

SECTION 3.0  
DESCRIPTIONS OF METHODS

This section contains a short description of each of the methods listed in Table 1. Each description includes:

- The scope and application of the methodology;
- A short summary of the method;
- Interferences, including matrix problems, if any are known;
- Method target compounds: i.e., all compounds for which the methodology is validated; and
- Applicable CAA Amendments Pollutants: i.e., hazardous air pollutants listed in the CAA Amendments to which the methodology may be applied.



## EPA METHOD 0010

### Modified Method 5 Sampling Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 0010 is used to determine the Destruction and Removal Efficiency (DRE) of semivolatile principal organic hazardous constituents (POHCs) from incineration systems. This method may also be used to determine particulate emission rates from stationary sources, as per EPA Method 5 (see the Reference Table included in the description of Method 0010 in SW-846). Method 0010 has been applied to semivolatile compounds, including polychlorinated biphenyls (PCBs), chlorinated dibenzodioxins and dibenzofurans, polycyclic organic matter, and other semivolatile organic compounds.

#### 2.0 SUMMARY OF METHOD

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin (typically XAD-2® or polyurethane foam for PCBs). The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species (compounds with a boiling point above 100°C). Comprehensive chemical analyses, using a variety of applicable analytical methodologies, are conducted to determine the identity and concentration of the organic materials.

### 3.0 INTERFERENCES

Oxides of nitrogen ( $\text{NO}_x$ ) are possible interferents in the determination of certain water-soluble compounds such as 1,4-dioxane, phenol, and urethane. Reaction of these compounds with  $\text{NO}_x$  in the presence of moisture will reduce their concentration. Other chemical reactions are possible, since  $\text{SO}_2$ ,  $\text{O}_3$ , and other reactive species may be present in the emissions. Other problems that could produce a positive or a negative bias, depending upon the compounds of interest, are:

- Stability of the compound of interest in methylene chloride, since at least one of the common analytical methods relies upon methylene chloride extraction of the sorbent media from the sampling train;
- Formation of water-soluble organic salts on the resin in the presence of moisture (compounds that form water-soluble salts can be recovered by appropriate control of pH during the extraction process); and
- Solvent-extraction efficiency of water-soluble compounds from aqueous media.

When gas chromatography/mass spectrometry is used as the analytical technique, compounds that coelute chromatographically can frequently be deconvoluted if their mass spectra are different. Using two or more ions per compound in quantitative analysis can overcome interference at one mass; however, if the concentration of the compound of interest is sufficient to saturate the detector at a given mass, an alternative mass MAY NOT be selected. In this case, the extract must be diluted to bring the concentration of the compound of interest into the calibration range in order to obtain accurate quantitative analysis.

#### 4.0 METHOD TARGET COMPOUNDS

Method 0010 is an extremely powerful and versatile methodology. A single analytical methodology cannot simultaneously address all semivolatile compounds for which Method 0010 might serve as a sampling methodology. Appropriate target compounds are listed under the pertinent analytical methodology in Table 1. Method detection limits are a function of volume sampled, and the volume that is sampled will also vary according to the analyte.

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acetamide (Method 8270)\*  
acetophenone (Method 8270; 8270 target)  
2-acetylaminofluorene (Method 8270)  
acrylamide (Method 8270)  
acrylic acid (Method 8270 with derivatization)  
4-aminobiphenyl (Method 8270; 8270 target)  
aniline (Method 8270; 8270 target)  
o-anisidine (Method 8270)  
benzidine (Method 8270; 8270 target)  
benzotrichloride (Method 8270)  
benzyl chloride (Method 8270)  
biphenyl (Method 8270; also Method 8310)  
bis (2-ethylhexyl) phthalate (Method 8270; 8270 target)  
bromoform (Method 8270)  
caprolactam (Method 632)  
captan (Method 8270)  
carbaryl (Method 632)  
catechol (Method 8270)  
chloramben (Method 515/615)

chlordan (Method 8270; 8270 target)

chloroacetic acid (Method 8270 with derivatization)

2-chloroacetophenone (Method 8270)

chlorobenzene (Method 8270)

chlorobenzilate (Method 8270)

o-cresol (Method 8270; 8270 target)

m-cresol (Method 8270)

o-cresol (Method 8270; 8270 target)

cresylic acid (mixture of cresol isomers; Method 8270)

cumene (Method 8270)

2,4-D salts and esters (2,4-D, Method 8270; 8270 target; salts and esters, Method 515/615)

DDE (Method 8270; 8270 target)

dibenzofurans (Method 8280, Method 8290)

1,2-dibromo-3-chloropropane (Method 8270)

dibutyl phthalate (Method 8270; 8270 target)

1,4-dichlorobenzene (Method 8270; 8270 target)

3,3'-dichlorobenzidine (Method 8270; 8270 target)

dichloroethyl ether (Method 8270)

1,3-dichloropropene (Method 8270)

dichlorvos (Method 8270)

diethanolamine (Method 8270, possibly Method 632)

N,N-diethylaniline (Method 8270)

diethyl sulfate (Method 8270)

3,3'-dimethoxybenzidine (Method 8270)

dimethylaminoazobenzene (Method 8270; 8270 target)

3,3'-dimethylbenzidine (Method 8270)

dimethyl carbamoyl chloride (Method 531)

dimethyl formamide (Method 8270)

dimethyl phthalate (Method 8270; 8270 target)

dimethyl sulfate (Method 8270)

4,6-dinitro-o-cresol and salts (Method 8270 for 4,6-dinitro-o-cresol;  
Method 515/615 for 4,6-dinitro-o-cresol and salts)

2,4-dinitrophenol (Method 8270; 8270 target)

2,4-dinitrotoluene (Method 8270; Method 8270 target)

1,4-dioxane (Method 8270)

1,2-diphenylhydrazine (Method 8270; 8270 target)

epichlorohydrin (Method 8270)

ethylbenzene (Method 8270)

ethyl carbamate (Method 632)

ethylene dibromide (Method 8270)

ethylene glycol (Method 8270)

ethylene thiourea (Method 632)

glycol ethers (Method 8270)

heptachlor (Method 8270; 8270 target)

hexachlorobenzene (Method 8270; 8270 target)

hexachlorobutadiene (Method 8270; 8270 target)

hexachlorocyclopentadiene (Method 8270; 8270 target)

hexachloroethane (Method 8270; 8270 target)

hexamethylene-1,6-diisocyanate (Method 8270)

hexamethylphosphoramide (Method 632)

hydroquinone (Method 8270)

isophorone (Method 8270; 8270 target)

lindane (Method 8270)

maleic anhydride (Method 8270)

methoxychlor (Method 8270; 8270 target)

methyl isobutyl ketone (Method 8270)

4,4'-methylene bis(2-chloroaniline) (Method 8270)

methylene diphenyl isocyanate (Method 8270 or Method 632)  
4,4'-methylenedianiline (Method 8270)  
naphthalene (Method 8270; 8270 target; also Method 8310)  
nitrobenzene (Method 8270; 8270 target)  
4-nitrobiphenyl (Method 8270; also Method 8310)  
4-nitrophenol (Method 8270; 8270 target)  
2-nitropropane (Method 8270)  
N-nitroso-N-methylurea (Method 8270, possibly Method 632)  
N-nitrosodimethylamine (Method 8270; 8270 target)  
N-nitrosomorpholine (Method 8270, possibly Method 632)  
parathion (Method 8270)  
pentachloronitrobenzene (Method 8270; 8270 target)  
pentachlorophenol (Method 8270; 8270 target)  
phenol (Method 8270; 8270 target)  
p-phenylenediamine (Method 8270)  
phthalic anhydride (Method 8270)  
polychlorinated biphenyls (Method 8270 with very high detection limits;  
Method 680)  
1,3-propane sultone (Method 8270)  
beta-propiolactone (Method 8270)  
propoxur (Method 632)  
quinoline (Method 8270)  
quinone (Method 8270)  
styrene (Method 8270)  
styrene oxide (Method 8270)  
2,3,7,8-tetrachlorodibenzodioxin (Method 8280, Method 8290)  
1,1,2,2-tetrachloroethane (Method 8270)  
tetrachloroethylene (Method 8270)  
toluene (Method 8270)



2,4-toluenediamine (Method 8270, Method 632)  
2,4-toluenediisocyanate (Method 8270, Method 632)  
o-toluidine (Method 8270)  
toxaphene (Method 8270; 8270 target)  
1,2,4-trichlorobenzene (Method 8270)  
1,1,2-trichloroethane (Method 8270)  
2,4,5-trichlorophenol (Method 8270; 8270 target)  
2,4,6-trichlorophenol (Method 8270; 8270 target)  
trifluralin (Method 8270)  
xylenes: o-xylene, m-xylene, p-xylene (Method 8270)  
polycyclic organic matter (Method 8270; Method 8310)

\* The appropriate analytical methodology for each pollutant is shown in parenthesis.



## EPA DRAFT METHOD 0011

### Sampling for Formaldehyde Emissions from Stationary Sources

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 0011 is used to determine the Destruction and Removal Efficiency (DRE) of formaldehyde. Although this methodology has been applied specifically to formaldehyde, many laboratories have extended the application to other aldehydes and ketones. Compounds derivatized with 2,4-dinitrophenylhydrazine (DNPH) can be detected in concentrations as low as  $6.4 \times 10^{-8}$  lbs/cu ft (1.8 ppbv) in 40 cu ft of stack gas sampled over a 1-hour period.

#### 2.0 SUMMARY OF METHOD

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic DNPH solution. Formaldehyde (and other aldehydes and ketones) present in the emissions reacts with DNPH to form the dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high-performance liquid chromatography.

### 3.0 INTERFERENCES

A chromatographic method is subject to interference from coeluting components of the matrix. A decomposition product of DNPH, 2,4-dinitroaniline, can be an analytical interferent if concentrations are high. High concentrations of oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde and that also absorb at 360 nm will interfere with the analysis. Contamination of the aqueous acidic DNPH reagent with formaldehyde and 2,4-dinitroaniline is frequently encountered. The reagent must be prepared within five days of field use and must be stored in an uncontaminated environment both before and after sampling in order to minimize blank problems. Because acetone is ubiquitous in laboratory and field operations, some level of acetone contamination is unavoidable; however, it must be minimized to the extent possible.

### 4.0 METHOD TARGET COMPOUNDS

Aldehydes

Ketones

### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetophenone

acrolein

2-chloroacetophenone

formaldehyde

isophorone

methyl ethyl ketone

methyl isobutyl ketone

propionaldehyde

quinone

## EPA METHOD 0012

### Multi-Metal Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 0012 is used to determine metals from municipal waste incinerators and similar combustion processes. In addition, the method may be modified to determine particulate emissions.

#### 2.0 SUMMARY OF METHOD

Method 0012 consists of a stack sampling train and a number of analysis techniques for the recovered samples. The source sample is withdrawn isokinetically from the stack through a heated probe. The majority of the particulate emissions are collected on a filter in a heated filter holder that is located after the probe outside the stack. The gaseous emissions are collected in a series of chilled impingers located after the filter. Two of the impingers contain dilute nitric acid in hydrogen peroxide, and one or two contain acidic potassium permanganate solution.

Sample train components are recovered and digested in acid as separate fractions. The impingers and digested probe and filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy. All the sampling train components, except the permanganate solution, can be analyzed by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic spectroscopy (GFAAS) is used for

analysis of arsenic, cadmium, lead, antimony, selenium, and thallium if greater analytic sensitivity is required. For convenience, AAS may be used to analyze for all metals and/or a combined sample in a single analytical determination, provided the resulting detection limits meet the data quality objectives of the testing program. Detection limits for the target compounds range from 0.11 to 27  $\mu\text{g}/\text{m}^3$  for all methods except GFAAS. For selected metals, detection limits range from 0.03 to 0.8  $\mu\text{g}/\text{m}^3$  with GFAAS.

### 3.0 INTERFERENCES

Organic interferences will be removed with complete digestion. Use of the train to quantify particulate emissions may impact on mercury determinations, although data acquired to date show that less than 2 percent of the mercury is lost in the particulate catch.

Iron can be a spectral interference during analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Matrix modifiers should be used to eliminate interferences in all GFAAS analyses. Refer to EPA Method 6010 (SW-846) for details on potential interferences.

### 4.0 METHOD TARGET COMPOUNDS

arsenic\*  
barium\*\*  
beryllium\*  
cadmium\*  
chromium\*  
copper\*\*  
lead\*  
manganese\*\*  
mercury\*

nickel\*

phosphorus\*\*

selenium\*\*

silver\*\*

thallium\*\*

zinc\*

\*Primary target compounds

\*\*Secondary target compounds

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

NOTE: Draft Method 0012 analytical methods do not speciate inorganic cc

antimony compounds

arsenic compounds

beryllium compounds

cadmium compounds

chromium compounds

cobalt compounds

lead compounds

manganese compounds

mercury compounds

nickel compounds

selenium compounds

titanium tetrachloride

## EPA METHOD 0030

### Volatile Organic Sampling Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 0030 is used to calculate destruction and removal efficiency (DRE) of volatile principal organic hazardous constituents (POHCs) from stack gas effluents of hazardous waste incinerators, and enable a determination that DRE values are equal to or greater than 99.99 percent. For the purpose of definition, volatile POHCs are those POHCs with boiling points less than 100°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may break through the sorbent under the conditions of the sample collection procedure.

#### 2.0 SUMMARY OF METHOD

A 20-L sample of effluent gas is withdrawn from an emission source at a flow rate of 1 L/min, using a glass-lined probe and a volatile organic sampling train (VOST). The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent resin traps. Liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap (front trap) contains approximately 1.6 g Tenax® and the second trap (back trap) contains approximately 1 g each of Tenax® and petroleum-based charcoal (SKC lot 104 or equivalent), 3:1 by volume.



An alternative set of conditions for sample collection has been used. This method involves collecting a sample volume of 20 L or less at a reduced flow rate. (Operation of the VOST under these conditions has been referred to as SLO-VOST.) This method has been used to collect 5 L of sample (250 mL/min for 20 min) or 20 L of sample (500 mL/min for 40 min) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 35°C.

### 3.0 INTERFERENCES

The sensitivity of this method depends on the level of interferences in the sample and the presence of detectable levels of volatile POHCs in the blanks. The target detection limit of this method is 0.1 µg/m<sup>3</sup> (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99 percent for volatile POHCs that may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Laboratory development data have demonstrated a range of 0.1 to 100 µg/m<sup>3</sup> (ng/L) for selected volatile POHCs collected on a pair of sorbent traps using a total sample volume of 20 L or less. Interferences arise primarily from background contamination of sorbent traps prior to or after use in sample collection. Many interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites. A sufficiently high background level in the source (for example, a THC level above 100 ppm) can make trace analysis in the samples impossible.

