C4FF New Proposal – Air Quality: Pollution Measuring and Monitoring System

Using an optical sensing method where an infrared light emitting diode (IR LED) and a photosensor are optically arranged in the device. The photosensor detects the reflected IR LED light by dust particles in air. The SMART Dust Sensor can detect small particles, such as smoke, pollens, and common dust. It can also distinguish between small and large particles by the amplitude of the signal output. The strengths of both laser and infrared (IR) solutions needs assessment.

For PM 2.5, a laser light emitting diode (laser LED) and a photosensor are optically arranged in the device. The photosensor detects the reflected laser LED light by dust particles in air, including particles sizes below PM2.5. The dust sensor can detect small particles, such as cigarette smoke, and distinguish small particles, such as smoke from large house dust, by the pulse pattern of the signal output.

CO_2 Sensor is a nondispersive infrared (NDIR) CO_2 sensor that implements a single channel diffusion sampling method for automotive HVAC applications

NO2 Gas detector tubes are glass tubes that are filled with a chemical reagent that absorbs and reacts with the target gas or vapour being measured. Gastec tubes do not contain hazardous substances

A colorimetric stain (a colour change) is created. For most tubes, the concentration is read directly from the pinpoint accurate measurement scale on each tube.

The Gastec detector tube system is comprised of a handheld [Gastec air sampling pump](#) and Gastec detector tubes

Membrane heating –

Diffusion Tubes are made from clear plastic, with a rubber stopper at each end. Designed for passive monitoring of gaseous airborne **NO2**. They are commonly used by Local Authorities to obtain data in addition to those from high- end fixed monitoring stations

Palmes-type diffusion tubes are widely used in the UK for indicative measurement of ambient concentrations of nitrogen dioxide (NO2) in the context of Local Air Quality Management. However, no UK or international standard method currently exists for diffusion tube preparation or analysis. Consequently, there is considerable variation in procedures among both supplying laboratories and end users. It is believed that this variation in methods and procedures is contributing to the observed variation in NO2 diffusion tube performance, and that by reducing (as far as practicable) the interlaboratory variation in methods, it will be possible to reduce inter-laboratory variation in results.

Diffusion tubes are passive samplers: they consist of small plastic tubes containing a chemical reagent to absorb the pollutant to be measured directly from the air (Figure 2-1). In the case of Palmes-type nitrogen dioxide diffusion tubes, the absorbent used is triethanolamine (TEA). Stainless-steel mesh grids at the closed end of the tube are coated with a water-based or acetone-based solution of this absorbent.

How is **nitrogen dioxide** (**NO_2**) **measured**? **Nitrogen dioxide** is commonly **measured** using automatic analysers that run 24 hours a day. The main **measuring** method is to use a chemiluminescence continuous analyser (chemiluminescence means the emission of light as a result of a chemical reaction).

Nitrogen Dioxide

Many techniques have been developed to measure nitrogen dioxide, but few can measure NO2 at concentrations below parts per billion, and few have been demonstrated to be free of interference from other atmospheric constituents. The standard way to measure NO2 in almost all air quality studies has been to use surface-conversion techniques to convert NO2 to NO and to subsequently detect the NO by chemiluminescence. The conversion techniques include the use of heated catalytic metal surfaces and surfaces coated with ferrous sulfate or other compounds. However, the development of the photolytic NO2-to-NO converter several years ago (Kley and McFarland, 1980) offered a potentially more specific conversion technique, albeit less simple. A recent comparison (Fehsenfeld et al., 1987) made a detailed study of the performance of surface and photolytic methods. In this study, the ferrous sulfate and photolytic converters agreed well at NO2 concentrations of 1 ppb and greater. However, the ferrous sulfate converter systematically reported higher values at lower concentrations, reaching a factor of 2 higher at 0.1 ppb. Spiking tests showed that the ferrous sulfate converter also was converting peroxyacetyl nitrate (PAN) to NO. Hence, whenever PAN is significant in comparison to the NO2, the ferrous sulfate converter gives results that overestimate the concentration of NO2. A heated molybdenum oxide surface converter was found to convert NO2, PAN, and HNO3 to NO, indicating that heated-surface converters also cannot be considered specific for NO2 or for NOx.

