



REGIONAL SEAS

UNITED NATIONS ENVIRONMENT PROGRAMME

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Guidelines for the determination of selected trace metals in aerosols and in wet precipitation

*Reference Methods For Marine Pollution Studies
No. 42 (draft)*

Prepared in co-operation with



WMO



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NOTE

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PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes ten regions and has over 120 coastal States participating in it. (1), (2)

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources, and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies are being developed and are recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations system as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, of analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

Marine Environmental Studies Laboratory
International Laboratory of Marine Radioactivity
International Atomic Energy Agency
c/o Musée Océanographique
MC98000 MONACO

which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

(1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No. 1 UNEP, 1982.

(2) P. HULM: A Strategy for the Seas. The Regional Seas Programme: Past and Future UNEP, 1983.

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1. SCOPE AND FIELD OF APPLICATION

This publication describes sampling and analytical procedures suitable for the collection and analysis of representative samples of atmospheric aerosols and wet precipitation for selected trace metals.

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3. PRINCIPLES

Most trace metals exist in the atmosphere associated with very fine particulate matter. Mercury is an important exception, being present in the atmosphere mainly in a gaseous form. The particulate matter in the atmosphere ranges in size from 0.1 μm to about 10 μm , though particles larger than 2 μm tend to settle out rapidly under gravity and hence are rare away from immediate sources. Many of the trace metals of interest (e.g., Pb, Zn, Cu, Cd) are found predominantly associated with the finer fractions of aerosols except very close to sources. Crustal material such as clays tends to be associated with somewhat coarser particles as is also the case for sea-salt.

Particles are removed from the atmosphere by wet and dry deposition. For large dense particles, dry deposition is the dominant removal process, and hence dominates close to sources. Away from sources the relative importance of wet deposition increases due to the slow gravitational settling (and hence inefficient dry deposition) of fine particles. Dry deposition rates are usually estimated from the atmospheric particulate concentrations and a term called the dry deposition velocity. Wet deposition rates are measured directly via sampling of precipitation. This precipitation includes particles scavenged from the atmosphere both in clouds and below clouds. Some of the particles, such as sea-salt, are readily soluble while others, such as clay particles, are relatively insoluble. In practice there will be a range of particles and solubilities with factors such as rainwater acidity and mode of formation controlling the balance. In this method, the presence of particulates in precipitation is recognised, though the samples are generally analysed without separation of particulate and dissolved components.

Sampling of precipitation may be achieved both manually and automatically. Manual collection equipment consists essentially of a funnel and collection bottle. An automatic precipitation collector includes a cover which covers the sample container during dry periods but which moves away automatically during precipitation to allow sample collection. Rigorous precautions are necessary for the preparation and deployment of sampling equipment to prevent contamination of the sample. Collection periods vary with the aims and scale of a survey together with the resources available, though daily sampling is preferable.

Suspended particulate matter is sampled by passing volumes of air through a filter. Sampling systems divide into high and low volumes with the choice being governed by ambient concentrations, sampling times and resources. As for precipitation, great care is necessary to avoid contamination of the samples. After collection, samples are dissolved by acid digestion. Both precipitation and digested particulates are generally analysed by graphite furnace atomic absorption spectrophotometry (GFAAS). In areas with unusually high atmospheric trace metal concentrations, a flame atomic absorption spectrophotometer may have sufficient sensitivity for the analysis. Increasing the volume of air sampled or pre concentration of the rainwater sample may also allow a flame atomic absorption spectrophotometer to be used. Alternative measurement methods are available (see section 8).

The methods presented here are applicable to most trace metals. Minor modifications are required for the analysis of mercury and these are noted. However, this method is concerned with atmospheric particulates and precipitation, and it should be noted that the bulk of the mercury in the atmosphere is present as a gas.

As noted above, the concentrations of trace metals in precipitation and aerosols in areas away from major sources are low requiring considerable care in collection and analysis of samples. To illustrate this, Tables 1 and 2 present a compilation of some recently reported aerosol and precipitation data for some trace metals. These samples have been collected with great care and probably are representative of the range of values likely to be encountered. In these tables the distinction between rural and remote is arbitrary but is generally between populated areas away from urban centres and essentially unpopulated areas.

