Methods for gas-phase measurements of ozone, ozone precursors and aerosol precursors

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Abstract

The techniques currently available to measure the ambient atmospheric concentrations of O_3, O_3-precursors (including the odd-hydrogen free radicals), the oxidation products of these compounds, and gas-phase aerosol precursors are outlined below. This critical review focuses on the recent developments, and, in particular those developments that have been reported in the published literature since 1990. In general, the techniques are described in terms of the results of formal and informal comparisons of the techniques in measuring the compounds of interest in the ambient atmosphere. The article concludes with a brief discussion of calibration methods and standards and tests that should be routinely performed when measurements in ambient atmosphere are undertaken. Published by Elsevier Science Ltd.

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1. Introduction

1.1. The importance of the determination of measurement capability and uncertainty

The ability to make unequivocal ambient measurements of ozone (O_3), ozone and aerosol precursors, oxidants, important co-pollutants and key tracer compounds is an essential first step in understanding the processes that control tropospheric O_3 and aerosol concentrations, and in assessing the progress of management of these two pollutants. With reliable instruments and techniques that have trustworthy estimates of their measurement uncertainties: (i) observations and theory can be compared meaningfully, (ii) results from separate field studies can be merged reliably, (iii) spatial gradients derived from separate data sets can be characterized credibly, and (iv) time series from different organizations can be used to establish longer trend records.

1.2. The role of formal and informal intercomparisons

Intercomparison of instruments used to measure chemically labile atmospheric species has been an area of active investigation for many years. Such instrument validation is in response to the need for reliable measurements that could be used to understand and monitor acid deposition, urban and regional air quality, global climate change, and stratospheric O_3 depletion. As new techniques were devised, they were field tested to demonstrate sensitivity, specificity, accuracy and precision and to determine the necessary housekeeping procedures (calibration, zeroing, routine maintenance). This progression of instrument validation has been described more fully elsewhere (Albritton et al., 1990; Seinfeld et al., 1991; Fehsenfeld, 1995). Newly developed instruments combined with a strong laboratory program of accuracy, precision and interference testing have been called upon to make important measurements of great value. However, such measurements should be regarded as preliminary until the instrument is more fully validated through informal and formal intercomparisons. In the discussion below, capability and reliability of instrumentation are based, where

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possible, on the quantitative results from these intercomparisons.

However, no single intercomparison can be considered definitive proof of suitability, capability or reliability when measurement circumstances change significantly. Each time the sampling configuration is altered to fit the requirements of a new platform or is adapted to operation in a location with substantially different chemical, meteorological, or dynamical conditions than previously encountered, the validation must be reviewed.

1.3. Aim of the paper

The instruments and techniques available for the measurement of atmospheric concentrations of O_3, O_3 and aerosol precursors, and related trace gases, the basic operating principles of these devices, and the highlights of the tests done thus far to determine instrument reliability are summarized below. Because these devices have been the subject of many periodic reviews, this discussion will attempt to focus on significant developments in instrument capability that have occurred during the past decade and only briefly mention earlier developments. Table 1 defines acronyms for instrumental techniques that are used in multiple sections of the paper; others are defined in the section where they appear. Finally, the issues regarding instrument calibration and data verification are briefly addressed.

2. Oxidant precursors

2.1. Nitrogen oxides and their oxidation products

The nitrogen oxides enter the troposphere primarily as nitric oxide (NO) and nitrogen dioxide (NO_2). In the presence of sunlight there is rapid interconversion of NO

Table 1
Acronyms for some of the techniques that have wide applicability in ambient atmospheric measurements

CIMS	Chemical Ionization Mass Spectrometry
DIAL	Differential Absorption LIDAR
DOAS	Differential Optical Absorption Spectroscopy
FTIR	Fourier transform infra-red Spectrometry
GC-ECD	Gas Chromatography with Electron Capture Detection
GC-FID	Gas Chromatography with Flame Ionization Detection
LIDAR	Light Detection and Ranging
LIF	Laser Induced Fluorescence
MIESR	Matrix Isolation with Electron Spin Resonance Detection
TDLAS	Tunable Diode Laser Absorption Spectrometry

and NO_2. One of the important byproducts of this interconversion is the photochemical production of O_3 in the troposphere. In addition, the nitrogen oxides, NO_x ($NO + NO_2$), are converted to a variety of other organic and inorganic nitrates. These are the compounds that make up the total reactive oxidized nitrogen family, NO_y (NO_x + organic nitrates + inorganic nitrates).

2.1.1. Nitric oxide (NO)

The reliability of two techniques to measure NO has been well established. The chemiluminescence technique (Fontjin et al., 1970; Ridley and Howlett, 1974) is based on the chemical reaction of the ambient NO with added O_3 and the detection of radiation from the excited NO_2 product, which is proportional to the concentration of the NO in the sampled air. The LIF technique (Bradshaw et al., 1985) relies on the absorption of radiation by NO in the sampled air and the subsequent re-radiation at different wavelengths. Instruments using the chemiluminescence and the LIF techniques were compared in ground based and airborne studies (Gregory et al., 1990c; Hoell et al., 1985,1987b). The measurements agreed within 30% for the concentration range of 5 to 200 parts per trillion by volume (pptv) of NO.

In intercomparisons of NO_2 and NO_y measurement techniques (Fehsenfeld et al., 1987; Williams et al., 1998) the chemiluminescent detection of NO has been extensively used and has proven itself as a reliable method (see below for details of NO_2 and NO_y measurement techniques). Although the instruments in these intercomparisons used the same NO detection method, the differences in instrument configuration lends additional confidence in the ability of the chemiluminescence technique to measure NO.

Laboratory tests of TDLAS systems for the measurement of NO have been reported (Hastie et al., 1983; Fried et al., 1993), but have not been applied to ambient measurements. It is likely that this application is limited by inadequate detection limits.

In resume, these results strongly indicate that NO can be measured reliably under most field conditions by either chemiluminescence or LIF. It should be noted that reasonably high quality chemiluminescence instruments are available commercially.

2.1.2. Nitrogen dioxide (NO_2)

A wide variety of techniques have been applied to the measurement of NO_2. In many air quality studies, NO_2 measurements have been based on surface conversion of NO_2 to NO and the subsequent detection of NO using the well characterized chemiluminescence technique described in the preceding section. The conversion surfaces have included heated catalytic metal surfaces and those coated with ferrous sulfate or other compounds. Though they are simple and rugged, these surface conversion techniques have proven to be relatively nonspecific for

NO_2. Since these surfaces can convert other nitrate compounds to NO, these techniques tend to overestimate NO_2 (Fehsenfeld et al., 1987; Gregory et al., 1990c). By contrast, photolytic NO_2 to NO conversion by a broadband arc lamp (Kley and McFarland, 1980) or a narrowband eximer laser (Sandholm et al., 1990) has been shown to provide a more specific conversion technique (see discussion below), albeit less simple. The arc lamp and eximer laser photolysis systems were followed by chemiluminescence and LIF detection of the product NO, respectively. Parrish et al. (1990) discuss in detail the field performance and possible interferences in the arc lamp photolysis system.

Three other in situ techniques for the measurement of NO_2 are TDLAS, luminol chemiluminescence, and cryogenic trapping on a cold finger (matrix isolation) followed by electron spin resonance (MIESR) (Mihelcic et al., 1985). The TDLAS (Schiff et al., 1987; Walega et al., 1984) instrument measures the absorption of laser generated infrared radiation by the NO_2 molecules in an air sample within the multi-pass cell of the laser spectrometer. The luminol instrument (Schiff et al., 1987) detects NO_2 by measuring the chemiluminescence produced by the oxidation of the luminol by NO_2. The TDLAS technique provides a specific spectroscopic method to measure NO_2, the luminol technique provides a sensitive, portable method with low power requirements, and the MIESR technique provides relatively precise, average measurements for approximately 30 min periods.

A ground based intercomparison (Fehsenfeld et al., 1990) tested the photolysis/chemiluminescence, TDLAS and luminol techniques. The TDLAS technique, while having a somewhat higher detection limit than the photolysis/chemiluminescence technique, appears capable of reliable NO_2 measurements. However, the data retrieval algorithms for the TDLAS are complicated and can compromise the veracity of the measurements when the absorption by the NO_2 in the sampled air nears the detection limit of the system. Results from the luminol technique indicated that peroxyacetyl nitrate (PAN) and O_3 constituted interferences in the NO_2 measurement. Presently, stratagems are being developed to remove or separate these interferences from the ambient air prior to sampling into the luminol detector. However, the effectiveness of these stratagems have not been verified by a field intercomparison.

An airborne intercomparison of the TDLAS, photolysis/LIF, and photolysis/chemiluminescence techniques was conducted (Gregory et al., 1990c). The results from this intercomparison indicated a general level of agreement (on the order of 30–40%) in ambient air for $NO_2 > 100$ pptv. For $NO_2 < 50$ pptv, the TDLAS overestimated the NO_2 mixing ratio, presumably due to data reduction uncertainties. At these low levels, the agreement between photolysis/LIF and photolysis/chemiluminescence measurements was within 20 pptv

with an equal tendency for one to be higher or lower than the other. This 20 pptv agreement is within the stated uncertainties of the two techniques at $NO_2 < 50$ pptv.

Zenker et al. (1998) intercompared photolysis/chemiluminescence, TDLAS and MIESR measurements for 50 pptv $< NO_2 < 600$ pptv at the Izaña surface site in the Canary Islands. Within relatively large uncertainties (30–50%), the correlations between the three techniques agreed with unity and there was no evidence for any significant offset for any instrument.

Sickles et al. (1990) have compared 24 h average NO_2 measurements from TDLAS, two luminol instruments and a transition flow reactor (a filter collection technique) at a semi-urban site for 13 days. One of the luminol instruments and the transition flow reactor agreed with the reference TDLAS system to about 10% with good correlation ($r \geqslant 0.94$). The larger differences found with the other luminol system were attributed to the electronic temperature compensation of that instrument.

Two informal intercomparisons have been reported for DOAS measurements of NO_2 with chemiluminescence instruments. Harder et al. (1997c) compared the photolysis/chemiluminescence technique with DOAS over a 10 km path in a rural area. Although the comparison was difficult due to the large spatial and temporal inhomogeneity of the NO_2 levels, data from the period most amenable to analysis suggested agreement within 10% at NO_2 levels > 300 pptv. Stevens et al. (1993) compared a surface conversion/chemiluminescence instrument with DOAS in an urban area. For NO_2 levels up to 50 parts per billion (ppbv), good correlation ($r^2 = 0.93$) between the techniques was found, with the DOAS results systematically higher by 14% plus a positive 2.65 ppbv offset. Some of the systematic difference found in this study was also attributed to spatial and temporal inhomogeneities.

Finally, as discussed in the peroxy radical Section 3.2.2 below, the measured NO_2/NO ratios should be consistent with the levels of the peroxy radicals. Several studies have shown such agreement (within rather large uncertainties) for measured (Cantrell et al., 1992,1997,1996) and modeled (Ridley et al., 1992b; Frost et al., 1998) peroxy radical levels. Although such comparisons are certainly not definitive, they do lend further credence to the NO and NO_2 measurements.

In summary, three in situ techniques (photolysis/LIF, photolysis/chemiluminescence, TDLAS) have been successfully subjected to several intercomparisons. Properly used, the photolysis/LIF and the photolysis/chemiluminescence techniques are capable of NO_2 measurement to levels well below 100 pptv, with no significant artifact or interference. These techniques should therefore be capable of measuring the NO_2 levels in most locations and from most platforms. The TDLAS technique is less sensitive, but with proper attention to data retrieval at low levels, is also accurate. The luminol chemiluminescence

instruments are sensitive, compact and easily operated, but the elimination of interferences identified in early intercomparisons has not yet been demonstrated in field intercomparisons.

The successful measurement of NO_2 by any of the in situ methods must correct for inlet effects associated with the rapid interconversion of NO and NO_2 by through-the-inlet calibration of the system with NO and NO_2. Finally, although it has acquitted itself well in intercomparisons, the photolysis/chemiluminescence technique requires considerable attention to detail. The combined chemiluminescence of NO present in the ambient sample as well as the photolysis-generated NO from the sampled NO_2 are detected. Because the conversion efficiency of NO_2 to NO by photolysis is less than unity, a separate, accurate, parallel determination of NO must be made if NO_2 (or indeed NO_x) is to be measured accurately.

2.1.3. Pan ($CH_3C(O)OONO_2$) and other peroxy acyl nitrates

The presently accepted method for the determination of peroxyacetyl nitrate, or PAN ($CH_3C(O)OONO_2$),[1] is GC-ECD. Two instruments, both employing cryogenically enriched sampling with separation on packed GC columns (Ridley et al., 1990; Singh and Salas, 1983), have been compared in the remote maritime free troposphere (Gregory et al., 1990b). The intercomparison indicated that for PAN < 100 pptv, the two instruments differed on average by 17 pptv with a 95% confidence interval of ± 9 pptv. At mixing ratios between 100 and 300 pptv, the difference was on the order of $25\% \pm 6\%$. A linear regression comparing all data below 300 pptv from the two instruments resulted in a slope of 1.34 ± 0.12 and an intercept of 4 ± 12 pptv. Although one instrument was consistently higher relative to the other for ambient measurements, the level of agreement was usually within the stated accuracy and precision of the two instruments. These results are reassuring; however, their significance is reduced because of the similarity in the two instruments. Since this intercomparison, the introduction of capillary gas chromatography (Helmig et al., 1989; Roberts et al., 1989; Roumelis and Glavas, 1989) has increased the sensitivity of the GC-ECD technique, and reduced the need for cryogenically enriched sampling.

Chromatographic techniques combined with luminol chemiluminescence detection have been proposed for the measurement of PAN (Blanchard et al., 1990; Gaffney et al., 1998). The method was informally compared over a twenty-four day period with two GC-ECD systems similar to those described above (Blanchard et al., 1990).

The reported agreement between the two GC-ECD techniques was good (slope $= 1.14$; $r^2 = 0.99$). If the data collected over three days during the comparison were neglected, the agreement between the GC/luminol and the GC-ECD was excellent (slope $= 0.98$; $r^2 = 0.90$). However, the method employing the luminol detector was judged to have a detection limit of approximately 25 pptv, which is insufficient for quantifying the trace levels of PAN often encountered in the atmosphere.

Other peroxy acyl nitrates of interest include peroxypropionyl nitrate (PPN, $CH_3CH_2C(O)OONO_2$) and peroxymethacrylyl nitrate (M-PAN, $CH_2C(CH_3)C(O)OONO_2$). These compounds, like PAN, have been measured with the GC-ECD. To date, there have been no comparisons that address the reliability and accuracy of this method for the detection of these compounds. In addition, these species have not always been separately calibrated; it is often assumed that because the chemical and physical properties of these compounds are so similar to those of PAN, these compounds have instrumental responses identical to PAN. However, laboratory tests indicate instrument responses can differ by as much as 40% for the three peroxyacyl nitrates mentioned above.

Two key concerns of any chromatographic system used to measure peroxy acyl nitrates are the methods that are used to calibrate and (in some systems) to pre-concentrate the sample prior to injection into the chromatographic column. Since these peroxy acyl nitrates are chemically and thermally unstable, care must be exercised in preparing and handling these compounds for calibration. In this regard the calibration gases should be introduced through the inlet to account for losses that could occur as these compounds pass through the system. The calibration gas can be added to a sample flow of zero air or, preferably, ambient air that has been heated to decompose ambient peroxy acyl nitrates, but is otherwise unmodified. Accepted methods for pre-concentration and calibration are described in the literature (Bertman et al., 1993; Buhr et al., 1990; Gaffney et al., 1984; Ridley et al., 1990).

2.1.4. Other organic nitrates ($RONO_2$)

A variety of alkyl nitrates (Atkinson et al., 1984) have been detected in air samples. These are thought to be present primarily as products of the photochemical reactions of non-methane hydrocarbons with NO_x. The measurements also have been done with direct injection into a GC/ECD (Buhr et al., 1990) or by collection on charcoal traps (Atlas and Schauffler, 1991), Tenax (Bertman et al., 1995; Roberts et al., 1996) or cryogenically cooled glass beads (Flocke et al., 1991) followed immediately by GC/ECD analysis. The samples collected on charcoal and Tenax are found to be reasonably stable, so atmospheric samples can be stored on these traps for later analysis (Atlas and Schauffler, 1991). No intercomparison between these methods has been reported.

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[1] From the standpoint of chemical structure peroxy acetyl nitrate (PAN) can be more correctly described as peroxyacetic nitric anhydride.

Consideration of the tropospheric chemistry of the wide variety of ambient hydrocarbons and other volatile organic compounds suggests that a wide variety of additional, multifunctional organic nitrates should be present at low levels in the troposphere. Their presence often is inferred from the imbalance between measured NO_y (see Section 2.1.7 below) and the sum of the independently measured NO_y components (see, e.g., (Parrish and Buhr, 1993)). No existing techniques have successfully measured these species in the atmosphere, but their development is underway (Muthuramu et al., 1993). There is a potential for these expected species to be readily incorporated into aerosols, which may lead to potential sampling artifacts caused by disturbance of the ambient gas–aerosol equilibrium during sampling and measurement.

