

3. Sampling methods

3.1 Precipitation amounts and determination of major ions in precipitation samples

3.1.1 Introduction

The purpose of sampling and chemical analysis of precipitation in the EMEP network is generally to give an accurate indication of precipitation chemical composition, which can be used to derive deposition by scaling with precipitation amounts, both on short-term (day-month) and on long-term bases.

In connection with the determination of transboundary fluxes and deposition of air pollutants, the concentrations of sulphate, ammonium and nitrate in precipitation are particularly important. However, determination of one or more of the sea-salt constituents (Na, Cl, Mg) is also necessary in order to determine the fraction of sulphate concentration which is due to marine sea-spray aerosols; and determination of the base cations Ca, K, and Mg is desirable in order to give an indication of the large-scale deposition of bases which is needed in connection with the determination of critical loads.

Finally, pH and conductivity should also be determined in order to give an indication of the overall composition of the samples, and to check the consistency of the chemical analyses.

3.1.2 Principle

Precipitation is collected in a vessel, with a defined horizontal opening. The collecting vessel must be constructed from a material, which does not alter the chemical composition of the sample, and shall give a reliable measure of the amount of precipitation on a daily basis. The concentration of the major anions and cations are determined by chemical analysis.

3.1.3 Site requirements

In order for the measurements to be useful for validation of models of long-range transport and deposition of air pollutants the site for precipitation collection should be chosen, and the collection of rain and snow for analyses should be made in such a way that the concentrations are representative of rainfall composition over a larger area. For this purpose, the following requirements have been worked out:

1. The annual precipitation amount at the site, as measured by an ordinary meteorological precipitation gauge, should not differ markedly from the precipitation amounts at adjacent sites in the national precipitation network, and the daily precipitation amounts should also be correlated with those from the adjacent sites.
2. The location of the sampler should conform to WMO site requirements for precipitation gauges (WMO, 1971). There should be no obstacles, such as trees, above 30° from the rim of the precipitation collector, and buildings, hedges, or topographical features which may give rise to updraughts or

downdraughts should be avoided. Consideration of the prevailing wind directions during precipitation events is recommended in connection with locating the sampler.

3. Of particular concern is the sedimentation of soil dust particles from the immediate surroundings. Gravel roads, farmyards, and tilled agricultural fields in the near surroundings within a distance of 100 m to 1 km should be avoided. Other potential local contamination sources include local residential heating with wood, peat or coal. Potassium is an indicator of such contamination. Local high ammonia concentrations from farming activities should also be avoided.

Supply of electricity is necessary for the operation of wet-only precipitation samplers. For the operation of the sampling site a small room is needed to store samples, equipment, and documents. This must be equipped with a refrigerator for the storage of collected precipitation samples.

3.1.4 Sampling equipment

The sampling equipment consists in principle of a funnel and a receiving vessel, as indicated on Figure 3.1.1. In order for the sample not to be contaminated from the ground during heavy rain, the rim of the funnel should be positioned 1.5–2 m above the ground level. It is recommended that the sampler be further protected from sedimentation of dust and adsorption of gases during dry periods by an automatic lid, which opens after activation of a precipitation sensor. The precipitation sensor is usually based on measuring the electrical conductivity between a pair of gold-plated electrodes on a suitable non-conducting surface. The sensor is electrically heated to a temperature of 1–2 degrees above the ambient temperature so that the water film evaporates after the precipitation event. The sensitivity of the sensor is important, a precipitation amount of 0.05 mm/h should be sufficient for the lid opening mechanism to be activated.

Precipitation collectors are commercially available and a list of instruments and manufacturers' addresses is given below (Table 3.1.1). In selecting one of these, reference should be made to available field test results (e.g. Winkler et al., 1989; Granat et al., 1993), and the climatic conditions at the site should also be considered.

Bulk samplers are recommended only if it can be shown that the contamination by dry deposition of dust and gases e.g. ammonia is negligible, and during periods when the precipitation is mainly in the form of snow. Wet-only samplers are unsuitable for collection of snow, because of generally poor aerodynamic designs, and because heating of the funnel to melt the snow may cause serious evaporation and concentration of the sample. The response of the conductivity sensors to dry snow is also poor.

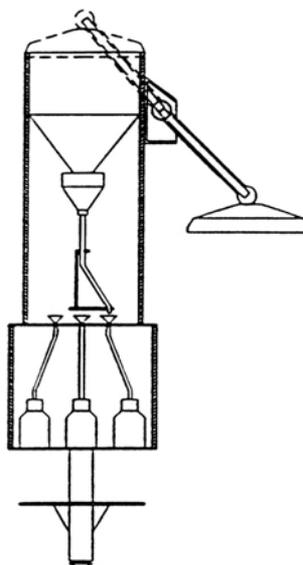


Figure 3.1.1: Precipitation collector type PR1410.

Table 3.1.1: Commercially available wet-only collectors.

Name	Manufacturers address	Comments
ERNI	Firma Eigenbrodt, Königsmor/ Kr. Harburg, D-21255 Germany. http://www.eigenbrodt.de	Rather bulky design. Old models have a relatively insensitive precipitation sensor, and funnel made from stainless steel. Replacement of these parts is possible.
MISU	Department of Meteorology, Stockholm University, S-106 91, Stockholm, Sweden. http://www.misu.su.se	Simple design, modest size and good collection efficiency.
ECN (PR1410)	Van Essen Instruments BV, PO Box 553, NL-2600 An Delft, The Netherlands. http://www.vanessen.com/	Good geometrical design. Can be used to collect up to 7 (daily) samples without attention.
APC 70	Hydrolog Limited 63 Constitution Street Edinburgh EH6 7AF, UK http://www.hydrolog.co.uk/	
WADOZ	Dipling, A. und Kroneis, W., Werkstätten für Messgeräte G.M.B.H., Iglaseegasse 30-32, A-1190 Wien, Austria. http://www.kroneis.co.at	

All materials that come in contact with the sample must be chemically inert. Polyethylene, tetrafluoroethylene and tetrafluoroethylene-fluorinated ethyl-propylene copolymer are generally recommended because of their excellent chemical properties. The mechanical properties of these materials must be taken into account in the construction of samplers, however. Polyethylene may become brittle when exposed to sunlight, and should be replaced after 1 year of use involving exposure to sunlight. Borosilicate glass should be properly acid-washed and rinsed in deionized water prior to use, but the use of glass is not generally recommended. Soft glass will contaminate the sample with alkali and alkaline earth cations. Metals and artificial materials with unknown chemical properties or

composition should be avoided. If such materials have to be used in joints or in other constructional details, boil a sample of the material in deionized water and analyze the water afterwards as a precipitation sample!

The construction principles for precipitation gauges are relatively simple. The sampler should not be too large or bulky, because this will obstruct the air flow around the sampler. On the other hand, the diameter of the collector must be large enough to provide samples large enough for chemical analysis. In practice, a diameter of 20 cm is sufficient. If a funnel is used, there should be a vertical section of at least 5 cm height.

For a general review of errors in the collection of precipitation in precipitation gauges, reference is made to Sevruck (1989). There are 4 sources of error if the sampler is equipped with a sensor-activated automatic lid:

- (1) aerodynamic error, when the gauge fails to catch the same amount of precipitation which falls on the surface,
- (2) evaporation errors, when part of the precipitation evaporates after the precipitation event, and before the amount is collected or measured, and
- (3) the wetting error, which occurs because not all of the precipitation is transferred to the measuring cylinder,
- (4) Failure of the lid to open in situations with light precipitation or snow.

The aerodynamic error is reduced by proper design of the collector, and by choosing the sampling site carefully. It cannot be entirely eliminated and may be very serious at windy sites, and particularly for snow. Use of a windshield (Nipher or Wyoming) may be necessary for sites where a large fraction of the precipitation is in the form of snow.

However, at many sites the collected amounts of precipitation will be a good measure of the precipitation amounts even if no particular measures have been taken. Consultation and co-operation with meteorological services running precipitation gauge networks is strongly recommended when selecting sites and precipitation collecting equipment.

The evaporation effect is reduced if an automatic closing lid is used, but the lid must form an airtight seal with the rim of the collector. For bulk collectors of the funnel and bottle type, diffusion through the funnel stem reduces the evaporation effect.

The wetting error is due to the liquid film on the inside of the collector. The equivalent volume of this liquid film is related to the internal surface of the collector, and may be determined experimentally, for example by weighing the collector in dry condition, spraying with water, "emptying", and weighing again.

It is not unusual to find a wetting error corresponding to 0.2 mm of precipitation. Winkler et al. (1989) have measured the wetting film on several commercially available precipitation collectors.

Evaporation changes are particularly serious, since this may result in a significant concentration of the sample. Electrical heating of the precipitation collector in

order to melt precipitation in the form of snow is therefore not recommended. It is acceptable, however, to apply electrical heating when the lid is firmly closed.

In order to obtain a more accurate measure of the precipitation amount, WMO GAW has equipped their sites with a rain gauge in addition to the wet-only collector. This improves the measurements of deposition, and will, provided that the Steering Body agrees, be implemented also for EMEP sites as one step in a harmonization process.

When precipitation is in the form of snow, it is advisable to use a special snow collector, in the form of an open polyethylene cylinder of diameter 20 cm. The height of the cylinder should be at least twice the diameter to prevent "blow-out". The snow collector should be equipped with a tight-fitting polyethylene lid, which is put on when the collector and sample is brought indoors for the sample to melt.

Proper design, construction and maintenance of the sampling equipment is essential in order to avoid serious errors because of poor performance of the precipitation sensor and automatic lid system. The sensor should be designed with a response which will cause the lid to open when the precipitation intensity exceeds 0.05 mm/h.

Additional equipment at the sampling site will include:

- Spare parts for precipitation collectors,
- Distilled(deionized) water storage bottle,
- Polyethylene spray bottle,
- Filter paper or tissue paper for cleaning,
- Disposable plastic gloves,
- Acetone for cleaning,
- Measuring cylinders,
- Funnel,
- Balance, 0-500 g.,
- Storage bottles, transport containers.

3.1.5 Sampling procedure

Samples are collected on a daily basis, at the same time as used in the official precipitation measurement network. Usually this will be at 0800 local time. If daylight savings time (summer time) has been introduced, samples should be collected according to the "normal" time. The daily sample collection involves transfer of the sample to a sample storage and transport bottle, measuring the sample volume, and cleaning of the equipment which has been used. The exact procedure will vary according to the equipment used at the sites. A detailed, written standard operating procedure must be worked out for each site and should be readily available at the site, in the national language of the operator. As an example, the procedure could consist of the following steps:

1. Collect the equipment needed for change of samples. Label the storage and transport bottle with station code and name, and start and end of the sampling period.

2. If there is any chance for the operator to touch the inside of the collecting funnel, disposable polyethylene gloves should be put on.
3. Exchange the collection bottle in the precipitation sample collector and put on a screw-stopper. Check that the collection equipment functions correctly by putting a drop of water on the precipitation sensor. Examine the collector funnel for visible contamination such as insects, leaves or tree-needles, organic debris. If this is found, remove the contamination and rinse with distilled water. If a bulk collector is used, the collecting funnel should be rinsed with distilled water every day. After the distilled water has drained off, put on the new collection bottle.
4. Take the collection bottle indoors to the room assigned to function as the sampling laboratory.
5. Weigh the bottle, transfer a suitable aliquot (50-100ml) to the labelled storage and transport bottle. (Alternatively, measure the volume in a graduated cylinder. Use a large cylinder (0-250 ml) for large samples, and a small (0-25 ml) cylinder for small samples).
6. Put the storage and transport bottle in the refrigerator until it can be sent to the laboratory for chemical analysis.
7. Pour out the remainder of the sample, rinse with distilled water and place the collecting bottle upside down in a clean place to dry. Also rinse the graduated cylinders.
8. Take off and discard the disposable plastic gloves.
9. Fill in the field sample registration form, and take time to record usual and unusual events which may have influenced the sampling. Examples are given below (these should be elaborated for each site, because of the different conditions):
 - Visible contamination of the sample or the collection funnel (describe the contamination, see 3 above)
 - Agricultural tilling and sowing (in the surroundings or on adjacent fields).
 - Fertilizing
 - Liming
 - Manure spreading
 - Burning of stubble, or other fires in the area
 - Construction work
 - Unusual smell, (try to describe the smell)
 - Strong haze (visibility)
 - Pollen
 - Visible deposition of dust
 - Strong winds, e.g. in connection with thunderstorms.

3.1.6 Chemical analyses

Most of the major ions in precipitation samples may be determined by ion chromatography, which is the generally recommended method for anions such as chloride, nitrate and sulphate. Table 3.1.2 gives a list of alternative recommended methods, with reference to more detailed descriptions and procedures in Section 4. It is not recommended to filter samples.

Table 3.1.2: Recommended and alternative methods for chemical analysis of precipitation within EMEP.

METHODS		
Component or parameter	Recommended methods	Alternative
Conductivity	Conductivity cell and resistance bridge	
Hydrogen ion (H ⁺)	Potentiometry (glass electrode) pH<5.0	Titration
Ammonium ion (NH ₄ ⁺)	Ion chromatography	Spectrophotometry (indophenol blue colour reaction)
Sodium ion (Na ⁺)	Atomic absorption spectrophotometry (AAS)	Ion chromatography
Potassium ion (K ⁺)	AAS	Ion chromatography
Magnesium ion (Mg ²⁺)	AAS	Ion chromatography
Calcium (Ca ²⁺)	AAS	Ion chromatography
Sulphate ion (SO ₄ ²⁻)	Ion chromatography	
Nitrate ion (NO ₃ ⁻)	Ion chromatography	Reduction to nitrite and diazotation
Chloride ion (Cl ⁻)	Ion chromatography	Displacement of SCN ⁻ in Hg (SCN) ₄ ²⁻ , determination of coloured Fe(SCN) complex.
Bicarbonate ion (HCO ₃ ⁻)	Titration	
Formate ion (HCOO ⁻)	Ion chromatography	
Acetate ion (CH ₃ COO ⁻)	Ion chromatography	

The last three anions are not part of the ordinary EMEP measurement programme. They are included here, however, because they are found in precipitation samples in concentrations comparable to some of the other ions, and may be necessary to explain the ion balance and measured conductivities, particularly for samples with pH above 5. Note that most of the components can be determined by ion chromatography, which is strongly recommended for the anions sulphate, nitrate and chloride. However, ion chromatography holds no advantages over conventional methods when it comes to determination of ammonia and base cations.

3.1.7 Calculation and reporting of results

The amount of precipitation is to be calculated from the collected sample volume, simply by dividing by the area of the sampling orifice. No corrections are to be made for sampling errors, such as undercatch, evaporation or the part of the

sample remaining in the collector because of the wetting effect. An assessment of these errors should be performed and be available.

Additionally, the amount of precipitation measured by rain gauge should be reported to the CCC.

Conductivity and pH is reported in $\mu\text{S}/\text{cm}$ and in pH units, respectively. All other parameters are reported as elemental concentrations in mg/litre. Note especially that nitrate, ammonium and sulphate concentrations are to be given as equivalent weight concentrations of nitrogen and sulphur. Table 3.1.3 gives reporting units and conversion factors.

Table 3.1.3: Units and conversion factors.

Ion	Reporting form	Mol /mg
Sulphate (SO_4^{2-})	mg S/litre	$31.19 \cdot 10^{-6}$
Nitrate (NO_3^-)	mg N/litre	$71.39 \cdot 10^{-6}$
Chloride	mg Cl/litre	$28.21 \cdot 10^{-6}$
Hydrogen (H^+)	(pH)	
Ammonium (NH_4^+)	mg N/litre	$71.39 \cdot 10^{-6}$
Sodium (Na^+)	mg Na/litre	$43.50 \cdot 10^{-6}$
Potassium (K^+)	mg K/litre	$25.57 \cdot 10^{-6}$
Magnesium (Mg_2^+)	mg Mg/litre	$41.13 \cdot 10^{-6}$
Calcium (Ca_2^+)	mg Ca/litre	$24.95 \cdot 10^{-6}$
Conductivity	$\mu\text{S}/\text{cm}$	

Before the results are sent to the CCC, they should be examined for internal consistency by the responsible laboratory. The procedure for this examination is given under Section 6, which also contains data flags and gives information on data reporting.

3.1.8 Quality assurance

Site operation

Standard operation procedure must be available at the site, together with necessary equipment, deionized water for cleaning and rinsing, replacement parts for precipitation collector. Operators should be trained and required to carry out all necessary operations under the surveillance of an experienced analytical chemist or person responsible for the quality control. Operators should also be instructed on how to fill in the field sample registration form with the remarks column (see above) and to use this column extensively for reporting of conditions at the site.

If bulk samplers are used the funnel and collecting vessel must be cleaned every day.

The site should be inspected at least once a year, and the operation of the site examined by the National Quality Assurance Manager.

Field blanks and control samples

In order to check on possible contamination on the site, field blank tests should be carried out at least once every month. For this purpose, 50–100 ml deionized water samples are to be poured into the sample collector at the time of collection a day without precipitation, and subjected to the same procedure as an ordinary precipitation sample.

The quality of the precipitation chemistry data is strongly linked with the performance of the chemical laboratory. Control samples should be prepared, and analysed regularly as ordinary precipitation samples, in order to keep an independent check on the chemical analyses performed. Standard rainwater samples are available from NIST and BCR, and it is advised to use such samples as an external reference solution analysed only 2–4 times during the year, and in-laboratory prepared control samples for daily control work. The control samples should approximate the expected mean concentration level in the precipitation samples, and may be prepared from the following compounds:

(NH₄)₂SO₄
Nitric acid
CaSO₄ · 2H₂O
MgSO₄ · 7H₂O
NaCl
KCl

Sample transportation

The transportation time should be as short as possible and the samples contained together with freezer packs in insulated boxes.

Chemical laboratory

It is expected that the chemical laboratory is accredited under one of the laboratory accreditation systems, or is performing close to these standards, e.g. ISO 17025.

The laboratory must keep check on its performance, with respect to detection limits, precision and repeatability, by repeated analyses of control solutions of known composition, analyses of synthetic rain samples prepared by other laboratories (preferably traceable to NIST or other certified standards), and reanalysis of at least 5% of all samples.

Quality control samples are to be included in the sample series each day, and if results are differ more from the expected than the targets for accuracy and precision, full reanalysis of the sample series must be carried out. Results of the analyses of control samples are to be reported to the CCC.

Data reporting and validation

The chemical analysis data should be used to check the data for consistency, by calculating the ion balance and by comparing measured and calculated electrical conductivity (Section 6).

Results from the analysed control samples should also be checked, in order to ascertain that the chemical laboratory's performance has been acceptable.

Results should also be compared with the site operator's notes, to see if untypical results are due to special activities or conditions at the site. If it is decided to reject or to correct data, the reason for the correction should be stated, and the data should be flagged. Examples of such permissible corrections may include contamination from nearby fields due to manuring or tilling, high concentrations of potassium and ammonium indicating contamination by bird droppings, a.o. Such samples should be excluded from the calculation of monthly, or yearly weighted mean concentrations.

Comparison of reported sample volumes with daily precipitation amounts from a standard meteorological rain gauge at the site is strongly advised, since this gives an independent control of the sample collection.

This assessment of the data should be carried out on a monthly basis, as soon as chemical analysis data are available.

3.1.9 Special problems in precipitation sampling and analysis

The above procedures relate to normal operations of a precipitation site, assuming that there are no particular problems with the collection of the samples. This is normally the case, at least for the main constituents, at most of the EMEP sites.

By collecting samples on a daily basis, and storing the collected samples refrigerated and in the dark, it is generally hoped to avoid biodegradation of the samples. As the precipitation is now gradually becoming less acid, there may be more reason to make sure that such bio-degradation does not take place. Bacterial growth will primarily reduce the concentration of ammonium ions and organic ions.

The acidity of a sample is usually determined by the concentrations of non-marine ("excess") sulphate and nitrate, less the concentration of base cations such as ammonium, calcium, potassium and magnesium. However, if the pH is higher than 5, dissociation of dissolved carbonic acid and organic acids such as formic and acetic acid may also contribute to the observed concentration of hydrogen ions, and the equilibrium concentration of ammonium ion is a function both of the pH and the ambient concentration of gaseous ammonia. For a discussion of the chemical equilibria involving ammonia and carbon dioxide, reference is made to Charlson and Rodhe (1982). Formic and acetic acid are thought to be formed mainly by oxidation of hydrocarbons via formaldehyde and acetaldehyde, and concentrations in precipitation samples are typically 2–20 micro-equivalents/litre (Keene and Galloway, 1988). Other organic acids may also be present, either as a result of photochemical oxidation processes, or generally from decay of organic materials.

While the contamination of the sample by soil dust of local origin should be avoided, there is also evidence of large-scale atmospheric transport of fly ash, soil dust and desert dust. The input of base cations from such sources is large enough to be of importance in the assessment of critical loads in relation to soil acidification.

Installations of emission control devices in the latest decades have reduced the emissions of fly ash and other alkaline dust. Only total emissions in weight units are usually available, data on the chemical composition and size distributions are lacking.

Wind erosion may be a serious problem in agricultural areas, and the soil dust has sometimes been transported over quite considerable distances. Significant amounts of soil dust and alkaline material also becomes airborne in connection with agricultural tilling and harvesting operation. Burning of straw and stubble also releases alkaline material in addition to soot.

Desert dust from Sahara is frequently observed in the Mediterranean countries, occasionally also in Northern Europe. In addition to quartz and feldspar minerals, Sahara dust also contains calcite, which is readily soluble in precipitation samples.

Feldspar and clay minerals may be partly soluble in precipitation samples and contribute to the concentrations of base cations. Aluminium ions may also be present in the precipitation samples.

Determination of the main inorganic ions and pH also allow the calculation of the ionic balance of the samples, provided that the pH is less than 5. For samples with higher pH, determination of the concentrations of anions of weak acids, e.g. formate, acetate, and bicarbonate, may be necessary in order to determine the ion balance and to explain measured conductivities.

3.1.10 References

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WMO (1971) Guide to meteorological instrument and observing practices. Geneva, World Meteorological Organization (WMO No. 8 TP 3).

3.2 Sampling of sulphur dioxide, sulphate, nitric acid, ammonia, nitrate and ammonium using the filter pack method

3.2.1 Introduction on the various sampling methods

The most commonly used method for sulphur dioxide measurements in EMEP today is the alkaline impregnated filter method. This is the recommended method, preferably in combination with ion chromatography, because it combines a small extraction volume and low measurement uncertainty with a large air volume, and therefore gives a good measurement accuracy even at low sulphur dioxide concentrations. At sites with annual average above $10 \mu\text{g S/m}^3$ the absorbing solution method can still be recommended and would give satisfactory results. Only few of the EMEP sites experience such concentrations at present. The UV-fluorescence monitor is the recommended procedure in EU; and many sites in EMEP also prefer using this due to its convenient sampling procedure and high time resolution. However, one disadvantage is the need of regular maintenance and skilled workers. The monitor needs frequent calibration, which is often difficult because most of the background stations are in remote areas. The sensitivity of the monitor is generally not as good as the manual method, giving uncertain results at concentrations below $1 \mu\text{g S/m}^3$. UV-fluorescence is therefore not recommended on background stations within the EMEP network.

Nitric acid in the gaseous state readily reacts with other atmospheric constituents to form nitrates in the form of atmospheric particles. If ammonium nitrate is formed, the reaction is reversible, and its presence requires a dissociation product of gaseous nitric acid and ammonia, which in turn depends on temperature and relative humidity (Stelson and Seinfeld, 1982). Sampling artifacts due to the volatile nature of ammonium nitrate, and possibly due to interaction with other atmospheric constituents make separation of these gases and particles by a simple aerosol filter unreliable. This can be achieved using denuders where one takes advantage of the different diffusion velocities of gas and aerosol particles in a sampling device, which is simply a tube coated on the inside by an absorbing reagent, usually sodium chloride or sodium carbonate. The same sampling principle may also be used for sampling of ammonia, using citric, oxalic, or phosphoric acid as the absorbent. Because the diffusion speed of ammonia in air is about twice that of nitric acid, a shorter diffusion tube will achieve >95% absorption. If the flow is laminar, minimal deposition of particles occur, and if the tube has proper dimensions in relation to the flow rate and the diffusion speed of gaseous nitric acid in air, nitric acid is efficiently deposited to the walls of the tube.

Two different denuder systems are available for sampling and determination of gaseous nitric acid and ammonia. The first procedure uses simple cylindrical tubes, as introduced by Ferm (1979). The second procedure uses so-called annular denuders, where the air is passed through the annular space between two concentric cylinders as described by Allegrini et al. (1987). This arrangement allows the airflow rate to be increased, and makes the subsequent chemical analyses somewhat less demanding. Two large field intercomparisons have been made for gaseous nitric acid, one in Italy (Allegrini et al., 1989), and one in the USA (Hering et al., 1988). Reference is made to these publications for further information on the performances of different sampling systems. Methods for

sampling and determination of ammonia have been compared in the field by Allegrini et al. (1992). The principles of using denuders are described in [section 3.4](#).