### 4.0 METHOD TARGET COMPOUNDS

None

## 5.0 APPLICABLE CLEAN AIR ACT LIST OF CHEMICALS

acetaldehyde<sup>++</sup>  
acetonitrile<sup>++</sup>  
acrolein<sup>++</sup>  
acrylonitrile<sup>++</sup>  
allyl chloride<sup>\*</sup>  
benzene<sup>\*</sup>  
bromoform<sup>\*\*\*</sup>  
carbon disulfide<sup>\*</sup>  
carbon tetrachloride<sup>\*</sup>  
chlorobenzene (validated)<sup>\*\*\*</sup>  
chloroform<sup>\*</sup>  
chloromethyl methyl ether<sup>++</sup>  
chloroprene<sup>\*</sup>  
cumene<sup>\*\*\*</sup>  
1,4-dichlorobenzene<sup>\*\*\*</sup>  
1,3-dichloropropene<sup>\*\*\*</sup>  
1,1-dimethylhydrazine<sup>++</sup>  
1,4-dioxane<sup>++</sup>  
epichlorohydrin<sup>++</sup>  
1,2-epoxybutane<sup>++</sup>  
ethyl acrylate<sup>++</sup>  
ethylbenzene<sup>\*\*\*</sup>  
ethyl chloride<sup>\*\*</sup>  
ethylene dibromide<sup>\*\*\*</sup>

ethylene dichloride<sup>\*</sup>  
ethylidene dichloride<sup>\*</sup>  
hexane<sup>\*</sup>  
methyl bromide<sup>\*\*</sup>  
methyl chloride<sup>\*\*</sup>  
methyl chloroform<sup>\*</sup>  
methyl ethyl ketone<sup>++</sup>  
methyl hydrazine<sup>++</sup>  
methyl iodide<sup>\*</sup>  
methyl isobutyl ketone<sup>++</sup>  
methyl isocyanate<sup>++</sup>  
methyl methacrylate<sup>++</sup>  
methyl tert-butyl ether<sup>++</sup>  
methylene chloride<sup>\*</sup>  
propionaldehyde<sup>++</sup>  
propylene dichloride<sup>\*</sup>  
propylene oxide<sup>++</sup>  
1,2-propylene imine<sup>++</sup>  
styrene<sup>\*\*\*</sup>  
1,1,2,2-tetrachloroethane<sup>\*\*\*</sup>  
tetrachloroethylene (validated)<sup>\*\*\*</sup>  
toluene (validated)<sup>\*\*\*</sup>  
1,1,2-trichloroethane<sup>\*\*\*</sup>  
trichloroethylene<sup>\*</sup>  
2,2,4-trimethylpentane<sup>\*</sup>  
vinyl acetate<sup>++</sup>  
vinyl bromide<sup>\*\*</sup>  
vinyl chloride (validated)<sup>\*\*</sup>  
vinylidene chloride<sup>\*</sup>

xylenes\*\*\*

o-xylene\*\*\*

m-xylene\*\*\*

p-xylene\*\*\*

- \* Boiling point between 35°C and 100°C. Should work well with this methodology.
- \*\* Special precautions must be taken to avoid breakthrough when these compounds are analytes.
- \*\*\* Boiling point above 100°C. Can be observed using VOST methodology but VOST should not be used to provide quantitative data unless specific validation is performed.
- ++ Polar and/or water soluble. In general, perform well in the VOST methodology. Recovery can be improved by modifying the standard purge and trap analytical method by elevating the purge temperature to 60°C and adding 1 g of sodium chloride or sodium sulfate to condensate before purging (see EPA-600/8-87-008). With modified analytical methodology, the VOST methodology may be applicable to these compounds (validation required before use of the methodology to generate regulatory data).



## EPA DRAFT METHOD 0050

### Isokinetic HCl/Cl<sub>2</sub> Emission Sampling Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 0050 is used to collect hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. Collected samples are analyzed using EPA Method 9057. Method 0050 collects the emission sample isokinetically and is therefore, particularly suited for sampling at sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets). Method 0050 is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm. This method may also be used to collect samples for subsequent determination of particulate emissions (EPA Method 5).

#### 2.0 SUMMARY OF METHOD

Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets. The cyclone is not required if the source emissions do not contain liquid droplets (See EPA Method 0051). The Teflon® mat or quartz-fiber filter collects other particulate matter, including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl<sub>2</sub>, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl<sub>2</sub> dissolved in the liquid in the cyclone and/or on the filter is vaporized and ultimately collected in the impingers

by pulling Ascarite II®-conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions. The Cl<sub>2</sub> gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H<sup>+</sup>), chloride ions, and hypochlorous acid (HClO). Chloride ions in the separate solutions are measured by ion chromatography (EPA Method 9057). If desired, the particulate matter recovered from the filter and the probe can be analyzed (EPA Method 5).

### 3.0 INTERFERENCES

Volatile materials that produce chloride ions upon dissolution during sampling are interferences in the measurement of HCl. Cl<sub>2</sub> disproportionates to HCl and HClO upon dissolution in water, and will interfere with the HCl analysis. Cl<sub>2</sub> exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of HCl greatly reduces the dissolution of any Cl<sub>2</sub> present.

### 4.0 METHOD TARGET COMPOUNDS

chlorine  
hydrogen chloride

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

chlorine  
hydrogen chloride

## EPA DRAFT METHOD 0051

### Midget Impinger HCl/Cl<sub>2</sub> Emission Sampling Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 0051 is used to collect hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using EPA Method 9057. Method 0051 is designed to collect HCl and Cl<sub>2</sub> in their gaseous forms; sources such as those controlled by wet scrubbers that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl<sub>2</sub> sampling train (EPA Method 0050).

#### 2.0 SUMMARY OF METHOD

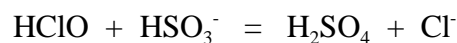
An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter removes particulate matter, such as chloride salts, that could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions. The Cl<sub>2</sub> gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H<sup>+</sup>), chloride ion, and hypochlorous acid (HClO). The chloride ions in the separate solutions are measured by ion chromatography (EPA Method 9057).



### 3.0 INTERFERENCES

Volatile materials that produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferent for HCl is Cl<sub>2</sub>, which disproportionates to HCl and HClO upon dissolution in water. The Cl<sub>2</sub> gas exhibits a very low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of HCl greatly reduces the dissolution of any Cl<sub>2</sub> present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl<sub>2</sub> with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl<sub>2</sub> results in a positive bias of 3.4 percent in the HCl measurement.

Reducing agents such as SO<sub>2</sub> may cause a positive bias in the Cl<sub>2</sub> measurement by the following reaction:



### 4.0 METHOD TARGET COMPOUNDS

chlorine

hydrogen chloride

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

chlorine

hydrogen chloride

## EPA METHOD 5040

### Analysis of Sorbent Cartridges from Volatile Organic Sampling Train

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 5040 is used to analyze Tenax® and Tenax®/charcoal cartridges containing volatile principal organic hazardous constituents (POHCs) from wet stack gas effluents from hazardous waste incinerators. Volatile POHCs are defined as those POHCs with boiling points less than 100°C. Method 5040 is based on the quantitative thermal desorption of volatile POHCs from the Tenax® and Tenax®/charcoal traps and analysis by purge-and-trap gas chromatography/mass spectrometry (GC/MS).

#### 2.0 SUMMARY OF METHOD

POHCs are collected on Tenax® and Tenax®/charcoal sorbent cartridges using a volatile organic sampling train (VOST), EPA Method 0030. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 minutes at 180°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free water, and trapped on an analytical adsorbent trap. After the 10 minute desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature-programmed gas chromatography and detected by low resolution mass spectrometry. The concentrations of the volatile POHCs are calculated using the internal standard technique.

EPA Method 5030 and 8240 may be referenced for specific requirements for the thermal desorption unit, purge-and-trap unit, and GC/MS system.

### 3.0 INTERFERENCES

Interferences from hydrocarbons may be a problem if a source with significant hydrocarbon content is sampled. The mass of low molecular weight POHCs (such as acetonitrile, with a mass of 41) would coincide with the mass of ions common to all hydrocarbons, and acetonitrile would thus not be identifiable by low resolution mass spectrometric techniques.

### 4.0 METHOD TARGET COMPOUNDS

Volatile POHCs.

### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetonitrile\*

acrylonitrile\*

allyl chloride

benzene

bis(chloromethyl) ether\*

carbon disulfide

carbon tetrachloride

chlorobenzene\*\*

chloroform

chloromethyl methyl ether\*

chloroprene

1,1-dimethylhydrazine\*

1,4-dioxane<sup>\*</sup>  
1,2-epoxybutane<sup>\*</sup>  
ethyl acrylate<sup>\*</sup>  
ethylbenzene<sup>\*\*</sup>  
ethyl chloride<sup>\*\*\*</sup>  
ethylene dibromide  
ethylene dichloride  
ethylene imine<sup>\*</sup>  
ethylidene dichloride  
hexane  
methyl bromide<sup>\*\*\*</sup>  
methyl chloride<sup>\*\*\*</sup>  
methyl chloroform  
methyl ethyl ketone<sup>\*</sup>  
methyl hydrazine<sup>\*</sup>  
methyl iodide  
methyl isobutyl ketone<sup>\*,\*\*</sup>  
methyl isocyanate<sup>\*</sup>  
methyl methacrylate<sup>\*</sup>  
methyl tert-butyl ether<sup>\*</sup>  
methylene chloride  
propylene oxide<sup>\*</sup>  
1,2-propylene imine<sup>\*</sup>  
tetrachloroethylene<sup>\*\*</sup>  
toluene<sup>\*\*</sup>  
1,1,2-trichloroethane<sup>\*\*</sup>  
trichloroethylene  
triethylamine<sup>\*</sup>  
2,2,4-trimethylpentane

vinyl acetate\*

vinyl bromide\*\*\*

vinyl chloride\*\*\*

vinylidene chloride

\* A protocol has been developed for sample analysis for water-soluble volatile POHCs and PICs (EPA-600/8-87-008). Application of this protocol may improve recoveries for polar water-soluble compounds.

\*\* Boiling point above 100°C.

\*\*\* Boiling point below 30°C. Special care must be taken to avoid breakthrough on sorbent.

## EPA DRAFT METHOD 5041

### Protocol for the Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-Bore Capillary Column Technique

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 5041 is used to analyze Volatile Principal Organic Hazardous Constituents (POHCs) collected from the stack gas effluents of hazardous waste incinerators using the VOST methodology which uses EPA Method 0030 for sampling. Draft Method 5041 is most successfully applied to the analysis of non-polar organic compounds that vaporize between 30°C and 100°C. Data are applied to the calculation of destruction and removal efficiency (DRE).

The VOST methodology may also be used to collect and analyze many compounds that boil above 100°C. However, sampling method collection efficiency, sampling tube desorption efficiency, and analytical method precision and bias should be determined for these compounds. An organic compound with boiling point below 30°C may break through the sorbent under the conditions used for sample collection. The quantitative value obtained for such a compound must be qualified, since the value represents a minimum value for the compound if breakthrough has occurred.

The VOST analytical methodology can be used to quantify volatile organic compounds (VOCs) that are insoluble or slightly soluble in water. When volatile water-soluble compounds

are included in the VOST organic compound analyte list, quantitation limits can be expected to be approximately ten times higher than quantitation limits for water-insoluble compounds (if the compounds can be recovered at all) because the purging efficiency from water (and possibly also from Tenax®) is so poor. Purging efficiency from water can be improved by modifying the VOST analytical methodology to include addition of salt (sodium chloride or sodium sulfate) to the purge water and heating the purge water (see EPA-600/8-87-008).

Overall sensitivity for the method depends on the level of analytical interferences encountered in the sample and the presence of detectable levels of volatile POHCs in the blanks. The target detection limit for the method is  $0.1 \mu\text{g}/\text{m}^3$  (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99 percent for volatile POHCs that may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by the dynamic range of the analytical instrumentation, the overall loading of organic compounds on the exposed tubes, and breakthrough of the volatile POHCs on the sorbent traps used to collect the sample.

## 2.0 SUMMARY OF METHOD

Sorbent tubes are thermally desorbed by heating and purging with organic-free helium. The gaseous effluent from the tubes is bubbled through pre-purged organic-free water and trapped on an analytical sorbent trap in a purge-and-trap unit. After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore column under subambient conditions. The VOCs desorbed from the analytical trap are separated by temperature-programmed high resolution gas chromatography and detected by continuously-scanning low resolution mass spectrometry. Concentrations of VOCs are calculated from a multi-point calibration curve, using the method of response factors.

### 3.0 INTERFERENCES

Sorbent tubes that are to be analyzed for VOCs can be contaminated by diffusion of VOCs (particularly Freon® refrigerants and common organic solvents) through the external container (even through a Teflon®-lined screw cap on a glass container) and the Swagelok® sorbent tube caps during shipment and storage. The sorbent tubes can also be contaminated if organic solvents are present in the analytical laboratory. The use of blanks is essential to assess the extent of any contamination. Field blanks must be prepared and taken to the field. The end caps of the tubes are removed for the period of time required to exchange two pairs of traps on the VOST sampling apparatus. The tubes are recapped and shipped and handled exactly as the actual field samples are shipped and handled. At least one pair of field blanks is included with each six pairs of sample cartridges collected.

At least one pair of blank cartridges (one Tenax®, one Tenax®-charcoal) must be included with shipment of cartridges to a hazardous waste incinerator site as trip blanks. These trip blanks will be treated like field blanks except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination that may occur during storage and shipment.

Analytical system blanks are required to demonstrate that contamination of the purge-and-trap unit and the gas chromatograph/mass spectrometer has not occurred or that, in the event of analysis of sorbent tubes with very high levels of organic compounds, no compound carryover is occurring. Tenax® from the same preparation batch as the Tenax® used for field sampling should be used in the preparation of the method (laboratory) blanks. A sufficient number of cleaned Tenax® tubes from the same batch as the field samples should be reserved in the laboratory for use as blanks.

Cross-contamination can occur whenever low-level samples are analyzed after high-level samples, or when several high-level samples are analyzed sequentially. When an unusually



concentrated sample is analyzed, this analysis should be followed by a method blank to establish that the analytical system is free of contamination. If analysis of a blank demonstrates that the system is contaminated, an additional bake cycle should be used. If the analytical system is still contaminated after additional baking, routine system maintenance should be performed: the analytical trap should be changed and conditioned, routine column maintenance should be performed (or replacement of the column and conditioning of the new column, if necessary), and bakeout of the ion source (or cleaning of the ion source and rods, if required). After system maintenance has been performed, analysis of a blank is required to demonstrate that the cleanliness of the system is acceptable.

If the emission source has a high level of non-target organic compounds (for example, hydrocarbons at levels of hundreds of ppm), the presence of these non-target compounds will interfere with the performance of the VOST analytical methodology. If one or more of the compounds of interest saturates the chromatographic and mass spectrometric instrumentation, no quantitative calculations can be made and the tubes that have been sampled under the same conditions will yield no valid data for any of the saturated compounds and may not yield valid data for other compounds. In the presence of a very high organic loading, even if the compounds of interest are not saturated, the instrumentation is so saturated that the linear range has been surpassed. When instrument saturation occurs, it is possible that compounds of interest cannot even be identified correctly because a saturated mass spectrometer may mis-assign masses. Even if compounds of interest can be identified, accurate quantitative calculations are impossible at detector saturation. No determination can be made at or beyond detector saturation, even if the target compound itself is not saturated. At detector saturation, a negative bias will be encountered in analytical measurements and no accurate calculation can be made for the DRE if analytical values may be biased negatively.

