CO_2 Capture Mongstad - Project A – Establishing sampling and analytical procedures for potentially harmful components from post-combustion amine based CO_2 capture

Task 2: Procedures for Manual Sampling

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EXECUTIVE SUMMARY

Treated flue gas from amine post-combustion capture (PCC) plants is expected to contain trace levels of compounds derived from the amine solvents. These may include some of the amine itself but also various degradation products produced in the plant. Some of these compounds are known to be toxic so it will be necessary to analyse the stack emissions to ensure that PCC plants operate within national environmental guidelines. Procedures are therefore required for the collection of samples of the treated flue gas for subsequent analysis. The purpose of Task 2, which is reported here, was to examine and recommend methodologies suitable for manually collecting samples of gases and entrained aerosols from PCC plant stacks.

Stack sampling is well established and there are many internationally recognised standard methods available covering a wide range of materials emitted from combustion processes. Despite the variety of published stack sampling methods, very few appear to be directly applicable to PCC plants because most of the compounds that have been suggested as possible constituents of PCC flue gases are not normally encountered in conventional combustion processes. Of the standard stack sampling methods currently available, the following have the most promise for use in a PCC plant:

- German Standard VDI 2066 – particulate matter
- USEPA Method 5 – particulate matter
- USEPA Method 0011 – aldehydes and ketones
- Japanese Standard JIS-K0099 – ammonia

Although the range of relevant stack sampling methods is small, there are numerous other methods for monitoring ambient air quality or workplace exposures. Many of the classes of compounds anticipated in PCC flue gas are covered by one or more of these methods. Since the general principles of stack sampling methodology apply regardless of the material being sampled, it is likely that some of these non-stack methods can be successfully adapted for use in PCC stacks. In adapting these methods, however, attention must be given to the equipment, potential interferences, preservation of the samples, detection limits, and the uncertainties of the methods.

When designing a sampling regime for a complex system such as an amine PCC plant, it must be remembered that the sampling procedures cannot be considered in isolation from the laboratory procedures needed to analyse the materials. Since these are also evolving, the sampling methods proposed here should be considered a first attempt based on the best information currently available. It is very likely that as developments are made in analytical chemistry and operational experience is gained with real-world amine plants, the sampling procedures will also evolve over time. Because of this uncertainty, rather than attempt to provide a set of prescriptive methods (that may need to be changed), we have developed a set of more general guidelines and recommendations that can assist experienced staff in setting up sampling regimes at the Mongstad PCC plant.

The main recommendations resulting from this investigation are:

Sampling Apparatus

- Many of the target species are likely to be dissolved in liquid droplets entrained in the gas flow. Because of the presence of liquid (and possibly solid) aerosols, sampling should be undertaken isokinetically unless reliable measurements of the particle distribution within the PCC plant show that this is not necessary (i.e. the Stokes diameter is sufficiently small). High quality stack sampling equipment should be used to maintain isokinetic conditions. Automatic samplers or closed loop controlled stack samplers are preferred since they provide increased accuracy and precision especially when the stack flow is variable. All equipment should be calibrated against traceable reference standards. The capture and transmission efficiency of the sampling system for target compounds should be quantified. This information may be supplied by the manufacturer for some compounds if a commercial apparatus is used.

- Components of stack sampling equipment in contact with flue gas and its condensates should be made from at least 316 stainless steel that has been polished and acid passivated. For many of the compounds targeted, silanised borosilicate glass or quartz, or Teflon will be more appropriate.

- Tube connections within the probe should have smooth transitions with taper angles < 30° to eliminate areas for gas flow to stagnate.

- Only high quality vane pumps of a sealed and pressure pulse-free design should be used in the sample train, and especially when dry gas meters are used to measure gas volumes. All materials in the pump and sample train must be amine free; o-rings should be Teflon encapsulated and contained within “captured” o-ring grooves.

- Heated probes and lines should be used where possible to eliminate condensation, but only for thermally stable compounds. Sorption cartridges should be used with heated sampling probes and lines and operated above the dew point of the flue gas.

Sampling Methods

- Some species may be amenable to analysis at the site using FTIR or micro gas chromatography but the system will have to be fully heated to prevent condensation in the sampling train and analytical instrumentation. If suitable equipment is available, this would be a worthwhile approach as it has been used successfully to measure ammonia and other trace organic compounds in high moisture, condensing industrial environments.

- There are relatively few stack methods that can be applied to a PCC plant without modification. Those recommended for use at Mongstad are:

    USEPA Method 5, VDI 2066, other standard particulate methods. Although particulates will only be a minor component of the flue gas, the general principles of isokinetic sampling will be applicable to sampling liquid aerosols.

    USEPA Method 0011 for aldehydes and ketones.

USEPA Method 18 for volatile organic compounds. This is not an isokinetic method, but it could easily be set up as such. Samples may be analysed at the stack or extracted into a heated Tedlar bag then analysed by gas chromatography. Alternatively, solid sorbents may be used, which provides considerable scope for adapting many of the ambient air methods to stack sampling in amine PCC plants.

JIS K 0099 for ammonia.

- It will be necessary to measure moisture in the stack gas. The most appropriate method is to assume that the gas is saturated at the measured temperature (according to method BS EN 14790:2005).
- There are numerous sampling methods designed for monitoring ambient air quality and workplace exposures. Most of these use solid sorbent materials to collect the target compound and many will be suitable for the range of compounds expected in amine PCC treated flue gas. Methods applicable to the Mongstad plant are:

  Nitrosamines – Most methods use commercially prepared ThermoSorb/N cartridges since they have been shown to overcome most interferences. Relevant methods are: NIOSH 2522, OSHA Method 27, OSHA Method 31, and USEPA Method TO 7.

  Amides – Silica gel is suitable for collecting amides; a relevant method is OSHA Method 2084.

  Amines – Silica gel or XAD-2 sorbent is used to collect amines from ambient air in workplaces. Methods include OSHA Method 60, NIOSH Methods 2002, 2007 and 2010. Alternatively, ISO 177734-2, which uses midget impingers containing dibutylamine, can be used for a range of amines.

  Ammonia – In addition to the stack-specific method JIS K 0099, OSHA Method ID 188 is also used for monitoring air quality. Both methods use acid impregnated sorbents.

  The main modification required to adapt these methods to stack sampling is that the sorbent cartridge will be attached to the sampling train in place of the impingers. As well, the sample line and perhaps the cartridge may need to be heated to prevent condensation in the system. These variations mean that the sampling methods will each have to be validated; i.e. the recovery efficiency will need to be determined for each material, preferably by using reference materials.

- To fully sample all of the material of interest using standard methodology, it is likely that a number of sample trains will be required.
- The composition of the flue gas from the Mongstad plant is largely speculative. Hence, it is suggested that early in the process of commissioning the plant that a bulk sample of condensate be collected for detailed analysis. Although this material may be subject to degradation due to unwanted reactions occurring in the liquid, it will nevertheless provide valuable qualitative information on the nature of the compounds

present. An extension of this simple approach is to cryogenically cool the condensate immediately after sampling which would effectively quench all degradation reactions.

Further Work

- A programme of stack sampling method development needs to be undertaken to design new procedures specific to compounds not currently covered by international methods. Examination of the current methodology shows that some of the characteristics of existing methods could be used to produce new robust stack sampling methods suitable for most of the materials expected at Mongstad. In particular, combining some of the features of isokinetic sampling used in USEPA Method 5 with the procedures of Method 18 and many of the ambient air methods would provide considerable flexibility.

- Cryogenic cooling of material collected from the stack may be a relatively simple method to preserve samples. If successful it may be possible to fully sample the stack emissions from a single sample train. This should therefore be investigated further to determine its collection efficiency and practicality for use in stack sampling. This work will, of course, need to be conducted in close cooperation with the analytical method development.

- None of the sampling methods suggested for use at Mongstad have been used at an amine PCC plant before. Consequently their performance in this application is largely unknown. It is therefore essential that all methods are properly validated, especially in relation to their collection efficiency, to ensure that sampling is representative of the stack conditions.

1 INTRODUCTION

Amine scrubbing is currently being considered as a method for reducing atmospheric emissions of CO_2 from fossil-fuelled power plants. The technology is relatively mature and has been used for many years in industrial gas cleaning processes. However, the scale of plants needed for post-combustion CO_2 capture (PCC) will be much larger than current industrial installations and the effect of emissions from these plants on the environment is not yet fully understood.

Atmospheric emissions are likely to include a certain amount of the amine solvent that escapes from the process (slippage) but degradation products, such as ammonia and various other compounds produced in the plant may also be emitted. Some of the materials that have been suggested as possible constituents of the exhaust gas are:

- *N*-Nitrosamines
- Alkylamines
- Amines (including alkanolamines)
- Amides
- Aldehydes
- Ammonia

Many of these compounds are toxic and consequently it will be necessary to quantify their emissions to ensure that acceptable environmental standards are maintained. Emission data are also needed for process optimisation purposes. Procedures are therefore required for representative sampling and analysis of the target species in the flue gas.

In Task 1, the design and location of the sampling points in the stack were considered (Halliburton et al., 2010). Particular attention was paid to the number and location of the sampling points necessary to achieve representative sampling. As well, measurement of the velocity of the gas stream and total gas flow was considered, since this is essential when reporting emission fluxes from plants.

The next step in the sampling process is the collection of the sample itself. Some of the gaseous components of the stack gas may be amenable to continuous online methods of analysis, and these are considered in detail in a separate study (Task 3, Riley et al., 2010). Most stack gas components, however, will need to be sampled manually, where samples from the stack are extracted for subsequent laboratory analyses.

Manual sampling involves inserting a probe into the gas flow from outside the stack, a pump to withdraw the gas, and collecting the sample in some form of sorbent or impinger train. The overall design of the entire sample train may be quite complex and depends on the physical state of the sample (e.g. solid particulate matter, liquids or gaseous material), its aerodynamic properties, the chemical nature of the target compound, but also on chemical interferences with other components that can occur during or after sampling.

To extract a representative sample from an exhaust stack, the sampling environment must be well understood; different environments generally require different sampling procedures. In industries where international stack sampling methods exist, this understanding has developed over many years of practical experience. Provided that the sampling location complies with recognised standards, and that the sampling methods are adhered to, these methods can be depended upon to yield representative samples. For new processes, or processes where sampling conditions differ from those defined by recognised methods, the sampling environment must be well characterised so that scientifically based modifications to existing methods can be made or new methods developed. For a new facility, such as the proposed Mongstad facility, recommendations can only be based on a model of what we consider to be the most likely conditions at the sampling location. Clearly, recommendations will require validation after construction of the facility.

The purpose of the study reported here (Task 2) was to examine the sampling process from the treated flue gas in an amine PCC plant such as that proposed at Mongstad. Attention is given to the equipment necessary, potential interferences, preservation of the samples, detection limits, and the uncertainties of the methods. We also examine some of the numerous stack sampling methods currently available and discuss their applicability to amine capture plants.

Finally, procedures for sampling various classes of compounds are recommended. However, it should be remembered that designing a regime for properly sampling such a complex system cannot be accomplished in isolation from the laboratory procedures needed to analyse the materials. Since this is also evolving (see Tasks 4 and 5, for example) the sampling methods proposed here should be considered a first attempt based on the best information that is currently available. It is very likely that as developments are made in analytical chemistry and operational experience is gained with real-world amine plants, the procedures will also evolve over time.

2 OVERVIEW OF SAMPLING AT THE MONGSTAD FACILITY

Treated flue gas emitted from the proposed Mongstad PCC plant is expected to be somewhat different to more usual stack emissions (from power stations, for example) so sampling conditions will also be different. As such, it is important to define these expected conditions and highlight how these differences will affect the suitability of sampling apparatus and international methods. The following is an overview of the sample conditions that are expected at the Mongstad facility and it is on this basis that recommendations for stack sampling and further research are based.

For the purpose of this study, we have assumed that the flow conditions at the sampling location will be compliant to an international standard i.e. the flow stream is relatively free from the effects of flow disturbances and is non-cyclonic (Halliburton et al., 2010). Sampling will most likely be multiphase which will pose challenges for the representative sampling of target species. The proposed design of the Mongstad plant and expected flue gas characteristics have been suggested as:

- Stack dimensions: 2.5-6.7 m diameter, square or circular section
- Flow Rate: 400 kg s^{-1}
- Temperature: 25-50 °C
- Composition:
    - Oxygen 15 mol %

- Nitrogen 81.5 mol %
- Carbon Dioxide 0.5 mol %
- Ammonia <50 ppmv
- Water 5 mol %
- Amines <5 ppmv

The Mongstad gas-fired facility is unlikely to produce significant levels of primary particles. However, the absorber will probably generate aerosols that will be entrained into the exhaust gas flow. Most of these aerosols would exist as condensed liquid droplets with a wide range of aerodynamic diameters. Solid phase aerosols may also be present as a result of secondary particle formation processes although it is expected that the mass of solid particles would be very low.

Many of the compounds of interest are highly soluble in water so a large proportion will be dissolved in the liquid droplets with the gas and liquid phases in dynamic equilibrium. This partitioning of a species between different phases is likely to vary according to plant operating conditions and may be difficult to predict or model. Thus many recommended sampling procedures may require further development after the Mongstad plant is commissioned.

For highly soluble species and for essentially insoluble species with slow dissolution kinetics, partitioning may have only a small impact on the sampling accuracy since the bulk of the species will reside in only one phase. However, for partially soluble species, partitioning the liquid and gas phases may provide challenges for obtaining quantitative samples. This latter aspect is an important difference between a “normal” stack sampling situation and sampling at the proposed Mongstad facility.

Another important difference is the temperature of the stack gas. Most conventional stack sampling is undertaken where the exhaust gas temperature is higher than its dew point whereas the Mongstat flue gas will be much cooler. Multiphase or condensing environments such as this provide significant challenges for the collection of the target species because it can be difficult to quantitatively collect both gas and liquid aerosol phases simultaneously without changing the phase equilibrium. Application of Henry’s Law helps in understanding the influence of gas phase solubility on stack sampling measurements; the Henry coefficients are useful in determining the significance of the phase partitioning upon sample accuracy.

During normal stack sampling, the temperature of the sample stream is kept above its dew point to prevent condensation in the sampling system. Highly condensing situations, on the other hand, can produce large volumes of condensate that can pose both collection and analytical problems. Hence even if the target material is normally a liquid, it may be preferable to collect the sample in the gas phase using sorbent cartridges or treated filters, for example (see Section 3.3.2). Where collection by condensation is necessary, it may still be preferable to transport the target species to the condensation trap in the gas phase to minimise interactions of the target species with the probe surfaces.

3 COLLECTION PROCEDURES

Occasionally, samples from stacks can be collected with minimal conditioning and directly analysed on site. This is the case for online continuous analysis systems (see Task 3 for a detailed discussion of these systems; Riley et al., 2010), but in some applications, other instruments may be taken on site for specific tasks. Examples are the use of micro gas chromatographs, or portable electrochemical cell analysers for periodic analyses of flue gases.

Non-routine analyses can also be achieved in this manner. In one example with which we are familiar, Park et al. (2005) used high resolution Fourier transform infrared spectroscopy (FTIR) to analyse trace gaseous products from steam gasification of coal. In this system, the gas stream was analysed directly using a 3 m multipass gas cell which was heated to 110 °C to prevent moisture condensation (Figure 3.1). Despite the very high concentrations of moisture in the sample, ammonia and various other nitrogen-containing compounds were quantitatively analysed. This technique is also the basis of NIOSH Method 3800 for analysing a range of organic and inorganic gases.

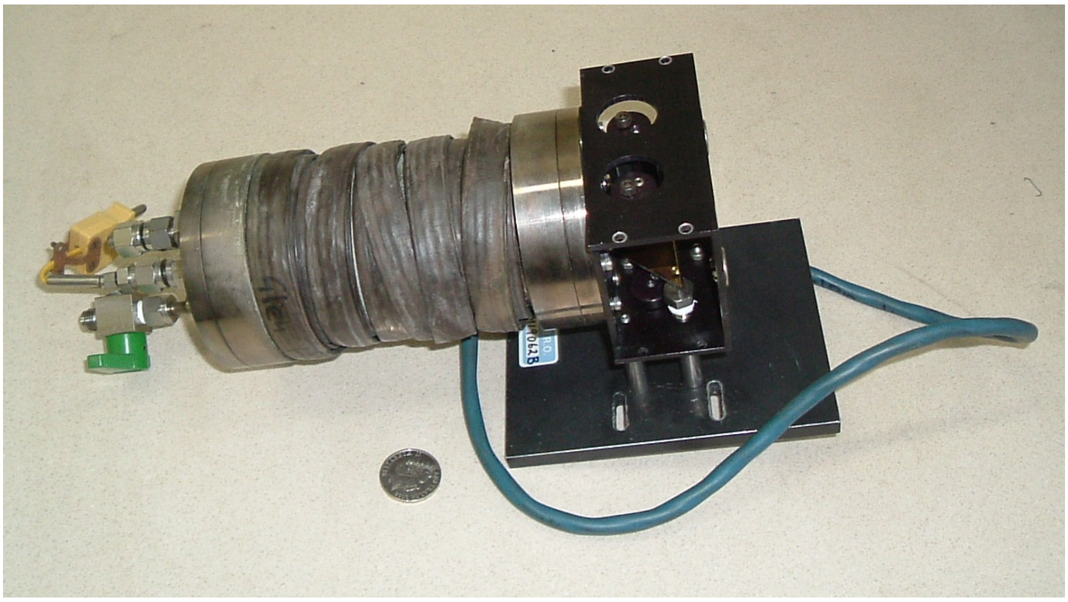

Figure 3.1 Heated cell for FTIR analysis of flue gas.

