



Figure 3-24. Estimated biogenic emissions of volatile organic compounds in the United States as a function of season.

Source: Fehsenfeld et al. (1992).

summertime anthropogenic VOC effect should be somewhat larger for southern regions. This is a very small change, however, relative to the uncertainty associated with VOC emission estimates. In an earlier discussion of the NAPAP inventory, VOC emissions from manmade sources were considered to be almost independent of season.

Increases in O_3 precursor emissions during the peak O_3 season will have a tendency to enhance O_3 production. Ozone production in rural areas is usually NO_x -limited (Fehsenfeld et al., 1992). Thus, enhanced summertime emissions of NO_x from soils and lightning will add NO_x to the atmosphere in rural regions, which in turn will lead to the production of more O_3 . Larger summertime emissions of VOCs will enhance O_3 production in urban areas. Biogenic VOC sources in the vicinity of urban areas can contribute significant quantities of reactive hydrocarbons to the urban O_3 precursor mix (Cardelino and Chameides, 1990).

3.4.2 Concentrations of Precursor Substances in Ambient Air

The volatile organic compounds, excluding CH_4 , often are referred to as NMOCs. The class of NMOCs most frequently analyzed in air are the nonmethane hydrocarbons (NMHCs). The NMHC measurements often provide an acceptable approximation of the NMOCs. The NMHCs and the NO_x within urban areas tend to have morning concentration peaks. These result from vehicular traffic in combination with limited mixing depths. Later in the morning into the afternoon hours, concentrations of NMHCs and NO_x decrease, but to varying extents (Purdue et al., 1992), because of chemical reactions and increases in mixing depths and consequent increases in dilution volumes. Photochemical

atmospheric reactions also can rapidly convert NO to NO₂, and hydrocarbons to carbonyls, PANs, and other products (Sections 3.2.4, 3.4.2.1, and 4.9). Late afternoon and early evening peaks might be expected in NMHC and NO_x concentrations because of increased vehicular traffic at urban locations, but such increases often are not discernible (Purdue et al., 1992). This effect probably results from the presence of substantial mixing depths in the warmer months that persist through these hours in many urban locations.

Because of the emphasis on early morning inputs of NMOCs and NO_x for models such as the Empirical Kinetics Modeling Approach (EKMA), most of the measurements available emphasize the 6 a.m. to 9 a.m. period. The variations in the concentrations of NMOCs and NO_x, their ratios, and the composition of NMOCs are important factors in the generation of O₃ and other photochemical products.

3.4.2.1 Nonmethane Organic Compounds

In earlier measurements based on GC analyses made during a number of different studies in urban areas between 1969 and 1983, the mean 6 a.m. to 9 a.m. NMHC concentrations were reported to range from 0.324 to 3.388 ppm carbon (ppmC) (U.S. Environmental Protection Agency, 1986a). The highest NMHC concentrations were those measured at sites in Los Angeles.

A program for analysis of NMOCs and NO_x in the months of June through September was conducted in a considerable number of U.S. cities during the 1980s. The results obtained from measurements made during the 6 a.m. to 9 a.m. period at sites in 22 cities in 1984 and 19 cities in 1985 have been subjected to statistical analysis and interpretation (Baugues, 1986). The total NMOC measurements throughout the June through September periods in these cities were obtained by the cryogenic preconcentration-direct flame ionization detection method (PDFID) (McElroy et al., 1986). In addition, during about 15% of the 6 a.m. to 9 a.m. periods, canister samples were collected for subsequent GC analysis (Seila et al., 1989). In 1984, the lowest median NMOC value obtained was 0.39 ppm C from measurements in Charlotte, NC, whereas the highest median NMOC value obtained was 1.27 ppmC from measurements in Memphis, TN. In 1985, the lowest median NMOC value obtained was 0.38 ppmC from measurements in Boston, MA, whereas the highest median NMOC value obtained was 1.63 ppmC in Beaumont, TX. The overall median values from all urban sites were approximately 0.72 ppmC in 1984 and 0.60 ppmC in 1985 (Baugues, 1986). The GC analyses made on samples collected in 1984, 1985, and 1986 have been reported (Seila et al., 1989). The more abundant individual hydrocarbons include C₂-C₆ alkanes, C₂-C₅ alkenes, C₆-C₉ aromatics, and acetylene. Based on the 48 most abundant concentrations, the overall median concentrations by class of hydrocarbon (NMHCs) were as follows: paraffins, 0.266 ppmC, 60% of total; aromatics, 0.166 ppmC, 26% of total; olefins, 0.047 ppmC, 11% of total; and acetylene, 0.013 ppmC, 3% of total (Seila et al., 1989). Additional individual NMHCs (totaling about 0.100 ppmC) were detected at concentrations \leq 0.002 ppm C each. Most of these compounds were identified by class but not by structure.

Detailed hydrocarbon analyses for C₂-C₁₀ NMHCs were obtained during the 17 intensive days of the Southern California Air Quality Study (SCAQS) in 1987 (Lonneman et al., 1989; Rasmussen, 1989; Stockberger et al., 1989). The average percentage ambient composition from eight Southern California sites during 11 intensive sampling days of the summer of 1987 by class of NMHCs were as follows: paraffins, 53.4; aromatics, 27.2; olefins, 12.1; carbonyls, 7.7 (Main and Lurmann, 1993).

In Atlanta, during the summer of 1990, hydrocarbon concentrations were measured at six sites with automated GCs. Results were reported on 54 hydrocarbons, with 24-h average concentrations ranging from 0.186 to 0.397 ppmC (Purdue et al., 1992).

A comparison of NMHC measurements made by GC analyses over a period of years in Los Angeles and in the New York City area has been reported (Lonneman and Seila, 1993). In the Los Angeles area, the NMHC concentrations averaged 2.81 ppmC in 1968, compared to 1.02 ppmC in 1987. In the New York City area, the NMHC concentrations averaged about 1.1 ppmC in 1969, compared to 0.62 ppmC from 1986 to 1988. In both the Los Angeles and New York areas, there were significant decreases in NMHC concentrations as well as compositional changes in NMHCs during these years, with increases observed in the percentage of paraffin hydrocarbons and decreases in the percentage of aromatic hydrocarbons and acetylene (Lonneman and Seila, 1993).

Aldehydes and ketones occur in urban air as O₃-oxidant precursors from emissions such as vehicular exhaust and as products of reactions of OH radicals with NMHCs, reactions of alkenes with O₃, and, at night, reactions with NO₃ radicals. Early morning aldehyde concentrations have been predicted to result to a greater extent from atmospheric reactions of alkenes than from emission of vehicular exhaust (Altshuller, 1993). During the day, aldehydes and ketones are rapidly produced from reactions of OH radicals with aliphatic and aromatic hydrocarbons and of alkenes with O₃. Carbonyl concentrations tend to increase through the daytime hours (Grosjean, 1982, 1988; Grosjean et al., 1993b).

Measurements of ambient air concentrations of carbonyls indicate the total loading of aldehydes and ketones from all processes. Ambient urban air concentrations of HCHO and total aldehydes were tabulated for the 1960 to 1981 period (Altshuller, 1983a). Subsequent studies by 2,4-dinitrophenylhydrazine high-performance liquid chromatography (DNPH-HPLC) techniques (Section 3.5.2.3) have shown consistently that HCHO and acetaldehyde are the most abundant aldehydes; however, a number of other carbonyls (including propanal, acrolein, acetone, butanal, crotonaldehyde, methyl ethyl ketone, pentanal, hexanal, benzaldehyde, and tolualdehyde) also have been measured (Fung, 1989; Grosjean 1982, 1988, 1991; Kalabokas et al., 1988; Zweidinger et al., 1988). The ratios of HCHO to acetaldehyde concentrations (in parts per billion volume) can vary from less than 0.5 in cities in Brazil, where there is high use of ethanol fuels, up to 4.0 to 5.0 at a few urban sites (Grosjean et al., 1993). However, at most urban sites, the ratios of HCHO to acetaldehyde concentrations occur in the 1.0 to 3.0 range.

A compilation of the maximum, average range of HCHO concentrations from many studies in Southern California carried out between 1960 and 1989 is available (Grosjean, 1991). A downward trend in HCHO concentrations occurs, probably because of decreased production from precursor alkenes and decreased emission in vehicular exhaust (Sigsby et al., 1987; Dodge, 1990). For example, the maximum HCHO concentrations decreased from above 100 ppbv in the 1960s to the 10- to 30-ppbv range during the last decade (Grosjean, 1991). In other U.S. cities in the early 1980s, the maximum HCHO concentrations ranged from 5 to 45 ppb (Salas and Singh, 1986).

Several studies have reported concurrent morning hydrocarbon and carbonyl concentrations in downtown Los Angeles (Grosjean and Fung, 1984); Raleigh, NC (Zweidinger et al., 1988); and Atlanta (Shreffler, 1992; Grosjean et al., 1993b). The average percentage of carbonyls relative to total NMHCs were reported as follows: Los Angeles, 3%; Raleigh, 2%; and Atlanta, 2% (formaldehyde + acetaldehyde concentrations) at two different

sampling sites. In SCAQS, carbonyls were measured at eight sites in the summer and five in the fall of 1987 (Fung, 1989; Fujita et al., 1992). The average percentage of C₁ to C₆ carbonyls relative to NMHCs was 7.6% in the summer and 3.7% in the fall.

Compilations of NMHC concentrations of nonurban and remote locations are available (U.S. Environmental Protection Agency, 1986a; Altshuller, 1989a). Total NMHC concentrations reported ranged from less than 0.01 to 0.14 ppmC. At remote locations over the Pacific, NMHC concentrations generally were less than 0.01 ppmC. Over both continental and oceanic locations there can be contributions from biogenic sources of NMHCs.

Interest in the contribution of biogenic hydrocarbons has existed for many years, and earlier work has been reviewed (Altshuller, 1983b). Photochemical modeling in the United States predicts significant effects of biogenic hydrocarbons on O₃ production (Chameides et al., 1988; Roselle et al., 1991). Similar modeling of the effect of biogenic hydrocarbons on O₃ production within urban plumes over southeastern England predicted a 2- to 8-ppb increase in plume and background O₃ concentrations (MacKenzie et al., 1991). Because of lower emissions of biogenic and lower overall NMOC/NO_x ratios, O₃ production over southeastern England is predicted to be limited by the availability of anthropogenic hydrocarbons.

Compilations of results of earlier measurements of isoprene and terpene concentrations are available (Altshuller, 1983b; U.S. Environmental Protection Agency, 1986a). Average concentrations of isoprene ranged from 0.001 to 0.020 ppmC and terpenes from 0.001 to 0.030 ppmC. When concurrent measurements of biogenic and anthropogenic NMHCs were available, the biogenic NMHCs usually constituted much less than 10% of the total NMHCs (Altshuller, 1983b).

Among more recent studies are two investigations of terpene and isoprene emissions in the central valley of California and in Louisiana (Arey et al., 1991b; Khalil and Rasmussen, 1992). Both studies reported a large number of individual terpenes, measured by using enclosure methods. When ambient air measurements were made, most of the terpenes measured in the enclosures were not detectable (Khalil and Rasmussen, 1992). In ambient air, isoprene was the predominate hydrocarbon, accounting on average for 70% of the biogenic species and 36% of NMOCs. It has been concluded that the bag enclosure method can lead to large overestimates in biogenic emissions (Khalil and Rasmussen, 1992).

In two other recent studies in deciduous forests, the isoprene oxidation products were measured as well as isoprene itself (Pierotti et al., 1990; Martin et al., 1991). Both studies report the ambient concentrations of methacrolein and methyl vinyl ketone. In an investigation in a central Pennsylvania deciduous forest in the summer of 1988, average midday concentrations of isoprene were in the 0.005- to 0.010-ppmC range; whereas the corresponding concentrations of methacrolein and methyl vinyl ketone were in the 0.001- to 0.002-ppmC range (Martin et al., 1991). In the study conducted in California forests with samples collected between noon and 4:00 p.m. in late spring and summer, the upper quartile of isoprene concentrations was within the 0.010- to 0.025-ppmC range, whereas methacrolein concentrations were within the 0.001- to 0.003-ppmC range, and methyl vinyl ketone concentrations were within the 0.0005- to 0.0015-ppmC range (Pierotti et al., 1991).

Higher-molecular-weight semivolatile carbonyls have been measured in a number of rural-remote areas (Jüttner, 1986; Yokouchi et al., 1990; Nondek et al., 1992; Ciccioli et al., 1993). The compounds identified include C₅-C₁₂ aliphatic aldehydes, aliphatic ketones, and aromatic aldehydes. Comparisons of the measurement of these carbonyls relative to aromatic

hydrocarbons in two studies indicated higher carbonyl concentrations and much lower aromatic hydrocarbon concentrations in the rural-remote sites compared to the urban areas (Yokouchi et al., 1990; Ciccioli et al., 1993). Widely varying natural sources have been associated with these carbonyls, including emissions from forest species (Nordek et al., 1992) and short vegetation (Ciccioli et al., 1993) and as secondary products of natural emissions of terpenes (Ciccioli et al., 1993) or oleic acid (Yokouchi et al., 1990). Among other oxygenates reported to be of natural origin are higher-molecular-weight alcohols (Jüttner, 1986; Nordek et al., 1992; Goldan et al., 1993). These oxygenates contribute to the "Other VOCs" category in the biogenic emissions inventory (Section 3.4.1.3).

In an urban-scale study in Atlanta during the summer of 1990 (as part of the Southern Oxidant Study), isoprene concentrations rose in late morning and into the afternoon, with early evening peaks observed at residential and rural-residential sites (Purdue et al., 1992). A similar diurnal profile for isoprene was observed at a Pennsylvania forest site (Martin et al., 1991). The median concentration at the sampling sites in Atlanta early in the evening ranged from 0.006 to 0.020 ppmC. The isoprene as a percentage of total NMHCs in the early evening ranged among the sites from 2 to 12% (Shreffler, 1992).

