



Project Summary

Investigation of the Performance of Sulfation and Nitration Plates

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An inexpensive method for measuring atmospheric pollutants, which has been in use for several decades, is the passive reactive monitor. Such a device contains a reactive substance that is exposed to ambient air for a period of time. The pollutants in the surrounding air react with the reactive surface of the monitor. A quantitative chemical determination is made of the reaction product. A calibration factor is then applied to estimate the pollutant concentration in the ambient air averaged over the exposure period. Passive monitors, known as sulfation and nitration plates, are available from commercial suppliers.

The objective of this study was to evaluate the performance of commercial sulfation and nitration plates. The sensitivity of plate calibration factors to pollutant concentration (SO_2 and NO_2), simulated wind, speed, humidity, and temperature was determined. Sulfur dioxide was collected as SO_4^{2-} on both sulfation and nitration plates. Nitrogen dioxide was collected effectively only on the nitration plates and is retained as NO_2^- . Nitration plates were subject to SO_4^{2-} and NO_2^- loss upon storage and should be analyzed promptly after use. No SO_4^{2-} loss was observed for sulfation plates.

For sulfation and nitration plates, test results indicate that sulfation calibration factors were extremely sensitive to wind speed. A slight effect of relative humidity was observed for sulfation calibration factors on both types of plates and for nitration calibration factors on nitration plates. Nitration calibration factors were extremely sensitive not only to wind

speed, but to NO_2 concentration and temperature as well.

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 are fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) are released in large quantities by anthropogenic sources. These gases are the major precursors of the acids that contribute to acidic precipitation. Inexpensive, reliable, accurate means are needed to monitor SO_2 and NO_2 in the atmosphere.

One type of method, which has been used with varying degrees of acceptance for two decades, is the passive reactive monitor. Such a device is exposed for a period of time, so that the pollutant in the surrounding ambient air reacts with the reactive surface of the monitor. The monitor is then returned to the laboratory, where a chemical determination of the reaction product is made. By considering the duration of exposure and the reactive surface area, a product flux (F) is determined. This product flux is used along with a calibration factor (CF) to estimate the gas phase concentration of the pollutant (C). Historically this calibration factor, which relates ambient air pollutant concentration to product flux ($\text{CF} = \text{C}/\text{F}$), has been assumed to be constant. The magnitude of this calibration factor may depend on several variables, such as pollutant

concentration, wind speed, humidity, and temperature.

Passive monitors for SO₂ and NO₂ are available from commercial suppliers. These devices are known as sulfation and nitration plates. The objective of this study was to evaluate the performance of commercial sulfation and nitration plates. The study was designed to determine the sensitivity of plate calibration factors to pollutant concentration, simulated wind speed, humidity, and temperature.

Experimental

An exposure apparatus was designed and built; it permits the simultaneous exposure of up to 40 plates, with half exposed at a high gas velocity and half at a low gas velocity. In the high velocity (HV) channel, the gas velocity at the centroid averaged 471 cm/s, and in the low velocity (LV) channel, the centroidal velocity averaged 66.6 cm/s. The test section was approximately 152 cm long; it contained two parallel channels, and each channel had dimensions of 6.35 by 10.2 cm. The exposure apparatus was contained in a temperature-controlled environmental chamber that can maintain temperature to within $\pm 0.5^\circ\text{C}$.

Air sampling occurred both up- and downstream of the test section on a 30-min cycle controlled by a Chronrol timer. A Monitor Labs Model 8440 Nitrogen Oxides Analyzer and Model 8450 Sulfur Monitor were used to determine the pollutant concentrations in the test apparatus. An EG&G Model 880 was used to monitor dew point, and a shielded thermistor was used to measure temperature. Sulfation and nitration plates were acquired from SERCO (P.O. Box 625, Cedar Falls, Iowa 50613) for testing. The sulfation plate is a 5.0-cm diameter petri dish with a lead dioxide (PbO₂) coating that is reactive with SO₂. The nitration plate is identical to the sulfation plate, except it has a coating of triethanolamine (TEA) that is reactive with both SO₂ and NO₂.

The experimental program consisted of eight exposures. The exposures were designed to study the effects of SO₂ and NO₂ concentrations, temperature, relative humidity, and wind speed on the sulfation and nitration plates.

