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## Atmospheric Chemistry of Aldehydes: Enhanced Peroxyacetyl Nitrate Formation from Ethanol-Fueled Vehicular Emissions

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■ A preliminary study of the effects of enhanced acet-aldehyde emissions from vehicles using ethanol and ethanol-containing fuel on peroxyacetyl nitrate (PAN) concentrations in urban air has been conducted in Rio de Janeiro. During this study, part of the second Rio de Janeiro Aerosol Characterization Study (RIO-JACS II), high concentrations of aldehydes (with low HCHO/CH<sub>3</sub>CHO ratios) were related to enhanced PAN formation rates, especially in the a.m. hours, leading to PAN concentrations as high as 5 ppbv even in the presence of high NO concentrations. Model simulations of smog photochemistry with high aldehyde emissions were in substantial agreement with observations, except nitric acid levels were higher than observed due in part to HNO<sub>3</sub> loss mechanisms not included in the model (e.g., uptake onto aerosol particles).

### Introduction

There has been increased interest in the use of ethanol and other biomass-derived alcohol fuels as alternative energy sources, both in developing countries where simple alternatives for wood-derived fuels are needed and in industrialized countries where continued reliance on a liquid fuel based economy will also make these bio-sourced fuels attractive. Recently, increased usage of "gasohol" has also been proposed as a control measure for elevated carbon monoxide (CO) levels in urban areas of the western U.S. Increased woodburning in western cities has added to the motor vehicle derived levels of CO. During wintertime inversions this has led to more numerous violations of the CO standard. Addition of alcohol to motor vehicle fuels has been proposed as a "solution" to reduce CO levels below the established air quality standards, since alcohol

fuel combustion produces reduced CO emissions, along with primary aldehyde emissions which are not currently regulated.

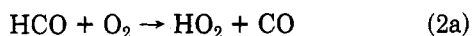
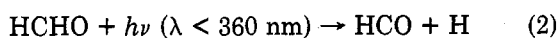
The tradeoffs and potential impacts of alcohol fuel usage leading to increased aldehyde emissions into the atmosphere must be carefully studied since low molecular weight aldehydes and ketones are partially oxidized organics of great significance to photooxidation processes (smog formation) in ambient air (1). Formaldehyde (HCHO) and acetaldehyde (CH<sub>3</sub>CHO) are the most abundant carbonyl compounds in the atmosphere (2), although significant fractions of total carbonyls (ca. 10%) may be present as propanal, acetone, acrolein, and benzaldehyde (3). Some difunctional aldehydes and ketones have been predicted by photochemical models, but ambient measurements are scarce. Ambient concentrations of HCHO in the range of 5-60 parts per billion by volume (ppbv) have typically been reported in polluted atmospheres in the United States and elsewhere (2-7), with CH<sub>3</sub>CHO levels on the order of 60% of formaldehyde values. Commercial production of HCHO in the United States is estimated at  $(1.5-2.0) \times 10^9$  kg/yr, with acetaldehyde production about one-third of that value (1).

In general, the lifetimes of aldehydes are on the order of hours (1, 8, 9), with principal gas-phase loss routes by photolysis and reaction with OH radicals. Heterogeneous losses by wet and dry deposition processes are also significant, especially the former for formaldehyde due to its high aqueous solubility (10). Aldehydes are formed through photooxidation reactions of methane and isoprene [dominant processes in remote areas (11)] and other biogenic and anthropogenic hydrocarbons. In industrialized areas of the world they are also directly emitted during manufacturing processes and by transportation sources. It is clear from emissions and ambient concentration data that transportation sources substantially in-

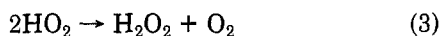
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crease the concentrations of HCHO and CH<sub>3</sub>CHO in polluted urban areas. Controls on vehicular sources, where in use, are effective in reducing aldehyde emissions (1).

Formaldehyde and acetaldehyde levels are important since these compounds substantially influence photochemical smog processes in complex ways, including accelerating the formation of secondary products (12, 13) and increasing ozone maxima (14). For example, gas-phase photochemistry of HCHO in the atmosphere can lead via reaction with OH (reaction 1) or via photolysis (reaction 2) to the net formation of one or two hydroperoxyl (HO<sub>2</sub>) radicals (9, 15):

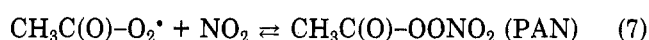
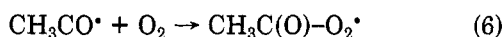
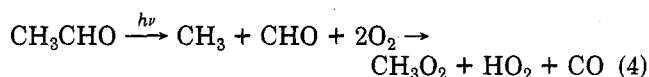


These hydroperoxyl radicals may oxidize nitric oxide (NO) molecules to NO<sub>2</sub> and OH (15) or recombine by reaction 3. This reaction produces increased levels of gas-phase



hydrogen peroxide, an important oxidant of dissolved S(IV) in cloudwater and precipitation (16).

Photolysis of acetaldehyde in the atmosphere leads to the formation of HO<sub>2</sub> radicals, CO, and methylperoxyl radicals (12, 17, reaction 4) and by reaction with OH to the peroxyacetyl radical and peroxyacetyl nitrate (PAN) via reactions 5–7. In the presence of high concentrations



of NO, the formation of PAN is suppressed, since acetylperoxyl radicals formed in reaction 6 can also oxidize NO to NO<sub>2</sub>. However, in polluted urban air daytime decomposition of CH<sub>3</sub>CHO via reaction with OH is expected to be a major route of PAN formation (12, 18), especially away from the immediate vicinity of NO emission sources. This process, of course, also contributes to elevated ozone levels downwind in an urban plume (1). The formation of peroxyacetyl nitrates has substantive health implications since PAN and higher alkyl homologues are known to be potent phytotoxins and along with their aromatic homologues (e.g., peroxybenzoyl nitrate) are strong lachrymators (19). The reasonably long lifetime of PAN, particularly at colder temperatures, has also made it an important agent for transporting NO<sub>x</sub> on regional and global scales (20).

The use of ethanol-based fuels by motor vehicles in Brazil has afforded an opportunity to examine the potential for increased atmospheric production of PAN when primary acetaldehyde emissions are increased. For example, in Rio de Janeiro, motor vehicles are currently using sugar cane derived ethanol as a constituent of gasohol (20% v/v in normal usage) and in pure form as a fuel in a smaller portion (10–15%) of vehicles with engines designed to burn hydrated ethanol. This fuel usage with no catalytic controls is expected to lead to increased primary emissions of formaldehyde, acetaldehyde, and other higher aldehydes.

