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CHARACTERISATION OF INCINERATOR STACK EMISSIONS

CHAPTER 2

CHARACTERISATION OF INCINERATOR STACK EMISSIONS

1. INTRODUCTION

The Guidelines for Class 2B (medical waste) incinerators stipulate that the Chief Officer may require that the certificate holder have tests carried out by an accredited person or body to determine stack and/or ground level concentrations of the following substances:

Max 0.05 mg/m^3 (as measured in the chimney)
Cadmium and compounds as Cd
Mercury Hg

Max 0.5 mg/m^3 (as measured in the chimney)
Lead Pb

Chloride as	HCl	<30 mg/m^3
Sulphur dioxide	SO_2	<25 mg/m^3

The average dioxin and furan concentration in the emissions of Class 2B incinerators should not exceed 80 ng/m^3 total dioxin and furans if measured for a period of 6 to 16 hours, or 0.2 ng International Toxic Equivalent (TEQ) /m^3 , or result in an excess cancer risk of 1:100 000 on the basis of annual average exposure.

The total particulate emissions should not exceed 180 mg/m^3. All pollutant concentrations should be expressed at 0 °C and 101.3 kPa, dry gas and 11 per cent oxygen.

The opacity of the smoke should not exceed 20 per cent.

All the emissions to air other than steam or water vapor should be odourless and free from mist, fume and droplets.

The Chief Officer may request analytical information on any other substances deemed necessary, eg polycyclic aromatic hydrocarbons, benzene, etc. It is known that a wide range of other metals are of interest, and stack surveys normally focus on a wider range of substances than those listed in the guidelines for medical waste incinerators. Medical waste may contain a wide range of hazardous metals, and the list under Schedule 2, Process 39 of the Atmospheric Pollution Prevention Act is likely to be inadequate.

Recommended sampling and analytical methods are described in the sections below. These are methods prescribed by the USA Environmental Protection Agency

[USEPA, 1996], and are used by the leading analytical laboratories in South Africa. The methods are recognised internationally. Other methods may be used, eg those from the American Society for Testing and Materials (ASTM), British methods, or any other official methods that have been validated. There are no official local methods for stack sampling, eg SABS methods or standards.

2. PRIORITY SUBSTANCES FOR MONITORING

The list of hazardous air pollutants (HAP's) compiled under the USA Clean Air Act Amendments of 1990, provides a reference for the selection of toxicants that may be relevant in certain emission sources. Although the list in the South African guidelines for medical waste incinerators is rather limited, it is important to note that many of the substances in the HAP's list may be of concern in medical waste incineration. The list is presented in Table 2.1. Of course, there are many substances in the list that are not of any interest in medical waste incineration.

This section presents some background information on substances that may be present in medical waste, or that may form in the combustion process. The part on dioxins and furans is presented in more detail, because of the special significance of this class of compounds in medical waste incineration.

2.1 METALS CLASSIFIED AS HAZARDOUS AIR POLLUTANTS

Although it is generally acknowledged that toxicity varies among compounds of an element where one or more of the compounds of an element are known to be toxic or carcinogenic, USEPA concluded that all compounds of such an element should be included in the list. USEPA has also stated that in the absence of better site-specific information, metals that take part in the combustion process may be assumed to convert completely into the lowest molecular mass oxides of the particular metals.

The metals discussed below were selected from the lists of emission guidelines for medical waste incinerators for the European Union, Germany, and USA.

2.1.1 **Antimony compounds**

There is sufficient evidence from animal studies and limited evidence from human epidemiologic studies that antimony trioxide (Sb_2O_3) is carcinogenic. This is based on data for total lung tumors in antimony trioxide-exposed female rats [Groth *et al,* 1986]. These animal studies followed reports of excess lung cancers in British antimony workers. The human data were however not complete and conclusive. Although the issue is complex, it is considered prudent in the interest of public health protection to consider all airborne antimony compounds as potential carcinogens.

2.1.2 Arsenic compounds

Inorganic compounds are confirmed human carcinogens producing tumors of the mouth, esophagus, larynx, bladder, and paranasal sinus. Arsenic compounds are recognised carcinogens of the skin, lungs, and liver. Some arsenic compounds have been shown to

be teratogenic in test animals [Calabrese and Kenyon, 1991]. The compound that can be expected to form is As_2O_3.

The formation of focal emphysema in the lungs eventually leads to dyspnoea and a low gas transfer factor. USEPA has classified cadmium as a Class B1 human carcinogen, based on occupational studies that showed cancer of the respiratory tract [HEAST, 1990].

Table 2.1: USEPA list of hazardous air pollutants

Acetaldehyde
Acetamide
Acetonitrile
Acetophenone
2-Acetylaminofluorene
Acrolein
Acrylamide
Acrylic acid
Acrylonitrile
Allyl chloride
4-Aminobiphenyl
Aniline
o-Anisidine
Asbestos
Benzene (including from gasoline)
Benzidine
Benzotrichloride
Benzyl chloride
Biphenyl
Bis(2-ethylhexyl)phthalate (DEHP)
Bis(chloromethyl)ether
Bromoform
1,3-Butadiene
Calcium cyanamide
Caprolactam
Captan
Carbaryl
Carbon disulfide
Carbon tetrachloride
Carbonyl sulfide
Catechol
Chloramben
Chlordane
Chlorine
Chloroacetic acid
2-Chloroacetophenone
Chlorobenzene
Chlorobenzilate
Chloroform
Chloromethyl methyl ether
Chloroprene
Cresols/cresylic acid (isomers and mixture)
o-Cresol
m-Cresol
p-Cresol
Cumene
2,4-D, salts and esters
DDE
Diazomethane
Dibenzofurans
1,2-Dibromo-3-chloropropane
Dibutylphthlate
1,4-Dichlorobenzene(p)
3,3-Dichlorobenzidene
Dichloroethyl ether (bis(2-chloroethyl)ether)
1,3-Dichloropropene
Dichlorvos
Diethanolamine
N,N-Diethylaniline (*N,N*-dimethylaniline)
Diethyl sulfate
3,3-Dimethoxybenzidene
Dimethyl aminoazobenzene
3,3'-Dimethyl benzidene
Dimethyl carbamoyl chloride
Dimethyl formamide
1,1-Dimethyl hydrazine
Dimethyl phthalate
Dimethyl sulfate
4,6-Dinitro-*o*-cresol and salts
2,4-Dinitrophenol
2,4-Dinitrotoluene
1,4-Dioxane (1,4-Diethyleneoxide)
1,2-Diphenylhydrazine
Epichlorohydrin (1-chloro-2,3-epoxypropane)
1,2-Epoxybutane
Ethyl acrylate
Ethyl benzene
Ethyl carbamate (urethane)
Ethyl chloride (chlorethane)
Ethylene dibromaide (dibromoethane)
Ethylene dichloride (1,2-dichloroethane)
Ethylene glycol
Ethylene imine (aziridine)
Ethylene oxide
Ethylene thiourea
Ethylidine dichloride (1,1-dichloroethane)
Formaldehyde
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexamethylene-1,6-diisocyanate
Hexamethylphosphoramide
Hexane
Hydrazine
Hydrochloric acid
Hydrogen fluoride (hydrofluoric acid)
Hydroquinone
Isophorone
Lindane (all isomers)
Maleic anhydride
Methanol
Methoxychlor
Methyl bromide (bromomethane)
Methyl chloride (chloromethane)
Methyl chloroform (1,1,1-trichloroethane)
Methyl ethyl ketone (2-butanone)
Methyl hydrazine
Methyl iodide (iodomethane)
Methyl isobutyl ketone (hexone)
Methyl isocyanate

