MEDITERRANEAN ACTION PLAN
MED POL

UNITED NATIONS ENVIRONMENT PROGRAMME

WORLD METEOROLOGICAL ORGANIZATION

MED POL MANUAL ON SAMPLING AND ANALYSIS OF AEROSOLS AND PRECIPITATION FOR MAJOR IONS AND TRACE ELEMENTS

MAP Technical Reports Series No. 123

UNEP
Athens, 1998

P.O Box 18019, Athens, Greece

ISBN 92-807-1741-3

For bibliographic purposes this volume may be cited as:
UNEP/WMO: MED POL Manual on Sampling and Analysis of Aerosols and Precipitation for Major Ions and Trace Elements MAP Technical Reports Series No.123, UNEP, Athens, 1998

This volume is the one hundred and twenty-third issue of the Mediterranean Action Plan Technical Report Series.

This series will collect and disseminate selected scientific reports obtained through the implementation of the various MAP components: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas, Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea, Environment Remote Sensing and Protection of Historic Sites.

Foreword

In 1981, recognizing the significance of the airborne pollution of the sea, the Contracting Parties to the Barcelona Convention for the Protection of the Mediterranean Sea against Pollution included monitoring of the transport of pollutants into the sea through the atmosphere and research on pollutant-transfer processes at air/sea interface in the Long-term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL-Phase II) and the World Meteorological Organization (WMO) became the co-ordinating agency for these activities.

The first version of the MED POL Airborne Pollution Monitoring and Modelling Programme was prepared by a WMO/UNEP workshop on this matter held in Belgrade in November 1987. In May 1988 the Scientific and Technical Committee for MED POL agreed that this programme should be initiated in as many countries as possible.

The results of modelling and measurements of atmospheric deposition of pollutants on the Mediterranean Sea obtained during MED POL – Phase II had confirmed that for many pollutants their atmospheric inputs could be as big as the riverine inputs. The conclusion is important not only from the scientific point of view, but also for the development of strategies, policies and legal instruments to protect the marine environment what would be a priority for the Programme for the Assessment and Control of Pollution in the Mediterranean Region (MED POL —Phase III) scheduled for 1996-2005.

The present manual has been prepared for the MED POL Airborne Pollution Monitoring Programme. The sampling and analytical procedures used in this programme were recommended in a series of workshops and expert meetings held during the MED POL-Phase II stage of the programme. Although a variety of aerosol and precipitation sampling and analytical techniques are available, only those methods which were recommended at those meetings are included in the manual.

Techniques similar to the ones used in the MED - POL Airborne Pollution Monitoring Programme are also used in other networks around the world. The procedures described in the manual are partly derived from the experience of the author and partly compiled and adapted from other manuals and reports prepared for application of similar procedures in those networks. The following reports and manuals have been utilized to different degrees in the preparation of this manual:

- Abott (1984). Operating and quality assurance procedures for the Abbot Ambient Monitoring Programme. University of Illinois, Urbana, IL.

- Eaton W. C., Tew E. L. (1985). NADP/NTN site visitation programme work plan.

- EMEP (1977). Co-operative Programme for Monitoring and Evaluation of the Long - range Transmission of Air Pollutants in Europe. Manual for sampling and chemical analysis.

- HELCOM (1992). Intercalibrations and intercomparisons of measurement methods for airborne pollutants. Balt. Sea Environ. Proc. No. 41.

- IAEA (1992). Sampling and analytical methodologies for instrumental neutron activation analysis of airborne particulate matter. IAEA Training Course Series No. 4.

- Iverfeldt A. and Sjöberg K. (1992). Intercomparison of methods for the determination of mercury deposition to convention waters. Report prepared for the Paris Commission, Goteborg, November 1992.

- James K. O. W. (1987) Quality assurance report for the NADP/NTN deposition monitoring.

- Meszaros E. and Whelpdale D. M. (1985). Manual for BAPMoN station operations. WMO Technical Document WMO/TD No 66.

- Rovinsky F. Y. and Wiersma G. B. (1987) Procedures and methods for integrated global background monitoring of environmental pollution. WMO Technical Document WMO/TD No. 178.

- Santroch J. (1993). Chemical analysis of precipitation for GAW: Laboratory analytical methods and sample collection standards. WMO Technical Document WMO/TD No. 550.

- *See R. B. and Schroder J. L. (1989). External quality assurance results for the* National Atmospheric Deposition Programme and the National Trends Network during 1987. USGS Water - Resources Investigations Report 89-4015.

- Sjöberg K. (1992). Report from workshop on the collection and analysis of trace metals in precipitation. Göteborg 28 - 30 September.

- UNEP (1985). Sampling of aerosols and wet precipitation for analysis of chemical pollutants. Reference Methods for Marine Pollution Studies No. 24.

- UNEP (1988). Guidelines for the determination of selected trace metals in aerosols and in wet precipitation. Reference Methods for Marine Pollution Studies No. 42.

- Vermette S. and Larson S. (1985). Air sampling manual - sampling considerations and instrumentation. Prepared for the short course on air sampling and analysis at University of Illinois at Urbana Champaign, Urbana, IL.

- Willoughby T. C. and See R. B. (1989). Stability of nitrate ion concentrations in simulated deposition samples used for quality assurance activities by the U.S. Geological Survey. USGS Water - Resources Investigations Report 89-4042.

- WMO (1988). International operations handbook for measurement of background atmospheric pollution. WMO Technical Document WMO/TD No. 491.

- WMO (1991). Report of the WMO meeting of experts to consider the aerosol component of GAW. WMO Technical Document WMO/TD No. 485.

- WMO (1992). Report of the WMO meeting of experts on the quality of assurance plan for the Global Atmosphere Watch. WMO Technical Document, WMO/TD No. 513.

The main part of this manual (Chapters I-V) was prepared by Dr Gurdal Tuncel, Middle East Technical University, Ankara, Turkey.

The Annex dealing with intercomparison of high-volume air samplers and intercalibration of metal analyses in aerosol filters was prepared by P. Rossini, S. Guerzoni, G. Quarantotto, V. Boccini, G. De Falco, C. Ori and G. Rampazzo, Italy.

The first draft of the manual was prepared in 1994 and presented to the WMO/EMEP Expert Meeting on Airborne Pollution of the Mediterranean Sea held in Paris, France from 31 October to 4 November 1994. The Meeting adopted the draft manual and recommended that it should be amended taking into account the results of the intercomparisons of high-volume samplers and laboratory analyses conducted in 1995 as well as recommendations made by the Meeting with respect to the activities on monitoring, modelling, assessment and control of pollution of the Mediterranean Sea through the atmosphere which should be implemented within the Programme for Assessment and Control of Pollution in the Mediterranean Region (MED POL – Phase III).

CONTENTS

Background

The Long Term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL), designed as the environmental assessment component of the Mediterranean Action Plan, has been successfully operational since 1975. Its first phase (MED POL-Phase I) was implemented from 1975 until 1980 and it included seven basic baseline studies covering the major marine pollution problems in the Mediterranean. In 1981 the Contracting Parties to the Barcelona Convention approved a new ten-year programme (MED POL-Phase II, 1981-1990) which included both monitoring and research. In 1991 the Contracting Parties decided to extend MED POL phase II to allow the completion of the programme as well as the formulation of the next phase which began in 1997.

In 1985, the GESAMP* Working group No 14 on the Interchange of Pollutants between the Atmosphere and the Oceans reviewed the information available for the Mediterranean Sea and concluded that for some elements such as Hg, Cd, Pb, Cr and transuranic elements, their atmospheric inputs are at least comparable in magnitude to inputs from rivers into the Mediterranean.

The fourth Ordinary Meeting of the Contracting Parties to the Convention for the Protection of the Mediterranean Sea against Pollution and its Related Protocols, held in 1985, recommended that a pilot project on studying air pollution deposition in the region and pollutant concentrations in air should be initiated in 1986 in as many countries as possible. Cd was selected as a pilot contaminant for the project. Monitoring the transport of pollutants into the Mediterranean Sea through the atmosphere became one of the four components of the MED POL Phase II in 1988, following the recommendation of the Scientific and Technical Committee for MED POL.

Two workshops, one in November 1987 in Belgrade, the other in April 1991 in Monaco and a group of experts meeting in May 1993 in Ankara were held. Recommendations made at these meetings have formed a basis for the MED POL airborne pollution monitoring programme, and for the formulation of procedures given in this manual

The following recommendations of the Belgrade and Monaco workshops and the Ankara expert meeting have been taken into consideration in the preparation of this manual:

○ Major goals of the programme were identified as:

  - to evaluate the importance of atmospheric transport and deposition of land-based contaminants to coastal and open Mediterranean waters,
  - to assess the airborne contamination levels of potentially harmful substances,
  - to identify sources and source areas of these atmospheric contaminants,
  - to develop predictive models for assessing airborne pollution load.

○ Two horizontal scales were identified for studies:

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* *GESAMP – IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection*

  - local scale for impact studies close to hot spots (sea-side cities and industries),
  - large scale for an evaluation of the level of contamination of the open Mediterranean Sea (permanent reference stations distant enough from local pollution sources with complementary information from ships).

- The monitoring of the following three types of chemical parameters were recommended:

  - inorganic, ionic and radioactive contaminants of concern for marine waters, marine life and human life along coastline,
  - tracers of natural and anthropogenic sources,
  - meteorological parameters.

  In the aerosol measurements, priority should be given to sampling of inorganic contaminants, including radionucleides. Following chemical parameters should be analyzed in aerosols:

  - heavy metals (Cd, Pb- first priority, Cu, Zn - second priority),
  - other inorganic elements (indicators of natural and anthropogenic contributions: Na, Al, $SO_4^{=}$),
  - radionucleides: Cs, transuranic elements (because of very low levels of these contaminants, the analysis may require the use of composite filters integrating up to a month of sampling),
  - organic species: PCBs, DDTs, HCHs (hexachlorocyclohexanes), PAHs and other particulate hydrocarbons.

  When feasible other possible parameters to be studied would be:

  - elemental carbon and fluorides,
  - heavy metals such as Hg, Sn, As, Se.

- Nutrients (N and P compounds) should be added to the list of priority measurement parameters. Priority should be given to the measurement of nutrients in precipitation (measurement of nutrients in aerosols is difficult, particularly for nitrogen species).

- Flux calculations are difficult because of the uncertainties in the dry deposition rates. Data on particle size distributions must be used to estimate dry deposition fluxes.

- Wet and dry deposition must be sampled separately to avoid contamination of wet samples by alkaline species.

- Sampling duration for both aerosol and rain should not exceed one week. Higher sampling frequency on a daily basis or shorter would be desirable.

- The use of high volume samplers is recommended for aerosol sampling.

- Whatman-41 filters should be used particularly when the sampling period is less than one week.
- Particle size distributions of atmospheric contaminants could be obtained through the use of high volume cascade impactors.
- Dry deposition fluxes should be estimated from aerosol measurements.
- Wet deposition should be collected on event basis using a fully automated device. If daily sampling is not feasible, then wet deposition samples should be collected on a weekly basis.
- The first priority should be given to the implementation of two rain collectors. One for major ions and one for heavy metals.
- Sampling sites should be located as close as possible to a major meteorological station. If meteorological station is not available, at least wind speed and direction should be measured at the station.
- The use of best analytical techniques in laboratories was recommended.
- Intercomparison and intercalibration exercises should be carried out. These exercises should be organized by host countries and international laboratories.
- Analytical intercomparison exercises could be held with the exchange of fractions of a common high volume reference sample to be prepared by one of the participants.
- WMO was requested to send reference rain samples for intercomparison of analytical procedures.
- Four levels of studies were identified:
  - studies to obtain information on the amount of total deposition of metals,
  - studies to obtain information on long term trends,
  - studies to obtain information on wet and dry deposition separately,
  - studies to obtain information on long term trends of bulk (wet + dry) deposition.
- Weekly collected aerosol samples were recommended for assessment of trends in concentrations.
- Samples should be collected using Hi-Vol samplers (using glass or cellulose fiber filters).
- Simultaneous use of one wet-only and one bulk sampler, both collecting bi-weekly samples is the best way to assess dry deposition.
- Collection of dry deposition on surrogate surfaces is proposed as the second alternative.

- Daily aerosol samples must be collected using Whatman-41 filters to obtain information on sources.
- To obtain information on the sources of pollutants in precipitation, wet-only and bulk samplers must be deployed simultaneously. Daily samples must be collected with a wet-only sampler and bulk samples must be collected weekly.
- Field blanks must be taken at regular intervals. Procedures applied to blank filters must be identical with those for sample filters.
- For bulk deposition sampling samples should be collected biweekly. But sampling duration may be increased in areas with low frequency of rain.
- If possible samplers must be located in areas with permanent vegetation.
- Areas with low wind speed should be preferred.
- The sizes of bottles and funnels must be defined for each station depending on the amount of rain in a two week period.
- When bulk samplers are used, triplicate sampling must be performed at least for a limited period of time to assess the uncertainty.
- Either two separate rain collectors must be used or the collected sample must be filtered and separated into two portions immediately after sampling. One portion should be saved for major ions and the other portion must be acidified for metal analysis.
- The measurement of major ions must be performed as soon as possible.

CHAPTER I
SITE SELECTION AND NECESSARY FACILITIES

1.1 Site selection

Selection of the sampling site is dictated by the purpose of the study. A set of very different rules can be formulated for site selection to study global background aerosols, regional aerosols/precipitation and urban or industrial aerosol/precipitation.

There are two basic objectives in the MED POL programme which determine the site selection criteria. These are: (1) the data generated must give information on the fluxes of pollutants from the atmosphere to the Mediterranean Sea and (2) the data generated should give information on the source regions of the measured pollutants. The first of these objectives requires that stations cannot be far from the Mediterranean Sea and samples should represent the region in which they are collected. The latter objective requires that samples should not be influenced by local sources[1].

Based on these requirements, the sampling sites in the MED POL programme should meet the following criteria[2]:

- Stations must be within 10 km from the shoreline[3].
- Major pollution sources (power stations, cities with population more than 10,000 etc.,) must be at distances greater than 5 km.
- The site should be at least 1 km from major roads, landfills and small towns (population less than 1,000).

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[1] *It is well established (at least for the northwestern Mediterranean) that the main sources of pollution in the region are the sources in Europe. Air masses transporting pollutants from sources in Europe to receptors in various parts of the Mediterranean are depleted in aerosol due to removal of particles by dry and wet removal mechanisms during the transport. Any strong local source can easily mask the pollutants arriving at the receptor site as a result of long range transport*

[2] *Most of the points in this list had been recommended in the Belgrade meeting in 1987. Slight additions to clarify certain points are made.*

[3] *It is preferable to have the station at 1 - 2 km from the shoreline.However, stations at the immediate vicinity of the shoreline will be under the direct influence of sea spray and too much NaCl deposition on the filters may interfere with some of the subsequent analyses.*

- The site should be at least 250 m away from single residences, parking lots and local roads.

- Open storage of agricultural products, fuels and other foreign material should be avoided within 250 m of the site.

- Electricity should be available at the site for the operation of instruments and heating (if necessary).

- Stations should be located at elevation less than 1,000 m to ensure that the results are representative for average regional conditions.

- The site must be co-located or located near a meteorological station making surface and (if possible) upper-air observations.

- Sites on or near slopes should be avoided.

- Wind pattern over the site should not be disturbed by nearby topographical features which may cause large disturbances in the wind field.

- Security of the site against potential vandalism should be ensured.

- Local meteorology should be taken into consideration. Sites where winds are predominantly from unfavourable sector should be avoided[4].

1.2. Central laboratory

A central laboratory has four main functions: (1) to provide spare parts and technical assistance during regular operation of the stations to ensure uninterrupted sampling of aerosols, precipitation and dry deposition, (2) to act as technical information center for solving problems which come out during the operation of a station, (3) to act as an analytical laboratory and carry out most of the sample handling and analyses and (4) to handle and interpret the generated data.

Various arrangements for the responsibilities of the central laboratory are possible. For example, the central laboratory may be responsible for continuous operation of the station or stations by providing technical assistance and co-ordination during regular operations

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[4] *If the sampling site is close to shoreline, one would like to receive clean marine air, but winds may be predominantly from land. Such a site could be used if no better alternatives are available.*

and during problems, but sample handling and analyses may be performed by a local laboratory, or some of the analyses may be performed at the central laboratory and some at a local laboratory. The responsibilities of the central laboratory primarily depend on the number of stations in operation (which determines the number of samples generated) and how well the central laboratory is equipped with trained personnel and analytical equipments. In the MED POL programme, the responsibilities of the central laboratory are not yet defined. In the organization of this manual, it is assumed that the central laboratory is responsible for co-ordination between stations, providing technical assistance during regular operations and during problems and carry out most of the sample handling and analyses. Although, this may be the most convenient scheme if one or two stations are in operation (which is the case in most of the Mediterranean countries for the time being), it may not be convenient if very large number of aerosol and precipitation samples are generated in a number of stations. In such a case either capacity of the central laboratory should be increased or analyses load should be distributed among local laboratories.

The following specific tasks should be performed by the central laboratory:

- To co-ordinate the activities of stations (if there are more than one station).
- To provide technical assistance for the maintenance of stations during regular operations.
- To solve or provide assistance to solve problems at the station or stations.
- To provide spare parts for the equipments installed at the stations.
- To provide pure water (with conductivity less than 1.2 $mS \cdot cm^{-1}$), necessary reagents and labware to the stations.
- To prepare aerosol filters and precipitation sample bottles for sampling and for transferring them to the stations.
- To prepare exposed filters and precipitation samples sent from stations for analyses.
- To analyze collected samples for major ions and trace metals (and for other parameters if they are monitored)

- To train the station personnel and work with them to ensure that the monitored data meet the expected quality criteria for the monitoring programme.

1.3. Laboratory facilities

1.3.1. Personnel

Since a central laboratory is expected to provide technical assistance and to perform analytical work, it must have experienced personnel in both technical and analytical components. Personnel with the following orientation may be helpful for the central laboratory to perform its functions:

- Researcher or researchers experienced in sampling and analyses of aerosols and precipitation as well as in data evaluation.

- Technicians experienced in the maintenance of high volume air samplers and automated rain samplers.

- Technicians experienced in ion chromatography (IC) and atomic absorption spectrometry (AAS) analyses of particles and rain water.

- Electricians and mechanics.

It may not be possible to find people with such specific experience in some of the countries. If such people are not available, then people should be trained with the help of international organizations, such as the UNEP and/or WMO.

1.3.2. Laboratory space

Any medium size laboratory well-equipped with relevant instruments and facilities can be used for chemical analyses of precipitation and aerosol samples collected at the station.

The area of the analytical laboratory should be adequate to house the instruments used and to analyze samples. A minimum of 2 m^2 should be available for each analyst on laboratory benches for preparing reagents and samples. An additional 15 - 20 m^2 space is needed for equipment in the laboratory.

The flooring and wall coverings should be washable, fabricated from an inert material(e.g. epoxy polymer, plastic or tile). The height of the laboratory room should be at least 2.5 m.

1.3.3. Back-up facilities

The laboratory must be equipped with the following facilities to support handling and analyses of the samples:

- A sink placed near the working bench with hot and cold water should be provided for washing the glassware, plasticware and plastic bottles. Waste water should be disposed according to national standards.

- The electrical system should provide 220 volts (or 115 V) with adequate wattage capacity for all the electrical devices in the laboratory. If voltage in remote areas varies, a voltage regulator should be used. All electrical equipment should be carefully grounded.

- The windows and electrical lighting in the laboratory should provide sufficient light to perform analytical procedures and to read scales and glassware lines.

- Laboratory temperature should be maintained at 20 - 25 °C without excessive temperature fluctuations. In summer or in hot climatic regions, air in the laboratory should be cooled by air conditioning to below 25°C.

- Compressed gas is needed for the ion chromatograph changer. Any inert gas is acceptable (e.g. nitrogen in 10L bottles) and its purity is not crucial. Clean acetylene and nitrous oxide (two 40 L bottles) and clean air from a compressor (with a cleaning unit) or cylinder (two 40 L bottles) are needed for the atomic absorption spectrometer.

- A vacuum pump or an inert gas pressure filtration system is needed for filtering precipitation samples to remove particulate or other impurities.

- An exhaust ventilation system, such as a fume hood, is necessary to protect the laboratory personnel from toxic acid vapors. Acids are used for sample digestion in metal analyses and to clean plasticware and sample bottles. The air flow through the fume hood should be 25 - 35 $m^3 \cdot min^{-1}$. The atomic absorption spectrometer also requires a separate exhaust system.

- An adequate storage space should be available in the laboratory for storing reagents, glassware, plasticware, filters and sample bottles. Closed cabinets are preferred for glassware and plasticware to protect from dust pollution.

- A refrigerator is needed to store reagents and precipitation samples. Precipitation samples must be stored in a refrigerated space away from reagents and other chemicals which can contaminate them.

1.3.4. Distilled water

Distilled water is used to prepare reagents, to dilute samples and to rinse glassware, plasticware and plastic sample bottles. Distilled water made from commercially available equipment can be used for rinsing, but it is not pure enough to dilute samples. Even double or triple distilled water contains contaminants and should be purified with ion-exchange resin. The cost of producing distilled water in the laboratory distillation systems is relatively low, but will require periodic shutdowns and periodic cleaning. The new ion exchange systems which are commercially available produce high quality water and they are relatively maintenance free. In the last stage of treatment, a membrane filter with 0.2 mm-diameter pores should be used to remove micro-organisms. An activated charcoal filter should also be used to remove organic contaminants.

Water with a conductivity less than 1.2 mS/cm is acceptable for dilution of precipitation samples and reagent solutions. Good quality deionizing units produce fresh deionized water with a conductivity of about 0.2 mS/cm. After a short time, the conductivity of the water increases to about 0.8 - 1.2 mS/cm depending on the CO_2 concentration and temperature in the laboratory. An on-line conductivity meter to monitor the quality of the deionized water should be installed directly at the output of the deionizing unit.

The deionized water should be collected in acid-washed polyethylene bottles. The conductivity of used deionized water should be checked with each set of analyzed precipitation samples.

1.3.5. Clean area

Since concentrations of ions and metals in aerosol and precipitation samples collected in MED POL reference stations are relatively low, contamination of samples during sample handling is a major problem. One of the sources of sample contamination is dust deposition from laboratory air, during sample processing. This problem is particularly serious for precipitation samples where the concentrations are low. If no precautions are taken to avoid this problem, deposition of few dust particles during filtration of a precipitation sample is sufficient to change the chemical composition of the sample. Consequently, possibility of dust deposition on samples during sample processing should be avoided or minimized.

Sample contamination can be reduced by performing all sample manipulations under air which is passed through **H**igh **E**fficiency **Pa**rticulate filters (known as HEPA filters). These filters are certified to remove particles with diameters down to 0.1 mm with up to 99.9999999% efficiency. The ideal solution to such a contamination problem is to use a "clean room" (preferably class-100[5]) where no metal containing surfaces exist and several HEPA filters and associated pumping units are so arranged that approximately 90% of the air recirculated and continuously refiltered. Although clean rooms are commercially available they are prohibitively expensive.

An alternative solution is to use "Laminar flow clean hoods" where only one HEPA filter is used. The air is filtered and send to the work area without any recirculation. The price of such hoods varies, depending on the surface area of the filter and work space, but generally prices are reasonable. The use of Laminar flow clean hoods is strongly recommended in the MED POL programme. If the price is the main constraint even for a clean hood, one can purchase a "clean room module" which basically consists of a prefilter (to remove large particles), a HEPA filter and a blower and which is not expensive[6]. The air produced by the clean room module is identical with the quality of air produced by a clean hood.

If a clean hood is not available, then a corner of a room (preferably without windows) which is away from regular laboratory activities should be designated as a sample-handling area and should be arranged as follows:

- Clean the area carefully with detergent.
- Cover the bench (or table) with a clean sheet of paper.
- Place a sheet of Plexiglas over the paper lining.
- Clean the Plexiglas with a damp tissue paper before using it for sample processing.
- Cover the Plexiglas with a sheet of polyethylene when it is not used.

Although this would not eliminate the possibility of dust settling completely, it will reduce it.

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[5] *Class-100 means that there are less than 100 particles per cm^3 of room air*

[6] *The price of a "clean room module" is approximately 1/5 to 1/10 that of a similarly sized "clean hood".*

1.3.6. Equipment

The following equipment should be available in the central laboratory:

- an ion chromatograph,
- an UV-VIS spectrophotometer,
- an atomic absorption spectrophotometer,
- an analytical balance,
- a pH meter,
- a conductivity meter,
- a water purification system,
- an oven for drying glassware and plasticware.

1.4. Facilities at a station

1.4.1 General requirements

Both aerosol and precipitation samples that are collected at reference stations have low concentrations of ions and metals. Hence, they are susceptible to contamination.
The station should be equipped bearing three main objectives in mind. These are:

- *To maximize the sample collection* or to minimize interruptions in the operation due to equipment failure, etc

- *To minimize chances of sample contamination*. Procedures for sample handling should be designed in such a way that possibility of sample contamination be minimized.

- *Proper preservation of samples*. Procedures should be developed so that samples should retain their integrity until they are transported to the central laboratory for analyses.

The station usually consists of two components: (1) a platform on which samplers are installed, and (2) a closed space, preferably a container or a room in a building where all sample handling takes place (field laboratory).

The platform is an open area with dimensions of approximately 10 m x 10 m (the larger the better). Wooden or concrete platforms are preferable, because it is recommended to install high volume samplers on a firm surface. If such a covering is not available, the ground covered by grass, other types of vegetation or gravel also produce satisfactory results. Under normal conditions, the platform should not be fenced, but if a fence must be installed to protect equipment from stray animals, potential contamination of aerosol and precipitation samples by particles from wires should be taken into account[7].

The following equipment should be installed on the platform[8]:

- a high volume sampler,
- a high volume cascade impactor,
- a bulk or automated wet/dry (or automated wet-only) sampler for ion analyses,
- a bulk or automated wet/dry (or automated wet-only) sampler for metal analyses[9],
- a recording or manual rain gauge[10].

The field laboratory (container or any other sheltered space) acts as a relatively clean environment where samples can be changed, handled and stored until they are shipped to the central laboratory. If sampling is done in the immediate vicinity of the central laboratory, one does not need such a sheltered area. All sample handling can be done in the central laboratory.

The field laboratory should be equipped with:

- a desk or a table on which sample handling can be done,

- a refrigerator to store precipitation samples until they are shipped to the central laboratory,

- a small storage area where clean and exposed filters can be stored,

- glassware and plasticware necessary for handling aerosol, precipitation and dry deposition samples (e.g., plastic tweezers, disposable polyethylene or latex gloves, polyethylene funnels, cutting devices, etc),

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[7] *Plastic covered wires are available in most countries and should be used*

[8] *Instruments listed are recommended at the Belgrade and Monaco meetings*

[9] *The use of two separate precipitation sampler was recommended at the Belgrade meeting This approach is convenient if the station or stations are located in remote places where skilled technicians are not available But if the samples are collected by experienced researchers, then one sampler can be used. The sample collected should immediately be divided into two parts and one of them should be acidified immediately for metal analyses.*

[10] *The rain gauge and the precipitation collector serve different functions. The rain gauge measures the amount of precipitation. The automatic precipitation collector collects samples for chemical analyses The two devices are not interchangeable*

- a pH meter to measure pH of the collected precipitation samples,

- a "clean area". Ideally sample handling should be performed under HEPA filtered air. But, installation of a "clean hood" to each of the stations may not be possible. However, a part of the table can be designated as clean area and can be kept as clean as possible by the following arrangement:

  - clean the area carefully with detergent,
  - cover the bench (or table) with a clean sheet of paper,
  - place a sheet of Plexiglas over the paper lining,
  - clean the Plexiglas with a damp tissue paper before using it for sample processing,
  - cover the Plexiglas with a sheet of polyethylene when it is not used;

- a closed space to store spare parts of the instruments installed on the platform,

- distilled deionized water (with conductivity less than 1.2 $mS{\cdot}cm^{-1}$) Availability of ultrapure water at the station is essential. If it can not be generated in field laboratory, it should be provided by the central laboratory.

Since the facilities available at the station can not be as good as the facilities available at the central laboratory, operations at the stations site should be kept at a minimum to avoid sample contamination. Only the operations related to sample changing and preservation should be performed at the site. Most of the sample handling must be done at the central laboratory. Since pH may change during storage, pH of the collected precipitation samples must be measured at the field laboratory.

1.4.2. Installation of samplers on a platform

Placement of precipitation samplers, rain gauges and high volume samplers must be such that unbiased samples should be collected. Since there will be a number of samplers on the platform, their operations should not interfere with each other. This can be accomplished by taking the following points into account:

- the rain gauges should be installed in such a way that their opening be horizontal over the ground,

- samplers should be at least 20 m from trees, buildings or other large obstacles (a general placement rule is that the sampler should be located at least twice as far away from the obstacle as the height of the obstacle),

- samplers must be at least 2 m away from each other,
- the height of the rain gauge opening should be at least 2 m from the ground to avoid re-entrainment,
- the high volume sampler inlet should be 2 - 7 m from the ground,
- wet/dry collectors should be oriented parallel to the prevailing wind direction, with the wet bucket upwind from the dry bucket (so that the dry bucket does not obstruct the wet bucket),
- the rain gauge must be oriented parallel to both the precipitation sampler and the prevailing wind direction (if the standard rain gauge has an access door to a recorder, the door should be kept closed, and the gauge should be mounted with the door facing away from the wind),
- location of samplers on roof tops should be avoided,
- if possible, samplers must be placed on grass covered areas to avoid contamination of samples by suspended local dust (it is preferable to have a wooden or concrete platform on which samplers are placed),
- the access road should be travelled at speeds low enough to prevent dust suspension and should be located at least 250 m from the sampling instruments,
- samplers must be bolted or anchored to the platform so that they can stand the strongest winds that can be expected in that location,
- an electrical surge suppresser and a ground fault interrupter are recommended the protect the samplers from transient voltage spikes and for safety.

CHAPTER II
SAMPLING OF ATMOSPHERIC AEROSOL

2.1. General

2.1.1 Atmospheric aerosol

Atmospheric aerosol is a three phase system, consisting of a solid nucleus surrounded by a liquid film which is floating in a gaseous surrounding. However, in reality any solid particle which can stay in the air for an appreciable period of time is referred to as atmospheric aerosol.

Aerosols are generated by three mechanisms which are: (1) dispersal of material from earth's surface, (2) chemical reaction of atmospheric gases and vapors and (3) burning of fossil fuels and biomass.

Dispersal of materials from Earth's surface is the main source of airborne mineral material and sea salt which are important components of the aerosol mass even in the remotest parts of the Earth. Airborne mineral particles are produced by the action of wind on terrestrial surfaces, particularly in the arid regions. Consequently, composition of such particles are the same as the composition of crustal material, which is characterized by high concentration of litophilic elements such as Al, Si, Fe, Sc, etc. Since these elements are not enriched in particles released from other sources, these, so called, crustal elements are frequently used to quantify the mass of mineral material in collected samples. Although, most of the crustal material in the atmosphere have natural sources, human activities increase their concentrations through the desertification process.

Sea salt particles in the atmosphere are mainly produced by the bubble bursting process in the sea. Bursting bubbles produce *jet drops* which are giant particles that fall down quickly from the atmosphere and *film drops* which are sub-micron particles and can stay in the atmosphere for longer periods of time. Composition of sea salt particles is the same as the composition of sea water. However, since the surface microlayer of the sea is enriched with chalcophilic elements complexed to organic material, and film drops are formed from the surfaces of bubbles, these sub-micron particles from the sea are believed to be enriched by elements such as Cd, Zn, Co, etc. At coastal stations large particles dominate in the sea salt aerosol component.

Both mineral aerosols and sea salt particles have diameters larger than 1.0 µm. Hence, they make up the *coarse fraction* of the aerosol mass at a given receptor site.

Some of the particles in the atmosphere are formed as a result of chemical reactions of gas phase species. In a reaction between atmospheric gases, if the product or one of the products has low vapour pressure, it can condense as fine particles when the reaction occurs. The best known example of these secondary aerosol is H_2SO_4 which forms by the oxidation of SO_2. Particles generated by this mechanism are very small (less than 10 nm) but since particles in this size range have large coagulation coefficients, they rapidly grow in size through coagulation with other particles. Particles in aitken size range (less than 100 nm) are produced exclusively by this mechanism. Secondary aerosol are important because of their role as cloud condensation nuclei. Aerosols produced by condensation predominate over the total aerosol number but their contribution to the total aerosol mass is important only in very remote regions where larger particles do not exist.

On a global scale, particles in the aitken size range are mainly of natural origin (most of them are $SO_4^=$ particles produced by the oxidation of SO_2 released from the ocean as dimethyl sulfide). But, in urban and industrial areas, gases released from fossil fuel combustion also produce such ultra-fine particles.

The third mechanism of particle generation is the combustion process, particularly combustion of fossil fuels and biomass. Combustion produces both coarse and fine particles. Coarse particles consist of refractory fraction in the fuel while fine particles are carbonaceous material. Particles produced by combustion are rich in elements like As, Se, Sb, Zn, Cd. It is believed that these elements are released from the stacks in the gas phase (they all have volatile oxides) and condense on particles at ambient temperatures. Since condensation depends on surface area of the particles, these elements are enriched on fine particles with large surface area. Due to this mechanism, elements like As, Se, Sb etc., are used as tracers of anthropogenic emissions.

Particles generated by these mechanisms cover a wide range of sizes and conventionally described by a three modal size distribution shown in Figure 2.1. Particles which are smaller than 0.1 µm are named as *aitken particles* or *condensation nucleus*. Particles between 0.1 - 1.0 µm in size are called *accumulation mode particles* and particles with sizes larger than 1.0 µm are called *large* or *coarse* particles. Particles in the aitken and coarse range have short residence times in the atmosphere due to high coagulation and sedimentation rates, respectively. Consequently, aged aerosol in the atmosphere are dominated by accumulation mode particles.

Particles are removed from the atmosphere by wet and dry deposition mechanisms. In wet deposition process, either particles are incorporated into cloud droplets and removed from atmosphere by rain (rainout) or they are washed by falling hydrometeors (washout). In either case, measurement of chemical composition of rain provides information on the quantity of wet deposition at a given receptor site.

In the absence of rain or other types of precipitation, particles are removed from the atmosphere by dry deposition. Dry deposition is dominated by the sedimentation of large particles. However, fine particles which are resistant to sedimentation can be brought to the surface by wind and can stick to canopy when they hit it.

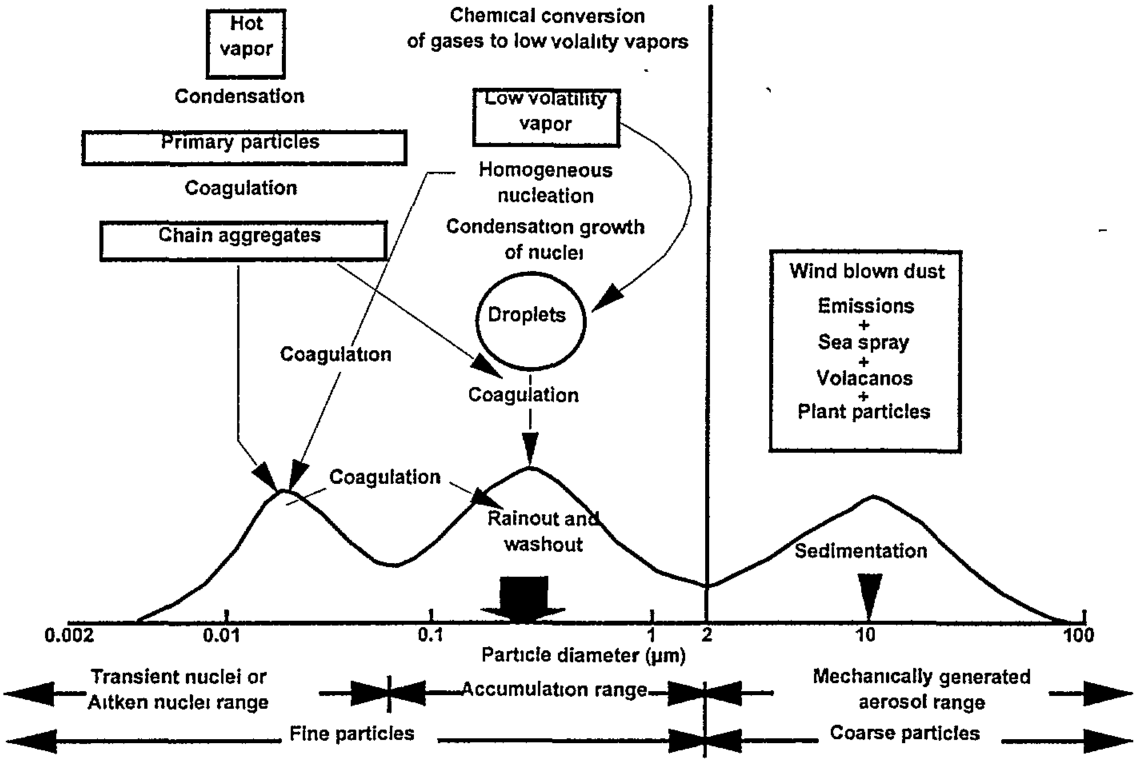

Figure 2.1 Three modal size distribution of particles

Atmospheric aerosol is important and studied because:

- they control visibility, affect intensity of solar radiation reaching the Earth surface, and terrestrial radiation escaping to the space,
- ions and radioactive products are attached to the aerosols, so they control electrical and radioactive properties of the atmosphere,
- aerosols act as cloud condensation nuclei and ice crystal nucleus affecting the water cycle,

- high concentration of aerosols in urban and industrial areas can cause visibility degradation and can affect the human respiratory system,

- deposition of atmospheric particles can be an important source of pollution including marine pollution.

2.1.2. Sampling of atmospheric aerosol

Information on atmospheric aerosols can be obtained by measuring interaction of particles with solar or terrestrial radiation, number of particles (number concentration), mass of particles (mass concentration) or chemical composition of particles. Study of interaction of particles with natural radiation and measurement of number concentrations usually involve in situ measurements of light extinction due to particles (natural or artificial light of various wavelengths). These techniques are not recommended in the MED POL programme and their discussion is beyond the scope of this manual. Since most of the work conducted in the MED POL programme involve measurements of mass or chemical composition, principles of techniques which are commonly used for these measurements will be briefly discussed in this section.

Measurements of mass or chemical composition of particles require collection of a sample on a certain substrate, which is then analyzed for its chemical composition and mass. Depending on the purpose of the work, either all particles regardless their size or shape are collected (whole filter sampling), or they are separated into several size classes and each size is separately sampled (size separated sampling).

In the whole filter sampling particles from the atmosphere are collected by passing a known volume of air through a filter. Particles are retained on the filter while air is passing through. Collected particles are subsequently analyzed for chemical components or their mass can be measured. Although all particle sizes are collected in the whole filter sampling, generally a size separating device such as an impactor or cyclone is placed before the filter, and particles larger than 10 μm are separated and not allowed to reach the filter (PM-10 sampling).

Duration and frequency of sampling, type of filter, flow rate needed, flow control and measurement are important considerations in the whole filter sampling which are dictated by the purpose of the work, location of the sampling site and analytical facilities available. There are large variety of samplers, filters and accessories in the market, and it may be extremely difficult task to select one, unless one knows why the sampling is being performed and at least has a general idea about the characteristics of equipments, filters and accessories.

An important consideration in aerosol sampling is to collect sufficient material on the filter for subsequent mass or chemical composition determinations. This can be ensured by proper selection of sampling time and flow rate through the filter. The sampling time is generally 24 hours. Consequently, the flow rate is the determining factor. Low flow sampling at flow rates around 1 $m^3 \cdot h^{-1}$ are used at areas with high atmospheric loading of particles. Since quantity of particles collected on the filter will be low in low volume sampling, analytical techniques with high sensitivity are required for subsequent analysis. If such sensitive techniques are not available, or if the atmospheric loading of particles is low, so that parameters needed can not be measured no matter how sensitive the analytical methods are, then high-volume sampling with flow rates about 60 - 70 $m^3 \cdot h^{-1}$ is preferred. High volume sampling was recommended for the MED POL programme in the Monaco Workshop and the Ankara Expert Group Meeting. In the high volume sampling with the 60 $m^3 \cdot h^{-1}$ flow rate, approximately 1,400 m^3 of air are filtered during a 24 h sampling time. Even in regions with relatively low atmospheric particle loading where particulate concentrations are around 15 $\mu g \cdot m^{-3}$, approximately 20 mg of particle mass can be collected. This amount of material is sufficient for both gravimetric mass determination and chemical measurements with most of the available analytical methods. However, in the same concentration of aerosols, low volume sampling with a flow rate of 1 $m^3 \cdot h^{-1}$, would result in a particle mass of 0.36 mg on the filter, which requires a sensitive microbalance and highly sensitive analytical techniques to measure mass and chemical composition of particles.