Data from the United States about gasoline fuels (1, quoting J. M. Heuss, personal communication) indicated

that formaldehyde:acetaldehyde mole ratios in auto exhaust averaged  $7.5 \pm 2.2$  for noncatalyst vehicles. The mole fraction of total aldehyde emissions present as HCHO and CH<sub>3</sub>CHO averaged  $80 \pm 5\%$ . The values for similar tests with catalyst-equipped cars were more variable, depending on the catalyst: ratios of average HCHO and CH<sub>3</sub>CHO concentrations were  $2.3 (+2.9/-1.1)$ , and the  $(\text{C1} + \text{C2})/\text{total aldehyde fractions} = 78 \pm 7.5\%$ . Earlier data were inconclusive concerning aldehyde emissions factors from vehicles using alcohol and alcohol-containing fuels vis-a-vis gasoline fuel (21). Blends of 20% ethanol were reported to produce marginally higher aldehyde emissions, but the HCHO/CH<sub>3</sub>CHO ratio was not specified. Some recent measurements (22) of Brazilian vehicular emissions in a test chamber with pure ethanol fuel suggest that abnormally high emission ratios of acetaldehyde to formaldehyde are obtained. This observation, plus the fact that Brazilian passenger cars are not equipped with catalytic converters, suggests that high ambient levels of acetaldehyde should be observed in polluted urban air in Brazil. Furthermore, enhancement of PAN formation rates and ambient concentrations, as well as changes in the diurnal patterns of PAN levels from those reported in other locations, might occur due to the use of their ethanol and ethanol-containing fuels.

As a result of these considerations of fuel-dependent emission factors, some preliminary measurements of aldehyde and PAN concentrations were performed during the second Rio de Janeiro aerosol characterization study (RIO-JACS II) which was conducted from 29 June to 11 July 1985 at two sites in Rio de Janeiro. Although the measurements were limited temporally and spatially and did not include all species critical to the evaluation of PAN formation rates, the results are used in this work, in conjunction with a simple photochemical model, to test the hypothesis that alcohol fuel derived acetaldehyde emissions enhance ambient PAN formation rates and change diurnal concentration patterns. The results of these studies as well as a comparison of the measurements with a simple photochemical model are presented here. The implications of this work with regard to ethanol-based fuel usage are discussed.

### Experimental Section

**Description of Sampling Sites.** The Vila Isabel site has been described in detail previously (23); it is located at the intersection of two heavily travelled streets near the Maracana stadium, about 6 km east of the downtown section of Rio and a few km south of a heavily industrialized area near the port facilities of the city. The other site was located on the roof of the seven-floor building housing the Chemistry Department on the campus of the Pontifical Catholic University of Rio de Janeiro (PUC/RJ), about 2 km from the ocean in the residential Gavea section of Rio.

**Aldehyde Measurements.** Aldehydes (formaldehyde and acetaldehyde) were sampled at 2.0 L/min by two reverse-phase (C18) Sep-Pak microcolumns (Waters Associates) connected in series; the microcolumns were coated with 2,4-dinitrophenylhydrazine as described in detail elsewhere (22). The retained 2,4-dinitrophenylhydrazones were eluted with acetonitrile and analyzed directly by a Waters Associates high-pressure liquid chromatograph equipped with a U6K injector and a Model 240 variable wavelength UV-visible absorbance detector set at 365 nm. Formaldehyde and acetaldehyde were efficiently (>95%) retained on the first Sep/Pak microcolumn; the second column collected no additional aldehydes (results not significantly above the field blanks). The analytical col-

umn (15 cm  $\times$  3.9 mm i.d.) contained spherical C18 reverse-phase material (5  $\mu$ m). The mobile phase was 43% v/v acetonitrile/water flowing at 1.2 mL/min. Coated Sep-Pak blanks (sealed at the end) were taken to the field and later analyzed along with the samples. Hydrazone standards dissolved in acetonitrile were used to prepare calibration curves.

**Measurements of PAN and Organic Nitrates.** Peroxyacetyl and peroxypropionyl nitrates (PAN and PPN, respectively) were measured by a gas chromatograph equipped with an electron capture detector (GC-ECD) and an automated 5-cc stainless steel sampling valve. Ambient air was continuously sampled through the valve, and at 30-min intervals, a 5-cc sample was injected onto a 1.8-m, 0.3 cm o.d., polypropylene column containing 3% Carbowax 400 on Chromosorb G (80/100 mesh) support. With a carrier gas flow rate of 30 cc/min of ultrahigh-purity nitrogen and a column temperature of  $35 \pm 1$  °C, the retention times of PAN and PPN were 4.9 and 6.0 min, respectively. The PAN peak is fully resolved both from the air peak (observed at about 0.9 min, with considerable tailing) and from PPN. Methyl nitrate can also be determined by the GC-ECD system employed in this work, its peak appearing at about 3.0–3.2 min on the tail of the air peak. Under the conditions used, the methyl nitrate peak is not resolved from  $C_2$ -chlorinated hydrocarbons, the latter frequently present in urban air; hence, it was not quantitated.

A source of gas-phase PAN for use in calibrating the GC-ECD was prepared by nitration of peracetic acid (24), stored in tridecane solvent (25), and evaporated into a stream of high-purity  $N_2$ . Direct calibrations done by serial cylinder dilution of gaseous PAN with  $N_2$  were only partially successful. Calibrations performed by comparing integrated GC-ECD signals from several PAN source dilutions with those of  $NO_x$  determinations by using a standard ozone chemiluminescent  $NO_x$  analyzer were reproducible to about  $\pm 20\%$  when a nylon filter was used to remove nitric acid impurities in the PAN source. Fourier transform infrared spectroscopy was used to confirm the purity of the PAN source.