Although such systems are very useful, it is often the case that the analyses required cannot be performed on site. In these cases, the stack gas must be manually sampled, which involves withdrawing a sample of material from the stack that can then be analysed in a laboratory. The equipment necessary for manual sampling depends on the type of material being collected, and may be quite elaborate. It generally has a probe that can be inserted into the stack, a pump and metering system to measure the gas flow, and some sort of collection device for retaining the sample. The complete system is known as the sampling train. Manual sampling has advantages for analysis of species at trace concentrations since a sample can be collected over an extended period of time and concentrated, which improves the detection limit of the method.

Broadly speaking, manual sampling systems collect material on three types of media:

- Filters – usually for solid particulate matter;

- Liquids – where the sample may be collected either as liquid condensate or by reacting with a specific reagent;
- Solid sorbents – sorbent material typically used for retaining gas phase components of the gas stream.

In the following sections, the various components of the sampling train are discussed.

3.1 Design of Sample Trains

The sampling train comprises a number of components that may include a sample nozzle and probe, filter holder, particle sizing device and/or impinger train, pump and associated flow control system, and a system for measuring the volume of sample gas collected. Stack sampling is conducted in a wide range of gas streams that can be corrosive, at high temperatures or with entrained abrasive particles. Thus the materials used for the system must be sufficiently robust to cope with these conditions. The surfaces of the components in contact with the sample stream must also be compatible with the target analyte compounds.

Stack sampling is widely practised and there are several commercial suppliers that sell off-the-shelf complete sample trains for both isokinetic and gaseous sampling (see Appendix B for a list of some common suppliers). These systems include the sample nozzle and probe, filter holder, impingers, pump and gas flow meter and are designed to comply with the requirements of most common stack sampling standards. An example of a commercial isokinetic sampling train is shown in Figure 3.2.

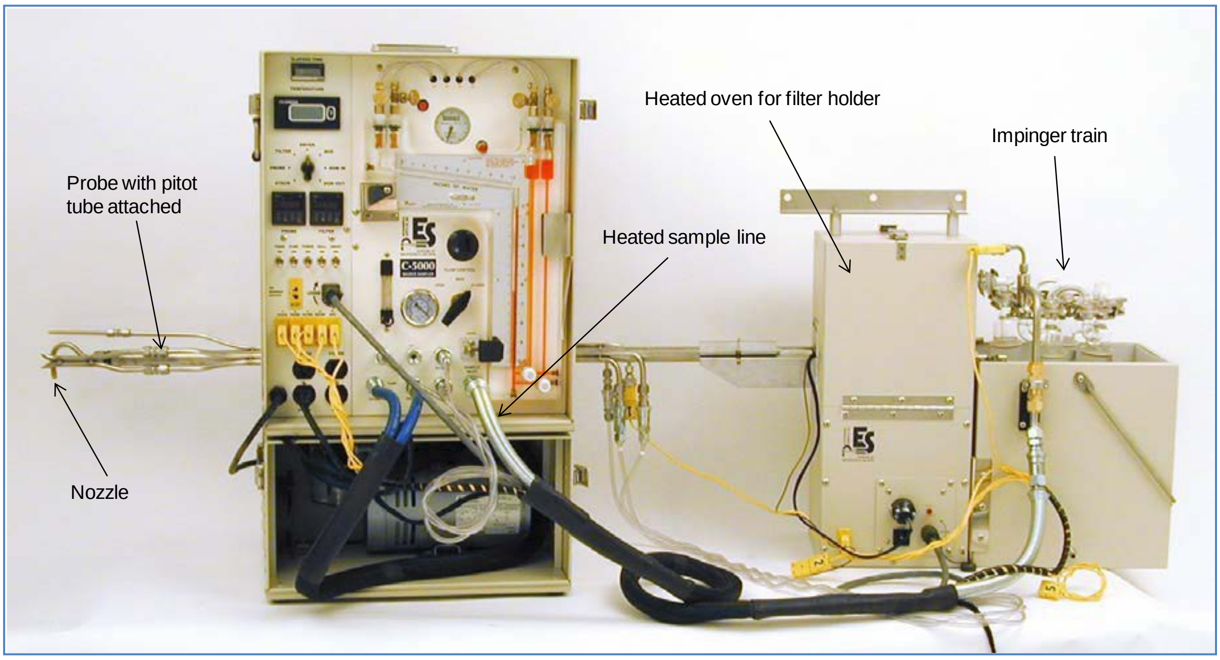

Figure 3.2 An example of a commercially available sampling train apparatus.

Commercial stack sampling systems designs are fundamentally similar, regardless of the manufacturer and will produce a representative sample from the environments for which they were designed. However, for sampling conditions that deviate from the normal sampling environment that is prescribed in standard international methods, the use of commercial stack sampling apparatus and systems must be carefully considered and evaluated.

A number of stack sampling operators also manufacture their own sampling apparatus. It is important where this occurs that the apparatus be well constructed so that it conforms to the appropriate international standards and is calibrated to traceable standards. For unusual sampling environments that differ from conventional stationary sources (like the proposed Mongstad facility), it is likely that commercial sampling systems will require some modifications. Any deviation from accepted international stack sampling methods must be based on a thorough understanding of the principles of sampling and the sampling environment.

3.1.1 Sample Nozzle and Probe

In the simplest case, the sample probe is a tube that can be placed in the desired location within the gas flow of the stack. Provided that the material is not reactive or subject to corrosion, a simple probe may be satisfactory for sampling many gases and would also be suitable for most applications where the sample is analysed on site (either an online or other instrumental method as described above).

When aerosols are present in the exhaust gas it is most likely that isokinetic sampling will be required. Halliburton et al. (2010) describe why and when isokinetic sampling is required and how mass biases can occur when aerosols are not isokinetically sampled. Additionally, the conditions when isokinetic sampling is not required are described. It is assumed that at the proposed Mongstad plant the Stokes diameter of the aerosol droplets in the flue gas will be sufficiently large to require isokinetic sampling. Many of the compounds of interest are also highly soluble in water so they may be dissolved in the liquid droplets. As already mentioned in Section 2, some compounds will partition between the gas and liquid phases so careful sampling of both the gas and aerosols will be required.

Isokinetic sampling involves the aspiration of an aerosol, either solid or liquid, into the inlet of a sampling device without changing the velocity or trajectory of the particles, and without influencing the aerosol size distribution of the sample. The sample nozzle is a tube with a sharp leading edge that cuts the sample from the flowing gas stream but with minimal perturbation to either the aspirated sample or the gas flow around the nozzle (Figure 3.3).

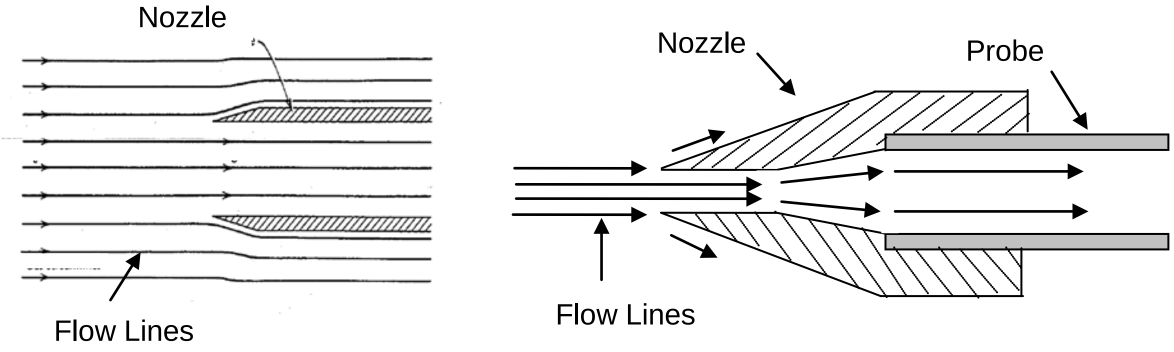

Figure 3.3 Nozzle designs. Copyright Hinds 1999 (left diagram) CSIRO (right diagram)

Figure 3.3 (left) shows a simple nozzle design. In this case the nozzle is simply a tube with a polished, sharp-edged chamfer of 15° machined into its end. This diagram also shows the flow lines that are expected during isokinetic sampling.

In all but the simplest of sampling, a range of nozzle opening diameters is required to maintain isokinetic velocity over a wide range of stack gas velocities. Figure 3.3 (right) shows the nozzle and the transition to the sampling tube. In this case the nozzle consists of a polished cone that fits over the sample tube. The opening diameter of the nozzle is calculated to maintain the isokinetic velocity at the nozzle tip. To accommodate the range of flows encountered, nozzles are supplied as a set with different sized tapered inlets, which allows the operator greater flexibility in controlling the sampling flow rate to maintain the isokinetic criterion. Nozzles also have smooth and polished transitions from the nozzle opening diameter to the probe diameter. This form of nozzle is often used when a particle sizing device such as a cyclone or cascade impactor is used.

Where out-of-stack sampling methods are used or where the filter assembly is placed out of the stack (usually in a heated box) a slightly different nozzle and flow transition piece is used. Since the probe is inserted perpendicular to the flow direction, the nozzle contains a smooth 90° bend so that the inlet orifice is facing directly into the gas stream (Figure 3.4). The nozzle opening is also chamfered at 15° and the transition between the nozzle opening diameter and the diameter of the sampling probe occurs within the bent nozzle. When this system is used, a range of bent nozzle pieces each with different diameters is supplied.

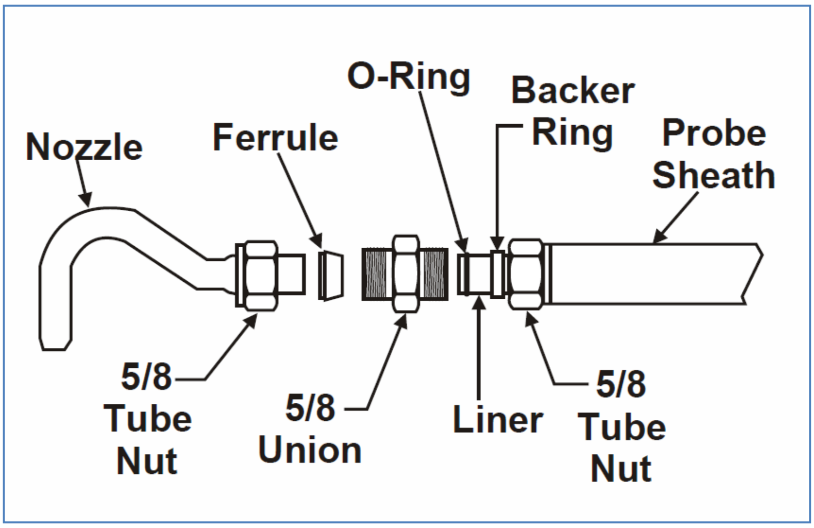

Figure 3.4 Nozzle used for isokinetic sampling

Nozzles are usually made from stainless steel but aluminium, glass and quartz are also used. During out-of-stack sampling the liner is usually made of the same material as the nozzle to maintain the integrity of the sample.

The materials used for the construction of the probe as well as how these materials are prepared and passivated prior to operations are likely to be important at the Mongstad facility due to the chemical reactivity of some of the compounds present. Thus inert materials will be necessary for all wetted surfaces. As has been discussed in Halliburton et al. (2010) copper and its alloys should be avoided due to corrosion problems with amines. As a minimum, 316L grade stainless steel should be used. Commercial stack sampling probes are usually constructed from this material. However, for amine plants, the stainless steel surface should be acid passivated to increase its corrosion resistance. Additionally, the corrosion resistance should be monitored until it has been confirmed that there is no degradation within the amine environment. If corrosion is observed, either quartz or a high chromium content alloy such as a 900 grade stainless steel should be used.

If necessary, additional passivation may be achieved by silanisation of the internal surfaces of the probe. Silanisation is a process where the surface of usually glass (but also quartz and some metal oxides) is modified to increase its hydrophobicity by attaching a layer of alkyl groups to the substrate material. Teflon may also be used as a liner; however, it is not suitable for out-of-stack sampling of particulates because particles tend to agglomerate on this material.

The nozzle is connected to a probe liner directly or through a sizing device such as a filter holder or cascade impactor. As it is expected that few primary particles will be encountered in the Mongstad stack gas, particle sizing devices are not considered in this report. When in-stack sampling methods are used, the filter holder containing the particle filter is located between the nozzle and the liner. While in-stack sampling is operationally more difficult, it has a number of advantages for collecting representative samples. These include:

- A very short sample tube between the nozzle opening and the sample capture device that minimises contact of the target species with the wetted surface area of the probe.
- Probe liners do not need to be cleaned out to recover material that deposits before reaching the collection device.
- The probe and liner do not need to be heated or constructed of exotic materials since the capture device is placed upstream of the probe.

The disadvantage of in-stack sampling is that the whole probe must be removed from the stack every time the filter or sizing device requires changing. However, it is recommended that in-stack sampling be utilised where possible to minimise the influence of the sample probe.

The nozzle, particle sizing/filtering device (if used) and liner are supported by the probe sheath. This is often a length of stainless steel tube between 25 and 50 mm in diameter and is of sufficient strength to comply with the minimum sag requirement of international methods. Typically a maximum of 2° sag over the length of the probe when supported at its maximum extension is tolerable. The probe sheath also mechanically protects the liner and provides a conduit for the other associated instrumentation attached to the sample probe (e.g. temperature, flow and dew point of relative humidity measuring devices).

The probe sheath connects the nozzle to the pump and sample capture devices that are located outside the stack. Suitable materials for the probe sheath have been discussed above.

3.1.2 Filter Holder and/or Particle Sizing Devices

Solid particulate matter is usually collected on a pre-weighed glass, quartz or Teflon filter, thus a suitable holder is required to support the filter during sampling. The holder is usually made from stainless steel, borosilicate glass or quartz. For some elemental work aluminium has been used, although it is not suitable in high pH environments. For sampling at the proposed Mogstad plant, it is recommended that passivated 316 grade stainless steel or silanised glass or quartz be used.

Filter holders should be designed to enable a smooth gas flow transition between the sampling nozzle and the filter (in-stack method) or between the probe liner and the filter holder (out-of-stack sampling) with a taper angle of no more than 30° at the inlet of the filter holder. All joints and angular transitions should be well fitting and preferably sealed with “captured” o-rings to reduce the exposure of the o-ring to the gas sample. The o-ring material should be compatible with amines; Teflon encapsulated o-rings are recommended. The filter, nozzle assembly and joints should contain no areas that allow gas stagnation where fine particles can collect. Figure 3.5 shows a schematic diagram of a nozzle filter assembly highlighting smooth transitions between each component.

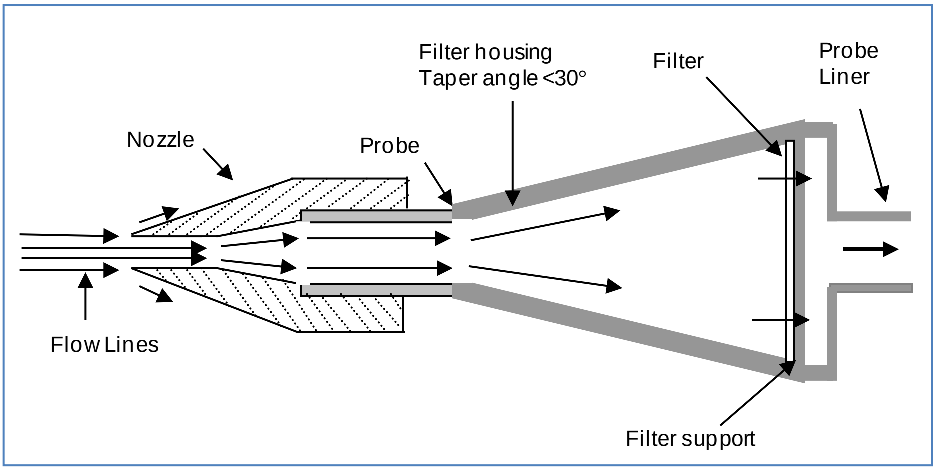

Figure 3.5 Filter transition design

Filters may be either in-stack where the holder is inserted into the bulk gas stream (Figure 3.6) or out-of-stack where it is connected to the nozzle via the sample probe.

Figure 3.6 In-stack sample probe fitted with a 90 mm stainless steel filter holder

The use of correctly configured impactors has the advantage that particle size distribution may be determined. For example, ISO 23210 splits the sample into three size fractions: >10 μm; 10 μm to 2.5 μm; < 2.5 μm. Figure 3.7 shows an in-stack, seven-stage cascade impactor that is equipped with a >10 µm sizer upstream of the cascade impactor assembly. This device was used both upstream and downstream of the filter device in a coal-fired power station.