Selection of proper filter is also very important in aerosol sampling. Four essential considerations in the selection of filters are:

- *Pressure drop across the filter* (the resistance it shows for passage of air). The pressure drop across the filter determines the air flow rate which can be attained in the sampling. If the pressure drop across the filter is high a powerful pump is needed to sample at the required flow rate. For example, filters with high pressure drop can not be used in standard high volume samplers, as blowers used in the construction of these high volume samplers are not powerful enough.

- *Blank values* (concentrations of analytes in the filter matrix). Blank values of filters must be as low as possible. The mass of a certain chemical element or compound in the particulate material collected on the filter must be significantly higher than the mass of the same specie in the filter matrix. Blank levels are particularly important if the filter is dissolved along with the collected sample for subsequent chemical analysis (as in the case of measurement of metals by atomic absorption spectrometry).

- *Chemical compatibility*. Filters must be compatible with subsequent chemical analysis. For example, Si can not be measured in samples collected on glass or quartz fiber filters.

- *The price*. Filters must be cheap enough to be used in large quantities. This requirement is particularly important in the networks where large number of samplers are collected.

A filter that has low pressure drop, low blank values, inert for most chemical analysis and cheap, can be used in any type of aerosol sampling programme. But, unfortunately it is not possible to find a filter which combines all of these attractive features. Consequently, a type of filter which is the most suitable for a particular work should be selected from almost infinite possibilities.

Filters are conventionally divided into two groups as fibrous and membrane filters. Fibrous filters consist of fibers (which can be made of variety of materials) in a mesh like structure. The most important feature of the fibrous filters is relatively low pressure drop across the filter. Their low resistance to the passage of air makes them a very convenient substrate for high volume samplers which are not equipped with powerful pumps. The two most well known fibrous filters used in all high volume air samplers are glass fiber and cellulose fiber filters. Glass fiber filters are the most widely used filter type for total particle mass determinations. But, because of their high metal blanks, they are not as widely used to collect aerosol samples for metal analysis. Cellulose filters, on the other hand, are convenient for metal analysis due to their relatively low metal blanks.

Membrane filters consist of porous structure with well defined pore size. These filters are made of variety of materials (e.g., Teflon, polyethylene, nylon, polycarbonate, cellulose esters etc.). They are made in an assortment of thickness, diameters and pore sizes. Membrane filters with pore sizes of 0.1 - 0.5 μm are nearly 100% efficient for the collection of particles in the entire particle size range. Most of these filters can be used for collection of atmospheric aerosol for chemical analysis. One specific type, namely the Nuclepore consists of a polycarbonate matrix with uniform cylindrical holes. To obtain such uniform holes, the polycarbonate is bombarded with fission recoil fragments and nuclear tracks are chemically etched out. Nuclepore filters are frequently used for aerosol sampling due to their very low element blanks (with the exception of Br). Teflon filters are also suitable to collect atmospheric particulate for metal analysis due to the same reason. Although most of these filters are used in low-volume aerosol sampling for different purposes, they are not suitable for high volume aerosol sampling, because the pressure drop across membrane filters is too high for blowers used in standard high volume samplers.

Determination of size distribution and chemical composition of each size fraction is more difficult than determination of mass and chemical composition of total aerosol mass, because aerosol sizes vary by several orders of magnitude and composition and shape of particles can be different.

There is no one single instrument which can measure size distribution over the whole size range. However, different parts of the size spectrum can be measured using different instruments. Size distribution of aerosols can be studied in situ by using optical and laser methods, or can be studied by capturing each size fraction separately on a suitable substrate.

Particle size distribution in aitken range can be determined using diffusion batteries, thermal precipitators or electrical mobility analyzers.

Diffusion battery is the instrument capable of sizing particles smaller than 0.01 µm. It consists of the ensemble of capillary tubes, through which the air is drawn at low velocity. Very small particles deposit on the walls of the tubes due to their brownian motion. Particle loss is a function of their velocity in the tubes. Large particles are captured on a back-up filter.

Thermal precipitators and electrical mobility analyzers are suitable for size measurements between 0.01 - 0.5 µm. Thermal precipitators consist of a metal wire which is heated to produce temperature gradient. Aerosol particles move away from the wire in the direction of cold surface where they are collected. Collected particles are counted by means of an electron microscope.

In electrical mobility analyzers, particles are charged and forced to move in a variable electrical field and captured on a wire due to their mobility in the electric field. Particle movement is a function of size and voltage applied. By varying the voltage between electrodes, particles with different sizes can be captured on the electrode. Particles which pass through the mobility analyzers (different sizes between 0.015 and 0.5 µm at different voltages) are measured by total particle counters such as CNC counter.

Particles less than 0.1 µm are not very interesting for the MED POL airborne pollution monitoring programme because:

- these particles have high coagulation coefficients in the air and, though they have high number concentrations close to sources, their concentration is low in aged aerosols which are collected at the MED POL reference stations;

- research conducted at MED POL stations includes measurements of mass and chemical composition of particles and contribution of particles with diameters less than 0.1 μm diameter to the total mass is insignificant (mass is proportional to r^3);

- at the regional and global scale, particles in this size range (Aitken size) almost exclusively consist of secondary sulfate.

Particles larger than 0.5 μm can be sampled by *impactors* using their inertia. Impaction occurs when particles can not follow the path of an air stream around an obstacle and collide with (impact on) the obstacle. The process is illustrated in Figure 2.2. Since the process of impaction is size dependent, it is the basis for numerous particle sizing instruments, including cascade impactors, virtual impactors and cyclones.

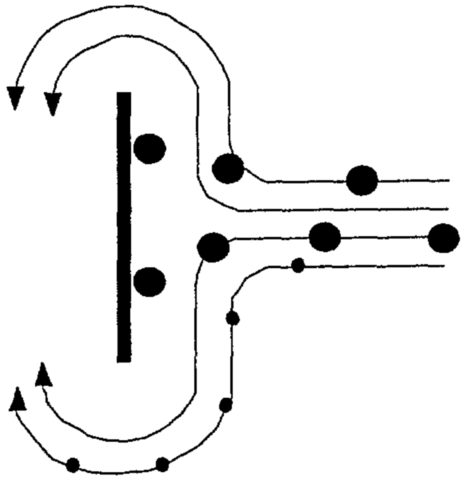

Figure 2.2 Basic principle of impaction (Vermette and Larson)

The efficiency with which particles are collected by impaction varies with particle size. In the ideal efficiency curve all particles greater than a certain size are collected and all particles less than that size follow the air stream around the impaction and so are not collected. In the actual curve, some particles larger than the cut off diameter (or critical diameter) follow the air stream, and some particles smaller than the cut off diameter are collected. The cut-off diameter (dp_{50}) is considered to be the particle size at which 50% of the particles at that size are collected and 50% follow the air stream. Consequently, an impactor plate with a dp_{50} of 10 μm has a 50% chance of collecting particles of size 10 μm. In practical use of this instrument, however, we would assume that all particles with sizes greater than 10 μm are collected by this plate and all particles smaller than 10 μm are not collected.

A *cascade impactor* has a series of stages, and each stage collects a different size fraction of the aerosol particles. The largest particles are collected on the upper stages The last stage is often a filter to collect remaining particles from the air stream. After sampling the stages can be removed and the material collected can be analyzed. The particles are actually collected on an *impactor substrate*, which can be a filter, glass slide, aluminum foil that fits to the impaction stage (one can also collect particles on the impaction stage itself). The impactor stage with the largest dp_{50} is first in the air flow and will typically have the largest jet. The stage with the smallest dp_{50} is last in the air flow and typically has the smallest jet. The jets can be single or multiple, round or slits. Multiple jet impactors help to minimize particle reintrainment (or bounce-off) and allow a larger sample to be collected.

Cascade impactors typically can collect particles ranging in size from 0.05 to 30 µm but they can also be designed for larger particles. To collect very small particles, impactors can be operated at lower pressures (e.g., in low pressure impactors) or use very small jets (e.g , as in the MOUDI, MOI, Berner impactor).

The bounce off problem in cascade impactors has been eliminated in virtual impactors. Virtual impactors with two stages are called *dichotomous samplers.* A dichotomous sampler is illustrated in Figure 2.3. In these instruments, air stream which carries particles is rapidly forced to change direction. Particles larger than 2.5 µm can not make the turn and follow the initial path ending on the coarse filter. Air stream containing particles with diameters smaller than 2.5 µm passes through a filter where *fine* particles are collected. Generally, small amount of air (equal to 10% of the total air flow) is pulled through the coarse filter to reduce the trapping of the coarse particles in the main air flow and hence to sharpen the size separation. However, this diverted air flow should be taken into account in calculation

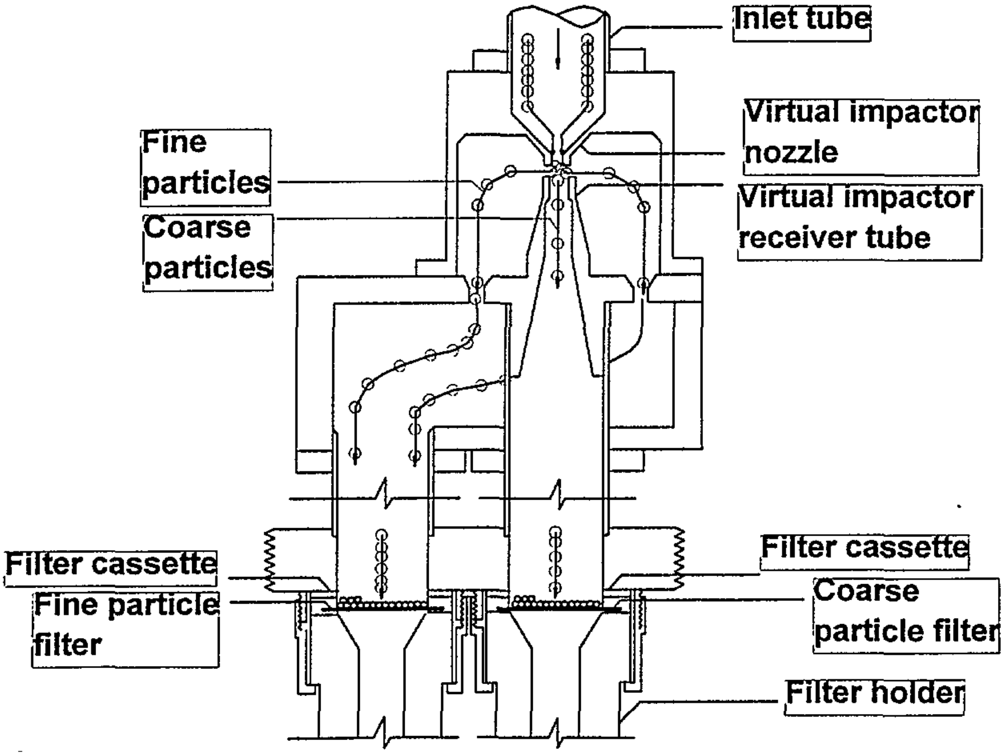

Figure 2.3 Schematic diagram of a virtual impactor
(From Sierra-Andersen, Series 241 Dichotomous sampler instruction manual)

of particle concentrations. Since there are no substrates on which coarse particles are impacted, there is no particle bounce off problem in the virtual impactor. In dichotomous samplers, both coarse and fine particles are collected on membrane filters. Currently the most frequently used filter type is Teflon (PTFE) which is an excellent substrate for most chemical analyses.

There had been some problems with the original inlets of dichotomous samplers. After 1980 new inlets have been designed which have better aerodynamic properties. These new inlets also remove particles larger than 10 µm. In most of the recent models particles collected on coarse filters are between 10 µm and 2.5 µm in diameter.

The dichotomous samplers are also excellent for sampling of aerosols for source apportionment studies, where most of the marker elements occur in the fine fraction and are not masked by coarse particles which are collected separately. However, the dichotomous samplers do not seem very promising to be used in routine monitoring programmes, because technicians who operate the sampler must be specially trained, and flow rate (16 $L \cdot m^{-1}$) is too low.

Another comparable system is the *stacked filter unit*. In the stack filter unit, two filters with different pore sizes are placed in series. Coarse particles are collected on the first filter and fine particles on the second. Pore sizes of the filters and flow rate determine the cut point. Generally, PTFE or nuclepore filters with 8 µm pore size in the first, and 0.4 µm pore size in the second are used When these filters are used with a flow rate of 16 $L\ m^{-1}$, particles with diameters larger than 2.5 µm are collected in the first and particles with diameters smaller than 2.5 µm are collected on the second filter. A preimpactor can be used to remove particles larger than 10 µm before they reach the filters.

The stack filter units are significantly cheaper than dichotomous samplers, but change in the flow rate due to clogging of filters and associated change in the sizing characteristics is a problem, particularly in areas with high atmospheric concentrations of particles. Like dichotomous samplers, the stacked filter units also operate at low flow rates and may not be suitable for MED POL reference laboratories.

One of the most common problems in measuring concentrations of airborne particles is the accurate quantification of the volume of air sampled. If the airborne concentrations are to be expressed as a mass of a measured substance per volume unit of air, then the total quantity of that substance and the total volume of air sampled must be carefully determined. Since the desired quantity is a ratio, excellent precision and accuracy in the analysis of numerator (mass of a substance) is meaningless if the volume of air sampled (denominator) is only known with a limited degree of accuracy. Most of the laboratories invest large sums to equip themselves with very sophisticated instruments for accurate analysis, but instruments for accurate flow measurements are generally at the bottom of the priority list. It should be clearly understood that reported airborne concentrations will always be wrong if flow measurements are incorrect, no matter how sensitive and accurate instrument is used for the analysis.

Thermal conduction flow control devices are used in most of the high volume samplers. It has been shown that there can be considerable errors in flow measurements with thermally-based mass flow controllers if particular care is not taken in the calibration of the controller for the temperature and altitude conditions under which the sampler is employed.

An alternative to mass flow control is the volumetric flow control with *critical orifices*. As the cross-sectional area of the tube through which the air flows is reduced, the velocity of the air in the tube increases. At certain diameter of the tube, the speed of the flow approaches to the speed of sound. At that point, the air molecules can not move faster, and the flow is therefore is limited to that value. It is possible to obtain a critical orifice even for very high air flows. These devices assure constant volumetric flow and are now commercially available. It is possible to obtain reliable and accurate flow information either by mass flow or volumetric flow control. It is necessary that control and calibration be an integral part of the quality control/quality assurance programme developed as a part of the design of any field sampling campaign.

The thermal mass flow controller and the critical orifice provide flow control. If less precision is required in the total volume of air sampled, the flow rates can be measured by means of rotameters, wet and dry test meters. However, these devices must be carefully calibrated before use.

Ambient barometric pressure is not always one atmosphere. In sampling at high elevations, the reduced atmospheric pressure must be taken into account if proper flow measurements are to be achieved. Normally rotameter measurements are made at the beginning and at the end of the sampling and the flow rate is assumed to vary linearly between these values over the sampling time. This linear behaviour is unlikely and typical volumetric errors are in the range of ±10 to ±30%.

Total mass flow meters (dry gas meters) are also used in the measurement of sampled air-volume. Dry gas meters which can accommodate 60-120 $m^3 \cdot h^{-1}$ are commercially available. These can be either purchased or rented from local gas companies.

2.2. High volume sampling at a station

The use of high-volume samplers at the MED POL stations had been recommended at the Belgrade and Monaco workshops as well as at the expert meeting held in Ankara. Based on these recommendations, procedures formulated in this part of the manual are exclusively for high volume samplers.

Although different types of high volume samplers are being used at different MED POL stations, most of them have similar basic features. The differences between different makes and models of high volume samplers are mainly in their control mechanisms and in accessories.

2.2.1. Basic equipment

A typical high volume sampler consists of three basic components. a filter holder, a blower which generates air flow through the filter and a housing which protects the sampler from any external impact. In most of the high volume samplers, the roof of the housing acts as a preimpactor to limit the particle sizes reaching the filter. The filter holder is located upstream from the motor and sampled particles are captured on a filter. If not regulated, the blower motor will run at full power and this level will vary between motors. The motors need to be adjusted to maintain a constant air flow, usually between 1.13 and 1.7 $m^3 min^{-1}$. Knowledge of the mass collected on the filter, duration of sampling, and the volume of air passing through the filter allows for the calculation of concentrations of suspended particulate matter, usually expressed as $\mu g\ m^{-3}$.

Samplers collect particles over a wide range of sizes, but generally smaller than 100 μm. A size selective inlet can be added to restrict the upper size range of the collected particles to less than 10 μm. There are numerous accessories to improve the convenience and accuracy of sampling

Particles are either collected on 22 cm x 28 cm filter sheets or 10 cm filter disks. Glass-, quartz- and cellulose-fiber filters can be used for gravimetric and/or chemical analysis.

2.2.2. Additional components

2.2.3. *Filter Cartridge* (*recommended*)

With a basic sampler, the filter paper is positioned or removed at the field site. While possible, filter changes under windy or wet conditions are difficult. The excessive handling may damage or contaminate the filter The use of a filter cartridge avoids these problems.

The filter cartridge consists of a screen, faceplate and dust cover. Removal of the complete filter cartridge allows the operator to handle the filter under controlled and clean conditions.

Sample Saver

With the basic sampler, a positioned filter is exposed to passive deposition. The passive loading may be of concern if there is a long time gap between the positioning /removal of the filter and the time when a sample was taken, especially if the sampler is located at a dusty site.

The sample saver is easily added with few modifications to the housing. Essentially, the filter is covered with a retractable lid when the sampler is off, and the lid is retracted into the housing when a sample is taken.

Sample Timer

With the basic sampler, the motor can only be turned on and off manually, requiring someone to operate the sampler. To avoid this problem, a number of timers are available, ranging from mechanical timers to electronic ones. Both types allow one to set the sample start time, the length of the sampling period, and the time between samples to be taken. Battery backups (in case of short term power failures) are also available. While there is no essential difference in the capabilities of the mechanical and electronic timers, the mechanical timers tend to be more reliable but less versatile, while the electronic timers offer more programming options.

The timers can be particularly recommended if interrupted sampling is to be performed over a week.

Flow Controller (recommended)

With the basic sampler, air flow can be adjusted using a voltage regulator and calibrator. However, variations in line voltage or resistance from increasing filter load will not be compensated. The flow controller consists of a probe placed just below the filter and in the path of the airflow. Flow controllers serve to maintain air flow at the calibrated rate, adjusting the speed of the motor to account for variations in voltage and resistance. Sophisticated controllers can automatically adjust the motor speed to correct variations in voltage, temperature, pressure and filter loading.

Flow Recorder With Clock Driven Chart

Reliance on the timer, while providing means to programme the start and shut off timers, does not provide a way to confirm that a sample was taken as programmed. An elapsed time counter is helpful in recording the duration of sampling. Additionally, a flow recorder with a clock driven chart (actually a pressure transducer) can provide a permanent record of the sample timing and duration.

Manometer

A manometer is an instrument used to measure pressure/vacuum, and when calibrated can be used to measure the air flow. Installation of a manometer (or vacuum gauge between the filter and the motor) while not essential can provide a quick check of air flow during the sampling. Significant variations in the air flow which are translated into an increase or decrease of vacuum, indicate that the sampler needs to be recalibrated.

Size Selective Inlet

With the basic sampler, particles with diameters less than 100 µm are collected on the filter. The size selective inlet restricts the upper size range of particles collected on the filter to less than 10 µm. The inlet is easily installed, replacing the peaked roof of the high volume sampler.

Particle separation within the inlet is based on inertial separation. Airflow is forced along a tortuous path and particles of large enough size leave the air stream. The sampled air and particles first enter the inlet and follow the air flow down another series of tubes. The momentum of particles greater than 10 µm carry these particles to an impaction surface (the surface is greased to retain large particles). Particles smaller than 10 µm are carried upward with the air flow and through the series of tubes on to the filter.

2.2.3. Sampling procedures using a high volume sampler

A number of models of high volume samplers and accessories are available. While the operating instructions are specific for a particular model, the instructions and operating hints can apply generally to all high volume samplers.

The specific high volume sampler discussed here is an Andersen high volume sampler, equipped with a G312 flow controller/digital timer, a G3000 filter cartridge, and a G8WT well type manometer, with both the traditional peaked roof, and a SA1200 PM-10 selective inlet.

Preparation of the Filter Cartridge

- In your laboratory or at the sampling site lay the filter cartridge on a clean surface. Snap off the dust cover and unscrew and remove the face plate.
- Obtain a preweighted sample filter and carefully center it on the screen. Avoid touching the filter - use plastic gloves or forceps.

- Replace the face plate, making certain that the screen is covered by the filter and the gasket will form an air tight seal.

- Lastly, snap on the dust cover, and seal the filter cartridge in a plastic bag. The plastic bag is not necessary but is advisable for transporting the filter cartridge to the field site.

Installation of the Filter Cartridge

- Upon arrival of the sampler check it over to make certain that the connections are secure, electrical power is on, and that generally everything looks in working order.

- Open the peaked roof of the sampler (or the size selective inlet).

- Retract the sample saver (if installed) and place a dust cover on the exposed filter cartridge in the sampler.

- Loosen the four (4) swing bolts to remove the exposed filter cartridge (assuming that there is an exposed cartridge on the sampler).

- With a lint free cloth wipe away any loose dust that may have been collected within the enclosure.

- Prior to positioning the new filter cartridge it is advisable, from time to time, to check the accuracy of the air flow. To do this, place a spare filter cartridge over the inlet screen, fasten the cartridge down with the swing bolts and manually start the sampler by placing the *sampler* switch in the 'on' position. After five minutes read the manometer. If the reading is similar to that during the last calibration the air flow is correct, otherwise the sampler needs to be recalibrated. Turn the sampler off by placing the *sampler* switch in the 'off' position.

- Place the new filter cartridge over the inlet screen of the sampler. Tighten the swing bolts to secure the filter cartridge. Sufficient pressure is required to avoid an air leak between the gasket and sampler housing. However, swing bolts should not be overtightened as this may damage the gasket. *Note: erratic motor speed usually indicates an air leak in this area.*

- Remove the dust cover and close the peaked roof (or size selective inlet).

Setting the Timer

When the above described procedures have been completed the high volume sampler is ready to collect sample. However, if a programmed sampling is desired, a programmable timer should be used. The following procedure is given for an Andersen high volume sampler equipped with Model G312 digital timer. Most of the high volume samplers do have electronic or mechanical timers as an option. Although the basic features of programming using a timer are more or less the same, the exact procedures for different makes and models of timers are given in their respective user manuals.

- Open the cover of the timer enclosure.

- The elapsed time indicator records the total sampling time. Record the number before and after sampling to confirm the length of time the sampler had operated.

- Set the *display* switch to 'time of day' to check the timer clock. If the clock needs to be reset, use the *fast/slow* switch to reset the clock[11].

- Set the *display* switch to 'sample start time'. Use *fast/slow* switch to set the sample start time[12].

- Set the *sample after* knob to the number of days to be skipped before the first sampling period. Position "0" will initiate the sampling the first time of the day when the clock reads the sample start time (e.g. if the current time is 10:00 and the start time is set for 08:00 the sampling will start at 8 am in the next morning). Position "1" will delay the start time until the clock reads the sampling start time for a second time, etc.

- The *sample every* knob allows to set the sampling frequency. In position "1" samples are taken every day, in position "2" - every two days, in position "6" - every six days.

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[11] *digits will flash until set*

[12] *Sample start time must be at least 30 minutes ahead of time of day, and the "display" switch must not be in the "sample start time' position for the sampler to start.*

- Set the *sample period* knob for the number of hours the sampler is to remain sampling for each sampling period.

- Momentarily toggle the *set* switch down to the 'timer' position[13].

- Place the *sampler* switch to the '*timer*' position. Close the cover of the enclosure[14],[15].

2.2.4. Calibration of a high-volume sampler

Calibration is a verification that the high volume sampler is sampling at the correct air flow. Calibration should be performed periodically (at least once every 4 months) and every time after the motor brushes (or the entire motor) is replaced.

The calibrator which is shown in Figure 2.4 consists of an orifice and mounting plate, tubing and flow meter (or manometer). The following procedure can be used for the calibration of a high volume sampler.

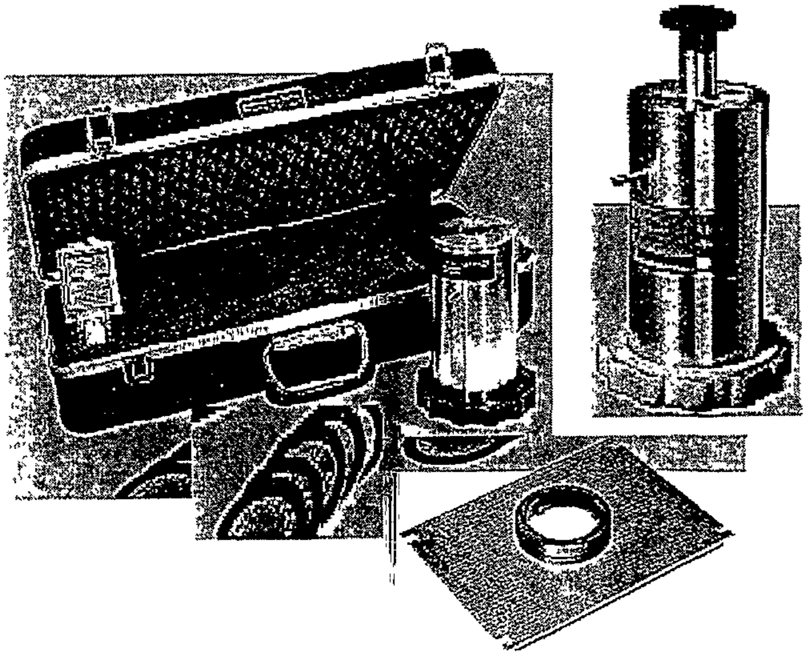

Figure 2.4 The top loading orifice flow calibration kit for Hi-Vol samplers (Andersen)

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[13] *The previous steps can be done in any sequence, but this step must be the last in the sequence.*

[14] *The timer can be bypassed by placing the* ***"sampler"*** *switch in the 'on' position The 'off' position turns the sampler power off.*

[15] *The time of the day and sample start time should be checked to ensure the clock is accurate, and that the* ***"sampler"*** *switch is in the 'timer' position*

- Assemble the calibrator, positioning the filter, mounting plate and orifice over the inlet screen, hanging the meter (or manometer) over the lip over the shelter door.

- Attach the tubing to the orifice and meter. Ensure that the orifice is fully turned to counterclockwise to open the inlet ports[16].

- Open the shelter door and the door on the timer\flow controller. Start the sampler and wait for at least 5 minutes for the flow to stabilize.

- Turn the flow adjustment screw, located on the front face of the timer flow controller either clockwise or counter clockwise to bring the sampler air flow into agreement with the calibration chart.

- Observe the reading on the manometer within the enclosure. While not considered accurate enough for purposes of calibration, changes in the readings of manometer over time are an indication of airflow changes[17].

- Close the timer/flow controller and shelter doors. Disassemble the calibrator.

2.2.5. Useful hints for the use of high volume samplers

The housing protects the filter and motor from external effects. In addition to this function, it also acts as a preseparator and prevents particles larger than 100 µm to reach the filter. These large particles are of local origin and can not be considered as representative for the background pollution. However, removal of large particles using the inlet of a standard high volume sampler is not efficient. Size selective inlets and cyclones which are specially designed for removal of particles larger than 10 µm, and which fit to most standard high volume samplers are commercially available. Their use is especially recommended at MED POL reference stations, because large particles which consist of local dust can mask elements with anthropogenic origin which are valuable tracers of long range transport.

Brush type motors are prone to problems. Unfortunately these are the most common motor types used in high volume samplers. Brushes in the motor wears out approximately after 500 hours of operation and the brushes or the entire motor have to be replaced after few months of continuous operation.

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[16] *If a size selective inlet is being used, hinges on the inlet should be unscrewed to allow the calibrator to fit on the inlet screen.*

[17] *If there is a change in the airflow the sampler needs to be recalibrated*

High volume samplers themselves generate particles. These particles are not in sufficient concentrations to influence mass determination. But, particles originating from the motor are rich in metals (they are particularly rich in Cu) and may interfere with subsequent metal measurements. If subsequent analysis include metal determination, then the motor exhaust must be directed away and downwind from the sampler.

If the sampling is being done intermittently (one sample in every few days), one has to be careful about the deposition of particles on the filter when the sampler is not operating. Normally, the housing is designed in such a way that particles can not easily reach the filter if the blower is not operating, but during a long idle period, some of the particles may still reach the filter. This should be checked by leaving the filter on the sampler for a few days and inspecting for deposits at the end of the trial period. If deposition of particles on the filter is observed, then filter should not be left on the sampler when it is not operating. The best solution would be to load the sampler just before it starts operating and not to leave any filter on during the idle period. *Sample savers* to avoid such passive deposition are commercially available for some makes and models of high volume samplers. When a sample saver is used, the filter on the high volume sampler is covered with a retractable lid. The lid is retracted into the housing during the operation of the sampler.

The flow rate should be measured at the beginning and at the end of the sampling period (and preferably also in between). Most of the high volume samplers are equipped with calibrated rotameters or manometers which can be used for a quick check of the air flow rate. Under normal conditions the flow rate does not change more than 5% during a 24 h sampling time But in the locations where the atmospheric dust loading is high, or in the locations where humidity is high, the filter may be clogged and flow range may change significantly. If such clogging becomes a frequent problem, sampling time or air flow rate should be reduced. If the problem can not be avoided by reducing the sampling time and air flow rate, then a total mass flow meter (dry gas meter) with high capacity should be used. A gas meter measures total volume of air passed during the sampling time, no matter how the flow rate changed[18,19].

In the regions where the humidity is high, prolonged exposure of cellulose filters, such as one week may not be possible, as the filter material may loose the physical integrity. This should be taken into account in determining the sampling time and/or the filter type.

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[18] *But, if the flow rate decrease too much, it may damage the motor.*

[19] *If the pressure at the station is less than 1 atmosphere, the volume registered on the gas meter, at the end of the sampling should be corrected.*

In the locations with cold winters where snow and frost is frequent, the filter holder should be heated to avoid condensation and freezing of the filter. Most of high volume sampler manufacturers provide heated filter holders as an option. It is recommended to purchase this accessory if freezing temperatures are common at the station site[20].

2.2.6. Filter material

Every researcher in the field of aerosol measurements is aware that, there is a wide range of filter types which are all used for sampling of atmospheric particles. But, most of them can not be used with high volume samplers, mainly because **standard** high volume samplers do not have powerful motors (high volume sampler motors are the same as the motors used in vacuum-cleaners). Consequently, the filters used should have low resistance (low pressure drop) for the passage of air. This requirement leaves out most of the membrane type filters, which have very favourable features, such as low blanks, but also have high pressure drop (high resistance for the passage of air).

The two filter types which are widely used in standard high volume sampling are glass fiber and cellulose fiber (the best known is Whatman 41) filters. They have surface area of approximately 500 cm^2 and weight of 4 g. Both glass and cellulose fiber filters have low pressure drop, sufficiently high tensile strength and more or less similar prices. Glass fiber filters are excellent for mass determinations, but known to have high blanks, particularly for metals. The glass matrix contains metals. Organic and inorganic binders used in manufacturing glass fiber filters further increase the blank values. A new glass fiber filter which became available only recently (Whatman 2000) is claimed to have low metal blanks. However, this new product should be tested in field before it can be recommended for use in large monitoring programmes. Quartz fiber filters have the same characteristics as glass fiber filters and have very low metal blanks. However, quartz fiber filters are more expensive than both glass and cellulose fiber filters.

Another problem with the glass fiber filters is the artifact ion formation. It is documented that gases like SO_2, HNO_3 and NH_3 are partially converted into $SO_4^=$, NO_3^- and NH_4^+ on the surface of the glass fiber filter causing erroneous results, if the sample is analyzed for these ions. Consequently, the use of glass fiber filters is not recommended if the samples will be analyzed for major ions.

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[20] *Freezing is probably not an important problem in the MED POL programme, except for high altitude stations*

Because of their low blanks, cellulose fiber filters, such as Whatman 41, are the most suitable one for *high volume*[21] sampling of atmospheric particles for *metal and/or major ion* measurements. However, cellulose fiber filters are also not free from interferences. One of the best known interference is the adsorption of gaseous halogens (particularly Br and I) on the filter resulting in erroneous Br and I measurements. Another artifact is the volatilization of NO_3^- from the filter[22] which renders NO_3^- measurements incorrect. However, at stations located very close to the sea (like most of the MED POL stations) filter is coated with NaCl and accurate measurement of NO_3^- may be possible.

In both glass and cellulose fiber filters, blank values change significantly from one batch of filters to another. Consequently, large number of blank filters should be analyzed. Number of blank filters analyzed over a year should be approximately equal to 5% of total number of samples collected at a sampling site.

To reduce the blank variability, it is recommended to order as much of filters as would be sufficient to operate all sampling sites for at least one year. Ask the distributor in your country to provide the filters from the same batch (they usually communicate with manufacturer to fulfill this request). Filters are usually provided in boxes of 50 or 100. It is recommended to spare at least one filter in every box for blank determination.

2.2.7. Sampling time and frequency

Sampling time and frequency is dictated by the purpose of the study, physical constraints such as atmospheric loading of aerosols, physical integrity of filters and analytical capabilities. This issue was extensively discussed during the Belgrade and Monaco workshops and at the Ankara meeting. In these meetings it was recommended that:

- Sampling time should be weekly if the purpose of the study is to determine the long term trends in concentrations of parameters that are being measured. Samples should be collected continuously[23] to fulfill the indicated purpose.

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[21] *There was an extensive discussion on the efficiency of Whatman 41 filters for sampling of atmospheric aerosols in 1987. Now it is quite well established that, efficiency of these filters for high volume sampling is close to 100% and constant But, Whatman 41 filters can not be recommended for low volume sampling, because (1) their efficiency is poor and variable in low volume sampling, (2) there are filters, such as teflon or polycarbonate (like nuclepore) with much lower blanks which can be used in low volume sampling.*

[22] *Volatilization of NO_3^- as HNO_3 is not specific only to Whatman 41 filter. It occurs on all filter types (except nylon filters)*

[23] *Continuously means that samplers are only stopped to change samples*

- If the atmospheric loading of particles is high and causing rapid drop in the air flow rate and if the flow rate can not be reduced, then three day long samples should be collected continuously.

- If the analytical laboratory can not handle large number of samples generated by three day sampling, then one three-day-long sample should be collected in every week.

- Sampling time should not exceed one week for the determination of long term trends in concentrations.
- If the purpose of the study is to obtain information on the sources of pollutants effecting the receptor site, then daily samples should be collected continuously to have sufficient resolution in the generated data set.

2.2.8. Blanks

Processing and handling of blank filters is as important as collection of samples. Blank levels should be paid even more attention to if the collected samples are subsequently analyzed for trace elements, because in the metal analysis, the filter is dissolved and elements in the filter matrix are added to the elements in the collected particles. The cellulose fiber filters which are recommended for high volume sampling for trace element analysis at the MED POL stations, do contain metals in different quantities. The elemental concentrations in Whatman 41 filters are given in Table 2.1.

In a typical 24 hrs operation of a high volume sampler, at a flow rate of 60 - 70 $m^3 \cdot h^{-1}$, approximately 1,400 - 1,700 m^3 of air is filtered. Even at a low concentration of atmospheric particles, such as 10 $\mu g \cdot m^{-3}$, approximately 14 mg of aerosols can be collected on the filter, which is sufficient to detect most of the metals without significant interference of filter blanks. Sample-to-blank ratios obtained using 24 hr sampling periods and Whatman 41 filters in the *Black Sea atmosphere*[24] are given in Table 2.2. High blank levels is a problem only for W, Cr, Au and Mo. Among these, only Cr is included in the MED POL programme. Although there are filter clean-up procedures which can reduce the blank values in Whatman 41 filters, these procedures are not recommended for the MED POL programme because (1) blank values are not a serious problem in the high volume sampling of aerosols at the Mediterranean atmosphere, if necessary precautions are taken for proper handling of filters and contamination free sampling operations, and (2) attempts to clean filters in laboratories where HEPA filtered air is not available, may cause more serious contamination problems.

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[24] *Concentrations of elements in the Black Sea atmosphere are quite similar to the corresponding concentrations in the Northwestern Mediterranean basin.*

Table 2.1. Average concentrations of trace elements in Whatman 41 cellulose filters.

Element	Avg. Blank Conc. (ng/100cm^2 filter)
Na	20520 ± 5300
Mg	8500 ± 2750
Al	5400 ± 1900
Cl	60000 ± 5800
K	4800 ± 3300
Sc	0.56 ± 0.11
Ti	820 ± 260
V	14 ± 7
Cr	1000 ± 260
Mn	100 ± 30
Fe	3400 ± 520
Co	3.7 ± 1.1
Zn	215 ± 80
Ga	480 ± 190
As	2.96 ± 1.48
Se	3.7 ± 0.7
Br	300 ± 75
Rb	9 ± 2
Sr	410 ± 20
Mo	20 ± 7
Cd	9.2 ± 12.2
In	0 67 ± 0.37
Sb	3.0 ± 0.5
Cs	1.5 ± 0.7
Ba	890 ± 400
La	2.6 ± 1.1
Ce	5.2 ± 1.9
Nd	12 ± 6
Sm	0.37 ± 0.04
Eu	0.44 ± 0.19
Gd	0.3 ± 0.2
Tb	0.28 ± 0.07
Dy	3.7 ± 0.6
Yb	0.25 ± 0.09
Lu	0.05 ± 0.03
Hf	0.5 ± 0.3
Au	0.37 ± 0.3
Hg	4.26 ± 0.75
Th	0 52 ± 0.11
U	5.6 ± 2.6

¶Concentrations were obtained by analysing 25 field blanks by INAA.

Shaded elements are the ones measured in the MED POL programme

Filters are not the only source of high blank values in the sampling of atmospheric particles. Sample handling, reagents and water used in laboratory procedures, glassware and plasticware used, transportation of the filters between a laboratory and a station could add to the blank values of the parameters that are being measured. Consequently, not only the highest quality of reagents, water and plasticware must be used, but also contribution of all these factors to the total blank values must be carefully determined.

Table 2.2. Blank subtraction (in %) for trace elements measured in the aerosol samples collected in the Eastern Mediterranean atmosphere

	% Blank Subtraction		% Blank Subtraction
Au	57.8	**Co**	8.1
Ga	46.9	**Zn**	7.9
Cd	34.6	**Yb**	7.6
Ba	33.5	**Al**	7.1
Ni	31.8	**Na**	7.1
Dy	23.5	**Gd**	6.8
Hg	23.0	**Mg**	6.5
In	22.9	**Cs**	6.1
Tb	22.0	**Fe**	5.6
Zr	21.8	**Mn**	5.4
Mo	21.6	**K**	5.4
Sr	20.0	**Br**	5.2
Eu	19.4	**La**	5.0
Ta	18.1	**Sm**	5.0
Pb	17.2	**Ce**	4.8
Cl	16.1	**Rb**	4.6
Cr	13.9	**Se**	4.2
Ca	12.6	**Sc**	3.9
Nd	12.3	**Th**	3.7
Hf	10.8	**Sb**	2.7
Lu	8.7	**V**	2.7
Ti	8.3	**As**	1.8

Samples were collected using a Hi-Vol sampler and analyzed by INAA. Blank subtraction may be higher in AAS due to contribution of reagents and procedures used in sample digestion to blank values

Field and laboratory blanks should be routinely analyzed along with the samples. The field blanks are more important, because they include all sorts of blanks introduced at every step of sampling and analysis and they are the values that will be subtracted from sample data. The field blanks are filters that are exposed to exactly the same procedures and handling as the sample filters, except air is not pulled through or pumps are operated for only very short time (such as one minute). As a rule, the number of field blanks analyzed for a sampling site should approximately be equal to 5% of total number of samples collected at that particular site in a year. This means that in a daily sampling programme, 18 field blanks must be prepared and analyzed along with samples every year. However, the number of blank samples depends on the variability in the blank values and larger than 18 blanks may be needed if the blank values are variable and comparable with sample concentrations in magnitude.

The following procedure can be recommended for preparation and handling of blank filters.

- Prepare field blank filters using exactly the same procedures you use for sample filters.

- Send packaged blank filters to the station in the same manner as used for the sample filters. It is recommended to send the blank filters to the site along with sample filters and not as a separate batch.

- At the station site, load a blank filter to the high volume sampler like a sample filter, using procedures given in section 2.2.3.

- Allow it to stay on the sampler for 1 or 2 minutes. Unload the blank filter from the sampler using the procedure given in section 2.2.3.

