiling point less than 100°C, while a semivolatile organic compound for the SemiVOST is any organic compound with a boiling point above 100°C. The Multiple Metals Sampling Train (SW-846 Draft Method 0012) is the methodology most commonly used for sampling and analyzing metals and inorganic compounds. Appendix A can be used as a pathway to an initial decision tree, below.

Table 3

Sampling and Analytical Methodology for Stationary Source non-Point Emissions

Compound/Chemical	Sampling and Analysis	Comments
Acetaldehyde	TO-5 TO-11	
Acetamide	TO-13	Modified to use GC/MS.
Acetonitrile	TO-14	
Acetophenone	TO-5 TO-13	Modified to use GC/MS.
2-Acetylaminofluorene	TO-13	Modified to use GC/MS or HPLC.
Acrolein	TO-5 TO-11	
Acrylamide	TO-13	Modified to use GC/MS.
Acrylic acid	TO-13	Modified to use GC/MS; analysis optimized with derivatization.
Acrylonitrile	TO-1 TO-14	
Allyl chloride	TO-1 TO-2 TO-14	
4-Aminobiphenyl	TO-13	Modified to use GC/MS or HPLC.
Aniline	TO-13	Modified to use GC/MS.
o-Anisidine	TO-13	Modified to use GC/MS.
Benzene	TO-1 TO-2 TO-14	

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Benzidine	TO-13	Modified to use GC/MS or HPLC.
Benzotrichloride	TO-1 TO-13	Modified to use GC/MS.
Benzyl chloride	TO-1 TO-13	Modified to use GC/MS.
Biphenyl	TO-13	Modified to use GC/MS.
Bis (2-Ethylhexyl) phthalate	TO-13	Modified to use GC/MS; recovery is optimized with acid extraction.
Bis (chloromethyl) ether	TO-1 TO-14	
Bromoform	TO-1 TO-14	
1,3-Butadiene	TO-1 TO-2 TO-14	
Caprolactam	TO-13	Modified to use GC/MS or HPLC.
Captan	TO-4 TO-10	
Carbaryl	TO-13	Modified to use HPLC.
Carbon disulfide	TO-1	Compound may decompose upon standing.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Carbon tetrachloride	TO-1 TO-2 TO-14	
Carbonyl sulfide	TO-1 TO-14	
Catechol	TO-13	Modified to use GC/MS.
Chloramben	TO-13	Modified to use HPLC.
Chlordane	TO-4 TO-10	
Chloroacetic acid	TO-13	Modified to use GC/MS; compound requires derivatization for analysis.
2-Chloroacetophenone	TO-5 TO-11 TO-13	Modified to use GC/MS.
Chlorobenzene	TO-1 TO-14	
Chlorobenzilate	TO-13	Modified to use GC/MS.
Chloroform	TO-1 TO-2 TO-14	
Chloromethyl methyl ether	TO-1 TO-14	
Chloroprene	TO-1 TO-14	