Figure 3.7 In-stack, seven-stage cascade impactor for particulate sampling

3.1.3 Heating of Sampling Components

International stack sampling methods usually stipulate that the sampling probes and liners must be heated to above 100 °C to eliminate condensation within the sample tube. Probe heating is essential to avoid condensation when the dew point of the stack gas is greater than ambient temperature. Without heating, liquid water may condense on the filter or other sorbent surface, which may affect the collection efficiency of the collection medium. As well, solid ionic phases that would normally be collected by the filter may dissolve into the mobile aqueous phase and be transported through the filter, and not captured. This latter aspect is important for gravimetric measurements as a reduced mass will be reported.

It is recommended that heated probes be used for thermally stable classes of compounds and the temperature be maintained above the dew point of the stack gas. However, this heating will cause deposition of ionic species onto the probe surface and hence the probe will require rinsing between separate samples. The use of heated probes is discussed in Section 3.3.2.

3.1.4 Impingers

Impingers are usually glass vessels such as Dreschel bottles containing water or some other reagent selected to react with the target compound and to quench decomposition reactions. With impinger sampling, a known volume of sample gas is passed through the impinger train where the liquid will chemically react with or dissolve the compound of interest. To prevent sample carry over, the impingers are frequently connected in series as shown in Figure 3.8.

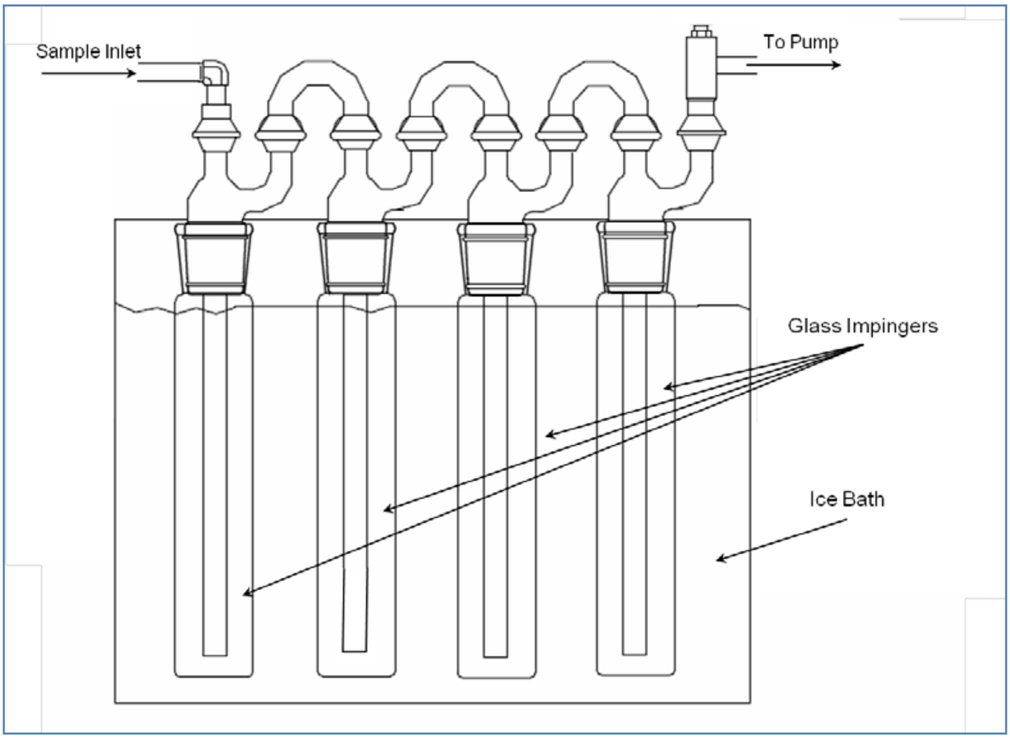

Figure 3.8 Typical impinger train used for stack sampling

Impingers are often used to measure the moisture content of stack gases where the sample stream (which is collected through a heated probe to prevent condensation in the sample system) is collected in chilled impingers. Particulate matter may also be collected in water-filled impinger trains. When impingers are used for species that are highly soluble in the solvent, collection efficiency can approach 100 % although it is important to give the gas sufficient residence time in the impinger to allow the species to be scrubbed from the gas phase. Excessive flow rates through impingers can reduce collection efficiency which increases the chance of sample breakthrough.

Although most impingers use liquids to trap the sample, in some cases, dry impingers may be used to collect condensable material.

3.1.5 Sorbents and Sample Cartridges

Not all species can be collected efficiently using impingers. For these compounds it may be possible to use cartridges containing sorbent materials. In some cases, the analyte may be physically adsorbed onto the surface of the collection medium. Common examples of this type of adsorbent include Tenax, charcoal, and alumina. As well as physical adsorbents, some compounds may be collected chemically by reacting the target species with a chemical reagent impregnated in a supporting substrate. Derivitisation cartridges containing 2,4-dintrophenylhydrazine (DNPH) used for sampling of aldehydes and other carbonyl compounds are examples of chemical sorbent sampling media. A third possibility for sorbents is a combination of physical and chemical sorbents. ThermoSorb/N, which is often used for the collection of nitrosamines (see Section 3.2.5) contains a solid adsorbent material along with a reagent to prevent unwanted side reactions from occurring during sampling.

Properly selected sorbent cartridges may have the advantage that they quench the decomposition of the target species; however, the suitability of a cartridge depends upon the operating temperature, flow rate and backpressure of the sampling system. They must also be operated above the dew point of the stack gas to eliminate condensation within the cartridge.

Many of the compounds thought to be possible components of amine PCC flue gas are amenable for collection on solid sorbents (see Sections 3.2 and 3.3; Table 3.1). Hence sorbents are likely to be used extensively for sampling at the Mongstad facility but supplementary heating of the cartridge and probe may be needed to prevent moisture condensation.

3.1.6 Pumps

A leak free pump is required to suck the sample from the stack and through the sample train. It is often placed after the impingers so that the sample does not pass through the pump. This is important because some of the target species may interact with the pump components. The increase in pressure within the pump may also cause enhanced decomposition of target compounds. The pump must have sufficient capacity to maintain isokinetic flow during the sampling operation; typically this would be in the range of 10 to 50 L min^{-1}. For species at trace concentrations, larger volumes are generally required to obtain sufficient sample for analyses and higher flow rates may be required. For instance, Halliburton et al. (2004) required in excess of 12 hours of sampling at 100 L min^{-1} to obtain sufficient material from a coal-fired power station stack. The choice of pump should be made with due consideration of the type of flow metering system used (see Section 3.1.7).

Recommended pumps include:

- *Carbon vane pumps*. Only high quality sealed carbon vane pumps should be used for sampling. These pumps have the advantage of a smooth pulse-free action and are suitable for use with dry gas meters. The flow rate can be regulated by microprocessors and electronic pump controllers.

- *Diaphragm pumps*. These pumps produce pulsations from the pumping action and generally require pressure dampeners between the pump and flow gas meter. Teflon diaphragm pumps have advantages when the stack gas is of a corrosive nature.

- *Piston pumps*. Piston pumps are generally not suitable unless they are of the sealed bellow variety or they are placed after the flow meter, as generally piston pumps have some degree of leakage past the sealing piston rings. In addition, pistons produce pulsations from the pumping action and require pressure dampeners between the pump and flow meter.

- *Blower and fan type pumps*. Only high quality sealed blowers are suitable for sampling. These have some advantages where larger volumes of stack gas are to be sampled. Blower pumps have a pulse-free operation, are easily controlled by microprocessors and motor speed controllers, and are compatible with dry gas meters.

3.1.7 Flow Metering and Flow Control

Commercial stack sampling apparatuses have either manual or automated flow metering systems. In manual systems, the operator must monitor the flows to maintain the isokinetic sampling velocity at the sampling nozzle. The sample flow rate is metered by a needle valve and the flow rate is determined by the operator and manually monitored. In this system, liquid filled manometers are often used for measuring stack gas velocity (with a pitot tube), the pressure difference between barometric pressure and stack pressure and the pressure at the dry gas meter. This system is robust and has been historically used to achieve representative samples. However, it requires significant operator interaction and judgement to maintain representative sampling. International stack sampling methods assume a minimum of a manual stack sampling system and the requirement regarding the tolerance for maintaining isokinetic sampling criterion reflects this (within 10% USEPA Method 5, 95% to 115% VDI 2066).

Automated stack samplers utilise electronic flow metering and mass flow controllers to accurately control the flow within a stack sampler. Using a microprocessor, an automated sampler continuously controls the flow to maintain the isokinetic criterion at the nozzle. These systems can usually accommodate multiple electronic sensors to measure the gas composition of the stack gas in real time. Sensors may include dew point or relative humidity, temperature, barometric pressure, absolute duct pressure, differential pressure at various points over the sampling system, instantaneous gas flow rate, as well as gas composition (O_2, CO_2, CO, NO_x concentrations etc.). Real time measurement of the concentration of the permanent gases in the stack has the advantage that the gas density can be calculated instantaneously.

Automatic samplers can provide accurate and instantaneous calculation of the isokinetic flow rate and allow the nozzle velocity to track the stack velocity in situations where the stack flow changes throughout the sampling period. It is recommended that fully instrumented automatic samplers be used for stack sampling at the Mongstad plant due to their increased precision and accuracy for maintaining isokinetic sampling conditions.

Regardless of the type of sampler, all flow measuring devices must be protected from moisture and corrosive gases. Ice filled or refrigerated condensers followed by a desiccant filled drier are used to prevent moisture from entering the flow measuring system as well as ensuring that a true dry gas measurement is achieved. It is also essential that the collection efficiency of the sampler be validated and all sensors for gas flow, temperature, pressure and moisture content etc. be calibrated against traceable standards.

3.2 Standard Methods

Stack sampling is routinely conducted in many industries to demonstrate compliance with statutory emission standards. Accordingly, there are numerous standard methods available for sampling a wide variety of pollutant compounds from flue gases. Many of these methods have been designed specifically for collecting samples from the stacks of large stationary sources, especially fossil-fuelled power stations but also industrial incinerators and other combustion processes. The following list includes the USEPA approved methods designed for isokinetic stack sampling.

- Method 5 - Determination of Particulate Emissions from Stationary Sources
- Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources
- Method 8 - Determination of Particulate, Sulfuric Acid Mist, and Sulfur Dioxide Emissions from Stationary Sources
- Method 12 - Determination of Inorganic Lead Emissions from Stationary Sources
- Method 13A - Determination of Total Fluoride Emissions from Stationary Sources - SPADNS Zirconium Lake Method
- Method 13B - Determination of Total Fluoride Emissions from Stationary Sources - Specific Ion Electrode Method
- Method 17 - Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration)
- Method 26 - Determination of Hydrogen Chloride Emissions from Stationary Sources
- Method 26A - Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources - Isokinetic Method
- Method 23 - Determination of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans from Stationary Sources
- Method 29 - Determination of Trace Metal Emissions in Exhaust Gases from Stationary Source Combustion Processes
- Method 101A - Determination of Particulate & Gaseous Mercury Emissions from Sewage Sludge Incinerators
- Method 104 - Determination of Beryllium Emissions from Stationary Sources
- Method 201A - Determination of PM10 Emissions (Constant Sampling Rate Procedure)
- Method 202 - Determination of Condensable Particulate Emissions from Stationary Sources
- Method 306 - Determination of Chromium Emissions from Decorative & Hard Chromium Electroplating & Anodizing Operations

- Method 0010 - Determination of Destruction & Removal Efficiency (DRE) of Semi Volatile Principal Organic Hazardous Constituents (POHCs) from Incineration Systems - SEMI-VOST

- Method 0011 - Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources

- Method 0050 - Determination of Hydrogen Chloride and Chlorine Emissions In Stack Gas Emission Samples from Hazardous Waste Incinerators

Methods from other countries are also widely used and the methodologies are broadly similar to those of the US methods. Since emissions are frequently reported on a dry gas basis, methods are also available for measuring the moisture content of the stack gas. Accurate emission measurements also require the temperature and pressure of the sample gas stream to be measured.

In general, the standard stack sampling methods currently in use are not intended for collecting compounds expected to be in the treated flue gas from amine PCC plants (with the exception of aldehydes and ammonia). Nevertheless, some methods may be applicable with certain modifications. Although not specific to sampling in stacks, there are numerous ambient air and occupational workplace methods for many of the compounds expected in amine PCC plant off gases. Some of these may be adaptable to stack sampling. A summary of the international standard methods that may be applicable to sampling at the proposed Mongstad facility are listed in Table 3.1. Some of the more relevant of these with the potential for application at amine PCC plants are discussed in the following sections.

Table 3.1. Summary of standard methods pertaining to compounds expected in PCC treated flue gas. The individual analytes covered by each method are listed in Appendix A.

Compound	Country	Standard	Sampling Medium	Collection Method	Analytical Method	Detection Limits	Interferents
N-Nitrosamine	USA	USEPA Method T0-7	Ambient air	Thermosorb/N cartridge	GC-MS	1 μg m^{-3}	Compounds of similar retention times
	USA	NIOSH Method 2522	Ambient air	Thermosorb/N cartridge	GC, TEA	0.003 mg m^{-3}	None with TEA
	USA	OSHA method 27	Ambient air	Thermosorb/N cartridge	GC, TEA	0.13 μg m^{-3}	
	USA	OSHA method 31	Ambient air	Gelman Type A glass fibre filters	GC, TEA	0.42 μg m^{-3}	
Aldehydes	USA	USEPA method TO-11A	Ambient air	DNPH cartridge	HPLC		
	USA	USEPA method TO-5	Ambient air	DNPH Impinger	HPLC		Formaldehyde contamination of DPNH
	USA	USEPA method 323	Natural gas fired stationary combustion source	Impinger	Colorimetric with acetyl acetone		Formaldehyde contamination of DPNH
	USA	USEPA method 0100	Ambient air	DNPH cartridge	HPLC		
	USA	USEPA method 0011	Stationary source	DNPH Impinger	HPLC	90 ppbv	Formaldehyde contamination of DPNH, high NO$_x$ levels
	USA	USEPA method 8520	Ambient air	Pararosaline scrubber/Na$_2$SO$_3$ reagent	UV-Vis spectrophotometer	6 μg m^{-3}	
	USA	NIOSH method 2539	Ambient air	Piperidine on XAD-2 resin	GC/MS &FID	2 μg/sample	
	USA	NIOSH method 2016	Ambient air	DNPH cartridge	HPLC	0.07 μg/sample	Ketone and other aldehydes react with DNPH
	USA	NIOSH method 2541	Ambient air	Piperidine on XAD-2 resin	GC-FID	1 μg/sample	None, acid sorbent inactivation
	USA	NIOSH method 3500	Ambient air	PTFE membrane + 1% Na$_2$S	Vis spectrophotometer	0.5 μg/sample	Oxidisable organics, phenols, high MW alcohols, olefins, aromatic hydrocarbons.
	USA	OSHA	Ambient air	Piperidine on XAD-2 resin	GC N selective detector	1000 μg m^{-3}	

		method 68					
Amines	ISO	17734-2	Ambient air	Impinger DBA in toluene	LC-MS		
	USA	NIOSH 2002	Ambient air	Silica gel absorbent	GC-FID	0.01 mg/sample	
	USA	NIOSH 2010	Ambient Air	Silica gel absorbent	GC-FID	0.02 mg/sample	
	USA	NIOSH 2007	Ambient Air	Silica gel absorbent	GC-FID	0.005 mg/sample	
	USA	NIOSH 3509	Ambient Air	Hexanesulfonic acid impinger	Ion chromatography	7-20 μg/sample	Na+ and NH_4+
	USA	NIOSH 2540	Ambient Air	Napthylisothiocyanate on XAD-2 resin	HPLC	0.9 μg/sample	Primary and secondary amines
	USA	OSHA method PV2111	Ambient Air	Napthylisothiocyanate on XAD-2 resin	HPLC		
	USA	OSHA method PV2018	Ambient Air	Napthylisothiocyanate on XAD-2 resin	HPLC		
	USA	OSHA method 60	Ambient Air	Napthylisothiocyanate on XAD-2 resin	HPLC	0.037-0.016 μg m^{-3}	Primary and secondary amines
	USA	OSHA method 60	Ambient Air	Napthylisothiocyanate on XAD-2 resin	LC		
Amide	USA	OSHA method 2084	Ambient Air	Silica gel absorbent	GC-NPD		
Alkylamines	USA	OHSA Method 40	Ambient air	NBD chloride on XAD-7 resin	HPLC	35 μg m^{-3}	
	USA	OHSA Method 36	Ambient air	NBD chloride on XAD-7 resin	HPLC	29 μg m^{-3}	
	USA	OHSA Method 34	Ambient air	NBD chloride on XAD-7 resin	HPLC	43 μg m^{-3}	
	USA	OHSA Method 41	Ambient air	NBD chloride on XAD-7 resin	HPLC	160 μg m^{-3}	
Ammonia	Japan	JIS-K0099	Flue gas	Boric acid impinger	Indophenol blue absorption spectrophotometry	1.2 mg m^{-3}	
	Japan	JIS-K0099	Flue Gas	Boric acid impinger	Ion chromatography	0.5 mg m^{-3}	
	USA	NIOSH 6016	Ambient Air	H_2SO_4 silica gel sorbent	Ion chromatography	2 μg/sample	Amines
	USA	NIOSH 3800	Ambient Air	Direct reading	FTIR	IR absorption peak overlap	Instrument dependant
	USA	NIOSH 6015	Ambient Air	H_2SO_4 silica gel sorbent	Vis spectrophotometer	0.5 μg/sample	
	USA	OSHA method ID-	Ambient Air	H_2SO_4 on carbon beads	Ion chromatography	1.5 ppm	