Compounds that coelute chromatographically with the compounds of interest may interfere with the analysis if the coeluting compounds have ions at the same masses as the compound of interest. An alternate ion can be selected for the compound of interest (provided

that detector saturation has not occurred) to avoid the interference at the primary quantitation mass.

#### 4.0 METHOD TARGET COMPOUNDS

acetone  
acrylonitrile  
benzene  
bromodichloromethane  
bromoform  
bromomethane  
carbon disulfide  
carbon tetrachloride  
chlorobenzene  
chlorodibromomethane  
chloroethane  
chloroform  
chloromethane  
dibromomethane  
1,1-dichloroethane  
1,2-dichloroethane  
1,1-dichloroethene  
trans-1,2-dichloroethene  
1,2-dichloropropane  
cis-1,3-dichloropropene  
trans-1,3-dichloropropene  
ethylbenzene  
iodomethane  
methylene chloride

styrene  
1,1,2,2-tetrachloroethane  
tetrachloroethene  
toluene  
1,1,1-trichloroethane  
1,1,2-trichloroethane  
trichloroethene  
trichlorofluoromethane  
1,2,3-trichloropropane  
vinyl chloride  
xylenes

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetonitrile (requires modification of the methodology for water-soluble  
compounds, but may require high resolution mass spectrometry)  
acrylonitrile  
allyl chloride  
benzene  
bis(chloromethyl) ether (will require modification of the methodology for  
water-soluble compounds)  
bromoform  
carbon disulfide  
carbon tetrachloride  
chlorobenzene (above 100°C boiling point)  
chloroform  
chloromethyl methyl ether (water-soluble)  
chloroprene  
1,1-dimethylhydrazine (water-soluble)

1,4-dioxane (water-soluble)  
ethyl acrylate (water-soluble)  
ethylbenzene (above 100°C boiling point)  
ethyl chloride (low boiling point; requires special care)  
ethylene dibromide (above 100°C boiling point)  
ethylene dichloride  
ethylene imine (water-soluble)  
ethylidene dichloride  
hexane  
methyl bromide (low boiling point; requires special care)  
methyl chloride (low boiling point; requires special care)  
methyl chloroform  
methyl ethyl ketone (water-soluble)  
methyl hydrazine (water-soluble)  
methyl iodide  
methyl isobutyl ketone (above 100°C boiling point; water-soluble)  
methyl isocyanate (water-soluble)  
methyl methacrylate (water-soluble)  
methyl tert-butyl ether (water-soluble)  
methylene chloride  
propylene dichloride  
propylene oxide (water-soluble)  
1,2-propylene imine (water-soluble)  
styrene (above 100°C boiling point)  
1,1,2,2-tetrachloroethane (above 100°C boiling point)  
tetrachloroethylene (above 100°C boiling point)  
toluene (above 100°C boiling point)  
1,1,2-trichloroethane (above 100°C boiling point)  
trichloroethylene

triethylamine (water-soluble)

2,2,4-trimethylpentane

vinyl acetate (water-soluble)

vinyl bromide (low boiling point; requires special care)

vinyl chloride (low boiling point; requires special care)

vinylidene chloride

xylene (above 100°C boiling point)

## EPA METHOD 8080

### Organochlorine Pesticides and PCBs

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs) in soil at levels of parts-per-billion. The method can be modified in order to analyze air samples. Method 8080 should be used only for non-stack stationary sources.

#### 2.0 SUMMARY OF METHOD

Prior to analysis, appropriate sample extraction techniques must be used. Water samples are extracted with methylene chloride using either EPA Method 3510 or EPA Method 3520. Solid samples are extracted using EPA Method 3540 or EPA Method 3550. The extraction solvent must be exchanged to hexane. A modification to accommodate air samples may be necessary. Once sample preparation is completed, the sample is injected, either manually or by an autosampler, into a gas chromatograph (GC). The compounds in the GC effluent are detected by an electron capture detector or a halogen-specific detector. The identification and concentration of the target compounds are based on a comparison of the retention times and peak areas of calibration standards with the sample peaks. A minimum of five concentration levels is required for calibration.

Method 8080 recognizes an Aroclor profile rather than individual PCBs. Since Aroclors are made up of numerous PCBs, their chromatograms are multi-peak and identification of an Aroclor is by pattern recognition. Method 8080 should not be applied to stack samples because Aroclors that have been combusted no longer exhibit the pattern of an Aroclor and consequently will not be identified. Spiking each sample, standard, and blank with the surrogates dibutyl chlorodane and/or 2,4,5,6-tetrachloro-meta-xylene is recommended in order to monitor the performance of the extraction, cleanup (when used), and analytical system.

### 3.0 INTERFERENCES

DDT and endrin degrade easily in the injection port of the GC as a result of buildup of high-boiling residue from sample injection. The degradation products of these compounds can interfere with peak detection and identification of certain compounds. Therefore, proper GC maintenance procedures are recommended in order to avoid these problems.

### 4.0 METHOD TARGET COMPOUNDS

aldrin  
alpha-BHC  
beta-BHC  
delta-BHC  
lindane  
chlordan  
4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
dielrin  
endosulfan I  
endosulfan II

endosulfan sulfate  
endrin  
endrin aldehyde  
heptachlor  
heptachlor epoxide  
methoxychlor  
toxaphene  
Aroclor-1016  
Aroclor-1221  
Aroclor-1232  
Aroclor-1242  
Aroclor-1248  
Aroclor-1254  
Aroclor-1260

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

polychlorinated biphenyls  
4,4'-DDE  
heptachlor  
lindane  
methoxychlor  
toxaphene  
chlordane





## EPA METHOD 8270

### Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. It is also applicable to an extract from sorbent media in conjunction with Method 0010. Direct injection of a sample may be used in limited applications.

Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

The following compounds may require special treatment when being determined by this method:

- Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor.
- Alpha-BHC, gamma-BHC, endosulfan I and II, and endrin are subject to decomposition under the alkaline conditions of the extraction step. Neutral extraction should be performed if these compounds are expected.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- N-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- N-Nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine.
- Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the gas chromatographic system is contaminated with high-boiling material. Derivatization can help to stabilize the chromatographic performance of these compounds.
- Acrylic acid will require derivatization to apply the analytical methodology.
- The phthalate esters exhibit better recoveries under acid extraction conditions.
- Bromoform, chlorobenzene, cumene, 1,3-dichloropropene, 1,4-dioxane, epichlorohydrin, ethylbenzene, ethylene dibromide, methyl isobutyl ketone, 2-nitropropane, styrene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, toluene, 1,1,2-trichloroethane, and *o*-, *m*-, and *p*-xylene are within the boiling point range for Method 8270, but they are sufficiently volatile that care must be taken in sample concentration to avoid loss. An adjustment in chromatographic conditions will be required to resolve the relatively volatile compounds from the solvent.
- 4-Aminobiphenyl, aniline, *o*-anisidine, benzidine, 3,3'-dichlorobenzidine, N,N-diethylaniline, 3,3'-dimethoxybenzidine, dimethylaminoazobenzene, 3,3'-dimethylbenzidine, 4,4'-methylene bis (2-chloroaniline), 4,4'-methylenedianiline, *p*-

phenylenediamine, quinoline, and 2,4-toluenediamine are basic nitrogen-containing compounds and careful control of pH during extraction is required to optimize recovery.

The practical quantitation limit for Method 8270 is approximately 50 µg/mL of extract. The entire sorbent module with filter is typically extracted and concentrated to 1 mL (a final volume of 5 mL is used to avoid loss of volatile compounds), and this final extract volume represents the entire volume of gas sampled.

## 2.0 SUMMARY OF METHOD

Method 8270 describes conditions for gas chromatography/mass spectrometry (GC/MS) to allow for the separation of the semivolatile compounds on the method target list. Sample extraction, purification, and concentration techniques are addressed in other methods. EPA Methods 3510, 3520, 3540, 3550, 3580 may be applicable to the sample preparation. The following purification methods may be used prior to GC/MS analysis:

phenols, Methods 3630, 3640, 8040  
phthalate esters, Method 3610, 3620, 3640  
nitrosamines, Method 3610, 3620, 3640  
organochlorine pesticides and PCBs, Method 3620, 3640, 3660  
polynuclear aromatic hydrocarbons, Method 3611, 3630, 3640  
nitroaromatics and cyclic ketones, Method 3620, 3640  
haloethers, Method 3620, 3640  
chlorinated hydrocarbons, Method 3620, 3640  
organophosphorus pesticides, Method 3620, 3640

petroleum waste, Method 3611, 3650

all priority pollutant base, neutral, and acids, Method 3640.

### 3.0 INTERFERENCES

Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. If an interference results from the preparation and/or cleanup of samples, corrective action can be taken to eliminate the problem. If the problem is a very high sample background of alkyl or aromatic hydrocarbons, very little can be done to resolve the problem other than dilution of the samples, which raises the detection limit. If chromatographic coelution occurs, deconvolution of the coeluting components by mass spectrometric techniques will be effective if the compounds are not chemically related and their mass spectra can be resolved. If isomers coelute and their mass spectra are similar, the coelution cannot be resolved.

Contamination by carryover can occur whenever high level and low level samples are analyzed sequentially. To reduce carryover, the sample syringe must be rinsed carefully with solvent between sample injections. The chromatographic column should be allowed to remain at a high temperature until all late-eluting components have eluted from the column in order to avoid chromatographic carryover problems. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of clean solvent to check for cross-contamination. If contamination is observed, the injections of solvent should be repeated until the contamination is no longer observed before another sample injection is performed.

### 4.0 METHOD TARGET COMPOUNDS

acenaphthene

acenaphthylene

acetophenone

aldrin

aniline  
anthracene  
4-aminobiphenyl  
Aroclor-1016  
Aroclor-1221  
Aroclor-1232  
Aroclor-1242  
Aroclor-1248  
Aroclor-1254  
Aroclor-1260  
benzidine  
benzoic acid  
benzo(a)anthracene  
benzo(b)fluoranthene  
benzo(k)fluoranthene  
benzo(g,h,i)perylene  
benzo(a)pyrene  
benzyl alcohol  
alpha-BHC  
beta-BHC  
delta-BHC  
gamma-BHC (lindane)  
bis(2-chloroethoxy)methane  
bis(2-chloroethyl)ether  
bis(2-chloroisopropyl)ether  
bis(2-ethylhexyl) phthalate  
4-bromophenyl phenyl ether  
butyl benzyl phthalate  
chlordan

4-chloroaniline  
1-chloronaphthalene  
2-chloronaphthalene  
4-chloro-3-methylphenol  
chrysene  
4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
dibenz(a,j)acridine  
dibenz(a,h)anthracene  
di-n-butyl phthalate  
1,3-dichlorobenzene  
1,4-dichlorobenzene  
1,2-dichlorobenzene  
3,3'-dichlorobenzidine  
dichloroethyl ether  
2,4-dichlorophenol  
2,6-dichlorophenol  
dieldrin  
diethyl phthalate  
p-dimethylaminoazobenzene  
7,12-dimethylbenz(a)anthracene  
alpha-, alpha-dimethylphenethylamine  
2,4-dimethylphenol  
dimethyl phthalate  
4,6-dinitro-2-methylphenol  
2,4-dinitrophenol  
2,4-dinitrotoluene  
2,6-dinitrotoluene

diphenylamine  
1,2-diphenylhydrazine  
di-n-octyl phthalate  
endosulfan I  
endosulfan II  
endosulfan sulfate  
endrin  
endrin aldehyde  
endrin ketone  
ethyl methanesulfonate  
fluoranthene  
fluorene  
heptachlor  
heptachlor epoxide  
hexachlorobenzene  
hexachlorobutadiene  
hexachlorocyclopentadiene  
hexachloroethane  
indeno(1,2,3-cd)pyrene  
isophorone  
methoxychlor  
3-methylcholanthrene  
methyl methanesulfonate  
2-methylnaphthalene  
2-methylphenol  
4-methylphenol  
naphthalene  
1-naphthylamine  
2-naphthylamine



3-nitroaniline  
4-nitroaniline  
nitrobenzene  
2-nitrophenol  
4-nitrophenol  
N-nitrosodi-n-butylamine  
N-nitrosodimethylamine  
N-nitrosodiphenylamine  
N-nitrosodipropylamine  
N-nitrosopiperidine  
pentachlorobenzene  
pentachloronitrobenzene  
pentachlorophenol  
phenacetin  
phenanthrene  
phenol  
2-picoline  
pronamide  
pyrene  
1,2,4,5-tetrachlorobenzene  
2,3,4,6-tetrachlorophenol  
1,2,4-trichlorobenzene  
2,4,5-trichlorophenol  
2,4,6-trichlorophenol  
toxaphene

## 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetamide  
acetophenone (8270 target)  
2-acetylaminofluorene  
acrylamide  
acrylic acid  
4-aminobiphenyl (8270 target)  
aniline (8270 target)  
o-anisidine  
benzidine (8270 target)  
benzotrichloride  
benzyl chloride  
biphenyl  
bis(2-ethylhexyl) phthalate (8270 target)  
bromoform  
catechol  
chlordan (8270 target)  
chloroacetic acid  
2-chloroacetophenone  
chlorobenzene  
chlorobenzilate  
o-cresol (8270 target)  
m-cresol  
p-cresol (8270 target)  
cresylic acid (mixture of cresols)  
cumene  
2,4-D  
DDE (8270 target)

1,2-dibromo-3-chloropropane  
dibutyl phthalate (8270 target)  
1,4-dichlorobenzene (8270 target)  
3,3'-dichlorobenzidine (8270 target)  
1,3-dichloropropene  
dichlorvos  
diethanolamine  
N,N-diethylaniline  
diethyl sulfate  
3,3'-dimethoxybenzidine  
dimethylaminoazobenzene (8270 target)  
3,3'-dimethylbenzidine  
dimethyl formamide  
dimethyl phthalate (8270 target)  
dimethyl sulfate  
4,6-dinitro-o-cresol (8270 target)  
2,4-dinitrophenol (8270 target)  
2,4-dinitrotoluene (8270 target)  
1,4-dioxane  
1,2-diphenylhydrazine (8270 target)  
epichlorohydrin  
ethylbenzene  
ethylene dibromide  
ethylene glycol  
glycol ethers  
heptachlor (8270 target)  
hexachlorobenzene (8270 target)  
hexachlorobutadiene (8270 target)  
hexachlorocyclopentadiene (8270 target)

hexachloroethane (8270 target)  
hexamethylene-1,6-diisocyanate  
hydroquinone  
isophorone (8270 target)  
lindane (8270 target)  
maleic anhydride  
methoxychlor (8270 target)  
4,4'-methylene bis(2-chloroaniline)  
methylene diphenyl diisocyanate  
4,4'-methylenedianiline  
naphthalene (8270 target)  
nitrobenzene (8270 target)  
4-nitrobiphenyl  
4-nitrophenol (8270 target)  
N-nitroso-N-methylurea  
N-nitrosodimethylamine (8270 target)  
N-nitrosomorpholine  
parathion  
pentachloronitrobenzene (8270 target)  
pentachlorophenol (8270 target)  
phenol (8270 target)  
p-phenylenediamine  
phthalic anhydride  
polychlorinated biphenyls  
polycyclic organic matter  
1,3-propane sultone  
beta-propiolactone  
quinoline  
quinone

styrene  
styrene oxide  
1,1,2,2-tetrachloroethane  
tetrachloroethylene  
toluene  
2,4-toluenediamine  
2,4-toluene diisocyanate  
o-toluidine  
toxaphene (8270 target)  
1,2,4-trichlorobenzene (8270 target)  
1,1,2-trichloroethane  
2,4,5-trichlorophenol (8270 target)  
2,4,6-trichlorophenol (8270 target)  
trifluralin  
xylenes: o-xylene, m-xylene, p-xylene

## EPA METHOD 8280

### The Analysis of Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 8280 is used to determinate tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in chemical wastes, including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil, and water.