**Measurement of Aerosols,  $SO_2$ , and Nitric Acid.** The techniques for sampling and analysis of aerosol constituents, sulfur dioxide, and nitric acid using the Brookhaven National Laboratory high-volume filter pack have been described in detail (26), as have the methods for pretreatment and preparation (26, 27). The filter pack consists of acid-treated quartz, NaCl-impregnated cellulose, and  $K_2CO_3$ -impregnated cellulose filters in series. Strong acid, ammonium, sodium, calcium, sulfate, nitrate, and chloride ions were determined on pH 4 aqueous extracts of the quartz filter by Gran titration ( $H^+$ ), indophenol colorimetry ( $NH_4^+$ ), atomic absorption spectroscopy ( $Na^+$ ,  $Ca^{2+}$ ), and ion chromatography ( $SO_4^{2-}$ ,  $NO_3^-$ , and  $Cl^-$ ). Nitric acid was determined by automated colorimetry of aqueous extracts of the NaCl-impregnated, 12.5 cm diameter filters (S&S 2W). Sulfur dioxide was determined by ion chromatography as sulfate following extraction of the  $K_2CO_3$ -impregnated cellulose filters (also S&S 2W) in water containing 2% hydrogen peroxide. Organic and elemental carbon levels were determined by thermal evolution and conversion to  $CO_2$  for determination by non-dispersive infrared (NDIR) spectroscopy (28). The  $^{13}C/^{12}C$  isotopic ratios and, on composited samples,  $^{14}C$  (radio-carbon) content were determined by isotopic ratio mass spectrometry and gas proportional counting, respectively. Only the nitric acid data will be considered in this manuscript due to its relationship to photochemical formation

of PAN. The aerosol carbon data and its relationship to anthropogenic source allocation will be discussed elsewhere (29).

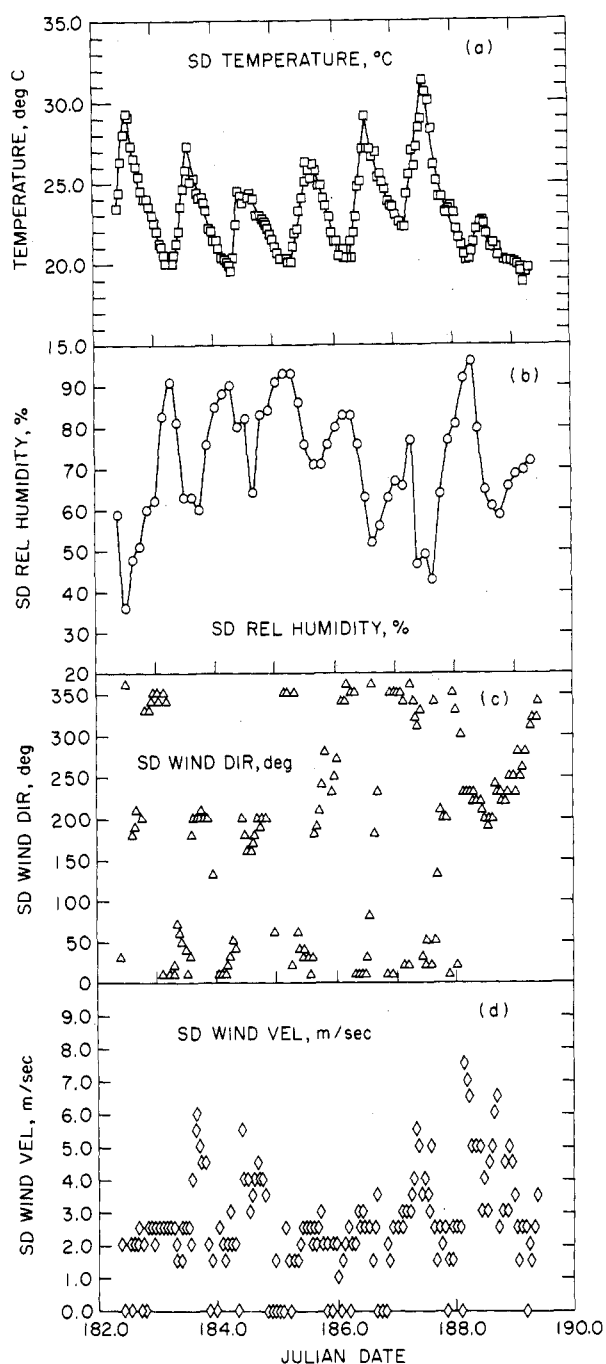
**Estimates of Ozone and Nitrogen Oxide Levels.** Previous monitoring data from the Vila Isabel site showed very low levels of ozone (23), presumably due to the proximity of large vehicular sources of nitric oxide. In fact, levels of ozone were usually below the limit of detection of the ethylene chemiluminescence instrument used ( $<2$  ppbv). Since background levels of ozone (daily maxima) might be expected to be about 50 ppbv at latitude  $23^\circ S$  in the austral midwinter (30), a lower limit of 50 ppbv of  $NO$  was present throughout the day at this site for reaction with boundary layer ozone. The total  $NO_x$  ( $NO$  and  $NO_2$ ) was expected to exceed  $NO$  initially (at dawn) by at least 10 ppbv due to  $NO$ -ozone reaction. This led to a lower limit estimate of 60 ppbv for the average concentration of  $NO_x$  at the Vila Isabel site. Concentrations of  $NO_x$  are estimated to be substantially lower (depending on local wind circulation) at the PUC/RJ site, but no monitoring data for either ozone or nitrogen oxides ( $NO_x$ ) were available at this location.

**Meteorological Data.** Meteorological observations were made at two airports in the Rio de Janeiro area: Galeao (International) airport located about 7 km north of the Vila Isabel sampling site and about 11 km north of the PUC/RJ site and Santos Dumont (downtown) airport located about 5 km east of the Vila Isabel site and 8 km northeast of the PUC/RJ site. Hourly observations of temperature, wind speed, and wind direction, and 3-h observations of relative humidity were made at both airports. In addition, balloon soundings to determine the mixing depth of the boundary layer were made daily at 0900 local time at the Galeao airport.

#### *Photochemical Model Description*

Photochemical modeling studies were performed with a photochemical box model which incorporates time-varying dilution rates, primary emission rates, temperature, and photolysis rates. The mechanisms used for these simulations were taken largely from that of Atkinson and co-workers (31) incorporating suggested improvements of Leone and Seinfeld (32). As appropriate, rate constants have been updated with the recommended values of Atkinson and Lloyd (33). The homogeneous gas-phase photochemical mechanism used consisted of 103 reactions and excluded  $SO_2$  chemistry. Hourly photolytic rates for 15 species were incorporated into the model by prior external calculations, with photolysis rates at intermediate times calculated by an interpolation procedure. Actinic flux calculations were made specifically for the appropriate dates and latitude of Rio de Janeiro, Brazil, for clear sky conditions with typical urban values for particle-induced light scattering incorporated into the calculations. The radiation field was calculated by the source method as described by Meier et al. (34).

