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Analyses of contaminants

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Analyses of contaminants

3.1 Introduction

This section provides information on the analytical methods and associated quality control requirements for the contaminants of concern at gasworks sites.

This module covers the following:

- analytical methods for organic contaminants
- analytical methods for inorganic contaminants
- sampling and sample preservation
- analytical field methods
- quality assurance requirements

Additional information on the analysis of contaminants can be found in Section 3 of the Users' Guide, including:

- ▲ reference analytical methods (Section 3.9)
- ▲ analytical field methods (Section 3.9.1)

3.2 Analytical methods for organic contaminants

The major organic contaminants found at gasworks sites include:

- polycyclic aromatic hydrocarbons (PAHs)
- benzene, toluene, ethylbenzene, xylene (BTEX)
- phenols

3.2.1 GC or GC/MS methods

Gas chromatography (GC) is the established procedure for analysing most organic contaminants in environmental samples, because of its relatively high sensitivities and its ability to separate groups of chemically similar compounds. When coupled with mass spectrometry (GC/MS), the technique becomes even more powerful in both these respects. Sample extraction and clean-up procedures are usually required with either of these analytical techniques.

The United States Environmental Protection Agency has published a series of sample clean-up and analytical procedures (SW-846, Test Methods for Evaluating Solid Waste, US EPA 1994) which are now well established, both in New Zealand and elsewhere, for these analyses. These cover:

- sample extraction procedures 3500 series
- sample clean-up 3600 series
- analysis 8000 series¹

3.2.2 Immunoassay methods

¹ The methods for volatiles (8260) and semivolatiles (8270) have comparable methods in the EPS 600 series for wastewaters; namely 624 for volatile organics in wastewater or groundwater and 625 for semivolatiles. EPA has another equivalent series (500 series) for drinking water analysis. Thus, method 524.2 (volatile organics by capillary column GC/MS) is essentially equivalent to method 8260, while method 525.1 (determination of organic compounds in drinking water using liquid/solid extraction and capillary GCMS) is similar to method 8270.

Enzyme linked immunoassay methods are proving their worth in many applications in the environmental field. The methods are based on combining selective antibodies with sensitive enzyme reactions to produce analytical systems capable of detecting very low levels of specific chemicals. The systems were initially introduced as rapid screening techniques for use in the field, but have now been developed to the stage where some of them are approved by the US EPA as screening methods (EPA 4000 series).

The main advantage of immunoassay systems is the speed of analysis, typically 30 minutes for a complete test, from sample extraction through to the result. In addition, the systems are easily set up for field use, and this makes them well suited to investigations of contaminated sites. They should be particularly useful during site clean-ups, where decisions on the extent of any work may be dependent on analytical results.

Immunoassay test kits are commercially available for PAHs and total petroleum hydrocarbons (Millipore, Ohmicron and Ensys).

The relevant standard test methods are:

- EPA 4030 Petroleum Hydrocarbons Soil Screening by Immunoassay
- EPA 4035 PAHs Soil Screening by Immunoassay

Immunoassay field methods should be pre-calibrated against GC laboratory analyses with typical samples taken from the site under investigation.

3.2.3 Phenols by colorimetry

Several methods are available for the analysis of phenols in waters and wastewaters using colorimetric procedures (APHA 5530, ASTM D 1783-91, ISO 6439: 1990 and EPA 9065, 9066 and 9067). These generally indicate the concentration of total phenols in the sample (i.e. phenol + cresols + xylenols, etc.). The total phenol level determined, therefore, represents the minimum concentration of phenolic compounds present.

These methods can suffer interference from the presence of sulphur compounds such as sulphides, and from oils and tars, in which some phenolics could be dissolved. These interfering compounds are commonly found in gasworks samples.

These methods are not suitable as reference methods or for confirming compliance with any clean-up criteria. They may be useful, however, as screening methods during the initial stages of any site investigation and clean-up. They are generally cheaper than any of the EPA GC methods, and can be carried out using less sophisticated laboratory equipment. Simple field test kits for phenols (in waters) are also commonly available.

3.2.4 Total petroleum hydrocarbons methods

The advantage of GC analysis as a total petroleum hydrocarbon (TPH) screening technique is that it can give an indication of the type of hydrocarbon fraction(s) or product types present in the samples. For example, the hydrocarbon “fingerprint” pattern obtained could indicate the presence of compounds typical of coal tar fractions, including PAHs. Such samples could then be further examined by GC/MS for confirmation and measurement of the specific PAH content.

A GC method is being developed by RJ Hill Laboratories as a New Zealand standard TPH method for inclusion in oil industry guidelines. This method would also probably be suitable for the analysis of gasworks samples.

Other techniques for the estimation of TPH content of soil samples include EPA 3560 (Total Recoverable Petroleum Hydrocarbons by Supercritical Fluid Extraction) and EPA 4030 (Petroleum Hydrocarbons Soil Screen by Immunoassay).

3.2.5 Other methods for organics

Method	Description
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Solid phase extraction	Most solid phase extraction systems are based on plastic cartridges similar in appearance to the barrel of medical syringes, but packed with a section of a selective absorbent. Samples are flushed through the tube, usually with a number of different solvents, to separate and extract the analyte fractions of interest. Solid phase extraction is now included in EPA SW-846 as a standard extraction method (EPA 3535).
Head space analysis	Headspace methods can be very useful in avoiding the matrix effects sometimes encountered with solvent extraction of complex wastes. Headspace techniques can also be used as a field screening method in conjunction with an organic vapour detector such as a photo ionisation detector (PID) or flame ionisation detector (FID). This can be a very useful technique for screening samples during the remediation phase of a site project. In gasworks samples, headspace analysis would be used mainly for BTEX analyses. A headspace screening method is included in EPA SW-846 (EPA 3810).