Table 1: Trace metal concentrations in precipitation from rural and remote area ($\mu\text{g l}^{-1}$)*

	rural	remote
Cd	0.04-0.7	0.002-0.093
Cu	1.4-24	0.013-1.8
Pb	3.0-15	<0.04-2.4
Mn	1.3-6.8	0.01-5.4
Ni	0.8-17	0.2-0.7
V	0.4-1.0	0.02-1.0
Zn	4-50	0.05-12

*Adapted from Barrie et al., 1987.

Table 2: Trace metal concentrations in aerosols from rural and remote areas (ng/m^3)*

	rural	remote
Cd	0.1-22	0.005-0.4
Ca	0.5-110	0.014-3.3
Pb	1.8-97	0.027-8.0
Mn	3-20	0.014-2.6
Ni	0.085-3.2	0.08-0.7
V	0.75-4.5	0.009-1.5
Zn	4.7-110	0.12-15

*Adapted from Wiersma and Davidson, 1986.

4. SITE SELECTION

In a study of atmospheric trace metals, site selection is a critical step. The first step is clearly to define the purpose of the measurements. If the input to a single specific location (e.g., a reservoir or city centre) is required then this will obviously dictate the sampling location. However, if a measurement of a regional

background level is required, it is important to recognise the potential sources of local contamination which can compromise such an objective. Local trace metal inputs will arise from essentially all industrial sources, automobile traffic, cultivated fields, smoke stacks, air ducts and any other sources of dust such as areas of sand or concrete. Sites selected must be remote from such sources under all wind directions unless sampling is only carried out when winds are from "clean" areas, a procedure which can be done automatically. It is impossible to generalise as to the area affected by a particular source, but large sources such as cities and major industrial emissions can affect hundreds or thousands of square kilometers, while a single dwelling may only affect a few hundred square meters. In many cases practical considerations of manpower availability and the cost of site operation will constrain the choice of site and the best available site should then be selected. The results of the analysis of samples must be carefully scrutinised for evidence of local contamination. If resources permit, the simultaneous collection of samples throughout the area of interest can assist in the identification of local effects.

In order to reduce local effects some workers have constructed towers from which to sample, while others recommend large clearings in forests and others flat or gently sloping grass (non-seeding) fields. While the forest clearings can provide remote well sheltered sites, the possibility of contamination from dust and debris on the surrounding trees may present a major problem. Further considerations are site security, electrical power and potential land use changes. The availability of meteorological data, such as rainfall, wind measurements, pressure and humidity, for the area can be a considerable advantage.

Once a site is selected, the samplers for trace metals should be sited well away from, and upwind under normal conditions, of other collectors or structures on the site. Access to the site, particularly by automotive traffic should be carefully controlled.

5. LABORATORY FACILITIES AND SAMPLER CLEANING

It must be recognised that the collection and analysis of precipitation and aerosols for trace metal analysis is a demanding task. The concentrations are generally low and the potential for contamination is high. A laboratory dedicated to the analyses of low level trace metal samples is necessary and this should be equipped with a laminar flow, filtered air clean bench, or equivalent, to allow sample handling with reduced risk of contamination.

Supplies of high purity water and acids are also necessary. High purity acids are now available commercially, but if relatively large quantities are required the purchase or construction of a sub-boiling distillation system may be cost effective. A similar system can also be used to produce high purity water, though a carefully constructed and operated glass laboratory still used to redistil deionised water can yield an acceptable supply of water. The trace metal content of all

reagents should be checked before use and subsequently at regular intervals. When handling samples plastic disposable gloves should be worn and these should not be of the prepowdered sort. Graphite furnace atomic absorption spectrophotometry (GFAAS) facilities are normally required for final analysis, though as noted earlier flame systems may be appropriate in some cases.

In all trace metal analyses thorough cleaning of sample collection and storage equipment is essential to avoid contamination of samples by trace metals adsorbed to surfaces. It is important that sampling equipment be designed using material which minimizes contamination effects. Polytetrafluorocarbons (PTFE), clear polyethylene and clear polypropylene plastics should be used and filled (i.e., opaque or coloured) plastics should be avoided. For the collection of rainwater samples for mercury analysis, glass and PTFE only should be used. Any plasticware with obvious inclusion of other material within the plastic should be discarded. Various cleaning procedures for plasticware have been described in the literature. All have the same general features of preliminary cleaning with soap and solvent followed by extensive soaking in strong acid solution. Heating steps are often included but these can present safety problems. Some procedures also include the use of concentrated nitric acid, but such a step can lead to polyethylene and polypropylene becoming brittle over time.