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
o-Cresol	TO-8 TO-13	Modified to use GC/MS.
m-Cresol	TO-8 TO-13	Modified to use GC/MS.
p-Cresol	TO-8 TO-13	Modified to use GC/MS.
Cresylic acid	TO-8 TO-13	Modified to use GC/MS.
Cumene	TO-1 TO-13 TO-14	Modified to use GC/MS.
2,4-D salts and esters	TO-10	
DDE	TO-4 TO-10	
Diazomethane	NIOSH 2515	
Dibenzofurans	TO-9	
1,2-Dibromo-3-chloropropane	TO-13	Modified to use GC/MS.
Dibutyl phthalate	TO-13	Modified to use GC/MS.
1,4-Dichlorobenzene	TO-1 TO-13 TO-14	Modified to use GC/MS.
3,3'-Dichlorobenzidine	TO-13	Modified to use HPLC or GC/MS.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Dichloroethyl ether	TO-13	Modified to use GC/MS.
1,3-Dichloropropane	TO-1 TO-14	
Dichlorvos	TO-13	Modified to use GC/MS.
Diethanolamine	TO-13	Modified to use GC/MS or HPLC.
N,N-Diethylaniline	TO-13	Modified to use GC/MS.
Diethyl sulfate	TO-13	Modified to use GC/MS.
3,3'-Dimethoxybenzidine	TO-13	Modified to use GC/MS or HPLC.
Dimethylaminoazobenzene	TO-13	Modified to use GC/MS.
3,3'-Dimethylbenzidine	TO-13	Modified to use GC/MS or HPLC.
Dimethyl carbamoyl chloride	TO-13	Modified to use HPLC.
Dimethyl formamide	TO-13	Modified to use GC/MS or HPLC.
1,1-Dimethylhydrazine	TO-1 TO-14	Compound is unstable.
Dimethyl phthalate	TO-13	Modified to use GC/MS.
Dimethyl sulfate	TO-13	Modified to use GC/MS.
4,6-Dinitro-o-cresol and salts	TO-13	Modified to use HPLC.
2,4-Dinitrophenol	TO-13	Modified to use GC/MS.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
2,4-Dinitrotoluene	TO-13	Modified to use GC/MS.
1,4-Dioxane	TO-1 TO-14	
1,2-Diphenylhydrazine	TO-13	Modified to use GC/MS or HPLC.
Epichlorohydrin	TO-13	Modified to use GC/MS or HPLC.
1,2-Epoxybutane	TO-1 TO-14	
Ethyl acrylate	TO-1 TO-14	Compound is very reactive and polymerizes easily.
Ethylbenzene	TO-1 TO-14	
Ethyl carbamate	TO-13	Modified to use HPLC.
Ethyl chloride	TO-1 TO-2 TO-14	
Ethylene dibromide	TO-1 TO-13 TO-14	Modified to use GC/MS.
Ethylene dichloride	TO-1 TO-2 TO-14	
Ethylene Glycol	TO-13	Modified to use GC/MS or HPLC.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Ethylene imine	TO-1 TO-14	
Ethylene oxide	TO-14	
Ethylene thiourea	TO-13	Modified to use HPLC.
Ethylidene dichloride	TO-1 TO-14	
Formaldehyde	TO-5 TO-11	
Glycol ethers	TO-13	Modified to use GC/MS or HPLC.
Heptachlor	TO-4 TO-10	
Hexachlorobenzene	TO-13	Modified to use GC/MS.
Hexachlorobutadiene	TO-1 TO-13 TO-14	Modified to use GC/MS. May not be quantitative.
Hexachlorocyclopentadiene	TO-13	Modified to use GC/MS.
Hexachloroethane	TO-1 TO-13 TO-14	Modified to use GC/MS.
Hexamethylene-1,6-diisocyanate	TO-13	Modified to use GC/MS or HPLC.
Hexamethylphosphoramide	TO-13	Modified to use GC/MS or HPLC.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Hexane	TO-1 TO-14	
Hydrazine	18	
Hydroquinone	TO-13	Modified to use GC/MS or HPLC.
Isophorone	TO-5 TO-11 TO-13	Modified to use GC/MS.
Lindane	TO-4 TO-10	
Maleic anhydride	TO-13	Modified to use GC/MS or HPLC.
Methanol	TO-14	GC/MD.
Methoxychlor	TO-4 TO-10 TO-13	Modified to use GC/MS or HPLC.
Methyl bromide	TO-1 TO-2 TO-14	Breakthrough problem.
Methyl chloride	TO-1 TO-2 TO-14	Breakthrough problem.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Methyl chloroform	TO-1 TO-2 TO-14	
Methyl ethyl ketone	TO-1 TO-5 TO-11 TO-14	
Methyl hydrazine	TO-1 TO-14	
Methyl iodide	TO-1 TO-14	
Methyl isobutyl ketone	TO-1 TO-5 TO-11 TO-14	
Methyl isocyanate	TO-1 TO-14	
Methyl methacrylate	TO-1 TO-14	
Methyl tert-butyl ketone	TO-1 TO-5 TO-11 TO-14	
4,4'-Methylene bis (2-chloroaniline)	TO-13	Modified to use GC/MS or HPLC.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Methylene chloride	TO-1 TO-2 TO-14	
Methyl diphenyl diisocyanate	TO-13	Modified to use GC/MS or HPLC.
4,4'-Methylene dianiline	TO-13	Modified to use GC/MS or HPLC.
Naphthalene	TO-13	Modified to use GC/MS or HPLC.
Nitrobenzene	TO-1 TO-14	
4-Nitrobiphenyl	TO-13	Modified to use GC/MS or HPLC.
4-Nitrophenol	TO-13	Modified to use GC/MS.
2-Nitropropane	TO-1 TO-13 TO-14	Modified to use GC/MS.
N-Nitroso-N-methylurea	TO-13	Modified to use GC/MS or HPLC.
N-Nitrosodimethylaniline	TO-1 TO-7 TO-13	Very reactive. Modified to use GC/MS or HPLC.
N-Nitrosomorpholine	TO-7 TO-13	Modified to use GC/MS or HPLC.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Parathion	TO-4 TO-10	
Pentachloronitrobenzene	TO-13	Modified to use GC/MS or HPLC.
Pentachlorophenol	TO-13	Modified to use GC/MS or HPLC.
Phenol	TO-13	Modified to use GC/MS.
p-Phenylenediamine	TO-13	Modified to use GC/MS or HPLC.
Phosgene	TO-6	
Phthalic anhydride	TO-13	Modified to use GC/MS.
Polychlorinated biphenyls	TO-13 with 680 or 8080	
1,3-Propane sultone	TO-13	Modified to use GC/MS.
beta-Propiolactone	TO-13	Modified to use GC/MS.
Propionaldehyde	TO-5 TO-11	
Propoxur	TO-13	Modified to use HPLC.
Propylene dichloride	TO-1 TO-14	
Propylene oxide	TO-1 TO-14	
1,2-Propyleneimine	TO-1 TO-14	

