

## 4. Chemical analysis

### 4.1 Determination of sulphate, nitrate, chloride, ammonium, sodium, potassium, calcium, and magnesium with ion chromatography

#### 4.1.1 Scope and Application

Ion chromatography can be used for the determination of the ions in the following samples:

- Precipitation
- Extracts of aerosol filters
- Extracts of impregnated filters
- Extracts of coated denuders

The pretreatment of the samples before analysis is described together with the sampling in the preceding Sections. Special conditions for the different sample matrices are given in these Sections.

The concentration range of the method is typically 0.01–10 µg/ml.

#### 4.1.2 Principle

A small volume of the sample, typically less than 0.5 ml, is introduced into the injection system of an ion chromatograph. The sample is mixed with an eluent and pumped through a guard column, a separation column, a suppressor device and a detector, normally a conductivity cell.

The separation column is an ion exchange column which has the ability to separate the ions of interest. The separation column is often preceded by a shorter guard column of the same substrate as in the separation column to protect the separation column from overloading and particles. Different types of separation columns, eluents and suppression devices have to be used for anions and cations respectively. Each ion is identified by its retention time within the separation column. The sample ions are detected in the detection cell, and the signals produced (chromatograms) displayed on a strip chart recorder or a PC equipped with the necessary software for measurement of peak height or area.

The ion chromatograph is calibrated with standard solutions containing known concentrations of the ions of interest. Calibration curves are constructed from which the concentration of each ion in the unknown sample is determined.

#### 4.1.3 Interferences

Any species with a retention time similar to that of the main ions could interfere. With the exception of  $\text{NO}_2^-$ , precipitation or filter extracts do normally not contain such species. Large amounts of one of the ions may interfere by reducing the peak resolution of the next ion in the elution sequence. Sample dilution can then be necessary.

In some systems the so-called negative water dip in the start of the chromatogram may interfere with the  $\text{Cl}^-$  determination. This can be avoided by adding a small

amount of concentrated eluent to all samples and calibration standards to match the eluent concentration.

When analyzing alkaline impregnated filters and denuders, the sample matrix may influence the shape of the chromatogram peak and give wrong results if comparisons are made with calibration standards made from pure water solutions. In some cases this can be avoided by using the peak area instead of the peak height, but using the peak area in the low concentration range may often fail.

It is strongly recommended to match the calibration solutions with the sample matrix. For some samples, e.g. extracts from impregnated filters, the sample matrix may cause a slight distortion of the chromatogram. This may cause erroneous results if the calibration solution does not have a similar ionic composition. If ordinary calibration solutions are used, it must regularly be checked if this causes a problem by using control samples with known concentration of the ions with the same matrix as in the samples. One way of doing this is to extract unexposed impregnated filters with the normal calibration standards and with the same volume of water as the samples. Analyses of these samples should not give deviating results from the calibration standard concentrations.

Samples that contain particles larger than 0.45  $\mu\text{m}$  and reagent solutions that contain particles larger than 0.20  $\mu\text{m}$  require filtration to prevent damage to the instrument columns and flow systems. If the sample is left undisturbed in the sample tube for some days before analysis, these problems can be avoided by simply place an in-line filter in the tubing in front of the columns.

The presence of air bubbles in the columns, tubing or conductivity detector cell will cause baseline and peak variability. Using boiled solutions as eluents will help to minimize the introduction of air.

#### **4.1.4 Instrumentation**

Different commercial instruments are available using different columns and suppressor devices. Two main types of instruments using different suppressor techniques, chemical and electronic suppression, are on the market. One example of specific equipment for each of these two types is given below. The examples below do not exclude a use of other commercial equipment which allow the analyses to be carried out with the required accuracy and precision.

##### **4.1.4.1 The Dionex (Dionex Corporation, Sunnyvale, CA, USA) system**

Modern versions of Dionex instruments are usually equipped with injection valve, pump constructed from inert material (both gradient and isocratic pumps are available), separation column, suppressor system and a conductivity detector (in some cases a UV/Vis absorbance detector may be used). The instruments may be operated with manual injection or automated using an autosampler. The chromatograms are recorded on a strip-chart recorder, an integrator or direct on a PC-based Chromatography Workstation.

The chemical suppressor in the Dionex system has undergone significant improvements during the last years, as ordinary packed ion exchange columns which had to be chemically regenerated, have been replaced initially by hollow fibre suppressors and then by micro-membrane suppressors with higher suppression capacity and a smaller dead volume. The last versions of these suppressors are equipped with a self-regenerating system based on electrolysis of water from the eluent itself.

Table 4.1.1 shows the guard columns, separation columns and suppressors which are recommended for the different sample types in 1994.

*Table 4.1.1: Columns and suppressors recommended by Dionex in 1994.*

	Samples	Separation/ Guard columns	Suppressor
Anions	All types mentioned above	AS9-SC/AG9-SC	AMMS-II or ASRS, 4mm
	All samples excluding KOH-impregnated filters	AS4A/AG4A	AMMS-II or ASRS, 4mm
Cations	(Both monovalent and divalent) Aerosol filters and precipitation	CS12/CG12	CSRS, 4mm

Producers of ion chromatographs also specify the eluent to be used and its concentration. Therefore no specific instructions regarding eluents are given in this manual. The column is delivered with a test chromatogram showing the separation of the different ions and the retention times. When installing a new column, it should be checked if the performance is as stated in the test chromatogram.

For other details on running the instruments, reference is made to the appropriate Instrument Manual.

#### **4.1.4.2 The Waters (Waters Association, Milford, MA, USA) system**

The Waters system is an electronically suppressed system, i.e. without a chemical based device to reduce the conductivity of the eluent, but with the possibility to subtract the conductivity of the eluent.

The following description of one possible instrument set-up and column choice is given by the Air Quality Department of Finnish Meteorological Institute (FMI):

### **Equipment**

Pump	Waters HPLC pump Model 501 (with pulsation suppression)
Injector and autosampler	Waters Model 712 WISP and Waters Model 717 96 or 48 samples analyzed sequentially
Detector	Waters Model 431
Microcomputer	NEC 486/66i, 20/240 MB
Software	Waters Maxima 820 and Baseline

### **Conditions for anions (precipitation, aerosol filters and alkaline impregnated filters)**

Eluent	Borate/Gluconate
In-line filter	Waters Guard Pak (0.22 µm)
Column	Precipitation and aerosol filters: Waters IC-Pak A HR (4.6 x 75 mm, 6µm, 30 ± 3 µeq/ml) Impregnated filters: Waters IC-Pak A (4.6 x 50 mm, 10µm, 30 ± 3 µeq/ml)
Flow rate	IC-Pak A HR: 1.0 ml/min IC-Pak A: 1.2 ml/min
Injected volume	20-200 µl
Run time	Appr. 16 min (Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> )

### **Conditions for cations (precipitation samples)**

Eluent	EDTA/HNO <sub>3</sub>
In-line filter	Waters (0.22µm, Cat no. 32472, Millipore)
Column	Waters IC-Pac C M/D (3.9 x 150 mm, 5 µm, 2.0 ± 0.2 meq/ml)
Flow rate	1.0 ml/min
Injected volume	20-200 µl
Run time	Ca. 18 min (NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>++</sup> , Ca <sup>++</sup> )

### **Detection limits**

The analytical detection limits (in mg/l) obtained at FMI with the described equipment, defined as 2x (peakheight of lowest standard/height of baseline noise), are given in Table 4.1.2.

*Table 4.1.2: Detection limits for Waters systems at FMI.*

	Detection limits	Lowest calibration standard
Cl <sup>-</sup>	0.010	0.05
NO <sub>3</sub> <sup>-</sup> -N	0.010	0.05
SO <sub>4</sub> <sup>2-</sup> -S	0.020	0.05
NH <sub>4</sub> <sup>+</sup> -N	0.002	0.02
Na <sup>+</sup>	0.002	0.02
K <sup>+</sup>	0.006	0.02
Mg <sup>++</sup>	0.003	0.02
Ca <sup>++</sup>	0.005	0.02

More practical hints on the use of the Waters system written by Anni Reissell, FMI are available from the CCC.

#### 4.1.5 Reagents and standards

All reagents must be of recognized analytical grade. The water used for dilution should be deionized and filtered. The water should have a resistance > 10 MΩ/cm and not contain particles larger than 0.20 µm. The sample, calibration standards and reagent solution bottles should be made of polyethylene or polypropylene. For the anions, borosilicate glass may also be used.

##### 4.1.5.1 Eluent solutions

The chemicals and concentrations to be used are normally given by the manufacturers of the different separation columns.

##### 4.1.5.2 Stock standard solutions

Stock standard solutions e.g. 1000 mg (based on the element)/litre, may be purchased as certified solutions from different manufacturers or NIST (National Institute for Standards and Technology, USA), or prepared from salts or oxide dried in the prescribed way, dissolved and diluted to 1000 ml as listed in Tables 4.1.3 and 4.1.4:

Table 4.1.3: Preparation of stock standard solutions. The salt amount indicated gives 1000 mg of the anions per litre.

Salt	Weight (g)	Drying temp. °C	Drying time (hours)
NaCl	1.6485	150	1
Na NO <sub>3</sub>	6.0679	105	2
Na <sub>2</sub> SO <sub>4</sub>	4.4299	105	24

Table 4.1.4: Preparation of stock standard solutions. The salt amount indicated gives 1000 mg of the cations per litre.

Salt	Weight (g)	Drying temp. °C	Drying time (hours)
NH <sub>4</sub> Cl	3.8190	105	1
NaCl	2.5421	150	2
KCl	1.9067	105	1
CaCO <sub>3</sub>	2.4971	180	1
MgO	1.6581	–	–

The CaCO<sub>3</sub> should be added to approximately 600 ml of water. Then add concentrated hydrochloric acid (HCl) slowly until the entire solid has dissolved, and dilute to 1000 ml with water.

The MgO should be dissolved in 10 ml concentrated nitric acid (HNO<sub>3</sub>) before diluting to 1000 ml with water.

The other salts should be dissolved directly in water.

These stock standards are stable for at least 1 year.

#### **4.1.5.3 Calibration solutions**

Five calibration solutions and one zero standard (blank, normally water) are needed to generate a suitable calibration curve. The range to be used will depend on the concentration range for the different samples.

One example is given for each of the ion types:

0, 0.5, 1.0, 2.5, 5.0 and 10.0 ml of each of the anion stock standards are transferred with calibrated pipettes to 1000 ml volumetric flasks and diluted to volume with deionized water. These calibration standards will contain 0, 0.5, 1.0, 2.5, 5.0 and 10.0 mg/l respectively calculated on the basis of Cl, NO<sub>3</sub>-N and SO<sub>4</sub>-S.

0, 0.5, 1.0, 2.5, 5.0 and 10.0 ml of each of the cation stock standards are transferred with calibrated pipettes to 1000 ml volumetric flasks and diluted to volume with deionized water. These calibration standards will contain 0, 0.5, 1.0, 2.5, 5.0 and 10.0 mg/l respectively calculated on the basis of NH<sub>4</sub>-N, Na, K, Ca and Mg.

If control samples have shown the necessity to match the matrix in the calibration solutions with the sample matrix (see 4.1.3 Interferences), addition of the matrix must be done before diluting to volume.

The calibration standards may be stored for 3 months in acid-cleaned polyethylene or polypropylene containers in a refrigerator. Special attention should be paid to control contamination from ammonia in the laboratory air.

#### **4.1.6 Procedure**

The ion chromatograph should be operated according to the manufacturers description.

The calibration solutions and control samples should be used as described in Section 5.

The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each ion.

However, it is important to use the experience of the analyst in the interpretation the chromatograms.

#### ***4.1.7 Calculation of the results***

The concentration of the different ions in the sample solutions are found by using the calibration curve manually or directly from a computer or integrator. To calculate the air concentrations for air samples from these values, use the appropriate formulas given in the actual sections on sampling.

#### ***4.1.8 References***

Small, H. (1989) Ion Chromatography. New York, Plenum Press.

## 4.2 Determination of sulphate in precipitation

Although ion chromatography is the method of choice for the determination of sulphate, spectrophotometric determination with barium perchlorate and thorin will also give useful results, particularly if the determination is automated (Autoanalyser or FIA).

### 4.2.1 Spectrophotometric by the barium perchlorate-Thorin method

#### 4.2.1.1 Field of application

This method is applicable to the determination of sulphate in precipitation within the range 0.05 mg S/l to 4 mg S/l. Samples containing higher concentrations must be diluted prior to the analysis.

#### 4.2.1.2 Principle

Ba(ClO<sub>4</sub>)<sub>2</sub> is added in excess to precipitate the sulphate as barium sulphate in an organic solvent. The organic solvent will minimize the solubility product of barium sulphate.

The excess concentration of barium (II) ions in the solution is determined spectrophotometrically at 520 nm through the reaction with Thorin (the sodium salt of 4-(ortho-arsenophenyl-azo)-3-hydroxy-2,7-naphtalenedisulphonic acid).

Several organic solvents may be used. The most favourable calibration curve is obtained with dioxane.

#### 4.2.1.3 Instrumentation

- Spectrophotometer for measuring absorbance at 520 nm.
- Optical glass spectro-photometer cells; 20 mm
- Micro pipette: 250 µl
- Bulb pipettes: 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ml
- Burette: 50 ml
- Ion exchange columns: 15 cm length, 1 cm diameter
- Test tubes: 30 ml
- Volumetric flasks: 50, 100 and 1000 ml

All glassware should be of borosilicate and should be thoroughly rinsed in distilled water before use.

#### 4.2.1.4 Chemicals

All chemicals, except Thorin, must be of recognized analytical grade. The water used for dilution and rinsing must be double distilled or deionized.

- Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) 0.05 M
- Perchloric acid, (HClO<sub>4</sub>) 72 %
- Barium perchlorate (Ba(ClO<sub>4</sub>)<sub>2</sub>), anhydrous
- Dioxane or isopropanol

- Thorin (disodium salt)
- Cation exchange resin, strongly acidic (e.g. Dowex 50 W x 8, 50-100 mesh).

#### **4.2.1.5 Reagents**

- (1) 0.1 M perchloric acid (HClO<sub>4</sub>).
- (2) 0.01 M perchloric acid (HClO<sub>4</sub>).
- (3) Barium perchlorate stock solution 210.0 mg anhydrous barium perchlorate, (Ba(ClO<sub>4</sub>)<sub>2</sub>), is dissolved in 0.1 M HClO<sub>4</sub> to a volume of 100 ml in a volumetric flask.
- (4) Barium perchlorate reagent solution 10.0 ml of solution (3) is diluted to 1000 ml with dioxane or isopropanol.
- (5) Thorin reagent solution 125.0 mg of the disodium salt is dissolved in 5 ml 0.01 M HClO<sub>4</sub> and diluted to 50 ml in a volumetric flask. A fresh solution should be prepared each day.
- (6) Sulphate standard solution 31.25 ml 0.05 M H<sub>2</sub>SO<sub>4</sub> is diluted to 1000 ml in a volumetric flask. The concentration is equal to 50 mg S/l.

#### **4.2.1.6 Calibration**

Prepare a series of standard solutions containing 0, 0.5, 1.0, 1.5 ..... 4 mg S/l by diluting 0, 1, 2, 3, ..... 8 ml of the sulphate standard solution in Section 4.2.1.5 (6) to 100 ml with water in volumetric flasks. Transfer 4 ml of each of these standard solutions to a test tube. Add 10 ml barium perchlorate reagent solution and 250 µl Thorin solution. Use a micro pipette for the Thorin solution. Mix thoroughly (do not use rubber stoppers!)

Transfer the solutions to optical cells. The spectrophotometer wavelength is set at 520 nm, and 0% transmission is adjusted according to the procedure in the manual of the photometer. Then gain and/or slit width is adjusted to give a reading of 0.80 absorbance units with the blank (0 mg S/l) in the sample compartment. Measure the absorbance of the solutions within 10 minutes after addition of the Thorin solution. This is especially important for low concentrations of sulphate and for the blank because the barium-Thorin compound may precipitate from the solution.

A calibration graph is constructed from the absorbance readings obtained from the standard solutions. The calibration curve is not linear below 0.5 mg S/l. This is suppressed by adding sulphate in a quantity corresponding to 0.5 mg S/l to all samples and blanks. The detection limit is then 0.05 mg S/l.

#### **4.2.1.7 Analytical procedure**

Cations are removed by treating the sample with a strongly acidic cation exchange resin.

Transfer 4 ml of the pretreated sample to a test tube and proceed according to Section 5.2.1.6.

Determine the sulphur concentration of the sample from the absorbance reading by means of the calibration curve.

With suitable equipment, the barium perchlorate-Thorin method can be made automatic. This method is described in detail in the next Section.

#### **4.2.1.8 Interferences**

Phosphate will interfere with this method.

#### **4.2.1.9 References**

Persson, G.A. (1966) Automatic colorimetric determination of low concentrations of sulphate for measuring sulphur dioxide in ambient air. *Air Water Pollut.*, 10, 845-852.

### **4.2.2 Automatic Spectrophotometric by the barium perchlorate-Thorin method**

#### **4.2.2.1 Field of application**

This automatic method can be used to determine the concentration of sulphate in precipitation within the range 0.05 to 2.5 mg S/l.

#### **4.2.2.2 Principle**

The basis principle is the same as in the manual method above.

A known amount of  $(\text{Ba}(\text{ClO}_4)_2)$  is added in excess to the sample and the sulphate is precipitated as barium sulphate. The excess of barium ions reacts with the Thorin indicator to form a red compound. The concentration is determined colorimetrically at 520 nm.

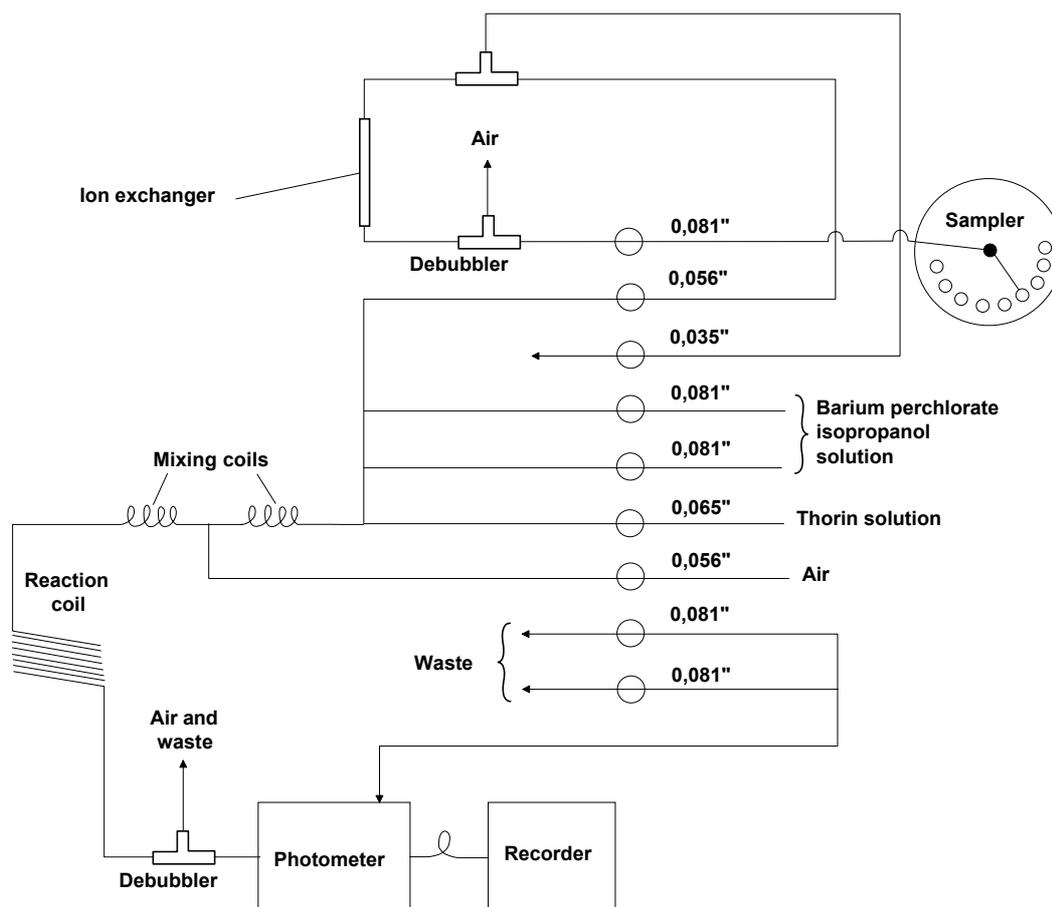


Figure 4.2.1: Flow scheme for automatic spectrophotometric analysis of sulphate.

#### 4.2.2.3 Instrumentation

- Automatic sampler with 6 ml cups
- Peristaltic pump
- Filter photometer with power supply and recorder output.
- Flow cell, pathlength 1.0 cm
- Filter, transmission 520 nm
- Recorder with zero suppression up to 100%
- Cation exchange column: A 10 cm glass (or polyethylene) tube i.d. 2 mm filled with a strongly acidic cation exchange resin. Glass wool in both ends of the tube keeps the resin in place. The resin should always be moist.
- Flexible tubings, connecting tubes, pulse suppressors, debubblers and mixing coils.

#### 4.2.2.4 Chemicals

All chemicals, except Thorin, must be of recognized analytical grade. The water used must be double-distilled or deionized.

- Isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH)
- Barium perchlorate (Ba(ClO<sub>4</sub>)<sub>2</sub> anhydrous)

- Perchloric acid (HClO<sub>4</sub>)
- Thorin (disodium salt)
- Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) 0.05 M
- Sodium acetate (CH<sub>3</sub>COONa)
- Acetic acid (CH<sub>3</sub>COOH)
- Cation exchange resin, strongly acidic (e.g. Dowex 50 W x 8, 50-100 mesh).
- EDTA (disodium salt)
- Sodium hydroxide (NaOH)

#### 4.2.2.5 Reagents

- (1) Barium perchlorate solution:  
Dissolve 900 mg (Ba(ClO<sub>4</sub>)<sub>2</sub>) in 1000 ml water and add 8.6 ml of HClO<sub>4</sub>.
- (2) Sodium acetate buffer:  
Add 1M CH<sub>3</sub>COOH to 100 ml 1M sodium acetate to pH 5.6.  
Use a pH-meter.
- (3) Barium perchlorate - isopropanol reagent:  
To 1000 ml of isopropanol, add 10 ml of barium perchlorate solution (1) and 4 ml of sodium acetate buffer (2).  
Mix well.
- (4) Thorin solution:  
Dissolve 100 mg of Thorin in a little water in a 500 ml volumetric flask. Fill up to the mark with water. Prepare a fresh solution every day.
- (5) Standard sulphate solution, 50 mg S/l:  
Transfer 31.25 ml of 0.05 M H<sub>2</sub>SO<sub>4</sub> to a 1000 ml volumetric flask using a burette. Dilute to 1000 ml with water. Store refrigerated.
- (6) Cleaning solution:  
100 g of EDTA and 10 g NaOH are diluted to 2 litres with water.

#### 4.2.2.6 Calibration and analytical procedure

Prepare a series of standard solutions containing 0.0, 0.1, 0.5, 1.0 ..... 2.5 mg S/l by diluting 0, 2, 10, 20 ..... 50 ml of the standard sulphate solution (5) to 1000 ml with water in volumetric flasks.

Start the pump and check the flow, all connections, tubings and debubblers with water running through the instrument. Turn on the photometer and the recorder (paper speed 5 mm/min.). Connect the tubings to the reagents and check that the baseline is stable.

Fill the cups of the automatic sampler with samples and standard solutions. Sampling time is 130 seconds and rinsing time with water after each sample is 180 seconds. Start with the series of standard solutions, and run a series of standard solutions after every tenth sample.

When isopropanol is used as organic solvent, the tubings must be thoroughly cleaned after use. Flush water through the system until all the reagents are rinsed out, then run the cleaning solution for 5 minutes. Rinse again with water. Turn off the recorder, photometer, sampler and pump, and loosen the tubings in the pump so they are not stretched.

Prepare a calibration curve from each of the series of standard solutions by plotting the recorder response in mm (absorbance) against the concentration of the standards.

#### **4.2.2.7 Expression of results**

Convert the recorder response (absorbance) of the sample to mg S/l by means of the calibration curve obtained just before or after the sample.

The use of a transparent sheet with several vertical scales corresponding to the different responses from the standard solutions will save time when many samples are to be handled.

#### **4.2.2.8 References**

Henriksen, A. and Bergmann-Paulsen, I.M. (1974) An automatic method for determining sulphate in natural soft water and precipitation. *Vatten*, 2, 187-192.

Persson, G.A. (1966) Automatic colorimetric determination of low concentrations of sulphate for measuring sulphur dioxide in ambient air. *Air Water Pollut.* 10, 845-852.

### **4.3 Determination of nitrate in precipitation**

Ion chromatography is the preferred method for determination of nitrate, spectrophotometric determination either the manual or the automatic method can also be used and will give useful results. It should, however, be noted that the Griess method in both versions described in the following gives the sum of nitrate and nitrite.

#### **4.3.1 The manual spectrophotometric Griess method**

##### **4.3.1.1 Field of application**

This method is applicable to the determination of the nitrate content in precipitation with the range 0.02-0.23 mg NO<sub>3</sub>-N/l (0.1-1.0 mg NO<sub>3</sub>/l).

##### **4.3.1.2 Principle**

Nitrate is reduced to nitrite using cadmium treated with copper sulphate as a reducing agent, in presence of ammonium chloride. Thus, by this method the sum of nitrate and nitrite is determined.

Nitrite and sulphanilamide form a diazo compound which couples with N-(1-naphthyl)-ethylenediamine-dihydrochloride to form a red azo dye. The concentration in the solution is determined spectrophotometrically at 520 nm.

##### **4.3.1.3 Instrumentation**

- Spectrophotometer
- Optical glass cell, 20 mm. If more than one cell is used, the cells should be matched photometrically.
- Shaking machine
- Erlenmeyer flasks: 25 ml with stoppers
- Volumetric flasks: 100 and 1000 ml
- Test tubes
- Pipettes: 1.0, 2.0, 4.0, 6.0, 8.0, 12.0 and a 20.0 ml graduated
- Micro pipettes: 100, 250, 500 µl
- pH-meter
- Beaker: 200 ml

##### **4.3.1.4 Chemicals**

During analysis, use only chemicals of recognized analytical grade. The water used for dilution and rinsing must be double-distilled or deionized and distilled.

- Ammonium chloride (NH<sub>4</sub>Cl)
- Sulphanilamide
- (1-naphthyl)-ethylenediamine dihydrochloride
- Cadmium, 40-60 mesh
- Copper sulphate (CuSO<sub>4</sub>·5H<sub>2</sub>O)
- Hydrochloric acid (HCl)
- Potassium nitrate (KNO<sub>3</sub>)
- Ammonia (NH<sub>3</sub>)

#### **4.3.1.5 Reagents**

- (1) 5% ammonium chloride solution:  
Dissolve 5 g ammonium chloride in water in a 100 ml volumetric flask. Adjust the pH of the solution to 8.6 using diluted ammonia. Dilute with water to the mark.
- (2) 1.2 M hydrochloric acid:  
Dilute 10 ml concentrated hydrochloric acid to 100 ml with water in a volumetric flask.
- (3) 2 M hydrochloric acid:  
Dilute 16.7 ml concentrated hydrochloric acid to 100 ml with water in a volumetric flask.
- (4) 1% sulphanilamide solution:  
Dissolve 1.0 g of sulphanilamide in some 1.2 M hydrochloric acid (2) in a 100 ml volumetric flask. Dilute with 1.2 M hydrochloric acid (2) to the mark.
- (5) 0.1% N-(1-naphthyl)-ethylenediamine dihydrochloride solution:  
Dissolve 0.1 g N-(1-naphthyl)-ethylenediamine dihydrochloride in some water, in a 100 ml volumetric flask. When all is dissolved, dilute to the mark.
- (6) 2% copper sulphate solution:  
Dissolve 2.0 g copper sulphate in water in a 100 ml volumetric flask, and dilute to the mark.
- (7) Reducing agent for nitrate:  
Transfer 10 g of cadmium to a beaker, add 2 M hydrochloric acid (3) to cover the cadmium and stir. Rinse well with water. Add immediately 100 ml of the 2% copper sulphate solution (6), and mix well. Pour off excess of solution. Rinse with water until there is no more precipitated copper in the washing water. The reducing agent must not be exposed to the air.
- (8) Standard nitrate solution I, 1000 mg NO<sub>3</sub>/l:  
Dissolve exactly 1.6305 g potassium nitrate in water in a 1000 ml volumetric flask. Dilute to the mark.
- (9) Standard nitrate solution II, 100 mg NO<sub>3</sub>/l:  
Dilute 10 ml of standard nitrate solution I with water to 100 ml in a volumetric flask.

#### **4.3.1.6 Calibration**

Preparation of the calibration curve:

- (1) Transfer to 100 ml volumetric flasks 0, 100, 250, 500 and 1000 µl of standard nitrate solution II. Dilute with water to the mark and mix well. The

concentration of nitrate in the five flasks are 0.0, 0.1, 0.25, 0.50 and 1.00 mg NO<sub>3</sub>/l.

- (2) By means of a pipette, transfer 4.0 ml of each of these standard solutions to a 25 ml Erlenmeyer flask. Add 6.0 ml 5% ammonium chloride solution using a pipette, and approximately 0.5 g of the nitrate reducing agent to the Erlenmeyer flask. Shake vigorously for 10 minutes. Transfer 8.0 ml of this solution by means of a pipette to a test tube. Add 2.0 ml 1% sulphanilamide solution and 2.0 ml of 0.1% N-(1-naphthyl)-ethylenediamide dihydrochloride solution using pipettes. Mix well, and leave for 10 minutes for the colour to develop. Transfer this solution to a 20 mm cell. Measure the absorbance of the solution at 520 nm.

Prepare a calibration curve by plotting the absorbance of each of the standard solutions against its concentration of nitrate.

#### **4.3.1.7 Analytical procedure**

Transfer 4.0 ml of the precipitation sample to a 25 ml Erlenmeyer flask, using a pipette. Proceed according to Section 4.3.1.6 (2).

Convert the absorbance of the sample to mg NO<sub>3</sub>/l by means of the calibration curve. The concentration may be expressed as mg N/l by multiplying with 0.226.

Samples containing more than 1 mg NO<sub>3</sub>/l must be diluted before the analysis.

Do not waste the cadmium used in the analysis. It may be regenerated and used again.

With suitable equipment this method can be made automatic. A detailed description of the automatic method is given in Section 4.3.2.

#### **4.3.1.8 References**

Morris, A.W. and Riley, J.P. (1963) The determination of nitrate in sea water. *Anal. chem. Acta*, 29, 272-279.

### **4.3.2 Automatic spectrophotometric Griess method**

#### **4.3.2.1 Field of application**

This method can be used to determine the concentration of nitrate in precipitation within the range 0.03-1.13 mg NO<sub>3</sub>-N/l (0.13-5.0 mg NO<sub>3</sub>/l). The method can be extended to include determination of ammonium in solutions, see Section 4.4.2 and Figure 4.3.1.

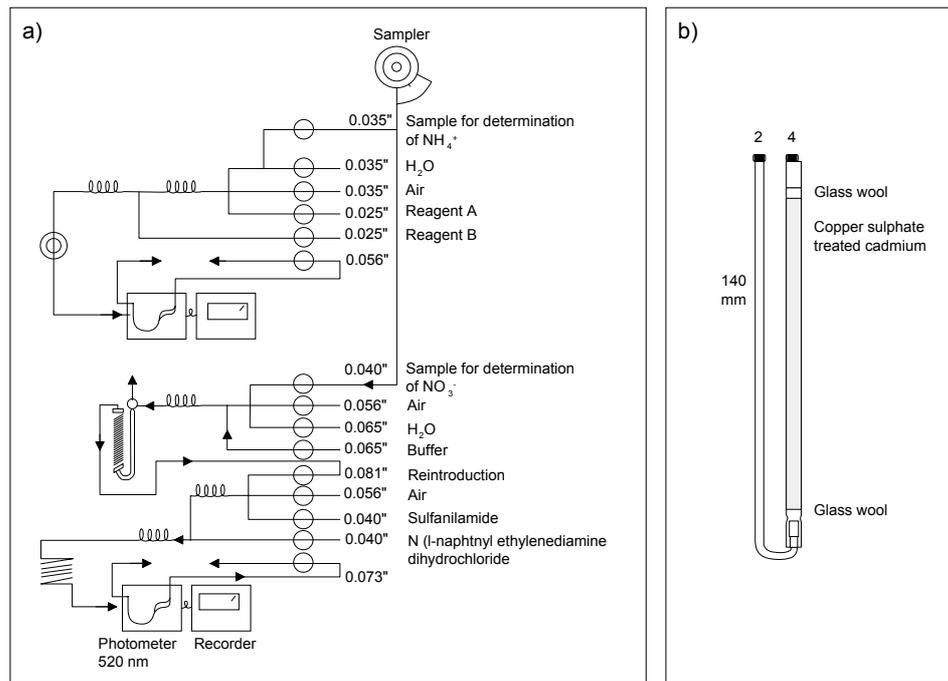


Figure 4.3.1: a) Automatic determination of nitrate and ammonium in precipitation samples.  
 b) Reduction column for the determination of nitrate in precipitation samples.

#### 4.3.2.2 Principle

The basis principles are the same as for the manual methods (see Section 4.3.1).

Nitrate is reduced to nitrite using cadmium treated with copper sulphate as reducing agent in the presence of ammonium chloride. Nitrite and sulphanilamide form a diazo compound which couples with N-(a-naphtyl)-ethylenediamine dihydrochloride to give a red azo dye. The concentration of the nitrate in the solution is determined spectrophotometrically at 520 nm. By this method the sum of nitrate and nitrite is determined.

#### 4.3.2.3 Instrumentation

- Peristaltic pump, 20-channels
- Automatic sampler with 4 ml cups
- Photometer(s) for measuring absorbance at 520 nm (and 630 nm if ammonium is determined with the same equipment)
- Recorder(s)
- Oil bath with thermostat, 70° C
- Flexible tubings, connecting tubes, pulse suppressors, debubblers, mixing coils and reduction column (Figure 4.3.1).
- Pipettes: 50, 25, 20, 10, 5, 2.5 and 2 ml
- Analytical balance
- Desiccator

#### 4.3.2.4 Chemicals

All chemicals must be of recognized analytical grade. The water used for dilution and rinsing must be double-distilled or de-ionized and distilled.