Table 2.1: USEPA list of hazardous air pollutants (continued)

Methyl methacrylate
Methyl-*t*-butyl ether
4,4-Methylene bis(2-chloroaniline)
Methylene chloride (dichloromethane)
Methylene diphenyl diisocyanate (MDI)
4,4'-Methylenedianiline
Naphthalene
Nitrobenzene
4-Nitrobiphenyl
4-Nitrophenol
2-Nitropropane
N-Nitroso-*N*-methylurea
N-Nitrosodimethylamine
N-Nitrosomorpholine
Parathion
Pentachloronitrobenzene (quintobenzene)
Pentachlorophenol
Phenol
p-Phenylenediamine
Phosgene
Phosphine
Phosphorus
Phthalic anhydride
Polychlorinated biphenyls (aroclors)
1,3-Propane sultone
β-Propiolactone
Propionaldehyde
Propoxur (Baygon)
Propylene dichloride (1,2-dichloropropane)
Propylene oxide
1,2-Propylenimine (2-methylaziridine)
Quinoline
Quinone
Styrene
Styrene oxide
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin
1,1,2,2-Tetrachloroethane
Tetrachloroethylene (perchloroethylene)
Titanium tetrachloride
Toluene
2,4-Toluene diamine
2,4-Toluene diisocyanate
o-Toluidine
Toxaphene (chlorinated camphene)
1,2,4-Trichlorobenzene
1,1,2-Trichloroethane
Trichloroethylene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
Triethylamine
Trifluralin
2,2,4-Trimethylpentane
Vinyl acetate
Vinyl bromide
Vinyl chloride
Vinylidene chloride (1,1-dichloroethylene)
Xylenes (isomers and mixtures)
o-Xylene
m-Xylene
p-Xylene

Antimony compounds
Arsenic compounds
Beryllium compounds
Cadmium compounds
Chromium compounds
Cobalt compounds
Coke oven emissions
Cyanide compounds
Glycol ethers
Lead compounds
Manganese compounds
Mercury
Fine mineral fibers
Nickel compounds
Polycyclic organic compounds
Radionuclides
Selenium compounds

2.1.3 Cadmium compounds

Cadmium salts are poorly absorbed from the gastrointestinal tract, and inhalation is the major exposure route of concern. Absorbed cadmium is bound to plasma proteins and transported to the liver from where it is finally accumulated in the kidneys [Friberg, Nordberg and Vouk, 1979]. Toxic effects are due to two biochemical mechanisms, ie through replacement of the essential metals zinc and copper, and as a result of the formation of metallothionein, a low molecular mass protein with a high proportion of sulphur-containing amino acids in its structure. In the kidneys, cadmium ions are released and stimulate the formation of more metallothionein. Eventually this leads to kidney damage.

2.1.4 Chromium compounds

The most important features of chronic effects of chromium compounds are changes in the skin and mucous membranes, and allergic dermal and pulmonary effects [Calabrese and Kenyon, 1991]. Important systemic effects occur in the kidneys, liver, gastrointestinal tract, and circulatory system. However, these are found for occupational exposures at high concentrations of chromates and are unlikely to occur with environmental exposures. The absorption of chromium aerosols depends on the physical and chemical properties of the compounds and the activity of alveolar macrophages and lymphatic drainage.

Hexavalent chromium salts (especially those with low water solubility) are human carcinogens of the lungs, nasal cavity and paranasal sinus. These compounds are also suspected carcinogens of the stomach and larynx [HEAST, 1990].

2.1.5 Cobalt compounds

Cobalt is considered a micro-nutrient based on its necessity as a functional part of the vitamin B 12 molecule. This is however its only known nutritional benefit to humans. It is now recognised that chronic exposure to cobalt may cause pulmonary hypersensitivity and diffuse interstitial fibrosis of the lung. Burning of coal has been identified as one of the major sources of cobalt in the atmosphere [Calabrese and Kenyon, 1991].

2.1.6 Copper

Inhalation of dust by test animals has demonstrated hemolysis of the red blood cells, deposition of hemufuscin in the liver and pancreas, and damage to the lung cells.

Chronic exposures to copper and certain copper compounds can lead to irritation of the skin and conjunctivae which may be an allergic phenomenon. Some compounds are irritating to the eyes and upper respiratory tract. Chronic exposure through ingestion may lead to local gastrointestinal irritation [HEAST, 1990].

Although copper is not classified as a carcinogen, it has been observed that there is an excess of cancer cases in the copper smelting industry [Lewis, 1996].

2.1.7 Lead compounds

Inorganic lead is poorly absorbed from the gastrointestinal tract. Pulmonary absorption is much more effective. Organo-lead compounds can be absorbed through the skin. The human skeleton acts as the main depository of lead [Friberg, Nordberg and Vouk, 1979]. USEPA has listed central nervous system effects as the primary result of chronic exposure to environmental levels [HEAST, 1990]. Lead anaemia occurs only from inorganic lead poisoning and manifests itself late in the disease.

Lead is classified by USEPA as a Class B2 (probable) human carcinogen [HEAST, 19901. There are however many uncertainties, especially with regard to lead pharmacokinetics, and current risk assessment techniques cannot be applied. The National Ambient Air Quality Standard (NAAQS) for lead is considered the best ambient air level goal. The NAAQS assumes that 80 per cent of the lead intake of humans comes

from non-air sources.

2.1.8 Manganese compounds

Manganese is an essential trace element in the human body. The rate of absorption from the gut is very slow and the major route of exposure is therefore through inhalation. After absorption, plasma clearance occurs rapidly. The metal tends to accumulate in tissues rich in mitochondria, mainly the liver, but also in the kidneys, and to a much lesser extent, the bone [Friberg, Nordberg and Vouk, 1979].

The central nervous system is the major site of damage as a result of chronic manganese poisoning. The onset is slow and early symptoms are non-specific. These include headache, lassitude, sleeplessness and pains in the joints and muscles. Neurological signs are due to damage of the basal ganglia and they resemble those of Parkinson's disease quite closely.

2.1.9 Mercury

Inhalation is a prominent route of exposure, because approximately 80 per cent of inhaled mercury vapour is absorbed from the lungs [Friberg, Nordberg and Vouk, 19791. During subsequent distribution in the body it is rapidly oxidised and bound to protein. Elemental mercury can cross the blood-brain barrier and the placenta. Inorganic mercury compounds do not cross these barriers, but are distributed widely to other tissues. Absorption of metallic mercury from the gastrointestinal tract is low, but absorption of organic mercuries is virtually complete. Organic mercury compounds rapidly penetrate the blood-brain barrier and the placenta. The kidneys, and to a lesser extent the liver, carry the greatest body burden of mercury.

2.1.10 Nickel compounds

Nickel is poorly absorbed from the gastrointestinal tract, but is distributed widely in the human body. The inhalation route is a prominent exposure pathway, and it is known that the lungs and brain contain the highest concentrations of nickel. Some nickel compounds are highly irritating to the lungs [Friberg, Nordberg and Vouk, 1979]. All airborne nickel dusts are regarded as carcinogens by inhalation. The formation of carcinoma of the nasal passages and air sinuses are prominently related to nickel exposure [Calabrese and Kenyon, 1991]

2.1.11 Selenium compounds

Selenium is an essential element for normal growth in some animals. Elemental selenium has low acute systemic toxicity. Chronic effects of exposure to selenium include amyotrophic lateral sclerosis in humans, irritation of the upper respiratory tract, and vague gastrointestinal disturbances. It may also cause liver damage. Selenium compounds are experimental carcinogens. In the atmosphere, selenium is predominantly associated with particulates. Up to 90 per cent of the selenium content in ambient air is emitted from fossil fuel burning, in the form of elemental selenium and selenium dioxide.