- Prepare the blank filter for transportation using the procedures given in section 2.4.2. for sample filters.

- Send blank filters to the central laboratory along with the sample filters.

In order to have reliable results, concentrations of parameters measured in untreated filters, in water used for washing glass and plasticware in the laboratory and dilution and in acids used in digesting samples must be well known. These are called laboratory blanks. Reagents and material used in the laboratory and their requested purities will be discussed in subsequent sections. But no matter how pure reagents are used, they should be analyzed periodically. Knowing concentrations of parameters that are measured in these matrices is critical both to minimize field blank levels and to pinpoint contamination problems. It is recommended to:

- Analyze at least one filter from each box of filters that is opened.

- At least one sample should be taken from each acid bottle and analyzed.

- If pure water is generated in batches, one sample should be analyzed from each batch. If water is generated continuously, samples should be taken periodically for analysis.

2.3. Size separated sampling of aerosols

There are variety of techniques and devices available for determination of sizes of atmospheric aerosols. Some of these techniques are briefly introduced in section 2.1.1. However, since the purpose of size separation at the MED-POL stations is subsequent chemical analysis, only impactors will be discussed in this section. Although devices like virtual impactors and cyclones are also based on impaction principle, the discussion will be confined to high volume cascade impactors, as virtual impactors and cyclones are not frequently used at the MED POL stations.

Principles of operation of the cascade impactors are discussed in section 2.1.1. Detailed procedures to operate one specific type of a cascade impactor are presented in this section.

2.3.1. Sampling procedure

No specific cascade impactor type is recommended to be used at the MED-POL stations. Since the stations operating in the MED-POL programme are located in rural areas with relatively low atmospheric loading of particles, the cascade impactors which cold be employed should be capable of operating at high flow rates, otherwise material collected on the stages, in a reasonable sampling time, will not be sufficient for chemical analysis.

Although different makes and models of high volume cascade impactors are available, operating instructions and hints given for a specific high volume impactor in this section, fully or partly, apply to most of the other impactors.

The impactor described as an example is a Sierra model 236 high-volume cascade impactor. It is a 5 stage impactor which fits to most regular high volume samplers. The impactor consists of 5 impaction stages and a base plate which also holds a back-up filter. Impaction plates are made of anodized aluminum to prevent corrosion and reduce possible sticking of collection substrates to plates. Impaction plates are 15.2 x 17.8 cm in size and have 9 or 10 slits which act as jets during the operation of the impactor.

In this particular model, size separated aerosol samples are collected on specially slotted collection substrates which can be glass fiber, cellulose or aluminum foil, depending on the application for which the impactor samples are going to be used. The assembled and dismantled views of the impactor are depicted in Figure 2.5.

Suspended particles enter the Sierra Model 336 (or 236) cascade impactor through parallel slots in the first impaction stage, and particles larger than the particle cut-off size of the first stage impact on the slotted collection substrate. Air stream then passes through the slots in the collection substrate, accelerates through narrower slots in the second impactor stage, and remaining particles greater than the particle cut-off size of the second stage impact on the second collection substrate and so on. The width of the slots is smaller for each succeeding stage, and most of the smaller particles eventually acquire sufficient momentum to impact on one of the collection substrates. After the last impactor stage, remaining fine particles are collected by the back-up filter in the high volume sampler.

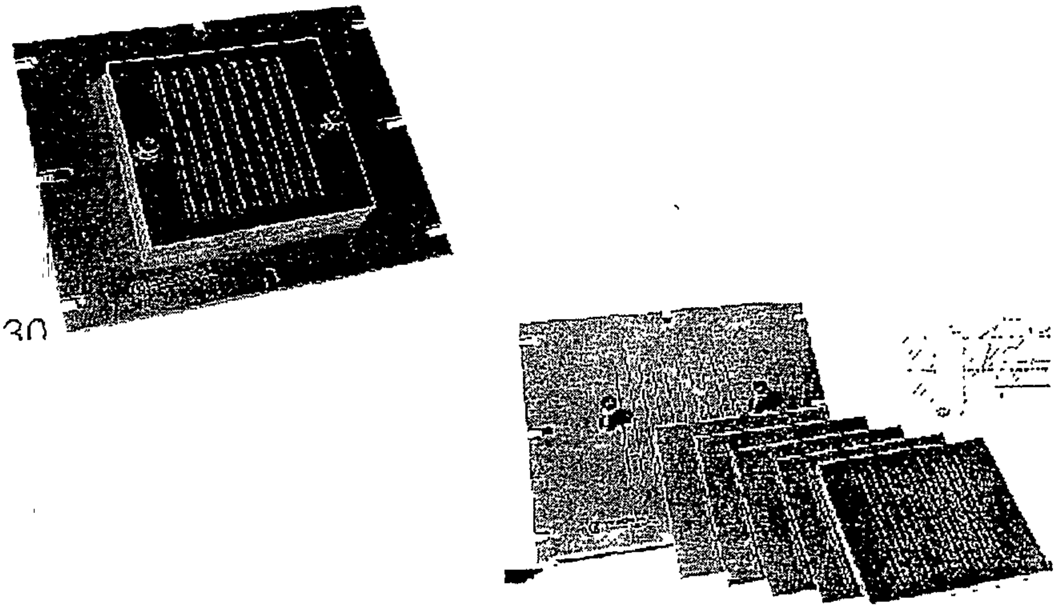

Figure 2.5 Assembled and dismantled views of a high volume cascade impactor (Andersen, Series 230)

The following procedure can be used to load and unload the impactor:

- Place the base plate on a clean surface in the field laboratory.

- Using tweezers, carefully place a preweighed collection substrate on the impaction stage (number 5) so that the slots are exposed[25].

- Place the impactor stage number 5 down over the two threaded studs on the substrate. The number should be in the upper right corner.

- Using tweezers, carefully place a preweighted collection substrate on the impaction stage so that the slots are exposed.

---

[25] *If a glass fiber filter is used, it should be vigorously tapped before inserting it into the impactor to shake off any excess fibers*

- Place the impactor stage number 4 down over the two threaded studs on the substrate. The number should be in the upper right corner.

- Using tweezers, carefully place a preweighted collection substrate on the impaction stage so that the slots are exposed.

- Place the impactor stage number 3 down over the two threaded studs on the substrate. The number should be in the upper right corner.

- Using tweezers, carefully place a preweighted collection substrate on the impaction stage so that the slots are exposed.

- Place the impactor stage number 2 down over the two threaded studs on the substrate. The number should be in the upper right corner.

- Using tweezers, carefully place a preweighted collection substrate on the impaction stage so that the slots are exposed.

- Place the impactor stage number 1 down over the two threaded studs on the substrate. The number should be in the upper right corner.

- Hand tighten the knurled knots holding the impactor stages together. Only a light torque is required, because the pressure drop through the instrument adequately seals it.

- Take the assembled impactor to the high volume sampler. The entire assembly fits on the sample holder of a standard high volume samplers.

- Place a 20 x 25 cm filter on the stainless steel screen.

- Place down the large base plate over the filter with the name *SIERRA INSTRUMENTS* in the lower left hand corner. The rubber gasket on the bottom of the base plate fits around the periphery of the of the filter.

- Hand tighten the wing-nuts (or thumb-nuts) on the high volume sampler to hold the base plate down.

- The impactor is now ready for sampling. Start the high volume sampler (see section 2.2.3).

- Allow the flow to stabilize. Set the high volume sampler to run at a flow rate of 40 cfm (about 67m^3.h^{-1}) (see section 2.2.3). Set the timer/programmer.

At the end of the sampling

- Stop the sampler.
- Fill in the necessary parts on the sample record form, (e.g., time when the sampler was stopped, duration of the operation).

- Remove the round chart paper from the flow recorder (if the high volume sampler is equipped with one).

- Loosen the wing-nuts on the high volume sampler.

- Remove the impactor assembly from the high volume sampler without tipping or jarring.

- Carry to a building (or a container or a vehicle) where samples are regularly changed.

- Beginning with the first impactor stage, carefully remove the collection substrates, one at a time, from the cascade impactor, fold each in half (exposed surfaces facing each other), place in an individual acid washed polyethylene bag (the polyethylene bags which are used to carry the substrates to the station can be used).

- Heat-seal the polyethylene bags containing collection substrates and back-up filter.

- Complete the sample record sheet.

- Place the polybags containing collection substrates, back-up filter and the sample record in a larger polyethylene bag and heat-seal.

- Write an appropriate Identification (ID) number on the polybag along with sampling information and store it in a convenient place until it is shipped to the central laboratory.

- Assemble the impactor for the next run.

2.3.2. Useful hints for the use of impactors

Type of a collection substrate is determined by the subsequent use of the collected sample. Three types of substrate material, namely, glass fiber, cellulose (Whatman 41) and aluminum foil are commercially available. Glass fiber substrates are convenient for mass determinations, but generally have high metal blanks and consequently not preferred if the collected samples are going to be analyzed for trace elements. Whatman 41 substrates have relatively low metal blanks and are preferred if collected samples will be analyzed for metals. Aluminum foil is usually selected for organic analysis. The collection plates themselves can also be used for collection of particles, but removal of particles from the plate requires washing of the plates which increases the chance of sample contamination.

Although the width of the slits change from one plate to the next, widths of the perforations in the collection substrates are identical. Substrates in a given batch can be randomly used in any of the stages.

Application of a thin layer of silicone grease is recommended if aluminum collectio§n substrates are used, or if the particles are collected on impactor plates themselves. A thin layer of silicone grease can significantly reduce particle reintrainment (particle bounce-off).

Proper selection of sampling time is also important in impactor sampling. Too short sampling times may not yield sufficient sample and may result in blank problems, while unnecessarily long sampling time may cause bounce-off problems or change in the jet-to-plate distance. One has to keep in mind that particle mass that is collected on one filter in a filter sampling is now collected on 6 or 7 different substrates (mass is not divided equally between stages). Consequently, sampling times for impactors should be significantly longer than sampling times used in filter sampling. There is no standard sampling period which applies everywhere, because atmospheric particle load changes significantly from one sampling site to another. Generally, if reasonably good sample-to-blank ratios are obtained with 24 hour regular high volume sampling at a given site, one should start with weekly sampling with a high volume cascade impactor. If the sample-to-blank ratio in each stage is sufficiently high, sampling time can be reduced. However, prolonged sampling can cause particle bounce-off which results in the collection of large particles in later stages.

Loading and unloading of the impactor must be done in a field laboratory preferably in a *clean area*. Proper handling of collection substrates may be difficult in rainy or windy weather.

If glass fiber substrates are used in a humid environment, the substrate may adhere to impaction stages. In such a case, it may be proper to condition the impaction stage with a small amount of baby-powder or talcum powder. But, all excesses must be removed before sampling.

The impactor stages should be carefully cleaned before runs. If no unusual contamination is observed, wiping away loose dust particles using a lint free cloth is sufficient. If the stages are dirty, they should be cleaned with alcohol (or water) and a clean cloth. Hold each stage up to the light to see if the slots are partially blocked, if so clean by washing in a detergent water solution or in an ultrasonic bath and then rinse and dry thoroughly.

Particle size distribution is normally presented as cumulative plots on a log-normal paper. To prepare the cumulative size distribution plot the following should be done: (1) total mass in all stages (including the back-up filter) is summed up, (2) percent of mass which less than the cut-off size of each stage is plotted against the particle size (d_p). On a log-normal paper the plot should be close to a straight line. Once the cumulative size distribution plot is prepared, two major parameters of particle size distribution can be determined. One of them is the mass median diameter ($d_{p,50\%}$) which corresponds to particle size at 50% efficiency is an overall measure of the particle size. The second one is the geometric standard deviation s_g which is the ratio of $d_{p,50\%}/d_{p,16\%}$ and which is the measure of the spread in the particle size distribution (if $s_g = 1$ then the particles are monodisperse but s_g is usually larger than 1). An example of cumulative plot is given in Figure 2.6.

Whatever the type of impactor is, one has to be careful about correct installation of stages. Correct installation ensures accurate jet to plate distance which in turn is crucial for attaining correct cut-off diameters.

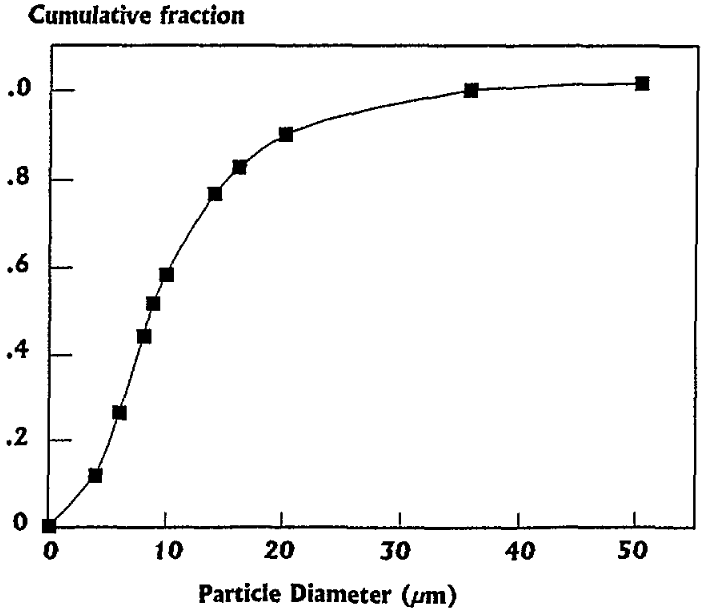

Figure 2.6 A cumulative plot obtained from impactor data

A precut (removal of large particles) should be preferred to reduce bounce-off effects, because the bounce-off problem is the most serious with large particles. This can be a size selective inlet in high-vol impactors or it may be a cyclone before the first stage of low volume impactors (high volume impactors can also be used with a cyclone and the results are as good as results obtained with size selective inlets).

Preparation and handling of blanks which was discussed in section 2.2.8. for high volume filter sampling also applies for size separated sampling of aerosols.

2.4. Sample handling

Since the contamination of collected samples is one of the most important issues in sampling and analysis of aerosols, proper handling of filters during preparation for shipment to the sampling site, at the sampling site and when they are returned from the station is very important to generate a reliable data set.

2.4.1. Preparation of filters for shipment to a sampling site

Handling of filters should be done by paying extreme attention to avoid contamination. All of the procedures given below should be carried out in a *clean area* (see section 1.3.5). Laboratory gown and polyethylene gloves should always be worn. Filters should never be touched by hand (even if you are wearing polyethylene gloves) Touch the filters only with Teflon, high density polyethylene or polyamide forceps (which are acid washed if the samples are to be analyzed for metals).

The following procedures could be recommended for preparation of filters to shipment.

- Visually inspect the filters for their physical integrity using a light table. Remove loose fibers with a soft brush. Discard the filters with pinholes and other defects (or return them to the supplier).

- Assign an acid-washed polyethylene bag and a serial number for each filter and write down the filter ID number on the polyethylene bag. Do not write anything on the filter. The polybags used to store filters must be washed with acid and dried. The following procedure can be used to clean plastic bags:

  - Wash with dilute detergent solution.
  - Rinse several times with distilled water.
  - Soak in 20% HNO_3 for 48 hours.
  - Rinse several times with distilled water (or until pH reads between 6 and 7).

  - Rinse at least 6 times with distilled deionized water.
  - Dry under HEPA filtered air or in the clean area.

- Equilibrate the filter in a conditioning environment for 24 hours before weighing it to minimize the errors in weight. Longer periods of equilibration will not affect accuracy. Temperature of the conditioning environment should average between 20°C and 25°C and not vary more than ± 3°C with a relative humidity (RH) <60% without varying more than ± 5% RH. Equilibration for 24 hours is sufficient if a few samples are to be weighed. However, if large lots (containing 50 - 100 filters) are to be processed at once, it is recommended to increase equilibration time to 3 - 4 days.

- Clean filters are usually processed in lots - that is, several at one time. Clean filters must not be folded or creased prior to weighing or use. Before weighing the first filter, check the balance by weighing standard Class-S weight of between 3 and 5 g. If the actual and measured values agree within ± 0.1 mg, weigh each filter to the nearest 0.1 mg. It is recommended to place the balance in the equilibration chamber for weighing. If this is not possible, weigh each filter within 30 seconds after it is removed from the equilibration chamber. Record the tare weight and the ID number of the filter in the laboratory log-book.

- Place the weighed filter in an acid washed plastic bag. Heat-seal the bag and write the filter ID number on both sides of the bag.

- Prepare a sample record sheet which should contain all necessary information relevant to that particular filter and place the polybag which contains the filter in a second polybag (not necessarily acid washed) along with the sample record sheet and heat-seal this *outer bag* as well. Now the filter is ready for transportation to the sampling site.

- Process all the filters in the lot using the same procedure.

2.4.2. Handling of filters at a station

At a monitoring station, like in a central laboratory, all the necessary precautions should be taken to reduce the risk of sample contamination. Wear lab-coat and polyethylene gloves all the time you deal with the filters. Never touch filters with your hands (even if you have your gloves on), always use acid washed Teflon, high density polyethylene or polyamide forceps.

One should be even more careful in handling filters at the station site, because facilities available in the central laboratory are usually not available in the field. Basic requirements that should be provided at the sampling site were discussed in section 1.4. One of them was a relatively clean area where samples can be changed. The contamination problem can be minimized by establishing a small area with HEPA filtered air. If HEPA filtered air is not available in the field station, at least a small bench space in a the field station should be allocated and cleaned thoroughly for sample changing. The area allocated for sample change should be prepared using the procedures discussed in section 1.4.

Do not attempt to install a new filter while in the field; rather, replace the entire exposed filter cartridge assembly with a cartridge containing a new filter. If two cartridges are not available, remove the cartridge assembly containing the exposed filter and carry it to the field laboratory where the exposed filter can be replaced with a clean one.

The following procedures can be recommended for replacing exposed filters on the sampler with the clean ones.

- Shut off the sampler motor.

- Record the following information in the station data log-book.

    - Stop time and elapsed time
    - Existing conditions that may effect the results (e.g. activities around the station, subjective evaluation of meteorology)
    - Initials

- Place the sampler to the servicing position by loosening the four wingnuts and tipping the sampler head back.

- Place the aluminum cover of the filter cartridge over the exposed filter.

- Remove the cartridge and carry it to the area allocated for changing samples.

- Remove the aluminum cover and faceplate.

- Using acid-washed forceps, remove the exposed filter from the back-up screen and fold it once so that exposed surfaces face each other.

- Place the filter in the acid washed polyethylene bag in which it was sent to the station and heat-seal the bag.

- Complete the sample record sheet.

- Place the poly-bag containing the exposed filter and the sample record sheet in another polyethylene bag and heat-seal this outer bag as well[26,27].

- Using a damp tissue paper, remove any loose dust or fibers from the previous filter, from the metal screen of the filter cartridge and from the rubber gasket of the face-plate.

- Check the gasket of the face-plate for any sign of wear. If you detect wearing in the gasket, it must be replaced with a new one, because an old gasket may leak air during sampling.

- Open the outer polybag containing the clean filter, remove the sample record sheet and lay it on an appropriate place.

- Lay the inner polybag on the clean Plexiglas, cut one edge and using acid-washed tweezers, remove the clean filter from the bag and lay and center it on the back-up screen of the filter cartridge

- Place the faceplate in the proper position on the back-up screen and the filter, and tighten the two thumbscrews just enough to prevent leakage during operation. Excessive tightening may cause the filter to stick and damage the face plate gasket.

- Place the aluminum cover on the filter cartridge assembly.

- Place the inner and outer bags which belong to the installed clean filter on the clean Plexiglas and cover the whole sample change area with a sheet of polyethylene.

- Carry the filter cartridge assembly to the sampler, place it and tighten four wingnuts just enough to prevent leakage. Excessive tightening may damage the gasket.

- Remove the aluminum cover.

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[26] *If the sampler is equipped with the flow-recorder, the circular graph paper which includes flow tracing should be removed from the sampler and be included in the bag along with exposed sample and sample record.*

[27] *The outer polybag can be the one in which the sample and record sheet was sent to the site*

- Lower the sampling head into operational position and tighten the four outside wingnuts.

- Start the sampling by turning the motor on using procedures given in section 2.2.3.2

2.4.3. Handling of filters after they are returned to a central laboratory

- In a clean area, open the outer polybag and remove the sample record sheet (and circular graph paper containing flow tracing if the sampler is equipped with a flow recorder) and the inner polybag containing the exposed filter.

- Lay the inner polybag which contains the exposed filter on a clean piece of Plexiglas and cut one edge carefully without damaging the filter.

- Using acid-washed tweezers, remove the exposed filter from the polybag and lay it on a clean piece of Plexiglas.

- Check the filter for signs of leakage. Leakage may result from worn out faceplate gasket or improper installation of the filter. When a filter is removed from the filter cartridge a rim at the edges which is approximately 1 - 2 cm thick should be free from particles (because it is covered by the faceplate gasket). A leak during sampling manifests itself by the presence of particles (coloration) at certain parts of this rim. If leakage signs are observed, void the sample, determine the cause and notify the field operator to replace the faceplate gasket or for more careful installation of the filters. Generally, a gasket deteriorates gradually, and thus the operator can decide well in advance to change the gasket before a total failure results.

- Check the exposed filter for physical damage that may have occurred during or after sampling. Physical damage after sampling would not invalidate the sample if all the pieces of the filter were put in the polybag. However, sample losses due to leakages during the sampling or losses of loose particles after the sampling (e.g., loss when folding the filter) would invalidate the sample, so mark such sample void before forwarding them to the weighing area.

- Check the appearance of the particles. Any changes from normal colour, for example, may indicate new or different sources or construction activity in the area and should be noted in the sample record sheet.

- Check the sample record sheet, to see whether all data needed to verify the sample and to calculate the concentration have been provided. Void the sample if data are missing and unobtainable after inquiry to the field operator or if the sampler malfunction is evident.

- Examine the inner (acid-washed) polybag. If the sample material has been dislodged from the filter, recover as much as possible by brushing it from the bag onto the deposit on the filter with a soft clean brush.

- Examine the filter. If insects are imbedded in the sample deposit, remove them with an acid-washed tweezer, but disturb as little as possible the sample deposit. If more than 10 insects are observed on the filter discard the sample.

- Gently place the exposed filters in the equilibration chamber (see section 2.4.1), two to a shelf so that no overlaps occur.

- Check the relative humidity every day. Record the hydrometer readings, any equilibration chamber malfunctions, and discrepancies or maintenance in the laboratory data log.

- Weigh the exposed filters to the nearest 0.1 mg on the analytical balance. It is recommended to place the analytical balance in the equilibration chamber, but if the facilities do not permit this, the balance must be placed as close to the chamber as possible and filters must be weighed within 30 seconds after they are removed from the chamber.

- Record the weight on the data record sheet.

- Lay the filter on a clean piece of Plexiglas. Cut the filters into two halves[28] and cut one of the halves into two quarter pieces. Name each piece by giving them proper ID numbers[29].

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[28] *A sharp home-made cutter is recommended to cut the filters You can make a knife by taking a proper piece of plexiglass and sharpening one end Knifes made of nickel coated stainless steel can be used (they are much more efficient than home made knives) if the samples are not going to be analyzed for Ni Stainless steel knives should be avoided as they can contaminate samples.*

[29] *The division of filters into two quarter and one half pieces is tentative. The loading of particles on the filter actually determine the way the filters should be divided The important point is that a piece spared for each analysis should have enough sample to detect parameters that will be measured. One piece must be spared for future analysis, just in case sample spared for IC or AAS analysis can be lost due to a variety of reasons, or you may want to apply a totally different analytical method to measure some additional parameters in the samples.*

- Weigh each piece[30] to the nearest 0.1 mg and record the weights in the data record sheet.

- Place one of the quarter pieces in a clean polybag and save it for the analysis of anions.

- Place the second quarter piece in an acid washed polybag and save it for the analysis of metals.

- Place the one-half piece in a third clean polybag and save it in the archive for any future analysis.

2.4.4. Transportation of samples between a central laboratory and station sites

If the central laboratory and the station are located in the same place, then there is no problem of sample transportation, because samples are changed in the central laboratory. But, stations are usually located far from the laboratory where samples are analyzed. Consequently, clean and exposed filters should be sent back and forth between the laboratory and the station site by means of postal services, cargo companies, airlines etc. Postal services are reliable for transportation of clean filters and collected samples, but handling of packages may be rough in most of the countries. Cargo can be send through airlines. Although airway transport is fast and reliable it may be expensive, particularly if filters are sent to more than one station. Special surface cargo companies or intercity bus services can also be used for sample transportation. It is almost impossible to recommend procedures for transportation, because very different means may be convenient for different stations. Whatever is the mean of transportation, reliability is the most important point. It is recommended to send clean and exposed filters in batches at regular intervals, such as 15 days. In case one batch do not reach to the destination due to problems in transportation, there must be sufficient extra clean filters to enable uninterrupted operation of the station until a new batch is sent. It is recommended to call the field operator when a new batch is sent and receive a confirmation when the batch is received at the station.

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[30] *It is recommended to reequilibriate pieces before weighing*

CHAPTER III

SAMPLING OF PRECIPITATION AND DRY DEPOSITION

3.1. General

An important process for removal of trace constituents from the atmosphere is the mechanism of precipitation scavenging. In the most general sense, wet deposition is the particulate matter that is removed from the atmosphere and deposited on the Earth's surface in precipitation. Dry deposition is gaseous and particulate matter that is transferred to Earth's surface by means other than precipitation. Deposition by fog impaction can also be important in certain areas. To remain representative on a regional scale, precipitation monitoring must exclude dry deposition. If dry deposition is avoided, scavenging processes within and below clouds are the mechanisms that control the composition of the sample. Both particles and some reactive gases are entrapped by precipitation and proper sampling and analysis of precipitation provides a measure of the burden of the trace substances in the lower troposphere and of the ability of the atmosphere to cleanse itself.

One of the most important constituents of the precipitation is sulfate. Its presence in the atmosphere, particularly on a regional scale, is due to human activities, notably the combustion of fossil fuels, which releases SO_2 into the atmosphere with subsequent oxidation to sulfate.

Nitrogen compounds in precipitation are equally important. A long series of observations in England, from 1900, show an unmistakable long term increase in their concentration; a similar trend is shown in other parts of Europe and in North America for the last 20 years. The major source of these compounds is the synthesis of nitrogen oxides from atmospheric nitrogen and oxygen during combustion at high temperatures. These oxides later appear in precipitation as nitrate. Both nitrate and sulfate derived from the processes outlined above, become strong acids when incorporated into precipitation and therefore, they lower pH of the precipitation Values of pH about 3 have been found on occasions in rural parts of Europe and North America. The acidity of precipitation is frequently used as a quantitative measure of the effect of these acids on aquatic and terrestrial systems. Sometimes, however, precipitation is highly alkaline. This is due to neutralizing effects of NH_3 and the incorporation of calcareous particulate matter. Alkalinity, a well-recognized property of sea water, is used as a measure of this effect.

Measurements of high priority are pH and the electrical conductivity. The latter is very easy to measure and is related almost linearly to total dissolved salts in precipitation. Measurement of pH is likewise relatively easy to make and have been used extensively to describe environmental conditions in relation to biological systems. There are for instance pH values established as limiting conditions for the viability of various fish species in sensitive lakes. Although scientists are not in universal agreement with respect to significance of pH measurements, this parameter is included in the high priority list.

Chloride ion and the metal ions of sodium, potassium, magnesium and calcium are normally not considered to be pollutants. Sodium, magnesium and chloride ions are largely derived from sea spray in oceanic areas. Calcium and potassium originate from deserts, from semi-arid regions and from intensely cultivated agricultural areas. They all have some biological significance and should be included wherever analytical facilities exist. In coastal areas, analysis of chloride and magnesium from precipitation is needed to estimate the part of the sulfate coming from the sea salt. In addition, measurement of all major ions in precipitation provides a means of quality control of sample analysis.

3 1.1. Sampling of precipitation

Sampling of precipitation can be divided into two categories as *bulk* sampling and *wet-only* (or wet and dry) sampling. Bulk sampling is generally performed to determine long-term total deposition trends at a given location and because of this purpose, the sampling time is long, ranging between two weeks to one month. Bulk sampling is not proper for more ambitious purposes, such as determination of sources or source regions of pollutants, or separate characterization of wet and dry deposition patterns. When bulk samplers are deployed along with a wet-only sampler the dry deposition can be estimated from the difference in concentrations. With all uncertainties in the determination of dry deposition, simultaneous deployment of a bulk and a wet-only sampler and estimating the dry deposition from the difference appears to be better than estimation of dry deposition using surrogate surfaces.

The use of bulk and wet-only sampling is recommended in the MED POL programme for different purposes. Collection of biweekly bulk deposition samples is recommended if the purpose of the study is to determine long term total deposition trends[31].

Bulk samplers were also recommended to determine dry deposition separately. If determination of dry deposition of major ions and/or trace elements is the purpose of the work or one of the purposes of the sampling performed at a station, then the recommended procedure is to deploy one bulk sampler and one wet-only sampler simultaneously and to estimate the dry deposition from the difference in measured concentrations. Recommended sampling time was again two weeks[31].

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[31] *Recommended at the Ankara meeting*

Simultaneous deployment of a bulk and wet only samplers with shorter sampling times were also recommended to obtain information on the sources of pollutants in precipitation and dry deposition. In such a case, the sampling time for the wet only sampling was one day and the sampling time for bulk sampling was 7 days[31].

Collection of wet-only samples was recommended to estimate long-term wet deposition patterns and to obtain information on the sources of pollutants in the precipitation. Recommended sampling time was 2 weeks to determine long-term wet deposition patterns and one day to obtain information on sources[31].

Since bulk, wet-and-dry and wet-only samplers are being used at the MED POL stations, procedures for all three types are presented in the following sections. However, since wet-and-dry samplers are not suitable to collect precipitation samples for trace element analysis and the wet-only sampler distributed by the UNEP/WMO to MED POL laboratories is one of the best automated samplers available in the market for sampling of precipitation for metal analysis, procedures presented in the following sections are prepared for wet-and-dry sampling for major ion analysis and wet-only sampling for trace element analysis

3.1.2. Bulk sampling.

In bulk sampling, the collector consists of a funnel and a bottle. The funnel can be an inverted bottle with its bottom cut. Such a funnel is shown to have good collection efficiency. When a bulk collector is deployed, it collects both precipitation and dry deposition during the sampling time. If precipitation occurs during sampling time wet plus dry deposition sample is collected, but if precipitation does not occur, then only dry deposition sample is collected. A typical funnel and bottle collector is shown in Figure 3.1.

The type of material used in the collection system is polyethylene or polypropylene if major ions and metals will be analyzed in the collected sample. A glass or stainless steel bottle and funnel is more appropriate for collection of samples for organic analysis, while a quartz or Teflon bottle (not necessarily funnel) should be used to collect samples for mercury analysis

The diameter of the funnel and the size of the bottle are determined by the frequency and intensity of rain and sampling time. For example, a funnel with diameter of 15 cm coupled to a 2 L collection bottle will produce approximately 200 mL sample in one week at a site where the precipitation intensity is 10 mm (typical for temperate latitudes). In dry climate which is more representative for the Mediterranean region, larger funnel diameters (such as 30 cm) and longer sampling times (such as two weeks) should be used. However, too long sampling time such as one month should be avoided to reduce the risk of sample evaporation and detoriation which results in erroneous high concentrations.

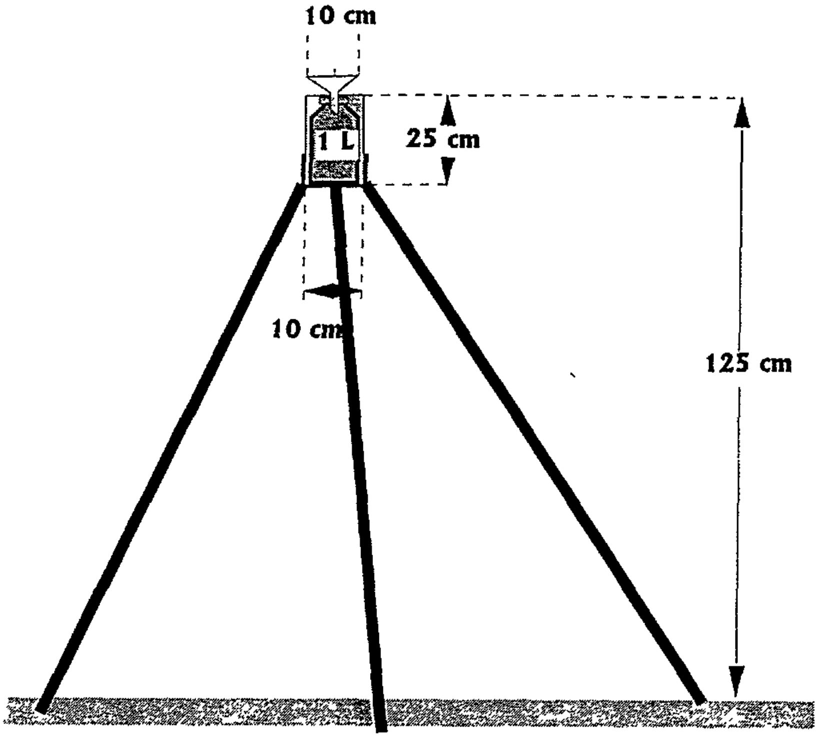

Figure 3.1 A funnel and bottle (bulk) precipitation sampler
(from Iverfeldt and Sjoberg, 1992)
(Dimensions change from one application to another)

The collection system (funnel and bottle) should be placed in an opaque cover made of PVC or similar material. The cover not only provides protection from any impact, but also the darkness within the cover prevents algae growth in the water sample which may be a problem in the warm Mediterranean sites. The cover should be cylindrical to minimize the possibility of splash[32]. It should be mounted on a plastic or wooden post which is approximately 2 m high.

If bulk samplers are to be used, two of them should be deployed in each station. One of the sampler should be used to collect samples for major ion analysis and the other one is to collect samples for the analysis of trace elements.

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[32] *In regions with cold climate additional protection to avoid freezing of water in the funnel and accumulation of snow may be needed. But, these precautions will not be discussed here as such temperatures are not expected in the Mediterranean coastal areas where most of the MED POL stations are situated*

Most of the intercalibration exercises for bulk samplers have shown that one has to be very careful to obtain desired reproducibility. Consequently, three to five samplers should be simultaneously deployed, at least for a short period to check the reproducibility of the sampling at a particular site.

Bulk samplers should be prepared in a central laboratory under clean air conditions and not in the field laboratory. Clean funnels and bottles should be supplied to the station by the central laboratory and exposed bottles and funnels should be returned to the central laboratory at regular intervals.

3.1.3. Wet-only (or wet-and-dry) sampling

Separate characterization of wet and dry deposition can be accomplished by collecting wet deposition samples during rain events and collecting dry deposition samples during nonraining periods. The important requirement in such a sampling scheme is that a wet collector should not be exposed during dry periods and a dry collector should be tightly sealed during rain events. Samplers which allow this type of sampling are called "wet-and-dry" (or wet/dry) samplers. Wet-and-dry sampling is used to determine wet and dry deposition patterns, and data generated can also be useful to answer questions on sources and source areas of measured pollutants (if sampling time is short enough and data are supplemented by trajectory analysis). If the purpose of the study is to identify source regions of pollutants or to study relation between deposition and ecosystem responses, collection of dry deposition does not provide any useful information, because (1) dry deposition is dominated by locally generated large particles and (2) there are significant uncertainties in the collection efficiencies of buckets and other surrogate surfaces used in wet-and-dry samplers. It is well established that surrogate surfaces such as Teflon or polyethylene dishes, slides or buckets do collect large particles fairly efficiently, but their collection efficiencies are poor for small particles. Furthermore, material such as Teflon and polyethylene are quite inert for the collection of gases, while vegetation surfaces and sea surface are not. Such limitations make collection of dry deposition using surrogate surfaces useless if the purpose of sampling is to study the interaction between the atmosphere and biosphere, or hydrosphere. However, collection of dry deposition samples using surrogate surfaces is useful to establish long term trends in dry deposition or to compare with studies where dry deposition samples are collected using similar surrogate surfaces.

Wet deposition, on the other hand, can be measured accurately, by analyzing precipitation samples and data can be related to long range transport, sources and wet deposition fluxes. Consequently, it is generally the only deposition that is sampled. Sampling of wet deposition only is called "wet-only" sampling. The main requirement for wet-only sampling is that the collector should not be exposed during non-raining periods[33]. This can be accomplished either by deploying the collector when rain starts and removing it when it stops (manual wet-only sampling), or by opening and closing the collector automatically with a lid which is activated by a sensor that senses the start and end of a rain event (automated wet-only sampling).

Manual wet-only (or wet-and-dry) sampling have attractive features such as economy (if personnel is already on site), no need for power source or batteries, no requirements for maintenance or repair, limited splash in very heavy rain, greater suitability for event sampling, good collection efficiency. However, it is not a practical method in long monitoring programmes, because of difficulties involved in allocating personnel who can deploy the sampler in the middle of the night for several years. However, it should be realized that manual sampling is the best approach for collection of contamination-free precipitation samples for the analysis of very trace constituents such as trace elements in short sampling campaigns.

The more common approach used to collect wet-only (or wet-and-dry) samples in monitoring programmes which continue for years is to use automated collectors. Automated samplers are attractive, because they provide more flexibility in station siting as there is no need for a 24 h-staffed station. Also, sampling is more reliable, i.e., all events and all of the rain in each event are collected. A wet-only sampler consists of a collector, a lid, a sensor, a motor which moves the lid and electronic components.

The sensor consists of an electrical circuit which is shorted by water when the rain starts. With the first drops of rain the sensor circuit is closed and this activates the motor to move the lid away from the collector funnel. Sensor is heated, so that water evaporates at a certain rate. Since there will be continuous supply of water to the sensor during rain, the lid remains away from the collector. When the rain stops, the heating element in the sensor evaporates all water, and the sensor circuit is broken and the lid is moved onto the collector funnel. The sensitivity of the sensor is important, because the highest concentrations of ions (and metals) occur in the beginning of a rain event. Consequently first drops of a rain have the highest concentrations. The sensor must be sensitive enough to open the lid immediately at the start of the rain and close it as soon as rain stops. However, a too sensitive sensor would result in frequent lid opening and closing in a light drizzle. It is preferable to have a sensor with adjustable sensitivity for different precipitation regimes and at different times of the year. The sensor should operate in the AC mode to avoid electrolysis and corrosion. Sensor grid mountings require special attention and protection against short circuiting owing to excess water.

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[33] *In wet-only sampling it is assumed that no dry deposition occurs during a rain event*

There are two important requirements in the design of the lid: (1) it should make a tight seal with the sample container to prevent the entry of the blowing dust, insects etc. into the collector and to prevent sample evaporation and exchange of gases and (2) it should avoid reintrainment of rain droplets into the collector (splash). Although there are variety of lid designs, the collectors used at the MED POL stations have lids which either slide across the collector funnel or completely moved away from the opening. The later is preferable over the first one[34]. The motor that moves the cover must be sufficiently strong to move it during heavy snowfall or freezing rain and to close it firmly on the orifice. Switches that activate the motor for cover positioning must be precise and reliable. To prevent damage to the motor, it should automatically disengage when the lid fails to open.

Automated wet-only samplers should have sufficiently rugged construction and mechanical strength to stand large temperature differences, wind buffeting and conditions of heavy snow loading and freezing precipitation. Materials and mountings must be corrosion-resistant. The cover assembly in particular, must be strong enough to stand snow load and freezing precipitation, and must position itself accurately.

Collection efficiency of the sampler should be as high as possible[35]. Consequently, the sampler should have proper aerodynamic design to maximize sample collection efficiency. In any case, a standard national rain gauge should be installed at the sampling site and precipitation amount corresponding to each sample should be determined from the rain captured by the gauge[36].

Evaporation of a collected sample is an important problem, particularly in the Mediterranean region due to relatively high temperatures. The problem of sample evaporation is more serious than incomplete sample collection, because evaporation results in erroneous high concentrations of measured parameters.

Collector materials should be polyethylene or polypropylene[37]. Teflon containers are the best, particularly if the collected sample will be subsequently analyzed for trace elements, but they are expensive.

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[34] *If the lid is not designed to avoid the splash, a screen laid on the lid may reduce the possibility of splash*

[35] *Due to their lid mechanism, wet-only (or wet and dry) samplers can not be 100 % efficient.*

[36] *Recording rain gauges also provide information on the intensity of precipitation and should be preferred.*

[37] *Assuming that a collected precipitation sample will be analyzed only for inorganic ions and trace elements Glass or stainless steel collectors are more suitable for determination of organics and collectors must be made of quartz or teflon for analysis of mercury in precipitation.*

3.2. Preparation of sampling bottles at a central laboratory

Sample handling in a central laboratory before sample bottles are sent to a field station includes cleaning and weighing of bottles and preparation of sample record sheets[38].
The first step is to prepare a sample record sheet for each of the bottles that will be send to the station. Sample ID, site ID and the weight of the empty bottle should be filled in at the central laboratory.