3.2.6 Recommendations

Contaminant	Method
BTEX and other volatile organics	<ul style="list-style-type: none"> EPA 8260B (soil/solid waste or all sample matrices) EPA 624 or EPA 602 (wastewaters or groundwaters) EPA 524.2 (drinking water) EPA 8020 (Volatile aromatics in solid samples)
PAHs and other semivolatile organics ²	<ul style="list-style-type: none"> EPA 8270C (soil/solid waste) EPA 625 (wastewaters or groundwaters) EPA 525.1 (drinking water)
Phenols ³	<ul style="list-style-type: none"> EPA 8270C or EPA 8041 (all sample matrices)
Total petroleum hydrocarbons (TPH)	<ul style="list-style-type: none"> GC Method being developed by RJ Hill Laboratories for the Oil Industry Guidelines (this is provisional on this method being found suitable once developed) Alternative methods could be those (non-standard) GC/FID-GC/MS techniques discussed in Douglas et al 1992, and Roques et al 1994.

3.3 Analytical methods for inorganic contaminants

The major inorganic contaminants expected at gasworks sites are cyanides, heavy metals, inorganic sulphur compounds, and ammonia. Unlike the organic contaminants, the analytical requirements for each of these groups of chemicals are quite different.

3.3.1 Cyanides

Cyanide may be present at gasworks sites in a number of different forms:

- free cyanide
- metal-cyanide complexes
- thiocyanate.

It is important that analyses can differentiate between these forms as the toxicities or potential toxicities are quite different.

Note: Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrogen cyanide. All manipulations and distillations must be done in a fume hood so that any HCN gas that might escape is safely vented. This equally applies to other tests on gasworks samples that may release the cyanide

² These methods should, however, be modified to include, in addition to the 16 EPA priority pollutant PAH compounds, dibenzofuran and selected PAH alkyl homologues (C1-C4), such as 2-methylnaphthalene (Douglas et al 1992). The US Gas Research Institute has also compiled its own list of PAHs specific to gasworks (GRI 1987, Thomas and Lester 1994). A number of compounds, not likely to be present on gasworks sites could be deleted from the standard EPA 8270 list. These could include chlorinated compounds and pesticides.

³ These methods should cover phenol, cresols (methylphenols) and xylenols (dimethylphenols).

content, for example, acid extraction for metal analysis. Many of the reagents used in these test methods are highly toxic. Reagents and test solutions must be disposed of properly.

APHA Standard Methods (19th Edition 1995) (APHA, AWWA, WEF 1995) specifies a number of different methods for cyanide analysis in water and wastewaters in section 4500-CN, Cyanide. The section contains the following parts:

A	Introduction
B	Preliminary treatment of samples
C	Total cyanide after distillation
D	Titrimetric method (of determination)
E	Colorimetric Method (of determination)
F	Cyanide-Selective Electrode Method (of determination)
G	Cyanides Amenable to Chlorination after Distillation
H	Cyanides Amenable to Chlorination without Distillation
I	Weak Acid Dissociable Cyanide
J	Cyanogen Chloride
K	Spot Test for Sample Screening
L	Cyanates
M	Thiocyanate

Most of these have as their starting point a distillation step which separates the cyanide from the sample matrix. Various pre-treatments are also used at this stage to distinguish between the different cyanide forms. Subsequent analysis can be by a variety of procedures including (titration, colorimetry, ion selective electrode). The choice of method is dictated by the desired detection limits, and availability of instrumentation.

APHA methods 4500-CN (C) and (I) should be acceptable for the analysis of total cyanide and free cyanide, respectively, in gasworks samples. Section 4500-CN (A) contains procedures for the extraction of cyanides from solid waste samples (A.2). The colorimetric determination procedure (4500-CN (E) should have adequate sensitivity for the required detection levels.

An analysis for total cyanide can be used as a 'screen' to decide if further analysis for free or complex cyanides is necessary. It would only be necessary to analyse for free cyanide if the total cyanide level exceeds the 'trigger' level for free cyanide.

Many ions and compounds may interfere with these cyanide determinations. The most significant in the case of gasworks materials are sulphides, sulphites, thiocyanate and other sulphur compounds. Sulphide will distill over with cyanide and adversely affect the colorimetric procedure. It must, therefore, be removed prior to the distillation step. Sulphide can convert cyanide to thiocyanate, especially at the pH of the base stabilised sample. Oxidising agents such as chlorine decompose most cyanides during storage and manipulation and their presence should, therefore, be tested for. The presence of either oxidising agents or sulphides should be determined, and they should be removed, if present, before the addition of sodium hydroxide normally used to preserve cyanide samples. Methods for preserving samples and eliminating interfering compounds are given in APHA 4500-CN, section B.

Samples should be protected from exposure to ultraviolet (UV) light, as photodecomposition of some metal-cyanide complexes may significantly increase the concentration of "free" cyanide in the samples. Samples should be stored in closed, dark bottles in a cool place and analysed as soon as possible.

Comparable methods for the analysis of cyanides are found in the ISO, ASTM and EPA collections of methods (e.g. EPA 9012).

Soils and solid wastes can also be analysed by the above procedures using an extraction pre-treatment such as is described in APHA 4500-CN (A-2) or EPA 9013 Cyanide Extraction Procedure for Solids and Oils.

Thiocyanates can be determined by the following methods:

- APHA 4500-CN (M) Thiocyanate

- ASTM D4193-89 Thiocyanate in Water

A more recent published standard method is ASTM D4374-93 Cyanides in Water - Automated Methods for Total Cyanide, Dissociable Cyanide, and Thiocyanate.

The US Gas Research Institute has carried out research on methods for the analysis of cyanides in gasworks wastes (Gas Research Institute 1989).

3.3.2 Heavy metals

The analysis of samples for heavy metals usually involves a digestion step followed by instrumental analysis of the resulting solution, using techniques such as atomic absorption (AA) or inductively coupled plasma (ICP). These techniques are well established and in common use, and so it is unnecessary to provide any detailed coverage of the various options or requirements for the range of different methods.