The latter reacts with water to form selenious acid, which is an irritant. In an urban atmosphere, inhalation of selenium will not add significantly to the body burden [Medinsky *et al,* 1985].

2.1.12 Thallium

It appears that the thallium contents of South African coals have not been of any interest, and levels are not known. Some of the thallium compounds are very toxic [Lewis, 1996], and the element is listed in the South African guidelines for control of incinerator emissions at the same level as cadmium and mercury.

2.1.13 Tin

The toxicity of tin after inhalation or dietary exposure is low. Some organotin compounds are highly toxic, especially triethyltin [Friberg *et al*, 1980].

2.1.14 Vanadium compounds

The predominant critical effects associated with vanadium pentoxide exposure is irritation of the upper respiratory tract with mucous discharge, lower respiratory tract irritation with bronchitis, bronchospasm and coughing, and depending on concentrations, eye irritation and skin irritation in the form of a sensation of heat or itching.

2.2 HYDROCHLORIC ACID

It is generally accepted that the major health effects associated with hydrochloric acid is irritation. Allowable ambient air concentrations have been proposed as 0.15 mg/m^3 for a 24-hour time-weighted average, and 0.007 mg/m^3 for an annual average.

2.3 SULPHUR DIOXIDE

Sulphur compounds dispersed into the air undergo conversion in a complex process with many interrelated variables. The presence of particulates and catalysis play a significant role in the conversion reactions. Photochemical reactions also occur. SO_2 dissolves readily in water to form sulphurous acid. This may be oxidised slowly to sulphuric acid by oxygen from the air. Sulphur dioxide can also react catalytically or photochemically in the gas phase with other air pollutants to form sulphur trioxide, sulphuric acid, and sulphates. Sulphur trioxide is highly reactive and is transformed rapidly to sulphuric acid in the presence of moisture. Overall, the half-life of sulphur dioxide in air is estimated to be three to five hours.
The toxicology of sulphur dioxide has been studied widely over many years, and a large volume of data can be found in some of the older references. Inhaled sulphur dioxide is absorbed from the respiratory tract into the blood system, from where it is distributed widely through the body [WHO, 1979]. The water solubility of sulphur dioxide enhances absorption by the nasal mucosa.

Ambient air polluted with sulphur dioxide contains, as a general rule, also H_2SO_3 and

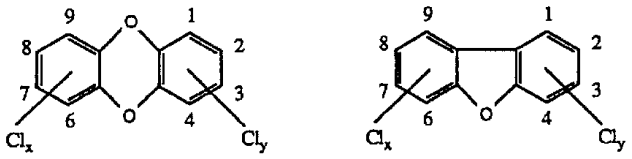
H_2SO_4. These acids may be the actual stimuli of the receptors. A basic physiological response to inhalation of sulphur dioxide is a degree of bronchial constriction, which is reflected in a measurable increase in flow resistance [Doull *et al*, 1980]. This is accompanied by a decrease in compliance of the lungs, resulting in a decrease in frequency of breathing. The finding that sulphur dioxide is deposited in the upper airways does not reduce its impact as a chronic, bronchoconstrictive irritant, but eliminates it as a single cause of lung tissue destruction. Recent work confirmed consistent effects on forced vital capacity (FVC) and forced expiratory volume at one second (FEV1) for nitrogen dioxide, sulphur dioxide and particulate matter (PM10) in a cross-sectional population-based sample of adults [Ackermann-Liebrich *et al*, 1997]. In recent studies on 12 European cities in the APHEA project (Air Pollution Health: a European Approach), it was found that an increase of 50 $\Phi g/m^3$ in sulphur dioxide was associated with a 3 % increase in daily mortality. These results confirmed older data on short-term health effects [Jaeger, 1982]. Sulphur dioxide is not listed as a carcinogen.

2.4 POLYCHLORINATED DIOXINS ANF FURANS

Dioxins and furans have been characterised as among the most toxic "man-made' chemicals ever studied. These compounds are extremely potent in producing a variety of effects in experimental animals based on traditional toxicology studies at levels hundreds or thousands of times lower than most synthetic chemicals of environmental interest. In addition, human studies demonstrate that exposure to dioxins and related compounds is associated with subtle biochemical and biological changes whose clinical significance is as yet unknown and, at higher levels with chloracne, a serious skin condition. Laboratory studies indicated that exposure to dioxin-like compounds may be associated with other serious health effects, including cancer [USEPA, 1994].

Polychlorinated dibenzodioxins (CDD's) and polychlorinated dibenzofurans (CDF's) are chemically classified as halogenated aromatic hydrocarbons. There are 75 possible congeners of CDD's and 135 different CDF congeners. Only 7 of the 75 possible CDD congeners and 10 of the 135 possible CDF congeners, those with substitution in the 2,3,7,8 positions, are believed to have dioxin-like toxicity. Basic structures are presented in Figure 2.1.

X =1 to 4, Y = 1 to 4, X + Y ≥ 1



PCDDs PCDFs

Figure 2.1: Chemical structures of dioxins and furans

Dioxin-like compounds are defined to include those compounds with non-zero Toxicity Equivalency Factor values (TEF's) as defined in a 1989 international scheme, I-TEF's/89. This procedure was developed under the auspices of the North Atlantic Treaty

Organizations Committee on Challenges of Modern Society (NATO-CCMS, 1988) to promote international consistency in addressing contamination involving CDD's and CDF's. The procedure relates the toxicity of 210 structurally related individual CDD and CDF congeners and is based on a limited data base of *in vivo* and *in vitro* tests. By relating the toxicity of 209 CDD's and CDF's to the highly-studied 2,3,7,8-tetrachloro dibenzodioxin (TCDD), the approach simplifies the assessment of risks involving exposures to mixtures of CDD's and CDF's.

The United States of America Environmental Protection Agency (USEPA) has adopted the I-TEF's/89 as an interim procedure for assessing the risks associated with exposure to dioxin mixtures. Table 2.2 lists Toxicity Equivalency Factors for CDD's and CDF's.

2,3,7,8-Tetrachloro dibenzodioxin has been classified by the Human Health Assessment Group of the USEPA as a Class B2 carcinogen. Sufficient evidence exists for carcinogenicity in animals, but there is inadequate or a lack of evidence in humans. In the interpretation of toxicological information it is inferred that humans and animals are similar in intrinsic susceptability to toxic chemicals and that animal data can be used as a surrogate to human data. USEPA considers the likelihood that a chemical will have adverse health effects in humans to increase as similar results are observed across sexes, strains, species, and routes of exposure in animal studies. As a matter of science policy, the study on the most sensitive species (the species showing the toxic effect at the lowest administered dose) is selected as the critical study for the basis of the toxicity value.