Volume of a collected sample should be measured by weighing the collected sample, because the use of a graduated cylinder would increase the risk of contamination. Since the density of rain water is approximately 1.0 $g \cdot mL^{-1}$ at 20°C , the weight of the sample will be equal to its volume. Weight of the sample should be determined from difference of the weights of the empty and filled bottle Consequently, all the bottles should be weighed before they are shipped to the station. Size of the bottles used depends on the sampling time. The balance should be capable of handling the sample size (or water amount) that is used in the monitoring programme. For example, for bi-weekly sampling, the balance should be capable of weighing 5 kg to the nearest 10 g. In weekly sampling the balance should be capable of weighing 2 kg to the nearest 1 g. In case of daily sampling, the balance used should be capable of weighing 1 kg to the nearest 1 g. The weight of the bottle should be recorded in the sample record sheet that will be sent to the station along with the sample bottle.

Cleaning of sample bottles and other plastic equipment used in sampling and analysis is one of the most important steps in the contamination-free sampling Cleaning procedures differ significantly for bottles used in sampling for metal analysis and those used in sampling for ion analysis.

Acids can not be used to wash sample bottles which will be used to collect samples for ion analysis, because acids which are commonly used for cleaning plasticware, such as HNO_3 and HCl increase blank levels in the NO_3^- and Cl^- measurements, respectively Since ions measured in precipitation are all water soluble, careful cleaning of bottles and other plasticware using detergent and distilled deionized water is generally sufficient to remove most of the ions. The following procedure can be used to clean sample bottles, funnels of bulk samplers and all plasticware used in the analysis of ions:

- Rinse with detergent (e.g., luquinox) in hot deionized water

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[38] *Assuming that samples collected in buckets in wet/dry samplers are transferred to sample bottles in the field station If buckets are transferred back and forth between the central laboratory and the field station, they should also be cleaned in the central laboratory*

- While rinsing remove particulates and dirty films from the previous sample using a plastic brush.

- Rinse six times with distilled deionized water.

- Check the conductivity of the final rinse. It should be less than 2 mS cm $^{-1}$
- Air dry in the clean area (see section 1.3.5).

Concentrations of trace elements in precipitation are very low. Thus, accurate measurements of trace element concentrations in wet deposition require a protocol which is even more rigorous than the methods used in the collection of precipitation for pH and major ion measurements. The following guidelines should be followed to minimize the risk of contamination in precipitation sampling for metal analysis:

- Sampling bottles and containers used in the laboratory should be polyethylene or polypropylene.

- All the plasticware should be vigorously washed with strong acids.

- The water used should be very pure (nano-Q)[39].

- All acids used should be very pure[40].

Metals are adsorbed on the walls of the container and do not come out by simple rinsing with detergent and distilled deionized water Consequently, bottles that will be used in sample collection and other plasticware used in the analysis should be washed vigorously with strong acids.

There is no standard cleaning procedure to wash polyethylene sampling bottles. Different cleaning procedures are being used by different laboratories. The common feature in all cleaning procedures is to use strong acids such as HNO_3 and HCl to desorb metals from walls of the containers. The following cleaning procedure can be used to clean all plasticware used in the sampling and analysis of precipitation for trace elements[41]:

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[39] *Deionizers which produce nano-Q water are commercially available (but they are not cheap). Either water from such units should be used or distilled deionized water produced in the laboratory should be further cleaned by subboiling distillation in an all quartz still*

[40] *Ultra pure acids are commercially available. Either such high purity acids should be purchased, or reagent grade acids should be cleaned by subboiling distillation in a all-quartz still.*

[41] *From Tramontano J. M., Scudlark J R., Church T M , A method for the collection, handling, and analysis of trace metals in precipitation. Environ Sci. Technol., **21**, 749-753 (1987)*

- Wash with detergent and deionized water.
- Rinse 3 times with deionized water.
- Shake off the excess water.
- Soak inside with Spex-grade acetone for 10 minutes.
- Shake off excess acetone.
- Swirl inside with concentrated reagent ACS HCl.
- Rinse 3 times with distilled water.
- Swirl inside with concentrated reagent ACS HNO_3.
- Rinse 3 times with distilled water.
- Place in warm 6N reagent ACS HNO_3 for 2-3 days.
- Transfer to 2N HNO_3 bath and soak for 2-3 days.
- Rinse outside of the container with deionized water.
- Rinse inside of the container 3 times with double-distilled water.
- Rinse inside of the container with nano-Q water.
- Dry under filtered air in a clean hood or bench.

Sample bottles that will be used in precipitation sampling for trace metal analysis should be acidified to avoid on-wall losses. Acid can be added to the bottle before or after sampling. Although, addition of acid before deploying the bottle in the station avoids adsorption of metals on the walls, it introduces logistic problems, such as the requirement of a special protocol to transport acid containing bottles to the station, or technical problems such as evaporation of acid in the sampler during summer. There are some evidence which suggest that addition of acid after sampling can completely desorb metals from the container walls. However, additional research is needed on the success of post sampling acidification.

- For the MED POL programme, addition of acid before sample bottles are deployed at the station was recommended[42]. However, acid content should be adjusted after sampling so that final sample should have 0.5% HNO_3 in it[43].

Bottles washed and dried (and acidified if they will be used for metal analysis) should be placed in polyethylene bags. It is recommended not to write on the bottles which will be used for sampling of precipitation for metal analysis. Information should be written on the polyethylene bag (information can be written on a sticky paper which is then sticked on the bag, or it can be directly written on the bag with a marker and water insoluble ink). Polyethylene bags which contain sampling bottles should be placed in a second polybag together with the sample record sheet.

3.3. Sampling and sample handling at a station

Sampling and sample handling at a station includes deploying bulk samplers, changing buckets in a wet/dry sampler, changing bottles in a wet only sampler, transferring precipitation samples from a wet-side bucket to a sample bottle, solubilization of dry deposition samples in the dry-side bucket and transferring the suspension to a sampling bottle, measurement of conductivity and pH, preparation of sample bottles for transportation and storage of the bottles until they are shipped to a central laboratory.

The main philosophy presented throughout this manual is to perform minimum sample handling in the field station where conditions may not be appropriate for handling precipitation samples with very low concentrations of ions and metals. However, even the minimum sample handling requires certain activities such as transferring samples from collectors to bottles, measuring conductivity and pH, etc. All necessary precautions to minimize the risk of sample contamination which were discussed in various parts of this manual, such as wearing labcoat, polyethylene or latex gloves, not touching collectors and bottles by hands, to use plastic or polyamide tweezers etc., should be taken.

3.3.1. Bulk deposition sampling

The following procedure is recommended for bulk deposition sampling and processing of collected samples at a station. The procedure is quite simple, because in bulk sampling, the whole sampler will be transferred between the central laboratory and the station.

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[42] *Ultra pure HNO_3 can be added to the sample bottles in the central laboratory or in the field laboratory. Since addition of acid in the field laboratory can increase the risk of contamination, it is recommended to add the acid in the bottle at the central laboratory*

[43] *Recommended at the Ankara meeting*

- Investigate both ion and metal samplers[44]. Make sure that the posts and bird-rings are firm.

- Remove the exposed ion sampler from the PVC cover loosening two screws located at both sides of the cover.
- Place the whole sampler in a clean polyethylene bag and carry it to the field station making sure that it is not tilted during the trip.

- In the field station, remove the sampler from the polybag, and investigate the funnel. Report any unusual observations (such as collection of large objects, accumulation of too many insects, etc.) to the sample record sheet.

- Unscrew the funnel, put the cap on the bottle and carefully tighten the cap.

- Measure the electrical conductivity and pH using the procedures given in sections 3.3.9 and 3.3.10.

- Place the exposed bottle and funnel in separate polyethylene bags and seal each of the bags.

- Write the following information on each of the bags:
  - Sample ID
  - Sampler-on date and time
  - Sampler-off date and time

- Repeat the procedures for the exposed metal sampler on the platform[45].

- Carry two clean samplers to the sampling platform. Make sure one of the samplers is designated as the metal collector (to collect samples for analysis of trace elements) and contains acid and the other one is designated as the ion collector (to collect samples for ion analysis)[46].

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[44] ***Metal sampler*** *refers to the bulk sampler which collects samples for trace element analysis and* ***ion sampler*** *refers to the bulk sampler which collects samples for the analysis of major ions*

[45] *Conductivity and pH measurements should not be performed for the samples collected for metal analysis, because bottles are acidified in the central laboratory.*

[46] *It is recommended to color-code samplers for metal and ion analysis. Identical color coding should also be on the PVC covers or the posts at the platform*

- Carefully remove the ion sampler from the polyethylene bag in which it is sent, making sure that the insect net which should be at the neck of the funnel is in its place. If the net is dislocated, put it to the neck of the funnel using a clean tweezer.

- Place the sampler in the PVC cover which is fixed on a plastic or wooden post and have similar colour coding with that on the sampler. Make sure that the sampler snugly fits to the cover and the funnel slightly protrudes from the top of the PVC cover. Secure the sampler in the cover by tightening two screws on both sides of the cover.
- *Secure the clean metal collector in its cover using the procedures given for the ion* collector.

3.3.2. Sampling precautions

Samples should be stored in a cool container A refrigerator with +4°C is the ideal storage place.

Since the temperature at most of the Mediterranean stations will be between 30 - 40°C during summer season, growth of algae and detoriation of samples can be a problem if the sampling time is long (such as two weeks). If preservation of the sample integrity when the sampler is exposed is a problem, then collected samples can be transferred to a bottle at regular intervals (such as every day or once every two days) and the bottle can be stored in a refrigerator. However, such a procedure should be avoided as much as possible, because any unnecessary sample handling in the field laboratory increases the risk of contamination.

Sampling units should be inspected once a week to see that everything is in order.

At certain sites, birds have the habit of sitting on the funnel, if such problem is encountered, "bird rings[47]" should be used. Bird rings should not be made of metal or should be coated with plastic.

All the following precautions should be taken to avoid sample contamination during sampler change:

- Technicians should wear polyethylene or latex gloves and labcoats.

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[47] *Bird ring is a cogged circular cover which has diameter slightly larger than the diameter of the funnel. It should be positioned at approximately 10 cm above the top of the funnel and should be fixed to the PVC cover.*

- Never touch the inside of the bottle even if you are wearing a glove. If the insect net should be positioned, this should be done using tweezers.

- Never touch the neck of the sampling bottle when the funnel is being removed.

- Perform all activities in a clean area (see section 1.4) in the field laboratory.

Any unusual event should be reported in the sample record sheet.

3.3.3. Wet-and-dry and wet-only deposition sampling

A number of automated precipitation samplers and accessories are available. While the operating instructions are specific for a particular model, the instructions and hints given in this section can apply generally to most automated deposition samplers.

Two specific deposition samplers discussed here are the Andersen Acid Deposition Sampler and the Karl Bleymehl, Model KFA wet-only collector. The Andersen sampler represents a design which is being used by a number of manufacturers (such as AeroChem Metrics). It is one of the most widely used wet-and-dry samplers. Although its performance proved to be good for precipitation and dry deposition sampling for analysis of pH and major ions, it use can not be recommended if the collected samples will be analyzed for trace elements.

The Karl Bleymehl, Model KFA collector is specifically designed for collection of precipitation samples for subsequent trace element analysis. The sampler was provided by UNEP and WMO to a number of laboratories participating in the MED POL programme, and it is presently one of the standard equipments at the MED POL stations.

3.3.4. Sampling of wet and dry deposition using the Andersen wet/dry sampler

The sampler consists of two symmetrically placed collector-holders each containing 15 L capacity polyethylene buckets, a lid which slides across the buckets, a motor which drives the lid, a sensor which activates the motor when rain starts and stops, and a cycle counter which basically records the number of times the wet side bucket is closed and opened.

The sensor detects precipitation episodes and activates the cover drive mechanism to seal the dry deposition collector and expose the wet deposition collector. When the precipitation ends, the heated sensor dries and activates the cover drive mechanism to seal the wet collector and expose the dry deposition collector.

The instrument has such advantages as relatively low price (compared to other automated precipitation collectors), quite rugged structure to operate trouble-free in the field and a reliable sensor. However, the sensor is fixed and its position is not sufficiently far from the wet side bucket to avoid the splash. Similarly, the cover has a peaked roof and splash of raindrops is possible, at least during heavy rain, when it is situated on the dry side bucket.

The Andersen rain sampler and instruments which have the same design are widely used to collect wet and dry deposition samples for pH and major ion analysis. The buckets are large and collected samples should be transferred to sample bottles in the field station[48]. After sample transfer, collectors should be cleaned and dried again in the field. All of these procedures increases the risk of sample contamination Collection of precipitation samples for trace element analysis is not recommended with this type of sampler[49]. The general view of an Andersen wet/dry sampler is shown in Figure 3 2

Collection of wet and dry deposition samples with the Andersen sampler includes replacing exposed wet and dry side buckets at the end of the sampling time, transferring the collected precipitation samples from buckets to sample bottles, transferring the dry deposit to another sample bottle, cleaning and drying buckets for the next sampling period[50].

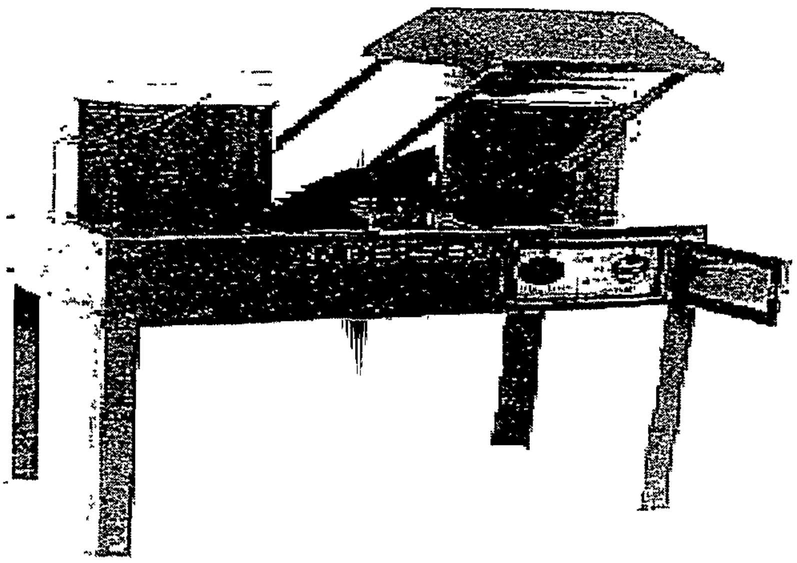

Figure 3.2 A wet-and-dry sampler (Andersen Acid Precipitation Sampler)

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[48] *In major networks where instruments with similar design are used (such as NADP/NTN network), whole buckets are send back and forth between the central laboratory and the station. But this requires large number of buckets and can not be recommended for the MED POL programme*

[49] *Samplers with similar design were used for metal measurements after certain modifications to reduce chance of contamination.*

[50] *In the formulation of the sample changing procedure, it is assumed that four buckets are available at a field station.*

The following procedure can be used to change collectors and to handle them in the field laboratory.

3.3.5. Removal of the wet-side bucket from the sampler

- Inspect the site and equipment for any damage.

- Inspect the contents of the dry side bucket and note any water that may be present.

- Short out the sensor grid with water. **DO NOT USE METALS TO SHORT THE GRID**. Apply enough water to ensure that the collector stays open for 5-10 minutes. After the collector has been open for 5-10 minutes, check to make sure the sensor plate is warm.

- Allow the lid mechanism to move over and cover the dry-side bucket. Observe the movement of the lid. It should operate freely with little motor noise and rest snugly over the bucket.

- Examine the contents of the wet side bucket for any sign of contamination.

- Remove the clean bucket-lid from the polyethylene bag in which it is carried to the platform.

- Place the bucket lid on the wet side bucket.

- Loosen the two springs which secure the bucket to the bucket holder and remove the bucket and the lid.

- Remove the clean bucket and lid from the polyethylene bag in which they are carried to the platform and place them in the wet-side bucket holder.

- Secure the bucket in the holder by the two springs which are fixed on the bucket holder.

- Remove the bucket-lid from the bucket and allow the sampler lid to move onto, and sit snugly on the wet-side bucket (by blowing the water off the sensor).

- Carefully transport the exposed bucket and lid back to the field laboratory.

3.3.6. Removal of dry-side bucket from the sampler

Procedures to remove dry-side bucket from the sampler is identical with the procedure to remove wet-side bucket, which is given in the previous section[51].

3.3.7. Handling of wet-side buckets in a field laboratory

- In the field laboratory, open the lid and lay it on a clean peace of polyethylene.
- Remove one of the clean sample bottles from the polyethylene bag and place it in the bottle holder.
- Remove a funnel from the polyethylene bag in which it is stored and place it in the funnel holder.
- Make sure that the tip of the funnel extends into the sample bottle.
- Carefully, pour the sample collected in the bucket, into the sample bottle, through the funnel.
- Place the cap of the sample bottle and tighten it.
- Carefully wash the funnel with several aliquots of distilled deionized water and dry on a clean sheet of polyethylene.
- Place the sample bottle containing the sample on the balance and determine the weight to the nearest 1 g. Record the weight on the sample record sheet.
- Measure the conductivity and pH using the procedures given in sections 3.3.9 and 3.3.10.
- Wash the bucket thoroughly, with detergent and tap water first, then rinse it with several aliquots of distilled deionized water.
- Allow it to drain by turning it upside down on a clean surface.
- When it is completely dry, place the bucket, the lid and the funnel in separate polyethylene bags and store until the next bucket change.

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[51] *Except the sampler lid should stay on the wet-side bucket while the dry-side bucket is being replaced.*

3.3.8. Handling of dry-side buckets in a field laboratory

The procedure for handling dry deposition samples is different from that of wet deposition samples. Dry deposition samples must be solubilized for subsequent analysis. The procedure to remove dry deposit from the bucket depends on the parameters that will be determined in the sample. If only ions are going to be measured, then rinsing the bucket with distilled deionized water is sufficient, but if metals are to be analyzed in the central laboratory, then water that will be used to remove dry deposit from the bucket should include pure HNO_3. The following procedure is given as an example assuming only ions will be subsequently analyzed.

- In the field laboratory, open the lid and lay it on a clean peace of polyethylene.

- Remove one of the clean sample bottles from the polyethylene bag and place it in the bottle holder.

- Remove a clean funnel from the polyethylene bag in which it is stored and place it in the funnel holder.

- Make sure that the tip of the funnel extends into the sample bottle.

- Fill a volumetric flask (with 500 mL capacity) with distilled deionized water and adjust the volume up to 500 ml.

- Slowly pour approximately 100 mL of water from the flask into the dry-side bucket, carefully swirling the bucket and rinsing the sides.

- Pour the mixture from the bucket through the funnel into the sample bottle.

- Repeat the rinsing of the bucket and transferring the deposit to the sample bottle (previous two steps) for five times with approximately 100 mL aliquots of distilled deionized water from the volumetric flask.

- Make sure that all the water and dry deposit in the dry-side bucket is transferred to the sample bottle.

- Close the cap of the sample bottle.

- Wash the bucket and the funnel thoroughly, with detergent and tap water first, then rinse it with several aliquots of distilled deionized water.

- Allow it to drain by turning it upside down on a clean surface.

- When it is completely dry, place the bucket, the lid and the funnel in separate polyethylene bags and store until the next bucket change.

3.3.9. Conductivity measurement

The procedure given below is recommended for bulk, wet and dry deposition samples. It is assumed that dry deposition samples are transferred from bucket to the sample bottle.

- Rinse the conductivity cell at least three times with distilled deionized water.
- Rinse once with 75 $mS \cdot cm^{-1}$ standard[52] solution.

- Measure the electrical conductivity of a 75 $mS \cdot cm^{-1}$ standard solution with the cell.

- If your conductivity meter has a calibration control, standardize the meter following the procedures given in the operation manual using the 75 $mS \cdot cm^{-1}$ standard solution.

- Record the value to the nearest 0.1 $mS \cdot cm^{-1}$ in the sample record sheet (in the space marked STANDARD MEASURED).

- Calculate the correction factor to the nearest 0.001 by dividing the standard certified (75.0 $mS \cdot cm^{-1}$) by the standard measured.

- Record the value in the sample record sheet.

- Rinse the cell three times with distilled deionized water, discharging each rinse. Use a fourth portion to determine conductivity(or specific conductance) of the distilled deionized water.

- Record the reading in the sample record sheet[53].

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[52] *The standard electrical conductivity solution should be supplied by the central laboratory.*

[53] *This value should be the lowest reading you are able to obtain after repeated rinsing. It should not exceed 2 If a value more than 10 is measured do not continue with measurements Instead obtain a new supply of distilled deionized water and repeat the procedure*

- Rinse the cell three times with distilled deionized water, discarding each rinse.

- Open the cap of the sample bottle and lay it on a clean surface.

- Pour approximately 20mL of aliquot from the sample into a clean disposable cup.

- Put the cap back on the sample bottle and tighten it. After making sure the seal is good, lay the bottle on a clean surface.

- Pour approximately 3 mL of the sample in the cup in a sampling vial.

- Rinse the conductivity cell with the sample in the sampling vial.

- Pour additional 3-4mL of the sample to the same sampling vial.
- Measure the sample conductivity using the sample in the vial.

- Record this value to the nearest 0.1 $mS \cdot cm^{-1}$ to the sample record sheet.

- Multiply this factor with the correction factor and record the result of calculation in the sample record sheet.

- Rinse the cell three more times with distilled deionized water, and then fill the cell with water.

- Cover the cell with parafilm or inverted sampling vial to prevent evaporation.

3.3.10. pH measurement

Like the conductivity measurement described in section 3.3.9, the procedure given for the pH measurement is recommended for both wet and dry deposition samples.

- Adjust the temperature control on the pH meter to room temperature[54].

- Rinse the electrode several seconds in a flowing stream of distilled deionized water[55].

- Fill one of the sample vials with the pH 7.00 buffer

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[54] *If a thermometer is not available, adjust the temperature control to 25^{0}C*

[55] *Make sure that any accumulated salts are dissolved from the tip of the electrode*

- Insert the electrode into the vial and allow it to remain there for 30 seconds.

- Discard the buffer and without any rinses refill the "conditioned vial" with the pH 7.0 buffer.

- Insert the electrode tip into the vial, allow sufficient time for the reading to become stable (within 0.001 pH units)

- Adjust the calibration control to read 7.00.

- Rinse the electrode thoroughly with distilled deionized water.

- Gently blot the electrode tip with a clean laboratory wipe (such as Kimwipe)
- Fill a clean vial with the pH 4.00 buffer.
- Repeat the conditioning rinse as described before for the pH 7.00 buffer.

- Remove the electrode and dump the buffer.

- Refill the vial with the pH 4.00 buffer and insert the electrode again.

- Allow sufficient time for the reading to become stable (approximately 30 seconds).

- Adjust the "slope control" of the pH meter to read pH 4.00.

- Rinse the electrode thoroughly with deionized or distilled water and gently blot the electrode tip.

- Fill a clean vial with sample, by pouring from the cup containing sample aliquot.

- Insert the electrode into the vial and allow it to remain there for 30 seconds.

- Remove the electrode and dump the conditioning rinse.

- Refill the vial with the sample and reinsert the electrode directly into the refilled vial.

- Allow the system to stabilize for approximately 30 seconds.

- Read the pH value of the sample and record it in the sample record sheet.

- Discard any remaining sample aliquot and any used sample vials.

- Rinse the electrode thoroughly with distilled deionized water and blot the tip with a clean absorbent laboratory wipe.

- Wrap the tip of the electrode with parafilm.

- Store the pH meter and electrode in a suitable place.

- Place the sample bottle in a clean polyethylene bag and heat-seal it.

- Place the polyethylene bag containing the sample bottle and sample record sheet into a second polyethylene bag and heat seal the bag.

- Record the same information on the inner bag to the outer bag as well.

- Store the sample at +4°C until it is sent to the central laboratory.

3.3.11. Wet-only sampling using the Karl Bleymehl sampler

As mentioned in the previous section, the Karl Bleymehl, model KFA wet-only sampler was provided to a number of MED POL stations. The equipment is designed to collect precipitation samples for metal analysis. It consists of a polyethylene collection funnel of 27.6 cm in diameter which is placed on a heatable mantle. The funnel is connected to a 5 L capacity polyethylene collection bottle through a filtration unit which contains a 0.45 mm pore size membrane filter to remove insoluble particles from the precipitation.
A heatable lid seals the sampler during non-raining periods. The sampler lid is completely removed from the vicinity of the funnel during rain, to avoid reintrainment of rain droplets to the funnel.

The sensor which activates the lid is separated from the collector and can be mounted up to 2 m away from the sampler.

The sampler also has a 7 day automatic sampling option. If this option is used, precipitation from each day is collected in a separate 1 L polyethylene bottle. The collector can operate both on AC line voltage and on a car battery. Schematic view of the sampler is shown in Figure 3.3.

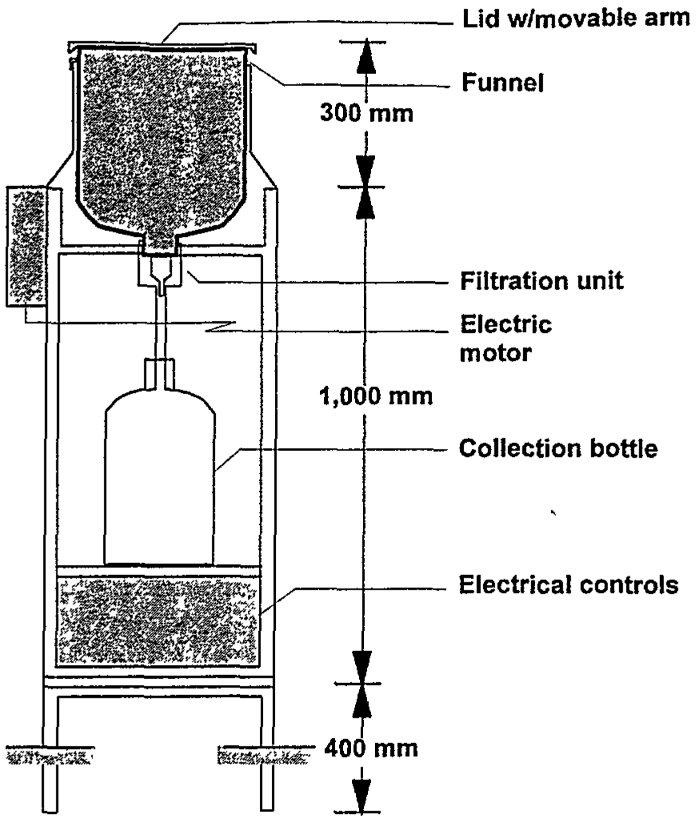

Figure 3.3 Schematic view of a wet-only precipitation sample (Karl Bleymehl, Model KFA)

Since samples are collected in bottles and no transfer of collected samples is necessary, sampling procedures are relatively straightforward. The following set of instructions can be used to change bottles and clean the sampling system:

- Open the door of the aluminum housing of the collector, exposing the filtration system and the collection bottle.

- Carefully remove both the bottle and filtration system from the sampler, place them in a clean polyethylene bag and carry to the field laboratory.
- In the field laboratory, remove the filtration unit and the tubing which connects it to the sampling bottle by unscrewing the cap from the bottle.

- Tightly close the bottle containing a precipitation sample with a clean cap.

- Using clean tweezers, remove the membrane filter from the filtration unit and place it in a clean petri dish[56].

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[56] *If the insoluble fraction is not be analyzed, the filter should be discarded*

- Carefully clean the filtration unit and the tubing, first with dilute HNO_3 solution then with several aliquots of distilled deionized water.

- Clean the funnel in the sampler using the same procedure.

- Place the exposed sample bottle and the petri dish containing the filter in a clean polyethylene bag and heat-seal.

- Place the polyethylene bag containing the sample bottle and the petri dish in a second polybag together with the sample record sheet.

- Store the bag in a refrigerator until it is shipped to the central laboratory.

- Place a clean membrane filter in the filtration unit.

- Remove a clean acidified sample bottle from the polyethylene bag in which it is transported from the central laboratory, remove its cap and screw the filtration unit to the sample bottle.

- Carry the sample bottle and the filtration unit to the sampler and tightly screw to the funnel.

- Close the door of the aluminum housing.

In the formulation of the procedure for changing sample bottles in the wet-only sampler it was assumed that the bottles are acidified at the central laboratory before they are shipped to the station. This scheme is convenient if a separate sampler is being used to collect precipitation samples for ion analysis[57]. However, if the sampler is the only precipitation sampler at the station, and both ion and metal measurements are to be conducted on the same sample, then bottles can not be acidified before sample collection. In this case, precipitation samples should be collected in bottles which are not acidified. At the end of the sampling, some part of the sample should be poured into another clean acidified polyethylene bottle for metal measurement The conductivity and pH should be measured in non-acidified aliquot using the procedures given in sections 3.3.9 and 3.3.10.

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[57] *Recommended at the Belgrade meeting*

3.4. Blanks

In precipitation samples, particularly in samples collected for metal analysis, blank measurements play a very important role. Contamination of precipitation samples by ions and metals is a strong possibility, as mentioned many times in this manuscript, because of very low concentrations being measured. Frequent analysis of field blanks is the only way to detect and correct any contamination problem before substantial time, effort and money is wasted.

Requirements for laboratory blanks in precipitation and dry deposition samples are the same as for the laboratory blanks in aerosol samples which are discussed in section 2.2.8. Laboratory blanks include analysis of reagents and simulation of processes in the laboratory, and they are important to estimate the contribution of each reagent and laboratory process to the field blank values.

Field blanks, which are the most important ones include simulation of all steps in sampling, sample handling and analysis. Procedures used in obtaining field blanks should be identical with procedures used to collect samples. Since, sampling procedures for bulk, wet/dry and wet-only samplers used in the MED-POL stations are different, procedures for collecting field blanks with these samplers also differ. Whatever the type of sampler, number of blanks analyzed should make-up 5 - 10% of total samples collected at the site.

The following procedure can be used to collect field blanks with bulk samplers:

- Select one of the collectors prepared in the central laboratory for collection of a bulk deposition sample for blank collection.
- Deploy the sampler using procedures given in section 3.3.1.
- Carefully pour 100mL of distilled deionized water rinsing the sides of the funnel.
- Remove the sampler using procedures given in section 3.3.1.

Sample handling procedures both at the field station and at the central laboratory are identical with the those used for collected samples.

The following procedure can be used to obtain a blank sample for the wet-side bucket in a wet-and-dry sampler:

- Install a clean bucket to the wet-side compartment of the wet-and-dry sampler using procedures given in section 3.3.7.
- Carefully pour 200 mL distilled deionized water rinsing the sides of the bucket.
- Remove the wet-side bucket from the sampler using procedures given in section 3.3.5.
- Perform the sample handling procedures given in section 3.3.7 to transfer the blank into a sample bottle, and to measure the conductivity and pH.
- Clean the bucket using the procedures given in section 3.3.7.
- Indicate in the sample record sheet which comes with the bottle that the bottle contains wet deposition blank.
- Install a new, clean bucket to the sampler using the procedures given in section 3.3.7.

The bottles containing the blanks should be shipped to the central laboratory along with the collected samples. In the central laboratory they should be handled and analyzed using the procedures given for precipitation samples.

The following procedure can be used to collect a blank for the dry-side bucket in the wet-and-dry sampler:

- Install a clean bucket to the dry-side compartment of the sampler using procedures given in section 3.3.8.
- Allow the bucket to stay on the sampler (with the lid on the wet side) for approximately 10 minutes.
- Remove the bucket from the sampler using procedures given in section 3.3.6.
- In the field station use procedures given in section 3.3.8 to suspend the dry deposit (which does not exist in the blank), to transfer to a sample bottle, to measure the conductivity and pH (section 3.3.9 and 3.3.10 respectively).
- Indicate in the sample record sheet which comes with the bottle that the bottle contains dry deposition blank.

- Install a clean bucket to the dry-side compartment of the wet-and-dry sampler using the procedures given in section 3.3.8.

The procedures for the shipment of the blank to the central laboratory as well sample handling and analysis procedures in the central laboratory should be identical with those used for the samples.

The following procedure can be used to collect a blank sample from the wet-only sampler:

- After routine removal of a sample bottle from the sampler (along with the filtration system) and cleaning funnel (for the procedures see section 3.3.11) install a clean sample bottle to the sampler using procedure given in section 3.3.11.

- Carefully pour 100 mL distilled deionized water, rinsing the sides of the funnel.

- Remove the sample bottle (and the filtration system) from the sampler using procedures given in section 3.3.11.

- In the field laboratory, indicate in the sample record sheet which comes with the bottle that the bottle contains the blank.

The sample bottle containing the blank should then be sent to the central laboratory along with the samples. In the central laboratory, blank should be treated like a sample and analyzed accordingly.

3.5. Sample record sheets

No matter what type of sampler is used at the station, every sample should be accompanied with a sample record form. The form should be prepared in the central laboratory and sent to the station along with sample bottles. The lay-out of the form may vary, but it should include the following information:

- Sample ID (should be recorded in the central laboratory).

- Site ID (should be recorded at the central laboratory).

- Weight of the empty bottle (to be recorded in the central laboratory).

- Sampling start date and time (should be recorded at the station).

- Sampling end date and time (should be recorded at the station).
- Weight of the sample + bottle (should be recorded at the station).
- Conductivity measured at the station (should be recorded at the station).
- pH measured at the station (should be recorded at the station).
- Type of precipitation (should be recorded at the station).
- Comments which includes: (should be recorded at the station).
  - Objective evaluation of weather conditions at the start and at the end of the sampling (if the station is visited during a sampling period, weather conditions at that particular time should also be included).
  - Observations (unusual) on the sampler at end of the sampling.
  - Observations on the operation of samplers (e.g., lid failure, tilting of bulk samplers, power failures in case of automatic samplers etc.,).
  - Observations on the condition of the sample (e.g., possible contamination, excessive particulate material).
  - Observations on the sample handling in the field laboratory (e.g., spilled sample, failure of pH electrode etc.).

CHAPTER IV
ANALYSIS OF AEROSOL AND PRECIPITATION SAMPLES

4.1. General

Chemical analysis of precipitation and aerosol samples is characterized by the need for routine analysis of extremely low concentrations. Concentrations of both ions and trace elements are low, particularly in precipitation samples. Preparation of samples requires the utmost attention such as using ultra pure acids and water, use of expensive PTFE labware, use of analytical instruments with high sensitivity, etc. The need for routine analysis of such samples imposes additional constraints on the analysis. Any laboratory can analyze a few samples of low trace metal concentrations, paying careful care. However, analysis of hundreds or even thousands of such samples, paying the same attention may not be possible, unless a system is designed particularly for that purpose. Such a system requires standardized and proven procedures at every step from opening the sample, until its injection to the instrument. It also requires highly experienced researchers and technicians and a comprehensive data quality assessment procedure to detect problems. If a problem leading to erroneous results is detected some time after, substantial laboratory time and man power would be wasted and expensive samples could be lost.

Composition of aerosol and precipitation samples are quite similar, because ions and metals in precipitation are derived from the particulate material incorporated into rain by incloud and below cloud processes. Consequently, analytical techniques used for analysis of precipitation and aerosols are also the same. They only differ in sample preparation.

Most of the major ions are water soluble. Hence, precipitation samples can be analyzed for major ions without extensive sample preparation. This is also true for the major ions in aerosol and dry deposition samples. Ions can be easily dissolved by treating aerosol and dry deposition samples with distilled deionized water.

Sample preparation procedures for analysis of metals in precipitation and aerosols have to be more exhaustive, because metals are not as soluble as ions.

Precipitation samples collected for metal analysis are acidified either before or after sampling. Consequently, samples contain 0.5% HNO_3 when they arrive at the laboratory. Elements Cd, Pb, Cu and Zn are soluble in a dilute HNO_3 solution and can be directly analyzed without substantial sample treatment. But if elements like Al and Si which occur in an aluminasilicate matrix are going to be measured, then insoluble phase should be separated from the rainwater through filtration and digested with strong acid mixtures. Concentrations measured in both soluble and insoluble fractions should be added to obtain total concentrations of these elements in wet deposition.

Analysis of aerosols for metals requires total dissolution of particles collected on the filters and subsequent analysis by instrumental techniques. Elements that are measured in the MED POL programme include Na, Al, Cd, Pb, Cu and Zn[58]. With the exception of Al all of these elements are soluble in HNO_3. However, Al occurs in the silicate matrix of the crustal material and can not be solubilized by treatment with HNO_3. Consequently, aerosol samples should be treated at least with a mixture of HNO_3 and HF to dissolve Al. The main problem in the dissolution of aerosol samples is generally the filter rather than particles collected. The weight of the glass fiber or cellulose filters are approximately 4 g. Analysis of a quarter filter means that approximately 1 g of cellulose or glass fibers should be dissolved along with a few mg of particulate material[59].

Dissolution of filter matrix and particles collected on it is called sample digestion. The digestion can be carried out under pressure using high pressure Teflon digestion vessels (commonly called "digestion bombs") or under atmospheric pressure (called "open digestion").

A digestion bomb consists of a Teflon vessel placed in a heavy stainless steel jacket. A pressure relief mechanism is usually included in the design to avoid explosion if the pressure exceeds the certified value. Variety of these bombs are commercially available. A typical example is shown in Figure 4 1. In the digestion bomb, a sample filter and a few mL of acid mixture are placed in the Teflon vessel which in turn is put in the stainless steel jacket. The cap is tightly closed and the bomb is heated on a hot plate or in an oven for 1 - 1.5 h at approximately 150°C. During heating period, the acid mixture in the Teflon vessel quickly decomposes the filter and particulate material under high pressure and temperature. Generally, digestion which takes about two days under atmospheric pressure can be completed within 1 - 2 hours in the digestion bomb. At the end of heating, the bomb is removed from the hot plate (or from the oven) and cooled to room temperature. Contents are poured in a polyethylene or Teflon beaker and diluted for AAS analysis. Digestion bombs come with different volumes and pressure ratings. General purpose digestion bombs can stand pressures up to 1800 psig. But pressure developed

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[58] *Recommended at the Belgrade meeting*

[59] *This problem does not exist if samples are collected on inert filters such as teflon or polycarbonate In the digestion only particles are dissolved and the filter remains intact Consequently, smaller acid volumes are sufficient when samples are collected by such inert filters*

in the digestion bomb during the digestion of a one-quarter cellulose fiber filter from a high volume sampler (such as Whatman 41) frequently exceed 1800 psig. Special high pressure bombs which can stand pressures up to 5000 psig (which are more expensive than regular ones) should be used in the MED POL laboratories.

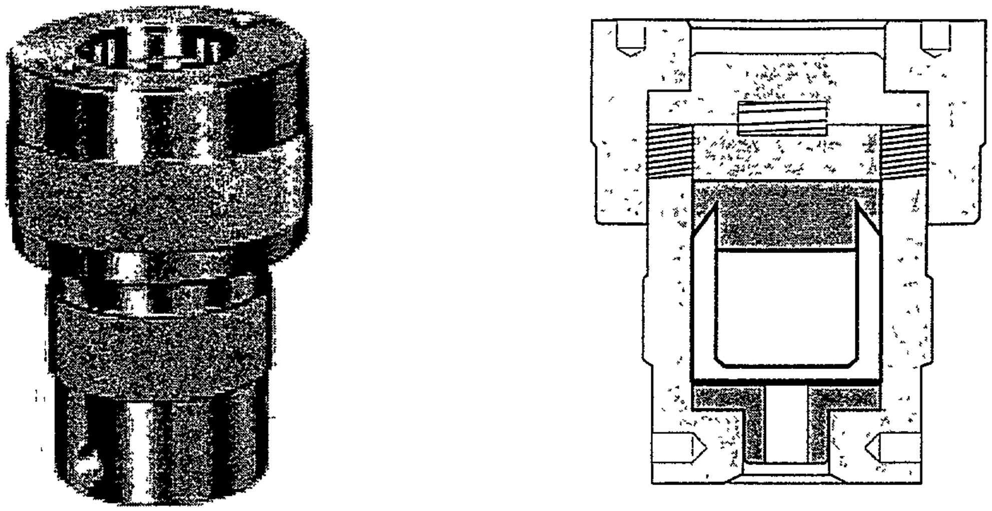

Figure 4.1 An example of a high pressure sample digestion system (Parr, Model 4746)

A recent development in the digestion bomb technology is the use of all Teflon bombs which are heated in a microwave oven. These bombs do not have any metal accessories and their heating by microwaves reduces substantially the heating time. A digestion which takes 90 min in a conventional bomb can be completed in 5 - 10 s in a microwave system. However, these bombs can not be used for the digestion of aerosol samples collected on cellulose filters, because they do not stand to high pressures developed during the digestion of filters.

