



Project Summary

Miniature Acid-Condensation System: Design and Operation

James L. Cheney

An extractive source sampling system was designed and constructed. The sampling system measures gaseous sulfuric acid and sulfur dioxide in combustion emissions. The miniature acid condensation system (MACS) includes a high-temperature quartz probe and quartz-filter holder. The temperatures of the probe and filter are maintained at or above 520°F during sampling with temperature controllers. After removal of particles from the source sample with a flat quartz filter, the sulfuric acid is collected in a glass-wool plug. The glass-plug temperature is maintained at 140°F with a water bath circulator. Subsequent midjet impingers containing hydrogen peroxide collect sulfur dioxide.

Since there is no commercially-available manual sampling system for measuring gaseous sulfuric acid at the present time, a prototype sampling system must be constructed for making such measurements. The purpose of this work is to provide a guideline for building such a sampling system. Also included is a discussion of two sulfate analytical methods, Barium-Thorin and Ion Chromatography. In addition, a brief discussion of sulfate analyses data handling and the results of some source emissions sampling are presented.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Measuring sulfuric acid (H_2SO_4) as a separate entity from particulate sulfate in

combustion source emissions requires specific procedures. As the quantitative determination of each relies on measuring the sulfate ions, the two must be separated prior to sample collection. An acceptable method of separation is to collect the particulate sulfate on a quartz filter at a temperature near 520°F while passing the gaseous H_2SO_4 through the filter.

Collecting the gaseous H_2SO_4 subsequent to particulate separation can be difficult due to the possible oxidation of sulfur dioxide (SO_2) which is always present in such gas streams. In addition to an SO_2 interference, collection efficiency problems are also encountered if attempts are made to collect the H_2SO_4 in impinger solutions. For these reasons, the H_2SO_4 is usually collected in a temperature-controlled condenser-type device. The condenser will separate H_2SO_4 from both SO_2 and moisture in the gas stream if the temperature is below the H_2SO_4 dew point but above the water dew point. For most combustion source gases, the temperature of the condenser is maintained at 140°F.

Two types of condensers currently are used: the traditional Goksoyr-Ross type, which consists of a water-jacketed spiral tube with a backup frit and a simplified type which consists of a water-jacketed straight glass tube packed with Pyrex glass wool. The simplified glass-wool plug was devised and evaluated in the Environmental Sciences Research Laboratory to overcome the high pressure drops and frit recovery of sulfate that persisted with the Goksoyr-Ross device.

As most source sampling that addresses H_2SO_4 and particulate sulfate also involves measurement of SO_2 , the sampling system usually includes impingers that contain 3% hydrogen peroxide (H_2O_2).