Initial concentrations and emission rates used for the model simulations presented are given in Table I. Lower limits for  $NO$  and  $NO_2$  were used to initiate the model (see discussion above) with primary emission rates of  $NO$  and  $NO_2$  appropriate for urban source areas included. Under these conditions, the major primary sources of  $OH$  radicals are photolysis of ozone and aldehydes, together with subsequent reactions [ $O(ID) + H_2O$ , and  $HO_2 + NO$ , respectively]. A dilution rate for the early morning hours are determined by a dilution factor derived from  $x = \ln(n)/t$ , where  $x$  is the dilution constant,  $n$  is the dilution factor, and  $t$  is the time to dilution. For the early morning hours



**Figure 1.** Meteorological data taken at Santos Dumont (downtown) airport in Rio de Janeiro from 1 to 8 July 1985 (Julian dates 182–189), hourly observations except humidity (every third hour): (a) temperature, °C; (b) relative humidity, %; (c) wind direction, deg; (d) wind velocity, m/s.

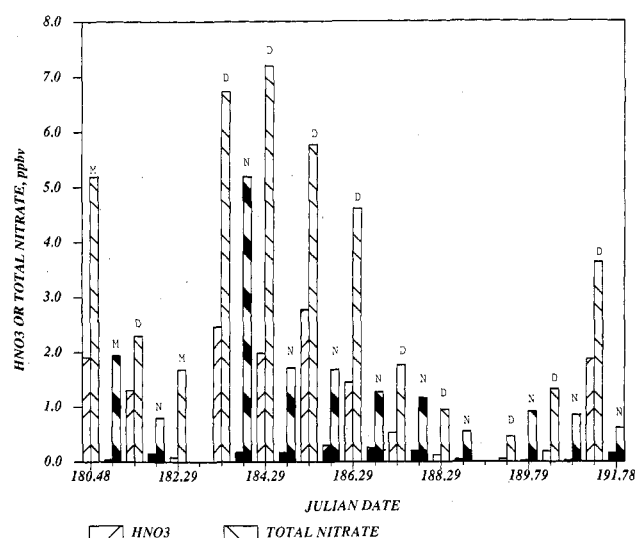
(0600–1000) a dilution factor of 3 was used to simulate the inversion breakup.

### Results

**Meteorological Data.** A summary of the meteorological data obtained from the Santos Dumont airport is shown in Figure 1. Although the study was conducted in the austral winter, weather conditions were sunny and moderate with temperature minima of 19–20 °C and maxima varying from 24 to 31 °C, low wind speeds, and no precipitation except for the early a.m. hours of 11 July, the last day of the study. The single exception to this pattern was 7 July in which cloudy conditions with strong SW winds and temperatures near 21 °C were observed. A sea-breeze circulation was observed on several days,

**Table I.** Initial Concentrations and Emission Rates of Species Used in Photochemical Box Model Simulation of High Primary Aldehyde Emissions Added to a Polluted Urban Situation (50% Relative Humidity, 298 K in Air)

molecular species	initial concn, ppbv	emission rate, ppbv h <sup>-1</sup>
NO	50	12
NO <sub>2</sub>	10	0.6
O <sub>3</sub>	2	
CO	3000	400
CH <sub>2</sub> O	25	0.4
CH <sub>3</sub> CHO	40	1.2
C <sub>3</sub> H <sub>8</sub>	20	0.9
alkane	140	4
ethene	15	0.4
propene	15	0.4
butene	20	0.5
benzene	20	0.1
toluene	10	0.4
xylene	20	0.5
acetone	10	0.4
HONO	10	



**Figure 2.** Averaged 12-h nitric acid and total inorganic nitrate (HNO<sub>3</sub> and particulate NO<sub>3</sub><sup>-</sup>) concentrations in Rio de Janeiro, 1–8 July 1985 at Vila Isabel site, 8–11 July 1985 at PUC/RJ site: D = daytime sampling period; N = nighttime sampling period; M = mixed day and night or nonstandard protocol.

characterized by light northerly winds blowing off Guanabara Bay in the a.m. hours and stronger winds blowing in from the Atlantic Ocean to the south for varying periods during the p.m. hours. The sea breeze from the south brought in slightly cooler and moister air, which reached the Santos Dumont airport as much as 2 h earlier than observed at the Galeao airport a few km further from the ocean. The stagnant conditions and sea-breeze recirculation of urban emissions were not dissimilar to conditions observed in the southern California air basin in the late summer months and resulted in the hazy, relatively polluted conditions detailed below.

**Nitric Acid Data.** As noted above, the presence of large, nearby sources of nitrogen oxides precluded the measurement of regionally characteristic ozone levels in the Vila Isabel (urban) site. An indication of photochemical reactivity could be obtained from the 12-h filter-pack nitric acid data, since the principal source of nitric acid is gas-phase oxidation of NO<sub>2</sub> by OH radicals (35):



Although filter-pack data for HNO<sub>3</sub> can be subject to ambiguities due to artifact gain or loss on upstream particu-

**Table II. Integrated 12-h Aldehyde and Filter-Pack Data from Nitric Acid, Sulfur Dioxide, and Total Nitrate<sup>a</sup> at the Vila Isabel Site, 29 June to 8 July 1985 (All Concentrations Reported Are in ppbv)**

date	start time	duration, h	HNO <sub>3</sub>	SO <sub>2</sub>	TN <sup>a</sup>	HCHO	CH <sub>3</sub> CHO
29 June	1138	16.43	1.91	29.4	5.2		
30 June	0404	3.12	0.03	12.8	1.9		
30 June	0713	11.80	1.30	15.2	2.3		
30 June	1901	11.85	0.15	14.5	0.8		
1 July	0652	1.78	0.08	59.7	1.7		
2 July	0713	11.85	2.50	74.2	6.7	15	17.3
2 July	1904	11.92	0.17	45.7	5.2	8.7	12.4
3 July	0704	11.88	1.88	56.4	7.2	11.4	13.3
3 July	1857	12.00	0.17	20.7	1.71	4.8	7.6
4 July	0704	11.87	2.77	70.6	5.77	11.6	14.8
4 July	1856	11.97	0.30	25.8	1.67	6.9	14.8
5 July	0654	12.15	1.44	53.1	4.61	10.1	14.2
5 July	1903	11.93	0.25	21.6	1.26		
6 July	0659	11.98	0.53	19.6	1.76		
6 July	1858	11.98	0.20	14.3	1.16		
7 July	0657	12.05	0.12	9.5	0.95		
7 July	1904	11.87	0.04	4.2	0.55		

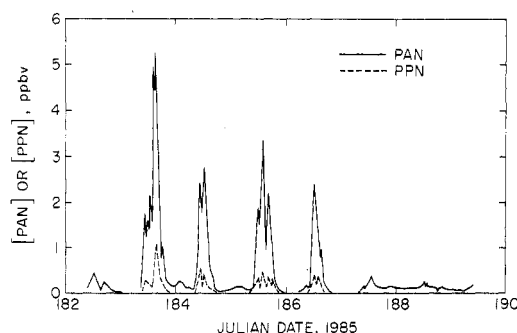
<sup>a</sup>TN = total nitrate = HNO<sub>3</sub> and particulate nitrate.

late filters (36), the general features of the data shown in Figure 2 are not thereby compromised.