3.4.2.2 Nitrogen Oxides

Measurements of NO_x were obtained with continuous NO_x analyzers at sites in 22 and 19 U.S. cities during the months of June through September of 1984 and 1985, respectively. These results have been evaluated and the 6 a.m. to 9 a.m. values tabulated (Baugues, 1986). In 1984, the lowest median NO_x concentration of 0.010 ppm was obtained from measurements in West Orange, TX; whereas the highest median NO_x concentration of 0.088 ppm was obtained from measurements in Memphis. In 1985, the lowest median NO_x concentration of 0.005 ppm was obtained from measurements in West Orange, whereas the highest median NO_x concentration of 0.100 ppm was obtained from measurements in Cleveland, OH. The median NO_x concentration values for sites in most of these cities in 1984 and 1985 ranged between 0.02 and 0.08 ppm. Because of high vehicular emission rates and shallow mixing depths, the median 6 a.m. to 9 a.m. concentration values in many of these cities exceeded the annual average NO_x values of 0.02 to 0.03 ppm in U.S. metropolitan areas between 1980 and 1989 (U.S. Environmental Protection Agency, 1991a). In the 1990 Atlanta study, the average summer NO_x concentration values at the six study sites ranged from 0.011 to 0.026 ppm (Purdue et al., 1992).

At nonurban sites, NO_x concentrations have been reported as mean 24-h seasonal or annual NO_x values. The available results have been compiled for work reported through 1983 (Altshuller, 1986). The average seasonal or annual NO_x concentrations ranged from less than 0.005 to 0.015 ppm. At remote sites in the earlier investigations, monthly average NO_x concentrations were less than 0.001 ppm. In more recent work, the statistics on NO_x concentrations have been reported for several relatively remote U.S. sites (Fehsenfeld et al., 1988). The 24-h average NO_x concentrations and the range in the central 90% of values were as follows: Point Arena, CA, spring 1985, 0.0004 ppm, 0.0007 to 0.001 ppm; Niwot Ridge, CO, summer 1985, 0.0005 ppm, 0.0001 to 0.002 ppm; and Scotia, PA, summer 1986, 0.002 ppm, 0.0007 to 0.009 ppm. It should be noted that each of these sites can be subject to anthropogenic influences, thus accounting for the higher NO_x values. For example, at Niwot Ridge, CO, with upslope flow from the Denver-Boulder, CO, urban area, higher NO_x

concentrations are measured. Nitrogen oxide concentrations at or below 0.0001 ppm occur at other remote surface locations (Fehsenfeld et al., 1988).

3.4.2.3 Ratios of Concentrations of Nonmethane Organic Compounds to Nitrogen Oxides

The ratios of 6 a.m. to 9 a.m. NMOC/NO_x have been obtained from the measurements in the U.S. cities discussed above (Baugues, 1986). In 1984, the lowest median NMOC/NO_x ratio of 9.1 was obtained in Cincinnati, OH, and the highest median NMOC/NO_x ratio of 37.7 was obtained in Texas City, TX. In 1985, the lowest median NMOC/NO_x ratio of 6.5 was obtained in Philadelphia, PA, whereas the highest median NMOC/NO_x ratio of 53.2 was obtained in Beaumont, TX. The range in daily 6 a.m. to 9 a.m. NMOC/NO_x ratios within a given city is large, with 10th percentile to 90th percentile NMOC/NO_x ratios varying usually by factors of 2 to 4 and, at several sites, by factors of 5 to 10 (Baugues, 1986). There appears to be a tendency for higher NMOC/NO_x ratios in the cities included in the southeastern (9) and southwestern (15) United States than in the northeastern (7) and midwestern United States (7) (Altshuller, 1989b). The NMOC-to-NO_x ratios at rural sites tend to be higher than the mean NMOC-to-NO_x ratios in urban locations, with mean values at several rural sites ranging between 20 and 40 (Altshuller, 1989b).

In SCAQS, the ambient NMOC (NMHCs + carbonyl)/NO_x ratios averaged 8.8 in the summer and 6.9 in the fall of 1987 (Fujita et al., 1992). However, the 6 intensive days in the fall between November 11 and December 11 were not characterized by elevated O₃ concentrations (Zeldin, 1993). These ambient ratios were 2 to 2.5 times higher than the corresponding emission inventory ratios. Discrepancies as large or larger have been discussed previously for urban and rural NMHC/NO_x ambient-to-emission ratios in the eastern United States (Altshuller, 1989b).

A trend analysis of NMHC/NO_x ratios in the South Coast Air Basin is available for the 1976 to 1990 period (Fujita et al., 1992). The ratios were consistently higher in the summer than in the fall. These ratios started decreasing slowly during the 1980s, from maximum ratios of about 12 in the summer and 9 in the fall to 8.5 in the summer and 7 in the fall by 1990. The ambient-to-emission inventory ratios over this period ranged from as high as 3.4 in the summer to 1.7 in the winter (Fujita, 1993).

Interest in the 6 a.m. to 9 a.m. NMOC/NO_x ratios is associated with their use in the EKMA type of trajectory model (Section 3.6.1.2). The analysis at 10 eastern and midwestern sites of upper-quartile O₃ days relative to other O₃ days indicated a significant difference ($p \leq 0.10$) by the two-sample Wilcoxon Rank Sum test at four of the 10 sites with NMOC/NO_x ratios (Wolff and Korsog, 1992). However, the correlation of NMOC/NO_x ratios with maximum 1-h O₃ concentrations was very weak. It was concluded that the use of the 6 a.m. to 9 a.m. NMOC/NO_x ratio in EKMA will not provide sufficient information to distinguish among NMOC, NO_x, or combined VOC-NO_x strategies as optimum strategies for urban areas.

A compilation of VOC/NO_x ratios between 1981 and 1988 in 10 cities in the northeastern and midwestern United States presents ratios ranging from 5.8 to 11.5, but generally below 10 (Wolff, 1993). Trends between 1986 and 1991 in VOC/NO_x ratios in four of these cities; New York; Newark, NJ; Philadelphia; and Washington, DC, show downward trends towards VOC/NO_x ratios between 4 and 6 (Zalewsky et al., 1993; Wolff, 1993). For Philadelphia, and the other sites, the downward trend in VOC/NO_x is associated with decreasing VOC concentrations with little change in NO_x (Zalewsky et al., 1993; Wolff,

1993). It has been pointed out that, in the National Academy of Science report (National Research Council, 1991), hydrocarbon control is considered more effective for VOC/NO_x ratios of about 10 or less, whereas NO_x control is considered more effective for VOC/NO_x ratios of 20 or more. Based on these results, it may be concluded that, in many cities in the northeastern and midwestern United States, continued VOC control, rather than NO_x control, will be more effective in reducing O₃ (Wolff, 1993). It also has been concluded by Wolff (1993) that models with greater spatial resolution than the Regional Oxidant Model (ROM), such as the UAM, are more applicable than ROM for determining appropriate O₃ control strategies in urban areas.

3.4.3 Source Apportionment and Reconciliation

3.4.3.1 Source Apportionment

Source apportionment refers to determining the quantitative contributions of sources to ambient air pollutant concentrations. In principle, it includes two fundamentally different approaches: (1) source-oriented and (2) receptor-oriented. In the source-oriented approach, a mathematical dispersion model is applied to an emissions inventory and meteorological data to produce an estimate of ambient pollutant concentrations that can be expected at a specified point in space and time. In contrast, the receptor-oriented approach depends on simultaneous ambient concentration measurements of a variety of pollutant species and a knowledge of the relative amounts of the species (source profiles) that are present in the emissions of the sources that are potential contributors. A mathematical receptor model operates on the source profile and ambient species concentration information to deconvolute the ambient concentrations into their source contributions, without the need of emissions inventory or meteorological information. Indeed, the desire to avoid the latter two kinds of information, whose acquisition is often problematical, has been an important motivation in the development of the receptor-oriented approach.

Although source apportionment, in its general sense, embraces both approaches, in recent years, it has come to be regarded as synonymous with the receptor-oriented approach (receptor modeling). The equivalence of source apportionment and receptor modeling is assumed in the following discussion. The most recent review of the field of receptor modeling has been given by Gordon (1988).

Because tropospheric O₃ is a secondary pollutant, the natural role of receptor modeling is in determining the quantitative source contributions of the VOC precursors of O₃. Historically, receptor modeling was first developed in the 1970s for the apportionment of ambient aerosol, and aerosol applications since then have been more extensive than VOC applications. The aerosol and VOC areas of receptor modeling application have more similarities than differences, however, so that much of the mathematical apparatus that has been developed for aerosol problems is readily adaptable to VOCs.

For reasons that will become apparent, the separation of emissions sources into anthropogenic and biogenic classes is a natural division for VOC receptor modeling and is used in the following.

Manmade Sources of Volatile Organic Compounds

A principal approach for receptor modeling of anthropogenic VOC sources is that of "mass balance". In this approach, a particular linear combination of source profiles is sought that best approximates (in a linear least-squares sense) the profile of VOC species

concentrations measured in an ambient sample. Here a VOC source profile is defined as the set of numbers giving the fractional amounts (abundances) of individual species in the emissions from the source. The profile may be normalized to the sum of the abundances of all VOC species emitted by the source or to a sum over some arbitrary subset of species. For the linear combination of profiles that gives the best fit, the coefficients are the source strengths (in the same units as the measured ambient concentrations) associated with each of the included source profiles.

Early efforts to use various versions of the mass balance approach include Ehrenfeld (1974), Mayrsohn and Crabtree (1976), and Mayrsohn et al. (1977) in Los Angeles and Nelson et al. (1983) in Sydney, Australia.

Of these studies, the work of Mayrsohn et al. (1977) is the most comprehensive: 900 samples from eight sites collected during June to September, 1974. The average results were automotive exhaust, 53%; whole gasoline evaporation, 12%; gasoline headspace vapor, 10%; commercial natural gas, 5%; geogenic natural gas, 19%; liquefied natural gas, 1%. The percentages are for NMHCs through C_{10} (i.e., not all of the total VOCs).

Together, the estimates for the first three vehicle-related sources account for 75% of the ambient NMHCs, which is the approximate percentage estimated in the other studies listed. Geogenic natural gas is obviously not anthropogenic but is included here for completeness. Its strength of 19% is striking; however, it seems unlikely that a contribution this large would be typical of other locales lacking a petroleum-related geology. In any case, accounting for the urban atmospheric concentrations of ethane and propane (the main NMHC constituents of natural gas) has remained an unsatisfactorily resolved problem, so the 19% result for geogenic natural gas has to be regarded skeptically.

Although dated, these early studies are of more than just historical interest. In one respect, they are superior to more recent studies in their recognition of two distinctly different kinds of gasoline evaporation: (1) headspace vapor, which represents the partial evaporation of gasoline in situations such as storage tank evaporation or vehicle diurnal evaporation, characterized by an enrichment of high-volatility species; and (2) whole gasoline emissions, which can arise from spillage, leakage, and vehicle hot-soak emissions, and has a composition resembling liquid gasoline itself. The implications of gasoline evaporation are discussed below.

In the mid-1980s, a useful degree of standardization was incorporated into the mass balance approach by the introduction of EPA's chemical mass balance (CMB) software. The current version, CMB7 (Watson et al., 1990), embodies a comprehensive treatment of error (including uncertainty in both ambient data and source profiles) and many diagnostics (including profile collinearity) and has been used frequently in recent VOC receptor modeling studies.

Recent studies include Wadden et al. (1986) in Tokyo, Japan; O'Shea and Scheff (1988) in Chicago, IL; Aronian et al. (1989) in Chicago; Sweet and Vermette (1992) in Chicago and East St. Louis, IL; Harley et al. (1992) in Los Angeles; Kenski et al. (1993) in Chicago, Beaumont, Detroit, Atlanta, and Washington, DC; Spicer et al. (1993) in Columbus, OH; and Lewis et al. (1993) in Atlanta.

The source categories covered by these studies taken together include vehicle exhaust, gasoline evaporation (whole gasoline and headspace vapor), industrial emissions (refineries, coke ovens, and chemical plants), architectural coatings, dry cleaning, wastewater treatment, auto painting, industrial solvents/degreasers, graphic arts (printing), and natural

gas. Each study gives estimates for the percentage contributions to measured ambient VOCs (or related quantity) for a selected subset of these source categories. The one exception is the work of Sweet and Vermette (1992) that estimates the percentage source contributions to individual species, rather than to total VOCs. Such species apportionment is always available from the CMB calculations, but often is not reported explicitly.

Usually, the source profiles used were generic; that is, from compilations of source measurements taken elsewhere (U.S. Environmental Protection Agency, 1993d). The work of Lewis et al. (1993) is unique in the use of profiles extracted from the ambient air data themselves.

Generally, for these urban-based studies, vehicle exhaust is found to be the dominant contributor to ambient VOCs. Exceptions are the Tokyo results of Wadden et al. (1986) that show an unreasonably small average contribution of 7% and the Beaumont results of Kenski et al. (1993), 14%. For all the rest, the average vehicle exhaust results fall in the range of $45 \pm 15\%$.

The results for gasoline evaporation contribution estimates are much less satisfactory. This is because the recent studies, with the exceptions of Harley et al. (1992) and Lewis et al. (1993), included a gasoline headspace vapor profile but not a whole gasoline profile in their calculations. The latter two studies suggest that this omission is a serious error. For example, Harley et al. (1992) found a remarkably large whole gasoline contribution (nearly the same as that of vehicle exhaust), and Lewis et al. (1993) find a whole gasoline contribution that is about 20% that of vehicle exhaust. Both, however, find a whole gasoline contribution about four times greater than the headspace contribution. Because vehicle exhaust and whole gasoline profiles are quite similar (except for the very light species that are absent in gasoline but present in exhaust as combustion products), excluding the whole gasoline profile will tend to overestimate the exhaust contribution. Although this error may not greatly affect the total mobile-source-related emissions estimate, it is misleading with regard to implied control strategies.