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Quinoline	TO-13	Modified to use GC/MS.
Quinone	TO-5 TO-11	
Styrene	TO-1 TO-14	
Styrene oxide	TO-13	Modified to use GC/MS.
2,3,7,8-Tetrachlorodibenzo-p-dioxin	TO-9	
1,1,2,2-Tetrachloroethane	TO-1 TO-14	
Tetrachloroethylene	TO-1 TO-14	
Toluene	TO-1 TO-2 TO-14	
2,4-Toluene diamine	TO-13	Modified to use GC/MS or HPLC.
2,4-Toluene diisocyanate	TO-13	Modified to use GC/MS or HPLC.
o-Toluidine	TO-13	Modified to use GC/MS or HPLC.
Toxaphene	TO-4 TO-10	

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
1,2,4-Trichlorobenzene	TO-1 TO-13	Modified to use GC/MS.
1,1,2-Trichloroethane	TO-1 TO-14	
Trichloroethylene	TO-1 TO-2 TO-14	
2,4,5-Trichlorophenol	TO-13	Modified to use GC/MS.
2,4,6-Trichlorophenol	TO-13	Modified to use GC/MS.
Triethylamine	TO-13	Modified to use GC/MS or HPLC.
Trifluralin	TO-4 TO-10	
2,2,4-Trimethylpentane	TO-1 TO-14	
Vinyl acetate	TO-1 TO-14	
Vinyl bromide	TO-1 TO-2 TO-14	Breakthrough may be a problem.
Vinyl chloride	TO-1 TO-2 TO-14	Breakthrough may be a problem.

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Xylenes (isomers and mixture)	TO-1 TO-14	
o-Xylene	TO-1 TO-14	
m-Xylene	TO-1 TO-14	
p-Xylene	TO-1 TO-14	
Antimony compounds	Draft 0012	
Asbestos	CARB 427 NIOSH 7400	
Arsenic compounds	Draft 0012	
Beryllium compounds	Draft 0012	
Cadmium compounds	Draft 0012	
Calcium cyanamide		
Chlorine	OSHA ID-101	
Chromium compounds	Draft 0012	
Cobalt compounds	Draft 0012	
Coke oven emissions	109	For visible emissions.
Cyanide compounds	NIOSH 7904/9010, 9012	Impinger solution modified to dilute (0.1 N) KOH