Table 2.2: Toxicity Equivalency Factors (TEF's) for CDD's and CDF's

COMPOUND	TEF
Mono-, Di- and TriCDD's	0
2,3,7,8-TCDD	1
Other TCDD's	0
2,3,7,8-PentaCDD's	0,5
Other PeCDD's	0
2,3,7,8-HexaCDD	0,1
Other HxCDD's	0
2,3,7,8-HeptaCDD	0,01
Other HpCDD's	0
OctaCDD	0,001
Mono-, Di- and TriCDF's	0
2,3,7,8-TCDF	0,1
Other TCDF's	0
1,2,3,7,8-PentaCDF	0,05
2,3,4,7,8-PentaCDF	0,5
Other PeCDF's	0
2,3,7,8-HexaCDF	0.1
2,3,7,8-HeptaCDF	0,01
Other HpCDF's	0
OctaCDF	0,001

In general, the assessment of human health risks to a mixture of dioxins and furans, using the TEF procedure, involves the following steps:

1. Analytical determination of the individual CDD's and CDF's in the sample.
2. Multiplication of congener concentrations in the sample by the TEF's in Table 2.1 to express the concentrations in terms of 2,3,7,8-TCDD equivalents (TEQ's).
3. Summation of the products in step 2 to obtain the total TEQ's in the sample.
4. Determination of human exposure to the mixture in question, expressed in terms of TEQ's.
5. Combination of exposure information with toxicity information on 2,3,7,8-TCDD to estimate risk.

2.5 VOLATILE ORGANIC COMPOUNDS

Potentially, a wide range of volatile organic compounds may form during combustion of medical waste. Guidelines do not prescribe measurement of particular VOC's. The term VOC's is used for organic compounds with boiling points typically below 100 °C, whereas semi-volatile organic compounds have boiling points above 100 °C. With analytical methods there is some overlap in determining compounds with boiling points between 80 and 120 °C. Sample preparation for semi-volatile organics involves a step where the sample is concentrated by evaporation of the extraction solvent. Some of the volatile organic compounds will be lost in this step, and the method is therefore suitable only for the higher boiling point substances. Volatiles, on the other hand, are injected into the analytical system by thermal desorption from the collection medium. Substances with higher boiling points will not be desorbed rapidly.

In the UK, measurement of total volatile organic compounds is required. This is normally a semi-quantitative measurement conducted with a flame ionisation detector. The temperatures that are maintained in secondary chambers of medical waste incinerators, under conditions of sufficient oxygen and adequate turbulence and mixing time, minimise the possibility of significant emissions of VOC's. The guideline concentration for total VOC's is determined on the potential that the VOC profile is made up out of the most toxic collection of compounds. The method is based on order-of-magnitude comparisons with numbers, and serves only as an indicator of significant hazards.

It is not practical to review toxicities of the entire list of organic HAP's presented in Table 2.1. Benzene is of prominent interest, because it forms in combustion processes, and is a confirmed human carcinogen with the haematopoietic (blood) system as the carcinogenic endpoint (leukemia). Many chlorinated organic compounds are lung, liver, and kidney toxicants, often with carcinogenic potency. Aliphatic hydrocarbons tend to have effects on the central nervous system. Whilst aldehydes are known to be irritants, formaldehyde is a probable human carcinogen (cancer of the nasal cavity).

It is not simple to select organic substances as targets for monitoring. The only criterion is an assessment of the likelihood of formation of certain compounds, based on published monitoring information. Fortunately, the analytical method used for identification of organic compounds covers a wide range of substances. From a single sample, a wide range of aromatic and aliphatic compounds, as well as their halogen-substituted families, can be determined with a gas chromatograph-mass spectrometer system (GC-MS).

There are some limitations with chromatographic columns over the entire range of compounds from the non-polar to the polar end of the range, but this can be overcome in the analytical process. A more important limitation lies in the sampling step. Different methods are required for different classes of VOC's, as outlined in the sections below. In summary, it can be stated that sampling and analytical methods are available to determine the entire list of volatile organics in the HAP's list.

2.6 SEMI-VOLATILE ORGANIC COMPOUNDS

Polynuclear aromatic hydrocarbons (PAH's) [EPRI, 1994] are known to form in combustion processes, especially as products of incomplete combustion. They consist of aromatic rings (benzene) that do not have carbon substitution within the ring structure of the side chains. For example, nitrogen substituted cyclic compounds are classified as amines and are not considered in the category of PAH's. The number of rings appears to affect carcinogenic potential. In general, it is the four and five ring compounds that likely to be carcinogenic, while the two and three ring compounds or those greater than five rings are not likely to exhibit tumor production activity. There are exceptions, however.

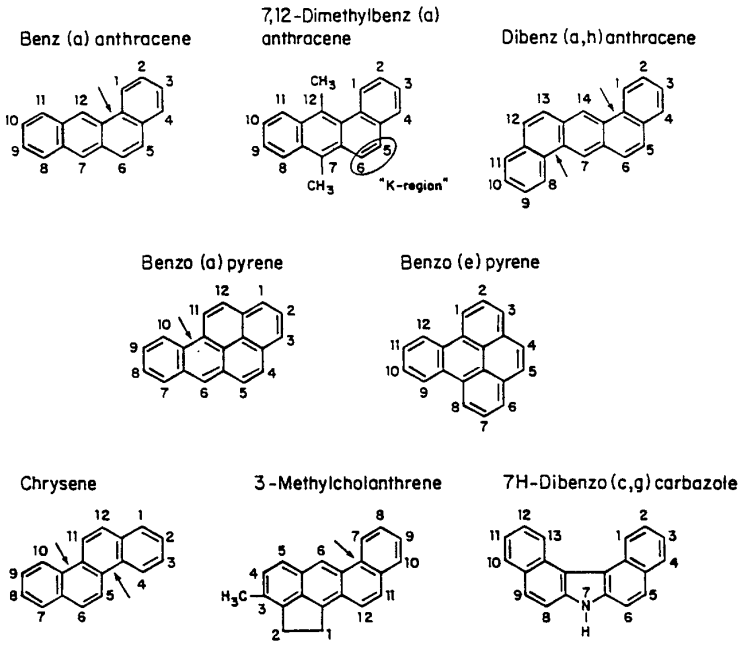


Figure 2.2: Examples of polynuclear aromatic hydrocarbons

The following PAH,s have caused cancer in laboratory animals through ingestion, dermal contact, or inhalation:

Benz[a]anthracene	Benzo[a]pyrene	Benzo[b]fluoranthene
Benzo[k]fluoranthene	Chrysene	Dibenzo[a,h]anthracene
Indeno[1,2,3-cd]pyrene		

Many PAH's have been assayed for carcinogenicity with negative results. Of those,

naphthalene and fluoranthene are the most highly studied, and these are often used as surrogates to model the behaviour and toxicity of other noncarcinogenic PAH's.

PAH compounds that have not been demonstrated to be carcinogenic are the following:

Acenaphthalene	Acenaphthene	Anthracene
Benz[a]acridene	Benzo[a]fluorene	benzo[b]fluorene
Benzo[c]fluorene	Benzo[ghi]perylene	Benzo[c]phenanthrene
Benzo[e]pyrene	Coronene	Dimethyl naphthalenes
1,4-Dimethylphenanthrene	Fluoranthene	Florene
1-Methylchrysene	3-Methylfluoranthene	1-Methylphenanthrene
1-Methyl naphthalene	3-Methyl naphthalene	Naphthalene
Perylene	Phenanthrene	Pyrene
Triphenylene		

Carcinogenic PAH's may also produce noncarcinogenic effects through various routes of exposure. Typically, carcinogenic effects take precedent over noncarcinogenic health effects when considering human health effects from chemical exposure. Information on noncarcinogenic health effects in humans or animal following inhalation exposure to the list of PAH's above, is limited.