Open digestion does not require any special instrumentation. Samples are placed in an approximately 250 mL capacity Teflon beakers and refluxed first with concentrated HNO_3 then with concentrated HF. The volume of acid used depends on the amount of filter being digested, but generally it is about 30 – 50 mL for HNO_3 and 3 – 8 mL for the HF. These acid volumes are substantially higher than 1 - 3 mL of HNO_3 and 1 mL of HF used in the digestion bombs. In the final step, a sample is brought to dryness to evaporate all of the HF and redissolved in HNO_3 for analysis. Typical duration of an open digestion procedure is 1 - 3 days.

Microwave digestion technology is also possible for an open digestion system. The application of microwaves in heating reduces the digestion time significantly. Unlike the application of microwaves to bomb digestion, its use in the open digestion system looks very promising. But, the commercial open digestion systems are new and has to be tested before they can be recommended.

Both open and pressurized digestion techniques have their own advantages and disadvantages. Digestion bombs have attractive features such as, fast decomposition, small risk of contamination, small volumes of acid needed and small risk of loosing volatile elements. However, volumes of digestion bombs are small and high pressures may develop during a digestion of a 1 g cellulose or glass fiber matrix. Although, the digestion period is between 1 - 1.5 h, cooling the massive stainless steel jacket may take approximately 3 - 4 hours. Since the digestion is being carried out in a Teflon lining placed in a stainless steel jacket, any leakage of acid during digestion may corrode the jacket and contamination of the Teflon lining and a sample by metals from the jacket becomes a problem as the bombs get older. The bombs are quite expensive, significant funding should be allocated to purchase a set of digestion bombs if large number of samples need to be digested simultaneously. Open digestion on the other hand provides a cheaper alternative for sample digestion. All that is needed is a Teflon beaker[60] and a hot plate with adjustable temperature control. Since the system is not expensive, many samples can be digested at once. Although the procedure is longer (typically 1 - 3 days), this disadvantage can be overcome by digesting large number of samples at a time. Usually much larger volumes of acid is used which increases both the cost (high purity acids are expensive if purchased commercially) and blank levels of elements.

A universal digestion procedure for aerosol samples collected on cellulose or glass fiber filters is not available. Various digestion procedures are used by different laboratories. The common feature in all these procedures is to use a mixture of HNO_3 and HF at different proportions depending on the quantity of refractory material on filters and the quantity of filter which will be digested. Three such procedures are presented in section 4.4.2 as an example. Heating times and acid volumes should be optimized before using one of these procedures in the laboratory

Similar analytical techniques are used for the analysis of precipitation, dry deposition and aerosol samples. The ion chromatography (IC) is the most common analytical technique for measurement of $SO_4^=$, NO_3^- and Cl^- ions. Although there are wet chemical methods for the analysis of these anions, ion chromatography is quite well established due to its simplicity, speed (all three anions are determined simultaneously) and lack of important interferences.

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[60] *Teflon beakers can be drilled from solid teflon in a machine-shop Although solid teflon is quite expensive, homemade teflon beakers and covers are half the price of teflon beakers commercially available.*

In the ion chromatography, sulfate, nitrate, and chloride ions in a sample are separated on an ion exchange column because of their different affinities with the exchange material. The exchange material commonly used for anion separation is polymer coated with quaternary ammonium active sites. After separation, the anions pass through a strong acid cation exchange column (called suppresser column) which exchanges all cations for H ions. Chloride, nitrate, and sulfate are detected as acids by a conductivity detector. A typical chromatogram of a precipitation sample containing chloride, orthophosphate, and sulfate is shown in Figure 4.2. Procedures used in the IC analysis, which is given in section 4.5 of this manual are identical for precipitation and aerosol samples.

For measuring ammonium in aerosol and deposition samples, the automated or manual colorimetric determination with phenate is used. A sample is mixed with alkaline phenol and hypochlorite to form an indophenol blue complex. A 50° C controlled temperature heating bath is used to increase the rate of color formation. The transmitted light energy (630-nm wavelength) measured through the sample is a function of the concentration of the ammonium ion in the sample. The detection limit of the method is 0.03 mg/l and the concentration range is 0.003-2.00 $mg{\cdot}L^{-1}$ as NH_4^+. This range could be extended by sample dilution.

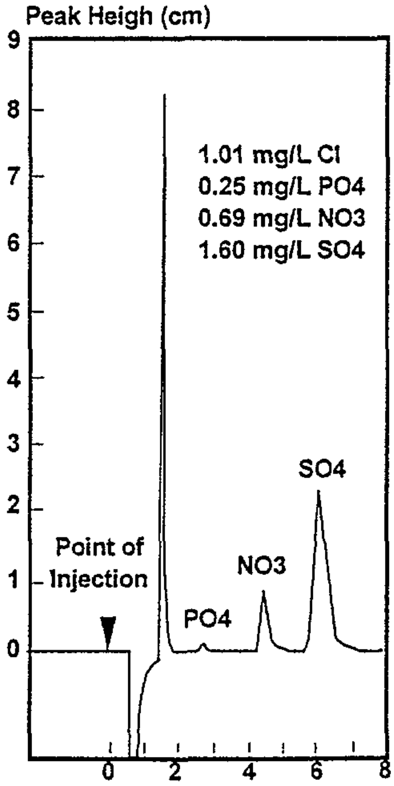

Figure 4.2 A typical chromatogram of rain water
(From WMO report No. 85)

Measurement of metals in the samples can be accomplished by various instrumental techniques. The type of the sample, detection limit of the technique, price per sample are the major constraints on the selection of an analytical method. The methods that can be used for the trace element analysis of aerosol and deposition samples include flame and flameless atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP), ICP-mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA), proton induced X-ray emission spectrometry (PIXE).

Among the analytical methods listed, the INAA, XRF and PIXE are non destructive, multielement techniques. They are excellent for analysis of aerosol samples because they do not need a sample dissolution step, many elements can be measured simultaneously, and samples can be used for other measurements after the analysis[61]. They have been extensively used for the analysis of aerosol samples, because the measurement of 20 - 30 elements in aerosols can provide valuable information for detailed studies involving determination of sources contributing to the observed concentrations at a receptor site. But, they all are expensive techniques which can be used if the necessary facilities are available. The INAA requires a nuclear research reactor, a quite sophisticated counting system and well trained personnel. In addition to this it is a slow technique for the analysis of a few samples (one has to wait for a month for short lived isotopes to decay so that long lived ones can be measured)[62]. But, the INAA has excellent detection limits and up to 35 trace elements can be detected. The PIXE requires an accelerator which is available only in nuclear reactors. It is a very fast technique (up to 100 samples can be analyzed during a working day). Twelve elements can be simultaneously measured with very high sensitivity. The XRF is commercially available, fast and can measure up to 22 elements. However, it is expensive and detection limits are poor compared to INAA, PIXE and GFAAS One of the disadvantages of the INAA, PIXE and XRF is that handling of liquid samples, such as rainwater is not standard and is difficult.

The ICP, ICP-MS and AAS require sample dissolution prior to analysis. The ICP is a multielement technique, but it suffers from relatively poor detection limits for many elements. The detection limit problem is solved in the ICP-MS where the sensitivity is

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[61] *Although this statement is strictly true for the XRF and PIXE, it is not for the INAA Samples analyzed by XRF and PIXE can be used for other measurements immediately after analysis But, in the INAA radioactive isotopes with varying half lifes are generated as a result of neutron irradiation. Although it is theoretically true that samples can be analyzed for other parameters after INAA, one has to wait for several years for the induced activity to decay before the irradiated samples can be used for other measurements.*

[62] *However, when large number of samples are analyzed it is not so slow because, with a proper arrangement of irradiations, one can count samples while waiting for some others to decay.*

sufficient for direct measurement of up to 20 trace elements in rainwater simultaneously. However, the instrument is expensive and do not exist in most of the laboratories.

The method which is most widely used in the MED POL laboratories is the atomic absorption spectrometry. The instrument is inexpensive relative to other techniques, detection limits are good enough for the measurement of most of trace elements in both rain water and aerosols and can be used with a limited training of the technicians.

Atomic absorption spectroscopy is a simple and rapid procedure that can be used to determine trace elements in precipitation and aerosol samples. Detection limits, sensitivities, and optimum ranges vary depending on the manufacturer and the model.

A flame atomic absorption spectrometer consists of a hallow cathode lamp, a flame to generate atoms, a monochromator and a photomultiplier tube detector. The sample which is in solution is sprayed into a flame (through a nebulizer mechanism). In the flame temperature (2000 - 2500°C) solvent evaporates and atoms of the analyte element is formed. The light from the hallow cathode lamp passes through the flame where it is absorbed by the atoms of the analyte element and attenuation of the light intensity is measured by the detector and is related to the concentration. A schematics of a flame AAS is shown in Figure 4.3.

Although the flame analysis is simple, rapid and relatively free of interferences, detection limits are not good enough for direct measurement of elements such as, Cd and Cr in precipitation and aerosol samples.

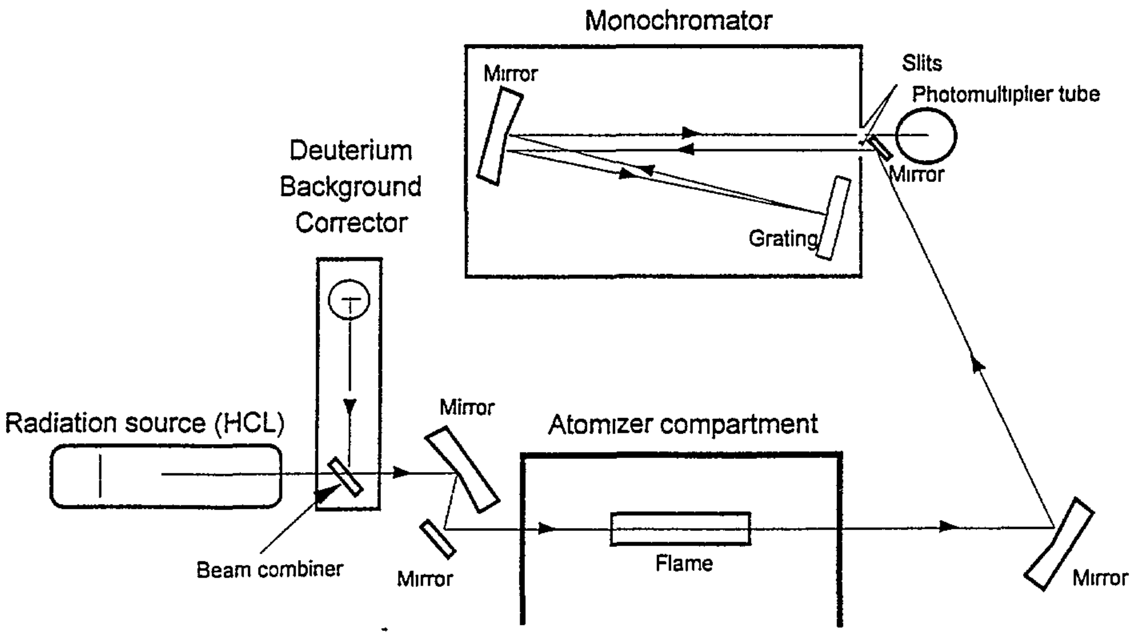

Figure 4.3 Schematic diagram of a flame atomic absorption spectrometer (Perkin Elmer 1100B)

Most of the elements included in the MED POL protocol can be analyzed without an enrichment step using graphite furnace (GF) as the atomization source in the AAS (GFAAS or ETA-AAS). In this technique, the basic equipment is the same, but a graphite furnace which consists of a small carbon tube restively heated by two graphite electrodes is used as the atomization source. A 10 - 50 mL sample is injected into the tube, which is then heated to evaporate the solvent, to ash the organic material and to form free atoms which absorb radiation from the hollow cathode lamp (or an electrodeless discharge lamp - EDL). The heating rate is usually programmed so that evaporation of solvent and ashing of organic matrix take place at low temperatures, and the system is quickly heated to 2500°C in the atomization step. Schematic picture of a graphite furnace unit is shown in Figure 4.4.

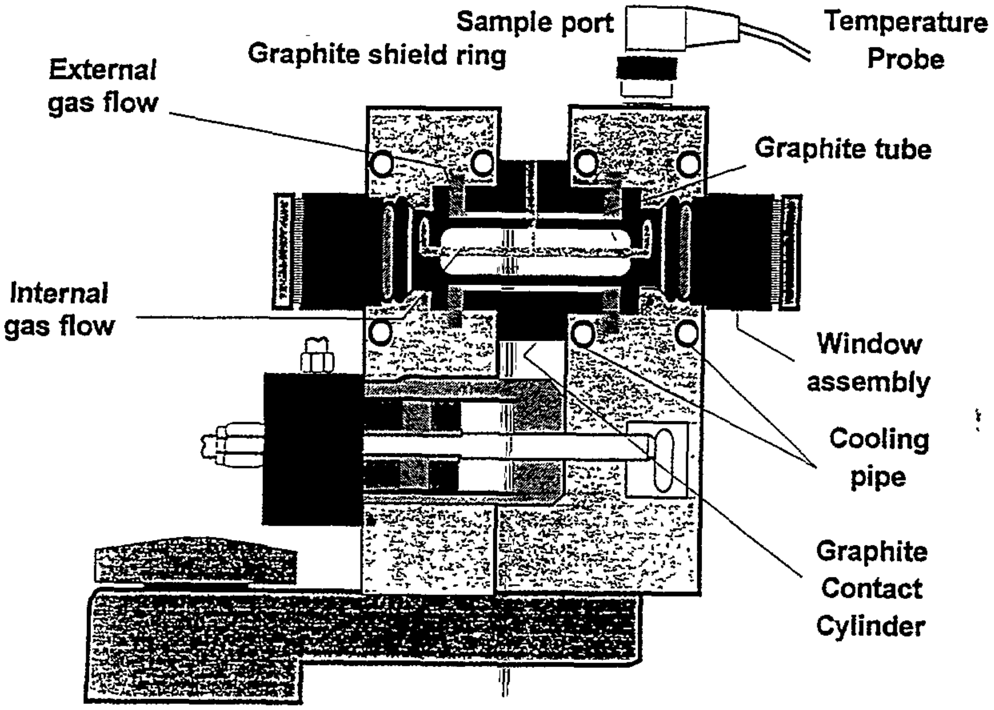

Figure 4.4 Schematic diagram of a graphite furnace atomization unit (Perkin Elmer, HGA 700)

Normally the graphite tube is filled with an inert gas such as Ar to avoid oxidation of carbon. But, the inert gas flow is stopped during the atomization step to increase the residence time of atoms in the tube. Since, atoms which are formed during the atomization step reside in the furnace until the measurement is completed and the inert gas flow is restored (approximately 10 sec, unlike in the case of flame atomization where atoms pass through the light beam at the flame velocity), the sensitivity of electrothermal atomization is two to three order of magnitude better than the sensitivity of the flame atomization.

The GFAAS is significantly slower (each injection in GFAAS takes about one minute, including cleanup cycle and cooling time, while each injection in the flame AAS takes approximately 10 sec), has poorer reproducibility and is more prone to interferences compared to the flame AAS. Consequently, the flame atomization should always be preferred unless concentrations of the elements which are analyzed are below the detection limit of the flame system. If a laboratory uses AAS for the first time for aerosol and precipitation samples, approximately 10 samples should be dissolved and scanned using the flame method for all the elements. The ones which can not be detected by the flame method should then be scanned by using the graphite furnace. An example of this approach is given in Table 4.1. However, the information in Table 4.1 can only be a starting point, because the required atomization mode for each element may change from one sampling site to another.

Table 4.1. Elements measured by flame and graphite furnace AASs at the Eastern Mediterranean station located near Antalya, Turkey

Element	Aerosol	Precipitation
Al	FAAS	FAAS
Ca	FAAS¶	FAAS¶
Cd	GFAAS	GFAAS
Cr	GFAAS	GFAAS
Cu	GFAAS	GFAAS
Fe	FAAS	FAAS
K	FAAS¶	FAAS¶
Mg	FAAS	FAAS
Na	FAAS¶	FAAS¶
Ni	GFAAS	GFAAS
Pb	GFAAS	GFAAS
Sb	GFAAS	GFAAS
V	GFAAS	GFAAS
Zn	FAAS	FAAS

¶Can also be measured in flame emission mode

4.2. Preparation of precipitation and dry deposition samples for major ion analysis

Since major ions are water soluble, they can be analyzed without significant sample preparation. However, particulates in the sample can clog the ion chromatographic column and they should be removed by filtration before IC analysis.

If the volume of a sample is low, the analysis should be made in the following priority order:

- pH,
- conductivity,
- sulfate,
- nitrate,
- chloride,
- ammonium,
- sodium,
- potassium,
- calcium,
- magnesium,
- acidity.

The following procedure can be recommended to prepare precipitation, dry and bulk deposition samples for major ion analysis.

- Remove sample bottles from polyethylene bags (in case of bulk deposition samples, spare the funnels for cleaning).
- After allowing them to equilibrate at room temperature, weigh to the nearest 1 g[63] and record the weight in the laboratory log book[64].
- Measure conductivity using the procedure given in section 3.3.9 and record the laboratory conductivity in the laboratory log book.
- Measure pH using the procedure given in section 3.3.10 and record the result in the laboratory log-book.
- Prepare an all-plastic pressure or vacuum filtration unit which should be washed using the procedures given in section 3.2. Install a cellulose acetate or cellulose nitrate membrane filter with 0.47 mm pore size on the filtration unit[65].
- Filter the sample by applying gentle pressure or vacuum to the filtration system. If the filtration becomes too slow due to clogging of the filter by particles in the

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[63] *To the nearest 10 g if 5 L bottles are used in bi-weekly sampling.*

[64] *Difference between the field weight and laboratory weight can provide information on whether any of the sample was spilled during the transport of samples*

[65] *If some analysis is required on the insoluble fraction, the type of the filter is determined by the type of the analytical technique*

sample, stop the filtration, replace the clogged filter with a clean one and resume filtration.

- After the filtration is completed take three 25 mL aliquots of the sample, by pouring into separate 25 mL capacity polyethylene bottles. One of the aliquots will be analyzed for Cl^-, NO_3^- and $SO_4^=$ using the procedure given in section 4.5, the second aliquot will be analyzed for Na^+, K^+, Mg^{++} and Ca^{++} with the procedure given in section 4.7, and the third one will be used for analysing ammonium. Save the remaining sample until all analysis are completed just in case that something goes wrong and the sample needs to be reanalyzed[66,67].

- All aliquots should be stored at +4°C (in a refrigerator) until analysis.

4.3. Preparation of precipitation and dry deposition samples for metal analysis

Samples collected for trace element analysis are acidified either at a central laboratory before they are shipped to a station or at the station, before sampling. Most of the anthropogenic elements such as, Pb, Cu, Cd, Cr, Zn, As, Se, Br, Sb are soluble in dilute nitric acid solutions and consequently these elements can be analyzed (at least more than 90% will be determined) without any sample treatment. However, some of the elements, particularly those associated with soil particles are insoluble in dilute HNO_3. Elements like V and Mn are partly soluble at acid levels that exist in the samples. Consequently, the type of the sample treatment is determined by the elements that will be analyzed. In the MED-POL programme the measurements of Cd, Pb, Cu and Zn were recommended. Based on this list, extensive digestion of samples is not necessary because Al can only be dissolved after extensive digestion using HF.

The following procedure can be recommended for preparation of samples for AAS analysis:

- In a clean area, open polyethylene bags used for transportation and remove sample bottles. Make sure that labcoat and disposable polyethylene gloves are worn.

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[66] *The ion balance is a good and quick way of checking the quality of the data. If the ratio of Σanions to Σcations is 1.0 ± 0.3 the data are of probably reasonable quality. But, if the ratio for a given sample is beyond this range, it may be necessary to reanalyze the sample for anions, cations or both Consequently it is recommended to keep the fourth aliquot until the ion balance is calculated.*

[67] *If the volume of the sample is not enough to take 25 mL aliquots, the volume of each aliquot can be reduced, because each IC injection requires only 100 - 200 μL, each NH_4^+ analysis requires approximately 5 mL and a total of 20 mL is needed for AAS analysis of cations.*

- Prepare an all-plastic pressure or vacuum filtration unit which should be washed using the procedures given in section 3.2. Install a cellulose acetate or cellulose nitrate membrane filter with 0.47 mm pore size on the filtration unit[68,69].

- Filter the sample by applying gentle pressure or vacuum to the filtration system.

- At the end of the filtration, collect a 25 mL aliquot of the filtered sample, pouring the filtered sample into a 25 mL capacity polyethylene bottle washed with the procedures given in section 3.2[70].

- Analyze trace elements in the 25 mL sample aliquot and store the remaining sample at 4°C until all the analyses are completed.

- Disassemble the filtration unit and remove the filter.

4.4. Preparation of aerosol samples for analysis

Preparation of aerosol samples for analysis depends on the subsequent analytical method and the parameters that will be measured. For example, while preparation of aerosol samples for metal analysis by atomic absorption spectrometry requires exhaustive sample digestion, sample preparation methods for the same metals by a non-destructive instrumental activation analysis or by XRF do not require any digestion. Consequently, the description of detailed procedures for all available analysis methods are well beyond the scope of this manual. However, the aerosol samples in the MED POL programme are collected either for analysis of major ions or for analysis of metals, AAS (with both graphite furnace and flame atomization) and ion chromatography are the most frequently used methods for determinations of metals and ions, respectively. In the procedures described in this section, it is assumed that samples will be subsequently analyzed by AAS for metals and by IC for ions.

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[68] *If some analysis is required on the insoluble fraction, the type of the filter is determined by the type of the analytical technique*

[69] *It is recommended to install a set of 5 - 10 filtration units at once so that after filtering 5 - 10 samples the filtration units can be washed using the procedure given in section 3 2*

[70] *The actual sample size depends on the mode of atomization in the AAS analysis Each injection into the graphite furnace requires approximately 10 - 50 µL, but each aspiration into the flame requires only 1 mL*

4.4.1. Preparation of aerosol samples for Cl^-, NO_3^-, $SO_4^=$ and NH_4^+ analysis.

The Cl^-, NO_3^-, $SO_4^=$ and NH_4^+ ions which are recommended to be measured in the MED POL programme are water soluble. Consequently, the sample preparation for ion measurements consists of dissolving these ions in water. The following simple procedure can be used to dissolve ions from aerosol samples for ion chromatographic measurements[71]:

- Using clean tweezers, remove one quarter of the filter allocated for ion measurements from the polyethylene bag in the "clean area".
- Place the filter in a clean polyethylene beaker (folding if necessary) and add 50 mL of distilled deionized water. Cover the beaker with a polyethylene lid.
- Place the beaker in an ultrasonic bath. Operate the bath and sonicate the sample for 30 min[72].
- At the end of the 30 min period, stop the ultrasonic bath and remove the beaker.
- Since the cellulose or glass fiber filters themselves and most of the particles collected on them will not be dissolved in water, you will not have a clear solution at this point. Filter the solution through a cellulose acetate or cellulose nitrate membrane filter with 0.47 mm pore size to remove particles and filter material which can clog the IC column[73].
- Transfer the eluent to a 50 mL capacity sample bottle and store in a refrigerator until IC analysis.

Although the procedure to dissolve ions is quite simple and straight forward, there are few points one has to be careful about:

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[71] *The procedure must be carried out in the clean area (see section 1.3.5) All the precautions, such wearing labcoat and polyethylene or latex gloves must be taken to avoid sample contamination*

[72] *Certain procedures suggest heating the sample filters at 80°C for complete dissolution of ions. Although this is not necessary due to high water solubility of these ions, heating will not effect the results. Ultrasonic baths which can also heat the solution are commercially available.*

[73] *A vacuum filtration is recommended to speed up the filtration*

- Activities which involve HNO_3 should not take place in the room where samples are being dissolved for ion analysis (HNO_3 vapors in the room may easily change NO_3^- concentrations in the sample solutions[74]).

- The sample storage bottle should not be washed with acid.

- The quality of plastic bottles is important. Sample solutions may evaporate and concentrations of ions may change in poor quality bottles where the cap does not seal the bottle properly. If you have to use local polyethylene bottles (which are generally much cheaper), make sure the bottle is air tight or improve the sealing using a sheet of parafilm or a sheet of clean polyethylene.

- The 50 mL volume used in the above procedure is tentative and depends on the concentrations of ions in the collected sample. Since, the ion chromatography generally requires for injection only a few hundreds of µL, the sample volume can be reduced.

Since the stability of ions in the water solution is questionable (particularly that of NO_3^-), never store water extracts for extensive periods of time. Dissolve samples in small numbers and try to analyze immediately after dissolution.

4.4.2. Preparation of aerosol samples for metal analysis using AAS

Preparation of aerosol samples for subsequent trace element analysis using flame and flameless AAS involves the acid digestion of samples. The acids that are used in the digestion are determined by the elements that will be measured. Such elements as Na, Mg, and K are water soluble and acid digestion is not necessary. Treatment of exposed filters in warm water (preferably in ultrasonic bath) is sufficient to dissolve Na, K and Mg. Elements such as Cu, Zn, Cd, Sb, Pb are soluble in HNO_3. Consequently, when the purpose of the sampling is measurement of one of these elements, it may be sufficient to digest the sample with HNO_3. However, elements like Al, Fe, Si, Sc, etc. occur in the aluminasilicate structure of the crustal material and digestion using a mixture of HNO_3 and HF is necessary for their complete dissolution. Neither HNO_3, nor HF can dissolve organic material. If complete dissolution of organic matter is needed, $HClO_4$ should be added to the digestion mixture.

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[74] *The same point should also be taken into consideration in the preparation of distilled deionized water HNO_3 should not be used in the room where the water is distilled or deionized The HNO_3 vapors may increase the NO_3^- concentration in the feed water or in the produced distilled deionized water significantly increasing the blank values*

Measurements of Na, Al, Cd, Pb, Cu and Zn in aerosol samples were recommended for the MED POL programme[75]. Since the list includes Al, a mixture of HNO_3 and HF should be used in the digestion procedure. Although the cellulose filters are readily dissolved in a mixture of HNO_3 and HF, careful adjustment of acid volumes is important for complete dissolution of both filters and particles (if added acid is not enough to dissolve cellulose fibers, particles may remain undissolved as well).

There is no standard acid digestion procedure which is proven to be complete for all aerosol samples. The following three procedures could be used in the digestion of aerosol samples collected on cellulose fiber filters for trace element determinations. They provide information on the important points in the digestion but none of them can be recommended for the use without any optimization. All of the procedures can be successfully used after careful optimization of volumes and heating times. Please note that volumes of acids used depend on the quantity of the filter digested rather than the amount of particulate material on the filter.

Procedure 1

- Remove one quarter of the filter allocated for metal analysis from the polyethylene bag where it is stored.

- Using plastic tweezers, transfer the filter into a Teflon bomb (folding if necessary) and squash it to the bottom of the vessel.

- Add 1 mL of aqua-regia, 1 mL of HF and close the bomb tightly.

- Submerge the bomb in boiling water for 1 h.

- After cooling, open the stainless steel jacket and remove the Teflon vessel[76].

- Inspect the Teflon vessel for the sign of leakage. Any sign of acid on the neck of the Teflon which may have greenish blue color due to dissolution of some Cu from the metal jacket may indicate that the acid leaked during heating (probably due to excessive pressure). Samples should be discarded when such indication of acid leak is observed. If the leak is observed frequently, this may indicate that Teflon

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[75] *Recommended at the Belgrade meeting*

[76] The bomb should be cooled in air and should not be submerged in water to speed up cooling

bomb is too small for the quantity of the filter used. Either the amount of filter should be reduced or larger digestion bombs should be used.

- Each digestion bomb is equipped with a relief mechanism which consists of a thin film of metal which is broken if too much pressure develops. Check the thin metal film for any distortion which indicate excess pressure. If the metal film is not broken, the sample should be undistorted, but any distortion on the film indicates that the pressure is at the margin.

- If there is no indication of leakage, decant the contents through a polypropylene funnel into a 25 mL polypropylene volumetric flask containing 0.93 g boric acid and approximately 5 mL of distilled deionized water[77].

- Wash the Teflon vessel several times with small volumes of water, each time collecting the washing water in the 25 mL volumetric flask.

- Shake the volumetric flask to complete the dissolution and make up to 25 mL with distilled deionized water.

- Prepare a blank solution using the same procedure omitting the filter.

- Store prepared solutions in polyethylene or polypropylene bottles until the AAS analysis.

Procedure 2

The following procedure had been recommended for the digestion of samples collected on cellulose and glass fiber filters[78].

- Remove one quarter of the filter allocated for metal analysis from the polyethylene bag where it is stored.

- Place the filter in a PTFE beaker.

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[77] *The solution may contain small black carbon particles. They do not interfere with subsequent metal analysis if they are allowed to settle to the bottom of the flask.*

[78] *From "Guidelines for the determination of selected trace metals in aerosols and in wet deposition" UNEP publication, Reference Methods for Marine Pollution Studies No 42 (1988).*

- Add 5 mL of concentrated HNO_3.
- *Slowly boil the mixture to dryness.*
- Add 2 mL of 1:1 mixture of HNO_3 and HF.
- Gently boil the solution to dryness.
- Redissolve the residue in 1% HNO_3.

Procedure 3

- Place a quarter of the filter in a 250 mL PTFE beaker.
- Add 30 mL of concentrated HNO_3 and cover the beaker with a plastic (but preferably Teflon) cover.
- Place the beaker on a sand bath and set the temperature control to 130 ± 10°C. Turn the sand bath on and monitor the temperature throughout the digestion by inserting a thermometer in the sand.
- Allow HNO_3 to reflux for 10 - 12 hours. If the solution is not clear at the end of 12 hours, add 20 mL of concentrated HNO_3 and reflux for additional 6 - 8 hours.
- Remove the cover and continue heating until the volume decreases to 10 mL.
- Add 5 mL of HF, cover the beaker and reflux for 6 - 8 hours.
- Remove the cover, continue heating to evaporate the solution to **near** dryness[79].
- Add 5 mL of concentrated HNO_3 and evaporate to near dryness or until dense white fumes of HF is no longer visible. If HF fumes do not disappear before the sample reaches to near dryness, repeat the addition of HNO_3 and evaporation two or three times until no HF remains[80].

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[79] *Do not dry the sample completely.*

[80] *Any HF which remains in the sample beyond this point may damage the nebulizer system of AAS in subsequent analysis.*

- Bring the sample to dryness, remove the beaker from the sand bath and allow to cool for a few hours.

- Redissolve the residue in 1% HNO_3, transfer to a 50 mL plastic volumetric flask and make up to 50 mL with the same 1% HNO_3 solution.

- Transfer the solution to a 50 mL sample bottle and store in a refrigerator until analysis.

4.4.3. Precautions in sample digestion

The PTFE beakers can only tolerate gentle heating. They may melt at high temperatures.

Technicians that perform the digestion should be experienced in chemical laboratory manipulations. The HNO_3 and HF are dangerous. Goggles, plastic gloves and labcoats must be worn all the time. The digestion should be carried out in a fumehood.

Acids used in digestion should have the same purity as the acids used in the preacidification of the precipitation sample bottles (see section 3.2). However, HF can not be purified by subboiling distillation (because it attacks to quartz). The highest purity HF available commercially should be purchased and used.

If the digested samples are not analyzed immediately after digestion it is recommended that the cap should be covered with a parafilm to avoid evaporation of samples which may result in erroneous concentrations.

4.5. Analysis of major ions

The following procedure is formulated for the analysis of Cl^-, NO_3^- and $SO_4^=$ ions using ion chromatography. The make and model of the instruments vary significantly which does not allow formulation of detailed operational procedures. In this section only the basic steps in the operation of an ion chromatograph are included. Detailed operation instructions must be obtained from the user's manuals of each instrument. The operation principles of ion chromatography are given in section 4.1.

4.5.1. Apparatus

- Ion chromatograph (e.g., Dionex) with autosampler (optional) and a conductivity detector.
- Anion separator column.

- Anion suppresser column.
- Pipettes - various sizes.
- 0.8 mL capacity injection syringe with stainless steel needles.

4.5.2. <u>Reagents and solutions</u>

- Concentrated eluent (0.6M $NaHCO_3$/0.48M Na_2CO_3)
    - Dissolve 100.8707g of $NaHCO_3$, and 101.7509g of Na_2CO_3 in 2L of hot deionized water.

- Working eluent (0.003M $NaHCO_3$/0.48M Na_2CO_3)
    - Dilute 20 mL of concentrated eluent to 4 L with deionized water; transfer to a polyethylene bottle with 4 L capacity.

- Regenerant (2.0M H_2SO_4)
    - Add 111.1 mL of concentrated H_2SO_4 to 3 L of deionized water in a polyethylene bottle with 3 L capacity.

- Concentrated buffer (14%)
    - Dilute 7 mL of the concentrated eluent to 59 mL with deionized water.

- Mixed stock solution (1000 mg·L^{-1} of $SO_4^=$ and NO_3^-, and 200 mg·L^{-1} of Cl^-)
    - Dissolve 0.3297 g of NaCl, 1.6305 g of KNO_3 and 1.8142 g of K_2SO_4 in 1 L of deionized water.

- Standard solution A (100 mg·L^{-1} of $SO_4^=$ and NO_3^-, and 20 mg·L^{-1} of Cl)
    - Dilute 10 mL of the mixed stock solution to 100 mL with deionized water.

- Standard solution B (10 mg·L^{-1} of $SO_4^=$ and NO_3^-, and 2 mg·L^{-1} of Cl^-)
    - Dilute 10 mL of the standard solution A to 100 mL with deionized water.

- Working standards (concentrations of 10, 5, 1 mg·L^{-1} of $SO_4^=$ and NO_3^-, and 2, 1 and 0.2 mg·L^{-1} of Cl^-).
    - Prepare from standard solutions by diluting 10, 5, and 1 mL of standard solution to 100 mL with deionized water.

4.5.3. Measurement procedure

- Regenerate the suppresser column with 1.0N of H_2SO_4 for 5 min and rinse with deionized water for 15 min.

- Set up the instrument for the most sensitive range.

  Recommendations for optimum dionex sensitivity:
  - 0.003M $NaHCO_3$/0.0024M Na_2CO_3 eluent.
  - 0.8 mL injection loop.
  - Flow rate for column backpressure is 650 psi.

- Begin to pump the eluent through the columns.

- Fill the autosampler with standards and samples, starting with the highest concentration standard decreasing the concentrations or inject in the same order manually.

- Turn on the autosampler to start analyzing the samples.

4.6. Analysis of NH_4^+

This section describes a method of ammonium determination in wet deposition and aerosol samples. The automated method using an equipment such as a Technicon autoanalyzer should follow the manufacturer's instructions.

4.6.1. Apparatus

- Colorimeter with a 630 nm setting.
- Heating bath (50°C).
- Glass test tubes with ground-in stoppers.

4.6.2. Reagents and solutions

- Stock solution (100 mg/l of ammonium)
  - Dissolve 0.2965g of NH_4Cl (dried at 105°C)in deionized water and dilute to 1000 mL.
- Alkaline phenol

  - Dissolve 3.5g of sodium hydroxide (NaOH) plus 8.5 ml freshly distilled phenol plus 0.04 g sodium nitroprusside in 100 ml deionized water, refrigerate the solution at 4°C for a period not exceeding 1 week, prepare fresh weekly.

- Sodium hypochlorite (NaOCl) solution
  - Dilute 250ml of 5.25% NaOCl to 500 ml with deionized water.

4.6.3. <u>Measurement procedure</u>

- The spectrophotometer should be switched on 30 min before the analysis starts.

- Put 5 ml of a sample in the test tube, add 15 ml of deionized water, 0.5 ml of alkaline phenol solution, and 0.5 of sodium hypochlorite solution; close the test tube with the glass stopper.

- Set the heating bath for 50°C, leave the sample in the heating bath for 2 hours, measure with the spectrophotometer at 630 nm.
- The elevated concentrations of ammonium in the laboratory will result in a positive interference. Wash the sample cups with deionized water immediately prior to use and rinse cups again with a portio of the standard or the sample to be analyzed.

4.7. Analysis of metals by atomic absorption spectrometry

Analysis of elements by AAS includes the following steps which will be discussed in this section:

- Preparation of stock solutions and working standards for elements.

- Preparation of the calibration curve.

- Preparation of the instrument.

- Measurement of atomic absorption signal.

- Computation of concentrations.

Apparatus

- Atomic absorption spectrophotometer – a single or double-beam instrument having monochromator; or dual-channel, single- or double- beam instrument having monochromator; photomultiplier detector; adjustable slit; a wavelength range of 190 to 800 nm; a burner system; power supply; an amplifier; a suitable recorder or PC; a graphite furnace atomization unit and its power supply, and an autosampler for the graphite furnace system (optional).

- EDL or hallow cathode lamps for Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu, Zn, Al, Cd, Pb (single element lamps are preferred but multi-element lamps may be used; EDL's are more intense than hollow cathode lamps).

- Compressed gases and pressure-reducing valves, cylinders of acetylene and nitrous oxide are necessary; the air may be supplied from a laboratory compressor (with a cleaning unit) or a cylinder with compressed air.
- Pipettes and volumetric flasks of various sizes.

4.7.2. Preparation of stock solutions and working standards

Stock solutions for Na, K, Ca, Mg, Cu, Zn, Al, Cd and Pb can be prepared from pure compounds (it is preferable to use elemental forms of metals if they are available, but if elemental forms are not available oxides and other non-hygroscopic compounds of elements can be used). The compound which will be used to prepare a stock solution, should be dried at high temperature and weighed (after equilibirating at room temperature) and dissolved so that the final concentration of element in the stock solution is 1000 $mg \cdot L^{-1}$ (ppm). For all of the elements, 1000 ppm stock solutions are also commercially available. These solutions can be purchased and also used.

Working standards of elements are prepared by dilutions from stock solutions and are used in the preparation of calibration curves. Concentrations of elements in the working standards should be such that the concentration of an element in the sample should be between the standards used in the construction of the calibration curve. It is not possible to give the concentrations of elements in working standards, because concentrations of elements in samples change significantly from one site to another. Consequently different sets of working standards are needed for different sample concentrations. Concentrations of elements should be optimized in each laboratory for typical concentrations observed in precipitation and aerosols[81].

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[81] *Concentrations of elements at a given site may change by an order of magnitude Concentrations of elements in samples and that in standards should not be very different from each other If*

4.7.3. Construction of the calibration curve

Aerosol samples prepared for analysis carry some acids, decomposed cellulose matrix and other species from the sample which can enhance or suppress the analyte signal in AAS. Consequently, the method of standard additions is the best approach for correct determinations of concentrations. However, with large number of samples, the method of standard additions is too slow to be practical. There are two approaches which can be taken:

- Since HNO_3 is the dominant source of signal suppression, the calibration curve can be prepared by using HNO_3 solution instead of pure water[82]. This approach can be used in the analysis of rainwater, because the concentrations of other interfering species are very low, and in the analysis of elements in aerosol samples if they are analyzed by flame atomization, because interferences are not as significant in flame as they are in electrothermal atomization. But, this method can not be recommended for elements in aerosols which require graphite furnace atomization, because the samples contain interferants other than HNO_3 in significant concentrations (such as, leftover cellulose decomposition products, organics, etc.).

- Calibration curve can be prepared using one of the samples instead of pure water. To construct the calibration curve a standard addition curve should be first prepared by using the following:

  - Divide one of the samples into 4 - 5 aliquot.
  - Add different amounts of the working standard so that the final concentrations in aliquots cover a range where most of the sample concentrations are observed[83].
  - Prepare a standard addition curve using the peak heights of the signals.

  Once the standard additions curve is prepared, the calibration curve can be constructed using the slope of the standards addition curve.

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concentrations of an element in all samples can not be covered by a single calibration curve, two calibration curves should be prepared with different working standards Dilution of samples with high concentrations of elements is not recommended, because the matrix which determines the slope of the calibration curve is also diluted If a dilution is absolutely necessary (if sample concentration is not in the linear range of the system) then a new calibration curve should be prepared using a diluted sample and used.

[82] *The HNO_3 concentration in the standards should be the same as that in samples.*

[83] *The volume of the working standard added should be much smaller than the sample aliquot, otherwise dilution of the sample (matrix effects) may change*

This approach is the best for analyses of elements in aerosols which require graphite furnace atomization. Construction of the calibration curve from a standard addition curve includes an assumption that the slope of the standard additions curve does not change from one sample to another. Although this can not be guaranteed, the method is obviously better than the construction of the calibration curve by using water or HNO_3 solution. The standard additions curve should be prepared at the beginning of every day using different samples and the slope should be checked (by injecting one of the standards) at every 15 th sample[84].