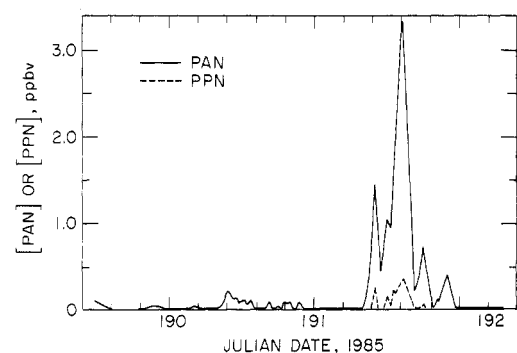
Nitric acid levels determined at the Vila Isabel site show strong diurnal variations which were much more pronounced than the trend exhibited by the sum of nitric acid and particulate nitrate (total inorganic nitrate). Significant levels of HNO<sub>3</sub> were being generated during daylight hours by photochemical oxidation of NO<sub>2</sub> (see reaction 8) and being lost during nighttime hours by absorption onto aerosol particles and also by dry deposition. Relatively high [NO] kept surface ozone levels near zero and probably prevented, within the urban boundary layer, a significant nighttime production rate of HNO<sub>3</sub> by the ozone-NO<sub>2</sub> reaction to form nitrate radical and dinitrogen pentoxide and their subsequent reactions with liquid water. Thus, 12-h daytime [HNO<sub>3</sub>] reached 2.8 ppbv on 4 July at the Vila Isabel site but never exceeded 0.3 ppbv at night. Nighttime [HNO<sub>3</sub>] reached a low of 22 pptv on 8-9 July at the near-coastal PUC/RJ site with SW winds off the South Atlantic Ocean. Overall, the average concentration-weighted fraction of total inorganic nitrate present as nitric acid was 37% for daytime samples and only 10% for nighttime samples.

**Aldehyde Data.** Data were obtained for both formaldehyde and acetaldehyde by the Sep-Pak cartridge/LC analysis technique described above. Twelve-hour data were obtained for 4 days (1-5 July) at the Vila Isabel site, and these were supplemented by 1- or 2-h data obtained on 2 and 4 July at Vila Isabel and 9 July at PUC/RJ. This data is shown in Tables II and III. The average of the 1- and 2-h samples is significantly higher than the 12-h data, suggesting that the collection efficiencies may not have been identical. For example, on 2 July the daytime levels of HCHO and CH<sub>3</sub>CHO were 15.0 and 17.3 ppbv, respectively, but the average of ca. 2-h data were 26.0 and 31.0 ppbv, respectively. The collection efficiency during the 12-h samples was apparently only ca. 57% of that observed during the 2-h sampling, assuming no artifact formation during collection. The HCHO/CH<sub>3</sub>CHO ratio was constant, however, at  $0.85 \pm 0.02$  with both sampling protocols.

The nighttime average ratio for all the 12-h data was HCHO/CH<sub>3</sub>CHO =  $0.57 \pm 0.12$ , somewhat lower than the daytime ratios of  $0.80 \pm 0.07$ . The nighttime ratios agree very well with ratios observed in samples taken in the Santa Barbara tunnel in Rio in April 1985; HCHO/CH<sub>3</sub>CHO =  $0.60 \pm 0.02$ . The daytime levels of HCHO and



**Figure 3.** Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) data from Vila Isabel site in Rio de Janeiro, 1-8 July 1985.



**Figure 4.** Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) data from the PUC/RJ site in Rio de Janeiro, 8-11 July 1985.

CH<sub>3</sub>CHO observed at the PUC/RJ site on 9 July (under the influence of strong sea-breeze circulation) were an order of magnitude lower than at the downtown site, although well above the marine background levels reported by Lowe and Schmidt (9) in the South Atlantic.

**Peroxyacetyl Nitrate Data.** Data for peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) were determined from 342 analyses at the Vila Isabel site from 1 to 8 July and from 135 analyses at the PUC/RJ site from 8 to 11 July. These data are presented in Figures 3 and 4. Strong diurnal trends in PAN levels were observed at the Vila Isabel site from 2 to 5 July and again at the PUC/RJ site on 10 July with daytime maxima over 2 ppbv (5.4 ppbv on 2 July was the highest value observed) and nighttime minima  $<0.25$  ppbv. For some extended periods, PAN levels were below the limit of detection (LOD) of the GC-ECD technique—about 0.07 ppbv (70 pptv). In con-

**Table III. Integrated 1- and 2-h Aldehyde Data in Rio de Janeiro for the Vila Isabel Site, 2 and 4 July 1985, and for the Pontificia Universidade Catolica (PUC/RJ) Site, 9 July 1985**