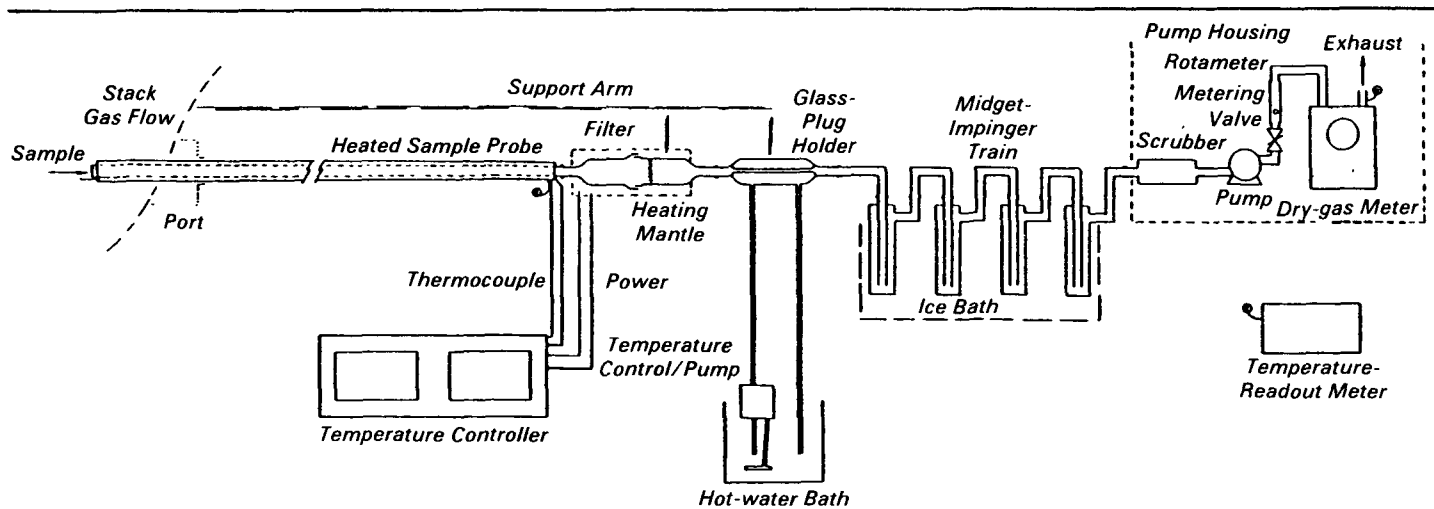


Figure 1. The miniature acid condensation system.

During the past few years ESRL's Stationary Sources Emissions Research Branch has conducted numerous source emissions studies involving the separation and measurement of gaseous H_2SO_4 and particulate sulfate. The methods used for such sampling and analysis have been continually updated. One product of this research is the Miniature Acid Condensation System (MACS), a highly portable and easily operable sampling system for gaseous H_2SO_4 and SO_2 .

While numerous systems of this type have been constructed by various source sampling groups, no such total system is commercially available. Sampling for gaseous H_2SO_4 in combustion source emissions, therefore, currently must be preceded by fabrication of a sampling system. One purpose of this project report is to provide guidelines for constructing such a system. The report includes drawings of system parts with suggested

dimensions, a listing of possible sources for parts, and the approximate construction cost. Also included is a discussion of sampling train operation and sample recovery. Topics covered include the interpretation of results, selective solvent recoveries, and procedures for sulfate ion analysis by

barium-thorin titration and ion chromatography.

Figure 1 depicts the MACS. The system consists of a high-temperature probe and filter holder, a temperature-controlled glass-wool plug, a midget impinger system and accompanying pump, a gas meter, and electronic components.

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Project Summary

Development of the MESOPUFF II Dispersion Model

J. S. Scire, F. W. Lurmann, A. Bass, and S. R. Hanna

The development of the MESOPUFF II regional-scale air quality simulation model is described. MESOPUFF II is a Lagrangian variable-trajectory puff-superposition model that has been designed to treat transport, transformation, diffusion, and removal processes of pollutants emitted from multiple point and/or area sources at transport distances beyond the range of conventional straight-line Gaussian model (i.e., beyond ~ 10-50 km).

The major features of this model and enhancements over its predecessor, MESOScale PUFF (MESOPUFF), include the use of hourly surface meteorological data, twice-daily rawinsonde data, and hourly precipitation data; separate wind fields to represent flows within and above the boundary layer; parameterization of vertical dispersion in terms of micro-meteorological turbulence variables; transformation of sulfur dioxide (SO_2) to sulfate (SO_4) and nitrogen oxides (NO_x) to nitrate (NO_3); a resistance model for dry deposition; time- and space-varying wet removal; and a computationally efficient puff-sampling function. The scientific and operational bases of the methods used in the model are discussed. The results from several model algorithms also are compared against experimental data.

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Introduction

The regional and long-range transport and transformation of sulfur oxides and nitrogen oxides emitted from major point sources have been of considerable concern. There is a need for easily usable, cost-efficient air-quality models that can realistically treat the various physical processes important on these scales. The MESOScale PUFF (MESOPUFF) model has been extensively modified to revise and more realistically treat the transport, vertical dispersion, chemical transformation, and dry and wet removal processes. The new model, designated MESOPUFF II, is one element of an integrated modeling package that includes components for preprocessing of meteorological data (READ56, MESOPUFF II) and for postprocessing of predicted concentrations (MESOFILE II).

Major Model Features

MESOPUFF II uses a puff-superposition approach to represent continuous plumes. The pollutant material in each puff is transported independently of that in other puffs and is also subjected to dispersion, chemical transformation, and removal processes. Some of the general features of the MESOPUFF II modeling system are as follows:

- (1) Hourly surface meteorological data, twice-daily rawinsonde data, and hourly precipitation data are read from magnetic tapes.
- (2) Wind fields to represent the mean flow in the boundary layer and above the boundary layer are constructed, although several options are given.