Sampling and analysis for PAH compounds can be done efficiently with standard USEPA methodologies, following the techniques for semi-volatile organic sample collection and analysis. The full range of PAH's can be determined in a single sample, covering both the gas phase and particulate-associated compounds.

Many other semi-volatile compounds are also collected during sampling, and can be quantified if they are of interest. It is not possible, however, to privide a list of target compounds that would be representative of emissions of all medical waste incinerators.

3. SAMPLING AND ANALYTICAL TECHNIQUES

3.1 CHARACTERISATION OF PHYSICAL STACK PARAMETERS

Incinerator stacks have to be characterised in terms of gas flow rates, pressures, moisture content, and temperature. The static pressure in the stack is measured to adjust concentrations to a standard pressure of 1 atmosphere (101.3 kPa). For the same reason, temperature is measured to express concentrations at 0 °C. Moisture is also determined, to apply corrections to express concentrations on a dry basis. The stack gas concentration, usually expressed as $\mu g/m^3$, is converted to a release rate, taking into account the volumetric flow rate, and is expressed as kg/h. This is required to assess actual releases. The stack gas concentration itself is not a measure of the total release of a substance. Small incinerators with high stack gas concentrations can cause less pollution than large units with lower stack gas concentrations of pollutants. The Guidelines of Schedule 2, Process 39 of the Atmospheric Pollution Prevention Act, based on stack gas concentrations, can therefore be misleading. Release rates are also used as the input data for mathematical dispersion modelling, to estimate ground level concentrations of

toxicants.

3.1.1 USEPA Method 1: Sample and velocity traverses for stationary sources

This method describes the selection of measurement positions in a stack, to collect a representative sample of the stack gas if a composite sample is collected from all those positions. The method is applicable to sampling of particulates larger than approximately 7 μm, where sampling has to be conducted isokinetically, ie sampling with a probe of specific geometry, at a flow rate that corresponds with the linear velocity of the stack gas, to avoid discrimination according to particle size in sample collection. Particles smaller than approximately 7 μm behave like a gas, and sampling has not to be conducted isokinetically.

A typical traversing plan is illustrated in Figure 2.3. Normally, it is required that a stack is equipped with two sampling ports at 90 degrees to each other, to enable traversing of all the sampling points.

Traverse point number on a diameter	Number of traverse points on a diameter									
	6	8	10	12	14	16	18	20	22	24
1	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5	85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6	95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7		89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8		96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9			91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10			97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11				93.3	85.4	78.0	70.4	61.2	39.3	32.3
12				97.9	90.1	83.1	76.4	69.4	60.7	39.8
13					94.3	87.5	81.2	75.0	68.5	60.2
14					98.2	91.5	85.4	79.6	73.9	67.7
15						95.1	89.1	83.5	78.2	72.8
16						98.4	92.5	87.1	82.0	77.0
17							95.6	90.3	85.4	80.6
18							98.6	93.3	88.4	83.9
19								96.1	91.3	86.8
20								98.7	94.0	89.5
21									96.5	92.1
22									98.9	94.5
23										96.8
24										98.9

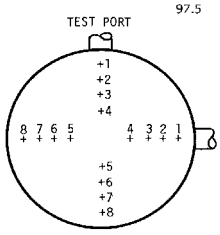


Figure 2.2: Diagram showing circular stack cross section with location of traverse points indicated

The number of traverse points depends on the stack dimensions, and can be planned from tables compiled by USEPA for different stack diameters. Sampling ports should be positioned at least eight stack diameters downstream and ten diameters upstream from the any point of turbulence, to enable true isokinetic sampling. Turbulence is caused by bends, changes in stack or duct diameter, obstructions, and burners/flames. If the outlined sampling criteria are not practical, a convenient sampling location is chosen and the minimum number of sampling points estimated from tables that take into account the number of stack diameters upstream and downstream from points of turbulance.

In stacks with diameters smaller than 0.3m it is not possible to use the standard equipment to measure flows, and a standard type pitot tube is used. It becomes difficult and inaccurate the sample isokinetically from small-diameter stacks and ducts. Special

approaches are also required when sampling cyclonic-flow (or swirling) stacks.

3.1.2 USEPA Method 2: Determination of stack gas velocity and volumetric flow rate

Based on the requirements discussed in EPA Method 1, a pitot tube is used to determine the average gas velocity, by measurement at various positions in the stack, and from the gas density.

A Type S (Stausscheibe or reverse type) pitot tube is illustrated in Figure 2.4.

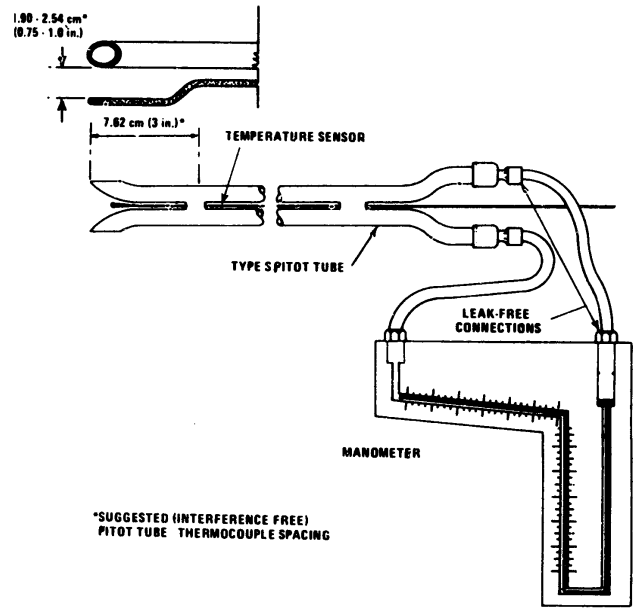


Figure 2.3: S-Type S pitot tube and inclined manometer

Pitot tubes are normally made from stainless steel according to specific design specifications, and are calibrated to determine characteristic coefficients. The configuration and sizes of the nozzles are critical parameters. In an assembly as shown in Figure 2.4, dynamic pressures are measured, which
are used together with the pitot tube coefficient, gas temperature, and gas density, to calculate gas velocity. Measurement at various traverse points enables determination of average velocity and volumetric flow rate.

A standard pitot tube is of smaller dimensions, and is illustrated in Figure 2.5. The major limitation with the use of standard pitot tubes is the possibility of plugging in particulate-laden gas streams. As stated above, standard pitot tubes should be used in small-diameter stacks.

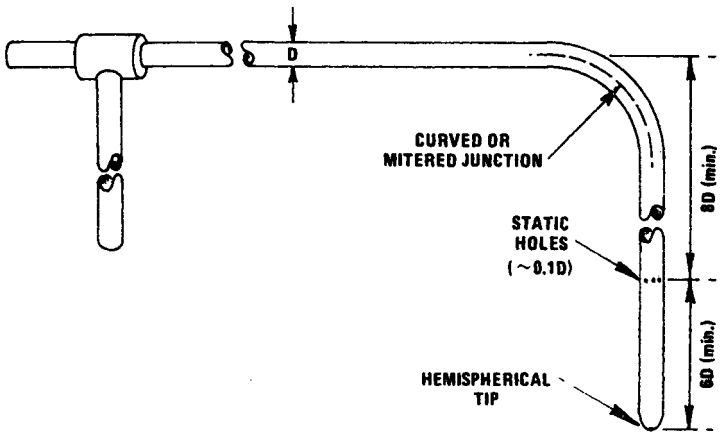


Figure 2.4: Diagram of a standard pitot tube

Thermocouples for temperature measurement form part of some pitot tube designs, or are used separately to determine stack gas temperature.