Beyond the ubiquitous vehicle-related contributions, other anthropogenic source contribution estimates tend to be smaller or locale-specific.

Biogenic Sources of Volatile Organic Compounds

The possible role of biogenic VOC emissions in O_3 formation is being considered much more seriously now (Chameides et al., 1988) than was the case a decade ago. Because of the severe experimental problems in accurately measuring biogenic emissions directly, receptor modeling approaches are of considerable interest. Compared with anthropogenic sources, however, the application of receptor modeling methodology to biogenic sources has been very limited. The principal reason is that it has not been possible to find VOC species that are simultaneously distinctive components of biogenic emissions, emitted in an approximately fixed proportion to the total VOC biogenic emissions, and relatively unreactive. Without these conditions, the construction of a credible stable biogenic source profile is not possible, and, consequently, the CMB approach is unusable.

In this situation, a crude form of receptor modeling has been used in which the ambient concentration of a VOC species, whose only source is thought to be biogenic, is divided by the estimated abundance of the species in the total VOC biogenic emissions. Typical candidates include isoprene (deciduous emission) and the terpenes α - and β -pinene (coniferous emission), α -caranene, and limonene. Because these are all highly reactive, any

such estimate can be regarded only as a lower limit of the contribution that biogenic emissions make to total ambient VOC, if the loss resulting from atmospheric transformation is not taken into account. As an example, Lewis et al. (1993) used isoprene, the most prominent biogenic species measured in downtown Atlanta during the summer of 1990, to infer a lower limit of 2% (24-h average) for the biogenic percentage of total ambient VOC at that location. Isoprene emissions have a strong diurnal dependence. Lower limits for biogenic emissions at other hours, inferred from average isoprene concentrations, were 1% at 8:00 a.m., 5% at noon, 6% at 4:00 p.m., and 2% at 9:00 p.m.

The recent review article by Fehsenfeld et al. (1992) lists other prominent biogenic species and calls attention to the newly recognized importance of alcohols, such as methanol (CH_3OH), as biogenic primary emissions. Goldan et al. (1993) reported the C_5 alcohol, 2-methyl-3-buten-2-ol to be the most abundant VOC of biogenic origin present in a predominantly lodgepole pine forest in Colorado. Ciccioli et al. (1993) present data from sites in Germany and Italy showing substantial contributions from various aldehydes and argue that their dominant source is biogenic primary emissions, rather than photochemical oxidation products.

A more sophisticated form of biogenic receptor modeling involves the radiocarbon isotope ^{14}C . The approach depends on the fact that ^{14}C constitutes a nearly fixed fraction (approximately 10^{-12}) of all carbon present throughout the biosphere. In contrast, the ^{14}C in dead organic material older than 40,000 years, certainly the case for fossil fuels, has been reduced by at least 99% through radioactive decay. This leads to a simple estimate of the biogenic fraction of a carbon-containing sample given by f_s/f_0 , where f_s is the ^{14}C fraction in the sample, and f_0 is the ^{14}C fraction in living material. Besides its conceptual simplicity, the approach is appealing for VOC apportionment because ^{14}C retains its identity in the reaction products that may result from atmospheric transformation of reactive VOC. The method appears to be reliable for particulate phase organics (Lewis et al., 1988, 1991) but is still under development for VOC applications (Klouta et al., 1993).

3.4.3.2 Source Reconciliation

Source reconciliation refers to the comparison of measured ambient VOC concentrations with emissions inventory estimates of VOC source emission rates for the purpose of validating the inventories. Because concentrations and emission rates are specified in different units, the comparisons are done in terms of percentages: the percentage contribution of a source to ambient total VOCs as estimated by receptor modeling versus the emission rate of the source as a percentage of the total VOC emission rate of the inventory.

Nearly all the receptor modeling studies listed above have included such a percentage comparison. Typically, the agreement is quite good for vehicle exhaust, generally the dominant VOC source in urban airsheds. Gasoline evaporation comparisons are much less consistent, at least partly for the reasons already indicated. Typically, there is at least qualitative agreement for the other anthropogenic sources: they are small in the inventory, and the receptor-estimated contributions are small. An interesting exception is refinery emissions in Chicago (Scheff and Wadden, 1993), for which the receptor estimate was 7%, five times greater than the inventory estimate. Another is the significant (5 to 20%) natural gas/propane contribution estimated in Los Angeles, Columbus, and Atlanta but not reflected in their inventories. The few biogenic source estimates provided by receptor modeling are generally smaller than those given in emissions inventories, at least partly because of the previously

referred to reactivity problem. Credible ^{14}C measurements on VOC samples would be extremely helpful in validating the magnitude of the biogenic component of emissions inventories.

Lewis et al. (1993) has noted that comparisons based on percentages are quite insensitive for dominant source components, and the comparisons are more dependent on how "total VOC" is defined than is often appreciated (the definition varies for the studies listed). Thus, unfortunately, the generally good agreement (receptor versus inventory estimates) found for vehicle exhaust does not translate into a definitive judgment on the current concern that this source component may be significantly underestimated in existing inventories. For example, if the emission rate of vehicle exhaust in a typical inventory were arbitrarily doubled, the resulting change in the percentage of this component in the inventory is well within the range of what can be produced in the receptor estimate by merely choosing a different definition of total VOC from plausible alternatives. Such alternatives relate to questions such as which subset of hydrocarbons are summed? and whether unidentified chromatographic components are included in the sum? In the future, this situation can be improved by more consistency in the total VOC definition and by transforming the receptor modeling results from a concentration-based representation to an emission-rate one. This unavoidably involves introducing some limited meteorological information (Lewis and Conner, 1991).

3.5 Analytical Methods for Oxidants and Their Precursors

3.5.1 Sampling and Analysis of Ozone and Other Oxidants

3.5.1.1 Ozone

Introduction

The measurement of O_3 in the atmosphere has been a subject of research for decades because of the importance of this compound in atmospheric chemistry and because of its potential and demonstrated effects on human health and welfare.

Because of the importance of O_3 in the air of populated regions, widespread O_3 monitoring networks have been operated for many years, and the development of measurement and calibration approaches for O_3 has been reviewed extensively (e.g., U.S. Environmental Protection Agency, 1986a). This section focuses on the measurement of O_3 in the ambient atmosphere at ground level and summarizes the current state of ambient O_3 measurement and calibration. No attempt is made here to cover the full history of development of these methods because that has been documented elsewhere (e.g., U.S. Environmental Protection Agency, 1978, 1986a). Instead, this section concentrates on those methods currently used and on new developments and novel approaches to O_3 measurement.

Although no method is totally specific for O_3 , current methods for O_3 must be distinguished from earlier methods that measured "total oxidants". The wet chemical methods used earlier for total oxidants have been replaced for essentially all ambient measurements by two more specific instrumental methods based on the principles of chemiluminescence and UV absorption spectrometry. These two approaches are described below. In addition, recent developments in spectroscopic measurements, in other chemical approaches, and in passive sampling devices for O_3 are described.

Chemiluminescence Methods

Gas-Phase Chemiluminescence. The most common chemiluminescence method for O_3 is direct gas-phase reaction of O_3 with an olefin to produce electronically excited products, which decay with the emission of light. This approach was first used nearly 30 years ago for chemical analysis by Nederbragt (Nederbragt et al., 1965), and development of a portable monitor (Warren and Babcock, 1970) and application to atmospheric measurements (Stevens and Hodgeson, 1970) followed soon after. Typically, an O_3 monitor based on this approach functions by mixing a constant flow of about 1 L/min of sample air with a small constant flow ($\approx 50 \text{ cm}^3/\text{min}$) of ethylene. Mixing occurs in a small inert reaction chamber fitted with a sealed window through which light can pass to the photocathode of a photomultiplier tube. Electronically excited formaldehyde molecules, generated by a small fraction of the O_3 -ethylene reactions, produce a broad band of emission centered at 430 nm. The emission intensity is linearly proportional to the O_3 concentration over the range of 0.001 ppm to at least 1 ppm. Calibration of the monitor with a known O_3 source provides the relationship between monitor response and O_3 concentration. Detection limits of 0.005 ppm and a response time of less than 30 s are easily attained, and are typical of currently available commercial instruments.

Although no interference has been found from common atmospheric pollutants, a positive interference from atmospheric water vapor has been reported (California Air Resources Board, 1976; Kleindienst et al., 1993, and references therein) and has recently been confirmed (Kleindienst et al., 1993; Hudgens et al., 1994). The recent results indicate a positive interference of about 3% per percent H_2O by volume at 25 $^{\circ}\text{C}$, based on tests at O_3 concentrations of 0.085 to 0.32 ppm, and at H_2O concentrations of 1 to 3% (i.e., dew point temperatures of 9 to 24 $^{\circ}\text{C}$). It has been estimated that the interference of water in ethylene chemiluminescent measurements at 30 $^{\circ}\text{C}$ and 60% relative humidity could be as high as 13 ppbv of O_3 , or 11% of the O_3 reading at 120 ppbv (Kleindienst et al., 1993). Calibration with known O_3 concentrations in air of temperature and humidity, similar to that of the sample air, can minimize this source of error.

A separate potential problem with the ethylene chemiluminescent method is leakage of the pure ethylene reagent gas. Because O_3 and hydrocarbon measurements are often co-located for monitoring purposes, leakage of ethylene could cause difficulty in obtaining valid measurements of total nonmethane hydrocarbons (TNMHC) in ambient air.

The measurement principle set forth by EPA for compliance monitoring for O_3 is the chemiluminescence method using C_2H_4 (Federal Register, 1971). Methods of testing and the required performance specifications that commercial O_3 monitors must meet to be designated a reference or equivalent method are documented (Federal Register, 1975). A monitor may be designated a reference method if it employs gas-phase chemiluminescence with C_2H_4 as the measuring principle and achieves the required performance specifications. An equivalent method must show a consistent relationship with the reference method and must meet the required performance specifications. Table 3-15 shows those specifications for O_3 monitors. Note that ethylene chemiluminescence monitors typically have response times far superior to those required in Table 3-15.

The list of commercial O_3 monitors designated as reference or equivalent methods by EPA is shown in Table 3-16 (updated as of August 1, 1994). Details on three monitors not described in the 1986 EPA criteria document for O_3 and other oxidants are presented in Table 3-17. All of the reference methods are C_2H_4 chemiluminescence instruments, as required by the definition of a reference method. The equivalent methods are based on either gas-solid

chemiluminescence or UV-absorption measurements. Those methods are described below. A gas-liquid chemiluminescence analyzer for O₃, which may be submitted for EPA equivalency in the near future, also is described below.

Gas-Solid Chemiluminescence. The reaction of O₃ with Rhodamine-B adsorbed on activated silica gel produces chemiluminescence in the red region of the visible spectrum. This was the first chemiluminescence method ever developed for ambient O₃ measurement

Table 3-15. Performance Specifications for Automated Methods of Ozone Analysis

Performance Parameter	Units	Specification
Range	ppm	0 to 0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interference	ppm	±0.02
Total interference	ppm	0.06
Zero drift, 12 and 24 h	ppm	±0.02
Span drift, 24 h		
20% of upper range limit	%	±20.0
80% of upper range limit	%	±5.0
Lag time	min	20
Rise time	min	15
Fall time	min	15
Precision		
20% of upper range limit	ppm	0.01
80% of upper range limit	ppm	0.01

Source: Federal Register (1975); Code of Federal Regulations (1994).

(Regener, 1960, 1964). The emitted light intensity is linearly related to the O₃ concentration, and the detection limit can be as low as 0.001 ppm. No direct interferences from other gas-phase pollutants are known; however, decay of the sensitivity because of surface aging can occur (Hodgeson et al., 1970). Addition of gallic acid to the surface stabilizes the response characteristics, apparently by allowing direct reaction of O₃ with the gallic acid, rather than with the Rhodamine-B (Bersis and Vassiliou, 1966). A commercial analyzer (Phillips Model PW9771) based on this approach has been designated an equivalent method for ambient O₃ (see Table 3-16), but gas-solid chemiluminescence currently is used rarely for ambient measurements.

Gas-Liquid Chemiluminescence. A recently developed commercial monitor uses the chemiluminescent reaction of O₃ with the dye eosin-Y in solution (Topham et al., 1992). The monitor functions by exposing a fabric wick, wetted with the eosin-Y solution, to a flow of sample air within view of a red-sensitive photomultiplier tube. The monitor, designated the LOZ-3, is compact, portable, and requires no reagent gases. The LOZ-3 provides very fast response: a lag time of 2 s, a rise time of 3 s, and a fall time of 2 s, all relative to a step change of 400 ppbv O₃, are reported (Topham et al., 1992). Instrument noise at zero and at 382 ppbv ozone is 0.05 ppbv or less, calculated as the standard deviation of 25 successive 2-min averages. The precision of the LOZ-3 is reported to be 0.80 ppbv at 100 ppbv O₃ and 1.87 ppbv at 400 ppbv O₃, both calculated as one standard deviation of six repeated measurements at these levels (Topham et al., 1992). The instrument provides linear response up to 200 ppbv, with a gradually decreasing slope of the response curve above that

**Table 3-16. Reference and Equivalent Methods for Ozone
Designated by the U.S. Environmental Protection Agency^a**

Principal Method	Designation Number	Method Code
<u>Reference Methods</u>		
(Ethylene Chemiluminescence)		
Beckman 950A	RFOA-0577-020	020
Bendix 8002	RFOA-0176-007	007
CSI 2000	RFOA-0279-036	036
McMillan 1100-1	RFOA-1076-014	514
McMillan 1100-2	RFOA-1076-015	515
McMillan 1100-3	RFOA-1076-016	016
Meloy OA325-2R	RFOA-1075-003	003
Meloy OA350-2R	RFOA-1075-004	004
Monitor Labs 8410E	RFOA-1176-017	017
<u>Equivalent Methods</u>		
(UV Absorption)		
Advanced Pollution Instrument 400	EQOA-0992-087	087
Dasibi 1003-AH,-PC,-RS	EQOA-0577-019	019
Dasibi 1008-AH,-PC,-RS	EAOA-0383-056	056
EnviroNics 300	EQOA-0990-078	078
Lear-Siegler ML9810	EQOA-0193-091	091
Monitor Labs 8810	EQOA-0881-053	053
PCI Ozone Corporation LC-12	EQOA-0382-055	055
Thermo Electron 49	EQOA-0880-047	047
<u>Equivalent Methods (Gas/Solid CL)</u>		
Philips PW9771	EQOA-0777-023	023

^aAs of August 1, 1994; see Appendix A for abbreviations and acronyms.

level. Temperature and pressure sensitivity are corrected by internal circuitry (Topham et al., 1992). An initial large positive interference from SO₂ that becomes smaller and negative as the eosin solution ages is reported, and a positive interference from CO₂ is also present. Topham et al. (1992) report that a pretreatment technique applied to the eosin reagent solution minimizes both of these interferences. Several of the performance characteristics of the LOZ-3 are impressive, but verification of the reported interference levels and the effectiveness of temperature and pressure corrections appears to be needed.