		188					
PCB/PCDD	Germany	DIN EN 1948-1	Stationary source waste incinerator	XAD-2 or PU foam	HRGC/HRMS		
	USA	USEPA method 0023A	Stationary Source	XAD-2	HRGC/HRMS		
Volatile Organic Compounds	USA	USEPA method TO-14A	Ambient air	Canister	GC-MS	Sub ppbv	
	USA	USEPA method TO-1	Ambient air	Tenax resin cartridge	GC-MS		Cartridge contamination
	USA	USEPA method 8265	Ambient air	Direct sampling	Ion trap mass spectrometry	50 ppbv	
	USA	USEPA method 0030	Stationary source waste incinerator	Tenax/Tenax/charcoal impinger train	GC-MS	0.1 μg m^{-3}	Absorbent contamination
	USA	USEPA method 0031	Stationary source.	Tenax/Anasorb-747 sorbent trap liquid condensate impinger trap	GC-MS	0.1 μg m^{-3}	
	USA	USEPA method 0031					
	United States of America	USEPA method 18	Stationary source	Tedlar bag or sorbent or direct measurement	GC	<1 ppm	
	USA	USEPA method 0040	Combustion source	Tedlar bag	GC-MS		Bag contamination
Gaseous and particulate organics	USA	USEPA modified method 10	Stationary source waste incinerator	Filter/XAD-2/condensate trap	GC-MS		NO_x
Condensable particulate matter	USA	USEPA method 202	Stationary source	Impinger	Methylene chloride extraction and weighing		Ammonia
	USA	USEPA method 28	Stationary source	Water dropout impinger, Greenberg Smith impinger, CPM filter	Methylene chloride extraction and weighing		

3.2.1 Particulate Matter

Particulate matter (PM) is one of the six “criteria” pollutants (the others being SO_2, NO_x, carbon monoxide, lead and ozone) and is frequently a significant component of emissions from coal-fired power stations. As a consequence, there are a number of standard methods designed for collecting solid PM from large flues. Generally, the PM associated with these installations is derived from the ash in the fuel. While the off-gas from amine PCC plants would normally be expected to have very low primary PM emissions (i.e. solid material produced in the combustion process), solid heat-stable salts have been shown to form in amine capture plants (CSIRO unpublished results; Rooney et al., 1996), and there is the possibility that secondary aerosols of these salts could be emitted from the plant. Hence, particulate measurements may be relevant to amine PCC plants. More importantly, however, many of the compounds of interest in PCC flue gases will be present as condensed aerosols and the principles of isokinetic sampling used in the standard particulate methods will be applicable to these plants.

Methods for sampling PM comprise a significant proportion of all of the available standard methods. Some of the most important methods for sampling particulate matter are:

- USEPA Method 5 – Determination of Particulate Matter from Stationary Sources
- US EPA Method 201 (1996) Determination of PM10 Emissions (Exhaust Gas Recycle Procedure)
- US EPA Method 201A (1997) Determination of PM10 Emissions (Constant Sampling Rate Procedure)
- US EPA Method 202 (1996) Determination of Condensable Particulates Emissions from Stationary Sources
- ASTM D3685 / D3685M - 98(2005) Standard Test Methods for Sampling and Determination of Particulate Matter in Stack Gases
- ASTM D6331 - 98(2005) Standard Test Method for Determination of Mass Concentration of Particulate Matter from Stationary Sources at Low Concentrations (Manual Gravimetric Method)
- ISO 9096 (2003) Stationary source emissions. Manual determination of mass concentration of particulate matter
- ISO 12141 (2002) Stationary source emissions - Determination of mass concentration of particulate matter (dust) at low concentrations - Manual gravimetric method
- ISO 23210 (2009) Stationary source emissions - Determination of PM10/PM2,5 mass concentration in flue gas - Measurement at low concentrations by use of impactors
- AS 4323.2 (1995) Stationary source emissions - Determination of total particulate matter - Isokinetic manual sampling - Gravimetric method

All of these methods involve isokinetically sampling the flue gas stream and collecting the entrained material on either a pre-weighed filter or an impactor train. Some of the most relevant methods are described below.

3.2.1.1 USEPA Method 5 – Determination of Particulate Matter from Stationary Sources.

Method 5 is designed to sample particulate matter from large stacks and is the reference method for PM emissions reporting in the US. The sample plane is defined by USEPA Method 1 and the stack gas velocity is measured according to USEPA Method 2 or 2F (see Halliburton et al., 2010 for details).

The gas stream is sampled isokinetically using a probe inserted through the stack or duct wall and particulates are collected on an external filter. The probe and filter are heated to 120 °C to prevent condensation of moisture during sampling. A chilled impinger train or condenser is located downstream of the filter to collect water from the sample stream so that the moisture content of the stack gas can be determined either by measuring the volume or weight of the water condensed from the sample stream. A schematic diagram of the sampling system for Method 5, identifying the main components, is shown in Figure 3.9.

After the sample has been collected, it is transported to a laboratory and weighed to calculate the mass concentration of the particulate matter in the stack gas stream.

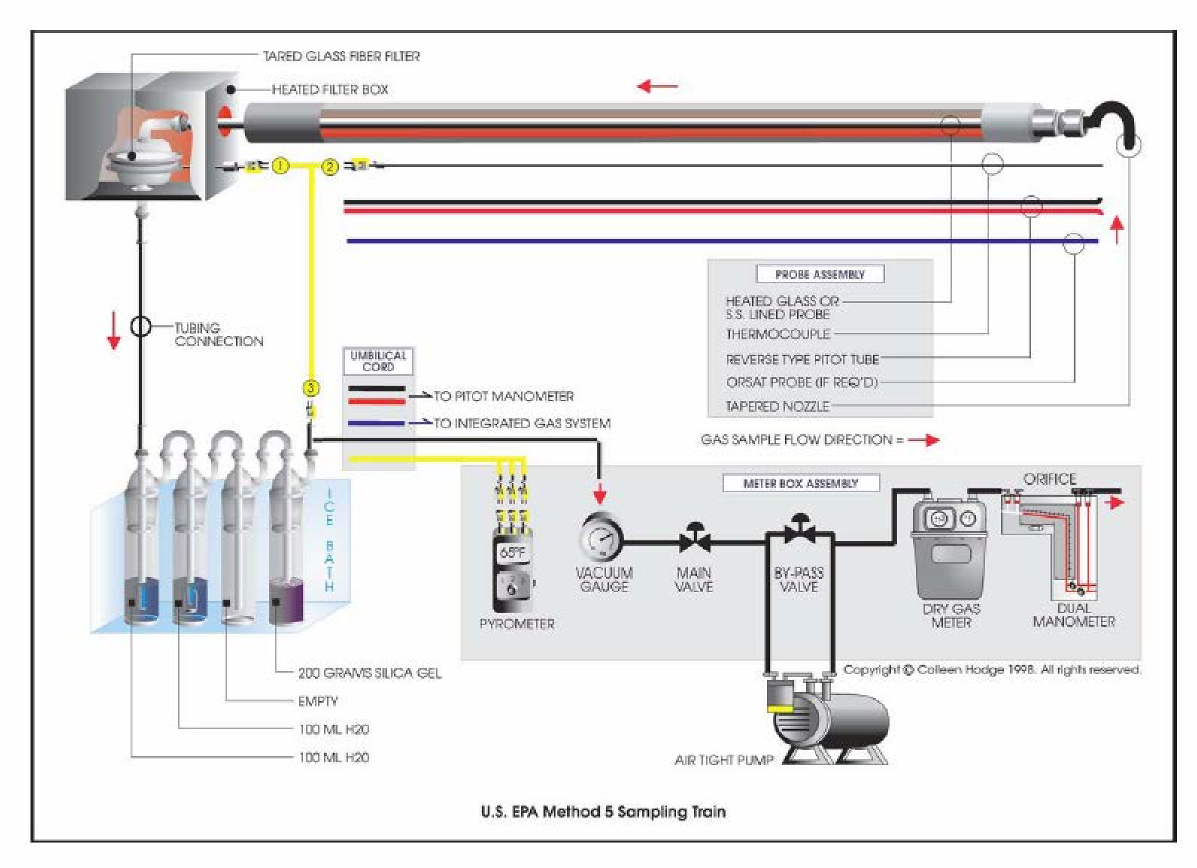

Figure 3.9 Schematic diagram of the isokinetic sampling system used for USEPA Method 5 (Copyright © 2000 - 2010 ActiveSET.org. All Rights Reserved)

3.2.1.2 VDI 2066 – Particulate matter measurement. Dust measurement in flowing gases. Gravimetric determination of dust load.

This method is a German standard and is used for compliance monitoring and calibration of online dust monitoring instrumentation. It is a comprehensive method and describes not only the sampling procedure but the selection of the sampling plane and the method for measuring the stack gas velocity.

The sample is withdrawn from the gas stream isokinetically and the dust particles are deposited onto a pre-weighed filter. If the gas flow is free of water droplets, the filter holder is placed within the stack directly in the gas flow (in-stack sampling). In this situation, the filter holder is not heated since the temperature of the gas stream is sufficient to prevent water droplets collecting on the filter. However, when the gas is saturated and water droplets are present, the method specifies that an out-of-stack filter be used and the filter and sampling line must be heated to prevent condensation in the line or on the filter.

Moisture is removed downstream of the filter by a chilled condenser, but there is no requirement to measure the water collected. The results are reported on a dry gas basis (i.e. as measured by the metering system). As for USEPA Method 5 it is necessary to rinse the probe with a suitable solvent between individual sampling runs and combine the results of analyses of these washings with the final emission measurement.

3.2.1.3 USEPA Method 202 – Determination of Condensable Particulate Emissions from Stationary Sources.

This method is intended to collect condensable material that can pass through a heated filter. The equipment and procedure are very similar to Method 5 described above, and is shown schematically in Figure 3.10. The gas stream is isokinetically sampled from the stack through a heated probe. A filter, which is also heated to 120 °C, traps solid particulate material. This filter may be either in- or out-of-stack (out-of-stack configuration is shown in Figure 3.10). The probe for this method must be either Teflon or glass lined. After the filter, the gas stream passes into an impinger train, the first three of which contain deionised water, while the fourth is filled with silica gel (note that in Figure 3.10 there is an error which shows the third impinger as being empty; this is the case for Method 5 only). Both the probe and filter are heated to 120 °C. It is apparent that the set up is very similar to Method 5; the main differences being that the probe must be glass lined (stainless steel is allowed for Method 5) and the line connecting the filter to the impinger must be Teflon.

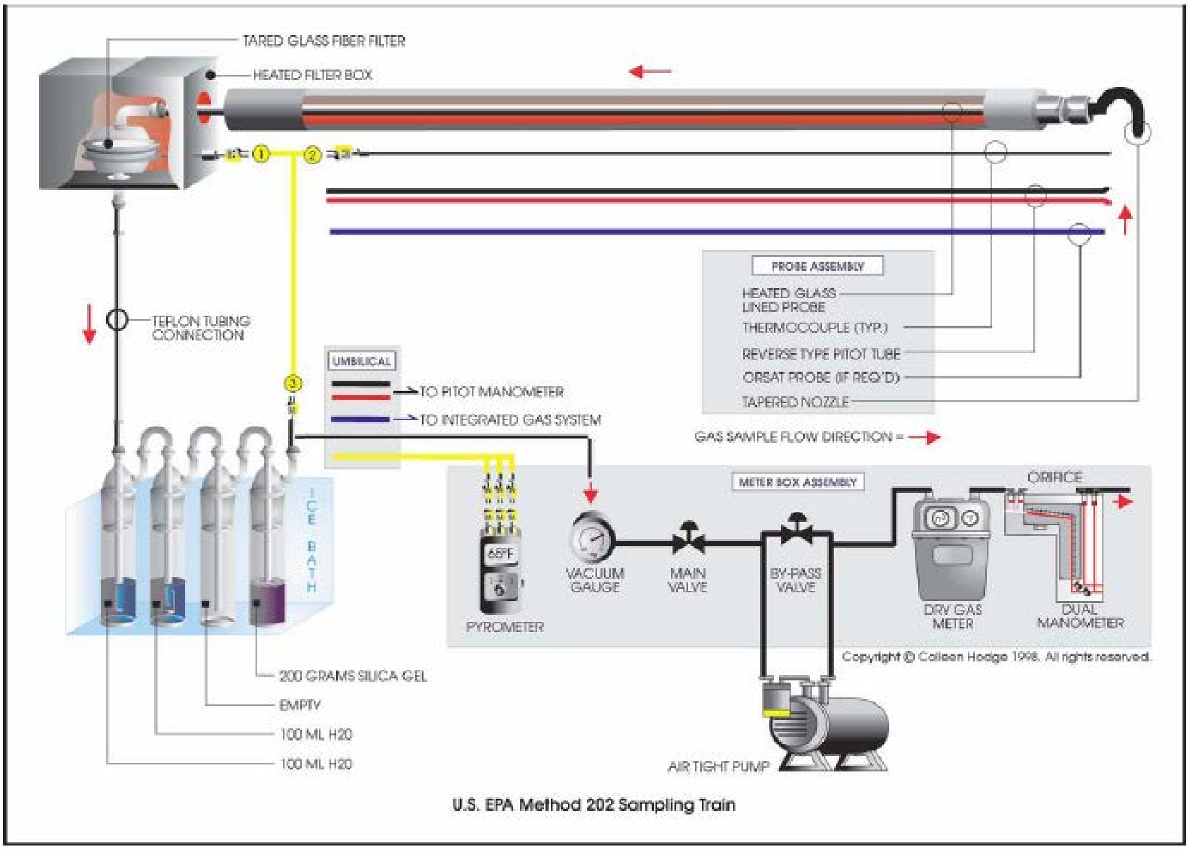

Figure 3.10 Schematic diagram of the isokinetic sampling system used for USEPA Method 202 (Copyright © 2000 - 2010 ActiveSET.org. All Rights Reserved)

Particulate matter retained on the filter is determined gravimetrically. Any condensable material is collected in the water filled impingers. After sampling, the liquid in the impingers is extracted with methylene chloride to remove the organic fraction. Both the aqueous and organic fractions are then evaporated to dryness to determine the condensable component.

Recently, variations to this method have been examined for use in industrial applications with lower stack temperatures (Schmelter, 2007). In one study, the sampling was performed at the stack temperature (~30 °C). The total amount of condensable material collected using this method was identical to the reference Method 202 but about 50 % of the particulate material was retained by the filter rather than collecting in the impingers. In the reference method, all of the condensable material passed through the filter to accumulate in the impinger train.

3.2.1.4 Potential Interferences

Some solid particulates may be prone to absorb moisture from the air. The measurements rely on measuring weight gain on the collection filters and hence the filter mass must be weighed and reported to a standard temperature and humidity to allow comparison of results. However, the amount of material collected can be affected by the operation of the sampling train. One of the main aspects that can lead to errors is deviation from isokinetic flow during sampling. Others points that may lead to errors are blocking of the sample nozzle, or sticking of the particles on the sample probe (which may happen if Teflon tubing is used).

For condensable particulates, there are other potential sources of error. In USEPA Method 202, ammonia is identified as an interfering compound. This is because the method is sometimes used for measuring emissions from installations where ammonia is injected into the process to control emissions of HCl. This leads to the formation of NH_4Cl particles that present as particulate matter. Although ammonia will probably be a significant component of the Mongstad plant emissions, it is unlikely to affect the particulate matter since HCl will not be present.

3.2.2 Moisture

Since emissions are usually reported on a dry gas basis, it is necessary to measure or estimate the moisture content of the stack gas. Standard methods for determining the moisture in flue gases are available, two of which are described below.

3.2.2.1 USEPA Method 4 – Determination of Moisture Content in Stack Gases

This method is very similar to the procedure described in Method 5 for the determination of water. The sample gas is sucked at a constant rate from the stack through a heated line and filter then passed through a chilled impinger train to condense the vapour to liquid water. The amount of water collected is then measured volumetrically or gravimetrically. However, it is noted in the procedure that when water droplets are present in the gas, this method tends to overestimate the actual moisture content of the stack gas. Under these conditions, Method 4 specifies that the moisture content be estimated simultaneously by a second technique where the temperature of the gas stream is measured. It is assumed that the gas is saturated and the moisture content is then estimated from the vapour pressure of water at the stack temperature. The lower of the two results is taken to be the stack gas moisture content.