#### 2.0 SUMMARY OF METHOD

This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high resolution capillary column gas chromatography/low resolution mass spectrometry techniques. An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases is needed. Fused silica capillary columns are required, and one of the following is recommended: (1) 50 m CP-Sil-88; (2) DB-5, 30 m x 0.25 mm ID, 0.25  $\mu$ m film thickness; or (3) 30 m SP-2250. However, any capillary column that provides separation of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) from all other TCDD's with higher isomers may be used.

Two types of calibration procedures are required: An initial calibration is required before any samples are analyzed, and routine calibration conducted intermittently throughout the sample

analyses. The routine calibration consists of analyzing the column performance check solution and a mid-range concentration calibration solution.

Samples are analyzed with Selected Ion Monitoring mass spectrometry techniques. Strict identification criteria for PCDDs and PCDFs are listed in the method. The concentration of individual isomers is determined using relative response factors that were calibrated using data obtained from the analysis of multi-level calibration standards.

Because of the extreme toxicity of many of the compounds listed as analytes, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. Laboratory personnel must ensure that safe handling procedures are employed.

### 3.0 INTERFERENCES

The sensitivity of this method depends on the level of interferents within a given matrix. Interferents coextracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as PCBs and polychlorinated diphenyl ethers, which may be found at higher concentrations than that of the analytes of interest.

### 4.0 METHOD TARGET COMPOUNDS

tetrachlorodibenzo-*p*-dioxin

tetrachlorodibenzofuran

pentachlorodibenzo-*p*-dioxin

pentachlorodibenzofuran  
hexachlorodibenzofuran  
hexachlorodibenzo-p-dioxin  
heptachlorodibenzo-p-dioxin  
heptachlorodibenzofuran  
octachlorodibenzofuran  
octachlorodibenzo-p-dioxin

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

dibenzofurans  
2,3,7,8-tetrachlorodibenzo-p-dioxin.





## EPA DRAFT METHOD 8290

### Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 8290 provides for the detection and quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), polychlorinated dibenzo-p-dioxins (PCDDs; tetra- through octachlorinated homologs), and polychlorinated dibenzofurans (PCDFs; tetra- through octachlorinated homologs) in a variety of environmental matrices and at part-per-trillion (ppt) concentrations. This method has been applied to samples from the following matrices: soil, sediment, fly ash, water, sludges, fuel oil, still bottoms, fish tissue, paper pulp, human adipose tissue, and gaseous and particulate emissions.

Because of the extreme toxicity of many of the compounds listed as analytes, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. Laboratory personnel must ensure that safe handling procedures are employed.

## 2.0 SUMMARY OF METHOD

This procedure uses matrix-specific extraction, analyte-specific clean-up, and high resolution capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques. A specified amount of matrix (or the entire sorbent sampling trap plus filter from a sampling train for gaseous emissions) is spiked with a solution containing specified amounts of the nine isotopically-labeled ( $^{13}\text{C}_{12}$ ) PCDDs/PCDFs. The sample is then extracted according to a matrix-specific extraction procedure. The extracts are submitted to an acid/base washing treatment and dried. Following a solvent exchange, the residue is purified by column chromatography on neutral alumina and carbon on Celite 545®. Preparation of the final extract for HRGC/HRMS analysis is accomplished by adding a solution containing the isotopically-labeled recovery standards to the concentrated carbon column eluate. The recovery standard is used to determine the percent recoveries of isotopically-labeled standards spiked at the beginning of the extraction process. An aliquot of the concentrated extract is injected into a HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

Compound identification for the compounds for which an isotopically-labeled standard is used is based upon elution at the exact retention time established by analysis of standards and simultaneous detection of the two most abundant ions in the molecular ion region. Compounds for which no isotopically-labeled standard is available are identified by their relative retention times, which must fall within the established retention windows, and the simultaneous detection of the two most abundant ions in the molecular ion region. The retention windows are established by analysis of a GC Performance Evaluation solution. Identification is confirmed by comparing the ratio of the integrated ion abundance of the molecular ion species to the theoretical abundance ratio.

Quantification of the individual congeners, total PCDDs and PCDFs, is based upon a multipoint (seven points) calibration curve for each homolog, with each calibration solution being analyzed once.

### 3.0 INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of the laboratory analysis by analyzing laboratory method blanks. Analysts should avoid using polyvinyl chloride gloves. High-purity reagents and solvents help minimize interference problems. Purifying solvents by distillation in all-glass systems may be necessary.

The sensitivity of the method is dependent upon the level of interferences within a given matrix. Interferences co-extracted from the sample matrix will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated xanthenes which may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards, and these values must correspond to the established retention time windows. While certain purification techniques are included as part of this method, unique samples may require other additional purification steps to achieve lower detection limits.

#### 4.0 METHOD TARGET COMPOUNDS

polychlorinated dibenzo-p-dioxins

polychlorinated dibenzofurans

2,3,7,8-tetrachlorodibenzo-p-dioxin

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

dibenzofurans

2,3,7,8-tetrachlorodibenzo-p-dioxin

## EPA METHOD 8310

### Polynuclear Aromatic Hydrocarbons

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 8310 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in ground water and wastes at parts-per-billion levels. By extension, the methodology should be applicable to material extracted from a solid sorbent module of a sampling train from EPA Method 0010, which is used to sample gaseous emissions from a stationary source.

Extension of the methodology to PAH containing functional groups should be possible, depending upon the ability to adjust analytical conditions and the availability of standards for the compounds of interest.

Use of Method 8310 presupposes a high expectation of finding the specific compounds of interest. To screen samples for any or all of the method target compounds (see listed below), independent protocols for the verification of identity must be developed. One method that can be used to certify identity is gas chromatography/mass spectrometry (GC/MS).

Method detection limits are compound-dependent, ranging from 0.4 µg/L for indeno(1,2,3-cd)pyrene in ground water to 230,000 µg/L for acenaphthylene in non-water miscible waste. Detection limits for PAH in gaseous emissions have not been determined directly.

This methodology has not been directly and specifically applied to the determination of polycyclic organic matter other than the PAH specifically listed in the methodology. A quantitative analysis of other PAH and functionalized PAH will require adjustment of analytical conditions and the use of appropriate standards. An additional method such as GC/MS, if applicable, may be required to identify additional compounds.

If coelution of compounds is encountered in samples taken from gaseous emissions of stationary sources, Method 8310 may not be applicable unless analytical conditions can be adjusted to achieve chromatographic resolution.

## 2.0 SUMMARY OF METHOD

Prior to using Method 8310, appropriate sample extraction methods must be used. A 5- to 25  $\mu$ L aliquot of extract is injected into a high performance liquid chromatograph (HPLC), and compounds in the effluent are detected by ultraviolet (uv) and fluorescence detectors. If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone purification using silica gel column cleanup (EPA Method 3630).

## 3.0 INTERFERENCES

The sensitivity of the method usually depends on the level of interferences rather than instrumental limitations. The limits of detection above for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower, if analysis is possible at all.

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis

by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of Method 8310, individual samples may require additional cleanup approaches to achieve the desired sensitivity.

The chromatographic conditions described in Method 8310 allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

#### 4.0 METHOD TARGET COMPOUNDS

acenaphthene  
acenaphthylene  
anthracene  
benzo(a)anthracene  
benzo(a)pyrene  
benzo(b)fluoranthene  
benzo(ghi)perylene  
benzo(k)fluoranthene  
chrysene  
dibenzo(a,h)anthracene  
fluoranthene  
fluorene  
indeno(1,2,3-cd)pyrene  
naphthalene  
phenanthrene  
pyrene



## 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

naphthalene\*  
4-aminobiphenyl  
benzidine  
biphenyl  
chlorobenzilate  
3,3'-4 dichlorobenzidine  
3,3'dimethoxybenzidine  
dimethylaminoazobenzene  
3,3'-dimethylbenzidine  
4,4'-methylene bis(chloroaniline)  
methylene diphenyl isocyanate  
4,4'-methylenedianiline  
4-nitrobiphenyl  
p-phenylenediamine  
2,4-toluenediamine  
2,4-toluene diisocyanate  
o-toluidine  
polycyclic organic matter

\* Method 8310 is directly applicable only to this compound.

## EPA DRAFT METHOD 8315

### Determination of Formaldehyde by DNPH Derivatization, Solid Sorbent Extraction, and HPLC Detection

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 8315 uses high performance liquid chromatography (HPLC) to determine formaldehyde in liquid environmental matrices and leachates of solid samples applicable to the determination of formaldehyde and acetaldehyde. Extension of the methodology to HPLC determination of formaldehyde and acetaldehyde in gaseous emission samples is feasible, and the methodology can also be applied to other aldehydes and ketones. When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique such as gas chromatography/mass spectrometry.

Actual detection limits are compound- and matrix-dependent. However, for a list of aldehydes and ketones tested, detection limits were approximately 2 ppbv when reagent capacity (for sampling by EPA Draft Method 0011) was 60-100 ppm.

#### 2.0 SUMMARY OF METHOD

In Draft Method 0011, the 2,4-dinitrophenylhydrazine (DNPH) derivative of aldehydes in the emission stream is formed during sampling, since the emissions are bubbled through impingers containing an aqueous acidic solution of DNPH. This solution is returned to the laboratory and

extracted with methylene chloride. The methylene chloride extract is concentrated to less than 10 mL using the Kuderna-Danish procedure. Liquid chromatographic conditions described in Draft Method 8315 which permit the separation and measurement of formaldehyde (and other aldehydes and ketones) in the extract by absorbance detection at 360 nm.

### 3.0 INTERFERENCES

Analysis for formaldehyde is especially complicated by its ubiquitous occurrence in the environment. The volatile aldehydes, such as formaldehyde and acetaldehyde, may be contaminants in volatile organic solvents. Since formaldehyde is widely used in building insulation, great care is required to determine whether the laboratory atmosphere is contaminated with formaldehyde. Blanks and controls that are treated under the same laboratory conditions as samples are of crucial importance in assessing background levels of aldehydes. Solvent blanks for each lot of solvents used in sample preparation are important. Glassware must not be rinsed with acetone in the cleaning process.

Matrix interferences will result from contaminants that are coextracted from the sample, and will vary from source to source. Since the analytical methodology is HPLC, quantitative analysis of compounds of interest depends on the absence of coeluting interferences.

### 4.0 METHOD TARGET COMPOUNDS

acetaldehyde\*  
acetone/propionaldehyde  
acrolein  
benzaldehyde  
butyraldehyde  
dimethylbenzaldehyde  
formaldehyde\*

hexaldehyde  
isovalderaldehyde  
methyl ethyl ketone  
o-, m-, and p-tolualdehyde  
valeraldehyde

- \* The target compounds actually cited in Draft Method 8315 are formaldehyde and acetaldehyde. The other listed compounds have been determined by DNPH derivatization followed by HPLC analysis.

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetophenone  
acrolein  
2-chloroacetophenone  
formaldehyde  
isophorone  
methyl ethyl ketone  
methyl isobutyl ketone  
propionaldehyde  
quinone



## EPA DRAFT METHOD 8318

### N-Methyl Carbamates by High Performance Liquid Chromatography (HPLC)

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Draft Method 8318 is used to determine the concentration of N-methylcarbamates in soil, water, and waste matrices. Extension of the methodology is required to allow preparation and analysis of samples from stationary sources.

#### 2.0 SUMMARY OF METHOD

N-Methylcarbamates are extracted from aqueous samples with methylene chloride, and from soils, oily solid waste, and oils with acetonitrile. The extract solvent is exchanged to methanol/ethylene glycol, and then the extract is cleaned up on a C-18 cartridge, filtered, and eluted on a C-18 analytical column. After separation, the target analytes are hydrolyzed and derivatized post-column, then quantified fluorimetrically.

Due to the specific nature of this analysis, confirmation by a secondary method is not essential. However, fluorescence due to post-column derivatization may be confirmed by substituting the NaOH and o-phthalaldehyde solutions with deionized water and reanalyzing the sample. If fluorescence is detected, then a positive interference is present and care should be taken in the interpretation of the results.

The sensitivity of the method usually depends upon the level of interferences present, rather than on the instrumental conditions. Waste samples with a high level of extractable fluorescent compounds are expected to yield significantly higher detection limits.

### 3.0 INTERFERENCES

Fluorescent compounds, primarily alkyl amines and compounds that yield primary alkyl amines on base hydrolysis, are potential sources of interferences. Coeluting compounds that are fluorescence quenchers may result in negative interferences. Impurities in solvents and reagents are additional sources of interferences. Before processing any samples, the analyst must demonstrate daily, through the analysis of solvent blanks, that the entire analytical system is interference-free.

### 4.0 METHOD TARGET COMPOUNDS

aldicarb (Temik)  
aldicarb sulfone  
carbaryl (Sevin)  
carbofuran (Furadan)  
dioxacarb  
3-hydroxycarbofuran  
methiocarb (Mesurol)  
methomyl (Lannate)  
promecarb  
propoxur (Baygon).

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

carbaryl

propoxur

ethyl carbamate





## EPA METHOD 9057

### Analysis of Samples from HCl/Cl<sub>2</sub> Emission Sampling

#### REFERENCE :

*Test Methods for Evaluating Solid Waste*, Third Edition. Report No. SW-846. U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. Washington, DC: 1986.

#### 1.0 SCOPE AND APPLICATION

EPA Method 9057 is used to determine hydrogen chloride (HCl) and chlorine (Cl<sub>2</sub>) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midjet impinger HCl/Cl<sub>2</sub> sampling train (Method 0051) or the isokinetic HCl/Cl<sub>2</sub> sampling train (Method 0050).

The lower detection limit is 0.1 µg of chloride ions per mL of sample solution. Samples with concentrations that exceed the linear range of the analytical instrumentation may be diluted.

Method 9057 is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

#### 2.0 SUMMARY OF METHOD

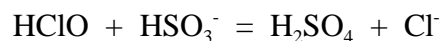
The stoichiometry of HCl and Cl<sub>2</sub> collection in the sampling train (Methods 0050 and 0051) is as follows: in the acidified water absorbin solution, the HCl gas is solubilized and forms chloride ions. The Cl<sub>2</sub> gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton

(H<sup>+</sup>), chloride ion, and hypochlorous acid. Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the chloride ion.

### 3.0 INTERFERENCES

Volatile materials that produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One likely interferent is Cl<sub>2</sub>, which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl<sub>2</sub> exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of HCl greatly reduced the dissolution of any Cl<sub>2</sub> present in the emissions.