- Ammonium chloride ( $\text{NH}_4\text{Cl}$ )
- Ammonia ( $\text{NH}_3$ )
- Sulphanilamide
- N-(1-naphthyl)-ethylenediamine dihydrochloride
- Cadmium, 40-60 mesh
- Copper sulphate ( $\text{Cu SO}_4 \cdot 5\text{H}_2\text{O}$ )
- Potassium nitrate ( $\text{KNO}_3$ )
- Hydrochloric acid ( $\text{HCl}$ )

#### 4.3.2.5 Reagents

Reagents for the determination of nitrate:

- (1) Buffer solution:  
Dissolve 100 g ammonium chloride in ca. 700 ml water in a 1000 ml volumetric flask. Adjust pH to 8.6 with diluted ammonia. Dilute with water to the mark.
- (2) Sulphanilamide solution:  
Dissolve 10 g sulphanilamide in a 10% HCl solution in a 1000 ml volumetric flask. Dilute with the acid solution to the mark.
- (3) 0.1% N-(1-naphthyl)-ethylenediamine dihydrochloride solution:  
Dissolve 1 g N-(1-naphthyl)-ethylenediamine in some water in a 1000 ml volumetric flask. When all is dissolved, dilute to the mark with water.
- (4) Reducing agent:  
Prepare a 2% copper sulphate solution. Wash the cadmium with 0.1 M hydrochloric acid and water. Add some of the 2% copper sulphate solution to the freshly washed cadmium and stir for 1–2 min. Pour off the solution and wash the reducing agent with water. Repeat until the washing water is clear. Fill the column as shown in Figure 1b. The reducing agent must not be exposed to air.

The reducing agent may be recovered in the following way:

Remove the cadmium from the column and wash with 0.1 M hydrochloric acid. Add some of the 2% copper sulphate solution and stir until the blue colour of the solution has disappeared.

- (5) Standard solutions (for nitrate and ammonium):  
Standard solution I, 500 mg  $\text{NO}_3/\text{l}$  and 200 mg  $\text{NH}_4/\text{l}$ :  
Dry potassium nitrate and ammonium sulphate for 1 hour at 105 °C, and then cool for 20 minutes in a desiccator.

Dissolve exactly 0.815 g potassium nitrate and exactly 0.735 g ammonium sulphate in water in a 1000 ml volumetric flask. Dilute to the mark with water. Store the solution refrigerated in the dark.

- 6) Standard solution II, 5.0 mg NO<sub>3</sub>/l and 2.0 mg NH<sub>4</sub>/l:  
Dilute 5 ml of standard solution I (5) to 500 ml with water in a volumetric flask.

#### 4.3.2.6 Calibration and analytical procedure

Prepare a series of calibration solutions according to Table 4.3.1.

Table 4.3.1: Calibration solutions for nitrate and ammonium.

Calibration solution No.	mg NO <sub>3</sub> /l	mg NH <sub>4</sub> /l	
1	5.0	2.0	Standard solution II
2	2.5	1.0	Dilute 100 ml of standard solution II to 200 ml with water
3	0.5	0.2	Dilute 20 ml of standard solution II to 200 ml with water
4	0.25	0.10	Dilute 10 ml of standard solution II to 200 ml with water
5	0.125	0.05	Dilute 5 ml of standard solution II to 200 ml with water
6	0.0	0.0	Water

These solutions may be stored in the refrigerator for a few days.

Start the pump and check the flow, all connections, tubings and debubblers with water running through the instrument. Turn on the photometers and the recorders (paper speed 10 mm/min.). Connect the tubings to the reagents and check that the baseline is stable.

Avoid air in the column containing the reducing agent. Therefore, do not connect the column to the pump before the apparatus is filled with liquids.

Fill the cups of the automatic sampler with samples and standard solutions. Sampling time is 90 seconds and rinsing time with water after each sample is 105 seconds. Start with the calibration solutions and run the calibration solution no. 1, 3, 5 and 6 between every tenth sample.

After analyses, run water through the system until all reagents are rinsed out. Turn off the recorder, photometer, sampler and pump, and loosen the tubings in the pump so they are not stretched.

Prepare a calibration curve by plotting the absorbances at 520 nm (each of the standard solutions against its concentration of nitrate).

#### **4.3.2.7 Expression of results**

Convert the recorder response (absorbance) of the sample to mg N/l by means of the calibration curves obtained just before or after the sample.

#### **4.3.2.8 Interferences**

Nitrite will interfere with the determination of nitrate.

#### **4.3.2.9 References**

Henriksen, A. and Selmer-Olsen, A.R. (1970) Automatic methods for determining nitrite in water and soil extracts. *Analyst*, 95, 514-518.

## 4.4 Determination of ammonium in precipitation

Ammonium may be determined together with the other major cations in precipitation if ion chromatograph equipment for cations is available. If not, the method described below is a good alternative.

### 4.4.1 Spectrophotometric by the indophenol blue method

#### 4.4.1.1 Field of application

This method is applicable to the determination of the ammonium content in precipitation within the range 0.04 to 2.0 mg NH<sub>4</sub>/l.

#### 4.4.1.2 Principle

In an alkaline solution (pH 10.4-11.5) ammonium ions react with hypochlorite to form monochloramine. In the presence of phenol and an excess of hypochlorite, the monochloramine will form a blue coloured compound, indophenol, when nitroprusside is used as catalyst. The concentration of ammonium is determined spectrophotometrically at 630 nm.

#### 4.4.1.3 Instrumentation

- Spectrophotometer
- Optical cell, 10 mm. If more than one cell is used, the cells should be matched photometrically
- Water bath with thermostat, 50 °C
- Test tubes: 30 ml
- Volumetric flasks: 10, 500 and 1000 ml
- Pipettes: 1.0, 2.0, 4.0, 5.0, 10.0, 20.0, 25.0, 50.0 ml.
- Micropipette: 250 µl

#### 4.4.1.4 Chemicals

During analysis, use only chemicals of recognized analytical grade. The water used for dilution and rinsing should be double-distilled or de-ionized and distilled.

- Phenol (C<sub>6</sub>H<sub>5</sub>OH)
- Sodium nitroprusside (Na<sub>2</sub>Fe(NO) (CN)<sub>5</sub> · 2H<sub>2</sub>O)
- Sodium hydroxide (NaOH)
- Sodium hypochlorite solution (NaOCl) 1M:
- Make a solution containing approx. 3.5% active chlorine (35 g/l) in 0.1 M NaOH (e.g. British Drug House no. 23039)
- Ammonium chloride (NH<sub>4</sub>Cl)
- Sodium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>)

#### 4.4.1.5 Reagents

- (1) Reagent A:  
Dissolve 3.5 g phenol and 0.040 g sodium nitroprusside in 100 ml water. Store the solution refrigerated in the dark. If the colour of the solution turns greenish, it must be discarded, and a fresh solution prepared.
- (2) Reagent B:

Dissolve 1.8 g sodium hydroxide in some water in a 100 ml volumetric flask. Add 4.0 ml 1 M sodium hypochlorite solution, and dilute with water to the mark. Store the solution refrigerated in the dark. If the solution is stored for weeks, the concentration should be checked by titration with a sodium thiosulphate solution.

- (3) Standard ammonium solution I, 100 mg NH<sub>4</sub>/l:  
Ammonium chloride must be dried for one hour at 100 °C.  
Dissolve 0.2965 g of the dried salt in water in a 1000 ml volumetric flask. Dilute to the mark with water. The solution is stable for six months when stored in a refrigerator.
- (4) Standard ammonium solution II, 4 mg NH<sub>4</sub>/l:  
By means of a pipette, transfer 20.0 ml of standard ammonium solution I to a 500 ml volumetric flask. Dilute with water to the mark. This standard ammonium solution, and the ammonium solutions made for preparing the calibration curve, must be freshly made.

#### **4.4.1.6 Calibration**

Preparation of calibration curve:

- (1) Transfer to 100 ml volumetric flask 0.0, 1.0, 2.0, 5.0, 10.0, 25.0 and 50.0 ml of standard ammonium solution II. Dilute to the mark with water. The concentrations of these solutions are 0.00, 0.04, 0.08, 0.2, 0.4, 1.0 and 2.0 mg NH<sub>4</sub>/l. Transfer 5.0 ml of each of these standard solutions and 5.0 ml of water to a 30 ml test tube.
- (2) Add to the test tube 250 µl reagent A using a micro pipette, and mix well. Add then 250 µl reagent B using a micro-pipette and mix well. Cover the opening of the tube with some inert material. Place the tube in the water bath at 50 °C for two hours.
- (3) Cool the solution to room temperature, and transfer it to a 10 mm cell. Measure the absorbance at 630 nm.
- (4) Prepare a calibration curve by plotting the absorbance of each of the standard solutions against its concentration of ammonium. Prepare a new calibration curve for each series of samples.
- (5) In order to check for ammonium in the reagents, take a photometric reading of the blank (0.00 mg NH<sub>4</sub>/l) against water. The absorbance should not exceed 0.020.

#### **4.4.1.7 Analytical procedure**

Transfer 5.0 ml of the sample and 5.0 ml of water to a 30 ml test tube. Proceed according to Section 4.4.1.6 (2) and (3). Convert the spectrophotometric readings of the sample to mg NH<sub>4</sub>/l by means of the calibration curve. The concentration may be expressed as mg N/l by multiplying with 0.778. Samples containing more

than 2.0 mg NH<sub>4</sub>/l must be diluted. With suitable equipment the “Indophenol method” can be made automatic. A detailed description is given in Section 4.4.2.

#### **4.4.1.8 Interferences**

Iron (III) may interfere if the concentration is more than 2 mg/l. This concentration of iron (III) does not occur very often in precipitation samples.

If the pH-value of the sample is lower than 3, the sample should be neutralized.

If the sample is turbid, both the sample and the blank should be filtered through a white band filter.

#### **4.4.1.9 References**

Koroleff, F. (1970) Direct determination of ammonia in natural waters as indophenol blue. In: *Information on Techniques and Methods for Seawater Analysis*. Charlottenlund, Internat. Counc. Exploration of the sea (Interlab. Rept. 3). pp. 19-22.

### **4.4.2 Automatic spectrophotometric determination of ammonium by the indophenol blue method**

#### **4.4.2.1 Field of application**

This method can be used to determine the concentration of ammonium within the range 0.05 to 2.0 mg NH<sub>4</sub> /l.

#### **4.4.2.2 Principle**

The basic principles are the same as for the manual methods (see Section 4.4.1).

The reaction between ammonium and hypochlorite in an alkaline solution (pH: 10.5 to 11.5) gives monochloramine. In the presence of phenol and an excess of hypochlorite, the monochloramine will form a blue coloured compound, indophenol, when nitroprusside is used as catalyst. The concentration of ammonium in the solution is determined spectrophotometrically at 630 nm.

#### **4.4.2.3 Instrumentation**

- Peristaltic pump, 20-channels
- Automatic sampler with 4 ml cups
- 2 Photometers for measuring absorbance at 520 nm and 630 nm
- 2 recorders
- Oil bath with hermostat, 70° C
- Flexible tubings, connecting tubes, pulse suppressors, debubblers, mixing coils and reduction column (Figure 4.4.1).
- Pipettes: 50, 25, 20, 10, 5, 2.5 and 2 ml
- Analytical balance
- Desiccator

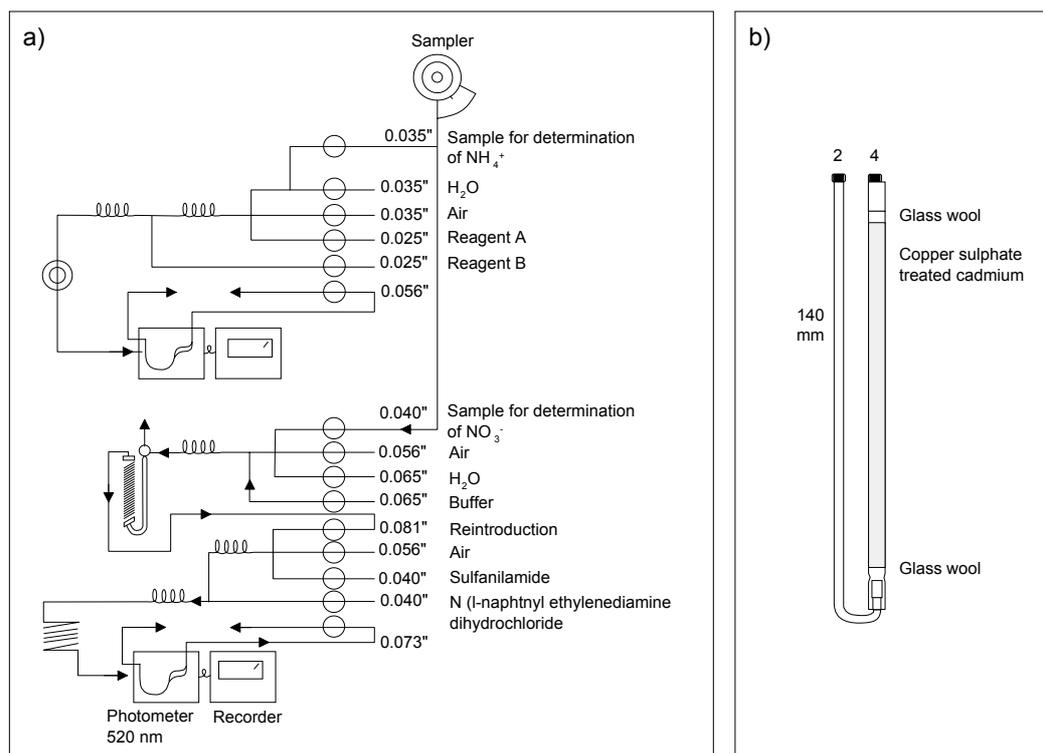


Figure 4.4.1: a) Automatic determination of nitrate and ammonium in precipitation samples.

b) Reduction column for the determination of nitrate in precipitation samples.

#### 4.4.2.4 Chemicals

All chemicals must be of recognized analytical grade. The water used for dilution and rinsing must be double-distilled or deionized.

Potassium nitrate ( $\text{KNO}_3$ )

Phenol ( $\text{C}_6\text{H}_5\text{OH}$ )

Sodium nitroprusside ( $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 \cdot 2\text{H}_2\text{O}$ )

Sodium hydroxide ( $\text{NaOH}$ )

Sodium hypochlorite solution ( $\text{NaOCl}$ ) 1M: Use a solution containing approximately 3.5% active chlorine (35g/l) in 0.1M  $\text{NaOH}$  (e.g. British Drug House, no. 23039)

Ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ )

Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ )

#### 4.4.2.5 Reagents

Reagents for the determination of ammonium:

- (1) Dissolve 3.5 g phenol and 0.040 g sodium nitroprusside in 100 ml water. Store the solution refrigerated in the dark. If the colour of the solution turns greenish, a fresh solution must be prepared.

- (2) Dissolve 1.8 g sodium hydroxide in some water in a 100 ml volumetric flask. Add 4.0 ml hypochlorite solution and dilute with water to the mark. Store the solution refrigerated in the dark. If the solution is stored for weeks, it should be checked by titration with a sodium thiosulphate solution.

Dilute reagent (1) and reagent (2) with water 1:4 before use. These solutions must be prepared daily.

Standard solutions (for nitrate and ammonium):

- (3) Standard solution I, 500 mg NO<sub>3</sub>/l and 200 mg NH<sub>4</sub>/l:  
Dry potassium nitrate and ammonium sulphate for 1 hour at 105 °C, and then cool for 20 minutes in a desiccator. Dissolve exactly 0.815 g potassium nitrate and exactly 0.735 g ammonium sulphate in water in a 1000 ml volumetric flask. Dilute to the mark with water. Store the solution refrigerated in the dark.
- (4) Standard solution II, 5.0 mg NO<sub>3</sub>/l and 2.0 mg NH<sub>4</sub>/l:  
Dilute 5 ml of standard solution I (3) to 500 ml with water in a volumetric flask.

#### 4.4.2.6 Calibration and analytical procedure

Prepare a series of calibration solutions according to Table 4.4.1.

Table 4.4.1: Calibration solutions for ammonium and nitrate.

Calibration solution No.	mg NO <sub>3</sub> /l	mg NH <sub>4</sub> /l	
1	5.0	2.0	Standard solution II
2	2.5	1.0	Dilute 100 ml of standard solution II to 200 ml with water
3	0.5	0.2	Dilute 20 ml of standard solution II to 200 ml with water
4	0.25	0.10	Dilute 10 ml of standard solution II to 200 ml with water
5	0.125	0.05	Dilute 5 ml of standard solution II to 200 ml with water
6	0.0	0.0	Water

These solutions may be stored in the refrigerator for a few days.

Start the pump and check the flow, all connections, tubings and debubblers with water running through the instrument. Turn on the photometers and the recorders (paper speed 10 mm/min.). Connect the tubings to the reagents and check that the baseline is stable.

Avoid air in the column containing the reducing agent. Therefore, do not connect the column to the pump before the apparatus is filled with liquids.

Fill the cups of the automatic sampler with samples and standard solutions. Sampling time is 90 seconds and rinsing time with water after each sample is 105 seconds. Start with the calibration solutions and run the calibration solution no. 1, 3, 5 and 6 between every tenth sample.

After analyses, run water through the system until all reagents are rinsed out. Turn off the recorder, photometer, sampler and pump, and loosen the tubings in the pump so they are not stretched.

Prepare a calibration curve by plotting the absorbances at 630 nm of each of the standard solutions against its concentration of ammonium.

#### ***4.4.2.7 Expression of results***

Convert the recorder response (absorbance) of the sample to mg N/l by means of the calibration curves obtained just before or after the sample.

#### ***4.4.2.8 Interferences***

Iron (III) ions may interfere with the determination of ammonium if the concentration is higher than 2 mg/l. This does not often occur in precipitation samples.

#### ***4.4.2.9 References***

Harwood, J.E. and Huysen, D.J. (1970) Automated analysis of ammonia in water. *Water Res.*, 4, 695-704.

## 4.5 Determination of chloride in precipitation

When an ion chromatograph is not available, chloride may be determined spectrophotometric as described below.

### 4.5.1 Spectrophotometric mercury thiocyanate-iron method

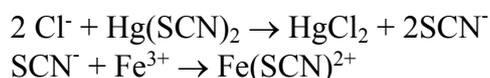
#### 4.5.1.1 Field of application

The method can be used for direct determination of the chloride ion content in precipitation samples within the range 0.05 to 5 mg/l.

#### 4.5.1.2 Principle

Chloride ions will substitute the thiocyanate ions in undissociated mercury thiocyanate. The released thiocyanate ions react with ferric ions forming a dark red iron-thiocyanate complex.

The absorbance is measured at 460 nm.



#### 4.5.1.3 Instrumentation

- ◆ Spectrophotometer, equipped with 50 mm optical cells
- ◆ Pipettes
- ◆ Volumetric flasks
- ◆ Erlenmeyer flasks

#### 4.5.1.4 Chemicals

During the analysis, use only chemicals of recognized analytical grade and only double-distilled or deionized and distilled water.

- ◆ Perchloric acid (HClO<sub>4</sub>) 72%
- ◆ Mercury (II) (thiocyanate (Hg(SCN)<sub>2</sub>))
- ◆ Iron (III) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O)
- ◆ Sodium chloride (NaCl)
- ◆ Ethanol (C<sub>2</sub>H<sub>5</sub>OH)

#### 4.5.1.5 Reagents

- (1) Perchloric acid, 1:1  
Mix 1 volume 72% perchloric acid with 1 volume of water.
- (2) Mercury (II) thiocyanate solution, saturated:  
Shake 1 g Hg(SCN)<sub>2</sub> with 1000 ml ethanol. Filter the solution after 24 hours. The solution may be stored in a glass bottle at room temperature.
- (3) Iron (III) nitrate solution, 6%:  
Dissolve 6 g Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O in 100 ml 1:1 perchloric acid. Filter the solution after 24 hours.

- (4) Standard chloride solution I, 1000 mg/l:  
Dissolve 412.5 mg NaCl dried at 140-200 °C, in water and fill it up to 250 ml with water.
- (5) Standard chloride solution II, 10 mg/l:  
Dilute 10.0 ml standard chloride solution I to 100 ml with water.

#### **4.5.1.6 Calibration**

Preparation of the calibration curve:

- (1) Transfer 2.5, 5.0, 7.5, 10, 15, 20 and 25 ml of standard chloride solution II to 50 ml volumetric flasks, and fill up to the mark with water. These solutions contain 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 and 5.0 mg Cl/l.
- (2) Transfer 25 ml of the calibration solutions to 100 ml Erlenmeyer flasks. to each flask add with pipettes 5 ml mercury (II) thiocyanate solution and 2 ml iron (III) nitrate solution. Mix well between and after the additions. After 20 minutes, measure the absorbance in 50 mm cells at 460 nm.

As reference, use 25 ml water mixed well with 5 ml of reagent (2) and 2 ml of reagent (3).

Plot the readings against the concentrations and draw the calibration curve.

#### **4.5.1.7 Analytical procedure**

Transfer 25 ml of the precipitation sample to a 100 ml Erlenmeyer flask. Proceed according to 4.5.1.6 (2). Read the chloride content of the sample from the calibration curve.

#### **4.5.1.8 Interferences**

Bromide and iodide will give the same absorbance as the equivalent amount of chloride.

#### **4.5.1.9 References**

Iwasaki, I., Utsumi, S., and Ozawa, T. (1952) New colorimetric determination of chloride using mercuric thiocyanate and ferric ion. *Bull. Chem. Soc. Japan*, 25, 226.

Zall, M., Fisher, D., and Gamer, Q. (1956) Photometric determination of chlorides in water. *Anal. Chem.*, 28, 1665-1668.

## **4.6 Determination of sodium, potassium, magnesium, and calcium in precipitation**

Sodium, potassium, magnesium, and calcium in precipitation can be analysed by atomic spectroscopic methods or with ion chromatography. Both flame (AAS and AES) and plasma (ICP-AES and ICP-MS) based methods can be used, but only the flame methods are described in this manual. For these ions ion chromatography have no special advantage concerning sensitivity, precision and accuracy over the spectroscopic methods, but analysis of all the ions in one run is not possible with flame AAS or AES.

### **4.6.1 Determination by flame atomic spectroscopy (AAS or AES)**

#### **4.6.1.1 Field of application**

The method can normally be used for the determination of sodium, magnesium, potassium and calcium in precipitation within the range 0.01-2 mg/l, but this will depend to a certain degree on the commercial instruments used.

#### **4.6.1.2 Principle**

The ions in the sample solution are transformed to neutral atoms in an air/acetylene flame. Light from a hollow cathode or an electrodeless discharge (EDL)-lamp is passed through the flame. The light absorption of the atoms in the flame, which is proportional to the ion concentration in the sample, is measured by a detector following a monochromator set at the appropriate wavelength. The described principle holds for the measurement performed in the AAS-mode. In the AES-mode, the light emitted from the atoms exited in the flame is measured. Most commercial instruments can be run in both modes. Sodium may be measured more favorably in the emission mode.

#### **4.6.1.3 Interferences**

In atomic absorption spectroscopy both ionization- and chemical interferences may occur. These interferences are caused by other ions in the sample, and result in reduction of the number of neutral atoms in the flame. The ionization interference is avoided by adding a relative high amount of an easily ionized element to the samples and calibration solutions. For the determination of sodium and potassium, caesium is added. For the elimination of chemical interferences from e.g. aluminium and phosphate, lanthanum can be added to the samples and calibration solutions.

#### **4.6.1.4 Instrumentation**

Atomic absorption spectrophotometer with a digital readout, suitable recorder or a PC. The wavelength range must be 200-800 nm. Preferably the spectrophotometer should also have the possibility to be run in the emission mode.

EDL or hollow cathode lamps for Na, K, Mg and Ca. Single element lamps are preferred, but multi-element lamps may be used. EDLs are more intense than hollow cathode lamps, and is preferred for K and Na. When performing analyses in emission mode, no lamps are needed.

Pipettes and volumetric flasks in various sizes.

#### **4.6.1.5 Chemicals**

- Deionized water
- Hydrochloric acid (HCl), suprapur, 37%
- Caesium chloride (CsCl), suprapur or Cs-solution specially produced for AAS
- Lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), 99.99% or La-solution specially produced for AAS
- Sodium chloride (NaCl), spectrapure
- Potassium chloride (KCl), spectrapure
- Magnesium oxide (MgO), spectrapure
- Calcium carbonate (CaCO<sub>3</sub>), spectrapure

Compressed gas and pressure-reducing valves. Both acetylene and air are needed. The air may be supplied from a compressor with a cleaning unit.

#### **4.6.1.6 Reagents**

*Caesium-Lanthanum-solution, 100.000 mg Cs/l + 50.000 mg La/l*

Transfer 5,865 g La<sub>2</sub>O<sub>3</sub> and 12,67 g CsCl to a 100 ml volumetric flask. Add about 50 ml deionized water and 25 ml suprapure HCl, and dilute to the mark with deionized water.

Commercial available solutions specially produced for AAS may be used.

It is very important that the caesium and lanthanum-solutions used have a low content of sodium, potassium, magnesium and calcium since a relative high concentration of this solution is added to the sample.

#### **4.6.1.7 Calibration solutions and stock solutions**

*Na, 1000 mg/l:*

Transfer 2,542 g NaCl, dried at 140 °C for 1 hour before weighing, to a 1000 ml volumetric flask, add 50 ml of deionized water and 1 ml HCl and shake until all is dissolved. Dilute to the mark with deionized water. Store the solution in a polyethylene bottle.

*K, 1000 mg/l:*

Transfer 1,907 g KCl, dried at 110 °C for 1 hour before weighing, to a 1000 ml volumetric flask. Add 50 ml of deionized water and 1 ml HCl and shake until all is dissolved. Dilute to the mark with deionized water. Store the solution in a polyethylene bottle.

*Mg, 1000 mg/l:*

Transfer 1,658 g MgO to a 1000 ml volumetric flask. Add 10 ml HCl and shake until all is dissolved. Dilute to the mark with deionized water. Store the solution in a polyethylene bottle.

*Ca, 1000 mg/l:*

Transfer 2,497 g CaCO<sub>3</sub>, dried at 180 °C for 1 hour before weighting, to a 1000 ml volumetric flask. Add 50 ml of deionized water, and dissolve slowly with a minimum of HCl. Dilute to the mark with deionized water. Store the solution in a polyethylene bottle.

*Working standard solution, Na, K, Mg and Ca 10 mg/l:*

Pipette 10,0 ml of each of the stock solutions Na, K, Mg, and Ca 1000 mg/l to a 1000 ml volumetric flask. Dilute to the mark with deionized water. Store the solution in a polyethylene bottle. The solution should be made fresh each time the calibration solutions are prepared.

*Calibration solutions for Na, K, Mg and Ca:*

Pipette 1, 2, 5, 10, 15, 20, 40, and 50 ml of the working standard solution, 10 mg/l to each of eight 100 ml volumetric flasks. Add 1 ml of the Cs-La-solution and dilute to the mark with deionized water. The concentrations in the solutions will be 0,1, 0,2, 0,5, 1,0, 1,5, 2,0, 4,0 and 5,0 mg/l respectively. A solution with 1 ml Cs-La- solution diluted to 100 ml is used as a blank.

The calibration solutions and the blank should be stored in polyethylene bottles and made fresh the day of analysis.

#### **4.6.1.8 Calibration of the instrument**

After a warm-up time of the instrument, set the wavelength for the element to be analysed as given in Table 4.6.1, and the slit width and the air/acetylene ratio as given in the instruction manual for the instrument. Ignite the flame. Adjust the reading of the instrument to zero by spraying the blank into the flame. Run the calibration solutions and read the absorption (or emission) signals from the readout. Plot the calibration graph.

The instrument should be recalibrated after every 20-30 samples. A control solution should also be run after each calibration.

*Table 4.6.1: Wavelength settings for the analyses.*

Element	Sodium	Potassium	Magnesium	Calcium
Wavelength nm	589.6	766.5	285.5	422.7

#### **4.6.1.9 Analytical procedure**

Transfer 10 ml of the sample to a test tube. Add with a micro pipette 100 µl of the Cs-La solution and mix well. Run the samples and read the absorption (or emission) signal from the readout. Use the calibration graph to find the concentration in the sample.

**Note:** Read and follow the instructions for the instrument carefully.

## 4.7 Determination of pH in precipitation

### 4.7.1 Potentiometric method

#### 4.7.1.1 Principle

The method is based on the determination of the potential difference between an electrode pair consisting of a glass electrode sensitive to the difference in the hydrogen ion activity in the sample solution and the internal filling solution, and a reference electrode, which is supposed to have a constant potential independent of the immersing solution. The measured potential difference is compared with the potential obtained when both electrodes are immersed in a solution or buffer with known pH or hydrogen ion concentration. The pH is defined by the formula:

$$\text{pH}_{(\text{sample})} = \text{pH}_{(\text{reference})} + (E_{(\text{sample})} - E_{(\text{reference})}) F/RT \ln 10$$

where E are the electrode potentials, R is the universal gas constant, T the absolute temperature and F is the Faraday constant.

This is an operationally defined pH. Buffers of known pH are specified by National Bureau of Standards, now the National Institute of Standardized Technology (NIST). The primary standard and the most widely used buffer for pH-meter calibration is 0.05 M potassium hydrogen phthalate, which has a pH of 4.00 at 20° C, and a hydrogen ion activity of  $10^{-4}$  M. This latter hydrogen ion activity is based on theoretical calculations (the Bates-Guggenheim convention).

In precipitation samples, the ionic strength will typically be in the region  $10^{-3}$  to  $10^{-5}$ . The activity coefficient for monovalent cations such as the hydrogen ion will therefore be in the range 0.95-0.99. This corresponds to <0.02 pH-units difference between pH and  $-\log(\text{H}^+)$ . Much more critical is the assumption of a constant reference electrode potential when going from a relatively concentrated potassium hydrogen phthalate solution to extremely dilute precipitations samples. The problem arises because of the inherent possibility of building up a liquid junction potential between the internal solution of the reference electrode, and the sample solution. This liquid junction potential may be larger if the ionic strength difference between the two solutions is large. It is reduced by making the boundary between the concentrated filling solution and the sample as sharp as possible. Various designs of pH cells meeting this criterion have been proposed. Tests of commercial electrodes against dilute acid solutions and low ionic strength buffers with known pH or hydrogen ion concentrations have shown, however, that this problem has largely been overcome with modern pH instrumentation and electrode systems.

However, it is strongly recommended to check the electrode system at regular intervals, by measuring the “apparent pH” of a solution with low ionic strength with known pH or hydrogen ion concentration. The pH readings should be within 0.02 or 0.05 pH-units of the “theoretical” result. If this is not the case, or if the reading is unstable during stirring of the solution, the reference electrode should be replaced. New glass electrodes should be tested against at least two buffers to see that the response is Nernstian.

The reference electrode should preferably be stored in dilute potassium chloride solution (0.1M).

#### **4.7.1.2 Instrumentation**

pH-meter with the possibility of reading to the nearest 0.02 pH-units or preferably to the nearest 0.01 pH-unit.

A glass electrode and a reference electrode must be used with the pH-meter. The reference electrode should be suitable for measurement in low-ionic strength solutions and preferably be of the calomel type filled with saturated potassium chloride. Other reference electrodes or combination electrodes may be used, but all electrodes should be checked for acceptable performance.

Magnetic stirrer, with teflon coated stirring bar.

Beakers used for the test solution should be made of borosilicate glass or polyethylene.

#### **4.7.1.3 Chemicals**

Buffer solutions for the calibration of the pH-meter. Preferably the two buffer solutions given in Section 4.7.1.4, which are recommended as standards by the U.S. National Institute of Standards and Technology (NIST).

#### **4.7.1.4 Reagents**

National Bureau of Standards solutions with known pH.

- (1) 0.05 M potassium hydrogen phthalate ( $C_6H_4(COOH)(COOK)$ )  
pH = 4.00 at 20 °C  
pH = 4.01 at 25 °C

Dissolve 10.12 g potassium hydrogen phthalate,  $C_6H_4(COOH)(COOK)$ , dried at 120 °C, in 1000 ml distilled water.

- (2) 0.025 M potassium dihydrogen phosphate ( $KH_2PO_4$ ) and 0.025 M disodium hydrogen phosphate ( $Na_2HPO_4$ )  
pH = 6.88 at 20 °C  
pH = 6.86 at 25 °C

Dissolve 3.39 g potassium dihydrogen phosphate,  $KH_2PO_4$ , and 3.53 g disodium hydrogen phosphate,  $Na_2HPO_4$ , dried at 120° C, in 1000 ml distilled water. Instead of the anhydrous disodium hydrogen phosphate, 4.43 g of undried dihydrate,  $Na_2HPO_4 \cdot 2 H_2O$ , may be used.

Commercial available buffer solutions may also be used, but should be checked against the primary standard buffers described above. The buffers should be kept in the dark in well closed bottles of borosilicate or polyethylene.

#### **4.7.1.5 Calibration**

Calibrate the pH-meter according to the instruction manual for the instrument using one, or preferably two, buffer solutions. The temperature of the buffer solutions must be known. The calibration should be checked after each set of samples.

#### **4.7.1.6 Analytical procedure**

Measure the pH-value of the sample according to the instruction manual for the instrument. The solution may be stirred, but not vigorously. The temperature of the sample solution must be the same as the temperature of the buffer solution used for calibration.

Rinse the electrodes thoroughly with distilled water between each measurement, and wipe off the excess water with a soft paper.

Store the electrodes in 0.1 M KCl-solution or according to the manufacturers recommendations. The reference electrode should not be stored in distilled water!

#### **4.7.1.7 Performance test of the electrode pair**

As mentioned in Section 4.7.1.1 the behaviour of the reference electrode is the main source of errors in pH-measurements, especially in low ionic strength solutions. In order to check the performance of the reference electrode, control measurements should be made on solutions of dilute acids or dilute buffers to verify that correct values are obtained for solutions of lower ionic strengths. A solution which should give a pH ~4.00 could be used for the test. A  $10^{-4}$ M HCl-solution should give a pH of  $3.99 \pm 0.05$ .

Electrode pairs should also show minimal differences between measurements made in stirred and unstirred low ionic strength solutions.

Usually the liquid junction between the solution and the saturated KCl-solution in the reference electrode is formed in a porous plug of ceramic fibre. Slow stirring removes the concentrated KCl-solution which slowly runs out through this capillary.

If the stirring is too vigorous, the ionic medium in the plug itself may be diluted. This will increase the liquid junction potential, and should be avoided. The liquid junction potential may also increase if the porous plug is clogged up by impurities.

#### **4.7.2 References**

Bates, R.G. (1965) Determination of pH, theory and practice. New York, Wiley.

Linnet, N. (1970) pH measurements in theory and practice. Copenhagen, Radiometer.

Westcott, C.C. (1978) pH measurement. New York, Acad. Press.

Davison, W. and Woof, C. (1985) Performance tests for the measurement of pH with glass electrodes in low ionic strength solutions including natural waters. *Anal. Chem.*, 57, 2567-2570.

## 4.8 Determination of strong and weak acids in precipitation

### 4.8.1 Coulometric titration method

#### 4.8.1.1 Field of application

This method is applicable to determination of strong acids in precipitation samples within the concentration range  $10^{-5}$  to  $10^{-3}$  M. Higher concentrations of acidity are not expected in precipitation. The lower concentration limit is close to the concentrations at background sites without alkaline mineral dust.