3.2.2.2 BS EN 14790:2005 – Stationary source emissions – Determination of the water vapour in ducts

A sample of gas is extracted from the stack at a constant rate and collected in an impinger train where it is condensed or absorbed. The mass of water collected in the system is weighed at the end of the sampling period. Like the USEPA method above, the presence of water droplets is recognised as a potential source of positive bias so, in such instances, the collection of a sample is not recommended. Instead, it is assumed that the gas stream is saturated with water and the moisture concentration is calculated from the theoretical mass of water per unit volume at the temperature and pressure of the gas stream.

3.2.3 Volatile Organic Material

3.2.3.1 USEPA Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography.

In this method, a gaseous sample is collected for analysis by gas chromatography. The analysis can be conducted off-site or in some cases, the gas sample can be analysed directly by connecting the sample probe to a suitable gas chromatograph. The method specifies that the sample probe be Teflon, borosilicate glass or stainless steel. Since this method is intended for gaseous samples, there is no requirement for isokinetic sampling. However, by fitting a suitable nozzle to the probe and adjusting the flow rate, it would be a simple matter to sample under isokinetic conditions if necessary (i.e. when liquid aerosols are present).

Samples that are not analysed directly are collected in either Tedlar bags or solid sorbents. For bags, a Tedlar bag is filled with sample gas by evacuating a rigid air-tight vessel that holds the bag (Figure 3.11).

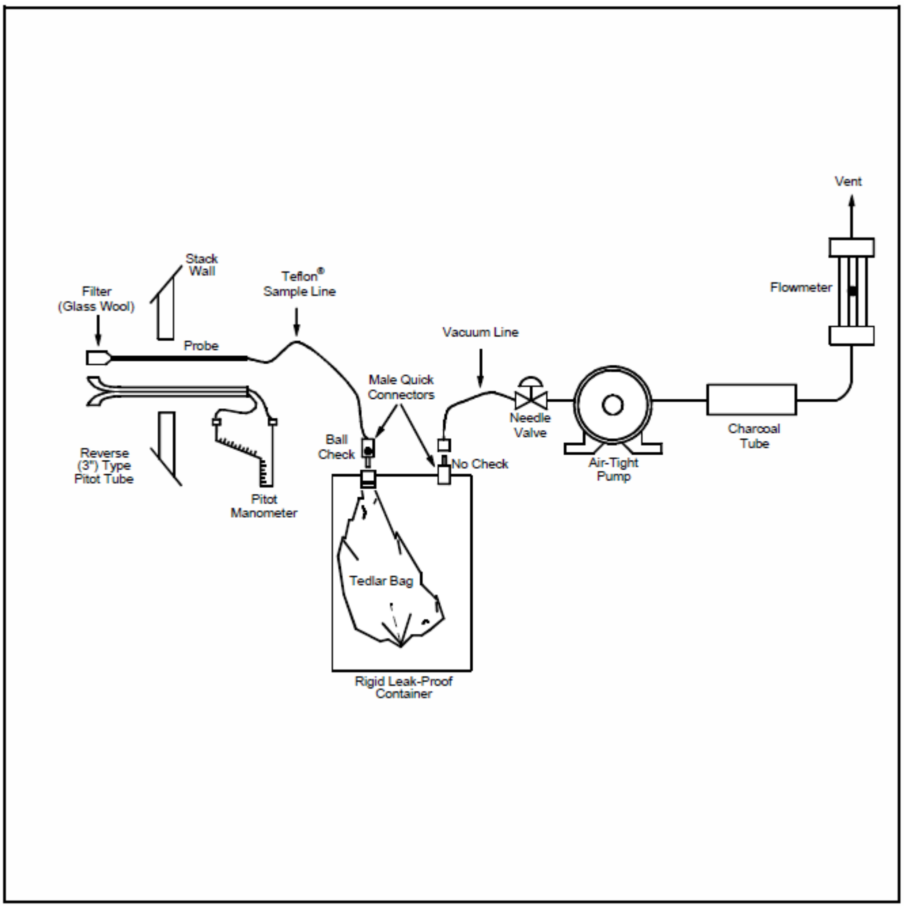

Figure 3.11 Sampling system used to collect gaseous samples from stacks according to USEPA Method 18

If there is a possibility of condensation, the bag can be heated to 120 °C (heating must be maintained until the sample is analysed). Alternatively, the bag can be partially filled with a known volume of inert diluent gas (e.g. nitrogen).

This method also allows the use of sorbent materials for collecting the sample, which has the potential advantage of concentrating the analyte. The sorbent used is selected according to the nature of the target compound.

Method 18 states that the procedure is not suitable for compounds that are polymeric (i.e. have high molecular weight), can polymerise before analysis, or have very low vapour pressures.

This method may have application for an amine capture plant, especially if the samples are heated to keep the components in the vapour phase. Ammonia and amines may be determined using this sampling technique because they can be separated by gas chromatography, even in the presence of water (see Varian Application Note 1994 GC). The use of sorbent tubes as the collecting medium also allows considerable scope to adapt many of the ambient air methods described in the following sections to stack sampling. In these cases, the sorbent tubes specified for particular classes of compound could simply be attached to the sampling system as described in Method 18. Due to the likely presence of liquid aerosols, it would be necessary to modify the procedure slightly to ensure that sampling was isokinetic, but this would be straightforward, especially if a standard sampling train was used.

3.2.3.2 USEPA Method 0030 – Volatile Organic Sampling Train.

This method applies to the sampling of organic compounds with boiling points below 100 °C from stacks. However, it can also be used for many compounds with higher boiling points. Note that this method is specific to gaseous species and consequently, isokinetic sampling is not required.

There are two variations; the FAST-VOST and the SLO-VOST. In the FAST-VOST, 20 L of sample gas is collected at a flow rate of 1 L min^{-1}. The SLO-VOST is for use when the target compounds have boiling points below 35 °C. For these materials, the flow rate may be too high and cause the material to carry through the impinger train. Hence this method allows collection of less than 20 L at lower flow rates. Note that the method specifies that the efficiency of the sample train must be determined by laboratory testing (i.e. need to make sure that there is no carry-over from the impingers).

The sample is withdrawn from the stack at 130 °C or more in a heated probe which is glass or quartz lined. The gas is then cooled to <20 °C and passed through the first impinger containing 1.6 g of Tenax resin. It then goes through a condensate trap before passing into a second trap with a 3:1 mix of Tenax and charcoal.

Tenax and charcoal, however, have been found to be prone to sampling artefacts (due to surface reactions that lead to the formation of nitrosamines). Hence Method 0030 as published is not suitable for sampling nitrosamines. The use of an alternative sorbent such as ThermoSorb/N would be preferable.

3.2.4 Aldehydes and Ketones

Of all the standard sampling methods available, USEPA Method 0011 is one of the few directly applicable to sampling the treated flue gas from the Mongstad PCC plant.

3.2.4.1 USEPA Method 0011 – Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources.

In this method, stack gases are sampled isokinetically into an acidic solution of DNPH. The method was primarily designed to check the destruction efficiency of commercial incinerators and is intended for sampling for the following species:

- Formaldehyde
- Acetaldehyde
- Acetophenone
- Isophorone
- Propionaldehyde

These compounds react with DNPH to form stable derivatives that that can be separated and detected by high pressure liquid chromatography (HPLC) and an ultraviolet detector.

The sample is withdrawn from the stack through a glass or quartz lined probe that is heated to 120 °C, and then passed through a chilled (immersed in an ice bath) impinger train comprising at least five glass impingers connected in series (Figure 3.12). The first three impingers contain the DNPH solution, while the fourth is empty and the fifth contains silica gel to protect the pump and metering system from contamination with water. The impinger train is a slight modification of that specified in Method 5; the main differences are the addition of a fifth impinger and the filter used in Method 5 is not required. However, Method 0011 allows the filter to be retained, if necessary.

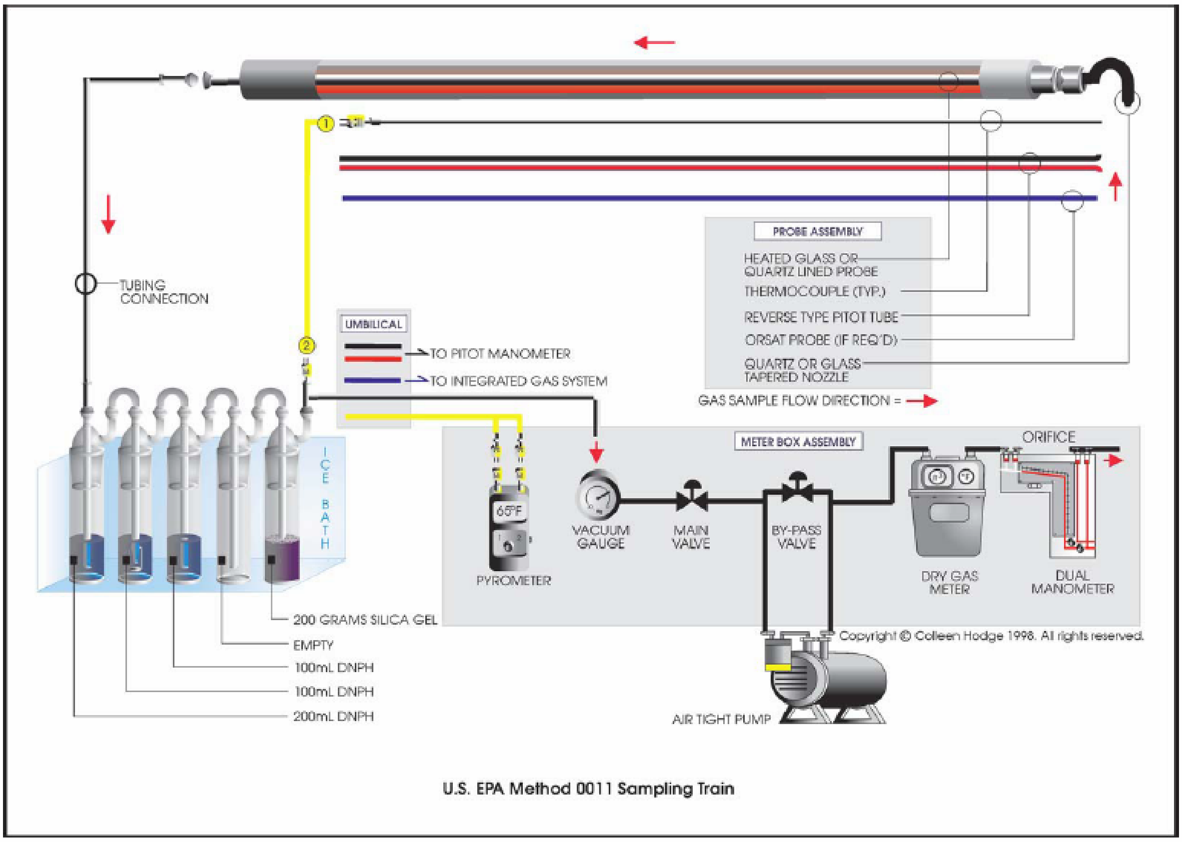

Figure 3.12 Schematic diagram of the isokinetic sampling system used for USEPA Method 0011 (Copyright © 2000 - 2010 ActiveSET.org. All Rights Reserved)

A number of potential sources of interference that can affect the method have been identified (see section 3.2.4.3).

The detection limit of the sampling method is determined by the volume of gas collected and the sensitivity of the instrumentation used for the analysis. The method requires that a minimum volume of 45 ft^3 (about 1275 L) should be collected although the actual volume would be adjusted to ensure sufficient analyte was available for adequate sensitivity. According to Method 11, the detection limits for the various compounds are as shown in Table 3.2.

Table 3.2. Detection limits quoted in USEPA Method 0011 for various carbonyl compounds

Compound	Detection Limit (ppb)
Formaldehyde	90
Acetaldehyde	40
Propioaldehyde	60
Acetophenone	10
Isophorone	10

It is likely, however, that these detection limits are very conservative because the analytical procedure for these compounds is very sensitive. For example, detector sensitivity to formaldehyde measured at 360 nm is typically around 55 pg per 20 µL injection; equivalent to 0.003 µg mL^{-1} (Waters Corporation, 1994). On this basis, a method detection limit for gas phase samples of around 0.15 µg m^{-3} (0.12 ppbv at 25 °C of formaldehyde) would be achieved for samples collected on commercial 2,4-DNPH cartridges. This assumes a 100 L volume of sample gas and 5 mL cartridge extraction volume. Lower detection limits could be achieved by increasing the sample volume, however, care must be taken to ensure that the capacity of the cartridge is not exceeded. Compare this to the 90 ppb (110 µg m^{-3}) detection limit quoted in Method 11 for an 849 L gas sample. USEPA Method 8315 (Determination of carbonyl compounds by HPLC) also suggests a detection limit of 0.03 ppb for formaldehyde on a 500 L sample of ambient air, which is consistent with value of 0.12 ppb calculated above. It seems therefore, that in practice, much lower detection limits should be achievable than suggested in Method 0011.

3.2.4.2 USEPA Method 323 – Measurement of Formaldehyde Emissions from Natural Gas Fired Stationary Sources – Acetyl Acetone Derivatisation Method

This method has been developed for the measurement of formaldehyde emissions in the exhaust of natural-gas fired stationary combustion sources and is formaldehyde specific Either a stainless steel or quartz glass lined stainless steel sampling probe is used in conjunction with a Teflon tubing connection to the impinger train which is contained within an ice bath. Heating of the sample line is not required. The sampling train consists of three midget impingers, the first impinger being used to remove moisture and the second being filled with reagent water (deionised, distilled organic free water). The third impinger contains silica gel for removal of residual water. To achieve the instrumental detection limit of 0.2 ppmv it is recommended that a liquid concentration of 10 times the detection limit be achieved. The samples should be held on ice prior to analysis which should be performed as soon as possible as limited data suggest that some degradation does occur even in refrigerated conditions. An aliquot of the sample solution is reacted with acetyl acetone and the absorbance at 412 nm determined by spectrophotometry.

3.2.4.3 Potential Interferences

A number of inferences that can affect the accuracy of Method 11 are listed in the procedure document:

- High concentrations of acetone or other oxygenated compounds with similar retention times as the formaldehyde derivative will interfere with the analysis.
- Dimethylolurea creates a slight positive interference.
- Hexamethylenetetramine and paraformaldehyde can decompose to formaldehyde in the acidic reagent and thus interfere with the determination of formaldehyde.
- If tolualdehyde is present it may interfere with the determination of acetophenone because they coelute.
- The DNPH reagent is frequently contaminated with formaldehyde, acetone and 2,4-dinitroaniline so special care is required to produce pure solutions. Note however,

that commercially prepared cartridges are rarely affected by this type of contamination.

For Method 323, interference from acetaldehyde, amines formaldehyde polymers and sulphates can arise via reaction with the acetyl acetone reagent.

3.2.5 Nitrosamines

There are currently no standard methods for sampling nitrosamines from stacks. However, methods do exist for ambient air or occupational health and safety monitoring that may be applicable with some modification. These methods rely on sorbing nitrosamines onto the commercially available sorbent material Thermosorb/N. Other sorbents such as Tenax, XAD and activated carbon have also been used previously but these are generally considered to be prone to sampling artefacts and are no longer used in standard methods. Some of these methods are briefly described below.

3.2.5.1 NIOSH Method 2522

This method is intended for determining a range of nitrosamine compounds in ambient air. Air is sampled at a flow rate between 0.2 to 2 L min^{-1} using a small pump and passed through a prepacked cartridge containing Thermosorb/N, which collects the nitrosamine compounds. The total volume of air sampled should be within the range of 15 to 1000 L, depending on the concentration of nitrosamines. For high concentrations, where there is a chance of overloading the sorbent cartridge, a second tube may be added in series to trap any carry-over. The nitrosamines are then analysed by gas chromatography with a thermal energy detector (GC/TEA). The range of concentrations over which the method is applicable is 0.003 to 10 mg m^{-3}.

3.2.5.2 OSHA Method 27

This method was developed in the context of occupational health and safety and is based upon sorption of volatile nitrosamines on ThermoSorb/N Cartridges followed by gas chromatography analysis with Thermal Energy Analyser (TEA) detection. The compounds specifically targeted are:

N-Nitrosodimethylamine (NDMA)

N-Nitrosodiethylamine (NDEA)

N-Nirtoso-n-propylamine (NDPA)

N-Nitrosodi-n-butylamine (NDBA)

N-Nitrosopiperidine (NPIP)

N-Nitrosopyrrolidine (NPYR)

N-Nitrosomorpholine (NMOR)

The sampling method is quite similar to NIOSH 2522 above, except that the volume of air sampled is 75 L. The sampling rate is nominally 1 L min^{-1}, although flows between 0.2 and 2 L min^{-1} are permissible. A ThermoSorb/N cartridge is used in preference to other sample collection techniques as it is claimed that artefactual formation of analytes is excluded through use of a proprietary amine trap and nitrosation inhibitor. The reliable quantitation limit for this method varies from 0.13 to 0.20 μg m^{-3} depending upon the particular nitrosamine species.