3.1.3 USEPA Method 4: Determination of moisture

The moisture content of medical waste incinerator stack gas is of interest for expressing concentrations of emitted substances on a dry basis. Different methods may be followed, but USEPA Method 4 is simple and provides adequate data as required for the calculations. It is based simply on the collection of moisture in chilled impingers, followed by s silical gel cartridge, by pumping stack gas through the sampling train at a specified flow rate for a selected time.. From the collected volume of water and increase in weight of the silica gel cartridge for a known gas volume, the moisture content of the stack gas can be calculated. Figure 2.6 illustrates the impinger train set.

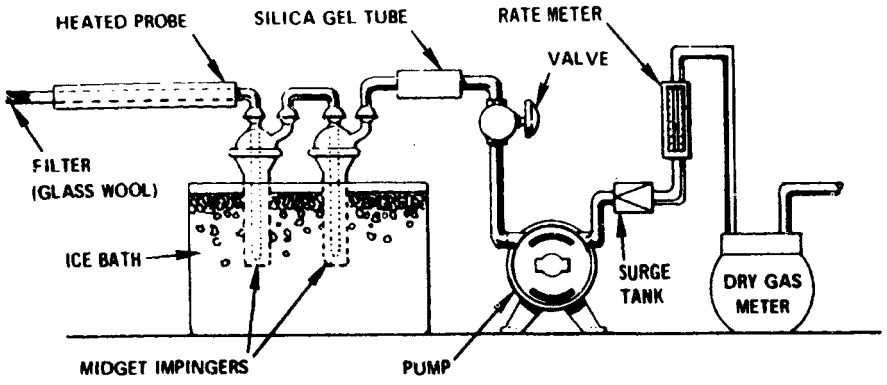


Figure 2.5: Sampling train to determine moisture in stack gas

3.1.4 Other parameters required for calculations

In addition to the concentration of a pollutant in the stack gas, and the parameters discussed in Sections 3.1.1 to 3.1.3 above, oxygen, nitrogen, carbon monoxide and carbon dioxide must also be determined, to enable calculation of the stack gas density. These parameters are normally measured with a combustion analyser, and estimated from mass.balance calculations. The stack gas density is required in the calculation of volumetric flow rate.

3.1.5 Opacity measurements

Smoke density is defined as the degree of blackness (opacity) of a plume expressed in terms of some arbitrary scale. The apparent blackness or stack plume opacity depends on the concentration of particulates, the size of the particulate matter, the depth of the smoke column, natural lighting conditions such as direction of the sun relative to the observer, and the colour of the particulates.
One of the oldest and most common methods of determining opacity is to compare the smoke to the shades of gray on the Ringelmann chart. The Ringelmann system is a scheme whereby shades of grey are graduated in equal steps between white and black. The observer glances from the smoke to the chart and notes the number on the chart that corresponds the closest with the shade of the smoke. A clear stack is recorded as no 1, and black smoke as no 5. Although instruments that give direct opacity readings have replaced the Ringelmann chart, it is still in use in many places.

Although useful, opacity measurements have many limitations. The measurements are not useful when there is a detached plume that becomes visible some distance beyond the stack, or when stack gases are opaque due to condensed water vapour. Direct reading instruments also have limitations, among others the difficulty to maintain dust-free optics, problems with calibration after installation, the dependence of light reflection on particle size, and the fact that only a small portion of the gas stream is observed. Opacity measurements should be used only to indicate major deviations from normal conditions resulting from poor combustion, failure of particulate collection systems, or soot blowing.

3.2 DETERMINATION OF PARTICULATE EMISSIONS

Sampling for particulates must be conducted isokinetically, using USEPA Methods 5 or 17. Method 5 employs a heated filter box at the end of the probe outside the stack, whereas Method 17 uses a thimble holder or filter holder at the front end of the probe inside the stack. Method 17 is the preferred approach, because it eliminates the problem of deposition of particulates on the inside
walls of the sampling probe. Where particulate sampling is combined with sampling for substances associated with the particulates, in-stack sampling represents a situation of equilibrium and is truly representative of the stack gas at that point. It is therefore also preferable from that point. Figure 7 shows an impinger train set with a filter assembly for the collection of particulates. A thimble assembly is similar, but designed to accommodate a thimble in the place of the filter. Filter and thimble material is normally glass fibre, to account for the presence of moisture. The impinger set is used to determine

the moisture content of the stack gas.

USEPA Method 17 should not be used where the filter assembly covers more than five per cent of the stack cross-sectional area, because of the turbulence that would be caused.

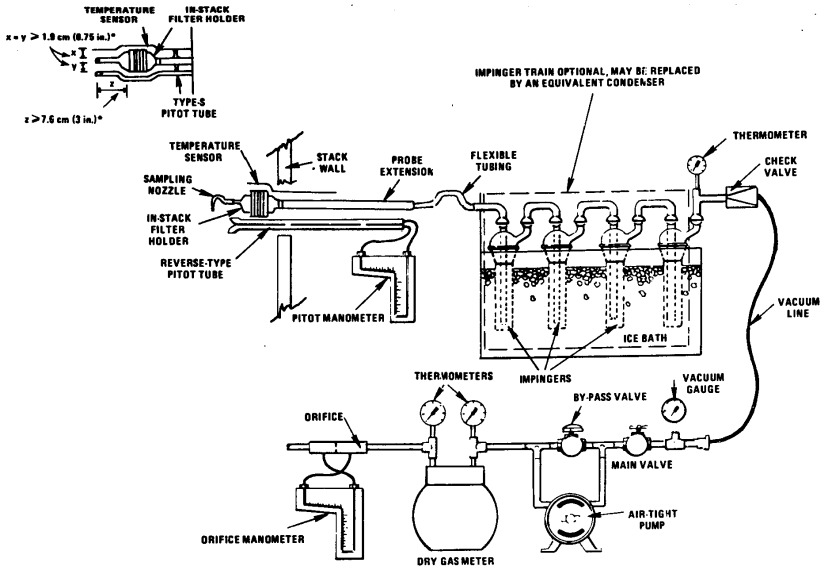


Figure 2.6: USEPA Method 17 sampling train for collection of particulates

3.3 DETERMINATION OF METALS

Although the South African guidelines for medical waste incinerators specify only a few metals of
interest (cadmium, mercury and lead), a wide range of metals may be specified for determination. The multi-metals sampling train (USEPA Method 0012) is recommended for the sampling. The method samples particulates for determination of associated metals, and stack gas for volatile metals in the gas phase. Figure 2.8 illustrates the sampling configuration.

Volatile metals are collected in the impinger train set. In Figure 8, the isokinetic probe is fitted with an external filter, but the in-stack filter assembly according to USEPA Method 17 may also be used. In fact, this may be the preferred method, because sampling will reflect the distribution of metals between particulates and the gas phase under the specific the stack gas conditions.

The impinger train set has been developed to sample for gas-phase compounds of antimony, arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, nickel, phosphorus, selenium, and titanium. Particulates can be analysed for any metals of interest.