2.1.5. Nitrate radical (NO_3)

Two methods have been used to measure NO_3 in the atmosphere: DOAS and MIESR. The DOAS technique relies on the measured absorption occurring in the NO_3 absorption bands between 600 and 700 nm. Total and height resolved NO_3 abundances have been measured using the moon and near-dawn sunlight as light sources (Noxon et al., 1978; Solomon et al., 1989a,b,1987). Measurements of NO_3 have also been made in the troposphere with the DOAS technique using lamps and a horizontal long-path (Noxon et al., 1980; Platt and Perner, 1980; Platt et al., 1979,1984). The MIESR technique (Mihelcic et al., 1978) relies on the cryogenic trapping of NO_3 and peroxy free radicals (HO_2 and RO_2) in a water matrix followed by the detection of the free radical using electron spin resonance. Problems with interferences in the ESR spectra have been overcome by using D_2O instead of H_2O as the isolation matrix. This substitution has improved the signal to noise ratio and spectral resolution, allowing the identification of different free radical species during field measurements (Mihelcic et al., 1985,1990). No attempt has yet been made to compare NO_3 measurements made using these techniques.

2.1.6. Nitric acid (HNO_3)

A comparison (Hering et al., 1988) carried out at an urban–suburban site involved six HNO_3 measurement methods: (1) filter pack, (2) denuder difference, (3) annular denuder, (4) transition flow reactor, (5) TDLAS, and (6) FTIR. The reported HNO_3 concentrations varied among methods by more than a factor of 2. These differences were substantially larger than the estimated precision of these instruments. Tests indicated that artifacts or interferences existed for some of the sampling methods that were associated with either the field sampling components (e.g., inlet/lines), operating procedures, detector specificity, or alteration during sampling in the physical or chemical makeup of the ambient air, such as shifts in the gas- and solid-aqueous-phase equilibrium of HNO_3,

ammonia, and ammonium nitrates. Further studies have given additional information regarding the performance of the annular denuder systems (Vossler et al., 1988) and comparison between the annular denuder and filter pack methods (Dasch et al., 1989).

Very recently, an informal intercomparison of gas-phase HNO_3 measuring techniques was carried out that involved two new CIMS systems along with a filter pack (Fehsenfeld et al., 1998). The two CIMS techniques (Huey et al., 1998; Mauldin et al., 1998) provide continuous, fast-response (> 1 Hz), molecule-specific measurement of HNO_3 with detection limits of approximately 10 pptv for a 1 s measurement. Although both systems were flow reactors of significantly different design, in each system the gas-phase HNO_3 detection relied on the equilibrium association of HNO_3 with the reagent ion of choice, SiF_5^- (Huey et al., 1998) or HSO_4^- (Mauldin et al., 1998). In each system the HNO_3 concentration was deduced from the ratio of the reagent ion signal to the signal of the reagent ion clustered to HNO_3. Both systems were calibrated by the standard addition of HNO_3 though the inlet.

Throughout the study the two CIMS techniques were in general agreement as shown in Fig. 1. In contrast, under certain conditions the gas-phase concentration of HNO_3 measured by the filter pack gave values that were somewhat higher. An analysis of these results suggested that the HNO_3 collected by the nylon filter in the filter pack suffered an interference associated with the volatilization of ammonium nitrate containing aerosols that were collected on the Teflon prefilter. These findings substantiate the concerns about the filter pack technique (Dasch et al., 1989), and indicate that powerful new tools are becoming available for the measurement of HNO_3.

The verification of HNO_3 measurement techniques aboard aircraft has been limited. One aircraft study compared three different measurement techniques in the sub-ppbv range: nylon filter collection, tungstic oxide denuder, and TDLAS (Gregory et al., 1990a). In general, measurements made by the filter collection system were 10–20% higher than those made by the denuder, with no correlation observed between the filter and denuder instruments for $HNO_3 < 150$ pptv; this agreement was well within the accuracy and precision estimated for the two techniques. The comparison of the denuder and TDLAS techniques indicated that the TDLAS measurements were consistently higher – for $HNO_3 > 300$ pptv, by a factor of approximately two. It was concluded that there was substantial disagreement among the three techniques, even at mixing ratios well above their respective detection limits.

Even with the advent of new detectors for HNO_3, the inlets used to transfer ambient HNO_3 into the detectors remains a critical issue, especially when HNO_3 is measured from an aircraft. In the interpretation of these measurements, the possibilities of errors associated with
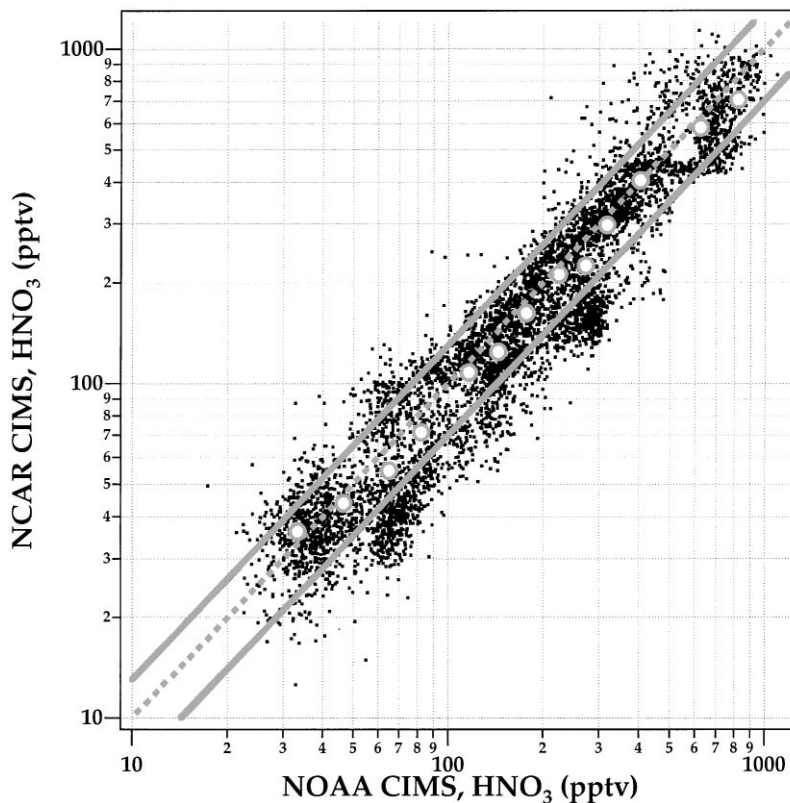
Fig. 1. A comparison of all the simultaneous HNO_3 measurements from the CIMS instruments developed by the National Center for Atmospheric Research (NCAR CIMS) and the National Oceanic and Atmospheric Administration (NOAA CIMS) (Fehsenfeld et al., 1998). The data are 6216 20 s averages. The open symbols indicate averages for 13 equal fractions of the 20 s averages sorted by increasing HNO_3 as measured by the NOAA CIMS. The dashed line indicates the 1:1 relation and the solid lines indicate the 1 : 1 relationship $\pm 30\%$.

sampling must be considered. Zahniser et al. (1995) report a TDLAS system for the measurement of HNO_3 that is designed for rapid equilibration with ambient air, and describe some preliminary results regarding its performance.

2.1.7. Nitrous acid (HONO)

Two classes of instruments have been utilized to measure HONO: optical analysis and surface collection followed by ion chromatographic analysis. The optical technique that has been principally applied is DOAS (Platt and Perner, 1980; Pitts et al., 1984). A second optical technique, UV-photofragment/laser-induced fluorescence, has been developed (Rodgers and Davis, 1989), but applied only in a limited demonstration campaign. The surface collection techniques include circular (Sjodin, 1988) and annular (Harrison and Kitto, 1994) denuders with Na_2CO_3 coatings, a parallel plate denuder (Simon and Dasgupta, 1995) and a diffusion scrubber (Vecera and Dasgupta, 1991).

The surface collection techniques have widely recognized artifacts from NO_2, SO_2, PAN and perhaps other atmospheric species. Researchers attempt to account for these artifacts by various methods including the use of sequential identical collectors or preceding denuders to remove interferants (Febo et al., 1993). However, results often show relatively high (several tenths of a ppbv or higher) daytime levels of HONO (Vecera and Dasgupta, 1991; Staffelbach et al., 1997). Since HONO is rapidly photolyzed in the daytime, such high levels cannot be explained by the chemical mechanisms that have been suggested for the formation of HONO in the troposphere. Consequently these high daytime levels must be viewed with skepticism, especially since the heterogeneous reaction of NO_2 on wet surfaces is one of the major mechanisms proposed for the formation of HONO (Notholt et al., 1992), and the surface collection methods use such surfaces as the active interface between the instrument and the atmosphere. Other studies report only very low daytime levels (Kitto and Harrison, 1992).

Two informal intercomparisons between DOAS and surface collection measurement techniques have been reported. Each concludes that there was good correlation with near unity slopes between the compared techniques, but there were significant systematic offsets as indicated by non-zero intercepts. However, these results cannot resolve the veracity of the reported high daytime values, since one study found the surface collection technique (compared to the DOAS result) to be about 1.6 ppbv high (Appel et al., 1990), while the other found it to be about 0.7 ppbv low (Febo et al., 1996). These inconsistencies and uncertainties emphasize the need for a formal intercomparison of HONO measurement techniques involving both optical techniques (if possible) and several surface collection techniques.

2.1.8. Total reactive nitrogen oxides (NO_y)

Our understanding of the reaction pathways can be aided by the measurement of the total abundance of reactive oxidized nitrogen compounds, NO_y (NO_x + PAN + HNO_3 + $\cdots$) as well as by the measurement of the individual species composing NO_y. For example, it is NO_y rather than NO_2 that is of primary interest in establishing the inflow/outflow regional budgets for tropospheric acid transport and deposition. However, the measurement of NO_y is fundamentally different from other measurements in that it detects the sum of many individual species.

Several NO_y measurement techniques have been proposed. In general, all rely on the reduction of NO_y to NO followed by the detection of NO. However, recently there have been increasing concerns regarding the suitability of this method due to possible interferences from reduced nitrogen species, such as HCN and NH_3, that are not associated with either NO_x or its oxidation products.

Early in the development of NO_y measurement techniques, ground based intercomparisons were undertaken to establish the reliability of the NO_y reduction methods. Fehsenfeld et al. (1987) report an intercomparison of instruments using the Au-catalyzed conversion of NO_y to NO in the presence of CO and the reduction of NO_y to NO on a heated molybdenum oxide surface. Except for a few cases, these instruments were found to give similar results in ambient air under conditions that varied from typical urban air to clean continental background air, with NO_y ranging between 0.4 and 100 ppbv.

Recently, an informal intercomparison of NO_y measurement techniques was conducted at a Nashville, Tennessee suburban site that was heavily influenced by urban pollution (Williams et al., 1998). The seven instruments tested relied on the reduction of NO_y to NO followed by chemiluminescence detection of NO and used either Au-catalyzed conversion of NO_y to NO in the presence of CO or H_2 (three instruments) or the reduction of NO_y to NO on a heated molybdenum oxide surface (four instruments). Spike tests were conducted with known levels of individual NO_y species (NO, NO_2, PAN, HNO_3) and one interfering compound (NH_3) added to the ambient air sample through the inlet. The mixing ratio of NO_y ranged from 2 ppbv to about 100 ppbv. Although the NO_y levels were highly variable, a good correlation was found among the different data sets. Some of the results are shown in Fig. 2. No significant differences were found in the effectiveness of NO_y conversion at these levels of NO_y using the Au-catalyzed conversion of NO_y to NO by CO or H_2 or the reduction of NO_y to NO on a heated molybdenum oxide surface. Within the estimated uncertainty limits, there was general agreement between the sum of the separately measured NO_y species and the NO_y measured by five of the seven techniques. The conversion of NH_3 to NO by these converters was nominally less than a few percent under typical operating conditions. These results indicate that these instruments can reliably measure NO_y in urban and suburban environments.

In contrast, the comparison of measurements of NO_y aboard aircraft has been much less successful and has lead to questions concerning the utility of the current technology for measurement of NO_y from aircraft platforms and/or measurements made in the remote troposphere (Crosley, 1996). This concern comes from the comparison of two NO_y instruments simultaneously operated aboard the NASA DC8. Although the inlet/converter designs were very different (Kondo et al., 1996; Sandholm et al., 1990) both measurements used Au-catalyzed converters with CO acting as the reducing agent. All measurements were made in the free troposphere. The results indicate that there were sometimes large differences, a factor of two or greater, in the measured NO_y concentrations with little systematic correlation between the two results.

Tests aimed at identifying the cause and possible management of these troubling problems have been reported (Bradshaw et al., 1998; Fahey, 1991; Fahey et al., 1985b, 1986; Kliner et al., 1997; Kondo et al., 1997). These tests specifically addressed: (1) the loss of reactive and/or polar constituents, such as HNO_3, in the inlet, (2) the incomplete reduction of some oxidized nitrogen species, such as HNO_3, by the converter, and (3) the oxidation to NO of reduced nitrogen species, such as HCN and NH_3, that are not part of the NO_y family by the converter or on heated sections of the inlet immediately preceding the converter. Although these tests suggested that the problems were manageable, they also indicated that frequent through-the-inlet additions of HNO_3 and HCN or NH_3 are required to verify proper operation. A recent inter-aircraft intercomparison (Weinheimer et al., 1998) indicated these problems can indeed be avoided; agreement within estimated systematic errors (± 20 pptv) was achieved at low (40–60 pptv) NO_y levels.
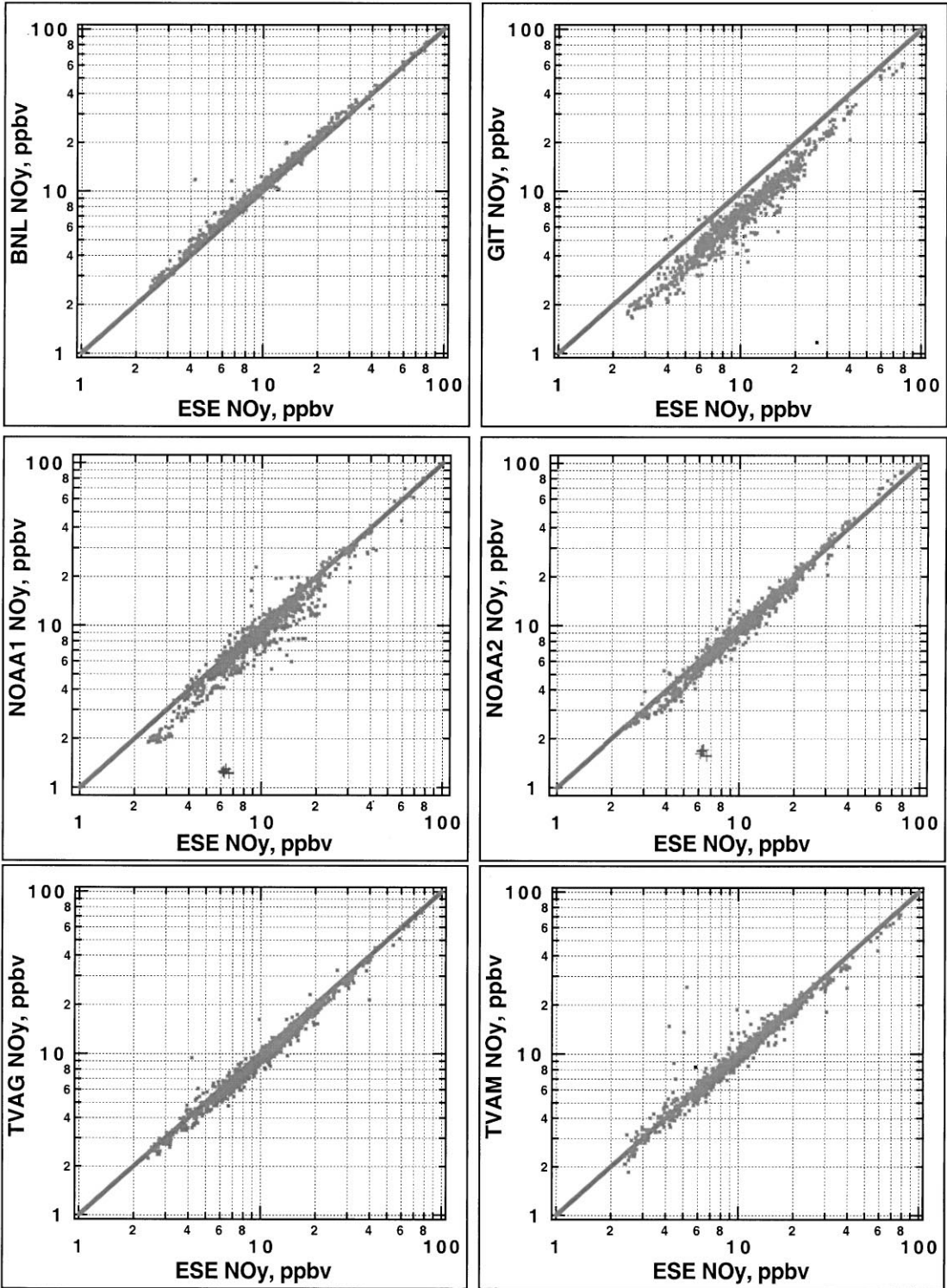
2.2. Carbon monoxide and volatile organic compounds (VOCs)

2.2.1. Carbon monoxide (CO)

Four techniques currently used for the measurement of background CO levels have been subjected to intercomparisons reported in the literature. These are: (1) grab samples followed by GC analysis (Rasmussen and Khalil, 1982), (2) gas filter correlation, non-dispersive infrared absorption spectroscopy (NDIR), and two different applications of laser infrared absorption, (3) differential absorption CO measurement (DACOM) (Sachse et al., 1987) and (4) TDLAS (Fried et al., 1991a,b). The NDIR (Dickerson and Delany, 1988) technique relies on the absorption of wide-band infrared light from a continuum source, while DACOM and TDLAS rely on the absorption of wavelength resolved, laser generated infrared radiation by CO within the multi-pass cell.

