9.5 Measurement Techniques of Acid Deposition

9.5.1 Introduction

One of the well known global environmental issues is acid deposition. Acid deposition, sometimes socially referred to as "acid rain", is air pollution on a continental scale. Combustion of fossil fuel injects sulfur and nitrogen oxides into the atmosphere. These oxides are subsequently converted to sulfuric and nitric acids by atmospheric photochemical processes, which result in the acidification of the atmosphere [1]. Sulfuric and nitric acids thus formed are deposited onto the earth's surface by wet and dry deposition processes. The deposited acids then acidify terrestrial and aquatic environments, which will cause adverse effects on various environmental elements including structural and ornamental materials and human health.

An important thing to note here is this environmental issue should not be recognized to be "acidification of rainwater" or "acidic fallout". The deposition of chemical species from the atmosphere to the earth's surface is the end result of a complex chain of physical and chemical processes in the atmosphere and is an input to another complex chain of processes that take place in terrestrial and aquatic ecosystems.

In other words, atmospheric deposition is also known to provide a primary pathway for the entry of nutrients and toxic chemicals into terrestrial ecosystems and oceans. The scientific description of this issue is acidification of the atmosphere as well as the environment. We should term this environmental issue "global acidification" because fossil fuel combustion also cause as global warming by emitting carbon dioxide.

Wet deposition is the deposition of chemical species associated with precipitation processes: in-cloud and below-cloud scavenging. Dry deposition is the deposition of the species in the gaseous and particulate forms by the atmospheric turbulent processes in the boundary layer and physico-chemical interactions with the surface of various substances in the receptor. Although numerical and experimental evaluations so far have reported that dry deposition will be as important as wet deposition, it is difficult to evaluate dry deposition on large spacial and temporal scales with sufficient certainty.

In this chapter, the basic concept of measurement techniques of wet deposition will be discussed below. Details of measurement techniques have already been addressed elsewhere [3)-7)].

9.5.2 Points for Wet Deposition Measurement Techniques

Measurement techniques used in wet deposition programs depend heavily on the program objectives. Definition of program objectives requires consideration of all factors influencing the nature and outcome of the program. In practice, measurement program objectives are always constrained by monetary and logistical factors. It is extremely important that all such constraints be identified at the beginning of the program so that they can be accounted for in the design of the measurement system. Typical constraints include budget limitations, manpower availability, access to instrumentation, access to electrical power, proven chemical analysis capabilities, and availability of computers for data handling.

The most appropriate data is obtainable only when necessary and sufficient methods are utilized. Not only will simple compromise or applications of unnecessarily sophisticated techniques produce data sets with inconsistent quality, they would also waste human energy, time, and funds. Proper measurement program design ensures that the program objectives will be satisfied, that the program constraints will be met, and that the program will be implemented in a timely and efficient manner. Adhering to this process reduces the amount of system alternation during the execution of the program.

Measurement techniques will be grouped into the four categories: 1) siting, 2) sample collection and handling, 3) chemical analysis, and 4) quality control and quality assurance. Different techniques will produce different descriptions of the same phenomenon. Before a comparison of different sets of data, one should clearly ensure the difference in the utilized techniques. In order to derive the proper conclusions from a data set, the impacts of the measurement quality on the data quality should be evaluated. The uncertainty of the conclusions derived from the data set should be consistent with the data quality. Each of the four categories made above will be individually discussed.

(1) Siting

Once a site has been selected, it is very difficult to relocate it with ease. The siting is the most decisive issue of all. What is important in site selection is whether the site is representative of the region of interest. Potential sources of pollutants to the samples are evaluated on three scales: on-site (ca. 1-100 m from collector), local (ca. 100 m-10 km from collector), and regional (ca. 10-50 km). Site representativeness is defined as the degree to which data accurately and precisely represents a characteristic of a population or parametric variation at a sampling point, a process condition, or an environmental condition. This element of data quality is generally evaluated in terms of semi-quantitative ratings. It is essential to make clear the nature of the measurement at the site which will provide different siting standards.

(2) Sample collection and sample handling

The wet deposition of a chemical species is calculated as the product of precipitation amount and species concentration. Precipitation amount is measured using standard precipitation gauges. The concentration is measured using precipitation chemistry collectors. The collector is usually a wet-only collector which is composed of a funnel-and-bottle with a movable lid on the funnel, that remains open only during precipitation. Another type of collector, bulk collector which remains open during both wet and dry periods, might be utilized on some occasions although the bulk sample will be contaminated by dry deposition during the dry period.

The sampling period is the length of time that a sample collection bottle stays in a wet deposition collector before being removed for shipping to a chemical analysis laboratory. There are a variety of sampling periods commonly used in precipitation sampling programs from daily to monthly. In major wet-deposition measurements networks of the world, samples are collected on a daily or event-basis.