The procedure listed below has been reported to effectively clean new sample bottles, though its efficiency can be checked by looking for increases in trace metal concentrations, over time, of high purity distilled water stored in the cleaned bottles.

Cleaning procedure for sample bottles:

- a. Rinse with acetone.
- b. Wash with laboratory detergent and deionised water.
- c. Rinse thoroughly with deionised water.
- d. Fill with 50% (v/v) reagent grade hydrochloric acid in deionised water and allow to soak for at least 48 hours.
- e. Drain and fill with 10% (v/v) reagent grade nitric acid in deionised water and allow to soak for at least 48 hours.
- f. Drain and fill with high grade deionised water acidified to 0.1% with high purity nitric or hydrochloric acid and store thus until required.
- g. Before use, rinse with high purity water, drain, dry by standing open on a clean bench and transport to and from sampling location in clean plastic bags.

After use sample bottles are rinsed with deionised water and stored soaking in 0.1% acid as in step (f).

This procedure can present problems of safety for large items such as funnels particularly with respect to the large volumes of 50% acid required in step (d). In such cases the omission of step (d) may be acceptable though the efficiency of the cleaning procedure should then be checked. Plastic liners for automatic rain collectors can usually be cleaned by a brief soak in 10% acid, though the efficiency of this procedure should again be checked, since the blank will vary with the source of the bags. Once cleaned in this manner, plasticware should be dedicated to trace metal sampling.

For mercury analysis nitric acid is usually used at all stages of the cleaning procedure instead of hydrochloric acid. It should be recognised that these cleaning procedures involve large amounts of strong acids and great care is necessary to ensure safe handling.

6. SAMPLING WET DEPOSITION

The continuous deployment of open collectors will result in the sampling of both wet and dry deposition (generally called "bulk" sampling). This procedure has the advantage of simplicity, but, by integrating sampling over long periods of time, increases the potential for local contamination. Furthermore, this approach loses a lot of useful information which can be derived from sampling wet and dry deposition separately. In general wet-only collection procedures, in which sampling is only carried out during periods of precipitation, are to be preferred, though it is recognised that in some situations deployment of open collectors is the only available practical method. The procedures for deployment, collection and preservation of bulk samples is the same as that for manual sampling of wet-only precipitation described below, except for the longer sampling intervals. Wet-only deposition can be sampled by either manual or automatic procedures.

Manual sampling involves manually opening collectors as soon as precipitation starts. This is usually done by deploying the collector encased in a plastic bag and simply removing the bag at the start of precipitation. This approach does not require the purchase and maintenance of automated collectors or the availability of power on site but does require manning of the site by trained operators. In practice it is usually impossible to define exactly when the precipitation starts and finishes, and periods of several hours can elapse between the cessation of precipitation and closure of the collectors. Manual sampling is thus labour intensive and often does not generate as distinct definition of wet and dry deposition as automatic procedures. If the site is not to be manned continuously it may be possible to sample on pre-selected precipitation events. However, this may be difficult if sophisticated meteorological facilities are not available nearby for predicting events. Despite these problems manual operation is in some circumstances a useful and cost effective procedure for sampling wet deposition.

The dimensions of the sampling system can be varied to suit local conditions. Unless the design is matched to that of a standard rain gauge, the collection efficiency for precipitation will be uncertain. However, it is common practice to use a collector of this type to sample the precipitation and then use information from a standard rain gauge to

Manual collection systems consist of a collection funnel attached to a sample bottle. If the collection programme is for wet-only precipitation, the use of mesh coverings to prevent large pieces of debris entering, or devices to minimise evaporation are not necessary. For bulk sampling programmes such additions may be useful, though it should be recognised that the simplest apparatus is the easiest to keep clean, and that a mesh covering can be a source of contamination and of reduced sampling efficiency.