Standard procedures for the analysis of metals in water and wastewaters are given in the APHA Methods (3030-Preliminary Treatment of Samples, 3111-Metals by Flame Atomic Absorption Spectroscopy, 3113-Metals by Electrothermal Atomic Absorption Spectroscopy, 3120-Metals by Plasma Emission Spectroscopy) and methods in the EPA 200 series (200.2-Sample Preparation, 206-Arsenic, 213-Cadmium, 239-Lead, 245-Mercury, 249-Nickel, 289-Zinc). Methods for the determination of metals in solid waste and soil are given in EPA SW-846, 3050A-Acid Digestion of Sediments, Sludges and Soils, 3051-Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, 6010B-Inductively Coupled Plasma-Atomic Emission Spectroscopy, 6020-Inductively Coupled Plasma-Mass Spectrometry and the 7000 series of Atomic Absorption Methods.

Given the wide range of metals that may be present at gasworks sites, multi-element techniques such as ICP and ICP/MS are the preferred analytical methods and these will be taken as the reference methods.

Multi-element X-Ray Fluorescence (XRF) may also be suitable, especially as a cost-effective screening technique. A semi-quantitative XRF scan can determine the concentrations of 57 (mostly metallic) elements from levels of 100% to a minimum detectable level of 0.001% (10mg/kg) in about 20 minutes. This can provide useful information on the overall composition of the material analysed and also indicate if higher than background levels of common elements are present.

3.3.3 Inorganic sulphur compounds

Sulphur may be present at gasworks sites as elemental sulphur, sulphates, sulphides, or thiocyanates, and each of these require a different analytical method. Alternatively, all forms may be determined as total sulphur in solid samples by, for example, the XRF technique described above.

Other methods for total sulphur are much less convenient and involve some type of total digestion step such as oxygen bomb combustion (EPA 5050), perchloric acid oxidation or fusion.

Elemental sulphur is only likely to be of interest in solid samples, and this is most easily determined using XRF (gasworks samples may contain over 50% sulphur). An alternative method for the determination of elemental sulphur is given in Method 31, Draft ANZECC Guidelines for the Analysis of Contaminated Soils (ANZECC 1994).

There are numerous methods available for sulphate analysis in water and wastewater samples. For soils, the extraction method in the ANZECC Guidelines (ANZECC 1994) will be suitable; for aqueous samples the APHA Standard Methods should be used. In both, the determinative step should be by either the APHA standard Ion Chromatographic method (4110) or the Turbidimetric method (4500-SO₄²⁻) and these should be taken as the reference method.

Sulphides in aqueous samples can be determined by APHA methods 4500-S²⁻, by the methylene blue procedure (method D), or by ion-selective electrode (method G). Suitable methods for soil samples are EPA 9030A-Sulphides and EPA 9031-Extractable Sulphides.

3.3.4 Ammonia

There are several methods that are suitable for the analysis of ammonia in aqueous samples. These include APHA 4500-NH₃, ASTM D 1426-93 and ISO 5664:1984. A suitable method for the extraction of ammonium in soils is given in Method 10 in the ANZECC Guidelines (ANZECC 1994). The extract solution is then analysed by the ion-selective electrode method given in APHA 4500-NH₃ (sections D or E).

3.3.5 Acidity

A method for analysing acidity of water is given in APHA 2310. A method for determination of the pH of soil or waste is given by EPA 9045B. An alternative method for determining soil pH is given in Method 6 in the ANZECC Guideline (ANZECC 1994).

3.3.6 Moisture content

For many chemical analyses, the moisture content is determined so that chemical concentrations can be expressed on a dry weight basis. A suitable method is given in Method 5 in the ANZECC Guidelines (ANZECC 1994).

3.3.7 Toxicity characteristic leaching procedure

This procedure, EPA 1311, is an agitated extraction test designed to simulate leaching in a sanitary landfill. The filtered extract from the toxicity characteristic leaching procedure (TCLP) is analysed to determine if any of the thresholds for the 40 toxicity characteristic constituents have been exceeded. This procedure is discussed more fully in the Draft Health and Environmental Guidelines for Selected Timber Treatment Chemicals (MfE/MoH 1993), and in the ANZECC Guidelines (ANZECC 1994).

This will be an important test to carry out on gasworks wastes if they are intended to be disposed of to a landfill or if a risk assessment of the leachability of the material in situ is to be determined. TCLP volatiles and TCLP semi-volatiles and metals must be determined on separate samples.

3.4 Sampling and sample preservation

Extensive discussions on correct sampling procedures and sample preparation and storage requirements are given in several other publications (ANZECC 1994, Ministry for the Environment/Ministry of Health 1993, CCME 1993) and are not, therefore, repeated in detail here. Some requirements more specific to gasworks samples are discussed briefly below (Department of the Environment 1987, ANZECC 1994).

To obtain reproducible results laboratories must use standardised procedures for the preparation of samples. It is important to ensure that no bias is introduced in the analytical results. For example, certain gasworks contaminants can be driven off or modified during drying or handling procedures. Volatile organics may evaporate, PAHs are photosensitive, aerobic biodegradation of phenols may be accelerated, sulphide and cyanide may volatilise as the acid gases, metal complex cyanides can photodissociate to release free cyanide and oxidation may occur, for example, of sulphur to sulphate or to decompose cyanides.

Table 3.1 Sample preparation

Sample	Preparation
Soils Non-volatile or "stable" contaminants	<ul style="list-style-type: none"> examine visually and record observations obtain a representative sub-sample of the laboratory sample, of at least 50% of the sample or 200g, whichever is the smaller, taking into consideration amounts required for repeat analyses,