#### 4.8.1.2 Principle

In the coulometric titration method (Liberti et al., 1972), the acid is titrated at constant current with hydroxyl ions liberated at a platinum electrode, a silver-silver bromide electrode serving as the counter electrode. The overall reaction is:



The emf of a glass-calomel electrode pair is read at intervals and the results are used to construct a Gran's plot (Gran, 1952; Rosotti and Rosotti, 1965), which gives the endpoint of the titration by extrapolation of the straight part of the curve.

The only necessary modification is the addition of a constant, known amount of acid to the sample before the titration, in order to facilitate the titration of weakly acidic or alkaline samples without interference from carbon dioxide.

#### 4.8.1.3 Instrumentation

- Expanded-scale pH-meter (Radiometer PHM 26 or an instrument with similar specifications).
- Constant current source (2-10 mA adjustable)
- A 4.5 V dry battery with an adjustable series resistance and a mA meter is sufficient for measurements, but "coulometers" are available commercially (e.g. Metrohm).
- Titration vessel, 100 ml  
This should have a suitable lid with holes to serve as support for the electrodes and the nitrogen inlet, and be supplied with a thermostat jacket.
- Thermostat ( $25\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$ )
- Sensing electrodes  
An ordinary glass electrode (pH range 0-10) and a calomel reference electrode, or a combined electrode.
- Working electrodes  
The platinum electrode ( $2 \times 2\text{ cm}^2$ ) is made of bright platinum (sheet or net).  
The silver electrode is made from 99.9% pure silver, 1.0 mm dia. wire, about 30 cm long and coiled to a suitable dimension.
- Pipette : 50 ml
- Micro pipettes : 0.5, 1.0 ml
- Volumetric flask : 1000 ml

#### 4.8.1.4 Chemicals and reagents

During analysis, use only reagents of recognized analytical grade. The water used for dilution and rinsing must be double-distilled or de-ionized and distilled.

Nitrogen gas (N<sub>2</sub>) 99.9%  
Potassium bromide (KBr)  
Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) 0.05M  
Buffer solution pH = 4.00

Solution I: 1 M KBr and 2.5 · 10<sup>-3</sup> M H<sub>2</sub>SO<sub>4</sub>  
Transfer 120.0 g KBr and exactly 50 ml of 0.05M H<sub>2</sub>SO<sub>4</sub> to a 1000 ml volumetric flask. Fill up to the mark with water.

#### 4.8.1.5 Analytical procedure

Turn on all instruments, and allow heating for ½ hour. Adjust the pH-meter to pH = 4.00, using the buffer solution. Transfer 50 ml of the sample into the thermostated titration vessel, and add 1 ml of solution I. Start nitrogen purging and adjust flow to give continuous agitation of the solution. The bubbles should not disturb the solution between the sensing and the working electrodes. Measure the pH of the solution. If the pH of the sample is above 5.6 it may be necessary to add more than 1 ml of solution I.

Wait until pH reading is constant. Switch pH-meter to read millivolts (range 0-240 mV with glass electrode positive) and start the electrolysis current.

Read the glass electrode potential vs the calomel electrode every 20 seconds and continue until the potential changes sign (at pH ca. 8). Stop the electrolysis.

Plot Gran's function,  $\Psi$ , at 25°C, see Table 4.8.1 against electrolysis time (in seconds). The plot intercepts the abscissa at the equivalence point,  $t_e$  (F = Faradays constant, R = the universal gas constant, T = absolute temperature).

$$\psi = 10^{\frac{EF}{RT \ln 10}}$$

$$\psi = 10^{\frac{E}{59.15}} \text{ at } 25^\circ\text{C}$$

Table 4.8.1: Gran's function.

$E_{mV}$	$\psi$	$E_{mV}$	$\psi$	$E_{mV}$	$\psi$	$E_{mV}$	$\psi$
1	1.04	41	4.93	81	23.4	121	111
2	1.08	42	5.13	82	24.4	122	115
3	1.14	43	5.33	83	25.3	123	120
4	1.17	44	5.55	84	26.3	124	125
5	1.22	45	5.77	85	27.4	125	130
6	1.26	46	5.98	86	28.4	126	135
7	1.31	47	6.22	87	29.6	127	140
8	1.36	48	6.47	88	30.7	128	146
9	1.42	49	6.75	89	32.0	129	152
10	1.48	50	7.00	90	33.3	130	158
11	1.54	51	7.28	91	34.6	131	164
12	1.60	52	7.57	92	36.0	132	171
13	1.66	53	7.87	93	37.4	133	177
14	1.73	54	8.19	94	38.8	134	185
15	1.80	55	8.51	95	40.4	135	192
16	1.90	56	8.85	96	42.0	136	199
17	1.94	57	9.20	97	43.6	137	207
18	2.02	58	9.57	98	45.3	138	216
19	2.10	59	9.94	99	47.2	139	224
20	2.18	60	10.3	100	49.1	140	233
21	2.26	61	10.7	101	51.0	141	242
22	2.36	62	11.1	102	53.1	142	252
23	2.45	63	11.6	103	55.2	143	262
24	2.54	64	12.1	104	57.4	144	272
25	2.65	65	12.5	105	59.7	145	283
26	2.75	66	13.0	106	61.9	146	294
27	2.86	67	13.5	107	64.4	147	306
28	2.97	68	14.1	108	67.0	148	318
29	3.09	69	14.6	109	69.7	149	331
30	3.21	70	15.2	110	72.4	150	344
31	3.34	71	15.8	111	75.3	151	351
32	3.48	72	16.5	112	78.3	152	371
34	3.61	74	17.1	113	81.5	153	386
34	3.75	74	17.8	114	84.7	154	402
35	3.90	75	18.5	115	88.1	155	418
36	4.06	76	19.3	116	91.6	156	434
37	4.23	77	20.0	117	95.1	157	452
38	4.39	78	20.8	118	98.9	158	470
39	4.56	79	21.7	119	103	159	489
40	4.74	80	22.5	120	106	160	507

#### 4.8.1.6 Expression of results

The concentration of strong acid in the sample is calculated from the formula:

$$C_{H^+} = \frac{i \cdot t_e}{F \cdot V_o} - \frac{N_{H_2SO_4} \cdot V_{H_2SO_4}}{V_o}$$

or

$$C_{H^+} = \frac{i \cdot t_e \cdot 1000}{96\,500 \cdot 50} - 1 \cdot 10^{-4} \text{ moles/l}$$

where

i	=	electrolysis current in ampères
t <sub>e</sub>	=	electrolysis time at equivalence point (seconds)
F	=	Faradays constant (coulombs/mol)
V <sub>o</sub>	=	initial sample volume (litres)
N <sub>H<sub>2</sub>SO<sub>4</sub></sub>	=	normality of added sulphuric acid
V <sub>H<sub>2</sub>SO<sub>4</sub></sub>	=	volume of added sulphuric acid (litres)

#### Notes:

Borosilicate glass can be used for storage of samples.

The glassware must be treated with hot dilute acid and thoroughly soaked in distilled water prior to use. 12 hours with 10% hydrochloric acid at 90°C followed by 24 hours soaking in distilled water is considered adequate. Otherwise, alkali metals from the glass will diffuse into the samples.

Equipment for the automatic plotting of Gran's function is available. The equipment is described in Section 4.8.2.

#### 4.8.1.7 References

Gran, G. (1952) Determination of the equivalence point in potentiometric titrations. Part II. *Analyst*, 77, 661-671.

Liberti, A., Possanzini, M. and Vicedomini, M. (1972) The determination of the non-volatile acidity of rain water by a coulometric procedure. *Analyst*, 97, 352-356.

Rosotti, F.J.C. and Rosotti, H.J. (1965) Potentiometric titrations using Gran's plots. *Chem. Educ.*, 42, 375-378.

## **4.8.2 Coulometric titration of strong acid by means of an instrument for automatic plotting of Gran's function**

### **4.8.2.1 Field of application**

This automatic method can be used to determine the concentration of hydrogen ions in precipitation within the range  $10^{-5}$  to  $10^{-3}$  M.

### **4.8.2.2 Principle**

The basic principle is the same as for the manual method described in Section 4.8.1.

In the present method, the pH is continuously monitored by feeding the output from the pH-meter into an instrument for automatic plotting of the Gran's function (APGRAF), which gives a recorder output from 1.0 mV at pH 7 to 10 V at pH 3. This signal is thus proportional to the hydrogen ion concentration in the solution. Since the volume of the solution is not altered during the coulometric titration, and the hydroxyl ions are supplied at a constant rate, the recorder output gives the Gran's function directly.

The APGRAF consists of two amplifiers and a current source capable of delivering a constant current for coulometric titration ranging from 3.5 to 7.5 mA. The range can be extended to maximum 20 mA. The APGRAF is designed to work with the pH-meter RADIOMETER PHM 26c.

### **4.8.2.3 Instrumentation**

- Expanded scale pH-meter (RADIOMETER PHM 26c or instrument with equal specifications).
- Constant current source (2-10 mA adjustable).
- Instrument for automatic plotting of Gran's function (APGRAF, see below)
- Thermostated titration vessel, 100 ml, equipped with a lid with holes for electrodes and nitrogen inlet.
- Thermostat ( $25^{\circ} \pm 1^{\circ}\text{C}$ ).
- Sensing electrodes: Glass electrode (pH range 0 to 10) and calomel electrode, or a combined electrode.
- Working electrodes: Platinum electrode, sheet or net ( $2 \times 2 \text{ cm}^2$ ) made of bright platinum. Silver electrode made of 99.9% silver wire 30 cm long and 1.0 mm diameter, coiled to suitable dimensions.
- Volumetric flask, borosilicate glass 1000 ml.
- Pipettes : 25 ml, 50 ml.
- Micro pipettes : 0.5 ml, 1.0 ml.
- Recorder.

### **Construction of the APGRAF**

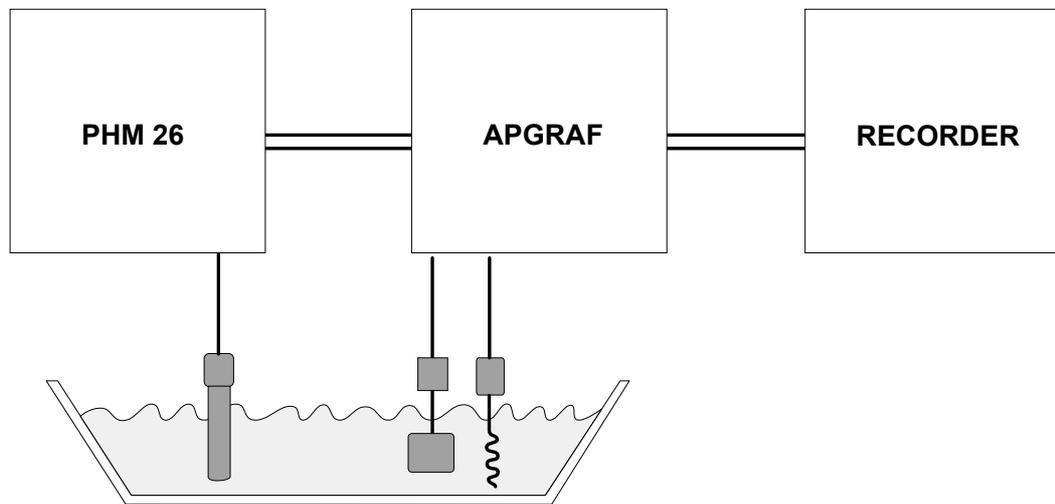
Figure 4.8.1 shows a block diagram of the layout, and a complete wiring diagram is shown in Figure 4.8.2. The 10 mV/pH output from the pH-meter is used as input signal to the preamplifier A1. The latter is adjusted to a gain of 1000 mV  $\text{pH}^{-1}$  and balanced to +2.0 V at pH 7 and -1.0 V at pH 4. The log amplifier A2 has

an output of 1 decade per volt input, connected in the antilog of voltage mode, i.e. +10V out for a -2V input and +10 mV for a +1V input.

The gain is adjusted by the 5 k $\Omega$  input resistor (potentiometer). The balance is adjusted by the 100  $\Omega$  potentiometer connected via 10 k $\Omega$  to pin 3 on A1. The ZF 5.6 zener is used to stabilize “Balance” versus temperature changes.

Amplifier A3 is a unity gain, non-inverting amplifier providing a low source resistance for amplifier A4 (current source). A4 supplies a current that is proportional to the input voltage, but the output polarity is reversed.

The desired current is set by selecting one of the outputs of the voltage divider which is fed into A3.



*Figure 4.8.1: Instrumental layout for automatic plotting of Gran's function.*

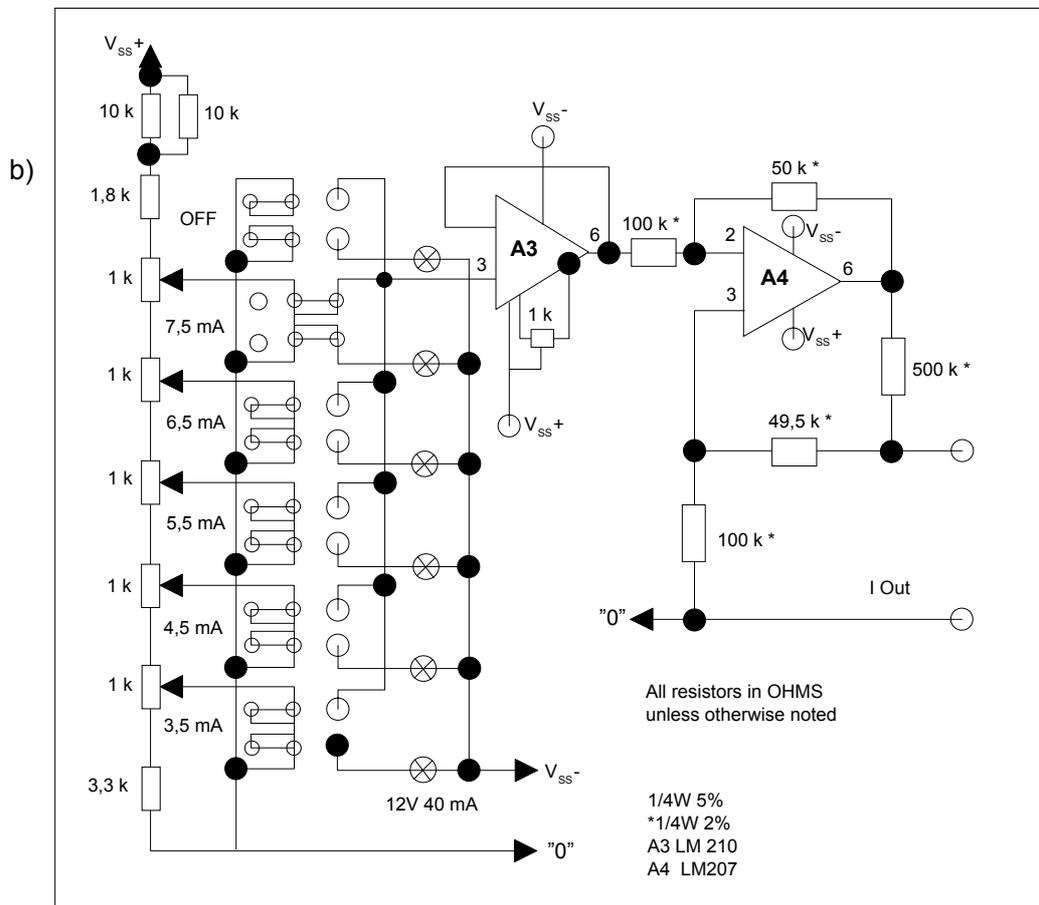
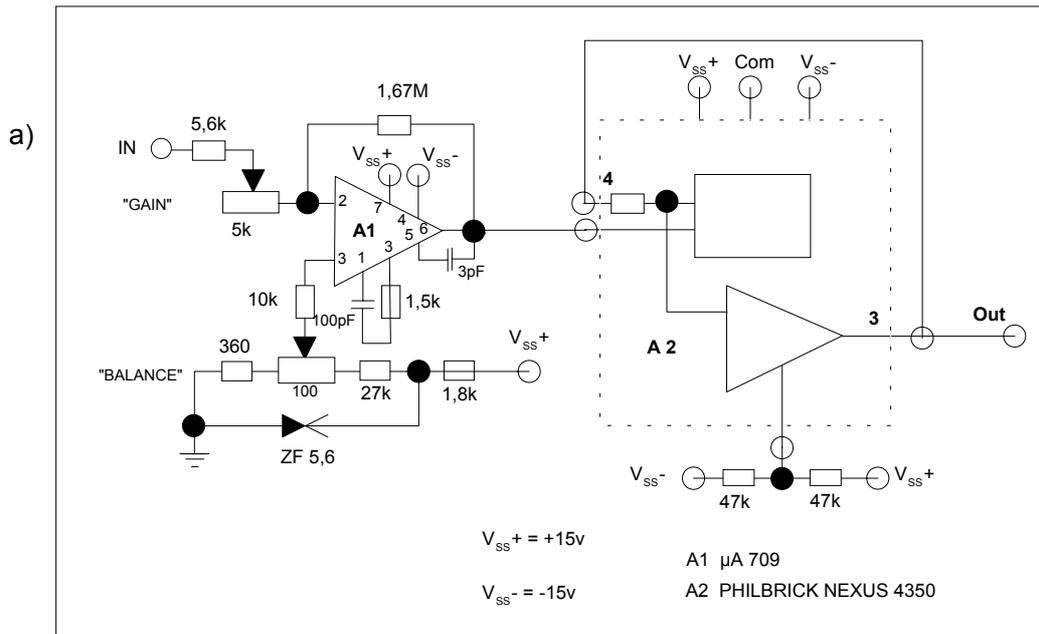


Figure 4.8.2: Wiring diagrams of a) amplifier and b) constant current source of the APGRAF (7.5 mA selected).

#### 4.8.2.4 Chemicals and reagents

Use only reagents of recognized analytical grade. The water must be double-distilled or deionized and distilled.

- Potassium bromide (KBr)
- Sulphuric acid 0.05 M (H<sub>2</sub>SO<sub>4</sub>)
- Nitrogen 99.9% (N<sub>2</sub>)

Solution I: 1M KBr and  $2.5 \cdot 10^{-3}$  M H<sub>2</sub>SO<sub>4</sub>:

Transfer 120.0 g KBr and exactly 50 ml 0.05 M H<sub>2</sub>SO<sub>4</sub> to a 1000 ml volumetric flask. Fill up to the mark with water.

#### 4.8.2.5 Calibration

- (1) Connect the APGRAF to the pH-meter.
- (2) Place the calomel electrode in a buffer solution with pH 4.
- (3) Let the output from the preamplifier (A1) stabilize.
- (4) Read the output voltage from the preamplifier.
- (5) Adjust the output to approximately -1.0V
- (6) Recheck pH and preamplifier output, note the values.
- (9) Check gain.

Example:	pH 4.0	output -0.900 V
	pH 7.0	output +2.230 V
Difference	pH 3.0	Difference output 3.130 V

$$\frac{3130 \text{ mV}}{3 \text{ pH - units}} = 1043 \text{ mV / pH - unit}$$

This should be adjusted to 1000 mV/pH-unit.

Try a couple of clockwise turns on “gain” potentiometer.

Repeat the procedure 1 through 9.

“Gain” and “Balance” interact. If gain is correctly set and balance has to be changed, recheck gain and readjust if necessary (“tracking”).

#### 4.8.2.6 Analytical procedure

Turn on all instruments, and allow 30 minutes warm-up. Adjust the pH-meter to pH = 4.00, using the buffer solution. Transfer 50 ml of the sample into the thermostated titration vessel, and add 1 ml of solution I. Start nitrogen purging and adjust flow to give continuous agitation of the solution. The bubbles should not disturb the solution between the sensing and the working electrodes. Measure the pH of the solution. If the pH of the sample is still above 4.0 add more of solution I until the pH is less than 4.0.

Switch the pH-meter to the mV position, and turn on the recorder (paper speed 1 mm/sec). Select the electrolysis current (3-5 mA) and start the titration. This

will result in a “jump” on the recorder trace, because the electrode potential is affected by the potential between the working electrodes. Minimize this effect by proper positioning of the electrodes. Mark the starting point on the paper. Continue the electrolysis until the recorder signal is zero (baseline). Stop the electrolysis and the recorder. Note the sample identification, electrolysis current, and the amount of acid (solution I) added, on the recorder sheet.

#### 4.8.2.7 Expression of results

Draw a vertical line from the starting point on the paper, to the baseline. Extrapolate the first straight part of the titration curve until it reaches the baseline, see Figure 4.8.3. (The curve is usually not a straight line at the end of the titration.) Measure the distance (mm) along the baseline between these two points (l).

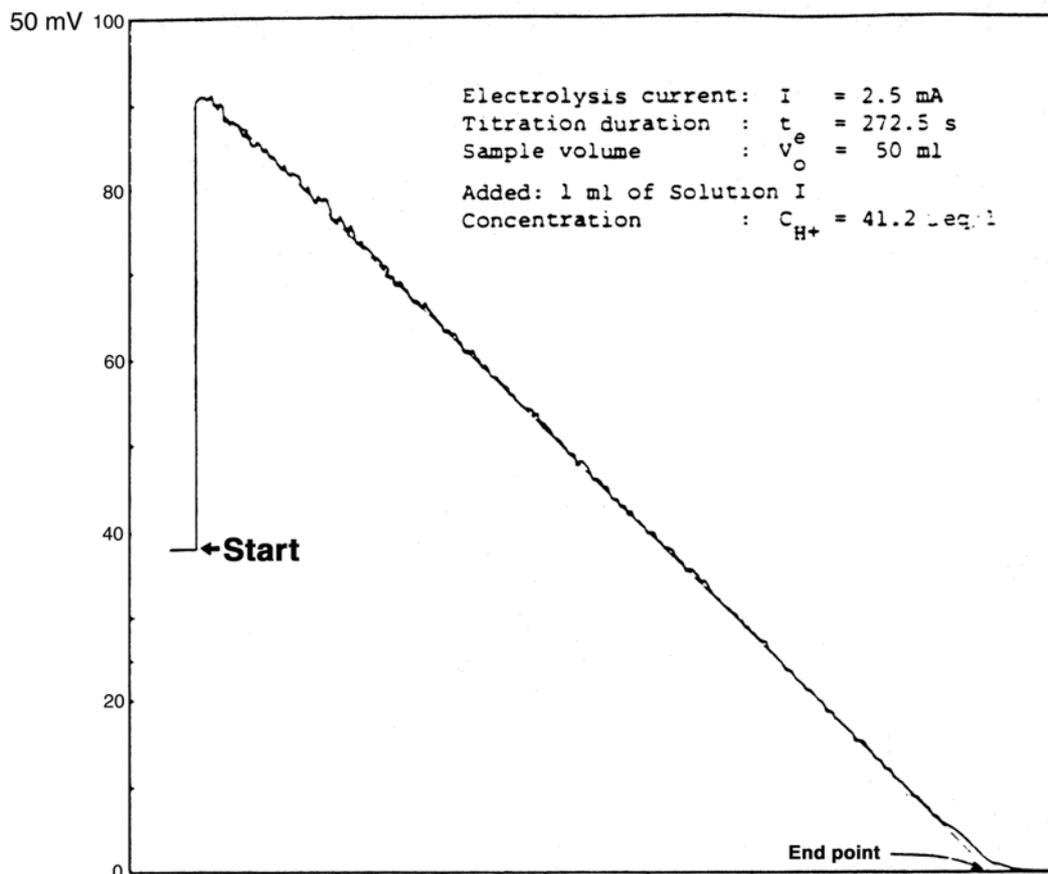


Figure 4.8.3: Titration graph for an actual precipitation sample.

The concentration of strong acid (in moles/litre) is calculated from:

$$C_{H^+} = \frac{1000 \cdot i \cdot t_e}{F \cdot V_o} - \frac{N_{H_2SO_4} \cdot V_{H_2SO_4}}{V_o}$$

where

- i = electrolysis current (A)
- $t_e$  = duration of analysis (s), determined from the distance between the start of titration and the end point on the chart, and the paper chart speed.
- F = Faraday constant (96500 C/mol)
- $V_o$  = sample volume (ml), normally 50 ml
- $N_{H_2SO_4}$  = normality of added sulphuric acid
- $V_{H_2SO_4}$  = volume (ml) of added sulphuric acid

## 4.9 Determination of conductivity

The conductivity of precipitation samples depends on the concentrations of the various ion species and their different ability to transport electric charges in a solution, i.e. the ion species equivalent conductivity. This conductivity is temperature dependent and increases approximately 2% per degree in aqueous solutions for most ion species. Conductivity measurements can through comparison with estimated conductivity and in combination with ion balance calculations and records of old data help identify ion concentrations which are wrong or inaccurate.

### 4.9.1 Principle

Conductance is the inverse of resistance in a solution and the conductivity the inverse of specific resistance. Conductivity is measured with a bridge and a measuring cell, and it is dependent upon distance between the electrodes and their area, in the measurement cell. This is expressed by the cell constant which is a characteristic of the measurement cell. The resistance,  $R$ , can be expressed as

$$R = \rho \frac{l}{A}$$

where  $l$  is distance between the electrodes and  $A$  their area.  $\rho$  is the specific resistivity. The specific conductance, or conductivity  $\kappa$  is

$$\kappa = \frac{l}{\rho} \text{ or } \frac{l}{R} \cdot \frac{l}{A}$$

where  $\frac{l}{A}$  is the cell constant.

### 4.9.2 Instrumentation

The conductivity meter applied should have a measurement range 1–1000  $\mu\text{S}/\text{cm}$ , a precision within this range of 0.5% and an accuracy within 1%. Conductivity meters may be able to give the result at a pre-selected reference temperature while the actual measurement is carried out at room temperature. Other meters need a waterbath for the measurement cell in order to give a result at 25 °C, which is the temperature used for EMEP's and WMO GAW's conductivity measurements. Besides the conductivity meter itself, a platinum conductivity cell is needed, and possibly a water bath and a thermometer.

### 4.9.3 Chemicals

- Deionized water, conductivity < 0.5  $\mu\text{S}/\text{cm}$
- Potassium chloride p.a. quality

#### 4.9.4 Calibration solutions

##### *0.1M KCl stock solution*

Transfer 7.4560 g KCl, dried at least 2 hours at 110°C, to a volumetric flask and dilute to 1000.0 ml with deionized water. The solution should be transferred to a plastic flask. The stability of the solution is one year at most.

A series of calibration solutions based on the 0.1 M KCl stock solution is used for the calibration procedure, as seen from Table 4.9.1. The solutions should be kept well closed in plastic flasks at room temperature. The stability is 6 months at most.

Table 4.9.1: Calibration standards for conductivity at 25°C.

Concentration M KCl	Conductivity μS/cm	Upper limit μS/cm	Lower limit μS/cm
0.0500	6668	6801	6535
0.0200	2767	2822	2711
0.0100	1413	1441	1395
0.0050	717.8	735	700
0.0010	147.0	149	145
0.0005	73.9	77.8	70.2
0.0001	14.94	16.5	13.5

#### 4.9.5 Calibration of the instrument

##### *Calibration of the cell constant*

The cell constant should be calibrated whenever the conductivity of the 0.0010 M KCl calibration solution is outside the upper and lower limits given in Table 4.9.1. The age of the calibration solution must be checked before the calibration. Enter the new constant after having followed the cell constant calibration procedure given in the instrument manual. Reference temperature (or measurement temperature) should be 25°C.

##### *Calibration with calibration solutions*

Before running a series of precipitation samples, measurements should be carried out with the 0.0001, 0.001 and 0.0100 M KCl calibration solutions. Check the age of the calibration solutions. If the measurements are outside the limits given in Table 4.9.1 the instrument must be checked as specified in the manufacturers instrument manual followed by measurements with all calibration solutions in Table 4.9.1. Reference temperature should be 25°C. Results obtained at other temperatures can be corrected to 25°C as seen in the next Section.

#### 4.9.6 Measurement procedure

The procedure given in the instrument manual must be followed. In general the measurement cell has to be rinsed well with deionized water, dried with a Kleenex, and rinsed again with the measurement solution a few times before a correct reading can be made. The display will also need some time to stabilize

before the reading. The reference temperature should be 25°C, and the result expressed in  $\mu\text{S}/\text{cm}$ . If the measurement is carried out at a different temperature, the result should be corrected to 25°C. The temperature coefficient for aqueous solutions is approximately 2% pr. degree. The formula below will give the conductivity,  $\kappa_{25}$ , corrected to 25°C when the measurement  $I_t$  is carried out at a temperature  $t$ .

$$\kappa_{25} = \frac{\kappa}{(1.0 + 0.02(t - 25))}$$

#### ***4.9.7 Maintenance and storage of measurement cell***

It is essential that the manufacturers instructions are followed. Cleaning of the measurement cell is needed if a contamination is discovered.

## **4.10 Determination of sulphur dioxide as sulphate ions on impregnated filters**

The extraction of sulphate from the alkaline impregnated filters is described in Section 3.6. For the Thorin method the extract has a too high pH to permit a direct analysis and the solution has to be treated with a cation resin before analysis.

### ***4.10.1 Determination of sulphur dioxide as sulphate by ion chromatography***

The procedure after the extraction from the filter (Section 3.6) for Dionex systems and Waters systems are described in Section 4.1.

### ***4.10.2 Determination of sulphur dioxide as sulphate spectrophotometric by the barium perchlorate – Thorin method***

#### ***4.10.2.1 Field of application***

This method can be used for the determination of sulphur dioxide in ambient air after the sulphur dioxide has been absorbed on a potassium hydroxide impregnated filter (see Section 3.6). The concentration range is 0.1 to 8 mg SO<sub>2</sub> per litre leaching solution.

#### ***4.10.2.2 Principle***

Sulphur dioxide is absorbed on a potassium hydroxide impregnated filter as sulphite. During the sampling period and storage the sulphite will be partly oxidized to sulphate. The filters are extracted with water, and hydrogen peroxide is added to oxidize the remaining sulphite to sulphate. Before analysis by the Thorin method (see Section 3.6.3), the extracted solution has to be treated with a cation exchange resin to remove the potassium and to neutralize the solution.

#### ***4.10.2.3 Instrumentation***

Same as listed in Section 4.2.1 In addition 100-150 ml polyethylene beakers or 30 ml centrifuge tubes are needed for the extraction.

#### ***4.10.2.4 Chemicals***

Same as listed in Section 4.2.1. In addition: Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), 30%. Traces of sulphate can be removed from the ion exchange resin by washing with 0.1 M sodium hydroxide, 0.1 M hydrochloric acid and distilled water before use.

#### ***4.10.2.5 Reagents***

Same as listed in Section 4.2.1.

#### ***4.10.2.6 Calibration***

Proceed as described in Section 4.2.1.

#### ***4.10.2.7 Analytical procedure***

1. Leaching of the filters; proceed as described in Section 3.6.1.2.
2. Analysis; proceed as described in Section 4.2.1.

#### **4.10.2.8 Expression of results**

The concentration of sulphur dioxide in the air expressed as microgram of sulphur per cubic metre, is given by:

$$C = 1000 \frac{a \cdot v_1}{v_2}$$

a = concentration of sulphur in milligrams per litre in the leaching solution, read from the calibration curve.

v<sub>1</sub> = the volume, in litres, of the leaching solution.

v<sub>2</sub> = the volume, in cubic metres, of the air sample.

#### **4.10.2.9 References**

Healy, C. and Atkins, D.H.F. (1975) The determination of atmospheric sulphur dioxide after collection on impregnated filter paper. Harwell, U.K. Atomic Energy Authority (AERE-R 7956).

## **4.11 Determination of nitrogen dioxide as nitrite**

The TGS method is only described in the previous version of this manual (EMEP/CHEM 3/77). The recommended method for NO<sub>2</sub> is sampling with iodide impregnated glass sinter filters followed by the nitrite determination described below.

### ***4.11.1 Determination of nitrite in extracts from impregnated glass sinters***

#### ***4.11.1.1 Scope and application***

This method is applicable to the determination of nitrite in extracts from iodide impregnated glass sinter filters (see Section 3.3.1) in the range 0.02–3 µg NO<sub>2</sub><sup>-</sup>-N/ml. Samples containing higher concentrations must be diluted prior to the analysis and the impregnation matrix have to be added in the dilution step to match the matrix of the calibration standards.

#### ***4.11.1.2 Principle***

Nitrite (NO<sub>2</sub><sup>-</sup>) and sulphanilamide form a diazo compound in acid solution which by a coupling reaction with NEDA, N-(1-naphthyl)-ethylenediamine-dihydrochloride, gives a red azo dye. The concentration in the solution is determined spectrophotometrically at 540 nm. The calibration standards must match the sample solutions by addition of an iodide matrix.

#### ***4.11.1.3 Instrumentation***

Spectrophotometer or filter photometer capable of measuring at 540 nm.

Optical glass cells, 10, 20 or 50 mm.

Bulb pipettes, micropipette (adjustable) and dispenser (adjustable).

Capped vials or reagent tubes, 10ml.

Volumetric flasks.

#### ***4.11.1.4 Chemicals***

All reagents must be of recognized analytical grade. The water used for dilution should be deionized. The water should have a resistance > 10 MΩ/cm. The sample, calibration standards and reagent solution bottles should be made of borosilicate glass, polyethylene or polypropylene.

Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), conc.

Sulphanilamide (NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH<sub>2</sub>)

NEDA, N-(1-naphthyl)-ethylenediamine-dihydrochloride  
(C<sub>10</sub>H<sub>7</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>\*2HCl)

Sodium iodide (NaI)

Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)

Sodium nitrite (NaNO<sub>2</sub>)

#### **4.11.1.5 Reagents and solutions**

##### ***Iodide matrix solution***

(10x concentration of leachate): 9.8 g NaI, 1.46 g Na<sub>2</sub>CO<sub>3</sub> and 133 µl triethanolamine dissolved and diluted to 100 ml with deionized water.

##### ***Mixed reagent***

(Sulphanilamide-NEDA solution): To a 1000 ml volumetric flask add about 500 ml deionized water, 8 ml phosphoric acid, 8 g sulphanilamide and 0.2 g NEDA. Dissolve and dilute to 1000 ml with deionized water.

##### ***Sodium nitrite stock solution, 1000 µg NO<sub>2</sub>-N/ml***

Dissolve 4.927 g NaNO<sub>2</sub> which has been dried 1 hour at 105 °C in some deionized water and dilute to 1000 ml with deionized water. This solution can be stored for several months if stored in a borosilicate bottle in a refrigerator.

##### ***Nitrite working standard, 10 µg NO<sub>2</sub>-N/ml***

10 ml of the sodium nitrite stock standard is diluted to 1000 ml with deionized water. This solution can be used for 1 month if stored in a borosilicate bottle in a refrigerator.