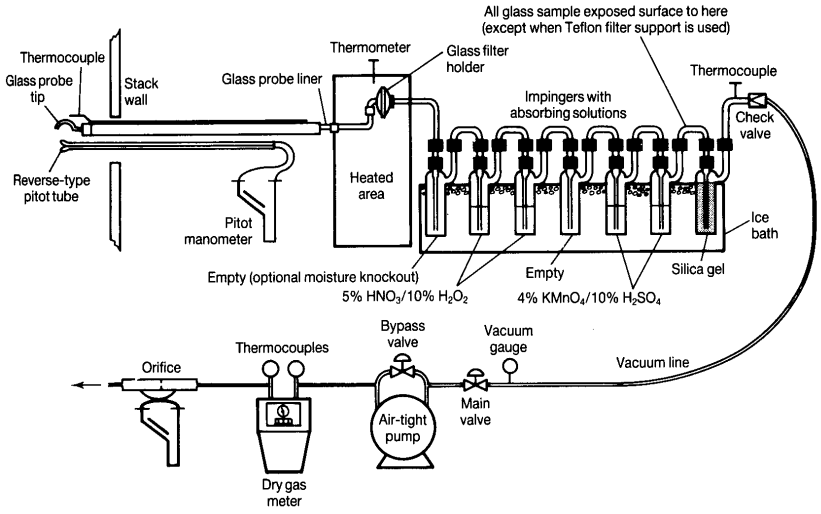


Figure 2.7: Multi-metals sampling train

Analytical methods that may be used are cold-vapour atomic absorption spectrometry, atomic absorption spectroscopy (AA), inductively coupled argon plasma emission spectrometry (ICP-AES), and ICP-mass spectrometry. It is important to select analytical methods and sampling times to determine the metals at low levels in the stack.

Data reported as below method detection limits may present problems when such data are used in risk assessments. The term "minimum detection limit" is used rather loosely in the analytical profession, but it should refer to the lowest level of a substance that can be quantified in a sample at a specified level of confidence. If no instrument signal is observed for the substance, its concentration is not given as zero, but indicated as below the limit of detection. Such data points are referred to as "non-detects". There is a concentration range at the lower end of the analytical ability of the detection system in which it may be possible to confirm that the substance is present in the sample, but the concentration may be too low to quantify at any level of confidence. Such cases are reported as below the method detection limit, but the preferred term to use is *below the limit of quantification*. Where no evidence of the compound is observed, it is fair to say that it is *not detected*. The problem is that the compound may be present at a level lower than the detection limit.

In risk assessment it is not permitted to use a zero concentration where a substance has not been detected, or where the concentration was below the limit of quantification (QL). These non-detected data points are assessed according to different conventions. The values used most often are QL, QL/2, and $(QL/2)^{½}$. The choice of the value to use depends on the goals of the risk assessment and level of confidence required. Different regulatory bodies may prefer different values, but QL/2 has been recommended as the preferred approach, especially where several non-detects may be observed.

The potential problem with using non-detected data points in a risk assessment lies in data generated by analytical methods that have relatively high detection limits for

substances that are toxic at low levels. In such cases the calculated risk based on QL/2 may be unacceptable. The assessment becomes an issue where corrective action has to be taken on the basis of such flimsy evidence. In fact, the possibility that the substance is not present at all in such a case, cannot be ruled out. The dilemma can be avoided by careful planning of the sampling and analytical survey, using analytical techniques with appropriate lower limits of quantification to ensure that non-detected data points would not indicate unacceptable risks when used as QL/2 in the assessment.

3.4 HYDROCHLORIC ACID

Sampling for hydrochloric acid is conducted non-isokinetically using USEPA Method 26. An integrated sample is extracted from the stack and passed through dilute sulphuric acid. HCl is dissolved to form chloride ions. The chloride ions are quantified with ion chromatography. A diagram of the sampling train is presented in Figure 2.9.

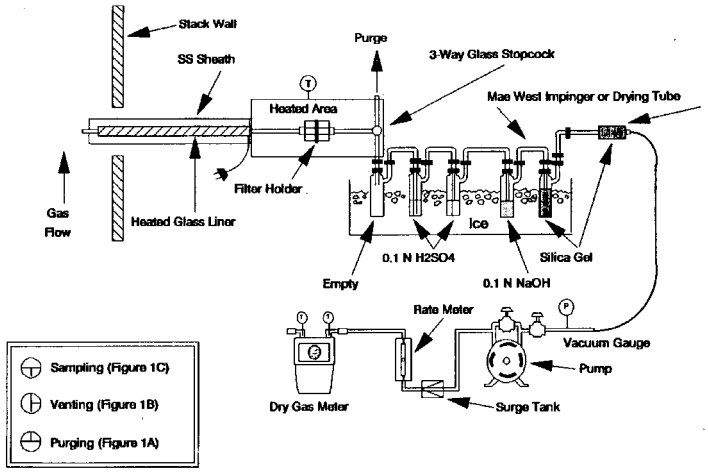


Figure 2.8: Impinger train for sampling of HCl

3.5 SULPHUR DIOXIDE

Several methods are available for the determination of sulphur dioxide, some of which also provide for the determination of sulphur trioxide. Although there may be variations, a simple approach is outlined in USEPA Method 6, as illustrated in Figure 2.10.

The first bubbler (which may also be an impinger) is filled with 80 per cent propanol, and the subsequent two impingers with 3 per cent hydrogen peroxide. The last impinger is empty. Glass wool filters and the isopropanol bubbler remove cations and fluorides that may interfere with the analysis. Sulphur dioxide combines with the hydrogen peroxide to form sulphuric acid, which is quantified by alkali titration or with ion chromatography.

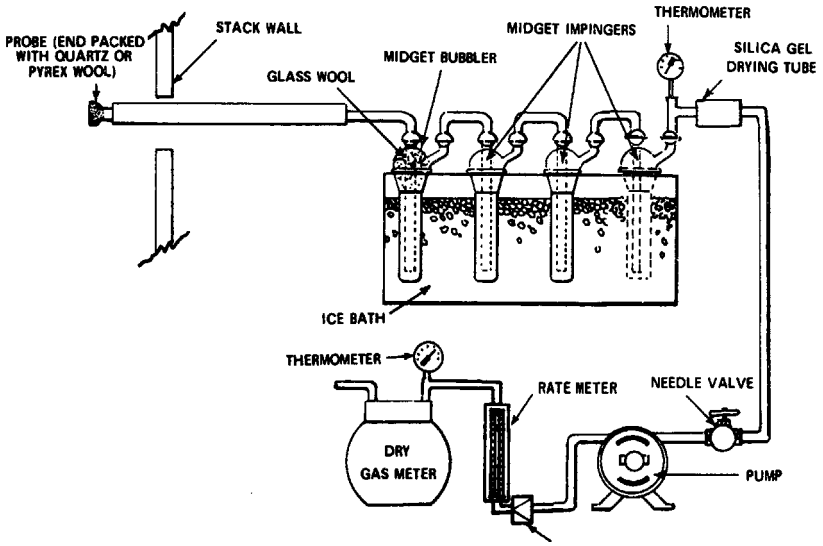


Figure 2.9: Sulphur dioxide sampling train

3.6 POLYCHLORINATED DIOXINS AND FURANS

USEPA Method 23 is applicable to the determination of dioxins in incinerator stack gas.