Two of these methods, GC and DACOM, were subjected to two rigorous intercomparisons (Hoell et al., 1985,1987a). The airborne intercomparison (Hoell et al., 1987a), involved the DACOM system and two GC systems. One of the GC systems collected a sample at ambient atmospheric pressure in a passivated container, while the other concentrated the sample cryogenically. For CO between 60 and 140 ppbv, the level of agreement observed for the measurements was well within the overall accuracy stated for each instrument. For all instruments, the correlation observed between measurements from respective pairs of instruments ranged from 0.85 to 0.98, with neither an interference nor a constant or proportional bias found among any of these instruments.

An informal intercomparison (Fried et al., 1991a,b) between the TDLAS and the NDIR techniques was carried out at a suburban location at the western edge of the Denver metropolitan area. The NDIR instrument was a modified (Parrish et al., 1994) commercial instrument (Thermo Electron Corp., Model 48). For CO between 100 ppbv and 1500 ppbv, the two instruments agreed within their combined uncertainty. On average, the NDIR technique was 6% higher than the TDLAS system, but there was no constant systematic offset.

A recently developed instrument based upon vacuum UV excited resonance fluorescence of CO (VUV) is capable of providing accurate and precise measurements of CO at high time resolution from an aircraft platform. Gerbig et al. (1996, 1998) report a precision (1σ) of 1.5 ppbv at a CO concentration of 100 ppbv for a 1 s averaging time. Holloway et al. (private communication, 1997) describe a similar instrument with improved wavelength selection that eliminates the water interference that required drying of the sample stream by Gerbig et al. (1996). This latter instrument has been intercompared informally with NDIR and TDLAS systems on aircraft flights; agreement on average to within 10% has been found.

In summary, there are presently a variety of instruments that are capable of measuring CO in the troposphere. The choice of instrument depends on the accuracy, precision and time resolution demanded of the measurements. Grab samples, collected by carefully designed and controlled procedures, returned to a central laboratory and analyzed by GC techniques with mercuric oxide reduction detection with carefully prepared and managed calibration standards (Novelli et al., 1991) have provided detailed information regarding latitudinal and seasonal variations of CO (Novelli et al., 1992,1998). The modified commercial NDIR instrument is capable of continuous, unattended measurements at 2 ppbv precision (1σ) for one-hour averaging times of the slowly varying ambient CO levels that are found in the rural and remote troposphere. The TDLAS, DACOM and VUV instruments can provide precise ($\leqslant 1$ ppbv), high frequency (≈ 1 Hz) measurements required for aircraft studies.

2.2.2. Non-methane hydrocarbons (NMHCs)

NMHC measurements are difficult due to the extreme complexity of the hydrocarbon mixtures that can be present in the atmosphere. Over 850 different hydrocarbons have been detected in the vapor over gasoline, and over 300 different hydrocarbons from a vehicle exhaust-polluted air sample have been identified. Natural hydrocarbons emitted by vegetation, which are estimated to account for approximately 50% of the NMHC emitted into the atmosphere in the United States, are mainly highly reactive olefinic compounds. Air samples obviously can contain a very great number of different hydrocarbons of natural and anthropogenic origin; the oxidation of each of these species creates a mixture containing many additional oxidation products as well. It is clear

Fig. 2. Simultaneous measurements of NO_y made by seven different systems during from the 1994 Nashville Middle Tennessee NO_y Measurement Intercomparison (Williams et al., 1998). The following converters were used: (1) BNL, Brookhaven National Laboratories, molybdenum oxide converter, (2) TVAG, Tennessee Valley Authority, gold catalyzed converter with CO, (3) TVAM, Tennessee Valley Authority, molybdenum oxide converter, (4) NOAA1, NOAA/Aeronomy Laboratory, gold catalyzed converter with CO, (5) NOAA2, NOAA/Aeronomy Laboratory, gold catalyzed converter with H_2, (6) ESE, Environmental Science and Engineering, molybdenum oxide converter and (7) GTI, Georgia Institute of Technology, molybdenum oxide converter. The individual instruments had different inlet and converter configurations but all used chemiluminescence detectors to measure the NO produced from the reduction of the NO_y species.

that the analysis of the NMHC and their oxidation products is a formidable task.

The standard approach for atmospheric hydrocarbon measurements is based upon GC separation of the individual hydrocarbons and the detection of each using a flame ionization detector (FID). Singh (1980) has summarized the general procedures employed in the analysis of ambient hydrocarbon samples. The gas chromatographic column and temperature programming of the column are selected to give the desired resolution of the compound peaks. Over the years, a great deal of progress has been made in achieving better separation and integrity of compounds passing through the chromatographic column by development of improved column packing compounds or coatings for open tubular columns. The FID is a nonspecific hydrocarbon detector with a response that is nearly linearly proportional to the number of carbon atoms in the hydrocarbon molecule, with a slightly diminished response for aromatic and olefinic carbon atoms (Ackman, 1968).

During recent years mass spectrometry (MS) has provided an increasingly attractive alterative to the FID. This technique offers increased sensitivity. Moreover, the MS can provide identification when compounds co-elute from the chromatographic column. This becomes an important issue when attempting to separate trace compounds contained in a complex matrix, but it is still problematic to positively identify co-eluting NMHCs of the same class, due to similar fragmentation patterns. Relieved of some of the burden of non-specificity associated with the FID, the MS can accommodate rapid response columns that do not fully separate peaks and, hence, provide much more frequent measurements. However, the obvious advantages of the MS method is accompanied by the increased complexity, weight, cost, and power consumption of this detection system.

When very low concentrations of hydrocarbons are measured it is necessary to pre-concentrate the hydrocarbons before injection into the column. This is done cryogenically or in a trapping matrix. Nitrogen, oxygen, argon and carbon dioxide, which compose the bulk of the air sample, pass through the trap, and subsequent heating evolves the hydrocarbon compounds to be measured. With pre-concentration, hydrocarbons with mixing ratios at or below 5 pptv have been measured with good precision by GC-FID systems. However, there are potential problems in using this method to measure reactive hydrocarbons at low concentrations. Large amounts of compounds, particularly high-carbon-number compounds, can be retained by the trapping medium. In addition, reactions between the hydrocarbons and oxidants, such as residual O_3 that survives the collection procedures, may destroy some hydrocarbons and produce other compounds not originally present (Goldan et al., 1995). Additional methods are required to reduce the oxidants to negligible levels before pre-concentration

without altering the hydrocarbons to be analyzed (Helmig, 1997).

Often measurements of NMHC in the field are done under circumstances that require maximum portability, low power consumption, and/or in an adverse environment for the operation of sensitive instruments. Consequently, many NMHC measurements are done by acquiring an air sample in a suitably prepared container and subsequently transferring this sample to laboratory GC-FID. Sample containers have been made from glass, treated metal, and special plastics. Often sampling procedures require that the containers are purged before the air sample is obtained and that the sample be stored in the container above atmospheric pressure. Although much has been done to ensure the integrity of the compounds of interest in these containers, many of the difficulties attendant to this approach are associated with the stability of the sample during collection, transport and storage before the analysis is completed. When samples of hydrocarbons are analyzed after storage for several days, substantial losses of the heavier hydrocarbons can be expected (Holdren et al., 1979). In addition, for reasons that are not understood, there is a tendency for the levels of light, unsaturated NMHCs such as ethyne, ethene, propene and butene to increase in samples collected in canisters on time scales from minutes (P.D. Goldan, private communication) to weeks (Singh et al., 1988). Finally, the results from the containers may depend upon the history of use and handling. Contamination due to sampling of particularly polluted air, or improper handling of the canisters may leave residues that can influence the determination of some or all NMHCs.

The Environmental Protection Agency has sponsored the development of automated GC systems to collect and analyze NMHCs (Oliver et al., 1996). These systems are widely deployed in the Photochemical Assessment Monitoring Station (PAMS) sites that states have been mandated to establish to measure ozone, its precursors and meteorological parameters in ozone non-attainment areas. The instrument is designed to automatically sample for about 1 h into adsorbent traps, remove ambient water, thermally desorb the NMHCs into a cryogenic trap for refocusing, and analyze them by GC/FID techniques. Large data sets are being accumulated by these PAMS sites. However, it is of critical concern that the technique has not been subjected to a formal field intercomparison. Internal consistency tests (see e.g. Parrish et al., 1998) of PAMS data sets suggests the presence of significant errors, including poor precision, systematic measurement errors, and unreported NMHCs that were expected to be present at levels significantly above the instrument detection limit. The application of some of these consistency tests to the PAMS data is given by Parrish (1996) and in Section 5.2. below.

New techniques are emerging for NMHC measurement. One based on the chemiluminescence reaction

between alkenes and O_3 has been developed to measure alkenes (Hills and Zimmerman, 1990; Guenther and Hills, 1998). Although the instrument was developed for the fast-response measurement of isoprene for eddy correlation flux studies, it has a significant response to a variety of other compounds including ethene, propene and reduced sulfur species (Guenther and Hills, 1998). In its current state of development, the instrument is capable of detecting isoprene with a signal to noise ratio of one for 140 pptv of isoprene using a 10 s signal integration.

The application of CIMS techniques to NMHC measurements is a developing area of great promise. Proton transfer from H_3O^+ can ionize most NMHCs, usually without fragmenting the parent ion; CIMS instrumentation using this technique can detect a wide variety of NMHCs with excellent time response (Hansel et al., 1995). The sensitivity and specificity of this approach is limited by the manifold of NMHCs with nearly the same mass. Improvements are promised by the development of ion chemistry specific to a more limited set of NMHCs; for example Leibrock and Huey (in preparation) report a CIMS technique specific for isoprene.

Optical techniques appear promising since they can provide a relatively unambiguous identification of the species present in the atmosphere. Measurements of the column densities of selected hydrocarbons have been made using FTIR and measured infrared absorption at frequencies characteristic of a few specific hydrocarbons. However, the generality and sensitivity of the technique are not sufficient at present to extend it to the whole spectrum of hydrocarbons. TDLAS systems have been applied to the detection of selected hydrocarbon species, but presently the technique does not have adequate sensitivity to offer a practical method for measurement of most atmospheric hydrocarbons at trace concentrations. DOAS techniques have been developed to the point that monocyclic aromatic hydrocarbons can be monitored with sup-ppbv sensitivity on minute time scales; these capabilities are adequate to provide useful measurements for urban areas (Volkamer et al., 1998).

Thus far, no formal intercomparison of NMHC measurement systems and sampling canisters has been completed. However, one such intercomparison is underway, the NO_n-Methane Hydrocarbon Intercomparison Experiment (NOMHICE), a support activity of the International Global Atmospheric Chemistry (IGAC) project. The intercomparison is managed by the National Center for Atmospheric Research (NCAR) and thirty-six laboratories have participated in the intercomparison. Participants received canisters containing aliquots of gas samples prepared by NIST or commercial gas suppliers. The analyses of all samples were independently verified by the preparer, NCAR, and in some cases EPA. The first three stages of this intercomparison have been analyzed

(Apel et al., 1994,1999); they reveal some of the problems mentioned above.

The first task of the intercomparison was aimed at checking the analytic methods of the participating laboratories and the accuracy of standards they used. The distributed samples contained a two component mixture of n-butane and benzene with mixing ratios in the ppbv range. The combined results reported by the participating laboratories gave an average deviation of 4.2% below the NIST/NCAR value with a standard deviation of 29%. The twelve laboratories that had results deviating by more than 20% from the accepted value for the measurement of either compound were informed and asked to redo their analysis.

The second task of the intercomparison was aimed at checking the techniques for the identification and quantification of a limited number of compounds. Aliquots of a sample containing 16 separate compounds were sent to the twenty-eight participating laboratories. Twelve of the laboratories did very well at quantifying the compounds they identified (ten laboratories of the twelve identified all sixteen compounds). For those twelve, the percent standard deviation compared to the NIST/NCAR values was 10% or less. However, seven of the laboratories were less successful, having a standard deviation of all the compounds they quantified 20% or greater compared with the NIST/NCAR value. For individual compounds the average of the twenty-eight laboratories usually did quite well in reproducing the expected mixing ratios of the compounds, with deviations generally less than ten percent. However, with certain compounds the scatter in the results was large. For example, in the case of propane the average composite determination was 4% less than the NIST/NCAR value with a standard deviation of 12%. In the case of isoprene, the average composite determination was 2% less than the NIST/NCAR value, but the standard deviation was 63%.

The third task expanded the tests of the second task to a greater range of species that more nearly represents those typically found in the atmosphere. Two different mixtures were prepared in humidified nitrogen; each included fifty-seven NMHCs: twenty-eight alkanes from ethane to undecane, sixteen alkenes from ethylene to hexene plus isoprene and α-pinene, acetylene, and ten aromatics. The reference concentrations were 1–30 ppbv as determined jointly by the NCAR and EPA laboratories that organized and conducted the exercise. These levels are higher than generally found in the troposphere, even in urban areas. Aliquots were sent to twenty-nine participating laboratories without information regarding composition or concentration. Thirty-three analyses were reported. They varied in range of hydrocarbons analyzed; laboratories were equipped either to measure only the light ($\leqslant C_6$), through the moderately heavy ($\leqslant C_{8 \text{ or } 9}$), or the full range of the NMHCs. Qualitatively, the analyses were generally successful; on average
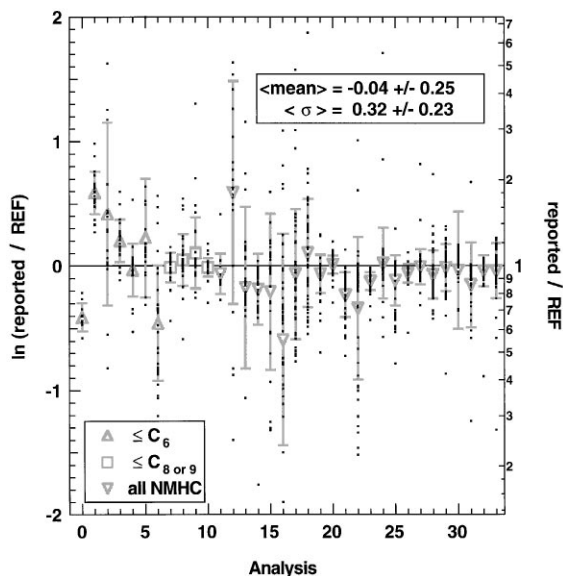
Fig. 3. Results from the blind analysis of aliquots containing a mixture of NMHCs in humidified nitrogen in the NOMHICE campaign (Apel et al., 1999). Twenty-nine laboratories reported thirty-three analyses of the fiftys-even NMHCs that were contained in the samples at levels of 1–30 ppbv. Each black dot indicates the result from a given analysis for a single NMHC ratioed to the reference concentration as determined jointly by NCAR and EPA laboratories. Each light symbol (coded according to the range of NMHCs analyzed) and error bar shows the geometric average and standard deviation of the ratios for all the compounds reported in the analysis. The average and standard deviation of the natural logs of all of the geometric means and standard deviations are indicated in the legend. The left ordinate gives the natural logarithm of the ratios, and the right ordinate gives the corresponding logarithmic scale of the ratios.

80% (median 86%) of the NMHCs within each laboratory's analysis range were identified and measured, although this fraction varied from 30 to 100%. The number of misidentified species (i.e. those reported, but not present) varied from 0 to 5 with a mean of 1.4 (median 1).