##### ***Nitrite calibration standards***

To 100 ml volumetric flasks add 0, 0.5, 1.0, 5.0, 10.0 and 30.0 ml nitrite working standard, 10 µg NO<sub>2</sub>-N/ml and 10 ml iodide matrix solution. Dilute to the mark with deionized water. These calibration standards contain 0, 0.05, 0.10, 0.50, 1.0 and 3.0 µg NO<sub>2</sub>-N/ml and have the same iodide concentration as the samples. The range of the calibration solutions may be different if only low concentrations occur, but five calibration standards in addition to a blank should be used. These calibration standards should be made new every day.

#### **4.11.1.6 Analytical procedure**

Transfer 0.5 ml sample leachate to a 10 ml vial or test tube and add 3.0 ml mixed reagent. Close the vial or test tube, shake well and read the absorbance at 540 nm after at least 15 min. Treat 0.5 ml of the nitrite calibration solutions the same way and plot the calibration curve. The concentration of the samples in µg NO<sub>2</sub>-N/ml are found from the calibration curve. Leachates from field blanks are also treated in the same way, and a representative value for the field blank in µg NO<sub>2</sub>-N/ml should be subtracted before the calculation in Section 3.3.1.10.

#### **4.12 Determination of nitric acid and ammonia absorbed on impregnated filters**

Nitric acid, ammonia (and hydrochloric acid) collected on an impregnated filter behind an aerosol filter will not generally reflect the true air concentrations due to physical processes and chemical reactions on the filter, mainly with sulphuric acid. By adding the amount of ions in the aerosol filter and on the impregnated filters, the sum of the concentrations of nitric acid and aerosol nitrate, ammonia and aerosol ammonium, and hydrochloric acid and aerosol chlorides can be determined. Separate determination of the two components can be achieved by use of denuders.

The recommended analytical procedures for nitrate and ammonium after the extraction from the impregnated filters (3.6.1.2) are given in Sections 4.1, 4.3 and 4.4. If the extract containing the nitrates is too alkaline for the method applied, it should be treated with a cation resin as described in Section 3.6. If the sample containing the ammonium extracts is too acid for the methods described in Section 4.4, the solutions may be neutralized by adding sodium hydroxide or buffers with sufficient capacity

##### ***4.12.1 Determination of nitrate ions by ion chromatography***

The analytical method is described in Section 4.1.

##### ***4.12.2 Spectrophotometric determination of nitric acid by reduction to nitrite and reaction with sulphanilic acid***

The analytical method is described in Section 4.3.1.

##### ***4.12.3 Automatic spectrophotometric determination of nitric acid by reduction to nitrite and reaction with sulphanilic acid***

The analytical method is described in Section 4.3.2.

##### ***4.12.4 Determination of ammonium ions by ion chromatography***

The analytical method is described in Section 4.4.1.

##### ***4.12.5 Spectrophotometric determination of ammonia as ammonium by the indophenol blue method***

The analytical method is described in Section 4.4.2.

##### ***4.12.6 Automatic spectrophotometric determination of ammonia as ammonium by the indophenol blue method***

The analytical method is described in Section 4.4.3.

## **4.13 Determination of sulphate in aerosol filters**

### **4.13.1 Determination of sulphate ions by ion chromatography**

The procedures after the extraction from the aerosol filter (Section 3.6.2) for Dionex systems and for Waters systems are described in Section 4.1.

### **4.13.2 Determination of sulphate spectrophotometric by the barium perchlorate – Thorin method**

#### **4.13.2.1 Field of application**

This method is applicable for the determination of water-soluble particulate sulphate collected on a filter. The working range is within 1 to 80 µg S per filter.

#### **4.13.2.2 Principle**

Particulate sulphate collected on a filter is dissolved in water. The concentration of sulphate in the solution is determined spectrophotometrically as described in Section 4.2.1 or 4.2.2.

#### **4.13.2.3 Instrumentation**

Same as listed in Section 4.2.1. In addition: 50 ml Erlenmeyer flasks.

#### **4.13.2.4 Chemicals**

Same as listed in Section 4.2.1.

#### **4.13.2.5 Reagents**

Same as listed in Section 4.2.1.

#### **4.13.2.6 Calibration**

Proceed as described in Section 4.2.1.

#### **4.13.2.7 Analytical procedure**

Transfer the exposed filters and blank filters to 50 ml Erlenmeyer flasks. Add 20 ml of water, shake well and leave for 30 minutes. (For small filters and low concentrations of sulphate use only 10 ml of water). Proceed according to Section 4.2.1.7 or 4.2.2.6.

#### **4.13.2.8 Expression of results**

The concentration of water soluble particulate sulphate in the air sample expressed in micrograms of sulphur per cubic metre, is given by:

$$C = 1000(a - b) \frac{v_1}{v_2}$$

a = concentration of sulphur, in milligrams per litre, read from the calibration curve.

b = concentration of sulphur in the blank sample

v<sub>1</sub> = the volume of water, in litres, used to extract the filter.

#### **4.14 Determination of nitrate and ammonium in aerosol filters**

Nitrate, ammonium (and chlorides) collected in an aerosol filter will not generally reflect the true air concentrations due to physical processes and chemical reactions on the filter, mainly with sulphuric acid. By adding the amount of ions in the aerosol filter to the amounts on alkaline and acid impregnated filters behind the aerosol filter, the sum of the concentrations of nitric acid and aerosol nitrate, ammonia and aerosol ammonium, and hydrochloric acid and aerosol chlorides can be determined. Separate determination of the gaseous and aerosol components can be achieved by use of denuders.

Extraction from aerosol filters is described in Section 3.6.

##### ***4.14.1 Determination of nitrate ions by ion chromatography***

The analytical method is described in Section 4.1.

##### ***4.14.2 Spectrophotometric determination of nitrate by reduction to nitrite and reaction with sulphanilic acid***

The analytical method is described in Section 4.3.1.

##### ***4.14.3 Automatic spectrophotometric determination of nitrate by reduction to nitrite and reaction with sulphanilic acid***

The analytical method is described in Section 4.3.2.

##### ***4.14.4 Determination of ammonium ions by ion chromatography***

The analytical method is described in Section 4.1.

##### ***4.14.5 Spectrophotometric determination of ammonium by the indophenol blue method***

The analytical method is described in Section 4.4.1.

##### ***4.14.6 Automatic spectrophotometric determination of ammonium by the indophenol blue method***

The analytical method is described in Section 4.4.2.

## 4.15 Determination of light hydrocarbons

The analytical method described below is by gas chromatography and FID.

NILU had several years of experience with a hand-made, quite time consuming, non-automated method. This method was based on a two-step concentration of up to one litre of air, dried with  $K_2CO_3$  and NaOH on support (revocation of  $CO_2$ ), a gas chromatographic separation on  $Al_2O_3$  PLOT column and FID detection (Schmidbauer and Oehme, 1985, 1986).

Considering the high number of samples which needed to be analysed within a very short time after sampling, automated instrumentation was needed. A prototype of a new instrument was presented by Jack Mowrer (IVL, Gothenburg, Sweden) at the Lindau workshop (EMEP/CCC-Report 3/90). This was an instrument for continuous unattended measurements of  $C_2$ - $C_5$  hydrocarbons at background levels. The instrument was designed and built together with Chrompack (Middelburg, The Netherlands). In the years after Lindau this instrument was further modified by Chrompack in cooperation with H. Bloemen (RIVM, Bilthoven, The Netherlands). More and more laboratories, especially within the EUROTRAC/TOR community, have since then based their on-line measurements of hydrocarbons on a commercial available type of this instrument. The last aspect – the increasing number of users – was one of the reasons for our decision to do the analyses for EMEP with this instrument. The instrument, as it comes from the factory, has to be modified to some extent to act as proper as some of the various homemade devices. The users have introduced some good improvements.

A brief description of the set-up and procedures are given below. The analysis is complicated and should preferably be learned by training.

### 4.15.1 Instrumentation

#### 4.15.1.1 VOC air analyser (Chrompack, Middelburg, The Netherlands)

Figure 4.15.1 shows the set-up with the original Nafion dryer (not used by NILU) and the 10 canister stream-selector.

Figure 4.15.2 shows the set-up with the dryer as it is used at NILU.

A drying-tube with backflush and heating option has been added between valve V3 and V4. (10 cm teflon-tube 1/4" with 20 micron steel-sinters on both ends, filled with 3 cm of  $K_2CO_3$  on both ends and 4 cm NaOH on support in the middle.)

The first trap is a 1/4" glass-tube packed with Carbosieve, Carbotrap and Carbotrap C - the refocussing trap a 10 cm piece of coat fused silica (Poraplot U).

Figures 4.15.3 and 4.15.4 show the flow-schemes of the seven different steps in an analytical cycle of the thermodesorption unit.

#### **4.15.1.2 Gas chromatography (GC 9000 Chrompack)**

Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column, 50 m, 0.32 i.d. (Chrompack).

VG Minichrom PC based chromatographic data handling system.

#### **4.15.1.3 Gases and materials**

All gases are grade 4 or better. They are further cleaned by passage through two different 200 ml cylinders filled with activated charcoal and molecular sieve. This is sufficient for the FID gases, but not for the helium as carrier gas. Helium is further cleaned in a 1/4" steel trap filled with molecular sieve at liquid nitrogen temperature. All tubes which are in contact with the sample are premium grade stainless steel or teflon (drying tube).

#### **4.15.2 Analytical Procedure**

The analytical procedure for this type of equipment is given in Figures 4.15.3 and 4.15.4.

*Table 4.15.1: Settings of temperatures, gases, flow-directions and gas-flows in the different steps of an analytical cycle of the thermodesorption unit.*

Step	Trap 1	Gas	Direction	Flow	Trap 2	Gas	Time
I	270°C	He	Back	20 ml	120°C	He	26 min
II	Ambient	He	Back	20 ml	Ambient	He	60 min
III	-30	He	Back	20 ml	Ambient	He	6 min
IV	-30	Sample	Front	25 ml	Ambient	He	14 min
V	-30	Sample	Front	25 ml	-180	He	6 min
VI	-30	He	Front	5 ml	-180	He	1 min
VII	250	He + HC	Back	8 ml	-180	He + HC	8 min

The consume of liquid nitrogen is about 2 litres per sample.

A chromatogram is given in Figure 4.15.5.

#### **4.15.3 Quality assurance**

##### **4.15.3.1 Calibration**

NILU is using calibration-gas-mixtures from NIST (USA) to determine the carbon-number-response for the FID.

The standard-gas-mixture is analysed with the same conditions as a sample (same pressure, flowrate, volume and time period) connected to one of the ten ports of the stream-selector. The absolute precision of the read-out of the massflow-controller is therefore not a critical point in calculating concentrations.

NILU is using the n-butane response calculated from a 10 ppb NIST standard as a basis for calculation of carbon-number-response.

The standard gas is connected to port 1 of the multistream-selector and therefore always the first and thereafter every tenth injected sample.

All hydrocarbon peaks in the chromatograms are identified and integrated by hand.

For identification purposes ppm standard-gas-mixtures from Scotty or self-made standards are injected via a home-made injection system.

#### **4.15.3.2 Maintenance**

The blank values of the carrier gas are checked by direct connection to one of the ports of the multiposition-valve. A good performance of carrier-gas cleaning is of fundamental importance for a reliable analysis of the very volatile hydrocarbons.

The blank values of the instrument especially of the traps have to be controlled quite often. High boiling compounds on the traps may decompose and give higher background noise of several compounds.

A need for change of the drying-agents is indicated by bad chromatographic performance. On a routine basis the tube is renewed every week.

A record of the raw-area of the standard-runs is very useful to judge the instruments behaviour over longer time.

All gas-flows need to be checked quite often.

#### **4.15.4 References**

Schmidbauer, N. and Oehme, M. (1985) Analysis of light hydrocarbons (C<sub>2</sub>–C<sub>6</sub>) at ppt levels by high resolution gas chromatography. *J. High Res. Chrom. & Chrom. Commun.*, 8, 404-406.

Schmidbauer, N. and Oehme, M. (1986) Improvement of a cryogenic preconcentration unit for C<sub>2</sub>–C<sub>6</sub> hydrocarbons in ambient air at ppt levels. *J. High Res. Chrom. & Chrom. Commun.*, 9, 502-505.

EMEP (1990) EMEP Workshop on measurement of hydrocarbons/VOC. Lindau, Federal Rep. of Germany, November, 6–9, 1989. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Report 3/90).

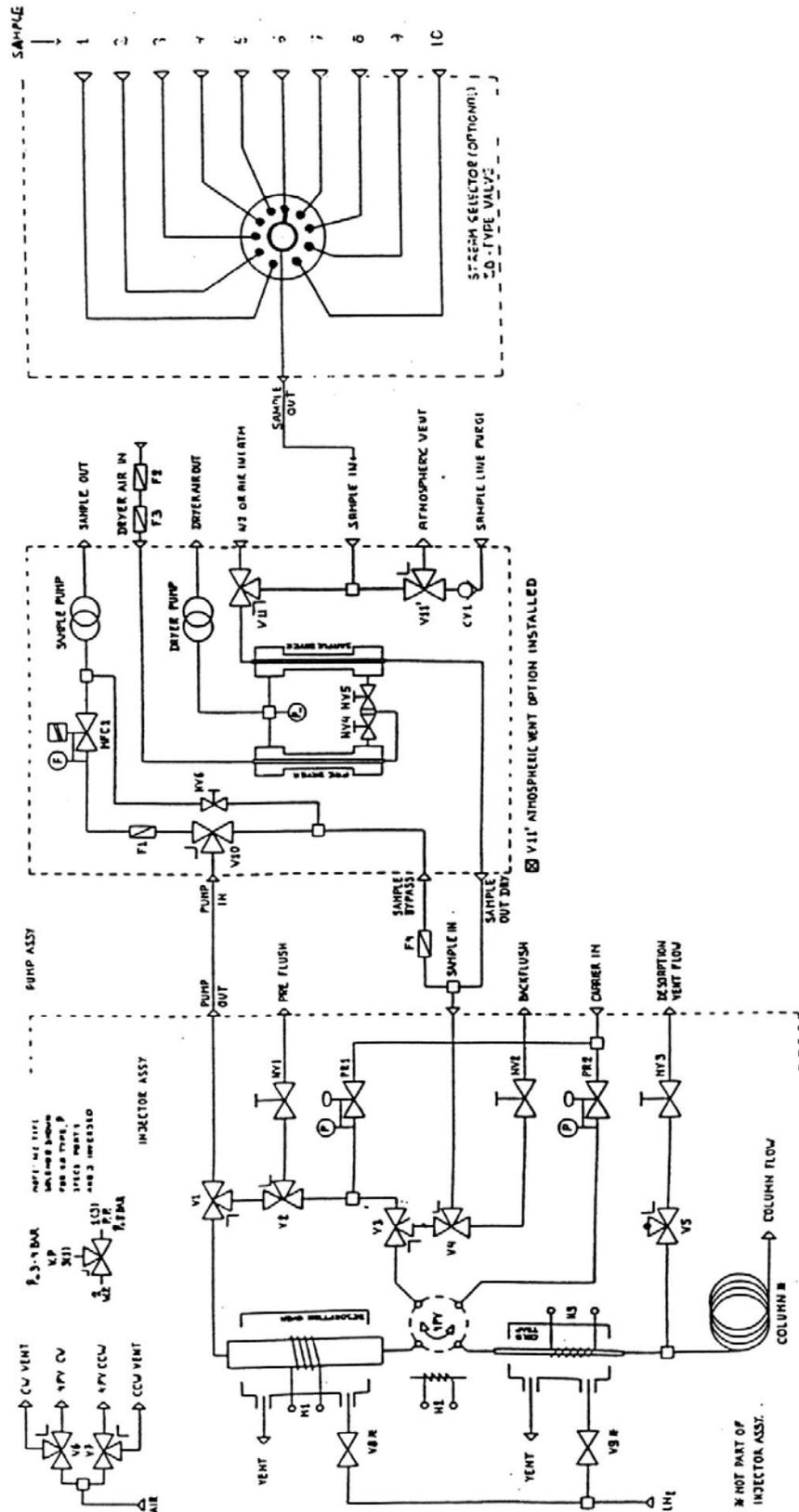


Figure 4.15.1: Original set-up with Nafion dryer (not used by NILU) and the 10 canister stream.

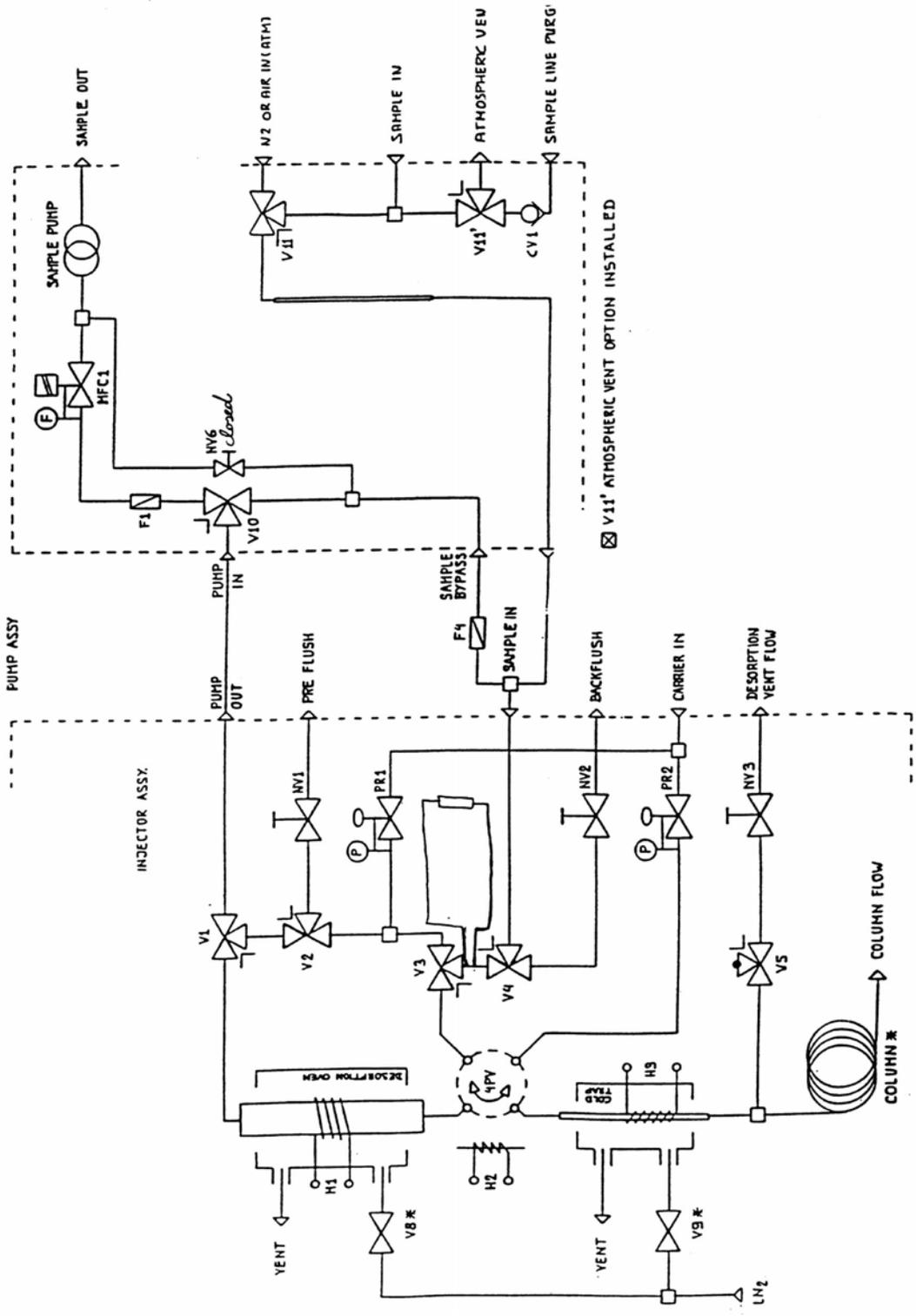
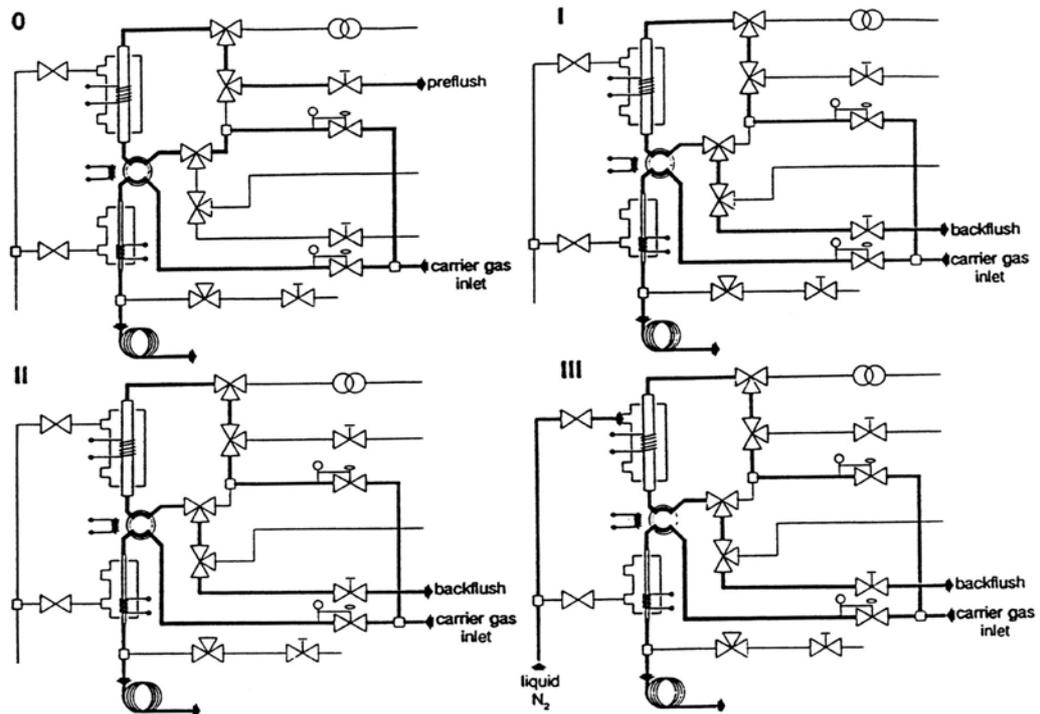


Figure 4.15.2: Instrument set-up with dryer as used at NILU.



#### 0 Run

The system is put into the Run mode by pressing the <Standby> key, turning off the LED. See B: Run mode, above.

NOTE From software revision SWL 1.03L onwards, the system cannot be started from any other stage.

#### I Backflushinjection

The cold trap is flash heated and the sample, which was cryo-focussed in stage 7, is injected into the capillary column. At the same time the adsorption tube is heated and cleaned by a backflush gas flow to prepare it for the next sample collection.

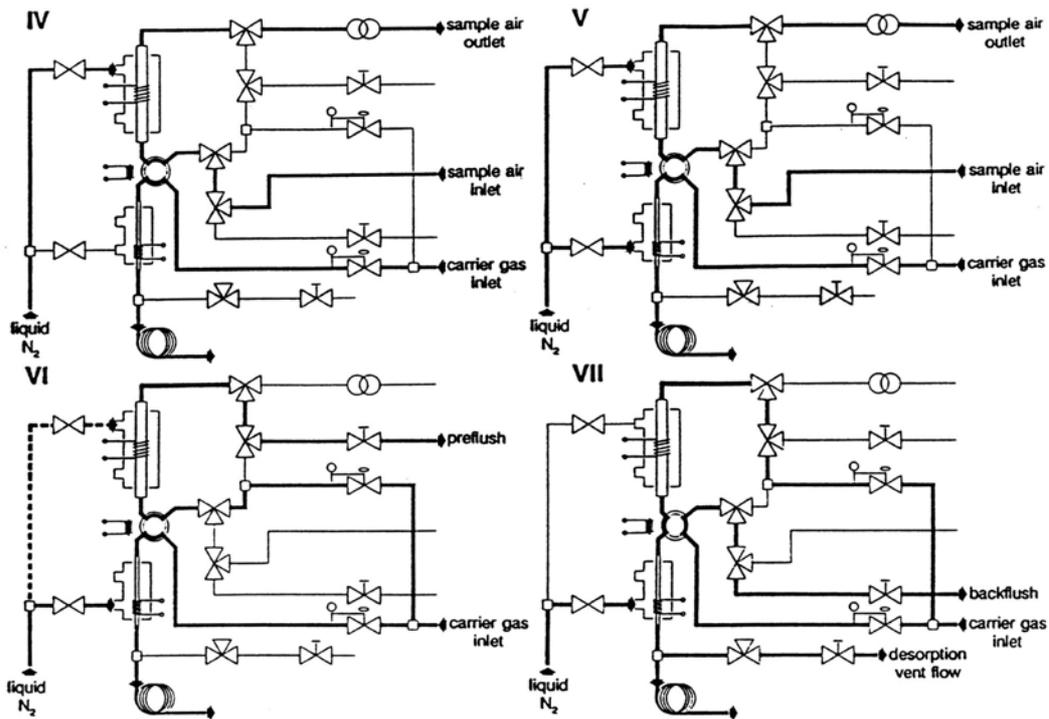
#### II Backflush/Stop-wait

This stage allows the user to synchronize the auto-TCT with the GC temperature program or his daily sample frequency (see Auxiliary run functions: Stop).

#### III Backflush/Oven precool

The sample tube is cooled down to between  $-170^{\circ}\text{C}$  and approximately  $28^{\circ}\text{C}$  to prepare it for the next sample collection.

Figure 4.15.3: Analytical procedure - step 0-III.



#### IV Sample collection

The air sample is sucked through the adsorption tube by means of a vacuum or pushed through by means of pressure.

#### V Sample collection/Trap precool

While sample collection is still in progress, the cold trap is cooling down to between  $-100^{\circ}\text{C}$  and  $-150^{\circ}\text{C}$  to prepare it for cryo-focussing of the collected components onto the fused silica trap.

#### VII Preflush

If necessary, water is removed from the adsorption tube by a dry carrier gas flow before the actual desorption starts and the components are transferred to the cold trap.

#### VII Desorption/trapping

The adsorption tube is heated and the components are transferred to the cold trap by the carrier gas flow and ayofocussed.

Figure 4.15.4: Analytical procedure - step IV-VII.

Injection C: <N20> 3 CS040393,1,1

Acquired on 09-Mar-93 at 20:15:33

Reported on 09-Mar-93 at 23:14:18

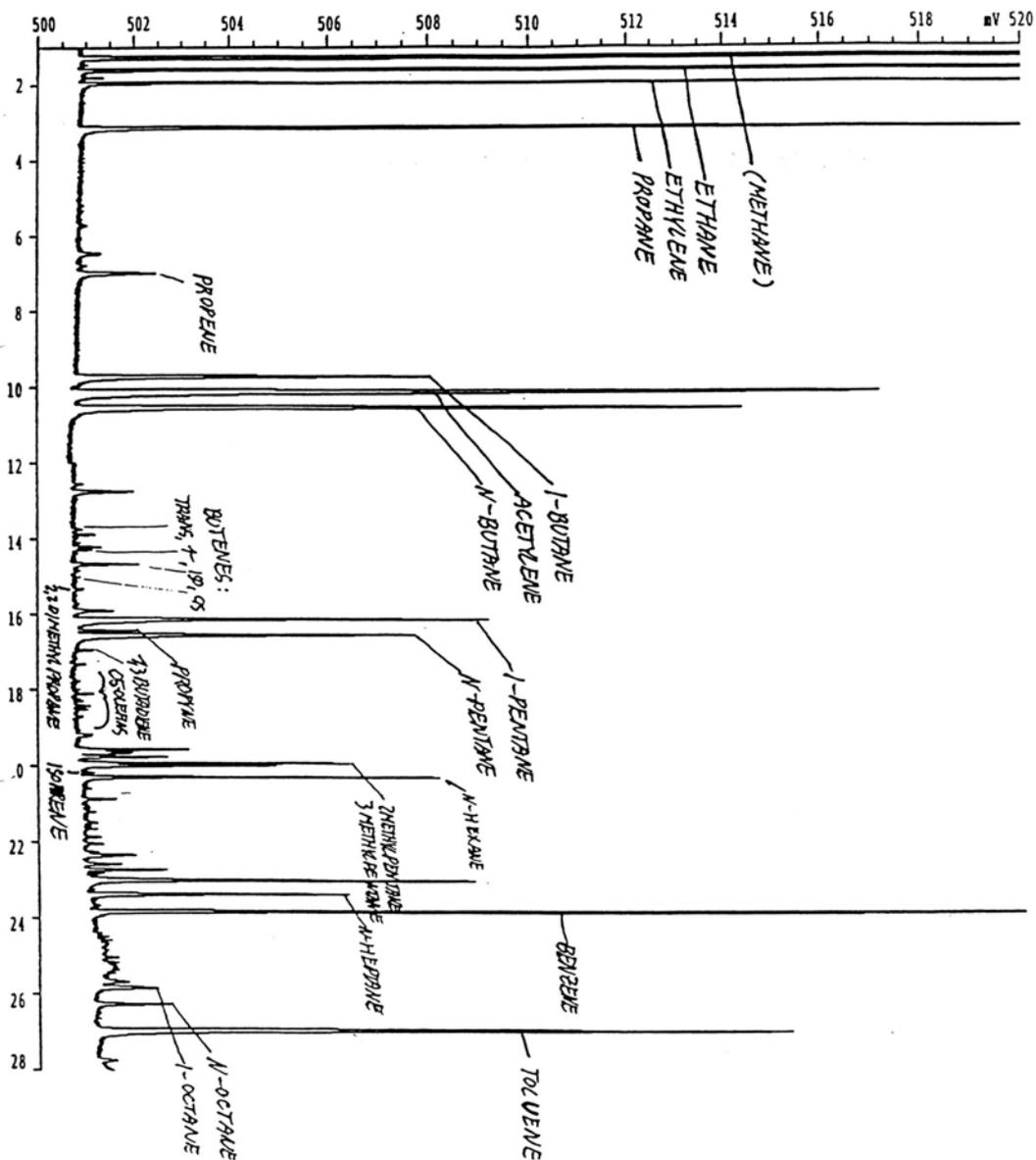


Figure 4.15.5: Chromatogram of light hydrocarbons by GC.

#### 4.16 Determination of aldehydes and ketones in ambient air

Aldehydes and ketones sampled as 2,4-dinitrophenylhydrazones in impregnated tubes can be analysed in extracts with high performance liquid chromatography (HPLC).

##### 4.16.1 Instrumentation

The following instruments and equipment may be used:

- A Hewlett-Packard 1050 modular system, consisting of a 79852A quaternary solvent supply system, a G1306A diode array detector, and a 79855A autosampler.
- Nova-Pak C<sub>18</sub>, 4 µm particles (No. 86344, Waters Associates), 150 mm \* 3.9 mm i.d.).
- Waters In-line Precolumn Filter, No 84560.
- Syringes and volumetric glassware.

##### 4.16.1.1 Chemicals

- Acetonitrile, HPLC-quality, Rathburn Chemicals Ltd., No. RH 1016.
- Methanol, Merc No. 6009.
- Tetrahydrofuran, Merck No 8101.
- Water, quartzdistilled and ion exchanged from a Millipore "MilliQ" water purification system.
- Potassium iodide, p.a, Fluka No. 60400.
- Sulfuric acid, Merc No 714.
- Ethanol.
- Carbonylcompounds needed.
- 2,4-Dinitrophenylhydrazine, Fluka No 42210.

##### 4.16.2 Analytical procedure

Fill a 5 ml syringe with acetonitrile. (Collect the sample extract in a 3 ml narrow neck flask). Eluate the derivatives by slowly (approximate 1.5 ml/min) pushing acetonitrile through the cartridge. Stop the elution when the 3 ml mark is reached. Transfer approximately 0.5 ml of the sample solution to a 2 ml autosampler vial and seal the vial. The sample is now ready for HPLC analysis.

10 µl of a sample or standard solution is separated by using a quaternary mixture of methanol/water/acetonitrile/tetrahydrofuran. Table 4.16.1 shows the gradient profile which is used.

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).

Following carbonylcompounds should be measured: methanal, ethanal, propenal, propanal, propanone, 2-methyl-propenal, butanal, 2-butanone, 3-buten-2-one, pentanal, hexanal, benzenecarbaldehyde, ethandial, oxopropanal.

Table 4.16.1: Quaternary gradient which separates the carbonylhydrazones of interest (EMEP) at a flowrate of 0.8 ml/min.

Time	% Tetrahydrofuran	% Acetonitrile	% Water	% Methanol
0.0	18.0	22.0	60.0	0.0
0.5	18.0	22.0	60.0	0.0
20.0	8.4	37.4	54.2	0.0
24.0	0.0	0.0	34.0	66.0
40.0	0.0	0.0	15.0	85.0
41.0	0.0	0.0	15.0	85.0
45.0	0.0	100.0	0.0	0.0
48.0	18.0	22.0	60.0	0.0

#### 4.16.3 Blanks

Each day analyses of carbonylcompounds are performed, a laboratory blank should be prepared. Periodically field blanks should be obtained once every week. The blank levels of methanal, ethanal, and propanone will probably change with cartridge batchnumber and the batchnumber of acetonitrile. The blank level should not exceed 0.05 µg/m<sup>3</sup> of the carbonylcompound in a sample volume of 750 litres.

#### 4.16.4 Preparation of hydrazones

1. Dissolve 400 mg 2,4-dinitrophenylhydrazine in 2 ml 96% sulphuric acid. This solution is then added, *with stirring*, to 13 ml 75% ethanol. Any undissolved solid is removed by aid of a pasteurpipette.
2. A volume corresponding to 500 mg of the carbonylcompound is transferred to 20 ml ethanol.
3. The carbonylsolution (step 2) is than transferred to the DNPH solution (step 1) with stirring. Let the solution stand for 15 minutes to complete the reaction.
4. Filter the solution in step 3, and recrystallize the hydrazone from aqueous ethanol. (Hydrazones from unsaturated/aromatic carbonyls should be recrystallized from aqueous acetonitrile.)
5. Dry the hydrazone and do a purity test (HPLC-UV).

#### 4.16.5 Calibration

Prepare a stock solution from each carbonylhydrazone by dissolving approximately 5 mg (+/- 1%) in 100 ml acetonitrile. (These stock solutions will be ready for use.) Calibration solutions are prepared by dilution of the stock solutions (1 µg/ml to 2 µg/ml is suitable for most analyses).