One successful design for manual collection is the global-bulk collector designed by Keene and Galloway. This consists of a 2 litre polyethylene bottle attached directly to a 27.9cm diameter polyethylene funnel via a screw thread machined into the plastic base of the funnel. A drip shield over the join prevents water running down the outside of the funnel and into the bottle. For samples for mercury analysis, glass funnels and PTFE bottles are recommended with a glass shroud to act as a drip shield.

Automatic wet-only collectors are available. These incorporate a precipitation sensor which opens the lid of the collector as precipitation starts and then closes it at the end of the precipitation event. Such equipment is available commercially or can be manufactured. Such collectors offer a standardised process of collection and only require visits from trained personnel at appropriate sampling intervals. Several of the available machines are reliable though interruptions of sampling programmes due to instrumental failure are inevitable. The equipment requires an electricity supply. The features of these instruments are reviewed in Reference Method 24 of this series.

Commercial wet-only collectors require some modification prior to use for trace metal work and in some cases such options are available at the time of purchase. Such modifications include the use of a plastic covered lid, covering of all other exposed metal with plastic or PTFE and the displacement of the metal precipitation sensor grid to a side arm away from the sample collector. The buckets provided for sample collection are a source of contamination but this can usually be eliminated by lining the inside of the bucket with an acid cleaned heavy-duty clear plastic bag and collecting the sample in this bag. Some experience and care is necessary when installing bags to ensure that they do not blow out of the bucket under windy conditions. The lid should move away from the collecting bucket sufficiently far to avoid drops from the lid falling into the bucket. For this reason the collecting bucket should be upwind of the rest of the collector under normal prevailing wind conditions. The underside of the lid should be regularly wiped clean with deionised water and paper tissue, and checked to see that it forms a good fit over the bucket.

Both manual and automatic collectors can suffer problems with heavy snow falls. Many of these can be overcome by minor modifications to the collectors (see Topol, 1986) which are now standard on many models, though in some cases a heater system may need to be installed.

Collectors of all types should be deployed on non metal, plastic/PTFE coated or painted metal supports with the collectors well above the support. If collectors are to be deployed for extended periods, biological growths can occur in the samples. This effect can be reduced by darkening the collectors via black outer bags. The addition of biological inhibitors is probably counter-productive because of their potential for contamination. Shorter deployment times are the best

In the case of rainwater samples collected for mercury analysis the possible loss of mercury by volatilisation is usually countered by putting high purity nitric acid in the collection bottle prior to deployment. The volume of acid required depends on the rainfall, which is of course unknown. However, 2ml of concentrated acid should be sufficient to maintain a very acid solution under all but the heaviest rainfall conditions. In the case of prolonged deployments when losses of mercury may be more of a problem, further additions may be necessary, and both gold chloride and potassium permanganate have been used. In the case of long deployments the aim will be to achieve conditions that are similar to those used for storage. For mercury recommended conditions are pH 1.0 and 30ppm Au/L.

For all other trace metals, for which volatility is not a problem, pre-acidification of the samplers before deployment is not recommended for three reasons. Firstly concentrated acids will damage any plastic sampler other than PTFE. Secondly the first rain collected will be subject to very acid conditions which may affect the particulates associated with the rain. The third reason is that volatilisation of the acids can damage the collector and contaminate other samplers on the site which may be being used for the collection of rainwater to determine the acids in the rain. For these reasons post-depositional acidification is recommended. Samplers are collected from the field, covered with plastic bags and returned to the laboratory. The samplers are weighed to estimate the volume of water collected and then acidified, under clean bench conditions, with high purity concentrated nitric or hydrochloric acid to give a final solution that is 0.4% (v/v) in acid. If the sample is to be stored in a different container, then the sample should be left soaking in the sampler for 24 hours in order to desorb any adsorbing trace metals. The sample is then decanted into a storage bottle and under these acid conditions the sample is stable indefinitely.

Under the above acid storage conditions most particulate matter is dissolved, though clay lattices will remain intact. However, agitation of samples prior to injection into the GFAAS system usually ensures that representative samples of such fine particulate matter are injected into the furnace and hence analysed.

