

## SAMPLING, MEASUREMENT AND ASSESSMENT

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### Summary

Measurements play a key role in the protection of the environment. They are needed to identify problems and to monitor the effectiveness of control and abatement technology. Decisions on vital questions such as the habitability of an area, the safety of drinking water, and the continued operations of an industrial plant are often based on measurement data. Equipment and technology for quantitative measurement are increasingly better developed these days, enabling us to identify new problems that may have existed for a long time. Consequently, stringent regulations can be set, and a cleaner environment can be assured with suitable enforcement.

In this article, sampling and sample pretreatment, instrumental analysis and the quality assurance of environmental measurements will be addressed.

### 1. Introduction

The analysis of chemical pollutants in environmental media entered a new phase in the 1990s. Modifications in instrumentation, sampling, and sample preparation techniques have become essential to keep up with the requirements of achieving ppt to low ppb detection levels, as well as to achieve faster speed of analysis. In addition, more stringent quality-control (QC) requirements in analytical methods have become necessary to obtain high quality data. This has led to the many new methodologies that are different from the conventional macro and semi-micro analytical approach.

Environmental analysis today, like any other scientific field, relies heavily on instrumentation. Organic pollutants are primarily determined by gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), and high performance liquid chromatography (HPLC), methods.

There is, however, also a growing interest in alternative techniques, such as Fourier transform infrared spectroscopy (FTIR). Specially designed capillary columns have come up for GC analysis to achieve high resolution and better separation of many closely eluting isomers. Another major development in organic analysis is HPLC determination using post-column derivatization. Many classes of substances such as aldehydes, ketones, and carboxylic acids may be accurately determined by using such techniques.

Most organic compounds are best analyzed by GC/MS. Such GC/MS or GC analysis, however, is preceded by either a “purge and trap” concentration step or a liquid or solid phase extraction step using a suitable organic solvent. The purge and trap method for aqueous samples is applicable for volatile substances that have lower solubility in water. A mass spectrometer should be used wherever possible to identify the compounds more correctly. Although it has a lower sensitivity than other GC detectors, mass spectrometry is, by far, the most confirmatory test for compound identification.

Methodologies for inorganic anions and metals have undergone rapid growth similar to chromatographic techniques. Notable among these technologies are the atomic absorption and emission spectroscopy and ion chromatography (IC). The latter is a rapid method to determine several anions, simultaneously. The IC approach may be modified further to measure such weak anions as carboxylates and cyanide.

Sample preparation is a key step in all environmental analysis. Two major areas of development in this area have been solid phase extraction of pollutants from aqueous and non-aqueous matrices. These processes, along with gel permeable chromatography, are relatively simple, fast, and less expensive, and provide efficient methods of removing interferences.

The methods of analysis of pollutants in ambient air have developed tremendously in recent years. Although these methods employ the same analytical instrumentation (i.e. GC, GC/MS, HPLC, IR, atomic absorption, ion chromatography, and the electrode methods), the air sampling technique is probably the most important component of such analysis. The use of cryogenic traps and high pressure pumps has supplemented the impinger and sorbent tube sampling techniques.

The numbers of pollutants that are currently regulated constitute only a fraction of those found in the environment. In addition, their chemical characteristics and concentrations may vary widely. New and alternative methodologies that are simple, rapid, and reliable need to be developed. Enzyme immunoassay and portable GC and IR techniques need greater attention.

This article presents an outline description of various environmental analytical methodologies, including sampling, sample preparations, cleanup, and instrumentation to identify different classes of substances and selected individual compounds and also to

derive a method to analyze uncommon pollutants based on their physical and chemical properties, as well as quality assurance and quality control.

## 2. Sampling and samples pretreatment

### 2.1. Samples pretreatment for metals (sample digestion for metals)

Aqueous and non-aqueous samples must be digested with an acid before their analysis by atomic absorption or atomic emission spectrophotometry. The metals and their salts present in the sample are converted into their nitrates due to the fact that the nitrates of all metals are soluble in water.

Therefore, concentrated nitric acid by itself or in conjunction with hydrochloric acid, sulfuric acid, perchloric acid, or hydrofluoric acid is used in sample digestion for the determination of total metals. Nitric acid alone is, however, adequate for digestion of most metals. Acid digestion is performed using a small volume (5 to 10 mL) of nitric acid alone or in conjunction with one of the previously mentioned acids on a hot plate. Alternatively, a laboratory-grade microwave unit, specifically designed for hot acid digestion, can be used. When the sample is boiled with acid, the latter should not be allowed to dry. The acid extract after boiling and cooling is diluted with water to a measured final volume for analysis.