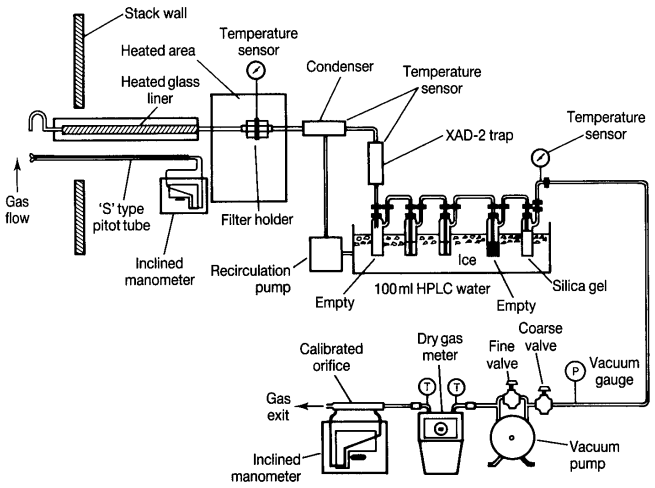


Figure 2.10: USEPA Method 23 sampling train for dioxins and furans

The sampling train is similar to the isokinetic trains used for collection of semi-volatile organic compounds, which are basically modified versions of the standard particulate sampling train. The filter outside the stack in Figure 2.11 can also be positioned in-stack, as with USEPA Method 17. Because of the low concentrations at which dioxins have to be determined, glassware and other equipment used for dioxin sampling go through special cleaning processes and are not used for other sampling purposes.

Dioxins may be particulate-associated, or in the gas phase. During sampling, a known

volume of stack gas is pumped through the sampling train. The collected particulates are submitted to a soxhlet extraction process. All probe washes and impinger solutions are also collected for solvent extraction. The XAD-2 resin is spiked with isotope-labelled dioxin standards prior to sampling, and surrogate standards are also added to go through the extraction, to assess efficiency of recovery of dioxins through the entire process of sampling and extraction. After concentration of the dioxin extracts through solvent evaporation, samples go through an extensive cleanup process to remove as much as possible of the other organic compounds that were collected from the stack gas. Another standard is added to monitor this step. Final analysis is conducted with combined high resolution gas chromatography-high resolution mass spectrometry. All the congeners of interest are quantified separately, to enable calculation of the total toxicity equivalent for health risk assessment.

3.7 VOLATILE ORGANIC COMPOUNDS

The USEPA volatile organics sampling train (VOST) is suitable for the collection of a wide range of alkanes, alkenes, alkynes, aromatic compounds, and halogenated volatile organic compounds. It is not effective for sampling of aldehydes and ketones.

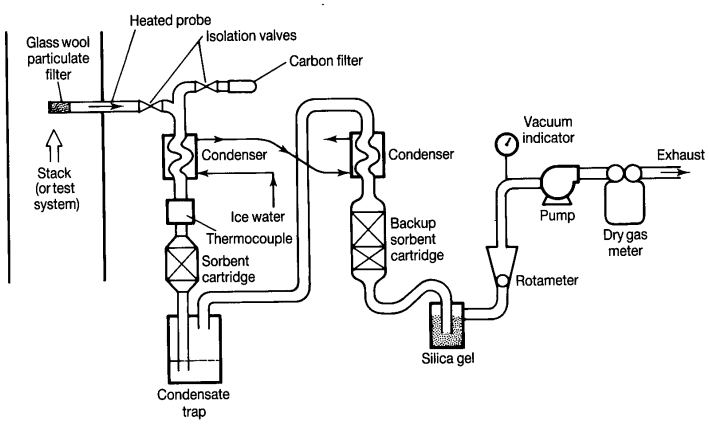


Figure 2.11: USEPA volatile organics sampling train

Sorbent traps normally consist of coconut charcoal and Tenax. After sampling, the traps are mounted in a thermal desorption unit, from where the adsorbed volatile organic compounds are desorbed by flash heating, into the inlet system of a gas chromatograph-mass spectrometer (GC-MS). The GC-MS not only identifies the constituents in the mixture, but can also quantify them against standard mixtures of VOC's.

3.8 ALDEHYDES AND KETONES

USEPA Method 0011 was developed for the determination of formaldehyde, but it has been applied subsequently also for the measurement of other volatile aldehydes.

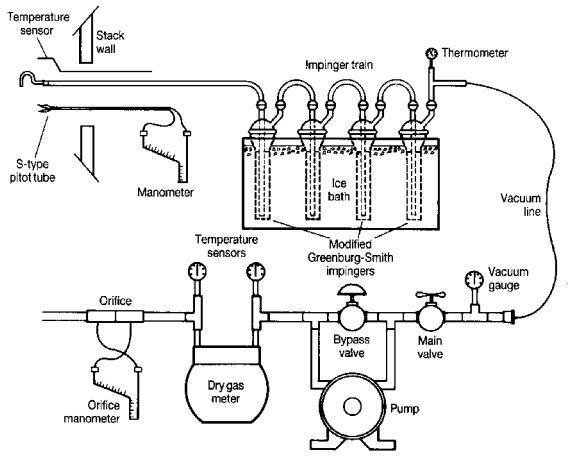


Figure 2.12: USEPA Method 0011 for aldehydes and ketones

Gaseous and particulate contaminants are withdrawn isokinetically from the incinerator stack and collected in an aqueous acidic solution of dinitrophenylhydrazine (DNPH). All the gas contact surfaces are glass or quartz. The aldehydes present in the stack gas react with the dinitrophenylhydrazine to form an aldehyde-dinitrophenylhydrazone derivative. After extraction into dichloromethane, analysis is conducted with high performance liquid chromatography. Variations on the chemical reaction also make it possible to conduct the analysis with gas chromatography.

3.9 SEMI-VOLATILE ORGANIC COMPOUNDS

The isokinetic sampling train for semi-volatile organic compounds is similar to the train used for dioxin sampling, except for differences in size and design of some of the components. Figure 2.14 shows a typical sampling train, and a diagram of an XAD-2 resin cartridge. This is known as the

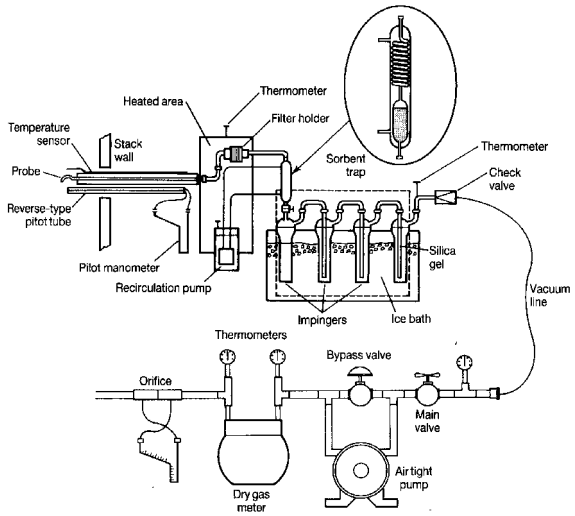


Figure 2.13: USEPA Modified Method 5 sampling train

USEPA Modified Method 5 sampling train. The heated filter assembly can be replaced with a unit for in-stack sampling, similar to Method 17. All components of the sampling train are made from glass or quartz, and Teflon.

Sampling and extraction are similar to the procedures followed for dioxin sampling. Soxhlet extraction is followed by concentration in Kuderna Danish evaporative concentrators, followed by analysis with combined gas chromatography-mass spectrometry. The GC-MS technique has the ability to determine a wide range of semi-volatile organic compounds in a sample during a single analysis. Determination of polynuclear aromatic hydrocarbons (PAH's) can be conducted as target-compound analysis, limiting the mass spectrometer scans to characteristic mass peaks of the selected compounds, or as full-scan data together with other semi-volatile organics.

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