Fig. 3 summarizes the results of the thirty-three analyses, coded by symbol according to the range of NMHCs measured in each analysis. The logarithm of the ratio of each reported measurement to the reference concentration is shown; this format provides a convenient method to summarize the overall accuracy and precision of the measurements. Working with the logarithms of the ratios is necessary to properly account for the highly skewed distributions of ratios that result from data sets with significant scatter. Here it is assumed that the reference concentrations are accurate, and that any deviations in the reported measurements represent errors in their determination. For each analysis the geometric

mean ratio (i.e. the antilog of the mean of the logs of the ratios, which are indicated by the symbols in Fig. 3) indicates the average fractional systematic error of that analysis. The mean of the geometric mean ratios of the thirty-three analyses is 0.96, which indicates that, on average, the analyses were 4% lower than the reference concentrations. This excellent agreement lends confidence to both the accuracy of the reference measurements and to the standards in use in the NMHC measurement community. However, the average systematic errors of the individual analyses varied from 45% low to 85% high.

The geometric standard deviation of the ratios for each analysis (i.e. the antilog of the standard deviation of the logs of the ratios, which are indicated by the error bars) gives a measure of the 1σ precision of the measurements in the analysis. An average random error of a factor of 1.38 is indicated, i.e. approximately 2/3 of the measurements fell in the range 27% below to 38% above the reference concentrations. The average random error of the individual analyses varied from a factor of 1.07 (i.e. $\pm 7\%$) to a factor of 2.4 (i.e. -58% to $+140\%$).

The measurement accuracy and precision can also be examined as a function of NMHC identity. Generally the heavier NMHCs were underestimated to a larger extent than the lighter ones. For example, the average error in undecane was -25%. With regard to NMHC class, the scatter in the aromatic determinations was larger (factor of 1.67) than for the alkanes (factor of 1.38) and the alkenes (factor of 1.47). The biogenic NMHCs included in the mixtures (isoprene and α-pinene) were among the most poorly determined with respect to average accuracy ($+17\%$ and -41%) and average precision (factors of 1.8 and 3.3, respectively).

This study probably provides the most accurate, quantitative assessment of the current capabilities of the NMHC measurement community. However, it must be noted that it tested only the identification and quantification capabilities under the best of experimental circumstances. The difficult procedures of sample collection and concentration in an ambient air matrix, the proper identification of species in the full manifold of ambient VOC species, and measurements at the low levels typical of the ambient troposphere were not tested in this study. Clearly one of the most critical needs of the ambient NMHC measurement community is a rigorous field intercomparison of measurement techniques. Such an intercomparison will more clearly define measurement capabilities and identify prevalent problems that must be addressed.

2.2.3. Aldehydes, ketones and alcohols
2.2.3.1. Formaldehyde (CH_2O). Thus far, five techniques have emerged for the measurement of formaldehyde: (1) TDLAS (Fried et al., 1997; Harder et al., 1997a), (2) enzymatic fluorometry (EF), which involves the

absorption of CH_2O from a sampled air stream into water, followed by detection of the fluorescence from the reaction of the aqueous CH_2O with beta-nicotinamide adenine dinucleotide catalyzed by the enzyme formaldehyde dehydrogenase (Heikes et al., 1996), (3) the absorption of CH_2O from a sampled air stream into an aqueous solution by a diffusion scrubbing technique (DSF) (Fan and Dasgupta, 1994) or a glass coil scrubber (Kelly and Fortune, 1994), followed by detection of the fluorescence from the product of the reaction of the aqueous CH_2O in the Hantzsch reaction, (4) reaction of carbonyls with 2,4-dinitrophenylhydrazine (DNPH) forming hydrozones that are extracted and analyzed using high pressure liquid chromatography (Lee and Zhou, 1993; Zhou and Mopper, 1993), and (5) DOAS (Harder et al., 1997b).

Several intercomparisons have been reported for various combinations of these techniques: Kleindienst et al. (1988) at a rural site in North Carolina, Lawson et al. (1990) at an urban location in the Los Angles basin, Heikes et al. (1996) at the remote Mauna Loa Observatory in Hawaii, Harder et al. (1997a) in the Colorado mountains, Gilpin et al. (1997) at a location on the western edge of the Denver/Boulder metropolitan area and Apel et al. (1998) at a rural, forested site in Tennessee. The CH_2O mixing ratios investigated by these intercomparisons spanned a range of approximately 0.01 ppbv to 100 ppbv.

Kleindienst et al. (1988) compared four techniques for the measurement of CH_2O at the lower concentrations typically found in rural air where ambient concentrations of CH_2O ranged from 1 to 10 ppbv. In this study, no large systematic errors were observed in synthetic air mixtures with and without added interferants such as NO_2, SO_2, O_3, and H_2O_2, for the TDLAS, EF and DNPH techniques. Although reasonably low levels of CH_2O were encountered during this intercomparison no attempt was made to establish the detection limit for these instruments.

Lawson et al. (1990) evaluated four instruments using the DSF, EF and DNPH methods in an urban environment. In this evaluation two additional techniques were included, DOAS and FTIR (Lawson et al., 1990). Because of their lower sensitivity, these latter two techniques could not measure CH_2O much of the time. However, because they are highly specific optical techniques, they provided independent measurements for comparison with other techniques. During the course of the ten day study, the average hourly ambient CH_2O ranged from 4 to 20 ppbv. The spectroscopic techniques agreed to within 15%. The DNPH technique yielded values 15–20% lower than the mean of the spectroscopic techniques, while the DSF technique yielded values 25% lower than the mean. Measurements obtained with the EF method were found to be 25% higher than the mean. Measurements reported in the study by both the DSF

and ET were closer to the spectroscopic mean early in the intercomparison; problems reportedly developed in these instruments as the intercomparison progressed. The slight negative bias in the values obtained with the DNPH technique was tentatively attributed to a negative O_3 interference (O_3 ranged from 0 to 240 ppbv in this field study). Based on the results from this study and the intercomparison of Kleindienst et al. (1988) described above, Schiff and Mackay (1989) in an overview of the results concluded that the CH_2O methods involved were capable of measuring CH_2O in rural air to within approximately 35%. However, larger discrepancies were found in the more polluted urban air, even between the "absolute" spectroscopic techniques.

Heikes et al. (1996) reported an intercomparison of five CH_2O measurement techniques: TDLAS, EF, cartridge and coil DNPH measurements, and DSF. The intercomparison was carried out at the Mauna Loa Observatory with various combinations of the instruments during four six-week measurement periods in the fall, winter, spring and summer of 1991 and 1992. Typical mixing ratios of CH_2O encountered at the site were about 0.1–0.2 ppbv. Because the concentrations were low, the precision of the measurements was not good, and the standard deviation in the determinations were often comparable to the mixing ratio. Hence, it was difficult from the correlations among the measurements to identify specific conditions that were unfavorable to the determination of the CH_2O by any one technique. However, the DNPH cartridge technique measured systematically higher than the other techniques. This was ascribed to improper accounting for the blank levels of CH_2O on the cartridges. Other differences between measurements made by the techniques were rationalized as problems in calibration procedures and methods.

Harder et al. (1991) reported the comparison of the TDLAS technique with DOAS. During this intercomparison, the DOAS measured CH_2O over a ten kilometer path with the TDLAS located near the retroreflector location of the DOAS path. Because of the complex terrain, the most uniform CH_2O mixing ratios were expected when the wind was from the western "clean" sector. Under these conditions (28% of the measurements), the two techniques agreed well with the linear correlation between the two instruments having a slope of 1.05 ± 0.28. Larger discrepancies were expected, and indeed found, when the wind was from the more populated areas to the east.

Gilpin et al. (1997) reported an intercomparison of six CH_2O measurement techniques. This intercomparison involved TDLAS, DSF using cyclohexanedione as a fluorescing agent, EF, and three types of DNPH: continuous aqueous extraction followed by derivitization with hydrazones analyzed by high pressure liquid chromatography (HPLC), cartridges containing DNPH on a silica gel substrate, and cartridges containing DNPH on a

octadecylsilica (C-18) gel substrate. The intercomparison included analyses of spiked zero air and ambient air. In evaluating the results, the TDLAS was used as the reference method and presumed to be correct. Although the measurements seemed to correlate well, there were large systematic differences (approximately a factor of two) observed in the deduced CH_2O mixing ratios of the various methods compared to the TDLAS. Since none of the instruments, with the exception of the TDLAS, were calibrated with standard additions of CH_2O through the inlet, these differences were attributed to differences in the calibration and the collection efficiencies of the different systems.

Finally, Apel et al. (1998) report measurements by two different DNPH cartridge techniques in laboratory prepared air streams and in ambient air. These tested cartridges are routinely used in ambient air sampling programs such as the Photochemical Assessment Monitoring Stations (PAMS) network. Reported CH_2O levels varied between < 1 and 62 ppbv. Various ozone scrubbing strategies were investigated. For measurements made in their standard field configuration, poor correlation was found ($r^2 = 0.51$) when the total ambient data set was compared, although the correlation improved ($r^2 = 0.89$) when 15% of the measurements were eliminated as "outliers". For this smaller data set, a slope of 1.08 with an intercept of 0.55 ppbv was found, indicating relatively good agreement for high (> 1 ppbv) levels. However, the large magnitude of the reported levels is of concern; extensive aircraft measurements in the boundary layer (1412 3 or 5 min averages) in this region during the same time period (Lee et al., 1998) found a median of < 4 ppbv with $\approx$ 1% of the values above 10 ppbv and a maximum of $\approx$ 13 ppbv. In contrast, the 72 3 h average values in the most extensive cartridge data set (Si-Gel$_{MTE}$ with KI scrubber) in the intercomparison, had a similar median ($\approx$ 3.5 ppbv), but found 35% of the values above 10 ppbv with a maximum of 62 ppbv. The systematic and random errors identified in the intercomparison, as well as the contrast between the ground and aircraft data sets, indicate that the problem of ozone interference in the DNPH cartridge technique does not seem to have been completely solved.

The net result of these intercomparisons indicates that for the low levels found in rural and remote regions, through-the-inlet calibration with standard additions of gas-phase CH_2O and careful zeroing procedures are essential, and that the techniques used for "routine" monitoring in rural and urban locations are not yet routine. Careful attention must be paid to problems with interferences and/or blank levels for all methods employed in all locations.

2.2.3.2. Alcohols and higher aldehydes and ketones. The measurement of alcohols and higher molecular weight aldehydes and ketones has been reported using DNPH

cartridges (Grosjean, 1982), GC-FID (Montzka et al., 1993), and GC-MS (Starn et al., 1998). The DNPH technique has been the standard method for most field measurements of the carbonyls and has been demonstrated to have adequate selectivity. However, it suffers from low time resolution and sensitivity when compared to the GC techniques. Also, since the DNPH technique involves liquid extractions of the compounds of interest from the cartridge, blank levels have been reported to be a problem at carbonyl levels expected in the rural environment. The GC techniques offer the advantages of reasonable sensitivity, as well as high resolution, when capillary columns are used. These techniques can afford detection limits ranging from < 10 to 200 pptv in one liter of air (compound dependent). In GC analysis of ambient air, artifact formation of carbonyl compounds can arise in the cryogenic or sorbent collection of an air sample.

An informal comparison of DNPH (C-18 and silica gel) methods and two independent GC-MS instruments was carried out at a suburban site near Nashville, Tennessee during the 1995 Southern Oxidant Study (Apel et al., 1998). Two cylinders of synthetic air containing a mixture of NMHCs, carbonyls and alcohols were provided for the study. The compounds in these cylinders were stable, indicating that standards of these compounds at the ppbv mixing ratios contained in high pressure cylinders of synthetic air are feasible. Spiking studies carried out in synthetic air revealed differences that were associated with the presence of O_3. Agreement among the systems ranged from poor to relatively good and appeared to improve as the study progressed. The conclusion drawn from the study was that additional research was required to determine the potential sources of systematic error when using these methods.

Chemical ionization mass spectrometry (CIMS) has been used to detect a variety of partially oxygenated compounds. The compounds particularly suitable for detection by the CIMS method are those with proton affinities greater than that of water vapor (Hansel et al., 1995; Viggiano, 1993). Using this approach, Arnold et al. (1986) have measured acetone in the upper troposphere and lower stratosphere and Warneke et al. (submitted) have measured methanol, acetaldehyde, ethanol, acetone and methyl ethyl ketone emitted from dry and decaying vegetation. The approach holds great potential as a molecule-specific, sensitive (sub ppbv), fast-response, continuous method to measure these compounds.

2.2.4. Organic acids

A variety of measurement techniques for collecting organic acids have been developed; however, few tests have been made to assess their validity. In 1986 an intercomparison of techniques for collecting aerosol and vapor phase formic and acetic acid was held (Keene et al., 1989). The acids were collected by mist chamber, cold

plate condensate, resin cartridges, sodium hydroxide coated denuder tubes, sodium hydroxide impregnated glass filters, nylon filters, and both sodium and potassium impregnated cellulose filters. This intercomparison was limited to ambient air sampling. After collection, all of the samples were analyzed by ion chromatography. The mist chamber and denuder tube gave results that were statistically indistinguishable. The cold plate technique gave results that were in general agreement with the mist and denuder techniques but showed significant differences on some occasions. The nylon filters were found to not retain the acid vapors quantitatively. The sodium carbonate filters gave concentrations somewhat below the mist and denuder techniques. The resin cartridges, sodium hydroxide impregnated glass filters, and both sodium and potassium impregnated cellulose filters gave concentrations substantially larger than the mist chamber and denuder tubes. Although this intercomparison was not able to establish a generally reliable method to measure organic acids, several correctable problems with the compared techniques were identified. The conclusion was reached that strong base coated filters and GC resin techniques suffer from large positive interferences.

2.2.5. Total non-methane organic carbon (TNMOC)

The direct measurement of the reactive organic carbon loading in an atmospheric sample provides useful information for the evaluation of potential ozone production in an air mass and a check on the completeness of VOC speciation analyses. The TNMOC quantity is taken to include all gas-phase carbon species in the atmosphere except CO_2, CO and methane. McElroy et al. (1986) describe a TNMOC measurement technique involving cryogenic sample collection at a temperature that allows methane to escape, followed by FID analysis. They compare these results with the sum from NMHC speciation determinations for ambient samples, and find agreement within a few percent at high ($\geqslant 100$ ppbC) TNMOC levels; however; their speciation analysis (and presumably their TNMOC measurement) did not include any oxygenated VOCs. The FID operated in the standard fashion has a variable response to oxygenated VOCs. Roberts et al. (1998) report a more sophisticated measurement technique for TNMOC (which they refer to as C_y) that separates the VOCs from methane, CO and CO_2 by a backflush GC technique, oxidizes them to CO_2, reduces them to methane and finally detects them by FID. The advantages of their system include sensitivity to oxygenated VOC's, uniform sensitivity to all VOC species, and lower detection limits ($\leqslant 10$ ppbC).

One additional aspect of TNMOC measurements is the use of radio carbon analysis to distinguish the contributions of biogenic and anthropogenic (from fossil fuel combustion) emissions to TNMOC. Klouda et al. (1996) describe the techniques required and report results from 2 prototype samples from Atlanta, GA showing relatively small biogenic contributions. Contrasting results are presented by Tanner et al. (1996) who report a major fraction ($\approx 80\%$) of biogenic contribution to formaldehyde levels at a site downwind of the major North American source regions. The radiocarbon analysis of ambient organic compounds is potentially of great interest, but must be considered in its infancy.

3. Oxidants

3.1. Ozone (O_3)

A variety of techniques have been developed to measure O_3. These include UV absorption, DOAS, chemiluminescence and chemical titration methods, particularly electrochemical techniques, and most recently light detection and ranging (LIDAR). Each of these techniques has special advantages for certain tropospheric O_3 measurements.

3.1.1. In situ

UV absorption provides a reasonably straightforward and accurate means to measure O_3. Most instruments rely on the 254 nm emission line emitted from a low pressure mercury discharge lamp as the UV light source. Several high quality, reliable, commercially available instruments use this method; their response times are generally on the order of 10–20 s. A UV absorption instrument with a 1 s response time has been reported by Proffitt and McLaughlin (1983).

The chemiluminescence produced by the reaction of O_3 with NO forms the basis for a very sensitive, specific O_3 instrument (Ridley et al., 1992a). The chemiluminescent reaction of O_3 with unsaturated non-methane hydrocarbons such as ethene and with Eosin dye have also been used. Although the chemiluminescence approaches tend to be more involved than the UV absorption method, they have increased sensitivity, and thus have the capability for fast response O_3 measurements. These techniques have been used to measure O_3 fluxes that can be deduced from the correlation of O_3 variation with vertical wind speed variations.