Suggested Citation:"7 Techniques for Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

The photolytic converter/chemiluminescence and ferrous sulfate/chemiluminescence techniques were compared during aircraft flights over the eastern Pacific Ocean and the southwestern United States at altitudes of 0.6 to 7.3 kilometers (km) (Ridley et al., 1988). In agreement with the intercomparison discussed above, the ferrous-sulfate-equipped instrument was found to be much less specific for NO2. It registered levels about three times larger than the photolytic converter, presumably because of the conversion of PAN and perhaps other organic nitrates to NO.

Newer technology is emerging to measure NO2. Three techniques that show considerable promise are photofragmentation/2-photon laser induced fluorescence (LIF), tunable-diode laser absorption spectrometry (TDLAS), and luminol chemiluminescence. The LIF and TDLAS techniques provide specific spectroscopic methods to measure NO2; the luminol technique provides a sensitive, portable method with low power requirements. Two recent studies have tested these techniques against the photolysis/chemiluminescence technique (Fehsenfeld et al., 1990; Gregory et al., 1990).

A ground-based comparison (Fehsenfeld et al., 1990) tested the photolysis/ chemiluminescence technique against the TDLAS and luminol techniques. For NO2 concentrations above 0.2 ppb, no interferences were found either for the photolytic converter/chemiluminescence technique or for TDLAS. However, interpretation of the results from TDLAS showed that correlation coefficients should not be used to select the data that are near the detection limit of NO2 for the instrument (Fehsenfeld et al., 1990). At these levels the background noise is normally distributed about the reference NO2 spectrum. Selection of the data with high correlation coefficients would lead to NO2 concentrations that are too high (Fehsenfeld et al., 1990). This test indicated that interferences from PAN and ozone influence the NO2 measurements made using the luminol technique. However, during the comparison those interferences were consistent enough that for NO2 concentrations above 0.3 ppb, they could be corrected using simultaneously measured values of ozone and PAN (Fehsenfeld et al., 1990). Techniques are being developed to remove or separate interfering substances from the ambient air prior to analyses by the luminol detector. However, the effectiveness of these techniques has not been verified by field tests.

An airborne comparison of TDLAS with LIF and photolytic converter/chemiluminescence was conducted by Gregory et al. (1990). The intercomparing of these three instruments in ambient air for NO2 > 0.1 ppb indicated a general level of agreement among the instruments of 30-40%. For NO2 < 0.05 ppb the results indicated that TDLAS overestimates the NO2 mixing ratio, presumably because of the use of correlation coefficients as the data selection criterion. At these low concentrations, agreement between LIF and photolytic converter/chemiluminescence measurements was within 0.02 ppb with an equal tendency for one to be high or low compared to the other. This 0.02 ppb agreement is typically within the expected uncertainties of the two techniques at NO2 mixing ratios < 0.05 ppb.

Suggested Citation:"7 Techniques for Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

It is believed that, properly used, the LIF, TDLAS, and the photolytic converter/chemiluminescence techniques measure NO2 concentrations well below 0.1 ppb, free of significant artifact or interference. These techniques should therefore be able to measure NO2 concentrations throughout the troposphere above North America.

Peroxyacetyl Nitrate

Two instruments, both of which use cryogenically enriched sampling with electron-capture gas chromatography detection, have been intercompared in the remote maritime troposphere (Gregory et al., 1990). At mixing ratios of <0.1 ppb, the two instruments differ on average by 0.017 ppb with a 95% confidence interval of ± 0.009 ppb. At PAN mixing ratios of 0.1-0.3 ppb, the difference between the instruments was 25% ± 6%. A linear regression equation developed by comparing all data < 0.3 ppb from the two techniques gave a line with a slope of 1.34 ± 0.12 and an intercept of 0.0004 ± 0.012 ppb. Although one instrument was consistently high relative to the other for ambient measurements, these levels of agreement were usually within the stated accuracy and precision of the two instruments. These results are reassuring. Nevertheless, their significance is reduced by the similarity in the design and operation of the two instruments.