Reducing agents such as SO<sub>2</sub> may cause a positive bias in the chlorine measurement by the following reaction:



### 4.0 METHOD TARGET COMPOUNDS

chlorine

hydrogen chloride

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

chlorine

hydrogen chloride

## METHOD TO-1

### Determination of Volatile Organic Compounds in Ambient Air Using TENAX® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-1 is used to collect and determine volatile, non-polar organics (aromatic hydrocarbons, chlorinated hydrocarbons) that can be captured on Tenax® and determined by thermal desorption techniques. The compounds to be determined by this technique have boiling points in the range of 80-200°C.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a cartridge containing 1-2 g of Tenax®. The cartridge is analyzed in the laboratory and purged with an inert gas into first a gas chromatograph (GC) followed by a mass spectrometer (MS). Only capillary GC techniques should be used. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points. The MS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics.

### 3.0 INTERFERENCES

The most common interferences are structural isomers.

### 4.0 METHOD TARGET COMPOUNDS

aromatic hydrocarbons

chlorinated hydrocarbons

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acrylonitrile

allyl chloride

benzene

bis(chloromethyl) ether

bromoform

1,3-butadiene

carbon disulfide

carbon tetrachloride

carbonyl sulfide

chlorobenzene

chloroform

chloromethyl methyl ether

chloroprene

cumene

1,4-dichlorobenzene

dichloroethyl ether

1,3-dichloropropene

1,1-dimethylhydrazine

1,4-dioxane  
1,2-epoxybutane  
ethyl acrylate  
ethylbenzene  
ethyl chloride  
ethylene dibromide  
ethylene dichloride  
ethylene imine  
ethylidene dichloride  
hexachlorobuadiene  
hexachloroethane  
hexane  
methyl bromide  
methyl chloride  
methyl chloroform  
methyl ethyl ketone  
methyl hydrazine  
methylene chloride  
methyl iodide  
methyl isobutyl ketone  
methyl isocyanate  
methyl methacrylate  
methyl tert-butyl ether  
nitrobenzene  
2-nitropropane  
N-nitrosodimethylamine  
propylene dichloride  
propylene oxide  
1,2-propyleneimine

styrene  
1,1,2,2-tetrachloroethane  
tetrachloroethylene  
toluene  
1,2,4-trichlorobenzene  
trichloroethylene  
2,2,4-trimethylpentane  
vinyl acetate  
vinyl bromide  
vinyl chloride  
vinylidene chloride  
m, p, o-xylenes

## METHOD TO-2

### Determination of Volatile Organic Compounds in Ambient Air by Carbon Molecular Sieve Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-2 is used to collect and determine highly volatile, non-polar organics (vinyl chloride, vinylidene chloride, benzene, toluene) that can be captured on carbon molecular sieve and determined by thermal desorption techniques. The compounds to be determined by this technique have boiling points in the range of -15-120°C.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a cartridge containing 0.4 g of a carbon molecular sieve (CMS) adsorbent. The cartridge is analyzed in the laboratory by flushing with dry air to remove adsorbed moisture and purging the sample with helium while heating the cartridge to 350-400°C. The desorbed organics are collected in a cryogenic trap and flash evaporated into first a gas chromatograph (GC) followed by a mass spectrometer (MS). Only capillary GC techniques should be used. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points. The MS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics.



### 3.0 INTERFERENCES

The most common interferences are structural isomers.

### 4.0 METHOD TARGET COMPOUNDS

benzene  
toluene  
vinyl chloride  
vinylidene chloride

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

allyl chloride  
benzene  
carbon tetrachloride  
chloroform  
ethyl chloride  
ethylene dichloride  
methyl bromide  
methyl chloride  
methyl chloroform  
methylene chloride  
toluene  
trichloroethylene  
vinyl bromide  
vinyl chloride  
vinylidene chloride



## METHOD TO-4

### Determination of Organochlorine Pesticides and Polychlorinated Biphenyls (PCBs) in Ambient Air

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*

U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-4 is used to analyze a variety of organochlorine pesticides and polychlorinated biphenyls (PCBs) in ambient air.

#### 2.0 SUMMARY OF METHOD

A modified high volume sampler consisting of a glass fiber filter with a polyurethane foam backup absorbent cartridge is used to sample air at a rate of 200-280 L/min. PCBs and pesticides are recovered by Soxhlet extraction with 5 percent ether in hexane. The extracts are reduced in volume with a Kuderna-Danish concentration technique and subject to column chromatography cleanup. The extracts are analyzed using gas chromatography with electron capture detection.

#### 3.0 INTERFERENCES

Extraneous organic compounds may interfere. It may be difficult to identify an individual pesticide or PCBs in a multiple component mixture.

#### 4.0 METHOD TARGET COMPOUNDS

organochlorine pesticides

polychlorinated biphenyls

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

DDE

heptachlor

lindane

methoxychlor

parathion

toxaphene

## METHOD TO-5

### Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-5 is used to analyze individual aldehydes and ketones in ambient air.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a midjet impinger containing dinitrophenylhydrazine (DNPH) reagent and isooctane where the target compounds are derivatized. The organic fraction is evaporated to dryness and dissolved in methanol. The derivatives are determined using reverse phase high performance liquid chromatography HPLC with an ultra-violet detector.

#### 3.0 INTERFERENCES

Isomeric aldehydes or ketones may be unresolved by the HPLC system.

#### 4.0 METHOD TARGET COMPOUNDS

aldehydes

ketones

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acetaldehyde

acetophenone

acrolein

formaldehyde

methyl ethyl ketone

methyl isobutyl ketone

propionaldehyde

quinone

trifluralin

## METHOD TO-6

### Determination of Phosgene in Ambient Air Using High Performance Liquid Chromatography (HPLC)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-6 is used to determine phosgene in ambient air at the 0.1 ppbv level.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a midjet impinger containing an aniline/toluene mixture. The solution is heated to dryness and dissolved in acetonitrile. The sample is analyzed by reverse phase high performance liquid chromatography (HPLC) with an ultraviolet detector.

#### 3.0 INTERFERENCES

Chloroformates and acidic materials may interfere.

#### 4.0 METHOD TARGET COMPOUNDS

phosgene

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

phosgene



## METHOD TO-7

### Determination of N-Nitrosodimethylamine in Ambient Air Using Gas Chromatography (GC)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-7 is used to determine N-nitrosodimethylamine in ambient air.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a Thermosorb/N adsorbent cartridge at a rate of 2 L/min. The cartridges are pre-eluted with dichloromethane to remove interferences. The sample is eluted with acetone and injected into a gas chromatograph (GC) that is followed by a detection system such as mass spectrometer (MS). A Carbowax 20M capillary column should be used in the GC. The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points. The MS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished using a library search routine on the basis of GC retention time and mass spectral characteristics.

### 3.0 INTERFERENCES

Compounds with similar GC retention times and similar detectable MS ions may interfere.

### 4.0 METHOD TARGET COMPOUNDS

N-nitrosodimethylamine

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

N-nitrosodiethylamine

N-nitrosomorpholine

## METHOD TO-8

### Determination of Phenol and Methyl Phenols (Cresols) in Ambient Air using High Performance Liquid Chromatography (HPLC)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-8 is used to determine cresols and phenols in ambient air at the 1-5 ppbv level.

#### 2.0 SUMMARY OF METHOD

Air is drawn through two midjet impingers, each containing sodium hydroxide. The solution is adjusted to pH 4 in the laboratory after sampling, and analyzed by reverse-phase high performance liquid chromatography (HPLC) with ultraviolet, electrochemical, or fluorescent detection.

#### 3.0 INTERFERENCES

Compounds having the same HPLC retention times will interfere with this method. The phenolic compounds of interest may be oxidized during sampling.

#### 4.0 METHOD TARGET COMPOUNDS

cresols

phenols

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

cresylic acid

o-cresol

m-cresol

p-cresol

## METHOD TO-9

### Determination of Polychlorinated Di-Benzo-p-Dioxins (PCDDs) in Ambient Air Using High Resolution Gas Chromatography/ High-Resolution Mass Spectrometry (HRGC/HRMS)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-9 is used to determine p-dioxins in ambient air, especially 1,2,3,4- and 2,3,7,8-tetrachlorodibenzo-p-dioxins (TCDDs), polychlorinated dibenzo-p-dioxins (HxCDDs) and octachlorodibenzo-p-dioxin (OCDD). With careful attention to reagent purity, the method can detect PCDDs at levels below 15 pg/m<sup>3</sup>.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a glass fiber filter with a polyurethane foam (PUF) back-up absorbent cartridge. Silica gel can be used in place of PUF to give lower detection limits, but silica gel does not always give consistent sample recoveries and will require extensive clean-up. The filters and PUF adsorbent cartridge are extracted together with benzene, diluted with hexane and cleaned up using column chromatography. The sample is injected into a high resolution gas chromatograph (HRGC) in line with a high-resolution mass spectrometer (HRMS). In the HRGC, temperature is increased through a temperature program and the sample compounds are eluted from the column on the basis of boiling points. The HRMS identifies and quantifies the compounds by mass fragmentation patterns. Compound identification is normally accomplished

using a library search routine on the basis of HRGC retention time and mass spectral characteristics.

### 3.0 INTERFERENCES

Polychlorinated biphenyls (PCBs), methoxybiphenyls, chlorinated hydroxydiphenylethers and naphthalenes, DDE, DDT, and other compounds with similar retention times and mass fractions are analytical interferences. Inaccurate measurements can occur if PCDDs are retained or absorbed onto particulate matter, the filter, or PUF cartridge, or are chemically changed during sampling and storage in ways not traceable with isotopically labelled spikes.

### 4.0 METHOD TARGET COMPOUNDS

polychlorinated dibenzo-*p*-dioxins  
polychlorinated dibenzofurans

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

dibenzofurans  
2,3,7,8-tetrachlorodibenzo-*p*-dioxin

## METHOD TO-10

### Determination of Organochlorine Pesticides in Ambient Air Using Low Volume Polyurethane Foam (PUF) Sampling with Gas Chromatography/Electron Capture Detector (GC/ECD)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-10 is used to determine organochlorine pesticides in ambient air. This method is applicable to multi-component mixtures containing the compounds of interest in concentrations of 0.01 to 50  $\mu\text{g}/\text{m}^3$ . The sampling procedure is also applicable to other pesticides that may be determined by gas chromatography coupled with a nitrogen-phosphorus detector, flame photometric detector, Hall electrolytic conductivity detector, or a mass spectrometer (MS). For some organopesticides, high performance liquid chromatography coupled with ultraviolet or electrochemical detection may be preferred.

#### 2.0 SUMMARY OF METHOD

A low volume sampler is used to collect source vapors onto a sorbent cartridge containing polyurethane foam. Pesticides are extracted from the cartridge with 5 percent diethyl ether in hexane and recovered by Soxhlet extraction with 5 percent ether in hexane. The extracts are reduced in volume with a Kuderna-Danish concentration technique and subjected to an alumina chromatographic cleanup procedure. The sample extracts are analyzed by gas chromatography coupled with an electron capture detector (ECD).

### 3.0 INTERFERENCES

ECD and other detectors (except the MS) will be subject to responses from a variety of compounds other than the compounds of interest. Polychlorinated biphenyls in particular may interfere. Certain organochlorine pesticides (e.g., chlordane) are complex mixtures of individual compounds that can make accurate quantification of a particular compound in the mixture difficult.

### 4.0 METHOD TARGET COMPOUNDS

organochlorine pesticides

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

captan

2,4-D salts and esters

DDE

heptachlor

lindane

methoxychlor

parathion

toxaphene

trifluralin



## METHOD TO-11

### Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC)

#### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006,  
600/4-87-013).

#### 1.0 SCOPE AND APPLICATION

Method TO-11 is used to determine formaldehyde in ambient air. Other aldehydes and ketones can be detected with a modification of the basic procedure.

#### 2.0 SUMMARY OF METHOD

Air is drawn through a midjet impinger sampling train (without impinger) containing a silica gel cartridge coated with acidified dinitrophenylhydrazine (DNPH). The cartridge is eluted with acetonitrile in the laboratory to form a formaldehyde-DPNH derivative. The concentration of formaldehyde is determined with isocratic reverse phase high performance liquid chromatography (HPLC) with ultraviolet absorption detection.

#### 3.0 INTERFERENCES

Isomeric aldehydes and ketones, and other compounds with the same HPLC retention times as formaldehyde may interfere with this method.

#### 4.0 METHOD TARGET COMPOUNDS

formaldehyde

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acetaldehyde

acetophenone

acrolein

2-chloroacetophenone

formaldehyde

isophorone

methyl ethyl ketone

methyl isobutyl ketone

phosgene

propionaldehyde

quinone

## METHOD TO-13

Determination of Polynuclear Aromatic Hydrocarbons (PAHs) in Ambient Air Using High Volume Sampling with Gas Chromatography/Mass Spectrometry (GC/MS) and High Resolution Liquid Chromatographic (HRLC)

### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

### 1.0 SCOPE AND APPLICATION

Method TO-13 is used to determine benzo(a)pyrene and other polynuclear aromatic hydrocarbons (PAHs) in ambient air. Nitro-PAHs are not included with this method.

### 2.0 SUMMARY OF METHOD

Air is drawn through a filter and adsorbent cartridge containing XAD-2® or polyurethane foam. The filters and adsorbents are extracted by Soxhlet apparatus. The extract is reduced in volume with a Kuderna-Danish concentration technique and subjected to cleanup with silica gel column chromatography. The sample is further concentrated with a Kuderna-Danish evaporator and analyzed by either gas chromatography equipped with flame ionization or a mass spectrometer, or high performance liquid chromatography.

### 3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and sampling hardware. Matrix interferences may be caused by contaminants that are co-extracted with the sample. Heat, ozone, nitrogen dioxide, and ultraviolet light may cause sample degradation.

### 4.0 METHOD TARGET COMPOUNDS

polynuclear aromatic hydrocarbons

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acetamide

acetophenone

2-acetylaminofluorene

acrylamide

acrylic acid

4-aminobiphenyl

aniline

o-anisidine

benzotrichloride

benzyl chloride

biphenyl

bis(2-ethylhexyl) phthalate

caprolactam

carbaryl

catechol

chloramben

chlordanes  
chloroacetic acid  
2-chloroacetophenone  
chlorobenzilate  
o,m,p-cresol, cresylic acid  
cumene  
1,2-dibromo-3-chloropropane  
dibutyl phthalate  
1,4-dichlorobenzene  
3,3'-dichlorobenzidine  
dichloroethyl ether  
dichlorvos  
diethanolamine  
N,N-diethylaniline  
diethyl sulfate  
3,3'-dimethoxybenzidine  
dimethylaminoazobenzene  
3,3'-dimethylbenzidine  
dimethyl carbamoyl chloride  
dimethyl formamide  
dimethyl phthalate  
dimethyl sulfate  
4,6-dinitro-o-cresol and salts  
2,4-dinitrophenol  
2,4-dinitrotoluene  
1,2-diphenylhydrazine  
epichlorohydrin  
ethyl carbamate  
ethylene dibromide

ethylene glycol  
ethylene thiourea  
glycol ethers  
hexachlorobenzene  
hexachlorobutadiene  
hexachlorocyclopentadiene  
hexachloroethane  
hexamethylene-1,6-diisocyanate  
hexamethylphosphoramide  
hydroquinone  
maleic anhydride  
methoxychlor  
methylene diphenyl isocyanate  
4,4'-methylenedianiline  
4,4'-methylene bis(2-chloroaniline)  
naphthalene  
4-nitrobiphenyl  
4-nitrophenol  
2-nitropropane  
N-nitroso-N-methylurea  
N-nitrosodimethylamine  
N-nitrosomorpholine  
pentachloronitrobenzene  
pentachlorophenol  
phenol  
p-phenylenediamine  
phthalic anhydride  
polychlorinated biphenyls  
1,3-propane sultone

beta-propiolactone

propoxur

quinoline

styrene oxide

2,4-toluediamine

o-toludine

1,2,4-trichlorobenzene

2,4,5-trichlorophenol

2,4,6-trichlorophenol

triethylamine

o-, m-, p-xylenes





## METHOD TO-14

Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Polished Canister Sampling and Gas Chromatography (GC)

### REFERENCE :

*Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.*  
U.S. Environmental Protection Agency. EPA-600/4-89-017 (Supplements: 600/4-87-006, 600/4-87-013).