3.2.5.3 US OSHA Method 31

Method 31 was developed specifically for the analysis of N-nitrosodiethanolamine (NDELA) and requires collection of the sample on a Gelman Type A glass fibre filter followed by GC analysis using a TEA detector. Because NDELA is unstable the filter must be protected from light during and after sampling. A sample volume of 480 L is recommended to be collected at a sampling rate of 2 L min^{-1}. The practical detection limit of the method is 0.42 μg m^{-3}. Potential interferences may arise from the formation of NDELA by reaction of di- and tri-ethanolamine with nitrosating species such as nitrogen oxides. Also, if NDELA precursors are present and are collected and retained, artefactual NDELA may also be produced. Although nitrosation artefacts may be formed, other collection strategies suffer similar problems and the glass fibre filter was selected as being the most convenient and least expensive sampling technique.

3.2.5.4 US EPA Method TO 7 – Method for the Determination of N-Nitrosodimethylamine in Ambient Air using Gas Chromatography

Like the NIOSH and OSHA Method 27, Method TO-7 involves drawing ambient air through a Thermosorb/N cartridge. The flow rate of the sample is 2 L min^{-1} to give a total volume of 300 L. After sampling the ends of the sorbent tube are capped then analysed in a laboratory. The main difference between this method and the other two above is that the analysis is by GC/MS, rather than GC/TEA.

Details of the analytical procedures of NIOSH Method 2522, OSHA Method 27 and Method TO-7 are provided in the report for Task 4 (Tibbett et al., 2010).

3.2.5.5 Potential Interferences

Nitrosamines are generally stable in neutral and basic media in the absence of light. However, they decompose in ultraviolet light to form aldehydes, nitrogen, nitrous acid, amine and nitrous acid (Ikeda and Migliorese, 1990). Consequently the samples must be adequately protected from light during and after sampling. Another problem is that if NO_x is present, it may react with amines to produce nitrosamines within the sampler. To prevent this, a small amount of an inhibitor such as sulphamic acid or ascorbic acid is added to the sampling solution. The inhibitors work by out-competing the amines for the NO_x nitrosating agent.

For gas phase sampling, many common solid sorbents have been found to be prone to sampling artefacts caused by retained amines reacting with NO_x to produce nitrosamines. However, ThermoSorb/N, which is a proprietary blend of metal silicates and other additives, has been shown to be free from such artefacts (Rounbehler et al., 1980; Goff et al., 1980) and is therefore the sorbent specified in most methods for nitrosamines.

3.2.6 Amides

As for nitrosamines, there are currently no standard methods for sampling nitrosamines from stacks. However, methods do exist for ambient air or occupational health and safety monitoring that may be applicable with some modification. One of these methods is briefly described below.

3.2.6.1 USA OSHA method 2084

This method is for the determination of acetamide in ambient air to assess occupational exposure. The sample is collected on a silica gel absorbent, desorbed with methanol and analysed using gas chromatography and a nitrogen-phosphorus detector. The practical detection limit of the method is given as 0.4 ppm, ~1 mg m^{-3} (based upon a 10 L air sample).

3.2.7 Amines.

Despite an extensive literature search, no standard methods for sampling of amines from stack gases were found. However, several methods have been developed for the determination of amines in ambient air with respect to occupational health and safety requirements.

3.2.7.1 OSHA Methods

The US Occupational Safety and Health Administration has developed four methods (Methods 60, PV2018, PV2111, and PV2145) for the determination of specific amines and alkanolamines in ambient air. However, most of these methods (those prefixed “PV”) are provisional and are yet to be fully evaluated. The methods are based upon the sorption of the amine on an XAD-2 resin coated with 1-naphthylisothiocyanate (NITC) followed by analysis using HPLC. It is noted that the presence of primary or secondary amines could reduce the capacity of the sampler. The US National Institute of Occupational Safety and Health (NIOSH) have also developed five methods for the determination of amines in ambient air. Of these, three (Methods 2002, 2007, and 2010) are based upon sorption of the amine onto a silica gel absorbent followed by gas chromatography analysis using an FID detector. Although no interferences are known it was noted that silica gel has a reduced capacity for collection of organic compounds at high humidity, suggesting that the flue gas may need to be dried before passing through the silica gel. NIOSH Method 3509 for the determination of aminoethanol compounds is based upon the drawing of an ambient air sample though a midget impinger containing hexanesulphonic acid followed by ion chromatography analysis. It is noted that higher molecular weight amines that may be trapped do not elute in the subsequent analysis so do not interfere. However, other low molecular weight amines may interfere as also may sodium and ammonium ions. Method 2540 is similar to the OSHA methods described above in that it also makes use of sorption on napthylisothiocyanate on XAD-2 resin followed by HPLC analysis.

The reliable detection limits with Method 60 are:

- Ethylenediamine 0.15 ppm (0.37 mg m^{-3})
- Diethylenetriamine 0.004 ppm (0.016 mg m^{-3})
- Triethylenetetramine 0.004 ppm (0.026 mg m^{-3})

The three provisional methods suggest detection limits of:

- Monoethanolamine (MEA) 0.060 ppm (0.15 mg m^{-3})
- Diethanolamine 0.040 ppm (0.172 mg m^{-3})
- 2-amino-2-methyl-1-propanol (AMP) 0.040 ppm (0.146 mg m^{-3})

3.2.7.2 ISO 17734-2

The ISO standard 17734-2 for the determination of amines and aminoisocyanates in workplace air uses dibutylamine (DBA) as a sorbent followed by liquid chromatography mass spectrometry. A known volume of air is drawn through a midget impinger containing a solution of DBA in toluene. The sampling rate is typically 1 L min^{-1} and the collection volume approximately 30 L.

3.2.8 Alkylamines.

Although there are no standard methods for sampling of alkyl amines from stack gases there are four methods developed by the USA OSHA (methods 34, 36, 40, and 41) for the determination of specific alkylamines in ambient air. The methods are based upon sorption of the alkylamine on XAD-7 resin coated with 7-chloro-4-nitrobenzo-2-oxa-1,3diazole (NBD chloride). Practical detection limits for the technique range from 29 μg m^{-3} to 160 μg m^{-3} depending upon the specific alkylamine analyte. Limited testing with other volatile alkylamines suggested that there was no interference but it is not known if other compounds will interfere with the collection efficiency.

3.2.9 Ammonia

Ammonia is an important industrial pollutant and there are a number of standard methods available for sampling in ambient air. There is also one method designed for sampling ammonia emission from stacks.

3.2.9.1 Japanese Industrial Standard JIS K 0099

This method is for the determination of ammonia in flue gas by absorption into boric acid and subsequent determination of ammonia by either absorption spectrophotometry or ion chromatography. The sampling tube may be made of glass, quartz, stainless steel or PTFE (Teflon). If condensation of moisture is a possibility, the flue gas should be heated to 120 °C prior to the absorption train which is comprised of two impingers containing the boric acid solution. Ammonia content is then determined either by absorption spectrometry after reaction of the absorbent with indophenol blue or by ion chromatography. Although no detection limits for either analytical method are reported the working range of the spectrophotometric method is given as 1.3 to 1200 mg m^{-3} and 1.2 to 11.8 mg m^{-3} for the ion chromatographic method.

3.2.9.2 OSHA Method ID 188

This method is used to determine workplace ammonia concentrations. The method uses a sorbent tube containing carbon beads impregnated with H_2SO_4 where ammonia passing through the tube reacts to form ammonium sulphate. Air is sampled at either 100 or 500 mL min^{-1} to give a total sample volume of between 7.45 and 24 L. After sampling, the material collected is desorbed by rinsing with deionised water then analysed by ion chromatography.

The method has stated detection limits as low as 0.6 ppm (4.2 mg m^{-3} at 25 °C) but it has been validated to concentrations of more than 100 ppm (69.5 mg m^{-3}).

3.2.9.3 Potential Interferences

In JIS K 0099, the spectrophotometric method is affected by the following concentrations of the interferents (relative to ammonia concentration): 100× NO_2, 10× amines and SO_2 and equivalent volume of H_2S. If these values are exceeded then ion chromatography should be used.

According to OSHA Method ID 188, ammonium salts may interfere with the analysis since they will be washed out of the tube along with the ammonium sulphate formed by the ammonia. Amines such as monoethanolamine, isopropanolamine, and propanolamine (some of which may be present in a PCC plant) may also lead to positive interference.

3.3 Non-Standard Methods

It is apparent that the standard methods currently available for stack sampling will not be adequate for sampling all of the compounds of potential interest from an amine PCC plant. It will be necessary, therefore to develop new methods specific to the various classes of compound. Some of these new methods may be based upon the sampling systems used in many of the ambient air methods described above. Since the range of materials to be sampled is quite diverse, it is probable that more than one sampling train will be needed to adequately sample all of the target compounds.

When developing new methods, the chemist is confronted with a circular problem: designing the sampling system requires some knowledge of the compounds present in the bulk material but obtaining this information is dependent on representative sampling. Consequently, sampling and analytical methods must be developed together. Moreover, method development is an iterative process and methods will change from time to time as new information becomes available.

Fortunately, some of the current analytical methods are capable of determining many of the compounds of interest in PCC treated flue gas, even in complex matrices. For instance, ion chromatography (IC) can be used to separate and quantify many amines and their degradation products. IC in line with an MS system can also be used to identify unknowns if suitable retention time calibrants are not available. IC can also be used to identify and quantify the suite of negative ions expected to be present in any PCC liquor, i.e. NO_2^-, NO_3^-, Cl^-, $HCOO^-$, CH_3COO^-, $HC_2O_4^-$, HSO_3^-, SO_4^{2-} (the effects of carbamates and bicarbonate need to be investigated using IC). Reverse phase HPLC-MS can be used to identify/quantify the non-ionic polar analytes such as non-volatile nitrosamines, and some degradation products.

In the following sections, some ideas for alternative sampling apparatus are considered. As well, some class-specific methods for sampling various target compounds are discussed based on methodology described in the open literature.

3.3.1 Bulk Liquid Phase Collection

In the first instance, it is suggested that a bulk sample of the flue gas condensate is collected from an amine PCC plant. This should be performed using procedures as close as possible to recognised isokinetic stack sampling methodology such as USEPA Method 5 or VDI 2066 with chilled impinger trains maintained at or near 0°C. If necessary, reagents could be added to the impinger solution to preserve specific compounds (e.g. in the case of nitrosamines, adding citrate/ascorbate prevents reaction with nitrite). Sampling in this way would yield a liquid sample of the flue gas condensate that could be subject to detailed analysis in a suitably equipped laboratory. While there is the possibility that the components collected could degrade within the collection vessel, this approach would nevertheless provide valuable operational information that will guide further refinement of specific sampling and analytical protocols.

Standard methods like USEPA Method 5 use ice bath cooling of the impingers, however, since decomposition reactions are temperature dependent this opens the possibility of an obvious, and somewhat novel, approach to sample collection. By cryogenically cooling the sample with liquid nitrogen, the kinetics of any unwanted reactions will be quenched. Low temperature cooling would ensure that sample integrity is preserved until the sample is ready for analysis. Since the vapour pressure of all gas phase species will be negligible at this temperature, gas phase target species will also be efficiently trapped.

The method may pose a few practical and safety issues for the operators but with careful design of the equipment, these should readily be overcome. For example, tubing and impingers would be designed to prevent blockages due to icing. Alternatively, liquid collected in conventional impingers could be transferred to a cryogenic vessel immediately after sampling. Such a system may provide an efficient method of collecting all target species with minimal degradation of the sample. This approach would, however, require development of appropriate techniques to thaw the sample before analysis. When thawing the sample for analysis, some of the reactions will begin to occur as the temperature increases. In some cases, experiments to investigate the kinetics of these reactions will yield rate data so that appropriate corrections can be applied.

3.3.2 Vapour Phase Collection

An alternative sampling approach to cryogenic cooling is to increase the temperature of the sampled flue gas to force all species into the vapour phase. This then allows the use of gas phase collection techniques such as treated filters and cartridges to collect specific species. Clearly this technique is only possible for thermally stable compounds. An advantage of this approach is that filters and cartridges can be connected in series with each removing a specific target species from the sample gas. Degradation reactions are also arrested. Such a system would also enable the use of non-stack collection methods, such as those that have been developed for ambient sampling that would otherwise be unsuitable or difficult to use at the Mongstad facility.

For vaporising the sample, it may be possible to simply use a heated probe; however, this would cause the non-volatile but soluble components to precipitate within the probe. Additionally, it will be important to ensure that all liquid aerosols have been volatilised before the sample reached the collection system. A better approach may be to utilise a small efficient heat exchanger after an in-stack filter to quickly volatilise the liquid aerosol. In this design the non-volatile but soluble species would be deposited within the heat exchanger and this deposited sample could then be analysed.

CSIRO has produced a number of stack sampling devices that have been successfully utilised to collect unique particle samples from power stations. CSIRO has also developed systems for sampling in systems within concentrated liquid aerosol environments. Utilising previous and new sampling designs and concepts it may be possible to develop a new sampling apparatus that would allow the use of treated filters and sample cartridges at the Mongstad facility. Clearly any new apparatus would require significant development and validation before it could be confidently used for the sampling of amines. However, if successful this system would allow the possible use of analysis and collection methods designed for ambient air, greatly reducing the difficulty of sample collection, in addition to minimising sample degradation after collection and resulting in a more accurate and representative sample.

3.3.3 Nitrosamines

Most sampling of gas phase nitrosamines is related to environmental monitoring, however, emissions from motor vehicles and cigarette smoke have also been investigated (Goff, et al., 1980; Rundlof et al., 2000). In general, most reported studies have used two approaches for collecting nitrosamines for laboratory analyses: (1) by dissolution in a liquid reagent in impingers or (2) by collecting onto a solid sorbent packed into a cartridge. The latter is the more common method.

In the first method, glass impingers (usually two to prevent sample breakthrough) are filled with an aqueous phosphate-citrate solution buffered to a pH of between 4 and 4.5. It is usual practice to add a small amount of an inhibitor, such as sulphamic acid or ascorbic acid to prevent the formation of nitrosamines in the solution itself. This can occur if amines present in the sample react with NO_x to form nitrosamines that are then detected during the analytical procedure. The impinger train is usually chilled in an ice bath and protected from light during and after sampling.

With solid sorbents, sample air is passed through a tube packed with a porous collection material. Various common sorbents have been tested for nitrosamine sampling, where the analyte is physically adsorbed onto the material’s surface. However, most are prone to the formation of artefacts caused by the nitrosation of amines that are also retained by the sorbent. It is suggested, however, that ThermoSorb/N is not subject to this problem.

ThermoSorb/N is normally supplied in prepacked cartridges intended specifically for air sampling. Furthermore, they do not require cooling during sampling and hence are more convenient to use in the field than liquid reagents. The cartridges are supplied already impregnated with inhibitors, and supplementary inhibitors are generally not required (Mahanama, and Daisey, 1995). The inlet of the tube comprises an amine trap, followed by a solid sorbent bed where the N-nitrosamines are retained. In high NO_x environments, a pre-cartridge containing sulphamic acid can be used to scrub out the NO_x (Rounbehler et al., 1980) but even in diesel exhaust TheromSorb/N cartridges have been found to perform satisfactorily without scrubbers (Khalek et al., 2009).

The capacity of the ThermoSorb/N cartridges is about 1500 μg (OSHA Method 27); higher capacities can be accommodated by connecting additional cartridges in series, if required.

For both impingers and sorbent tubes, the flow rate of the sample stream is around 1 to 2 L min^{-1}; the total volume sampled is determined by the level of analyte expected (consistent with the capacity of the tubes). Non-reactive materials such as Teflon should be used for sampling lines etc.

In summary, although stack sampling methods specific to nitrosamines are not currently available, the techniques currently used for ambient and vehicle exhaust can probably be applied to the Mongstad facility. The most suitable method will rely on the use of ThermoSorb/N cartridges.

3.3.4 Nitramines

Nitramines are often a component of explosives. Much of the work relating to these compounds is therefore concerned with either forensic investigations or environmental studies of discharges from manufacturing facilities into soil and groundwater.

Air samples for nitramine analysis are usually collected on solid-phase sorbents. In one reported study (Sigman et al., 2001), samples of common explosive derivatives were collected on either Tenax TA or a silica sol-gel preparation. Sorbent tubes were packed with the sorbent material and various calibration standards were spiked onto the tubes for analyses by thermal desorption/GC. The results validated the recovery of the materials.

3.3.5 Amines and Ammonia

Acid-impregnated filters have been found to be effective for collecting basic components such as ammonia and amines in ambient air (Dye et al., 2009). In this system, filters are prepared by impregnating with citric or oxalic acids. The system described by Dye et al. used 15 cm diameter filters mounted in plastic holders, however, for in-stack sampling, metal or other suitable materials could be used as well. Whatever the material, it should be selected to ensure that it is not itself a source of amines.

The filter holder would normally include a pre-filter (that did not contain the acid reagent) to remove particulates. It was suggested by Dye et al. that this system would be suitable for use in environments containing high levels of liquid aerosols such as sea spray or fog which indicates that the method may be applicable with little modification to the stack of an amine PCC plant.