Denuders can be rather impractical and are relatively expensive, and as filter packs are mostly more reliable and less demanding in terms of sampling and sample preparation, this procedure is often chosen. However, since the filter pack technique is poorer when it comes to separate gas and particle phase, only the sum of nitric acid and nitrate and for the sum of ammonium and ammonia are obtained. Information on the partition between the gaseous and the particle formed may sometimes be inferred also from filter pack data. This may be the situation in areas where the concentration of gaseous ammonia is usually high, or where the concentrations of both nitric acid and ammonia gas concentrations are so low that the partial pressure product necessary for ammonium nitrate to be present is not reached. The separation of $\text{SO}_2/\text{SO}_4^{2-}$ is good in both techniques.

3.2.2 Principle of using filter pack

The first filter in the air stream is an aerosol filter for collecting the airborne particles containing sulphate, ammonium and nitrate. This is followed by an alkaline impregnated filter which will collect HNO_3 , SO_2 , HNO_2 , HCl , and other volatile acidic substances. Nitric acid and sulphur dioxide will react with potassium hydroxide on this impregnated filter to give potassium nitrate and potassium sulphite. The absorption of SO_2 is quantitative at a relative humidity above 30% at temperature down to -10°C (Lewin et al., 1977). Oxidizing species in air e.g. ozone are believed to convert most of the sulphite to sulphate during the sampling. It is also possible to include a third acid-impregnated filter for alkaline air component such as NH_3 . Ammonia is effectively retained on a filter impregnated with citric or oxalic acid. When a 3-filter pack is applied the acid impregnated filter should be the last in the air stream

Since the filter pack method cannot separate gaseous nitrogen compounds from aerosols only the sum can be given. In other words, the concentration of nitrates in air equals the sum of the nitrate found on the aerosol filter and nitrate found on the alkaline impregnated filter. The same for ammonium where the sum of ammonium concentration equals the sum of ammonium collected on the aerosol front filter and ammonia collected on the acid impregnated filter.

The filter material should not absorb SO_2 and should have acceptable collection efficiency for submicron particles. Cellulose filters are acceptable for this purpose, e.g. Whatman 40 filters, but membrane filters, e.g. teflon, are preferred.

3.2.3 Interference

During sampling, salts can react with aerosol particles containing sulphuric acid. The resulting volatile acid, e.g. nitric acid and hydrochloric acid will react with the potassium hydroxide on the impregnated filter to give potassium nitrate and potassium chloride. This will, however, not affect the measured concentration of sulphate in airborne particles or sulphur dioxide.

A bias may be introduced if the aerosol filter becomes wet during sampling since it is possible to have an absorption of sulphur dioxide on cellulose based filters.

This gives an overestimation of the sulphate concentrations in aerosols and a corresponding underestimation of the sulphur dioxide. Another source of error could be that the absorption of sulphur dioxide on the impregnated filter is not 100 per cent effective. Experiments with a second KOH-impregnated filter behind the first have, however, not given measurable amount of sulphur dioxide.

It may be possible to loose components before the analysis due to incomplete extraction from the filter.

3.2.4 Sampling equipment

Air intake and filter pack

A diagram showing the sampling principle is given in Figure 3.2.1. The air intake should have a cylindrical, vertical section 15 cm wide and at least 25 cm high. This air intake reduce the sampling efficiency for particles larger than 10 μm a.e.d., such as soil dust particles, large sea spray droplets, large pollen, and fog droplets. The filter pack is placed directly in the air intake, and it should have separate supports for the aerosol and the impregnated filters in order to avoid contamination from one filter to the next. An exploded view of a filter pack and its components is shown in Figure 3.2.2.

It is important to avoid leaks in the filter pack. The filter pack in Figure 3.2.2 should be tightened to the torque specified by the producer. Care should be taken to avoid materials in the filter pack which may be a source of contamination or absorb sulphur dioxide or other air components which are to be determined. Teflon, polyethylene, polypropylene, PVC, and polycarbonate are recommended materials. Ordinary rubber and nylon contains sulphur and should be avoided. Nylon will absorb nitric acid.

Since the absorption of sulphur dioxide is only quantitative at relative humidities above 30, sampling with a filter pack should take place outdoor, only sheltered from the ambient air by the air inlet. Additions of glycerol may improve the absorption efficiency of the impregnated filter at low humidities. Typical air volume, sampling rate, and flow velocity through the filters are respectively 20 m^3 , 15 l/min., and 15 cm/s.

Pump and gas meter

The filter pack should be connected to the sampling line with an airtight seal, using either a nut and gasket, or push-fitted tubing. The sampling line connects the air intake and filter pack to a pump and a gas meter in series. The pump should be a membrane pump of sufficient capacity to allow 15 l/min. against a pressure difference of 10-20 kPA (0.1 atm.), which is the typical pressure drop across two filters. It is essential that the pump is leakproof against outside air in order to allow reliable metering of the air volume at the outlet of the pump. A dry bellows-type gas meter may be used for recording of the air sample volume. This is a relative inexpensive instrument, which is readily available commercially. The accuracy of commercial gas meters is typically within $\pm 5\%$; calibration not less than once or twice a year is therefore mandatory. Better accuracy is obtainable with a wet gas meter. Both devices will record the air volume at the temperature and pressure conditions in the pump. If the pump and gas meter is kept at room temperature, no corrections are usually required, and the air volume is then

assumed to be the sample air volume at 20 °C. If deviations of more than ± 5 °C are expected, the temperature in the gas meter surroundings has to be recorded and the air volume corrected accordingly.

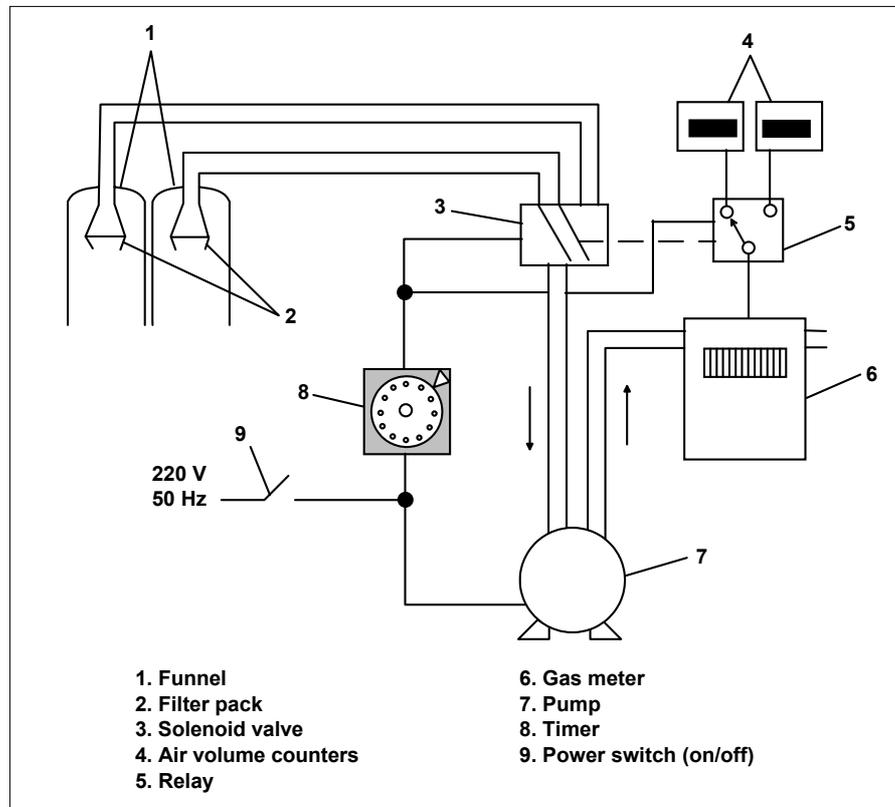


Figure 3.2.1: Sampling principle.

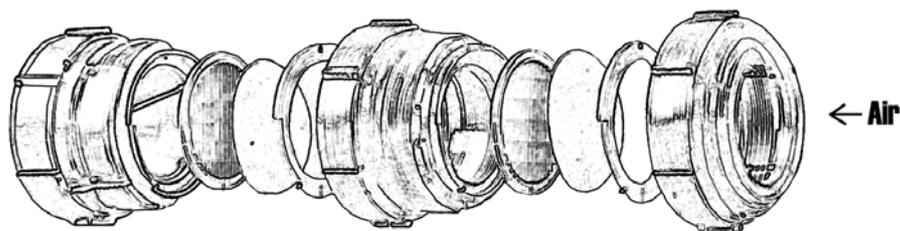


Figure 3.2.2: Filter pack with one aerosol filter and one impregnated filter for gases.

Sequential sampling

In order to facilitate operation of the sampler, it is possible to connect two or more air inlet and filter pack units to the same pump and gas metering device, letting timers control valves. This enables a collection of samples (exposed filter packs) and an inserting of new filter packs at a convenient time and without interruption of the sampling process. A schematic indication of how this may be carried out is indicated in Figure 3.2.1.

Mass flow controllers

It is possible to use mass flow controllers to control the sampling rate or to provide dynamic dilution of span gases for calibration purposes. In principle, these determine the heat capacity of the gas or air flowing through a capillary, and the temperature difference between two points is used to control the position of a needle valve. The disadvantage of this system is, besides the costs, the pressure differences 0.7–1.1 atm (10–16 psi) required over the needle valve to make the control function reliable. This makes it impractical to use this type of device to control the sampling rate in front of the pump unless the needle valve is replaced by another control valve requiring less pressure drop. The device can, however, preferably be used at the outlet of the pump to keep the sampling rate constant over the sampling period. Low-pressure mass flow controllers are available. The flowmeter must be properly calibrated, and a suitable recording instrument added, if a mass flowmeter is to be used as the only measure of the sample volume.

Commercial supply

A list containing only some of the suppliers of the various types of equipment is given below:

Prefilter for collection of aerosols:

Teflon filter by Gelman, Zefluor 2 µm.

Cellulose filters for impregnation with potassium hydroxide to be used for sampling of sulphur dioxide:

47 mm Whatman 40 (W40) cellulose filter

Whatman International Ltd., Maidstone, England

Filter packs for two or three filters, with clamp and wrench:

NILU Products, P.O. Box 100, NO-2027 Kjeller, Norway

Membrane pump:

GAST, Model DOA-P101-BN

MFG. Corp., Benton Harbor, Mich. USA

Gas meter:

FLONIDAN

Gallus 2000 G1.6

Islandsvej 29

DK-8700 Horsens, Denmark

Mass flow controller:

TYLAN GmbH

Kirchhoffstrasse 8

Eching, Germany

3.2.5 Site requirements

The sampler should be located at least 100 m from small-scale local sources, e.g. generators or houses heated with petroleum, coal, or wood.

Samplers for gas and aerosols should normally be located in a shelter with temperature regulation. The gas meter should be kept at 20 °C ± 5 C.

Nitric acid is very reactive and is readily absorbed by vegetation and by other surfaces. It is therefore particularly important for this species that the site is well exposed and is not sheltered by tall vegetation close to the sampler. Ammonia is emitted mainly from decomposition of urine, and from the application of manure. To find representative sites for this component may therefore be very difficult, as a basic rule the measurements at the site should not be influenced by emissions, which take place within a radius of 2 km from the site. Within this radius there should be no stabling of domestic animals, no grazing by cattle or sheep on fertilized pastures, and no application of manure to agricultural fields.

Even more pertinent to ammonia than to other pollutants is the reporting of activities, which could affect the data, e.g. spreading of manure in adjacent agricultural areas. These data need to be flagged in the database.

3.2.6 *Sampling procedure*

Mounting and dismounting of filter packs

It is recommended that the filter pack is assembled and dismounted in the laboratory only. When assembling the filter pack, the parts should be tightened to the torque specified by the manufacturer to prevent leaks. Airtight protection covers need to be mounted in both ends of the filter pack. One random selected complete filter pack should be checked every second week for leaks. Each filter pack should be tagged with the site code in the laboratory before it is sent to the site.

Exposed filter packs should be opened in the laboratory and the filters put into plastic bags, which in advance, have been tagged with site code, start and stop of sampling, and filter type. The filters are now ready for a chemical treatment and the analysis. Normally there is a delay between this step and the time when actual chemical treatment and the analysis takes place. During this period the samples are to be kept in a refrigerator.

It is important to wear a pair of disposable plastic gloves when working with the filters and the filter packs.

Changing of filter packs at the site

At the site, and before the filter pack is mounted in the sampling line, the site operator has to write the start date on the filter pack, and likewise the end date of the sampling after exposure. Further details are to be written into the site journal and copied into site reporting forms, worked out for this purpose.

The sampling procedures may be slightly different from one air sampling system to another. When a two line sampling system is used with a timer, the exposure of a new filter pack starts at a preset time; an example of a recommended procedure at the site is as given below. The start and end of exposure should be between 0700 - 0900 local time:

- mark an unexposed filter pack with start date,
- read the pressure behind the exposed filter pack and record the reading in the journal,

- read the counter in the volume meter and record the volume in the journal,
- remove (unscrew) the air intake or funnel covering the exposed filter pack and remove (unscrew) the filter pack,
- dismount the covers from the new unexposed filter pack and mount them on the exposed filter pack,
- mount the new unexposed filter pack and the air intake,
- read the pressure behind the unexposed filter pack and record the reading in the journal,
- reset if necessary the counter or volume meter of the new filter pack,
- write the start of the exposure of the new filter pack in the journal,
- activate or programme the timer if necessary,
- put the exposed old filter pack in a plastic bag, seal it and put it in the refrigerator,
- copy the information from the journal into the site reporting form.

Transportation of samples from and to the laboratory

It is recommended to ship a one weeks supply of filter packs from the laboratory to the site, and vice versa, once every week. One extra filter pack, complete with filters, should be added as a field blank (i.e. one field blank every week). This filter pack should be handled in every way as the ones to be exposed, returned with the other filter packs from the batch, dismounted, and the filters given the same chemical treatment and analysis as the exposed filters.

Once every week the field operator fetch the seven exposed filters from the refrigerator as well as the one unexposed (field blank) filter pack, and put the filter packs in the transportation box together with the site reporting form covering the past week. Field reporting forms should always be put in a separate plastic bag in case of accidental leaks from precipitation samples, which may be contained in the same transportation box. Mail the transportation box to the laboratory.

Maintenance and calibration

The sampling equipment should be maintained in accordance with the manufacturer's specifications.

Accurate volume readings are important for the resulting measurement's accuracy, and the volume meters may need frequent calibrations. Calibrations should under no circumstances be less frequent than once or twice every year. The accuracy must be better than 5%.

Written instructions for maintenance and calibration need to be available at the site, and the operator should be familiar with the contents.

Use of filter blanks

It is recommended that 10 samples from each new batch of filters are analysed as laboratory filter blanks. The purpose of the filter blanks is to control the quality of the filters rather than to estimate the laboratory detection limit. Normally, the blank values should be sufficiently low that their values can be ignored. If high blank values are found a problem has occurred which has to be identified and

solved, e.g. by using filters or chemicals from another batch, and by inspection of the routines in the laboratory.

3.2.7 *Cleaning of filters*

Cellulose filters may contain small amounts of impurities and a cleaning of filters may therefore be necessary before use.

The cleaning process is demanding and it may therefore be omitted if the filter blanks from a new batch of filters are lower than the requirements given in Table 3.2.1, otherwise cleaning must be done. Following the cleaning, some filters are impregnated and the requirements for impregnation and extraction solutions are the same as those given in Table 3.2.1. See more details in 3.2.8 and 3.2.9.

Membrane filters should be tested at regular intervals in order to see if impurities occur. NILU make use of teflon filters; impurities have not been detected so far.

Table 3.2.1 Recommended requirements.

SO ₄ ²⁻	Better than	0.01 µg S/ml
Cl ⁻	“ “	0.01 µg Cl/ml
NO ₃ ⁻	“ “	0.01 µg N/ml
NH ₄ ⁺	“ “	0.01 µg N/ml

General procedure for cleaning

Figure 3.2.3 presents equipment, made of teflon, used for cleaning of filters. The procedure below is designed for cleaning of Whatman-40 cellulose filters (W40). The contents from 5-7 packages of W40 filters are put into a filter container with a perforated disk in each end, after which 20 litres of the cleaning solution is pumped through the filter container. After cleaning the filters should be rinsed with 20 litres deionized water.

After the rinsing, the clamps in both ends of the container should be tightened in order to force as much water as possible out from the filters. A filter pack loaded with aerosol filter, an alkaline impregnated filter, and an acid impregnated filter should next be connected to the intake side of the filter container, and the outlet side be connected to a vacuum pump in order to remove most of the remaining water in the cleaned filters.

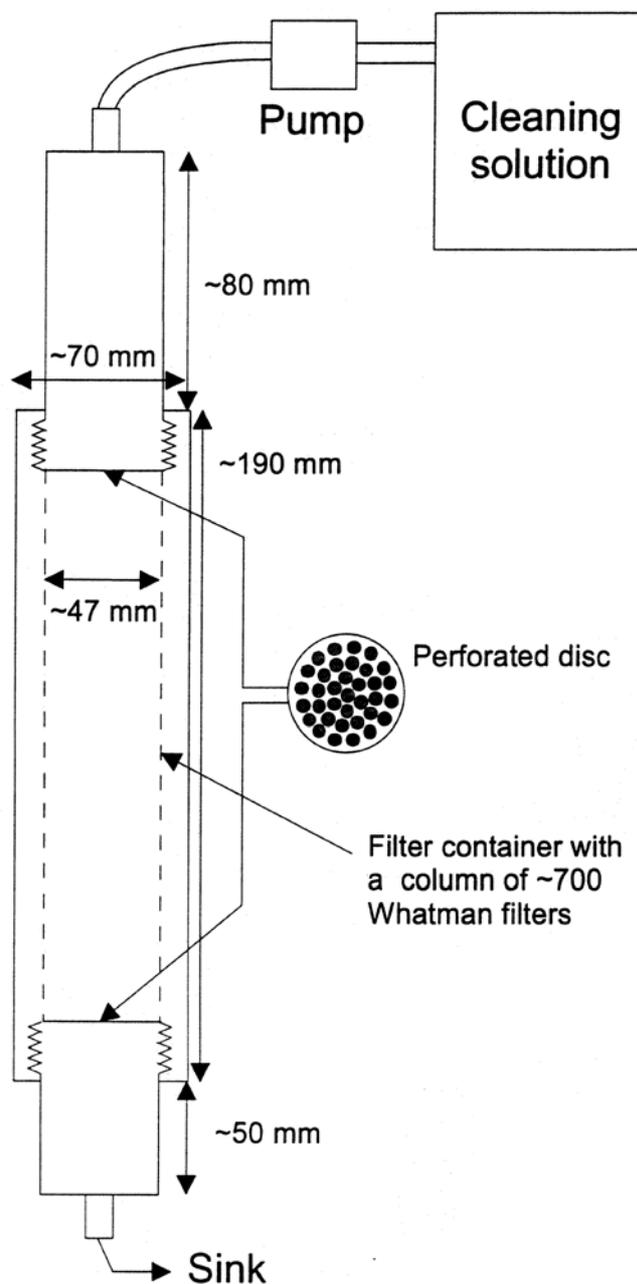


Figure 3.2.3: Equipment for cleaning of filters.

In the final step the container which still should be connected to the vacuum pump and filter pack, should be heated to, and kept overnight, at 100°C with the vacuum pump operating, in order to remove the last trace of water. After cooling the cleaned filters should be put in a plastic bag equipped with a zipper and the bag put in a desiccator. The filters inside the bag must not be bent, but must remain flat as in the original package. Before the filters are put into the bag, the bag should be labelled with the date of cleaning and cleaning reagent.

Tweezers and disposable gloves must always be used when handling filters.

After the cleaning 5 filters should be selected at random and the concentrations of cations and anions contained in the filters be determined as described in this manual. The concentrations found should be filled into the laboratory journal, and the label on the plastic bag signed and dated again if the concentrations are less than the detection limit of the analytical instrument. If one of the concentrations is higher than the detection limit, the cleaning must be repeated.

Cleaning of filters to be impregnated with KOH

The cleaning procedure is as described above. In order to avoid excessive blank values, the Whatman 40 filters used for acid gases may be washed with 20 litres 0.1 M K_2CO_3 (14 g K_2CO_3 pr. litre solution). After cleaning the filters should be rinsed with 20 litres water. If the SO_2 , HNO_3 or NH_3 concentrations are high in the laboratory, the filters should be dried in a dry box, which is supplied with clean air.

Cleaning of filters to be impregnated with citric or oxalic acid

The cleaning procedure is as described above. The filters should be cleaned with 20 litres 0.1 M citric acid (25 g citric acid dihydrate pr. litre solution) if citric acid will be used for impregnation, or with 20 litres 0.1 M oxalic acid (13 g oxalic acid dihydrate pr. litre solution). After cleaning the filters should be rinsed with 20 litres of water.

3.2.8 Impregnation of filters

General procedure for impregnation solutions

A solution to be used for impregnation should be prepared the same day the impregnation of a new series of filters will take place. Before impregnation, the purity of the solution must be checked by adding 300 μ l of the impregnation solution to 10 ml of the extraction solution, and the sample analysed. The following requirements to the impregnation solution should be met, or the concentrations should be lower than the instrument detection limit, table 3.2.1.

The recommended chemicals are given in Table 3.2.2.

Table 3.2.2: Specifications for chemicals used for impregnation.

Reagent	Quality	Formula
Oxalic acid	Merck p.a. 495 or corresponding	Oxalic acid dihydrate
Citric acid	Merck p.a. 244 or corresponding	Citric acid monohydrate
Potassium hydroxide	Merck p.a. 5033	KOH

The concentrations found should be filled into the laboratory journal.

Particularly for ammonia the chance for contamination is severe, since the ammonia concentrations in laboratories may reach 1-5 μ g N/m^3 . The control of the impregnation solution is therefore important. The chemicals used for impregnation should be stored separated from the other laboratory chemicals. In

particular, the container with citric or oxalic acid should be stored together with the impregnated filters in a desiccator.

Procedure for impregnation of filters

The following procedure may be used. The filters are placed on plastic stoppers after which the impregnation solution is dripped on the filter (Table 3.2.3). The filters may be dried in air, usually is half an hour sufficient. When the filters are dried they must be placed in plastic bags and the zippers closed. The bags should be labelled with type of filters and date.

Disposable gloves and tweezers must be used when handling the filters.

Table 3.2.3: Impregnation of filters and recommended requirements to purity after impregnation.

Impregnation solution	Preparation	Volume	Purity requirement:
Alkaline filter: 1.0 M KOH/10% glycerol in methanol	5.6 g KOH, 10 ml glycerol, methanol to 100 ml volume	300 µl	Cl ⁻ < 0.01 mg Cl/l NO ₃ ⁻ <0.01 mg N/l SO ₄ ²⁻ <0.01 mg S/l
Acid filter: 0.33 M oxalic acid	3.0 g oxalic acid, methanol to 100 ml volume	300 µl	NH ₄ ⁺ <0.01 mg N/l
or 0.1 M citric acid	2.1 g citric acid, methanol to 100 ml volume	300 µl	NH ₄ ⁺ <0.01 mg N/l

Control of the impregnated filters

5 filters should be selected at random after drying and analysed as described in this manual. The requirements to the concentrations are identical to the ones in Table 3.2.3. If the requirements are not met, all filters from the impregnation batch should be thrown and a new batch made. If the requirements are met the bags should be signed and dated.

The concentrations found should be filled into the laboratory journal.

Storage of impregnated filters

The bags filled with impregnated filters should be stored in desiccators; alkaline impregnated filters in one desiccator and acid impregnated ones in a different one. The desiccator for KOH impregnated filter should have KOH at the bottom, and the one for acid impregnated filter should have citric acid at the bottom.

Impregnated filters should not be stored more than 3 months before use.

Summary of quality assurance steps

- Disposable gloves and tweezers should be used when handling the filters.
- Cellulose filters should be cleaned if necessary before use.

- After each cleaning and drying process 5 filters should be analysed for major ions and all concentrations meet strict requirements.
- An impregnation solution should be used the day it is prepared.
- An impregnation solution should be analysed for major ions before used, and all concentrations meet strict requirements.
- Impregnated filters should be kept inside dated and signed plastic bags with zippers, and the bags kept in a desiccator together with the impregnation reagents.
- The desiccator should be filled with the (solid) impregnation reagent at the bottom. Oxalic acid may be replaced by citric acid.
- After impregnation and drying, 5 filters should be analysed for major ions and all concentrations meet strict requirements.
- Impregnated filters should not be stored more than 3 months.
- All quality assurance steps and results should be recorded in the laboratory journal.

3.2.9 *Extraction from filters*

This section contains procedures for extraction of major ions collected on impregnated filters as well as on aerosol prefilters. The procedures given are the recommended ones provided that the procedures for filter impregnation in Section 3.2.8 have been followed.