#### 4.16.6 Quantification

The concentration of carbonyl compounds in the air sample expressed as  $\mu\text{g}/\text{m}^3$ , is given by:

$$C = \frac{H(p)cvk}{H(s)V}$$

- C : Concentration of the carbonyl compound in the air sample [ $\mu\text{g}/\text{m}^3$ ]  
 c : Concentration of the carbonyl compound in the standard [ $\mu\text{g}/\text{ml}$ ]  
 H(s) : Peak height/area of the carbonyl compound in the standard [counts]  
 H(p) : Peak height/area of the carbonyl compound in the sample [counts]  
 k : Conversion factor (e.g. from hydrazone to carbonyl)  
     methanal:0.1429, ethanal:0.1964, propenal 0.2373 etc.  
 V : Sample volume [ $\text{m}^3$ ]  
 v : Volume of the prepared sample [ml]

#### 4.16.7 Interferences

Failure to remove ozone by the ozone scrubber will result in serious underestimating of some carbonylhydrazones.

#### 4.16.8 References

- Vairavamurthy, A., Roberts, J.M. and Newman, L. (1992) Methods for determination of low molecular weight carbonyl compounds in the atmosphere: a review. *Atmos. Environ.*, 26A, 1965-1993.
- Slemr, J. (1991) Determination of volatile carbonyl compounds in clean air. *Fresenius J. Anal. Chem.*, 340, 672-677.
- Dye, C. and Oehme, M. (1992). Comments concerning the HPLC separation of acrolein from other  $\text{C}_3$  carbonyl compounds as 2,4-dinitrophenylhydrazones: a proposal for improvement. *J. High Res. Chrom.*, 15, 5-8.

## 4.17 Analytical methods for determination of heavy metals

### 4.17.1 Introduction

At the EMEP WMO-GAW workshop (EMEP, 1997a), inductively coupled plasma mass spectrometry (ICP-MS) was chosen to be the reference technique within EMEP. The exception is mercury where cold vapour atomic fluorescence spectroscopy (CV-AFS) was chosen, but this technique is described in the separate mercury manual. Other techniques may be used, if they are shown to give results of equal quality as obtained with the recommended method. The choice of technique is dependent on the detection limits desired. In

Table 4.17.1 the techniques described in this manual are presented with minimum detection limits. 23 countries, within the EMEP network, monitor and report heavy metal data. As shown in Table 4.17.2 various techniques are used (Berg et al, 2000). In this manual methods including the following four techniques are described: ICP-MS, graphite furnace atomic absorption spectroscopy (GF-AAS), flame-atomic absorption spectroscopy (F-AAS) and CV-AFS. The methods described are generally derived from development and experience gained within the EMEP network as well as information provided by EPA through the Ambient Monitoring Technological Information Centre (AMTEC).

*Table 4.17.1: Minimum detection limits. These detection limits are the ultimate values since the blank value from the reagents and filter not have been taken into account.*

Element	ICP-MS ng ml <sup>-1</sup> <sup>a)</sup>	GF-AAS ng ml <sup>-1</sup> <sup>b)</sup>	F-AAS ng ml <sup>-1</sup> <sup>c)</sup>
As	<0.01	0.056	0.02
Cd	<0.01	0.0014	0.5
Cr	<0.01	0.0038	2
Cu	<0.01	0.015	1
Ni	<0.03	0.072	2
Pb	<0.001	0.007	10
Zn	<0.02	0.006	0.8
Hg		0.2	0.001

<sup>a)</sup> Fisons Scientific equipment, VG Instrument Group, Bulletin No.5M/AMSG/390, England

<sup>b)</sup> Perkin Elmer, "new Analyst<sup>TM</sup> 800 detection limits", technical note, Norwalk, USA, 1998

<sup>c)</sup> Parsons, M.L. and Forster, A.L., *Applied Spectroscopy*, **37** (1983) 411-418

Table 4.17.2: Analytical techniques for metal determination within the EMEP network (Berg et al. 2000).

Techniques	Number of laboratories	Described in this manual
NAA	0	
ICP-MS	6	X
GF-AAS	4	X
ICP-AES	1	
PIXE	1	
XRF	1	
F-AAS	5	X
CV-AFS	7	X

#### 4.17.2 Washing procedures

**All reusable labware** (glass, teflon, polyethylene etc) should be carefully rinsed before use to avoid contamination of the samples. Sampling cans and bottles should be rinsed with de-ionized water and soaked in 3% HNO<sub>3</sub> for 24 hours. After the acid bath the bottles for storing of precipitation samples should be rinsed 3 times and then filled with 1% HNO<sub>3</sub> and stopped.

The sampling cans should be rinsed 3 times with de-ionized water, dried, stopped and packed in two clean plastic bags with zip-locks.

**Disposable pipette tips** should be placed in a plastic bottle filled with 1% HNO<sub>3</sub>. Turn the bottle upside down a few times to assure that the tips are filled with the acid solution. Leave the tips in the acid solution for minimum 12 hours. Pour out the acid solution and rinse the tips by filling the bottle with de-ionized water 3 times. Shake as much as possible of the water out of the bottle and tips, and keep them in the stopped bottle until use.

**The rings and filter supports** from the filterpacks should be soaked in 1% HNO<sub>3</sub> for 12 hours, rinsed 3 times with de-ionized water.

**Autosampler tubes and cups** (polystyrene or polyethylene) should be rinsed with de-ionized water, soaked in 1% HNO<sub>3</sub> for minimum 12 hours and rinsed 3 times with de-ionized water before use.

#### 4.17.3 Determination of Cd, Pb, Cu, Zn, Cr, Ni and As by the use of inductively coupled plasma mass spectrometry (ICP-MS)

##### 4.17.3.1 Introduction

ICP-MS is a multi-element technique that is suitable for trace analysis. The technique offers a long linear range and low background for most elements. The detection limits obtained are better or comparable to what is obtained by graphite furnace atomic absorption spectroscopy (GF-AAS). The technique is prone to some interferences that will be described below. Different sample introduction devices may be used in combination with ICP-MS to allow introduction of non-

liquid samples such as solid samples, slurries and gaseous samples. In this chapter, only conventional solution introduction will be described.

#### **4.17.3.2 Principles**

ICP-MS is a technique where ions produced in an inductively coupled plasma, are separated in a mass analyser and detected. The sample solution is fed into a nebulizer by a peristaltic pump. The nebulizer converts the liquid sample into a fine aerosol that is transported into the plasma by an Ar gas flow, most often called carrier gas or nebulizer gas. With an ordinary pneumatic nebulizer, only 1-2% of the sample reaches the plasma. In the plasma the sample is evaporated, dissociated, atomised and ionised to varying extent. The produced positive ions and molecular ions are extracted into the mass analyser. A simple quadrupole gives a resolution of 1 amu or more at a peak width of 10% of the peak height. The ions are separated by mass to charge ratio ( $m/z$ ) and measured by a channel electron multiplier. Detailed description of the ICP-MS technique can be found in various textbooks (Jarvis et al. 1992; Montaser, 1998).

#### **4.17.3.3 Interferences**

In analysis by ICP-MS, the following interferences should always be considered:

##### ***Isobar overlap***

Isobar overlaps exist when two elements have isotopes of essentially the same mass. To overcome this problem 1) a different isotope of the analyte can be chosen or 2) by determining the signal for another isotope of the interfering element and by using the natural abundance information, subtracting the appropriate signal from the analyte isotope signal.

##### ***Isobar overlap by polyatomic ions***

Isobar overlap may occur due to formation of poly-atomic species. As the name suggests, polyatomic species consist of two or more atomic species, e.g.  $\text{ArO}^+$ . They are formed by rapid ion-molecule reactions between components of solvent or sample matrix with the constituents of the plasma. The dominant species in the plasma and its surrounding are Ar, O, N and H. These elements can combine with each other to give a variety of polyatomic ions. The main elements of the solvent or acids used during sample preparation may also participate in these ion-molecule reactions. A large number of polyatomic species may therefore cause interference by isobar overlap. To which extent formation of polyatomic ions occur, depends on several parameters including sampling geometry, plasma and nebulizer conditions, choice of acids and solvents and the nature of the sample matrix. By careful optimisation of the ICP-MS instrument, it is possible to keep the formation of polyatomic species at the minimum and the elemental sensitivity close to maximum. If interference from polyatomic species cannot be avoided by selecting alternative isotopes of the analyte, appropriate corrections should be made to the data.

##### ***Isobar overlap by doubly charged ions***

Doubly charged ions are detected at half mass ( $m/2$ ). Most of the ions produced in the plasma are single charged. The elements that might produce doubly charged

ions are typically the alkaline metals, alkaline-earth metals and some transition metals. At conventional operating conditions of the plasma and nebulizer, the level of doubly charged ions is small (< 1%).

### ***Physical interferences***

Physical interferences are associated with nebulization and transport processes as well as with ion-transition efficiencies. The efficiency of the nebulization and transport processes depends on the viscosity and surface tension of the aspirated solution. Therefore, physical interference (matrix effect) may occur when samples and calibration standards have different matrix. In addition to matrix-matching of samples and calibration standards, the use of internal standard may reduce these problems.

ICP-MS systems are not tolerant to solutions containing significant amounts of dissolved solids. Clogging of nebulizers and salt build-up at the tip of the cones leads to poor sensitivity and considerable signal drift over a short period of time. A level of total dissolved solid (TDS) in the region of 0.1-2 (w/w) % is recommended (Perkin Elmer, 1993)]. High matrix concentration generally leads to poor precision. Memory effects may also be severe and time-consuming washout periods required. The use of flow-injection sample introduction may reduce some of these problems.

### ***Memory effects***

If there is a considerable difference in concentration between samples or standards that are analysed in sequence, memory effect may occur. The memory effect is caused by sample deposition on the cones, and in the spray chamber. The effect is also dependent on which type of nebulizer that is used. The washout time between samples must be long enough to bring the system down to blank value.

### ***Interference control***

It is recommended to determine the concentrations of the main components in the sample to be able to predict possible interference effects on the analytes of interest. Following ions should be monitored in the analysis programs:

$^{25}\text{Mg}$ ,  $^{24}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{31}\text{P}$ ,  $^{34}\text{S}$ ,  $^{35}\text{Cl}$ ,  $^{44}\text{Ca}$ ,  $^{55}\text{Mn}$  and  $^{57}\text{Fe}$  (see Table 11.2).

### ***Reagents and standards***

Nitric acid	( $\text{HNO}_3$ ) 65%
Sodium arsenite	( $\text{NaAsO}_2$ )
Cadmium metal	(Cd)
Potassium chromate	( $\text{K}_2\text{CrO}_4$ )
Copper sulfate	( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ )
Nickel sulfate	( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ )
Lead nitrate	( $\text{Pb}(\text{NO}_3)_2$ )
Zinc metal	(Zn)

ICP-MS stock solutions may be purchased or prepared from chemicals of ultra pure quality (99.9% or better). The standards should be dissolved in an appropriate acid ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$ ) of suprapure quality. In addition to the chemical compound from which the stock solution is made, the acid that is used

should be specified. This makes it possible to calculate the contents of ions that may cause problems by interference ( $\text{Cl}$ ,  $\text{SO}_4^{2-}$ ).  $\text{HNO}_3$  gives a very simple spectrum and is for this reason considered as the ideal matrix. Only de-ionised water must be used (resistance  $> 18 \text{ M}\Omega/\text{cm}$ ). Argon gas of high purity grade (99.99% or better) must be used.

***Standard stock solutions (1000  $\mu\text{g ml}^{-1}$ )***

As 1000  $\mu\text{g ml}^{-1}$ :

Transfer 9.733 g  $\text{NaAsO}_2$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Cd 1000  $\mu\text{g ml}^{-1}$ :

Transfer 1.000 g cadmium metal to a beaker. Dissolve the metal in 10 ml 1:1  $\text{HNO}_3$ . Transfer the solution to a 1000 ml volumetric flask. Dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Cr 1000  $\mu\text{g ml}^{-1}$ :

Transfer 3.734 g  $\text{K}_2\text{CrO}_4$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Cu 1000  $\mu\text{g ml}^{-1}$ :

Transfer 3.930 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Ni 1000  $\mu\text{g ml}^{-1}$ :

Transfer 4.477 g  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Pb 1000  $\mu\text{g ml}^{-1}$ :

Transfer 1.599 g  $\text{Pb}(\text{NO}_3)_2$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Zn 1000  $\mu\text{g ml}^{-1}$ :

Transfer 1.000 g zinc metal to a beaker. Dissolve the metal in 10 ml 1:1  $\text{HNO}_3$ . Transfer the solution to a 1000 ml volumetric flask and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Commercially available standard solutions may also be used.

***Preparation of secondary stock standard***

When making mixed calibration standards there might be convenient to prepare a secondary stock standard containing 1000 ng/ml of all the elements of interest, conserved with 10 % (v/v)  $\text{HNO}_3$ . This secondary stock standard may be stored

and used for 1 year. *Care must be taken in the preparation of mixed stock standards so that the elements are compatible and stable.*

#### ***Preparation of mixed calibration standards***

Mixed calibration standards are made by dilution of the secondary stock standard solution to levels within the linear range for the instrument. The same acid concentration and method of spiking must be used in calibration standards as in the samples.

#### ***Internal standards***

In most analysis there is an advantage to implement three internal standards; one for the low mass region, one for the mass region in the middle and one for the high mass region. Care must be taken in the choice of elements to be used as internal standards:

- The internal standard should not be present in the sample in measurable amounts.
- The internal standard should not suffer from an isobar overlap or polyatomic ion interference or indeed generate them on isotopes of interest.

The following elements are often used as internal standards:

Sc	m/z 45
Rh	m/z 103
In	m/z 115
Re	m/z 185

Sc may be susceptible to isobar overlap from  $^{89}\text{Y}^{2+}$ ,  $^{14}\text{N}_2^{16}\text{OH}^+$ ,  $^{28}\text{Si}^{16}\text{OH}^+$  and  $^{44}\text{CaH}^+$ . This is a problem only when the concentrations of the mother ions are very high. If there is a risk for isobar overlap, Sc should be omitted when calculating the results.

When spiking the samples with internal standard, the precision of the addition of the spike solution should be better than 1%. Internal standard solution may be added before or after dilution to volume, but *equal method of spiking must be used in calibration standards, blanks and samples!*

#### ***Quality control standard***

The QC-standard (quality control standard) is the initial calibration verification solution. This standard must be an independent standard made from a certified reference solutions that are traceable to certified reference samples. An independent standard is defined as a standard composed of analytes from a different source than the calibration standard. The QC-standard must be prepared in the same acid matrix as the calibration standards and contain the same concentration of internal standard. The concentrations of the QC-standards are determined of the applications in which the standards are used. A typical concentration is  $10 \text{ ng ml}^{-1}$ . The maximum acceptable deviation will vary from element to element depending on sensitivity, background signal etc. The measured concentration should be within 3 standard deviations of the mean value based on results from analysis of a series of the QC standard. If the measured concentration is more than 3 standard deviations, a re-calibration must be done.

**Blank solutions**

Three different blank solutions are required; calibration blank, procedural blank and rinse blank.

- **Calibration blank** is used for establishing the calibration curve. The calibration blank consists of the same concentration(s) of the acid(s) used to prepare the final dilution of the calibration standards. In addition, an appropriate concentration of internal standard is added.
- **Procedural blank** (or reagent blank) is used to monitor for possible contaminations resulting from the sample preparation procedure. The procedural blank must be carried through the same procedure and contain the same volume of reagents as the sample solution. In addition an appropriate concentration of internal standard is added.
- **Rinse blank** is consist of 1-2 % (v/v) HNO<sub>3</sub> and is used to flush the sample introduction system between standards and samples.

**Tuning solution**

Tuning solution is used for tuning and mass calibration of the instrument. The solution is prepared by diluting the secondary stock solution with 1 (v/v) % HNO<sub>3</sub> to produce a concentration of 10 ng/ml for each element. Usually the tuning solution contains elements to cover the entire mass range like Be, Co, In, La, Pb and U.

**Sample preparation**

Add 100 µl of 10 ng ml<sup>-1</sup> internal standard solution to the appropriate amount of autosampler tubes. Transfer 10 ml of the sample digest to the tubes. The samples are now ready for analysis.

**4.17.3.4 Calibration and standardisation****Optimisation and stabilising of the instrument**

Allow at least 30 min for the instrument to equilibrate after ignition of the plasma before analysing any element. The optimisation procedures will vary with varying types of instruments. The instrument manual should be consulted with regards to optimisation procedures and specification values. In general all ICP-MS systems shall be optimised to give maximum sensitivity and minimum level of oxides and doubly charged ions. The instrument parameters to adjust are as follows;

- XYZ-position of the torch box
  - setting of the ion lenses
  - nebulizer gas flow rate.
- 1) Aspirate a standard solution containing a suitable concentration (usually 10 ng/ml) of an element in the middle of the mass region (<sup>103</sup>Rh or <sup>115</sup>In). Adjust the instrument parameters mentioned above, as described in the instrument manual, to obtain maximum sensitivity of the aspirated element.

- 2) Aspirating a standard solution containing 10 ng/ml  $^{140}\text{Ce}$  can check the oxide level at the condition chosen in 1). The ratio between the signal obtained at m/z 156 and m/z 140 should be low (consult instrument specifications for exact value).
- 3) Aspirating 10 ng/ml  $^{138}\text{Ba}$  can check the level of doubly charged ions. The ratio between the signals obtained at m/z 69 and m/z 138 should be low (consult instrument specifications for exact value).
- 4) If equal sensitivity in both the low and the high mass region is required, the lens setting should be adjusted to give equal response for 10 ng/ml  $^{24}\text{Mg}$  and  $^{207}\text{Pb}$ . This will lead to a minor decrease in the sensitivity obtained in point 1).

If poor sensitivity is obtained, following actions should be taken:

- check the sample flow rate of the peristaltic pump and change tubing if necessary.
- check if the sampler and skimmer cones need cleaning
- check nebulizer, spray-chamber, and torch for possible salt depositions, blockages or eventually leaks.
- look for eventually leaks in the torch-spray chamber-nebulizer assembly.
- increase the detector voltage

### ***Mass calibration***

A mass calibration check should be conducted to ensure that the masses measured by the instrument, for the tuning solution, are accurate with respect to the standard spectrum. If a signal shift of more than 0.1 amu is observed, mass calibration should be adjusted as described in the instrument manual.

### ***Sequence of analysis***

Three calibration blank standards should be analysed to establish a representative blank level. Then the calibration standards are analysed. After calibration, the quality control standard should be analysed to verify the calibration. Flush the sample introduction system with rinse blank, and analyse the blank solution to check carry-over and blank level. Analyse samples if blank level is acceptable. If blank values are too high, repeat flushing of the sample introduction system and analysing of blank solution until acceptable blank level is reached. The calibration blank value, which is the same as the absolute value of the instrument response, must be lower than the method detection limit.

Samples having concentration higher than the established linear concentration range should be diluted into range and reanalysed.

*Table 4.17.3: Example of a typical sequence of analysis.*

Sequence no.	Sample type	
1-3	Calibration blank	Establish blank level
4-9	Calibration standards	Calibration
10	Quality control standard	Calibration verification (accuracy)

11	Calibration blank	Check for "carry-over"
12-41	Samples	
42	Quality control standard	
43	Calibration standard	
44	Calibration standard	

*Table 4.17.4: Isotopes of the priority heavy metals and some possible interferences.*

Element	Isotope mass	Relative abundance	Isobar overlap (% abundance)	Poly-atomic species
Cr	<b>52</b>	83.76		ArC <sup>+</sup> , <sup>35</sup> ClOH <sup>+</sup> ,
	53	9.55		<sup>37</sup> ClOH <sup>+</sup>
Ni	58	67.88	<sup>58</sup> Fe	<sup>42</sup> CaO,
	<b>60</b>	26.23		<sup>44</sup> CaO,
	61	1.19		
	62	3.66		<sup>46</sup> CaO
	64	1.08		<sup>48</sup> CaO
Cu	<b>63</b>	69.09		TiO <sup>+</sup> , ArNa <sup>+</sup> , PO <sub>2</sub> <sup>+</sup>
	65	30.91		ArMg <sup>+</sup>
Zn	64	48.89	<sup>64</sup> Ni (1.8)	SO <sub>2</sub> <sup>+</sup> , SS <sup>+</sup> , ArMg <sup>+</sup>
	<b>66</b>	27.81		ArMg <sup>+</sup>
As	<b>75</b>	100		Ar <sup>35</sup> Cl <sup>+</sup>
Cd	<b>111</b>	12.75		<sup>93</sup> MoO <sup>+</sup>
	114	28.86	<sup>114</sup> Sn (0.66)	
Pb	204	1.48	<sup>204</sup> Hg (6.85)	
	206	23.6		
	207	22.6		
	<b>208</b>	52.3		

#### **4.17.4 Determination of Cd, Pb, Cu, Zn, Cr, Ni and As by the use of graphite furnace atomic absorption spectroscopy (GF-AAS)**

##### **4.17.4.1 Introduction**

Graphite furnace atomic absorption spectroscopy (GF-AAS) is a powerful technique suitable for trace analysis. The technique has high sensitivity (analyte amounts 10<sup>-8</sup>-10<sup>-11</sup> g absolute), the ability to handle micro samples (5-100 µl), and a low noise level from the furnace. Matrix effects from components in the sample other than the analyte are more severe in this technique compared to flame-AAS. The precision is typically (5-10) % using GF-AAS.

##### **4.17.4.2 Principles**

A graphite tube is located in the sample compartment of an AA spectrometer with the light from an external light source passing through it. A small volume of sample is placed inside the tube, which then is heated by applying a voltage across its ends. The analyte is dissociated from its chemical bonds and the fraction of

analyte atoms in the ground state will absorb portions of light. The attenuation of the light beam is measured. As the analyte atoms are created and diffuse out of the tube, the absorption rises and falls in a peak-shaped signal. Beer-Lamberts law describes the relation between the measured attenuation and concentration of analyte. A detailed description of the GF-AAS technique can be found in various textbooks (Montaser, 1998).

#### **4.17.4.3 Interference**

##### ***Background absorption***

Background absorption is non-specific attenuation of radiation at the analyte wavelength caused by matrix components. To compensate for background absorption, correction techniques such as continuous light source (D<sub>2</sub>-lamp), Zeeman or Smith-Hieftje should be used. Enhanced matrix removal due to matrix modification may reduce background absorption.

##### ***Non-spectral interference (Matrix effect)***

Non-spectral interference arises when components of the sample matrix alter the vaporization behaviour of the particles that contains the analyte. To compensate for this kind of interference, method of standard addition can be used. Enhanced matrix removal by matrix modification or the use of a L'vov platform may also lead to a reduction of non-spectral interferences.

#### **4.17.4.4 Instrumentation**

Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipment for flameless atomization (graphite furnace) and a suitable recorder or PC. The wavelength range must be 190-800 nm.

Hollow cathode lamps for As, Cu, Cr, Ni, Pb and Zn. Single-element lamps are preferred, but multi-element lamps may be used if no spectral interference can occur. Electrodeless discharge lamps may be used if available.

Pyrolytically coated graphite tubes.

#### 4.17.4.5 Reagents and standards

All chemicals must be of analytical grade or better.

Distilled de ionized water

Nitric acid	(HNO <sub>3</sub> ) 65%
Sodium arsenite	NaAsO <sub>2</sub> )
Cadmium metal	(Cd)
Potassium chromate	(K <sub>2</sub> CrO <sub>4</sub> )
Copper sulphate	(CuSO <sub>4</sub> * 5H <sub>2</sub> O)
Nickel sulphate	(NiSO <sub>4</sub> *6H <sub>2</sub> O)
Lead nitrate	(Pb (NO <sub>3</sub> ) <sub>2</sub> )
Zinc metal	(Zn)
Palladium nitrate	(Pd(NO <sub>3</sub> ) <sub>2</sub> )
Magnesium nitrate	(Mg(NO <sub>3</sub> ) <sub>2</sub> )
Lanthanum nitrate	(La(NO <sub>3</sub> ) <sub>2</sub> *6 H <sub>2</sub> O)
Ammonium phosphate	((NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub> )

Argon (Ar) as purge gas.

#### ***Standard stock solutions (1000 µg ml<sup>-1</sup>)***

##### As 1000 µg ml<sup>-1</sup>:

Transfer 9.733 g NaAsO<sub>2</sub> to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1 HNO<sub>3</sub> and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

##### Cd 1000 µg ml<sup>-1</sup>:

Transfer 1.000 g cadmium metal to a beaker. Dissolve the metal in 10 ml 1:1 HNO<sub>3</sub>. Transfer the solution to a 1000 ml volumetric flask. Dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

##### Cr 1000 µg ml<sup>-1</sup>:

Transfer 3.734 g K<sub>2</sub>CrO<sub>4</sub> to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1 HNO<sub>3</sub> and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

##### Cu 1000 µg ml<sup>-1</sup>:

Transfer 3.930 g CuSO<sub>4</sub>\* 5H<sub>2</sub>O to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1 HNO<sub>3</sub> and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

##### Ni 1000 µg ml<sup>-1</sup>:

Transfer 4.477 g NiSO<sub>4</sub>\*6H<sub>2</sub>O to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1 HNO<sub>3</sub> and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

##### Pb 1000 µg ml<sup>-1</sup>:

Transfer 1.599 g  $\text{Pb}(\text{NO}_3)_2$  to a 1000 ml volumetric flask. Add distilled de-ionised water to dissolve the salt. Add 5 ml 1:1  $\text{HNO}_3$  and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Zn 1000  $\mu\text{g ml}^{-1}$ :

Transfer 1.000 g zinc metal to a beaker. Dissolve the metal in 10 ml 1:1  $\text{HNO}_3$ . Transfer the solution to a 1000 ml volumetric flask and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Commercially available standard solutions may also be used.

**Calibration standards**

Calibration standards are prepared by single or multiple dilutions of the stock metal solutions. Prepare a reagent blank and at least 3 calibration standards in graduated amount in the appropriate range of the linear part of the curve. The calibration standards must contain the same acid concentration as in the samples following processing. For precipitation samples, that would be 1% (v/v)  $\text{HNO}_3$  and for suspended particulate matter 10% (v/v)  $\text{HNO}_3$ . The calibration standard should be transferred to polyethylene bottles.

Table 4.17.5: Calibration range.

	As	Cd	Cr	Cu	Pb	Ni	Zn
Calibration range ( $\mu\text{g l}^{-1}$ )	0-100	0-5	0-40	0-50	0-50	0-40	0-5

**4.17.4.6 Instrument procedure**

The operating instructions will vary between various brands and models of satisfactory instruments, making it virtually impossible to give precise details of a proposed GF-AAS method that is guaranteed to reduce interference effects on all commercial instruments. *The instrument manual should be confirmed in regards of operating instructions.* A careful interference study and calibration procedure as given in the particular instrument manual must be carried out by the analyst. Some general guidelines are given below.

- Allow the light source(s) a stabilisation time of 10-15 minutes before analysing.
- Set the monochromator to the appropriate wavelength.
- Align the furnace for maximum transmission of radiation.
- Carefully balance the intensity of the hollow cathode lamp and the  $\text{D}_2$ -lamp if such background correction is used.
- A temperature calibration of the furnace should be done.
- Optimise the injection position of the autosampler capillary in such a way that the sample droplet is gently placed in the bottom of the graphite tube. A convenient sample volume for most analyses is 20  $\mu\text{l}$ .

- Make sure that the silica windows in the furnace compartment are clean to ensure maximum transmission of radiation.
- All new graphite tubes must be thermally conditioned as described by the manufacturer.
- For quantification of absorption signals peak area is recommended.

#### 4.17.4.7 *Setting up a temperature programme*

A temperature programme consists most commonly of four steps: Drying, pyrolysis, atomization and cleaning.

**Drying step:** A quick ramp (5 s) to 15°C below the boiling point of the solvent. Then a slow ramp (25 s) to reach a temperature just above the solvents boiling point. This provides a gentle evaporation without sputtering. Hold the furnace at the selected temperature until drying is complete (5- 10 s). The drying time will vary with sample volume and salt content. A purge gas flow of 250-300 ml min<sup>-1</sup> is normally used.

**Pyrolysis step:** A pyrolysis curve should be made to find the appropriate temperature to use in this step without losing any analyte. Consult the instrument manual for the procedure of making a pyrolysis curve. In a pyrolysis step a typical ramp will vary between 20-50 °C s<sup>-1</sup>. Too steep ramp may cause sputtering. A purge gas flow of 250-300 ml min<sup>-1</sup> is normally used.

**Atomization step:** An atomization curve should be made to find the appropriate temperature to use in this step. Consult the instrument manual for the procedure of making an atomization curve. The lowest temperature that still gives maximum signal should be used in order to extend the lifetime of the graphite tube. Zero ramp time is used in this step. Gas stop during atomization is recommended.

**Cleaning step:** A tube cleaning cycle after the analyte measurement should be done to remove any remains of sample and thereby avoid memory effects. A purge gas flow of 250-300 ml min<sup>-1</sup> is normally used.

*All times and temperatures are guidelines only.*

#### 4.17.4.8 *Instrument performance*

The characteristic mass (sometimes called sensitivity) is defined as the absolute mass of an element that will absorb 1% of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU). The characteristic mass may be used as an indicator of instrument optimisation. Values of the characteristic masses are most often given in the instrument documentation. Experimental values for comparison can be determined by measuring the absorbance signal (area) of a known mass of analyte and calculate using the following formula:

$$m_0 = V_s * C_s * 0.0044 \text{ AU} / \text{observed peak area}$$

$m_0$ : Characteristic mass (ng)

$V_s$ : Standard volume injected (ml)

$C_s$ : Standard concentration ( $\text{ng ml}^{-1}$ )

*Table 4.17.6: Proposed instrument parameters.*

	$\lambda$ , nm	slit	Drying temp	Pyrolysis temp	Atomization temp	Chemical modifier	Pyrolysis temp.	Atomization temp.
As	193.7	0.7	120	500	2300	$\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$	1300	2300
Cd	228.8	0.7	120	350	1800			
Cr	357.9	0.7	120	1350	2660	$\text{Mg}(\text{NO}_3)_2$	1650	2500
Cu	324.7	0.7	120	900	2600			
Pb	217.0	0.7	120	550	2000	$(\text{NH}_4)_3\text{PO}_4$ or $\text{La}(\text{NO}_3)_2$	700	1800
Ni	232.0	0.2	120	1200	2600			
Zn	213.9	0.7	120	350	1800	$\text{Mg}(\text{NO}_3)_2$	700	1800

Other operating parameters should be set as specified by the particular instrument manufacturer.

#### **4.17.4.9 Chemical modifiers**

In order to achieve better separation between analyte and matrix prior to atomisation, a chemical modifier can be used. The role of the modifier is most often to stabilise the analyte making higher temperatures in the pyrolysis step possible without any loss of analyte. The concentration level of most modifier mixtures is usually in the ppm level. The injection volume most often is in the 5-20  $\mu\text{l}$  region. The modifier mixture should be injected and dried prior to sample injection. For suggestions of chemical modifiers for the various elements see Table 4.17.6.

#### **4.17.4.10 Sequence of analysis**

- Start the analysis with an “empty tube” run. If a significant signal is obtained, a cleaning step (2650°C, 2-3 s) should be run repetitively to remove the remains in the tube. If this is not sufficient, the graphite tube should be replaced.
- The chemical modifier solution (if used) should be checked for contamination in a separate run.
- The blank solution should be analysed to establish a blank level.
- In addition to the blank standard, at least 3 standards should be selected to cover the linear range. Repeat the analysis until good agreement between replicates and a linear calibration curve is obtained.
- A quality control standard should be analysed to verify the calibration.
- Samples that are found to have concentration higher than the highest standard should be diluted into range and reanalysed.
- To monitor the performance of the graphite tube, a mid-level standard and a blank standard should be run after every 10<sup>th</sup> sample.

#### **4.17.5 Determination of zinc by flame atomic absorption spectroscopy (F-AAS)**

##### **4.17.5.1 Introduction**

F-AAS is a very specific technique prone to few interference effects. F-AAS is a single element technique with analyte determinations in the  $\text{mg l}^{-1}$  region as routine for most elements.

##### **4.17.5.2 Principles**

A liquid sample is nebulized to form a fine aerosol, which is mixed with fuel and oxidant gasses and carried into a flame. In the flame the sample is dissociated into free ground state atoms. A light beam from an external light source emitting specific wavelengths passes through the flame. The wavelength is chosen to correspond with the absorption energy of the ground state atoms of the desired element. The measured parameter in F-AAS is attenuation of light. Lambert-Beers law expresses the relationship between the attenuation of light and concentration of analyte.

##### **4.17.5.3 Interferences**

F-AAS is known as a technique with few problems related to interference effects. The interferences that occur are well defined, as are the means of dealing with them. For analysis of a few elements the type and temperature of the flame are critical; with improper conditions ionisation and chemical interferences may occur.

##### ***Ionisation***

Ionisation of the analyte atoms in the flame depletes the levels of free ground state atoms available for light absorption. This will reduce the atomic absorption at the resonance wavelength and lead to erroneous results. The degree of ionisation of a metal is strongly influenced by the presence of other ionisable metals in the flame. By addition of an excess of a very easily ionised element to the blanks, standards and samples the effect of ionisation can usually be eliminated. Ionisation is most common in hot flames such as nitrous oxide- acetylene flames. In an acetylene-air flame ionisation is most often limited to be a problem in analysis of the alkali- and alkaline earth metals.

##### ***Chemical interference***

The most common type of chemical interference occurs when the sample contains components that forms thermally stable compounds with the analyte and thus reduce the rate at which it is atomised. Adding an excess of a compound that form thermally stable compounds with the interfering element eliminates chemical interference. For example, calcium phosphate does not dissociate completely in the flame. Addition of Lanthanum will tie up the phosphate allowing calcium to be atomised. A second approach to avoid chemical interference is, if possible, to use a hotter flame. Using the method of standard addition can also control chemical interference.

##### ***Physical interference***

If the physical properties as viscosity and surface tension vary considerably between samples and standards, the sample uptake rate or nebulization efficiency may be different and lead to erroneous results. Dilution of samples or method of standard addition or both can be used to control these types of interferences.

#### ***Background absorption and light scattering***

Matrix components that are not 100% atomised and that has broadband absorption spectra may absorb at the analytical wavelength. Tiny solid particles in the flame may lead to scattering of the light over a wide wavelength region. The background absorption can be accounted for by using background correction techniques such as continuous light source ( $D_2$ -lamp) or Smith-Hieftje.

#### ***4.17.5.4 Instrumentation***

Atomic absorption spectrophotometer single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, equipped with a air-acetylene burner head and a suitable recorder or PC. The wavelength range must be 190-800 nm.

- Hollow cathode lamp for Zn.
- Electrodeless discharge lamp for Zn may be used if available.
- Pressure reducing regulators for acetylene and air.
- Pipettes ( $\mu$ l) with disposable tip in various sizes.

#### ***4.17.5.5 Reagents and standards***

All reagents must be of analytical grade or better.