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Hydrochloric acid	18 26	
Hydrogen Fluoride	14 18	
Lead compounds	Draft 0012	
Manganese compounds	Draft 0012	
Mercury compounds	Draft 0012	
Mineral fibers	CARB 427	Does not differentiate between mineral fibers and asbestos.
	NIOSH 7400	
Nickel compounds	Draft 0012	
Phosphine	Draft 0012 18	
Phosphorus	Draft 0012	
Polycyclic organic matter	TO-13	Modified to use GC/MS or HPLC.
Radionuclides	0020/EPA Docket No. A-79-11	Method will detect gaseous and particulate forms.
Selenium compounds	Draft 0012	

Table 3

Continued

Compound/Chemical	Sampling and Analysis	Comments
Titanium tetrachloride	Draft 0012 13A or B	Method measures total titanium, not species; compound decomposes at ambient moisture levels.

Information presented in Table 1 will give information on the tentative assignment of the volatile, semivolatile, or inorganic analyte to a combined sampling/analytical methodology. With the summary information presented in Table 1, the sampling and analytical methodology can be examined to determine the range of applicability of the methods and any difficulties which might be expected with the analyte in using the tentatively assigned methodology. Other decision trees will be possible on the basis of information from Table 1 and from the discussions of the sampling and analytical methods (see Figure 1 and Figure 2). The Figures provide only a general guideline, however, and several checks must be made to be sure that the methodology will be applicable. After a tentative methodology is identified, Section 3.0, which contains a summary of the method, with a description of the analytes from the Clean Air Act Amendments to which the methodology ought to be applicable, must be checked to be sure that the tentative method is appropriate. With such a broad range of analytes, many methods must be modified or adapted for reasonable results. For example, a polar water-soluble organic compound with boiling point less than 100°C requires adaptation of Method 5040 or Draft Method 5041 for any hope of successful analysis.

2.4 Validation of Proposed Methodology

Methodology without validation data can be used only for screening purposes. Validated methodology should be used, whenever possible, to generate data to determine regulatory compliance. Table 1 identifies many analytes which require validation of the sampling and analytical methodology. Some analytes indicate that they are a "target compound" for SW-846 Method 8270. A "target compound" for Method 8270 is an organic compound for which the analytical methodology has been validated: that is, the precision and bias of the analytical methodology have been established in an interlaboratory study. However, validation of the analytical methodology determines

only that if the compound is introduced to the analytical instrument, a successful analysis can be performed. Successful analysis does not mean or even imply that successful sampling can be performed; the successful functioning of the field sampling methodology must be demonstrated and documented.

If a validated method is required for a given analyte, a source owner or operator must validate a proposed methodology to generate data which will meet EPA requirements. A procedure for performing this validation is available from EPA ("Protocol for the Field Validation of Emission Concentrations from Stationary Sources," Method 301). This protocol states that if EPA currently recognizes an appropriate test method or considers a proposed test method to be satisfactory for a particular source, the Administrator may waive the use of the validation protocol or may specify a less rigorous validation procedure. The list of validated methods from the Federal Register includes Methods 1 through 28A. Where these methods are applicable to analytes from the Clean Air Act Amendments, they are usually applicable to only a single analyte or, at most, a small group of analytes. Since the goal of this program was to make the sampling and analytical methodology as broad as possible, these validated methods are not used extensively in Table 1. As a general observation, the sampling and analytical methodology cited in Table 1 does not, except for a few analytes, have a known precision and bias for a given analyte at a particular type of source. The need for validation of the proposed methodology, or the availability of partial validation information, is indicated in Table 1.