Acids combination	Suggested use
HNO <sub>3</sub> -HCl	Sb, Sn, Ru and readily oxidizable organic matter
HNO <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub>	Ti and readily oxidizable organic matter
HNO <sub>3</sub> -HClO <sub>3</sub>	Difficult to oxidize organic materials
HNO <sub>3</sub> -HF	Siliceous materials

Table 1: Acid combination suggested for sample preparation

For the determination of acid-soluble metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and improperly cleaned laboratory apparatus with which the sample comes into contact, are all potential sources of contamination. Sample containers can introduce either positive or negative errors in the measurement of metals by (a) contributing contaminants through leaching or surface desorption and/or (b) by depleting concentration through adsorption.

Laboratory glassware, including the sample collection container and the polyethylene sample storage bottle, as well as the filtering apparatus, should be thoroughly washed with detergent and tap water; thoroughly rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap water and finally de-ionized distilled water in that order. At the time of sample collection, the sample container is rinsed with the sample solution and the rinse portion discarded.

The container is then filled with approximately 800 mL of sample, acidified with 2mL of (1+1) nitric acid and mixed. For most ambient waters the acid addition will lower the pH to near 2, but not lower than 1.75. The container is sealed, placed in an ice chest at 4 °C,

and returned to the laboratory. The date and time of preservation should be recorded on the sample tag. The sample should not be held more than 3 days at 4 °C from the day of collection before processing is started. The filtrate is estimated to be stable for 30 days.

For determination of total recoverable elements in solid samples (sludge, soils, and sediments), the sample should be mixed thoroughly to achieve homogeneity and a portion of the sample, of 1.0±0.01 g, accurately weighed and transferred to a 250 mL Phillips beaker. Nitric acid, 4 mL (1+1), and 10 mL (1+4) hydrochloric acid are then added, and the mixture covered with a watch glass. The sample is heated on a hot plate and gently refluxed for 30 min. Very slight boiling may occur, but vigorous boiling must be avoided to prevent the loss of HCl-H<sub>2</sub>O azeotrope.

For determination of total recoverable elements in biological tissues, appropriate individual tissue samples should be taken soon after collection and must be taken prior to freezing. If dissection of the tissue cannot be performed immediately after collection, it should be placed in a plastic bag, sealed and placed on ice or refrigerated at approximately 4 °C. Prior to dissection, the tissue should be rinsed with metal-free water and blotted dry. Dissection should be performed within 24 hours of collection.

Each individual tissue sample should also be rinsed with metal-free water, blotted dry, and frozen at less than -20 °C. Tissue samples of up to 5 g should be taken using a special implement and handled with plastic forceps. A maximum holding time for frozen samples has not been determined.

Of the elements in the Periodic Table more than two thirds are metals. Although many of these metals are toxic, only a few are major environmental pollutants, because of their widespread use. USEPA has classified 13 metals as priority pollutants: aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc.

The Resource Conservation and Recovery Act has listed eight metals whose mobility in the soil is measured to determine the characteristic of toxic wastes. These metals include arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver all but one from the above list of priority pollutant metals.

Metals in general can be analyzed by the following techniques:

- Colorimetry
- Atomic absorption or atomic emission spectrophotometry

In addition, some metals may be determined by other methods, including ion-selective electrode, ion chromatography, electrophoresis, neutron activation analysis, redox titration, and gravimetry. Atomic adsorption or emission spectro-photometry is the method of choice, because it is rapid, convenient, and gives the low detection levels as required in the environmental analysis. Although colorimetry methods can give accurate results, they are time consuming and a detection limit below 10 ug/L is difficult to achieve for most metals.

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### **Bibliography**

Barcelo D. (2000). *Sample Handling and Trace Analysis of Pollutants: Techniques, Applications and Quality Assurance*. Elsevier Science. [This book introduces the analytical method on trace pollutants of the samples]

Patnaik P. (1997) *Handbook of Environmental Analysis: Chemicals Pollutants in Air, Water, Soil, and Solid Wastes*. CRC Press, Inc. [This book presents the chemical analysis of pollutants in different matrices in the environment]

Smolery K. (1992). *Methods for determination of Metals in Environmental Samples*. CRC Press, Inc. [This book describes the determination of metals in the environmental samples]

Subramanian G. (1995). *Quality Assurance in Environmental Monitoring*. Weinheim, New York. [This book introduces Quality Assurance when doing environmental monitoring]

Yen T. F. (1999). *Environmental Chemistry: Essentials of Chemistry for Engineering Practice, Volume 4A*. Prentice-Hall, Inc. [This book presents basic concepts on environmental chemistry in the engineering process]

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