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Local Measurement of Tropospheric HO_x

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PREFACE

Direct detection of the important OH radical in the clean troposphere has posed an extraordinary challenge to experimentalists. There is now a nearly two-decade history of attempts to measure this elusive species, primarily in the United States and Germany. Much of the early effort was devoted to the technique of laser-induced fluorescence, culminating in a series of intercomparison tests concluding that the first generation of OH instruments was not capable of the needed sensitivity. A workshop held at SRI International in August 1985 assessed the prospects then available for detection of OH, HO₂, and H₂O₂ in the near future.

Recently, there has been significant development of both laser and nonlaser methods for the determination of OH, and further development of HO₂ methods as well. Thus this is an opportune time to discuss further the available methods. Local measurement of OH and HO₂ is the topic of the present workshop, held at SRI International on 23 to 26 March 1992 (the term local measurement is meant to distinguish the methods from global, regional, and diurnal averages). Many methods are now available, far more than in 1985, and all were discussed. Importantly, there are now nonlaser local OH determination techniques, subject to different experimental errors than the spectroscopic methods. The topic of instrument intercomparison for OH was selected as a subject for special discussion.

As in 1985, the workshop was structured to encourage considerable discussion. The participants were the field measurement experimentalists, other atmospheric chemists, and chemical physicists familiar with the pertinent experimental methods. They were divided into five subpanels, with representation from each scientific specialty. Discussion within these was alternated with full group discussion. The conclusions, recommendations, and ideas from the subpanels were collected as summary notes, and form the basis for this report.

Additionally, notes compiled by Leah Williams and Gregory Smith of SRI, and discussions with them, have assisted greatly in my reconstructing the workshop deliberations. The report has been circulated in draft form to all the participants, and most of the comments received have been incorporated. I hope that I have managed to fairly represent all of the ideas expressed, not just a majority opinion; in any case I am responsible for this interpretation of those ideas.

The major support for this workshop was provided by the National Science Foundation, Atmospheric Chemistry Division, and the National Aeronautics and Space Administration, Tropospheric Chemistry Program. Additional funds for travel expenses for participants were furnished by the Chemical Manufacturers' Association, the Alternative Fluorocarbons Environmental Acceptability Study, Battelle Pacific Northwest Laboratories, the Electric Power Research Institute, and the National Oceanographic and Atmospheric Administration. I wish to thank all of these sources for making the workshop possible.

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1. The first part of the document discusses the importance of maintaining accurate records of all transactions. It emphasizes that this is crucial for the company's financial health and for providing reliable information to stakeholders.

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3. The third part of the document addresses the role of the accounting department in this process. It highlights the need for clear communication and collaboration between different departments to ensure the accuracy and timeliness of the records.

4. The fourth part of the document discusses the importance of regular audits and reviews. It explains how these activities help to identify any discrepancies or errors and ensure that the records are up-to-date and accurate.

5. The fifth part of the document provides a summary of the key points discussed and offers some final thoughts on the importance of maintaining accurate records for the long-term success of the company.

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EXECUTIVE SUMMARY

The OH radical plays a major role in tropospheric photochemistry, and its measurement forms an extremely useful test of our knowledge of that chemistry. Accordingly, a major effort has been devoted to developing means for its direct detection on a rapid time scale (seconds to minutes) and a local spatial scale (a few km). Such measurements are quite difficult, owing to the low concentration of reactive, transient OH, of the order of 10^6 molecules per cm^3 . In 1985, following a series of intercomparison tests showing that methods then available were incapable of detecting OH at these levels, a workshop held at SRI International appraised detection schemes for OH, HO₂, and H₂O₂. Since that time there has been significant development of means for detection of local OH, using both laser-based and nonlaser methods.

In March of 1992, a second workshop was held at SRI International to assess the current state of measurement techniques for both OH and HO₂. The workshop participants consisted of the experimentalists involved in measurement of the two radicals, other atmospheric chemists, and chemical physicists familiar with the measurement techniques. The format consisted of brief presentations including considerable discussion, with further discussion within five smaller groups. A special session was devoted to intercomparison studies.

Many instruments or concepts were represented at the workshop. Five laser-induced fluorescence schemes for OH detection were presented, and five laser-based absorption techniques. Importantly, four nonlaser methods were also presented. These are subject to very different experimental errors than the laser-based techniques, and the absence of any nonlaser techniques in 1985 was felt to be a serious deficiency. HO₂, at concentrations about a hundredfold those of OH, also plays an important role in tropospheric chemistry. Six instruments or concepts for HO₂ detection were discussed, based on chemical amplification, conversion to OH with subsequent OH detection, or spectroscopic detection of the HO₂ itself.

There were several major conclusions from the workshop:

1. OH measurements are valuable and form crucial tests of models of tropospheric photochemistry. There are recent surprising indications that local concentrations could disagree significantly with model predictions (a factor of three or more). With currently available instruments, local OH measurements can be made at sensitivities useful for this purpose. Low-pressure laser-induced fluorescence, long path absorption, ion-assisted mass spectroscopy, and ¹⁴C¹⁸O oxidation are now ready for field studies.

2. Measurements of OH are not useful without a large suite of supporting measurements to determine the other variables that control the OH concentration. These include measurement of H₂O, O₃, CH₄, CO, NO, NO₂, J(NO₂), J(O₃), and in some cases NMHCs. Care must be taken to ensure meaningful comparison with model predictions and among different instruments in those cases where not all of the measurements are averaged over the same temporal or spatial scales.
3. HO₂ measurements can be made reliably with a variety of techniques at needed levels of precision and sensitivity. These are useful both alone and in conjunction with OH measurements. The methods are chemical conversion to OH with subsequent OH detection, chemical amplification which determines the sum of HO₂ and RO₂, and matrix isolation electron spin resonance.
4. Intercomparison studies are vital to establishing the credibility of the OH measurement methods and must be undertaken. A ground-based series, probably in 1995 at the earliest, should precede any flight tests. A formal blind intercomparison should be held, with previous participation in at least one informal intercomparison a prerequisite. The site should be carefully chosen (by a panel convened for the purpose) to provide variation in the variables controlling OH, and the full set of those variables should be measured simultaneously. This could be part of a more general photochemistry mission if the objective of OH intercomparison is not thereby compromised.
5. Sampling inlets are a major concern for obtaining reliable OH measurements, as loss can occur between sampling and detection. Effort should be directed at sharing and comparing inlet designs, although a common inlet is not necessarily a good idea, or even possible. A standard OH calibration source would be very valuable, although none is now available. If available, one could be circulated among experimentalists to ensure common calibration even if absolute accuracy is not determined. Absorption in a limited spatial region offers the best absolute OH calibration.

INTRODUCTION

OH in the Troposphere

The hydroxyl radical is central to the chemistry of the troposphere. It is the primary oxidizing agent responsible for the removal of most trace gases, including CH₄ and other hydrocarbons, CO, H₂, and hydrogenated halocarbons. OH oxidizes SO₂ to sulfuric acid and NH₃ to NO; it is important in establishing the balance between NO and NO₂ and the partitioning between these two species and the HNO₃ reservoir.

The primary formation mechanism for OH is O₃ photolysis at wavelengths below 315 nm, producing O(¹D) atoms which react with H₂O vapor to form the radicals. (At sufficiently high NO concentrations, the reaction NO + HO₂ can also be significant.) OH is destroyed primarily by reaction with CO and CH₄. A simple balance between approximate production and destruction rates, with appropriate values of solar flux and concentrations of these reactants, leads to a chemical lifetime for OH of about 1 s and typical daytime concentrations of about 3×10^6 molecules/cm³ in the clean troposphere. Because of this short lifetime, the OH concentration responds rapidly to changes in the ambient concentrations of other atmospheric species, such as O₃, H₂O, NO, etc. On this time scale, it is not affected by surface sources and sinks, and a measurement of its concentration thus constitutes an excellent test of models of the fast, homogeneous photochemistry of the troposphere.

Because of this important role, considerable effort has been expended, primarily in the United States and in Germany, to develop a means for determination of hydroxyl concentrations in the troposphere. For the most constraining, stringent comparison with model predictions, one desires measurements made on a rapid time scale (seconds to minutes) and local spatial scale (averaging over distances less than a few km at most). An instrument capable of operation from an aircraft platform is also valuable, owing to its ability to sample varying conditions in the atmosphere outside the planetary boundary layer, thereby determining the response of [OH] to changes in the variables that control it. Such measurement methods we term "local", as distinct from techniques which average over regional or global scales, and the seasonal as well as diurnal variation of OH concentration.

In the 1970s, three methods were proposed and developed for this purpose. These are long path absorption of laser radiation, averaging over several km but yielding a direct absorption measurement without need for external calibration; laser-induced fluorescence (LIF), whose design

parameters promised the needed sensitivity and selectivity for measurements made within a volume of a few cm³; and ¹⁴CO oxidation, a chemical conversion process also operating on a local scale. The latter two methods are capable of flight operation. A 1982 workshop report¹ contains full descriptions of the laser-based methods, including spectroscopic and collisional considerations, and a careful delineation of the analysis used to extract OH concentrations from the measured signals.

During the development of the LIF effort toward levels of sensitivity capable of detection of ambient tropospheric OH, it became apparent that there existed interference problems unanticipated from tests at higher concentration. The primary problem was photolysis of O₃ by the laser beam. Operation at a laser wavelength of 282 nm and observation at 310 nm had been designed to avoid scattered laser light. However, laser photolysis of ozone at 282 nm produced spurious OH molecules in the path of the laser beam, often in much higher concentration than the ambient OH. Attempts to avoid the problem by reduction in laser intensity also reduced the already small LIF signal due to natural OH. A secondary but clearly noticeable problem was background fluorescence due to aerosols and unidentified gaseous compounds absorbing the laser light.

These enduring problems and the controversies associated with their proper solution led to the concept of an instrument intercomparison study. This was performed as CITE-1, the first of the Chemical Instrumentation Test and Evaluation missions, with OH experiments at a ground station in 1983 and aboard flights the following year. Two LIF packages and the ¹⁴CO experiment were tested, although only the laser-based instruments yielded data. No intercomparison data were obtained in the ground portion of the tests. A total of eight simultaneous LIF measurements were made during the flight segments. These data and their analyses were reviewed by an external panel (R. N. Zare, A. L. Schmeltekopf, and D. R. Crosley). The conclusion reached by this panel was that definitive measurements of tropospheric OH had not been demonstrated.² The background levels due to nonresonantly excited fluorescence and solar scatter presented serious problems. It was clear that the schemes tested in CITE-1 were unable to provide reliable measurements of OH at the concentration levels useful for testing our knowledge of tropospheric photochemistry.

HO₂ in the Troposphere

The HO₂ radical is also of crucial importance in tropospheric photochemistry. It is linked to the OH concentration through the HO₂ + NO → OH + NO₂ reaction, its formation as a product of the reaction between OH and both O₃ and H₂O₂, and as a result of the oxidation of CH₄ and CO initiated by OH. Its removal proceeds largely by reaction with O₃, NO, and itself, with relative concentrations depending on local conditions. HO₂ reaction with itself forms H₂O₂, whose wet deposition and reaction with OH form major routes for the destruction of odd hydrogen. HO₂ is

also important in partitioning NO_2 into HO_2NO_2 , one of the temporary reservoirs for NO_x . HO_2 is present typically at concentrations one hundred times that of OH, except in the presence of NO concentrations as high as 1 ppb; and HO_2 has a chemical lifetime of minutes, again about a hundred times that of OH. Accordingly, HO_2 is subject to the influence of some sink and source terms on the surface. Nonetheless it also constitutes a valuable test of tropospheric photochemistry and its measurement is also highly desirable.

Until recently, there existed only two methods for HO_2 determination, matrix capture with electron spin resonance measurement, and chemical amplification followed by NO_2 determination. First used in the stratosphere, chemical conversion to OH with sensitive detection of the latter radical has recently been developed for tropospheric instruments, although, as with all chemical conversion methods, this is subject to interferences. HO_2 has never been the focus of an intercomparison campaign.

OH Detection Development, 1985 - 1992

After the CITE-1 experiments demonstrated the inability of the then-current instruments for the detection of local OH, it was felt useful to proceed further, looking to new methods for detection of OH radicals. In 1985, a workshop was held to assess future prospects and directions for the detection of all odd hydrogen containing compounds, H_xO_y , in the troposphere.³ The participants were invited from three groups of scientists: modelers of atmospheric chemistry, experimentalists measuring OH, HO_2 , and H_2O_2 , and chemical physicists familiar with the physical principles on which the experimental techniques were based, but not themselves involved in atmospheric monitoring.

There were four major conclusions from this workshop concerning local detection of the OH radical. First, it was felt that measurements made by laser techniques would be ready within 2 or 3 years of that time to furnish reliable determinations at the level of 10^6 molecules/cm³. Second, measurements at this level of sensitivity and with attainable levels of precision (within 30% or better) could indeed be used to make useful and interesting tests of the fast photochemistry of the troposphere. These measurements, however, must be carefully designed, with respect to spatial and temporal averaging, if there is to be a meaningful comparison made between results from two different experimental methods or between measurement and model. Third, while laser-based methods appeared very promising, it would be extremely valuable to have one or more nonlaser, nonspectroscopic local methods for comparison, although no nonlaser candidate was identifiable. Finally, intercomparison among experimental methods is crucial to establishing credible measurements of OH concentrations; such tests, both planned and open comparison, and blind

tests such as CITE, should be considered an essential part of the developmental effort with results made public.