	<p>other analyses to be carried out on this same sample and the moisture content of the sample</p> <ul style="list-style-type: none"> remove large stones (> 5mm) and vegetation and record the proportion by weight, together with the description, of each fraction of material removed air-dry or in draught oven (<30°C, <65% relative humidity) grind sample (mortar and pestle) and sieve to <2mm (weigh and retain the larger particles for later analysis if required) mix and quarter (if necessary) the fraction <2 mm diameter transfer to sealed glass container store at 4°C in the dark, pending extraction and analysis
Soils Semi-volatile analytes ⁴	<ul style="list-style-type: none"> follow 1st three steps above grind sample in a mortar and pestle to produce a homogeneous test sample transfer to sealed, air tight glass container and store at 4°C in the dark, pending extraction and analysis dry a separate, weighed portion of the original sample to determine moisture content. Report the moisture content with the analytical result so that the analyte concentrations may be estimated on a dry weight basis
Soils Volatile	<ul style="list-style-type: none"> using a clean spatula, rapidly homogenise the cold laboratory sample by stirring in its original container if large stones (> 5 mm) and vegetation can be removed rapidly without risk of significant analyte losses, do so quickly and return the sample promptly for cold storage. If not, no material is to be removed and the analysis portions are to be taken from the homogenised, “as received” sample. Record the proportion by weight, with the description, of each fraction of material removed
Liquid ⁵	<ul style="list-style-type: none"> filter out solids, except from samples for sulphide analysis stabilise as necessary by cooling to 4°C separate distinct liquid phases, if present, for separate analysis

Table 3.2 Sample preservation

Sample	Preservation
Soil	<ul style="list-style-type: none"> sampling containers should be filled to the brim, in order to exclude air glass containers are preferred, although polyethylene and polypropylene are probably satisfactory (other than for organic analytes), if analysis follows promptly where volatile contaminants are of interest, gas tight bottles should be used samples should be placed in the dark and in cool storage (4°C) as soon as possible extracts should be prepared as soon as possible stored under optimum conditions sensitive determinands should be analysed as soon as possible, preferably on site or within hours, and certainly within 2 days
Water	<p>Stabilisation can normally be achieved by addition of a chemical agent on site, or in the laboratory. Preservatives for one determinand may disturb the stability of other contaminants and thus cause a bias in their analysis. A common practice for water samples from gasworks sites is to split the sample four ways and treat each as follows (Department of the Environment 1987):</p> <ul style="list-style-type: none"> for ammonia determination, stabilise with sulphuric acid for sulphide determination, stabilise with zinc acetate and sodium hydroxide for metal determination, stabilise with nitric acid for phenols, semivolatile organics and cyanide, store at 4°C and in dark for volatile organics a separate sample should be taken
Cyanides	<ul style="list-style-type: none"> sample containers should be filled to the top if possible so as to exclude air, and should be protected from strong sunlight to minimise cyanide oxidation and photodecomposition. Analyse as soon as possible after collection samples likely to contain oxidising agents should be pre-treated with sodium hydroxide solution to give a pH of at least 12. Sulphide content must be removed prior to this preservation treatment
Heavy metals	<ul style="list-style-type: none"> sample containers should be pre-washed with detergent and acid, and AR nitric acid added as a preservative. Water samples should be pre-filtered in the field if significant quantities of solids/sludges are present in the samples (sludges may be collected separately for independent analysis).

⁴ Drying may lead to losses - this could include AHs

⁵ Samples heavily contaminated with coal tar present particular difficulties in that they can be extremely cohesive. Analysis of these should not be necessary and visual assessment will indicate the need for remedial measures

Sulphur compounds	<ul style="list-style-type: none"> there are no special requirements for total sulphur, elemental sulphur or sulphate. For sulphide, stabilise with zinc acetate and sodium hydroxide.
Ammonia	<ul style="list-style-type: none"> use tightly sealed containers and analyse samples as soon as possible after collection. Most reliable results are obtained on fresh samples. If samples are to be analysed within 24 hours of collection, refrigerate unacidified at 4°C. For preservation for up to 28 days, freeze at -20°C unacidified, or preserve samples by acidifying with sulphuric acid to pH <2 and storing at 4°C. If acid preservation is used, neutralise samples with NaOH or KOH before the determination (APHA, AWWA, WEF 1995).

Table 3.3 EPA Method 6010 Sample Holding Times, Required Digestion Volumes and Recommended Collection Volumes for Metal Determinations (CCME 1993)

Measurement	Digestion* Volume (mL)	Collection volume (mL)	Preservative	Holding Times
Metals (except Cr VI and Hg)				
Total recoverable	100	600	HNO ₃ to pH <2	6 months
Dissolved	100	600	Filter on site, HNO ₃ to pH<2	6 months
Suspended	100	600	Filter on site	6 months
Total	100	600	HNO ₃ to pH <2	6 months
Chromium VI	100	400	Cool to 4°C	24 hours
Mercury				
Total	100	400	HNO ₃ to pH <2	28 days
Dissolved	100	400	Filter, HNO ₃ to pH <2	28 days

* Solid samples should be at least 200g and usually require no preservation other than storing at 4°C.

Table 3.4 Sample collection, preservation and storage (CCME 1993 and EPA SW-846)

Method Number	Sampling and Preservation	Storage
EPA-8260A Cap GC/MS Volatile organics	Liquid samples: Use a 40-ml glass screw-cap VOA vial with Teflon -faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven dried at 105 ⁰ C for 1 h). If residual chlorine is present, collect sample in a 125 ml soil VOA container that has been pre-preserved with 4 drops of 10% sodium thiosulphate. Mix gently and transfer to a 40-mL VOA vial. Add 4 drops of concentrated HCL and cool to 4 ⁰ C. Collect bubble-free samples in duplicate.	The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4 ⁰ C for a maximum of 14 days from date of collection.
	Soil/sediments and sludges: Use an 125 ml widemouthed glass with Teflon -faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105 ⁰ C for 1 h). Do not heat septum for more than 1h. Tap slightly to eliminate free air space. Collect in duplicate and cool to 4 ⁰ C.	
EPA-8270B Cap GC/MS (B/N/A) Semi-volatile organics	<i>Liquid samples:</i> Use a 1 gal. or 2 x 0.5 gal amber glass bottle with a screw-top Teflon -lined cover. Prewash with detergent and rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4 ⁰ C. If residual chlorine is present, add 3 ml of 10% sodium thiosulphate per gallon and cool to 4 ⁰ C.	Liquid samples must be extracted within 7 days and extracts analyzed within 40 days. Soil/sediments and sludges may be stored for a maximum of 14 days. Do not store in the presence of exhaust fumes.
	<i>Soil/sediments and sludges:</i> Use a 250 ml widemouthed glass with a screw-top Teflon -lined cover. Prewash with detergent and rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4 ⁰ C.	
EPA-524.2 Rev 3 Cap GC/MS Volatile organics	Use a 60- to 120 mL screw cap vial (prewashed with detergent, rinsed with distilled water, and oven-dried at 105 ⁰ C) with a Teflon-faced silicone septum. If residual chlorine is in the water, add about 25 mg of ascorbic acid to each vial before sample collection. Collect bubble-free samples. Add hydrochloric acid until a pH of <2 is achieved and immediately cool samples to about 4 ⁰ C.	The maximum holding time is 14 days from the date of collection. Do not store samples in a refrigerator where other volatile chemicals are stored as their vapours may contaminate these samples.
SM-6420B Phenols by GC/FID or ECD (equivalent to US EPA Method 604)	Collect grab samples in 1-L amber glass bottles fitted with a screw cap lined with Teflon. Wash and rinse bottle and cap liner with acetone or methylene chloride and dry before use. Collect composite samples in refrigerated glass containers. Optionally, use automatic sampling equipment as free as possible of plastic tubing and other potential sources of contamination, incorporate glass sample containers for	Keep samples at 4 ⁰ C from time of collection until extraction. Extract samples within 7 days of collection and analyse completely within 40 d of extraction.