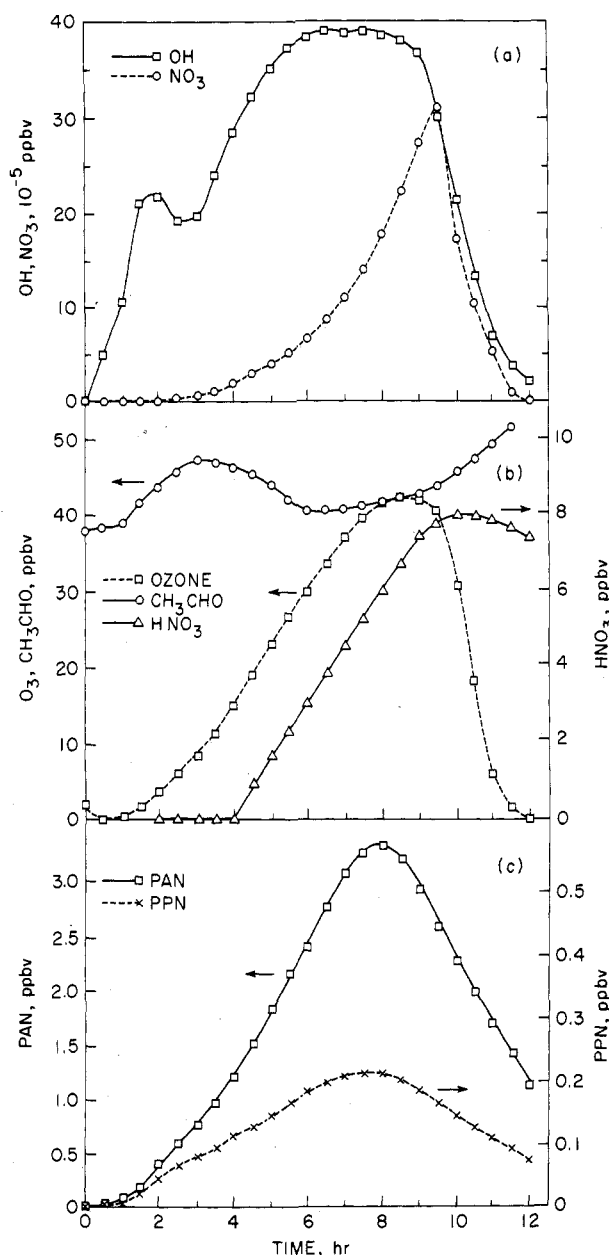
date	start time	duration, min	HCHO, ppbv	CH <sub>3</sub> CHO, ppbv
Vila Isabel Site				
2 July	0807	92	35	47
	0930	191	24	27
	1241	127	22	24
	1449	108	25	30
	1638	112	27	33
4 July	0729	62	36	54
	0831	60	23	30
	0931	186	20	23
	1237	40	26	36
	1317	58	26	34
	1415	55	20	35
	1510	50	21	42
	1600	55	30	43
	1655	52	34	55
	1747	75	27	44
PUC/RJ Site				
9 July	0750	60	2.4	3.1
	0850	60	1.6	5.4
	0950	60	2.0	4.6
	1050	60	2.4	4.0
	1150	140	1.2	1.9
	1410	60	1.8	3.9
	1510	80	1.4	3.0
	1630	60	2.2	4.6
	1730	60	2.2	3.4
	1830	77	1.2	3.2

trast, for the remaining days at both sites PAN levels never exceeded 0.5 ppbv all day; indeed, on 7 July with SW winds at the urban site and on 8 and 9 July with a strong sea breeze at the near-coastal site, PAN levels were seldom above LOD of 70 pptv. PPN levels were infrequently above LOD (about 70 pptv as per PAN) but when observed were about 15–20% of the PAN levels. The maximum PPN levels observed of >1 ppbv suggest that substantial propionaldehyde emissions (ca. 10% of the acetaldehyde) are likely to be occurring.

It should be noted that the PAN data exhibit considerable sample-to-sample variability: this is to be expected since the sampling technique is not continuous—instead, a single grab sample is injected every 30 min. However, there is an apparent structure to the data in addition to the sample-to-sample variability. That is, a smooth diurnal variation with a single clear maximum in the mid to late afternoon is not observed, as has been reported for southern California measurements. In Rio for the days with maxima >2.5 ppbv, an early rise, a leveling off, and one or more afternoon maxima between 1230 and 1630 h are a more typical pattern at the urban site. The data for 10 July at the PUC/RJ site, on which day sea-breeze recirculation of aged urban emissions is implicated, are more uniform with a maximum of about 3.3 ppbv at ~1500 h.

**Photochemical Model Results.** The results of the photochemical box model simulations are presented in Figure 5. Note that the rates of PAN formation under the average conditions of the urban Rio site observed during this study are qualitatively reproduced by the model. The PAN maximum is predicted to occur around 1400 h and is predicted to decrease due to peroxyacetyl radical reaction with NO. PAN maxima of ~4 ppbv are predicted with the estimated values for the polluted urban air of Rio de Janeiro.

The acetaldehyde concentrations are predicted to be in the 30–60 ppbv concentration range using estimated levels



**Figure 5.** Results of photochemical box model simulations with high aldehyde concentrations: (a) nitrate and hydroxyl radical concentrations,  $10^{-5}$  ppbv ( $10^{-8}$  ppbv  $\approx 2.5 \times 10^5$  molecules/cc); (b) ozone, nitric acid, and acetaldehyde concentrations, ppbv; (c) PAN and PPN concentrations, ppbv. Time is in h since start of simulation at sunrise (~0600 h).

of aldehyde and other pollutant emissions (Table I). The model also indicates that there should be a decrease in aldehyde concentrations occurring around midday followed by an increase in the concentrations in the late afternoon. For the Vila Isabel hourly average aldehyde data (Table III) this behavior was observed.

This simple box model simulation estimates that ozone should reach levels approaching 50 ppbv during the day. The available ozone data which have been collected near ground level and adjacent to vehicular sources are typically below 5 ppbv. This data indicates that NO in Rio de Janeiro urban sites exceeded 50 ppbv. It would be interesting to measure ozone aloft to compare with the models estimates of available ozone. Note that the model predicts a much more rapid dropoff late in the day for ozone than for PAN due to the afternoon rush-hour traffic vehicular emissions of nitric oxide. This is consistent with the NO reaction with ozone being much more rapid than



with PAN, since the latter compound must first decompose to the peroxyacetyl radical and  $\text{NO}_2$  before it can be titrated by nitric oxide.

The simulation also estimates that nitric acid will be produced photochemically at levels approximately 4 times that of PAN on the basis of the estimated  $\text{NO}_x$  levels used for the simulations (see Table I). The model does not contain a deposition term for nitric acid or aerosol conversion and as such, should be considered an upper limit estimate. It should be also noted here that this model does not contain any dilution estimates late in the day. It is clear from the meteorological data that any offshore winds that bring in clear air from the ocean to the Vila Isabel site will strongly affect the diurnal behavior of PAN and nitric acid data, causing the concentrations of both to drop off in the late afternoon and evening at rates larger than predicted in these simple simulations.