Distilled de-ionized water

Nitric acid ( $HNO_3$ )

Zinc metal (Zn)

Acetylene gas (99,99% or better)

Air supply

#### ***Standard stock solutions (1000 $\mu$ g $ml^{-1}$ )***

Zn 1000  $\mu$ g  $ml^{-1}$ :

Transfer 1.000 g zinc metal to a beaker. Dissolve the metal in 10 ml 1:1  $HNO_3$ . Transfer the solution to a 1000 ml volumetric flask and dilute to the mark with distilled de-ionised water. Store the solution in a polyethylene bottle.

Commercially available standard solutions may also be used.

#### ***Calibration standards***

Calibration standards are prepared by single or multiple dilutions of the stock metal solution. Prepare a reagent blank and at least 3 calibration standards in graduated amount in the appropriate range of the linear part of the curve. The calibration standards must contain the same acid concentration as will result in the samples following processing. For precipitation samples, that would be 1% ( $v/v$ )  $HNO_3$  and for suspended particulate matter 10% ( $v/v$ )  $HNO_3$ . The calibration standard should be transferred to polyethylene bottles.

#### 4.17.5.6 Instrumental procedure

The operating procedure will vary between instrument brands, *so the instrument manual should be followed carefully*. The position of observation and the fuel:oxidant ratio must be optimised. Some general guidelines are outlined below

- Light the hollow cathode lamp or electrode discharge lamp and D<sub>2</sub>-lamp if such background correction is used. Set the lamp current to the value specified by the manufacturer.
- Position the monochromator at wavelength 213.9 and choose slit with 0.7 and slit height “high”.
- Carefully balance the intensity of the hollow cathode lamp and the D<sub>2</sub>-lamp if such background correction is used.
- Align the burner head to assure that the centre of the light beam passes over the burner slot.
- Light the flame and regulate the flow of fuel and oxidant to produce an oxidising flame (lean blue).
- Aspirate calibration blank and establish a zero point.
- Aspirate standard solutions and construct a calibration curve.
- Aspirate distilled water after each standard or sample.

#### 4.17.5.7 Instrument performance

The “characteristic concentration” (sometimes called sensitivity) is defined as the concentration of an element (mg l<sup>-1</sup>) that will absorb 1 % of the incoming radiation. This equals a signal of 0.0044 absorbance units (AU). The “characteristic concentration” is instrument dependent and is calculated as follows:

$$C = (S * 0.0044 \text{ AU}) / \text{measured absorbance}$$

C: Characteristic concentration (mg l<sup>-1</sup>)

S: Concentration of measured standard (mg l<sup>-1</sup>)

Knowing the “characteristic concentration” allows the analyst to check if the instrument is correctly optimised and performing up to specifications.

#### 4.17.5.8 Sequence of analysis

- Aspirate calibration blank and establish a blank level
- Aspirate calibration blank and standard solutions and construct a calibration curve. Use at least 3 standard solutions in addition to the calibration blank to cover the linear range. Every point at the calibration curve should, if possible, be based on replicate analysis. Distilled water should be aspirated after each standard and sample.
- A quality control standard should be analysed to verify the calibration.
- A calibration blank should be analysed to check for memory effects.
- Aspirate unknown samples.
- Aspirate a quality control standard for every 10th sample to check for drift.

- Samples that are found to have concentration higher than the highest standard should be diluted and reanalysed.

#### **4.17.6 References**

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## **4.18 Analysis of mercury in precipitation and air**

### ***4.18.1 Analysis of mercury in precipitation***

#### ***4.18.1.1 Instrumentation***

The most common procedure for the analysis of mercury in precipitation is oxidation with BrCl, pre-reduction with NH<sub>2</sub>OH·HCl followed by reduction of the aqueous Hg to Hg<sup>0</sup>, purging onto gold traps and thermal desorption and analysis using Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS) (Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). The analysis procedure can be performed in manual or automated modes. A detection limit (defined as 3 times the standard deviation of the blank concentration) 2 ng/l is necessary for the accurate analysis of total mercury in precipitation samples from remote stations.

The most reliable technique for the analysis of mercury is atomic fluorescence spectrometry (AFS). Atomic absorption spectrometry (AAS) may be used but requires larger sample volumes due to higher detection limit. AFS and AAS instruments are available from a number of different manufacturers.

Borosilicate glass is the recommended material for the reaction and purging of flasks where mercury is reduced and volatilised for the pre-concentration step. Acid-washed Teflon tubing should be used. Ordinary polyethylene or rubber tubing is not suitable.

#### ***4.18.1.2 Sample storage and handling***

All water samples for mercury analyses must be handled with care in order to avoid contamination. Sample bottles should only be handled in laboratories where mercury or any mercury compounds in pure or concentrated forms have not been handled. Samples for analysis of total mercury should be preserved with low blank HCl (5 ml 30% acid/l). Precipitation samples should be stored in the collection bottles, in double plastic bags in the dark in a refrigerator or cold room. A storage time up to 6 months can be acceptable but it is absolutely necessary to test this under the conditions employed in the individual laboratories. Shorter storage times are recommended if methylmercury is analysed. Plastic gloves must always be used when the plastic bags are opened. If possible, the plastic bags should be left around the bottles during the analysis. The bottles should not be placed on laboratory surfaces that may have been exposed to mercury or chemical reagents containing mercury.

#### ***4.18.1.3 Chemicals and glassware***

*Purging flasks for SnCl<sub>2</sub>-reduction:*

Acid-cleaned borosilicate glass (Pyrex) wash-bottles are used.

*Hg-free Nitrogen/Hg-free Argon:*

The gas should go through a gold trap or coal filter

*High purity water:*

Purified water with >18 MΩ resistance and a low mercury blank.

*Air in laboratory:*

All glassware and samples should be handled in a laboratory containing low concentrations of mercury (not more than 10 ng/m<sup>3</sup> if possible). A clean bench (or some other clean zone arrangement) of class 100 should be used for handling reagents, for some sample treatment and for the drying of glassware.

*Hydrochloric acid:*

30% HCl (Suprapur) from Merck is recommended. Other manufacturers may provide equally high quality hydrochloric acid. Regular blank checks should be made. For the preparation of SnCl<sub>2</sub> solution, 37% HCl (P.A.) is necessary.

*Bromine monochloride solution:*

**Must be prepared in a fume hood with great care. Use safety goggles.** Add 11,0 g KBrO<sub>3</sub> and 15,0 g KBr to 200 ml high purity water. Stir the solution with a magnetic bar for 1 hour and add 800 ml 30% HCl **very slowly**. Large amounts of acid fumes and gaseous free halogens will form and will evaporate from the solution. The solution can be prepared in an empty HCl bottle.

*Hydroxylammonium chloride:*

Dissolve 120 g NH<sub>2</sub>OH·HCl in 1 l high purity water. This chemical reagent sometimes contains high mercury concentrations. Adding 1 g Chelex 100 ion exchange material can lower the mercury content. Blanks must be checked carefully.

*Stannous Chloride solution:*

Dissolve 200 g SnCl<sub>2</sub>·2H<sub>2</sub>O in 100 ml 37% HCl (p.a.) and dilute to 1 l with high purity water. Purge this solution with mercury-free N<sub>2</sub> for 12 hours and then store it in the dark. Aliquots of 100 ml may be removed and used as working solutions for analysis. These aliquots should be purged continuously with mercury-free N<sub>2</sub>.

*Mercury calibrating solution:*

Standard solutions can be prepared from commercially available mercury standards. A parallel check using two standard solutions of different origin is recommended. One of these can be made from pure chemicals (e.g. Hg<sup>0</sup> dissolved in concentrated HNO<sub>3</sub> and diluted to the appropriate volume).

**4.18.1.4 Pre-treatment**

The collected samples are preserved with HCl prior to storage or during sampling. Before analysis a chemical oxidation step is performed using BrCl. This reagent efficiently converts stable mercury forms to water soluble species that can be easily reduced by SnCl<sub>2</sub>. Before analysing the sample, excess BrCl is removed using a mild reducing agent such as NH<sub>2</sub>OH·HCl or ascorbic acid.

#### **4.18.1.5 Preparation of reducing vessels**

Fill the wash bottles with about 50 ml water containing 2.5 ml of the  $\text{SnCl}_2$  solution and 2 ml 30% HCl. Purge the solution with  $\text{N}_2$  for 20 minutes before checking the bubbler blank value.

At the end of each day, the bottles should be rinsed thoroughly with de-ionised water and then filled (at least covering the glass frit) with Aqua Regia until use. Before starting the next set of analyses, the Aqua Regia should be transferred to a storage bottle (Aqua Regia can be re-used for up to a month) and the reduction vessel rinsed, first with de-ionised water and then with high purity water (e.g. Milli-Q).

#### **4.18.1.6 Reduction step**

The bubbler blank value should be checked by connecting a gold trap to the bubbler and purging the solution with  $\text{N}_2$  for 20 minutes, then analysing the mercury collected. The mercury collected on the gold trap is the bubbler blank and should not exceed a few picograms.

In all collection and purging steps, a glass tube containing baked quartz wool should be connected between the bottle and the gold trap to avoid exposing the gold surface to droplets of acid solution.

After the bubbler blank has been checked, a clean gold trap should be connected to the outlet and an aliquot of the pre-treated precipitation sample added to the bubbler flask. The bubbler flask should then be placed on an electronic balance and the amount of sample added weighed. The reduction and purging should be allowed to proceed for 10 to 20 minutes.

#### **4.18.1.7 Detection**

The traps should be dried at about  $40^\circ\text{C}$  in a mercury-free  $\text{N}_2$  flow for 5 minutes prior to analysis. They should then be connected to the AFS detector on line with the helium gas flow. The mercury is then thermally desorbed either directly into the detector or onto an analytical trap. If an analytical trap is used, a second heating step should be performed before the detection. The advantage of the dual amalgamation is that the influence of any interfering substances adsorbed on the first trap may be reduced and also that the mercury adsorbed onto the second analytical trap will be more easily desorbed and a sharper peak obtained.

After the analytical step the gold trap should be allowed to cool. It should then be removed from the gas stream and stoppered with Teflon plugs. It should be stored in a plastic bag if not immediately used again.

#### **4.18.1.8 Calibration**

Standard solutions can be prepared from commercially available mercury standards. Calibration should be performed by using 4 standards in each run.

#### 4.18.1.9 Quality control - Quality assurance

The calibration step is critical. In general, the basic principle is always to use two independent calibrant solutions. One of these can be made from pure chemicals (e.g.  $\text{Hg}^0$  dissolved in concentrated  $\text{HNO}_3$  and diluted to the appropriate volume). For mercury, commercially available standard solutions can be used but regular checks against a reference standard must be made. Certified reference materials should be used if available, but reference standards can also be prepared from pure mercury compounds. Traceability is an important step and all standard solutions must be regularly checked against a reference material. In the absence of aqueous phase reference standards, solid materials may be used.

As an independent check on the analytical results, a  $\text{Hg}^0$  vapour source can be used consisting of liquid mercury in an enclosed vessel from which vapour samples can be drawn with a gas tight syringe.

#### 4.18.1.10 Special problems

The analysis of low level mercury concentrations in aqueous samples is associated with a number of potential errors mainly emanating from blank problems and poor recovery.

Blank values usually arise from the use of reagents of poor quality or from glass vessels or tubing. Careful checking and documentation of all steps in the analytical procedure is necessary in order to identify the source of the blank.

#### 4.18.1.11 Summary

	Recommendation	Acceptable alternatives
Sample pre-treatment	BrCl oxidation, $\text{NH}_2\text{OH}\cdot\text{HCl}$ pre-reduction	Ascorbic acid
Preconcentration	$\text{SnCl}_2$ reduction, purging, collection on gold traps	
Detection	AFS	AAS
Detection limit	< 2 ng/l	
QA/QC	Blank determinations, use of traceable reference materials	

#### 4.18.2 Analysis of mercury in air

Mercury collected on gold traps is analysed after desorption of the mercury.

##### 4.18.2.1 Sample pre-treatment

Before analysing the mercury content of the gold trap, a drying step is recommended. Small amounts of water vapour may have condensed on the gold surface and may interfere in the analysis step. The gold traps can be heated to 40-50°C for 5-10 min in a stream of dry  $\text{N}_2$  without any measurable loss of mercury.

#### **4.18.2.2 Analysis**

The analysis of mercury in air samples is generally made using double amalgamation CVAFS (Fitzgerald and Gill, 1979; Bloom and Fitzgerald, 1988). In this procedure, the gold trap is mounted in series with a second analytical trap in a gas stream (Hg-free argon) leading to the CVAFS detector. Heating is achieved with a heating wire (e.g. NiCr). In the first step the mercury is thermally desorbed from the first sampling trap onto the second analytical trap. The second trap is then rapidly heated and the mercury is transported into the CVAFS with an integrator.

The analytical steps are as follows:

1. thermal desorption from the field trap to the analytical trap: 500°C for 4 minutes, with 30 ml/min flow rate
2. thermal desorption from the analytical trap to the AFS: 800°C for 25 seconds, with 30 ml/min flow rate
3. Total gaseous mercury calculation: Peak Area of the integrated AFS Signal.

#### **4.18.2.3 Calibration**

Mercury-saturated air is supplied from a closed flask (ca 350 ml), containing 30-40 ml of mercury (Dumarey et al., 1985). The inner pressure is kept at atmospheric pressure by means of a side-arm, which has access to ambient conditions via a capillary. The flask is placed in a thermostat ( $20^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ ). 0.1 ml saturated air is removed via a septum by using a gas-tight syringe (Hamilton #1810). 0.1 ml of air at  $20^{\circ}\text{C}$  and 101,325 Pa contains 1.316 ng Hg according to Ideal Gas Law (Table 4.8). Its accuracy depends mainly on the temperature of the mercury-saturated air, which must be lower than the ambient temperature to prevent condensation of mercury in the syringe. By preconditioning the syringe, initial irreproducible measurements caused by sorption are avoided. Under optimal conditions the standard deviation of the injection with 0.1 ml ( $n=10$ ) should be better than 10%. The re-establishment of the equilibrium between liquid and gaseous mercury depends on the cleanness of the pool surface. After some time, mercury at the surface becomes oxidised by atmospheric oxygen and the upper layer must be removed.

Table 4.18.1: Concentrations of Hg calibration gas as function of temperature.

Temp °C	ng Hg/ml						
17.0	10.22	20.5	13.72	22.2	15.79	23.9	18.14
18.0	11.12	20.6	13.83	22.3	15.92	24.0	18.29
19.0	12.10	20.7	13.95	22.4	16.05	24.1	18.44
19.1	12.20	20.8	14.06	22.5	16.18	24.2	18.59
19.2	12.31	20.9	14.18	22.6	16.31	24.3	18.74
19.3	12.41	21.0	14.30	22.7	16.45	24.4	18.89
19.4	12.52	21.1	14.42	22.8	16.58	24.5	19.04
19.5	12.62	21.2	14.54	22.9	16.72	24.6	19.20
19.6	12.73	21.3	14.66	23.0	16.86	24.7	19.35
19.7	12.83	21.4	14.78	23.1	17.00	24.8	19.51
19.8	12.94	21.5	14.90	23.2	17.13	24.9	19.67
19.9	13.05	21.6	15.03	23.3	17.28	25.0	19.83
20.0	13.16	21.7	15.15	23.4	17.42	26.0	21.49
20.1	13.27	21.8	15.28	23.5	17.56	27.0	23.27
20.2	13.38	21.9	15.40	23.6	17.70		
20.3	13.49	22.0	15.53	23.7	17.85		
20.4	13.60	22.1	15.66	23.8	17.99		

#### 4.18.2.4 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.

To provide an internal control on the field results, one set of 3 or 4 gold traps is routinely kept in the glass container during a field study. The set is then analysed along with the other field samples. In almost all cases, a typical mercury blank result of 5-30 pg Hg was observed.

#### 4.18.2.5 Detection limit

The detection limit of the gold trap analysis is defined as 3 times the standard deviation of the trap blank provided that the trap blank is subtracted from the analysed amount. This detection limit, expressed in units of ng Hg, can be translated into an air concentration using the typical air volume sampled in this application. The detection limit can also be based on the requirement that the blank content of mercury on the traps should not exceed 10% of the total content of mercury collected during a normal sample period. The absolute value will depend on sampling time and air flow rate. As a guideline the following example can be used: in air containing 2 ng Hg/m<sup>3</sup> a sample collected for six hours at an air flow rate of 0.5 l/min contains 0.36 ng. In this case, the blank content on the trap

should not exceed 10% of 0.36, i.e. 0.036 ng. If the blank content is higher than this value, then the detection limit exceeds 2 ng/m<sup>3</sup> under the conditions employed, and a larger sample volume is required.

#### 4.18.2.6 *Special problems*

The analysis of mercury collected on gold traps is generally straightforward provided that the collection efficiency of the gold traps is checked regularly.

#### 4.18.2.7 *Summary*

	<b>Recommendation</b>	<b>Acceptable alternative</b>
Sample pre-treatment	Drying at 30-50°C if necessary.	
Analysis	Dual amalgamation CVAFS.	CVAAS.
Detection limit	3 $\sigma$ of trap blank and/or trap blank <10% of sample.	
QA/QC	Check gold trap collection efficiency and recovery.	

#### 4.18.3 *References*

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## 4.19 Determination of persistent organic pollutants (pesticides and PCBs)

### 4.19.1 Principle

This method covers the following groups of components:

Chlororganic pesticides:

- $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCH
- HCB
- Chlordanes (including acid labile components)
- DDTs
- The Dieldrin group
- Trifluraline
- $\alpha$ -Endosulphane

Polychlorinated biphenyls,

- PCB

These components may be determined in air samples, described in chapter, [3.13](#). 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).

### 4.19.2 Materials and equipment

#### 4.19.2.1 Glassware

- Beakers, 50, 100, and 250 ml, Schott Duran or similar
- Desiccator, 150 mm and 300 mm diameter with grinded glass rims, no grease to be applied
- Erlenmeyer flasks, 250 ml with glass stopper
- Funnels, 20 – 150 mm diameter, Schott – Duran or similar
- Sample vials
  - Vial, 0.9 ml, Chromacol 0.9-CTV or similar with septum cap (teflon-coated silicon seal), Brown cat. no.151261 or similar quality
  - Vial, 1.5 ml Brown cat. no.150900 with scew top and teflon seal, Brown cat. no.150931 or similar quality
  - Vial, 2 ml with a capillary opening (diameter 1.5 mm and length 20 mm) and screw cap (teflon seal Schott GL14), (home made)
  - Vial, 8 ml with screw cap (teflon seal), Supelco cat. No. 2-3295
  - vial with 100  $\mu$ l insert, Chromacol 0.3- FIV
- Hamilton syringes 5, 10, 25, 100, 250, 500  $\mu$ l
- Chromatography column, length 20 cm x 1.5 cm diam., Schott Duran
- Micropipettes, 10, 20, 25, 50 and 100  $\mu$ l with accuracy better than  $\pm 0.25$  %
- Volumetric flasks, with glass stoppers, and graduated for 10, 25, 50, 100 ml with accuracy better than  $\pm 0.025$  %, Schott Duran

- Cylinders, graduated for 25, 50, 100, 250, 500, 1000 ml, with accuracy better than  $\pm 0.75\%$ , Schott Duran or similar
- Pasteur pipettes 150 mm and 220 mm
- Flasks, round bottom, 100, 250, 500, with glass joints NS24/29, Schott Duran or similar
- Conical glasses for centrifugation, 10 ml
- Soxhlet extractors 200, 500, 2000 ml with condenser, 250 mm, Schott Duran or similar
- Sample tubes for TurboVap 500

#### **4.19.2.2 Other equipment**

- Aluminium foil
- Analytical balance, 0–160 g, precision  $\pm 0.0001$  g or better
- Cotton wool, chemical clean, (cleaning: section 2.6.4.6)
- Cellulose thimbles for Soxhlet, Schleicher & Schuell (pre-treatment: section 2.6.4.5).
- Gloves, disposable, of polyethylene
- Gloves, solvent resistant, of PE/EVOH/PE laminate
- Freezer for
  - samples, both untreated and extracts after chemical treatment
  - standards
- Evaporator with automatic stop, TurboVap 500, Zymark
- Oven, Hagan, Type 22, 200 - 1030°C, precision  $\pm 10^\circ\text{C}$
- Refrigerator, explosion safe, for storing diethyl ether and working standards
- Cork stands in various formats
- Membrane vacuum pumps
- Evaporator to be used with nitrogen gas supply, with activated charcoal cartridge and valve for fine adjustment of nitrogen gas
- Tweezers in various sizes
- Oven, Heraeus, RE 4125, 50–1100°C,  $\pm 5^\circ\text{C}$
- Syringes, 5, 10 and 25  $\mu\text{l}$ , fixed needle and steel plunger, Hamilton, and 1 ml, fixed needle and teflon tipped plunger, Hamilton
- Ultrasonic bath, Sonorex RK 100, Bandelieu, 100 W
- Pressure regulator for gas, L'Air Liquide BS 300
- Water purification equipment, MilliQ plus, Millipore
- Heaters for 500 ml spherical flasks
- Oven, 50–300°C with  $3^\circ\text{C}$  precision
- Vibrator for dry packing of columns

#### **4.19.2.3 Analytical equipment and accessories**

- Gas chromatograph combined with a low resolution mass spectrometer; HP 5890 II gas chromatograph, Hewlett Packard, Avondale, USA
  - HP 5890-II gas chromatograph with split/splitless injector and HP 7673 autosampler
  - HP 5989 mass spectrometer (MS Engine)
  - HP G1034C MS Chemstation integration system

- Gas chromatograph combined with high resolution mass spectrometer VG AutoSpec, MICROMASS, Wythenshawe Manchester, England
  - HP 5890-II gas chromatograph with split/splitless injector and HP 7673 autosampler
  - VG GC/MS interface with lock mass substance inlet system
  - VG AutoSpec three sector high resolution mass spectrometer with EI-ion source
  - EC 3100 data system with OPUS MS- software system
- Examples of GC capillary columns:
  - 60 m and 30 m length\* 0.25 mm i.d., 0.10 µm film thickness, 95% dimethyl –5% diphenyl polysiloxane, immobilized, e.g. Rtx-5 from Restek Corporation, Bellefonte, USA
  - 25 m length\* 0.20 mm i.d. \* 0.11 µm film thickness, 5% phenylmethyl-polysiloxane HP-5 (Ultra), Hewlett Packard Company, Amsterdam, Holland
  - 50 m length \*0.22 mm i.d. \*0.15 µm 8% phenylpolycarbonsiloxane e.g. HT-8 SGE, Australia
  - 30 m length \*0.25 mm i.d. \*0.10 µm, 14% cyanopropylphenyl – 86% methylpolysiloxane, immobilized, e.g. Rtx-1701 from Restek Corporation, Bellefonte, USA
  - 30m length \*0.25 mm i.d. \*0.10 µm, 90% biscyanopropyl 10% phenyl-cyanopropyl, e.g. Rtx-2301 from Restek Corporation, Bellefonte, USA
- GC syringes; Hamilton, 10 µL, fixed needle and metal plunger for HP auto-sampler, HP cat. no. 80397, and for manual injection, cat. no. 80366.

#### 4.19.2.4 Chemicals and gases

##### *Organic solvents*

- Acetone, Merck no. 12
- Diethyl ether, Rathburn RG 2013
- Iso-octane, Merck no. 15440
- Methanol, Merck no. 6011
- MS lockmass standard: perfluorokerosene (PFK) low boiling, Merck no. 10145
- n-Hexane, Merck no. 4371
- n-Nonane, Merck no. 806838
- Perfluorotributylamin MS calibration solution, HP cat. No. 0571-60571
- Cyclohexane, Merck no. 2817
- Tetradecane, Fluka no. 87140
- Toluene, Merck no. 8382

All solvents, except diethyl ether can be used without cleaning.

##### *Inorganic chemicals, adsorbents and various accessories*

- Active carbon 1.5 mm diameter, Merck no. 2514
- Aluminium oxide, ICN Biomedicals no. 02072 Alumina B, Act. I
- Cotton, Apotekernes Felleskjøp

- De-ionised water, Millipore equipment
- Glass wool, silanized, Alltech cat. no. 4037
- Molecular sieves, 0.5–2 mm, Merck no. 5707, activated at 300°C in a He flow
- Sodium sulphate, Merck no. 6649, heating, see 2.6.4.3
- RBS 25 laboratory detergent, KEBO
- 6 N hydrochloric acid, diluted from concentrated acid, Merck no. 319
- Silica gel, Merck no. 7734, pre-treatment, see 2.6.4.4
- Sulphuric acid, 96%, Merck no. 731

#### *Gases*

- Helium, Norsk Hydro 4.5, 99.995%
- Nitrogen, N<sub>2</sub> Norsk Hydro 4.0, 99.99%
- Methane, CH<sub>4</sub> 3.5, Messer Griesheim, 99.9%

### **4.19.3 Cleaning and pre-treatment**

#### **4.19.3.1 Cleaning of the sampler**

See chapter [3.16.3.1](#)

#### **4.19.3.2 Cleaning of PUF-plugs**

See chapter [3.16.3.2](#)

#### **4.19.3.3 Cleaning of glass equipment**

See chapter [3.16.3.3](#)

#### **4.19.3.4 Cleaning of other equipment**

See chapter [3.16.3.4](#)

#### **4.19.3.5 Check and pre-treatment of solvents and chemicals**

All solvents must be of "pesticide grade" or equivalent quality. The solvent must give chromatograms free from interfering peaks ( $S/N < 3$ ) in the elution range from  $\alpha$ -HCH to OCN. Performing a complete method blank test may also check this.

#### **4.19.3.6 Cleaning of diethyl ether**

The diethyl ether must be cleaned because it contains an inhibitor to prevent formation of peroxides: 250 ml diethyl ether is filtered using a chromatography column (diam. 20 mm) packed with 20 cm basic aluminiumoxide. Diethyl ether without inhibitor may, with time, form peroxides, which represents an explosion hazard, especially by pre-concentrating samples using a rotary evaporator. Therefore not more than an amount sufficient for one month's consumption is cleaned. The solvent is stored in the dark at a temperature  $< 5^{\circ}\text{C}$ .

#### **4.19.3.7 Pre-treatment of sodium sulphate**

Sodium sulphate is put in a porcelain dish and heated to 600°C for 8 hours in an oven. Let cool to room temperature in a desiccator. Store in a stoppered glass

bottle. The bottle must be labelled with the expiry date of the sodium sulphate. Maximum storage time is one month. After the expiry date the sodium sulphate is discarded.

#### **4.19.3.8 Pre-treatment of silica**

Ca. 400 g silica is put in a porcelain dish and heated at 600°C for at least 8 hours in an oven. After heating the silica is left to cool in a desiccator and shall not be used before it has reached room temperature. The silica is stored in a glass bottle with a glass stopper. The bottle must be labelled with the expiry date of the silica. Maximum storage time is one month

#### **4.19.3.9 Cleaning of soxhlet thimbles**

Soxhlet thimbles are cleaned by soxhlet extraction using n-hexane for 8 hours. The thimbles are dried in a fume hood at room temperature overnight and wrapped individually in aluminium foil.

#### **4.19.3.10 Cleaning of cotton wool**

Cotton wool is soxhlet extracted with 500 ml – 2500 ml (depending of amount of cotton) n-hexane or dichloromethane for 24 hours. The cotton is dried in a vacuum desiccator at 60°C.

### **4.19.4 Gas cleaning**

#### **4.19.4.1 Gas bottle exchange**

1. Gas bottles must be replaced when the pressure approach 20 bar. The bottle pressure should never be lower than 15 bar.
2. Before exchanging GC-carrier gas bottles, set GC-oven temperature below 50°C.
3. Bottle exchange should be performed rapidly. Collect the new bottle before disconnecting the old one.
4. If only one spare bottle is in the storage room, order a new batch.
5. Flush the bottle valve on the new bottle twice (ear protection) before connecting the pressure reduction valve.
6. Connect pressure reduction valve firmly and open it.
7. Check for leaks with leak detector (Ion Sciences: Gas Check B4 or Supelco: Snoop leak detector).
8. Mount valve protection cap on the empty bottle and transport the bottle to the storage room.
9. All bottles must be secured against falling over.

#### **4.19.5 Special procedures**

Helium GC carrier gas cleaning:

1. Chrompack Gas Clean Oxygen Filter (with charcoal) and Chrompack Gas Clean Moisture Filter are connected in series after the pressure reduction valve. Exchange the units after exchanging 5 bottles or once a year.
2. Two metal cartridges are mounted in series on the gas line before each GC inlet. The first is filled with active carbon, the second is filled with molecular sieves. Exchange adsorbents each 3 years and after irregularities (empty gas bottle).

Nitrogen used for final sample blow-down/pre-concentration is cleaned using a metal cartridge filled with active carbon. Exchange adsorbent when exchanging the gas bottle.

#### **4.19.6 Treatment of adsorbents**

Chrompack filters are discarded after use.

Re-activation of molecular sieves: Fill molecular sieves in a metal cartridge and activate at 300°C (3 h) in an oven, flushing the cartridge with 20 ml/min. pre-filtered helium.

Active carbon is discarded after use.

#### **4.19.7 Sample preparation**

Sample pre-treatment, e.g. weighing of filters and extraction, is discussed in chapter [3.17.5](#)

##### **4.19.7.1 Principle**

Small amounts of interfering substances may be removed from the sample with one single method. Depending on the components to be measured different cleaning procedures can be selected; treatment of the extract with sulphuric acid for acid-stable components, or with alkaline hydrolysis for acid-labile substances. Both treatments are followed by adsorption chromatography. When both acid-stable and -labile substances are measured and their relative amounts unknown, the concentrate should be divided into two equal parts before further treatment. After cleaning, the sample should be concentrated once more followed by addition of a recovery standard (TCN or OCN) in order to determine the amount of internal standard before the sample is ready for analysis by GC/MS.

##### **4.19.7.2 Sulphuric acid treatment of acid-stable substances**

The concentrated sample (0.5–1 ml volume) is transferred to a 10–15 ml centrifuge tube, 8-10 ml conc. sulphuric acid added, and placed in a rack until the next day. The hexane fraction is transferred to a new centrifuge tube and 1 ml MilliQ water added drop by drop. The water phase is removed and the hexane phase dried with ½ teaspoon Na<sub>2</sub>SO<sub>4</sub>.

#### **4.19.7.3 Alkaline hydrolysis of acid-labile substances**

To 1 ml concentrated sample is added a solution of 0.2 g KOH in 1 ml ethanol and 0.1 ml MilliQ water. The mix is heated on a water bath at 50°C for 30 min. Add 5 ml MilliQ water, shake the sample, separate by a centrifuge, concentrate the organic phase by evaporation, and add a recovery standard before the GS/MS analysis. If the hydrolysed sample is strongly coloured after evaporation, the sample may be cleaned using silica-chromatography (next Section).

#### **4.19.7.4 Silica chromatography**

Cotton is put at the bottom end of a glass column (20 cm x 1.5 cm) and the column is filled with 4 g silica activated at 600°C. A layer of 1g Na<sub>2</sub>SO<sub>4</sub> is added on top. Use a vibrator when filling. The column is washed with 30 ml 10 % diethyl ether in hexane. The column should never be allowed to run dry! The sample (0.5–1 ml volume) is transferred to the column after washing, and the sample container rinsed with additionally 2–3 ml diethyl ether/hexane mixture which is transferred to the column. Elute the column with 30 ml of diethyl ether/hexane mixture and the sample is collected in a TurboVap glass with 20 µl nonane as a keeper. The sample volume is carefully reduced with the TurboVap until 0.5 ml, and transferred to a sample glass with conical insert. The TurboVap vessel is rinsed three times with 0.15 ml hexane, and the liquid volumes added to the sample. The sample volume is reduced to the desired volume (0.1–0.5 ml) in a slow nitrogen stream. Recovery standard is added and the sample vessel sealed with a screw cap or a crimp cap with auto-injector septum. This sample is now ready for a GS/MS analysis. If the sample is not analysed at once (same day) it must be kept dark in a freezer at -20°C. If the sample is stored for more than 1 month, this should be noted in the data report.

#### **4.19.7.5 If the sample contains silica particles**

Flush a pasteur pipette with a piece of cotton wool at the bottom with hexane. Pass the sample through the pipette and collect the sample. Wash with a small amount hexane before volume reduction to 0.1–0.5 ml.

#### **4.19.8 Standards**

A standard mixture containing known concentrations of components of interest is used for identification/quantification. Standard components should preferably be provided as crystalline solids with purity better than 99 per cent. If they can be provided in solutions only, the solutions must be certified or calibrated against certified standards from an international standardisation bureau as NIST or BCR.

Concentrated standards containing only one, or a small number of components are prepared and checked by GC/MS in full scan mode before further use. If impurities are discovered, their concentrations should correspond to less than 3% of the main components area. The other standards; calibration standards, internal standards, and recovery standards, are all prepared as different diluted mixtures based on the concentrated standards.

Weighing the proper amounts of crystalline substance of the standards should be performed with great care. Use disposable gloves and a mask. Weighing ships and spatulas should be rinsed in toluene and hexane before use and (air) dried. The tare of the ship is set to zero and the standard component transferred to the ship by a thin spatula in an amount as close to the estimated one as possible. The spatula must be rinsed and dried between each weighing in order to avoid contamination. When all components have been weighed, the content of the ship is transferred to a volumetric flask with n-hexane or iso-octane. The flask is filled with n-hexane or iso-octane to the correct volume and placed in an ultrasonic bath until all solids are dissolved. The concentrated standard is transferred to a flask equipped with screw cap and a teflon seal.

The weighed amounts and standard concentrations, a standard number, and the weight of the standard flask must be recorded in the standards logbook. The concentrated standards should be kept in a refrigerator at 4°C. When preparing the more diluted solutions, the concentrated standards should be removed from the fridge two hours before use. The concentrated standard should be sonicated for 5 min. in order to dissolve any solid substance. This is of particular importance for heavily soluble components e.g.  $\beta$ -HCH. In order to maintain a high accuracy in the final concentration, the dilution should be less than 1:100 in all steps, i.e. at most 100  $\mu$ l in a 10 ml graduated flask. When more diluted solutions are needed, secondary standards should be prepared. The flask containing the concentrated standard should be weighed before and after removing a volume for dilution, and the weights recorded in the logbook.

Diluted solutions are prepared by using volumetric flasks and pipettes or syringes. Disposable pipettes are preferred to syringes used for different standards because of a possibility for contamination. The entire dilution process must be checked by weighing.