Blank procedures to check for contamination during sampling should be carried out at regular intervals. This can be done by deploying a collector, opening it briefly and pouring in 200ml of high purity water and then leaving the collector closed (and electricity disconnected for automatic collectors) for the normal period of sampling. After this time the sample is retrieved and treated as a sample. The "sampling blank" is assessed by comparing the concentration of trace metals in the acidified high purity water after storage in the sampler, with acidified high purity water that is stored in the laboratory. The sampling blank should be small compared to the concentrations found in samples and if this is not the case then the source of the contamination should be traced.

Samples of storage acid should be retained for analysis so that any blank from this source can be quantified. Occasionally samples will be recovered which contain obvious signs of contamination such as bird droppings, insects, visible soil dust or plant debris. In general, such visibly contaminated samples will be contaminated for trace metals, and in many laboratories it is considered pointless to analyse such samples. They are simply noted as having been collected, judged to have been contaminated and discarded. Regardless of the protocol, the samples should be inspected and any visible debris noted.

7. AEROSOL SAMPLING

Particulate trace metal aerosols are measured by drawing known volumes of air through a filter. In general two types of samplers are available - high volume samplers (hivols) with flows of 1-2m³ air/min and low volume samplers which displace 1m³ air/hr or less.

High volume samplers are described in reference method 24, and these systems have been adapted for trace metal sampling by replacing the stainless steel intakes and filter supports with cleaned plastic materials and by separating the filter assembly from the motor via a plastic pipe in order to avoid contamination from the motor. The filters used in these samplers are 500cm² glass fibre or cellulose filters and these should be pre-cleaned by acid washing. In areas of high aerosol concentration, filters may sometimes not need washing. Cellulose filters such as Whatman 41 have lower blanks for trace metals and are therefore usually preferred. Earlier concerns about the efficiency of collection of this type of filter appear to have been overcome. The full acid cleaning system described earlier will destroy the filter but if the filters are supported on polyethylene screens they can be soaked in more dilute acid solutions. Soaking for 24 hours in 10% (v/v) reagent grade concentrated nitric acid, rinsing with deionised water, soaking for 24 hours in 10% (v/v) reagent grade concentrated hydrochloric acid, soaking for 24 hours in high purity-deionised water and final rinsing in high purity deionised water followed by air drying, with all procedures carried out under clean room conditions, should yield filters with very low blanks. High volume air samplers can sample relatively large volumes of air in relatively short periods of time and thus have considerable advantages. In addition it is often possible to sub-sample the filter and analyse for several different purposes though this will depend on the compatibility of sampler design and cleaning procedures with other analyses (e.g., plastic samplers are incompatible with trace organic analyses and the sample cleaning procedures may compromise the filter for use in sampling for acid aerosols).

A simpler relatively inexpensive alternative to high volume sampling is a low volume sampling system. A standard 47mm polycarbonate filter holder with 0.45 µm membrane filters designed for conventional water filtration can be used. The filter head should be sheltered from precipitation and a shelter can either be made from polypropylene sheet or from 2 litre wide mouth polyethylene bottles. A plastic tube then leads from the filter assembly to an air pump with a gas meter mounted on the outlet to monitor the air flow. This should be located far enough away to avoid contamination of the sample. Flow rates of the order of 1m³/hr are used and in most environments this yields a suitable sample within 24 hours, though it will be necessary to experiment with sampling times at any location to determine to appropriate sampling interval. Flow rates should be regularly monitored. In order to minimize the risks of contamination, filters should be loaded in filter holders (both low and high volume systems) under clean room conditions then transported to the field in a plastic bag. The used filter assembly is then removed and placed in a plastic bag and the new one installed. Disposable plastic gloves should be worn throughout the filter changing procedure.

The sampling process can be made more sophisticated by the introduction of switching gear to allow sampling only when the wind is from certain directions and atmospheric condensation nuclei counts are low. Such devices can be very useful, but such sophistication should only be contemplated in a large and well developed programme, due to the inevitable complications which arise with more complex equipment. It is important to carry out regular "sampling blank" determination. For this procedure filters are deployed by the normal procedures and for the normal lengths of time but the pumps are switched off. The sampling blank is determined from any increase in trace metal concentrations on the filter compared to filters stored in the laboratory. The sampling blank should be small compared to sample concentrations and if they are not the source of contamination should be investigated and eliminated.

In the laboratory under clean room conditions, filters are removed from filter assemblies, folded over with the exposed face inward and stored in acid cleaned plastic bags or vials.