Table 3-17. List of Designated Reference and Equivalent Methods for Ozone

Designation Number	Identification	Source	Manual or Auto	Ref. or Equiv.	Federal Register		
					Vol.	Page	Notice Date
EQOA-0990-078	"Enviro-nics Series 300 Computerized Ozone Analyzer," operated on the 0-0.5 ppm range, with the following parameters entered into the analyzer's computer system: Absorption Coefficient = 308 ± 4 Flue Time = 3 Integration Factor = 1 Offset Adjustment = 0.025 ppm Ozone Average Time = 4 Signal Average = 0 Temperature/Pressure Correction = On and with or without the RS-232 Serial Data Interface	Enviro-nics, Inc. 165 River Road West Willington, CT 06279	Auto	Equiv.	55	38386	September 18, 1990
EQOA-0992-087	"Advanced Pollution Instrumentation, Inc. Model 400 Ozone Analyzer," operated on any full-scale range between 0-0.1 ppm ^b and 0-1 ppm, at any temperature in the range of 5 to 40 °C, with the dynamic zero and span adjustment features set OFF, with a 5-µm Teflon® filter element installed in the rear-panel filter assembly, and with or without any of the following options: Internal Zero/Span (IZS) Rack Mount with Slides RS-232 with Status Outputs Zero/Span Valves	Advanced Pollution Instrumentation, Inc. 8815 Production Avenue San Diego, CA 92121-2219	Auto	Equiv.	57	44565	September 28, 1992

Table 3-17 (cont'd). List of Designated Reference and Equivalent Methods for Ozone^a

Designation Number	Identification	Source	Manual or Auto	Ref. or Equiv.	Vol.	Federal Register	
						Page	Notice Date
EQOA-0193-091	"Lear Siegler Measurement Controls Corporation Model ML9810 Ozone Analyzer," operated on any full-scale range between 0-0.050 ppm ^b and 0-1.0 ppm, with auto-ranging <i>enabled</i> or <i>disabled</i> , at any temperature in the range of 15 to 35 °C, with a 5-µm Teflon® filter element installed in the filter assembly behind the secondary panel, the service switch on the second panel set to the <i>In</i> position; with the following menu choices selected: Calibration: <i>Manual</i> or <i>Timed</i> ; Diagnostic Mode: <i>Operated</i> ; Filter Type: <i>Kalman</i> ; Pres/Temp/Flow Comp: <i>On</i> ; Span Comp: <i>Disabled</i> ; with the 50-pin I/O board installed on the rear panel configured at any of the following output range settings: Voltage, 0.1, 1, 5, and 10V; Current, 0-20, 2-20, and 4-20 mA; and with or without any of the following options: Valve Assembly for External Zero/Span (EVS) Rack Mount Assembly Internal Floppy Disk Drive	Lear Siegler Measurement Controls Corp. 74 Inverness Drive East Englewood, CO 80112-5189	Auto	Equiv.	58	6964	February 3, 1993

^aDesignated since publication of the 1986 EPA criteria document for ozone and other photochemical oxidants (U.S. Environmental Protection Agency, 1986a).

^bUsers should be aware that designation of this analyzer for operation on any full-scale range less than 0.5 ppm is based on meeting the same absolute performance specifications required for the 0- to 0.5-ppm range. Thus, designation of any full-scale range lower than the 0- to 0.5-ppm range does not imply commensurably better performance than that obtained on the 0- to 0.5-ppm range.

This method is undergoing testing and is likely to be submitted for EPA certification as an equivalent method.

Ultraviolet Photometry

This method is based on the fact that O₃ has a reasonably strong absorption band with a maximum near 254 nm, coinciding with the strong emission line of a low-pressure mercury lamp. The molar absorption coefficient at the mercury line is well known, the accepted value being 134 (± 2) M⁻¹cm⁻¹ in base 10 units at 0 °C and 1 atmosphere pressure (Hampson et al., 1973). Ultraviolet absorption has frequently been used to measure O₃ in laboratory chemical and kinetics studies. Ultraviolet photometry also was used for some of the first atmospheric O₃ measurements, but the early instruments suffered from poor precision because of the small absorbances being measured (U.S. Department of Health, Education, and Welfare, 1970).

Modern digital electronics have now solved the precision problems resulting from measurement of small absorbances, and several commercial O₃ monitors now employ UV photometry. Several instruments based on this principle have been designated by EPA as equivalent methods for ambient O₃ (Tables 3-16 and 3-17). Ultraviolet photometry is now the predominant method for assessing compliance with the NAAQS for O₃. The commercial monitors use pathlengths of 1 m or less, and operate in a sequential single-beam mode. Transmission of 254-nm light through the sample air is averaged over a short period of time (as short as a few seconds) and is compared to a subsequent transmission measurement on the same air stream from which O₃ has been selectively removed by a manganese dioxide (MnO₂) scrubber. The electronic comparison of the two signals can be converted directly into a digital readout of the O₃ concentration. The method is in principle absolute, because the absorption coefficient and pathlength are accurately known, and the measured absorbance can be converted directly to a concentration.

Commercial UV photometers for ambient O₃ measurements have detection limits of approximately 0.005 ppm. Time response depends on the averaging time used, but is typically < 1 min. Long-term precision can be within $\pm 5\%$. The method has the advantage of requiring no gas supplies, and commercial instruments are compact and reasonably portable. Sample air flow control is not critical, within the limitations of the MnO₂ scrubber. Because the measurement is absolute, UV photometry also is used to assay O₃ calibration standards as in Section 3.5.1.1. Ambient air monitors using UV photometry are generally calibrated with standard O₃ mixtures to account for losses of O₃ in sampling lines.

A potential disadvantage of UV photometry is that any atmospheric constituent that absorbs 254-nm light and is removed fully or partially by the MnO₂ scrubber will be a positive interference in O₃ measurements. Potential interferents include aromatic hydrocarbons, mercury vapor, and SO₂. A recent study (Kleindienst et al., 1993) demonstrated that toluene and possibly aromatic reaction products, such as benzaldehyde, produce positive interferences in UV photometric O₃ measurements. This result was found using photochemically reactive mixtures of toluene and NO_x, at concentrations at a factor of 2 to 5 higher than those expected in polluted urban air. Consideration of the relative absorption coefficients of O₃ and the aromatics indicated that, at higher humidities, toluene can cause an interference of 0.1 ppbv O₃ per ppbv of toluene, whereas benzaldehyde may cause an interference as high as 5 ppbv O₃ per

ppbv benzaldehyde (Kleindienst et al., 1993). This interference may be humidity dependent. In earlier work at very low humidities, no interference was observed with toluene, and only a very small interference was observed with benzaldehyde (Grosjean and Harrison, 1985b). However, even at very low humidities, these investigators observed significant interferences from styrene, cresols, and nitrocresols. Evaluation of aromatic interference is limited by a lack of appropriate absorption spectra in the 250-nm range and by a lack of ambient measurements of most of the aromatic photochemical reaction products. The use of C₂H₄ chemiluminescence monitors in areas where aromatic concentrations are substantial has been suggested (Kleindienst et al., 1993).

The same study found no consistent effect of ambient water vapor on measured O₃ concentrations using UV photometry, in contrast to the effect noted using C₂H₄ chemiluminescence (Kleindienst et al., 1993). However, short-term disturbances in UV photometric O₃ readings were observed when the humidity of the sample air was changed substantially within a few seconds. This finding corroborates the observations of Meyer et al. (1991a) in an earlier study that indicated microscopic irregularities in the UV cell windows as the cause of such disturbances. This effect should be absent in UV photometric measurements of ambient O₃ at the ground but could be important in other applications, such as measuring vertical O₃ profiles from an aircraft (Kleindienst et al., 1993).

A different approach to evaluating potential interferences in O₃ measurements was taken by Leston and Ollison (1993). These investigators examined ambient O₃ data from instruments of different measurement principles co-located at monitoring sites. The focus of their study was the O₃ "design value", the fourth highest daily maximum hourly value from a monitoring station within an urban area, which is established in the 1990 Clean Air Act Amendments (CAAA) (U.S. Congress, 1990) as the basis for classification of the area relative to attainment of the NAAQS for O₃. Leston and Ollison (1993) examined hourly O₃ concentration data from co-located UV and C₂H₄ chemiluminescence instruments, from 1989 and 1990 at a site in Madison, CT, and from shorter periods at sites in East Hartford, CT, and Mobile, AL. They also examined 11 winter days of simultaneous O₃ data from UV and Luminox LOZ-3 instruments, from Long Beach, CA. Leston and Ollison (1993) reported positive biases in the UV data of 20 to 40 ppbv O₃ during "hot, humid, hazy conditions typical of design value days." They proposed that most O₃ data and all design values are biased high by known and suspected interferences, and that those interferences are exacerbated by water vapor. Leston and Ollison (1993) argue that the interference in UV measurements from benzene derivatives (e.g., styrene, cresols, benzaldehyde, nitro-aromatics) is poorly accounted for. For example, of these compounds, only styrene is measured in the Photochemical Aerometric Monitoring Stations (PAMS) VOC monitoring network (Leston and Ollison, 1993).

An experimental study by Hudgens et al. (1994) attempted to address the issues raised by Leston and Ollison (1993) by evaluating several aspects of both UV and chemiluminescence O₃ measurements. This study confirmed the positive interference of water vapor in the chemiluminescence method as 3% per percent water by volume (Kleindienst et al., 1993) and also confirmed that no comparable interference exists with the UV method. However, Hudgens et al. (1994) also showed that some UV instruments give noisier response when operated under conditions in which condensation of moisture may occur in the sampling lines, as in an air conditioned enclosure during hot, humid weather. Hudgens et al. (1994) also tested several aromatic hydrocarbons for both absorbance at 254 nm and behavior in the

O₃ scrubber of UV instruments. Both positive and negative potential interferences were found; the former by adsorption of UV-absorbing aromatics in the scrubber, and the latter by release of those stored compounds on an increase in sample humidity. Transient O₃ breakthrough also was said to occur under humid conditions (Hudgens et al., 1994). The combined effects of adsorbed material and sample humidity may contribute to the anomalous behavior reported for a few scrubbers from field instruments, but that behavior could not be reproduced with new scrubbers, even after continuous sampling of a smog chamber mixture for up to 13 weeks (Hudgens et al., 1994). The aromatic compounds present at highest concentrations in ambient air (e.g., benzene, toluene, xylenes, benzaldehyde) are relatively weak UV absorbers and are not efficiently removed by the O₃ scrubber. As a result, those compounds are not significant interferences in the UV method (Hudgens et al., 1994). However, less common aromatics (e.g., styrene, nitrotoluene) were found to absorb 254-nm light as effectively as does O₃ and to be efficiently adsorbed in the O₃ scrubber (Hudgens et al., 1994). The importance of such compounds as interferents in the UV method will depend on their ambient concentrations.

Interferences of the magnitude suggested by Leston and Ollison (1993) clearly would have serious implications for monitoring of ambient O₃. It is difficult to estimate whether interferences in the UV method could be as high as suggested, in part, because data are lacking on the ambient levels of potential interferents. Many potential interferents are photochemically reactive, and it is questionable whether such compounds could co-exist with ozone in sufficient quantities to constitute a significant interference. The results of Hudgens et al. (1994) also suggest that periodic replacement of the O₃ scrubber may minimize any interferences in the UV method. In any case, full evaluation of interferences in UV and ethylene chemiluminescence methods may require simultaneous measurements of O₃, humidity, temperature, and speciated organic compounds, and perhaps of other meteorological parameters and potential interferents.

Spectroscopic Methods for Ozone

Spectroscopic methods have the potential to provide direct, sensitive, and specific measurements representative of broad areas, rather than of single monitoring sites. This potential has led to investigation of spectroscopic approaches, primarily differential optical absorption spectrometry (DOAS), for O₃ measurement. Differential optical absorption spectrometry measures the absorption through an atmospheric path (typically 0.5 to 1.5 km) of two closely spaced wavelengths of light from an artificial source. One wavelength is chosen to match an absorption line of the compound of interest, and the other is close to but off that line, and is used to account for atmospheric effects. Platt and Perner (1980) reported measurements of several atmospheric species, including O₃, by DOAS, and various investigators have applied the technique since then (Stevens et al., 1993, and references therein). Stevens et al. (1993) described testing of a commercial DOAS instrument in North Carolina in the fall of 1989. Ozone was measured using wavelengths between 260 and 290 nm, over a 557-m path. A detection limit for O₃ of 1.5 ppbv was reported, based on a 1-min averaging time (Stevens et al., 1993). Comparison of DOAS results to those from a UV absorption instrument showed $(\text{DOAS O}_3) = 0.90 \times (\text{UV O}_3) \pm 2.5 \text{ ppbv}$, with a correlation coefficient (r^2) of 0.89, at ozone levels up to 50 ppbv. The sensitivity, multiple analytical capability, stability, and speed of response of the DOAS method are attractive, although further intercomparisons and interference tests are recommended (Stevens et al., 1993).