Preparation of extraction solutions

When the impregnation has followed the procedures in Section 3.2.8, the composition and amount of extraction solutions to be used are given in Table 3.2.4. The exposed impregnated filters are put into a test tube or other suitable vessel with additions of extraction solution. Hydrogen peroxide solution is used for the alkaline filter in order to oxidize any remaining sulphite to sulphate. The quality requirements to the reagents are given in Table 3.2.1.

Table 3.2.4: Preparation and amount of extraction solutions for impregnated filters.

Filter/solution	Preparation of extraction solution	Amount of extraction solution
Alkaline filter 0.3% H ₂ O ₂	10 ml 30% H ₂ O ₂ to 1000 ml deionized water	10.0 ml
Acid filter 0.01 M HNO ₃	10 ml 1.0 M HNO ₃ to 1000 ml deionized water	10.0 ml

After preparation, and every day before use, 10.0 ml of the extraction solution should be analysed for major ions and the concentrations meet the requirements in Table 3.2.1 or be less than the instrument detection limit.

The volume of the extraction solution used must be measured accurately and a 10 ml precision dispenser should therefore be used. It is known that the accuracy will change with time, and the accuracy needs to be checked at regular intervals by weighing 10.0 ml of the extraction solution.

The results of the control analysis of the extraction solution and the control of the dispenser volume should all be recorded in the laboratory journal.

Table 3.2.5: Specifications for chemicals used during extraction.

Reagent	Quality	Formula
Hydrogen peroxide	Merck p.a. perhydrol or corresponding	H ₂ O ₂
Nitric acid	Merck p.a. or corresponding	HNO ₃
Water	MilliQ-water or corresponding	

Extraction procedure for impregnated filter

The impregnated cellulose filters requires careful treatment not to loosen fibres, which will cause problems during the analysis. The filters should be extracted the day they are removed from the filter pack. They may be put directly into tubes made of polystyrene fit for an autosampler. The stopper should be put on the tube at once and even before adding the extraction solution unless this is done at the same time. Disposable gloves and tweezers should be used when handling the filters. The tubes should be kept in the refrigerator until analysis.

The filters are extracted with 10.0 ml of the extraction solution. The rack with the stopped tubes should be turned upside down by hand at least ten times to ensure a good extraction and a homogeneous solution. It is necessary to allow any fibres in the solution to settle a few hours before analysis. If the analysis will be performed the next day or later, the tubes should be stored in a refrigerator.

The solution containing the acid filters may develop gases during and after the extraction. It is advisable to keep the tubes with the solutions in the laboratory a few hours, then to open the tubes to let any gas out before the tubes are moved to the refrigerator.

Extraction from aerosol filter

The aerosol teflon filters should be given an ultrasonic treatment before analysis in order to obtain a complete extraction. The filters are put into tubes and 10.0 ml of deionized water added. The rack with the tubes should be kept in the ultrasonic bath for 30 minutes.

Pre-treatment of acid extract before analysis

The extracts from the acid-impregnated filters may be too acidic to allow a direct analysis with the indophenol method. It is necessary to raise pH ~12 with a buffer, or with potassium hydroxide, for analysis. When preparing control samples (spiked samples) for this analysis, the same extract, and additions of buffers or potassium hydroxide should be applied.

Pre-treatment of KOH extracts before analysis

For some analytical methods e.g. the spectrophotometric Griess method (section 4.3 and 4.11.3), the extract from an alkaline impregnated filter has a too high pH to permit a direct analysis. In this case, 10 mg moist cation resin is added to the solution in the tube and the contents mixed well. After half an hour check the pH in the solution by putting one drop on a pH-paper. The solution should be neutral or slightly acid.

The remaining ion exchange material is completely removed during analysis when the sample is passed through the column of ion exchange resin.

Summary of quality assurance steps

- Disposable gloves and tweezers should be used when handling the filters.
- After preparation and every day before use, 10.0 ml of the extraction solution should be analysed for major ions and all concentrations meet strict requirements.
- The extraction solution volume given by the 10.0 ml dispenser should be controlled at regular intervals by weighting the liquid.
- The filters should be extracted the same day as removed from the filter pack.
- The solutions should be kept in a refrigerator after extraction unless the analysis can be performed the same day.

3.2.10 Calculation of results

The concentrations of the sum of nitric acid and nitrate in aerosols in $\mu\text{g N/m}^3$ is obtained by adding the nitrate from the aerosol filter extract and the alkaline filter extract. If

a_1 expresses the concentration of nitrate from the aerosol filter in mg N/litre,

v_1 is the aerosol filter extraction volume in ml

a_2 expresses the concentration of nitrate from the impregnated filter in mg N/litre,

v_2 is the impregnated filter extraction volume in ml,

v_L is the air volume through the sampler, in cubic meter at approximately 20°C and corrected for height from elevated sites,

then the total nitrate concentration in $\mu\text{g N/m}^3$ is given by the following expression:

$$C = \frac{a_1 \cdot v_1 + a_2 \cdot v_2}{v_L}$$

The concentrations of the sum of ammonia and ammonium in aerosols in $\mu\text{g N/m}^3$ is obtained by adding the ammonium from the aerosol filter extract and from the acid filter extract. It can be calculated similar as for total nitrate.

The concentrations of sulphur dioxide in the air sample expressed in $\mu\text{g S/m}^3$ is given by:

$$C = \frac{a \cdot v_1}{v_2}$$

- a is concentration of sulphur in mg/l read from the calibration curve,
- v_1 is the liquid volume containing the sulphate ions, e.g. 10 ml if a 10 ml extraction solution were used,
- v_2 is the air volume from the sampler, in cubic meter at approximately 20 °C, and corrected for height from elevated sites.

3.2.11 Quality assurance

Handling of filters and filter packs in the laboratory

- Always wear disposable plastic gloves and use a pair of tweezers when handling filters,
- keep the impregnated filters in air-tight plastic bags,
- air-tight covers must be mounted in both ends of the filter pack once the filter pack has been assembled,
- filter packs should be tightened to the specified torque to avoid leaks after assembly,
- one filter pack selected at random should be checked for leaks every second week,
- each filter pack should be tagged with site code in the laboratory,
- exposed filter packs should only be opened in the laboratory, and the filters kept in air-tight plastic bags in a refrigerator before further chemical treatment.

Handling of filters and filter packs in field

- Filters should only be handled in the laboratory,
- each filter pack should be tagged with start time (day-hour-minute) by the field operator before being mounted in the sampling line, and with stop time when dismantled after exposure,
- covers removed from the new filter pack should be mounted on the exposed one when the samples are changed,
- filter packs should be kept in a plastic bag in the refrigerator at the site.

Maintenance and calibration of field equipment

- Maintenance performed in accordance with written instructions for the field instruments in question,
- calibrations of measuring devices at least once every year.

Field blanks

- As a field blank, one complete filter pack should follow the other filter packs every week,
- the field blanks should be analysed as the normally exposed samples to control the performance of the measurement system, and to give data for the assessment of the measurement detection limit.

Chemical analysis

- Calibration should be carried out in the beginning, and end of a series of samples, not to exceed 50, and at the end of the day at the latest. The average of the calibrations before and after a sample series should be applied,
- 5% of the samples should be split and the results used to quantify the analytical precision,
- 5% of the samples should have known, and realistic, concentrations and should be run between the normal samples to control the performance of the analytical system,
- 5% of the samples should be blank samples used to quantify the analytical detection limit.

Transportation

- Transportation time should be kept as short as possible.
- All quality assurance steps and results should be recorded in the laboratory journal.

3.2.12 References

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3.3 Sampling of nitrogen dioxide

A manual method based on absorption of nitrogen dioxide on a sodium iodide impregnated glass-sinter has been developed by Ferm and Sjödin (1993). Due to the reasons mentioned below, only the sodium iodide method has been included in this manual.

Several methods, both manual and continuous have been used for the measurement of nitrogen dioxide in ambient air. In urban air, the chemiluminescence method have replaced the manual absorption solution methods, and is introduced as an ISO standard (ISO, 1985a). The chemiluminescence method for NO₂ is based on reduction to NO by a heated catalytic converter and calculation of the concentration as the difference between (NO+NO₂) and NO (the signal without converter). For clean air sites commercial monitors are usually not sensitive enough, and since other reducible nitrogen compounds (e.g. HNO₃ and PAN) may exist in the same concentration level as NO₂, the method is not specific. However monitors with selective photolytic converters may be used if the sensitivity is adequate.

Also the liquid phase NO₂-luminol chemiluminescence reaction has been used in a commercial monitor for nitrogen dioxide at low levels (Schiff et al., 1986). This monitor has been shown to give almost interference-free values for NO₂ (e.g. Gehrig and Baumann, 1993). However a small interference from ozone has been observed by Kelly et al. (1990) and Hesterberg and Neftel (1993) found non-linearities under 1 ppb in addition to other systematic errors due to pressure variations in the inlet system and temperature changes in the reaction chamber. Since this monitor work with a liquid phase reaction, it needs more regular service than the ordinary chemiluminescence instruments.

The manual absorbing solution method based on direct Griess reaction during sampling (Saltzman method) has also been appointed an ISO standard (ISO, 1985b). This method is sensitive and more selective than the chemiluminescence method, but the colour to be measured spectrophotometrically is developed during sampling, and the measurement have to be performed immediately after sampling due to instability. This makes the method unsuitable if the exposed absorbing solution has to be transported to a chemical laboratory far from the sampling site, particular if temperature and light exposure cannot be controlled. Field inter comparison studies has shown that the Saltzman method is not suitable at concentration levels below 1 µg N/ m³ (EMEP, 1999).

Other absorbing solutions have been used in which nitrogen dioxide is absorbed and transformed to nitrite (EMEP, 1977). These methods are usually not sensitive enough in background areas, and also have the problem of instability of the exposed absorption solution during transport when the temperature and sunlight cannot be controlled. There has also been considerable uncertainty about the absorption efficiency of the absorbing solutions, and to which extent this varies with concentration. The use of experimentally determined absorption efficiencies has shown to be inadequate (Fährnich et al., 1993).

3.3.1 Determination of nitrogen dioxide using the iodide absorption method

3.3.1.1 Introduction

This method (Ferm and Sjödin, 1993) is based on the same principle as the method developed by Pavlenko and Volberg (1979, 1991). This method is recommended at EMEP stations with low concentrations of NO₂ and where the analysis has to be performed in a laboratory far from the sampling site.

3.3.1.2 Principle

Ambient air with a flow rate of about 0.5 l/min is drawn through an air intake (inverted funnel) and a glass filter impregnated with sodium iodide (NaI) and sodium hydroxide (NaOH). Nitrogen dioxide is absorbed in the filter and the iodide reduces NO₂ to nitrite (NO₂⁻). The hydroxide is converted to carbonate during sampling due to uptake of carbon dioxide. The nitrite formed on the glass filter is extracted with deionized water. After extraction the nitrite concentration can be determined photometrically by the Griess method described in Section 4.11.

This method can be used for measurement of nitrogen dioxide on a 24 h basis in ambient air within the range 0.1-10 µg NO₂-N/m³, assuming an air sample of 0.7 m³ and an extraction volume of 4 ml. Exposed samples are stable for several weeks and can be transferred to a laboratory for chemical analysis.

3.3.1.3 Sampling efficiency and interference

The sampling efficiency at a flowrate of 0.5 l/min and a relative humidity of 15% is higher than 98%. With a relative humidity higher than 60%, the sampling efficiency is higher than 98% even at a flowrate of 4 l/min. (Ferm pers. comm.).

Interference studies showed negligible formation of nitrate on the NaI/NaCO₃-substrate. Nitric oxide formation was also never observed behind the filter and no oxidation of nitrite by ozone is found. The absorption of PAN (peroxyacetyl nitrate) and the subsequent formation of nitrite on the alkaline NaI filter have been demonstrated with about 20% absorption (Ferm and Sjödin, 1993). This cause a positive interference which can be severe if the PAN-concentration is higher than the NO₂-concentration. This may happen in very remote areas, but not at most of the EMEP-sites.

3.3.1.4 Sampling equipment

Figure 3.3.1 shows the components of a suggested sampling system. The Figure shows an automated system, a simpler set-up with manual exchange of samples may also be used. The main components are:

Air inlet

An inverted funnel made of PTFE teflon, polypropylene, borosilicate or polyethylene should be used in order to prevent entrance of precipitation at the sampling point.

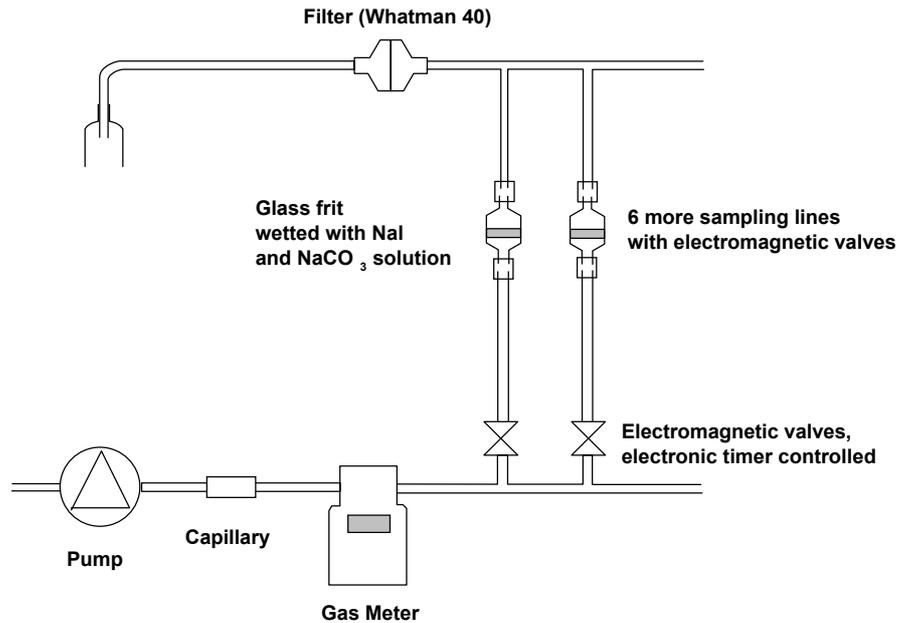


Figure 3.3.1: Sampling system for nitrogen dioxide.

Tubing

The sampling tube connection between the air inlet and the absorption system should be as short as possible, and made of PTFE teflon, polypropylene, borosilicate glass or polyethylene.

Filterholder with prefilter

A filterholder with a filter should be used in front of the absorption system in order to remove particulate matter. The filter must be inert to NO₂. A teflon membrane filter with a pore size 1–2 μm or a Whatman 40 cellulose filter or equivalent may be used. The filterholder and the connections to the sampling line must be airtight. The prefilter can be used for one week.

Absorption system

A 4 mm thick sintered glass filter 25 mm i.d. with a porosity of 40–60 μm enclosed in a glass bulb as shown in Figure 3.3.2 is used as a substrate for the impregnation. The glass bulbs should be connected to the sampling line using short pieces of silicon tubing. During transport the silicon tubing must be closed by pieces of glass or plastic rods.

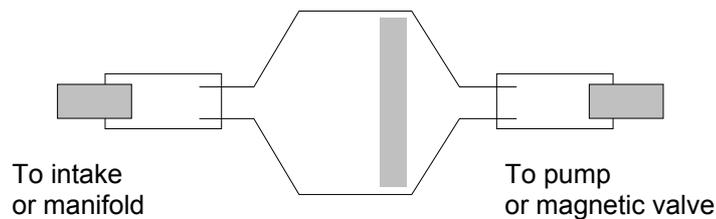


Figure 3.3.2: Sintered glass filter in a glass bulb.

Flow control device

In order to maintain a constant flow through the absorption system, a restrictor (glass capillary or hypodermic needle) or an electronic flow controller should be used.

Pump and gas meter

A membrane pump is recommended. If the pump is placed in front of the gas meter it must be leakproof. A calibrated dry or wet gas meter is recommended for recording the sampled air volume. Accurate air volume readings are most important for the accuracy of the measurement. Calibration of the gasmeter should be performed at least once a year. If the gas meter is placed in front of the pump, it must be assured that the pressure drop behind the absorption system is negligible.

3.3.1.5 Commercial supply***Pump:***

GAST, Model DOA-P101-BN
MEG. Corp., Benton Harbor, Mich, USA.

Gas meter:

FLONIDAN
Gallus 2000 G1.6
Islandsvej 29
DK-8700 Horsens, Denmark

Sinter glass filter in bulb:

Porosity 40-60 μm
Werner Glas & Instrument AB
Västra Rydsvägen 118
S-196 31 Kungsängen, Sweden
Tel.: +46 8 851 700 70, fax: +46 8 581 700 71

3.3.1.6 Site requirements

The site requirements for nitrogen dioxide are as for sulphur dioxide with respect to regional location and point sources. Particular attention should be paid to the possibility of contamination from motor vehicles, tractors, and other machinery with combustion engines. As nitrogen dioxide is taken up by vegetation, the air intake should not be sheltered by vegetation, but be freely exposed. The air intake should be 2–5 m above the ground. The sampling site should be at least 100 m away from any road open to public traffic, but the minimum distance to roads depends also on the traffic volume. This has been discussed in Section 2. The pump and sampling equipment should be placed in a room where the temperature is controlled at $20\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$.

3.3.1.7 Preparation of the absorption system***Impregnation solution***

The impregnation solution consist of 9 g NaI and 1 g NaOH in 90 g methanol or ethanol (7.9 g NaI and 0.88 g NaOH in 100 ml methanol or ethanol). The solution should be made fresh for every new batch of filters to be prepared, due to possible uptake of nitrogen dioxide from laboratory air.

Cleaning of exposed samplers

Used samplers must be carefully cleaned before use. They may be left overnight soaked in deionized water to release old marking labels etc. After that the samplers are then cleaned by flushing deionized water into the back end of the tube (in the opposite direction of the sampling flow). At 0.5 - 1 litre of deionized water should be flushed through each tube to ensure a proper cleaning. After cleaning the samplers should be dried in a laboratory oven at 100 - 105°C.

Preparation of the sinters

500µl impregnation solution is added to carefully cleaned glass sinters. The sinters should be dried with a flow of NO₂-free air. For cleaning the drying air, a NaI impregnated filter should be used. The glass bulbs should be closed as soon as possible after the drying. Well-protected impregnated sinters can be stored for several weeks before, as well as after sampling, preferably in a cool place.

3.3.1.8 Sampling procedure

Assemble the sampling equipment at the site as shown in Figure 3.3.1, and make sure that the glass bulbs are coded with site name and date. Control that the equipment is leak free. Check the initial flowrate with the gasmeter. It should be about 0.5 l/min. Record the gasmeter reading at the start and again at the stop. For a 24-hour sample the total air volume should be about 0.72 m³. If a sequential sampler for one week is used, it is possible to record the total volume for seven samples and then divide by seven, provided the flow rate is kept constant. When using a sequential sampler is it important to check that the right glass bulb is actually exposed.

After sampling the glass bulbs must be sealed and sent to the laboratory for chemical analysis.

3.3.1.9 Preparation of samples and chemical analysis

Preparation of samples

Open the front end of the glass bulb and add carefully 4.0 ml of a 0.001 M (133 µl = 149 mg triethanolamine to 1 litre water) solution of triethanolamine in deionized water. (The triethanolamine is added to reduce the iodine formed in the reaction with nitrogen dioxide to iodide). The open end should be closed again and the bulb shaken for about 15 min. The lower end should then be opened and placed in a vial or test tube. When the upper end is opened the leaching solution flows through the glass sinter and into the test tube. Some of the solution may be removed by blowing air into the open end of the bulb. About 0.5 ml of the leachate will however remain in the glass filter using this procedure, and need to be thoroughly washed out when preparing the filter for new sampling. The NO₂⁻ concentration can be determined as described in Section 4.11 or by an automatic version of the method either in the flow-injection (FIA) or continuous flow mode.

Blanks

All steps in the described procedure, which could contaminate the samples, should be controlled regularly and properly documented.

Before using the impregnation solution, it should be controlled for the content of NO₂⁻. In order to have the same concentration of the iodide reagent in this test

sample as in the normal samples, 0.5 ml of impregnation solution is mixed with 4 ml deionized water before analysis. The analysis is performed as described in Section 4.1.1. The impregnation solution blank value should be less than 0.005 µg N/ml.

When a new batch of impregnated filters have been produced, 5% of the filters should be leached as the exposed samples. The leaching solution should be analysed in the usual way for NO₂⁻. The amount of NO₂⁻ found should be less than 0.02 µg N/filter.

In every batch of impregnated filters sent to the sampling site, filters which shall remain unexposed (field blanks) must be included. For daily sampling, one field blank per station per week is needed.

3.3.1.10 Calculation of the air concentration

The concentration C of nitrogen dioxide in the air sample expressed as µg N/m³ is given by:

$$C = \frac{a \cdot v_1}{v_2}$$

where *a* is the concentration of NO₂⁻ in µg N/ml in the leachate,
*v*₁ is the volume of the leaching solution, normally 4 ml,
*v*₂ is the volume of the sampled air in cubic meter.

3.3.1.11 References

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3.4 Sampling of sulphur dioxide, sulphate, nitric acid, ammonia, nitrate and ammonium using annular denuders

3.4.1.1 Introduction

The procedure for the determination of nitric acid and ammonia is based on the work of Allegrini et al., (1987, 1989, 1992) with some simplifications. It is suitable for the determination of nitric acid and ammonia in the concentration ranges 0–50 $\mu\text{g}/\text{m}^3$ $\text{HNO}_3\text{-N}$ and 0–5 $\mu\text{g}/\text{m}^3$ $\text{NH}_3\text{-N}$, respectively. If higher ammonia concentration levels are expected, the sampling procedure must be modified.

Since the denuders give a possibility to determine the individual concentrations of $\text{HNO}_3(\text{g})$ and $\text{NO}_3^-(\text{particle})$; and $\text{NH}_3(\text{g})$ and $\text{NH}_4^+(\text{particle})$ it is a recommended method to use in the EMEP network. A detailed discussion of using denuders contra filter pack is found in chapter [3.2.1](#).

3.4.1.2 Principle

The air is drawn through a series of annular denuders, and filters. The two first denuders are internally coated with sodium carbonate (Na_2CO_3) and glycerol for the collection of nitric acid and sulphur dioxide, the third is coated with citric acid, oxalic acid or phosphorous acid for the collection of ammonia. Evaporation of the coating layer can be a problem. A new study done on the efficiency of different coating layers to determine ammonia has shown that phosphorous acid is the most suitable denuder coating reagent (Perrino and Gherardi, 1999).

The coated denuders are then followed by a three-filter pack system. The first filter is a membrane filter with high collection efficiency for submicron particles, followed by a filter impregnated with potassium hydroxide for collection of nitric acid which may have evaporated from the particle filter, and a filter impregnated with oxalic acid for the collection of ammonia which may also have evaporated.

Nitrous acid (HNO_2) is also absorbed in the alkaline denuders, but will normally not cause a significant interference as it is usually detected as nitrite in the sample extracts. Glycerol prevents oxidation of nitrite to nitrate by ozone. Nitrogen dioxide and PAN is partially absorbed as nitrite, this interference in the eventual determination of nitrous acid may be corrected for from the distribution of nitrite between the first and the second denuder.

3.4.1.3 Sampling equipment

A schematic description of the sampling equipment is given in Figure 3.4.1. It consists of a small insulated box, with a fan for internal air circulation and provisions for heating to a temperature ~ 2 °C above the ambient temperature, and with a rack for mounting the denuder sampling trains and filter packs, electromagnetic valves connecting the sampling trains to a manifold, a leak-proof membrane pump which gives a sampling rate of 15 l/min, and a gas meter for recording of the sample volume. The electromagnetic valves activating each of the sampling trains are operated by means of an electronic timer. Denuder and filter pack sampling trains can also be activated and changed manually.

The sampling train consists of an air intake, 2 annular denuders of length 242 mm, and one denuder of length 120 mm. The denuders are connected by special threaded connectors, and capped with threaded caps when not in use. A special connect is used to connect the denuder train to a 3-stage filter pack containing an aerosol filter, a KOH-impregnated filter and a citric- or oxalic acid-impregnated filter. The pump and sample volume recording instrumentation is identical to the equipment described under 3.2.4.