Of the four LIF-based methods discussed at the 1985 workshop, only one has undergone significant development since that time, the FAGE (Fluorescent Assay by Gas Expansion) method at Portland State University. The 1985 version of this method has been criticized as being prone to laser-generated interference, using a computer model of the photochemistry of the experimental technique.⁴ The Portland State apparatus has undergone substantial redesign and improvement, and two other groups (at Pennsylvania State University and KFA Jülich) have also now constructed instruments based on this approach. Little work has been done on the second method, two-photon LIF detection at Georgia Tech, largely due to difficulties in generation of suitable tunable infrared laser light, although new technologies for this purpose are now emerging. Efforts on the other two LIF methods discussed in 1985, lidar-based at the Jet Propulsion Laboratory, and low-pressure/frequency modulated at Ford Motor Company, have been abandoned. Development has continued on the long path laser absorption methods, performed at KFA Jülich and MPI Mainz, discussed in 1985, and new efforts with this approach have been undertaken at NOAA and Frankfurt.

Especially valuable is the emergence of new nonlaser methods for local OH detection. Comparison of results obtained using both spectroscopic and nonspectroscopic techniques could signal serious deficiencies that might be hidden in a comparison among similar methods with common systematic errors. These approaches include a redesign of the ¹⁴C¹⁸O oxidation method (Washington State), ion-assisted mass spectroscopy (Georgia Tech), dye fluorescence quenching (Arizona), and active chemical titration (Massachusetts Institute of Technology). Some of these have by now advanced to the field measurement stage whereas others have yet to undergo laboratory mockup.

In the 1985 workshop, considerably less attention was paid to HO₂ than OH. Only two methods were discussed: a chemical amplifier method (University of Denver) and conversion to OH with subsequent OH detection (Portland State). Each of these has undergone further development, chemical amplification at Denver and also York University and NCAR, and conversion to OH at Portland State, Pennsylvania State and KFA. The method of electron spin resonance following matrix capture (KFA) has demonstrated ambient HO₂ measurement, and tunable diode laser absorption of HO₂ has been proposed at Aerodyne and Southwest Sciences.

Thus it was felt that this was an opportune time for a new assessment of the methods available. As in the 1985 workshop, the participants consisted of modelers and other atmospheric chemists, researchers involved in field measurements, and chemical physicists familiar with the

principles underlying the methods. The scope of the workshop was limited to local measurement methods for tropospheric HO_x, that is, those that average over time periods of seconds or minutes and spatial scales up to a few km at most. Each technique for OH and HO₂ was discussed individually. Additionally, intercomparison studies among different methods and approaches for both relative and absolute calibration were specifically selected topics for discussion. The group was divided into five discussion panels, who met separately but whose conclusions and recommendations were presented to and discussed by the entire group of participants. The remainder of this report will discuss measurement requirements, prospects of the currently available and potential methods for meeting those needs, the issues of intercomparison and calibration, and finally laboratory data required for quantitative understanding of HO_x measurement schemes.

MEASUREMENT REQUIREMENTS

Although the absolute concentration of OH is the key to determining the local oxidizing power of the troposphere, the value of OH measurements lies not as an isolated measurement but rather as a test and constraint for models of tropospheric photochemistry. Several individual instruments discussed below appear now or in the near future capable of detecting OH at concentrations near 10⁶ molecules/cm³, with a background often below 10% of that value and a precision of 30% or better. As concluded in the 1985 workshop, this is adequate to form useful tests of our understanding of the fast photochemistry of the troposphere. We discuss here needs for measurement sensitivities and precision, present concerns about averaging over different time and/or distance scales when comparing measurement and model, and describe the ancillary species determinations needed for meaningful use of [OH] data as such a test.

OH Measurement Sensitivities

The approximate concentration of tropospheric OH can be obtained from knowledge of the major production and loss rates⁵. In continental mid-latitudes, the main OH production mechanisms are the reaction of O(¹D) with H₂O, and the reactions of HO₂ with O₃ and NO; OH is removed primarily by reaction with CO and CH₄. Then one can estimate its concentration from the following photostationary balance:

$$[\text{OH}] = \{[\text{HO}_2](k_7[\text{O}_3] + k_6[\text{NO}]) + 2k_2[\text{O}(\text{}^1\text{D})][\text{H}_2\text{O}]\} / \{k_3[\text{CO}] + k_4[\text{CH}_4]\} \quad (1),$$

where the $O(^1D)$ concentration is also given by the ratio of its production and removal rates:

$$[O(^1D)] = J_1[O_3]/\{k_{QN}[N_2] + k_{QO}[O_2]\} \quad (2).$$

Here, k_i is the rate constant for each relevant chemical reaction; k_{QN} and k_{QO} are the rate constants for quenching of $O(^1D)$ to $O(^3P)$ by nitrogen and oxygen, respectively. J_1 , an effective photolysis rate constant, includes solar flux, ozone absorption cross section and the quantum yield for $O(^1D)$ formation. With this balance, and concentrations of the controlling variables appropriate to continental mid-latitude air,⁵ one finds noontime maximum concentrations of OH between 1 and 2×10^6 molecules/cm³.

These values correspond to empirical values for the concentration of globally, diurnally, and seasonally averaged [OH]. Those concentrations⁶ may be derived through analysis of the budget for methyl chloroform, CH_3CCl_3 . This compound is released to the atmosphere by anthropogenic activity and removed by reaction with OH, having a chemical lifetime of about six years. Therefore its concentration reflects reaction with OH averaged over large temporal and spatial scales. Agreement with model predictions within about a factor of two is achieved; the difference can be ascribed to uncertainty in source strengths of some of the variables controlling [OH]. This is very useful information, but it appears unlikely that further measurements will pose new constraints on our knowledge of global [OH].

In contrast to these globally and seasonally averaged concentrations of OH, the local measurement techniques discussed at the workshop test on a rapid time scale and local spatial scale the response of [OH] to variation in other controlling variables under different conditions. They are thus able to test, sensitively, specific portions of the photochemical models, using well designed experiments in the presence of suitably changing conditions.

What do we expect to find with these local measurements? Testing model predictions requires some degree of precision (a precision the measurement techniques appear capable of achieving). Certainly the existence of OH at the $10^6/cm^3$ level is well enough established that an experiment which merely confirms that fact is hardly necessary. In addition, the diurnal variation of OH (its disappearance at night in a relatively clean environment) is quite well established on simple theoretical grounds. Thus an observation of this variation should be construed as confirmation of proper operation of the instrument, not confirmation of photochemical models.

A discussion of our knowledge of tropospheric [OH] photochemistry at the 1985 workshop concluded that we certainly do not expect local measurements to exhibit tenfold disagreement with model predictions, and that in fact "disagreement between measurement and

calculation at the factor of three level would likely signal a significant omission in our understanding of tropospheric photochemistry." However, recent evidence suggests that there indeed can be disagreement even more than this factor of three.

In the summer of 1991, measurements of OH were made simultaneously with two of the techniques discussed at the workshop, long path absorption and ion-assisted mass spectroscopy⁷. The primary focus of this experiment was an informal intercomparison study, as discussed below. However, the absolute [OH] concentrations determined by both methods can also be compared with predicted concentrations. These predictions are made using a photochemical model⁸ designed to describe the forested region in which the experiments were made, in particular the influence of isoprene and other nonmethane hydrocarbons. The model predicts concentrations some 3 to 5 times larger than the measured values. This discrepancy cannot be ascribed to an incorrectly low rate of OH removal by isoprene because the low OH concentration does not exhibit the correlation with ambient temperature that would then be expected, caused by the temperature dependence of the isoprene vapor pressure.

Thus there are surprises at a level signifying some significant deficiencies in our understanding of fast tropospheric photochemistry, well beyond those anticipated a few years ago. This makes even more compelling and exciting a measurement of local [OH], spanning a range of interesting conditions in the troposphere.

Accuracy and Precision

As a test of the photochemistry, the needed accuracy and precision in the measurement should be somewhat better than that in the model prediction. These are important considerations in addition to ultimate sensitivity. Early proposals for OH detection focused on a standard of 10% absolute accuracy at the 10^6 level¹, but this is an extremely difficult requirement and apparently was chosen somewhat arbitrarily. As discussed in the 1985 workshop, meaningful comparison with model predictions can be made with considerably relaxed demands. A precision of 30% or better in measurements of relative OH in the presence of different concentrations of the controlling variables should be sufficient for this purpose. Some of the instrumentation discussed at the present workshop appears to readily satisfy such criteria.

This is fortunate because a high degree of absolute accuracy in OH is difficult to attain. Potential calibration systems are discussed below. The primary standard must be absorption, which can potentially yield a high degree of accuracy; the oscillator strengths for the pertinent transitions are known to 3%. More difficult is establishing a path that is sufficiently uniform but still long enough to observe measurable absorption, although the folded path technique developed

at Frankfurt appears capable of this. Nonetheless, such a calibration source is only conceptual at the present time, and the availability of a working source capable of cross-calibrating other instruments by folded long path absorption remains several years in the future.

We examine here the degree of accuracy that is needed, compared with anticipated accuracy of the model predictions. Consider the major formation and removal rates for OH, as expressed in Eqs. (1) and (2). An uncertainty in OH due only to uncertainties in the input kinetic data may be predicted using a simple propagation of errors treatment. Errors in the rate constants in those expressions are taken from the recommendations of the NASA evaluation panel⁹ at the 1- σ level of deviation; these range from 20 to 40% for the rate coefficients appearing in the Eqs. (1) and (2) for [OH] and [O(¹D)]. We consider rates (i.e., concentrations) appropriate to nonurban, mid-latitude continental air⁵, where there is enough NO that the HO₂ + NO reaction constitutes nearly half the formation rate for OH. Under these conditions one computes an expected 1- σ uncertainty of 35% in the OH concentration. (One fifth of this is attributable to the 43% uncertainty in the O(¹D) concentration, Eq. (2).)

This range of uncertainty has also been investigated in a much more sophisticated fashion using a complete photochemical model.¹⁰ The model was run using different choices of the input kinetic data, varying them in a random Monte Carlo fashion within a distribution described by the same 1- σ uncertainties recommended by the NASA panel. The resulting uncertainty in [OH] was 25% in the marine low-latitude air, 32% in clean continental mid-latitude air, and 72% in urban mid-latitude air. The clean continental air case corresponds closely to the propagation of errors treatment described above, and the agreement between this model study and our simplified treatment is excellent.

Thus, within the $\pm 35\%$ range of the 1- σ deviation, a photochemical model cannot be expected to predict absolute [OH] better than a factor of 2, simply from the uncertainties in the input kinetic data alone. Uncertainties in the empirically determined concentrations of other species also needed as input have not been included, and that will enlarge the total uncertainty. Thus meaningful agreement on absolute [OH] between model and measurement better than this spread of a factor of two should not be expected at the present time. One might expect improved laboratory data in the future might reduce that to a factor of 1.5 (i.e., $\pm 20\%$) but not much better.

Therefore, it is more important to consider the attainable precision in an experiment, especially when comparing [OH] measured under different ambient conditions. For example, in continental mid-latitude air, [OH] increases threefold as the NO concentration increases from 10 to 100 ppt, and the [OH]/[HO₂] ratio varies markedly for NO between 10 ppt and 1 ppb.⁵ Of course, sampling air masses with such different concentrations, e.g., from an airplane, will likely involve

changes in $[O_3]$ and $[H_2O]$ as well. Thus a precision in $[OH]$ of better than 20% is indeed desirable in measurements that sample different concentrations of the controlling variables. Such precision appears attainable with some of the currently available instrumentation, for averaging times of the order of minutes or less.

Averaging Considerations

The OH concentration responds rapidly to changes in the concentration of other species whose chemical reactions form and remove the radical. The concentrations of these species can vary rapidly on temporal and spatial scales. (In a moving aircraft, of course, spatial averaging is necessarily associated with temporal averaging.) Examples of such variations can be seen in data from the 1983 CITE-1 flight portion, reproduced in Ref. 11. Occasional wide variations in O_3 , NO, and H_2O are seen, and even CO varies by as much as 20%.

The expressions describing $[OH]$, Eqs. (1) and (2), are nonlinear in the concentrations of these species. Thus the concentration of OH averaged spatially and/or temporally over actual variation of the concentrations of these variables is different from the concentration of OH computed from the average of each concentration over the same scales. A study of the effects of averaging, based on model calculations, is presented in Ref. 11. Two types of average OH concentrations were calculated. One, called "exact", was an average over the flight interval of the concentrations computed using the actual time-varying values of the controlling variables. The second, termed "approximate", was computed from the average values of those variables over the same periods. Ratios for "exact"/"approximate" of 1.3, 1.8, 1.0, and 0.9 were obtained for four different flights. However, if the data were preselected to exclude wide variations due to thundercloud encounters, the ratios for the first two flights are improved to 1.0 and 1.5. How faithfully this preselection can be carried out is of course difficult to ascertain; further modeling studies of this type could better establish such limits.

A closely related concern arises in connection with long path absorption measurements of OH. This method necessarily averages $[OH]$ over the entire path, which may not be uniform. Concentrations of the controlling variables may be obtained by absorption over the entire path, although the correspondence between measured and calculated OH is then subject to the same concerns expressed in the preceding paragraph. They are often measured at a pointwise location, typically near one end of the path. Differences between path-averaged quantities and pointwise measurements have been seen previously. For example, measurements of NO_2 were made at a field station using both long-path absorption and local chemiluminescence detection.¹² Although in most cases the agreement is within 50%, the long path measurements range between half and three times that of the chemiluminescence determinations, a spread of a factor of six. This can

cause variation in predicted [OH] of factors of four, at the ppb concentrations of NO₂ present in these experiments. Thus OH predictions based on variables determined with one averaging technique cannot be compared with confidence with OH measurements using a method that averages differently.