After exposure, each plate was desorbed in 50 mL of sodium bicarbonate-sodium carbonate eluent solution; the solutions were subjected to nitrite (NO₂⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻) analysis by ion chromatography

(IC). IC analysis provided a direct measure of pollutant reaction product loading in units of micrograms per plate. By using the area by plate (20.27 cm²) and the duration of exposure (day), the product flux in units of micrograms per square centimeter per day was determined. The pollutant gas phase concentration was determined by the gas monitor and converted from parts per billion into micrograms per cubic meter. The calibration factor is simply the ratio of the gas concentration to the product flux. It should be noted that the reciprocal of the calibration factor (adjusted by the appropriate stoichiometry and molecular weight) may be expressed as the deposition velocity in centimeters per second.

Results

The performance of commercially available passive monitors for SO₂ and NO₂ was evaluated. Sulfur dioxide can be collected as SO₄²⁻ on both sulfation and nitration plates. Nitrogen dioxide can be collected effectively only on the nitration plates and is retained as NO₂. Nitration plates were subject to SO₄ and NO₂ loss upon storage and should be analyzed promptly after use. No SO₄²⁻ loss was observed for sulfation plates.

The percentage changes in CF corresponding to changes in the tested environmental variables are given in Table 1, along with precision estimates. Sulfation CF, for both types of plates, were relatively independent of SO₂ concentration and temperature. They were dependent on wind speed and relative humidity. They were also subject to appreciable lot-to-lot differences, and for sulfation plates, to smaller within-lot, plate-to-plate differences. As the simulated wind speed was reduced from 4.7 to 0.7 m/s, the CF increased by factors of 3.1 and 4.5 on sulfation and nitration plates. As the relative humidity was reduced from 79 to 16% the sulfation CF increased on the average by 45% for sulfation and nitration plates. The lot-to-lot precision of SO₂ deposition to nitration plates was better than 1%; but for sulfation plates, this difference averaged 30%.

Nitration CF were sensitive to most of the tested variables. As the NO₂ concentration was increased from 20 to 200 parts per billion, the CF increased by a factor of 2.5. As the simulated wind speed was reduced from 4.7 to 0.7 m/s, the CF increased by a factor of 2.4. Reducing the relative humidity from 79 to 16% increased the nitration CF by 67%. A

temperature change from 27°C to 5.6°C increased the CF by a factor of 4.6 at the higher wind speed and 2.9 at the lower wind speed.

The lot-to-lot variation in nitration CF was small and was found to be less than 3%. At room temperature, the within-lot, plate-to-plate variability of NO₂ deposition to nitration plates averaged 2.7% at the high wind speed and 7.5% at the lower wind speed.

Test results indicated that for either sulfation or nitration plates, sulfation CF were extremely sensitive to wind speed. Nitration CF were extremely sensitive not only to wind speed, but to NO₂ concentration and temperature as well.

These findings identify and quantify many of the uncertainties associated with the use of sulfation or nitration plates in ambient air quality monitoring. They should provide insight toward the interpretation of data collected with such devices. Finally, these results should provide guidance on the quality of information that can be expected from these devices if their deployment is considered in future air quality studies.

Table 1. Summary of the Sensitivity and Precision of Calibration Factors for Sulfation and Nitration Plates

Plate Type	Calibration Factor	Percentage Change in CF Corresponding to Indicated Change of Environmental Variable				Precision (%)	
		Concentration 20 to 200 ppb	Wind Speed 4.7 to 0.7 m/sec	Humidity 79 to 16% RH	Temperature 27 to 5.6°C	Lot-to-Lot	Plate-to-Plate Within-Lot
Sulfation	CF _{SO₄²⁻}	±25	+310	+39	negligible ^a	±30	±5.3 ^b ±16 ^c
Nitration	CF _{SO₄²⁻}	±15	+450	+49	negligible ^a	negligible ^a	±3.5 ^b ±14 ^c
Nitration	CF _{NO₂}	+250	+240	+67	+460 ^b +290 ^c	negligible ^a	±2.7 ^b ±7.5 ^c

^a On the average the difference is less than 5%.

^b Result is for the high velocity wind speed.

^c Result is for the low velocity wind speed.

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J. W. Spence is the EPA Project Officer (see below).

The complete report, entitled "Investigation of the Performance of Sulfation and Nitration Plates," (Order No. PB 84-211 184; Cost: \$8.50, subject to change) will be available only from:

National Technical Information Service
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