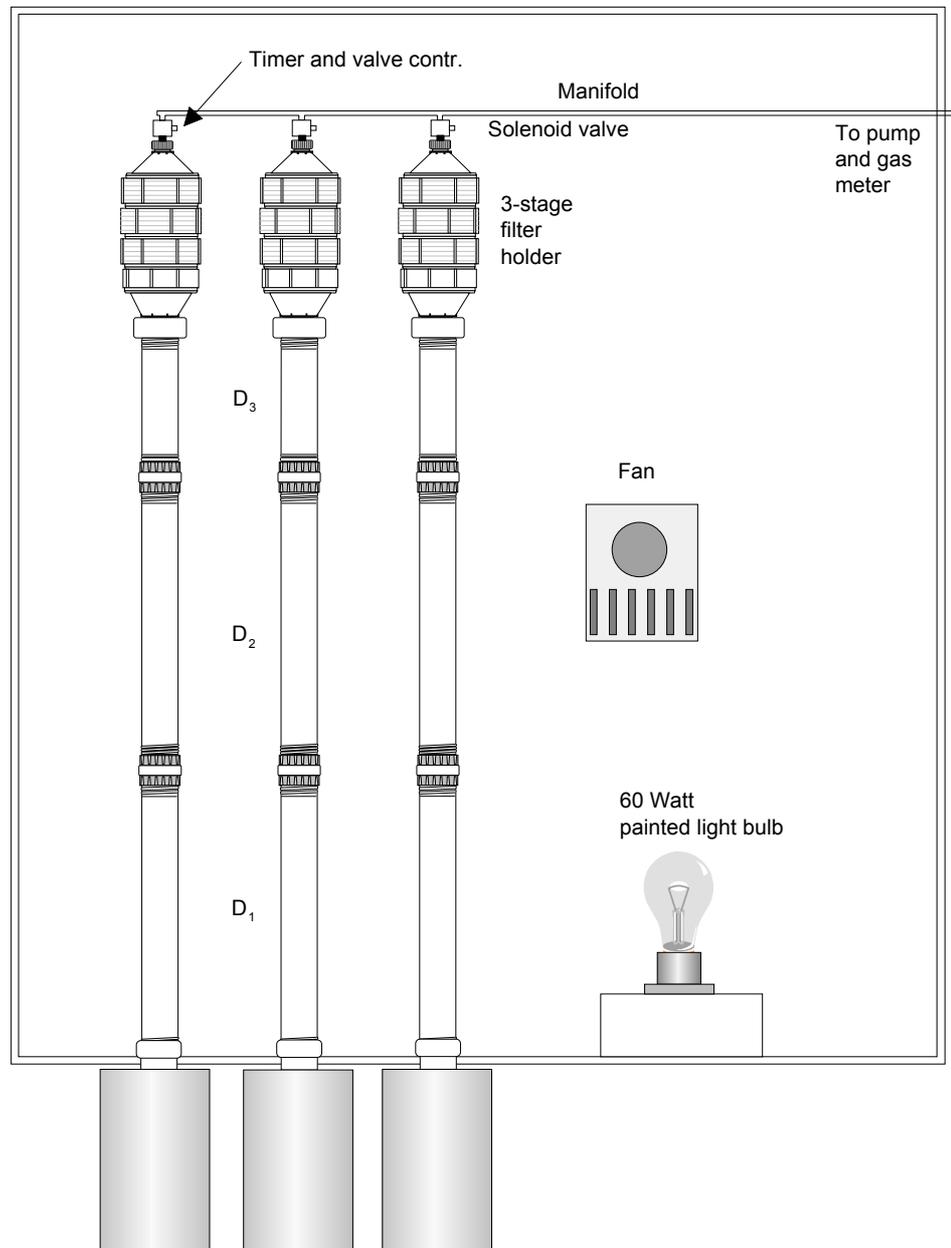


Figure 3.4.1: Sampling arrangement for denuder sampling. The number of sampling lines may be extended up to eight.

3.4.1.4 Commercial supply

Denuders:

242 mm URG-2000-30 BWH#30, annular denuder, heavy wall glass

120 mm URG-2000-30 BWH#30 as above

University Research Glassware, 118 E. Main St., P.O.Box 368 Carrboro, North Carolina 27510, USA.

3.4.1.5 Site requirements

See section [3.2.4.1](#)

3.4.1.6 Sampling procedure

Coating of denuders and preparation of filter packs

The preparation and coating of the denuders should take place in the laboratory that will carry out the chemical analyses of the collected samples. A solution of 1% Na₂CO₃ and 1% glycerol is prepared by dissolving 1 g of the analytical grade reagents in 50 ml of deionized water, and diluting to 100 ml with methanol.

Similarly, 1 g of citric acid (or oxalic- or phosphorous acid) is dissolved in a few drops of deionized water and diluted to 100 ml with ethanol.

The denuders have to be thoroughly cleaned, preferably by immersion in strong detergent for several hours, and then rinsed in deionized water.

For the coating procedure, a source of clean, dry air is needed. Compressed air must be filtered, and may have to be scrubbed. Passing the air through 2 tubes filled with cotton or filter paper impregnated with, respectively, sodium carbonate and citric acid will be safeguards against contamination. It is also possible to use clean and dry nitrogen from a steel cylinder.

Put on a screw-thread cap on one end of the denuder, add 2–3 ml of the coating solution, and rotate the denuder so that all internal surfaces are wetted. Pour off excess liquid, take off the screw-cap and put on another cap with connection to the dry air source. Pass dry air through the denuder, while rotating the denuder slowly. Observe the evaporation of the liquid film, and continue for a few seconds more to make sure that the evaporation is complete. Close the denuder with screw-caps.

At least 3 of the denuders should be set aside for the determination of blank values for each batch of denuders, which is being prepared in this way.

(Alternatively, sodium chloride may be used as an internal coating for the absorption of nitric acid in D1 and D2. This absorbent may partly absorb SO₂ and will not absorb nitrous acid or PAN).

Preparation of impregnated filters with potassium hydroxide and with oxalic acid, and determination of filter blank values, is described under Section 3.2.8. Filter packs with impregnated filters should also be prepared and loaded in the laboratory, and sealed for transport to the sampling site. One set of denuders and one filter pack should be reserved for use as field blanks every week. These are to

be sent to the field sampling site, and returned to the laboratory without being exposed at the site.

Sampling

Denuders and filter holders will have been prepared and should be transported to the sampling site in special transport containers. They are to be connected to the sampling equipment according to specific instructions, and should be marked with sampling date and time period (from-to) and denuder number (D1, D2, D3) in the laboratory before transport to the site. Make sure that connections are leak proof. Denuder and filter pack trains should be changed at 0800h in the morning or a timer and magnetic valve arrangement should be used to make an automatic sampling train change at 0800h. The gas meter should be read or recorded every day, together with the temperature in the gas meter.

The temperature of the ambient air and the temperature inside the box holding the denuder trains, should also be checked periodically, to avoid overheating and to check that the system functions properly.

A sampling form should be filled in, with date and identification of denuders and filterpacks, gas meter readings, and notes of observations, which may be of interest in connection with the evaluation of the results.

The denuders and filter packs should be capped after exposure, and put in the container used for transport to the chemical laboratory (together with the field blanks).

3.4.1.7 Preparation of samples for chemical analyses

The following solutions are recommended for extraction of the denuders and the filters in the filter pack:

D1 (Na ₂ CO ₃ -imp)	10 ml deionized water with H ₂ O ₂ (0.3%)
D2 (Na ₂ CO ₃ -imp)	10 ml deionized water with H ₂ O ₂ (0.3%)
D3 (Citric acid)	10 ml 0.01M HNO ₃
F1 (aerosol filter)	10 ml deionized water
F2 (alkaline imp. filter)	10 ml deionized water with H ₂ O ₂ (3%)
F3 (oxalic acid filter)	10 ml 0.01 M HNO ₃

Unscrew the cap at one end of the denuder to be extracted, add exactly 10 ml of the extraction solution with a pipette, put on the cap and shake the denuder, then transfer the extract to a stoppered test tube for subsequent analysis. It is essential to work quickly in order to minimize contamination hazards! The filters may be folded and transferred to the same kind of stoppered test tubes to which 5 ml of extraction solution is added. Stopper and agitate shortly. If a hydrophobic (e.g. fluoropore) membrane filter is used as the first filter in the filter pack, immersion in an ultrasonic bath may be useful. Chemical analyses of the extracts are to be made as follows:

Sample	Ions to be determined	Analysis methods	Reference
D1	NO ₃ ⁻ -N, SO ₄ ²⁻ -S (Cl ⁻ , NO ₂ ⁻ -N)	Ion chromatography	Section 4
D2	NO ₃ ⁻ -N, SO ₄ ²⁻ -S (Cl ⁻ , NO ₂ ⁻ -N)	Ion chromatography	Section 4
D3	NH ₄ ⁺ -N	Spectrophotometry or ion chromatography	Section 4
F1	NO ₃ ⁻ -N, SO ₄ ²⁻ -S, NH ₄ ⁺ -N (Cl ⁻ , NO ₂ ⁻ -N)	Ion chromatography and spectrophotometry	Section 4
F2	NO ₃ ⁻ -N, SO ₄ ²⁻ -S (Cl ⁻ , NO ₂ ⁻ -N)	Ion chromatography	Section 4
F3	NH ₄ ⁺ -N	Spectrophotometry or ion chromatography	Section 4

3.4.1.8 Calculation of results

The results from the chemical analyses will be given in µg/ml of the respective ions. After subtraction of blank values, the following algorithm have been proposed by Allegrini et al. (1987) for the subsequent calculation of the concentrations of HNO₃-N, SO₂-S and NH₃-N in air:

$$\text{HNO}_3\text{-N } (\mu\text{g}/\text{m}^3) = [(D1-D2)/0.94]*(10/V),$$

$$\text{SO}_2\text{-S } (\mu\text{g}/\text{m}^3) = [(D1-D2)/0.96]*10/V,$$

$$\text{NH}_3\text{-N } (\mu\text{g}/\text{m}^3) = D3*10/V,$$

where D1, D2, and D3 stand for the concentrations of the relevant components in the respective denuder extracts and V is the sample air volume in m³. The correction factors are based on theoretically calculated absorption efficiencies and it is assumed that interfering particles and other substances (e.g. PAN) are collected with the same efficiencies in D1 and D2. Correspondingly:

$$\text{NO}_3\text{-N}(\text{particles}) = (F1+F2+2.5*D2)*10/V,$$

$$\text{NH}_4\text{-N}(\text{particles}) = (F1+F3),$$

$$\text{SO}_4\text{-S}(\text{particles}) = (F1+2.5*D2).$$

Note that if the absorption capacity of denuder D3 for ammonia is exceeded, F3 will retain gaseous ammonia, which has passed through the denuder system. Therefore, if this amount of ammonium-N collected on F1 and F3 is significantly larger than the equivalent amount needed to balance the nitrate and sulphate on F1 and F2, the calculated excess should be added to the NH₃-N concentration determined from D3.

3.4.1.9 Quality assurance

Sampling

Written step-by-step instructions for the handling of denuders and the operation of the sampling equipment should be available at the site, together with appropriate sampling forms for the registering of sampling flow rates, change of samples, and air sample volumes. The gas meter and flow control device must be properly calibrated in the laboratory. Field calibration of the flow rate and sample volume recording apparatus should be carried out at least once every year.

Chemical analysis

Field blanks should be analysed regularly in order to check on the possible contamination. It is recommended to prepare, and analyse, one complete sampling train every week. Field blanks are to be prepared in the same way as the other samples, sent to the site, and returned unexposed to the laboratory.

Control samples should be included in each batch of chemical analyses. The control samples should contain the same reagents as the leachates, and known realistic concentrations of the analytes. 5% control samples will generally be sufficient.

Data consistency

Sulphur dioxide and sulphate aerosol will generally be determined by a separate filter-pack sampler, as described in Section 3.2.1. Sulphur dioxide is also quantitatively retained in D1 and D2, and the sum of nitric acid and nitrate in airborne particles may be determined from the filter pack data. Comparison of the results will give a good indication of the performance of the complete sampling and analysis procedure. The results should generally be within $\pm 10-15\%$.

3.4.1.10 Comments with respect to the denuder sampling procedure

This sampling technique is technically demanding and requires good control of chemical analyses and particularly of blank values. The sampling set-up is relatively simple, but needs to be defined in relation to the sampling site and practical arrangements in connection with transport of unexposed denuder sampling trains and filter packs. The recommended denuder tubes are both expensive and brittle. Even more expensive denuder tubes are available, which are unbreakable. More information with respect to the theoretical and practical aspects of denuder sampling for the phase-separated determination of nitrogen species in air can be found in the literature described in the general introduction, reference is also made to a general review article by Ali et al. (1989).

The denuder sampling technique is applicable also to the determination of atmospheric HCl, HF and HNO₂, but these components are not included in the EMEP measurement programme.

The simple tubular denuder systems described by Ferm (1979, 1982, 1986) require much less expensive equipment. If blank values (including field blanks) and chemical analyses can be controlled, this system is an alternative to the system described above.

More advanced systems are also available, e.g. for continuous monitoring of gaseous NH₃ (Keuken et al., 1988)

3.4.1.11 References

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3.5 Cleaning and impregnation of filters

See sections [3.2.7](#) and [3.2.8](#).

3.6 Extraction from filters

See section [3.2.9](#).

Pages 3-44 to 3-50 in earlier revision is included in the previous pages.

3.7 Determination of light hydrocarbons in air

3.7.1 Introduction

The EMEP-Workshop on measurements of hydrocarbons/VOC in Lindau 1989 recommended C2 to C5 hydrocarbons to be measured in spot-samples taken twice a week at 10 to 15 sites in Europe. Electropolished stainless steel canisters were recommended for the sampling.

3.7.2 Principle

A cleaned steel canister is flushed with air and then filled to a pressure about 40 psig (2.8 atm). The canister is brought to a laboratory and analysed within a week.

3.7.3 Sampling equipment

The sample cylinders are 1.8 litre "Summa" polished stainless steel canisters manufactured by Prof. R. Rasmussen. The clean air pump is from the same supplier. Both cylinders and pumps were widely used and tested in both USA and Europe. A number of tests and comparisons with other equipment have been undertaken, and are published in several articles and intercalibrations (McClenny et al., 1991; Pate et al., 1992; Westberg et al., 1984; Olivier et al., 1986).

3.7.4 Sampling procedure

See Figure 3.7.1.

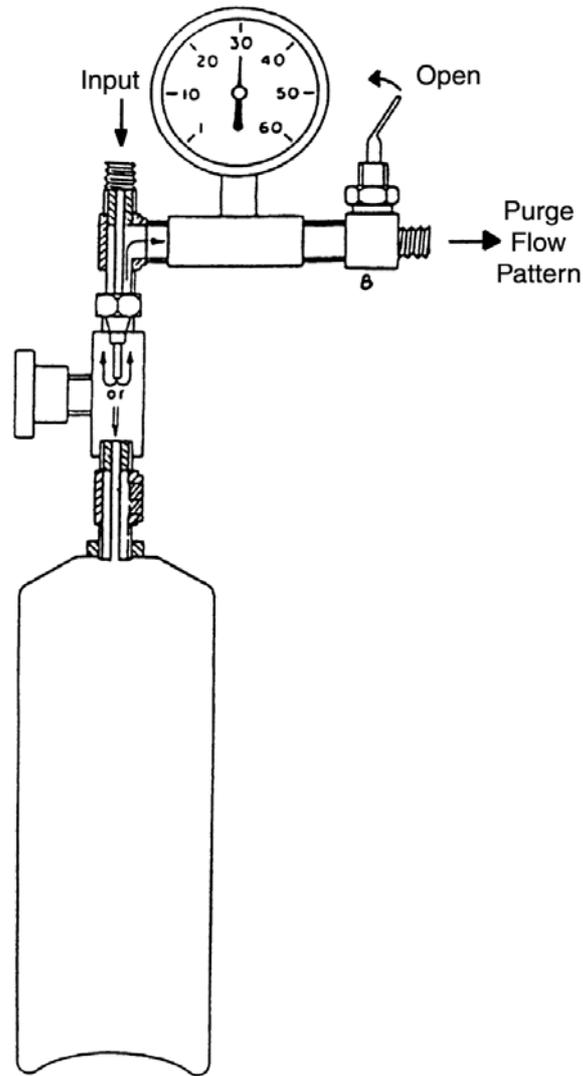
1. Can is evacuated
2. Remove swagelock-end-cap
3. Connect purge-tee and tighten
4. Switch on pump
5. Pressurize purge-tee
Vent by opening valve B
(minimum 10 times)
6. Open valve A - pressurize can to 15 psig
Vent by opening valve B
(minimum 5 times)
7. Pressurize can to max. pressure (about 40 psig)
8. Close valve A and switch off pump
9. Remove purge-tee and replace swagelock

Please use a pencil to fill in the label.

Please do not use force to tighten the green handle of the shut-off valve. Normal use of thumb and forefinger is sufficient!!

3.7.5 Cleaning of canisters before the first use

- (1) evacuate to a pressure of 10^{-7} mbar 24 hours, ambient temperature.
- (2) fill with 10 μ l water and purified helium 24 hours, 1 bar
- (3) evacuate to 1 mbar and fill with helium 5 times
- (4) humidify with 10 μ l water, evacuate to 1 mbar



- 1 Can is evacuated
- 2 Remove swagelock-end-cap
- 3 Connect purge-tee and tighten
- 4 Switch on pump
- 5 Pressurize purge-tee
 - Vent by opening valve B
(minimum 10 times)
- 6 Open valve A - pressurize can to 15 psig
 - Vent by opening valve B
(minimum 5 times)
- 7 Pressurize can to max. pressure (about 40 psig)
- 8 Close valve A and switch off pump
- 9 Remove purge-tee and replace swagelock

Please use a pencil to fill in the label.

Please do not use force to tighten the green handle of the shut-off valve. Normal use of thumb and forefinger is sufficient!!

Figure 3.7.1: Sampling procedure.

After step (1) a one-hour leak-test is performed. The canister shut-off valve is closed and no detectable increase of pressure should occur on the 10^{-7} mbar scale.

Blank runs of canisters should not show a single signal of more than 2000 μ Vs (30 ppt ethane or 10 ppt benzene).

From the 200 canisters we bought for the EMEP-program, 7 had a significant high level of C_6 hydrocarbons and chlorinated solvents. Those bottles were cleaned with methanol, acetone and water and cleaned as shown above. The evaporation in step (1) is performed with 70 °C instead of ambient temperature. The cleaning of a used bottle is done by 6 to 24 hours evacuation at 10^{-7} mbar and 50°C. (Turbomolecular pump from Pfeiffer Balzers modified at NILU to allow simultaneous cleaning of 6 bottles).

3.7.6 Commercial supply

Steel canisters:

Prof. R. Rasmussen, Oregon Graduate Center, Biospheric Research Cooperation.

3.7.7 References

McClenny, W.A. et al. (1991) Canister-based method for monitoring toxic VOCs in ambient air. *J. Air Waste Manage. Assoc.*, 41, 1308-1318.

Pate, B. et al. (1992) Temporal stability of polar organic compounds in stainless steel canisters. *J. Air Waste Manage. Assoc.*, 42, 460-46.

Westberg, H. et al. (1984) Analysis of individual hydrocarbon species in ambient atmospheres. In: *Identification and analysis of organic pollutants in air*. Ed. by L.H. Keith. Woburn, MA, Butterworth. pp. 323-327.

Olivier, K.D. et al. (1986) Sample integrity of trace level volatile organic compounds in ambient air stored in summa polished canisters. *Atmos. Environ.*, 20, 1403-1411.

3.8 Determination of aldehydes and ketones in ambient air

3.8.1 Introduction

Recent years several methods for simultaneous determining of aldehydes and ketones in air have been investigated. The most popular method so far utilizes a solid adsorbent coated with 2,4-dinitrophenylhydrazine (DNPH), and the resulting derivatives are subsequent analysed by high performance liquid chromatography and UV detection, e.g. Slemr (1991). This method has been modified for use in EMEP, and the procedure is described below.

The range of concentrations of the individual aldehydes and ketones which may be determined is typically from 0.1 $\mu\text{g}/\text{m}^3$ to 10 $\mu\text{g}/\text{m}^3$.

The detection limit of a typically sample (sample volume 750 litres) lies in the range 0.01 $\mu\text{g}/\text{m}^3$ –0.05 $\mu\text{g}/\text{m}^3$. Preliminary results from parallel sampling at Birkenes give a relative standard deviation of 6% for methanal (mean 0.30 $\mu\text{g}/\text{m}^3$) and propanone (mean 0.99 $\mu\text{g}/\text{m}^3$, and 12% for ethanal (mean 0.42 $\mu\text{g}/\text{m}^3$).

3.8.2 Principle

The air sample is drawn through a cartridge which contains 2,4-dinitrophenylhydrazine (2,4-DNPH)-coated silica packed in a polyethylene tube. Aldehydes and ketones react with the acidified 2,4-DNPH to form the corresponding hydrazones.

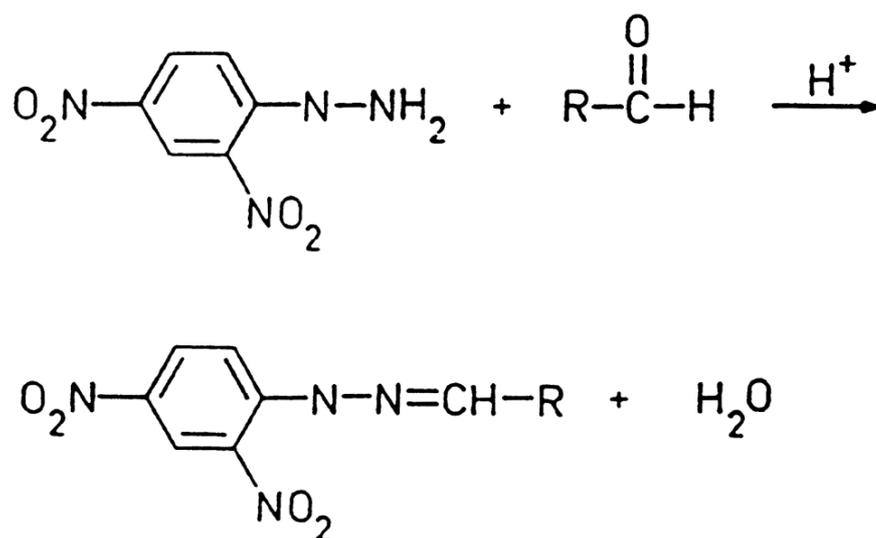


Figure 3.8.1: Reaction scheme.

After exposure the cartridge is eluted with acetonitrile, and the sample extract is analysed by reversed phase high-performance liquid chromatography, using UV-detection (diode array detector). The detection and quantification is carried out at 369 nm (band width 22 nm) using 474 nm (band width 50 nm) as the reference wavelength. The detection and quantification of dicarbonyls is carried out at 440 nm (band width 22 nm) using 337 nm (band width 50 nm).

3.8.3 *Sampling equipment*

- Sep-PAK DNPH-silica cartridges
- Air sampling pump, model DOA-p101-BN
- Gas meter, FLONIDAN, Gallus 2000 G1.6
- Copper tubing, length 1 meter, i.d. 0.46 cm

3.8.4 *Commercial supply*

Absorption tubes:

Sep.-PAK DNPH-silica, cartridges, No. 37500
Waters, Millipore Corporation
Waters Chromatography
Millford, MA, USA.

Membrane pump:

GAST, Model DOA-P101-BN
MFG Corp.,
Benton Harbor, Mich. USA

Gas meter:

FLONIDAN
Gallus 2000 G1.6
Islandsvej 29
DK-8700 Horsens, Denmark

The sampling equipment set-up is shown in Figure 3.8.2. The threads in the pump inlet, pump outlet, and gasmeter inlet require use of teflon tape to get the connections leakproof. Be careful and do not overtighten the connections!

Before use, the equipment should be leakproof-tested and tested for appropriate air flow rate (typically 1.5 litres/min–2 litres/min).

Leakproof-test: Plug the air inlet PE-tube with a male Luer plug (or your thumb) and start the pump. Keep the sampling line plugged for 2 minutes. During this time period the gas meter reading should be constant.

Air flow rate test: Connect the DNPH-silica cartridge (connect a cartridge which has been used and dried) to the air inlet tube (as shown in Figure 3.8.3) and start the pump. Measure the "sample" volume over a period of 5 to 10 minutes and calculate the flow rate in litres/min. If necessary adjust the needle valve until you have a flow rate of 2 litres/min or as high flowrate as possible not exceeding 2 litres/min (sometimes the cartridge-restriction makes it impossible to reach 2 litres/min).

3.8.5 *Preparation of ozone-scrubber*

Form a coil from a copper tube (1 meter, 0.46 cm i.d.). Fill the coil with a potassium iodide solution (dilute a saturated aqueous potassium iodide solution 1:1 with water) for 5-10 minutes. Drain the coil and dry it completely by passing nitrogen through the coil.