Prior to GFAAS determination, the atmospheric particles on the filters must be dissolved and this can be done by several procedures.

(a) Most contaminant elements are relatively soluble and soaking the filter in 20ml of 1% nitric acid will dissolve most of the metal, and this solution can then be analysed directly. This approach offers the advantages of simplicity and safety and can be useful in a semi-quantitative regional survey, but such an approach will present uncertainties in absolute concentrations and may be inappropriate for intercomparisons between various groups.

(b) The alternative, therefore, involves total digestion of the filter and the particles. This can be done by placing the filter in a PTFE beaker, adding 5ml of concentrated high purity nitric acid and slowly boiling the mixture to dryness. A 1:1 (v/v) mixture of high purity nitric and hydrofluoric acid is then added (2 ml) and the solution gently boiled to dryness. The residue is then redissolved in 1% hydrochloric or nitric acid. This approach should be adequate to completely dissolve a membrane filter and about a quarter of a glass fibre filter and associated particles, but since this does depend on the temperatures used this should be checked. Several safety features must be noted. First PTFE beakers will only tolerate gentle heating, high temperatures melt them. Secondly concentrated hydrofluoric and nitric acid are dangerous, particularly hydrofluoric acid and great care must be exercised. All handling must be done wearing highly acid resistant plastic gloves and in a very efficient fume cupboard. Persons unfamiliar with the use of these acids must consult appropriate texts on laboratory safety before using this method.

It should be noted that hydrofluoric acid cannot be redistilled in a glass apparatus since it destroys glass. The best available quality hydrofluoric acid should be purchased and stored safely.

(c) In many cases concentrated nitric acid alone is an adequate digestion method, though this will not be the case for aluminium and silicon.

(d) Some alternative techniques for dissolving solid samples collected on fibrous, porous and glass fiber filters are described by Rovinsky and Wiersma (1987).

Blanks of cleaned but unused filters should regularly be carried

8. ANALYSIS

Several analytical techniques have the sensitivity for analysis of trace metals at the concentrations encountered in these studies including neutron activation and electrochemical methods. Where facilities exist for using these techniques they can be used as an alternative to those described below and neutron activation of aerosols will have the advantage of allowing filters to be analysed without dissolution. However because of its more widespread availability, a method based on GFAAS is described here.

The dissolved filters and the acidified rainwater samples are both analysed by the same procedures. In most regions the concentrations of Al, Cd, Cu, Fe, Mn, Pb and Zn are high enough to allow direct measurement by GFAAS. For other elements this can usually be accomplished if the GFAAS system allows variable injection volumes to be used. If insufficient sensitivity is available it is possible to preconcentrate the sample, for relatively involatile elements, by putting 10ml samples in a PTFE beaker and gently evaporating the solution to dryness and redissolving the residue in 1% acid. The efficiency and contamination associated with this method should be determined by carrying standards spiked on aliquots of the sample and empty beakers treated as blanks through the method.

While direct analysis of these samples is usually possible, great care is necessary to check for interferences in the graphite furnace. These take two main forms which will be briefly discussed here. The instrument manual or a relevant textbook should be consulted for further detail. Non specific interferences can be corrected for with the background correction facilities that are available on most GFAAS machines. However, it cannot be automatically assumed that such facilities will correct all such interferences. Even if the lamps are properly aligned, the system will only operate up to a certain level of background. Therefore the background signal from a sample must be monitored to check that it is within the limits specified by the manufacturers.

Specific interferences can cover a wide range of effects from the physical effects on drying characteristics of the presence of salt to chemical effects arising from specific chemical interactions between the matrix and the analyte. A common example of this effect in atmospheric samples is the premature volatilisation (and hence loss before analysis) of Al, Cd and Pb as chlorides. These effects can be reduced by manipulation of drying and charring parameters but rarely eliminated. The use of platforms within the furnace can greatly reduce these interferences and such equipment is now available commercially for many types of GFAAS system. Matrix modification procedures are also available to overcome some interferences. In order to check for the presence of such effects, standard addition procedures should be used for calibration along with direct monitoring of background radiation. Whether such procedures are required for all samples will depend on the type and variability of the matrix. In areas near the sea the presence of relatively high and variable sea salt concentrations may require the routine use of standard addition procedures.