Personal and Passive Samplers for Ozone

A passive sampler is one that depends on diffusion of the analyte in air to a collecting or indicating medium. In general, passive samplers are not adequate for compliance-monitoring purposes because of limitations in specificity and averaging time. However, passive sampling devices (PSDs) for O₃ are of value as a means of obtaining personal human exposure data for O₃ and as a means of obtaining long-term O₃ measurements in areas where the use of instrumental methods is not feasible. Estimation of long-term population exposure and ecological monitoring for vegetation effects of O₃ in remote areas are examples of the latter application. Passive sampling devices have the advantages of simplicity, small size, and low cost, but also may present disadvantages, such as poor precision, loss of effectiveness during use or storage, and interference from other atmospheric constituents. New designs for PSDs have been implemented to overcome some of these limitations and to make them more useful for short-term ambient and indoor studies, personal exposure assessments, and validation of exposure models. Passive samplers for measuring O₃ at ambient concentrations are now commercially available.

The Ogawa PSD for O₃ (Ogawa, Inc., Pompano Beach, FL) contains 0.1 mL of a solution of NaNO₂ and NaCO₃ in glycerine on glass fiber filter paper. The nitrite ion reacts with O₃ to form nitrate. Following exposure, the PSDs are analyzed by extraction of the nitrate with deionized water, followed by ion chromatographic (IC) analysis. In a comparative ambient O₃ study over 24 weeks, this PSD demonstrated agreement within about 10% with the weekly real-time measurements taken by a UV O₃ monitor (Mulik et al., 1991). Extension of these measurements to a full year produced similar results (Mulik et al., 1991). The standard deviation of weekly average measurements by three collocated PSD samplers ranged from about ± 1 to ± 6 ppb, at weekly average O₃ levels of 12 to 45 ppb (Mulik et al. 1991). The Ogawa PSD also was used in a study of personal exposure to indoor and outdoor O₃, showing a correlation of $r = 0.91$, and relative errors of 15% (daytime) and 25% (nighttime) relative to UV photometric data (Liu et al., 1992).

Another PSD for O₃ has been developed that is based on the use of a colorant that fades when exposed to O₃ (Grosjean and Hisham, 1992; Grosjean and Williams, 1992). The plastic, badge-type PSD contains a diffusion barrier and a colorant-coated filter as the O₃ trap. The colorant used is indigo carmine (5,5'-disulfonate sodium salt of indigo, $\lambda_{\text{max}} = 608 \text{ nm}$). With a plastic grid or Teflon® filter as the diffusion barrier, detection limits of 30 ppb·day and 120 ppb·day, respectively, are achieved. Interferences from NO₂, HCHO, and PAN are 15, 4, and 16%, respectively, of the ambient interferent concentrations. For sampling ambient O₃ in most locations, these interferences are probably negligible (Grosjean and Hisham, 1992). Following sampling, the color change is measured by reflectance spectroscopy and no chemical analysis is required. The reported shelf life is 3 mo prior to O₃ exposure and 12 mo after O₃ exposure (Grosjean and Hisham, 1992).

Field tests of the indigo carmine PSD were conducted at five forest locations in California in the summer of 1990 (Grosjean and Williams, 1992). During these tests, ambient O₃ ranged up to 250 ppbv; 3-day average O₃ values at the sites ranged from 40 to 88 ppbv. The precision of the measurements was $\pm 12\%$ based on 42 sets of collocated samplers, over sampling durations of 3 to 30 days. The color change in the PSD was highly correlated ($r = 0.99$) with O₃ dose as measured by UV photometry. No effect of ambient temperature or

humidity variations was observed, and the total interference caused by other pollutants (NO_2 , PAN, aldehydes) was less than 5%.

A third PSD for O_3 also has been developed recently; it is based on color formation from the reaction of O_3 with an aromatic amine (Kirolos and Attar, 1991). The ChromoSense™ direct-read passive dosimeter is a credit-card-sized device that changes color proportionally to the integrated dose of exposure of the specific toxic material for which it was designed (U.S. Patent 4,772,560). The dosimeter consists of an outer polyester pouch that encloses a polymeric plate with a sorbent and membrane. A filtering layer is coated on the membrane to reduce the sensitivity of the detection process to NO_2 . The chromophoric layer, consisting of an aromatic amine that can react with O_3 and form color, is encapsulated so as to create a very high surface area. A polymeric barrier separates the chromophore from a UV-absorbing layer to reduce their interaction. The UV absorber (in a polymeric matrix) helps stabilize the chromophore toward intense light exposure when the device is used outdoors. The transparent polymeric plate keeps the wafer flat and allows uninterrupted optical viewing of the color of the reference and the sample area. An electronic reading device measures color on both the exposed (sample) and unexposed (reference) areas, and displays a digital reading that is proportional to the log of the O_3 dose. Visible color is formed at doses as low as 20 ppb 1 h. No interference from NO_2 is observed at NO_2 concentrations up to 350 ppb, and only a small effect of ambient humidity has been reported (Kirolos and Attar, 1991). No data on precision have yet been reported.

A popularization of a PSD for O_3 has been achieved in the form of the EcoBadge®, which employs color formation by reaction of O_3 with an undisclosed reagent in a filter paper (Vistanomics, Inc., Glendale, CA). The EcoBadge is available through several scientific equipment catalogs, primarily as a tool for classroom instruction on environmental issues. The badge is said to indicate both a 1-h and an 8-h average O_3 concentration. Comparison of color development to a standard chart indicates O_3 concentrations up to about 350 ppbv, with a limit of resolution of about 20 ppbv or more. The badge is stated to be unaffected by air velocity, humidity, or temperature, with only a slight interference from NO_2 . Test data apparently have not been published. The EcoBadge has been used in middle and high school programs promoting science and math and is included in the curriculum of the Global Thinking Project (1993), an international telecommunications and education network.

Calibration Methods for Ozone

Because it is an unstable molecule and cannot be stored, O_3 must be generated at the time of use to produce calibration mixtures. Electrical discharges in air or oxygen readily produce O_3 , but at concentrations far too high for calibration of ambient monitors. Radiochemical methods are expensive and require the use of radioactive sources, with associated safety requirements. For calibration purposes, low levels of O_3 nearly always are generated by photolysis of oxygen at wavelengths < 200 nm. Placing a mercury lamp near a quartz tube through which air is flowing produces small amounts of O_3 in the airstream. Commercial O_3 sources based on this approach typically adjust the lamp current to control the amount of light transmitted, and thus the O_3 produced.

Once a stable, low concentration of O_3 has been produced from a photolytic generator, that O_3 output must be established by measurement with an absolute reference method. The original reference calibration procedure promulgated by EPA in 1971 (Federal Register, 1971) was an iodometric procedure, employing 1% aqueous neutral buffered

potassium iodide (NBKI). A large number of studies conducted in the 1970s revealed several deficiencies with potassium iodide (KI) methods, the most notable of which were poor precision or interlaboratory comparability and a positive bias of NBKI measurements relative to simultaneous absolute UV absorption measurements.

Following investigations of problems with the NBKI method, EPA evaluated four potential reference calibration procedures and selected UV photometry on the basis of superior accuracy and precision and simplicity of use (Rehme et al., 1981). In 1979, UV photometry was designated the reference calibration procedure by EPA (Federal Register, 1979a).

The measurement principle of UV O₃ photometers used as reference standards is identical to that of O₃ photometers used for ambient measurements (see Section 3.5.1.1). A laboratory photometer used as a reference standard will typically contain a long-path cell (1 to 5 m) and employ sophisticated digital techniques for making effective double-beam measurements of small absorbances at low O₃ concentrations.

A primary reference standard is a UV photometer that meets the requirements set forth in the 1979 revision designating UV photometry as the reference method (Federal Register, 1979a). Commercially available O₃ photometers that meet those requirements may function as primary standards. The EPA and the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards [NBS]) have established a nationwide network of standard reference photometers (SRPs) that are used to verify local primary standards and transfer standards. A secondary or transfer standard is a device or method that can be calibrated against the primary standard and then moved to another location for calibration of O₃ monitors. Commercial UV photometers for O₃ often are used as secondary or transfer standards, as are commercial photolytic ozone generators and apparatus for the gas-phase titration of O₃ with NO.

The latter method, gas-phase titration (GPT) of O₃ with NO ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$), is a direct and absolute means of determining O₃, provided NO is in excess so that no side reactions occur. Under such conditions, GPT has the advantage that measurement of the NO or O₃ consumed or the NO₂ produced gives a simultaneous measurement of the other two species. All three modes have been used, and this method is often used for calibration of NO/NO_x analyzers. Gas-phase titration has been compared to UV photometry in several studies. The most detailed study is that of Fried and Hodgeson (1982), who used an NBS primary standard UV photometer, highly accurate flow measurements, photoacoustic detection of NO₂, and NBS (now NIST) Standard Reference Materials as sources of NO and NO₂. That study showed that decreases in O₃ as measured by the UV method averaged 3.6% lower than the corresponding decrease in NO and increase in NO₂ measured independently. Because of uncertainty about the origin of the small bias relative to UV photometry, GPT is used as a transfer standard but not as a primary reference standard.

3.5.1.2 Peroxyacetyl Nitrate and Its Homologues

During laboratory organic photooxidation studies, Stephens et al. (1956a,b) determined the presence of a number of alkyl nitrates and an unidentified species called "Compound X". The presence of Compound X in the atmosphere of Los Angeles was confirmed by Scott et al. (1957). In later work (Stephens et al., 1961), its structure was determined and Compound X was named peroxyacetyl nitrate, or PAN. Since the discovery of PAN, much effort has been directed toward its atmospheric measurement. In the following subsections PAN measurement and calibration techniques are described. The discussion on

measurement techniques includes a summary description and identifies limits of detection, specificity (interferences), reproducibility, and accuracy of each method. The relative merits of each method also are presented. The subsection on calibration techniques includes those methods most often employed during ambient air measurement studies.

Measurement Methods

Two methods generally have been employed to make atmospheric measurements of PAN. These methods are infrared spectroscopy (IR) and GC. Infrared spectroscopy permits the sampling and analysis to be conducted in real time. Because PAN is very reactive in the gas phase and exhibits surface adsorptive effects, the minimal contact time offered by IR makes this method very attractive. However, IR instrumentation is expensive and complex and requires a good deal of space. On the other hand, GC is inexpensive and requires minimal space and operator training. A GC can be set up to automatically sample and analyze air for PAN and PANs. Application of these methods for obtaining ambient concentrations of PAN and other organic nitrates recently has been reviewed by Roberts (1990).

Infrared Spectroscopy. Conventional long-path infrared spectroscopy and FTIR have been used to detect and measure atmospheric PAN. Sensitivity is enhanced by the use of FTIR. The most frequently used IR bands have been assigned, and the absorptivities reported in the literature (Stephens, 1964; Bruckmann and Willner, 1983; Holdren and Spicer, 1984; Niki et al., 1985; Tsalkani and Toupance, 1989) permit the quantitative analysis of PAN without calibration standards. Tuazon et al. (1978) have described an FTIR system operable at pathlengths up to 2 km for ambient measurements of PAN and other trace constituents. This system employed an eight-mirror multiple reflection cell with a 22.5-m base path. The spectral windows available at pathlengths of 1 km were 760 to 1,300, 2,000 to 2,230 cm^{-1} . Thus, PAN could be detected by the bands at 793 and 1,162 cm^{-1} . The 793- cm^{-1} band is characteristic of peroxy nitrates, whereas the 1,162- cm^{-1} band is reportedly caused by PAN only (Stephens, 1969; Hanst et al., 1982). Tuazon et al. (1981a,b) reported ambient measurements with this system during a smog episode in Claremont, CA, in 1978. Maximum daily PAN concentrations ranged from 6 to 37 ppb over a 5-day episode. A detection limit for PAN was 3 ppb at a pathlength of \approx 1 km. Hanst et al. (1982) modified the FTIR system used by Tuazon by changing it from an eight-mirror to a three-mirror cell configuration and by considerably reducing the cell volume. A detection limit for PAN was increased to 1 ppb at a similar pathlength.

The limited sensitivity (\approx 1 ppb) and the complexity of the above FTIR systems generally have limited their field use to urban areas such as Los Angeles. More recently, cryogenic sampling and matrix-isolation FTIR have been used to measure PAN in 15-L integrated samples of ambient air. The matrix isolation technique has a theoretical level of detection of \approx 50 ppt (Griffith and Schuster, 1987).

Gas Chromatography-Electron Capture Detection. Peroxyacetyl nitrate is normally measured by using a GC coupled to an electron capture detector (GC/ECD). The method was originally described by Darley et al. (1963) and subsequently has been refined and employed by scientists over the years. Key features of the method remain unchanged. The column and detector temperatures are kept relatively low (\approx 50 and 100 $^{\circ}\text{C}$, respectively) to minimize PAN thermal decomposition. Short columns of either glass or Teflon[®] generally are used (1 to 5 ft in length). Finally, column packing normally includes a Carbowax stationary phase coated onto a deactivated solid support. Using packed columns, detection limits of

10 ppt have been reported using direct sampling with a 20-mL sample loop (Vierkorn-Rudolph et al., 1985). Detection limits were further extended to 1 to 5 ppt using cryogenic enrichment of samples (Vierkorn-Rudolph et al., 1985; Singh and Salas, 1983). These studies have found only slight overall losses of PAN (10 to 20%) associated with cryosampling, provided samples are warmed only to room temperature during desorption.

Recently, improved precision and sensitivity have been reported using fused-silica capillary columns instead of packed columns (Helmig et al., 1989; Roberts et al., 1989). Signal-to-noise enhancement of 20 has been claimed (Roberts et al., 1989).