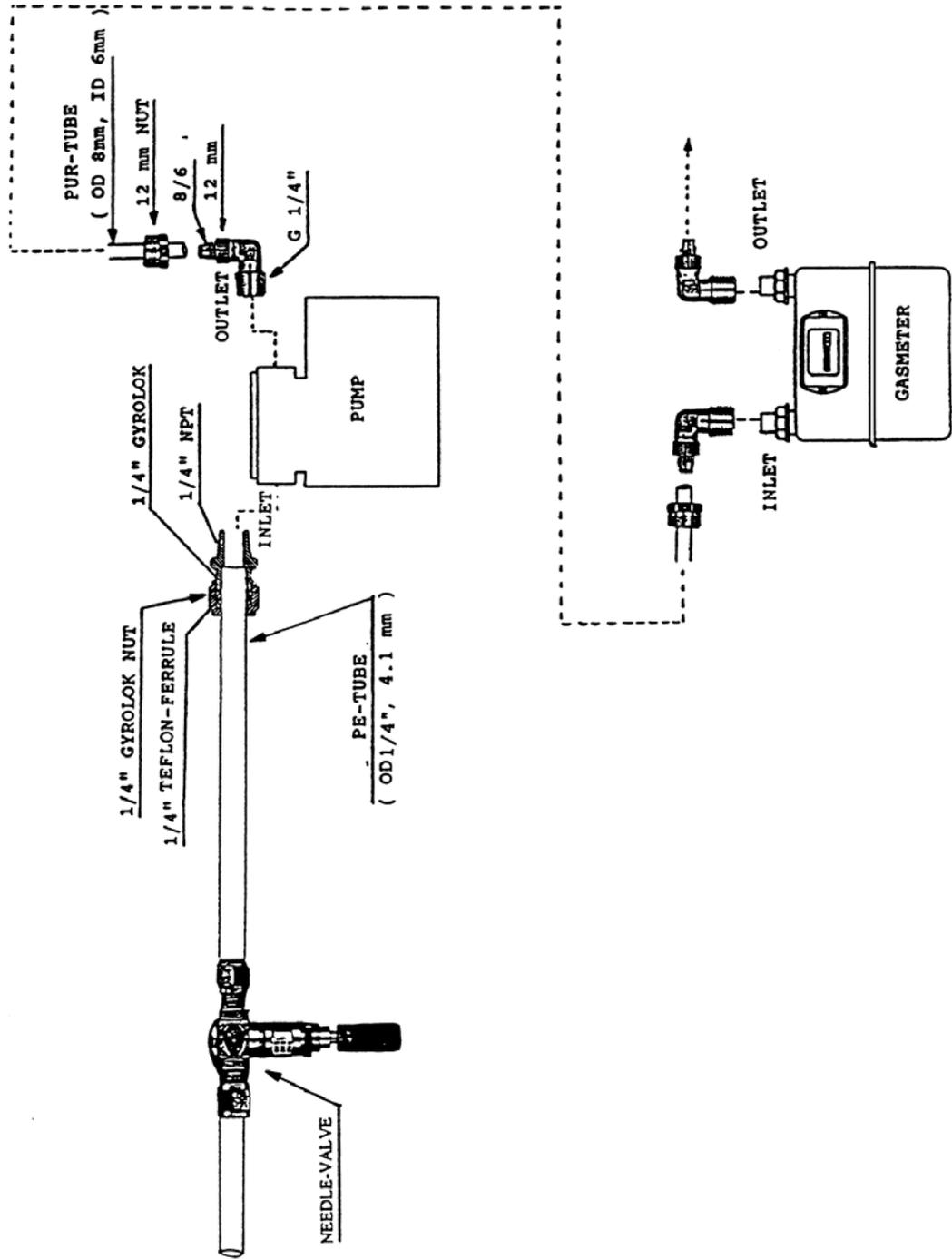


Figure 3.8.2: Sampling equipment set-up.

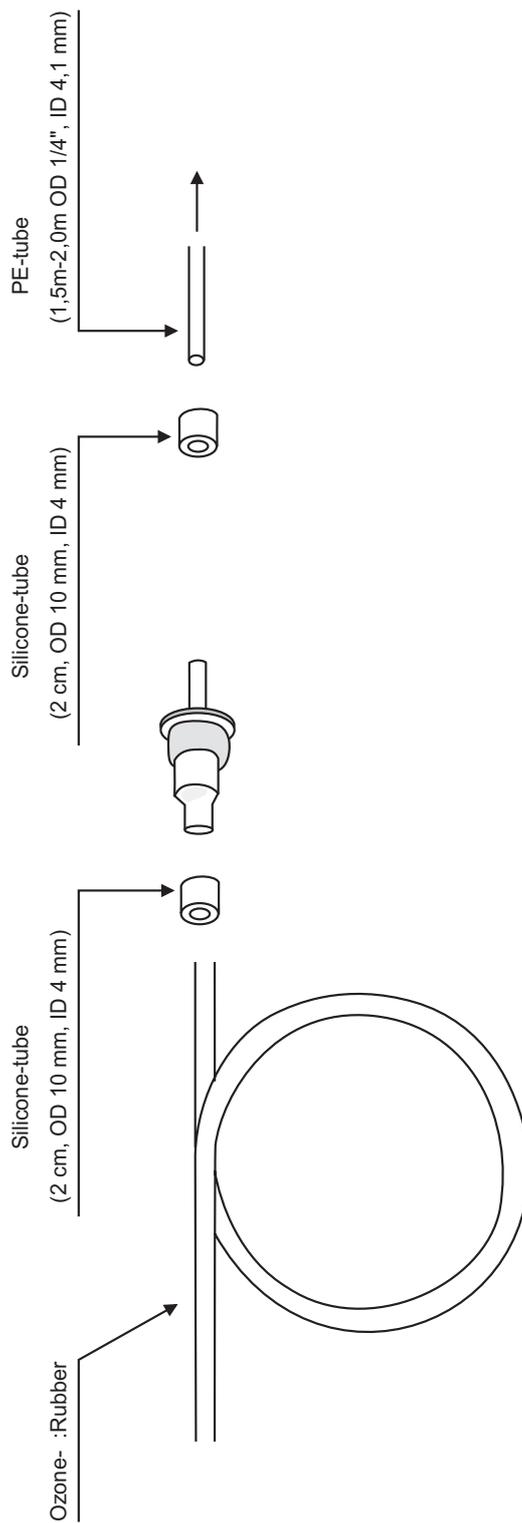


Figure 3.8.3: The figure shows how DNPH-silica cartridges and the ozone-scrubber are connected to the pump inlet polyethylene (PE) tube.

3.8.6 *Sampling procedure*

- The samples should be taken on Mondays and Thursdays from 0800 to 1600 hours local time.
- Sample information should be carefully recorded in the sampling form. The sampling form must follow the sample as an identification when the sample is sent to the laboratory. Each glasscontainer should be marked with "sample name" (Sample name = Station name, sampling date (example: London, 15/5-93 = 15 May 1993).

The "cookbook":

1. Record the following in the sampling form: Batch number (= Lot No.) of the sample cartridge, ozone scrubber number, sample name, outdoor temperature, indoor temperature, sampling technique and signature.
2. Remove the endcaps from the ozone scrubber.
3. Open the sealed pouch which contains the cartridge. Remove the Luer plug and cap and keep them in a place where they do not disappear (you need the plug and cap for sealing the cartridge after completed sampling).
4. Connect the ozonescrubber, cartridge, and the PE-tube in the manner shown in Figure 3.8.3. (The ozone scrubber should be mounted upstream of the cartridge.) The male Luer tip of the cartridge has to enter the PE-tube ("edge-to edge"), in such a way that the silicon tube becomes a support and not the main seal (then there will be no contact between the exhaust and the silicon tube).
5. Install the sampling equipment in sampling position.
6. Record the following in the sampling form: gasmeter reading and sampling start time. Then turn on the sampling equipment.
7. After a run time of 5-10 minutes optimize the flow rate.
8. Seal the cartridge with Luer cap and plug after completed sampling.
9. Record the following in the sampling form: gasmeter reading and sampling end time.
10. Seal the ozone scrubber with end caps.

In order to avoid the potassium iodide film being dissolved by water, a weather-protection "device" has to be mounted on the scrubber (teflon funnel or the upper half of a teflon bottle).

3.8.7 *Sampling handling*

- "Stock-cartridges" should be stored in the sealed pouches at 4°C.
- After completion of the sampling, the exposed cartridges should as soon as possible, be disconnected from the sampling line and sealed with the Luer plug and cap.
- The cartridges are put into glass containers with teflon lined screw-caps.
- *Label the glass containers* by using the sample name written on a self-adhesive label. The glass containers are then put into plastic containers and sent to the laboratory.
- If the exposed cartridges have to be stored for some days, it should be done in dark at a cool place (4°C), i.e. a refrigerator. **Do not store the cartridges at places where carbonyls are stored (acetone etc.).**

3.8.8 *Procedure for blank sample preparation*

1. After preparing the sampling equipment for sampling, open a sealed pouch with same batch number as the sample batch number.
2. Record the following in the sampling form: Batch number (= Lot No.) of the blank sample cartridge, starting time (= opening time for the pouch), sample name (= same as "real" sample name), indoor temperature and signature. Instead of recording gasmeter readings and sampling end time "BLANK" should be noted in the sampling form.
3. Place the cartridge nearby the sampling equipment during sampling. Do not remove the end cap and plug.
4. After completion of the real sampling the blank sample cartridge should be treated in same manner as the real sample. *Label the glass container with "sample name" and BLANK.*
5. The blank sample cartridge has to be mailed together with the real sample *in the same envelope*. Please do remember that the sampling forms have to be mailed together with samples.

3.8.9 *References*

- Dye, C. and Oehme, M. (1992) Comments concerning the HPLC separation of acrolein from other C₃ carbonylcompounds as 2.4-Dinitrophenylhydrazones: A proposal for improvement. *J. High Resolut. Chromatogr.*, 15, 5.
- Millipore Corp. (1992) Waters Sep-Pak DNPH-Silica Cartridge; Care and Use Manual. Milford, USA, Waters Chromatography Publications.
- Slemr, J. (1991) Determination of volatile carbonylcompounds in clean air. *Fresenius J. Anal. Chem.*, 340, 672.

3.9 Determination of ozone

3.9.1 Introduction

Both chemiluminescence and UV-absorption based methods have been used in the past 20 years for the measurement of ozone in ambient air. After many years of discussion and intercomparison between different wet-chemical methods for calibration of ozone generators used for calibration of the monitors, it is now generally accepted to use UV-photometry as the primary calibration method. Since the UV-absorption method has proven to be reliable and robust in field operations, this method is recommended and described in this manual. The description follows the principles from the International Organization for Standardization (ISO) (ISO 13964:1998).

The general requirements to regional sites are valid for ozone. In addition ozone is a reactive gas that is taken up by vegetation; measurements should therefore be carried out well away from plant life. The Canadian networks recommend sampling at 3-5 m above ground level and more than 20 m away from trees.

Details in the operating procedures for the O₃-instruments will be found in the Operator Manual for the different commercial monitors.

3.9.2 Field of application

The described method is applicable for continuous monitoring of ozone (O₃) in ambient air. The method can be used in the range 2 µg/m³ to 2 mg/m³ (1-1000 ppb).

3.9.3 Principle

Sample air is drawn continuously through an optical absorption cell where it is irradiated by monochromatic light at 253.7 nm from a stabilized low-pressure Hg discharge lamp. The absorption of this radiation by the sample air is a measure of the ambient air ozone concentration. To avoid interference from other gases absorbing light at the same wavelength and from instability in the light source, an ozone catalytic converter is used to selectively remove ozone from the sample stream either in the sample cell by alternately fill the sample cell with unscrubbed and scrubbed sample air, or by using another parallel sample cell.

The Beer-Lambert equation, shown below, is used to calculate the concentration of ozone from the ratio of the two light intensities measured:

$$I/I_0 = \exp(-acd)$$

where

I_0 is the light intensity measured with no ozone in the gas sample

I is the light intensity measured with ozone in the gas sample

a is the ozone absorption coefficient at 253.7 nm ($1.44 \times 10^{-5} \text{ m}^2/\mu\text{g}$)

c is the mass concentration of ozone in µg/m³

d is the optical path length in m

UV photometry is also the recommended primary calibration procedure. The use of transfer standards (including non-UV methods) is possible if they have been previously calibrated against the primary UV photometric method.

3.9.4 Reagents and materials

Sampling line

The sampling line shall be made of material that is inert to ozone, such as glass or fluorocarbon polymer and shall be as short as possible to keep the residence time to a minimum. Any ambient nitric oxide present in the sample air will react with some of the ozone during the residence time in the sampling line. The sampling line or manifold shall be clean and should normally be replaced after one year. If high amount of dust deposition in the sampling line is expected, it should be cleaned or replaced more frequently.

Particle filter

The sample air has to be drawn through a filter before entering the absorption cell. The filter and its support shall be made of material inert to ozone, such as fluorocarbon polymer, and shall remove all particles likely to alter the performance of the analyzer. It shall be changed on a regular basis, depending on the ambient particle concentrations at the sampling site. This is necessary because excessive accumulation of particles on the filter can cause loss of ozone from the sample air and an excessive pressure drop across the filter.

Normally, a filter pore size of 5 μm is used.

Generally, new filters need some time to be conditioned, and the first 5-15 minutes data after the filter change should be discarded.

Zero air

Zero air is required in the analyzer calibration procedure. The zero air shall be free of ozone, nitrogen oxides and any other interfering substance that can cause a positive or negative response in the UV photometer. The zero air supplied to the photometer during the I_0 measurement shall be the same as that used for generation of calibration ozone concentrations.

If synthetic air is used, the oxygen content shall be within 2% of the normal atmospheric concentration.

Details on a system for making zero air from ambient air is found in EPA (1979a).

3.9.5 Apparatus

3.9.5.1 UV photometric ambient ozone analyzer

The components of a typical UV photometric ozone measuring system are shown in Figure 3.9.1. The monitor should have specifications as listed below:

Range	:	0.002–2 mg/m ³
Output	:	0–10V full scale
Lag time	:	20 s
Rise time	:	15 s

Fall time	: 15 s
Warm-up time	: 2h
Zero instability	: $\pm 2 \mu\text{g}/\text{m}^3$ per week
Span instability	: $< 0.5\%$ per week
Repeatability	: $\pm 2 \mu\text{g}/\text{m}^3$
Period of unattended operation	: 7 d
Sample flow rate	: 1.5–2 l/min
Temperature range	: 0–45 °C

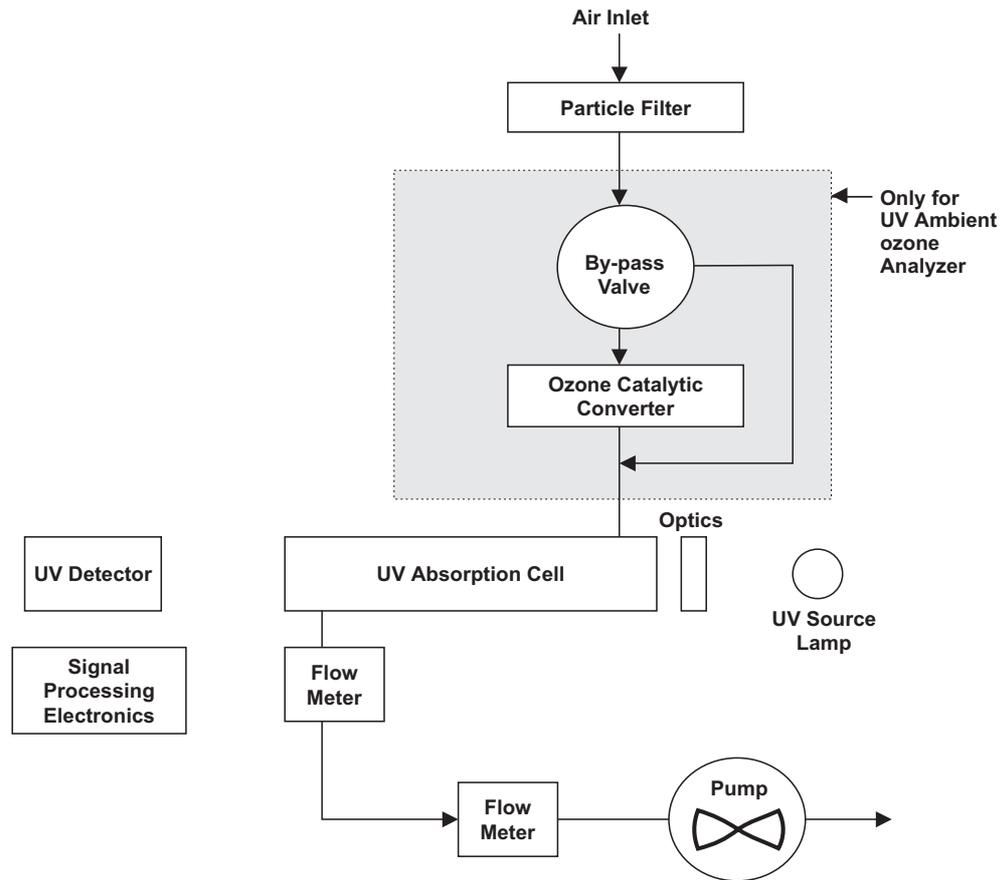


Figure 3.9.1: UV photometric ozone measurement system.

Commercial instruments that meet these specifications are readily available.

One important component of the instrument is the ozone-specific scrubber. Normally, instrument manufacturers give an average lifetime of such scrubbers, however, the actual lifetime will depend on the concentration of other pollutants at the sampling site. A scrubber failure will give a decrease in response to ozone.

Since the ozone absorption coefficient given in the formula in Section 3.9.3 is dependent of temperature and pressure, it is important that the instruments have temperature and pressure indicators capable of measuring the temperature and pressure in the absorption cell with an accuracy of $\pm 0.1^\circ\text{C}$ and $\pm 0.1\text{kPa}$ respectively.

3.9.5.2 Apparatus for calibration

A simplified scheme of a primary ozone calibration system is shown in Figure 3.9.2 and consists of an ozone generator and a UV calibration photometer.

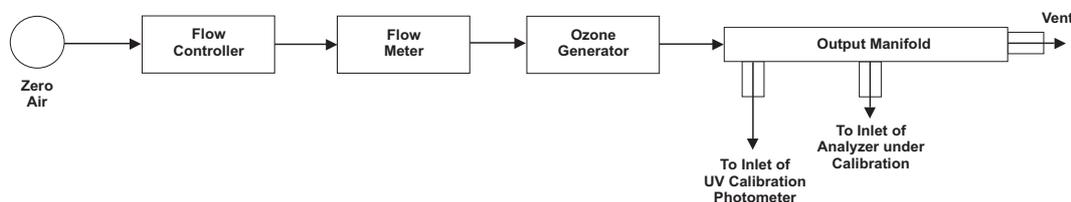


Figure 3.9.2: Primary ozone calibration system.

Primary UV calibration photometer

The primary UV calibration photometer shall be used for only that purpose and shall be carefully maintained under stable laboratory conditions. The different parts of the calibration photometer are the same as shown in Fig. 3.9.1 but without the catalytic ozone scrubber. Every part shall be manufactured optimum care.

When using the expression **primary** calibration photometer in this section, it will normally mean a laboratory or e.g. a country's primary calibration photometer. Such primary calibration photometers should preferably be traceable to the NIST (US National Institute of Standards and Technology) UV-photometer. One way of obtaining this is to buy from NIST a NIST-UV photometer which periodically will be checked by NIST. Another way is to have the laboratory or national primary calibrator calibrated against a NIST-UV photometer in another country e.g. once per year. To the CCCs knowledge there are at least three NIST-UV photometers in Europe:

Institute of Applied Environmental Research at the University of
Stockholm,
Air Pollution Laboratory, Stockholm, Sweden
Phone : + 46 8 674 70 00
Fax : + 46 8 612 08 49

Swiss Federal Laboratories for Materials Testing and Research (EMPA),
Dübendorf, Switzerland
Phone : + 41 1 823 55 11
Fax : + 41 1 821 62 44

Czech Hydrometeorological Institute
Prague, Czech Republic
Phone : +42 2 401 6719
Fax : +42 2 401 0800

Ozone generator

This apparatus generates the stable ozone concentrations that are measured by the calibration photometer described above. It shall be capable of producing steady

ozone concentrations in the range of interest at the required flow rate and throughout the calibration period. If a variable ozone generator is not available, the calibration system shall include a means of diluting the ozone with additional zero air, and a mixing chamber shall be installed before the output manifold.

Output manifold

The output manifold shall be of materials inert to ozone, such as glass or fluorocarbon polymer. It shall be of sufficient diameter and be vented to ensure equal pressure inside and outside the manifold. The vent shall be located so as to prevent intrusion of ambient air.

Procedure

In the next paragraphs the principles for the measurement and calibration procedures are described.

Operation of the ambient ozone analyzer

Install the instrument in a suitable location. The room for the analyzer shall be temperature controlled. For background ozone measurements, local sources of nitric oxide have to be avoided as it readily react with ozone. The air intake should be positioned at least 2 m above ground.

Follow the manufacturers instructions for the specific analyzer to set correctly the various parameters, including UV source lamp intensity, sample flow rate and activation of the electronic temperature/pressure compensation.

Introduce sample air into the instrument and record the ozone concentrations by means of a suitable recording device.

During continuous operation, checks on the instrument zero and operational parameters shall be made at least once per week. If an internal ozone source is available in the monitor, this can be used for a span check, but is normally not stable enough for making calibrations. It is recommended that a multipoint calibration be carried out every 3-4 months.

3.9.5.3 Calibration of the ambient ozone analyzer

Principle

The calibration system is shown in Figure 3.9.2. Various ozone concentrations (in air) are generated and accurately measured with the primary UV calibration photometer. These ozone calibration concentrations are simultaneously sampled by the ambient ozone analyzer to be calibrated via a common manifold. The analyzers response is plotted against the ozone concentrations measured by the primary UV calibration photometer.

Alternatively, a transfer standard calibration method can be calibrated against the primary ozone standard and then used to calibrate the ambient analyzer at the sampling location.

More details for the calibration procedure are given in EPA (1979a) and in the instrument manuals.

Transfer standard calibration procedure

A transfer standard has to be used whenever the primary calibration photometer is not readily available such as at the sampling site.

The transfer standard shall be calibrated against the primary UV photometric standard at least once per year and its accuracy shall be maintained within $\pm 5\%$ between successive primary calibrations.

The recommended (portable) transfer standard calibration method is a second UV photometer system with its own zero air and ozone supply. The other acceptable transfer standard calibration methods are the gas-phase titration of excess nitric oxide by ozone (or vice versa) and the laboratory-based neutral buffered iodide-potassium bromide (KIBR) method. For details see EPA (1979b).

3.9.6 Cooperation with WMO GAW on surface ozone measurements

WMO has produced a quality assurance plan for surface ozone including standard operating procedures (WMO GAW No. 97). WMO GAW and EMEP are trying to harmonize and will hopefully adopt the same SOPs, and cooperate with respect to audit and calibration.

3.9.7 References

EPA (1979a) Technical assistance document for the calibration of ambient ozone monitors. Research Triangle Park, N.C., United States Environmental Protection Agency (EPA-600/4-79-057).

EPA (1979b) Transfer standards for calibration of air monitoring analyzers for ozone. Research Triangle Park, N.C., United States Environmental Protection Agency (EPA-600/4-79-056).

WMO (1994) Quality assurance project plan for continuous ground based ozone measurements. Prepared by GAW QA/SAC. Geneva (WMO GAW No. 97).

3.10 Sampling of heavy metals in precipitation

3.10.1 Introduction

The Protocol to the Convention on long-range transboundary air pollution (LRTAP) on heavy metals was signed on 24th of June 1998 in Aarhus in Denmark. It targets three particularly harmful metals: cadmium, lead and mercury. According to one of the basic obligations, Parties will have to reduce their emissions of these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). The main sources for atmospheric deposition of heavy metals are mines, smelting plants and metal industry of various types as well as burning of coal and other fossil fuels. Additive of lead in gasoline is historically one significant source of lead; however, international agreements have decreased this problem.

From 1999, heavy metals have been part of the EMEP program; and it is therefore a need for harmonisation and standard procedures for sampling and analysis of heavy metals. The recommendations are mainly based on previous work of EMEP (NILU and IVL, 1993) and the conclusions from the EMEP and WMO-GAW workshops in Durham, Beekbergen, Moscow and Aspenäs (EMEP, 1993; EMEP, 1996b; EMEP, 1997a; EMEP, 1997b) and at the two first task force of measurements and modeling, TFMM (EMEP, 2000).

Due to the special properties of mercury, this needs a different sampling technique than the other elements and separate chapters have been written for sampling of mercury, chapter [3.12](#).

3.10.2 Siting criteria

Generally, as for the main components, the heavy metal measurements should not be influenced by emissions from local sources nor by local circulation effects and formation of stagnant air pockets, which cannot be reproduced in the regional scale models. The siting should follow the criteria written in Chapter [2](#); in addition, further precautions have to be taken to prevent local sources as e.g. metal dust from pumps, metal surfaces, building materials, paint etc.