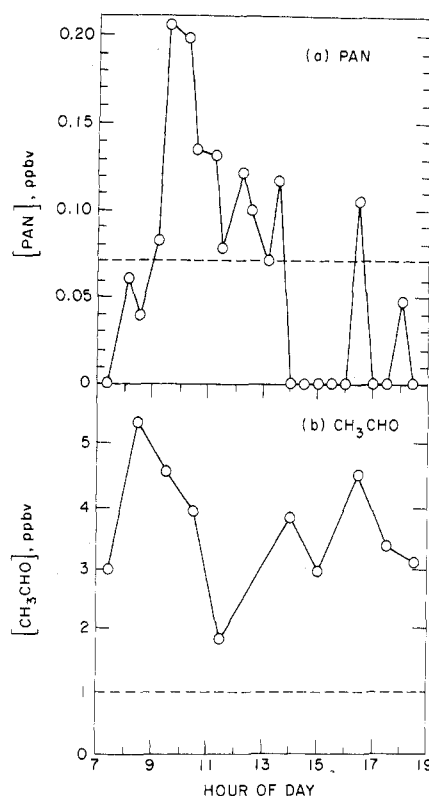
Considering the uncertainty in  $\text{NO}_x$  levels and that reactive hydrocarbon levels are unknown, the simple simulations presented here are consistent with both nitric acid and PAN levels being produced from photochemical processes. The levels of PAN are predicted to be elevated when compared to ozone particularly late in the day due to the slower reaction of PAN with locally emitted NO. As well, the increased levels of acetaldehyde from ethanol-based fuels are also contributing to increased PAN production. Once these polluted air masses are carried away from urban NO sources, it is expected that integrated dosages of ozone, PAN, and other oxidants will increase at downwind suburban and rural sites at such times as the urban plume impacts these areas following transport and further transformation.

#### Discussion

**Implications of High Urban Levels of Aldehydes with Low  $\text{HCHO}/\text{CH}_3\text{CHO}$  Ratios.** The aldehyde concentrations by the 1- or 2-h sampling protocol were quite high even for urban photochemical smog conditions, and the  $\text{HCHO}/\text{CH}_3\text{CHO}$  ratios were lower than reported elsewhere (2, 5). Differences were observed between 1- and 2-h aldehyde data and the 12-h average data, both measured at the Vila Isabel site; as noted above, the former are likely to be more accurate. This is reinforced by the fact that agreement between observed and model-predicted PAN formation rates (discussed below) requires the presence of ca. 50 ppbv of acetaldehyde during mid-morning hours.

The aldehyde results suggest that additional primary emission sources, especially of acetaldehyde, are ubiquitous to the Rio de Janeiro airshed and lead to elevated ambient concentrations of this atmospheric precursor to PAN. As noted above, these sources are likely to be ethanol- and gasohol-fueled motor vehicles. The high  $\text{HCHO}/\text{CH}_3\text{CHO}$  ratios in daytime samples are consistent with either additional  $\text{HCHO}$  emissions during daytime hours or, more likely, more rapid daytime sink processes for  $\text{CH}_3\text{CHO}$  than for  $\text{HCHO}$  (17, 37). Lower aldehyde levels and low  $\text{HCHO}/\text{CH}_3\text{CHO}$  ratios reported for 9 July at the PUC/RJ site suggest that the sea-breeze circulation isolated this site from industrial areas of Rio to the north, although evidence of local traffic emissions was observed. Comparisons of aldehyde and PAN data are described below.

Other loss mechanisms for low molecular weight aldehydes need to be considered, especially those involving nighttime chemistry. The most facile of these, reaction with  $\text{NO}_3$  radical (38), is not considered to be important in urban areas in which NO levels remain high (see Figure 5c).



**Figure 6.** Comparison of peroxyacetyl nitrate (PAN) and acetaldehyde ( $\text{CH}_3\text{CHO}$ ) data from PUC/RJ site, 9 July 1985; dotted line indicates approximate limit of detection of analytical techniques.

#### Diurnal Trends in PAN and Aldehyde Levels—Predicted versus Observed.

Comparison of diurnal variation of PAN and  $\text{CH}_3\text{CHO}$  concentrations at the Vila Isabel site on 2 and 4 July indicates that high levels of the latter shortly after dawn are followed by an early increase in PAN approximately 2 h later, in addition to the afternoon maximum in PAN on both days. The  $\text{CH}_3\text{CHO}$  levels appear to be dominated by direct emissions coupled with dilution accompanying the a.m. breakup of the surface boundary layer; this daytime variation is well mimicked in the model simulations (Figure 5c). The simulation for PAN shows the a.m. increase, but only a single concentration maximum at about the time of the observed maximum; however, only a single concentration and a single  $\text{CH}_3\text{CHO}$  emission rate were used in the simulation. Actual emission patterns would show emission rate maxima during the a.m. and p.m. rush hours if the dominance of vehicular sources of  $\text{CH}_3\text{CHO}$  is assumed.

Comparison of aldehyde and PAN data at PUC/RJ on 9 July (Figure 6) shows a rough correlation of observed concentrations if a delay time of 1–2 h between  $\text{CH}_3\text{CHO}$  emission and PAN formation is assumed. Unfortunately, no aldehyde data is available for 10 July when much higher PAN levels were observed and when transport and sea-breeze circulation of an aged urban plume from downtown Rio is suggested by the meteorological data.

**PAN-PPN Correlation.** The correlation between PAN and PPN concentrations during those periods in which PPN was present above the limit of detection is really quite good. With one outlier removed, the regression equation for 44 pairs for determinations is as follows:  $[\text{PPN}] = 0.204[\text{PAN}] - 0.046 \text{ ppbv}$  ( $r^2 = 0.89$ ). The strong correlation of PPN with PAN and the existence of PPN maximum levels of  $>1$  ppbv suggest that substantial propionaldehyde emissions (on the order of 10% of  $\text{CH}_3\text{CHO}$ ) are occurring. Information on 1-propanol content of hydrated ethanol fuel (300–400 ppm v/v; D.



Quast, Copersucar SP, personal communication, 1988) suggests that direct emissions of propionaldehyde from ethanol-fueled vehicles may not be the source. The correlation between PAN and PPN only indicates similarity in source distribution, so other vehicular sources may be implicated.