The GFAAS system is applicable to almost all trace metals, but for some volatile metals alternative systems can be used and these offer some advantages via increase in sensitivity and the removal of interferences. For As, Sb, Se and Sn, hydride generation methods can be used if available. For mercury cold vapour methods can be used and this can be coupled to gold amalgam to achieve greater sensitivity. Such systems are available commercially and need not be discussed further here.

For all analyses appropriate standards should be prepared in solutions of the same acidity as the samples. These can be prepared from commercially available stock solutions. While these standards can be used to calibrate the instrument and define the linear working range, great care should be taken, as discussed above, before using a calibration based on dilute acids for quantifying the samples.

9. ANCILLARY MEASUREMENTS

As mentioned earlier, rain collectors are generally less efficient at rain collection than standard meteorological rain gauges. A standard rain gauge should therefore be installed at the site and used for providing a record of rainfall. Many other meteorological measurements are useful for interpreting the results of aerosol and precipitation analyses. These include wind speed and direction plus times of rainfall. Equipment to measure these parameters can be installed and operated at the sampling site but if this site is close to a meteorological station, records from this source can be used. Local meteorological stations may also be able to provide the data for the estimation of back-trajectories or even calculate them. Such back-trajectories are of enormous value in determining the source of air masses and hence atmospheric contaminants.

In order to interpret trace metal measurements it is useful to have other measurements on the composition of the precipitation and aerosol. For precipitation the analysis of a separate sample for acids and major components will allow any correlations between acid, sea salts and trace metal contaminants to be assessed. Similarly, the analysis of a reference crustal and marine element such as aluminum and sodium allows the contributions of crustal and marine sources to the aerosol to be assessed using enrichment factors (see for example Wiersma and Davidson, 1986).

10. DATA PRESENTATION

Within national and international programmes dealing with the determination of selected trace metals in aerosols and wet precipitation there exists a number of formats for data presentation which differ in lay-out but contain mainly similar information summarized in Annexes I - IV.

ANNEX 1

Precipitation Samples: Field Reporting Form

1. Sampling station.....
2. Sample number.....
3. Type of sampler.....
4. Date and time sampler deployed.....
5. Date and time sampler opened (if known).....
6. Date and time sampler closed (if known).....
7. Date and time sampler retrieved.....
8. Weight of sample collector.....
9. Weight of sample collector + sample.....
10. Weight of sample.....
11. Amount, type and batch of acid added.....
12. Date and time of acid addition.....
13. Date and time of transfer of sample
from sampler to storage bottle.....
14. Rainfall measured by rain gauge.....
15. Estimated wind speed and direction
at deployment.....
16. Estimated wind speed and direction
at retrieval.....
17. General observations on sample
(e.g., debris, collector stuck, etc.).....
18. General observations on weather.....

ANNEX 11

Aerosol Samples: Field Reporting Form

1. Sampling station.....
2. Sample number.....
3. Type of sampler.....
4. Date and time sampler deployed.....
5. Date and time sampler switched on.....
6. Date and time sampler switched off.....
7. Date and time sampler retrieved.....
8. Total sampling time.....
9. Initial air flow.....
10. Final air flow.....
11. Note any intermediate measurements
of air flow.....
12. Volume of air sampled.....
13. Estimated wind speed and direction
at deployment.....
14. Estimated wind speed and direction
at retrieval.....
15. General observations on sample
(e.g. colour of filter).....
16. General observations on weather.....

ANNEX III

Precipitation Samples: Laboratory Report

Date of analysis (day/month/year).....

Numbers of sample.....

Numbers of sample blank.....

Laboratory blanks analysed.....

Sample preconcentration procedure.....

Recovery estimate (%).....

Element analysed for.....

Instrument setting wavelength (nm) slit width (nm) lamp current (mA) background correction (?)

Graphite Furnace:

instrument parameters -

graphite tube..... sample volume..... purge gas..... concentration of standards.....

Programme -

Table with 4 columns: step, temperature (°C), ramp/hold time (s), gas flow (ml/min)

Quantification procedure e.g. direct comparison with standards, standard additions, etc.:

Table with 6 columns: Run #, Conc. in sample, Conc. factor, Sample blank, Laboratory blank, Conc. in precipitation

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