Electrochemical sondes rely on the conversion of chemicals in a solution by ambient O_3 to alter the electric conductivity of the solution. A typical instrument, such as the electrochemical concentration cell (Komhyr, 1969), is composed of platinum electrodes immersed in neutral buffered potassium iodide solutions of different concentrations in anode and cathode chambers. When air containing O_3 is pumped into the cathode region of the cell, a current is generated that is proportional to the O_3 flux through the cell. These sondes are very light to be lifted by small balloons, and are widely used to measure O_3 profiles in the atmosphere. However, the measurements made by these instruments may suffer interferences

from compounds other than O_3 that tend to increase the instrument uncertainty (Barnes et al., 1985).

Over the years several formal and informal intercomparisons have been made of these techniques (Aimedieu et al., 1983; Hilsenrath et al., 1986; Kleindienst et al., 1993). Although the most comprehensive of these intercomparisons was aimed at evaluation of instruments used to measure stratospheric O_3, many of the findings were obtained in or can be applied to tropospheric O_3 measurements. The consensus from these intercomparisons indicates that the best UV absorption instruments are probably reliable for measurement of tropospheric O_3 with uncertainties less than 3%, and chemiluminescence instruments should be equally good. Kleindienst et al. (1993,1997) have shown that interferences in the UV absorption instruments due to absorption or scattering by species other than O_3 are negligible, except in highly polluted environments (see discussion below); the ethene based chemiluminescence instruments have a small bias due to water vapor ($\approx 4\%$ per % water vapor) that may be corrected for if humidity measurements are available or mitigated by calibration with humid air. The electrochemical sondes exhibited some interferences as mentioned above.

3.1.2. Remote

If a column of air has a uniform O_3 mixing ratio, there is little doubt that with present technology the column measurements of the average mixing ratio of O_3 along the path will agree with the mixing ratio measured in situ at any point along the path. This was recently illustrated by DOAS measurements made over two passes of a ten kilometer path compared to in situ, UV absorption measurements located near the retro-reflector of the DOAS path (Harder et al., 1997c). Even though the terrain was complex, the distribution of O_3 was remarkably uniform, especially under west winds, allowing definitive comparisons. Fig. 4 shows the fractional difference between the two measurements made under different wind regimes. Overall, the two techniques agreed for all measurements to within $\pm 7\%$. Stevens et al. (1993) report a comparison between a DOAS technique and a UV absorption instrument in an urban area. All measured O_3 levels were below 50 ppbv. For these conditions, good correlation ($r^2 = 0.89$) between the techniques was found, with the DOAS results systematically lower by 10% plus a negative 2.46 ppbv offset. Some of this systematic difference was attributed to spatial and temporal inhomogeneities.
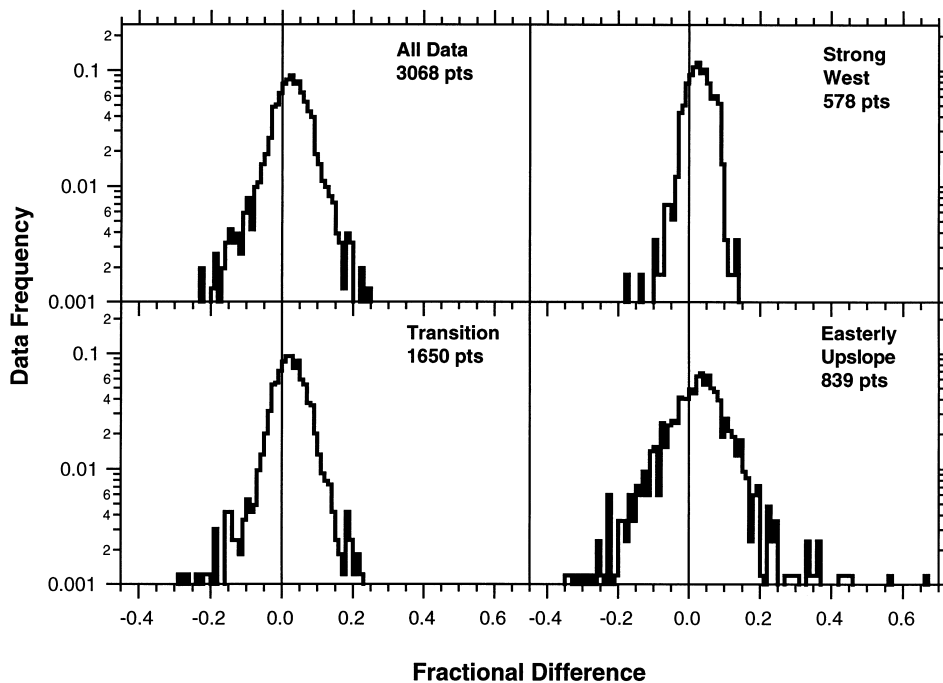

Fig. 4. Fractional difference histograms for O_3 measured by long-path absorption relative to the O_3 measured in situ near the retro-reflector of the long-path absorption path (Harder et al., 1997c). Three different wind regimes are plotted: (1) strong westerly winds, which should yield the most uniform conditions; (2) easterly upslope winds, which should yield the most variable conditions; and (3) transition periods when the winds are either more northerly, southerly or light and variable. Each panel shows the frequency that data fall into 0.01 fractional difference bins. The percentage of the points in each bin are shown on the logarithmic ordinate. The legends indicate the number of points in each wind regime.

During the past decade significant advances have been made in the development of differential absorption LIDAR (DIAL) systems for O_3 measurements. The method obtains spatially (horizontal or vertical) resolved distributions of O_3. Most of these instruments have been designed to operate in the wavelength range between 248 and 313 nm. These devices have been successfully used for profiles of stratospheric O_3 for almost twenty years (Godin et al., 1989; McDermid et al., 1990; Pelon et al., 1986). In the troposphere, lower O_3 mixing ratios and increased interferences from species such as SO_2 and aerosols make these measurements much more difficult.

An intercomparison of several LIDAR and in situ O_3 measurements was carried out in the Netherlands during June 1991. The project, Tropospheric Ozone LIDAR Intercomparison Experiment (TESLAS), was done under the auspices of EUROTRAC. Intercomparison of near-surface O_3 mixing ratios were made between two of the LIDARs, a DOAS and a commercial in situ UV monitor. The optical paths were approximately 20 m above a reasonably flat surface. The inlet of a commercial O_3 monitor (TECO Model 49) was located at one end of the 0.884 km optical path of the DOAS. The resolution of the two LIDARs were 0.75 and 0.15 km along paths that paralleled that of the DOAS. When averaged over fifteen minutes, the O_3 mixing ratio was found to be sufficiently homogeneous and consistent to afford a useful comparison. Considering the different air masses being sampled by the different techniques, the agreement was reasonably good, within about $\pm 30\%$. The LIDAR measured slightly higher mixing ratios than the in situ and DOAS instruments, but there were no differences in the systematic trends. These results suggest that LIDAR measurements are achieving significant gains in sensitivity and spatial resolution. However, more comparisons are needed to aid further development.

3.1.3. Urban

Measurements of ambient O_3 in urban areas have substantial economic implications since emission controls are mandated in non-attainment areas. Areas are designated as non-attainment where measured O_3 levels exceed the federal standard. Thus it is critical that the O_3 measurements in potential non-attainment areas be accurate. Such areas are generally urban areas with high ambient levels of VOCs. Laboratory studies have shown significant interferences in the UV absorption technique from aromatic hydrocarbons and their oxidation products (Kleindienst et al., 1993,1997). Nevertheless, this technique is commonly employed for routine monitoring in the areas where such interferences would most likely occur. From an analysis of possible errors in the UV absorption measurements, it has been plausibly argued that approximately half of the areas designated in 1993 as non-attainment, may actually have been in compliance

with the O_3 standard (Leston and Ollison, 1992). The errors found likely to occur in these monitors involved not only ambient interferants but also calibration uncertainties and anomalous operating conditions. These anomalous operating conditions include complex interactions of contaminated instrument components (O_3 scrubbers, absorption cells and other plumbing), sampling of high humidity air, and temperature cycling of the instruments's environment. Such errors often persist in ambient measurements by instruments that are found to operate well during calibration procedures in clean, dry air. The errors were found to be especially large during the hot, humid and stagnant conditions that are typical of O_3 standard violations. Such uncertainty in measured O_3 levels is not tolerable.

Even though significant evidence of interferences in the UV absorption technique has been reported, such interferences are not always observed, even in urban plumes. Ryerson et al. (1998) report simultaneous measurements of O_3 by UV absorption (TECO Model 49) and NO chemiluminescence instruments on the NOAA WP-3 aircraft. Through five field missions over four years, excellent correlations were found between the measurements of the two instruments, although the chemiluminescence instrument was systematically low ($\approx 5\%$) throughout some flights. The data sets include many passes through the Nashville urban plume with O_3 as high as 138 ppbv during the summer 1994 and 1995 Nashville/Middle Tennessee Ozone studies of the Southern Oxidant Study. There was never any indication ($<1\%$) that the UV instrument measured systematically higher in the urban plume.

Extensive field intercomparisons of a variety of different O_3 measurement techniques are critically needed in urban areas during the O_3 pollution season to quantitatively address the identified uncertainties. For O_3, field intercomparisons should be particularly effective, since several mature, in situ techniques have been developed. However, few if any field intercomparisons have been reported for the urban areas under the important high pollution conditions that lead to O_3 standard violations. If such intercomparisons are undertaken, DOAS, which is an absolute measurement technique with little chance of systematic interference, could be adapted for in situ measurements by use of a folded optical path.

UV absorption is a particularly efficient technique for ambient monitoring of O_3 and widely used, primarily because it does not require any reagent gases or liquids (which are required by techniques such as the chemiluminescence methods). The UV absorption technique has a further advantage in that it is, in principle, an absolute measurement; the measured absorbance is directly related to the O_3 concentration only through the optical path length and the absorption cross section of O_3. Conversion of the measured O_3 concentration to mixing ratio units requires only the accurate measure-

ment of temperature and pressure in the absorption cell. Given the absolute character of the measurement, "calibration" procedures, which involve adjusting the "span" control of the monitor until the instrument reading agrees with the output of a standard ozone generator in dry zero air, should be limited to only small adjustments. A much more critical assessment of a field O_3 monitor would be to frequently compare that instrument with another O_3 monitor that is carefully maintained in good operating order. These comparsions should include both instruments measuring ozone in ambient air, preferably during high pollution conditions. The comparisons would be particularly effective if the two instruments differed as much as possible: in manufacturers, in O_3 scrubbing medium, and even in technique (e.g. chemiluminescence versus. UV absorption). If the field instrument is found to disagree with the reference instrument, it should be repaired or cleaned to correct the problem.

In summary, the monitoring of O_3 in non-attainment areas has critical uncertainties with large economic and societal implications. Field intercomparisons during the conditions of O_3 exceedences are critically needed to reduce these uncertainties.

3.2. Odd-hydrogen free radicals

Cycles of reactions involving the odd-hydrogen free radicals, the hydroxyl radical (OH) and the peroxy radicals (HO_2, RO_2), are thought to be responsible for most atmospheric oxidation and the photochemical production and destruction of O_3.

3.2.1. Hydroxyl radical (OH)

Considerable effort was invested in the development of methods to measure OH in the decade between 1975 and 1985. However, a very careful assessment of the capabilities of these methods carried out by the Chemical Instrumentation and Evaluation (CITE) program of NASA concluded that the then available methods failed to have adequate sensitivity or suffered from interferences that prevented their accurate and precise measurement of ambient levels of OH (Beck et al., 1987). However, during the past decade considerable progress has been made toward the development of these techniques.

Two techniques have been continuously improved: (1) long-path absorption (LPA), where the amount of UV light that is emitted by a suitable light source and then absorbed by OH in the light path is detected at the end of the path ((Mount et al., 1997; Mount and Eisele, 1992), and the references therein), and (2) laser induced fluorescence (LIF), whereby laser emitted photons excite OH to an electronic state that decays by photon emission at a wavelength different from the exciting photon (see Crosley (1995) and the references therein). A version of the LIF instrument has been successfully and extensively used to measure OH in the upper troposphere and lower

stratosphere (Wenneberg et al., 1994). The principal modification in the LIF technique for operation at the higher pressures encountered in the middle and lower troposphere involved the expansion of the atmospheric sample into a low pressure chamber. In this approach (Hard et al., 1984; Mather et al., 1997; Stevens and al., 1997), termed fluorescence assay by gas expansion (FAGE), the lifetime of the excited OH is lengthened, which allows the separation of the fluorescence from the scattered excitation laser light, and greatly reduces the interference associated with the production of OH by the laser.

Methods of OH measurement in the troposphere have been extended during the past ten years by the emergence of a CIMS technique (Eisele and Tanner, 1991; Tanner et al., 1997). In this method, the reaction of SO_2 with OH in the CIMS is used to generate H_2SO_4 which in turn reacts with negative ions such as NO_3^- to form an exceptionally stable negative ion, HSO_4^-.

In 1991 an informal intercomparison was carried out between the LPA and CIMS techniques (Eisele et al., 1994; Mount and Eisele, 1992). The laser light source and detector for the LPA were co-located while a retro-reflector was located ten kilometers distant. The LPA measured the OH over this path while the CIMS was operated at a site near the retro-reflector. Because of complex terrain, the distribution of the very short-lived OH was expected to be very non-uniform, making a definitive comparison difficult. The study was carried out over a six week period during the summer. Unfortunately, instrument problems and adverse weather permitted comparisons to be made on only six days. The most uniform OH mixing ratios were expected when the wind was from the west, and under these conditions there was generally good agreement between the methods.

In 1993 a second intercomparison was held at this same location (Crosley, 1997). In addition to the LPA and the CIMS, the LIF-FAGE was included. Degraded laser performance prevented the LIF-FAGE from participating fully in this exercise. The optimum conditions for sampling again occurred when the wind was from the west. Under those condition the correlation between the LPA and CIMS measurements of OH was reasonably good, as shown in Fig. 5.

Finally, in 1994 an intercomparison of the LPA and the LIF-FAGE techniques was held in a rural site in northern Germany (Brauers et al., 1996; Hofzumahaus et al., 1998)). In this study, termed photochemistry of plant emitted compounds and OH radicals in Northeastern Germany (POPCORN), the LPA used an open optical path of 38.5 m with as many as 80 passes of the laser beam for a total path length of 3080 m (Dorn et al., 1996). The correlation between these measurements, shown in Fig. 6, was quite encouraging. Excluding one wind sector, a linear regression of 137 sets of simultaneous OH measurements by the two techniques (i.e., 70% of the
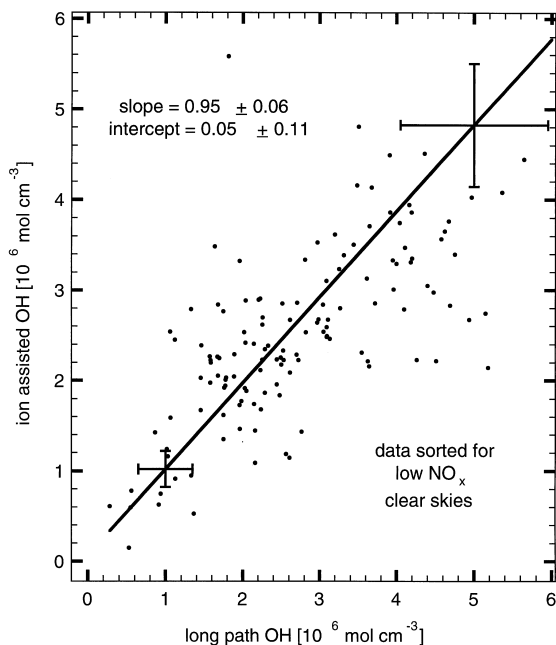
Fig. 5. Correlation of a set of simultaneous measurements of OH (units: 10^6 cm^{-3}) made over a four week period in September and early October of 1993 using the CIMS technique (listed as "ion assisted") and the LPA method (i.e., long path) (Crosley, 1997). The measurements were made on clear days during periods of low NO_x, as measured at the site of the CIMS instrument. These conditions were judged to be most favorable for uniform conditions along the path of the LPA. The correlation of these data was moderate: $r^2 = 0.62$. However, a large contribution to the low correlation was due to measurements made during two days in late September.
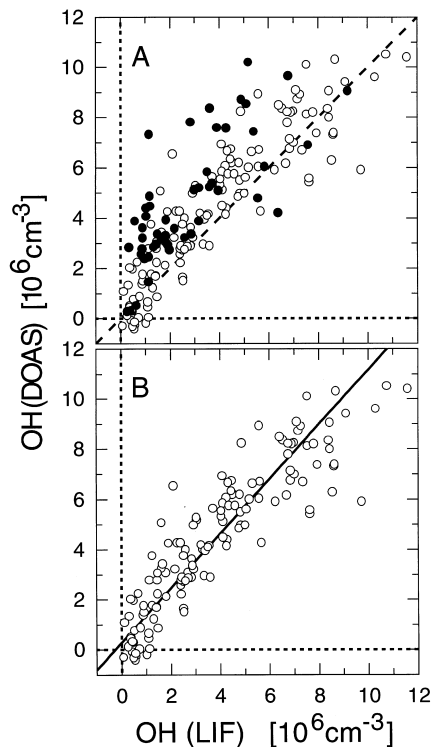

Fig. 6. The correlation of simultaneous measurements of OH made using folded path DOAS and LIF as a part of the POP-CORN study (Hofzumahaus et al., 1998 with kind permission from Kluwer Academic Publishers). The top graph (A) shows all simultaneous determinations (195) of OH made during eleven days in August 1994. For these measurements $r^2 = 0.72$. The measurements denoted by the solid symbols were made when the wind direction was unfavorable for the comparison. The bottom graph (B) shows the results with those points removed. In this case $r^2 = 0.81$. The solid line gives the fit to these measurements, $OH_{DOAS} = (1.01 \pm 0.04)OH_{LIF} + (0.28 \pm 0.15)10^6$ cm^{-3}.

data; see Fig. 6) resulted in a slope of 1.01 ± 0.04, an intercept of (0.28 ± 0.15) 10^6 cm^{-3}, and $r^2 = 0.81$. The intercomparison concluded that both OH instruments agreed excellently in their calibration and accurately measured OH.