**Prediction of PAN Formation, Concentrations Downwind of Large NO Sources.** A preliminary estimate of PAN levels downwind in the Rio urban plume on subsequent days can be made by the model described above. The assumptions are as follows: no nighttime chemistry, no emissions (except for 0.5 ppbv/h of butene) after day 1, and morning dilution due to mixing layer breakup each day. The results for PAN indicate maximum concentrations of 3.5 ppbv on day 2, and ca. 2.5 ppbv maximum through day 5. HO<sub>x</sub> chemistry forming, e.g., H<sub>2</sub>O<sub>2</sub> and peracetic acid, is suppressed by the large NO<sub>x</sub> levels until day 5. These results indicate that exposure of suburban Rio environs to ppb levels of PAN during stagnant weather conditions as a result of urban pollutant emissions is quite likely. These predictions are very sensitive to the addition of small concentrations of reactive hydrocarbons (biogenic or anthropogenic) to air masses downwind of the major NO<sub>x</sub> sources. The presence of substantial levels of contemporary organic carbon (based on <sup>14</sup>C measurements) in urban Rio aerosols (23, 29) suggests that gaseous biogenic emissions may also be significant and that further measurements of secondary pollutants downwind of Rio are warranted.

**Consistency of Predicted and Observed PAN and HNO<sub>3</sub> Concentrations.** An important comparison to be made is the predicted and observed concentrations of nitric acid and PAN. This is true because nitric acid is formed principally by the direct reaction of NO<sub>2</sub> and OH radicals (reaction 8), but PAN is formed by the secondary reaction of NO<sub>2</sub> with acetylperoxy radicals, the latter formed (rate-limiting step) by the competitive attack of OH on CH<sub>3</sub>CHO (reaction 5). The observation is that PAN formation rates sufficient to produce the concentrations observed at the Vila Isabel site are predicted (Figures 3 and 5c) but that observed daytime levels of HNO<sub>3</sub> are lower than predicted (Figures 2 and 5b). Loss of HNO<sub>3</sub> to the surface or uptake into aerosol particles was suggested above to explain these differences in "model performance". PAN dry deposition rates may be somewhat lower than those for HNO<sub>3</sub>, depending on the surface type and the presence of moisture. The diurnal data in Figure 2 do suggest that conversion of HNO<sub>3</sub> produced in daylight to aerosol nitrate at night is a major loss mechanism which maintains HNO<sub>3</sub> concentrations lower relative to model predictions than PAN.

**Suggestions for Future Studies.** This study was a preliminary one to investigate whether the differences in emission patterns accompanying the use of ethanol-containing fuels in Rio de Janeiro would result in enhanced PAN formation rates and other smog photochemistry-related changes within the urban airshed. The study was exploratory and, thus, far from complete. Nevertheless, the implications with respect to use of ethanol and ethanol-containing fuels are clear: acetaldehyde levels and PAN formation rates will be elevated relative to areas with gasoline-fueled fleets in the absence of catalytic controls. Use of methanol-containing gasohol, as proposed for areas of the western U.S., will not increase PAN formation but may substantially increase radical precursors to atmospheric oxidants.

Some of the limitations which should be addressed were the absence of measurements of key species, in particular,

NO and NO<sub>x</sub>, ozone, reactive hydrocarbons, propionaldehyde, and hydrogen peroxide. The studies should be extended geographically to include suburban and adjacent rural areas, whereby "next day" photochemistry within the urban plume but away from intense NO<sub>x</sub> sources could be examined.

#### Summary

The preliminary study reported in this paper demonstrates that changes in gaseous emission patterns accompanying the use of ethanol and ethanol-containing fuels in Rio de Janeiro, Brazil, result in predictable changes in formation rates and concentrations of secondary smog photooxidation products. In particular, increased acetaldehyde emissions from ethanol-fueled vehicles lead to an apparent increase in the formation rate for peroxyacetyl nitrate, even in the vicinity of large sources of NO and other nitrogen oxides. Model estimates of PAN formation and concentrations are in good agreement with observations at a polluted urban site; observed nitric acid levels are lower than predicted due in part to uptake onto aerosols and other loss mechanisms not included in the model.

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## In Situ Comparison of a Multistage Series Cyclone System and a Cascade Impactor for In-Stack Dust Sampling

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■ Dust samples were collected in the flue gas duct of a coal-fired power unit, with either an in-stack cascade impactor or a multistage cyclone system. A comparison of both sampling devices is made by consideration of the mass-size distributions obtained as well as some practical aspects. The cyclone system seems to offer a valid alternative to the cascade impactor, but the suitability of each sampler depends on the particular sampling conditions involved and on the kind of information required.

### Introduction

Although cyclone systems are widely used as dust collecting devices for industrial gas cleaning, they have been applied less frequently for dust emission sampling than cascade impactors. One reason for this might be the fact that the impaction theory is relatively straightforward and well established (1, 2). On the other hand, no general cyclone theory exists. Consequently several rather complex mathematical models are dealing with predicting cyclone efficiency as a function of cyclone dimensions, or alternatively empirical equations are established (3, 4).

In this paper a number of dust samples were taken in the flue gas stream of a coal-fired electric power generating unit, by either the Andersen-2000 Mark II in-stack cascade impactor or a five-stage series cyclone system developed at Southern Research Institute (Birmingham, AL) in association with the EPA and manufactured by Flow Sensor. The samplers are compared on a mainly practical basis, relying on the mass-size distributions obtained as well as on experience gained during sample treatment.

### Experimental Section

**Sampling Conditions.** Samples were taken after the electrostatic precipitator in the rectangular flue gas duct of a pulverized coal-fed unit, operating at full load [130 MWe (megawatt electrical power output)], burning American coal containing 1.7% sulfur and with an ash content of 17%. Three sets of two samples were collected: the impactor sample was taken first (6-25 min), immediately followed by the cyclone sample (120-240 min) at the same sampling point. For each set a different sampling location was selected.

**Sampling Train.** The sampling train is schematically shown in Figure 1 and is in accordance with the specifications of the Belgian Institute for Normalization (5). A quartz fiber disk (Whatman QM-A) was used as the backup filter for the Andersen impactor, while a glass fiber filter thimble (Schleicher & Schüll) was used instead of the conventional flat filter to avoid clogging in the case of the multistage cyclone.

**Sample Treatment.** All tare weights and sample weights were determined under the same circumstances. For the impactor samples the stainless steel impaction plates and the backup filter were heated to 150 °C (about the flue gas temperature) and allowed to cool in a desiccator prior to weighing.

After sampling, the external surfaces of the multistage cyclone sampler were carefully cleaned. Subsequently the sampler was dismantled, and the deposits were gently brushed into tared beakers. All the internal surfaces, including the connecting tubes, were rinsed with petroleum ether (30°-50°, Carlo Erba, RPE). The rinsing liquid from