Supporting Measurements

As noted above, an isolated measurement of OH is of little value. Its worth comes through the comparison with model predictions. For these to be made, supporting data on the other variables controlling OH need to be available. Such data can also be useful in understanding the quality of the OH measurements themselves, as found for the 1991 NOAA/Georgia Tech intercomparison measurements discussed below. The cost of a campaign to measure OH is too great to not include a comprehensive suite of simultaneous ancillary measurements.

The accuracy of these ancillary species measurements is of course reflected in the accuracy of the model predictions. Variables which need to be determined under all conditions are the concentrations of O₃, H₂O, NO, NO₂, CO and CH₄, and values of J(O₃) and J(NO₂). In special circumstances the concentrations of other species can be important; examples might be isoprene, other nonmethane hydrocarbons, or methyl hydroperoxide. In many cases, HO₂, RO₂, and H₂O₂ determinations are extremely valuable. Spatial and temporal averaging scales as discussed above must be considered. The accuracy with which these variables can be determined may vary with conditions; for example, a sensitive Lyman- α hygrometer may be needed for accurate enough H₂O vapor measurements high in the troposphere where the humidity is too low for frost point hygrometer determinations.

OH MEASUREMENT TECHNIQUES

The local OH measurement techniques discussed at the 1992 workshop fell into three categories. One set is based on the absorption of laser light by OH, the second on laser-induced fluorescence of OH, and the third on the determination of some species either removed or produced as the result of chemical reaction of OH with an added compound. The availability of nonspectroscopic techniques having the needed sensitivity is an extremely important advance in the last seven years. A list of the methods is given in Table 1, including presenter and affiliation. Short, one-page write-ups describing the method, detailing major problems, and with appropriate references, were requested from each presenter. These are included as Appendix A. Thus we will not describe here the principles or hardware involved in each method, but rather discuss the

conclusions and concerns expressed at the workshop both about these general detection categories and about the individual instruments.

Long Path Absorption

In a carefully designed experiment, absorption on the order of or somewhat better than one part in 10^5 of the incident beam can be detected. Thus path lengths on the order of km are necessary for the measurement of ambient OH near 10^6 cm^{-3} . Three methods to achieve this were discussed. The first, common to three instruments, is retroreflection of the laser beam by a single mirror located typically 3 to 5 km from the laser and receiving telescope (this will be referred to simply as "long path absorption"). In the second, termed "folded long path", a multiple pass arrangement (as many as 200 reflections) is used to attain suitable path lengths in a much smaller volume, using mirrors located about 6 m apart. Each of these methods is currently in operation. The third approach, presented only as a concept, is intracavity absorption of ultraviolet laser dye emission, greatly extending the effective absorption path length while probing over only about 1 m actual distance.

The most appealing characteristic of long path absorption techniques is that they form absolute measurements of [OH], without the need for calibration. Once the spectral lines are identified and fitted (accounting for interferences), the only parameter needed to determine absolute concentration is the path length. The other parameter, the integrated total absorption cross section, is known through laboratory lifetime measurements and spectroscopic studies to within about 3%. However, in practice, the effective absorption cross section at line center is used, with a resulting accuracy of 10-15% depending on instrumental resolution.

There are three instruments (NOAA, KFA, Mainz) in the several-km, two-pass category. These differ slightly in hardware but are otherwise similar. The two German instruments utilize a broadband, high repetition rate picosecond pulse length laser to avoid problems created when atmospheric turbulence scatters the return beam. Both of these and the NOAA instruments utilize diode array detectors, further avoiding turbulence problems because intensity fluctuations affect all wavelengths equally in the narrow interval used. The laser beam is expanded sufficiently that OH generated by laser photolysis of ozone does not interfere (below about 10^4 cm^{-3}). Each is capable of measurements of high enough sensitivity ($\sim 5 \times 10^5 \text{ OH}$ in 1 to 15 min.) to meet the measurement criteria discussed above. The averaging time needed for a given sensitivity can vary with local conditions due to differing levels of interfering absorptions.

The quantitative operation of the multipass folded long path absorption instrument (Frankfurt) was more difficult to understand on the basis of published information. It is a scanned

narrowband device, with rapid enough scanning to avoid atmospheric turbulence. A detailed analysis including statistical noise considerations would be useful to place the sensitivity analysis of this instrument on the same footing as the two-pass instruments.

Intracavity laser absorption is a method only in concept, in that no laser dyes yet operate in the 308 nm region needed for absorption measurements. This method (like the multipass technique) has the distinct advantage of being a truly local measurement, with minimum spatial averaging. However there was concern about the real linearity of the method (the effective path length is related to the length of time the signal is averaged following buildup of the initial laser oscillations). Laser generated OH might be present in the intense intracavity laser field; this could be avoided by appropriate beam expansion in the detection region but should be carefully checked. It was felt that the utility of this method was marginal enough that further consideration should await availability of the appropriate laser dyes (i.e., their development should not be undertaken for this particular purpose). Even then, the method may not be competitive with the other methods discussed here, given normal anticipated improvements in other methods over the same period of time.

There are two major problems with the long path absorption instruments. The first of these is the detailed analysis needed to extract the OH concentration. The laser spectrum in the absence of OH absorption cannot be determined over the same path at the same time (a nighttime measurement could yield some information but conditions, and thus the interfering species, might not be the same). Even in the relatively clean troposphere of Colorado, investigated with the NOAA instrument, considerable data analysis was needed to remove absorption due to NO₂, SO₂ and other unknown interferents (probably hydrocarbons). Many data were obtained in these NOAA experiments, but the analysis is not automatic and is quite time consuming. Moreover, only a portion of the raw data (perhaps half) were of sufficiently good quality to be of use. In the German experiments, performed in a more polluted region, SO₂ was identified in absorption and naphthalene was a possible interferent. In some cases, absorption could be seen on one OH line present in the spectral region covered, but not another. A signal with the proper ratio of absorption in different lines is essential to establishing the credibility of the measurement. A spectral region encompassing more than one OH absorption line is needed to ensure that what is attributed to OH is not some isolated unidentified interferent.

The folded long path absorption can be configured to measure the background spectrum in the presence of many of the interfering gases listed above but the absence of OH. This is done by covering the path so that it is fully isolated from solar flux for a time period long enough for the OH to disappear. (This approach could even be extended to a concept for an open air laboratory in which ultraviolet flux and trace gas concentrations are varied controllably).

The second problem with the long-path absorption is that it averages over very long distances. The questions of averaging over different spatial scales have been discussed above. A fully quantitative comparison with model predictions would require knowledge of the distribution of the other controlling variables (solar flux, O₃, H₂O, CH₄, NO_x, CO) over the same path. Normally, measurements of these parameters would be made at a point near one end of the path, or possibly quantities averaged over the same path would be determined by absorption (e.g., for O₃ or NO₂). Even in the latter case differences can occur, because, due to the nonlinearity of the processes, average [OH] is not the same as [OH] computed as a function of the average of all the variables. The same concerns can be raised for a comparison of long-path absorption with a pointwise local method, as discussed below in connection with an intercomparison study between the NOAA long path and the Georgia Tech ion-assisted chemistry method.

Therefore it was felt that the long path method would have limited utility in the long term future, as some of the more localized methods described below undergo further maturation. As the pointwise methods become more sensitive, and more detailed comparisons (including ancillary variable measurement) become available, measurements averaged over several km will appear less attractive. In addition, these experiments cannot be mounted easily on aircraft platforms, limiting their ability to sample at will regions of varying types of air mass to investigate OH changes under different conditions.

An alternative view for the very long term future is that long path absorption may mature so that it can be used to measure all relevant variables at once (using a large number of wavelengths). Many simultaneous measurements could then be made along the same path.

In addition to the ability to measure the background spectrum, the folded-long path method has the advantage of being a truly local method, averaging over only a few meters of actual atmospheric path length. As now configured, it too cannot be adapted for flight measurements to sample varying environments. It is likely that the path may never be folded enough times to do so, and mirror stability requirements also may well preclude such an adaptation. Nonetheless it can be meaningfully compared with models in conjunction with other pointwise data obtained at the same measurement location on the ground.

The number of passes cannot be increased indefinitely due to losses even on excellent mirrors. Then detection hardware and statistical noise considerations may present an ultimate limit of $\sim 5 \times 10^5 \text{ cm}^{-3}$ using this method. This is not as sensitive as one might anticipate that other local instruments can attain, given further development. This, together with the inability to fly the folded long path instrument, suggests the following scenario over a five to ten year period. This method, capable of sufficiently sensitive but still local absolute measurement of OH, will find its

ultimate long term value as the calibration and validation instrument for the somewhat more sensitive and portable instruments discussed below. The instrument can be readily moved to different ground stations and can participate in ground-based intercomparisons, thus producing many useful scientific results in nearer time frames.

This Frankfurt instrument appears very useful, both for direct OH measurements at the present time, and also as the future method for absolute calibration of all other instruments (see below). Therefore, three recommendations were made by the workshop participants. First, a full and quantitative analysis of the detection method and noise sources should be made and published by the individual investigators. Second, a similar (or identical) instrument should be built in the U.S., so both could be used in different studies. Third, close contact with other groups measuring long-path absorption (NOAA, KFA, Mainz) should be maintained so that new hardware and data analysis innovations can be incorporated.

Laser-Induced Fluorescence

Five laser-induced fluorescence instruments were discussed at the workshop. Four are designed specifically to address the problem of ozone interference encountered in the measurement of tropospheric OH. Three of these operate at low pressure; these are improvements on the FAGE (Fluorescent Assay by Gas Expansion) concept introduced by the Portland State group in 1979 and discussed as one of the two viable nonabsorption local measurements at the 1985 workshop. Significant progress with this method has occurred since that time. The fourth method, also discussed in 1985, is the two-photon excitation method of Georgia Tech. The fifth method, from Harvard, is an ER-2 instrument designed for OH detection in the lower stratosphere.

Three designs, from Portland State, Penn State, and KFA, use low-pressure operation and electronic gating to reduce interference problems. Electronic gating after the laser pulse discriminates against laser scatter and fluorescence from cell components and aerosols, and also against fluorescence from interfering SO₂ and CH₂O which have much shorter radiative lifetimes than OH. The low pressure reduces the quenching rate, thereby lengthening the effective OH upper state lifetime to make possible such gating. In addition, it slows the chemical reaction and energy transfer rates which form the photolytically generated OH that can be excited by the laser.

The early FAGE design, which operated using excitation in the 1,0 band at 282 nm, was nonetheless subject to problems due to ozone interference. The situation was greatly improved by changing to operation on the 0,0 band at 308 nm, which is the form of the present Portland State instrument. At 308, the O₃ absorption cross section is only 4% of that at 282, and the O (¹D) quantum yield 18% smaller, reducing the interference problem by a factor of 29. In addition, the

OH absorption is a factor of four larger, so the signal/interference ratio increases two orders of magnitude using the same laser power. The only disadvantage compared with excitation at 282 nm is the need for increased care in avoiding scattered laser light from the apparatus and aerosols. Some new questions concerning the fluorescence quantum yield appear for this scheme, for example, effects of polarization of the fluorescence and the temperature dependence of quenching due to water vapor (this latter effect can affect signal levels by a factor of two). This 0,0 band excitation approach has been independently adopted by the other two investigators in the development of their instrumentation.

It now appears that all the investigators have these interference problems under control, although explicit tests still should be performed. For example, OH produced following laser photolysis of O₃ is formed in $v = 1$ as well as highly excited rotational levels in $v=0$, none of which is populated thermally at tropospheric temperatures. Therefore the degree of photolytic interference could be gauged directly by tuning the laser to absorption from these levels. In any case, it would appear to be useful to set up a complete model of each system, separately addressing individual components of the instrument such as inlet nozzle flows, chemistry in the flow tube itself, fluorescence quantum yield in the detector gate, etc. This would involve both experiments and a computer model of the detection scheme. A model of the pertinent photochemistry has been constructed to describe the 1,0 pump approach and could be adapted to the 0,0 scheme. This should be combined with a model of the fluid flow and diffusion considerations specific to each apparatus as well. Furthermore, in moderately heavily polluted environments, new problems of laser-generated noise or interference may occur. These could include scattering from smoke, haze, or other aerosols, while photolysis of other compounds present at higher concentrations (e.g., HNO₃) could generate spurious OH even at 308 nm. These factors must be considered when planning experiments under such conditions, although they will not be present for operation in the clean troposphere.

The level of sensitivity claimed for each experiment in a field-operable mode appears quite adequate for meaningful tests of tropospheric photochemistry under a variety of conditions. To establish a credible OH measurement, it will be necessary to demonstrate an excitation scan encompassing several rotational lines, made with ambient OH. (This could be done over a longer averaging time than the nominal value used in monitoring purposes.)

The Harvard instrument is designed for OH detection in the lower stratosphere, operating from the ER-2 aircraft platform. In the stratosphere the mixing ratio of OH is higher and the atmosphere is drier, presenting larger signal levels and far less ozone-related photolysis interference compared to detection in the troposphere. Because of less concern with photolysis interference, this instrument was designed to operate using 1,0 excitation to avoid laser scatter.

Nonetheless, a high repetition rate, low peak power pump laser is used to minimize the effects of spurious OH production through photolysis of ozone or other compounds. Optimized for stratospheric detection, it has not been carefully evaluated for detection of OH under tropospheric conditions. The sensitivity quoted for this instrument in Table 1 is for stratospheric conditions. The instrument operates at ambient pressure, where the signal is linear in OH mixing ratio, not number density; and it is known empirically that the background is linear in pressure. Therefore the sensitivity for the same signal to noise ratio and averaging time is expected to be somewhat lower under tropospheric conditions. The ER-2 will fly briefly throughout the troposphere in ascent and descent but will not spend much time there; if signal levels look adequate, this instrument perhaps could be modified for optimal tropospheric detection. On the other hand, the modifications needed to avoid photolytic ozone interference in the troposphere at ambient atmospheric pressure with 282 nm excitation may be considerable, and the design must be carefully evaluated.