Nitric Acid

A test by Hering et al. (1988) focused on the capability to measure nitric acid (HNO3). Over an 8-day period at a site with urban and suburban characteristics, six methods were used to make simultaneous measurements: filter pack, denuder difference, annular denuder, transition flow reactor, tunable-diode laser, and Fourier transform infrared spectrometer. The reported concentrations of HNO3 varied by more than a factor of 2. These differences were substantially larger than the estimated precision of the instruments. The tests indicated that artifacts or interferences exist for some of the sampling methods associated with either the field sampling components (e.g., inlet lines), the operating procedures, detector specificity, or alteration during sampling in the physical or chemical make-up of the ambient air, such as shifts in the gas- and solid-aqueous-phase equilibrium of HNO3, ammonia, and ammonium nitrates.

Suggested Citation:"7 Techniques for Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

Several conclusions could be drawn from Hering's data set. The larger percentage differences in the techniques that were observed at higher HNO3 concentrations and the dependence of the differences on day or night sampling suggest uncontrollable shifts of the equilibrium (ammonium

nitrate evaporation) in samples obtained by some instruments. The annular denuder exhibited poor intramethod precision for HNO3, and its average value was substantially below the means of the spectroscopic methods and those of all methods. The results from tungstic acid adsorption tubes and filter packs (> 8-hr sample) deviated substantially from those two means. The falter packs exhibited a positive bias (systematically higher than average HNO3 concentrations) that increased as the sampling time average increased, indicating an artifact due to ammonium nitrate particle evaporation to release HNO3 (and ammonia). The denuder difference, transition-flow reactor, filter pack (<8-hr sample), and spectroscopic methods were in good agreement. This comparison provides a valuable start in assessing the problems of reliable measurement of HNO3.

A more recent test involved three different measurement approaches: nylon falter collection, tungstic oxide denuder, and TDLAS (Gregory et al., 1990). In general, the filter measurements were high relative to those reported by the denuder. No correlation was observed between the falter and denuder techniques for HNO3 < 0.15 ppb. Below 0.3 ppb, the difference between simultaneous measurements from the denuder and filter instruments was greater than the expected accuracy and precision stated for each instrument for more than 75% of the measurements. Comparing the denuder technique and TDLAS, TDLAS measurements were consistently higher; for HNO3 > 0.3 ppb, TDLAS results were systematically higher by a factor of approximately two. There was only one instance of overlap among all three techniques at concentrations of HNO3 well above detection limits. In that case, the measurements from the filter and TDLAS were in agreement, whereas those from the denuder (with only a 35% overlap) were about a factor of two lower. The paucity of simultaneous measurements from all three instruments prevented firm conclusions being drawn from the intercomparison. However, it was clear that there was substantial disagreement among the three techniques, even at mixing ratios well above their respective detection limits. These inter-comparisons clearly indicate that current techniques do not allow the unequivocal determination of HNO3 in the range of concentrations expected in the nonurban atmosphere.

Suggested Citation:"7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

One final comparison is worthy of note. A new technology is emerging to measure HNO3 and other soluble gases. For HNO3, this approach involves the absorption of HNO3 contained in air into ultraclean water followed by analysis with ion chromatography. The approach has been obvious for decades, but only recently have water purification and handling techniques become sufficiently advanced to allow measurement of low levels of these compounds (Cofer et al., 1985). A recent application of this approach is the mist-chamber technique (Cofer et al., 1985; Talbot et al., 1990), which is used to measure nitric acid and other atmospheric acids (Talbot et al., 1988). The mist-chamber technique was recently compared with the nylon Filter method (Talbot et al., 1990). Laboratory and field tests indicated that both techniques were capable of collecting and analyzing HNO3 emitted from permeation tube sources. However, in field measurements made at a rural site, the nylon Filter yielded HNO3 mixing ratios 70% larger than those measured simultaneously by mist-chamber techniqes. Subsequent tests revealed a small positive interference for ozone on the nylon filter, but this interference could not account for the large discrepancy noted above. Talbot et al. (1990) suggested that the nylon filter may suffer interference from other species as well. In any event, this comparison shows the need for caution in interpreting the measurements of HNO3 made with available techniques and underlines the need for further study to determine the reliability of the various methods.