### 1.0 SCOPE AND APPLICATION

Method TO-14 is used to determine semi-volatile and volatile organic compounds in ambient air. The sample canisters can be placed above or below atmospheric pressure. Pressurized samples can be detected at the ppbv level.

### 2.0 SUMMARY OF METHOD

Air is drawn through a sampling train into a pre-evacuated sample SUMMA® canister. The canister is attached to the analytical system. Water vapor is reduced in the gas stream by a Nafion dryer and VOCs are concentrated by collection into a cryogenically-cooled trap. The cryogen is removed and the temperature of the sample raised to volatilize the sample into a high resolution gas chromatograph (HRGC). The GC temperature is increased through a temperature program and the compounds are eluted from the column on the basis of boiling points into a detector. The choice of detector depends on the specificity and sensitivity required by the analysis. Non-specific detectors include nitrogen-phosphorus detectors, flame ionization detectors, electron capture detectors, and photoionization detectors. Specific detectors include a mass spectrometer (MS) operating in the selected ion mode or the SCAN mode, or an ion trap

detector. Identification errors can be reduced by employing simultaneous detection by different detectors.

### 3.0 INTERFERENCES

Interferences can occur because of moisture contamination in the dryer. Polar organic compounds may be lost with moisture removed in the GC/MS dryer.

### 4.0 METHOD TARGET COMPOUNDS

semi-volatile organic compounds

volatile organic compounds

Freons®

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

acetonitrile

acrylonitrile

allyl chloride

benzene

bis(chloromethyl) ether

bromoform

1,3-butadiene

carbon disulfide

carbon tetrachloride

carbonyl sulfide

chlorobenzene

chloroform

chloromethyl methyl ether

chloroprene  
cumene  
1,4-dichlorobenzene  
dichloroethyl ether  
1,3-dichloropropene  
1,1-dimethylhydrazine  
1,4-dioxane  
1,2-epoxybutane  
ethyl acrylate  
ethylbenzene  
ethyl chloride  
ethylene dibromide  
ethylene dichloride  
ethylene imine  
ethylene oxide  
ethylidene dichloride  
hexachlorobutadiene  
hexachloroethane  
hexane  
methanol  
methyl bromide  
methyl chloride  
methyl chloroform  
methyl ethyl ketone  
methyl hydrazine  
methylene chloride  
methyl iodide  
methyl isobutyl ketone  
methyl isocyanate

methyl methacrylate  
methyl tert-butyl ether  
nitrobenzene  
2-nitropropane  
propylene dichloride  
propylene oxide  
1,2-propyleneimine  
styrene  
1,1,2,2-tetrachloroethane  
tetrachloroethylene  
toluene  
trichloroethylene  
2,2,4-trimethylpentane  
vinyl acetate  
vinyl bromide  
vinyl chloride  
vinylidene chloride  
o-, m-, p-xylenes

## CARB METHOD 427

### Determination of Asbestos Emissions from Stationary Sources

#### REFERENCE :

*Stationary Source Test Methods, Volume III: Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources.* State of California Air Resources Board, Monitoring and Laboratory Division. Sacramento, CA: 1989.

#### 1.0 SCOPE AND APPLICATION

CARB Method 427 is used to determine asbestos emissions from stationary sources. The method describes a stack sampling method, but an alternate non-stack method (NIOSH Method 7400) can be used. The method of analysis described in NIOSH 7400 (light microscopy), and permitted under Method 427, does not distinguish asbestos from other mineral fibers.

#### 2.0 SUMMARY OF METHOD

The method consists of a stack sampling train designed to isokinetically collect a particulate sample from a known sample of gas, corrected to a dry basis. A probe is used to withdraw the sample isokinetically from the duct. A tared filter in filter holder is placed behind the probe within the stack to collect the bulk of the particulate sample. A series of impingers or a condenser following the filter assembly outside the stack is used to both measure the moisture present in the gas and protect the dry gas meter that is located at the end of the train.

The sample is composed of the particulate-laden filter and the dried washings of the probe, nozzle, and front half of the filter holder. Transmission electron microscopy (TEM) can be used to analyze the collected sample. TEM analysis is used to classify the fibers as chrysotile,

amphibole, or non-asbestos and to describe the aggregation of asbestos into single fibers, bundles, or mats.

### 3.0 INTERFERENCES

Phase contrast light microscopy will not differentiate between asbestos and other mineral fibers.

### 4.0 METHOD TARGET COMPOUNDS

asbestos

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

asbestos

mineral fibers

## CARB Method 429

### Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Stationary Sources

#### REFERENCE :

*Stationary Source Test Methods, Volume III: Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources.* State of California Air Resources Board, Monitoring and Laboratory Division. Sacramento, CA: 1989.

#### 1.0 SCOPE AND APPLICABILITY

CARB Method 429 is used to determine polycyclic aromatic hydrocarbon (PAH) emissions from stationary sources. The sensitivity that can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample, as well as the original sample size and instrument sensitivity.

The limitations on extension of the methodology to compounds other than the method target compounds listed in Section 4.0 are the availability of standards and the ability to perform chromatographic separations on vaporized compounds.

#### 2.0 SUMMARY OF METHOD

Particulate and gaseous-phase PAH are extracted isokinetically from the stack and collected on a filter, on XAD-2® resin, in the impingers, or in upstream sampling train components. Only the total amounts of each PAH in stack emissions can be determined with this method. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH.

The analytical method entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts (if necessary), and analysis of the processed extract for PAH using high-resolution capillary column gas chromatography coupled with either low resolution or high resolution mass spectrometry.

### 3.0 INTERFERENCES

Modified Method 5 sampling train can cause artifactual formation and PAH transformation. The fact that PAH can degrade or transform on sample filters is well documented. When trapped on filters, certain reactive PAH such as benzo[a]pyrene, benzo[a]anthracene, and fluoranthene can readily react with stack gases. Low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides have been known to react with these PAH.

PAH degradation may be of even greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water, they are converted into sulfuric acid and nitric acid, respectively. There is evidence that under such conditions certain PAH will be degraded. It is recommended that the levels in the impingers be used as a qualitative tool to determine if breakthrough has occurred in the resin.

In order to assess the effects of ozone, sulfur oxides, and nitrogen oxides, the tester should monitor concurrently for these gases during PAH sampling.



#### 4.0 METHOD TARGET COMPOUNDS

naphthalene  
acenaphthylene  
acenaphthene  
fluorene  
phenanthrene  
anthracene  
fluoranthene  
pyrene  
benz[a]anthracene  
chrysene  
benzo[b]fluoranthene  
benzo[k]fluoranthene  
benzo[a]pyrene  
benzo[ghi]perylene  
dibenz[a,h]anthracene  
indeno[1.2.3-cd]pyrene

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

polycyclic organic matter



## CARB METHOD 431

### Determination of Ethylene Oxide Emissions from Stationary Sources

#### REFERENCE :

*Stationary Source Test Methods, Volume III: Methods for Determining Emissions of Toxic Air Contaminants from Stationary Sources.* State of California Air Resources Board, Monitoring and Laboratory Division. Sacramento, CA: 1989.

#### 1.0 SCOPE AND APPLICATION

CARB Method 431 is used to determine ethylene oxide emissions from sterilization chambers in pounds per sterilization cycle. The method can be modified to determine emissions of ethylene oxide from other stationary sources.

#### 2.0 SUMMARY OF METHOD

A sterilization chamber is operated empty of items to be sterilized, minimizing interferences and simulating worst-case vented emission conditions. Volumetric flow of vented gas is monitored and vented gas is analyzed repeatedly by gas chromatography during chamber purging. Total emissions of ethylene oxide for the sterilization cycle are calculated from curves of flow and concentration over time.

Ethylene oxide is used in sterilizers at lethal concentrations. Contact with vented gas can cause skin burns. Inhalation can cause injury or death. Caution should be observed to avoid contact with or inhalation of vented gas.

The lower limit of sensitivity will vary according to the gas chromatography equipment and span gases used. With appropriate span gases the method is expected to achieve useful accuracy over the expected range of emissions from either controlled or uncontrolled sterilizers.

### 3.0 INTERFERENCES

Ethylene oxide is frequently used in sterilizers in a mixture with dichlorodifluoromethane (Freon 12). If the gas chromatographic conditions are not well selected, the ethylene oxide peak may be overwhelmed by the tail of the Freon 12 peak when testing emissions at low concentrations. This matrix problem is effectively eliminated by selecting a gas chromatographic column where ethylene oxide elutes before Freon 12.

### 4.0 METHOD TARGET COMPOUNDS

ethylene oxide

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

ethylene oxide

## NIOSH METHOD 2515

### Diazomethane

#### REFERENCE :

*NIOSH Manual of Analytical Methods, Part 1: NIOSH Monitoring Methods, Volume 1.* U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health. Cincinnati, Ohio: Revised 1985.

#### 1.0 SCOPE AND APPLICATION

NIOSH Method 2515 is used to determine 0.1 to 0.6 ppm (0.2 to 1 mg/m<sup>3</sup>) diazomethane for a 10 L air sample.

#### 2.0 SUMMARY OF METHOD

An air sample is obtained using a solid sorbent tube (octanoic acid-coated XAD-2® resin, 100 mg/50 mg) attached to a personal sampling pump with flexible tubing. The sample is collected at a known flow rate of  $0.2 \pm 0.03$  L/min for a total sample size of 6 to 30 L.

Analysis is by gas chromatography (GC) with flame ionization detector. A stainless steel column, 3 m x 3 mm OD with 5% SP-1000 on 100/120 mesh Chromosorb WHP preceded by a 15 cm x 3 mm OD stainless steel precolumn 80/100 mesh Gas Chrom Q is recommended.

Methyl octanoate (analyte) is desorbed in carbon disulfide with an internal standard (tridecane) for daily calibration over a range of 1 to 32 µg methyl octanoate per sample. The GC is set according to recommendations and conditions given in this method for optimum and the peak resolution samples are injected manually using the solvent flush technique or with an autosampler.

The concentration of diazomethane per sample is calculated by converting mg methyl octanoate to mg diazomethane by multiplying the corrected mg per sample by the molecular weight ratio, 41.04/158.24, and calculating the apparent concentration of diazomethane in the air volume sampled.

### 3.0 INTERFERENCES

The collection efficiency and reaction of diazomethane with the octanoic acid-coated resin may be strongly dependent on sample flow rates; therefore, all samples must be collected at a flow rate of 0.2 L/min only.

### 4.0 METHOD TARGET COMPOUNDS

diazomethane

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

diazomethane

## NIOSH METHOD 7400

### Fibers

#### REFERENCE :

*NIOSH Manual of Analytical Methods, Part 1: NIOSH Monitoring Methods, Volume 1.* U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health. Cincinnati, Ohio: Revised 1985.

#### 1.0 SCOPE AND APPLICATION

NIOSH Method 7400 gives an index of airborne fibers but will not differentiate asbestos from other mineral fibers. Fibers less than 0.25  $\mu\text{m}$  will not be detected by this method.

#### 2.0 SUMMARY OF METHOD

A sample is withdrawn through a 0.8 to 1.2  $\mu\text{m}$  ester membrane filter in a 25 mm cassette filter holder at 0.5 to 16 L/min. The sample is prepared according to the acetone/triacetin "hot block" method onto a phase-shift test slide. The fibers are counted manually using a light microscope and a Walton-Beckett graticule.

#### 3.0 INTERFERENCES

Any airborne fibers may interfere as all particles meeting the counting criteria will be counted. Chain-like fibers may appear fibrous. High levels of non-fibrous dust particles may obscure fibers in the field of view and increase the detection limit.

#### 4.0 METHOD TARGET COMPOUNDS

asbestos

various mineral fibers

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

asbestos

fine mineral fibers



## NIOSH METHODS 9010 AND 9012

### Total and Amenable Cyanide Analysis

#### REFERENCE :

*NIOSH Manual of Analytical Methods, Part 1: NIOSH Monitoring Methods, Volume 1.* U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health. Cincinnati, Ohio: Revised 1985.

#### 1.0 SCOPE AND APPLICATION

NIOSH Methods 9010 and 9012 are used to analyze an aqueous sample for total inorganic cyanide. The methods detect simple soluble salts or complex radicals, total cyanide, and cyanide amenable to chlorination.

#### 2.0 SUMMARY OF METHOD

The sample is refluxed with strong acid and distilled into an absorber/scrubber that contains sodium hydroxide solution. Cyanide is released as hydrogen cyanide. The cyanide ion is converted to cyanochloride by reaction with chloramin-T at a pH less than 8. Color is formed by addition of pyridine-barbituric acid reagent. The concentration of cyanide ion is determined colorimetrically (UV) either manually (Method 9010) or with an automated system (Method 9012) by comparison to known standards.

#### 3.0 INTERFERENCES

Sulfides, nitrates, or nitrites adversely affect the colorimetric procedure but can be eliminated as interferences by pretreating the sample.

#### 4.0 METHOD TARGET COMPOUNDS

inorganic cyanide

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

cyanide compounds

## OSHA METHOD ID-101

### Chlorine in Workplace Atmospheres

#### REFERENCE:

OSHA Method ID-101

#### 1.0 SCOPE AND APPLICATION

The method describes the collection and analysis of airborne chlorine for industries where chlorine is used as a bleaching agent or for chlorination of various organic compounds.

#### 2.0 SUMMARY OF METHOD

An air sample is drawn into a solution of 0.1 percent sulfamic acid. An aliquot of the sample is reacted with acidic potassium iodide. Chlorine oxidizes the potassium iodide to iodine which is measured by an ion specific electrode. The detection limit is 0.4 mg/m<sup>3</sup> for a 15 liter air volume.

#### 3.0 INTERFERENCES

Strong oxidizing agents including iodate, bromine, cupric ion and manganese dioxide can interfere with the analysis. High silver and mercuric concentrations (greater than 15 ppm) also can cause interference.

#### 4.0 METHOD TARGET COMPOUNDS

Chlorine.

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

Chlorine.

## EPA METHOD 6

### Determination of Sulphur Dioxide Emissions from Stationary Sources

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 60, Appendix A. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

EPA Method 6 is used to determine sulphur dioxide (SO<sub>2</sub>) emissions from stationary sources.