3.10.3 Sampling procedure

The sampling of heavy metals follows to a large extent the same procedures as for the main components in precipitation, Chapter [3.1](#), but due to the sensitivity for contamination extra precautions are needed. The concentrations of heavy metals in precipitation are typically only a few nanograms per millilitre and it is important that the standard procedures are followed carefully.

3.10.3.1 Equipment

It is recommended to use a wet only collector for precipitation sampling. When choosing which wet-only sampler to use, it is important that no parts of the precipitation collector are made of metal. Further that all parts can easily be cleaned and be of known composition. As for material, high-density polyethylene collectors are recommended. Among good wet-only collectors are the ARS type from Eigenbrodt in Germany and the one from MISU in Sweden. Other wet only collectors can be used if they have proven to be of the same or better quality.

Different sampler designs have different sampling efficiency, which may lead to incomparable results when calculating the wet deposition. A parallel measurement of precipitation amounts should be made to identify any discrepancies. It is strongly recommended to use a rain gauge in parallel with the sampling equipment. The difference in precipitation amount between the two collectors should not be greater than 10%. If systematic errors are found, the sampler design should be reconsidered. The precipitation amounts from both collectors should be reported to CCC.

Bulk collector may be used when proven to be quantitatively equivalent to the recommended method. Bulk collectors tend to give too high metal concentrations due to dry deposition, but in some areas there are practically no difference between the two types of collector i.e. in the Nordic countries. When a bulk collector can be used, it is recommended to use a sampler with separate collective funnel and collection bottle for easy cleaning. In addition the funnel should have high walls. Some of the traditional bulk collectors have a metal ring in the top; this has to be taken away before it can be used for heavy metal sampling. If a bird ring is needed it should be made of polyethylene. In the field comparison of heavy metals in precipitation performed in Deuselbach Germany in 1995 a variety of different bulk precipitation collectors were compared (Winkler and Roeder, 1997). It was discovered that the use of a fine meshed net (<1 mm) in the funnel neck caused troubles with wetting loss, sometimes hindered water from draining into the bottle and caused difficulties in sealing the funnel and bottle. It is therefore recommended to avoid using this type of net. However, in order to prevent insects leaves etc. to enter the collection bottle one can use a sieve made of i.e. polycarbonate with larger grid size. The sieve should be free and not tied up in the funnel neck. The sieve can for example just be the filter backing used in the filter folder system. For sites with snow in wintertime it is recommended to use the rain sampler also in this season, since a snow collector (cylindrical bucket) are difficult to clean thoroughly. However, for places with extremely much snow and strong wind it might be necessary to use a snow collector in the wintertime.

3.10.3.2 Cleaning

The concentration of heavy metals in precipitation samples and extracts from filters are very low, in the interval 0.01-10 ng/ml. Therefore, it is very important that all the equipment are thoroughly cleaned to prevent contamination. The precipitation bottles should be thoroughly cleaned between use. They should be stored minimum one day in 2% nitric acid and then washed several times (minimum three times) with de-ionized water, dried corked and packed in two clean plastic bags and zipped until used in the field. All reusable lab-ware should be cleaned in the same manner. The funnels should be washed in the field between every sampling and every month sent to laboratory for more thorough cleaning.

3.10.3.3 Standard operating procedure

Sample bottles, measuring equipment etc should always be handled with care to prevent contamination. Plastic gloves should be used when collecting the samples and the inside of the funnel or the tip of the collector should not be touched. All

bottles should be kept in double plastic bags during transport and storage. The station observer must wear clean clothes that do not give any dust or other kind of pollution.

In order to prevent contamination, the precipitation bottle should be sent directly to the laboratory without transferring any precipitation into smaller transport bottles, which are usually done when measuring the main components in precipitation. Immediately after disconnection the sample bottle must be closed e.g. with a screw cap and sent to the laboratory. The precipitation amount is measured by weight. The empty sampling bottle with screw cap is weighed before use and then weighed after the sampling period is finished.

The precipitation must be conserved in nitric acid which is added either before or just after (Chapter [3.10.4](#)) the sampling. To prevent growth of algae in the sample the acid should be added before the precipitation sampling. Before sending the precipitation bottle to the field it should then be filled with e.g. 2 ml concentrated HNO_3 . Choosing this sampling strategy it is, however, important to consider whether i.e. a possible evaporation of nitric acid may influence other measurements at the site.

Some trace metals may absorb on the surface of the funnel. Therefore, the funnel should be washed with an exact volume (200 ml) of acidic water (1% HNO_3), which is collected in a separate collection bottle. This is analysed to study the influence of absorption. This is especially important in the beginning of the sampling program, and if it turns out to have a significant influence this needs to be included in the sampling procedure as written in cursive below.

The standard sampling procedure is:

- Bring an empty clean precipitation bottle and screw cap to the precipitation sampler.
- Disposable polyethylene gloves are put on. One should change to new plastic gloves if touching the inside of the funnel is necessary.
- Disconnect the precipitation bottle and put on the screw cap.
- Examine the collector funnel for visible contamination such as insects, leaves or tree-needles, organic debris. If this is found, remove the contamination.
- *Wash the funnel using 200 ml acidic (1% HNO_3) water. Let it run into a separate bottle. Disconnect this bottle and set the screw cap on.*
- Without any collection bottle in place rinse the funnel twice using deionized water (\approx 100 ml) and let the water drain off.
- Connect the new clean precipitation bottle.
- The precipitation bottle (*as well as the bottle with the 200 ml acidic rinsing water*) is (*are*) put in separate double plastic bags and sent to the laboratory for analysis.
- **Also for periods without rain the empty bottles must be sent for cleaning.**
- The sampling bottle with screw cork is weighted to determine the precipitation amount.

- The funnel must regularly be sent to the laboratory for cleaning, the recommended frequency is every month. In the laboratory, the funnel is cleaned with 2% HNO₃.

Storage of equipment in the field should always be in plastic bags to prevent contamination and kept on as clean and dust-free place as possible. Especially it should be avoided to let the equipment be in contact with or close to metal surfaces as copper, zinc, aluminium etc. since these may often give off metallic dust.

The sampling procedures described above are similar for both wet-only and bulk collectors. However, when using bulk collector for snow sampling, the funnel is often full before the end of the sampling period. The station observer must therefore take the collector (both funnel and precipitation bottle) indoor whenever it is full, and close the funnel with a polyethylene lid. The lid must have been cleaned before use and it should be kept on during the entire melting process. While this sample is melting another collector and funnel is installed, and when the sampling period is finished, the samples are poured together in the last collector. Before pouring, the sample should be shaken to include possible solid residue. If the amount is too much, both collectors are sent to the laboratory. A major drawback of the bulk sampling approach is the likely reasons for contamination due to insects, bird droppings or other material in the sampling vessels. This is especially a problem for extended sampling periods. The risks of contamination are kept under control by using two or three parallel samplers. Contaminated samples can then be identified and discarded.

3.10.4 Conservation and filtering precipitation samples

3.10.4.1 Sample storage

Precipitation samples should be stored in the dark and refrigerated. A storage time up to 6 months can be acceptable providing that long time stability is checked. This includes the testing of blanks of samples stored for long time periods. However, to detect problems with contamination on an early stage, it is recommended to analyse as soon as possible after sampling.

After measuring the sampling volume by weighing the storage bottles, nitric acid should be added (this can also be added before sampling,). This can be done by adding one ml of suprapure concentrated nitric acid to each 100 ml precipitation. This will dissolve the metals that could be adsorbed to the walls of the container. The equipment used for this procedure must be carefully washed with 1% HNO₃ before use and plastic gloves must be worn. Acidified samples should be stored in the collection bottle for at least 24h before being transferred to acid cleaned storage bottles. The samples should be stored refrigerated (4°C) until analysis.

Filtering the samples should generally be avoided to prevent contamination; however it may be necessary for samples containing too much non-dissolved material, which is often the case for precipitation samples in South and Central Europe. Procedures for filtering are described in Chapter 3.10.4.2.

3.10.4.2 Filtration of precipitation

Acidify the collected precipitation in the sampling bottle as described in the section above. Equipment for vacuum filtration should be used. **All equipment used for filtration must be thoroughly cleaned in 2% HNO₃.** A cellulose acetate filter with 0.45 µm pore size (e.g. Sartorius, No. 1106-50-N) should be used. If sufficient amount of precipitation has been collected, filter about 20-50 ml of the sample to rinse the filter and discard the filtrate. Then filter 100 ml of the sample and transfer into an acid cleaned bottle for analysis. If less than 120 ml precipitation is collected, filter 20-50 ml 1% HNO₃ s.p. to rinse the filter and discard the filtrate. Then filter the collected precipitation and transfer into an acid cleaned bottle for analysis. Change filter and rinse the filtration flask with 1% HNO₃ s.p. between samples. Filtered blank samples should be prepared as a control for possible contamination during filtration.

3.10.5 Field blanks

Two extra sampling bottles are brought to the site; one containing about 100 ml diluted HNO₃ (or HCl for Hg sampling), pH 3 to 4, and one empty. After removing the regular sample bottle and washing the funnel as in the ordinary exchange procedure, the empty bottle is installed and the diluted acid is poured through the sampling device. The bottle is capped and brought to the laboratory for analysis. Field blank samples should be taken regularly, at least four times a year. If blank values exceed 20% of the concentration normally measured at the site measures should be taken to reduce the blanks (i.e. exchange or cleaning of sampling devices). The yearly average blank values are used to determine the detection limit and should be reported to CCC.

3.10.6 Measuring the influence of dry deposition

After a fixed period, i.e. one week without any rain, 100 ml diluted HNO₃ (or HCl for Hg sampling) are poured into the funnel and collected in the empty precipitation bottle. The bottled is disconnected and sent to the laboratory for analysis. The metal content will then indicate the importance of dry deposition. This type of field blank should be done regularly and especially important when a new station is installed, afterwards it should be done yearly. This exercise is especially important when considering the use of bulk collector for precipitation sampling.

3.10.7 Quality assurance

The low ambient concentration of trace elements will easily cause wrong measurements if strict precautions are not taken to prevent contamination and other sources of errors. The laboratories collecting trace element data for EMEP should therefore have a QA procedure, which is designed for their own sampling and analytical procedures. The QA procedures should among others include:

- **Field and analytical blanks.** Frequent use of field and laboratory blanks, which are important in order to discover weak part of the sampling, handling and analytical procedures. The blank results should also be used to correct the measurements when necessary. The detection limits for the methods need to be quantified, as three times the standard deviations of blanks.

- **Chemical blanks.** The chemicals used may themselves be a contamination source for some elements and have to be checked.
- **Cleaning.** Glassware and other materials used for storage of samples may both act as a source and a sink for some transition and heavy metal ions. Consequently, it is important to clean glassware and polyethylene equipment several times with dilute solutions of nitric acid followed by deionized water.
- **Gloves.** Plastic gloves must be used whenever working with the samples and sampling equipment.
- **Analytical intercomparison and reference material.** Interlaboratory exercises have to be a part of the measurement programme in order to ensure, as far as possible, a consistent data set. Certified Reference Material (CRM) of artificial precipitation samples and solid samples are available from various organisations, e.g. BCR, NIST and IAEA. Additionally the CCC will distribute samples, both of artificial precipitation and exposed filters. Once RMs certified for elemental composition of aerosol deposition on filters becomes available, they will be preferred.
- **Field intercomparison.** Field comparisons are especially important in the starting face of the measurement program to prevent erroneous data for a long time period. For example, it is important in the choice of using either a wet-only or bulk collector. In Scandinavia it has shown that the differences are small, but the situation might be very different in other parts of Europe.

3.10.8 References

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3.11 Sampling of heavy metals in particles

3.11.1 Introduction

The recommended sampling frequency for heavy metals in particles is weekly and is recommended to collect the PM₁₀ fraction. A cost efficient strategy may be to combine PM₁₀ measurements that also are part of EMEP's measurement program with particulate heavy metal sampling. However, since the PM₁₀ measurements are to be done on a daily frequency extracts should be combined into weekly samples to be analysed for heavy metals. Analysis on daily samples should be carried out during campaign studies. It is though important to realize that when collecting particles for heavy metal analysis it is necessary to take extra precautions to prevent contamination.

Either high- or low volume sampler may be used. The choice depends on the sampling period. For short sampling periods (daily) a high volume sampler is usually needed. With a high volume sampler it is possible to collect samples of 1600 m³ per 24 hours. Low volume samplers are in comparison in the range of 1-3 m³ per hour. The filter pack method, used for sampling of the main air components is a low volume sampler and can be used for heavy metal sampling if the sampling period is longer, i.e. weekly sampling. For clarification, many particle samplers that today are called low volume sampler have also been classified as medium volume sampler since they have been compared with the flow rate of absorption solution which has even slower rate.

Another important issue is which particle size should be sampled, fine (PM_{2.5}), coarse + fine (PM₁₀) or total particulate matter (TSP). Most of the high or low volume samplers provide the possibility to collect either total suspended particle matter or a fraction with a defined cut-off; which to prefer depends on the aim of the measurements. In order to obtain the best estimate of the deposition of heavy metals, a size distribution is preferred. However, several studies indicate that the mass distribution is different for the elements, and to obtain an informative size distribution there should be sampled 7-8 fractions. This is very expensive and for monitoring purposes it is generally sufficient to sample one fraction. Sampling of particles less than 10 µm will to a large extent contain the main fraction of long range transported heavy metals and it is recommended that this fraction is collected. A size distribution should be done at a few stations in Europe.

When collecting particles for heavy metal analysis it is necessary to take precautions to prevent contamination. All equipment used has to be cleaned carefully and gloves must be used whenever the filters are treated.

3.11.2 Sampling equipment

3.11.2.1 The air sampler

The same sampler as for PM₁₀ measurements described in 3.15 can be used.

In addition, low volume sampler for the filterpack system can be used. A general description of this sampling equipment is written in the Chapter [3.2](#) under sampling of the main components.

3.11.2.2 Filters

See general description under 3.15.3. It is strongly recommended to use either teflon or quartz filters for heavy metal sampling; however the teflon filters can not be used for high volume sampling with a prescribed flow, but may be used for low volume sampler. Glass filters do often have high blank values for certain elements. Teflon holders are recommended since they can be washed with acid before use and generally have low blank values. Quartz glass filters do have the advantage that they can be baked at 500°C prior use. Cellulose filters may be used as well; however, it must be checked whether the flow rate is maintained at given level.

All handling of filters should be made in a clean air facility (clean room or at least clean bench). Plastic gloves and acid washed utensils are necessary. All equipment should be stored in double plastic bags in a dust free environment. All parts that may be in contact with the filters should, if possible, be cleaned in nitric acid before the filters are inserted, and after exposure the filter should be stored in acid cleaned equipment.

3.11.3 Sampling procedure

In addition to the general siting criteria given in Chapter 2, it is important that the inlet is located far from any obstruction that might influence on the airflow, like building walls and trees etc. Some pumps have shown to give some dust containing copper. Air from the pump should therefore be transferred in a separate tube at least 10 metre from the filter intake.

The sampling procedures may be somewhat different from one air sampling system to another. Standard operating sampling procedures (SOP) should therefore be based on the sampler's operator manual. The procedure is also dependent on whether the filters need to be weighted for PM₁₀ measurements or not, see Chapter 3.1.

It is very important that the filters are stored within a plastic bag with zippers when it is transported between the laboratory and the field. One should also use tweezers made of not metallic material or covered with teflon when touching the filter. Never touch the filters with the fingers. After exposure the high volume filters are folded in two with the exposed side against each other, put in the plastic bag and sent to the laboratory for analysis. For low volume sampler the filter holder is sent to laboratory where it is dismounted.

Field reporting forms should always be put in a separate plastic bag in case of accidental leaks from precipitation samples, which may be contained in the same transportation box.

3.11.4 Field blanks

Field blanks should be taken regularly, at least every quarter a year. They should be handled similar as the other filters from the batch and given the same chemical treatment and analysis as the exposed filters. If blank values exceed 20% of the concentration normally measured at the site measures should be taken to reduce the blanks (i.e. exchange or cleaning of sampling devices). The yearly average

blank values are used to determine the detection limit and should be reported to CCC.

3.11.5 *Extraction from filters*

Filters used in high volume samplers should be cut into smaller pieces before extraction. The partition may be done by folding and cutting 1/4 or 1/8 of the filter using non-metallic tools. Another option is to use a well-defined form to cut a piece of e.g. 10% of the filter. The filter part is cut into smaller pieces and 6-7 ml of concentrated nitric acid is added to the filter in a teflon bomb. To extract particles from filters in a low volume sampler, the whole filter is included and 1.5 ml concentrated nitric acid is added to the bomb.

The bomb is kept at 150-170°C for 6-8 hours. The solution is cooled to room temperature and transferred to a 50 ml volumetric flask. If the analyses are to be performed using ICP-MS the internal standard is added to this solution and then diluted to the mark with distilled water. The solution should now contain 10% HNO₃.

3.11.6 *Filter blanks*

It is recommended that 5% randomly selected samples from each new batch of filters are analysed as laboratory filter blanks. The purpose of the filter blanks is to control the quality of the filters rather than to estimate the laboratory detection limit. Normally, the blank values should be sufficiently low that their values can be ignored. If high blank values are found a problem has occurred which has to be identified and solved, e.g. by using filters or chemicals from another batch, and by inspection of the routines in the laboratory.

3.11.7 *Calculation of results*

The flow volume is given in cubic feet per minutes (cfm) for some samplers, it should be given in cubic meter per hour.

$$1 \text{ foot}^3/\text{min} = 0.02832\text{m}^3 * 60 \text{ min/hour} = 1.698 \text{ m}^3/\text{h}.$$

When calculating airflow the average between start and stop flow is used. The total air volume in cubic meter is then given as:

$$\text{Total air volume} = \text{Average flow} * \text{total sampling time (h)}$$

The concentrations of the element in the air sample should be expressed in ng /m³; this is given by:

$$C = \frac{a \cdot v_{extr} - F_b}{v_{air}}$$

C is metal concentration in ng/m³
 a is concentration of the element in ng/ml
 v_{extr} is the extraction volume in ml

v_{air} is the air volume from the sampler, in cubic meter at approximately 20°C, and corrected for height from elevated sites.

F_b is average amount of metal in field blank (ng)

3.11.8 *Quality assurance*

See chapter [3.10.7](#).

3.12 Sampling of mercury in precipitation and air

3.12.1 Introduction

The availability of adequate techniques for the sampling and analysis of mercury in air and precipitation has grown during the last decade. Today, monitoring of mercury in air and precipitation is routinely done by a number of institutes throughout Europe and North America. From 1999, mercury has been part of the EMEP program; but at present, monitoring of the atmospheric content of mercury is carried out only at a minor number of EMEP stations.

Important anthropogenic sources of mercury are burning of fossil fuels, waste incineration plants and crematoriums.

Sampling of particulate phase mercury in air is one of the difficult steps in measurements of atmospheric mercury. This is mainly due to errors that may occur during both sampling and analysis. In ambient air the particulate fraction of mercury usually is less than 5%, with volatile mercury making up the remainder. This increases the risk of gas to particle conversion during sampling. For this reason, sampling and analysis of particulate phase mercury should be considered as an operationally defined method. The presence of particulate mercury in air will greatly influence the overall atmospheric deposition of mercury and further development of these techniques is highly desirable, and is needed before any recommended procedure can be given.

We are very grateful to OSPARCOM and John Munthe at IVL to allow us to use their guidelines on sampling and analysis of mercury. The text is with minor changes taken from their report (Munthe, 1996; OSPAR, 1997).

3.12.2 Sampling methods for mercury in precipitation

3.12.2.1 Sampler design and materials

Mercury is collected in special precipitation samplers. Two alternative materials may be used for funnels and collection bottles: borosilicate glass and a halocarbon such as Teflon or PFA. Borosilicate glass is often preferred due to lower costs and general availability. Quartz glass may also be used but is generally avoided due to high costs.

Precipitation can be sampled using either wide-mouthed jars or funnels and bottles. The sampling vessels can be bulk samplers which are open at all times or wet-only samplers which are open only during precipitation events. For monitoring purposes, bulk sampling using funnels and bottles is normally adequate (Iverfeldt, 1991a,b; Jensen and Iverfeldt, 1994). Wet-only samplers are used by the German national monitoring programme as well as by research groups working in the Great Lakes area (Landis and Keeler, 1996) and in the US National Atmospheric Deposition Programme (Vermette et al., 1995). Wet-only samplers have the advantage that they avoid particle dry deposition, although the contribution of gaseous or particulate mercury species to the wet deposition fluxes in non-industrialised or non-urban areas is probably not large (Iverfeldt and Sjöberg, 1992; Iverfeldt and Munthe, 1993).

For extended sampling periods it is necessary to prevent the diffusion of Hg^0 into the precipitation sample collected, since it could contribute to the mercury content of the sample via oxidation to water-soluble forms. This can be done easily by using a capillary tube between the funnel and the bottle. It is also necessary to shield the sample bottles from light to avoid photo-induced reduction of the mercury in the precipitation sample.

Samplers should be designed for sampling during all seasons and all climatic conditions. Thus a heating device should be included for melting snow and to prevent the formation of ice in the funnel and bottles during winter and, depending on climatic conditions, it may be useful to cool the samples in locations where high temperatures are expected during summer. Funnel area and bottle sizes should be modified to suit the sampling period used.

The bulk sampler design used in the Swedish national monitoring program for mercury is shown in Figure 3.13.1.

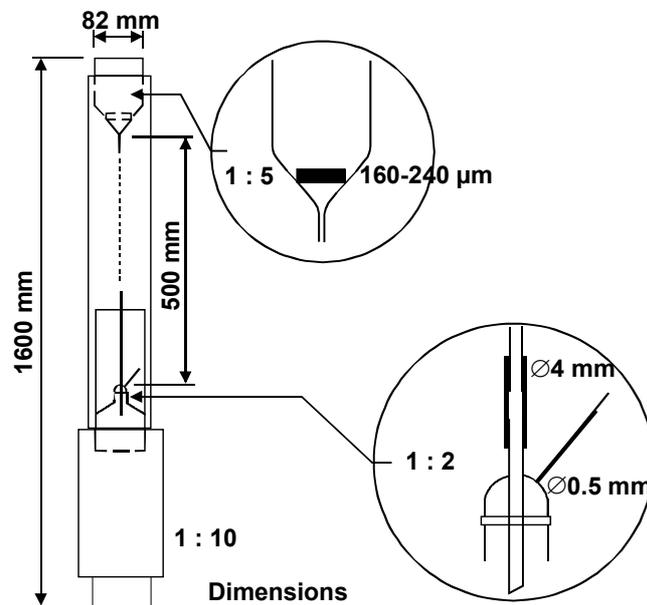


Figure 3.4: Schematic of bulk sampler for sampling of precipitation for mercury analysis from IVL-Gothenburg.

In the air pollution network of the German Federal Environmental Agency (Umweltbundesamt) a commercially available automatic (wet-only) precipitation collector (type: ARS 721) is used for mercury (Bieber, 1995). The funnel of this sampler is made of borosilicate glass while the collection bottle is made of halocarbon polymer (PFA) and has a heating system with a thermostat.

3.12.2.2 Washing procedure for glass equipment

All glass equipment used for sampling or for storing water samples for mercury analysis must be cleaned extensively before use. The glassware is washed extensively according to the following procedure.

Plastic gloves should be used during all steps of the washing procedure. Glassware that is not being leached in tanks should always be stored in double plastic bags.

1. Leach in an alkaline detergent for 24 hours. Rinse thoroughly with de-ionised water.
2. Leach in a solution of HNO₃ (Puriss): de-ionised water (1:3) for 7 days. This should be done in a polyethylene tank placed under a fume hood. Rinse thoroughly with de-ionised water.
3. Leach in a 0,1 M solution of HNO₃ (P.A.) in high-purity water (e.g. Milli-Q) for 7 days. Rinse thoroughly with de-ionised water.
4. Fill bottles with high purity water. Add 5 ml/l BrCl solution. Leave to stand for at least 24 hours.
5. Add 5 ml/l 12% NH₂OH·HCl. Leave to stand for 1 hour.
6. Pour out the above solution. Rinse with large amounts of de-ionised water followed by large amounts of high-purity water.
7. Add 2,5 ml 30% HCl (Suprapur) to the bulk sampler bottles (0,5 l borosilicate glass) All other bottles and containers should be filled with 5 ml/l 30% HCl (Suprapur). Other glassware should be air-dried in a clean zone.

Bottles that are believed to be contaminated are baked at 500°C for 5 hours and then washed according to the procedure above, but excluding step 1.

This procedure is generally sufficient for containers used for the sampling and analysis of precipitation. After analysing samples with extremely low concentrations of mercury the BrCl treatment steps according to steps 4-6 above is generally sufficient.

3.12.2.3 Sampling procedure

All samples and replacement sample bottles should be handled with care in order to avoid contamination during transport and storage. Sample bottles should only be handled using plastic gloves and all bottles should be kept in double plastic bags during transport and storage.