Method Number	Sampling and Preservation	Storage
	collecting a minimum of 250 mL. Refrigerate sample containers at 4 ⁰ C and protect from light during compositing. Fill sample bottles and, if residual chlorine is present, add 80 mg sodium thiosulphate per litre of sample and mix well. Cool samples immediately to 4 ⁰ C	
SM-3111B (metals-flame AA) SM-3112B (Hg - AA) SM-3113B (methods - electrothermal AA) SM-3114B (As, Se - hydride AA) SM-3120B (metals by ICP)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO ₃ to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4 ⁰ C to prevent loss in volume due to evaporation. Samples with metal concentrations of several milligrams per litre are stable for up to 6 months. For microgram-per-litre metal levels, analyse samples as soon as possible after collection.
EPA-6010 - Metals by ICP	Samples should be collected in borosilicate glass, linear polyethylene, polypropylene, or Teflon bottles that have been prewashed with detergent and tap water and rinsed with 1:1 nitric acid and tap water or 1:1 hydrochloric acid and tap water.	The maximum holding times from time of collection to time of extraction is shown in Table X3 for each type of analyte.
APHA SM 4500-CN EPA-9012 Colorimetric Automated UV Total and amenable cyanide	Collect samples in 1-L or larger plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed to remove soluble materials. Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI) - starch test paper at the time of collection; a blue colour indicates the need for treatment. Add ascorbic acid a few crystals, at a time until a drop of sample produces no colour on the indicator. Then, add an additional 0.6 g of ascorbic acid for each litre of water. Samples must be preserved by adding 10N sodium hydroxide (or NaOH pellets) until sample pH is >12 at time of collection. Oxidised products of sulphide convert cyanide to thiocyanate rapidly, especially at high pH. Sulphide will also distill over with cyanide and adversely affect the determination step. Samples therefore require testing for the presence of sulphide prior to stabilisation with NaOH. Test for sulphide by placing a drop of sample on lead acetate paper previously moistened with acetic acid buffer solution, pH 4. Darkening of the paper indicates presence of sulphide. Add lead acetate or lead carbonate to precipitate the sulphide. Filter sample before raising pH for stabilisation.	Samples should be stored at 4 ⁰ C in a dark place and analyzed as soon as possible.

3.5 Analytical field methods

3.5.1 Portable gas analysers

There are a several portable gas analysers on the market which have potential application in gasworks site investigations. These analysers give “real-time” measurements on levels of gases and vapours being emitted from a site and can store information, gained over a period of time, in a data logger. They would therefore be useful in testing for unsafe vapour concentrations in air, in cases of extreme contamination.

For organic vapours, the most universal systems are those based on the photoionisation detector (PID) or the flame ionisation detector (FID). These are used as total organic vapour monitors, or can be made more selective through coupling with a portable GC. Either configuration could be used as a screening device for detecting the presence of volatile organic compounds such as the BTEX compounds on a gasworks site.

Portable gas detectors, based on electronic sensors, could also be used in testing for ammonia or hydrogen sulphide concentrations, although the odours of these gases would usually make their presence quite apparent to workers on site. More important could be gas detectors for hydrogen cyanide which could form from the photodissociation of complex cyanides and reach elevated concentrations in confined spaces such as test pits, trenches or tanks.

3.5.2 Gas detector tubes, passive badges, sorbent tubes and filters

These are available for a wide range of gases and vapours, although the most likely applications at gasworks sites would be much the same as for the portable analysers noted above; i.e. volatile hydrocarbons, ammonia, hydrogen cyanide and hydrogen sulphide. These sampling devices give “average” readings of air contaminants, over either short or long time periods, unlike the gas analysers discussed above which give “real-time” readings. They do, however, have the advantage of being much less expensive.

Gas detector tubes, such as the Gastec or Drager products operate on the colorimetric principle. A detecting reagent is adsorbed on a support medium in the tubes and, upon exposure to the test substance in the air sample, a distinct colour change occurs, giving a quantitative indication of the concentration of the test substance via the calibrated scale on the tube. Gas detector tubes are available for ammonia, carbon dioxide, carbon monoxide, hydrogen sulphide, hydrogen cyanide, mercury, mercaptan, phenol, sulphur dioxide, total hydrocarbon vapours and the BTEX compounds.

Passive badges and diffusion tubes are either of the self-indicating type or the sorbent type which require subsequent laboratory analysis. Colour indicating badges are available for ammonia, carbon dioxide, carbon monoxide, hydrogen sulphide and sulphur dioxide. A direct indicating diffusion tube is available for hydrogen cyanide. Sorbent tubes and filters are available for a wide range of organic and inorganic gases, vapours and aerosols.