4.7.4. Preparation of the instrument for flame AAS determinations

Because of differences between atomic absorption spectrophotometers, detailed instructions cannot be formulated; the analysts should follow the manufacturer's operating instructions for the particular instrument. The following general steps should be performed to prepare the instrument for flame analysis:

- Turn the analyzer on.
- Align the light source for maximum response.
- Ignite the flame.
- Allow the instrument to warm up (at least 15 min).
- Reset the wavelength.
- Optimize and adjust the nebulization rate for maximum response.
- Adjust the burner position for maximum response.
- Prepare a full calibration curve and analyze one standard for every 20 samples.

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[84] *When a standard addition curve is prepared every day, one can get an idea on whether the slope of the curve is changing from one sample to another*

4.7.5. Preparation of the instrument for graphite furnace AAS determinations

Operating principles of a graphite furnace atomization system are discussed in section 4.1. In general GF-AAS is slower, more difficult to use and prone to interferences when compared to flame-AAS. Although it is more susceptible to problems, it is still being used for analysis of trace elements, because the sensitivity of the graphite furnace (or graphite cup) atomization is two-to-three orders of magnitude higher than typical sensitivities for the elements in flame AAS.

One of the important considerations in GFAAS is the selection of tubes. There are three types of tubes, namely *un-coated*, *pyrolitic graphite coated* tubes and *tubes with L'vov platform* which are commercially available. Although all of them can be used for all the elements, different types of tubes produce better results for specific elements. For the elements that are measured in the MED POL programme, pyrolytic graphite coated tubes are more suitable for Al, Cu and Zn, while uncoated tubes produce better results for Pb and Cd. Tubes with L'vov platform permit the atomization of the sample under nearly isothermal conditions. That results in reduction of interferences and allows for direct comparison with aqueous standards (at least theoretically). However, the tubes with L'vov platform are more expensive than regular coated and uncoated tubes. If tubes with L'vov platform are used, the platforms should be uncoated for Pb and Cd (uncoated platforms are not available commercially, but can be constructed in the laboratory).

The following set of instructions can be used to prepare the instrument (GF-AAS) for analysis:

- Install the graphite furnace unit into the atomization chamber of AAS.
- Turn the analyzer and graphite furnace power on.
- Align the light source and furnace position for maximum response.
- Set the wavelength and slit width.
- Optimize the drying time and temperature. The drying time should be optimized by injecting a 20 mL standard and changing the drying temperature and time so that no sputtering occurs (which can be heard) or no water vapor comes out from the sample injection hole when the system switches from drying to the ashing step. The tubes with L'vov platform require relatively high drying temperature (approximately 270°C). Slow ramp times should be selected.

- Optimize the ashing temperature and time. The ashing temperature should be high enough to destroy all organic material without atomization of the analyte element. Usually, dense fumes indicating combustion of organic material come out during ashing. The ashing time should be so adjusted that these fumes cease before the system switches to atomization. The temperature should also be adjusted so that no fuming occurs during the atomization step.

  One of the problems that is frequently observed in the GFAAS measurements is the loss of analyte element during the ashing step. Some elements like Pb are atomized at relatively low temperatures and they may be lost during the ashing step. In addition to common volatile elements, chlorides of some elements like Zn are also volatile. If the analyzed sample contains high concentration of Cl (most of the samples collected at the MED POL stations do contain high concentrations of Cl) then the element may form chloride and is volatilized at typical ashing temperatures. The volatility losses can be checked from the atomization signal for that element by temporarily reducing ashing temperature.

- Optimize the atomization temperature and time. The atomization typically takes 5 - 6 seconds. The profile of the atomization signal can be monitored on a screen in most of the recent instruments. The atomization time should not be unnecessarily long (since the inert gas flow from the tube is interrupted during the atomization step, high temperatures for prolonged time can reduce the graphite tube life-time) and also it should not be too short (erroneous concentrations may be obtained, if the peak area is being used in computations; incomplete atomization may also cause the analyte element to built-up on the graphite tube walls). The fastest possible ramp-time should be used in the atomization step.

The operating parameters for both flame and graphite furnace AAS determinations are given in Table 4.2a and 2b, respectively However, it should be kept in mind that these parameters may not be directly used. For example, Zn which is suggested to be analyzed by GFAAS in precipitation samples may be detected by flame AAS for most of the stations. The slit widths may slightly change from one instrument to another. The drying, ashing, and atomization times and temperatures should be used as starting points and optimized at every laboratory.

4.8. Blanks

Table 4.2a. Operating instrumental parameters used for the analysis of trace elements in aerosols and precipitaiton

	Wavelength (nm)	**Flame Type**	**Oxidant Flow (mL min^{-1})**	**Fuel Flow (mL min^{-1})**	**Slit width (nm)**	**Inert gas**
Al	309.2	N$_2$O - C$_2$H$_2$	5.0	7.0	0.7	
Zn	213.9	Air -C$_2$H$_2$	10.1	2.2	0.7	
Fe	459.4	Air -C$_2$H$_2$	9.8	2.2	0.7	
Ca	422.7	Air -C$_2$H$_2$	7.7	2.1	0.7	
Mg	285.2	Air -C$_2$H$_2$	8.0	2.0	0.7	
K	766.5	Air -C$_2$H$_2$	8.5	1.6	0.7	
Na	589.0	Air -C$_2$H$_2$	8.7	1.4	0.7	
Pb	283.3				0.7	Ar
Cr	357.9				0.7	Ar
V	318.4				0.7	Ar
Ni	232.0				0.2	Ar
Cu	324.8				0.7	Ar
Cd	228.7				0.7	Ar
Sb	217.5				0.2	Ar

In addition to field blanks which are analyzed regularly, digestion blanks, acid blanks and water blanks should be analyzed at regular intervals. If sample digestion is performed in batches, then one digestion blank should be prepared for each set of the digested samples. A digestion blank should be prepared by adding the acid mixture to the digestion vessel (digestion bomb or teflon beaker in open digestion) without adding the sample, and then should be subjected to the same procedures as the sample.

Acid blanks should be prepared whenever a new acid bottle is opened by taking an aliquot and diluting so that the final acid concentration in the blank is the same as the acid concentration in samples[85].

Small aliquot of water should be stored in a polyethylene bottle and analyzed as the water blank. It is preferable to prepare one water blank every time a batch of distilled deionized water is prepared.

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[85] *The acid concentration in the blank should be the same as the acid concentration in samples, otherwise a separate calibration curve is needed to analyze the blank.*

Table 4.2b. Graphite furnace temperature programmes used for analysis of elements in precipitaiton and aerosols.

Element	Step No.	1	2	3	4	5	6	7
Al	Furnace Temp., °C	90	130	750	2500	2650	1800	2650
	Ramp Time, Sec.	5	10	10	0	2	5	5
	Hold Time, Sec.	15	10	20	5	5	5	5
Cd	Furnace Temp., °C	90	130	700	1600	2000		
	Ramp Time, Sec.	5	10	10	0	2		
	Hold Time, Sec.	15	10	25	6	5		
Cr	Furnace Temp., °C	90	130	1600	2500	2650	1800	2650
	Ramp Time, Sec.	5	10	15	0	2	3	5
	Hold Time, Sec.	15	20	20	5	8	5	5
Cu	Furnace Temp., °C	90	130	1200	2300	2650		
	Ramp Time, Sec.	5	10	10	0	2		
	Hold Time, Sec.	15	15	25	5	5		
Ni	Furnace Temp., °C	90	130	1400	2500	2650	1800	2650
	Ramp Time, Sec.	5	10	10	0	2	3	5
	Hold Time, Sec.	15	15	25	5	5	5	5
Pb	Furnace Temp., °C	90	130	750	1800	2100		
	Ramp Time, Sec.	5	10	10	0	2		
	Hold Time, Sec.	15	15	25	5	8		
V	Furnace Temp., °C	90	130	1200	2650	2650		
	Ramp Time, Sec.	10	10	10	0	2		
	Hold Time, Sec.	15	15	25	7	8		
Sb	Furnace Temp., °C	90	130	800	2400	2600		
	Ramp Time, Sec.	5	10	20	0	2		
	Hold Time, Sec.	15	15	20	5	5		
Se	Furnace Temp., °C	90	130	800	2100	2600		
	Ramp Time, Sec.	5	10	10	0	2		
	Hold Time, Sec.	15	15	25	5	5		

CHAPTER V
ASSESSMENT OF DATA QUALITY

5.1. General

Since all the data on airborne pollution measurements collected within the framework of MED POL should be accumulated in one data centre (Coordinating Unit for the Mediterranean Action Plan – MEDUnit, Athens, Greece) to be used for regional assessments, the data generated by individual laboratories must be comparable, reliable and of known quality. This can be accomplished only by co-ordinated efforts of the participating laboratories and of UNEP in co-operation with WMO. However, the commitments of the laboratories themselves to generate reliable data are also very essential for the success of the programme.

Each laboratory should develop a data quality programme which should consist of data quality assurance and data quality assessment components. Strict adherence to the protocols generated for quality assurance and quality assessment can ensure the reliability of data generated by the laboratories.

The data quality assurance programme includes necessary precautions which should be taken in the sampling and analysis of aerosols and precipitation to ensure generation of reliable data. The necessary precautions should be listed stepwise in a protocol and the list should be closely followed during the sampling and analysis. Various precautions in all aspects of data generation had been discussed in different parts of the manual. They should be compiled into one list and distributed to relevant people. Strict and continuous adherence to the protocol is essential to generate reliable data.

5.2. Data quality assessment

Data generated by a laboratory are the product of several steps in sampling, sample handling and analysis. Overall accuracy and precision of the data is determined by the accuracy and precision of each of the steps. Consequently, a programme should be developed by each laboratory to assess the quality of their data, and the contribution of each of the sampling, sample handling and analysis steps to the overall accuracy and precision.

5.2.1. Assessment of sampling precision

Sampling precision should be established by duplicate sampling with collocated samplers at the station employing identical collection, handling, and storage procedures for all duplicated samples. Periodic visits to the station by experts and training of technicians are the main criteria to ensure that all collection procedures are followed and that no major changes have taken place at the site.

5.2.2. Assessment of precision and accuracy of laboratory measurements

Assessment of precision , accuracy, and validation of laboratory chemical analyses of samples should be an integral part of the quality control procedure of precipitation and aerosol analyses in every chemical laboratory.

5.2.3. Analytical precision

To estimate the contribution of analytical variabilities, the duplicate sample analysis should be performed on about 10% of routinely analyzed samples. Samples containing a large quantity of precipitation should be divided, one half being analyzed immediately after the first analysis, and the other half being refrigerated at about 4°C to be analyzed within a week. Analytical precision is then defined and reported as the standard deviation between the two analyses. The analytical precision is defined as

$$S_i=(Sd_i^2 /2N_i)\text{½}$$

where d_i denotes the difference between the two analyses, and N_i is the number of sample pairs in the reporting period. An additional factor of 2 is included in the denominator to take into account the random error associated with both measurements.

5.2.4. Accuracy of chemical analysis

Accuracy of the laboratory practices can be best assessed by participating in intercomparison exercises conducted by a central unit which can be within or outside the MED POL programme. In such an intercomparison exercise, samples closely resembling the aerosols and precipitation collected at the MED POL stations should be distributed to the laboratories for sample handling and analysis.

To control the laboratory performances in analysing precipitation samples, WMO regularly conduct intercomparison exercises by distributing simulated rainwater samples to participating laboratories for analyses. Although the concentrations of metals and ions in the distributed samples are higher than those observed in actual rain samples, these are the best ones available. Nordic countries, in their PARCOM and HELCOM programmes perform round-robin exercises using simulated rainwater samples for major ions and trace elements. If the concentrations of ions and elements in these samples are more realistic, possibility of distribution of these samples to MED POL stations should be investigated. All the MED POL stations should participate in these intercomparison exercises at regular intervals.

An intercomparison of aerosol analyses had been carried out by a laboratory in Italy, where aerosol samples were collected from the ambient atmosphere and distributed to the participating laboratories along with a recommended digestion procedure. Since the digestion procedure was specified, the exercise aimed to determine only analytical performances. Similar intercomparison exercises should be repeated at regular intervals with and without specifying the digestion procedure, so that both analytical performances and the reliability of the digestion procedures used by laboratories can be assessed. The MED POL laboratories should participate in these intercalibration exercises on a regular basis.

In addition to intercomparison exercises, where the quality of data generated by a laboratory can be compared with that generated by other laboratories, each laboratory should develop a system to assess the quality of its own data.

Laboratories should analyze standard reference materials at regular intervals. It can be recommended to analyze a reference material every morning before starting analysis, and repeat analysis at every 15 or 20 th sample during the day.

The reference materials should have the same matrix with the sample being analyzed. Unfortunately there are almost no good reference materials which exactly match with the aerosol and precipitation samples analyzed at the MED POL stations. For major ions in precipitation the standard reference simulated rain water standard (SRM 2694-I and SRM 2694-II) produced by the US National Institute of Standards and Technology (NIST) can be used. The standard is certified for most of the major ions and contains two bottles with different concentrations. For trace elements in rainwater the NIST standard reference material SRM 1643b (which is the standard of trace elements in water) can be used. Approximately 20 elements are certified and information values are provided for additional 2 elements. Some Sertified Reference Materials (SRM) containing major ions and trace elements in rainwater are produced by the National Water Research Institute in Canada.

There are also no reference material which includes particulates on a filter matrix, which is the actual aerosol matrix analyzed at the MED POL stations. The nearest reference materials are SRM 1648 which contains urban particulates (certified for 13 elements and information values are given for 21 additional elements), and SRM 1633a which contains coal fly ash (certified for 24 elements and information values are provided for 11 additional elements). Among these urban particulates are the one closest to the aerosol samples collected in the MED POL programme, but concentrations of elements are high and elemental ratios do not resemble the ratios found in a typical urban particulate material. The use of these standard reference materials do not give information on the accuracy of the digestion procedure, because they do not include a filter matrix.

In analysis of precipitation for major ions, computation of equivalent ratios of positively and negatively charged ions also provides information on the accuracy of measurements. If all the ions (organic and inorganic) in precipitation are measured, total equivalents of anions should be equal to total cation equivalents. Consequently, the ratio of the two should be equal to one. The ratio deviates from unity because of three reasons: (1) presence of organic anions, (2) presence of the HCO_3^- ion (if it is not measured) and (3) inaccurate measurements.

The cation-to-anion ratio may be less than unity owing to presence of organic anions from organic acids in the precipitation. The contribution of organic anions may be as high as 30% in equatorial regions where atmosphere is rich in organic matter. But, organic acids are not expected to contribute total anion mass significantly in the Mediterranean which is surrounded by arid and semi arid regions.

Contribution of the HCO_3^- ion to the total anion mass depends on pH of the sample. It can be significant and affect the cation-to-anion ratio at high pH. For example, the contribution can be as high as 30% at pH 5.6 but its contribution decreases quickly with the decreasing of pH. The HCO_3^- ion is insignificant at pH < 5. The concentration of HCO_3^- in precipitation can both be measured and calculated.

If the organics and HCO_3^- ion are not main sources for deviation of the cation-to-anion ratio from unity, then there should be some experimental problem. Consequently, computation of the cation-to-anion equivalent ratio provides a mean for the assessment of quality of the major ion data. The required criteria of the ion balance of precipitation analyses are given in Table 5.1. If the required ion balance criteria have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the results did not meet the required criteria.

Table 5.1. Required criteria for ion balance

Anions + cations (µeq L^{-1})	**Ion difference (%)**
< 50	60
> 50 < 100	30
> 100	15

From Santroch, 1993

Quality of major ion measurements in precipitation can be assessed by comparing the measured conductivity values with those calculated using equivalent conductances of ions at infinite dilution. For dilute solutions (e.g. below 10^{-3} M) of known composition, the equivalent conductances is the sum of the equivalent ionic conductances in solution at infinite dilution. From the relation between equivalent and specific conductance of individual ions the total conductance of a precipitation sample could be calculated as follows:

$$
\begin{aligned}
&(\text{Cond}) = (10^{3 \times \text{pH}}) \times 350 + 2 \times (SO_4^{2-}) \times 79.6 + (NO_3^-) \times 70.6 + \\
&(Cl^-) \times 75.5 + (NH_4^+) \times 74.5 + (Na^+) \times 50.9 \\
&+ (K^+) \times 74.5 + 2 \times (Ca^{2=}) \times 60 + 2 \times (Mg^{2+}) \times 53.1
\end{aligned}
$$

where the parentheses denote the ionic concentrations in mmol/l and individual constants express the equivalent conductance at infinitive dilution at 25°C which are given in Table 5.2.

Table 5.2. Equivalent conductivity at infinite dilution (25°)

Ion	**Equivalent conductivity (µS cm^{-1})**
H^+	350
Cl^-	75.5
NO_3^-	70.6
$SO_4^{2-}/2$	79.0
NH_4^+	74.5
Na^+	50.9
K^+	74.5
$Mg^{2+}/2$	53.1
$Ca^{2+}/2$	60.0

From Santroch, 1993

The calculated specific conductance (Cond) values can be compared with the measured values for precipitation samples by the relation

$$\text{Conductance [\% Difference]} = 100^* \, 9(\text{Cond})_{calc} - (\text{Cond})_{meas})/ (\text{Cond})_{meas}$$

The required comparison criteria of measured and calculated conductances are expressed in Table 5.3. If the required conductance comparison criteria have not been met, the analysis should be repeated or a flag should be entered into the data base indicating that the results did not meet the required criteria.

5.3. Site performance audit

Table 5.3. Required Specific Conductance Balance Criteria

Measured Conductance (µS cm-1)	**Conductance (% difference)**
< 5	50
> 5 < 30	30
> 30	20

Taken from WMO 85[86]

A site performance audit for a precipitation monitoring network should be made at least once per year. A site performance audit should include the steps described in the following sections.

5.3.1. Check of operation of a wet-only automatic sampler

To check the proper sampler operation, the auditor should add 1-2 drops of distilled or deionized water to the precipitation sampler sensor. The sampler is judge to be operating normally if, within a few seconds, the lid covering the wet bucket moves out. If the wet bucket is open, the cleanness of the bucket should be checked. After the wet bucket has been open for several minutes, the auditor should touch the sensor plate to check that it is heating. If so, the moisture is removed from the sensor plate by blowing. The sensor plate then dries more quickly and the lid should cover the bucket again.

5.3.2. Check of procedure for container cleaning

The auditor should check the procedure of container cleaning performed by a responsible person and the availability of containers on the site. The auditor should also check the quality of deionized water at the site (electrical conductance should be <1.2mS/cm).

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[86] WMO/GAW report No 85 Chemical analysis of precipitation for GAW: Laboratory analytical methods and sample collection standards. WMO/TD – 550

5.3.3. Review of site procedures and data documentation

The auditor should observe site personnel performing all the routine site operation duties. This should include reviewing of sample handling, of instrumentation procedures, and of data reporting. After observing sample handling, the auditor should than interview site personnel to gather detailed information on the operation of sampling devices, sample treatment, water supply, and data recording. The interview should also be used to asses the training levels of the operators.

ANNEX

INTERCOMPARISON OF HIGH-VOLUME AIR SAMPLERS AND INTERCALIBRATION OF METAL ANALYSES IN AEROSOL FILTERS

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Foreword

Monitoring of the transport of pollutants to the Mediterranean Sea through the atmosphere is one of the four components of the Long Term Programme for Pollution Monitoring and Research in the Mediterranean Sea (MED POL - phase II) for which the World Meteorological Organization (WMO), since 1982, has been responsible for initiating and co-ordinating activities related to airborne pollution of the sea (WMO, 1994). To improve comparability and accuracy of data generated by the MED POL stations, most of the available Hi/Vol equipment's normally in use within MED POL or other programmes, were compared and studied, in the same site and in the same period (13 may - 5 June 1995, Oristano, Italy). In addition, an intercalibration of samples treatment and metal analyses procedures used by the laboratories participating in the MED POL Airborne Pollution Monitoring Programme was organised (WMO, 1995) as recommended by the WMO/UNEP Expert Meeting on Quality Assurance held in Ankara, Turkey, from 27 to 30 May 1993 (WMO, 1994).

Introduction

In a paper published by Dulac *et al.* (1989), the authors pointed out that at present geochemists do not have available samplers adequate to characterise atmospheric mass-particle size distribution of elements in order to assess precisely their dry deposition rates to the sea from atmospheric measurements. An ideal sampling device should allow the fitting of elemental size distribution in the nucleation, accumulation and coarse modes, then over four orders of magnitudes in particle size, from 0.01 µm to 100 µm (Dulac *et al.*, 1989).

Having compared various sampling methods, Parker *et al.* (1977) demonstrated that a miniature dichotomous sampler, consisting of a 12 µm Nuclepore filter as the first stage followed by a 0.2 µm Nuclepore filter as the second stage, can separately collect fine and coarse particles from the atmosphere. The greatest percentage variations in the collection efficiencies occur near the 2 µm minimum of the bimodal distribution of particles. Comparing the performances of low, medium and high flow sampler inlets in a field study, Rodes *et al.*, (1985) show that the Sierra Andersen model 321 Hi/Vol inlet tended to collect significantly more particulate matter than the other samplers studied, and the GMW 9000 Hi/Vol inlet appear to significantly undercollect. Sampling methods for aerosol were compared also by Kashdan *et al.* (1986), Hering *et al.* (1990) and Tsai (1993), both in laboratories and in field studies. As reported by Hollander *et al.* (1990), the GMW Hi/Vol sampler for total suspended particulates, as far as the Sierra Andersen PM_{10} sampler studied, agreed satisfactorily with the particulate matter as determined by their reference dust sampler. Vawda *et al.* (1992) compared the performance of a May tunnel sampler to those of an Andersen 1 ACFM impactor and a May impactor, both sampling directly from the free wind. They concluded that the tunnel sampler offers a much enhanced performance for sampling large (>8 µm diameter) particles. During an intercomparison field experiment François *et al.* (1995) found a good agreement for the Low/Vol samplers for the majority of the measured elements. With the Hi/Vol Whatman 41 (W41) filter sampler, on the other hand, much higher results were obtained in particular for the sea-salt and crystal elements. The discrepancy was dependent upon the wind speed and was attributed to a higher collection efficiency of the Hi/Vol sampler for the very coarse particles.

As reported by Andreae (1996), a full assessment of aerosol effects on climate requires the incorporation of the aerosol component into fully interactive climate models. It appears essential to obtain comparability among the observational systems and homogeneous databases. Thus, there is a need to create simple and secure sampling networks (WMO, 1994).

Although being not isokinetic, Hi/Vol sampling is able to better collect very coarse particles (>10 µm), with respect to Low/Vol systems (François et al., 1995). Moreover, it allows the determination of low atmospheric concentrations, as are often found over remote marine areas, on short sampling time scales. Due to higher air volume collected, this sampling method decreases the blank/signal ratio (e. g. Kubilay and Saydam, 1995). Furthermore, Hi/Vol sampling permits to collect enough material to allow mineralogical and grain size analyses. The WMO/UNEP expert consultation on quality assurance for the MED POL airborne pollution measurements, that was held in Ankara, Turkey from 27 to 30 May 1993, suggested that samples should be collected by Hi/Vol samplers using glass-fibre or, preferably, cellulose W41 filters (WMO, 1994).

Sampling and Chemical Analyses Intercomparisons

Intercomparisons of high-volume samplers for the MED POL airborne pollution monitoring programme was organized by WMO and the Institute of Marine Geology (IGM), Italy, and took place from 8 May to 8 June 1995. Different air samplers were placed on the roof of the International Marine Center in Torregrande, Oristano, Italy (39°54' N, 8°36' E). The equipment compared were: Aquaero Tech 400XT aerosol sampler (A), MTX CVA 3000 air sampler (B), Sierra Andersen GMWL 2000H air sampler (C). In order to start and stop all instruments at the same time, the Aquaero and Sierra samplers were connected to the MTX sampler, that was equipped with a timer driving the sampling time.

During the intercomparison, 19 aerosol samples were collected by each sampler on 20 cm x 25 cm cellulose filters Whatman 41. Because Aquaero is a constant flow sampler, in this instrument the flow decreases when the obstruction of the filter increases. Thus, the total filtered air was slightly lower with respect to the other two samplers. The difference was only 10-20% because the sampling time of most (15/19) samples was 24 hours. In this way we have reduced the problem related to reduction of the flow by the filter clogging. The remaining four samples were collected with a 48 h sampling time.

Chemical analyses of samples were conducted, after digestion of filters and dissolution of soluble fraction following a common procedure (Molinaroli *et al.*, 1993), with graphite furnace AAS and Ion Chromatography. The following parameters were measured: total suspended particles; insoluble suspended particles; soluble suspended particles; non-sea salt soluble suspended particles; Na, Ca, Cl, NO_3, NH_4 in soluble fraction; Al, Pb and Cu total contents in air, and K, Mg, Ca, SO_4 in non-sea salt soluble fraction. (Table 1).

For the intercomparison of sample treatment and trace metal analysis procedures, taken place in 1994, reference aerosols samples (RAS) were collected on W41 filters with a Sierra Hi/Vol equipment. Blanks from the same stock have been prepared. Filters and blanks were fractionated and combined to produce equivalent aliquots (160 cm^2) that were put into 125 ml Teflon bottles. The acid digestion was done directly inside those bottles to avoid further manipulations, following the recommendation of the enclosed procedure. In total 15 reference and 15 blank samples were prepared in this manner for distribution among laboratories participating in the intercalibration. Each laboratory was provided with a detailed protocol (see Appendix I), together with one blank sample and one reference sample. The Participating Laboratories (PLs) sent to the Central Laboratory (CL) the analytical data together with one half of their digested solution. These solutions were analysed by the CL to check-up the analyses of the participating laboratories (called WMO check). Two RAS and two blanks were also analyzed by CL using several different techniques in several replicates to determine the true value (WMO, 1995).

Results and discussion

Intercomparison of Hi/Vol Air Samplers (IHVAS)

During the week of a workshop in Sardinia (8-12 May 1995) we have compared and studied three Hi/Vol samplers normally in use in the MED POL programme. At the beginning of the intercomparison a short (one week) training course was organised to discuss sampling problems and to exchange experiences. For the intercomparison Malta provided an Aquaero sampler, IGM (Italy)- a MTX sampler and IMC (Italy)- a Sierra. The Aquaero sampler is also in use in Cyprus, and the Sierra Andersen samplers are used in Turkey, Israel and Morocco.

As shown in Figure 1, during the intercomparison the prevailing wind direction was NW, *although calms (□ 1 m s^{-1}) were dominant. Prevailing mean wind speed was between 1* and 2 ms^{-1} (Figure 2). A comparison table with the main characteristics of each instrument (Table 2) was prepared for easy reference. At the workshop a lot of debate was raised with respect to contamination problems, in particular those caused by: filter holder, pump, cover, etc. As it can be seen in Figure 3, the total fluxes measured by each sampler were comparable. For the insoluble fraction (representative of the coarse fraction >2 µm) of the fluxes and for the levels of lead (representative of the fine-grained fraction < 2 µm) we observed similar performances of the samplers. But in the case of the Sierra sampler, we observed the levels of copper 60% higher than for the MTX and Aquaero samplers. This is probably due to the Sierra sampler engine, with copper brushes. In addition, because of that, in case of heavy utilisation (continuously for weeks/months), the Sierra sampler breaks easily.

Thus, the Aquaero and MTX samplers seem to be better than the Sierra sampler, especially because of the Cu-engine-related contamination.

The Aquaero and MTX are very different in term of performances, and among them the most important are: a) Aquaero has no flow regulation, no programming (i.e. sampling recording, data transfer, stop in case of rain, etc); b) MTX allows all kind of regulation, but it is more complicated (electronics). Another difference, in case of need of technical intervention, is that Aquaero and Sierra are from the USA and MTX is from Italy, i.e. from the Mediterranean itself.

The problem of flow-rate checking was also highlighted at the workshop. Most of the participants normally trusted the flow-rate recorder but it was recognised that, even with the factory kit (in the case of Sierra), there were a lot of problems related to the calibration of the flow without a filter ("open machine"), as it is suggested to do in the Sierra manual. We observed differences when an external flow meter was utilized. Therefore a common tool to standardise the flow measurement (hot wire calibration kit with one blank W41 inserted) was suggested. For this purpose, some measurements were done with the Aquaero sampler (a constant flux instrument) to read the "correct" gauge with one blank W41 inserted, and for different states of the filter clogging (that was surrogated by inserting 2 and 3 W41 instead of 1; see Table 3). In this instrument the flux decreases when the obstruction of the filter increases. Only the difference between the flux at the beginning and at the end of the sampling (□) can be read, and the enclosed table could be used for calibration purposes (Table 3).

The sampling performances of the two other instruments were also compared, and the results happened to be satisfactory.

The isokinetic high volume sampler was treated separately, because of its specificity and its probable scarce utilisation at the MED POL monitoring stations.

In addition, we have discussed the problem of weighting the filters, especially with W41, that is much more hydrophilic than the GFF filters, previously utilised. It was agreed that the best way is to make a Plexiglas glove box that can contain the balance and the filters, kept with salts (see Table 4) at constant humidity, where the weighting before and after sampling should be performed.

Figure 4 shows the box plots for total suspended particles (TSP), measured with the MTX CIS3100 isokinetic sampler and all other samplers, expressed as mass (mg) and total flux (µg m^{-3}). The total mass captured by the isokinetic sampler was lower than those sampled by all others, whereas the total fluxes (µg m^{-3}) were comparable. In Figure 5 the correlation between TSP measured with the MTX CIS3100 isokinetic sampler and mean wind speed is shown. The isokinetic sampling demonstrated high correlation between sampled mass and wind speed, and a higher sampling efficiency with respect to the other samplers at wind speed above 3.5 m s^{-1}. This indicates that the other samplers (non isokinetics), are performing well in moderate-low wind conditions

The results of the analyses of all 19 samples for each sample compared are summarized in Tables 1a-1c.

For the three instruments in use within MED POL (Aquaero, MTX and Sierra), we compared the recovery of TSP, insoluble suspended particles (ISP), Al, Pb, Cu (insoluble fraction) (Figure 6) and soluble suspended particles (SSP), Na, NO_3, non-sea salt Ca (nssCa), non-sea salt SO_4 (nssSO_4) (soluble fractions) (Figure 7). In order to avoid the rejection of outliers, that can affect the mean considerably, we utilized robust procedures, to calculate the median and the median absolute deviation (MAD) of our data sets, where MAD = [median of (|x-median|)]/0.6745, with x = data point (Analytical Methods Committee, 1989).

The robust estimates are completely insensitive to how outlying the extreme data values are and obtain most of their information from the values in the centre of the dataset. As it can be seen, the performances of the instruments were similar for all these parameters, except Cu (already examined) and Al. As far as this element concerns, usually a ratio Al/ISP ≈ 0.08 can be expected (Chester *et al.*, 1993). In our case, we observed Al/ISP ≈ 0.02. This can be caused by a bigger percentage of sand (Al poor material) in the collected mass, due to resuspension, that increased the insoluble fraction, and can explain the slight variability amongst samplers.

In Figure 8 the correlation between Al and Pb measured in all the samplers is presented. The low levels (0-7 ng m^{-3}) of Pb and Al (0-1 µg m^{-3}) demonstrate the remoteness of the site and well correlate each-other. Only a few samples were enriched in crustal components (Al), mainly when winds came from S-SE.

In Table 5 the amounts of trace metals present in the atmosphere under normal conditions in remote and coastal stations are compared. To obtain this values, we considered the concentrations found in atmosphere by different studies (see references in the table) and we supposed three different sampling times, at an air flow = 40 m^3 h^{-1} (which could be set up for each sampler, see Table 2). Table 6 shows the data obtained by all the samplers (except CIS3100) during the intercomparison. As it can be seen, for a remote site the sampling time must be at least 48 h, in order to avoid a too high blank/signal ratio. On the contrary, for a coastal station a 24-h-sampling time can be used.

Intercomparison on Metal Analyses in Reference Aerosol Samples (IMARAS)

The intercomparison of sample treatment and analysis procedures for heavy metals used by the laboratories participating in the MED POL Airborne Pollution Monitoring Programme was recommended by a WMO/UNEP Expert Meeting on Quality Assurance for the MED POL Airborne Pollution Measurements held in Ankara, Turkey from 27 to 30 May 1993 (WMO, 1994).

For such an intercomparison the Institute of Marine Geology (IGM) Bolognia, Italy, prepared two intercomparison samples: a blank Whatman 41 filter (W41F) and a Reference Aerosol Sample (RAS). The RAS filter (taken from the same set of filters as the blank one) was exposed to air pumping at a monitoring station in Sardinia, Italy. A Sierra Andersen high-volume sampler was used for sampling.

Two strips of each filter (taken from different parts of W41F and RAS to ensure better homogeneity) were put into Teflon bottles and two bottles (with parts of W41F an RAS) were sent to each of the laboratories participating in the intercomparison (in Croatia, Cyprus, Egypt, France, Israel- 2, Italy, Malta, Monaco, Morocco, Slovenia, Spain, Turkey- 2, Yugoslavia and the Marine Environment Laboratory (MEL) of IAEA in Monaco). The list of laboratories and the analytical methods they used are given in Table 7.

In accordance with the recommended procedure (see Appendix I) the participating laboratories (PLs) were advised to prepare aliquots of each sample (W41F and RAS) and to divide them into two parts. One part of each sample should have been analysed at the participating laboratory (laboratory data) and the second part should have been sent to WMO for further analysis at a central laboratory in Italy, (CL) (WMO check data). That procedure allowed to conduct the intercomparison of both sample treatment procedures and analyses.

Two RAS and two blanks were also analyzed by CL using several different techniques in several replicates to determine the "true value".

Table 8 lists the results obtained by each participant and the WMO checkouts are also displayed in form of graphs (Figure 9).

The comparison of the bias of the PLs (WMO, 1995), has been made for each element using the Z score where Z= (x - x_t) / □t, x = analytical value obtained by each laboratory, x_t = true value obtained by CL using several different techniques in several replicates, and □t = standard deviation of the true value (Pedersen and Cofino, 1994). The scores of |Z| = 2 would be equivalent to 2□ and values above this would equate to critical levels. Scores higher than |Z| = 4 must be considered unacceptable. The Z scores for Pb in reference aerosol samples and in blanks are given in Figure 10, for both PL and WMO checks. High values derived from the check-up analysis of the digested solution sent by the laboratory 4 have been observed also for Al, Cu, Na, Zn, and are probably due to a contamination in the PL (Figure 11).

The results of the intercomparison for RAS show that the main disparities have occurred in the analytical techniques rather than in the digestions. That stresses the importance for all laboratories to strictly follow the recommended digestion procedures and to take all the necessary precaution measures to avoid possible contamination of samples during the digestion. In this case the recommended protocol produces acceptable results.

It was also recommended that the laboratories participating in the MED POL Airborne Pollution Monitoring Programme be provided with certified standard solutions (with metals) to check their analyses and that another similar intercomparison exercise be organized in the future (WMO, 1995).

Conclusive remarks

- The three high-volume samplers in use within the MED POL programme compared in this study performed similarly in terms of efficiency, but the Aquaero and MTX samplers seem to be better than Sierra, especially because of the Cu-engine-related contamination.
- For the Aquaero sampler, a flux calibration table has been proposed.
- It has been decided that the best way for weighting the filters is to make a Plexiglas glove box that can contain the balance and the filters, kept with salts at constant humidity, where filter weighting before and after sampling should be performed.
- Through a comparison with an isokinetic high-volume prototype, it has been shown that the collection efficiency of non-isokinetic samplers is satisfactory in case of moderate low winds.
- Reference blanks for W41 filters have been prepared and analyzed, and reference values for trace metals blank contribution obtained. These, expressed as ng cm^{-2} of filter surface, are: for Al - 110, for Cd - 0.03, for Pb - 1, for Zn - 7.4.
- The sampling time needed to get an acceptable blank/signal ratio should be at least 48 h for a remote station and 24 h for a coastal one.
- The protocol for digestion and handling W41 filters utilized for IMARAS is believed to be sufficient to produce acceptable results.
- The results of IMARAS showed that the main discrepancies occurred in the analytical techniques rather than in digestion.