Before sending the precipitation bottle to the field they should be filled with 5 ml/L concentrated HCl. One should therefore be extra careful when handling these bottles.

The following procedure is recommended for bulk samplers of the design seen in Figure 3.13.1. For alternative sampling devices, this procedure can be adapted.

1. Bring a new collection bottle, plastic bags and container (squeeze bottle) with high purity water to the sampler. All equipment needed for the bottle exchange should be placed on a plastic cover either on the ground or available surface.
2. Remove outer plastic tube

3. Open double bags of the new collection bottle (but leave the bottle in the bags).
4. Carefully remove the ground glass joint connecting the bottle to the capillary. Use both hands, one for loosening the glass fitting the other for holding the funnel.
5. Remove the stopper from the new collection bottle and close the bottle containing the precipitation sample. This bottle is then put in double plastic bags.
6. Without mounting the new bottle, rinse the funnel and capillary with high purity water. If visible materials (dust, insect etc.) are present, disconnect the funnel from the capillary and rinse separately. New plastic gloves should be used if handling the watch glass or touching the inside of the funnel is necessary. If the funnel and capillary are visibly dirty even after rinsing, they must be exchanged with newly washed pieces.
7. Remove the new collection bottle from the plastic bags and place in the plastic casing. Connect the ground glass fitting and check all connections. Make sure that all connections are without gaps where the silicon tubing is exposed to the precipitation sample unnecessarily.
8. Replace outer plastic tube.

Samples for storage must be refrigerated and kept in the dark. They may be stored up to 6 months provided that the long-term stability is checked. This includes the testing of sample blanks stored for corresponding periods.

A critical step when evaluating wet deposition of mercury is the availability of correct data on precipitation amounts. Different sampler designs have different precipitation sampling efficiencies and this may lead to incomparable results when calculating the wet deposition of mercury, even if the analysis are harmonised. For all techniques, a parallel measurement of precipitation amounts should be made in order to identify discrepancies. A standard rain gauge should be used in parallel with the sampling equipment for mercury and the WMO recommendations should be followed. If systematic errors are found, the sampler design should be reconsidered.

3.12.2.4 *Quality control – Quality assurance*

Written instructions for personnel carrying out the sampling are necessary to avoid contamination. All routine handling of samples and sampling equipment should take place according to specified procedures. Furthermore, replacement parts should be easily available so that glassware can be exchanged if contamination is suspected.

The risks of contamination when using bulk samplers and extended sampling times are controlled by using two or three samplers in parallel. Contaminated samples can then be identified and discarded and the corresponding data excluded.

3.12.2.5 *Field blanks*

Field blanks should be taken at least four times each year.

Two extra sampling bottles should be brought to the site; one containing dilute HCl (pH 3 to 4) and one empty. After removing the regular sample bottle the empty bottle should be installed and the dilute HCl poured through the sampling device (*e.g.* funnel and capillary). The bottle should be stoppered, double bagged and brought to the laboratory for analysis. The mercury content of the dilute HCl should be compared to that of samples stored in a clean laboratory environment. If the blank values exceed 20% of the concentrations normally measured at the site, measures should be taken to reduce the blanks (for example, by exchanging or by cleaning the sampling devices).

The yearly average blank value is used to determine the detection limit and should be reported to CCC.

3.12.2.6 *Special problems*

When first starting to sample precipitation for mercury analysis numerous problems can arise, mostly associated with high blanks. Weekly sampling should be undertaken initially, even if monthly sampling is planned. In this way the number of sampling periods without results can be reduced.

The most common causes of sample contamination are insects, bird droppings or other material in the sampling vessels. This is the major drawback to bulk sampling. In areas with large numbers of birds in the vicinity, it may be necessary to install devices preventing birds from perching on the samplers.

Using two or three samplers in parallel controls the risks of contamination when using extended sampling periods. Contaminated samples can then be identified and the results discarded thus minimising the loss of information. Contamination of two samplers in parallel is very rare.

When temperatures are high, it may be necessary to cool the sample bottle to prevent the evaporation of mercury from the sample.

3.12.2.7 *Summary*

	Recommendation	Acceptable alternative
Material	Borosilicate glass.	Halocarbon materials, quartz.
Sampler design	Bulk samplers or wet-only samplers with gaseous Hg prevention and light shield. Heating and/or cooling of sample bottle depending on climatic conditions.	Event sampling using funnels and bottles or jars.
Sampling time	1 week to 1 month.	
Preservation of samples	Monthly sampling 5 ml/l HCl (Suprapur) prior to sampling.	Adding 10 ml/l HCl after sampling in sampling periods of <2 weeks and samples are cooled if necessary.
QA/QC	Field blanks. Written instructions for field personnel.	

3.12.3 *Sampling methods for total gaseous mercury in air*

3.12.3.1 *Sampler design and cleaning procedure*

The sampling of total gaseous mercury (TGM) in air is usually done using gold traps with gas meters or mass flow controllers for air volume measurements. During the last few years, automated instruments for the sampling and analysis of mercury in air have been made available. The automated method applies the same basic principles as the manual method and has been shown to generate comparable results (Schroeder et al., 1995; Ebinghaus et al., 1999).

Gold traps comprise 10-12 cm quartz glass tubes filled with gold adsorbent. The gold adsorbent can either be small pieces (1-2 mm) of 1 mm solid gold wire mixed with a crushed-quartz glass bearer or, alternatively, sand, glass beads or quartz glass coated with a thin layer of gold. The latter trap type usually generates lower blank values.

The gaseous mercury collected with the gold trap in the field is transferred by heating to a calibrated Au trap, using Hg-free argon with a purity of >99.998% (at a flow rate of 30 ml/min) as the carrier gas. This is known as the dual amalgamation technique. The sampling and transfer lines are made of Teflon tubing. Glass to glass connections (i.e. between the sampling trap and the analytical trap) are made with silicone tubing. The inlet filter is a quartz tube 75 mm in length (with an inner diameter of 4 mm and an outer diameter of 6 mm) with a quartz wool plug 15 mm in length. A brief summary of the equipment and cleaning procedure is as follows:

- material: glass, quartz, Teflon
- heating device: e.g. Perkin Elmer Part No. 102961 with a variable transformer
- cleaning procedure for the field trap: thermal desorption at 500°C for three minutes while purging with a Hg-free argon stream at a flow rate of 30 ml/min (three consecutive times)
- cleaning procedure for the analytical trap: thermal desorption at 800°C for 25 seconds while purging with a Hg-free argon stream at a flow rate of 30 ml/min (two consecutive times)
- cleaning procedure for the inlet filter: thermal desorption at 1200°C for 1.5 minutes while purging with an air-stream of 30 ml/min (three consecutive times)
- argon: > 99.998 Vol.% (Producer: e.g. Messer Griesheim)
- pump: automatic Dräger gas detector pump (“Quantimeter 1000”). One stroke volume = $100 \pm 5 \text{ cm}^3$.

3.12.3.2 *Sampling procedure*

The sampling of total gaseous mercury in air is relatively straightforward and without major difficulties. The site should be chosen with great care to avoid contamination or non-representative results. Sampling should be performed >1.5 m above the ground or other surfaces (walls *etc.*) in order to avoid the

influence of local fluxes. The sampling system contains 1 protective quartz wool plug followed by 2 gold traps in series.

The analytical method for sampling total gaseous mercury (including elemental, organic and inorganic mercury) is based on the amalgamation of mercury with gold. Total gaseous mercury is collected on the surface of the gold. For sample collection two of these traps are placed in series. With this arrangement a breakthrough of mercury is detected with a significant mercury amount on the second trap.

The sampling time and air volumes should be sufficient to collect enough mercury for analysis but not so large as to cause a breakthrough of mercury. Sampling flow rates in the range 0,1-0,5 l/min up to a maximum volume of 100-1000 litres is normally adequate.

The general configuration for the set-up of the sampling system for total gaseous mercury in air:

- One quartz wool plug followed by two field traps in series
- sampling flow: 0,100-0,500 ml/min
- sampling time: 12-24 hours (for TGM concentration in the range of 1-10 ng/m³)

3.12.3.3 Sample storage

Field traps should be exchanged according to a fixed procedure taking great care to avoid contamination. Before and after sampling the ends of the traps are closed with plastic caps and the traps are stored in a firmly closed glass bottle. To prevent contamination during storage 1 g of silver wool should be kept in the bottle to bind gaseous mercury diffusing into the storage vessel.

3.12.3.4 Volume standardisation

To convert the sample volume to a volume with standard conditions (0°C and 1 atm or 273.16°K and 1013.25 mB) it is necessary to multiply the pump volume with correction factors (calculated from the Ideal Gas Law).

$$V (\text{Std.}) = V (\text{current}) * 273.16 \text{ K/T (inlet) and } V (\text{Std.}) = V (\text{current}) * P (\text{inlet}) / 1013.25 \text{ mB.}$$

3.12.3.5 Quality control - Quality assurance

The necessary quality control steps are primarily associated with gold trap collection and analytical instrument reliability. All gold traps must be individually calibrated at regular intervals. This is most conveniently done using a source of gaseous mercury, *i.e.* a thermostated vessel containing liquid mercury from which gaseous samples can be drawn with a gas tight syringe. Gold traps with low recovery must be discarded.

Alternative methods for sampling mercury in air are not generally available. Commercially available iodated carbon traps have, however, been successfully used for sampling over extended periods, *i.e.* days (Bloom *et al.*, 1995).

3.12.3.6 *Special problems*

Under certain conditions, breakthrough of mercury can occur at air volumes considerably smaller than those recommended above. This is usually due to the presence of trace constituents in the air which block the gold surface. Possible contaminants are sulphur-containing volatile organic compounds and volatile inorganic species capable of forming solid salts on the gold surface via atmospheric reactions (*e.g.* $(\text{NH}_4)_2\text{SO}_4$). If this happens, considerably smaller sampling volumes should be used, *i.e.* <100 litres.

When using automated systems frequent re-calibration is necessary and this frequency will vary according to the temporal resolution of the sampling. Daily re-calibration is a minimum.

3.12.3.7 *Summary*

	Recommendation	Acceptable alternative
Material	Solid gold traps.	Coated gold traps.
Sampling design	1 protective quartz wool plug followed by 2 gold traps in series.	Teflon filter or quartz fibre filter followed by 2 gold traps in series.
Air flow rate	200 to 500 ml/min.	
Sample volume	100 to 800 litres.	
QA/QC	2 gold traps in series to check mercury breakthrough.	

3.12.4 *Intercomparisons*

Within any monitoring network where data are reported from different institutes, regular intercomparisons are necessary. The intercomparisons should be performed for all steps in the measurement procedure. The recently completed intercomparisons on the sampling and analysis of heavy metals organised by Umweltbundesamt in Germany together with EMEP/CCC, HELCOM, PARCOM and AMAP, is a good example of a successfully managed exercise with encouraging results (Winkler and Roeder, 1997).

In 1991 an intercomparison exercise for mercury deposition was held at Rörvik, Sweden (Iverfeldt and Sjöberg, 1992). The conclusions from that exercise was that the measured fluxes varied within a factor of 2 to 4 which was explained as systematic errors in the methods used by several of the participants. More encouraging results were found in the Mace Head intercomparison in 1995 (Ebinghaus *et al.*, 1999) where relatively good agreement between different methods for measurements of mercury in air and precipitation were obtained.

3.12.5 Commercial supply

The equipment list below shows examples of known good samplers. However there might be several others excellent products on the market, but if used they must anyhow also have been proven to give comparable and reliable results.

Sampler	Name	Manufacture	Materials
Wet only	MDN 1 sampler modified Aerochem Metric sampler used in US-NADP		Double system: glass funnel, glass capillary and bottle for Hg sampling the other PE or Teflon funnel and bottle for trace metals
	ARS 721	Eigenbrodt http://www.eigenbrodt.de/	Borosilicate glass funnel, PFA bottle, heating
Bulk	NSA 181 KD	Eigenbrodt http://www.eigenbrodt.de/	Quartz glass funnel, teflon tube teflon bottles, heating and cooling
	IVL and WDNR – modified IVL	IVL, P.O.Box 47086 S-402 58 Gothenburg Sweden http://www.ivl.se/	Borosilicate glass funnel, glass filter, capillary tube and glass bottle, heating in the modified version
	GKSS	International bureau of GKSS, Germany http://www.gkss.de/	Teflon funnel, brown glass bottle
Hg(g) sampler	Gold traps	Brooks Rand, US http://www.brooksrand.com/	
Hg-monitor For Hg (g)	Tekran 2537A	Tekran Inc, Toronto, Canada http://www.tekran.com/	Automatic, 5 min time resolution
Automated water Analysis systems	P.S. Analytical	P.S. Analytical, Kent, UK, http://www.psanalytical.com	
	Perkin Elmer	http://instruments.perkinelmer.com/index.asp	
	Tekran 2600	Tekran Inc, Toronto, Canada http://www.tekran.com/	
Detectors	P.S. Analytical	P.S. Analytical, Kent, UK, http://www.psanalytical.com	CV-AFS
	Tekran 2500	Tekran Inc, Toronto, Canada http://www.tekran.com/	CV-AFS

3.12.6 References

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3.13 Sampling of persistent organic pollutants pesticides and PCBs

3.13.1 Principle

This method covers the following groups of components:

Chlororganic pesticides:

- α -, β -, and γ -HCH
- HCB
- Chlordanes (including acid labile components)
- DDTs
- The Dieldrin group
- Trifluraline
- α -Endosulphane

Polychlorinated biphenyls,

- PCB

These components may be determined in air samples. The air samples can be collected with an air sampler with a particle filter followed by two PUF plugs. Filter and PUF plugs are extracted separately with a hexane/diethylether 9:1 mixture in a soxhlet extractor.

The extracts are concentrated and then cleaned by using adsorption chromatography (silica). After the concentration to the appropriate volume and addition of the recovery standard the components are separated and quantified by using gas chromatography combined with mass spectrometry (MS), see the chemical analysis chapter 4. 1x

3.13.2 Equipment for air sampling

Materials and equipment of similar or better performance or quality from other manufacturers may be used.

- Aluminium foil
- Glass fibre filter type A/E 142 mm diameter, Gelman no. 61635. Cleaning, see section 2.6.2
- Disposable gloves of polyethylene
- Tweezers
- Zip shut plastic bags
- Polyurethane foam plugs (PUF plugs), 11 cm x 5 cm (diam. X h.), density 25 kg/m³, (Ekornes industries). Cleaning see section 2.6.2.
- PUF air sampler

NILU PUF (polyurethane foam) sampler consists of a glass cylinder (10 cm i.d.) supplied with a filter holder in one end. The other end is connected to a Siemens ELMO vacuum pump 2BH5 via an adapter and tube. The PUF sampling unit is outlined in Figure 3.13.1.

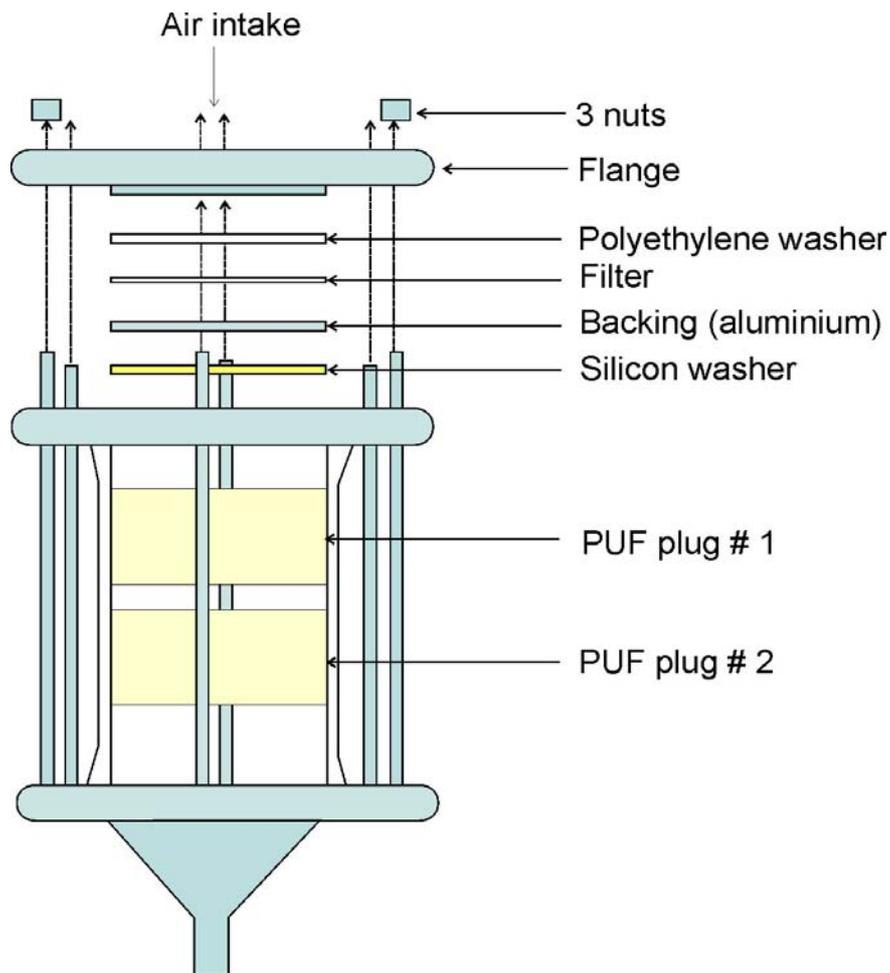


Figure 3.13.1: The PUF sampling unit.

3.13.3 Sampling procedure

Inserting unexposed filter and PUF plugs and starting sampling:

- Put on a pair of disposable gloves.
- Insert PUF plug # 2.
- Insert PUF plug # 1. Make certain that the plugs are not bent and have an even and smooth contact with the glass walls of the sampling unit.
- Insert the silicon washer.
- Mount the backing using a pair of tweezers.
- Insert the filter using a pair of tweezers.
- Insert the polyethylene washer.
- Mount the flange and tighten the three nuts.
- Start the pump.
- Adjust the airflow with the false air valve until the correct flow is obtained. Please note; the airflow decreases considerably during the first half hour (approximately) until the pump's working temperature is reached and stable conditions obtained. The airflow should then be increased until the correct flow again is reached.
- Record date, time, flow, and underpressure in the instrument logbook.

Stopping sampling and removing exposed filter and PUF plugs:

- Record date, time, flow, and underpressure in the instrument logbook.
- Stop the pump
- Loosen the three nuts and remove the flange.
- Remove the polyethylene washer using tweezers.
- Remove the filter. Fold the exposed filter over itself, exposed side against exposed side, wrap the filter in aluminium foil.
- Remove the backing with tweezers.
- Remove the silicon washer.
- Put on a pair of disposable gloves, remove PUF plug # 1 and wrap it in aluminium foil. Mark the foil “# 1”.
- Remove plug # 2 the same way and mark the aluminium foil ”# 2”.
- Filter and PUF plugs are placed in a plastic bag with zipper.

Please note: All handling of PUF plugs must be with disposable gloves. Exposed plugs and filters must be put in a freezer once the sampling is finished.

3.13.4 Weighing filters

If the weight of particles on the filter is to be determined, the filter must be weighed before and after sampling.

In this case the filter should be conditioned for 24 hours in a room where temperature and humidity are kept constant before sampling. The filter should be unwrapped from its aluminium foil, which can be used as a bed during weighing. The filter should be wrapped in the same foil after the weighing. When volatile substances such as HCH and HCB are measured, the filter must be weighed after a well-defined period, i.e. ½ to 1 hour in the conditioned room.

3.13.5 Extracting samples

After exposure the glass fibre filter containing the particle fraction of the sample is transferred to a 100 ml soxhlet extractor with 250-300 ml 10% diethyl ether/hexane mixture and an internal standard. The filter is extracted for 6-8 hours.

The PUF plugs are put into a 250 ml soxhlet extractor. This extractor should be mounted on the flask containing the particle extract and extracted for another 6-8 hours.

The filter and the PUF plugs may also be extracted independently in order to quantify the distribution between gas and particle phase. In this case the internal standard should be added to both extractors.

Na₂SO₄ is added to the extract in order to remove water before further treatment of the samples. When samples are considered to be “wet”, they should be extracted for 3 hours with acetone, followed by an extraction with diethyl ether/hexane. These extracts should be combined, dried with Na₂SO₄, and the volume reduced to 0.5 ml. The amount internal standard to be added depends on the concentration expected in the sample.

Keeper, 20 µl nonane should be added to the extract before evaporation to 0.5 ml with a TurboVap 500. Use “A” or “B” speed and 35°C water temperature. The sample is now ready for clean-up as described in the next section.

3.13.6 Cleaning of equipment

3.13.6.1 Cleaning of the sampler

The sampler is disassembled and glass, metal parts and gaskets are washed using lab detergent (RBS 25) diluted with warm water. The parts, except the gaskets, rinsed well with warm water, thereafter with distilled water and finally with acetone. The gaskets are rinsed well with warm water and distilled water, ***not with acetone.***

3.13.6.2 Cleaning of PUF-plugs

8 new plugs are put in a 2000 ml soxhlet extractor and extracted with toluene (24 h), acetone (8 h) and with toluene (8 h). Plugs, which have been previously extracted after sampling, are cleaned using soxhlet extraction with acetone (8 h) and toluene (8 h). After extraction the bulk of the solvent is removed by squeezing the plugs using solvent resistant lab gloves. The plugs are put in a desiccator placed in an oven and dried at 60°C under vacuum (100–200 mbar). Following drying the plugs are wrapped individually in aluminium foil. Pairs of plugs are stored in a zip-shut plastic bag together with a glass fibre filter (see below). Storage time should not exceed 6 months. Expiry date is written on a label on the plastic bag and batch number is written in a logbook kept in the cleaning laboratory. A sampling form is put in each plastic bag.

Toluene used in the third cleaning step for cleaning new plugs may be used later in the first cleaning step in order to reduce solvent consumption.

Glass fibre filters are heated in an oven to 450 °C (8 h). After cooling they are wrapped individually in aluminium foil. Storage time should not exceed 6 months.

3.13.6.3 Cleaning of glass equipment

All glass equipment used for sampling and/or analysis of air, water, deposition, sediment and biological samples must be colour coded in order to separate it from equipment used for samples containing high levels. After use the glass equipment is put in a 2.5% (v/v) water dilution of the lab detergent RBS (16 h). Thereafter it is rinsed 10 times with warm tap water and twice with de-ionised water. Finally the equipment is dried and cleaned in an oven at 450°C (6 h). All glass equipment is rinsed with n-hexane before it is used.

3.13.6.4 Cleaning of other equipment

Tweezers used for handling filters and PUF plugs are rinsed well with n-hexane.

3.14 Sampling of polycyclic aromatic hydrocarbons (PAH) in air

3.14.1 Principle

Sampling is performed using a high volume sampler. Particle bound polycyclic aromatic hydrocarbons (PAHs) are collected on a glass fibre filter, and more volatile PAHs are adsorbed to plugs of polyurethane foam (PUF) placed behind the filter. The filter and the plugs are Soxhlet extracted with cyclohexane after sampling. The pre-concentrated extracts are cleaned using liquid/liquid extraction and HPLC before analysis using high-resolution gas chromatography combined with mass spectrometry (GC/MS).

3.14.2 Sampling equipment and instruments

Sampler: NILU's PUF-High-volume sampler (see [3.13.2](#))

Pump: Siemens ELMO-vacuum pump 2BH5

Glass fibre filter: Type A/E, 142 mm, Gelman no. 61635 (cleaned)

PUF-plugs: 11 x 5 cm (diam. x h), density 25 kg/m³, white type (cleaned)

PUF may be replaced with XAD-2.

Aluminium foil

Plastic gloves

Tweezers

XAD-2, polystyrene divinylbenzene co-polymer, 0.3-0.85 mm particle size

Similar or better qualities from other manufacturers may be used. For sampling also Sierra, Anderson or similar high volume samplers may be used.

3.14.3 Cleaning of equipment

3.14.3.1 Glass equipment

All glass equipment must be decontaminated before use. Leave the equipment in 2.5% RBS in water for 16 hours. Flush well with hot tap water followed by MilliQ water. Leave to dry on a clean surface.

3.14.3.2 Glass fibre filter

Put ca 50 filters (Gelman-Type A/E, 142 mm) on an Al-foil and heat to 450°C for 8 hours. After cooling to room temperature wrap each filter in Al-foil.

3.14.3.3 Extraction timbles

Extract timbles for 8 hours ("1 day") with cyclohexane in a 600 ml Soxhlet extractor. Dry in a desiccator connected to a vacuum pump (capacity 2.4 m³/h, and 80 kPa (0.8 bar) at 100°C. Connect pump outlet to a cooler to condense solvent. Wrap dry timbles in Al-foil.

3.14.3.4 Sampler

Dismantle the sampler. Wash glass, metal parts and gaskets with warm detergent (2.5% RBS 25 in water). Flush all parts except the gaskets, with warm water, distilled water and acetone. Flush the gaskets with warm water, distilled water, *not acetone*.