Each instrument has different design details, for example the photon detector and filtering modes, and scattered light rejection. Optimally, the laser even for 0,0 excitation should have high repetition rate and low average power. The Harvard ER-2 instrument incorporates a new type of diode laser pumped Nd:YLF pump laser, having excellent performance characteristics (including ease of remote operation, ruggedness and reliability) for this purpose. Being a solid state device, it is highly preferable to the Cu vapor pump laser previously used. Although this device was expensive, it is now developed and could be incorporated at less cost into future designs of tropospheric instruments. Design ideas such as this should be shared among the investigators, to develop optimum instrumentation. Full details of the experimental designs, parameters, and tests should be published in reports or journal articles which are readily available to other workers in the field, so as to enhance this exchange.

A direct comparison of sensitivity between the Penn State and KFA instruments was made. The KFA device has higher photon detection sensitivity but poorer ultimate OH detection capability; this is due to a memory of laser scatter (principally from Rayleigh scattering off ambient atmospheric gases) persisting in the photomultiplier, leading to a much higher background. Incorporation of a new microchannel plate detector as in the Penn State instrument should improve the KFA sensitivity. These are examples where sharing of design details and tests can help each investigation.

Other specific comments were also made. First, the Portland State instrument had originally been configured in a multipass White cell arrangement, yielding a larger number of fluorescent photons per laser pulse. This was abandoned in the current version, because laser photolysis generated OH from one pass was detected in the next. However, this is done at the cost

of available signal level, leading in part to the lower expected sensitivity of this instrument compared with the Penn State and KFA versions. A multipass cell should be part of all instruments; however, it must be designed carefully to avoid problems of beam overlap and scattered light, even with a 308 nm pump scheme. Another important consideration concerns the flow rate and repetition rate. Much of the $O(^1D)$ produced during a given laser shot reacts after the laser pulse, forming much more total interference OH than during the laser pulse itself, the first 10 ns. If the flow rate is too slow or the repetition rate too fast, some photolysis-generated OH from one laser shot will be present in the detection region during the next shot, owing to back diffusion in the flow tube, and this can lead to high interference levels. The limit on the usable repetition rate can be determined by modeling of the flows and chemistry. Third, C_3F_6 as a chemical modulator (to remove ambient OH and thus determining the background) appears preferable to isobutane or other hydrocarbons, which can react with $O(^1D)$ to produce OH. Finally, the question of rotational cooling in the nozzle expansion into these low pressure regions should be considered, and tested using excitation scans.

The Portland State investigators presented a scheme designed to provide detection of several species based on laser light from the single Cu vapor pump laser. In addition to OH, and HO_2 determined by NO titration as discussed below, visible light would be used to determine NO and NO_2 , and photochemical conversion to measure $J(O_3)$ and $J(NO_2)$. The simultaneous determination of several variables in this category is certainly desirable. However, it was felt that in the near term the Portland State investigators should concentrate on optimization of the crucial and most difficult aspect, OH detection. (The other variables can be measured with confidence using other separate instruments.) In particular, intercomparison of this instrument with others would be a valuable and needed effort and should take priority over enhancing the instrument's capabilities for other species.

The method of two-photon detection was also designed to avoid problems of ozone interference and scatter due to residual aerosols and other unidentified fluorescing species. An elegant solution to these problems, it received an enthusiastic reception when presented in 1985, but the method has undergone little development since that time. The problem has been the lack of reliable generation of the 2.8 μm radiation needed for the first excitation step, having the right combination of pulse energy, bandwidth, tunability, and aircraft worthiness. Despite the near-term availability of a new solid state device (whose details remain proprietary to the laser company) to produce this radiation, this method had a mixed reception at the workshop. The technique is forecast to have a similar sensitivity to that of the low pressure LIF instruments. Compared with operation at 282 nm, two-photon LIF had some distinct advantages concerning interference. First, ozone photolysis in the 345 nm ultraviolet step forms only $O(^3P)$, not $O(^1D)$ and therefore no OH.

Second, aerosol and background fluorescence due to unidentified background species is always far to the red side of the 308 nm detection wavelength. However, operation of the low pressure instruments at 308 nm reduces both of these interference contributions compared to 282 nm excitation. The ozone absorption cross section is smaller at 308 nm. The maximum background fluorescence typically occurs some 20 to 40 nm to the red of the excitation, so with 308 nm excitation nearly all of the fluorescence is at longer wavelengths, instead of falling in the observation region. Thus the two photon method no longer has these earlier obviously significant advantages over low pressure instruments in their present configuration. The major appeal of this device is that it offers a second, very different means of OH detection, based on a highly selective spectroscopic approach. It is not subject to the type of complications found in the chemical conversion methods (discussed below), can operate at ambient pressure without the need to fly large pumps, and has quite different error sources than the low pressure methods. Its ability to totally avoid ozone interference even at high pressure may have some advantages for aircraft operation; the Georgia Tech group is certainly skilled in aircraft monitoring, having operated a two-photon NO/NO₂ LIF instrument for some time. However, significant further investment will certainly need to be made to develop this method, including hardware, assembly and testing time. (If begun now, it would probably be ready for aircraft operation at the same time as the low-pressure devices.) The workshop was divided on whether this investment was worthwhile, given the availability of other OH detection methods having the needed sensitivity.

A question was raised concerning the use of $v=2$ excitation at 1.4 μm instead of the $v = 1$ at 2.8 μm ; this latter wavelength is more difficult to generate. Although the 2-0 overtone infrared band has a smaller transition probability than the 1-0 fundamental, it is nearly balanced by the larger amount of more easily generated laser radiation at the shorter wavelength. Nonetheless, over 30 mJ radiation with a 0.1 cm^{-1} bandwidth would be required at 1.4 μm , and there is not yet a commercially available system capable of meeting the needed requirements. This approach had been considered (and used in the initial laboratory demonstration of the concept). The scheme had been discarded for the field instrument development because of presumed difficulties exciting the 1,2 band in the ultraviolet step. However, the 1,2 and 0,1 bands have similar transition probabilities, and this possibility should be reconsidered quantitatively with the possible advent of new laser sources.

A Fourier transform ultraviolet spectrometer developed at JPL was described. This is not an OH detection system in itself but could provide a useful high resolution detector to discriminate rotationally resolved LIF against laser scatter, with excitation in the same band. A major motivation for its development was a JPL concept, presented at the 1985 workshop, for lidar LIF detection of OH using an XeCl laser for 0,0 band excitation. However, it appeared that the

application of this device to tropospheric OH detection schemes under current operation or development remains in the longer term, with potential incorporation only following further development of the present LIF instrumentation. The susceptibility to mechanical vibration poses possible problems for aircraft operation.

Chemical Conversion Methods

At the 1985 workshop, it was lamented that the only methods then developed or even proposed for the detection of local OH were spectroscopically based. Nonspectroscopic methods are subject to different types of error sources, and their addition to a spectroscopic measurement suite would be invaluable in establishing the validity of each method. Since that time, four new methods have been developed or conceived, all based on reaction of OH with some other compound.

The ion-assisted mass spectroscopic measurement at Georgia Tech has been tested in the laboratory and has participated in the intercomparison study with the NOAA long path instrument, discussed below. It appeared to the workshop participants that this method is now producing real data on OH concentrations at the needed sensitivity and at an impressive rate. There is a complex chain of chemical reactions relating ambient OH and the HSO_4^- ion that is actually detected. These complications appear under control, and the reactions are fast enough that uncertainties in values of the reaction rate influence but little the derived concentration. However, a full computer model of the chemistry of the reaction sequence would be valuable, to address quantitatively the influence of any needed reaction rate or thermodynamic data. Also, there is significant background; the amount varies with conditions but is at the 10^6 level and often larger than ambient OH. This is distinguished in the apparatus by the addition of C_3H_8 to remove the ambient OH.

Several potential interferences (such as the effect of ambient NH_3) have been investigated, but all possibilities must be eliminated. During the 50 or more millisecond residence times in the flow tube, HO_2 can be cycled to produce OH, presenting problems in a polluted environment. Questions were raised as to the altitude (i.e., pressure) dependence of the conversion steps in flight operation, and the presence of these potential interferences in a more polluted atmosphere. Also, reaction with H_2O is one of the chemical conversion steps; for operation at altitudes high in the troposphere, which are drier, does H_2O need to be added to make the reaction sufficiently fast? If a reaction scheme using different reactants but still leading to ion detection could be devised, that would provide an extremely valuable check on the method. During the intercomparison studies, different apparent OH concentrations were observed with two different inlet systems, one 0.75m longer than the other. The instrument calibration had been carried out with the shorter tube, and these data were the ones used as the final results; however, this points up the need to carefully

consider the inlet as part of the overall detection system (more general concerns about inlet systems on all instruments are discussed below). It is not obvious that this instrument, requiring large diffusion pump capacity, can be readily adapted to aircraft operation without considerable modification. However, in light of the apparent success of the ion-assisted method, that question should be addressed soon.

The method of oxidation of ^{14}CO , practiced at Washington State, is based on observation of the rate of removal of the added labeled compound, in amounts which remove about 5% of the local OH. It consists of a chemical reaction producing small changes in the measured quantity, radioactivity from the labeled product $^{14}\text{CO}_2$, with the potential for errors entering at several stages. There were serious concerns about apparently complex physical separations to remove Rn interference and to separate the ^{14}CO , raised largely by those workshop participants grounded in spectroscopic detection. The combined and complex temperature/pressure dependence of the OH + CO reaction must be carefully incorporated. The long and delayed analysis times may present problems. It was felt that more convincing evidence needed to be supplied, in the form of calibration tests, a complete model of the measurement device, and participation in intercomparison studies. The addition of a scavenger (a hydrocarbon, or C_3F_6) to remove the ambient OH and measure the background signals, as well as operation at night, would be valuable.

The disappearance of a reactant dispersed throughout a local atmosphere, under development at MIT, appears to be well thought out in terms of method requirements (specific compound, reaction rate, etc.) and potential interferences. It is subject to technological challenges, that is, rapid release of a sufficient quantity, several moles, of the compound, dispersed rapidly to ppm levels. However, this measurement averages over several km and requires hours to perform, under rather stable atmospheric conditions. Therefore it samples a chemistry rather different from the other local techniques, somewhere intermediate between local and global. (The spatial average is similar to the two-pass long path methods, but the time averaging is much longer.) It was felt that this was therefore not suitable for intercomparison studies and would not form a primary method, such as the other local techniques. However, it would be very useful for comparisons with model predictions computed for the same averaging scales as used in the experiment.

The technique of reactive dye quenching is still in an early development stage at Arizona, and the investigators are aware that many questions have not been addressed. The question of selectivity of the dye quenching (at the low concentration of ambient OH) was raised at the workshop. Nothing is known about the effects of other oxidizing compounds such as O_3 , HO_2 , O_2 , RO_2 , H_2O_2 , PAN, etc. Note that for a compound present at the ppb level, a dye quenching rate only 10^{-6} of that for OH would produce interference. These must all be checked at conditions approaching ambient tropospheric concentrations. Nothing is known about the uptake coefficients

of OH (or these other species) into liquid solutions of this type, so whether one can process enough of the ambient OH to give a signal is not yet predictable. This could be measured by construction of a flow cell with known amounts of OH, calibrated by LIF at higher concentrations before dilution, and such an experiment should be an early priority to assess feasibility.

HO₂ MEASUREMENT TECHNIQUES

Four very different types of HO₂ methods were discussed. Two are direct (spectroscopic); however, the one in operation is relatively cumbersome and time-consuming while the other is still conceptual and, once developed, may be only marginal at best. The other methods rely on chemical conversion, either directly by reaction to form OH, or in a series of steps to produce many NO₂ molecules per ambient HO₂.

The method of conversion of HO₂ to OH is accomplished by reaction with added NO. The OH product can be detected by any of the rapid local techniques, and has been demonstrated directly in both the Portland State and Penn State apparatuses. It will be part of the KFA and Harvard instruments, and could be added to both the Georgia Tech two photon or ion-assisted chemistry schemes. (Because of the much longer residence time in the ¹⁴CO Washington State apparatus, RO₂ would be converted as well as HO₂.) HO₂ is present at concentrations on the order of 100 times the ambient OH, so that any instrument which is capable of detecting ambient OH will yield very large signals in the HO₂ mode. For example, this mode was used for LIF excitation scans using ambient species detection. A photochemical model of the earlier FAGE approach (using 282 nm excitation) confirms that ozone photolysis is not a problem even then, when HO₂ is measured.

Because the conversion chemistry is common to many instruments, a single presentation was made with open discussion from all investigators using this scheme. The question is that of quantitative conversion of the HO₂: addition of too much NO removes OH through the three body reaction to form HONO. Thus, there is a maximum conversion less than 100% which is dependent on apparatus design (particularly residence time between NO addition and OH detection). RO₂ can form some interference due to chain reactions, the level depending on the pressure and rate of flow through the particular instrument; note that the RO₂/HO₂ ratio can vary greatly in the atmosphere. Again, a chemical model of the process in each device, including wall effects and flow dynamics, is needed for credibility. With the help of such a model, tests should be devised to check questions and ambiguities. (Some modeling has been performed for the Portland State instrument.) There should be direct investigations of the flows (perhaps mapping

the patterns) and chemistry (using a moveable injector, and including other reactants), to define reaction times and interferences. These studies should be performed in detail and the results published in the available literature.