Bias is any systematic positive or negative difference between the measured value and the true value of a sample. Bias is established by comparing the results obtained from the application of the method against a reference value. Precision is the variability in the data obtained from the entire measurement system (both sampling and analysis) as determined from collocated sampling trains. At least two paired sampling trains must be used in order to establish precision. Standards for an acceptable level of bias and precision are given in the Validation Protocol, and exact

procedures for determination of bias and precision and calculating the values are presented. Bias and precision can also be determined when an alternative method to a validated method is being proposed. In general, spiking of the analyte in the field must be performed (an isotopically-labeled analyte may be used if gas chromatography/mass spectrometry is the ultimate analytical method), and replicate samples must be taken and analyzed. The field validation must incorporate:

- Summary of appropriate precision and bias calculations;
- Certification for the reference material(s) used and the value(s);
- Results from a performance audit, if performed, or an explanation of the inability to perform an audit;
- Results of the laboratory demonstration of the quality of the spiking system;
- A discussion of the laboratory evaluations;
- A discussion of the field sampling;
- A discussion of sample preparation and analysis;
- A report of the storage times of samples and/or extracts; and
- A discussion of the reasons for the elimination of any results.

There are many conditions under which a waiver from the Validation Protocol may be obtained. These conditions and the procedure for application for a waiver are described in the Validation Protocol.

2.5 Quality Assurance/Quality Control (QA/QC) Procedures

If appropriate Quality Assurance and Quality Control procedures are followed in the determination of emissions from stationary sources, the level of precision and accuracy will be documented, and acceptance limits for the precision and accuracy will be defined. If appropriate Quality Control information is included as part of the final data report, the process of reviewing the results will be straightforward and effective. The general format and required topics in a Quality Assurance Project Plan are presented in "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" (EPA QAMS-005/80, December 29, 1980). The points which must be addressed in the Quality Assurance Project Plan relative to the generation of data include:

- Quality Assurance objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability;

  Completeness is the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under optimal normal conditions.

  Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition.

  Comparability expresses the confidence with which one data set can be compared to another.

- Sampling procedures;

- Sample custody;

- Calibration procedures and frequency (for both laboratory and field operations);

- Analytical procedures;

  Modifications of standard methods must be identified, with reasons for the changes.

- Data reduction, validation, and reporting;
- Internal quality control checks and frequency;
- Performance and systems audits and frequency;
- Preventive maintenance procedures and schedules;
- Specific routine procedures to be used in the assessment of data precision, accuracy, and completeness of specific measurement parameters; and
- Corrective action to be taken in case problems are encountered at any stage of the sampling, analytical, or reporting procedures.

In general, Quality Control procedures for sampling and analysis of volatile organic compounds (boiling point <100°C) must consider the following elements:

- Results for blanks;
- Calibration of the analytical system(s);
- Performance of the sampling/analytical method at the level of 99.99% Destruction and Removal Efficiency;

Establish prior to taking samples that the analytical methodology is capable of sufficient sensitivity to detect and quantify the analyte at the expected concentration level which will be encountered for the stationary source.

- Determination of accuracy and precision;

Replicate spiking studies at the expected concentration level for the analyte must be performed to demonstrate the reproducibility and accuracy of the methodology.

- Assessment of method accuracy using calibration check standards and surrogate compounds;

- Breakthrough ratios of analytes on sorbent, if sorbents are used; and

  Sampling is not quantitative if the capacity of the sorbent exceeded.

- Determination of detection limits.

Quality control procedures for sampling and analysis of semivolatile organic compounds (boiling points >100°C) must consider the following elements:

- Demonstration of method performance at the 99.99% Destruction and Removal Efficiency level;
- Calibration of the analytical system;
- Assessment of method accuracy using calibration check standards, surrogate compounds, and spiked samples;
- Determination of method precision by analysis of replicate samples;
- Determination of the detection limit for the analytical methodology; and
- Analysis of appropriate laboratory and field blanks.

The following quality control elements must be considered in metals sampling and analysis:

- Definition of the need for analysis of metals, the definition of metal analytes of interest, and the concentration limits for regulatory purposes;
- Determination of the accuracy of the analytical procedures by use of calibration check samples, reference materials, and spiked samples;
- Assessment of method precision by preparation and analysis of replicate samples; and
- Determination of the method detection limit for a given matrix.

Sampling and analytical procedures presently available do not speciate inorganic compounds. Development of methodology is required for speciation of inorganic compounds. In addition, for each analytical method, there are specific quality control procedures which address the identification of analytes and performance of correct quantitative calculations to determine the concentration of the analytes in samples which have been taken in the field at a stationary source.