Gas Chromatography-Alternate Detection. As noted earlier, PAN is readily reduced to NO in the gas phase. To separate PAN, NO, and NO₂, Meyrahn et al. (1987) coupled a GC with a molybdenum converter and used a chemiluminescent analyzer to measure PAN as NO. Using a 10-mL sample loop, a detection limit of 10 ppb was reported.

A luminol-based detector also has shown sensitivity to PAN. Burkhardt et al. (1988) used GC and a commercially available luminol-based instrument (i.e., Scintrex LMA-3 Luminox) to detect both NO₂ and PAN. Using a sampling interval of 40 s, linear response was claimed from 0.2 to 170 ppb NO₂ and from 1 to 65 ppb PAN. Although the PAN calibration was nonlinear below 1 ppb, a detection level of 0.12 ppb was reported. Drummond et al. (1989) slightly modified the above approach by converting the PAN from the GC column to NO₂ and measuring the resulting NO₂ with a luminol-based instrument.

Peroxyacetyl Nitrate Stability

Peroxyacetyl nitrate is an unstable gas and is subject to surface-related decomposition as well as thermal instability. Peroxyacetyl nitrate exists in a temperature-sensitive equilibrium with the peroxyacetyl radical and NO₂ (Cox and Roffey, 1977). Increased temperature favors the peroxyacetyl radical and NO₂ at the expense of PAN. Added NO₂ should force the equilibrium toward PAN and enhance its stability. In the presence of NO, peroxyacetyl radicals react rapidly to form NO₂ and acetoxy radicals, which decompose in O₂ to radicals that also convert NO to NO₂. As a result, the presence of NO acts to reduce PAN stability and enhance its decay rate (Lonneman et al., 1982). Stephens (1969) reported that appreciable PAN loss in a metal sampling valve was traced to decomposition on a silver-soldered joint. Meyrahn et al. (1987) reported that PAN decayed according to first-order kinetics at a rate of 2 to 4%/h in glass vessels, and they suggested first-order decay as the basis for a proposed method of in-field PAN calibration. In contrast, Holdren and Spicer (1984) found that without NO₂ added, 20 ppb PAN decayed in Tedlar bags according to first-order kinetics at a rate of 40%/h. The addition of 100 ppb NO₂ acted to stabilize the PAN (20 ppb) in the Tedlar bags.

A humidity-related difference in GC/ECD response has been reported (Holdren and Rasmussen, 1976). Low responses observed at humidities below 30% and PAN concentrations of 10 and 100 ppb, but not 1,000 ppb, were attributed to sample-column interactions. A humidity effect was alluded to by Nieboer and Van Ham (1976) but details were not given. No humidity effect was observed by Lonneman (1977). Watanabe and Stephens (1978) conducted experiments at 140 ppb and did not conclude that the reduced response was from faults in the detector or the instrument. They concluded that there was no column-related effect, and they observed surface-related sorption by PAN at 140 ppb in dry acid-washed glass flasks. They recommended that moist air be used to prepare PAN calibration mixtures to avoid potential surface-mediated effects.

Another surface-related effect has been reported for PAN analyses of remote marine air (Singh and Viezee, 1988). Peroxyacetyl nitrate concentrations were found to increase by 20 to 170 ppt, an average factor of 3, when the sample was stored in a glass vessel for 1 to 2 min prior to analysis. This effect remains to be explained.

Preparation and Calibration

Because PAN is unstable, the preparation of reliable calibration standards is difficult. The more promising methods are described here. The original method used the photolysis of ethyl nitrite in pure oxygen (Stephens, 1969). When pure PAN is desired, the reaction mixture must be purified, usually by chromatography, to remove the major by-products, acetaldehyde and methyl and ethyl nitrates (Stephens et al., 1965). For GC calibration, purification is unnecessary; the PAN concentration in the reactant matrix is established from the IR absorption spectrum and subsequently diluted to the parts-per-billion working range needed for calibration purposes (Stephens and Price, 1973).

Static mixtures of molecular chlorine, acetaldehyde, and NO_2 in the ratio of 2:4:4 can be photolyzed in the presence of a slight excess NO_2 to give a near-stoichiometric yield of PAN (Gay et al., 1976). This method was adapted by Singh and Salas (1983) and later by Grosjean et al. (1984), using photolytic reactors to provide continuous PAN calibration units at concentrations between 2 and 400 ppb. In the former approach, the PAN concentration is established by measuring the change in acetaldehyde concentration across the reactor. In the latter approach, the PAN concentration is established by measuring the acetate in an alkaline bubbler where PAN is hydrolyzed.

A static technique involving the photolysis of acetone in the presence of NO_2 and air at 250 nm has been reported to produce a constant concentration of PAN (Meyrahn et al., 1987; Warneck and Zerbach, 1992). A Penray mercury lamp is inserted into a mixture of 10 ppm NO_2 and 1% acetone and irradiated for 3 min to yield 8.9 ± 0.3 ppm PAN.

Peroxyacetyl nitrate can be synthesized in the condensed phase by the nitration of peracetic acid in C_6H_{14} (Helmig et al., 1989), heptane (Nielsen et al., 1982), C_8H_{18} (Holdren and Spicer, 1984), or *n*-tridecane (Gaffney et al., 1984). Purification of PAN in the liquid phase is needed using the first two methods. The resulting PAN-organic solution can be stored at -20 to -80 °C with losses of less than 3.6%/mo and can be injected directly into a vessel containing air to produce a calibration mixture. The PAN concentration is normally established by FTIR analysis of the solution or the resulting PAN-air mixture.

Peroxyacetyl nitrate readily disassociates to NO , and chemiluminescence NO_x analyzers have near-quantitative response to PAN. Thus, under some circumstances, chemiluminescent NO_x response can be used for PAN calibration. One method uses the difference in NO_x signal measured upstream and downstream of an alkaline bubbler (Grosjean and Harrison, 1985a). Joos et al. (1986) coupled a chemiluminescence NO_x analyzer with a GC system to permit calibration of the ECD response by reference to the chemiluminescence NO_x analyzer that has been calibrated by traditional methods.

As noted previously, NO in the presence of PAN is converted to NO_2 . Approximately four molecules of NO can react per molecule of PAN. Lonneman et al. (1982) devised a PAN calibration procedure based on the reaction of PAN with NO in the presence of benzaldehyde, which is added to control unwanted radical chemistry and to improve precision. Using this approach and an initial NO -to-PAN ratio between 10 and 20 to 1, the change in NO concentration is monitored with a chemiluminescence NO analyzer, the change in PAN GC-

ECD response is monitored, and the resulting ratio (i.e., $\square\text{NO}/\square\text{PAN}$) is divided by the stoichiometric factor of 4.7 to arrive at a calibration factor for the ECD.

Peroxyacetyl nitrate and *n*-propyl nitrate (NPN) have similar ECD responses. Serial dilution of the more stable compound, NPN, has been used for field operations (Vierkorn-Rudolph et al., 1985). This approach is not recommended for primary calibration, however, because it does not permit verification of quantitative delivery of PAN to the detector (Stephens and Price, 1973).

3.5.1.3 Gaseous Hydrogen Peroxide

Although O_3 has long been considered to be the primary oxidant affecting air quality, atmospheric chemists recently have identified H_2O_2 , a photochemical reaction product, as another oxidant that also may play a significant role in diminishing air quality. In order to assess the role of atmospheric H_2O_2 , good measurement methods are needed. Early measurements in the 1970s reported H_2O_2 concentrations ranging from 10 to 180 ppb (Gay and Bufalini, 1972 a,b; Kok et al., 1978 a,b). However, these measurements are in error because of artifact formation of H_2O_2 from reactions of absorbed gaseous O_3 (Zika and Saltzman, 1982; Heikes et al., 1982; Heikes, 1984). Modeling results also indicate that H_2O_2 atmospheric concentrations should be on the order of 1 ppb (Chameides and Tan, 1981; Logan et al., 1981).

In the following section, the discussion focuses on those sampling and analytical methods most frequently used within the last decade to determine atmospheric levels of H_2O_2 . The measurement techniques are described and limits of detection, specificity (interferences), reproducibility, and accuracy are discussed.

Measurement Methods

In situ measurement methods that have been employed for determining gaseous H_2O_2 include both FTIR and tunable diode laser absorption spectrometry (TDLAS). Four methods involving sample collection via wet chemical means and subsequent analysis via chemiluminescent or fluorescent detection also have been used frequently: (1) luminol, (2) peroxyoxalate, (3) enzyme-catalyzed (peroxidase), and (4) benzoic acid-fenton reagent methods. Application of most of these methods for obtaining ambient concentrations of H_2O_2 recently has been reviewed by Sakugawa et al. (1990) and Gunz and Hoffmann (1990).

In Situ Methods. Fourier transform infrared spectroscopy was employed in the early 1980s for atmospheric measurements (Tuazon et al., 1980; Hanst et al., 1982). Even though the FTIR is very specific for H_2O_2 , it saw limited use because of the high detection level of $\square 50$ ppb when using a 1-km path length. The TDLAS also has very high specificity for H_2O_2 and was subsequently evaluated and shown to have a much improved detection limit of 0.1 ppb when using scan-averaging times of several minutes (Slemr et al., 1986; MacKay and Schiff, 1987a; Schiff et al., 1987).

Wet Chemical Methods. Numerous wet chemical techniques for measuring H_2O_2 have been reported. However, discussion in this section is limited to the four approaches most frequently used by researchers.

Luminol Method. Hydrogen peroxide concentrations in the atmosphere have been determined by the chemiluminescent response obtained from the catalyzed oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) by H_2O_2 . Copper²⁺ (Armstrong and Humphreys, 1965; Kok et al., 1978 a,b; Das et al., 1982) and hemin, a blood component (Yoshizumi et al.,

1984), have been reported as catalysts for the luminol-based H_2O_2 oxidation. Method sensitivity of ≤ 0.01 ppb has been achieved. Interference from O_3 , SO_2 , metal ions, and high pH have been reported along with ways to mitigate these effects (Heikes et al., 1982; Zika and Saltzman, 1982; Ibusuki, 1983; Lazrus et al., 1985; Aoyanagi and Mitsushima, 1985; Hoshino and Hinze, 1987).

Peroxyoxalate Method. The peroxyoxalate chemiluminescence method also has been employed by a number of researchers (Rauhut et al., 1967; Scott et al., 1980; Klockow and Jacob, 1986). Hydrogen peroxide reacts with *bis*(2,4,5-trichloro-6-phenyl)-oxalate to form a high-energy dioxetanedione (Stauff and Jaeschke, 1972). The chemiluminescence is transmitted to the fluorophore, perylene, which emits light on return to the ground state. Method sensitivity of ≤ 0.01 ppb is achieved, and no interferences are observed from O_3 and metal ions. A signal depression has been reported for trace levels of nitrite ($> 10^{-5}$ M), sulfite ($> 10^{-4}$ M), and formaldehyde ($> 10^{-3}$ M) (Klockow and Jakob, 1986).

Enzyme-Catalyzed Method (Peroxidase). This general method involves three components: (1) a substrate that is oxidizable; (2) the enzyme, horseradish peroxidase (HRP); and (3) H_2O_2 . The production or decay of the fluorescence intensity of the substrate or reaction product is measured as it is oxidized by H_2O_2 , catalyzed by HRP. Some of the more widely used chromogenic substrates have been scopoletin (6-methoxy-7-hydroxy-1,2-benzopyrone) (Andreae, 1955; Perschke and Broda, 1961), 3-(*p*-hydroxyphenyl)propionic acid (HPPA) (Zaitsu and Okhura, 1980), leuco crystal violet (LCV) (Mottola et al., 1970), and *p*-hydroxyphenylacetic acid (POPHA) (Guilbault et al., 1968).

Of the chromogens used, POPHA is one of the better indicating substrates. Hydrogen peroxide oxidizes the peroxidase and is itself reduced by electron transfer from POPHA. The POPHA radicals form a dimer that is highly fluorescent. Because the chemical reaction is sensitive to both H_2O_2 and organic peroxides, a dual-channel system with a H_2O_2 removal step (use of catalase) is used to distinguish H_2O_2 from organic peroxides (Lazrus et al., 1985; Wei and Weihai, 1987; Dasgupta and Hwang, 1985; Kok et al., 1986).

The peroxidase-POPHA-fluorescence technique has been used by several groups to measure gas-phase H_2O_2 concentrations (Lazrus et al., 1986; Tanner et al., 1986; Heikes et al., 1987; Van Valin et al., 1987; Dasgupta et al., 1988; Olszyna et al., 1988; Meagher et al., 1990). Method detection levels range from 0.01 to 0.1 ppb. However, artifact formation does occur as a result of the reaction of dissolved O_3 in the collection devices (Staehelin and Hoigne, 1982; Heikes, 1984; Gay et al., 1988). To overcome the O_3 interference, researchers have used NO to eliminate O_3 (Tanner, 1985; Tanner et al., 1986; Shen et al., 1988).

Fenton Reagent-Isomeric Hydroxybenzoic Acids Method. This technique involves the formation of aqueous OH radicals from the reaction of Fenton reagent (Fe^{2+} complex) with gaseous H_2O_2 . The OH radicals, in turn, react with benzoic acid (hydroxyl radical scavenger) to form isomeric hydroxybenzoic acids (OHBA). The OHBA fluoresces weakly at the pH necessary to carry out the above reactions. Fluorescence is enhanced by adding NaOH to the product stream (Lee et al., 1990) or by using a low pH Al^{3+} fluorescence enhancing reagent (Lee et al., 1993).

Comparison of Methods

The above techniques have been shown to measure H_2O_2 in the atmosphere with detection levels of ≤ 0.1 ppb. Kleindienst et al. (1988) compared several of these techniques using three sources of H_2O_2 : (1) zero air in the presence and absence of common interferences,

(2) steady-state irradiations of hydrocarbon-NO_x mixtures, and (3) ambient air. The measurements were conducted simultaneously from a common manifold. For pure samples in zero air, agreement within 23 % was achieved among methods over a concentration range of 0.06 to 128 ppb. A negative SO₂ interference was caused with the luminol technique. During the irradiation experiment, significant concentrations of organic peroxides were generated, and the agreement among techniques for H₂O₂ was very poor. For ambient measurements, the methods agreed reasonably well with an average deviation of 30 % from the mean values.