The other chemical conversion method of HO₂ detection is that of chemical amplification. The current models are improved versions of that first developed at the University of Michigan in the early 1980s. Added NO is converted to NO₂ by reaction with both HO₂ and RO₂ species; the OH and RO products of these reactions are reconverted by added CO to HO₂ radicals, to form a chain yielding up to several hundred NO₂ molecules per peroxy before chain termination occurs. Background NO₂, chain length, and wall losses are tested by replacing the CO by N₂ to suppress the chain, and calibration is via thermally decomposed H₂O₂ or PAN. Two instruments operating on this principle were represented at the workshop, that at NCAR and a modified form of the instrument from York University; Mainz and University of Denver instruments were not presented. The York apparatus has been designed to minimize potential interference problems in PAN-rich environments.

This method is responsive to both HO₂ and RO₂ radicals, with a chain length that varies depending on the particular reacting species. Therefore, the method measures some weighted sum of HO₂ plus RO₂, and is not as specific as is really desired. On the other hand, such a sum provides a useful measure of oxidant concentrations and can be valuable, and other considerations about atmospheric conditions may help deduce the approximate fraction that is HO₂.

Concerns were raised about changes in the chain length with ambient conditions, such as temperature, altitude and pressure. It is necessary to make sure the chain length is measured under operating conditions. Other possible interferences (e.g., PAN, PNA) must also be considered in different tropospheric conditions.

The technique of matrix isolation/esr detection has been performed at KFA for several years. This is a method in which a sample is collected by deposition onto a solid matrix, and kept at cryogenic temperatures to preserve the deposited HO₂. The solid sample is then investigated using electron spin resonance. Other species found in the same spectral region include NO₂, NO₃, and certain RO₂ radicals. These may be separated from HO₂ using spectral fitting methods, so the technique is capable of simultaneous measurement of several interesting species. This measurement is time consuming but produces unambiguous, selective detection of HO₂. Two questions were raised about this method. First, this approach actually measured the deposition rate of HO₂ onto the surface, but the sticking coefficient for this process is unknown. Second, what is the long term storage stability, between sample acquisition and measurement? In order to achieve sufficient sensitivity, a collection time of 30 min is necessary, perhaps somewhat longer than

desirable when sampling in an aircraft under varying conditions but suitable for ground-based sampling in a quiescent environment.

Tunable diode infrared absorption could be carried out in two different wavelength regimes, ~ 7 and $1.5 \mu\text{m}$, each with potential advantages. If HO_2 absorbs strongly enough to provide adequate sensitivity, this would be the method of choice for selectivity and ease of operation. A cell with many passes would be needed in any event. The current knowledge of absorption strengths and line broadening coefficients, particularly in the $1.5 \mu\text{m}$ overtone, is not complete enough to project detection sensitivities in a field instrument. Wings of strong lines, peaks due to other trace species, or weak lines of H_2O may interfere. Absorption due to $\text{HO}_2 \cdot \text{H}_2\text{O}$ clusters may pose a significant problem; these could be formed in the pressure reduction step which would be undertaken to narrow the absorption linewidth, thereby minimizing interferences. Even with the best technological schemes, this approach may be marginal. The method should be developed, by measurement of the needed basic parameters, but it should not be counted upon as a solution. One possible and perhaps important use would be the use of diode absorption at higher, artificially generated concentrations of HO_2 as a standard method to calibrate other techniques for absolute measurements.

INTERCOMPARISONS

The concept of instrument intercomparison in atmospheric chemistry measurements was established largely in response to the concern of the atmospheric chemistry community about the viability of tropospheric OH measurements in the 1970s. CITE-1 established that the two LIF and the ^{14}CO instruments of 1983/4 were not able to measure OH at the requisite levels of sensitivity and precision.² (Little if any OH data were produced in CITE-1 and it has therefore been criticized as an expensive mission; however, it was far less expensive than continuing to develop instrumentation incapable of useful OH measurements.) At the same time, CITE-1 established as quite credible different (spectroscopic and nonspectroscopic) methods for the determination of both NO and CO.¹³ The success of the CITE-1 mission for all three species has led to further intercomparison studies. CITE-2, carried out in 1986, was concerned with NO_y species¹⁴, and CITE-3, performed in 1990 but whose results have not yet been published, was devoted to sulfur containing compounds.

By now the concept of an intercomparison study for new techniques to determine trace atmospheric species is well established and accepted in the community. An intercomparison of the OH instrumentation discussed here is a necessary step in the establishment of the credibility of the

measurement methods. (During the workshop, the vast majority of the discussion of intercomparison referred to the OH molecule; in this context HO₂ was usually considered as an ancillary measurement, but the different techniques for its determination should be intercompared too.)

The other species that have been the subject of intercomparison campaigns have been long-lived chemical compounds, for which standard samples are available that are tested on a double-blind basis. OH must be handled quite differently. First, it is present at much lower concentration than the other compounds that have been subjects of the CITE studies. Second, no calibration source is available at this time, so the most important information to be derived from the tests is the correlation in [OH] determined by different methods, as its controlling variables change.

A definite protocol for an OH intercomparison study was established at the workshop. 1) A formal intercomparison, on a fully blind basis, must be held to establish the credibility of the OH techniques. This should accommodate up to five different instruments; more may pose logistical problems. 2) This formal intercomparison will be subject to the well-established rules of the CITE series, with all data analyzed on a blind, or when appropriate, double-blind, basis, submitted for review, and all results (positive and negative) published in readily available form. 3) Informal intercomparisons are crucial to instrument development, and no one may participate in the formal intercomparison without having first taken part in an informal study. 4) After meeting criterion (3) concerning an informal intercomparison, a principal investigator should submit a proposal (including the informal intercomparison results); selection of the participants in the formal intercomparison would be made by a peer review panel on the basis of these proposals. 5) The formal intercomparison study will be ground-based at a specially chosen site, with ample simultaneous measurement of ancillary variables related to OH concentration.

Despite the desirability of aircraft sampling of different regions of the troposphere, there is no doubt that a formal intercomparison must first be performed at a ground-based site where the challenges of both designing and operating the instruments are smaller. Once the credibility of ground-based OH measurements is established, we can move to planning an airborne intercomparison.

These conclusions were based on discussion of the CITE-1 experiments as well as the recent NOAA/Georgia Tech intercomparison. The CITE -1 intercomparison was performed at the limit of detectability, making a statistically significant intercomparison very difficult to achieve. A new intercomparison should take place where [OH] is high enough that this does not occur. The sensitivity and uncertainties limits achievable by currently available instrumentation are such that this should pose no problem.

An informal intercomparison is valuable in that it forms a more relaxed, slower paced situation in which problems with one or more instruments can be diagnosed and, one hopes, improved on a rapid time scale. Information should be shared among the different investigators, so as to improve all the detection instruments. Measurements of ancillary supporting data are essential to understanding the errors in, and discrepancies among, the different OH techniques.

One such informal intercomparison between two very different OH instruments has taken place⁷, and valuable lessons were learned in this exercise. The NOAA long path absorption method was one of the instruments, and the Georgia Tech ion-assisted mass spectroscopic technique, located at one end of the path, was the other. The site was a forested area in the mountains of Colorado; the long path measurement was, on the average, at a height of several hundred meters above the forest. Ancillary measurements were also made. O₃, H₂O, NO₂, SO₂, and CH₂O were simultaneously determined via absorption over the same path, and O₃, NO, NO₂, NO_y, H₂O, SO₂, aerosols, and solar flux were determined at one or both ends of the path. These were invaluable in understanding the patterns observed for the measured OH concentration, even in the absence of model calculations. For example, increased concentrations of SO₂, NO_x, CO and/or aerosols formed excellent indicators for the intrusion of polluted air from the east, which could often be correlated with variations in the OH concentration.

Although the campaign spanned a five week period, the instruments did not operate during all of that time. On only six days were data obtained which had good overlap between the two methods. Measurements were made every few minutes with the mass spectral instrument and four times each hour by absorption. Generally there was good agreement between the two methods for the temporal variation of the OH, in the absence of pollution episodes. In the presence of NO_x, correlation was often but not always achieved. These differences could usually be rationalized by the reasonable assumption of a nonuniform pollutant distribution along the absorption path. This nonuniformity could be seen in a comparison between absorption and pointwise measurements of other species; for very long lived compounds such as O₃, good agreement was obtained but for species with shorter lifetimes such as NO₂ these differently averaged determinations did not always agree. Finally, between 5 and 10% of the time, changes in OH and differences between the two techniques could not be explained on the basis of changes in NO_x, solar flux, etc. Therefore there are still unknown reactants and/or reactions that affect both the overall OH concentration and its measurement using different spatial averaging modes. This suggests that even more ancillary species must be measured at the same time.

In this intercomparison, the absorption measurement was considered the primary OH standard. The mass spectroscopic technique can now be calibrated with an external source of OH (184.9 nm Hg line photolysis of H₂O vapor), but that method was not available in 1991. Instead,

calibration using an ion ratio method had been performed earlier in the laboratory; as noted earlier, the calibration must be performed with the same inlet nozzle configuration used for sampling ambient OH. Measurements were also made at night, with null results corresponding to $< 4 \times 10^5$ by absorption and $1.5 \pm 1 \times 10^5$ by mass spectroscopy. Such null experiments are an essential part of any intercomparison method, informal or formal, and a careful delineation of the error or upper limit estimates must be made and published.

Considerable discussion was spent on the selection of a site and timing for the formal ground-based intercomparisons. One possibility is to schedule an OH intercomparison as part of an already planned campaign, because the intercomparison will require measurement of a large suite of ancillary species that will be found useful for testing photochemical models as well. On the other hand, a site and conditions that provide interesting and useful tests of photochemical models, particularly specific aspects of that chemistry, do not necessarily constitute ideal conditions for an intercomparison study. Making valid and useful intercomparison measurements, preferably in the presence of some variety of atmospheric conditions, must be the first priority of an intercomparison study. If this can be combined with another mission objective, that is fine, but establishing credibility in OH measurement methods is too important an objective to compromise.

The ideal conditions for testing OH measurement methods, i.e., a designer troposphere, and places they might be found, were discussed. One would like a site that is rather clean but not boringly so, with occasional mild pollution episodes well-characterized by the ancillary species measurements. The site should be predominantly sunny with brief cloudy spells, and have ample concentrations of both O_3 and H_2O . Periods of low wind are necessary. Aerosols should be absent, to provide viewing for long path absorption and also the absence of potentially complicating heterogeneous chemistry. NO_x should be present over a range of concentrations beginning with a few ppt at the low end; some participants suggested maximum NO_x concentrations as high as 1 ppb although others felt somewhat lower values, 100 to 300 ppt, would be more desirable. SO_2 and CH_2O must be at sufficiently low concentration, certainly < 1 ppb, that they pose no interference problems for the long path absorption. These concentration criteria for many trace species suggest we consider only sites which have already been well characterized in previous measurement campaigns.

Some but not all of these conditions could be found at different sites, and specific locations were suggested. Other criteria were also imposed. In particular, the site must be amenable to establishing long path absorption. For example, the distances involved make Mauna Loa a poor choice despite its meeting many other criteria, and rule out a location on the coast where aerosol scatter would preclude adequate light transmission. Having suitable support facilities (electricity, water, access, and technical services) is also important.

One site which was suggested was Colorado. This was the site of the 1991 informal intercomparison, and interpretation of the data required knowledge of the isoprene concentration due to the local forest. If such a site is used for other intercomparison, the campaign should span a time period starting in warm summer months (August) and continuing into cooler ones (late September at least) over which the concentration of these naturally occurring compounds varies greatly. Other possibilities that were mentioned include Arizona and SUNY stations where considerable meteorological and other supporting equipment is already available.

The instrument selection must include at least one absorption measurement, and preferably more, one of which is the folded long path technique. A discussion of instrument siting was held, but with no clear conclusion. Although OH is short-lived, it still can communicate with sources and sinks through reactions involving HO₂, NO, etc., if measured too close to the ground. The OH and all supporting measurements must be made where there are no gradients and unknown source/sink terms affecting the ability of the photochemical models to predict [OH] using empirical determinations of the other variables that control it. The primary issue was the height of the OH sampling inlets needed to ensure a lack of vertical and horizontal gradients related to nonuniform surface reactions. On the basis of previous studies of the distribution of other trace species (e.g., H₂O, NHO₃) different participants offered different suggestions. These ranged from inlet stations a few meters above the surface to a platform at least 250 m above the surface. (This latter height would clearly be difficult to achieve; should it prove necessary, the value of an aircraft sampling platform to avoid surface effects is strongly indicated.) It was recommended that this question of instrument siting be investigated through a modeling effort incorporating previously measured data for near-surface concentration gradients in other trace atmospheric species.

An intercomparison site selection committee should be established. Members should include persons with particular experience: someone skilled in tropospheric measurements (not necessarily OH); a modeler; an expert in the meteorological considerations. Such a committee should be convened soon to take advantage of potential future campaigns that could incorporate a formal OH intercomparison, if the conditions of such missions meet the criteria outlined above.

Prior participation in an informal intercomparison is a prerequisite for taking part in the formal intercomparison. This probably places the time scale for the formal mission no earlier than 1995, although that is a reasonable target date. Three informal intercomparisons are now planned: one between the Pennsylvania State low pressure LIF method, the ion-assisted mass spectrometry, and the NOAA long path absorption in Colorado in 1993; one between the Portland State low pressure LIF and the ¹⁴CO method in 1992; and one involving all of the German instrumentation, in Schauinsland in 1994. These plus the 1991 intercomparison include all the OH instrumentation that is now ready or soon will be for field measurements. Therefore, if these informal tests

indicate proper operation of the instruments, all will have met the prerequisite in time for a formal intercomparison in 1995.

Intercomparison of HO₂ methods was discussed little at the workshop. A major problem here is that, as already recognized, the different techniques measure somewhat different quantities: matrix isolation/esr is quite specific to HO₂, whereas RO₂ is included in the chemical amplification method and can affect the techniques which convert to OH by reaction with NO. Thus a comparison between the chemical amplifier and conversion to OH is not expected to lead to the same value. Because several of the OH instruments are capable of HO₂ detection via NO addition, an intercomparison on HO₂ determinations by those methods should be made as part of the OH intercomparison study.