3.5.3 Portable analytical equipment

A range of portable analytical equipment is now available but this has not been widely applied in New Zealand. This includes X-ray fluorescence equipment useful for the preliminary assessment of the spatial extent of elemental contamination, as well as portable GCs, GC/Mass Spectrometers, Thermal Desorption GC/MS, Infrared detectors (for organics) and Anodic Stripping Voltammeters (for trace metals).

3.6 Quality assurance requirements

Quality assurance procedures during analytical work are essential for the provision of meaningful results. This includes procedures for sample storage and preservation, sub-sampling, calibration and the analysis of quality control samples. Each of these is discussed briefly below, but laboratories should also examine the more comprehensive coverage given in some of the major references, such as EPA SWP-846 (US EPA 1994, MfE/MoH 1993, ANZECC 1994 and CCME 1993).

3.6.1 Sample containers and sample storage

Sample containers should be carefully chosen and pre-treated to ensure minimal or no interactions between the samples and the container materials. Specific recommendations for gasworks containers are given in the field sampling notes, elsewhere in these Guidelines.

Storage requirements for gasworks samples are also covered in the field sampling notes. It is essential that these be followed, to minimise the possibility of sample degradation or other changes in composition, before analysis.

3.6.2 Sample preparation and sub-sampling

Many of the samples collected from gasworks sites will be heterogeneous in nature and it is important that these be properly processed and sub-sampled prior to analysis, to ensure representative results.

Sample type	Requirements
Liquids	Samples containing visible amounts of sediment should be filtered before analysis, unless the method is intended to cover the total amounts of contaminant present in the sample. Even in this case it may be preferable to analyse the sediment separately from the liquid, because a “total” result will be affected by the relative amounts of sediment and liquids in sub-samples taken.
Soils ⁶ and sediments	<p>Where the amount of material required for an analysis is greater than 10g, samples may be analysed on an “as received” (i.e. wet) basis after removal of any stones and other large objects, and thorough mixing of the samples. Any superficial water should be decanted from sediment samples prior to mixing. Any analyses for volatile contaminants such as petroleum hydrocarbons, must be carried out on as received wet samples to avoid losses during drying, or samples which are highly heterogeneous, or when test portions less than 10g are required, samples should be dried, ground and sieved before collection of the analytical portion. Samples should be air dried (30-35 C, <65% relative humidity, 16 hours or longer if required) and ground so that less than 5% is retained on a 2mm sieve.</p> <p>If composite samples are to be analysed, these should be prepared from equal quantities of subsamples taken through the full drying and sieving process. No more than five subsamples should be used to form a composite, to avoid excessive dilutions of individual samples.</p> <p>Extreme care should be taken to avoid cross contamination during the sample preparation process and to minimise spread of dust in the laboratory. Equipment and containers used must be thoroughly cleaned before each sample to prevent cross-contamination. Cleaning procedures will vary according to the analytes being determined. Generally detergent washing, followed by deionised distilled water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid before distilled water rinsing. Solvent rinsing followed by air drying will normally be required before homogenising samples for organics analysis. Frequent laboratory reagent blank analyses will be required to check for contamination.</p>

3.6.3 Calibration and standards

All of the methods in these notes require some form of calibration to ensure the accuracy of the results. This will normally be achieved through the use of working standards, prepared as part of the analytical procedure. However, it is important that these standards be cross-referenced to primary standards, and preferably to an externally sourced reference materials as well.

It is essential that detailed procedures are in place to manage and document the traceability and validity of reference materials and derived solution standards used in analytical methods. Documentation should include at least the following:

- a suitable coding system for uniquely identifying all primary and derived standards
- records of receipt of all primary reference compounds or certified standards including source, purity and expiry date

⁶ **WARNING: Grinding of soils to fine dimensions may produce airborne particles which present a health hazard. Preparation should be performed in a fume hood, and appropriate respiratory protection should be worn.**

- records of preparation of all stock standard solutions including dates of preparation and expiry, weight of reference material, final volume and solvent of dilution, signature of check by laboratory manager or person responsible for quality assurance policy in the laboratory
- records of preparation of all primary dilution and calibration (working) standard solutions including aliquot volume(s) or weight(s) of stock standard(s), final volume and solvent of dilution, expiry date, signature of check by laboratory manager
- records of confirmation of identity and concentrations of analytes in standard solutions including GCMS, comparisons of concentrations with those of previous standards and comparisons of concentrations with those of standard solutions exchanged with other laboratories.

3.6.4 Quality control procedures

3.6.4.1 Recommended QC procedures

It is recommended that the QC steps described in Chapter 1, “Quality Control” of “Test Methods for Evaluating Solid Waste”, US EPA Publication SW-846 (US EPA 1994), be adopted for all soils analyses. They are also applicable to most water analyses.

In particular, it is expected that analysts would implement the following QC steps with each analytical batch, or with each twenty samples, whichever is the smaller.

	QC Control Procedure
Laboratory reagent blank	At least one determination of a blank to establish the contribution to the analytical signal by reagents, glassware etc. The blank should be subtracted from the gross analytical signal for each analysis before calculation of sample analyte concentration.
Replicate analysis	Duplicate analysis of at least one sample from the batch. The variation between replicate analyses should be recorded for each batch to provide an estimate of the precision of the method.
Quality control sample	Analysis of at least one control sample, either a standard reference material, a laboratory reference material or a control matrix fortified with analytes representative of the analyte class. Recovery check portions should be fortified at concentrations which are easily quantified but within the range of concentrations expected for real samples.
Surrogate analytes	Surrogates should be added to all analyses for determinations where it is appropriate (e.g. chromatographic analysis of organics). Surrogate spikes are known additions to each sample and matrix spike or reference sample analysis , of compounds which are similar to the analytes of interest in terms of: <ul style="list-style-type: none"> • extraction • recovery through clean-up procedures, and • response to chromatographic or other determinations, but which • are not expected to be found in real samples, • will not interfere with quantification of any analyte or interest, and • may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GC/MS system. Surrogates are added to the analysis portion before extraction to provide a means of checking, for every analysis, that no gross errors have occurred at any stage of the procedure leading to significant analyte losses.
Internal standards⁷	use of internal standards is highly recommended for chromatographic analysis of organics. Internal standards are added, after all extraction, clean-up and concentration steps , to each final extract solution. The addition is a constant amount of one or more compounds with similar qualities to 4(d), 4(e) and 4(f) above.