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Tab. 1a - IHVAS. Data obtained by chemical analyses of aerosol samples. A = Aquaero Tech 400XT aerosol sampler, TSP = total suspended particles, ISP = insoluble suspended particles, SSP = soluble suspended particles, nss = non-sea salt, sol = soluble, mws = mean wind speed (m s^{-1}), wdir = prevalent wind direction (degrees; 0 = wind□1 m s^{-1}). Units ng m^{-3} for Pb and Cu, and µg m^{-3} for others. $^{(1)}$ = corrected for water absorption (10 µg cm^{-2} at 40% humidity; Demuynck, 1975).

	mg$^{(1)}$	m^3	TSP $^{(1)}$	ISP$^{(1)}$	SSP	SSP nss	Na-sol	K-solnss	Mg-solnss	Ca-sol	Ca-solnss	Cl-sol	NO_3-sol	SO_4-solnss	NH_4-sol	Al	Pb	Cu	mws	wdir
A2	47,10	1135	41,50	1,85	39,65	4,21	10,76	0,045	0,000	0,589	0,176	19,90	1,45	1,60	0,93	0,076	0,00	2,71	5,2	315
A3	31,90	1056	30,21	7,44	22,77	7,54	2,51	0,142	0,004	0,250	0,152	11,56	2,76	3,95	0,53	0,137	0,00	5,26	2,0	315
A4	51,00	1046	48,76	30,00	18,76	9,11	3,26	0,074	0,004	0,998	0,871	4,90	3,67	3,03	1,46	0,565	0,22	8,75	1,1	0
A5	69,00	1054	65,46	38,87	26,59	11,76	5,32	0,067	0,038	1,531	1,325	7,06	4,72	4,08	1,57	0,376	0,93	2,85	4,8	180
A6	24,30	1014	23,96	9,23	14,73	8,59	2,10	0,049	0,007	0,586	0,503	3,06	2,97	3,79	1,28	0,333	1,11	8,58	2,2	360
A7	65,40	1967	33,25	12,66	20,59	11,08	3,49	0,058	0,012	0,577	0,442	4,42	3,29	5,65	1,64	0,251	0,65	7,05	1,9	0
A8	66,30	1056	62,78	33,77	29,02	12,23	6,25	0,103	0,053	0,648	0,406	7,66	3,99	5,20	2,54	0,283	1,56	9,09	1,2	0
A9	23,00	1039	22,14	4,67	17,47	10,58	1,54	0,110	0,024	0,687	0,626	4,61	2,87	5,20	1,77	0,380	4,98	7,29	1,5	0
A10	11,00	1080	10,19	0,00	15,45	12,78	0,92	0,085	0,036	0,619	0,582	1,29	3,17	6,80	2,15	0,528	4,38	4,86	1,3	0
A11	31,20	982	31,77	14,88	16,89	10,84	1,96	0,104	0,033	1,185	1,108	3,16	2,52	5,28	1,83	0,991	2,90	5,19	3,0	180
A12	48,30	1039	46,49	23,27	23,21	13,73	3,26	0,104	0,049	1,799	1,672	4,68	4,07	6,15	1,74	1,209	3,39	5,56	2,3	180
A13	89,80	1973	45,51	22,19	23,32	14,01	3,25	0,096	0,062	1,464	1,339	4,52	4,05	6,85	1,68	0,901	2,21	73,71	1,1	0
A14	83,90	1978	42,42	25,14	17,28	12,83	1,55	0,106	0,046	0,922	0,862	2,15	3,97	6,34	1,56	0,954	4,44	6,29	1,5	0
A15	56,60	1030	54,95	36,30	18,65	13,14	1,92	0,082	0,010	1,028	0,952	2,69	4,51	5,85	1,74	1,254	7,14	9,98	1,2	0
A16	83,20	1655	50,27	24,08	26,19	5,93	5,76	0,054	0,000	0,613	0,391	11,93	2,77	1,61	1,10	0,082	1,00	4,58	3,6	315
A17	76,80	1054	72,87	27,87	45,00	12,70	9,89	0,025	0,016	0,649	0,268	17,93	4,48	5,08	2,84	0,243	1,57	7,19	2,3	315
A18	38,90	1037	37,51	19,08	18,43	10,52	2,66	0,083	0,021	0,573	0,469	4,01	4,35	3,81	1,80	0,315	3,33	12,30	0,9	0
A19	21,90	1005	21,79	10,36	11,43	8,57	0,93	0,078	0,031	0,501	0,464	1,46	3,15	3,35	1,53	0,272	3,51	9,18	1,2	0
A20	33,70	1055	31,94	18,82	13,12	9,96	1,04	0,083	0,025	0,762	0,720	1,61	3,24	4,17	1,74	0,457	3,20	9,67	1,2	0

Tab. 1b - IHVAS. Data obtained by chemical analyses of aerosol samples. B = MTX CVA3000 air sampler, TSP = total suspended particles, ISP = insoluble suspended particles, SSP = soluble suspended particles, nss = non-sea salt, sol = soluble, mws = mean wind speed (m s^{-1}), wdir = prevalent wind direction (degrees; 0 = wind□1 m s^{-1}).Units ng m^{-3} for Pb and Cu, and µg m^{-3} for others [(1)] = corrected for water absorption (10 µg cm^{-2} at 40% humidity; Demuynck, 1975).

	mg[(1)]	M³	TSP [(1)]	ISP[(1)]	SSP	SSP nss	Na-sol	K-solnss	Mg-solnss	Ca-sol	Ca-solnss	Cl-sol	NO_3-sol	SO_4-solnss	NH_4-sol	Al	Pb	Cu	mws	wdir
B2	71,40	1159	61,60	2,47	59,13	7,08	15,85	0,017	0,000	0,787	0,176	35,63	2,53	3,32	1,00	0,087	0,00	0,13	5,2	315
B3	44,40	1199	37,03	6,51	30,53	7,42	7,26	0,103	0,000	0,585	0,304	12,65	2,66	2,62	1,73	0,133	0,31	2,13	2,0	315
B4	56,80	1199	47,37	29,27	18,10	8,42	3,29	0,087	0,000	0,936	0,806	4,92	3,31	2,78	1,44	0,521	0,19	9,32	1,1	0
B5	73,30	1199	61,13	28,94	32,19	13,01	6,51	0,068	0,008	1,774	1,521	9,73	5,34	4,61	1,48	0,833	2,19	20,33	4,8	180
B6	38,40	1204	31,89	17,77	14,12	8,39	1,87	0,052	0,001	0,483	0,408	3,04	3,13	3,58	1,18	0,421	1,56	5,48	2,2	360
B7	69,00	2212	31,19	11,17	20,03	10,44	3,38	0,062	0,028	0,582	0,450	4,63	3,02	5,32	1,59	0,281	0,95	2,98	1,9	0
B8	79,80	1203	66,33	30,84	35,49	14,55	7,12	0,069	0,000	0,646	0,370	10,62	5,18	6,52	2,43	0,292	2,00	6,05	1,2	0
B9	24,70	1198	20,62	5,84	14,77	10,18	1,43	0,119	0,017	0,636	0,578	2,48	3,00	4,77	1,73	0,460	2,32	6,26	1,5	0
B10	18,30	1199	15,26	0,75	14,51	12,09	0,83	0,091	0,027	0,661	0,625	1,18	3,03	6,31	2,04	0,532	3,19	3,82	1,3	0
B11	43,20	1200	36,00	16,92	19,08	11,00	2,61	0,112	0,025	1,310	1,206	4,29	2,88	5,09	1,68	0,956	1,88	6,00	3,0	180
B12	69,40	1202	57,74	33,36	24,38	13,64	3,66	0,123	0,049	1,832	1,688	5,32	4,09	6,08	1,71	2,118	3,43	9,61	2,3	180
B13	114,60	2300	49,83	28,57	21,26	12,70	3,08	0,099	0,048	1,394	1,275	4,05	3,69	6,12	1,53	0,811	2,22	65,19	1,1	0
B14	97,40	2400	40,58	25,50	15,08	11,08	1,44	0,113	0,040	0,861	0,804	1,87	3,35	5,35	1,46	0,808	2,84	7,16	1,5	0
B15	59,80	1199	49,87	30,78	19,10	13,68	1,93	0,150	0,057	1,198	1,121	2,58	4,51	6,12	1,74	1,195	5,25	7,51	1,2	0
B16	78,60	1791	43,89	21,89	22,00	5,86	6,09	0,057	0,000	0,568	0,332	7,32	1,67	2,79	1,04	0,308	0,59	2,76	3,6	315
B17	91,90	1202	76,46	28,62	47,84	12,90	10,57	0,004	0,000	0,609	0,201	19,84	4,62	5,16	2,88	0,271	1,00	2,37	2,3	315
B18	45,60	1200	38,00	19,58	18,42	10,50	2,61	0,099	0,012	0,585	0,481	4,11	4,34	3,80	1,78	0,329	2,94	7,44	0,9	0
B19	24,10	1198	20,12	8,51	11,60	8,76	0,88	0,102	0,021	0,523	0,486	1,54	3,49	3,27	1,45	0,358	5,13	6,32	1,2	0
B20	37,80	1197	31,58	18,55	13,03	10,28	0,94	0,099	0,026	0,787	0,747	1,42	3,26	4,40	1,73	0,841	3,45	6,58	1,2	0

Tab. 1c - IHVAS. Data obtained by chemical analyses of aerosol samples. C = Sierra Andersen GMWL 2000H air sampler, TSP = total suspended particles, ISP = insoluble suspended particles, SSP = soluble suspended particles, nss = non-sea salt, sol = soluble, mws = mean wind speed (m s^{-1}), wdir = prevalent wind direction (degrees; 0 = wind□1 m s^{-1}). Units ng m^{-3} for Pb and Cu, and µg m^{-3} for others. $^{(1)}$ = corrected for water absorption (10 µg cm^{-2} at 40% humidity; Demuynck, 1975).

	mg$^{(1)}$	m^3	TSP$^{(1)}$	ISP$^{(1)}$	SSP	SSP nss	Na-sol	K-solnss	Mg-solnss	Ca-sol	Ca-solnss	Cl-sol	NO_3-sol	SO_4-solnss	NH_4-sol	Al	Pb	Cu	mws	wdir
C2	79,90	1195	66,86	11,21	55,65	4,10	15,78	0,090	0,000	0,859	0,252	28,77	1,46	1,43	0,88	0,087	0,13	14,12	5,2	315
C3	39,10	1176	33,25	7,99	25,26	7,06	3,38	0,050	0,000	0,260	0,128	13,30	2,57	3,62	0,66	0,137	0,19	33,42	2,0	315
C4	53,20	1178	45,16	26,91	18,25	8,66	3,22	0,081	0,000	0,986	0,859	4,92	3,45	2,91	1,35	0,566	0,51	7,26	1,1	0
C5	86,30	1200	71,92	37,92	34,00	13,00	7,24	0,066	0,000	1,905	1,625	10,49	5,32	4,65	1,31	0,183	2,06	3,38	4,8	180
C6	34,50	1200	28,75	15,58	13,17	7,58	1,90	0,077	0,026	0,555	0,479	2,76	2,67	3,20	1,15	0,279	2,38	23,50	2,2	360
C7	81,60	2205	37,01	17,10	19,91	10,16	3,43	0,048	0,012	0,595	0,462	4,79	2,92	5,12	1,59	0,196	1,09	98,98	1,9	0
C8	71,10	1176	60,46	23,81	36,65	14,46	7,46	0,167	0,014	0,809	0,520	11,28	5,07	6,18	2,55	0,219	1,40	26,59	1,2	0
C9	30,60	1176	26,02	11,22	14,80	9,78	1,49	0,133	0,029	0,681	0,621	2,73	2,60	4,82	1,65	0,557	3,76	20,60	1,5	0
C10	17,20	1200	14,33	1,42	12,92	10,50	0,86	0,078	0,025	0,643	0,607	1,14	2,52	5,35	1,94	0,619	4,63	18,44	1,3	0
C11	51,10	1200	42,58	22,00	20,58	11,83	2,71	0,122	0,041	1,468	1,361	4,74	3,06	5,52	1,81	1,524	2,69	24,50	3,0	180
C12	83,10	1200	69,25	45,25	24,00	13,17	3,69	0,123	0,049	1,780	1,636	5,43	3,88	5,91	1,64	1,194	2,25	32,50	2,3	180
C13	110,30	2300	47,96	27,26	20,70	12,39	2,92	0,099	0,063	1,327	1,213	4,02	3,56	6,09	1,43	1,002	2,45	88,30	1,1	0
C14	94,00	2400	39,17	23,71	15,46	11,67	1,37	0,085	0,031	0,778	0,724	1,78	3,80	5,73	1,32	0,999	3,00	23,06	1,5	0
C15	59,40	1199	49,54	31,69	17,85	12,51	1,74	0,133	0,045	1,156	1,087	2,74	4,15	5,55	1,60	1,180	7,13	20,96	1,2	0
C16	93,30	1885	49,50	22,60	26,90	6,74	5,78	0,047	0,000	0,576	0,353	11,81	2,46	2,89	0,99	0,080	0,40	20,17	3,6	315
C17	77,80	1200	64,83	17,67	47,17	12,17	10,61	0,066	0,030	0,768	5,000	19,51	4,35	4,92	2,50	0,111	0,88	15,56	2,3	315
C18	50,50	1236	40,86	24,27	16,59	9,55	2,37	0,092	0,011	0,539	0,445	3,58	3,95	3,51	1,55	0,290	2,79	29,19	0,9	0
C19	40,00	1216	32,89	22,37	10,53	7,89	0,83	0,065	0,015	0,461	0,427	1,36	2,87	3,13	1,39	0,309	4,56	25,23	1,2	0
C20	35,00	1200	29,17	16,50	12,67	9,75	1,00	0,085	0,034	0,805	0,764	1,43	2,95	4,29	1,68	0,488	6,56	34,75	1,2	0

Tab. 2. Main characteristics of each instrument.

		Aquaero Tech 400XT	**MTX CVA 3000**	**Sierra Andersen GMWL 2000H**
Flow regulation		NO	YES	YES
Regulation range (for reliable values),	MIN	-	22 m³/h	35 m³/h
with a Watman 41 (W41) clean filter	MAX	46 m³/h	67–80 m³/h (1–1,2 HP pump)	100 m³/h
Flow regulation type		-	electromechanic (by pass)	electronic
Flow regulation sensor		-	Venturi	hot wire
Sampling time programming (start/stop)		YES	YES	YES
Total sampling time recording		YES (hours counter)	YES (display+output RS232)	YES (hours counter)
Direct reading of total volume sampled		NO (total time x mean flow)	YES (display+output RS232)	NO (total time x mean flow)
Sampling data recording (flow, time, wind direction, wind speed, rain)		NO	YES (*every data on output* RS232)	YES (*mean flow on a paper disc*)
Data maintenance in case of power failure		YES (hours)	YES (buffer battery: every data)	YES (hours + mean flow)
Programming and data transfer on a PC		NO	YES	NO
Sampling stop for undesired wind direction		YES	YES	NO
Sampling stop for undesired wind speed		YES	YES	NO
Sampling stop in case of rain		NO	YES	NO
Filter size holder		8”x10”	*∅ 240 mm or 8”x10”*	8”x10”
Filter type		Watman 41, glass fiber, quartz, fabric	Watman 41, glass fiber, quartz, fabric	Watman 41, glass fiber, quartz, fabric
Filter holder chemically inert		YES	YES	NO
Engine type		induction single-phase 220 VAC	Induction single-phase 220 VAC	with brushes 220 VAC
Engine pollution		NO	NO	YES (Cu + C)
Maximum power		~600 W	760–900 (1÷1,2 HP pump)	~960 W
Noising		very low	medium-low	low
Total weight		~60 Kg	~60 Kg	~20 Kg
Transport easiness		mean difficulty, bulky	mean difficulty	easy

Tab. 3. See text for explanation.

Aquaero Tech	Δ	$m^3 h^{-1}$	***% variation***	
1 W41				
reading	2.5	46.3	-3%	Max flow rate
calibration (hot wire kit)		47.6		
2 W41				
reading	1.5	34.8	-6%	
calibration (hot wire kit)		37.0		
3 W41				
reading	1.3	31.4	-4%	
calibration (hot wire kit)		32.8		

Tab. 4. % Humidity at 25 °C within a closed space when an excess of the substance indicated is in contact with a saturated aqueous solution of the given solid phase.

$LiCl$	14
CH_3COOK	21
$MgCl_2\ 6\ H_2O$	33
K_2CO_3	44
$Mg(NO_3)_2\ 6H_2O$	54
$NaCl$	76
K_2CrO_4	88
$BaCl_2\ 2H_2O$	90
KNO_3	94
$NaHPO_4$	96
K_2SO_4	97
K_2CrO_4	98

Tab. 5. Amounts of trace metals present in the atmosphere under normal conditions (air flow = 40 m^3 h^{-1}). 1 = Data from Guerzoni *et al.*, (1997). 2 = Data from Chester *et al.*, (1992). 3 = Data from Guieu (1991). Units = µg.

		Al	**blank %**	**Cd**	**blank %**	**Pb**	**blank %**	**Zn**	**blank %**
Remote[1]	24 h	137	40.0	0.029	51.7	7.01	7.6	3.3	113 6
	48 h	275	20.0	0.058	25.9	14.02	3.8	6.5	57 7
	72 h	412	13 3	0 086	17 4	21 02	2 5	9.8	38 3
Coastal[2, 3]	24 h	368	15 0	0 470	3.2	52.80	1.0	48.0	7.8
	48 h	735	7.5	0 941	1.6	105 60	0.5	96.0	3.9
	72 h	1103	5.0	1 411	1.1	158.40	0.3	144.0	2 6
Blank		55		0.015		0 53		3 7	

Tab. 6 - IHVAS. Amounts of atmospheric trace metals measured during the investigation with all the samplers (air flow = 40 m^3 h^{-1}). Units = µg.

		Al	**blank %**	**Pb**	**blank %**
present study	24 h	528	10.4	1.92	27.6
	48 h	1056	5.2	3.84	13 8
blank		55		0.53	

Tab. 7 - IMARAS. Analytical methods used by different laboratories. AAS = Atomic Absorption Spectrometry, ICP-MS = Inductively Coupled Plasma-Mass Spectrometry, F. Phot. = Flame Photometry, DPASV = Different Pulse Anodic Stripping Voltametry, DCUSA = D.C.U. - Shaped Arc, ASV = Anodic Stripping Voltametry, F/GF = Flame/Graphite Furnace.

Laboratory	**Laboratory's Country**	**Method**	**Notes**
CNR - Istituto di Geologia Marina	Italy	AAS	F/GF
State General Laboratory	Cyprus	AAS	F/GF
University of Malta - Dept. of Chemistry	Malta	AAS	F/GF
Ecole Mohammadia d'Ingénieurs – Atmospheric and Marine Pollution Laboratory	Morocco	AAS	
IAEA - Marine Environmental Laboratory	Monaco	ICP-MS	
Middle East Technical University - Dept of Environmental Engineering	Turkey	AAS	F/GF
Middle East Technical University - Institute of Marine Sciences	Turkey	AAS	F/GF
Meteorological and Hydrological Service - Water and Air Control Division	Croatia	F Phot -AAS-DPASV-DCUSA	
	True value	***AAS*-ICP-ASV***	****F/GF***

Table 8. IMARAS. Analytical results for aliquots of reference aerosol samples (RAS) as measured by the participating laboratories (8a) and by the central laboratory (8b). Units: µg/ml; for AC, Cu, Na, Pb and Zn and ng/ml for Cd.

Tab. 8a - IMARAS. Laboratory data.

Lab. code	**Al**	**Cd**	**Cu**	**Na**	**Pb**	**Zn**
1	27,6	5,22	1,41	70,8	0,42	0,34
2	na	<0.1	0,75	na	na	0,13
3	5,2	8,76	1,69	6400	0,11	0,36
4	na	0,35	<0.1	0,48	0,07	na
5	12,4	295	1	17,4	0,26	0,24
6	na	1,18	1,65	56,2	0,21	0,32
7	20,6	3,5	1,03	62,4	0,53	0,29
8	27,2	<0.1	0,05	75,3	0,33	<0.1
True value	***27,5***	***3,87***	***1,52***	***72***	***0,36***	***0,36***
st. dev.	***1***	***1,6***	***0,13***	***2,2***	***0,07***	***0,04***

Tab. 8b - IMARAS. WMO check data.

Lab. code	**Al**	**Cd**	**Cu**	**Na**	**Pb**	**Zn**
1	27,4	5,06	1,62	72,7	0,38	0,35
2	23,5	47,2	1,64	79,6	0,75	0,35
3	23,9	7,62	1,49	75,3	0,43	0,39
4	45,8	2,55	2,07	110,2	0,33	1,14
5	24,3	3,66	1,54	74,1	0,43	0,33
6	21,9	6,31	1,65	75,7	0,5	0,35
7	24,9	5,73	1,5	74	0,39	0,4
8	28,1	<0.1	0,2	74,5	0,34	<0.1
True value	***27,5***	***3,87***	***1,52***	***72***	***0,36***	***0,36***
st. dev.	***1***	***1,6***	***0,13***	***2,2***	***0,07***	***0,04***

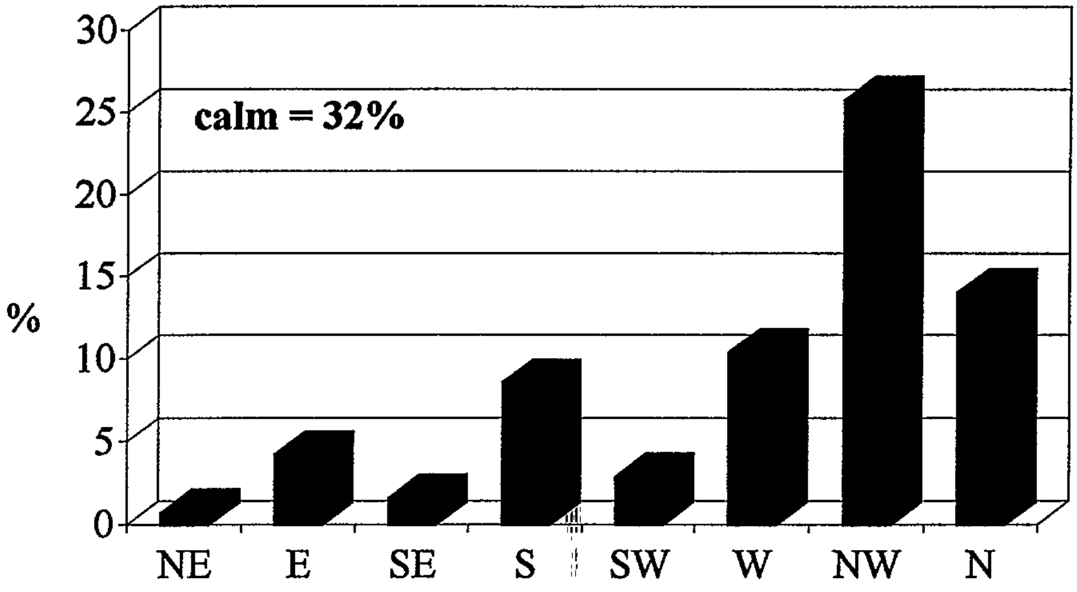

Fig. 1 - IHVAS. Wind direction during the intercomparison. Calm = wind speed ≤ 1 m s^{-1}.

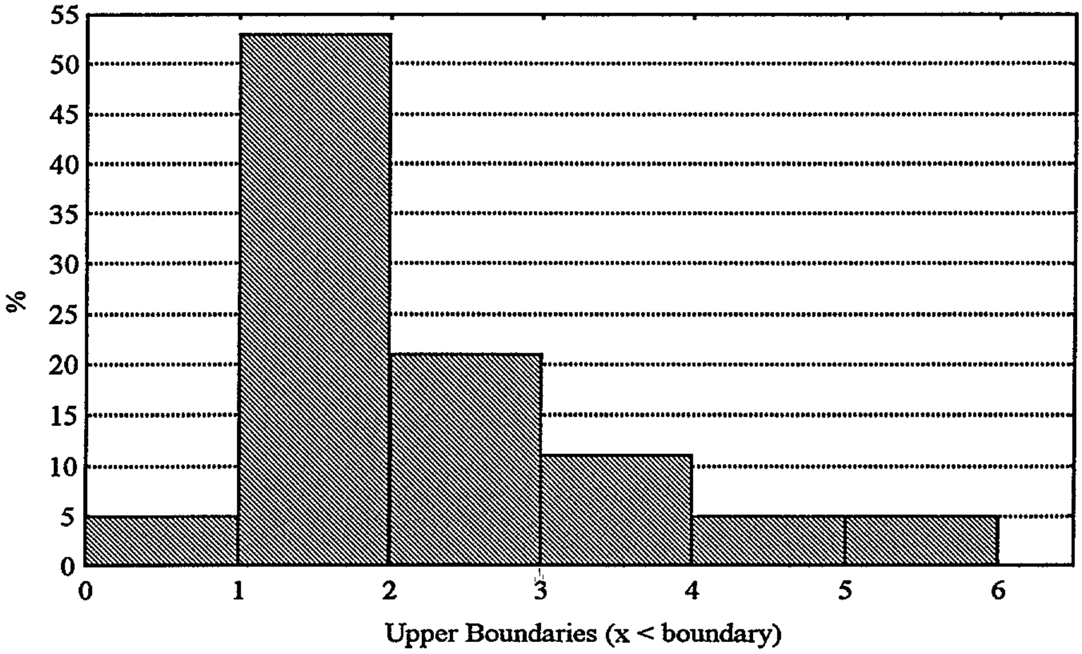

Fig. 2 - IHVAS. Mean wind speed during the intercomparison. Units = m s^{-1}.

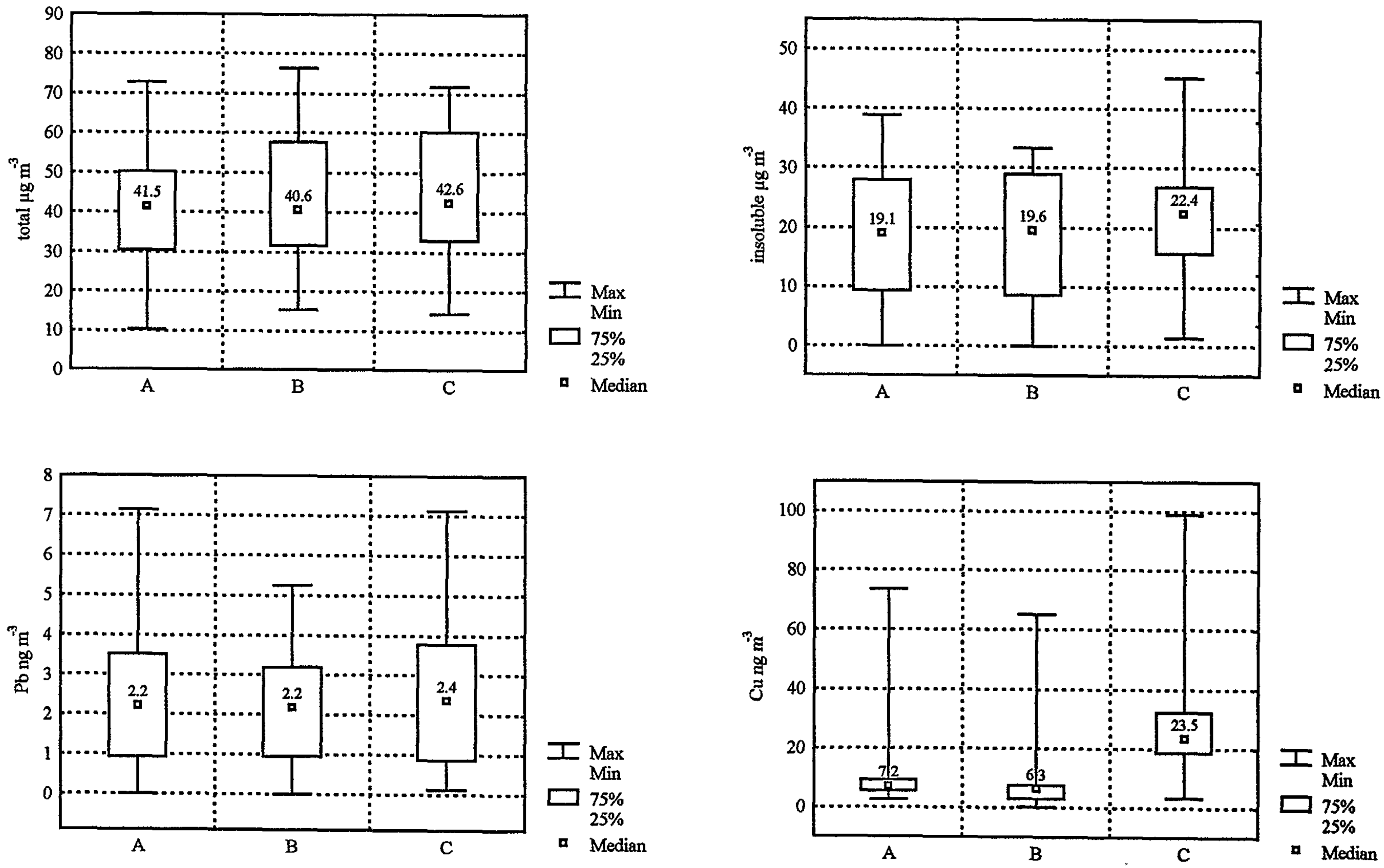

Fig. 3 - IHVAS. Descriptive statistic of main data collected during the intercomparison. Total = total suspended particles. Insoluble = insoluble suspended particles. A = Aquaero Tech 400XT aerosol sampler, B = MTX CVA 3000 air sampler, C = Sierra Andersen GMWL 2000H air sampler.

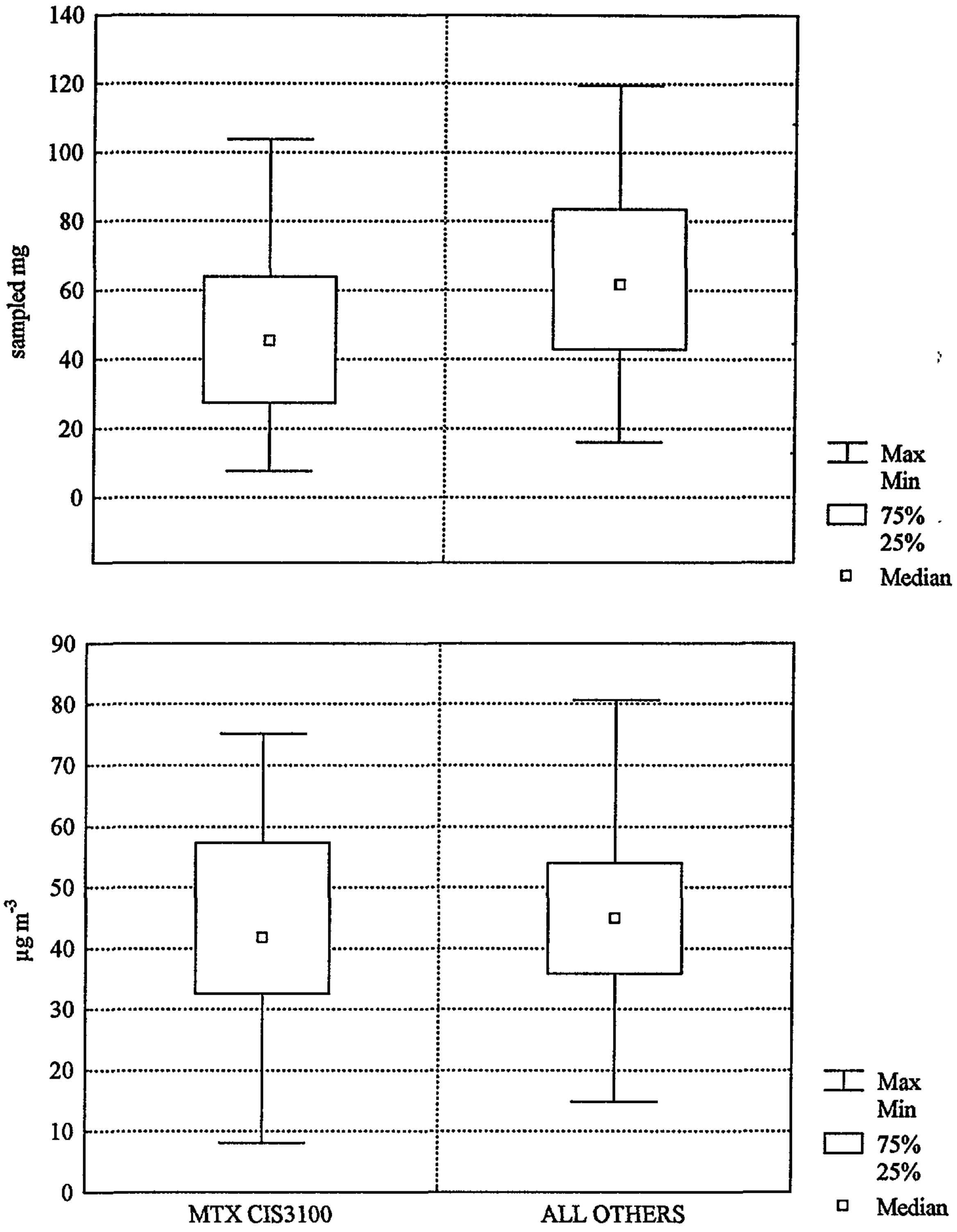

Fig. 4 - IHVAS. Box plots for total suspended particles (TSP) measured with MTX CIS3100 isokinetic sampler and all other samplers.

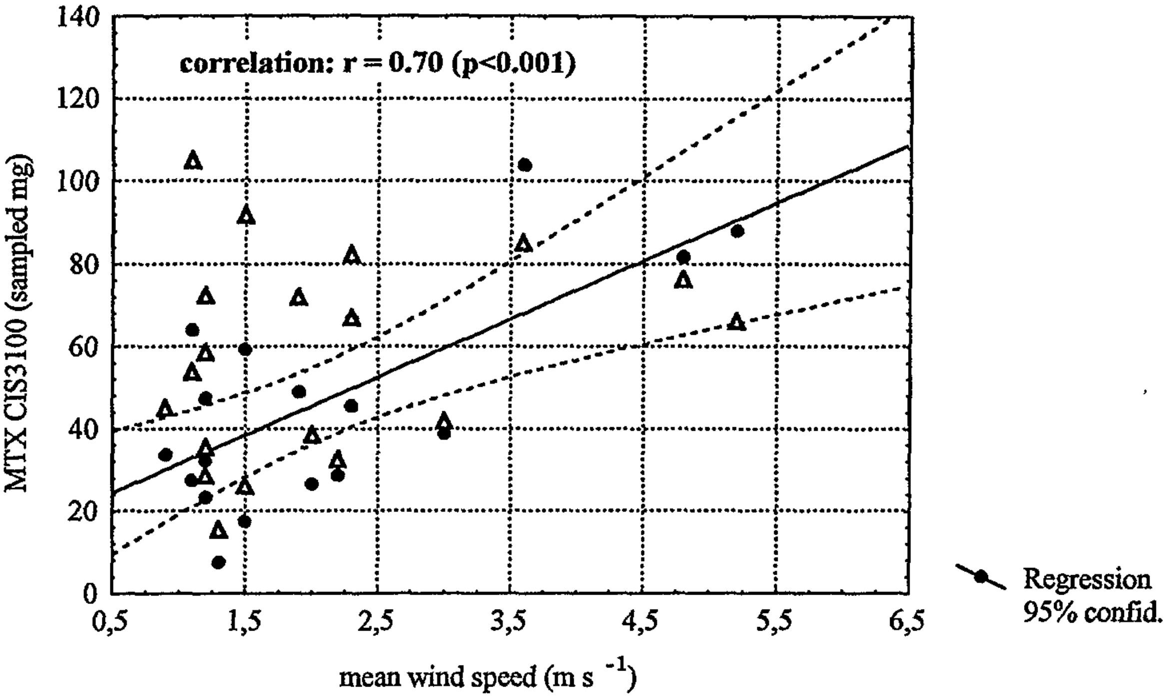

Fig. 5 - IHVAS. Correlation between total suspended particles (TSP) measured with all samplers and mean wind speed. • = MTX CIS3100, Δ = average of all other samplers. The regression curve is only referred to TSP values obtained with MTX CIS3100 isokinetic sampler.

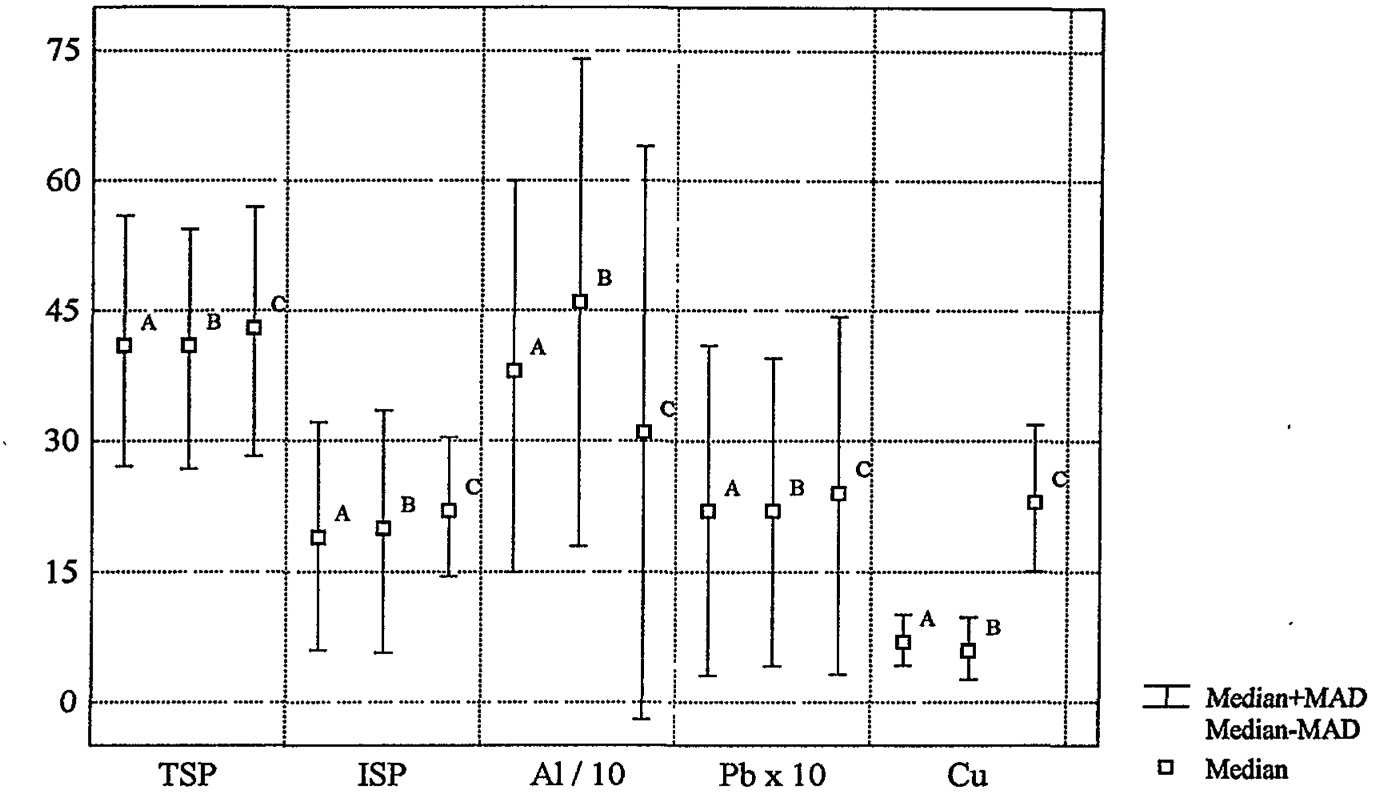

Fig. 6 - IHVAS. Amounts of total suspended particles (TSP), insoluble suspended particles (ISP), Al, Pb and Cu measured with each sampler. A = Aquaero Tech 400XT aerosol sampler, B = MTX CVA 3000 air sampler, C = Sierra Andersen GMWL 2000H air sampler. MAD, median absolute deviation = [median of (|x-median|)]/0.6745, with x = data point (Analytical Methods Committee, 1989). For TSP and ISP units = $\mu g\ m^{-3}$, for Al, Pb, Cu units = $ng\ m^{-3}$.

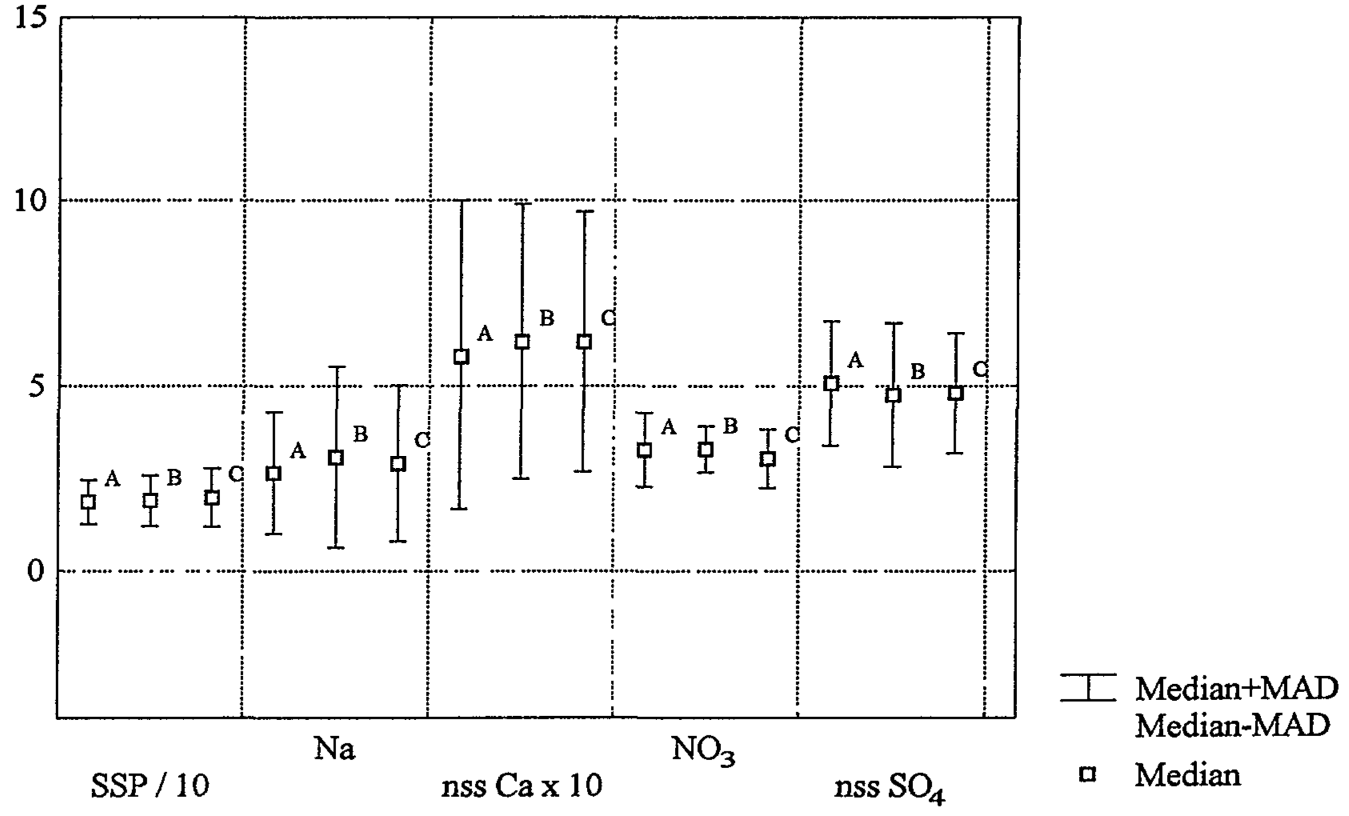

Fig. 7 - IHVAS. Amounts of soluble components measured with each sampler. SSP = soluble suspended particles. Nss = non-sea salt. A = Aquaero Tech 400XT aerosol sampler, B = MTX CVA 3000 air sampler, C = Sierra Andersen GMWL 2000H air sampler. MAD, median absolute deviation = [median of (|x-median|)]/0.6745, with x = data point (Analytical Methods Committee, 1989). Units = $\mu g\ m^{-3}$.