- (3) Boundary-layer structure is treated in terms of micrometeorological parameters that include the surface friction velocity, mixing height, convective velocity scale, and Monin-Obukhov length.
- (4) Space- and time-varying chemical transformation can be performed simultaneously for up to five pollutant species, including sulfur dioxide (SO_2), sulfate (SO_4^{2-}), nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), nitric acid (HNO_3), and nitrate (NO_3^-).
- (5) Dry deposition is prescribed by a resistance model in the surface-depletion mode, and the source-depletion method is optional.
- (6) Space- and time-varying wet removal is parameterized according to precipitation rate and scavenging coefficients.

The meteorological data inputs required by the preprocessors consist of the routine twice-daily upper air soundings, hourly surface meteorological observations, and hourly precipitation measurements reported by the National Weather Service. The preprocessor programs have been designed to read the standard-formatted meteorological data tapes available from the National Climatic Center in Asheville, North Carolina.

Wind fields for MESOPUFF II are constructed from the hourly surface wind observations, as well as from the twice-daily rawinsonde wind profile data. The surface station network data allow better temporal and spatial resolution than do the upper air sounding data, which involve much larger distances and less frequent measurements. The wind fields are constructed at two user-specified levels--a lower level representing the mean boundary-layer flow and an upper level representing flow above the boundary layer.

Boundary-layer structure is parameterized in terms of micrometeorological variables computed from the surface station data and information about surface characteristics (land use, or roughness lengths) provided by the user for each grid point. The surface friction velocity, u^* , the convective velocity scale, w^* , the Monin-Obukhov length, L , and the computed boundary-layer height, z_i , are computed.

Chemical transformation rate expressions were developed from the results of photochemical model simulations over a

wide range of environmental conditions. The rate expressions include gas-phase NO_x oxidation, gas- and aqueous-phase components of SO_2 oxidation, and the chemical equilibrium of the nitric acid, ammonia, and ammonia nitrate system. The parameterized transformation rates depend on solar radiation, background ozone concentration, and atmospheric stability. The SO_2 oxidation rate is empirically increased at high relative humidity to account for aqueous-phase reactions. In the case of NO_x , the transformation rate also depends on the NO_x concentration.

The spatial and temporal variations of dry deposition are treated by a resistance model. The pollutant flux is proportional to the inverse of a sum of resistances to pollutant transfer through the atmosphere to the surface. The resistances depend on the characteristics of the pollutant and the underlying surface and atmospheric conditions. MESOPUFF II contains options for the commonly used source-depletion method or for more realistic surface depletion, where pollutants are removed only from a surface layer in the three-layer mode.

Precipitation scavenging can be the dominant pollutant removal mechanism during precipitation periods. MESOPUFF II contains a scavenging ratio formulation for wet removal. The scavenging ratio depends on the type and rate of precipitation (derived from hourly precipitation measurements, if available) and the characteristics of the particular pollutant.

In addition, improvements were made in the method of summing the contributions of individual puffs to the total concentration at a receptor location. The model uses an integrated form of the puff-sampling function that eliminates the problem of insufficient puff overlap commonly encountered with puff-superposition models. This development allows continuous plumes to be more accurately simulated with fewer puffs, thereby saving computational time and reducing computer storage requirements.

MESOPUFF II Modeling System

The MESOPUFF II modeling package is schematically illustrated in Figure 1. The two meteorological preprocessor routines are READ56 and MESOPAC II. READ56 processes the rawinsonde data, and MESOPAC II reads the output file created by READ56 and the standard-formatted hourly surface meteorological data and precipitation data. A single output file is produced that includes all the time- and space-interpolated fields of

meteorological variables required by MESOPUFF II.

All source, receptor, and program-control information is input by formatted-card images. The control parameter inputs determine which options are used in the computations and what type of output is produced.

The model was run for a two-day period, to evaluate the SO_2 to SO_4^{2-} transformation mechanism and to qualitatively demonstrate the behavior of some other model algorithms. The modeled period was taken from the August 1978 Tennessee Plume Study, which was conducted near the Cumberland power plant in northwestern Tennessee. The two-day period (August 22-23) included chemical measurements by aircraft traverses through the plume at distances of 18 km to 160 km and represented 2 to 10 hours of travel. The predicted transformation rates were generally close to the observed rates derived from the pollutant measurements, especially for the drier, sunny period on August 22. During this period, SO_2 oxidation was probably dominated by gas-phase reactions, whereas on the 23rd, when plume-cloud interactions were observed, the transformation rates were underpredicted (values were two-thirds the observed rates). The larger observed values are attributed to greater contributions by aqueous-phase reactions.