(3) Chemical analysis

The dissolved inorganic ions of major concern to acid deposition measurement programs are the nine types of ions in Fig.9.5.1 [8]. The chemical analysis methods for the ions and conductivity are shown in Table 9.5.1. pH measurement is still high problematic, and more research is needed to solve measurement problems. However, seen from the viewpoint of the entire measurement systems, the problems of chemical analysis are not very great. Rather, it is important to be aware of essential problems other than those of chemical analysis, such as siting, sampling, and sample handling.

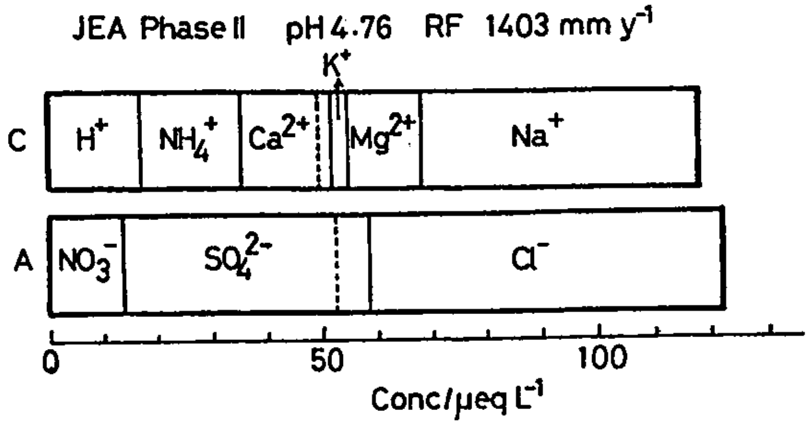

Fig.9.5.1 Nine types of ions [8] usually measured by the chemical analysis of precipitation

Table 9.5.1 Methods recommended for the analysis of the main components of rainwater

Measurement item	Equipment analysis methods
pH	Glass pole (poles with non-leaking internal cells are ideal)
Electrical conductivity rate	Electrical conductivity meter
Ion chloride, ion nitrate, ion sulfuric acid, ion nitrite, ion fluorides	Ion chromatography (ideally with a sub-laser attachment)
Ammonium ion	Ion chromatography Spectrometry (indophenol blue)
Sodium, potassium, calcium, magnesium ions	Ion chromatography Atomic absorption spectrometry / emission analysis
Phosphoric acid ion	Spectrometry
Heavy metals, aluminum, mercury	Atomic absorption spectrometry using a graphite furnace, ICP emission spectrometry, ICP/MS, metal trough mercury analyzer
Organic acids	Ion chromatography

(4) Quality Control/quality assurance (QA/QC)

Quality control and quality assurance to date have only emphasized the chemical analysis of standard reference materials. However, quality control should apply to all the items ((1) to (3) above) so that the overall data quality will meet the measurement objectives. Quality assurance is the quantitative evaluation of the data quality in terms of the above items. The purpose of the evaluation is to indicate to the data user the level of confidence he can place in the data for the analysis of interest so that one can select the pertinent data to their objectives. Even with data of low but clear quality, a proper interpretation is definitely needed to draw conclusions with such qualities are as consistent when the data quality itself [9]. However, if the quality of the data is unclear, the interpretations and associated conclusions will eventually be unclear as well.

The site is rated with respect to the representativeness in the three scales mentioned in the siting section. For the sample sampling, the sample history, such as the management of the sample collectors and storage bottles, shipping, storage until the chemistry is analyzed, should be recorded and handled as an important part of the data [6].

Validity of the chemical analysis is evaluated with respect to the ion balance and electric conductivity checks, in addition to analyzing standard reference materials. In the case of Fig.9.5.1, the balance of the full concentration of positive ions and negative ions is shown as being a very good one.

Data completeness is another element of quality assurance. This is defined as a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions. From a data set with poor data completeness, the missing values must not be estimated, nor the annual mean calculated. Wet deposition estimates should not be used if certain levels of completeness are not met.

The quality of a data summary is a function of the site representativeness and of the data completeness on which the summary is based. A qualitative assessment of the overall quality of a data summary can be obtained by combining the information in the categorization of the quality of a data summary. This overall data quality is an important attribute of the data one that plays a valuable role in assessing the usefulness of wet deposition data.

9.5.3 Summary

In order to make high quality wet-deposition measurements, the measurement system must be carefully designed, implemented, and operated. Particular care must be given to the selection of sites, sampling periods, instrumentation, sample collection and handling methods, analytical methods, data management, and data reporting. Ensuring that the measurements techniques produce data of suitable quality requires the operation of a quality assurance program. Considerable energy, money and attention should be dedicated to quality assurance programs [6].