Internal and surrogate standards are most use for trace analytes where analyte losses during extraction or chromatography and small final volumes can give rise to considerable errors.

⁷ Internal standards are used to check the consistency of the analytical step (e.g. injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation. The instrument is usually calibrated using the ratio of peak height or area for analytes compared with that for the internal standard(s). Surrogates are treated as analytes for quantification.

They are of lesser utility for samples with very high concentrations of analytes as the responses of small quantities of added standards are likely to be swamped or to be lost in dilution of final extracts.

In addition to the above within-batch QC samples, it is also strongly recommended that the laboratory participate in inter-laboratory sample exchange and collaborative study programmes, and periodically analyse certified reference materials. These QC activities provide invaluable experience and external reference to validate analytical methodology and give confidence in data produced.

It is also recommended that a field control sample, spiked with analytes in the mid-range of anticipated sample concentrations, be analysed for every matrix type from a site assessment study. Such samples provide information on the potential of the matrix to cause positive or negative bias. For soil and sediment samples the spike should be applied to fresh material which has already been dried, ground and sieved. An unspiked duplicate sample must also be analysed to establish the naturally occurring analyte concentrations.

3.6.5 Data management

Effective data management is an essential final stage of any analytical procedure, to ensure the overall validity of the results. This can involve the following steps:

- data recording and documentation, including data custody records and checks on any data transfer operations
- data validation, including checking that all calculations are correct, identification of outliers and instrument drift
- data verification, which includes checking that all the data is present and correct
- data handling, which includes data rounding and treatment of significant figures, in accordance with recognised methodologies.

This subject is more fully discussed in MfE/MoH 1993 and CCME 1993.

3.6.6 Laboratory accreditation

Where possible laboratories engaged in analytical work should be accredited by an appropriate agency such as Telarc.

3.7 References

- 1 Australian and New Zealand Environment and Conservation Council (ANZECC) 1994. Draft guidelines for the analysis of contaminated soil, December.
- 2 APHA, AWWA, WEF 1995. Standard methods for the examination of water and wastewater, 19th edition.
- 3 API 1987. Manual of Sampling and Analytical Methods for Petroleum Hydrocarbons in Groundwater and Soil, API Publication No. 4449, Appendix B-3.
- 4 CCME 1993. Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites; Volume I, Main Report, Report CCME EPC-NCS62E, December.
- 5 Department of the Environment 1987. Problems arising from the redevelopment of gasworks and similar sites. Second Edition. Environmental Resources Ltd, April.
- 6 Douglas G S et al 1992. The use of hydrocarbon analyses for environmental assessment and remediation, Journal of Soil Contamination, 1(3), 197-216.
- 7 Gas Research Institute 1987. Management of manufactured gas plants sites. Report GRI-87/02601, Vols. 1-4
- 8 Gas Research Institute (GRI) 1989. Cyanide in MGP Wastes, Investigation of Analytical Methods, Report GRI-89/0165
- 9 Ministry for the Environment and Ministry of Health (MfE/MoH) 1993. Draft Health and Environment Guidelines for Selected Timber Treatment Chemicals. December.
- 10 Roques D E, Overton E B, and Henry C B 1994. Using GC/MS Fingerprint Analysis to Document Process and Progress of Oil Degradation, Journal of Environmental Quality, 23, July-August.
- 11 Thomas A O and Lester J N 1994. The Reclamation of Disused Gasworks Sites: New Solutions to an Old Problem, The Science of the Total Environment 152 , 239-260.
- 12 US EPA 1994. EPA SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd Edition, November 1986, plus subsequent updates, to Proposed Update III, January.
- 13 US EPA 1995. Methods considered within the scope of existing wastewater methods under the EMMC performance-based methods system. Office of Science and Technology, June.

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Appendix 3A

Definitions⁸

Internal standard	A pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component. In practice internal standards are added prior to the final instrumental determining stage.
Surrogate analyte	A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction and is measured with the same procedures used to measure other sample components. Where mass spectrometric detection is used, internal standards or surrogate standards may be isotopically labelled analogues of one or more of the analytes.
Laboratory duplicates	Two sample aliquots taken in the analytical laboratory and analysed separately with identical procedures. Analyses of duplicates give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
Field duplicates	Two separate samples collected at the same time and placed under identical conditions and treated exactly the same throughout field and laboratory procedures. These give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.
Laboratory reagent blank (LRB)	An aliquot of reagent water or quartz sand that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.
Field control sample (FCS)	A sample of field matrix which contains levels of analytes of interest which are low compared to those expected in test samples. The FCS should otherwise be as similar as possible to the test samples. Aliquots of FCS, alone and fortified with analytes, carried through the complete method provide essential data on interferences, analyte recoveries and detection levels for a method as being applied in a given laboratory at a given time.
Laboratory performance check solution (LPC)	A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.
Laboratory fortified blank (LFB)	An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analysed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.
Laboratory fortified sample matrix (LFM)	A portion of an environmental sample, usually a field control sample, to which known quantities of the method analytes are added in the laboratory and then analysed exactly like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results, i.e. whether the matrix causes interferences or reduced recoveries of the analytes. The background concentrations of the analytes in the sample matrix alone must be determined in a separate aliquot and used to correct the measured values in the LFM.
Stock standard solution	A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a simple analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.
Primary dilution standard solution	A solution of one or more analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.
Calibration	A solution prepared from the primary dilution standard solution of the analytes and stock

⁸ Ministry for the Environment and Ministry of Health (1993). Draft Health and Environmental Guidelines for Selected Timber Treatment Chemicals, December.