CALIBRATION AND INLETS

It would be most desirable to have a calibration source for OH which could be used by all investigators with a similar sampling scheme. Different ideas to accomplish this were discussed. There are several questions that must be addressed, in particular concerning sampling from a calibration source. Although it was clear that the availability of a common source type was extremely desirable, it was expressed that it was important that the calibration be not much harder to do than the measurement of ambient OH itself.

Unlike chemically stable gases such as NO, there is no convenient source of OH at a known concentration. OH can be produced in flow tubes via several chemical or photochemical reactions. Even with very carefully metered gases and measured lamp intensities, the error bars on the rate coefficients relating OH concentration to these quantities result in OH concentration uncertainties of 30% or greater. Absorption measurements can yield more accurate measurements of OH, better than 10%, so the most reliable calibration source would appear to be photochemical production combined with a folded long path absorption method. Although this path is only a few meters in dimension, the ability to artificially generate OH homogeneously enough over the entire region remains a major question. It is desirable to produce the OH under various conditions and subject to different interferences, and at quantities not much greater than the ambient OH, i.e., no more than 10⁷/cm³.

Potential loss of OH between sampling and detection is an important consideration in the instrument design. Wall coatings such as teflon or halocarbon wax are known to greatly reduce the OH sticking coefficient and thus any wall losses, and are employed in many flow tube kinetics experiments as well as some of the current OH detection instruments. However, the passage of

large quantities of ambient air may alter that sticking coefficient, so the safest way to avoid wall losses is to avoid wall collisions altogether. Thus many of the instruments are designed with fast flow to deliver the sample of air containing ambient OH to the OH detection region without contact with the walls.

This in turn raises a crucial calibration issue. Can a calibrated source be designed that can reliably deliver the same amount of OH to each of the instruments that have sampling nozzles? The inlet flow rates employed on the different instruments vary by over two orders of magnitude, from less than a liter/s to over 200 liters/s. The calibration methods must be designed to handle the fastest flow; for slower flows, one will just discard some of the calibration source flow. The directionality of the inlet nozzles must also be considered to ensure that they all sample from the same distribution. Further, the calibrated flows should be designed so that the sampling is from the middle of the flow, and fluid flow models should be constructed to describe this sampling.

Several techniques for OH production were discussed; each has been developed and studied in conjunction with one or more of the OH detection instruments. In a flow cell, one can produce OH quantitatively by the reaction $H + NO_2$, where the hydrogen atoms are formed by a microwave discharge in H_2 ; this technique is however not easily adapted to pressures higher than about a Torr. Instead, schemes based on photochemical reactions are the most promising. These are: 1) the ultraviolet photolysis of O_3 by 253.7 nm Hg radiation to produce $O(^1D)$, which then reacts with H_2O vapor; 2) the photolysis of H_2O by Hg line radiation at 184.9 nm; 3) the photolysis of H_2O_2 in the ultraviolet. Each of these can be designed to deliver known quantities (subject to the rate coefficient uncertainties, of course) into the OH instruments.

To calculate reliable trace concentrations of OH in such sources, it is extremely important to rigorously exclude contaminants from the gases used in the flows. For example, 1 ppm of CO or some hydrocarbon would seriously alter the OH concentration by the time it is delivered to the detection region.

One of these methods should be chosen to design a common calibration source which could be used by all investigators. Building such a device would be a research task in itself, requiring complete testing for reproducibility, modeling to ensure lack of problematic concentration gradients, etc. Several copies of this source would be fabricated. Each investigator would keep one for optimization and day-to-day laboratory or field calibration of that instrument. In addition, there would be a single primary version that would circulate among investigators to provide comparison among instruments while they are still in laboratory development and testing stages. If possible, this must precede a formal intercomparison (and should be used in informal ones, if

available in time) to maximize the chances of uncovering problems before field measurements commence.

It is not necessary that this laboratory calibration source be calibrated by absorption for absolute [OH] at the outset. More important is the ability to produce a reliably reproducible concentration for comparison among instruments. The laboratory source can be calibrated later (directly or indirectly) via the folded long path method and any necessary numerical corrections in earlier data made at that time. That is, a common calibration source is urgently enough needed in the development of the detection instruments that the source development should not await its calibration for absolute OH.

Through this development, interaction among different investigators is vital to solving common problems such as proper inlet design. Knowledge and findings (including negative results) should be shared to avoid duplication of effort. Questions and concerns (such as the formation of clusters in nozzle flow) should be identified and also communicated.

One might direct such efforts toward the development of a nozzle and inlet system common to each apparatus (different flow requirements may preclude this in some cases). This would remove variation in sampling errors from instrument to instrument. On the other hand, it could increase the chance of a common systematic error going undetected. The formation of a working group to collect, regularly assess, and publicize inlet design and research would be very desirable.

Calibration of HO₂ (as its intercomparison) was not discussed in detail. Thermal decomposition of H₂O₂ over a catalyst has been used in the chemical amplifier method and appears to be a good source at the 30 to 50 ppt range, with accuracy estimates near 10%. Other possibilities include chain reactions which follow the photolysis of CH₃ONO with light of wavelength < 400 nm, or photolysis of CH₂O at 330 nm or less. It would be useful to construct a model of this chemistry in the flow tubes, to ensure that proper sampling is occurring here as well.

LABORATORY DATA NEEDS

A quantitative understanding and model of the physical chemistry operating in a given detection instrument requires various input parameters. Categories of such parameters include thermodynamic data, chemical kinetic rate coefficients, spectroscopic information, and collisional energy transfer and broadening cross sections. As part of a discussion, the workshop participants listed (without prioritizing) needs both for new laboratory data and also improved values of previously measured quantities. These are listed here in arbitrary order.

1. The bond energy of the $\text{HO}_2\bullet\text{H}_2\text{O}$ complex, and its effects on the chemical amplifier chain reactions.
2. The rates for $\text{O}(^1\text{D})$ removal by quenching to $\text{O}(^3\text{P})$ due to N_2 , O_2 , and H_2O , and its chemical reaction with both H_2O and N_2O , all measured by the same investigator.
3. The equilibrium constant for the reaction $\text{HO}_2 + \text{NO}_2 = \text{HO}_2\text{NO}_2$, which currently has an uncertainty of a factor of five.
4. Relative rates of reaction of OH with NO and SO_2 .
5. The rate constant, products, pressure dependence, and heterogeneous effects on the reaction $\text{SO}_3 + \text{H}_2\text{O}$.
6. The temperature dependence of the reaction $\text{NO}_3^- + \text{H}_2\text{SO}_4$.
7. The rate of reaction of $\text{OH} + \text{NO}$ at low temperature, and the formation of HONO in jets.
8. Clustering reactions in low-pressure inlets of the type used in OH sampling nozzles.
9. Relative rates of rotational relaxation and quenching of electronically excited OH at low temperature.
10. The sticking coefficient for HO_2 (and OH) on surfaces of both tropospheric interest (e.g., aerosols) and technological interest (i.e., flow tube walls and coatings).
11. Near infrared absorption coefficients for HO_2 .
12. Line broadening cross sections for HO_2 in both the near and far infrared.
13. Identification of the remaining unknown interfering absorbers in the long path absorption method.

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Table 1

OH TECHNIQUES

Laser-Induced Fluorescence

<u>Technique</u>	<u>Institution</u>	<u>Presenter</u>	<u>S/N</u> ^a	<u>Sens.</u> <u>10⁵/cm³</u>	<u>Avg Time</u> ^b <u>minutes</u>
Low-pressure	Portland State	O'Brien	2	10	7
	KFA-20Hz	Hofzumahaus	2	25	5
	10 kHz	Hofzumahaus	2	1	5
	Penn St.	Brune	2	7	0.5
	New Detector	Brune	2	0.3	0.5
Two-photon	Georgia Tech	Bradshaw	2	1	2
ER-2 Instrument ^c	Harvard	Wennberg	2	0.2	1

LONG PATH ABSORPTION

<u>Technique</u>	<u>Institution</u>	<u>Presenter</u>	<u>S/N</u> ^a	<u>Sens.</u> <u>10⁵/cm³</u>	<u>Avg Time</u> ^b <u>minutes</u>
Long path	NOAA	Mount	2	5	3
	KFA	Dorn	2	5	2-30 ^d
	Mainz	Kraft	3	20	15
Folded long path	Frankfurt	Amerding	1	3	0.2 - 1 ^d
Intracavity	Aerodyne	McManus	-	-	-

CHEMICAL CONVERSION

<u>Technique</u>	<u>Institution</u>	<u>Presenter</u>	<u>S/N</u> ^a	<u>Sens.</u> <u>10⁵/cm³</u>	<u>Avg Time</u> ^b <u>minutes</u>
Mass spectrometry	Georgia Tech	Eisele	2	1	5
¹⁴ C CO oxidation	Washington State	Campbell	6	2	2
Dispersed reactant	MIT	Sprengnether	2	5	60
Dye Quenching	Arizona	Gast	1	10	3

^a Signal/noise ratio

^b Averaging time needed for quoted sensitivity

^c For stratospheric conditions; see text

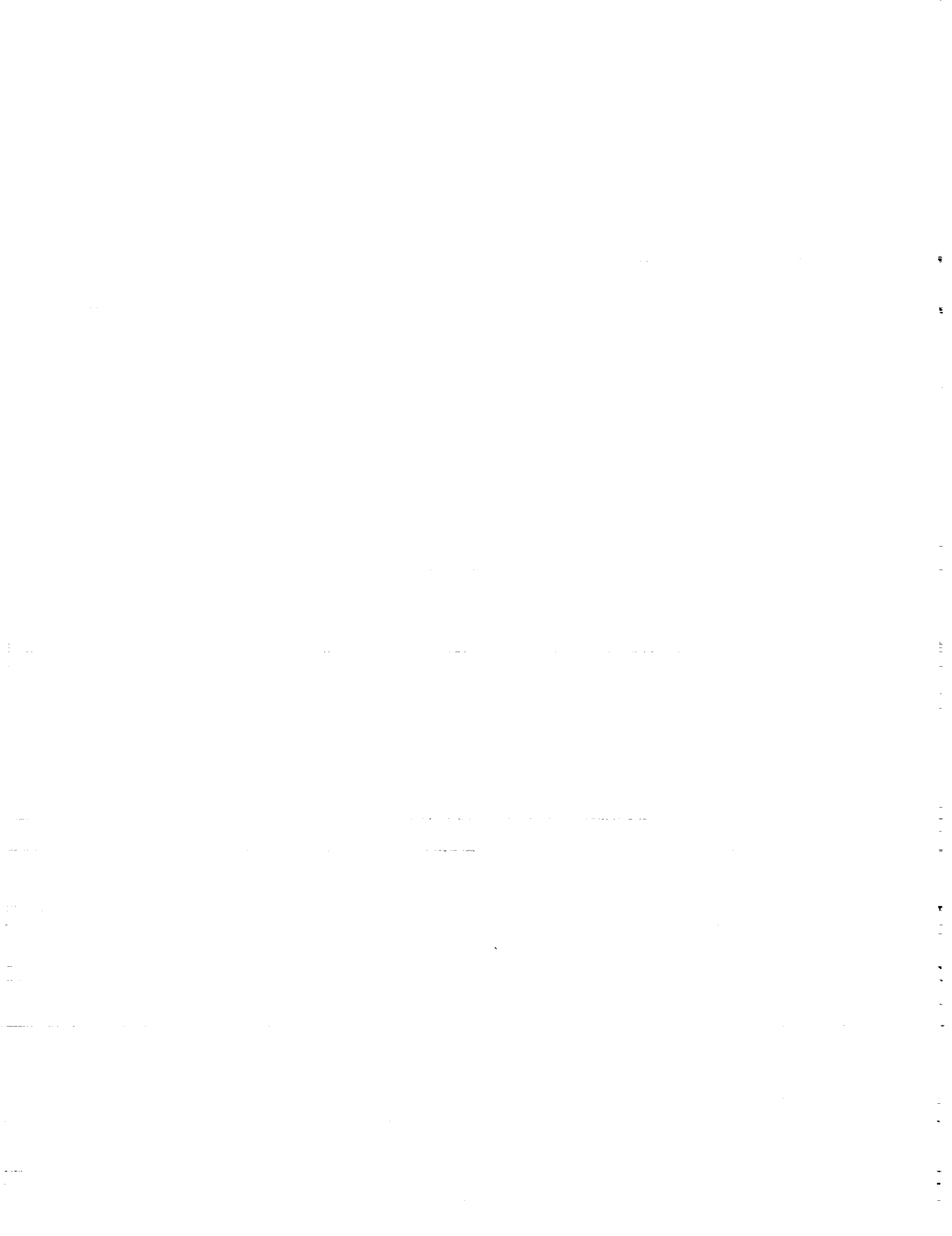
^d Depending on local conditions, see text

Table 2

HO₂ TECHNIQUES

<u>Technique</u>	<u>Institution</u>	<u>Presenter</u>
Chemical amplifier	York	Hastie
	NCAR	Calvert
Conversion to OH	Portland State ^a	Hard
Matrix-ESR	KFA	Mihelcic
Diode laser absorption	Aerodyne	Zahniser
	Southwest Sciences	Stanton