Based on these studies, the LIF-FAGE, CIMS and LPA techniques seem capable of measuring OH in the troposphere. The CIMS approach is less direct since it relies on a chemical reaction to convert OH to a compound that can be easily detected. However, the technique is robust and exhibits remarkable sensitivity and reliability. It has been used to make extensive OH measurements from ground sites and aircraft platforms.

3.2.2. Peroxy radicals (HO_2, RO_2)

Three techniques have been utilized for the measurement of HO_2 and RO_2. The most widely used method is the chemical amplifier (CA) technique (Cantrell et al., 1993,1997), where HO_2 and RO_2 are introduced into a reaction chamber in the presence of elevated concentra-

tions of NO and CO. Chain reactions involving NO and CO convert most RO_2 to HO_2 (a fraction of RO_2 forms alkyl nitrates upon reaction with NO and thus is not measured by this technique) and subsequently HO_2 to OH and back to HO_2, in the process forming NO_2; usually many NO_2 molecules are produced for each RO_2 or HO_2 that enters the reaction vessel. The NO_2 that is produced is subsequently detected by the luminol chemiluminescence. Hence, the technique measures HO_2 plus the fraction of RO_2 that oxidizes NO to NO_2. The LIF-FAGE technique for OH measurement can be adapted to detect RO_2 and HO_2 by the addition of NO to convert these species to OH, which is then detected as described above (Stevens et al., 1997). Presumably the time scales for the conversion allows HO_2, but not RO_2, to be detected. Finally, RO_2 and HO_2 have been detected by MIESR (Mihelcic et al., 1978). The unpaired spin

detected by MIESR is common to all peroxy radicals, but its environment is different enough in the HO_2 radical that the technique detects HO_2 separately from the organic RO_2 radicals. The RO_2 detected by MIESR include all peroxy radicals, not just the fraction that is capable of oxidizing NO to NO_2.

An informal intercomparison termed the Peroxy Radical InterComparison Exercise (PRICE) was carried out at a rural site in Germany with the CA technique and the MIESR method (Volz-Thomas et al., 1996). The two techniques generally agreed to within $\pm 40\%$, except under polluted conditions. Under these conditions the peroxy radical mixing ratios measured by the CA technique were considerably lower than those determined by MIESR. Zenker et al. (1998) report another informal intercomparison between three CA instruments and the MIESR technique conducted at the remote Izaña site in the Canary Islands. Two of the CA instruments agreed within 25% with the MIESR results (1.01 ± 0.20 and 0.98 ± 0.24, 95% confidence limit), while the third responded low (0.65 ± 0.32).

In addition to the techniques directly measuring RO_2 and HO_2, the imbalance in photochemical stationary state (PSS) has been used to infer the concentration of RO_2 and HO_2 (Parrish et al., 1986; Cantrell et al., 1992). In several studies, measurements made with the CA technique have been compared to the PSS concentrations (Cantrell et al., 1992,1996,1997). Although there is considerable uncertainty in the PSS peroxy radical concentration due to the lack of precision in the simultaneous measurements of NO, NO_2, O_3, and the photodissociation rate of NO_2, the two approaches have agreed within the large uncertainties in three very different locations.

Although these studies have produced encouraging results, much work remains to be done to remove uncertainties in the determination of the peroxy radical mixing ratios in the atmosphere.

3.3. Hydrogen peroxide (H_2O_2) and other peroxides

Four techniques have emerged for the measurement of H_2O_2 and related organic peroxides: (1) enzymatic derivitization with flourometric detection (EDFD) (Lazrus et al., 1986; Heikes, 1992), (2) Fenton derivitization with flourometric detection (FDFD) (Lee et al., 1993), (3) high performance liquid chromatography (HPLC) (Lee et al., 1995), and (4) TDLAS (Mackay et al., 1996). The first three techniques rely on collecting gas-phase peroxides in aqueous solutions in a scrubbing coil, followed with speciation by the respective techniques, while the fourth provides a specific, gas phase measurement of H_2O_2 only. The HPLC technique has also been utilized with samples collected cryogenically (Kok et al., 1995).

In the EDFD method the enzyme peroxidase catalyzes a reaction between the hydroperoxide and a hydrogen donor substrate (p-hydroxyphenylacetic acid) to form a fluorescent dimer, which is measured by UV fluorescence spectroscopy. In order to differentiate H_2O_2 from other peroxides, usually a second enzyme, catalase, is added in a second channel to preferentially remove H_2O_2 and thus determine H_2O_2 and the sum of other peroxides by difference. Alternatively, two sequential scrubbing coils can be used to differentiate between the highly soluble H_2O_2 (and perhaps other, multifunctional soluble peroxides) and the generally less soluble organic peroxides (Heikes, 1992).

In the FDFD method benzoic acid is oxidized by a Fenton reagent (Fe(II) and H_2O_2) and the hydroxylated products are detected by UV fluorometry. In the approach employed by Lee et al. (1993), three channels are used; one, to measure only H_2O_2, a second to convert hydroxymethyl hydroperoxide (HMHP) to H_2O_2, and a third to measure all peroxides by the EDFD method; differences between the channels then are used to determine the principle peroxide components. No formal intercomparison of this method with other techniques has been reported.

The HPLC technique analyzes the effluent from the scrubbing coil or a cryogenic sample, by injection into an HPLC system. The scrubbing coil technique (Lee et al., 1995) uses a 15 min analysis time and measures H_2O_2, methyl hydroperoxide (MHP), HMHP, ethyl hydroperoxide and peroxyacetic acid. The corresponding detection limits are approximately 0.01 ppbv or below for the first 3 peroxides, and below 0.1 ppbv for the latter 2. The HPLC technique using cryogenic detection requires as much as 45 min to collect a sample, and may introduce artifacts (Staffelbach et al., 1996).

In a 1986 intercomparison carried out at Research Triangle Park, NC, the EDFD and TDLAS techniques were compared. The results indicated that these two methods were sufficiently sensitive to measure H_2O_2 present in ambient air and agree with an overall accuracy of $\pm 30\%$ (Kleindienst et al., 1988).

The results from an intercomparison of Staffelbach et al. (1996) made during the Mauna Loa Observatory Photochemical Experiment II (MLOPEX II) (Atlas and Ridley, 1996) were less satisfactory. During two studies carried out at this remote mid-Pacific mountain site during fall 1991 and winter 1992, the peroxides were measured using TDLAS, the EDFD method in both the dual enzyme and sequential coil configurations, and the HPLC technique with cryogenic collection. The HPLC system, while sensitive to many hydroperoxides, detected only H_2O_2 and MHP, which simplified the interpretation of the EDFD measurements. The TDLAS system only measured H_2O_2. During the measurement periods the range of H_2O_2 varied from detection limits of the techniques to 2 ppbv. The reported MHP mixing ratios varied between 0.2 and 0.6 ppbv. Although there were periods of relatively good agreement between

H_2O_2 measured by the four methods (i.e., $\pm$ 20%), there were periods when the disagreement was greater than a factor of two. Even larger differences were recorded between the three techniques that measured methyl hydroperoxide. They concluded that there remain unsolved problems in making reliable measurements of H_2O_2 and MHP.

In summary, although the techniques for the measurement of H_2O_2 in moderately polluted areas have intercompared reasonably well, there is a need for further intercomparisons in less polluted regions. Through the inlet calibration by gas phase standards would seem to be a critical requirement to resolve some of the disagreement found in the more remote regions. A formal intercomparison of H_2O_2 systems including the FDFD and HPLC techniques as well as previously compared techniques is important. This intercomparison should include sampling a wide variety of ambient air masses through the inlets normally used. The measurement techniques for organic peroxides are much less well characterized; the one intercomparison that addressed this issue (Staffelbach et al., 1996), was in a region where only MHP was expected and indeed observed. A much more extensive, formal intercomparison is necessary before organic peroxide measurements can be accepted with confidence.

4. Gas-phase aerosol precursors

Secondary aerosols are formed in the troposphere by reactions involving oxidized nitrogen species, VOCs, ammonia and sulfur containing species; consequently there is a great deal of coupling between the photochemistry producing aerosols with that producing O_3 (Meng et al., 1997). The measurement of the VOCs is discussed above; however the VOCs that are important as aerosol precursors present special measurement problems. It is the heavier VOCs (C_7 and higher), primarily the aromatics in urban areas, and their partial oxidation products that constitute the VOC aerosol precursors (Odum et al., 1997). It is likely that these species will be particularly difficult to measure because, first, their semi-volatile nature will make them particularly vulnerable to loss in the sampling and analysis process, and second, it will be particularly difficult to avoid artifacts associated with disturbing the ambient equilibrium of the gas and aerosol phases during the measurement process.

4.1. Ammonia (NH₃)

A major difficulty associated with measurements of NH_3 is its presence in gaseous, particulate (e.g., $(NH_4)_2SO_4$ and NH_4NO_3) and liquid (i.e., $NH_4^+(aq)$ in cloud and fog droplets) forms in the atmosphere. The partitioning between these three phases is highly variable and a complete picture generally requires simultaneous but separate measurements of at least the gaseous and particulate phases. A second major difficulty results from the tendency of NH_3 to form strong hydrogen bonds with water and thus adsorb on the surfaces of most materials exposed to air. This can lead to high backgrounds and memory effects due to retention on sampling plumbing.

Most gaseous NH_3 measurements reported in the literature trap NH_3 with an acidic medium such as acid bubblers (Breeding et al., 1973; Junge, 1957), acid-coated filters (Shendrikar and Lodge, 1975), or acid-coated denuder tubes (Ferm, 1979). The extract from these samplers is then analyzed for NH_3 via colorimetry, ion-specific electrode, or ion chromatography. The diffusion denuders developed by Ferm (1979) separate gaseous NH_3 from particulate and droplet NH_4^+ by exploiting the large difference in the diffusion coefficient. Variants of this technique have become the de facto standard for gaseous NH_3 measurements. The detection limit depends on the sample time and denuder preparation, but levels below 0.01 ppbv appear to be possible for a 2 h sample. Similar limits may be obtained with acid-coated filters, which are also widely used, typically with a Teflon prefilter to collect the particulate phase. Filter packs are generally considered the standard technique for measuring particulate NH_4^+ and related species.

Several intercomparisons of the diffusion denuder and filter pack techniques for measuring gaseous NH_3 have been conducted in recent years. A field comparison of oxalic acid-coated paper filters and diffusion denuders described by Gras (1984) indicated that volatilization of particulate NH_4^+ collected on the Teflon prefilter led to high apparent gaseous NH_3 in the filter pack technique. This conclusion was also drawn from an intercomparison of filter pack, diffusion denuder, FTIR, and tungsten oxide denuder detectors (Appel et al., 1988; Wiebe et al., 1990). Harrison and Kitto (1990) also found evidence for particulate volatilization in filter packs.

Both filter packs and denuders offer the advantages of simplicity and relatively low cost, but the preparation and analysis of the sample is labor intensive. This makes the acquisition of large data sets with sufficient temporal resolution difficult. Automated diffusion denuder systems (Bos, 1980; Keuken et al., 1989) have been developed in which the acid solution coating is continuously replenished. An alternate approach for automated detection uses "permanent" acid coatings and thermal desorption. McClenny and coworkers (Harward et al., 1982; McClenny and Bennet, 1980) collected NH_3 on Teflon beads or tungsten oxide tubes and detected the thermally desorbed product by photoacoustic spectroscopy. Braman et al. (1982) developed a denuder tube coated with tungsten oxide/tungstic acid to collect NH_3. The collected NH_3 is thermally desorbed and subsequently converted to NO on a hot gold surface. The NO is then measured with a chemiluminescence detector. A similar

instrument, developed by Appel et al. (1984) agreed with the diffusion denuder measurements to within about a factor of two but exhibited a temperature dependent sensitivity. Thermal denuder systems based on other metal oxides are possible. Keuken et al. (1989) developed a system using vanadium pentoxide while Langford et al. (1989) used molybdenum oxide. The former instrument employs an oxide coated annular quartz denuder while the latter uses the oxidized surface of a molybdenum rod suspended in a quartz tube. Both vanadium and molybdenum oxide directly oxidize the NH_3 to NO or NO_x upon desorption, thus eliminating the need for a secondary converter.

Several other promising sampling techniques have been developed to measure gaseous NH_3. Abbas and Tanner (1981) described a fluorescence derivatization technique that collects NH_3 in a continuously flowing acidic solution and monitors fluorescence from 1-alkyl-thioisoindole formed in the subsequent reaction with *o*-phthalaldehyde. Farmer and Dawson (1982) used a cold plate to condense NH_3 and other soluble gases in water, analyzing the condensate by colorimetry or ion-selective electrode. Genfa et al. (1989) described an instrument in which NH_3 diffuses through a porous membrane into water. The NH_4^+ is then reacted with sodium sulfite and *o*-phthaldialdehyde and the resulting fluorescence from 1-sulfonatoisoindole is monitored. The technique offers potential for general use since it is relatively inexpensive, appears to be specific towards NH_3, and has a detection limit of $\leqslant 0.05$ ppbv for a 5 min sample time. At present, this technique has not been compared to other methods. Other instruments based on mist chamber techniques (Cofer et al., 1985) are under development in several laboratories and offer similar advantages.

It is clear, however, that direct spectroscopic detection of gaseous NH_3 without intervention of a collecting medium would be most desirable since this could provide both continuous measurements and unequivocal identification of the compound. Long path absorption techniques using CO_2 differential absorption lidar (DIAL) (Force et al., 1985) and FTIR (Biermann et al., 1988) have been used, but have very high detection limits (5 and 1.5 ppbv, respectively). TDLAS, an in situ spectroscopic technique (MacKay and Schiff, 1984), has excellent sensitivity and specificity but the application at low concentrations is limited by NH_3 losses on absorption cell walls. A photofragmentation/laser-induced fluorescence technique (PF/LIF) (Schendel et al., 1990) has been used which overcomes this problem by using very high flow rates ($\geqslant 1000$ l min^{-1}) through the excitation cell. This technique offers detection limits approaching 1 pptv for a one-minute integration time with no known interferences. However, in its present form the system is large, expensive and complicated. Nevertheless, the technique has great potential as a standard against which other measurements can be evaluated.

The PF/LIF technique was compared with citric acid diffusion denuders, a filter pack/colorimetry system, a tungsten oxide denuder, and a molybdenum oxide denuder (Williams et al., 1992b). In general, agreement to better than a factor of 2 was seen among all the NH_3 instruments at all times, even when large changes in the NH_3 mixing ratio occurred over very short time intervals. The conclusions from this study were that the PF/LIF technique and citric acid coated diffusion denuder systems agreed within the stated accuracies for all tests with no evidence of interferences; the filter pack/colorimetry system was systematically lower due to temperature related losses on the Teflon prefilter; the tungsten oxide denuder system agreed for separate inlet ambient sampling; and the molybdenum oxide denuder system exhibited a background level of ≈ 0.07 ppbv attributed to retention of NH_3 on the Teflon inlets and responded to both gaseous NH_3 and free NH_4^+ dissolved in cloud or fog droplets when the latter were present. An ancillary conclusion from the study is that even short inlet lines retain NH_3 and cause memory effects. In particular, Teflon appears to be unsuitable for NH_3 sampling inlets. Sampling through any type of inlet should be done using high flow rates (i.e., $\geqslant 100$ l s^{-1}) if sub-ppbv mixing ratios of NH_3 are to be measured.

Although there have been no comparisons to support its capabilities, an emerging new CIMS approach (Viggiano, 1993) is providing NH_3 measurements in the troposphere and stratosphere (Tanner and Eisele, 1991; Ziereis and Arnold, 1986). The CIMS technique is extremely sensitive for the detection of NH_3 because of the very high proton affinity of NH_3. The CIMS systems that are being used successfully in the negative ion (anion) mode for acids could be used in the positive ion mode (cation) mode for alkaline compounds.