3.14.3.5 PUF-plugs

Toluene

Clean new PUF-plugs with toluene (Merck no. 8389) in a 2000 ml soxhlet extractor. The extractor can take up to 8 plugs simultaneously. Use a 3000 ml round bottomed flask and fill toluene into the extractor until it empties the content into the round bottomed flask. Add ca. 500 ml toluene and mount the lid and cooler. Turn on the heater and the **cooling water**. Extract the plugs for 24 hours.

Acetone, cyclohexane

Squeeze toluene out of the plugs (solvent resistant gloves!) and transfer the plugs to another 2000 ml soxhlet extractor. Acetone is added as prescribed for toluene and the plugs are extracted for 8 hours.

Finally, extract with cyclohexane (new extractor) for 8 hours.

Observe! Used plugs (which previously have passed through the whole cleaning procedure, toluene included) can be cleaned as follows:

- 1) Soxhlet extraction with acetone for 8 h
- 2) Soxhlet extraction with cyclohexane for 8 h

Drying

After final extraction squeeze the cyclohexane out of the plugs. Place the plugs in a desiccator. Put the desiccator in an oven at 60°C, and connect desiccator to a vacuum pump. Dry for 16 hrs and wrap the plugs in Al-foil individually. Store pairs of plugs and a filter in zip-shut plastic bags.

3.14.3.6 XAD-2

Fill XAD-2 in a tumbler and put it in a soxhlet extractor. Extract for 8 h with each of the following solvents: Methanol, acetonitrile and diethyl ether. Leave the wet adsorbent on an Al-foil in a fume hood until it appears dry. Dry in an oven at 35°C overnight.

3.14.4 Sampling

NILU's high volume sampler consists of a glass cylinder (10 cm diam.) with a filter holder at one end. The other end is connected to a Siemens vacuum pump with a hose. Before starting sampling it is important that the plugs fit firmly to the glass wall without forming channels

See chapter [3.13.3](#) for the sampling procedure using the NILU PUF sampler.

All new samples are stored in a freezer until extraction.

For the most volatile PAHs, especially the bicyclic compounds, "break-trough" will occur at high air temperature and/or long sampling time. At sampling times longer than 6 h and temperature 20 °C (or higher) a break-trough will normally occur for the bicyclic PAHs, and these should not be reported with accreditation.

For sampling XAD-2 may be used instead of PUF.

3.14.5 Weighing filters

If the amount of particles in the sample is to be determined, the filter must be weighed before and after sampling. Condition the filter for 24 h at constant temperature and humidity before weighing.

3.14.6 Extraction

Fold the filter over twice and cut the rim with a scissors cleaned with cyclohexane. Transfer the filter to a timple (28 x 80 mm), in a 60 ml soxhlet extractor. Add internal standard directly to the filter using a 10, 20, 50 µl or 100 µl syringe or micropipette. Use 100 ml cyclohexane in a 250 ml round bottomed flask for the filter extraction.

Transfer the two PUF plugs to a 500 ml extractor, add internal standard, extract with 500 ml cyclohexane and use a 1000 ml round bottomed flask. Extract filter and plugs for 8 h (1 day).

If only the total PAH content in the sample is wanted, the whole amount of internal standard is added to the filter. Use 500 ml cyclohexane and a 1000 ml round bottomed flask for the extraction. After the filter extraction, remove the 60 ml extractor and replace with a 500 ml extractor containing the plugs. Continue the extraction without further addition of internal standard.

After the extraction, transfer the solvent in the extractor to the flask.

If the filter and plugs are to be analysed separately, the extracts must be cleaned separately. The extract is pre-concentrated before clean-up.

Extraction of XAD-2 is done using cyclohexane in a soxhlet extractor for 8 h. XAD-2 is transferred to a timple of suitable size and internal standard is added before the extraction is started.

3.14.7 Pre-concentration

Pre-concentration is normally performed using a TurboVap pre-concentration system. This system has an automatic stop at a final sample volume of 0.5 ml. Manual control must be made to stop the pre-concentration at 4 ml.

3.15 Measurement of PM₁₀ particles

3.15.1 Introduction

The Interlaken workshop in 1999 (EMEP, 2000) made a series of recommendations for measurements of particulate matter, and the first TFMM meeting in Vienna October 2000 built further on these conclusions and recommended a measurement program. This first TFMM meeting stressed the need for PM₁₀ measurements with a view to the current legislation in the European Union. The manual was adopted at the third TFMM meeting in Geneva 2002.

More measurement data within EMEP for assessment of the long-range transported part of the aerosol particulate mass in Europe are needed. This includes measurement of particulate mass, preferably determined according to EN 12341 (CEN, 1998), the reference method defined in EU Directive 1999/30/EC. In addition chemical characterisation and speciation of the particulate material is also highly desirable. Methods that give the added advantage of determining the chemical components in the sample are therefore recommended. The sampling period should be 24 hours and the samples should be changed daily together with the other sampling devices.

3.15.2 Sampling equipment

Different methods for the determination of aerosol particle mass have been extensively tested and compared (WHO, 1999; Guidance Document, 2001). Since different methods may give rise to systematic differences in the results, standardisation is necessary as specified by the European Union and the European Standards Organisation

EN 12341 specifies three reference methods for determination of PM₁₀. Two of these, the high- and low-volume samplers, may be used at EMEP sites to obtain daily samples for weighing and subsequent chemical analyses. EN 12341 also gives detailed instructions with respect to comparisons, which are required to show that alternative samplers are equivalent to the reference methods for determination of PM₁₀. These requirements are particularly relevant at sites where suspended dust and coarse particles form a major part of the airborne particulate matter. At many EMEP sites, however, particles < 2.5 µm may account for a large part of the total aerosol mass.

Direct recording instruments can be used if they have been shown to provide consistent results compared with gravimetric methods. They should be compared according to the CEN standard, preferably at the EMEP site and during all seasons and then used with possibly a correction factor. There are also instruments providing both gravimetric and online data measurements, which may be used if proven to give equivalent result to the standard. Monitoring with heated filters and/or inlets have a negative bias due to removal of water contained in the aerosol particles as well as evaporation of ammonium nitrate and semi-volatile organic compounds causing significant weight loss depending on season and location. It is difficult to avoid this problem even for standard gravimetric instruments where also losses of e.g. ammonium nitrate and semi-volatile organic compounds may occur during sampling and when filters are conditioned at constant RH and

temperature. But to minimize evaporation artefacts it is recommended to use monitoring instruments with unheated inlets and/or filters.

One example of instrument, which is in accordance with CEN standard (1998) for PM_{10} measurements, is the high volume sampler Sierra-Andersen/GMW model 1200 seen in Figure 3.15.1.

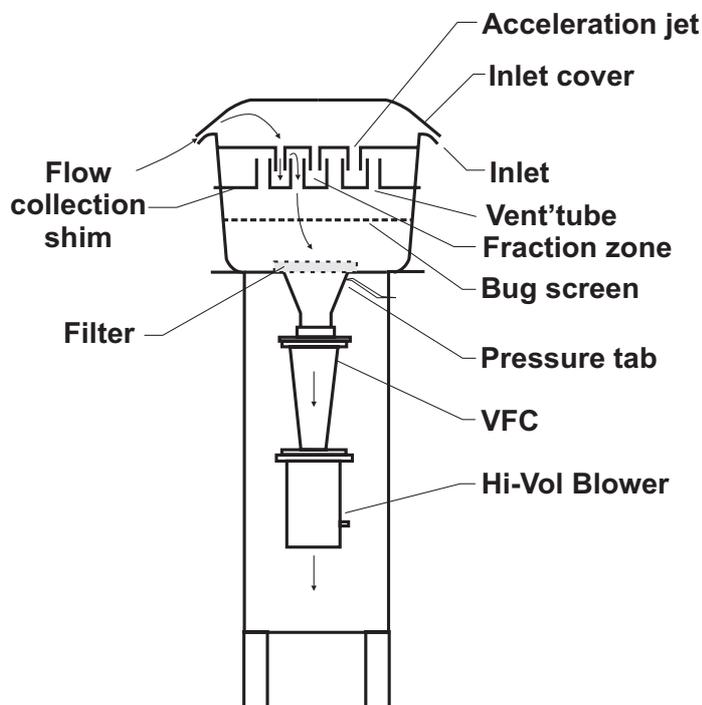


Figure 3.15.1: Schematic diagram of Sierra-Andersen/GMW Model 12000 with a volumetric flow controller (VFC).

3.15.2.1 Impactor inlet

Without any special intake (hood) of the high volume sampler the upper cut is between 50-100 μm , termed as total suspended particle matter (TSP). An intake hood should be connected to collect particles of defined size (PM_{10}); in practice this requires an impactor stage with a 50% cut-off at 10 μm a.e.d. When ambient air is drawn into the inlet, the acceleration nozzles fractionate particles larger than 10 μm , which are impacted onto a greased collection shim. The air containing the PM_{10} particle fraction is channelled through to the filter holder. The flow rate is critical to maintain the PM_{10} cut point and when using the standard impactor dimension, following the criteria for the CEN standard (EN 12341:1998), a constant flow rate of 68 m^3/h (1133 l/min) is needed for a high volume sampler and 2.3 m^3/h (38 l/min) for a low volume sampler.

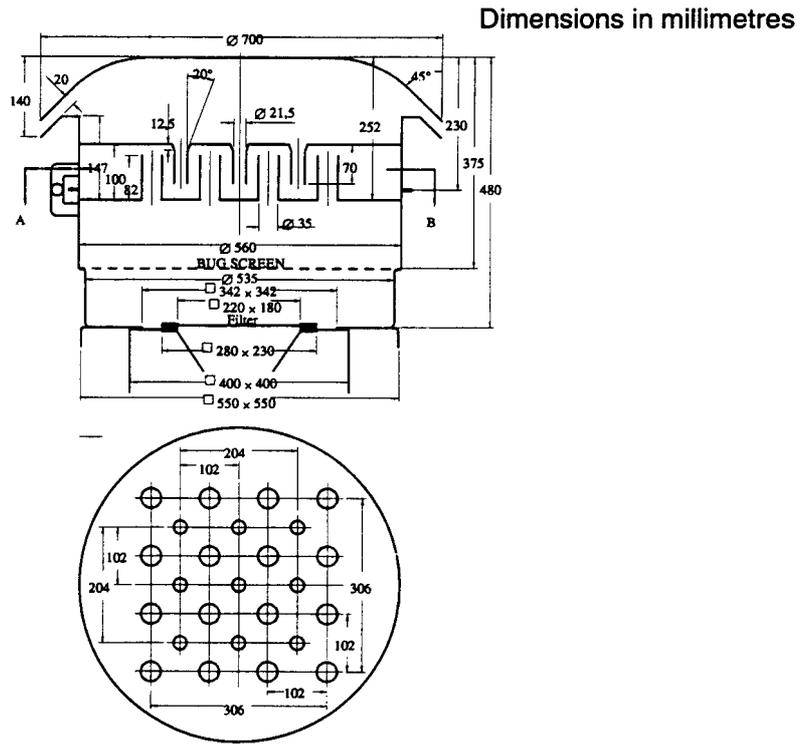


Figure 3.15.2: Design of 68 m³/h HVS-PM₁₀ sampling inlet (CEN, 1998).

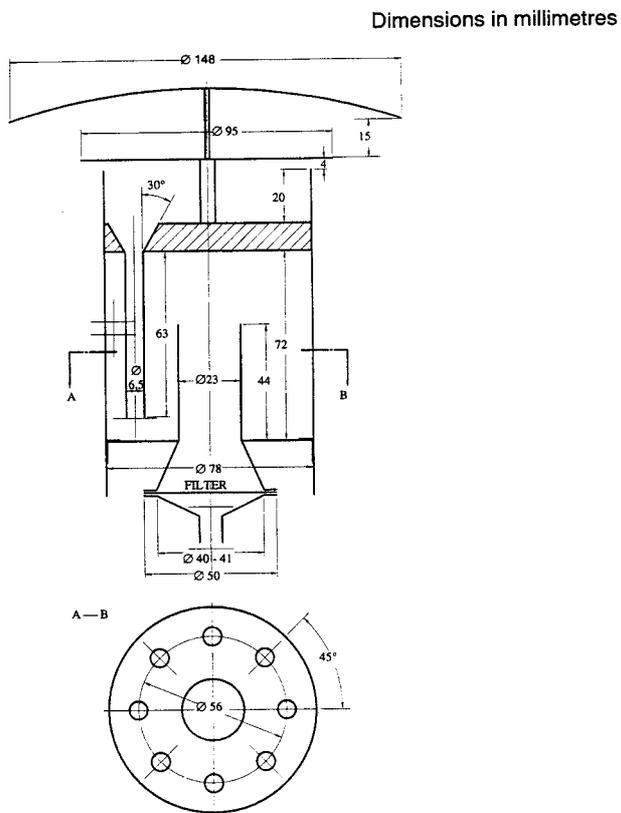


Figure 3.15.3: Design of the 2.3 m³/h MVS PM₁₀ sampling inlet (CEN, 1998).

The impaction nozzles and surface shall be cleaned and greased (e.g. with Vaseline) regularly, at least for every 20 samples. To facilitate cleaning and greasing the sampling inlet shall be constructed in such a way that the impaction plate can be pulled out of the housing. The construction and critical dimensions of the inlets of the high and low volume PM₁₀ samplers are shown in Figure 3.15.2 and Figure 3.15.3.

3.15.3 Filters

The choice of filter type is dependent on instrumentation and what type of analysis is going to be done after sampling. For PM₁₀ sampling, especially for high-volume sampling, it is necessary to use filter material with low flow resistance in order to maintain the prescribed flow rate. Quartz fibre filters should therefore be used for high-volume sampling. These filters have very good filtration characteristics with high flow and low pressure-drop, and their collection efficiency for small particles is excellent. The problem with the quartz fibre filters is their very large surface, and their adsorption of water vapour and other gases. Absorption of sulphur dioxide is not a serious problem when quartz fibre filters are used, but glass fibre and cellulose filters should not be used because of this possibility. Cellulose filters are also hygroscopic and are not suitable for particle mass measurements.

For low- or medium volume sampling, membrane filters may also be used, e.g. Teflon filters or filters made from mixed cellulose esters. But test should be carried out to see that this gives equivalent results.

When the amount of elemental- and organic carbon (EC/OC) is to be measured, sampling will have to be carried out on quartz filters. Membrane and cellulose filters contain organic material and are therefore unsuitable. Quartz filters do have the advantage that they can be baked at 500°C prior use, which may be necessary for measurements of the organic fraction to avoid high blank values. However heating filters may also result in evaporation of water in the filter structure; in addition, active sites are generated after baking the filters and volatile organic material will easier adsorb on the surface. Glass fibre filters will melt during the thermal process applied and cannot be used for sampling.

For mineral dust analysis however it is preferable to use membrane filters. Since quartz filters contain silicon and also has absorption problems when using X-ray techniques.

For heavy metal sampling, it is strongly recommended to use either Teflon or quartz filters. Glass filters do often have high blank values for certain elements.

Also cellulose filters have extensively been used for sampling of particulate matter followed by neutron activation analyses for mineral dust and trace metal analysis, but these filters cannot be used for weighing.

3.15.4 Interference

Positive interference may result from absorption of gaseous species, like SO₂ and HNO₃ on the filters followed by oxidation to sulphate and nitrate respectively.

This problems increase with filter alkalinity. If alkalinity is less than 25 microequivalent/gram filters little or no sulphate artefact should occur (EPA, 1997). Nitrate formation from nitric acid occurs on many filter types, including glass fibre, cellulose ester and quartz fibre. Nitrate can also give negative interference due to dissociation of volatile ammonium nitrate. Semi-volatile organic compounds may also cause sample weight-loss. The magnitude is dependent on location and ambient temperature.

3.15.5 Sampling procedure

In addition to the general siting criteria given in Chapter 2, it is important that the inlet is located far from any obstruction that might influence on the airflow, like building walls and trees etc. Some pumps have shown to release particles e.g. copper. Air from such pumps should therefore be removed in a separate tube at least 10 metre from the filter intake.

It is very important that the filters are stored in filter holders or in plastic bags with zippers when it is transported between the laboratory and the field. Tweezers should be used, preferably made of non-metallic material or covered with Teflon at least when heavy metals are to be determined. Never touch the filters with the fingers. After exposure the high volume filters are folded in two with the exposed side against each other, put in transport container and transferred to the laboratory for conditioning and analysis, ensuring that the filters never is exposed to higher temperature than reached during sampling.

The sampling procedures are different from one air sampling system to another. Standard operating sampling procedures (SOP) should therefore be based on the sampler's operator manual. Below some general points to remember is given:

- Inspect the filter for any pinholes, irregularities etc. If found select another one.
- Record the selected filter identification on the field log sheet.
- Always use tweezers when handling the filters. If not possible, always use anti-static powder free gloves.
- Make sure the filter is correctly placed and remember that the filters usually have a front side.
- Record the flow-rate before and after exposure or read the total flow if this is given.
- Note down the date time at the start and the end of the exposure.
- Record any unusual events, i.e. power brake down, storm, fires etc.

3.15.6 Maintenance and calibration

The sampling equipment should be maintained in accordance with the manufacturer's specifications. Accurate volume readings are important for the resulting measurement's accuracy, and the volume meters need frequent calibrations. The flow rate should be checked using a rotameter. Calibrations should under no circumstances be less frequent than twice every year. The accuracy must be better than 5%. Written instructions for maintenance and calibration need to be available at the site, and the operator should be familiar with the contents.

3.15.7 *Weighing procedure*

All handling of filters should be made in clean air. All equipment should be stored in plastic bags in a dust free environment.

It is required by EN 12341 that the filters are equilibrated, at 20° C (± 1) and 50% R.H. (± 5), for 48 hours. This equilibration should be performed before the filters are weighed previous to the sample collection, and after sampling, before the filter is weighed again with the collected sample.

Exposed filters should immediately be left to equilibrate, or stored in a fridge or cooling room ($< 10^{\circ}\text{C}$) prior to equilibration. Care must be taken to avoid condensation of water onto the filter.

Some filters are brittle, and special precautions should be taken in their handling. All the handling of filters must be done using tweezers. If one has to touch the filters, always use anti-static powder free gloves.

Filters from the high-volume sampler should be weighed to the nearest 0.1 mg. For the medium or low volume sampler, a balance capable of nearest 1 μg , should be used.

Two reference filters should be kept in the balance room and their weight checked daily. Weight changes per week should not exceed a mass which corresponds to more than 0.1 $\mu\text{g}/\text{m}^3$. If the changes are higher it might be an indication of a contamination in the conditioning/balance room. In addition one should daily weigh a standard weight to check the stability of the balance. These weights should be recorded in a logbook placed in the balance room.

Care should be taken to avoid electrostatic effects. It may be an advantage if the filters can be positioned in an upright position on the balance when the weighing is performed, at least for high volume filters. The use of ionising units, e.g. an alpha particle emitter (usually Polonium 210) is recommended, especially if membrane filters are used. For further guidance to the cause and control of static effects see: *Cahn Technical Note: Static Control for Balances*, 6/90. This document is available within the U.S. EPA's Ambient Monitoring Technology Information Center (AMTIC) PM monitoring information web page:

<http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/static.pdf>

3.15.8 *Filter blanks*

One filter blank per week is recommended. The filter blanks are to be pre-equilibrated under the same conditions as the loaded filters, they should be transported to the site, inserted into a sampler without sampling, taken out and stored in the transport container in a shelter for the sampling period, taken back to the equilibration room and weighted. If the field blank exceeds a mass that corresponds to more than 0.3 $\mu\text{g}/\text{m}^3$ it can be an indication of a contamination problem during transport or at the sampling site.

3.15.9 Commercial supply

EN 12341 specifies three reference methods for determination of PM₁₀ (CEN, 1998). Two of these, the high-volume sampler and a low -volume sampler, may be used at EMEP sites to obtain daily samples for weighing and subsequent chemical analyses. Commercial samplers that satisfy these specifications are given in the table below. Other samplers may also be used, provided that these give comparable results.

	Model	Manufacture
Low and medium volume sampler (KleinfILTERgerät)	ISAP 1050	Ingenieurbüro Schulze Im Heidewinkel 66 D-21271 Asendorf, Germany http://www.isap.com/
	LVS3D/ MVS6D	Ing. Büro Norbert Derenda, Bleibtreustrasse 7, D-10623 Berlin, Germany
	LVS3/ MVS6	Ing.-Büro Sven Leckel Leberstraße D-10829 Berlin. Germany http://www.leckel.de/
High volume sampler	ISAP 2000	Ingenieurbüro Schulze Im Heidewinkel 66 D-21271 Asendorf, Germany http://www.isap.com/
	ESM Andersen	ESM Andersen Instruments GmbH Frauenaauracher Straße 96, D-91056 Erlangen. Germany. http://www.esm-online.de/
	DA-80 H	DIGITEL Elektronik AG Alte Gasse 18, CH-8604 Hegnau Switzerland http://www.digitel-ag.ch/
Combined gravimetric sampler and beta monitor	ADAM SM2000	Opsis AB, Box 244, SE-244 02 Furulund. Sweden http://www.opsis.se

3.15.10 References

- CEN (1998) Air Quality. Determination of the PM₁₀ Fraction of Suspended Particulate Matter. Reference Method and Field Test Procedure to Demonstrate Reference Equivalence of Measurement Methods. Brussels (EN 12341).
- EC (2001) Working group on particulate matter. Guidance to member states on PM₁₀ monitoring and intercomparisons with the reference method. Draft Final Report, 16 March 2001
- EMEP (2000) EMEP-WMO Workshop on Fine Particles – Emissions, Modelling and Measurements, Interlaken, Switzerland, 22–25 November 1999. Kjeller, EMEP/CCC-Report 9/2000
- EPA (1997) Reference Method for the Determination of Particulate Matter as PM₁₀ in the Atmosphere. *Federal Register*, 62, No 138, Appendix M to part 50.
- WHO Regional Office for Europe, Copenhagen (EUR/ICP/EHB1040102, E62010, 10-13.)
- WHO (1999) Particulate Matter (PM₁₀ and PM_{2.5}). Results of Intercomparison Studies. Conference Held in Berlin 3-5 September 1998.

3.15.11 Measurements of PM_{2.5} and PM_{1.0}

To harmonize the measurements of particulate matter, the EMEP manual on PM_{2.5} and PM₁ will to a large extent follow the coming reference from the European Community as it does for PM₁₀. CEN is working on a reference method for PM_{2.5}, but this is not expected to be finalized before earliest in 2004. Even though a reference method is not yet adopted it is highly desired to include the measurements of smaller particles as soon as possible. PM_{2.5} and PM₁ has a larger fraction of long rang transported components than the PM₁₀ which in many cases are influenced by local pollution and/or resuspension. Those countries interested in starting PM_{2.5} and/or PM₁ measurements are encouraged to use one of the candidate CEN reference instrument and this manual for a general guidance on sampling and analyzing methods. For PM₁ it is not yet any CEN group established to decide on a reference method, but one may still use any of the reference or candidate instruments for PM₁₀ or PM_{2.5} with a PM₁ inlet. Some companies manufacturing PM₁ inlets are listed below.

3.15.11.1 List of Candidate CEN PM_{2.5} reference instruments

- MINI-WRAC, gravimetric, single filter from [Fraunhofer Institute for Toxicology and Aerosol Research](#) (FhG-ITA), Germany
 - RAAS 2.5-1, gravimetric single filter from [ESM Andersen](#), USA
 - LVS 3D, gravimetric, single filter from Derenda Company, Germany
 - [Partisol Plus](#), gravimetric, sequential and Partisol WINS, gravimetric, single filter from [Rupprecht & Patashnick](#), USA
 - SEQ 47/50, gravimetric, sequential from [Leckel Company](#), Germany
 - HVS-HDI 2, gravimetric, sequential from [Digitel Company](#), Switzerland
- Candidate Equivalence Instruments (automated)*
- ADAM, beta method, sequential [Opsis](#), Sweden

- TEOM SES, *sharp cut cyclon* [Rupprecht & Patashnick](#), USA
- FHG 2 I-R, *beta method, filter tape* [ESM Andersen Company](#), Germany
- BAM-1020, *beta method, filter tape* [Met One](#), USA

3.15.11.2 Manufactures with $PM_{1.0}$ inlet

- Cyclonic separation [PM-1 Inlet](#) from [Rupprecht & Patashnick](#), USA
- The PMX INLET from [Leckel Company](#), Germany
- The [Dekati](#) PM-10 impactor measure PM_{10} , $PM_{2.5}$, and PM_1 concentrations simultaneously.
- Standard and impactor sampling heads (PM_{10} , $PM_{2.5}$, $PM_{1.0}$) for ISAP2000 with optionally heating from [Schultze](#)
- Sharp Cut Cyclone, PM_1 ([SCC-2229](#)) from [BGI](#) incorporated, USA