Fournier et al., (2008) also used acid-impregnated filters for collecting primary and secondary amines in ambient air. The range of compounds investigated included ethanolamine and diethanolamine so is applicable to PCC emissions. This group used H_2SO_4 on 37 mm diameter filters held in cassettes. Cassettes were selected in preference to tubes because they are easier to use and are better suited to aerosols and vapours. Although the method proposed was aimed at sampling in ambient air, they heated some of the test compounds to 50 and 90 °C to ensure that the samples were in the vapour phase. This is relevant to stack sampling since it shows that it would be feasible to heat the sampling line to keep the material in the vapour phase which can be an advantage because it would prevent condensation in the sampling system. After sampling the filters were placed in a solution of dansyl chloride to derivatise the amines for HPLC/MS analysis. Recoveries were generally between 90 to 100 %.

In another approach, ethanolamines in ambient air have been sampled using an alumina sorbent in glass tubes, then subsequently analysed by mobile phase ion chromatography (Bouyoucos and Melcher, 1986). These tubes were home made and contained two beds of alumina (which had been cleaned to remove any organic material). Sampling was conducted over a 7 hour period to give about a 42 L total sample volume. Similar methods have been found to be suitable for sampling ambient amines up to 12 ppm in 100 % relative humidity, conditions that are comparable to the anticipated treated flue gas stack conditions at the Mongstad plant. Recovery of the material was good (in excess of 90 %) and provided that the tubes were refrigerated after collection, the samples were stable for at least one month.

Finally, ambient ammonia and NH_4^+ have been determined using commercial denuder cartridges (Baum and Ham, 2009). These cartridges consist of an initial impactor to collect particulates (usually PM10 or PM2.5), a denuder and a filter (or set of filters). The denuder is often a honeycomb glass structure coated with a reagent to react with the target gas. Aerosols that pass through the denuder are trapped on the filters. Typical flow rates through these devices are around 10 L min^{-1}.

3.3.6 Aldehydes

The main limitation to the DNPH/HPLC methodology is the co-collection of certain compounds which may affect its efficiency and/or its chromatographic performance. In ambient gas phase sampling, ozone affects the collection of certain carbonyls due to in situ interactions on the cartridge and the occurrence of artefacts in the chromatogram. This is overcome with the use of a potassium iodide, or other ozone scrubbing cartridge placed upstream of the sampling cartridge (Pires and Carvalho, 1998). However, this is not a likely issue for the PCC process collections.

Nitrogen dioxide (NO_2) is derivatised by DNPH to form an azide which may deplete the DNPH and hence reduce the capacity of the cartridge for reaction with carbonyl compounds. When sampling in high NO_x atmospheres an assessment of the likely NO_2 levels must be undertaken to determine if cartridge carrying capacity will be exceeded. Even where NO_2 levels will not deplete the DNPH, the NO_2 derived azide can interfere in chromatographic resolution of carbonyl analytes as it absorbs at the wavelength used for carbonyl hydrazone analysis and it elutes in the region close to formaldehyde. This is overcome by careful optimisation of the solvent mixture and gradient elution used for the chromatography to allow selectivity to this compound. In fact NO_2 can be accurately quantified in this way (Grömping et al., 1993). However, this is unlikely to be a problem in an amine capture plant where the NO_2 concentration in the flue gas is expected to be very low.

Acrolein has been found to degrade under the conditions of the acid catalysed derivatisation reaction, forming a by-product that will increase over time on-cartridge or in solution, and will present as an extra peak in the LC chromatogram. For this reason, the DNPH method is no longer recognised by some international agencies for acrolein analysis. However, acrolein is not of major priority in the assessment of process emissions.

Of particular relevance to this study with respect to gas phase sampling is the water content and temperature of the sample gas and the range over which the sampling cartridges are suitable. A sampling temperature of between 10 °C and 100 °C is specified by Waters (Waters Corporation, 1994) for their Sep-pak XpoSure™ cartridges. Supelco do not provide a temperature range for their cartridges but warn that elevated temperatures may result in an increased level of carbonyl impurities migrating from the cartridge body to the DNPH bed (email communication). They rate their cartridges as suitable above 20 % relative humidity and at high humidity, provided water does not condense to any large extent in the cartridge body. Condensation of small amounts of water in the cartridge has been evaluated and does not unduly affect their performance. Under these conditions a potassium iodide ozone scrubbing cartridge cannot be used as this is affected by excess moisture which in turn affects the collection to the DNPH cartridge. This scrubber is not required for flue gas sampling.

From the sampling and analytical viewpoint it is determined that cartridge collection with in situ DNPH derivatisation is a suitable method of collection of gas phase aldehyde compounds under the conditions of the sampling regime proposed. Where gas phase collection of condensate is performed, impingers charged with DNPH would be used. DNPH treatment of process liquids would require evaluation to ensure that matrix components do not adversely affect the efficiency of the carbonyl DNPH reaction. This would require method development and validation using real process liquid samples. On the basis that collection and treatment is found to be efficient, the HPLC chromatographic method using uv or diode array detection is the preferred determinative technique for routine analysis of the specified compounds formaldehyde and acetaldehyde.

4 DETECTION LIMITS

Detection limits are determined to a large extent by the sensitivity of the analytical technique rather than the sampling method. Usually, samples are not analysed directly, but need some preparation in the laboratory that includes extraction and concentration to yield a solution suitable for analysis. The role of the sampling method is to ensure that enough sample is provided to the laboratory so that a sufficiently concentrated solution can be prepared. For reliable quantification of the analyte, the concentration of the sample presented to the instrument should be at least five to ten times higher than the minimum detection limit.

In stack sampling, the amount of sample collected is merely determined by the volume of gas extracted from the stack. Thus for low concentration compounds, more gas is collected and hence a greater mass of the analyte is collected. However, there is a limit to the amount of sample that can be withdrawn. Firstly, very large volumes of gas may be difficult to handle through the sample train or may take an impractical length of time to collect. It is also possible that large volumes of gas being passed through impingers or solid sorbents may affect the collection efficiency of these materials. In general, practical sample volumes are within the range of about 10 to 1000 L and flow rates are limited to about 50 L min^{-1} (although there are exceptions).

Comparison of the detection limits quoted by different standard organisations is often difficult due to the various criteria that are used. For example NIOSH standards frequently quote an instrumental detection limit of µg or mg/sample which is difficult to translate to a practical working detection limit. The USEPA sometimes quote a method detection limit which is defined as “the minimum concentration of a substance that can be detected and reported with 99% confidence that the value is above zero.” Many of the NIOSH methods also quote an overall method accuracy varying from ±10 to 20 % of the recommended value. OSHA standards provide the most detailed error analysis and make the following distinctions:-

- Analytical detection limit. This is the amount of analyte that will give a peak approximately 5 times the height of adjacent contamination peaks or of baseline noise.

- Procedural detection limit. This is the amount of analyte spiked in the sample collection media which allows recovery of an amount of the analyte equivalent to the detection limit of the analytical procedure.

- Reliable quantitation limit. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96SD) of ±25% or better.

Notwithstanding these limitations, some estimates of the detection limits for various classes of compounds are shown below in Table 4.1. Detection limits for individual methods are shown in Table 3.1 Much greater detail on analytical methods and their detection limits is provided in the report for Task 4 (Tibbett et al., 2010).

Table 4.1 Detection limit ranges for various potential stack gas components

Compound Class	**Detection Limit Range**
Particulates	<0.2 mg m^{-3}
Nitrosamines	0.13-3 μg m^{-3}
Alkylamines	29-160 μg m^{-3}
Aldehydes	0.15 μg m^{-3}
Amides	~10 mg m^{-3}
Amines	0.016-0.37 mg m^{-3}
Ammonia	1.2 mg m^{-3}

5 SAMPLE INTEGRITY

Unless the samples are analysed immediately, samples will need to be preserved to prevent possible contamination or stop unwanted changes in composition occurring prior to analysis. Usually, standard sampling analytical practices are sufficient to ensure that the integrity of the sample is maintained. These practices include the use of clean, well maintained apparatus, ensuring that glassware and other containers are clean, and ensuring that reagents and sorbent tubes are free from contamination. Often samples are refrigerated after collection to reduce the rate of degradation reactions. All of the standard methods for the various classes of compound provide details on additional precautions that should be used, if required. Some of the specific requirements are highlighted below:

- Particulates are not usually subject to chemical transformations during sampling, but nevertheless, samples must be carefully handled to prevent contamination or loss of material as the filters are transferred to and from the filter holder. Most of the particulate matter associated with amine PCC plants will probably be ammonium salts. Since these compounds are soluble, exposed filters should be stored under conditions that prevent them from absorbing atmospheric moisture. It is recommended that filters be weighed under carefully controlled laboratory conditions.

- Although nitrosamines are reasonably stable, they will decompose in ultraviolet light. Hence samples should be collected in amber glassware or protected by from ultraviolet light by some other means. Nirtosamines may also react with nitrites so it is advisable when using liquid filled impingers to add citrate/ascorbate to the sampling solution to remove nitrite. Samples should also be refrigerated immediately after collection until required for analyses. Very little sample preservation is required for gas phase samples collected on Thermosorb/N tubes as sulphamic acid is incorporated into the assembly to inhibit nitrosation reactions. After exposure, the tube ends are capped to prevent contamination and sealed in foil pouches. According to NIOSH 2522, samples are stable for at least six weeks at 20 °C.

- Amines are prone to deposit on the walls of glassware which would tend to reduce the amine concentration of liquid samples. To avoid this possibility, it is recommended that all glassware used for amine sampling should be silanised, which increases the hydrophobicity of the glass surface.

6 UNCERTAINTIES

Every measurement is affected by either random or systematic errors that combine to produce a level of uncertainty in the measured value. Estimating the magnitude of this uncertainty is critical to the proper interpretation of the measurement, however, the process of uncertainty analysis can be a complicated procedure. Each source of error must be identified, its magnitude estimated, its effect on the overall measurement determined then finally the contributions from all errors combined to yield the uncertainty that is normally expressed as ± some value from the reported result. Often, statistical methods are used to deal with uncertainty analysis, and comprehensive procedures have been developed for this purpose (see for example The Guide to the Expression of Measurement Uncertainty, ISO/IEC, 2008).

Standard analytical methods, including many of those described in the preceding sections, often include estimates of the measurement uncertainty that can be expected if the procedures are closely followed. These estimates are based upon detailed experimental validation programmes, which in some cases have taken years of development and refinement (e.g. many of the USEPA methods). Although sampling itself does not normally have a quantitative estimate of uncertainty (after all nothing has been measured yet; only a quantity of material has been collected for analysis), there are nevertheless various aspects that must be considered to minimise errors. The main factors relating to stack sampling are discussed below:

Representative Sampling. One of the first things to consider is: how representative is the sample? Large stacks with multiphase streams such as that anticipated in the Mongstad plant often have uneven distribution of material within the gas flow. It is therefore essential to ensure that samples are representative of the bulk flow. This is best achieved by selecting the sampling plane and number of sampling points in accordance with proper methodologies (see Halliburton et al., 2010).

Stack Gas Velocity. Determining the emission flux for a particular material depends on measuring the volumetric flow rate of the stack gas. Hence the overall uncertainty will be strongly influenced by the reliability of measurement of the gas velocity. One of the main sources of error when measuring gas velocity is not properly accounting for the effects of non-axial flow. Traditional flow velocity measurement devices like pitot tubes may suffer from reduced accuracy when used to measure cyclonic flows so three-dimensional pitot probes are preferred in these instances (see Halliburton et al., 2010 for more detail in stack flow measurements).

Further uncertainty may be introduced if the volumetric flow rate is not adjusted for the temperature, pressure and composition (including moisture) of the gas flow. Accordingly, methods for stack sampling stipulate that these parameters must be measured during sampling. Temperature is generally measured by a thermocouple attached to the sample probe. Pressure can be measured directly in the gas stream, using a suitably calibrated pressure sensor. However, the use of national meteorological data is often suitable if the monitoring station is reasonably close to the measuring site. Allowance for height above sea level should also be applied if necessary.

The bulk composition of the stack gas should be measured so that the density can be determined. For the Mongstad plant it is probable that oxygen, nitrogen and moisture concentration data would be necessary.

Isokinetic Sampling. Since the gas stream will contain aerosols, most of the sampling will need to be performed under isokinetic conditions. When isokinetic sampling is required, care must be taken to ensure that these conditions are maintained during the sampling procedure, which may last for periods of more than an hour (or in some cases much longer). Accurate monitoring of isokinetic flow requires measurement of the gas velocity within the stack at the sampling point (either with a pitot tube or three-dimensional probe) and the flow rate of the sampling train. The sample train flow rate is normally measured using a calibrated flow meter or mass flow controller (see Section 3.1).

Deviation from isokinetic sampling of particulate material can result in sampling bias (i.e. the particle size distribution of the material collected is not representative of the bulk flow). As a consequence, most standard methods for sampling aerosols impose maximum allowable tolerances on the sampling flow rate. For example, the German standard, VDI 2066, requires the sample flow rate be maintained with 95 to 115 % of the isokinetic rate. Similarly, USEPA methods require that sampling be within 10 % of isokinetic conditions.

Measuring Sample Volume. A potentially large source of error is the measurement of the sample volume. This volume is usually measured on site with a dry gas meter but other types of flow meter or mass flow controllers are frequently used. Whatever the instrument, they should be calibrated against a traceable standard. All standard methods specify that flow measuring devices must be calibrated or that their uncertainty be within certain limits (e.g. VDI 2066 requires that the sample volume be measured to within ± 2 %).

The sample volume may also be affected by the presence of leaks in the sample system. Leaks can occur in most components of the sampling train including tubing connections, impingers, pumps or flow meters. Good practice dictates that sampling equipment should be maintained in good condition to reduce the risk of leaks but as well, thorough leak testing should be performed on the sample train on site. Many standard methods include a leak testing step in the procedure.

Sample Breakthrough. Some of the target species may pass through the collection medium if the collection efficiency is too low or the capacity of the medium is exceeded. This breakthrough is generally prevented by the use of backup media such as multiple impingers or sample tubes connected in series.

Standard methods generally specify how many impingers or tubes are required since the methods have been validated for the conditions of the sampling. However sampling methodology for treated flue gas from an amine PCC plant has not yet been validated so it is not known whether breakthrough will be a concern. Hence some initial testing will be necessary to determine if breakthrough will be a problem. It is suggested that in the first instance, a cautious approach should be adopted and thus use multiple impingers/sorbent tube to capture any breakthrough material. Subsequent analysis of the downstream media will confirm whether or not breakthrough has occurred. This will be a necessary step in the method validation procedures.

For particulate mater, it is usual to use only one filter (or impactor device) so it is important that they can retain the material in the gas flow. Standard methods for particulate sampling specify minimum performance characteristics of filter media (USEPA Method 5 requires better than 99.95 % retention of 0.3 μm particles; 99.9 % for 0.6 μm in VDI 2066).

Unwanted Reactions. One of the aims of effective sampling is to stop any unexpected reactions from occurring in the sample after collection. Often the sample is preserved by cooling or adding a preservative reagent. Some commercial sorbent tubes used for gas phase sampling are prepared with suitable preservatives already added. However, in some complex matrices, there may be certain reactive components that cannot be effectively prevented from undergoing unwanted chemical transformations. If such a situation occurs, it still may be feasible to perform quantitative analysis on the sample if the kinetics of the transformation process are understood. This approach has been used successfully to determine the concentration of unstable compounds in motor vehicle exhaust (Ye et al., 1997; Nelson et al., 2008). It does, however, necessitate detailed characterisation of the kinetics and an accurate knowledge of the time elapsed between sampling and analysis.

Contamination. Care must be taken to ensure that samples are not contaminated by material that did not originate from the stack. All containers and associated sampling equipment must be thoroughly cleaned before use. After sampling the collected materials must be adequately sealed to prevent contamination during transport to the laboratory.

The effects of contamination can be estimated by performing blank analyses and it is recommended practice to run a field blank during sampling campaigns. The field blank comprises sampling medium (impinger, sorbent tube or filter) that is handled on site the same way as the “real” samples, except that it is not exposed to the stack gas. Field blanks identify any contamination that has occurred during the sampling process. Analytical blanks on the fresh medium (i.e. they have not been handled) are also usually performed in the laboratory to determine the background level of contamination in the material.

The brief discussion above illustrates that there are a number of factors that can contribute to the overall uncertainty of when determining emissions. Because of this, it is essential that any new method is properly validated. Where possible this process should include the use of reference materials to measure sample recovery efficiencies for a particular method.

7 CONCLUSIONS AND RECOMMENDATIONS

The exhaust gas stream from an amine PCC plant will be significantly different from conventional stationary sources. The temperature of the gas stream will be lower than most combustion sources and as a consequence will contain both gas and condensed liquid aerosols. There may also be some solid particulate matter present due to heat stable salts produced through secondary reactions within the plant. Representative sampling from the stack of the proposed Mongstad amine PCC plant will therefore be a significant challenge. Procedures will be required that can effectively collect all of these components while ensuring that the samples do not degrade prior to analysis.

At present, the composition of the treated gas stream from the Mongstad plant is largely unknown and the analytical methods required are still undergoing development. Because of this uncertainty, rather than attempt to provide a set of prescriptive sampling methods that may need to be changed, we have developed a set of more general guidelines and recommendations that can assist experienced staff in setting up sampling regimes at the Mongstad PCC plant.