^a Also in use at Pennsylvania State, KFA, and Harvard

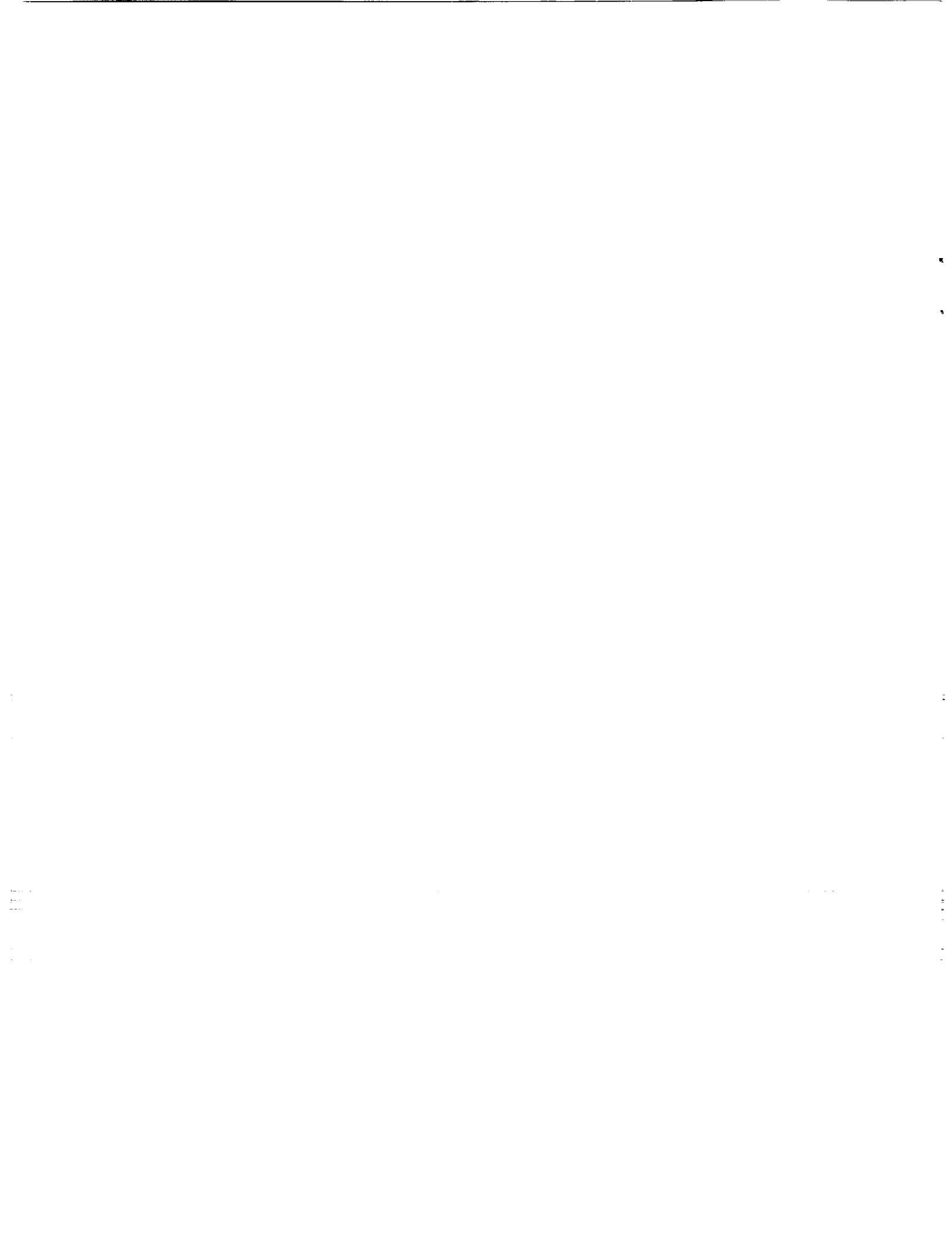


Appendix A

**ONE-PAGE DESCRIPTION OF EACH INSTRUMENT
OR CONCEPT PROVIDED BY EACH INVESTIGATOR**

omit

(Appendix A contains unedited verbatim abstracts.)



Two-Photon/Laser-Induced Fluorescence (TP/LIF) Sensor

John Bradshaw, Georgia Institute of Technology

2075 73

The TP/LIF technique is based on the stepwise excitation of the OH transitions, $X^2\Pi, v''=0 \rightarrow X^2\Pi, v''=1$ ($\lambda = 2.9\mu$) and $X^2\Pi, v''=1 \rightarrow A^2\Sigma, v''=0$ ($\lambda = 345$ nm) with background free fluorescence monitoring of the $A^2\Sigma, v''=0 \rightarrow X^2\Pi, v''=0$ transition near 309 nm. This technique has awaited the advent of a suitable mid-infrared (2.9μ) laser source¹. Tunable mid-IR lasers now exist that are capable of meeting the specifications required of a high sensitivity TP/LIF OH sensor^{2,3}.

Advantages:

The TP/LIF OH sensor samples air at ambient pressure/temperature conditions with no pre-concentration or conversion process. For a 100 second signal integration period the TP-LIF OH sensor should have a limit-of-detection (LOD) for $S/N = 2/1$ of $\sim 2 \times 10^5$ OH/cm³ in the free troposphere and $\sim 4 \times 10^5$ OH/cm³ in the tropical marine boundary layer. These LOD's will be achievable in less than 30 seconds with the implementation of 40 pps repetition rate lasers that will become available in the early fall of 1992. LOD's decrease linearly with, and measurement precision increases by the square root of increasing integration time, up to about 15 minutes (or with increasing laser repetition rate). Background signal levels have been determined to be less than an equivalent OH concentration of 1×10^5 molecules/cm³ for signal integration times up to 15 minutes (at 10 pps rep. rate). This technique is not susceptible to interferences from H₂O₂, HNO₃, or the so called O₃/H₂O interference for ambient OH concentrations $> 1 \times 10^4$ molecules/cm³. A continuous calibration mode will use the airborne proven technique⁴ involving quantitative photolysis of ambient ozone and subsequent reaction of O¹D + H₂O \Rightarrow 2OH through the use of a separate photolytic calibration laser. In addition, the sensor is equipped with a reference system that continuously monitors a constant OH mixing ratio for purpose of energy and wavelength normalization. Calibration accuracy is estimated at $\pm 20\%$ based on evaluation of O₃/H₂O and H₂O₂ methods during CITE-1. The OH sensor will be compatible with only minor modifications to the existing compact Georgia Tech TP/LIF airborne flight system. In addition, the Georgia Tech group has the experience of successfully making LIF measurements in four blind instrument intercomparisons and has accrued over 1000 flight hours of experience using similar Two-Photon/LIF detection techniques under a variety of tropospheric conditions. The sensor will also be compatible with the detection of HO₂ via the titration HO₂ + NO \Rightarrow OH + NO₂.

Disadvantages

The sensor uses in-situ sampling with air drawn in through a large diameter sampling inlet. Therefore, wall loss of ambient OH although considered to be small, can not be ruled out as a possible negative interference. The continuous O₃/H₂O calibration requires accurate simultaneous measurements of ambient O₃ and H₂O. In the upper free troposphere this would require the availability of H₂O measurements from a Lyman- α -fluorescence H₂O sensor. The TP/LIF sensor is not compatible with unattended mode operation. The sensor would not be available for ground-based intercomparison study until August 1993 (assuming requisite funding could be obtained).

¹Bradshaw, et al., Sequential TP/LIF: A New Technique For Detecting OH, *Appl. Opt.* **23**, pp.2134-2145 (1984)

²Bradshaw, et al., 2.9 μ Laser Source For Use In The TP/LIF Detection of Atmospheric OH, *SPIE* **1433**, pp.81-91 (1991)

³Bradshaw, Completion of a TP/LIF Technique For the Detection of Atmospheric OH Radicals, proposal to NSF (7/91).

⁴Rodgers, et al., A 2- λ LIF Field Instrument for Ground-Based and Airborne Measurements of Atmospheric OH, *JGR* **90**, pp. 12,819-12,834 (1985)

**In situ detection of tropospheric OH and HO₂ by laser-induced fluorescence
in a detection chamber at low pressure.**

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Method. Just as in the method of Hard and O'Brien, ambient air is pulled through a ~1 mm diameter inlet into a detection chamber that is maintained at a pressure of 2.4 torr. The ambient air stream travels through the detection chamber with a velocity of ≥ 100 m sec⁻¹ in a narrow stream, constrained by the addition of an inert gas flow (0.4 torr).

The OH molecule is both excited and detected in the $A^2\Sigma(v'=0) \rightarrow X^2\Pi(v''=0)$ transition at 308 nm. Light from a copper vapor-pumped dye laser (rep. rate = 10kHz; pulse length = 20 ns; linewidth = .1 cm⁻¹, and average power = 15 mW), resonant with the Q₁(3) transition, is multipassed through a White cell and intercepts the air stream as 24 non-overlapping 2mm by 5mm beams. A fast microchannel plate detector is turned off during the laser pulse to prevent saturation of the detector due to Rayleigh and chamber scattering. It is turned on 30-100 nsec after the end of the laser pulse for 300 ns to collect resonance fluorescence from OH. HO₂ is detected by chemical conversion to OH by reaction with reagent NO, followed by OH detection.

Both the detection sensitivity and the inlet characteristics must be understood for any in situ instrument. For the calibration of the detection sensitivity, OH is produced quantitatively by the fast $H + NO_2 \rightarrow OH + NO$ reaction in a low pressure, flowing discharge tube connected to the detection chamber. The inlet transmission of OH inlet is calibrated separately.

Advantages.

1. OH and HO₂ can be detected simultaneously.
2. The sensitivity, C , given as $signal = C \times [OH]$, is 4×10^{-6} (cts sec⁻¹)/(OH molecule cm⁻³, with a background signal of 15 cts sec⁻¹. Thus, an OH abundance of 5×10^5 cm⁻³ can be measured in 30 seconds, and 1.6×10^5 cm⁻³ can be measured in 5 minutes, with $S/N=2$. An improvement in S/N of a factor of 5 to 20 is currently being implemented, so that OH abundances smaller than 3×10^4 molecules cm⁻³ should be detectable in 5 minutes with $S/N = 2$. The sensitivity is linear with laser power and with OH.
3. Interference signals are unmeasurably small for all conditions encountered thus far. The signal from laser generated OH is almost unmeasurable for conditions with ozone = 300 ppbv and water vapor = 3%.
4. The background signal determined by spectral and chemical modulation are the same.
5. The sensitivity is directly related to Rayleigh scattering that is measured when the detection cell is filled with N₂.
6. The signal can be attributed directly to OH because the OH fluorescence spectrum can be directly observed during the day.
7. Uncertainties of ~ 20% in the absolute abundance of OH will be possible once the inlet transmission is properly characterized. HO₂ can be detected with the same uncertainty as OH. Accuracy of the OH/HO₂ ratio will be limited mainly by the precision of the OH measurement.
8. The instrument can be made light weight (< 500 lbs.), compact (DC-8 double rack), and energy efficient (< 1500 watts) for use in aircraft and at great heights above the ground. The instrument can be designed so that no operator is required for up to a day.

Disadvantages.

1. The largest potential problem is the uncertainty of the inlet transmission of OH. This disadvantage can be overcome to a large extent with proper calibrations and monitoring.
2. For the immediate future, the system probably cannot run without fairly constant monitoring at the present level of engineering.
3. The production of known amounts of OH at atmospheric pressure is a problem for the calibration of this instrument, just as it is for others. However, all the currently developed calibration techniques can be applied to this one.
4. A chemical conversion with reagent NO is required for HO₂ detection. Mixing and chemical reaction of reagent NO into the airstream requires careful attention to the internal flow.
5. The major cost of the system is the laser system, which currently costs of \$70,000 to \$100,000. As the price of solid state lasers declines, the cost per copy of this instrument will decrease.

Tropospheric HO Determination by FAGE
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Portland State University

207575

P. 1

In the measurement of tropospheric HO we have employed three low-pressure laser-excited fluorescence (LEF) experimental systems. These instruments operate by expanding the ambient air flow via a nozzle, followed by transit down a flow tube through a detection region traversed by the excitation laser beam. This sampling method we named FAGE (fluorescence assay with gas expansion). The instruments employed a hydrocarbon reagent, added below the nozzle, to remove HO for background measurement. In the second and third instruments, air sampling via parallel nozzles and tubes, with reagent addition alternating between two channels, permitted continuous signal measurement with simultaneous measurement of background. The first two instruments (FAGE1 and FAGE2) used 282 nm HO excitation by frequency-doubled tunable dye lasers, pumped by pulsed Nd:YAG lasers at 10-30 Hz repetition rate. The third instrument (FAGE3) uses 308 nm excitation in which the dye laser is pumped by a copper vapor laser, pulsed at 5600 Hz.

Progressive improvement in HO sensitivities is shown in Table 1. The results in Table 1 for FAGE1 and FAGE2 refer to ambient measurements whereas for FAGE3 they refer to calibration experiments. Sensitivities are determined by a combination of (1) scattering and fluorescence by the cell windows and walls initiated by the laser beam in the detection cell; (2) broadband fluorescence of components of the sampled air; (3) photolytically generated HO, due mostly to ozone, present in both channels; and (4) PMT dark current and/or ambient light leaking through the nozzle. The second source of background signal is found to be larger in the trimethylbenzene/NO_x atmosphere used for calibration than in ambient air, and consequently the HO sensitivity of ambient measurements is better than that of calibrations. The largest background source in FAGE1 and FAGE2 was wall scattering and nonresonant fluorescence, with photolytic HO significant when ozone was present. In the Cu-based system, single-pass excitation has allowed more efficient trapping and temporal gating of stray laser UV. Broadband "air" fluorescence is reduced by excitation at a longer wavelength, and photolytic signals have been demonstrated to be negligible in FAGE3 by experiments at very high ozone concentrations. A further advantage of FAGE3's lower pulse energy is the absence of transient saturation of photomultipliers, and the resulting ringing during the detection gate period. However, dark current or ambient light are significant in FAGE3, unlike FAGE2 whose duty cycle was much lower.