#### 2.0 SUMMARY OF METHOD

A heated probe is used to collect a sample from the source. The probe is equipped with a filter (either in or out of stack) to remove particulates and sulfuric acid mist (including sulphur trioxide). The sample is collected in impingers filled with isopropanol and hydrogen peroxide. The concentration of SO<sub>2</sub> is determined by titration of the sample with barium perchlorate to a thorin endpoint.

The impinger solution can be modified to allow sampling/analysis of other compounds.

#### 3.0 INTERFERENCES

Free ammonia, water soluble cations, and fluorides may interfere.

#### 4.0 METHOD TARGET COMPOUNDS

sulphur dioxide

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

ammonia

cyanide

## EPA METHODS 7C AND 7D

### Determination of Nitrogen Oxide Emissions from Stationary Sources-Alkaline-Permanganate Methods

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 60, Appendix A. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

EPA Methods 7C and 7D are used to determine nitrogen oxide ( $\text{NO}_x$ ) emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, among other sources.

#### 2.0 SUMMARY OF METHOD

An integrated sample is collected in a heated probe packed with glass wool for particulate collection. The sample is passed through a series of impingers containing alkaline potassium permanganate solution.  $\text{NO}_x$  is oxidized to nitrate ions. The nitrate is reduced to nitrite with cadmium and the nitrite is analyzed colorimetrically (Method 7C) or is analyzed as nitrate by ion chromatography (Method 7D) against known standards. The detection limits are 7 ppm  $\text{NO}_x$  when sampling at 500 cc/min for 1 hour.

#### 3.0 INTERFERENCES

Sulphur dioxide and ammonia may interfere.

#### 4.0 METHOD TARGET COMPOUNDS

nitrogen dioxide

nitrogen oxide

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

phosphine



## EPA METHOD 12

### Determination of Inorganic Lead Emissions from Stationary Sources

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 60, Appendix A. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

This method applies to the determination of inorganic lead emissions from specified stationary sources only.

#### 2.0 SUMMARY OF METHOD

Particulate and gaseous lead emissions are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame.

#### 3.0 INTERFERENCES

Sample matrix effects may interfere with the analysis for lead by flame atomic absorption. If matrix interference is suspected, the analyst may confirm the presence of these matrix effects and frequently eliminate the interference by using the Method of Standard Additions.

High concentrations of copper may interfere with the analysis for lead at 217.0 nm. This interference can be avoided by analyzing the samples at 283.3 nm.

#### 4.0 METHOD TARGET COMPOUNDS

lead compounds

#### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

lead compounds

## EPA METHOD 13A

### Determination of Total Fluoride Emissions from Stationary Sources by the SPADNS Zirconium Lake Method

#### REFERENCE :

*Standards of Performance for New Stationary Sources*. Compilation. U. S. Environmental Protection Agency, EPA-340/1-77-015.

#### 1.0 SCOPE AND APPLICATION

EPA Method 13A is used to determine fluoride emissions from stationary sources. It does not measure fluorocarbons.

#### 2.0 SUMMARY OF METHOD

Gaseous and particulate fluoride are withdrawn isokinetically from the source through a heated probe. A filter (with optional heating) is placed either before the first impinger or between the third and fourth impinger. The sample is collected in impingers containing deionized water and analyzed spectrophotometrically after distillation and addition of SPADNS reagent [4,5 dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalene-disulfonic acid trisodium salt]. The range of this method is 0 to 1.4  $\mu\text{g F/mL}$ . The sensitivity has not been determined.

#### 3.0 INTERFERENCES

Large quantities of chloride will interfere with the analysis. Grease on sample-exposed surfaces may cause low results because of adsorption of fluoride.

#### 4.0 METHOD TARGET COMPOUNDS

fluoride

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

hydrogen fluoride

## EPA METHOD 13B

### Determination of Total Fluoride Emissions from Stationary Sources by Specific Ion Electrode Method

#### REFERENCE :

*Standards of Performance for New Stationary Sources.* Compilation. U. S. Environmental Protection Agency, EPA-340/1-77-015.

#### 1.0 SCOPE AND APPLICATION

EPA Method 13B is used to determine fluoride emissions from stationary sources. It does not measure fluorocarbons.

#### 2.0 SUMMARY OF METHOD

Gaseous and particulate fluoride are withdrawn isokinetically from the source through a probe heated filter and collected in impingers containing deionized water. The sample is analyzed after distillation by a specific ion electrode that is calibrated with known standards.

#### 3.0 INTERFERENCES

Grease on sample-exposed surfaces may cause low results because of adsorption of fluoride.

#### 4.0 METHOD TARGET COMPOUNDS

fluoride

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

hydrogen fluoride

EPA METHOD 14  
Determination of Fluoride from Roof Monitors

REFERENCE :

*Standards of Performance for New Stationary Sources.* Compilation. U. S. Environmental Protection Agency, EPA-340/1-77-015.

1.0 SCOPE AND APPLICATION

EPA Method 14 is used to determine fluoride emissions from potroom roof monitors for primary aluminum plants when specified by New Source Performance Standards. It does not measure fluorocarbons.

2.0 SUMMARY OF METHOD

The sample is drawn into a manifold that is connected to a duct. A sample is withdrawn from the duct isokinetically and analyzed, either spectrophotometrically or by use of a specific ion electrode.

3.0 INTERFERENCES

Large quantities of chloride will interfere with the analysis. Grease on sample-exposed surfaces may cause low results because of adsorption of fluoride.

#### 4.0 METHOD TARGET COMPOUNDS

fluoride

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

hydrogen fluoride



## EPA METHOD 15

### Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide from Stationary Sources

#### REFERENCE :

*Standards of Performance for New Stationary Sources*. Compilation. U. S. Environmental Protection Agency, EPA-340/1-77-015.

#### 1.0 SCOPE AND APPLICATION

EPA Method 15 is used to determine hydrogen sulfide, carbonyl sulfide, and carbon disulfide from tail gas control units of sulfur recovery plants. Any method that uses the principle of gas chromatography separation with flame photometric detection can be substituted, providing that sample-line loss and the calibration precision are met.

#### 2.0 SUMMARY OF METHOD

Gas is drawn through a heated sample probe followed by a particulate filter (Teflon®) outside the stack. A sulfur dioxide (SO<sub>2</sub>) scrubber made up of impingers containing citrate buffer removes SO<sub>2</sub> from the sample. The sample then is diluted with clean dry air (9:1) and fed into a gas chromatograph (GC) equipped with a flame photometric detector ((FPD). In the GC, temperature is increased through a temperature program and the compounds of interest are eluted from the column on the basis of boiling point. Concentrations of the sulfur compounds of interest are determined by calibration of the GC/FPD against known standards. The minimum detectable quantity depends on the sample size and would be about 0.5 ppm for a 1 mL sample.

### 3.0 INTERFERENCES

Moisture, carbon monoxide, carbon dioxide, SO<sub>2</sub>, elemental sulfur, and alkali mist are possible interferences.

### 4.0 METHOD TARGET COMPOUNDS

carbon disulfide

carbonyl sulfide

hydrogen sulfide

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

carbon disulfide

carbonyl sulfide

## EPA METHOD 18

### Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

#### REFERENCE :

40 CFR Part 60, Appendix A.

#### 1.0 SCOPE AND APPLICATION

EPA Method 18 is used to analyze approximately 90 percent of the total gaseous organics emitted from an industrial source.

Method 18 does not include techniques to identify and measure trace amounts of organic compounds such as those found in building air and fugitive emission sources. This method will not determine compounds that: (1) are polymeric (high molecular weight); (2) can polymerize before analysis; or (3) have very low vapor pressures at stack or instrument conditions.

#### 2.0 SUMMARY OF METHOD

A presurvey must be performed on each source to be tested. The purpose of the presurvey is to obtain all information necessary to design the emission test. The most important presurvey data are the average stack temperature and temperature range, approximate particulate concentration, static pressure, water vapor content, and identity and expected concentration of each organic compound to be analyzed. Some of this information can be obtained from literature surveys, direct knowledge, or plant personnel. However, presurvey samples of the gas shall be obtained for analysis to confirm the identity and approximate concentrations of the specific compounds prior to the final testing. The presurvey samples shall be used to develop and confirm the best sampling and analysis scheme.

The major components of a gas mixture are separated with a gas chromatograph (GC) and measured with a suitable detector. The retention time of each separated component is compared with the retention time of a known compound under identical conditions. Therefore, the analyst confirms the identity and approximate concentration of the organic emission components beforehand. With this information, the analyst then prepares or purchases commercially available standard mixtures to calibrate the GC under conditions identical to those of the samples. The analyst also determines the need for sample dilution to avoid detector saturation, gas stream filtration to eliminate particulate matter, and prevention of moisture condensation. The range of this method is from about 1 part per million (ppm) to the upper limit governed by GC detector saturation or column overloading. The upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. The minimum detectable concentration is determined during the presurvey calibration for each compound. Gas chromatographic techniques typically provide a precision of 5 to 10 percent relative standard deviation (RSD), but an experienced GC operator with a reliable instrument can readily achieve a 5 percent RSD. For this method, the following combined GC/operator values are required:

1. Precision -- duplicate analyses are within 5 percent of their mean value.
2. Accuracy -- analysis results of prepared audit samples are within 10 percent of preparation values.

### 3.0 INTERFERENCES

Chromatographic resolution interferences that may occur can be eliminated by appropriate GC column and detector choice or by shifting the retention times through changes in the column flow rate and the use of temperature programming. If chromatographic resolution cannot be achieved by application of these techniques, quantitative results cannot be obtained from the application of this method.

The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen. Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample loop between samples.

To ensure consistent detector response, calibration gases are contained in dry air. To eliminate errors in concentration calculations due to the volume of water vapor in the samples, moisture concentrations are determined for each sample, and a correction factor is applied to any sample with greater than 2 percent water vapor.

### 4.0 METHOD TARGET COMPOUNDS

gaseous organics

### 5.0 APPLICABLE CLEAN AIR ACT LIST COMPOUNDS

acetaldehyde

allyl chloride

1,3-butadiene

carbon disulfide

carbonyl sulfide

chloroprene  
ethyl chloride  
ethylene imine  
ethylene oxide  
formaldehyde  
hydrazine  
methanol  
methyl bromide  
methyl chloride  
methyl iodide  
methyl isocyanate  
methylene chloride  
phosgene  
propylene oxide  
1,2-propylene imine  
vinyl bromide  
vinyl chloride

## EPA METHOD 23

### Determination of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources

#### REFERENCE :

Federal Register, February 13, 1991 (56 FR 5758). To be included in 40 CFR Part 60, Appendix A.

#### 1.0 SCOPE AND APPLICATION

EPA Method 23 is used to determine polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources.

#### 2.0 SUMMARY OF METHOD

A sample is withdrawn isokinetically from the stack through a probe, a filter, and a trap packed with a solid adsorbent. The PCDDs and the PCDFs are collected in the probe, on the filter, and on the solid adsorbent.

The sampling train used in this method is identical to that described in EPA Method 5 with the exceptions and modifications noted within this method.

The sample is analyzed using a gas chromatograph coupled to a mass spectrometer (GC/MS). A 1 to 5  $\mu\text{L}$  aliquot of the sample extract is injected into the GC and measured with the MS. The total PCDDs and PCDFs are the sum of the individual isomers. Strict identification criteria for PCDDs and PCDFs are listed in the method. Fused silica capillary columns are required, and one of the following is recommended:

- DB-5, 0.25 µm film thickness; or
- SP-2331 column to measure the 2,3,7,8-tetrachlorodibenzofuran isomer.

Two types of calibration procedures are required: an initial calibration is required before any samples are analyzed and intermittently calibrations are performed throughout sample analyses. The routine calibration consists of analyzing the column performance check solution and a concentration calibration solution.

The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the PCDDs or PCDFs in its homologous series.

### 3.0 INTERFERENCES

PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as polychlorinated biphenyls (PCBs) and polychlorinated diphenyl ethers, which may be found at higher concentrations than those of the analytes of interest.

### 4.0 METHOD TARGET COMPOUNDS

2,3,7,8-tetrachlorodibenzo-p-dioxin  
 2,3,7,8-tetrachlorodibenzofuran  
 1,2,3,7,8-pentachlorodibenzo-p-dioxin  
 1,2,3,7,8-pentachlorodibenzofuran  
 2,3,4,7,8-pentachlorodibenzofuran  
 2,3,4,7,8-hexachlorodibenzo-p-dioxin  
 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin  
 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin  
 2,3,4,6,7,8-hexachlorodibenzo-p-dioxin



1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin  
1,2,3,4,7,8-hexachlorodibenzofuran  
1,2,3,6,7,8-hexachlorodibenzofuran  
1,2,3,7,8,9-hexachlorodibenzofuran  
1,2,3,4,6,7,8-heptachlorodibenzofuran  
1,2,3,4,7,8,9-heptachlorodibenzofuran  
octachlorodibenzo-p-dioxin  
octachlorodibenzofuran

#### 5.0 APPLICABLE CLEAN AIR ACT CHEMICALS

dibenzofurans  
2,3,7,8-tetrachlorodibenzo-p-dioxin



## EPA METHOD 101

### Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants - Air Streams

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 60, Appendix B. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

This method applies to the determination of particulate and gaseous mercury emissions from chlor-alkali plants and other sources (as specified in the regulations), where the carrier gas in the duct or stack is principally air.

#### 2.0 SUMMARY OF METHOD

Particulate and gaseous mercury emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride solution. The mercury collected (in the mercuric form) is reduced to elemental mercury, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

#### 3.0 INTERFERENCES

Sampling SO<sub>2</sub> reduces iodine monochloride and causes premature depletion of the iodine monochloride.

Iodine monochloride concentrations greater than  $10^{-4}$  molar inhibit the reduction of the  $\text{Hg}^{\text{II}}$  in the aeration cell. Condensation of water vapor on the optical cell windows causes a positive interference.

#### 4.0 METHOD TARGET COMPOUNDS

mercury compounds

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

mercury compounds

## EPA METHOD 101A

### Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR, Part 61, Appendix B. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

EPA Method 101A applies to the determination of particulate and gaseous mercury emissions from sewage sludge incinerators and other sources as specified in the regulations.

#### 2.0 SUMMARY OF METHOD

This method is similar to EPA Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for collection.

Particulate and gaseous mercury emissions are withdrawn isokinetically from the source and collected in acidic potassium permanganate solution. The mercury collected (in the mercuric form) is reduced to elemental mercury, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

#### 3.0 INTERFERENCES

Excessive oxidizable organic matter in the stack gas prematurely depletes the potassium permanganate solution and prevents further collection of mercury.

Condensation of water vapor on the optical cell windows causes a positive interference.

#### 4.0 METHOD TARGET COMPOUNDS

mercury compounds

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

mercury compounds

## EPA METHOD 103

### Beryllium Screening Method

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR, Part 61, Appendix B. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICABILITY

EPA Method 103 details guidelines and requirements for methods acceptable for use in determining beryllium emissions in ducts or stacks at stationary sources.

#### 2.0 SUMMARY OF METHOD

Beryllium emissions are isokinetically sampled from three points in a duct or stack. The collected sample is analyzed for beryllium using an appropriate analytical technique.

#### 3.0 INTERFERENCES

Not specified in Method.