#### 4.19.8.1 Concentrated standard

The following components may be included in a set of standards:

<b>Pesticides</b>	<b>Abbreviation</b>	<b>Polychlorinated biphenyls</b>	<b>IUPAC no.</b>
Hexachlorobenzene	HCB	2,2',5'-TriCB	18
$\alpha$ -Hexachlorocyclohexane	$\alpha$ -HCH	2,4,4'-TriCB	28
$\beta$ -Hexachlorocyclohexane	$\beta$ -HCH	2,4',5'-TriCB	31
		2',3,4'-TriCB	33
		3,4,4'-TriCB	37
$\gamma$ -Hexachlorocyclohexane	$\gamma$ -HCH	2,2',4,4'-TetCB	47
Trifluralin	Trifl	2,2',5,5'-TetCB	52
Chlordene	CDen	2,3,4,4'-TetCB	60
Heptachlor	HepC	2,3',4,4'-TetCB	66
Oxy-Chlordane	oxy-CD	2,4,4',5'-TetCB	74
Cis-Heptachlorepoxyde	cis-Hepex	2,2',4,4',5'-PenCB	99
Trans-Chlordane	tr-CD	2,2',4,5,5'-PenCB	101
Cis-Chlordane	cis-CD	2,3,3',4,4'-PenCB	105
trans-Nonachlor	tr-NO	2,3,4,4',5'-PenCB	114
cis-Nonachlor	cis-NO	2,3',4,4',5'-PenCB	118
<b>Pesticides</b>	<b>Abbreviation</b>	<b>Polychlorinated biphenyls</b>	<b>IUPAC no.</b>
		2',3,3',4,5'-PenCB	122
$\alpha$ -Endosulfan	$\alpha$ -Endo	2',3,4,4',5'-PenCB	123
Dieldrin	Diel	2,2',3,3',4,4'-HexCB	128
Aldrin	Ald	2,2',3,4,4',5'-HexCB	138
		2,2',3,4,5,5'-HexCBC	141
Endrin	End	2,2',3,4',5',6'-HexCB	149
o,p'-Dichlorodipenyldichloroethane	op-DDD	2,2',4,4',5,5'-HexCB	153
p,p'-Dichlorodipenyldichloroethane	pp-DDD	2,3,3',4,4',5'-HexCB	156
o,p'-Dichlorodipenyldichloroethylene	op-DDE	2,3,3',4,4',5'-HexCB	157
p,p'-Dichlorodipenyldichloroethylene	pp-DDE	2,3',4,4',5,5'-HexCB	167
<b>Pesticides</b>	<b>Abbreviation</b>	<b>Polychlorinated biphenyls</b>	<b>IUPAC no.</b>
o,p'-Diklorodifenyltrikloroethane	op-DDT	2,2',3,3',4,4',5'-HepCB	170
p,p'-Diklorodifenyltrikloroethane	pp-DDT	2,2',3,4,4',5,5'-HepCB	180
		2,2',3,4,4',5',6'-HepCB	183
		2,2',3,4',5,5',6'-HepCB	187
		2,3,3',4,4',5,5'-HepCB	189
		2,2',3,3',4,4',5,5'-OctCB	194
		2,2',3,3',4,4',5,5',6'-NonCB	206
		2,2',3,3',4,4',5,5',6,6'-DecaCB	209
<b>Internal standard pesticides</b>	<b>Abbreviation</b>	<b>Internal standards PCB</b>	<b>IUPAC no.</b>
$^{13}\text{C}$ -p,p'-Dichlorodipenyldichloroethylene	$^{13}\text{C}$ -p,p'-DDE	$^{13}\text{C}$ -2,4,4'-Trichlorobiphe	$^{13}\text{C}$ -PCB-28
$^{13}\text{C}$ - $\gamma$ -Heksachlorosyklohexane	$^{13}\text{C}$ -2D- $\gamma$ -HCH	$^{13}\text{C}$ -2,2',5,5'-Tetrachlorobiphe	$^{13}\text{C}$ -PCB-52
$^{13}\text{C}$ - $\alpha$ -Heksachlorosyklohexane	$^{13}\text{C}$ - $\alpha$ -HCH	$^{13}\text{C}$ -2,2',4,5,5'-Pentachlorobiphe	$^{13}\text{C}$ -PCB-101
		$^{13}\text{C}$ -2,3',4,4',5'-Pentachlorobiphe	$^{13}\text{C}$ -PCB-118
		$^{13}\text{C}$ -2,2',4,4',5,5'-Hexachlorobiphe	$^{13}\text{C}$ -PCB-153
$^{13}\text{C}_4$ -Aldrin			
$^{13}\text{C}_4$ -Dieldrin			
$^{13}\text{C}_4$ -Heptachlor			
$^{13}\text{C}$ -Hexachlorobenzene	$^{13}\text{C}$ -HCB	$^{13}\text{C}$ -2,2',3,4,4',5,5'-Heptachlorobiphenyl	$^{13}\text{C}$ -PCB-180
<b>Recovery standards</b>			
1,2,3,4-Tetrachloronaphtalene	TCN		
Octachloronaphtalene	OCN		

#### **4.19.8.2 Calibration standard**

A standard for GC/MS should have concentrations similar to the expected concentrations of the components to be measured

#### **4.19.8.3 Internal standard (ISTD)**

The internal standard may be a solution with pesticides and/or PCBs which contains labelled isotopes.

#### **4.19.8.4 Recovery standard (RSTD)**

A solution containing tetrachloronaphtalene is used for this purpose. The recovery standard is added to the sample as the last step before quantification.

#### **4.19.8.5 Standard addition**

Amounts of standards added before extraction (ISTD) and after the sample preparation (RSTD) should be similar to the expected concentrations in the sample.

#### **4.19.8.6 Quality assurance of standards**

The purity of the standards is checked in the GC/MS full scan mode before acceptance. If impurities are discovered in the concentrated standard, the amounts as expressed by its area in the chromatogram must be less than 3 % of the main component's area. When concentrated standards are stored dark in a refrigerator, their stability will be very good. In order to document the stability, the full scan mode check is repeated at intervals not longer than 3 years. Normally this will be carried out when preparing a working standard after 2 years. The working standards are stored dark in a refrigerator, but new standards should be prepared every two years at most. Working standards kept in sample flasks with capillary tubes are not checked for weight loss (1 mg in 6 months when closed). The stability of working standards stored as described above is considered to be 2 years.

A newly prepared series of standards must always be compared with the previously used ones before use. Only differences considered to be less than the reproducibility of the analytical method are accepted. The working standards should be compared with certified reference material; NIST SRM 1492 "Chlorinated pesticides in hexane" and BCR CRM 365 "Polychlorinated biphenyls in iso-octane", at least once every year. Standards from laboratory comparisons may also be used. The standards should be stored in a refrigerator.

### **4.19.9 Separation and quantification**

#### **4.19.9.1 Principle**

The cleaned samples are analysed by gas chromatography/mass spectrometry (GC/MS). Standard mixtures are used for identification and quantification.

The individual components are identified by their GC retention and their mass fragments.

The quantification of the components is made by using internal standard. A calibration is performed with a standard mixture containing known concentrations of the components to be measured and one or more components not contained in the sample (internal standards). The calibration is followed by injection of the sample containing known amounts of internal standards. Quantification is relative to the internal standard. In this way, the sample extract volume will not be included in the calculations, and it is not necessary to accurately determine the final sample volume after evaporation or the injection volume.

#### **4.19.9.2 Gas chromatographic conditions**

The GC-parameters given are approximate and must be fine-tuned for each column, since equal columns may separate the actual compounds slightly differently.

Capillary column: Rtx-5, 60 m x 0.25 mm x 0.10  $\mu$ m:

Carrier gas: He, 185 kPa (1.85 bar, 27 psi)

GC-temperature program:

1  $\mu$ l injected splitless (autoinjector or "hot needle" injection) at 60°C, 2 min. at 60°C, 60–190°C with 20°/min., 190–230°C with 3°/min., 230–280°C and 280°C for 15 min. isothermally.

Capillary column: Rtx-5 or equivalent, 30 m x 0.25 mm x 0.10  $\mu$ m:

Carrier gas: He, 75 kPa (0.75 bar, 11.5 psi)

GC-temperature program:

1  $\mu$ l injected splitless (autoinjector or "hot needle" injection) at 60°C, 2 min. at 60°C, 60–150°C with 20 °/min., 150–280°C with 1 °/min. and 280°C for 10 min. isothermally.

Capillary column: Rtx-2330 or equivalent, 30 m x 0.25 mm x 0.10  $\mu$ m:

Carrier gas: He, 83 kPa (0.83 bar, 12 psi)

GC-temperature program:

1  $\mu$ l injected splitless (autoinjector or "hot needle" injection) at 60 or 100°C (depending on solvent), 2 min. at 60 or 100°C (depending on solvent), to 170°C with 20 °/min., 170–230°C with 3 °/min., 230–270°C and 270°C for 6.5 min. isothermally.

Capillary column: HP Ultra-2, 25 m x 0.20 mm x 0.11  $\mu$ m:

Carrier gas: He, 110 kPa (1.1 bar, 15 psi)

GC-temperature program:

1  $\mu$ l injected splitless (autoinjector or "hot needle" injection) at 60°C, 2 min. at 60°C, 60–150°C with 20 °/min., 150–230°C with 4 °/min. and 230–280 with 25 C/min and 275°C for 5 min. isothermally.

In addition the following parameters are used:

Split gas flow:  $40 \pm 10$  ml/min  
Septum purge flow: 3 ml/min  
Injector temperature: 260°C  
GC/MS-interface temperature: 260°C–280°C

To save carrier gas, the split gas flow is reduced to <5 ml/min when the instrument is not used.

Autoinjector conditions (approximate):

Solvent A: toluene  
Solvent B: n-hexane  
Sample wash: 0  
Sample pumps: 5  
Sample volume: 1  $\mu$ l  
Solvent A washes: 8  
Solvent B washes: 8

Solvents A and B for syringe cleaning must be exchanged each day. The solvent vials are cleaned when necessary.

The injector septum is exchanged after ca. 50 injections or once a week. The cleanness of the glass liner is checked after ca. 100 injections or if the GC-separation is poor.

#### **4.19.9.3 GC/MS-analysis**

For quantification GC/MS with either EI or NCI ionisation is used. To check the stability of the GC/MS-system, a calibration standard is injected before and after each sample batch.

Operation of the GC/MS-system is described in the instrument manuals.

#### *Calibration- and detection conditions for EI (VG-AUTOSPEC GC/MS)*

Gas chromatograph  
GC/MS-interface: 260°C  
Ion source:  
Electron impact (EI) ion source  
Ion source temperature: 260-300°C  
Max. acceleration voltage: 8000 V  
Electron energy: 30 eV-40 eV  
Lock substance: Perfluorokerosene (PFK)

By mounting the capillary column, 1-2 mm of the exit of the column (on the MS-side) should extend into the ion source.

Using mass fragment  $m/z = 330,97$  from perfluorokerosene (PFK, boiling point range 70°–240°C) the instrument is optimised manually for ion gain and mass

resolution. At resolution 10,000 (defined as  $m/\Delta m = 10,000$  at 5% valley) the signal/noise ratio for 500 fg of  $\gamma$ -HCH should be  $S/N \geq 3$ .

The mass scale for each SIM-function (single ion monitoring) is calibrated automatically if possible. Optimisation of ion source and mass resolution and calibration of mass scale is controlled for each single PFK-mass in each SIM-function.

To reduce the risk of false identification further, two masses in each fragment cluster are detected (see table SIM-program for pesticides).

The SIM-program described is sufficient for a semi-quantitative analysis. If a higher accuracy is desired, a  $^{13}\text{C}$ -labelled internal standard must be added to each SIM-group in order to compensate for differences in sensitivity between the different SIM-functions.

Since the mass spectrometer has a large linear range, injection of one calibration standard before a series of samples is sufficient.

#### Calibration

The response factor,  $Rf_i$ , for each compound,  $i$ , relative to the internal standard (*ISTD*) is determined from an analysis of a calibration standard with known concentrations:

$$Amount_i = \frac{Amount_{ISTD} \times Area_i}{Rf_i \times Area_{ISTD}}$$

$Rf_i$ :	Response factor of compound $i$
$Amount_{ISTD}$ :	Amount of internal standard injected
$Amount_i$ :	Amount of compound $i$ injected
$Area_i$ :	Peak area of compound $i$
$Area_{ISTD}$ :	Peak area of internal standard

#### Quantification

Using the response factors,  $Rf_i$ , determined during the calibration, a known amount of internal standard and the peak areas detected during the quantitative analysis, the amount of each compound  $i$  is calculated.

$$Amount_i = \frac{Amount_{ISTD} \times Area_i}{Rf_i \times Area_{ISTD}}$$

$Amount_i$ :	Amount of compound $i$ in the sample
$Amount_{ISTD}$ :	Amount of internal standard added to the sample
$Area_i$ :	Area of compound $i$
$Rf_i$ :	Response factor of compound $i$
$Area_{ISTD}$ :	Area of internal standard

Recovery of internal standard (added before sample clean-up) is computed relative to amount of recovery standard (RSTD) added before the quantification. Relative response factors based on the recovery standard ( $RRF_g$ ) is calculated for each ISTD-compound from the quantification standard analysis.

$$RRF_g = \frac{Amt._{RSTD} \cdot Area_{ISTD}}{Amt._{ISTD} \cdot Area_{RSTD}}$$

$$Rec.(%)_{ISTD} = \frac{Amt._{RSTD} \cdot Area_{ISTD} \cdot 100}{RRF_g \cdot Amt._{ISTD} \cdot Area_{RSTD}}$$

- $Amt._{ISTD}$  : Amount internal standard added before extraction  
 $Amt._{RSTD}$  : Amount of recovery standard added before quantification  
 $Area_{ISTD}$  : Peak area of internal standard  
 $Area_{RSTD}$  : Peak area of recovery standard

*SIM-program for PCB-compounds*

SIM-function	Isomer group	<sup>12</sup> C-Mass 1	<sup>12</sup> C-Mass 2	<sup>13</sup> C-Mass 1	<sup>13</sup> C-Mass 2
1	HCB PFK	283,8102 292,9825	285,8072	293,8244	295,8214
2	TCN TrCB TeCB PFK	263,9067 255,9613 289,9224 280,9825	265,9038 257,9584 291,9194	268,0016 301,9226	269,9986 303,9597
3	TeCB PeCB PFK	289,9224 325,8804 342,9792	291,9194 327,8775	337,9207	339,9177
4	PeCB HxCB HpCB PFK	325,8804 359,8415 393,8025 342,9792	327,8775 361,8385 395,7995	337,9207 371,8817	339,9177 373,8788
5	HxCB HpCB PFK	359,8415 393,8025 380,9760	361,8385 395,7995	405,8428	407,8398

*SIM-program for DDT-compounds*

SIM-function	Isomer group	<sup>12</sup> C-Mass 1	<sup>12</sup> C-Mass 2	<sup>13</sup> C-Mass 1	<sup>13</sup> C-Mass 2
1	TCN PFTBA DDE DDD DDT DDT(control)	263,907 218,986 246,000 235,008 235,008 246,000	265,904 247,997 237,005 237,005 247,997	258,041	260,038

All mass fragmentograms and area lists are printed after the analysis. Mass fragmentograms must be evaluated on the following properties:

- Clean undisturbed mass fragmentograms, missing or extra signals?
- Sufficient gas chromatographic separation?
- Correct retention times: deviation of relative retention time relative to OCN retention time shall be less than  $\pm 3$  sec.
- Intensity ratio: the area ratio of mass 1 to mass 2 for each compound is calculated. The deviation shall be less than 20% relative to the theoretical value
- Signal/noise ratio sufficient?  $S/N > 3$

*Calibration- detection conditions for NCI (HP 5989 GC/MS)*

- Gas chromatograph: see 2.4
- GC/MS-interface: 260°C
  
- Ion source:
- CI ion source
- Ion source temperature: 200°C
- Electron energy: 90-150 eV
- CI-gas pressure 0.4-0.6 torr (approximate values)
- CI-gas: Methane

The instrument parameters are optimised using perfluorotributylamine (PFTBA) either with automatic or manual tuning. To reduce the risk of false identification further, two masses (M and M+2) in each fragment cluster are detected (see table for SIM-program).

Since the mass spectrometer has a large linear range, injection of one calibration standard before a series of samples is sufficient. The analysis is performed using the same procedures described for EI GC/MS.

All mass fragmentograms and area lists are printed after the analysis.

*SIM-program for POP (for guidance)*

SIM-function	Isomer group	Mass 1	Mass 2
1	HCH	252.9	254.9
	<sup>13</sup> C-HCH	262.9	264.9
	Chlordene	263.9	265.9
	<sup>13</sup> C- <sup>2</sup> D-HCH	264.9	266.9
	HCB	282.8	284.8
	<sup>13</sup> C-HCB	295.8	297.8
	Trifluralin	335.1	336.1
	Heptachlor	299.8	301.8
2	TCN	263.9	265.9
	Aldrin	329.9	331.9
	Oksychlordane	349.8	351.8
	Heptachlorepoxyde	387.8	389.8
	Trans-Chlordane	407.8	409.8
3	o,p-DDE	245.9	247.9
	PCB 101, PCB-118	325.9	327.9
	<sup>13</sup> C-PCB-118	337.9	339.9
	Dieldrin, Endrin	379.9	381.9
	α-Endosulfane	405.8	407.8
	cis-Chlordane	407.8	409.8
	trans-Nonachlor	441.8	443.8
4	o,p-DDD	245.9	247.9
	p,p-DDE	315.9	317.9
	PCB 105	325.9	327.9
	PCB-153	359.8	361.8
	<sup>13</sup> C-PCB 153	371.8	373.8
	cis-Nonachlor	441.8	443.8
5	p,p-DDT	280.9	282.9
	PCB 138	359.8	361.8
	PCB 156	359.8	361.8
6	PCB 156	359.8	361.8
	PCB 180	393.8	395.8
	OCN	401.7	403.7
	<sup>13</sup> C-PCB 180	405.8	407.8

**4.19.10 Calibration of instruments**

The GC/MS-instrument should be calibrated every day. The sensitivity of the mass spectrometer can, for instance, be controlled daily by determining the signal-to-noise ratio for a given amount of a chosen component (one such component could be PCB-101).

**4.19.10.1 Control of concentrations of standards**

Every new working standard should be compared to the existing standard before it is taken into use. Deviations within the reproducibility of the procedure are acceptable. At least once a year, the working standards should be controlled against a reference standard from an intercomparison or which has been certified from an international reference laboratory.

The accuracy should be within the uncertainty of the procedure ( $\pm 20\%$ ). Measures to assure constant standard concentration is described in chapter [4.19.8.2](#) under "Quality assurance of standards".

#### **4.19.10.2 Frequency of GC injections of quantification standard**

The quantification standard should be injected at the beginning of the GC-run of every series of samples. A maximum of 10 samples should be analysed before a new injection of the quantification standard is carried out. If the sample series consists of less than 10 samples, the quantification standard should be injected after the last sample. A control standard should also be injected with every sample series.

#### **4.19.10.3 Analysis of control samples**

At the moment there is no certified reference material available that can be utilised for determination of organic compounds in air samples. It is therefore necessary for the laboratory to establish a control sample. This sample should be large enough to correspond to about 40 real air samples. The sample is extracted in the usual way. The extract is homogenised and split into 40 separate samples that are stored in suitable flasks at  $-20^{\circ}\text{C}$ . Each year, at least 4 of these control samples should be analysed. The results for at least one component from each component group (for instance  $\gamma$ -HCH, tr-CD and PCB-153) should be plotted on a quality control chart (QCC, Vogelsang, 1991). This quality control chart gives a good overview of the long time stability of the measurement results.

#### **4.19.11 Recovery test**

An internal standard (ISTD) should be added at the beginning of the procedure and a recovery standard (e.g. octachloronaphtalene) should be added just before the quantification step. In addition to this, recovery tests with spiked (including  $\text{C}^{12}$ -components) samples or solvents should be carried out for every 100 sample of a certain type. In this work, analysis of control samples and blank samples are also important parts. The recovery of the internal standard should be between 40% and 120%, while the spiked  $\text{C}^{12}$ -components should have a recovery that corresponds to the uncertainty of the procedure (for instance  $\pm 20\%$ ) relative to the theoretically added amount of each component. For volatile components, for instance HCB or HCH, which are prone to losses during the volume reducing steps, the lower recovery limit for the corresponding  $\text{C}^{13}$ -spiked components are 20%.

#### **4.19.12 Quality assurance**

##### **4.19.12.1 General principles**

The aim of quality assurance (QA) is to ascertain that the established results have the necessary accuracy and traceability.

The methods used for determination of organic compounds in environmental samples at very low concentrations may include a number of possibilities for errors:

- Loss and contamination during or after sampling or during sample preparation

- Reactions or breakdown after sampling
- Interferences
- Errors in detection or quantification due to a large and partially unknown number of organic compounds in various sample matrixes
- Errors in instrumentation or operator errors

To eliminate as many as possible of these error sources, the following demands should be fulfilled:

1. The laboratory personnel must have adequate competence and everyone involved must be familiar with the detailed routines
2. Equipment, chemicals and other materials should be well suited for their purpose. The quality should be regularly controlled and documented
3. The operating procedures should fit the purpose, be validated and adequately documented
4. Every working step and routine should be described
5. The results should be completely traceable

#### ***4.19.12.2 Administrative routines***

##### **Operating procedures**

The operating procedures are the fundament for every quality assurance measure taken. The procedures assure continuity and dependability in every working step carried out in the laboratory. They are also an important part of the education and training of new operators and of the continuous training of all personnel involved. The operating procedures should include descriptions and specifications of the following:

- Every working step and routine and all equipment, chemicals and instruments used from sampling to reporting
- Validation methods used (how to specify the "trueness" of the results)
- Calibration of instruments
- Handling of reference materials and working standards
- Administrative routines that should be followed. Examples are sample journal, sample handling form, reporting and storage

#### ***4.19.12.3 Sample journal***

As soon as the laboratory receives a sample, the sample should be registered in the sample journal or sample logbook. The journal should include information about sample type, sampling site, sampling date, sample amount, and, if necessary, place of storage. Every sample should be given a unique sample number, for instance year/serial number (99/102).

#### ***4.19.12.4 Sample handling form***

When the sample is registered in the sample journal a sample handling form for the sample should be established. In addition to information about sample type, sample number and so on, details of the important steps in the sample handling should be written on the form, especially deviations from the procedures.

Amounts of added standards and name and location of electronic data files should also be specified. All notes in the form should be signed (initials) and dated.

#### **4.19.12.5 Instrument logbook**

Every analysis instrument should have an instrument logbook. In this journal every sample run should be registered together with method used, temperature program or other vital instrument parameters. Instrument deviations, for instance poor separation or “tailing”, should be registered. In addition, instrument sensitivity and simple maintenance of the instrument, e.g. change of septum or cleaning of the glass liner, should be registered.

#### **4.19.12.6 Standard journal**

Every standard should be given a unique identification. The standards should be registered in the standard journal. Concentration, solvent, date of preparation and weight of the container should be specified. A container should be weighed at room temperature before and after removal of an amount of standard. Weight and date should be registered in the journal. It is not necessary to weigh a working standard in a glass container with capillary outlet.

#### **4.19.12.7 Acceptance of results**

The following criteria should be fulfilled in order to achieve a necessary degree of certainty in the identification and quantification of organic compounds:

- Blank values should correspond to the limit of detection or alternatively be less than 1/10 of the lowest concentration expected (for samples from background areas, for instance the Arctic, the blank values should be less than 1/5 of the lowest expected concentration). Alternatively, if the series contains more than 5 blank samples, the limit of quantification can be defined as the average of the blank values plus 3 standard deviations.
- Calibration: Special adjustments in multilevel calibrations should be controlled.
- Identification and quantification:
  - Are the mass fragmentograms pure and undisturbed or are there extra or missing signals?
  - Is the gas chromatographic separation adequate?
  - Retention times: Deviations in the relative retention times in relation to the isotopic marked quantification standards should be between +3 and 0 seconds. The deviation relative to non-isotopic marked quantification standards should be between +2 and -2 seconds.
  - The signal-to-noise ratio should be larger than 3:1.
  - The ratio between two measured isotope signals should be inside  $\pm 20\%$  of the theoretical value (alternatively the standard value).

#### **4.19.12.8 Reporting of results**

The report should include:

- Sample identification, sample type and amount

- Operating procedure and detection and quantification method
- Results with limit of detection
- Measurement uncertainty

#### **4.19.12.9 Storage**

The following should be stored:

- Sample handling form, sample journal, instrument journal, standard journal and reports should be stored for at least 5 years
- Data files should be saved on an adequate medium for 5 years

It is not necessary to store paper copies of chromatograms or fragmentograms

#### **4.19.12.10 Validation of the method**

There are always a number of possible errors that may affect the quality of the results. It is not possible to eliminate all these errors because samples are different due to a number of factors and because every step in the procedure has inherent possibilities for errors. Validation of a method must therefore be a continuous process.

The following is a list of some of the more important possible errors with measures or control routines:

1. Loss after sampling: Every sample should be wrapped adequately, for instance in aluminium foil and plastic bags with zip locks, and transported to the laboratory as soon as possible. If samples must be stored, they should be kept in the dark. Air samples should be stored at -20°C.
2. Loss during sample preparation and clean-up
3. Contamination during sampling, storing or sample preparation and clean-up: See chapter 4.19.10. "Testing of blank values".
4. A large number of partially unidentified organic compounds (sample matrix) are complicating the determination of organic compounds in air samples. It is not always possible to remove these organic compounds (or sample matrix) completely and in some cases this may give rise to interferences or faulty identifications (see chapter 5.3.2).

#### **4.19.12.11 Testing of blank values**

An important part of the quality control of the results is the comparison of the measured sample concentration with the blank values of the method (calculated on the basis of the sample amount). Before the preparation and clean-up of every new series of samples or new sample type is started, a blank sample should be run through the procedure. The result for this sample will represent the blank value of the method.

In the case of larger series of the same type of samples, it will be enough to run a blank sample (filter and PUFs) for every 30 real sample unless there are other considerations that make it necessary with more frequent blank samples. One such

consideration is the analysis of a sample with unexpected high concentration (more than 100 times above the normal level). A blank field sample (representing the blank value of the whole process including sampling, transport and preparation and clean-up) should be run 2 to 3 times a year for each sampling site.

*Criteria for acceptance of blank values*

The results of a blank sample is accepted if the blank values for every component to be quantified is lower than the limit of detection (signal-to-noise ratio larger than 3:1) or at lower than 1/10 of the lowest expected concentration level. For a larger blank sample series (more than 5 blank samples) the limit of quantification may be utilised. This level of quantification is defined as the average of the blank value (for a component) plus 3 standard deviations.

**4.19.12.12                    *Participation in laboratory intercomparisons***

Intercomparisons are an important tool for validating the operating procedure. The laboratory should try to achieve participation in at least one intercomparison a year for each sample type (air, precipitation, sediment and biological samples).

**4.19.13    *Reference***

Vogelsang, J. (1991) The quality control chart principle: Application to the routine analysis of pesticide residues in air. *Fresenius J. Anal. Chem.*, 340, 384-388.

## 4.20 Determination of polycyclic aromatic hydrocarbons (PAHs) in air

### 4.20.1 Introduction

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).

### 4.20.2 Equipment and instruments

#### 4.20.2.1 Gas chromatography/mass spectrometry (GC/MS)

Autosampler	: Hewlett-Packard 7673 or similar
Detector	: Hewlett-Packard 5970 Mass Selective Detector (MSD), 5973 MSD or similar
Gas chromatography	: Hewlett-Packard 5890 or similar with splitless injector
GC-column	: Capillary column, 25-30 m x 0.25 cm, CP-Sil 8CB, SE 52 or similar, 0.1 µm film thickness.
Integrator system	: Hewlett-Packard Pascal 3.2 ChemStation or similar

#### 4.20.2.2 Liquid chromatograph

Injector	: Rheodyne 7125 with 2 ml sample loop
Column	: Lichrosorb Si-60-5, 5 µm, 4.6 mm x 25 cm
Pump	: LDC Constametric model III
Syringe	: 1000 µl, Hamilton no. 1001
UV-detector	: LDC UVIII monitor model 1203
Valve for switching solvent	: Hamilton no. 86414

#### 4.20.2.3 Soxhlet equipment

Extractors	: 60 ml, male glass joint 24/29 and female glass joint 34/35 500 ml, male glass joint 24/29 and female glass joint 60/48 2000 ml, male glass joint 34/35 with flat lid, size 34/35
Extraction timbles	: 28 x 80 mm, cellulose, Schleicher & Schuell 53 x 145 mm, cellulose, Schleicher & Schuell 60 x 180 mm, cellulose, Schleicher & Schuell
Coolers	: double surface, 345 mm long with male glass joint 34/35 cooler, 260 mm long with male glass joint 34/35 cooler, 330 mm long with male glass joint 24/29
Connector	: female glass joint 34/35 to male glass joint 60/48

**4.20.2.4 Glass equipment**

Desiccator	:	internal diam. 30 cm, lid with vacuum connection
Micro pipettes	:	10, 20, 25, 50, 100 $\mu$ l, < +0.25%, Brand or similar
Graduated cylinders	:	100, 200 and 500 ml
Pasteur pipettes	:	150 and 230 mm long
Sample vials	:	1.5 ml (Brown cat.no. 150900) with screw cap, Teflon lined (Brown cat.no. 150930)
Round bottomed flasks	:	250, 500 and 1000 ml, ground glass joint 24/29 3000 ml, ground glass joint 34/35
Centrifuge tube	:	15 ml, conical with ground glass plug 14/15, graded to 10 ml

**4.20.2.5 Other equipment**

Analytical balance, 0-160 g, precision  $\pm$  0.02 mg  
 Gloves, thin polyethylene, KEBO  
 Gloves, solvent resistant of PE/EVOH/PE  
 Membrane vacuum pumps with Teflon membrane (solvent resistant), 2.4 m<sup>3</sup>/h  
 Metal cartridges (metal cylinders), for active carbon/ molecular sieve filter  
 Micro balance, capacity 3000 mg, precision + 1  $\mu$ g  
 Millipore, MilliQ plus, water purifier  
 Pressure valve GA 2 (L'Air Liquide) with needle valve ALG 2B (L'Air Liquide)  
 Porcelain dish  
 TurboVap 500 pre-concentrator, Zymark  
 Tissue paper Kimwipes, Kimberly-Clark  
 Ultrasonic bath  
 Heater mantles for round bottomed flasks for 500, 1000 and 3000 ml flasks  
 Oven, 50–500°C

**4.20.3 Chemicals and gases**

Helium, 4.6	99.996%,	Hydro
Nitrogen Hydro Ultra, 5.0	99.999%,	Hydro

Active carbon, 1.5 mm diam., Merck no. 2514  
 Chrompack Gas Clean moisture filter, no. 7971  
 Chrompack Gas Clean oxygen/charcoal filter, no. 7972  
 Molecular sieve, 0.5-2 mm diam., Merck no. 5707

Acetone, Merck no. 12  
 Acetonitrile, Rathburn no. RH1016  
 Diethylether, Rathburn no. RG2013  
 2,2-Dimethoxypropane, Merck no. 802936  
 Dimethylformamide, Rathburn no. RG2014  
 Acetic acid, Merck no. 62  
 Hexane, Merck no. 4371  
 Chloroform, Merck no. 2445  
 Methanol, Merck no. 6011

Sodium sulphate, Merck no. 6649

PAH-standards, see 6.1

RBS 25, lab detergent

Cyclohexane, Merck no. 2817

Toluene, Merck no. 8389

#### ***4.20.4 Cleaning of equipment and chemicals***

##### ***4.20.4.1 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.

##### ***4.20.4.2 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.

##### ***4.20.4.3 Extraction thimbles***

Extract thimbles 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 m<sup>3</sup>/h, and 80 kPa (0.8 bar) at 100°C. Connect pump outlet to a cooler to condense solvent. Wrap dry thimbles in Al-foil.

##### ***4.20.4.4 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***.

##### ***4.20.4.5 Sodium sulphate***

Heat ca. 100 g sodium sulphate in a porcelain dish at 600°C for ca. 20 hours. Store in a 250 ml Pyrex bottle with tight screw cap. Label the bottle with date for cleaning. Max. storage time is 1 month.

##### ***4.20.4.6 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

#### **4.20.4.7 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.

#### **4.20.4.8 XAD-2**

Fill XAD-2 in a thimble 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.

#### **4.20.5 Gas cleaning**

##### **4.20.5.1 Gas bottle exchange**

1. Gas bottles must be replaced when the pressure approach 20 bar. The bottle pressure should never be lower than 15 bar.
  2. Before exchanging GC-carrier gas bottles, set GC-oven temperature below 50°C.
  3. Bottle exchange should be performed rapidly. Collect the new bottle before disconnecting the old one.
  4. If only one spare bottle is in the storage room, order a new batch.
  5. Flush the bottle valve on the new bottle twice (ear protection) before connecting the pressure reduction valve.
  6. Connect pressure reduction valve firmly and open it.
  7. Check for leaks with leak detector (Ion Sciences: Gas Check B4 or Supelco: Snoop leak detector).
  8. Mount valve protection cap on the empty bottle and transport the bottle to the storage room.
- All bottles must be secured against falling over.

##### **4.20.5.2 Special procedures**

Helium GC carrier gas cleaning:

1. Chrompack Gas Clean Oxygen Filter (with charcoal) and Chrompack Gas Clean Moisture Filter are connected in series after the pressure reduction valve. Exchange the units after exchanging 5 bottles or once a year.
2. Two metal cartridges are mounted in series on the gas line before each GC inlet. The first is filled with active carbon, the second is filled with molecular sieves. Exchange adsorbents each 3 years and after irregularities (empty gas bottle).

Nitrogen used for final sample blow-down/pre-concentration is cleaned using a metal cartridge filled with active carbon. Exchange adsorbent when exchanging the gas bottle.

#### **4.20.6 Treatment of adsorbents**

Chrompack filters are discarded after use.

Re-activation of molecular sieves: Fill molecular sieves in a metal cartridge and activate at 300°C (3 h) in an oven, flushing the cartridge with 20 ml/min. pre-filtered helium.

Active carbon is discarded after use.

#### **4.20.7 Analysis**

Sampling, extraction, pre-concentration and weighing is described in chapters [3.14.4](#) - [3.14.7](#).

##### **4.20.7.1 Adding internal standards**

Depending of sample type the internal standard is added in an amount similar to the expected concentration level of the sample.

##### **4.20.7.2 Clean-up**

The extract is cleaned using liquid/liquid distribution between cyclohexane and dimethylformamide (DMF). Mix DMF and water in the ratio 9:1 (DMF:water), e.g. 180 ml DMF and 20 ml de-ionised water (MilliQ-plus).

1. The extract (4 ml) from 5.2 is transferred to a 15 ml centrifuge tube (graded to 10 ml).  $3.2 \pm 0.1$  ml DMF/water (9:1) is added with a pipette. Plug the tube and shake.
2. Centrifuge for 5 min. at ca 2500 rpm. Transfer the cyclohexane phase, using a Pasteur pipette, to a new tube and add  $1.2 \pm 0.1$  ml DMF/water (9:1). Shake well, centrifuge and add the DMF/water phase to the DMF/water from point 1. If no emulsion is formed after shaking the centrifuge step may be omitted. Discard the cyclohexane.
3. Add  $5.2 \pm 0.2$  ml (10 ml pipette) water and  $3.2 \pm 0.1$  ml cyclohexane to the DMF/water phase (totally 12.8 ml in the centrifuge tube). Shake well, centrifuge and remove (but keep) the cyclohexane phase. The DMF/water phase is extracted again with  $1.0 \pm 0.1$  ml cyclohexane and the two cyclohexane phases are combined. Discard the DMF/water.
4. Add 2 ml water to "wash" the cyclohexane phase. Transfer the cyclohexane extract to a new glass and dry by adding 1/2 teaspoon of water free sodium sulphate. The extract is transferred to a new tube and pre-concentrated to 0.5 ml.