Atmospheric intercomparison studies also have been conducted as part of the Carbon Species Methods Comparison Study (Calif, 1986). The results of the study indicated that the wet chemical methods still suffer from sampling artifacts and interferences from other atmospheric constituents (Dasgupta et al., 1990; MacKay et al., 1990; Kok et al., 1990; Sakugawa et al., 1990; Tanner and Shen, 1990). Lee et al. (1991) showed that substantial loss of airborne H₂O₂ can occur when air is drawn through Teflon® tubing of inlet sampling devices. In addition to reducing the H₂O₂ in incoming ambient air, this line loss also compromises the use of aqueous standards to calibrate a gas-phase monitoring system. More recently, Lee et al. (1994) have demonstrated a surfaceless inlet system to eliminate line loss problems. It is clear from the above studies that further comparisons of techniques are needed to resolve questions of errors and to provide improved measurement techniques.

Calibration Methods

The most frequently used method for generating aqueous standards is simply the serial dilution of commercial grade 30 % H₂O₂/water. The dilute solutions of H₂O₂ as low as 10⁻⁴ have been found to be stable for several weeks if kept in the dark (Armstrong and Humphreys, 1965). The stock H₂O₂ solution is standardized by iodometry (Allen et al., 1952; Hochanadel, 1952; Cohen et al., 1967) or, more recently, by using a standardized permanganate solution (Lee et al., 1991).

Gaseous H₂O₂ standards are not as easily prepared, and stability problems require the use of standard mixtures immediately. One method makes use of the injection of microliter quantities of 30 % H₂O₂ solution into a metered stream of air that flows into a Teflon® bag. The amount of H₂O₂ in the gas phase is determined by the iodometric titration method (Cohen and Purcell, 1967). Gas-phase H₂O₂ standards also have been generated by equilibrating N₂ with an aqueous H₂O₂ solution of known concentration that is maintained at constant temperature. Equilibrium vapor pressures and corresponding gas-phase concentrations are calculated using Henry's law constant (Lee et al., 1991).

3.5.2 Sampling and Analysis of Volatile Organic Compounds

3.5.2.1 Introduction

The term *volatile organic compounds* generally refers to gaseous organic compounds that have a vapor pressure greater than 0.15 mm and, generally, have a carbon content ranging from C₁ through C₁₂. As discussed in Sections 3.2 and 3.4, VOCs are emitted from a variety of sources and play a critical role in the photochemical formation of O₃ in the atmosphere.

The U.S. Environmental Protection Agency revised the ambient air quality surveillance regulations in Title 40, Part 58, of the Code of Federal Regulations to include, among other activities, the monitoring of VOCs. The revisions require states to establish VOC air monitoring stations in nonattainment areas as part of their existing State Implementation

Plan (SIP) monitoring networks. Authority for requiring the enhanced monitoring is provided for in Title I, Section 182, of the CAAA of 1990 (U.S. Congress, 1990). Several states have begun acquiring VOC data on 55 O₃ precursors at these PAMS, using methodology discussed in an EPA technical assistance document (U.S. Environmental Protection Agency, 1991c).

The term *nonmethane organic compounds* also is used frequently and refers to a subset of VOCs, because it excludes the compound CH₄. Numerous sampling, analytical, and calibration methods have been employed to determine NMOCs in ambient air. Some of the analytical methods utilize detection techniques that are highly selective and sensitive to specific functional groups or atoms of a compound (e.g., formyl group of aldehydes, halogen), whereas others respond in a more universal manner (i.e., to the number of carbon atoms present in the organic molecule). In this overview of the most pertinent measurement methods, NMOCs have been arranged into three major classifications: (1) NMHCs, (2) carbonyl species, and (3) polar volatile organic compounds (PVOCs). Measurement and calibration procedures are discussed for each classification.

3.5.2.2 Nonmethane Hydrocarbons

Nonmethane hydrocarbons constitute the major portion of NMOC in ambient air. Traditionally, NMHCs have been measured by methods that employ a flame ionization detector (FID) as the sensing element. This detector was originally developed for GC and employs a sensitive electrometer that measures a change in ion intensity resulting from the combustion of air containing organic compounds. Ion formation is essentially proportional to the number of carbon atoms present in the organic molecule (Sevcik, 1975). Thus, aliphatic, aromatic, alkenic, and acetylenic compounds all respond similarly to give relative responses of 1.00 ± 0.10 for each carbon atom present in the molecule (e.g., 1 ppm hexane = 6 ppmC; 1 ppm benzene = 6 ppmC; 1 ppm propane = 3 ppmC). Carbon atoms bound to oxygen, nitrogen, or halogens give reduced relative responses (Dietz, 1967). Consequently, the FID, which is primarily used as a hydrocarbon measuring method, more correctly should be viewed as an organic carbon analyzer.

In the following sections, discussion focuses on the various methods utilizing this detector to measure total nonmethane organics. Methods in which no compound speciation is obtained are covered first. Methods for determining individual organic compounds then are discussed.

Nonspeciation Measurement Methods

The original EPA reference method for NMOC, which was promulgated in 1971, involves GC separation of CH₄ from the remaining organics in an air sample (Federal Register, 1971). A second sample is injected directly to the FID without CH₄ separation. Subtraction of the first value from the second produces a nonmethane organic concentration.

A number of studies of commercial analyzers employing the Federal Reference Method have been reported (Reckner, 1974; McElroy and Thompson, 1975; Harrison et al., 1977; Sexton et al., 1982). These studies indicated overall poor performance of the commercial instruments when either calibration or ambient mixtures containing NMOC concentrations < 1 ppmC were used. The major problems associated with using these NMOC instruments have been reported in an EPA technical assistance document (Sexton et al., 1981). The technical assistance document also suggests ways to reduce the effects of existing problems. Other nonspeciation approaches to the measurement of nonmethane organics also

have been investigated. These approaches have been discussed in the 1986 EPA air quality criteria document (U.S. Environmental Protection Agency, 1986a). Again, these approaches also are subject to the same shortcomings as the EPA reference method (i.e., poor performance below 1 ppmC of NMHC).

More recently, a method has been developed for measuring NMOC directly and involves the cryogenic preconcentration of nonmethane organic compounds and the measurement of the revolatilized NMOCs using FID (Cox et al., 1982; Jayanty et al., 1982). This methodology has been formalized and is referred to as Method TO-12 and is published in a compendium of methods for air toxics (Winberry et al., 1988). The EPA recommends this methodology for measuring total NMOC and has incorporated it into the *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (U.S. Environmental Protection Agency, 1991c).

A brief summary of the method is as follows. A whole air sample is drawn through a glass bead trap that is cooled to approximately -185°C using liquid argon. The cryogenic trap collects and concentrates the NMOC, while allowing the CH_4 , nitrogen, oxygen, etc., to pass through the trap without retention. After a known volume of air has been drawn through the trap, carrier gas is diverted to the trap first to remove residual air and CH_4 . When the residual gases have been flushed from the trap, the cryogen is removed and the temperature of the trap is ramped to approximately 100°C . The revolatilized compounds pass directly to a FID (no analytical column). The corresponding signal is integrated over time (several minutes) to obtain a total FID response from the NMOC species. Water vapor, which also is preconcentrated, causes a positive shift in the FID signal. The effect of this shift is minimized by optimizing the peak integration parameters.

The sensitivity and precision of Method TO-12 are proportional to the sample volume. However, ice formation in the trap limits sampling volumes to ≤ 500 cc. The detection level is 0.02 ppmC (with a signal-to-noise ratio [S/N] of 3), and the precision at 1 ppmC and above has been determined to be $\leq 5\%$. The instrument response has been shown to be linear over a range of 0 to 10 ppmC. Propane gas certified by NIST is normally used as the calibrant. Accuracy at the method quantitation level (S/N = 10) is $\pm 20\%$.

Speciation Measurement Methods

The primary measurement technique utilized for NMOC speciation is GC. Coupled with FID, this analytical method permits the separation and identification of many of the organic species present in ambient air.

Separation of compounds is accomplished by means of both packed and capillary GC columns. If high resolution is not required and large sample volumes are to be injected, packed columns are employed. The traditional packed column may contain either a solid polymeric adsorbent (gas-solid chromatography) or an inert support, coated with a liquid (gas-liquid chromatography). Packed columns containing an adsorbent substrate normally are required to separate C_2 and C_3 compounds. The second type of column can be a support-coated or wall-coated open tubular capillary column. The latter column has been used widely for environmental analysis because of its superior resolution and broader applicability. The wall-coated capillary column consists of a liquid stationary phase coated or bonded (cross-linked) to the specially treated glass or fused-silica tubing. Fused-silica tubing is most commonly used because of its physical durability and flexibility. When a complex mixture is introduced into a GC column, the carrier gas (mobile phase) moves the sample through the

packed or coated capillary column (stationary phase). The chromatographic process occurs as a result of repeated sorption-desorption of the sample components (solute) as they move along the stationary phase. Separation occurs as a result of the different affinities that the solute components have for the stationary phase.

As described in the previous O₃ criteria document (U.S. Environmental Protection Agency, 1986a), the GC-FID technique has been used by numerous researchers to obtain ambient NMOC data. Singh (1980) drew on the cumulative experience of these researchers to prepare a guidance document for state and local air pollution agencies interested in obtaining speciation data. In general, most researchers have employed two gas chromatographic units to carry out analyses of NMOC species in ambient air. The more volatile VOCs (C₂ through C₅) generally are measured on one unit using packed-column technology, whereas the other GC separates the less volatile organics using a capillary column. In typical chromatograms of urban air, all major peaks are identified and, on a mass basis, represent from 65 to 90% of the measurable nonmethane organic burden.

Identification of GC peaks is based on matching retention times of unknown compounds with those of standard mixtures. Subsequent verification of the individual species is normally accomplished with gas chromatographic-mass spectrometric (GC/MS) techniques. Compound-specific detection systems, such as electron capture, flame photometry, and spectroscopic techniques, also have been employed to confirm peak identifications. The peak matching process is far from being a trivial task. Ambient air chromatograms are often very complex (>200 peaks/run) and require a good deal of manual labor to assure that the peak matching process is being carried out correctly by the resident peak identification/quantification software. Efforts to improve on the accuracy of peak assignment and diminish the labor hours normally associated with the objective recently have been reported. Silvestre et al. (1988) developed an off-line spreadsheet program that is menu-driven and used to identify and edit a chromatogram containing 200 peaks within 15 min. The accuracy of peak assignment was typically better than 95%. Mason et al. (1992) developed a novel algorithm that is embedded within the Harwell MatchFinder software package and demonstrated the potential of the algorithm for enhancing peak identification in complex chromatograms. The authors indicate that the software could be used to batch-process large volumes of chromatographic data. A commercial software package from Meta Four Software, Inc., was recently employed during the Atlanta Ozone Precursor Monitoring Study to batch process chromatographic data from over 6,000 GC runs (Purdue et al., 1992). This software was also used to validate peak identities from two GC databases and was shown to improve peak identities from the originally processed data by 10 to 20% (Holdren et al., 1993).

Because the organic components of the ambient atmosphere are present at parts-per-billion levels or lower, sample preconcentration is necessary to provide sufficient material for the GC-FID system. The two primary techniques utilized for this purpose are the use of solid adsorbents and cryogenic collection. The more commonly used sorbent materials are divided into three categories: (1) organic polymeric adsorbents, (2) inorganic adsorbents, and (3) carbon adsorbents. Primary organic polymeric adsorbents used for NMOC analyses include the materials Tenax®-GC and XAD-2®. These materials have a low retention of water vapor, and, hence, large volumes of air can be collected. These materials do not, however, efficiently capture highly volatile compounds such as C₂ to C₅ hydrocarbons, nor certain polar compounds such as CH₃OH and C₃H₆O. Primary inorganic adsorbents are silica gel, alumina, and molecular sieves. These materials are more polar than the organic polymeric adsorbents and

are thus more efficient for the collection of the more volatile and polar compounds. Unfortunately, water also is collected efficiently, which in many instances leads to rapid deactivation of the adsorbent. Carbon adsorbents are less polar than the inorganic adsorbents and, as a result, water adsorption by carbon adsorbents is a less significant problem. The carbon-based materials also tend to exhibit much stronger adsorption properties than organic polymeric adsorbents; thus, lighter-molecular-weight species are more easily retained. These same adsorption effects result, however, in irreversible adsorption of many compounds. Furthermore, the very high thermal desorption temperatures required (350 to 400 °C) limit the use of carbon adsorbents and also may lead to degradation of labile compounds. The commonly available classes of carbon adsorbents include various conventional activated carbons, carbon molecular sieves (Sphero carb®, Carbosphere®, Carbosieve®), and carbonaceous polymeric adsorbents (Ambersorb® XE-340, XE-347, SE-348).

