Accuracy in Trace Analysis

### Results

## **GC-MS** Calibration Samples

Three direct injection calibration samples, which contained all but one of the training set compounds, were analyzed [2]. Of the 77 compounds observed in the calibration runs, 84% were correctly identified. Of the 13 compounds not identified, three were correctly assigned by chemical class.

#### **GC-MS Field Samples**

The GC-MS data files for three field samples were also analyzed [3]. The identities of the target compounds were determined by using both GC retention times and a combination of forward and reverse spectral matching techniques with stringent matching parameters. The identification of other compounds not on the target list was based on a Finnigan search technique. The application of the pattern recognition scheme to the transformed data for the target compounds resulted in 88% correct classification. The compound identification results were 85% accurate.

There were 75 different nontarget compounds identified in 120 occurrences in the three samples. The classification results agreed very well for the two class 1 and class 2 spectra. However, a very large number of alkanes and alkenes were incorrectly classified as chlorocompounds. Further details of this study are given in references [2], [3], and [4].

Although the research described in this article has been funded by the U.S. Environmental Protection Agency under Cooperative Agreement CR-811617 with the University of Illinois at Chicago, it has not been subjected to Agency review. The mention of commercial products does not constitute endorsement or recommendation for use.

### References

- Wold, S., Albano, C., Dunn, W. J. III, Edlund, U., Esbensen, K., Geladi, P., Hellberg, S., Johansson, E., Lindberg, W., and Sjostrom, M., in B. R. Kowalski (Editor), Chemometrics: Mathematics and Statistics in Chemistry, Reidel, Boston (1984), pp. 17-96.
- [2] Dunn, W. J. III, Koehler, M. G., Emery, S. L., and Scott, D. R., Application of Pattern Recognition to Mass Spectral Data of Toxic Organic Compounds in Ambient Air, Chemometrics Intell. Lab. Sys., in press, Sept. (1987).
- [3] Scott, D. R., Dunn, W. J. III, and Emery, S. L., Classification and Identification of Hazardous Organic Compounds in Ambient Air by Pattern Recognition of Mass Spectral Data, Environ. Sci. Tech., in press, Sept. (1987).
- [4] Scott, D. R., Anal. Chem. 58, 881 (1986).

Annular Denuders and Filter Packs Designed to Measure Ambient Levels of Acidic and Basic Air Pollutants

### **Robert K. Stevens**

U.S. Environmental Protection Agency Research Triangle Park, NC 27711

Measurements of acidic (e.g., SO<sub>2</sub>, HNO<sub>3</sub>) and basic gases (e.g., NH<sub>3</sub>) that coexist with fine particles ( $< 2.5 \,\mu$ m) are used in models to assist in determining the origin and age of aerosols. Bias associated with each measurement method used to obtain this air quality data can degrade the real correlation between species. In addition, the sensitivity of most instrumental methods to measure SO<sub>2</sub>, NH<sub>3</sub>, HNO3 or HNO2 is limited to measurements at concentration levels above 2-5 ppb. Measurement of HNO<sub>3</sub> has also proven to be more difficult due to losses of HNO<sub>3</sub> in the sampling inlets used in some of the measurement procedures. Difficulties in differentiating atmospheric HNO<sub>3</sub> from HNO<sub>3</sub> produced by the dissociation of NH4NO3 during sampling, further complicates monitoring procedures.

Possanzini et al. [1] described the development of an annular denuder system which removes reactive gases (e.g.,  $HNO_3$ ,  $SO_2$ ) from air samples an order of magnitude more efficiently per unit length and at lower Reynolds number than open tubular denuder designs. Recently we developed an improved version of the annular denuder that incorporates several important features to minimize losses of key species during sampling and reduce the possibility of leaks in the components that join the various parts of the system.

To demonstrate the applicability of this improved design of the annular denuder, a series of field studies were conducted in Research Triangle Park, NC during the fall of 1986 and winter of 1987. An annular denuder system (fig. 1) is composed of four components: an inlet (to remove large particles), coated denuders (to collect the acidic and basic gases), filter pack (to collect fine particles and HNO<sub>3</sub> that may evaporate from the filter), and a flow controller-pump assembly. In this study a new glass Teflon-coated impactor inlet was designed with a short tube extending below the impactor to prevent large particles and rain droplets from entering the impactor. With the exception of the impactor surface, the entire inlet is

# Accuracy in Trace Analysis

coated with Teflon. The impactor surface is a sintered glass disc coated with silicone grease to prevent particle bounce. At 16.7 L/min, a 50%  $D_{AE}$ =2.64 µm cutpoint was obtained with an impactor nozzle jet diameter of 4.0 mm (Baxter and Lane [2]).

The first two denuder tubes were coated with a 1% solution of glycerine and Na<sub>2</sub>CO<sub>3</sub>. Anions collected on the second denuder are used to correct for any particle deposition that may have occurred in the denuders during sampling. Both denuders were extracted with ion chromatography eluent and analyzed for NO<sub>2</sub> (HNO<sub>2</sub>), NO<sub>3</sub> (HNO<sub>3</sub>), and  $(SO_2)$ . The two filters in the filter pack were extracted with 20 mL deionized water and analyzed for  $SO_4^=$  and  $NO_3^-$  content. For some portions of the study, a third annular denuder coated with citric acid was used to collect NH<sub>3</sub>. As a result of these experiments, we have demonstrated that a relatively inexpensive (\$150.00) Teflon-coated impactor will quantitatively transmit acidic gases to an annular denuder.

In addition, modifications to the annular denuder itself resulted in a reliable system for field investigations. Paired samples were run to compare the new denuder assemblies and the average percent differences between sampler results with different inlet configurations for SO<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>2</sub>. The differences were 3.4, 6.4, and 8.3%, respectively. During the second phase of the testing, an NH<sub>3</sub> denuder was incorporated into the assembly. The average % difference between two identical annular denuder systems for SO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>, SO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were 1.8, 5.5, 15, 16, 4.6 and 3.6%, respectively. Experiments by Appel et al. [3] indicated that HNO<sub>3</sub> was not retained in the Tefloncoated glass inlets.

In our study, intercomparison of denuder assemblies showed that ratios of  $HNO_3$  to particle nitrate tended to decrease with decreasing ambient temperature and increasing humidity. This is qualitatively consistent with previous theoretical phase equilibrium calculations of  $NH_4NO_3$ .

Disclaimer. Although the research described in this article has been funded wholly by the U.S. Environmental Protection Agency, it has not been subjected to review and therefore does not necessarily reflect the views of the agency and no official endorsement should be inferred.



Figure 1. Annular denuder.

### References

- Possanzini, M., Febo, A., and Liberti, A., Atmosph. Environ. 7, 2605 (1983).
- [2] Baxter, T. E., and Lane, D. D., Initial performance testing of a glass jet impactor designed for use in dry acid deposition sampling, Presented at the 1987 American Assoc. for Aerosol Research, Seattle, WA. 14-17, Sept. (1987).
- [3] Appel, B. R., Povard, V., and Kathney, E. L., Loss of nitric acid within inlet devices for atmospheric sampling, Paper presented at 1987 EPA APCA Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC. 3-6 May (1987).