Total Reactive Nitrogen Oxides

Understanding of reaction pathways can be advanced by the measurement of the total abundance of reactive nitrogen compounds, NOy' as well as by the measurement of the individual NOy species. For example, it is NOy' rather than such components as NO2, that is of primary interest in tracking the transport and deposition of tropospheric nitric acid on a regional basis.

Several NOy measurement techniques have been proposed. In general, all rely on the reduction of the NOy-species to NO followed by detection of the NO. A ground-based comparison of two of these techniques, the gold-catalyzed conversion of NOy to NO in the presence of carbon monoxide and the reduction of NO. to NO on a heated molybdenum oxide surface, has been done by Fehsenfeld et al. (1987). The instruments were found to give similar results for the measurement of NOy concentration in ambient air under conditions that varied from clean continental background air to typical urban air, with NOy ranging between 0.4 ppb and 100 ppb. However, it was found that when the molybdenum oxide converter was operated for extended periods (several hours) with NOy concentrations > 100 ppb, the conversion efficiency dropped significantly. For this reason the gold-catalyzed converter was judged more reliable when used in a polluted environment.

Suggested Citation:"7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

Measurement Techniques for Carbon Monoxide and Volatile Organic Compounds

Unlike the NOx measurement techniques described above, which are adequate, the techniques for measuring VOCs and their oxidation products do not meet current needs. The analysis of VOCs is complicated by the extreme complexity of the mixtures that can be present in the atmosphere. Over one hundred detectable VOCs can be present in air sampled from reasonably isolated rural sites (P.D. Goldan, pers. comm., Aeronomy Laboratory, NOAA, 1990). In urban locations this number is substantially greater (Winer et al., 1989). VOCs emitted by vegetation, estimated to account for 50% of the VOCs emitted into the atmosphere in the United States (Placet et al., 1990), are mainly highly reactive olefinic compounds. Moreover, it is believed that more than one-third of the natural compounds that are emitted are, as yet, unidentified. Air samples obviously can contain many different VOCs of natural and anthropogenic origin; the oxidation of each of these species creates a mixture that contains many additional oxidation products as well. This complex chemistry is discussed in detail in Chapters 5 and 6. It is clear that the analysis of VOCs and their oxidation products is a formidable task. The techniques that have been developed to measure these compounds, as well as several promising new methods, are described in the following sections.

The discussion of these measurement techniques is divided into five parts: (1) carbon monoxide (CO); (2) nonmethane hydrocarbons (NMHC), which are compounds other than methane (CH4) that are composed entirely of hydrogen and carbon; (3) formaldehyde (HCHO), the simplest aldehyde; (4) other aldehydes and ketones; and (5) organic acids. These are the compounds that most strongly influence the photochemical production of tropospheric ozone, which have the most atmospheric variability (as opposed to CH4), and for which measurement capability is a matter of the most concern. The term "volatile organic compound" refers to all the above compounds except CO, and also refers to other compounds, such as organic nitrates, peroxides, and radicals, that are discussed elsewhere in the report.

Carbon Monoxide

CO is ubiquitous in the atmosphere, and it has many sources, both natural (oxidation of methane and other natural VOCs and biomass burning) and anthropogenic (combustion processes). Its lifetime is long enough, on the order of a few months, that it is distributed globally, and its concentration ranges from 50 to 150 ppb in the remote troposphere.

Suggested Citation:"7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

Concentrations above this background can indicate air masses that have had recent anthropogenic pollution input. Given the relatively unreactive nature of the gas and its high concentrations, it is expected to be one of the more easily measured trace atmospheric species.

Three techniques are used widely for measurement of CO in the troposphere: collection of grab samples followed by analysis using gas chromatography (GC); tunable-diode laser absorption spectrometry (TDLAS); and gas filter correlation, nondispersive infrared absorption spectroscopy (NDIR). The first two of these methods have been compared in rigorous sets of tests (Hoell et al., 1987b, and the references therein). In the earlier ground-based comparison of three GC techniques (one with direct injection of samples) and one TDLAS system, there was a high degree of correlation between the results of all four techniques in ambient measurements and for prepared mixtures of CO in ambient air (Hoell et al., 1987b). The general level of agreement was within 15%. However, a day-to-day bias between the techniques was observed to result in differences between techniques as large as 38%.