#### 4.0 METHOD TARGET COMPOUNDS

beryllium compounds

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

beryllium compounds



## EPA METHOD 104

### Reference Method for Determination of Beryllium Emissions from Stationary Sources

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR, Part 61, Appendix B. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

EPA Method 104 is applicable to the determination of beryllium emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

#### 2.0 INTERFERENCES

Beryllium emissions are isokinetically sampled from the source, and the collected sample is digested and analyzed by atomic absorption spectrophotometry.

#### 3.0 INTERFERENCES

Not specified in method.

#### 4.0 METHOD TARGET COMPOUNDS

beryllium compounds

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

beryllium compounds

## EPA METHOD 106

### Determination of Vinyl Chloride from Stationary Sources

#### REFERENCE :

U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR, Part 61, Appendix B. Washington, D.C. Office of the Federal Register, July 1, 1987.

#### 1.0 SCOPE AND APPLICATION

EPA Method 106 is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, vinyl chloride, and polyvinyl chloride manufacturing processes. The method does not measure vinyl chloride contained in particulate matter.

#### 2.0 SUMMARY OF METHOD

An integrated bag sample of stack gas containing vinyl chloride is subjected to GC analysis using a flame ionization detector.

#### 3.0 INTERFERENCES

The chromatographic columns and the corresponding operating parameters described in Method 106 normally provide an adequate resolution of vinyl chloride. However, resolution interferences may be encountered on some sources.

#### 4.0 METHOD TARGET COMPOUNDS

vinyl chloride

## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

vinyl chloride

## EPA METHOD 114

### Test Methods for Monitoring Radionuclide Emissions from Stationary Sources

#### REFERENCE :

*Standards of Performance for New Stationary Sources.* Compilation. U. S. Environmental Protection Agency, EPA-340/1-77-015.

#### 1.0 SCOPE AND APPLICATION

EPA Method 114 contains guidance on continuous stack sampling for radionuclides and radiochemical methods used to analyze the sample. Radionuclides differ in the chemical and physical forms, half-lives, and type of radiation emitted. The appropriate type of sample extraction, collection, and analysis for an individual radionuclide depends on many interrelated factors, including the mixture of other radionuclides present. Therefore the procedure for radionuclide sampling and analysis described in Method 114 is actually a series of methods based on principles of measurement that provides the user with flexibility to choose the combination of sampling and analysis schemes most applicable to the effluent stream measured.

The analysis methods described in Method 114 are for commonly found radionuclides that have the greatest potential for public harm. The analyses are grouped according to the type of radiation emitted: alpha, beta, or gamma.

## 2.0 SUMMARY OF METHOD

### 2.1 Particulate Sampling

Continuous sampling can be performed according to EPA Method 5 or SW-846 Method 0020 to isokinetically sample radionuclides present as particulate matter. A probe is equipped with a filter that has a high efficiency for submicrometer particles. Additional guidance can be found in the American National Standards Institutes' "Guide to Sampling Airborne Radioactive Materials at Nuclear Facilities" (1969).

### 2.2 Gaseous Sampling

Radionuclides of hydrogen, oxygen, carbon, nitrogen, the noble gases, and in some cases iodine, will be in the gaseous form. Radionuclides of these elements will require direct flow into a counter or suitable bubblers to collect the radionuclides. The following are suggested media for gaseous sample collection:

<u>Radionuclide</u>	<u>Medium</u>
tritium	silica gel, molecular sieves, ethylene glycol, water
iodine	charcoal, metal zeolites, caustic solution
argon, krypton, xenon	charcoal or metal zeolites
oxygen, carbon, nitrogen, radon	caustic solution

## 2.3 Analysis

### 2.3.1 Alpha Analysis

The element of interest is separated from the sample matrix by precipitation, ion exchange, or solvent extraction; or by carriers using electrodeposition or coprecipitation. The alpha energy is measured by alpha spectrometry or an alpha counter. Particulate samples can be analyzed from the surface of the filter directly by alpha spectrometry or an alpha counter.

2.3.1.1 Uranium Analysis. Uranium is dissolved and extracted into hexane. The extract can be analyzed colorimetrically by adding dibenzoylmethane, or fluorometrically after fusion with sodium fluoride-lithium fluoride.

2.3.1.2 Radon-222. Radon in the gaseous form can be detected continuously using a calibrated scintillation cell

### 2.3.2 Beta Analysis

Gaseous samples can be continuously analyzed by flow through a ionization chamber or another beta detector such as a Geiger-Müller tube. In non-gaseous sample mixtures, the element of interest is separated from other radionuclides by precipitation, distillation, ion exchange, solvent extraction, or carriers. The extracted radionuclide is analyzed with a scintillation cell or a beta counter. Particulate samples can be analyzed directly from the filter with a beta counter when it is known that the sample contains only the radionuclide of interest.

### 2.3.3 Gamma Analysis

High resolution gamma spectroscopy can be used to directly measure gaseous, liquid, or particulate gamma-emitting radionuclides. Prior chemical separation is not usually necessary. For simple mixtures, low resolution gamma spectroscopy can be used. Single channel gamma spectrometry can be used when only one gamma-emitting radionuclide is present.

### 3.0 INTERFERENCES

Some analysis methods state that only one radionuclide can be present without interference in the analysis. Sufficient separation must occur to produce a pure sample from combined extracts and with a correction for chemical yield.

### 4.0 METHOD TARGET COMPOUNDS

carbon\*  
hydrogen\*  
iodine\*  
nitrogen\*  
noble gases (including argon)  
oxygen\*  
polonium-210  
radon-222  
tritium\*  
uranium

\* Usually gaseous

NOTE: Method target compounds are not limited to those listed above.



## 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

radionuclides



## EPA METHODS 515/615

Determination of Chlorinated Herbicides in Drinking Water (Method 515)  
Determination of Chlorinated Herbicides in Industrial and Municipal  
Wastewater (Method 615)

### REFERENCES:

Method 515 - Supplement to "Method for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water." EPA EMSL. September 1986.

Method 615 - Pressley, Thomas A., and Longbottom, James E., EPA EMSL. "The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater." January 1982.

### 1.0 SCOPE AND APPLICATION

EPA Methods 515 and 615 are used to determine certain chlorinated acid herbicides in drinking water (Method 515) and wastewater (Method 615). Chlorinated herbicides in air will be distributed between particulate and gas phase, depending upon temperature.

### 2.0 SUMMARY OF METHOD

Methods 515 and 615 need to be modified to allow extraction of solid sorbent used for air sampling. The original methods require acidifying approximately 1 L of sample. The acid herbicides and their esters and salts are then extracted with ethyl ether using a separatory funnel. The esters are hydrolyzed and converted to acid salts with potassium hydroxide solution. The aqueous phase containing the acid salts is then solvent-washed to remove extraneous organic material. After acidification, the acids are extracted into organic phase and the sample volume reduced to 5 mL in methyl t-butyl ether (MTBE) with a K-D concentrator. The acids are

converted to their methyl ester using diazomethane as the derivatizing agent. Excess reagent is removed and the esters are determined by electron capture gas chromatography.

### 3.0 INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, and glassware. Therefore, care must be taken during sample preparation to ensure minimal interferences.

The acid forms of the herbicides are strong organic acids that react readily with alkaline substances and can be lost during analysis. Glassware and glass wool must be acid-rinsed, and the sodium sulfate must be acidified prior to use to avoid this possibility.

Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the analysis. Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

### 4.0 METHOD TARGET COMPOUNDS

2,4-D  
2,4-DB  
dalapon  
dicamba  
dichlorprop\*  
dinoseb  
MCPA\*  
MCP\*  
pentachlorophenol (PCP)  
picloram

2,4,5-T

2,4,5-TP (silvex)

\* Method 615 only

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

2,4-D esters and salts

pentachlorophenol



## EPA METHOD 531

### Measurement of N-Methyl Carbamoyloximes and N-Methyl Carbamates in Drinking Water by Direct Aqueous Injection HPLC with Post-Column Derivatization

#### REFERENCE :

U.S. Environmental Protection Agency, EPA/600/485/054

#### 1.0 SCOPE AND APPLICATION

EPA Method 531 is used to identify and measure N-methylcarbamoyloximes and N-methyl carbamates in finished drinking water, raw source water, or drinking water at any treatment stage.

#### 2.0 SUMMARY OF METHOD

Air samples are collected using EPA sampling Method 0010. The solid sorbents used in Method 0010 are extracted with methylene chloride. Extensive modification of chromatographic conditions of Method 531 will be required to perform analysis of air samples.

In Method 531, a high performance liquid chromatographic (HPLC) system capable of injecting 200 to 400  $\mu\text{L}$  aliquots and performing binary linear gradients at a constant flow rate is used for sample analysis. The recommended column is a 10 cm long x 8 mm ID radially compressed HPLC column packed with 10  $\mu\text{m}$   $\mu$ -Bondapak  $\text{C}_{18}$  or equivalent. Use of a guard column is also recommended. A post-column reactor capable of mixing reagents into the mobile phase is needed. The fluorescence detector should be capable of excitation at 230 nm and detecting emission energies greater than 419 nm. Fluorometers should have dispersive optics for excitation and be able to utilize either filters or dispersive optics at the emission detector.

The water sample is filtered and a 400-μL aliquot is injected into a reverse phase HPLC column. Separation of the analytes is achieved using gradient elution chromatography. After elution from the HPLC column, the analytes are hydrolyzed with 0.05N sodium hydroxide at 95°C. The methyl amine formed during hydrolysis is reacted with o-phthalaldehydes to form a highly fluorescent derivative which is detected using a fluorescence detector.

The analytes are identified by comparing the retention times of the unknowns to the retention times of standards, and the concentration of individual compounds in the sample is determined.

### 3.0 INTERFERENCES

Any matrix interferences that will interfere with the chromatography are interferences for the method. Matrix interference that will produce saturation of the chromatographic system will interfere with the analysis of target compounds even if the fluorescence detector will resolve the compounds.

### 4.0 METHOD TARGET COMPOUNDS

- aldicarb
- aldicarb sulfone
- aldicarb sulfoxide
- carbaryl
- carbofuran
- 3-hydroxycarbofuran
- methomyl
- oxamyl

### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS



carbaryl

dimethyl carbamoyl chloride



## EPA METHOD 632

### Determination of Carbofuran, Fluometuron, Methomyl, and Oxamyl in Wastewater

#### REFERENCE :

U. S. Environmental Protection Agency, EMSL, Physical and Chemical Methods Branch.  
November, 1985.

#### 1.0 SCOPE AND APPLICATION

EPA Method 632 is a high performance liquid chromatographic (HPLC) method used to determine certain carbamate and urea pesticides in industrial and municipal wastewater discharges.

#### 2.0 SUMMARY OF METHOD

Air samples may be obtained using EPA Method 0010, and the solid sorbent extracted with methylene chloride.

When Method 632 is applied to wastewater, a measured volume of sample (about 1 L) is solvent-extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and concentrated to a volume of 10 mL or less. HPLC conditions are described that permit the separation and measurement of the compounds in the extract.

The HPLC analytical system should include high pressure syringes or sample injection loop, analytical columns, ultraviolet (UV) detector and strip chart recorder. A guard column is recommended for all applications. The recommended analytical column is a 30 cm long x 4 mm

ID stainless steel packed with  $\mu$ -Bondapak C<sub>18</sub> (10  $\mu$ m) or equivalent with Whatman Co. PELL ODS (30 - 38  $\mu$ m) guard column, 7 cm long x 4 mm ID. The UV detector should be capable of monitoring at 254 nm and 280 nm.

The HPLC system may be calibrated using either the external or internal standard technique. The standards and extracts must be in the solvent (acetonitrile or methanol) compatible with the mobile phase.

The sample extract is injected (around 10  $\mu$ L), the resulting peak size in area or peak height units is recorded, and the concentration of individual compounds in the sample is determined.

### 3.0 INTERFERENCES

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality sampled.

### 4.0 METHOD TARGET COMPOUNDS

aminocarb  
barban  
carbaryl  
carbofuran  
chlorpropham  
diuron  
fenuron  
fenuron-TCA  
fluometuron

linuron  
methiocarb  
methomyl  
mexacarbate  
monuron  
monuron-TCA  
neburon  
oxamyl  
propham  
propoxur  
siduron  
swep

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

caprolactam  
ethylene thiourea  
ethyl carbamate  
propoxur



## EPA METHOD 680

### Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry

#### REFERENCE :

U. S. Environmental Protection Agency, EMSL, Physical and Chemical Methods Branch.  
November, 1985.

#### 1.0 SCOPE AND APPLICATION

EPA Method 680 provides procedures for mass spectrometric determination of polychlorinated biphenyls (PCBs) and pesticides in water, soil, or sediment. These compounds in air will be mostly associated with particulate, although some can exist in the gas phase if the source temperature is high enough and the compound is sufficiently stable. A modification of the method in order to analyze air samples is possible.

#### 2.0 SUMMARY OF METHOD

Sample preparation consists of placing a 1-L water sample in a separatory funnel, extracting with methylene chloride, followed by hexane exchange. Method 680 must be modified, however, to allow for extraction of solid sorbent used for air sampling. Sample extract components are then separated with capillary column gas chromatography (GC) and identified and measured with low resolution electron ionization mass spectrometry. Two surrogate compounds and two internal standards are added to each sample. Because of the multi-compound characteristics of PCBs, they are identified and measured as isomer groups. A concentration is measured for each PCB isomer group, and total PCB concentration in each sample extract is obtained by summing isomer group concentrations.

### 3.0 INTERFERENCES

Interferences may be caused by contaminants in solvents, reagents, and glassware. Therefore, care must be taken in sample preparation to assure minimal interferences.

With both pesticides and PCBs, interferences can be caused by the presence of much greater quantities of other sample components that overload the capillary column. Therefore, additional sample cleanup procedures may be necessary to eliminate these interferences. Capillary column GC retention times and the compound-specific characteristics of mass spectra eliminate many of the interferences that formerly were of concern with pesticide/PCB determinations with electron capture detection. The approach and identification criteria used in this method eliminate interference by most chlorinated compounds other than other PCBs. With the isomer groups approach, coeluting PCBs that contain the same number of chlorines are identified and measured together. Therefore, coeluting PCBs are a problem only if they contain a different number of chlorine atoms.

### 4.0 METHOD TARGET COMPOUNDS

aldrin  
alpha-BHC  
beta-BHC  
chlordane  
delta-BHC  
4,4'-DDD  
4,4'-DDE  
4,4'-DDT  
decachlorobiphenyl  
dichlorobiphenyls  
dieldrin



endosulfan I  
endosulfan II  
endosulfan sulfate  
endrin  
endrin aldehyde  
heptachlor  
heptachlor epoxide  
heptachlorobiphenyls  
hexachlorobiphenyls  
lindane  
methoxychlor  
monochlorobiphenyls  
nonachlorobiphenyls  
octachlorobiphenyls  
pentachlorobiphenyls  
tetrachlorobiphenyls  
trichlorobiphenyls

#### 5.0 APPLICABLE CAA AMENDMENTS POLLUTANTS

chlordane  
4,4'-DDE  
polychlorinated biphenyls  
heptachlor  
lindane  
methoxychlor  
toxaphene