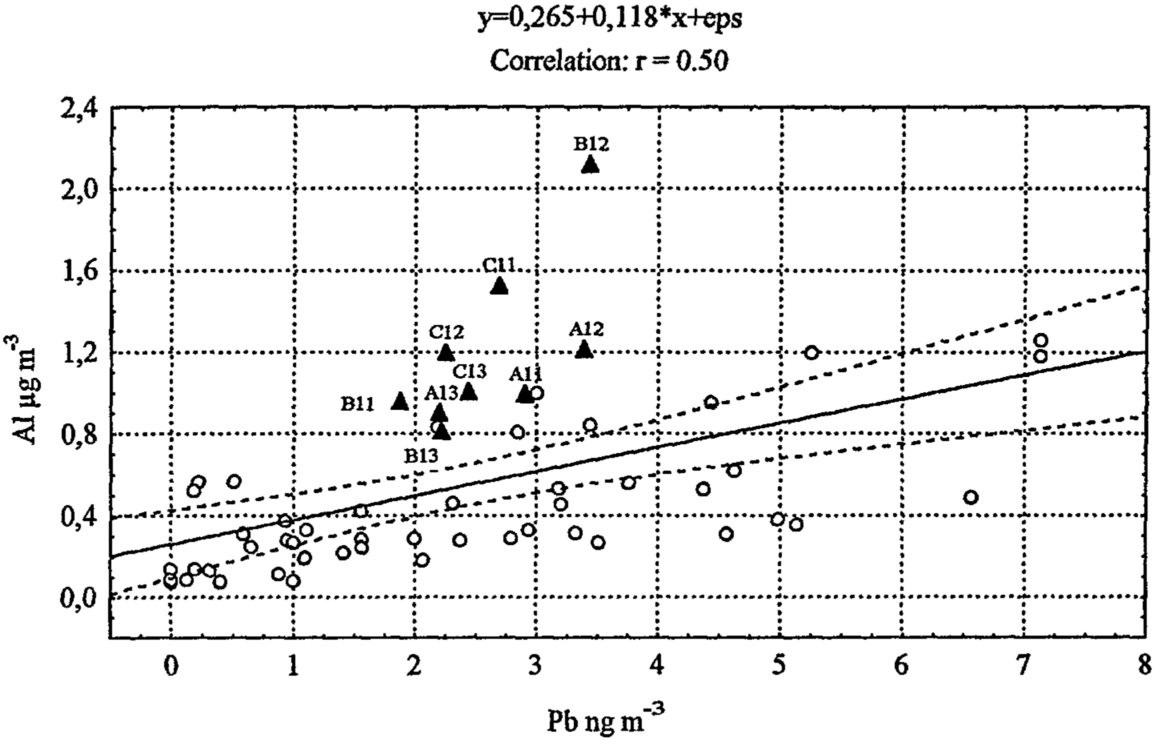

Fig. 8 - IHVAS. Correlation between Al and Pb concentrations measured with all the samplers.

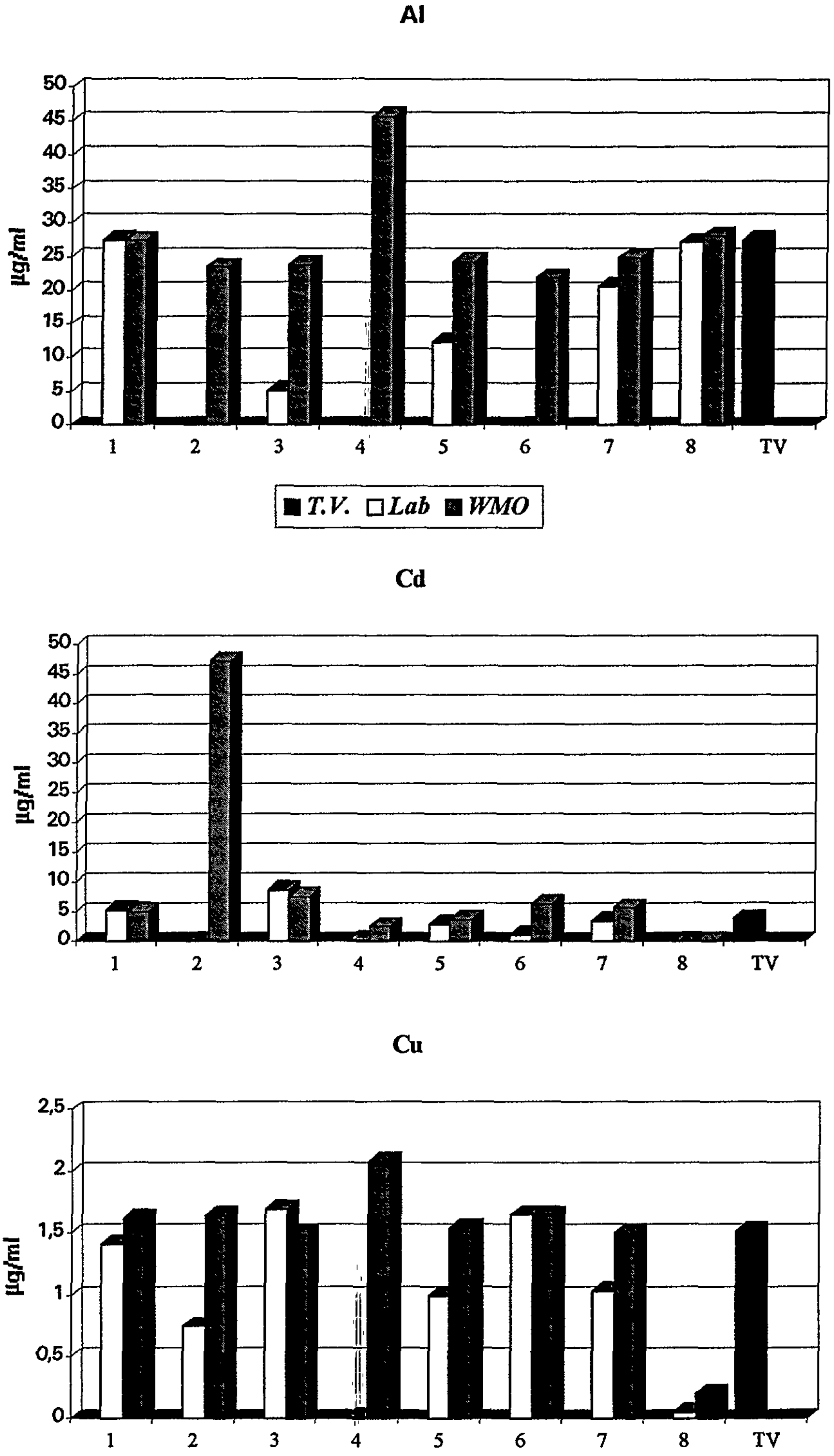

Fig. 9a - IMARAS. Concentration graphs. The results obtained by each participant from the analyses of test solutions are shown for each element. T.V.=true value. Lab=value obtained from the analysis of the test solutions by other laboratories. WMO= value obtained from the analysis of the same solutions by WMO Test Laboratory. The bold numbers (1 to 8) represent the laboratory intercalibration code.

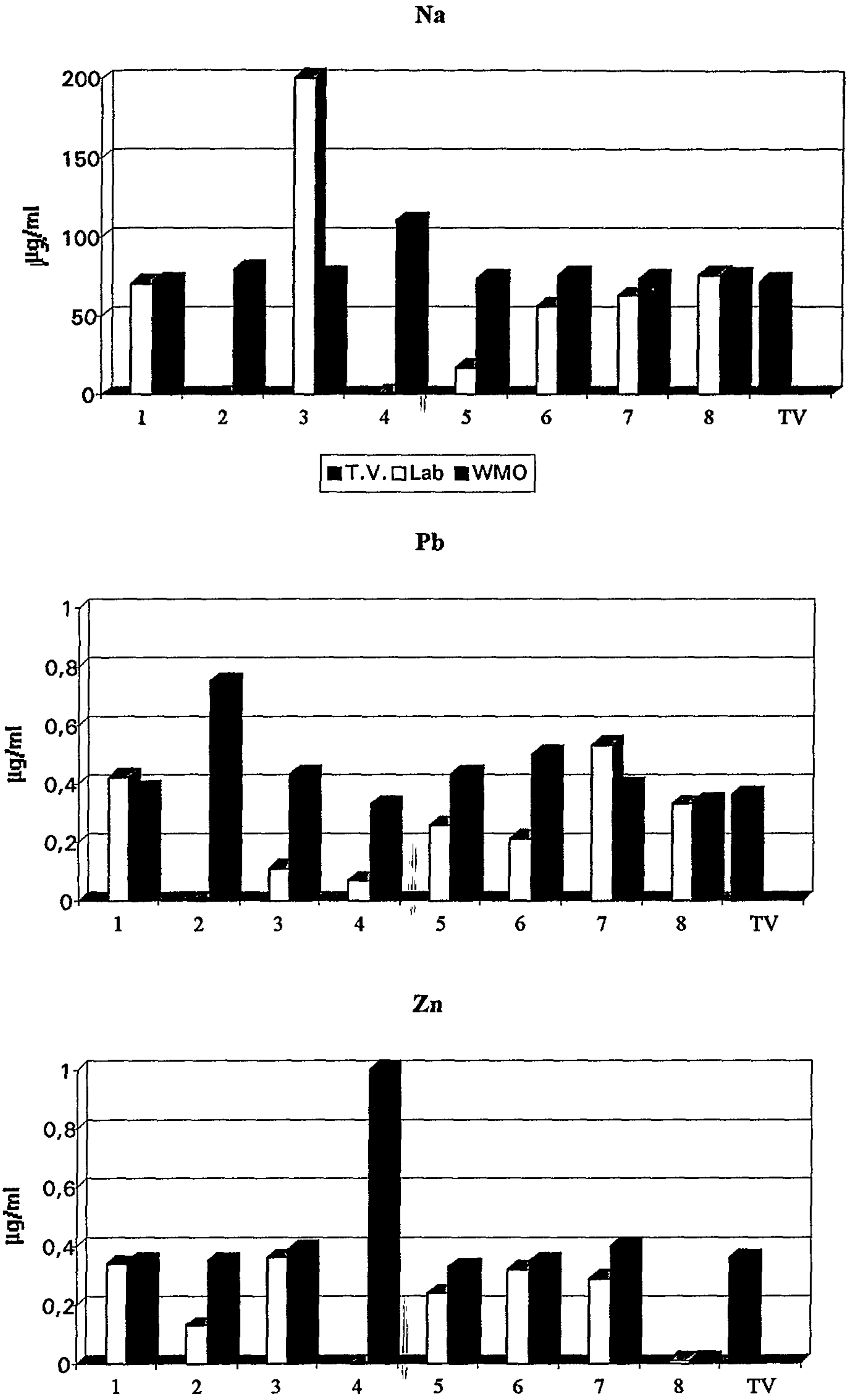

Fig. 9b - IMARAS. Concentration graphs. The results obtained by each participant from the analyses of test solutions are shown for each element. T.V.=true value. Lab=value obtained from the analysis of the test solutions by other laboratories. WMO= value obtained from the analysis of the same solutions by WMO Test Laboratory. The bold numbers (1 to 8) represent the laboratory intercalibration code.

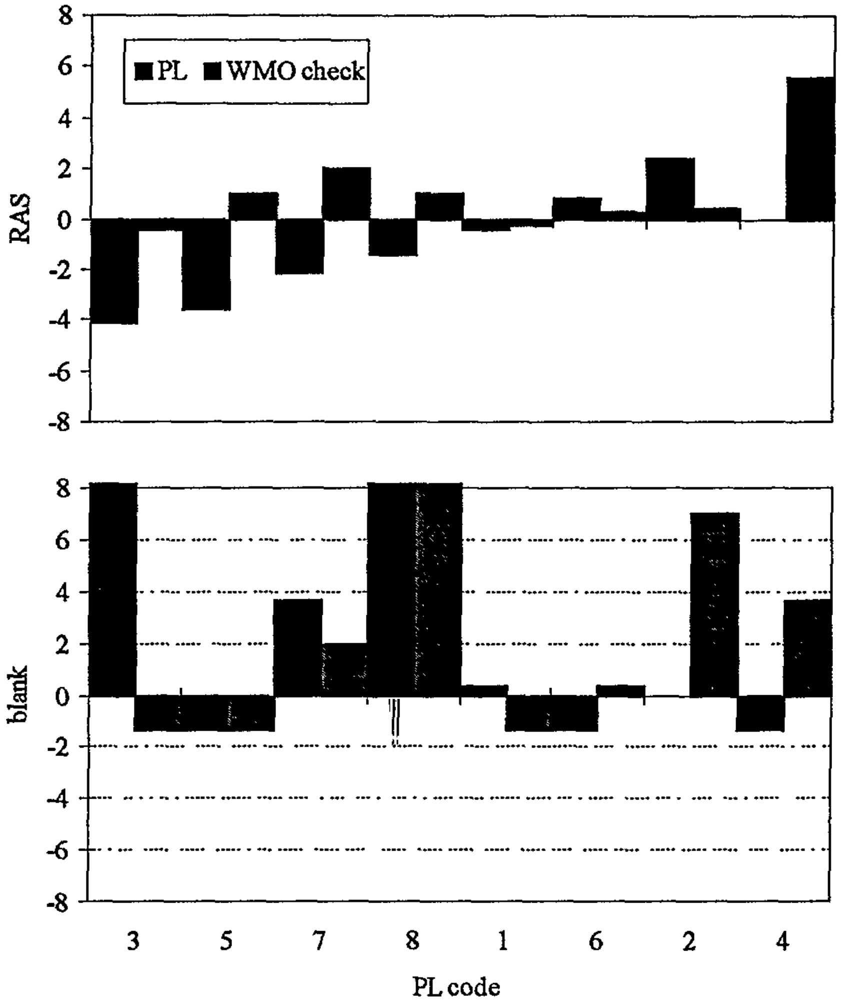

Fig. 10 - IMARAS. Z scores for Pb in reference aerosol samples (RAS) and in blanks. Z= (x - x_t)/σ_t, with x = analytical value obtained by each laboratory, x_t = true value, obtained by CL using several different techniques in several replicates, σ_t = standard deviation of the true value (Pedersen and Cofino, 1994). PL = Participating Laboratory. WMO check = Central Laboratory checkup. The numbers represent the laboratory intercalibration code.

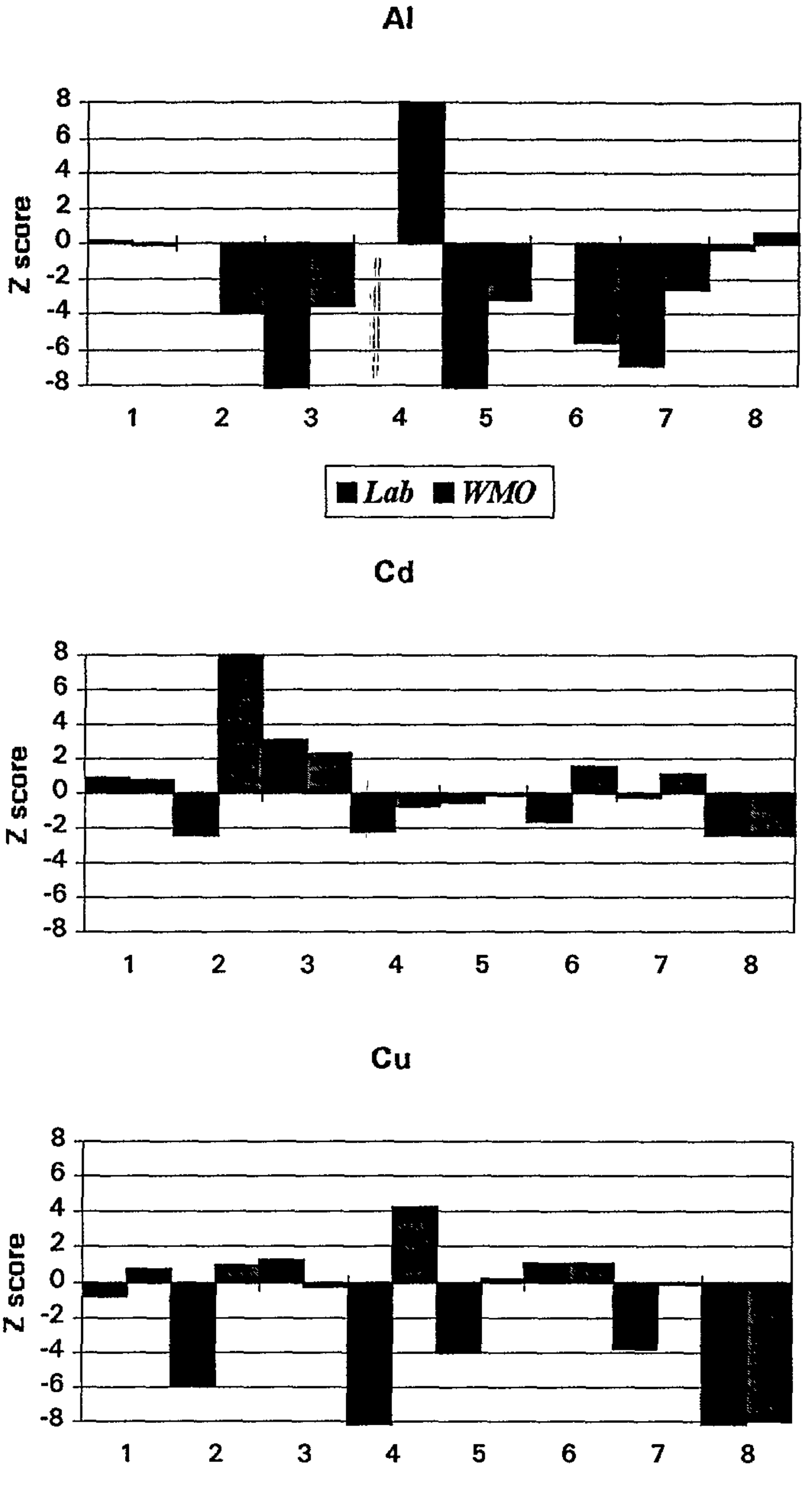

Fig. 11a - IMARAS. Z scores graphs. The comparison of the bias of laboratories has been made for each element using the Z score, where: Z= (x - x_t)/σ_t, with x = analytical value obtained by each laboratory, x_t = true value, obtained by CL using several different techniques in several replicates, σ_t = standard deviation of the true value (Pedersen and Cofino, 1994). Lab= Z score obtained from the analysis of the test solutions by other laboratories. WMO = Z score obtained from the analysis of the same solutions by WMO Test Laboratory. The bold numbers represent the laboratory intercalibration code.

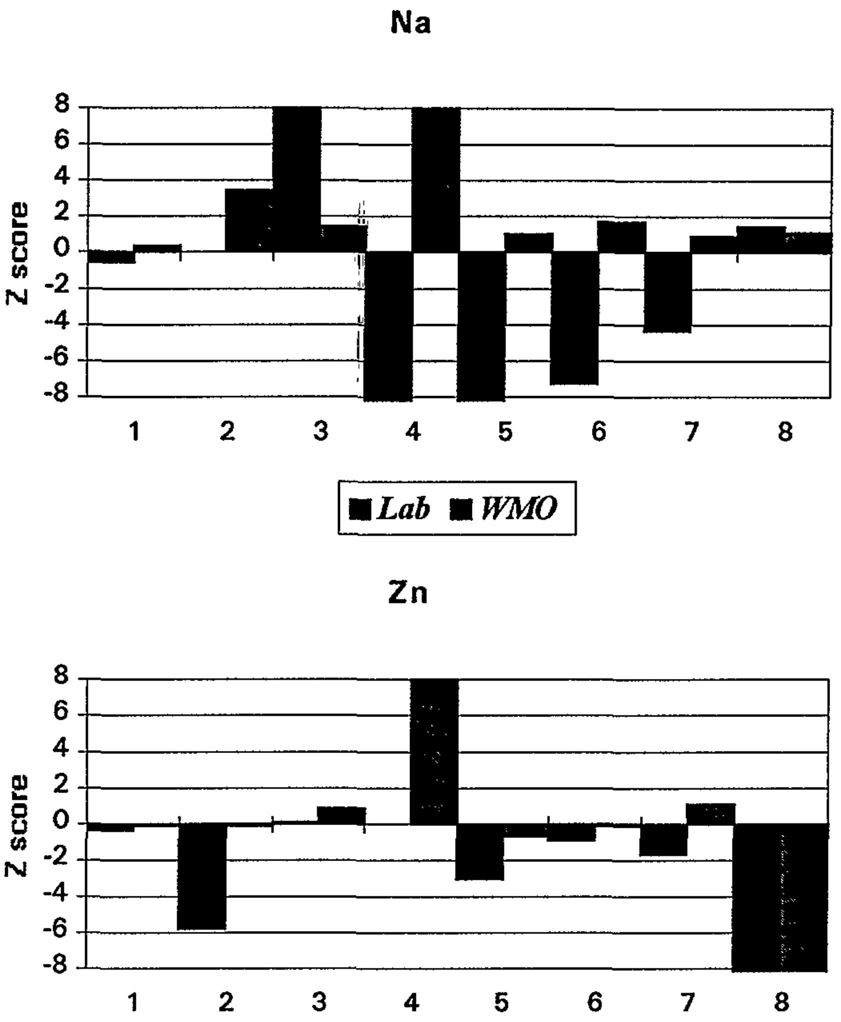

Fig. 11b - IMARAS. Z scores graphs. The comparison of the bias of laboratories has been made for each element using the Z score, where: Z= (x - x_t)/σ_t, with x = analytical value obtained by each laboratory, x_t = true value, obtained by CL using several different techniques in several replicates, σ_t = standard deviation of the true value (Pedersen and Cofino, 1994). Lab= Z score obtained from the analysis of the test solutions by other laboratories. WMO = Z score obtained from the analysis of the same solutions by WMO Test Laboratory. The bold numbers represent the laboratory intercalibration code.

INTERCOMPARISON OF METAL ANALYSES IN REFERENCE AEROSOL STANDARDS (IMARAS)

The procedure followed by the participating laboratories (PLs) for digestion and handling of W41 filters (Guerzoni et al., 1987; Molinaroli et al., 1993, WMO, 1995):

- Each PL received strips of a blank Whatman 41 filter and a Reference Aerosol Sample (RAS) in Teflon bottles. The Teflon empty bottles were kept closed and clean, for sending the aliquots for analyses to a central laboratory (see later).
- Each filter strip was transferred, using plastic tweezers, into a Teflon FEP 250 ml beaker.
- 30 ml of high purity concentrated HNO_3 was added and a plastic (Teflon if available) cover was put on the beaker.
- The beaker was put on a sand bath and the temperature controller set at 130±10 degrees centigrade. The bath was switched on and the increasing temperature was checked up to the desired value by inserting a thermometer into the sand. Thermometer was kept inserted to continuously check the temperature.
- The refluxing of HNO_3 was allowed for 10-12 hours. [Refluxing means that the acid does not escape the bottle due to the cover; it evaporates and recondenses continuously, so very little evaporation occurs. Normally during the refluxing there is no possibility of drying] After that, the clearness of the solution was checked.
- At this point the solution should be clear; if not, an additional step was made, by adding some more acid (up to a total of 20 ml) and allowing the refluxing (by leaving the cover on) for 6-8 more hours.
- The cover was removed from the beaker and the acid volume was reduced down to approximately 10 ml.
- 5 ml of concentrated HF were added, the beaker was covered and the refluxing was allowed for 6-8 hours. [Note: up to this stage the cover of the beaker was not left open except for acid additions.]
- The cover was removed from the beaker and the sample was carried to a dry stage (but avoiding to bake the sample).
- 5 ml of concentrated HNO_3 were added and evaporation until the near dry stage was repeated so that the white fumes of HF were not more visible. If necessary, this step was repeated two/three times. When the sample looked clear it was carried to dryness and the beaker was removed from the hot bath, to allow cooling. [This step is very important to remove completely HF from the solution, to avoid damages to nebulizer and other parts of the AAS]
- The residue was redissolved with 1% HNO_3, the solution was transferred to a graduated flask and made up to 50 ml (with the same 1% HNO_3).

Handling of the Final Solution:

- From the 50 ml flask with the prepared blank and RAS solutions, subsamples of approximately 25 ml were taken (exact volume was not important at this step) and the solutions were put back to the original Teflon bottles, rinsed and washed several times with double distilled water (DDW). The bottles were closed tightly and wrapped with parafilm to avoid any loss of the sample, then they were sent (clearly labelled) as soon as possible to the WMO. These were the samples for control analyses by the central laboratory.

- The remaining 25 ml of each of the subsamples were taken by each PL in Teflon or polyethylene bottles (pre-washed with 1% HNO_3 acid and rinsed several times with DDW) for the analyses in their laboratories.
- For major elements (Al, Na) a PL took 5 ml of the concentrated solution and diluted it 5 to 10 times.
- For trace elements (Cd, Cu, Pb, Zn) the determination was made directly using the concentrated solution.

General Comments:

- While using HF safety precautions have been taken. Gloves and protecting lenses have been worn. Contamination mainly during transfer from beaker to flask, during subsampling and from flask to the bottles should have been avoided.
- All labware and glassware were pre-washed with diluted acid and rinsed with DDW.
- All acids were of "suprapure-type".

WIND DIRECTIONS AND MEAN WIND SPEEDS DURING THE IHVAS

(Calm = wind speed ≤ $1 ms^{-1}$)

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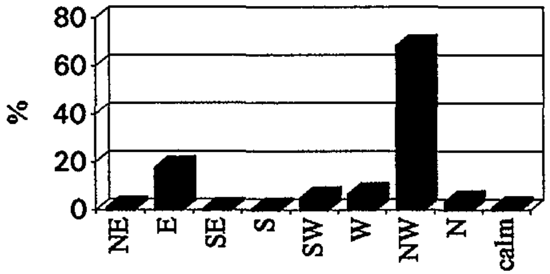

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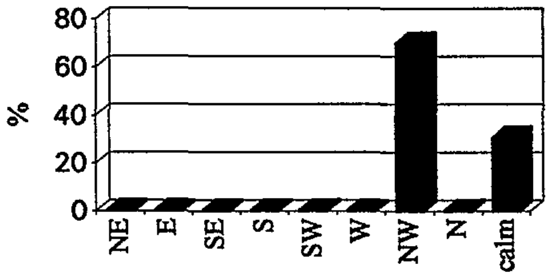

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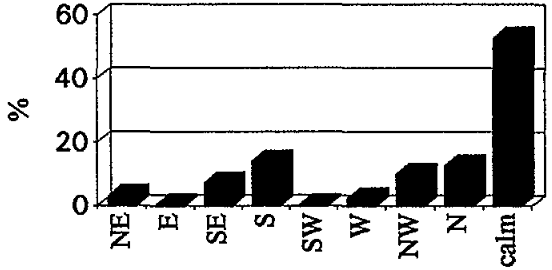

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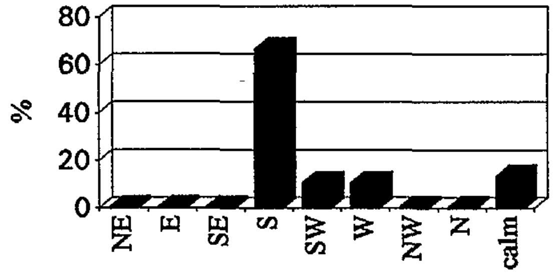

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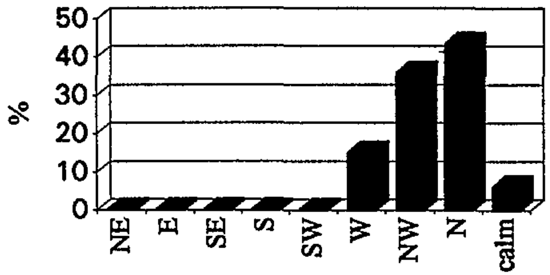

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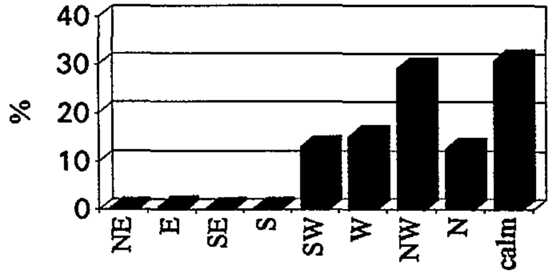

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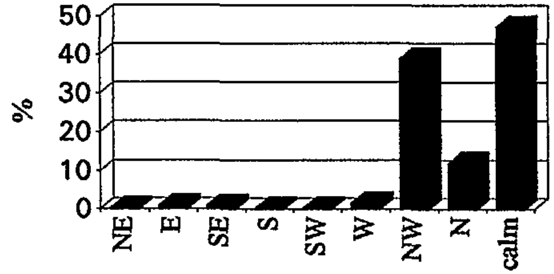

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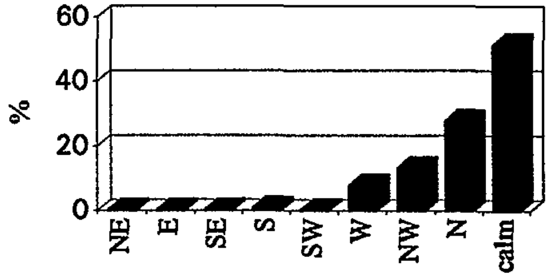

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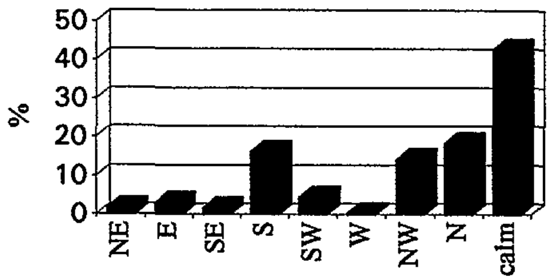

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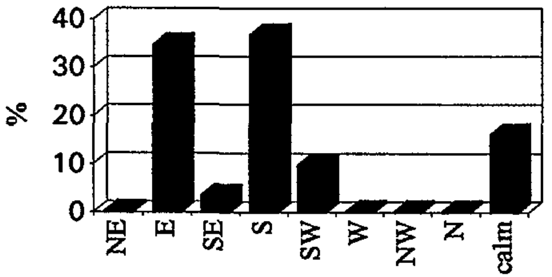

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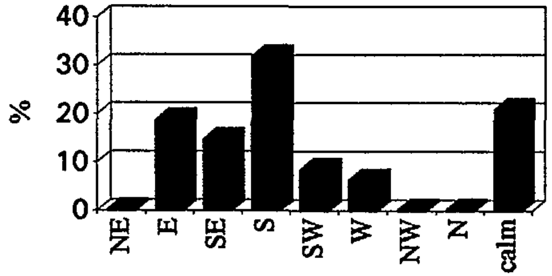

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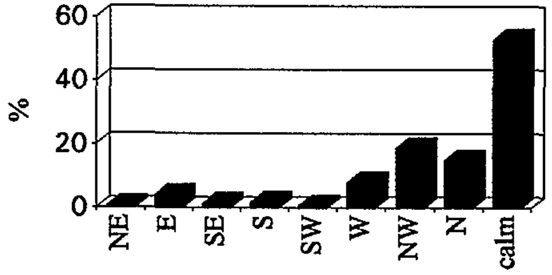

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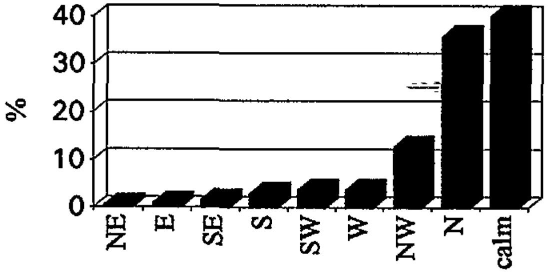

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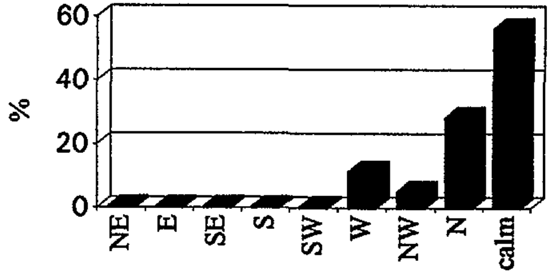

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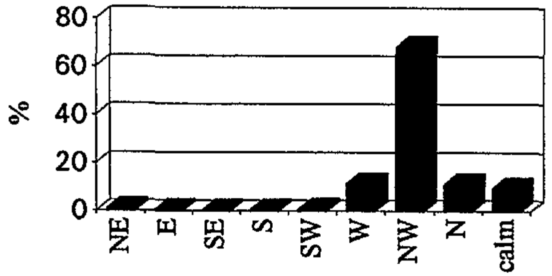

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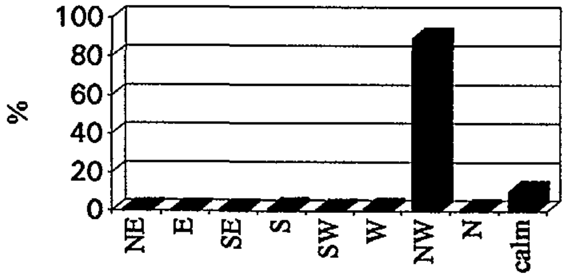

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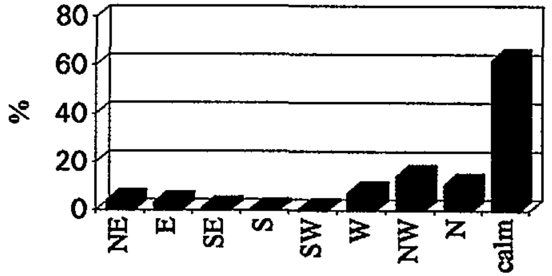

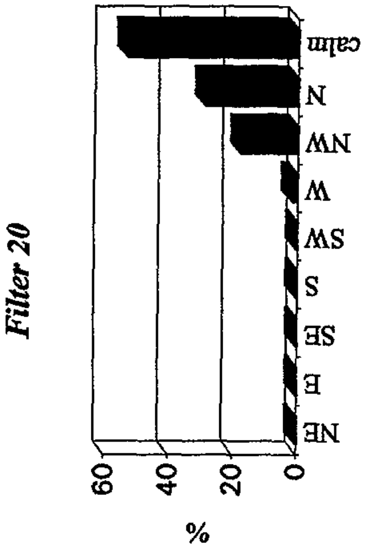

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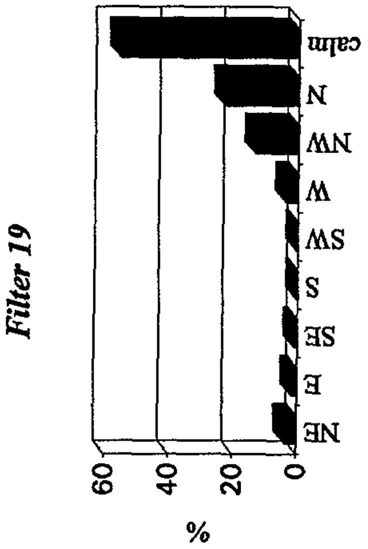

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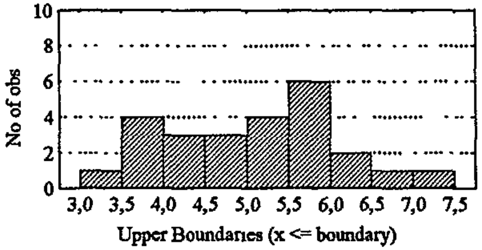

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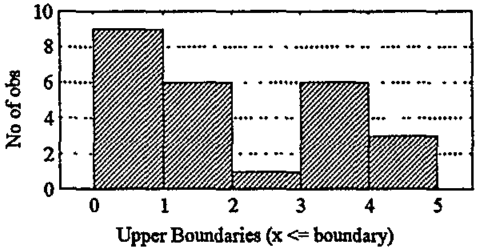

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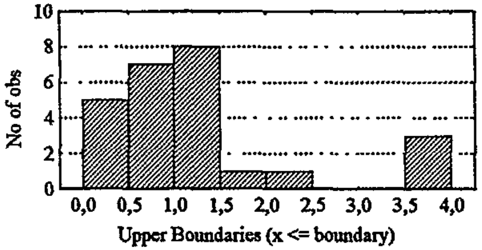

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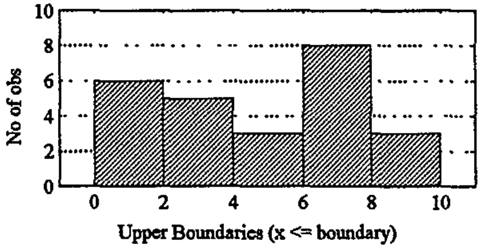

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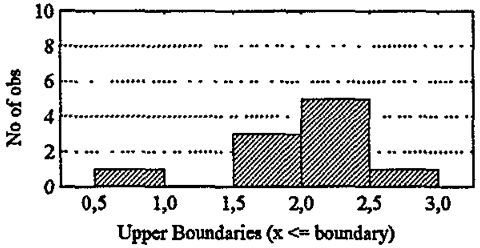

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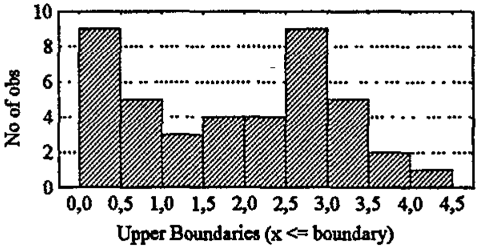

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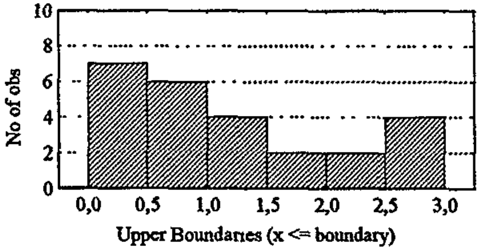

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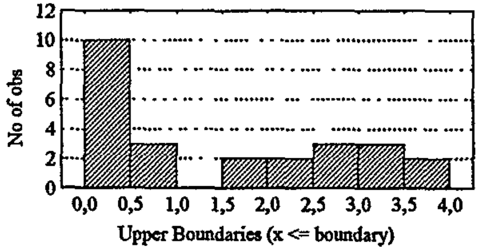

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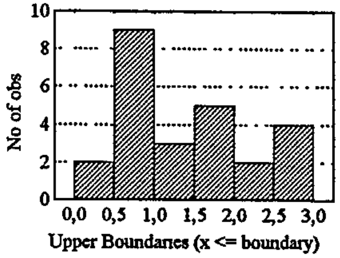

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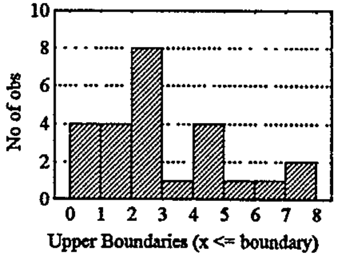

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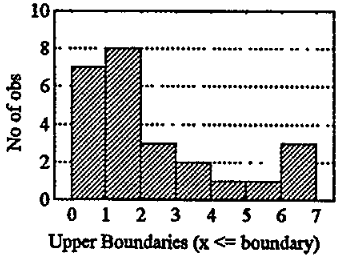

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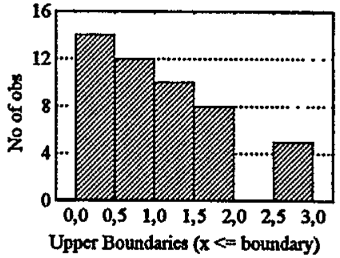

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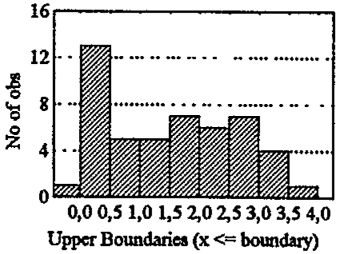

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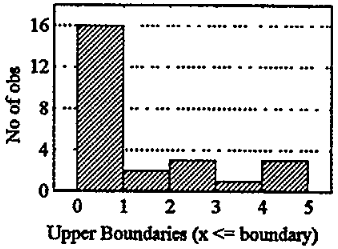

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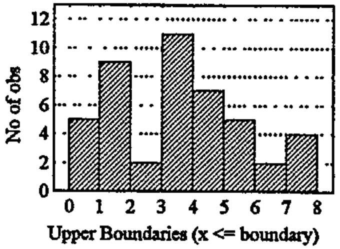

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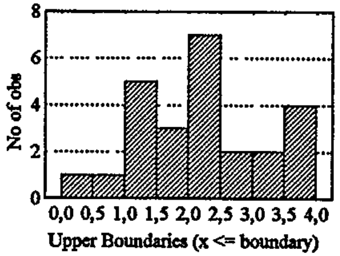

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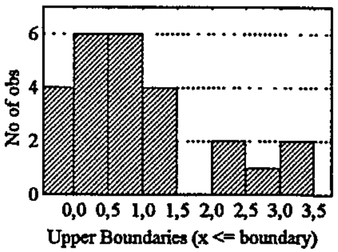

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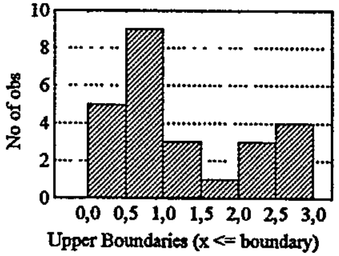

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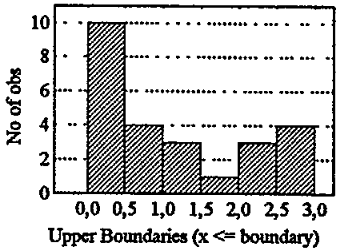

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Plan d'action pour la Méditerranée
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