In the later airborne comparison (involving the two grab sample GC and the TDLAS systems), the techniques had been refined to the point that, at mixing ratios of 60-140 ppb, the level of agreement observed for the ensemble of measurements was well within the overall accuracy stated for each instrument (Hoell et al., 1987b). The correlation coefficient determined from the measurements taken from respective pairs of instruments ranged from 0.85 to 0.98, with no evidence of the presence of either a constant or proportional bias between any of the instruments. Thus, the reliability of the measurement of CO has been rigorously established.

Nonmethane Hydrocarbons

Much of the reactive carbon entering the atmosphere is in the form of nonmethane hydrocarbons (NMHCs). The standard approach for measurement of NMHCs is based on GC separation of individual hydrocarbons and the detection of each using a flame ionization detector (FID). Singh (1980) summarized the general procedures used in the analysis of ambient hydrocarbon samples. The GC column and temperature programming of the column are selected to give the desired resolution of the compound peaks. Over the years, separation and the integrity of compounds that pass through the columns have been improved by development of better column packing compounds for packed columns or coatings for open tubular columns.

Suggested Citation:"7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

The FID is a nonspecific hydrocarbon detector with a sensitivity that, in general, is linearly proportional to the number of carbon atoms in a VOC molecule (Ackman, 1968). Compound identification is usually established by compound retention in the GC column. In addition, mass spectrometric identification of given peaks can be made to confirm the elution time assignments or can be used to help in the identification of an unknown peak.

When very low concentrations of the VOCs are measured, it is necessary to concentrate the samples before they are injected into the column. This is done by concentrating a volume of air cryogenically or with a trapping matrix before injection onto the column. By temperature programming the trap, it is possible to separate the VOC compounds to be measured from compounds that comprise the bulk of the air sample: nitrogen, oxygen, water vapor, argon, and carbon dioxide. As a consequence of these improvements, VOCs with concentrations as low as 5 ppt in air have been measured with good resolution by GC-FID systems. However, there can be problems with using this method to measure reactive VOCs at low concentrations in air. Large amounts of compounds, particularly high-carbon-number compounds, can be retained by the trapping medium. In addition, reactions between the VOCs and oxidants, such as residual ozone that survives the collection procedures, may destroy some hydrocarbons and produce other compounds not originally in the sampled air. Hence, additional methods are required to reduce the oxidants to negligible concentrations before preconcentration without altering the concentration of the hydrocarbons to be analyzed.

Often, measurements of NMHCs in the field are done under circumstances that require maximum portability and low power consumption, and they arc done in an environment adverse to the operation of a sensitive instrument. Consequently, many NMHC measurements are done by acquiring an air sample in a suitably prepared container and transferring it into the GC-FID. Sample containers have been made from glass, treated metal, and special plastics. Sampling procedures often require that the containers be purged before the air sample is obtained and that the sample be stored in the container above atmospheric pressure. Although much has been done to ensure the integrity of the compounds of interest in these containers, many of the difficulties attendant to this approach are associated with the stability of the sample during transport and storage. When samples of hydrocarbons are analyzed after having been stored for several days, substantial losses of the heavier hydrocarbons can occur (Holdren et al., 1979). This is significant because occasionally, several months may pass before hydrocarbon samples stored in these containers can be analyzed.

Thus far, there has been no rigorous comparison of the various versions of GC-FID systems and sampling containers. However, the limited comparisons that have been done indicate that the techniques could be satisfactory for measuring relatively high concentrations (> 10 ppb carbons) of simple, light hydrocarbon compounds (five carbons or fewer).

Suggested Citation: "7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

Formaldehyde

The oxidation of NMHC forms the carbonyl compounds, the aldehydes and ketones (CHO). Measurements of these compounds can test present understanding of the VOC oxidation mechanism. The oxidation of aldehydes and ketones can be an additional source of ozone and oxidizing free radicals, and the photolysis of aldehydes and ketones can be a primary source of radicals. The simplest aldehyde, formaldehyde (HCHO), is particularly important because it can be formed by the oxidation of methane. As a result, it is distributed throughout the troposphere. HCHO can also be emitted into the atmosphere as a direct product of hydrocarbon combustion (Lawson et al., 1990a). Thus the photolysis of HCHO could be a key process in the formation of tropospheric ozone.