Although a number of researchers have employed solid adsorbents for the characterization of selected organic species in air, only a few attempts have been made to identify and quantitate the range of organic compounds from C₂ and above. Westberg et al. (1982) evaluated several carbon and organic polymeric adsorbents and found that Tenax®-GC exhibited good collection and recovery efficiencies for C₆ organics; the remaining adsorbents tested (XAD-4®, XE-340®) were found unacceptable for the lighter organic fraction. The XAD-4® retained C₂ organic gases, but it was impossible to desorb these species completely without partially decomposing the XAD-4®. Good collection and recovery efficiencies were provided by XE-340® only for organics of C₄ and above. Ogle et al. (1982) used a combination of adsorbents in series and designed an automated GC-FID system for analyzing C₂ through C₁₀ hydrocarbons. Tenax-GC® was utilized for C₆ and above; whereas Carbosieve S® trapped C₃ through C₅ organics. Silica gel followed these adsorbents and effectively removed water vapor while passing the C₂ hydrocarbons onto a molecular-sieve, 5A adsorbent. More recently, Levaggi et al. (1992) used a combination of adsorbents in series for analyzing C₂ through C₁₀ hydrocarbons. Tenax GR, Carbotrap, and Carbosieve S-III were evaluated. At room temperature collection, excellent recovery efficiencies were obtained for all species except acetylene (breakthrough begins after 220 cc). Smith et al. (1991b) evaluated a commercially available GC system (Chrompack, Inc.) and found that a Carbotrap C, Carboxpack B, and Carboxieve S-III combination was effective for all C₂ and above species, if the trap temperature was maintained at ±30 °C during collection (600 cc). The above researchers also caution that artifact peaks do occur during thermal desorption and recommend closely screening the resulting data.

The preferred method for obtaining NMOC data is cryogenic preconcentration (Singh, 1980). Sample preconcentration is accomplished by directing air through a packed trap immersed in either liquid oxygen (B.P. -183 °C) or liquid argon (B.P. -186 °C). For the detection of about 1 ppbC of an individual compound, a 250-cc air sample normally is processed. The collection trap generally is filled with deactivated 60/80 mesh glass beads (Westberg et al., 1974), although coated chromatographic supports also have been used (Lonneman et al., 1974). Both of the above cryogenics are sufficiently warm to allow air to pass completely through the trap, yet cold enough to collect trace organics efficiently. The use of cryogenic preconcentration for collection of VOCs, in general, was automated to allow sequential hourly updates of GC data (McClenny et al., 1984), leading to the initial configuration of what are now referred to as automated GCs ("auto GCs") for O₃ precursor monitoring. The cryogenic collection procedure also condenses water vapor. An air volume

of 250 cc at 50% relative humidity and 25 °C contains approximately 2.5 mg of water that appears as ice in the collection trap. The collected ice at times will plug the trap and stop the sample flow; furthermore, water transferred to the capillary column during the thermal desorption step occasionally causes plugging and other deleterious column effects. To circumvent water condensation problems, Pleil et al. (1987) have characterized the use of a Nafion® tube drying device to remove water vapor selectively during the sample collection step. Although hydrocarbon species are not affected, polar organics are partially removed when the drying device is used. Burns et al. (1983) also showed that partial loss or rearrangement of monoterpenes, or both (e.g., α -pinene, limonene), occurs when the Nafion® tube is used to reduce water vapor.

The EPA has recently provided technical guidance for measuring VOCs that is based on the above studies as well as emerging and developing technology (U.S. Environmental Protection Agency, 1991c). Guidance for the use of auto GC sampling and analysis for VOCs has been derived from experience gained from application of this technology during an O₃ precursor study conducted by EPA in Atlanta during the summer of 1990 (Purdue et al., 1992). For that study, an auto GC system developed and manufactured by Chrompack, Inc., and modified for O₃ precursor monitoring (McClenny et al., 1991b) was used to obtain hourly VOC measurements. The GC system was equipped with a preconcentration adsorption trap, a cryofocusing secondary trap, and a single analytical column. The study was focused on the identification and quantitation of 55 O₃ precursor compounds, and resulted in accounting for 65 to 80% of the total NMOC mass. Sample volumes of 600 cc were used and a detection level of 0.1 ppb C was reported. External auditing indicated accuracy of $\pm 30\%$ at challenge concentrations of 2 ppbC (17-component audit mixture).

The study also revealed several weaknesses. First of all, excessive amounts of liquid cryogen were consumed in carrying out the measurements. The inferior quality of the cryogen containers and poor delivery schedules resulted in reduced data capture. Secondly, because of the single-column approach, numerous target species either co-eluted or were poorly resolved. Thirdly, several significant artifact peaks co-eluted with the target species and, therefore, biased the reported concentrations of those species, as well as the total NMOC (by summation of peaks). Additionally, Shreffler (1993) reported results from analyses of canister samples collocated with the automated field GC systems. In general, good agreement between the systems was found when comparing the sum of the 55 identified O₃ precursors. However, regression analysis indicated that the average total NMOC concentrations found from the analyses of canister samples were 50% higher than those measured with the field GC systems.

Based on these operational deficiencies, EPA has challenged commercial GC instrument makers with improving the current state of the art. One result has been the evolution of systems that require no liquid cryogen for operation, yet provide sufficient gas chromatographic resolution of target species (McClenny, 1993; Holdren et al., 1993). A recent comparison study of auto GCs at Research Triangle Park with five participating vendors has indicated that the newer auto GC designs use cryogenics more efficiently (Purdue, 1993).

In addition to direct sampling via preconcentration with sorbents and cryogenic techniques, collection of whole air samples is frequently used to obtain NMOC data. Rigid devices such as syringes, glass bulbs, or metal containers and nonrigid devices such as Tedlar®

and Teflon® plastic bags are often utilized during sampling. The primary purpose of whole-air collection is to store an air sample temporarily until subsequent laboratory analysis is performed. The major problem with this approach is assuring the integrity of the sample contents prior to analysis. The advantages and disadvantages of the whole air collection devices were summarized in the 1986 air quality criteria document (U.S. Environmental Protection Agency, 1986a).

The canister-based method is the preferred means for collecting VOCs and is described as part of the "EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (Compendium Method TO-14). McClenny et al. (1991a) recently reviewed the canister-based method and discussed basic facts about the canisters, described canister cleaning procedures, contrasted the canister collection system versus solid adsorbents, and discussed the storage stability of VOCs in canisters. Although storage stability studies have indicated that many target VOCs can be stored with integrity over time periods of at least 7 days, there are still many VOCs for which there are no stability data (Pate et al., 1992; Oliver et al., 1986; Holdren and Smith, 1987; Westberg et al., 1982, 1984; Gholson et al., 1990). Coutant (1993) has developed a computer-based model for predicting adsorption behavior and vapor-phase losses in multicomponent systems, based on the potential for physical adsorption as well as the potential for dissolution in condensed water for canister samples collected at high humidities. At present, the database for the model contains relevant physicochemical data for 78 compounds (including water), and provisions for inclusion of up to 120 additional compounds are incorporated in the software.

Calibration Methods

Calibration procedures for NMOC instrumentation require the generation of dilute mixtures at concentrations expected to be found in ambient air. Methods for generating such mixtures are classified as static or dynamic systems.

As described in the previous O₃ criteria document (U.S. Environmental Protection Agency, 1986a), static systems generally are preferred for quantitating NMOCs. The most commonly used static system is a compressed-gas cylinder containing the appropriate concentration of the compound of interest. These cylinder gases also may be diluted with hydrocarbon-free air to provide multi-point calibrations. Cylinders of calibration gases and hydrocarbon-free air are available commercially. Also, some standard gases such as propane and benzene, as well as a 17-component ppb mixture, are available from NIST as certified standard reference materials (SRMs). Commercial mixtures generally are referenced against these NIST standards. In its recent technical assistance document for sampling and analysis of O₃ precursors, EPA recommended propane (or benzene)-in-air standards for calibration (U.S. Environmental Protection Agency, 1991c). Some commercially available propane cylinders have been found to contain other hydrocarbons (Cox et al., 1982), so that all calibration data should be referenced to NIST standards.

Because of the uniform carbon response of a GC-FID system ($\pm 10\%$) to hydrocarbons (Dietz, 1967), a common response factor is assigned to both identified and unknown compounds obtained from the speciation systems. If these compounds are oxygenated species, an underestimation of the actual concentrations will be reported. Dynamic calibration systems are employed when better accuracy is needed for these oxygenated hydrocarbon species. Dynamic systems normally are employed to generate in situ

concentrations of the individual compound of concern and include devices such as permeation and diffusion tubes and syringe delivery systems.

3.5.2.3 Carbonyl Species

Historically, the major problem in measuring concentrations of carbonyls in ambient air has been to find an appropriate monitoring technique that is sensitive to low concentrations and specific for the various homologues. Early techniques for measuring HCHO, the most abundant aldehyde, were subject to some interferences and lacked sensitivity at low parts-per-billion concentrations (Altshuller and Leng, 1963; Altshuller et al., 1961; Altshuller and McPherson, 1963). However, spectroscopic methods such as FTIR and DOAS also lack sensitivity for HCHO in the low parts-per-billion concentration range. The 1986 air quality criteria document described two methods frequently used: (1) the chromotropic acid (CA) method for HCHO and (2) the 3-methyl-2-benzothiazolone hydrazone (MBTH) technique for total aldehydes (U.S. Environmental Protection Agency, 1986a). However, spectroscopic methods, on-line colorimetric methods, and the HPLC method employing DNPH derivatization are the preferred methods currently used for measuring atmospheric levels of carbonyl species.

Spectroscopic Methods

Three spectroscopic methods have been used to make measurements for atmospheric levels of HCHO and were recently intercompared at an urban site in California (Lawson et al., 1990). The FTIR method used gold-coated 30-cm-diameter mirrors and a total optical path of 1,150 m. The $2,781.0\text{-cm}^{-1}$ "Q-branch" adsorption peak was used to measure HCHO. The limit of detection was 3 ppb, and the measurement errors were within ± 3 ppb. The DOAS method was operated at an 800-m pathlength, and an absorption peak at 339 nm was used to measure HCHO; NO_2 and HNO_2 spectral features were subtracted. The limit of detection was 4.5 ppb, and the experimental error was $\pm 30\%$. A TDLAS method was operated at a pathlength of 150 m. Laser diodes were mounted in a closed-cycle helium cryocooler with a stabilizing heater circuit for constant temperature control. Radiation from the diode was collected and focused into the sampling by reflective optics. Formaldehyde absorption was measured at $1,740\text{ cm}^{-1}$. The limit of detection was 0.1 ppb and the measurement errors were within $\pm 20\%$. Additional information on FTIR and DOAS has been reported by Winer et al. (1987), Atkinson et al. (1988), and Biermann et al. (1988). A more complete description of TDLAS is given by MacKay and Schiff (1987a).

On-Line Fluorescence Method

A wet chemical method based on the derivatization of HCHO in aqueous solution to form a fluorescent product was developed by Kelly et al. (1990) and recently tested (Kelly and Fortune, 1994). The detection of fluorescent product was made more sensitive by using intense 254 nm light from a mercury lamp for excitation. This procedure allowed the use of a simple and efficient glass coil scrubber for collection of gaseous HCHO. A detection limit of 0.2 ppb was obtained with a response time of 1 min. The instrument is portable and highly selective for HCHO.

High-Performance Liquid Chromatography-2,4-Dinitrophenylhydrazine Method

The preferred and most current method for measuring aldehydes in ambient air is one involving derivatization of the aldehydes concurrent with sample collection, followed by

analysis using HPLC. This method takes advantage of the reaction of carbonyl compounds with DNPH to form a 2,4-dinitrophenylhydrazone:



Because DNPH is a weak nucleophile, the reaction is carried out in the presence of acid in order to increase protonation of the carbonyl.

In this method, atmospheric sampling initially was conducted with micro-impingers containing an organic solvent and an aqueous, acidified DNPH reagent (Papa and Turner, 1972; Katz, 1976; Smith and Drummond, 1979; Fung and Grosjean, 1981). After sampling was completed, the hydrazone derivatives were extracted, and the extract was washed with deionized water to remove the remaining acid and unreacted DNPH reagent. The organic layer was then evaporated to dryness, subsequently dissolved in a small volume of solvent, and analyzed by reversed-phase liquid chromatographic techniques employing a UV detection system (360 nm).

An improved procedure subsequently was reported that is much simpler than the above aqueous impinger method (Lipari and Swarin, 1982; Kuntz et al., 1980; Tanner and Meng, 1984). This scheme utilizes a midget impinger containing a C_2H_5N solution of DNPH and an acid catalyst. After sampling, an aliquot of the original collection solution is injected directly into the liquid chromatograph. This approach eliminates the extraction step and several sample-handling procedures associated with the DNPH-aqueous solution and provides much better recovery efficiencies. This method has been formalized by EPA as Compendium Method TO-5 (Winberry et al., 1988). The TO-5 Method has been further modified to include the use of a DNPH-impregnated solid adsorbent, rather than DNPH impinger solutions, as the collection medium. This modification and associated sampling conditions are referred to as EPA Method TO-11. The methodology can be used easily for long-term (1 to 24 h) sampling of ambient air. Sampling rates of 500 to 1,200 cc/min can be achieved and detection levels of 1 ppbv can be attained with sampled volumes of 100 L. The method currently calls for the use of SepPak[®] silica gel material as the sorbent material. However, researchers have noted that O_3 present in ambient air reacted more easily with carbonyl compounds collected on DNPH-coated silica gel cartridges than on DNPH-coated C_{18} -bonded silica material. To eliminate this negative bias, these researchers used an O_3 scrubber (Arnts and Tejada, 1989). Smith et al. (1989) noted that artifact peaks occurred when O_3 was bubbled through impingers containing DNPH solution. These artifacts were identified as DNPH- O_3 reaction products and were shown to cause positive interferences unless they were chromatographically resolved from the HCHO-hydrazone derivative. Although the TO-11 Method has been included in EPA's *Technical Assistance Document for Sampling and Analysis of Ozone Precursors* (U.S. Environmental Protection Agency, 1991c), a KI-coated denuder tube also has been recommended to remove O_3 upstream of the DNPH-coated cartridges.

Although both the Sep-Pak[®] C_{18} and silica gel cartridges have been used by researchers (either with or without O_3 scrubbers), there is still considerable uncertainty as to which type of cartridge gives the most reliable carbonyl results. Experiments are currently underway at several laboratories to investigate the effect of O_3 on the performance of DNPH-coated cartridges. However, results have not yet been reported in the literature.

Calibration of Carbonyl Measurements

Because they are reactive compounds, it is extremely difficult to make stable calibration mixtures of carbonyl species in pressurized gas cylinders. Although gas-phase