4.2. Sulfur containing compounds

4.2.1. Sulfate precursor compounds

Several techniques are available to measure reduced sulfur compounds. Considerable effort was expended during the 1980s as part of the United States National Acid Precipitation Assessment Program to develop techniques to measure the flux of sulfur compounds from natural sources. Instruments were designed, tested, and used to measure a variety of reduced sulfur species, including H_2S, COS, CS_2, CH_3SH, C_2H_5SH, CH_3SCH_3, and $CH_3S_2CH_3$. These techniques include: GC with flame photometric detection (GC-FPD) (Goldan et al., 1987; Lamb et al., 1987) metal foil collection followed by flash desorption and FPD (MFC-FD-FPD) (MacTaggart et al., 1987) and filter collection followed by extraction and spectrofluorometric analysis (Lamb et al., 1987; Natusch et al., 1972). They are adequate to measure sulfur compounds at the higher concentrations observed for reduced sulfur compounds in the effluent from flux

chambers. However, much lower detection limits are required to measure these compounds in the remote troposphere.

An intercomparison evaluated the capability of instrumentation for the airborne measurement of ambient concentrations of SO_2, H_2S, CS_2, DMS, and COS in the remote troposphere (Hoell et al., 1993). The study involved an intercomparison of sulfur calibration standards followed by airborne measurements of the ambient concentrations of the sulfur compounds of interest over the North Atlantic and the tropical Atlantic.

Six instruments designed to measure DMS participated in the intercomparison. The instruments utilized four different measurement approaches (1) isotope dilution – gas chromatograph (ID-GC) followed by mass spectrometric detection (MS) (Thornton et al., 1990), (2) GC followed by flame photometric detection (FPD), (3) GC followed by fluorination with electron capture detection (GC-F-ECD) (Johnson and Bates, 1993), and (4) gold wool absorption followed by flame photometric detection (Ferek and Hegg, 1993). The six instruments involved three fundamentally different detection principles (flame photometry, mass spectrometry, and electron capture detection), three collection/preconcentration methods (cryogenic, gold wool absorption, and polymer absorbent), and three types of oxidant scrubbers (solid phase alkaline, aqueous reactor, and cotton). The results (Gregory et al., 1993c) indicated that the instruments agreed to within a few pptv for DMS mixing ratios less than 50 pptv, and to within 15% for DMS mixing ratios above 50 pptv. The results also indicated that all these instruments were capable of measuring DMS mixing ratios from a few pptv to 100 pptv (the upper range of DMS mixing ratios encountered during the intercomparison).

Four instruments designed to measure COS, H_2S, or CS_2 participated in the intercomparison (Gregory et al., 1993a): GC-FPD for COS, H_2S, and CS_2, GC/MS for COS and CS_2 (Thornton et al., 1990), GC-F-ECD for COS and CS_2, and the Natusch technique for H_2S. During the intercomparison, COS generally varied between 400 and 600 pptv. The COS measurement techniques agreed on average to within about 5%, and individual measurements generally agreed to within 10%. The mixing ratios for H_2S reached a maximum of 100 pptv but were generally less than 25 pptv. For H_2S > 25 pptv, the instruments agreed on average to about 15%. For H_2S < 25 pptv, the techniques agreed to within about 5 pptv. In the case of CS_2, mixing ratios encountered were typically less than 10 pptv with a maximum of 50 pptv. The GC-FPD and GC-MS agreed to within 4 pptv with the GC-FPD measurements consistently higher on average by 4 pptv. For the same mixing ratio range, the GC-F-ECD technique measured consistently higher relative to the other two techniques by 3–7 pptv. At the lowest mixing ratios encountered (a few pptv or

less), the CS_2 levels were below the detection limits of the GC-F-ECD.

It should be noted that a high precision TDLAS system for the measurement of COS has been reported (Fried et al., 1991a,b), but has not participated in any intercomparison. These workers report a precision of $\pm$ 0.3 to $\pm$ 1%, for this gas, which typically occurs in the troposphere at concentrations near 0.5 ppbv.

Five instruments designed to measure SO_2 participated in the intercomparison (Gregory et al., 1993b): (1) GC-FPD, GC-MS (Driedger et al., 1987; Thornton et al., 1986) (2) chemiluminescence (Maser et al., 1991; Meixner and Jaeschke, 1981), (3) filter collection with ion chromatographic analysis, and (4) filter collection with the above mentioned chemiluminescence analysis. For SO_2 of a few pptv to 200 pptv, there was not general agreement among techniques and the results from the instruments were uncorrelated. The intercomparison did not unambiguously validate any of the measurement techniques involved as capable of SO_2 measurements, but identified a range of potential uncertainty in aircraft SO_2 instrumentation.

Recently, the intercomparison of SO_2 measurements techniques was revisited in the Gas-phase Sulfur Intercomparison Experiment (GAISE) sponsored by the National Science Foundation (Stecher et al., 1997). The intercomparison was stimulated by the importance of establishing some degree of confidence concerning the capability of current SO_2 instruments following the inconclusive results from the SO_2 intercomparison described above (Gregory et al., 1993b).

Seven techniques for the measurement of SO_2 were compared using samples of synthetic air mixtures and diluted ambient air. Complete descriptions of the instruments can be found in Luther and Stecher (1997). The seven techniques were: (1) aqueous chemiluminescence (Aq. CL) (Jaeschke et al., 1997), (2) pulsed resonance fluorescence detector (PRF) (Luke, 1997), (3) isotope dilution – gas chromatograph followed by mass spectrometric detection (ID-GC-MS) (Thornton et al., 1990), (4) mist chamber, ion chromatograph (Mist-IC) (Talbot et al., 1997), (5) diffusion denuder with sulfur chemiluminescence detector (DD-SCD) (Benner et al., 1997), (6) high performance liquid chromatography with fluorescence detector (HPLC-FD) (Gallagher et al., 1997), and (7) carbonate filter with ion chromatographic detection (Filter-IC) (Ferek et al., 1991,1997).

Six of the seven techniques compared well with no evidence of interference from O_3, NO_x, DMS, CO, CO_2, or CH_4. Problems with the DD-SCD technique were identified and considered manageable (Benner et al., 1997). The accuracy of the techniques seemed to depend on variations associated with the calibration standard. Indeed the intercomparison showed that there are presently no validated standards for low pptv concentrations of SO_2. Two techniques, ID-GC-MS and HPLC-FD,

were able to easily quantify standard additions of SO_2 to the gas mixture below 50 pptv. Two other techniques, mist-IC and Filter-IC, were judged capable of this if they were operated closer to their nominal operating conditions. All but the DD-SCD technique agreed well during the ambient measurements.

Stevens et al. (1993) report a comparison in an urban area between DOAS and PRF techniques for SO_2 measurements. For SO_2 levels up to about 20 ppbv, good correlation ($r^2 = 0.96$) between the techniques with a slope not significantly different from unity was found, although the PRF results were systematically offset by -1.78 ppbv. The PRF values were often below zero, emphasizing the importance of proper zeroing technique for the PRF instrument.

4.2.2. Sulfuric acid (H_2SO_4)

Although there have been no comparisons to support its capabilities, a CIMS approach (Viggiano, 1993), is providing considerable data concerning the concentration of H_2SO_4 in the troposphere and stratosphere. The CIMS technique is extremely sensitive for the detection of H_2SO_4 because it will react rapidly with most negative ions by transferring a proton to form the exceptionally stable negative ion, HSO_4^-. Arnold (Arnold et al., 1981; Mohler and Arnold, 1992; Schlager and Arnold, 1987; Viggiano and Arnold, 1983), Arijs (Arijs et al., 1983a,b), and their coworkers have deduced the concentration of H_2SO_4 in the upper troposphere and the stratosphere by measuring the atmospheric abundance of HSO_4^- relative to NO_3^-. With this approach they have determined atmospheric mixing ratios of H_2SO_4 as low as 10^4 cm^{-3}. More recently, this ion chemistry has been incorporated by Eisele and Tanner (1993) into a flow/drift CIMS capable of determining H_2SO_4 in the lower troposphere. H_2SO_4 mixing ratios as low as 10^5 cm^{-3} have been measured using this approach. Indeed, this ion chemistry forms the basis for the CIMS measurement of OH (see discussion in Section 3.2.1).

5. Support activities

5.1. Calibration issues

The demonstration of instrument capability through intercomparison is needed to provide measurement tools of assured reliability. However, in order to use these tools successfully in the field, reliable and accurate methods of in situ instrument calibration are required. Experience has demonstrated that calibrations must be done with a known quantity of the molecule of interest, added by standard addition to ambient air at the inlet of the system. It is desirable that the standard addition be done at levels representative of the ambient levels of the analyte compound to be sampled. For gases that can be manu-

factured and stored (e.g., NMHCs), calibration additions of small mixing ratio levels found in the atmosphere can be achieved by dilution of the calibration standard using a dynamic dilution system or by simply adding a small flow of the calibration gas mixture to a large ambient sample gas flow (Williams et al., 1992a). A sampling strategy using large carrier gas flows (i.e., $> 10^3$ l min^{-1}) has proven to be relatively effective at conditioning inlets for sampling a compound as difficult as NH_3 at low mixing ratios (i.e., ppbv or pptv levels) through relatively long sampling lines (Williams et al., 1992a).

For more reactive gases, through-the-inlet calibration becomes increasingly important and increasingly difficult. For this reason methods must be found to manufacture, store and introduce these compounds or to generate them in known quantities near the inlet.

5.1.1. Standard reference gas mixtures (SRM)

The preferred method of supplying standards is in the form of a dilute mixture (parts per million by volume (ppmv) or ppbv range) of the compound of interest in a suitable carrier gas (usually a synthetic mixture of N_2, O_2, i.e., "zero air"). Such calibration standards are limited to those compounds that remain stable and can be stored at the low concentrations in a high pressure gas mixture. The development of specially treated, chemically passive high pressure cylinders, careful gas handling procedures, and makeup gases free of contamination are required to produce these low concentration standards.

A variety of reference standards are available from national standards laboratories, for example the National Institute of Standards and Technology (NIST) in the United States or the National Standards Laboratory in the United Kingdom. Generally, these standards, when available, are prepared by microgravimetric techniques and supplied in specially treated cylinders at high pressure (Fried and Hodgeson, 1982). The stability of the SRM standards in these cylinders is assured by the supplier as a result of monitoring over a period of years. In addition, a variety of other standard mixtures are supplied by compressed gas manufacturers. These secondary standards are sometimes traceable to the primary SRM standards supplied by the national standards laboratories. However, there is no set procedure or protocol provided by the national standards laboratories to assure or even to gauge the quality of these manufactured secondary standards.

5.1.2. Permeation tubes

Another method to provide a small but known calibration addition to a system is through permeation tubes. This source for a known flow of an analyte of interest has been particularly useful for compounds that are difficult to store at trace concentration in high pressure cylinders. A variety of compounds in permeation tubes are available commercially. These "low loss" permeation tubes

are usually gravimetrically calibrated. The permeable membrane is made of a suitable inert material such as Teflon. The output of the tube is determined by the permeation rate of the material at a given temperature and area of the permeating surface. The rate of permeation can be altered by varying the temperature over a limited range of temperatures.

The versatility of the permeation tube calibration sources is somewhat offset by some inherent stability problems. Since the permeation rate is a strong function of temperature, the tubes must be held at a constant, known temperature. In addition, the calibrated rate of analyte permeation from these tubes can be subject to irreversible change. Commonly this is a result of overheating. Moreover, the mixture inside the tube can change due to permeation of atmospheric gases into the tube and chemical reactions that may occur within the tube. In this case part of the emission from the tube, and hence the weight loss, may be associated with the permeation of the volatile adulterants.

5.1.3. Diffusion/effusion sources

There are a variety of labile compounds that are sufficiently unstable that they cannot be prepared, stored and maintained in either high pressure cylinders or permeation tubes. In certain cases these compounds have been synthesized, stored at low temperature and then supplied in known amounts from diffusion or effusion sources. Examples in the literature include calibration sources that have been developed for PAN and N_2O_5. An accepted calibration source for PAN (Gaffney et al., 1984) is a capillary diffusion source containing PAN dissolved in tridecane and held at constant temperature and pressure. For N_2O_5, a flow of an inert carrier gas can be used to elute N_2O_5 vapor from an N_2O_5 storage trap (Fahey et al., 1985a).

5.1.4. Continuous chemical generation

Occasionally the compounds that are to be studied are sufficiently unstable so that they cannot be produced and stored for latter use. In such cases, rigorous calibration requires that the compound of interest be generated in known amounts at the inlet. An example is OH (Tanner et al., 1997); a calibration source produces known amounts of OH by photolyzing the measured amount of H_2O present in the sampled air with 184.9 nm light of known intensity from a mercury lamp.

5.2. The testing of routine measurements

During the past twenty years enormous resources have been expended to develop the measuring techniques described above. These instruments have achieved the level of performance needed to accomplish many of the most demanding geophysical measurements. However, this level of performance is achieved with several attendant drawbacks: great instrument complexity, highly specialized and expensive components, extraordinary instrument maintenance, and careful and frequent calibration and zeroing procedures. The instrument performance described in the comparisons discussed in the preceding text required all of these resources. The instruments were usually maintained by the scientists that developed the technique and built the instrument. They had the care of individuals who were staking their professional reputation on the results that were obtained. They carefully reduced and interpreted their data, often using ancillary measurements and their experience and intuition to determine if the instrument was operating properly and if the measurements were reliable. It is little wonder that these instruments do not perform to expectation when operated by individuals who are less trained, lack the scientific background to understand the demands that will be placed on the measurements, or are isolated from the data analysis and interpretation.

Clearly, the first information emerging from data reduction and interpretation is the quality of the instrument performance. A recent study of several NMHC data sets provides a case study of this truism (Parrish et al., 1998). Most reported NMHC measurements have been made using gas chromatography with flame ionization detection. The FID technique, while rugged and reliable, is non-specific. This introduces the opportunity for errors due to failure of the GC to uniquely resolve the FID-responsive compounds that enter the detector. Often before analysis, samples are stored in metal containers or on absorbent traps. In addition, to detect trace compounds, samples are cryogenically concentrated. Each of these steps introduces additional sources of possible error. Not surprisingly, when data sets employing these methods are analyzed, the analysis often casts suspicion on the claimed accuracy of the results.

The emission of NMHCs into the atmosphere is followed by their photochemical processing and dilution. In spite of the uncertainties associated with the mixture of compounds expected from the wide variety of sources and with the chemical and physical processes responsible for their dispersal in and removal from the atmosphere, common patterns still should be expected in NMHC measurements. Parrish et al. (1998) presented five specific tests that can be used to determine the representativeness and/or credibility of NMHC measurements collected in North America. The five tests were: (1) a lower limit for ethane concentrations, (2) a list of NMHCs that should typically be found to be detectable in North American continental air samples, (3) relative consistency in the ratio of concentrations of longer lived NMHCs with similar lifetimes and similar sources, (4) consistency in patterns of the concentrations of families of NMHCs and (5) limits on the variability in the ratios of concentrations of NMHCs. Although non-representativeness of the
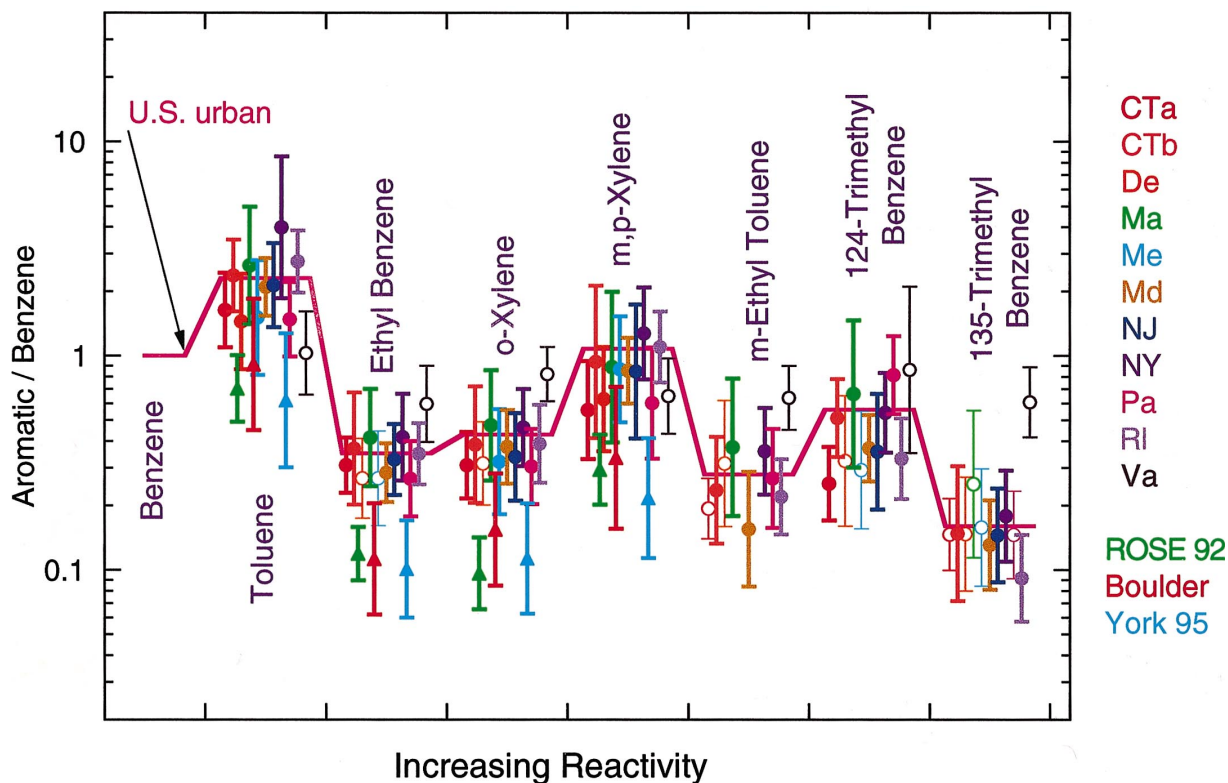
Fig. 7. Log plot of ratios of aromatic NMHCs to benzene in order of increasing OH reactivity of the aromatic. Each symbol and error bar give the geometric mean and standard deviation for the labeled ratio and the color indicated data set. The color key is given on the right; the PAMS and research data sets are indicated by circles and triangles, respectively. The symbol is closed only if more than 50% of the measurements find both NMHCs of the ratio above the detection limit. The ratios of the urban medians from Seila et al. (1989) are indicated by the solid line through the data.

emission sources is a valid reason why a set of measurements may fail one or more of these tests, in the cases where measurements were reevaluated, experimental problems were usually found to have caused the failure (Parrish et al., 1998).