Often samples may be ready for GC/MS at this stage. Dirty samples may require an additional HPLC-clean-up step.

#### 4.20.7.3 *Sample clean-up using HPLC*

Cleaned cyclohexane extracts, except low level samples from background areas, are cleaned using a silica-column (Lichrosorb SI-60-7, 250 x 4.6 mm). More polar compounds than unsubstituted PAHs will adsorb to the column, whereas the PAH-fraction elutes rapidly to be collected. The UV-detector is operated at 254 nm. The column is flushed with chloroform after each sample.

Between the pump and the eluent reservoirs a solvent switch makes it easy to change from one eluent to another. Cyclohexane, which is saturated with water, and chloroform are used as eluents. Water saturated cyclohexane is made by adding a few millilitres of water (MilliQ plus) to a bottle of cyclohexane. Sonicate the bottle for 30 min. Leave to separate overnight and decant the cyclohexane phase into another bottle the next day.

##### *Start up:*

1. Turn on the detector. Set sensitivity to 2.048 absorbance units.
2. Start the pump and set the flow to 1 ml/min. Check that there is no air in the tubes.

If there is, disconnect column, vent the air from the system and connect the column again.

3. Flush the column with cyclohexane for a few minutes. Turn on the recorder and check that the baseline is stable. The recorder settings are 10 mV and 30 cm/h.
4. Inject ca 1 ml (1000 µl syringe) of a naphthalene and coronene standard mix and mark the injection point on the recorder paper. Elute the compounds. Measure the distance from the injection point to the naphthalene peak start and from the injection point to the coronene peak end.

Use 90% of the distance to the naphthalene start and 125% of the distance to the coronene end, as measure for collecting the PAH fraction.

##### *Sample clean-up:*

1. Start the pump (1 ml/min) and the recorder and inject the sample with a clean syringe. Mark the injection point on the recorder paper.
- Collect the PAH-fraction in a 15 ml centrifuge tube after the measures described in the previous section.
3. Switch to the chloroform eluent reservoir and increase the flow to 2 ml/min.
4. After flushing most of the adsorbed compounds from the column (about 5 min), switch back to cyclohexane. When the baseline reaches the same level as before, the system is ready for the next injection.

5. After cleaning 10 samples, perform a new standard injection as described in 5.3.1.1.
6. Pre-concentrate the collected fraction, first using TurboVap and finally using a gentle nitrogen gas flow. Avoid evaporation of the sample to dryness.

#### **4.20.7.4 Cleaning of the column**

With time the columns separating performance will decrease and a cleaning is necessary. Make mixes of methanol/water 1:1 (50% vol. water) and methanol/water 19:1 (5% water) and hexane/acetic acid/dimethoxypropane 44:5:1 (88% vol. hexane, 10% vol. acetic acid, 2% vol. dimethoxypropane). Use the following solvents at a flow of 2 ml/min.:

1. Chloroform for ca 5 min.
2. Methanol for ca 5 min.
3. 1:1 Methanol/water for ca 30 min.
4. Methanol for ca 5 min.
5. Chloroform for ca 5 min.
6. Hexane/acetic acid/dimethoxypropane 44:5:1 for ca 20 min.
7. Chloroform for ca 5 min.
8. Methanol with 5% water for ca 5 min.
9. Chloroform for ca 5 min.
10. Cyclohexane saturated with water until the baseline is stable

#### **4.20.8 Calibration and quantification**

##### **4.20.8.1 PAH-standards**

The standards should have the highest possible purity and, if available, be certified.

Certified standards from Community Bureau of Reference (BCR):

	Purity (%)
Fluoranthene	99.49
Pyrene	99.75
Benzo[ghi]fluoranthene	99.4
Benz[a]anthracene	99.78
Chrysene	99.20
Triphenylene	99.77
Benzo[a]fluoranthene	99.5
Benzo[b]fluoranthene	99.5
Benzo[j]fluoranthene	99.5
Benzo[e]pyrene	99.0
Benzo[a]pyrene	99.3
Indeno[1,2,3-cd]pyrene	99.8
Dibenz[a,c]anthracene	99.5
Dibenz[a,h]anthracene	99.8
Benzo[ghi]perylene	99.0

Coronene	99.83
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Standards from Tokyo Kasei Kogyo, Ltd., Japan:

	Purity (%)
Biphenyl	>99
Acenaphthene	>99
Phenanthrene	Zone Refined, 30 passes
Anthracene	Zone Refined, 70 passes
Fluorene	Zone Refined, 70 passes

Standard from Dr. Ehrensdorfer GmbH, Germany:

	Purity (%)
Dibenzothiophene	99.7

Standards from Promochem GmbH, Wesel, Germany:

	Purity (%)
Naphtalene	99.8
1-Methylnaphtalene	97
2-Methylnaphtalene	98
Acenaphthylene	99.8
3-Methylphenanthrene	99.8
2-Methylphenanthrene	99
2-Methylanthracene	>99
9-Methylphenanthrene	99.9
Benzo[b]fluorene	99.5
Cyclopenta[cd]pyrene	99
Anthanthrene	>99
Perylene	99.6
Dibenzo[a,e]pyrene	99.8
Dibenzo[a,i]pyrene	99.9
Dibenzo[a,h]pyrene	99.8

Certified standards from Chem Service, Inc., West Chester, USA:

	Purity (%)
1-Methylphenanthrene	99.5
Dibenzofuran	98
Benzo[a]fluorene	99
Retene	85
Benzo[k]fluoranthene	99.0

Labelled standards from C/D/N Isotopes Inc., Canada:

	Purity (%)
2-Methylnaphtalene-D <sub>10</sub>	99.3
Acenaphthene-D <sub>10</sub>	99.7
Anthracene-D <sub>10</sub>	99.3
Fluoranthene-D <sub>10</sub>	98.8
Pyrene-D <sub>10</sub>	99.9
Benz[a]anthracene-D <sub>10</sub>	99.1
Benzo[e]pyrene-D <sub>12</sub>	99.6
Benzo[ghi]perylene-D <sub>12</sub>	99,1

#### 4.20.8.2 Main standard

The following compounds may be included in the main standard:

Naphtalene	Benzo[ghi]fluoranthene
2-Methylnaphtalene	Syklopenta[cd]pyrene
1-Methylnaphtalene	Benz[a]anthracene
Biphenyl	Chrysene
Acenaphthylene	Triphenylene
Acenaphthene	Benzo[b]fluoranthene
Dibenzofuran	Benzo[j]fluoranthene
Fluorene	Benzo[k]fluoranthene
Dibenzothiophene	Benzo[a]fluoranthene
Phenanthrene	Benzo[e]pyrene
Anthracene	Benzo[a]pyrene
3-Methylphenanthrene	Perylene
2-Methylphenanthrene	Indeno[1,2,3-cd]pyrene
2-Methylanthracene	Dibenz[a,c]anthracene
9-Methylphenanthrene	Dibenz[a,h]anthracene
1-Methylphenanthrene	Benzo[ghi]perylene
Fluoranthene	Anthranthene
Pyrene	Coronene
Benzo[a]fluoren	Dibenzo[ae]pyrene
Retene	Dibenzo[ai]pyrene
Benzo[b]fluoren	Dibenzo[ah]pyrene

#### ***Perform the weighing using the micro balance. Use gloves and a dust mask.***

Spatulas and other equipment should be rinsed with toluene before use. When all compounds are weighed, transfer them to a 25 ml volumetric flask using a Pasteur pipette and toluene. Fill the flask to the mark and sonicate until all PAH is dissolved. Compute the exact concentration for each compound (ng/μl). The individual concentration should be in the range 15±10 ng/μl. This corresponds to 300±100 μg of each single compound. Transfer mix to well labelled vial with Teflon lined screw cap. Weigh the vial and store it in a freezer.

#### 4.20.8.3 Internal standards

The internal standard includes the following compounds: 2-methylnaphtalene-D<sub>10</sub> (ISTD I), acenaphthene-D<sub>10</sub> (ISTD II), anthracene-D<sub>10</sub> (ISTD III), pyrene-D<sub>10</sub>

(ISTD IV), benz[a]anthracene-D<sub>12</sub> (ISTD V), benzo[e]pyrene-D<sub>12</sub> (ISTD VI), benzo[ghi]perylene-D<sub>12</sub> (ISTD VII).

Ca. 1 mg of ISTD I, II, III, IV and ca 0.5 mg of ISTD V, VI, VII are weighed as described under 6.1.1 and transferred to a 25 ml volumetric flask filled to the mark with cyclohexane. The concentration range is ca 20-40 ng/μl. Transfer mix to a well-labelled vial with Teflon lined screw cap. Weigh the vial and store it in a freezer.

Transfer ca. 1 ml to a sample vial. Label the vial and use as working standard. Weighing is not necessary. Store in a refrigerator.

#### **4.20.8.4 Recovery standard**

As recovery standard fluoranthene-D<sub>10</sub> may be used. Weigh in ca 1 mg, transfer to a 25 ml volumetric flask and fill to the mark with cyclohexane as described in 6.1.1. Transfer mix to well labelled vial with Teflon lined screw cap. Weigh the vial and store it in a freezer.

Transfer ca 1 ml to a sample vial. Mark the vial and use as working standard. Weighing is not necessary. Store in a refrigerator.

#### **4.20.8.5 Quantification standard**

Remove the flasks with main standard, internal standard and recovery standard from the freezer and leave to melt at room temperature. Use aluminium foil to protect the flasks against sunlight. Remove the foil and sonicate flasks for 5 minutes. Check that all PAH is dissolved. If crystals are visible, repeat sonication. Check the flasks for weight loss and compensate an eventual loss with solvent. 2 ml main standard is transferred to a 50 ml volumetric flask using a 2 ml pipette. To the same flask further 1 ml internal standard and 2 ml recovery standard are transferred. Fill the flask to the mark with cyclohexane. Transfer mix a well labelled vial with Teflon lined screw cap. Weigh the vial and store it in a freezer.

Transfer ca. 1 ml to a sample vial. Label the vial and use as working standard. Weighing is not necessary. Store in a refrigerator.

#### **4.20.8.6 Control standard**

This standard is used to check the GC/MS quantification performance (chapter 6.2.4). The standard may contain the following compounds:

- Biphenyl
- Phenanthrene
- Fluoranthene
- Benzo[a]anthracene
- Benzo[e]pyrene
- Benzo[ghi]perylene

First a mother standard is made as described under **6.1.1**.  $300 \pm 100$   $\mu\text{g}$  of each compound is weighed and dissolved in cyclohexane in a 10 ml volumetric flask. Label the flask, weigh and store in a freezer.

Working solution is made as described under **6.1.2**. 1 ml. The mother standard is diluted to 50 ml with cyclohexane in a 50 ml volumetric flask. Store the flask in a freezer.

Transfer ca. 1 ml to a 2 ml sample vial. Label the vial and use as working standard. Weighing is not necessary. Store in a refrigerator.

#### **4.20.8.7 Retention standard, HPLC**

This standard is used to check retention times before HPLC clean-up.

Ca. 5 mg naphthalene and ca. 10 mg coronene is dissolved in 100 ml cyclohexane. The concentrations are ca. 50  $\mu\text{g}$  naphthalene and ca. 100  $\mu\text{g}$  coronene pr. ml. Store in a refrigerator.

#### **4.20.9 Separation and quantification**

The cleaned sample extracts are analysed using gas chromatography combined with mass spectrometry (GC/MS). The compounds are identified according to their retention time and molecular weight and quantified using internal standards.

##### **4.20.9.1 GC separation**

GC conditions:

- Column : CP-Sil 8CB, 25 m x 0.25 mm x 0.12  $\mu\text{m}$  film thickness or similar.
- Injector temperature : 300°C
- Temperature program: 50-100°C with 20°C/min., 100-300°C with 10°C/min., 300°C for 5-10 min.
- Carrier, helium : 85 kPa
- Split gasflow : 40  $\pm$  10 ml/min.
- Sample volume : 1  $\mu\text{l}$  splitless, (Autosampler or "hot-needle" injection)

Autosampler conditions:

- Solvent A : toluene
- Solvent B : cyclohexane
- Sample wash : 0
- Sample pumps : 6
- Sample volume : 1  $\mu\text{l}$
- Solvent A, washes : 6
- Solvent B, washes : 6

Solvent A and B for syringe cleaning must be exchanged each day.

##### **4.20.9.2 Mass spectrometry (MS)**

Electron impact ionisation (EI) is used. Inject the quantification standard before each sample series and after each 10 samples.

*MS conditions for EI (MSD 5970 and MSD 5973):*

- GC/MS-interface : 290°C
- Electron energy : 70 eV
- Calibration compound : Perfluorotributylamine (PFTBA)

Automatic tuning (“Autotune”), or manual optimisation of mass scale and transmission of the mass filter (quadrupole) with PFTBA using mass fragments  $m/z$  69.0, 219.0 and 502.0. Mass resolution, signal width at half height:  $0.55 \pm 0.03$ . Calibration of mass scale at  $\pm 0.05$  amu.

The following SIM-program may be used for quantification:

SIM-function	Compound group	Mass	
1	Naphtalene	128.1	
	2-Methylnaphtalene	142.1	
	1-Methylnaphtalene	142.1	
	d <sub>10</sub> z-Methylnaphtalene	152.1	
	Biphenyl	154.1	
2	Acenaphthylene	152.1	
	Acenaphthene	154.1	
	d <sub>10</sub> Acenaphthene	164.1	
	Dibenzofuran	168.1	
	Fluorene	166.1	
3	Dibenzothiophene	184.1	
	Phenanthrene	178.1	
	Anthracene	178.1	
	d <sub>10</sub> Anthracene	188.1	
	3-Metylphenanthrene	192.1	
	2-Methylphenanthrene	192.1	
	2-Methylantracene	192.1	
	9-Methylphenanthrene	192.1	
1-Methylphenanthrene	192.1		
4	Fluoranthene	202.1	
	d <sub>10</sub> Fluoranthene	212.1	
	Pyrene	202.1	
	d <sub>10</sub> Pyrene	212.1	
	Benzo[a]fluorene	216.1	
	Retene	234.1	
	Benzo[b]fluorene	216.1	
	Benzo[ghi]fluoranthene	226.1	
Cyclopenta[cd]pyrene	226.1		
5	Benz[a]anthracene	228.1	
	d <sub>12</sub> Benz[a]anthracene	240.1	
	Chrysene/triphenylene	228.1	
	6	Benzo[b/j/k]fluoranthenes	252.1
		Benzo[a]fluoranthene	252.1
Benzo[e]pyrene		252.1	
d <sub>10</sub> Benzo[e]pyrene		264.1	
Benzo[a]pyrene		252.1	

SIM-function	Compound group	Mass
7	Perylene	252.1
	Inden[1,2,3-cd]pyrene	276.1
	Dibenz[a,c/a,h]anthracenes	278.1
	Benzo[ghi]perylene	276.1
	d <sub>10</sub> Benzo[ghi]perylene	288.1
	Anthanthrene	276.1
	Coronene	300.1
	Dibenzo[a,e]pyrene	302.1
	Dibenzo[a,i]pyrene	302.1
	Dibenzo[a,h]pyrene	302.1

If compounds occur at concentrations which saturate the detector these compounds may be quantified using the signal from the <sup>13</sup>C-isotope in the compound, detected at a mass one amu higher than the number indicated in the table.

#### 4.20.9.3 Quantification

1. Relative response factors,  $RRF_i$ , are computed for the single compounds relative to the internal standard (ISTD) after analysing the quantification standard with known concentrations.

$$RRF_i = \frac{Amt_{ISTD} \cdot Area_i}{Amt_i \cdot Area_{ISTD}}$$

- $RRF_i$  : Relative response factor of compound  $i$   
 $Amt_{ISTD}$  : Amount of internal standard injected  
 $Amt_i$  : Amount of compound  $i$  injected  
 $Area_i$  : Peak area of compound  $i$   
 $Area_{ISTD}$  : Peak area of internal standard

2. Quantification of samples is based on relative response factor, added amount internal standard and the peak area of each compound  $i$ .

$$Amt_{i,j} = \frac{Amt_{ISTD} \cdot Area_i}{RRF_i \cdot Area_{ISTD}}$$

- $Amt_{i,j}$  : Amount of compound  $i$  in the sample  
 $Amt_{ISTD}$  : Amount of internal standard added  
 $Area_i$  : Peak area of compound  $i$   
 $RRF_i$  : Relative response factor for compound  $i$   
 $Area_{ISTD}$  : Peak area of internal standard

Check the chromatogram for eventual interference and correct retention times before quantification.

3. Recovery of internal standard (added before sample clean-up) is computed relative to amount of recovery standard added before the quantification.

Relative response factors based on the recovery standard ( $RRF_g$ ) is calculated for each ISTD-compound from the quantification standard analysis.

$$RRF_g = \frac{Amt_{GSTD} \cdot Area_{ISTD}}{Amt_{ISTD} \cdot Area_{GSTD}}$$

$$Rec.(%)_{ISTD} = \frac{Amt_{GSTD} \cdot Area_{ISTD} \cdot 100}{RRF_g \cdot Amt_{ISTD} \cdot Area_{GSTD}}$$

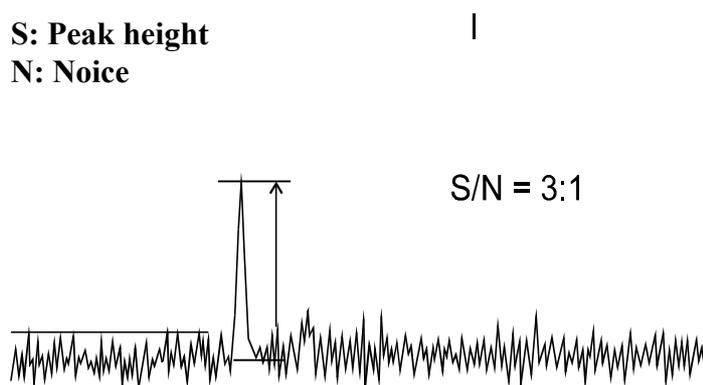
$Amt_{ISTD}$	:	Amount internal standard added before extraction
$Amt_{GSTD}$	:	Amount of recovery standard added before quantification
$Area_{ISTD}$	:	Peak area of internal standard
$Area_{GSTD}$	:	Peak area of recovery standard

#### 4.20.9.4 GC/MS-analysis

1. Before each sample series the quantification standard is injected twice. The first injection is used to deactivate the injector and is not used for quantification.
2. Inject the quantification standard not later than each 10 samples.
3. The last injection should be a quantification standard.

#### 4.20.9.5 Detection limit

The detection limit is defined as 3 times the noise level (compound signal/noise = 3:1) as shown in the following figure.



For outdoor air the detection limit is normally reported in the unit  $\text{pg}/\text{m}^3$ . The detection limit varies according to the concentration level in the sample, the sample volume, the purity of the sample extract, sample loss during clean-up and the pre-concentration factor.

#### **4.20.10 Quality assurance**

##### **4.20.10.1 Reception and storage of samples**

Incoming samples must be registered in a sample journal with date, a sample number and an analysis form which follows the sample during the whole analysis.

A cleaned sample extract ready for GC/MS may be stored up to 6 months in a freezer before analysis.

##### **4.20.10.2 Standard mixtures**

PAHs dissolved in cyclohexane and stored in a freezer (dark) are stable for years. The main standard, quantification standard, internal standard, control standard and recovery standard must be stored in a freezer ( $\leq 18^{\circ}\text{C}$ ). Control of weight and corrections for weight loss must be recorded. Max. storage time is 5 years.

The working solutions are stored in a refrigerator ( $4-6^{\circ}\text{C}$ ) and weight loss control is not necessary. Max. storage time is 6 months.

All new standards must be checked against the old standard and concentration deviations should be within  $\pm 10\%$ .

##### **4.20.10.3 Control standard**

To check the GC/MS quantification a control standard must be analysed. The standard covers the whole volatility range of the PAHs to be quantified.

The standard must be analysed after every 20<sup>th</sup> sample or every 14<sup>th</sup> day when less than 20 samples are analysed. For long periods without any activity (months), the standard must be analysed once a month.

Plots showing the single results for each compound and an average of the last 10 analyses must be available.

##### **4.20.10.4 Recovery of internal standard**

Before GC/MS-analysis a recovery standard is added to the sample in an amount according to the amount of internal standard added.

The recovery of the internal standards should be within the following limits:

ISTD	II	>10 to 100%
ISTD	III, IV	>20 to 100%
ISTD	V, IV, VII:	>30 to 120%

Since the results for bicyclic PAHs is uncertain and the interest for these compounds is low, no limit is given for ISTD I.

If recovery is outside limits a note about this must be given in the analysis report. Low recovery is caused by losses during clean-up and pre-concentration. The result will be less reliable than with normal recovery.

Too high recovery may be caused by interference on the ISTD-signal. In such cases the quantification should be based on another ISTD with normal recovery.

#### **4.20.10.5 Blanks**

Blank tests must be performed on clean filters and PUF plugs using the complete method. 2 unexposed plugs and 1 unexposed filter are extracted and analysed as if it was a normal sample. This must be done after each 20<sup>th</sup> sample.

#### **4.20.10.6 Control of results**

The following criteria must be fulfilled for a satisfactory identification and quantification:

- Clean, undisturbed mass fragmentograms
- Adequate GC separation
- Correct retention times. The retention time should be within  $\pm 3$  sec. relative to the retention time of the compound in the quantification standard
- Signal/noise ratio  $>3:1$
- Blank values should be 10 times lower than the lowest expected level in the samples.



## **4.21 Chemical speciation of particles**

### **4.21.1 Introduction**

The inorganic fraction of the aerosol mass consists mainly of sulphate, ammonium, and nitrate containing particles. Other ions contribute to a less extent to the inorganic fraction. It is recommended to measure all soluble base cations, sodium, potassium, calcium, and magnesium, as well as chloride. Participants applying ion chromatography for analysis of the EMEP filterpack aerosol filter for sulphate, nitrate and ammonium (see chapter 3.2) should be able to obtain the base cations and chloride concentrations on a daily basis.

The recommended measurement program also includes EC/OC measurements. The carbon fraction typically constitutes ~ 30 per cent of the mass and contains elemental carbon (EC) and a huge number of different organic carbon (OC) compounds. It is recommended to determine the amounts of EC and OC in at least one sample every week from each station in the start phase. A (partial) speciation of the organic fraction is also of great interest, but this will mainly be a research activity applying advanced laboratory equipment and rather complicated chemical procedures and not applicable on all EMEP sites

### **4.21.2 Extraction**

For extraction of water-soluble constituents from the PM<sub>10</sub> filters, it is recommended to use a punch to remove an accurately defined part of the exposed area of the sample filter. The diameter should be chosen to allow for a similar sub-sample to be taken for the determination of elemental and organic carbon (see below). A suitable size would be a circular punch, of diameter 3-5 cm. The extraction volume should be at least 10 ml. The filters are put in tubes and deionised water is added, the tubes should be kept in ultrasonic bath for at least 30 minutes to obtain a complete extraction. When quartz or other fibre filters are used, be careful to avoid breaking up the filter by unnecessary stirring, because loose fibres in the solution do not go well with the ion chromatograph! Filtration of the extract may be necessary.

If heavy metals are to be determined by e.g. ICP-MS it is necessary to use acidic extraction agent, see chapter 3.11.5

### **4.21.3 Determination of the inorganic components**

Chemical speciation should primarily include determination of sulphate, nitrate, ammonium and other water-soluble ions in filter samples. The latter will include sea-salt, which contributes significantly to the PM<sub>10</sub> in coastal regions in Western Europe. The concentrations of aerosol sulphate, nitrate and ammonium ions are usually determined in connection with the normal EMEP measurement programme, and the determination of these water-soluble ions by ion chromatography of filter extracts can be used to give data also for sodium, potassium, magnesium, calcium and chloride, particularly if the recommendations for sampling given in the chapter 4.1-4.6 are followed (see also Tørseth et al., 1999).

#### **4.21.4 Determination of heavy metals**

Heavy metals do not usually give a significant contribution to the particulate mass, and it is not important to measure these components just to obtain a mass closure. But aerosols play an important role as a carrier of heavy metals. Sampling methods of heavy metals in particles are found in chapter 3.11 and the analytical methods are found in 4.17. In addition, heavy metals may be determined using PIXE and INAA described under mineral dust, 4.21.7.

#### **4.21.5 EC/OC determination**

The quantification of elementary carbon and organic compounds (EC/OC) in aerosol particles is of considerable interest. The ratio between EC and OC is often used as a valuable tool for the elucidation of the origin of the air masses investigated. Elementary carbon is present in the form of chain aggregates of small soot globules, and is responsible for the light absorption of the material collected on filters. Unfortunately this light absorption depends on the size distribution of the soot particles and on the association of the soot particles with other substances in the aerosol particles and on sample filters. Optical methods to determine EC are therefore only semi-quantitative, and calibration factors may vary from one situation to another, see e.g. (Liousse and Jennings, 1993).

The recommended method to determine elementary carbon is therefore by successive volatilization and oxidation of the sample, and to determine the evolved CO<sub>2</sub>, either directly or after conversion to CH<sub>4</sub> by a flame ionization detector (FID). This procedure also gives the total carbon content, and a quantification of the amount of organic materials through the organic carbon content of the aerosol particles. The method is not free of artefacts, particularly the charring or incomplete removal of organic compounds may lead to the overestimation of EC. To compensate for this, optical detection of a darkening of the filter during the last stage of the OC volatilization is recommended (Chow et al. 1993; Huntzicker et al. 1982). This method is now part of the USEPA programme, and the equipment described by Birch and Cary (Birch and Cary, 1996) is commercially available (Sunset Laboratory Inc., USA). CCC has opportunity to analyse samples collected on quartz fibre filters and the equipment is also available in other laboratories in Europe. A factor of 1.4 is tentatively recommended to convert the measured OC content to total organic particulate mass.

Chemical analyses for further speciation of the organic component in aerosol particle samples are much more demanding, although some advances have been made in determining the water-soluble organic aerosol mass, and specific fractions of this mass. Quantification of selected chemical compounds by gas chromatography and other methods is also possible, but the number of individual compounds is very large, and chemical analyses should therefore be directed to determination of "signature" compounds, which are indicative of certain groups or specific emission sources (e.g. wood combustion).

#### 4.21.6 *Chemical characterization of the OC fraction*

High performance liquid chromatography (HPLC) combined with mass spectrometry (MS) have reached a state where identification of unknown compounds has become possible at quantities about 1 ng. From the accurate mass determined, the elemental composition of an unknown can be calculated. Combination of retention time data obtained during a HPLC run, the corresponding UV spectra, and the isotope pattern in the mass spectrum, makes possible calculations of possible elemental compositions. Commercially available chemistry databases should allow the identification of unknown compounds present in the aerosol samples. Based on the solubility, particulate matter can be defined as water soluble organic carbon fraction (WSOC) and water insoluble organic carbon fraction (WINSOC). According to Zappoli and co-workers (Zappoli et al. 1999), the WINSOC fraction can be further separated into solvent extractable polar organic compounds (SEPOC); solvent extractable non-polar organic compounds (SENOC) and non extractable organic compounds (NEC).

Derivatisation with alkylchloroformates is helpful for trace analytical purposes. Alkylchloroformates have unique properties which allows to derivatise nearly all polar compound classes simultaneously; phenols, organic acids, hydroxylated acids, amines etc. Derivatisation with alkylchloroformates will be used in order to obtain a complementary sample preparation to the approaches below.

For polar organic compounds, the following sample preparation and analytical methods can be used:

- Molecular size distribution of the organic content of particles will be obtained by LC/MS. The work may be supported by high resolution gel permeation chromatography.
- A LC/MS (TOF) method for the identification of polar to very polar organic compounds in particles of high carbonaceous content. The method will be an important tool to characterize sources.
- Comparison of the extract content of different solvent extraction methods in order to optimise yields and efficiency.
- Comparison of the developed method with (or without) conventional derivatisation and GC-MS analysis (high resolution MS) to compare information and for quality assurance.
- The development of a general derivatisation procedure based on alkylformates for polar to very polar organic compounds in particle extracts.

In order to distinguish between the water-soluble OC and water insoluble OC compounds the following techniques can be used:

- 1.) A gentle filter washing with water giving a water-soluble fraction and water insoluble fraction.
- 2.) The water insoluble fraction remaining on the filter is dried and divided into two parts. One part is analysed for cellulose. The other part is extracted with sodium hydroxide (NaOH) in two increasing concentration steps in order to obtain the "humic acids" and the "humin" fractions according to the procedure

in Havers et al. (Havers et al. 1998). The quantification of the humic acids and humic fractions will be performed via micro-combustion analysis. Combustion method is described in Puxbaum et al. (Puxbaum et al. 2000).

- 3.) The water-soluble fraction will be separated into three fractions by two-step solid phase extraction: weakly polar compounds (fatty acids, fatty aldehydes, fatty alcohols, esters), strong polar compounds (dicarboxylic acids and other multifunctional compounds), and macromolecular water soluble compounds ("fulvic acids"). Weakly and strong polar compounds can be determined as described by Limbeck and Puxbaum (Limbeck and Puxbaum, 1999). The macromolecular fraction is determined by the micro-combustion technique as mentioned above.

#### 4.21.7 Analysis of mineral dust

Mineral dust may often contribute significantly to the particle mass and to generate a total mass closure it is important to determine this fraction. Monitoring of air pollution has mainly been focused on anthropogenic sources, mineral dust has therefore traditionally not been measured because of its more natural origin, even though atmospheric dust can be an indirect result of land use and human activities. Mineral dust is a mirror of the earth crust and consists mainly of silicates and oxides of silicon, aluminium and iron. The relative importance of mineral dust in particulate matter depends on location, season and particle size, it is mainly concentrated in the coarse fraction. There can be large local variations depending on the source, e.g. Sahara dust can give a large contribution of the PM<sub>10</sub> concentration in southern Europe.

Mineral dust has in general low solubility and is therefore difficult to analyze using instruments like ICP-MS, ICP-AES, AAS etc. To dissolve e.g. silicon it is usually necessary to use strong solvents as hydrofluoric acid. This solvent is however not very practical for most instruments and needs special precautions. As a consequence XRF, INAA and PIXE are the most commonly used techniques for analyzing mineral dust, Table 4.21.1. These techniques have a major advantage that the sample can be analyzed directly from the filter avoiding uncertainties of whether everything is dissolved when using solvent techniques. An additional advantage using PIXE, INAA or XRF is the multielement analysis thereby the possibility to get information of the concentrations of heavy metals in particulate matter as well.

Table 4.21.1: Analytical methods used for analyzing mineral dust.

Analytical method	Disadvantages	Advantages
Proton induced X-ray emission (PIXE)	Demanding	Sensitive, multielement analysis
Neutron activation analysis (INAA)	Demanding, silicon cannot be analysed, time consuming	Sensitive, multielement analysis
X-ray fluorescence (XRF)	High detection limit for silicon, absorption	Multielement analysis
X-ray diffraction (XRD)	Insensitive	Composition of species
Microscopy	Difficult to quantify the species	Characterization of particles

Proton induced X-ray emission (PIXE) and neutron activation analysis (INAA) are excellent instruments for dust analysis, but they are demanding methods

needing a proton and neutron accelerator respectively, and for most laboratories X-ray-fluorescence (XRF) is easier accessible, XRF is however less sensitive. The theory behind the techniques are found in numerous textbooks (see e.g. a review by Török et al, 1996) and will not be described here, neither will a detailed analytical description, since it is dependent on the instrument, and the user manual from the manufacture should be used to set up a standard operational procedure.

One major problem analysing the content of mineral dust is the low sensitivity for silicon in most analytical techniques. PIXE is the only method that has proven to be suitable for this element. However, it is possible to analyse e.g. aluminium or iron to estimate the amount of crustal mass in the sample using the known composition of the earth's crust (Mason, 1966); although one should bear in mind that the chemical composition of the mineral dust is not necessarily consistent because of influence from sources where some of the crustal elements are enriched (Rahn, 1976 and 1999).

X-ray fluorescence (XRF) analysis can be used for all elements passed the first row in the periodic table and the detection limit is dependent on element ranging from 20 to 200 ng/cm<sup>2</sup> for 44 of 49 elements (Willeke and Baron, 1993). Two different types of instrumentation can be used, wavelength dispersive (WD-XRF) and energy dispersive (ED-XRF). ED-XRF provides simultaneous determination of multiple elements, whereas WD-XRF usually determines one element at a time. The latter technique has somewhat lower detection limits for elements with low atomic number and it has better spectral resolution compared with ED-XRF where interference and line overlap may be a problem (Claes et al, 1998). Absorption of primary and emitted X-rays can be a problem, but if the deposition is thin, X-ray is not absorbed in the matrix and conversion into concentrations is simplified considerably. The filters may also absorb X-rays; membrane filters where the aerosols are collected on the surface are much better compared to filters where the aerosol is collected in the material. Filters of low mass are also preferable to minimize the background scattering. Teflon membrane filters are frequently used. Glass fibre filter should not be used due to higher absorption and since the content of silicon then can't be determined. Nucleopore filters may also be used (Willeke and Baron, 1993; Claes et al., 1998). The particles should preferably be quite small and the deposition should be homogenous. This is even more critical for the PIXE technique where only a very small part of the filter is analyzed. PIXE differ from XRF in excitation source for X-ray fluorescence, using high-energy protons. Nucleopore filters should be used because fluoride in Teflon filter causes problems for PIXE analysis. This technique is described in more detail by e.g. Maenhaut (1987). INAA is similar to PIXE regarding limits of detection and it is also suitable to determine a large number of elements in the samples (Willeke and Baron, 1993). The advantage of INAA is the almost absence of matrix effects, self-absorption and interferences. It can be used to analyze thick and inhomogeneous samples; the disadvantage is of course the need for a nuclear reactor and special expertise.

X-ray diffraction (XRD) can sometimes be used depending on the concentration level. The great advantage of XRD is that it gives the composition of the minerals, which is not possible with the above mentioned element analysis. The most

important use of XRD has been for silica (Lodge, 1989). The problem with this technique is the low sensitivity and for background sites the concentration levels are usually too low. To improve the low peak intensity/background ratio the dust can be deposited on Ag-filters or silicon (5 1 0) plates (Queralt et al., 2001).

Microscopy can also be a powerful tool to identify the different minerals in particles; though, in practice not easy to use for quantification.

#### 4.21.8 References

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