standard (CAL)	standard solutions of the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
Quality control sample (QCS)	A sample matrix containing method analytes, portions of which are regularly analysed to check that a method is in control. A QCS can be a fortified sample matrix (either laboratory or external). A thoroughly homogenised field sample with analytes present as weathered residues can also be used as a QCS. The QCS may be locally prepared from a bulk sample containing analytes in relevant concentration ranges (laboratory reference material) or from external sources where the QCS may have been carefully validated by an inter-laboratory collaborative study.
Accuracy	Closeness of a result or the mean of a set of results to the true value. Accuracy is assessed by means of laboratory fortified matrix samples or external QC samples.
Precision	A measurement of the agreement of a set of replicate results amongst themselves without assumption of any prior information as to the true result. Laboratory precision is assessed by means of analysis of duplicate/replicate sub-samples.
Repeatability	The precision, usually expressed as a standard deviation, that measures the variability among results of measurements at different times on the same sample at the same laboratory.
Reproducibility	The precision, usually expressed as a standard deviation, that measures the variability among results of measurements of the same sample at different laboratories.
Replicates	Repeated but independent determination on the same sample by the same analyst at essentially the same time and under the same conditions.
Method detection level or limit (MDL)	The lowest concentration at which individual measurements for a specific analyte are statistically different from a laboratory blank with a specified confidence level for a given method and representative matrix. For a 95% confidence interval $MDL = 3 S_B/M$. where M = slope of calibration line for analyte S_B = standard deviation of the noise level or the background signal (usually from a field control sample).
Reliable detection level (RDL)	Lowest recommended concentration of analyte for making qualitative decisions based on individual measurements for a given method and representative matrix. Recommended to be 2 x MDL (CCME 1993)
Reliable quantitation level (RQL)	Lowest recommended concentration of analyte for making quantitative decisions based on individual measurements for a given method and representative matrix. Recommended to be 4 x MDL (CCME 1993).
Estimated quantitation limit (EQL)	Lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL.

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Appendix 3B

Summaries of test methods

Method	Comment
SW-846 Method 8270B (Capillary GC-MS for Semi-volatile Organics in Solid or Liquid Waste)	This is a screen based on solvent extracts prepared using the 3500 series protocols. However the low resolution mass spectrometric detection (full scan mode) covers a wider range of contaminants with higher selectivity than ECD or FID. The high resolution capillary column separation also improves selectivity and inertness in the analytical system.
EPA-600 Method 525.1, rev 2.2, 1991 (Determination of Organic Compounds in Drinking Water using Liquid/Solid Extraction and Capillary GCMS)	This screen is similar to SW 846 8270B in the determination of a wide range of contaminants using capillary GCMS except that revised phase adsorbents (column or disk) are used to concentrate contaminants from water samples.
SW-846 Method 8040A, rev. 1, 1990 (Phenols by gas chromatography)	<p>This concentrates on the determination steps but indicates that phenols can be recovered from waters by liquid-liquid partition (Method 3510 Separating funnel or Method 3520 Continuous liquid-liquid) or from solid waste by solvent extraction (Method 3540B Soxhlet or Method 3550B Sonication). Clean-up is by acid base partitioning (Method 3650A) and, for low levels in soil, gel permeation chromatography (Method 3640A).</p> <p>The specificity of packed column GC-FID is low and interferences from other acidic compounds may be expected. Also acidic phenols are liable to tailing and other adsorption effects in the GC, effects which can be variable and influenced by co-extractives and therefore lead to poor quantitation.</p> <p>The method also provides for a derivation step to form pentafluorobenzyl-ethers of the phenols which have more reliable GC performance and give high responses to the electron capture detector (ECD) However, a time-consuming silica gel chromatographic clean-up is required to remove interferences including derived co-extractives. The method has been validated for a range of phenolics including cresols.</p>
SW-846 Method 8260 (Volatile Organics by Gas Chromatography/Mass Spectrometry: Capillary Column Technique)	This is a screen based on a purge-and-trap extraction technique. The method is applicable to nearly all types of samples, regardless of water content, including groundwater, soils, and sediments. It covers 58 volatile organic compounds including all of the monocyclic aromatic hydrocarbons and naphthalene. The low resolution mass spectrometric detection (full scan mode) covers a wider range of contaminants with higher selectivity than ECD or FID. The high resolution capillary column separation also improves selectivity and inertness in the analytical system.
EPA 524	GC/MS method used for detection of extremely low levels of halocarbons and aromatic hydrocarbons in drinking water.
EPA 624	GC/MS method used for detection of ppb levels of halocarbons and aromatic hydrocarbons in wastewater or groundwater.
EPA 3510B	GC/MS method used for detection of ppb levels of halocarbons and aromatic hydrocarbons in wastewater or groundwater.
EPA 3540B	Soxhlet extraction procedure for the extraction of non-volatile and semi-volatile organic compounds from solids such as soil, sludges and wastes. The procedure is undertaken in such a way that will ensure intimate contact of the sample matrix with the extraction solvent.

EPA 3550A	Ultrasonic extraction procedure for the extraction of non-volatile and semi-volatile organics compounds from solids such as soils, sludges and wastes.
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	The procedure involves the use of a horn-type probe sonicator or equivalent device that will ensure intimate contact of the sample matrix with the extraction solvent.
EPA 3560	Supercritical fluid extraction procedure for the extraction with supercritical fluids of total petroleum hydrocarbons (TPH) from soils, sediments and other solid matrices which are amenable to extraction with conventional solvents. The method is suitable for use with any supercritical fluid extraction system that allows the temperature, pressure and flowrate to be adjusted to achieve separation of the TPHs from the matrices of concern. This method is not suitable for the extraction of low boiling TPHs such as gasoline.
EPA 3040	Prepares oily waste samples for soluble metals determination by AA and ICP methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease or wax (and tar) content.
EPA 3050	Prepares waste samples for total metals determination by AA and ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges and solid waste samples.
EPA 3051	Prepares sludges, sediments, soils, and oils for total metals determination by AA and ICP. Nitric acid is added to the representative sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.