Conclusions

The scientific and operational approaches to modification of the model are completely described in the report. The results of the model runs, including a comparison of observed and predicted transformation rates, the qualitative behavior of plume growth, plume fumigation, and dry deposition (surface depletion) are also presented. A companion report entitled "User's Guide to the MESOPUFF II Model and related Processor Programs" provides a brief technical description of the methods and a complete set of user instructions.

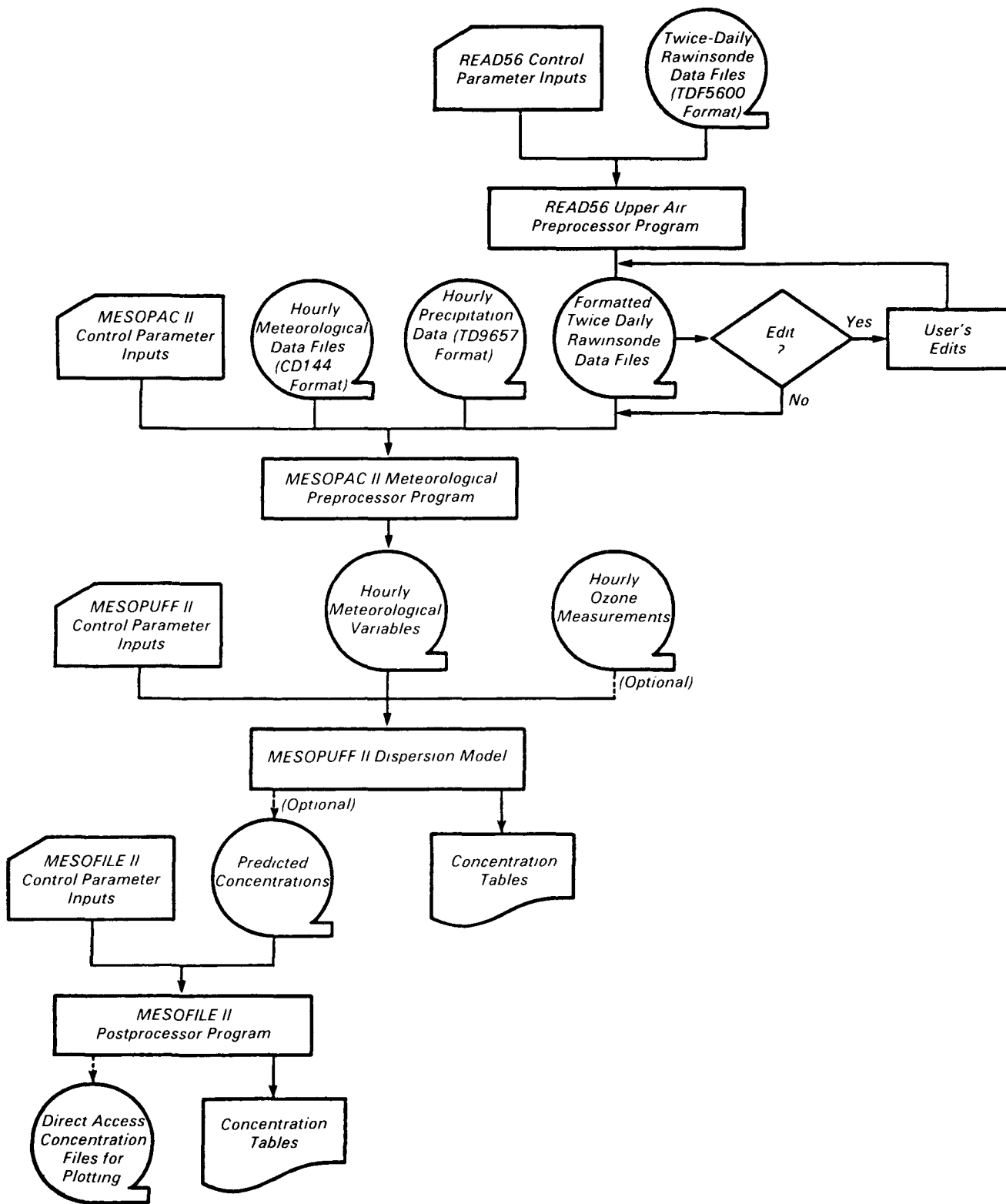


Figure 1. MESOPUFF II modeling package

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The complete report, entitled "Development of the MESOPUFF II Dispersion Model," (Order No. PB 84-183 753; Cost: \$11.50, subject to change) will be available only from:

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