Four techniques have emerged for the measurement of HCHO: TDLAS; enzymatic fluorometry (EF), which involves the absorption of HCHO from a sampled air stream into water followed by detection of the fluorescence from the reaction of the aqueous HCHO with b-nicotinamide adenine

dinucleotide, as catalyzed by the enzyme formaldehyde dehydrogenase; a diffusion scrubbing fluorescence (DSF) technique, which involves the absorption of HCHO from a sampled air stream into water followed by detection of the fluorescence from the reaction of the aqueous HCHO with ammonia and acetylacetone; and a derivatization technique, which involves trapping HCHO on a substrate impregnated with 2,4-dinitrophenylhydrazine (DNPH) followed by extraction of the derivatized compounds and ultraviolet absorption analysis. Two studies have been reported that compare these techniques for the measurement of HCHO in ambient air. In the first, Kleindienst et al. (1988) compared the four techniques for the measurement of HCHO at the lower concentrations (< 10 ppb) typically found in rural air. Because of its recent development, potential interferences for the DSF technique were not known in advance of the study and, as a consequence, the DSF technique was not involved in the ambient air measurements. In this study, no large systematic errors were observed in synthetic air mixtures with and without added interferants such as NO_2, SO_2, O_3, and H_2O_2, or, for the TDLAS, EF, and DNPH techniques, in ambient air where ambient concentrations of HCHO ranged from I to 10 ppb. Although reasonably low concentrations of HCHO were encountered during this comparison, no attempt was made to establish detection limits for these instruments.

In a more recent comparison, Lawson et al. (1990a) evaluated the four instruments in a reasonably polluted urban environment. In this evaluation two additional techniques were included, Fourier transform infrared spectrometry (FT-IR) and differential optical absorption spectrometry (DOAS). Because of their low sensitivity, these latter two techniques are not suitable for the measurement of HCHO in the nonurban atmosphere. However, because they are highly specific optical techniques that can measure higher concentrations of HCHO over limited paths in the free atmosphere, in this urban environment they provided independent measurements for comparison with the measurements made by the other techniques.

Suggested Citation:"7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Washington, DC: The National Academies Press. doi: 10.17226/1889.

During the course of the 10-day study, a systematic diurnal variation was observed in the HCHO; it reached a maximum during the day and a minimum during the night. The average hourly ambient HCHO ranged from 4 to 20 ppb. Because reasonably high concentrations of HCHO were observed during the early morning rush hour, it was surmised that formaldehyde was being emitted directly into the atmosphere as a primary pollutant. Over the study period, the three spectroscopic techniques agreed to within 15% of the mean of these three methods. DNPH yielded values 15-20% lower than the mean of the spectroscopic techniques, whereas DSF yielded values 25% lower than the mean. Measurements obtained with the EF were found to be 25% higher than the mean. Measurements reported early in the study for DSF and EF were closer to the spectroscopic mean; problems developed in these instruments as the comparison progressed. The slight negative bias in the values obtained with DNPH was tentatively attributed to a negative ozone interference (ozone concentrations ranged from 0 to 240 ppb in this field study).

Other Aldehydes and Ketones

The measurement of higher molecular weight aldehydes and ketones has been performed with two different techniques, DNPH cartridges and GC-FID. DNPH has been the standard method for most field measurements of the carbonyls. For these compounds, the method has proven to have adequate selectivity. However, it suffers from low resolution and sensitivity when compared to GC-FID. Also, because DNPH involves liquid extraction of the compounds of interest from the cartridge, blank levels are a problem for measurements of carbonyl compounds at concentrations expected in

the rural environment. GC-FID offers reasonable sensitivity and high resolution when capillary columns are used. This technique can achieve detection limits of <0.01-0.2 ppb in one liter of air, depending on the compound analyzed. In GC-FID analysis of ambient air, artifact formation of carbonyl compounds can arise in the cryogenic collection of an air sample. Thus

Suggested Citation: "7 Techniques For Measurement of Reactive Nitrogen Oxides, Volatile Organic Compunds, and Oxidants." National Research Council. 1991. *Rethinking the Ozone Problem in Urban*