Figs. 7 and 8 present an example of these tests applied to 16 data sets: 11 from Photochemical Assessment Monitoring Stations (PAMS) and 5 research data sets. The PAMS data are for August 1985 from stations included in the data base of the North American Research Strategy for Tropospheric Ozone (NARSTO) program for their Northeast 1995 Summer Ozone Study. They are labeled by the state in which the station was located. (Connecticut had 2 stations that are included separately, and Massachusetts had 4 stations that are included as a single data set.) These PAMS data were collected by automatic GC/FID systems described in Section 2.2.2 above. The research data sets (summarized in Table 2) were collected by groups that used state-of-the-art techniques to collect the highest quality data possible. Considerable resources were put into perfecting the

experimental techniques and reducing the collected chromatograms to ambient concentration values. With one exception, the data span relatively limited time periods, since the data collection and reduction is quite labor intensive. However, the Harvard Forest site is operated on a continuous basis; only the results from August 1995 from that site will be considered here.

The hypotheses upon which these tests are based are: (1) in all ambient measurements, the anthropogenic NMHC data should reflect urban concentration patterns, modified by dilution and photochemical removal, and (2) deviations from this expectation likely are due to measurement problems. The urban patterns of NMHC have been established by a large number of urban studies. Seila et al. (1989) analyzed 800 ambient air samples from 39 US cities. The median concentrations of the 48 compounds seen at the highest ambient levels are reproduced in Table 1 of Seinfeld (1989); they are assumed to characterize the urban concentration pattern. The ratios of these median concentrations will be compared with the measured ratios of ambient concentrations. These ratios
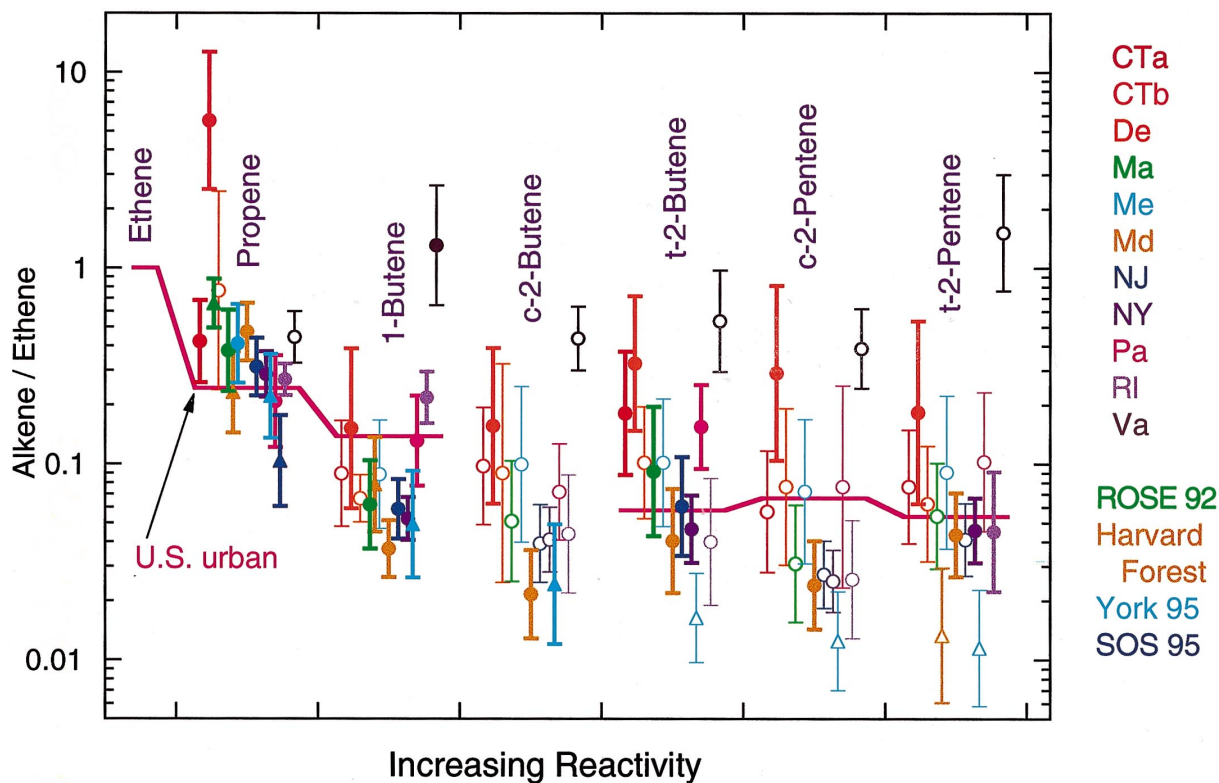
Fig. 8. Log plot of ratios of alkenes to ethene in order of increasing OH reactivity of the alkene. The format of the plot is described in the caption to Fig. 7. The gap in the ratios of the urban medians at the c-2-butene ratio occurs because this NMHC is not listed in the top 48 most abundant NMHC by Seila et al. (1989).

Table 2
Research data sets used for NMHC pattern evaluation

Data set	Research group	Study period, method, site type and location
ROSE 92	NOAA AL[a]	11/5–4/7 1992 – in situ GC/FID Rural surface site in Southern US
Boulder	NOAA AL[a]	3/2–15/2 1991 – in situ GC/FID Suburban surface site in Western US
York 95	York Univ[b]	26/6–20/7 1995 – canisters – GC/FID Aircraft collection in Southern US
SOS 95	NOAA AL[a]	7/6–22/7 1995 – in situ GC/FID Aircraft in Southern and Western US
Harvard Forest	Harvard Univ[c]	August 1995 – in situ GC/FID Rural surface site in Northeastern US

[a] For experimental details see Goldan et al. (1995).
[b] For experimental details see Young et al. (1997).
[c] For experimental details see Goldstein et al. (1995).

are expected to remain constant at the average emission ratio of the sources, except as the ratios are modified by the differential rate of photochemical removal of the NMHCs. The primary process for removal of NMHCs from the atmosphere is attack by OH radicals; the approximate summertime lifetimes of NMHCs span the range of tens of days for ethane at diurnally averaged OH to one hour or less at midday for the more reactive NMHCs.

The manifold of the aromatic NMHC ratios to benzene is examined in Fig. 7. Since the least reactive aromatic NMHC, benzene, is placed in the denominator of each ratio, photochemical removal is expected to decrease each ratio. The research data sets show, on average, significant evidence for photochemical processing — factors of 3–5 reduction in the concentration of the more reactive aromatic relative to benzene from the ratio of the urban medians. In contrast, the PAMS data show no consistent indication of photochemical processing. Remarkably, every mean ratio in every data set (except one) agrees with the ratio of the urban medians to within a factor of 2. The one exception is the Va site, which is evidently affected by some systematic error throughout the aromatic measurements. The generally excellent agreement between the ambient PAMS data and the urban median ratios is unexpected. At least some of the PAMS sites are located where fresh emissions are not

expected to dominate, especially during the photochemically active August period, and evidence for photochemical processing is expected as is seen for the research data sets. It may be that all of the selected PAMS stations are sited such that local, fresh automotive emissions dominate the aromatic NMHC concentrations. Alternatively, it could be that the adsorbent traps used in the PAMS systems are susceptible to contamination from the highest observed concentrations (i.e., the freshest emissions sampled), and that subsequent samples are contaminated. Such siting or measurements problems may well limit the usefulness of the PAMS data for evaluation of the areal NMHC levels, which is their intended purpose.

Fig. 8 compares the ratio of each alkene to ethene in all of the data sets. There is little consistency in the behavior of these data in contrast to the data in Fig. 7. Some systematic errors are obvious in data sets with ratios significantly above the US urban ratios, notably in the Ctb and Va sets generally and the Pa set, at least for t-2-butene. No consistent pattern of photochemical processing emerges in the PAMS data; propene appears generally too high, t-2-butene and t-2-pentene show generally no photochemical processing, while the other C_4 and C_5 alkenes seem to be aged. Substantial (approaching an order of magnitude) systematic errors are indicated in much of the PAMS alkene data. The research data sets seem to be in somewhat better agreement with expectations, but more detailed analyses (Parrish et al., 1998) indicate that many of these data suffer from systematic measurement errors as well. Indeed, it is not clear that any measurement technique reliably measures ambient alkenes.

In summary, the most pressing issue in the measurement of gas-phase NMHC species in the troposphere is the need for a rigorous, formal intercomparison of field measurements. Only then can the evident systematic measurement errors be reliably quantified, and the reliability of the techniques adequately assessed.

6. Conclusions

6.1. NO_y compounds

- Validated techniques appear to be available with adequate sensitivity to reliably measure NO, NO_2, and PAN throughout the troposphere.
- The available technique for PAN measurements does not provide for continuous acquisition of data. This limits the information that can be obtained when an instrument is operated from an aircraft.
- Chemiluminescence detectors for NO equipped with photolytic converters for NO_2 seem satisfactory for the measurement of the NO_x (NO + NO_2) throughout the troposphere. The measurements, while reliable,

are not routine. The instrumentation for measurements in the remote troposphere or from aircraft platforms are expensive and demanding.
- Alkyl nitrate techniques should be intercompared, and methods for measurement of multi-functional organic nitrates are required.
- New methods for the fast response measurement of HNO_3 are emerging, but reliable inlet systems, particularly for aircraft, remain a critical issue.
- Uncertainties in reported HONO levels clearly demonstrate the need for an intercomparison of measurement techniques for this species.
- Conversion of reduced nitrogen species (NH_3 and HCN) to NO on NO_y converters has been noted. However, these interferences may only constitute a problem for NO_y measurements that are made in remote regions. The performance of NO_y converters must be monitored regularly by standard additions through the inlet of a variety of NO_y species and possible interferants.

6.2. Carbon monoxide and volatile organic compounds

6.2.1. CO
- Commercial instruments using non-dispersive infrared absorption (NDIR) can monitor CO mixing ratios at continental surface sites.
- Fast response instruments [TDLAS, differential absorption CO measurement (DACOM) and resonance fluorescence (VUV)] having suitable sensitivity and rapid response are available for airborne measurements throughout the troposphere.
- Grab samples analyzed by GC techniques have proven valuable for characterizing latitudinal and seasonal variations of CO.

6.2.2. NMHC
- Although much has been done to ensure the integrity of NMHC measurements using canisters, difficulties associated with the stability of the sample during collection, transport and storage remain. When canisters are utilized for NMHC sample collection, some decreases (particularly of the heavier NMHCs) and increases (particularly of the alkenes) can be expected.
- The results from the canister samples depend on the history of use and handling. Contamination due to sampling of particularly polluted air or improper handling may leave residues that can influence the determination of some or all NMHCs.
- New specialized technology is emerging that offer the possibility of fast response, continuous measurements of certain key hydrocarbons (e.g., isoprene and monocyclic aromatic compounds).
- The first three stages of an international campaign to compare NMHCs have been completed. For samples

of synthetic air containing a wide range of compounds at the ppbv level, the overall accuracy and the precision seems good for many participating laboratories, but poorer for others.

- Routine measurements of NMHCs may have unacceptably large uncertainties due to experimental difficulties or non-representative site selection. Procedures have been devised to routinely check for these problems. These tests should be incorporated on-line into routine measurement programs.
- A field intercomparison including simultaneous ambient measurements to determine the capability of existing and emerging technology is probably the most critical need of the atmospheric measurement community.

6.2.3. CH_2O
- Several techniques are capable of measuring CH_2O in the troposphere, but attention must be paid to problems with interferences and/or blank levels.
- Through-the-inlet calibration with standard additions of gas-phase CH_2O is essential.
- Development of reliable calibration standards is important.

6.2.4. Alcohols and higher carbonyls
- Atmospheric measurements of the concentration of the carbonyls have been made for several years using 2,4-dinitrophenylhydrazine (DNPH). There remain questions concerning the reliability of the method to accurately measure the higher carbonyls in the presence of O_3 and other oxidants.
- Atmospheric measurement of the concentrations of the carbonyls and alcohols have been made using GC-FID and GC-MS.
- Chemical ionization mass spectrometry (CIMS) offers an attractive new approach to measure these compounds.
- Through-the-inlet calibration with standard additions of the carbonyls and alcohols is essential.
- Development of reliable calibration standards is important.

6.2.5. Organic acids
- Development of reliable, validated techniques is required.

6.2.6. Total non-methane organic carbon
- Measurements of the total atmospheric burden of organic carbon (excluding methane) provides a useful check upon speciated VOC measurements.
- Radiocarbon analysis of TNMOC potentially provides an indication of the contributions of biogenic versus anthropogenic sources of VOCs.
- A great deal of work remains before these measurements can be considered reliable.

6.3. Oxidants

6.3.1. O_3
- In situ measurement of O_3 can be made accurately and routinely with chemiluminescence and commercial instruments in non-urban areas.
- LIDAR techniques have been improved sufficiently so that O_3 profiling is becoming an increasingly attractive measurement tool.
- The veracity of urban O_3 measurements by UV absorption instruments has been questioned. Intercomparisons of O_3 measurement techniques during summer in high pollution regions are critically required to answer these questions.

6.3.2. OH
- Significant progress has been made in the development of new methods to measure OH.
- Intercomparisons have indicated that long path absorption (LPA), laser induced fluorescence (LIF-FAGE), and chemical ionization mass spectroscopy (CIMS) appear to be capable of measuring OH at levels observed in the troposphere.
- Issues of calibration for in situ measurements are being addressed.

6.3.3. HO_2 and RO_2
- Significant headway has been made in the development of new methods to measure HO_2 and RO_2. However, measurement differences determined by the comparisons that have been performed indicate that important issues remain.
- Calibration of measurements remains a significant problem.
- Within the precision and accuracy of the determinations, the imbalance of the photochemical stationary state can be attributed solely to HO_2 and RO_2.

6.3.4. H_2O_2 and other peroxides
- Significant developments have been made to measure H_2O_2 and other peroxides. However, intercomparisons indicate that important problems remain.
- Through the inlet calibration with standard additions of H_2O_2 and, where appropriate, other peroxides is essential.

6.4. Gas-phase aerosol precursors

6.4.1. NH_3
- Measurements made using the more sophisticated LIF technique and the more simplistic citric acid coated denuder tube compare well.
- A CIMS technique offers exciting new possibilities.
- Reliable inlet systems remain a critical issue.

6.4.2. Sulfate precursor compounds

- Recent intercomparisons indicate considerable advance in the measurement of sulfur compounds.
- Reliable calibration standards remain a problem.

6.4.3. H_2SO_4

- Fast response measurements of gas phase H_2SO_4 from ground sites and aircraft platforms have been reported using CIMS.

6.5. Calibrations

- Through-the-inlet calibration at near ambient concentrations of the compounds of interest is essential to determine instrument performance and to ensure instrument accuracy.

6.6. Testing of routine measurements

- In some cases, such as NMHC measurements, very useful internal consistency checks can be applied to data sets to check for potential problems.

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