EPA-625/R-96/010a

Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Chapter IO-4

DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES IN AMBIENT AIR USING THE ANNULAR DENUDER TECHNOLOGY

OVERVIEW

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June 1999

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OVERVIEW

Acid aerosols are found in the atmosphere as a result of atmospheric reaction of emissions from a variety of fossil fuel combustion sources, including power plants, industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Awareness of the effects of acid aerosols concentrations on human health and property has been documented over the past several years. The Clean Air Act Amendments of 1970 required the U. S. Environmental Protection Agency (EPA) to develop uniform national ambient air quality standards (NAAQS) for pollutants that were recognized as widespread (emitted by numerous mobile and stationary sources) and that endangered public health and welfare. Further, Section 109 of the Clean Air Act, as amended, requires EPA to periodically review the NAAQS as well as the scientific information and data on which they are based. New pollutants are identified for NAAQS development if the Administrator concludes that they may reasonably be anticipated to endanger public health and welfare.

To assist the Administrator in evaluating the need for new or revised NAAQS, the Clean Air Act created the Clean Air Scientific Advisory Committee (CASAC). This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge on new or revised NAAQSs. The Acid Aerosol Subcommittee of CASAC identified a need for a coordinated acid aerosol research program to assist the Agency in making recommendations on a proposed NAAQS for fine particle acid aerosol. The Subcommittee recommended a research program that addresses characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. As documented in the CASAC Report to the Administrator, the foundation for any research program and potential air quality standard development is "*…a measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes*." The National Exposure Research Laboratory (NERL) of EPA was directed by CASAC to obtain the information needed for scientifically assessing a possible fine particle standard for acid aerosols to protect human health.

In 1989, NERL conducted a workshop to determine and exchange views on the various methods that have been and are being used to measure aerosol acidity. The workshop was held in response to recommendations by CASAC to identify issues associated with characterizing aerosol acidity and acid aerosol measurement methods. The workshop was structured to accomplish two principal objectives. The first objective was to identify appropriate indicators and methodologies for characterizing aerosol acidity; the second was to develop ideas and recommendations for evaluating acid aerosol methods currently in use. The workshop participants identified the development of an accurate, reliable, and interference-free method as an important initial research objective.

The participants concluded that the most appropriate indicator of aerosol acidity is the fine particle strong acidity component of the atmosphere (i.e., the amount of strong acidity available in the fine particle component of the atmospheric aerosol). Sampling would involve the use of an annular denuder followed by a 37-mm Teflon® filter to trap the fine particle acid aerosol. After sampling, the filter is returned to the laboratory for extraction and analysis. After extracting the acid aerosol from the 37-mm Teflon® filter with an aqueous solution of perchloric acid at a pH of approximately 4.00 (to prevent dissociation of weak acids), the available hydrogen ion is measured either by titration or by pH. This defines atmospheric fine particle acid aerosol as free hydrogen ion (H^+) and hydrogen ion available from either undissociated sulfuric acid or

from undissociated bisulfate ion. Atmosphere acidity is reported as either nanomoles of hydrogen ion per standard cubic meter of air [nmoles/m^3 (nM/m^3)] or as equivalent sulfuric acid in micrograms per standard cubic meter of air (µg/m^3).

In December 1989 and February 1990, Intercomparison Studies were held at the EPA's NERL facility in Research Triangle Park, NC, to quantify the performance methods currently used to measure fine particle acid aerosol in epidemiology studies to ensure comparability of measurements by different groups. The criteria for selecting the participants for the initial Pilot Intercomparison Study was that they represented monitoring systems that were being used in epidemiological field studies currently in progress or that they had developed a prototype sampler under contract to EPA that the agency wanted evaluated. Based upon those criteria, three research groups were invited. They were: Harvard School of Public Health, Robert Wood Johnson (RWJ) Medical School and Research Triangle Institute (RTI). Each group used a variation of the annular denuder system (ADS) to determine fine particle acid aerosol of a standardized test atmosphere.

Based upon the findings of the Pilot Intercomparison Study, NERL developed this Chapter entitled *"Determination of the Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles in Ambient Air Using Denuder Technology."* This standard methodology represents a composite of the most viable features of the three research methods utilized in the Pilot Intercomparison Study. The following table identifies the annual denuder methods discussed in Chapter IO-4 along with the constituents monitored by those methods.

Method	Title	Constituent Detected
IO-4.1	Determination of the Strong Acidity of Atmospheric Fine Particles (< 2.5 µm) Using Annular Denuder Technology	Fine Particle Acid Aerosol (H^+)
IO-4.2	Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles in Ambient Air Using Annular Denuder Technology	HNO_3, NH_3, HCl, SO_2, NH_4^+, $SO_4^=$, NO_3G, Fine Particle Acid Aerosol (H^+)

The unique features of the annular denuder that separate it from other established monitoring methods are the elimination of sampling artifacts due to interaction between the collected gases and particles and the preservation of the samples for subsequent analysis. Compendium Method IO-4.1 utilizes a denuder for removing ammonia interference and a filter assembly for determining atmospheric fine particle acid aerosol in ambient air. The method does not, however, account for potential interferences from nitric acid (HNO_3), ammonium nitrate aerosol (NH_4NO_3), or other ammonium salts that might bias the acidity measurement. Compendium Method IO-4.2 does correct for potential biases by an additional denuder upstream of the filter assembly to selectively remove and quantitate acid gases (nitric acid vapor and sulfur dioxide) from the gas stream prior to filtration. In addition, to correct for biases due to the dissociation of ammonium nitrate aerosol captured on the Teflon® filter, Compendium Method IO-4.2 uses a backup Nylon® filter to capture the dissociated HNO_3 from NH_4NO_3.

The techniques, procedures, equipment, and other specifications comprising Compendium Methods IO-4.1 and IO-4.2 are derived and composited from those used by the contributing research

organizations and, therefore, are known to be serviceable and effective. At this stage, these methods are unified, consensus, tentative drafts intended for further application and testing. Users should be advised that the methods have not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgement and have not been subjected to ruggedness testing. In some cases alternative techniques, equipment, or specifications may be acceptable or superior. In applying these methods, users are encouraged to consider alternatives with the understanding that they should be tested to determine their adequacy and to confirm and document any advantages.