Based on examination of a wide range of international standard methods for stack and ambient air sampling, as well as our own experience, we offer the following observations and recommendations for sampling the treated flue gas at the Mongstad plant.

7.1 Sampling Apparatus

- Many of the target species are likely to be dissolved in liquid droplets entrained in the gas flow. Because of the presence of liquid (and possibly solid) aerosols, sampling should be undertaken isokinetically unless reliable measurements of the particle distribution within the PCC plant show that this is not necessary (i.e. the Stokes diameter is sufficiently small). High quality stack sampling equipment should be used to maintain isokinetic conditions. Automatic samplers or closed loop controlled stack samplers are preferred since they provide increased accuracy and precision especially when the stack flow is variable. All equipment should be calibrated against traceable reference standards. The capture and transmission efficiency of the sampling system for target compounds should be quantified. This information may be supplied by the manufacturer for some compounds if a commercial apparatus is used.

- Components of stack sampling equipment in contact with flue gas and its condensates should be made from at least 316 stainless steel that has been polished and acid passivated. For many of the compounds targeted, silanised borosilicate glass or quartz, or Teflon will be more appropriate.

- Tube connections within the probe should have smooth transitions with taper angles < 30° to eliminate areas for gas flow to stagnate.

- Only high quality vane pumps of a sealed and pressure pulse-free design should be used in the sample train, and especially when dry gas meters are used to measure gas volumes. All materials in the pump and sample train must be amine free; o-rings should be Teflon encapsulated and contained within “captured” o-ring grooves.

- Heated probes and lines should be used where possible to eliminate condensation, but only for thermally stable compounds. Sorption cartridges should be used with heated sampling probes and lines and operated above the dew point of the flue gas.

7.2 Sampling Methods

- Some species may be amenable to analysis at the site using FTIR or micro gas chromatography but the system will have to be fully heated to prevent condensation in the sampling train and analytical instrumentation. If suitable equipment is available, this would be a worthwhile approach as it has been used successfully to measure ammonia and other trace organic compounds in high moisture, condensing industrial environments.

- There are relatively few stack methods that can be applied to a PCC plant without modification. Those recommended for use at Mongstad are:

  USEPA Method 5, VDI 2066, other standard particulate methods. Although particulates will only be a minor component of the flue gas, the general principles of isokinetic sampling will be applicable to sampling liquid aerosols.

  USEPA Method 0011 for aldehydes and ketones.

  USEPA Method 18 for volatile organic compounds. This is not an isokinetic method, but it could easily be set up as such. Samples may be analysed at the stack or extracted into a heated Tedlar bag then analysed by gas chromatography. Alternatively, solid sorbents may be used, which provides considerable scope for adapting many of the ambient air methods to stack sampling in amine PCC plants.

  JIS K 0099 for ammonia.

- It will be necessary to measure moisture in the stack gas. The most appropriate method is to assume that the gas is saturated at the measured temperature (according to method BS EN 14790:2005).

- There are numerous sampling methods designed for monitoring ambient air quality and workplace exposures. Most of these use solid sorbent materials to collect the target compound and many will be suitable for the range of compounds expected in amine PCC treated flue gas. Methods applicable to the Mongstad plant are:

  Nitrosamines – Most methods use commercially prepared ThermoSorb/N cartridges since they have been shown to overcome most interferences. Relevant methods are: NIOSH 2522, OSHA Method 27, OSHA Method 31, and USEPA Method TO 7.

Amides – Silica gel is suitable for collecting amides; a relevant method is OSHA Method 2084.

Amines – Silica gel or XAD-2 sorbent is used to collect amines from ambient air in workplaces. Methods include OSHA Method 60, NIOSH Methods 2002, 2007 and 2010. Alternatively, ISO 177734-2, which uses midget impingers containing dibutylamine, can be used for a range of amines.

Ammonia – In addition to the stack-specific method JIS K 0099, OSHA Method ID 188 is also used for monitoring air quality. Both methods use acid impregnated sorbents.

The main modification required to adapt these methods to stack sampling is that the sorbent cartridge will be attached to the sampling train in place of the impingers. As well the sample line and perhaps the cartridge may need to be heated to prevent condensation in the system. These variations mean that the sampling methods will each have to be validated; i.e. the recovery efficiency will need to be determined for each material, preferably by using reference materials.

- To fully sample all of the material of interest using standard methodology, it is likely that a number of sample trains will be required.

- The composition of the flue gas from the Mongstad plant is largely speculative. Hence, it is suggested that early in the process of commissioning the plant that a bulk sample of condensate be collected for detailed analysis. Although this material may be subject to degradation due to unwanted reactions occurring in the liquid, it will nevertheless provide valuable qualitative information on the nature of the compounds present. An extension of this simple approach is to cryogenically cool the condensate immediately after sampling which would effectively quench all degradation reactions.

7.3 Further Work

- A programme of stack sampling method development needs to be undertaken to design new procedures specific to compounds not currently covered by international methods. Examination of the current methodology shows that some of the characteristics of existing methods could be used to produce new robust stack sampling methods suitable for most of the materials expected at Mongstad. In particular, combining some of the features of isokinetic sampling used in USEPA Method 5 with the procedures of Method 18 and many of the ambient air methods would provide considerable flexibility.

- Cryogenic cooling of material collected from the stack may be a relatively simple method to preserve samples. If successful it may be possible to fully sample the stack emissions from a single sample train. This should therefore be investigated further to determine its collection efficiency and practicality for use in stack sampling. This work will, of course, need to be conducted in close cooperation with the analytical method development.

- None of the sampling methods suggested for use at Mongstad have been used at an amine PCC plant before. Consequently their performance in this application is largely unknown. It is therefore essential that all methods are properly validated, especially in relation to their collection efficiency, to ensure that sampling is representative of the stack conditions.

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APPENDIX A

List of analytes covered by standard methods.

Compound Class	Method	Compounds Covered
N-Nitrosamine	USEPA Method T0-7	N-nitrosodimethylamine
	NIOSH Method 2522	N-nitrosodimethylamine; N-nitrosodiethylamine; N-nitrosodipropylamine; N-nitrosodibutylamine; N-nitrosomorpholine; N-nitrosopiperidine; N-nitrosopyrrolidine
	OSHA Method 27	N-nitrosodimethylamine; N-nitrosodiethylamine; N-nitrosodipropylamine; N-nitrosodibutylamine; N-nitrosopiperidine; N-nitrosopyrrolidine; N-nitrosomorpholine
	OSHA Method 31	N-nitrosodiethanolamine
Aldehydes and Ketones	USEPA Method TO-11A	Formaldehyde; Isovaleraldehyde; Propionaldehyde p-Tolualdehyde; Acetaldehyde; Valeraldehyde; Crotonaldehyde; Hexanaldehyde; o-Tolualdehyde; Butyraldehyde; 2,5-Dimethylbenzaldehyde; Methyl ethyl ketone; Acetone; m-Tolualdehyde; Benzaldehyde
	USEPA Method TO-5	Formaldehyde; Acetaldehyde; Acrolein; Propanal; Acetone; Crotonaldehyde; Isobutyraldehyde; Methyl Ethyl Ketone; Benzaldehyde; Pentanal; o-Tolualdehyde; m-Tolualdehyde; p-Tolualdehyde; Hexanal
	USEPA Method 323	Formaldehyde
	USEPA Method 0100	Acetaldehyde; Acetone; Acrolein; Benzaldehyde; Butyraldehyde; Crotonaldehyde; 2,5-Dimethylbenzaldehyde; Formaldehyde; Hexanal; Isovaleraldehyde; Propionaldehyde; m-Tolualdehyde; o-Tolualdehyde; p-Tolualdehyde; Valeraldehyde
	USEPA Method 0011	Formaldehyde; Acetaldehye; Acetophenone; Isophorone; Propionaldehyde
	USEPA Method 8520	Formaldehyde
	NIOSH Method 2539	Acetaldehyde; Acrolein; Butyraldehyde; Crotonaldehyde; Formaldehyde; Furfural; Heptanal; Hexanal; Isobutyraldehyde; Isovaleraldehyde; Propionaldehyde; Valeraldehyde
	NIOSH Method 2016	Formaldehyde
	NIOSH Method 2541	Formaldehyde
	NIOSH Method 3500	Formaldehyde
	OSHA Method 68	Acetaldehyde
Amines	ISO 17734-2	4,4'-methylenediphenyldiamine; 2,4- and 2,6-toluenediamine; 1,6-hexamethylenediamine; 4,4'-methylenediphenyl aminoisocyanate; 2,4-, 4,2- and 2,6-toluene aminoisocyanate; 1,6-hexamethylene aminoisocyanate
	NIOSH 2002	Aniline; o-Toluidine; 2,4-Xylidine; N,N-Dimethyl- p-toluidine; N,N-Dimethylaniline
	NIOSH 2010	Diethylamine; Dimethylamine
	NIOSH 2007	2-aminoethanol; 2-dibutylaminoethanol; 2-diethylaminoethanol
	NIOSH 3509	Monoethanolamine (MEA); Diethanolamine (DEA); Triethanolamine
	NIOSH 2540	Triethylenetetramine
	OSHA Method PV2111	Ethanolamine
	OSHA Method PV2018	Diethanolamine
	OSHA Method 60	Ethylenediamine; Diethylenetriamine; Triethylenetetramine
Amide	OSHA Method 2084	Acetamide

Alkylamines	OHSA Method 40	Methylamine
	OHSA Method 36	Ethylamine
	OHSA Method 34	Dimethylamine
	OHSA Method 41	Diethylamine
Ammonia	JIS-K0099	Ammonia
	JIS-K0099	Ammonia
	NIOSH 6016	Ammonia
	NIOSH 3800	Benzene; o-xylene; m-xylene; p-xylene; Styrene; Toluene; n-Hexane; Acetone; 2-Butanone; Methanol; Methylene Chloride; Vinylidene Fluoride; Trichloroethylene; Tetrafluoroethylene; Formaldehyde; Ethylene Oxide; Tetrahydrofuran; Nitrous Oxide; Carbon Disulfide; Sulfur Dioxide; Ammonia; Hydrogen Fluoride
	NIOSH 6015	Ammonia
	OSHA Method ID-188	Ammonia
PCB/PCDD	DIN EN 1948-1	Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)
	USEPA Method 0023A	PCDDs and PCDFs
Volatile Organic Compounds	USEPA Method TO-14A	Freon 12; Methyl chloride; Freon 114; Vinyl chloride; Methyl bromide; Ethyl chloride; Freon 11; Vinylidene chloride; Dichloromethane; Trichlorotrifluoroethane; 1,1-Dichloroethane; cis-1,2-Dichloroethylene; Chloroform; 1,2-Dichloroethane; Methyl chloroform; Benzene; Carbon tetrachloride; 1,2-Dichloropropane; Trichloroethylene; cis-1,3-Dichloropropene; trans-1,3-Dichloropropene; 1.1,2-Trichloroethane; Toluene; 1,2-Dibromoethane; Tetrachloroethylene; Chlorobenzene; Ethylbenzene; m,p-Xylene; Styrene; 1,1,2,2-Tetrachloroethane; o-Xylene; 4-Ethyltoluene; 1,3,5-Trimethylbenzene; 1,2,4-Trimethylbenzene; m-Dichlorobenzene; Benzyl chloride; p-Dichlorobenzene; o-Dichlorobenzene; 1,2,4-Trichlorobenzene; Hexachlorobutadiene
	USEPA Method TO-1	Benzene; Toluene; Ethyl Benzene; Xylene(s); Cumene; n-Heptane; l-Heptene; Chloroform; Carbon Tetrachloride; 1,2-Dichloroethane; 1,1,1-Trichloroethane; Tetrachloroethylene; Trichloroethylene; 1,2-Dichloropropane; 1,3-Dichloropropane; Chlorobenzene; Bromoform; Ethylene Dibromide; Bromobenzene
	USEPA Method 8265	Acetone; Benzene; Bromodichloromethane; Bromoform; Bromomethane; Carbon disulfide; Carbon tetrachloride; Chlorobenzene; Chloroethane; Chloroform; Chloromethane; Dibromochloromethane; 1,1-Dichloroethane; 1,2-Dichloroethane; 1,1-Dichloroethene; cis-1,2-Dichloroethene; trans-1,2-Dichloroethene; Dichloromethane; 1,2-Dichloropropane; cis-1,3-Dichlororopene; trans-1,3-Dichloropropene; Ethylbenzene; 2-Hexanone; Methyl ethyl ketone (MEK); Methyl isobutyl ketone (MIBK); Methyl-tert-butyl ether (MTBE); Styrene; 1,1,2,2-Tetrachloroethane Tetrachloroethene; Toluene; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethene; Vinyl acetate; Vinyl chloride; Xylenes
	USEPA Method 0030	volatile principal organic hazardous compounds with boiling points <100 °C
	USEPA Method 0031	Acrylonitrile; Benzene; Bromodichloromethane; Carbon disulfide; Carbon tetrachloride; Chlorodibromomethane; Chloroform; Chloroprene; Dibromomethane; 1,1-Dichloroethane; 1,2-Dichloroethane; 1,1-Dichloroethene;

		trans-1,2-Dichloroethene; 1,2-Dichloropropane; 1,3-Dichloropropene; Methylene chloride; Tetrachloroethene; Toluene; 1,1,1-Trichloroethane; 1,1,2-Trichloroethane; Trichloroethene; Trichlorofluoromethane
	USEPA Method 18	Gaseous organic compounds
	USEPA Method 0040	1,1,1-Trichloroethane; Trichloroethene; 1,1-Dichloroethane; 1,1-Dichloroethene; 2,2,4-Trimethylpentane; Allyl chloride; Benzene; Carbon tetrachloride; Methyl chloride; n-Hexane; Methylene chloride; Toluene; Trichlorofluoromethane; Vinyl bromide; Vinyl chloride; Methyl bromide; 1,3-Butadiene; Dichlorodifluoromethane; 1,2-Dichloro-1,1,2,2-tetrafluoroethane; 1,1,2-Trichlorotrifluoroethane; Chloroform; 1,2-Dichloropropane; Tetrachloroethene
Gaseous and particulate organics	USEPA modified method 10	Particulates and semi volatile organic compounds (i.e. boiling points > 100 °C)
Condensable particulate matter	USEPA Method 202	Condensable liquids
	USEPA Method 28	Condensable liquids

APPENDIX B

Commercial Stack Sampling Suppliers/Manufacturers

The following is a list of well known suppliers of stack sampling equipment. Please note that these are provided as a general reference; CSIRO has not evaluated these products and in no way endorses any of the companies listed.

CleanAir

CleanAir (http://www.cleanaireurope.com/page.php?u=texte&texte=presentation&lang=us) is a US based stack sampling equipment manufacturer providing a comprehensive range of stack sampling equipment including isokinetic sampling systems, continuous emission monitoring equipment and systems. The company has a European operation located in France. They also have equipment available for rental.

This company supplies manual stack sampling systems compliant to USEPA Method 5 and includes sampling nozzles, heated transfer lines, flow and temperature sensors, impinger train and a manual stack sampling control console. Probe lengths up to 3 m are available off-the-shelf so the probe will have difficulty undertaking measurements in ducts with diameters larger than 6 m. Probe liners available are borosilicate glass, quartz, 316 stainless steel, inconel and titanium.

While the sampler is not an automated unit the company provides a flow calculator to enable the correct isokinetic velocity to be easily calculated.

New Star Environmental LLC

New Star Environmental (http://www.newstarvironmental.com) is a US based stack sampling equipment manufacturer providing a comprehensive range of air monitoring equipment including isokinetic sampling systems, continuous emission monitoring equipment and systems. Their stack sampling system is a small portable device and is suitable only for small ducts.

TCR TECORA

TCR TECORA (http://www.tecora.it/en/main.php) is an Italian stack sampling equipment manufacturer providing a very comprehensive range of air monitoring equipment including isokinetic sampling systems, continuous emission monitoring equipment and systems. The company offers both manual and automated stack sampling systems that are compliant with international stack sampling methods.

Apex Instruments

Apex Instruments (http://www.apexinst.com) is a US based stack sampling equipment manufacturer providing a very comprehensive range of air monitoring equipment including isokinetic sampling systems, continuous emission monitoring equipment and systems and three-dimensional flow probes. The company offers both manual and automated stack sampling systems that are compliant with international stack sampling methods.

Manufacturer	Origin	Compliant Methods	Probe length	Probe Liner Material	Flow Rate Range (L min^{-1})
CleanAir	US	USEPA Methods, VDI 2066, European prEN 13284-1*	3 m**	316L SS, quartz, glass, titanium	3 – 27
New Star Environmental LLC	US	USEPA Methods	Telescopic probe	316 SS	2 – 12
TCR TECORA	Italy	USEPA Methods, VDI 2066, European prEN 13284-1*	2.5 m	316 SS	3 – 70
APEX Instruments	US	USEPA Methods, VDI 2066, European prEN 13284-1*	2.5 m*	316L SS, quartz, glass, titanium. Inconel, Teflon	3 - 70

* this probe would be compliant with other international stack sampling methods

** Custom probe lengths available.