The advantages of FAGE for HO determination are its ability to provide a continuous HO record with adequate sensitivity for daytime concentrations, and time resolution approaching that needed to follow the response of HO to changes in ambient irradiation and chemical composition. The disadvantages of FAGE are its need for a moderately large vacuum pump and a moderately complex laser system.

TABLE 1. Comparison of Successive FAGE Instruments, Referred to FAGE3

	FAGE1	FAGE2	FAGE3
HO excitation wavelength, nm	282	282	308
Laser beam dimensions, cm	0.2 diameter	0.6 diameter	0.1 x 0.3
Laser linewidth, cm ⁻¹	0.5	0.3	0.3
Laser repetition rate, Hz	6	30	5600
Detection total pressure, torr	5	4	4
Laser average power	0.1	3	1
Effective number of passes	15	8	1
HO absorption coefficient	0.26	0.26	1
Efficiency with respect to saturation ^a	0.45	0.35	1
Fluorescence efficiency	0.7	0.7	1
Photon collection efficiency	0.1	0.67	1
Signal per unit time	0.012	1.0	1
Averaging time, min ^b	107	60	9
Zero offset ^c	-4 × 10 ⁵	-2 × 10 ⁶	-3 × 10 ²

^a Efficiency relative to excitation with laser beam of same pulse energy, with diameter sufficiently large to prevent loss due to stimulated emission (calculated by model).

^b At ambient [HO] = 1 × 10⁶ molec cm⁻³, required for photon signal-to-noise ratio equal to 2.

^c In units of ambient [HO] in molec cm⁻³, at 50 ppb O₃ and 10 torr H₂O, using chemical modulation.

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P-1

DETECTION OF TROPOSPHERIC OH AND HO₂ BY LASER-INDUCED FLUORESCENCE
AT LOW PRESSURE USING THE 308NM EXCITATION OF OH

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Laser-induced fluorescence (LIF) spectroscopy is a highly sensitive method for the direct in-situ measurement of hydroxyl concentrations in the atmosphere. Its sensitivity and selectivity relies on the intense discrete UV-absorption lines of OH which are strongest around 282nm and 308nm.

We have developed a LIF-instrument (Hofzumahaus et al., 1990) based on the low-pressure experiment (FAGE) by Hard et al. (1984). However, we use 308nm instead of 282nm as excitation wavelength for OH, a concept that is also pursued by other groups. One advantage of the longer excitation wavelength is the higher detection sensitivity due to the about 6 times larger effective OH-fluorescence cross-section. Moreover, the O₃/H₂O-interference (OH self-generation by the laser) is about a factor of 200 smaller at 308nm than at 282nm. This keeps the interference level well below the projected detection limit of 10⁵ OH/cm³. Atmospheric HO₂-radicals are detected by chemical conversion of HO₂ into OH with NO.

In our experiment, ambient air is expanded through a sampling nozzle into a detection chamber, maintained at a pressure of about 1-2 mbar. The OH-radicals are excited at 308nm on the (0,0) vibrational band of the OH(A²Σ⁺ ← X²Π) transition and the OH-resonance fluorescence is detected around 309nm by a gain-switched photomultiplier (photon counting). The much larger laser stray-light signal (308nm, 10ns duration) is discriminated from the longer-lived OH-fluorescence (about 400ns lifetime) by temporal filtering. Residual background signals are distinguished by modulating the small-bandwidth (4-5 GHz) laser-wavelength on- and off-resonance. This system has recently been calibrated by a laminar flow tube experiment. Its 1σ detection sensitivity was found to be about (2-3)*10⁶ OH/cm⁻³ for a 10minute integration time, running the Nd-YAG-pumped tunable dye-laser system at its maximum repetition rate of 20 Hz. We are now going to replace the laser system by a high-repetition rate (2-20 kHz) dye-laser, pumped by a copper-vapour laser, in order to achieve an improved OH-detection limit of 10⁵ cm⁻³ with a time resolution of a few minutes.

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207577

P-1

SRI OH Workshop

Harvard ER-2 OH Laser Induced Fluorescence Instrument

Paul O. Wennberg and James G. Anderson

The Harvard ER-2 OH instrument is scheduled to be integrated into the NASA ER-2 high altitude aircraft ozone payload in August 1992. Design and fabrication is presently underway. This experiment is a descendant of a balloon borne instrument designed and built in the mid-1980s (see Stimpfle, R.M., et al., *Geophys. Res. Lett.*, 11, 1905, 1990).

The ER-2 instrument is being designed to measure OH and HO₂ as part of the NASA ozone payload for the investigation of processes controlling the concentration of stratospheric ozone. Although not specifically designed to do so, it is hoped that valid measurements of OH and HO₂ can be made in the remote free troposphere with this instrument.

Instrument Description:

- a. Laser System: 8 kHz prf, pulsed dye laser (diode-laser pumped Nd:YLF pump source). Frequency width: $.106 \text{ cm}^{-1}$. Pulse energy: $3 \mu\text{J}$. Pulse length: 5 ns. Transition Probed: Q1(2) or Q21(2), 2822 A. Light source weight - less than 20 Kg. Power consumption - less than 200 Watts.
- b. Detection Axis: Flow - Laminar entrance duct without boundary layer growth into the probed volume. Pressure - Ambient + ram. Temperature - Ambient + ram. Dual detection axes are used to follow the kinetics of the HO₂ titration reaction ($\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$) in a manner similar to the Harvard ClO instrument (see Brune et al., *Geophys. Res. Lett.*, 15, 144, 1988.) Laser White cell - 30 pass, $1 \mu\text{J}$ pulse (2mm X 2mm). Collection optics - Condensing lens system with uv interference filters. Wavelengths Detected - 3021 A (N₂ raman line), 3065-3110 A (OH fluorescence). Illuminated volume - about 1 cc. Fluorescence detection efficiency - 2×10^{-3} .
- c. Flight algorithm (prelim.). Laser tuned on and off resonance at 1/2 Hz. Gas addition (NO and OH remover) interspersed.
- d. Sensitivity (estimate): 1500 cps/ppm OH.
- e. Backgrounds (estimates: exact count rates will not be known until flight):
 1. Solar Infiltration: 10 cps
 2. Chamber Scatter: about 200 cps
 3. Scatter from air: about 200 cps
 4. Fluorescence from organics: Stratosphere - 0 cps; Troposphere - unknown.
- f. Calibration (laboratory): Low pressure titration of NO₂ in excess H atoms; direct absorption measurement in the White cell.
- g. O₃/H₂O Interference: signal equivalent to an OH density (molecule/cc) of less than $5 \times 10^3 \times \text{H}_2\text{O}$ (mixing ratio in ppm). Diagnostics: Variable pulse energies - .1 - 3 μJ . Chemical removal of ambient OH. Simultaneous in situ measurements of [O₃] and [H₂O]. Nighttime flights.

The ability of the Harvard ER-2 OH instrument to make OH measurements in the free troposphere will only be determined after test flights this summer. OH signal levels in the troposphere should be quite high (a few hundred counts per second), but noise levels are not known at this time. Long integration times will be difficult to obtain as the ER-2 platform is not designed to fly for long periods at low altitudes.

Photochemical production of OH by the laser should be quite low and knowable above 10 km. HO₂ measurements will have higher signal to noise, but extraction of the absolute number density will become increasingly problematic at higher pressures due to the fast three body reaction of OH with NO. Organic fluorescence and the O₃/H₂O interference is expected to prevent any HO₂ measurements in the mixed layer with this instrument.

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 Workshop on Local Measurement Techniques for Tropospheric OH and HO₂
 SRI International, March 23-26, 1992

P-1
JPL Fourier Transform Ultraviolet Spectrometer

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We will describe the Fourier Transform Ultraviolet Spectrometer (FTUVS), a new high resolution interferometric spectrometer for multiple-species detection in the UV, visible and near-IR. As an OH sensor, measurements can be carried out by remote sensing (limb emission and column absorption), or in-situ sensing (long-path absorption or laser-induced fluorescence). As a high resolution detector in a high repetition rate (>10 kHz) LIF system, OH fluorescence can be discriminated against non-resonant background emission and laser scatter, permitting (0,0) excitation.

Objectives

1. Measure column abundances and vertical profiles of key atmospheric trace molecules including OH, O₃, NO₂, NO₃, OClO, BrO, HONO, HCHO, SO₂ and possibly other species.
2. Acquire high resolution laboratory ultraviolet absorption and emission spectra of atmospheric molecules.

Instrument Description

- Michelson interferometer, planar optics, servo-controlled alignment.
- 0.06 cm⁻¹ unapodized resolution, resolving power 550,000 at 308 nm.
- 10 second scanning time.
- 5 cm dia. entrance aperture (etendue = $A\omega = 2 \times 10^{-4}$ cm² sr⁻¹).
- Spectral coverage 250 - 800 nm, 0.5 million spectral elements.

Advantages/Disadvantages Relative to Dispersive Spectrometers

Advantages

- Physically much smaller than grating instruments of comparable resolution.
- Insensitive to scattered light of different wavelengths.
- Frequency coverage is arbitrarily large.
- Low sensitivity to polarization of incident radiation.
- Spectrum wavelength scale is self-calibrated using reference laser.
- Single-element detector used (no pattern noise or q.e. variability).

Disadvantages

- Implementation in the UV is optically and mechanically difficult.
- Computation of spectrum from interferogram can be time-intensive.
- Contains critical moving parts; sensitive to mechanical vibration.

Absolute Determination of Local Tropospheric OH Concentrations

207579

P-1

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Long path absorption (LPA) according to Lambert Beer's law is a method to determine absolute concentrations of trace gases such as tropospheric OH. We have developed a LPA instrument which is based on a rapid tuning of the light source which is a frequency doubled dye laser. The laser is tuned across two or three OH absorption features around 308 nm with a scanning speed of $0.07 \text{ cm}^{-1}/\mu\text{s}$ and a repetition rate of 1.3 kHz. This high scanning speed greatly reduces the fluctuation of the light intensity caused by the atmosphere. To obtain the required high sensitivity the laser output power is additionally made constant and stabilized by an electro-optical modulator.

The present sensitivity is of the order of a few times 10^5 OH per cm^3 for an acquisition time of a minute and an absorption path length of only 1200 meters so that a folding of the optical path in a multireflection cell was possible leading to a lateral dimension of the cell of a few meters. This allows local measurements to be made.

Tropospheric measurements have been carried out in 1991 resulting in the determination of OH diurnal variation at specific days in late summer. Comparison with model calculations have been made.

Interferences are mainly due to SO_2 absorption. The problem of OH selfgeneration in the multireflection cell is of minor extent. This could be shown by using different experimental methods. The minimum-maximum signal to noise ratio is about 8×10^{-4} for a single scan.

Due to the small size of the absorption cell the realization of an open air laboratory is possible in which by use of an additional uv light source or by additional fluxes of trace gases the chemistry can be changed under controlled conditions allowing kinetic studies of tropospheric photochemistry to be made in open air.

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UV LASER LONG-PATH ABSORPTION SPECTROSCOPY

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P-1 Long path Differential Optical Absorption Spectroscopy (DOAS) using a picosecond UV laser as a light source was developed in our institute (see references below). Tropospheric OH radicals are measured by their rotational absorption lines around 308 nm. The spectra are obtained using a high resolution spectrograph. The detection system has been improved over the formerly used optomechanical scanning device by application of a photodiode array which increased the observed spectral range by a factor of 6 and which utilizes the light much more effectively leading to a considerable reduction of the measurement time. This technique provides direct measurements of OH because the signal is given by the product of the absorption coefficient and the OH concentration along the light path according to Lambert-Beers law. No calibration is needed. Since the integrated absorption coefficient is well known the accuracy of the measurement essentially depends on the extent to which the OH absorption pattern can be detected in the spectra. No interference by self generated OH radicals in the detection lightpath has been observed. The large bandwidth (>0.15 nm) and the high spectral resolution (1.5 pm) allows absolute determination of interferences by other trace gas absorptions. The measurement error is directly accessible from the absorption-signal to baseline-noise ratio in the spectra.

The applicability of the method strongly depends on visibility. Elevated concentrations of aerosols lead to considerable attenuation of the laser light which reduces the S/N-ratio. In the moderately polluted air of Jülich, where we performed a number of OH measurement campaigns, SO₂ and - to a minor extent - HCHO absorptions are present in most of the air spectra. In addition absorption features of unidentified species were frequently detected. A quantitative deconvolution even of the known species is not easy to achieve and can leave residual structures in the spectra. Thus interferences usually increase the noise and deteriorate the OH detection sensitivity. Using diode arrays for sensitive absorption measurements some specific problems of those detectors have to be solved experimentally (i.e. fixed pattern noise, dark signal noise, nonuniform efficiency of individual elements, spatial sensitivity variations). In order to improve the low spatial resolution we performed laboratory studies using a multiple reflection cell to convert the long path technique to a real in situ point measurement.

Under the conditions of field experiments in Jülich residual absorbance signals at present are about $1.5 \cdot 10^{-4}$ corresponding to an OH detection sensitivity of $2 \cdot 10^6$ OH/cm³ using a light path of 5.8 km. Total integration times for one measurement point vary between a few minutes and an hour.

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MEASUREMENT OF TROPOSPHERIC OH BY LASER LONG-PATH ²⁰⁷⁵⁸¹

ABSORPTION SPECTROSCOPY

P. 1

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OH-radicals are measured by laser long-path absorption spectroscopy. A tunable Nd:YAG/dye laser system provides broadbanded light at 308 nm. The beam is expanded to 0.3 m and pointed to an array of retroreflektors placed at a distance of 2800 m. The returning beam is separated from the outgoing beam and focussed into a spectrometer of 0.3 pm resolution. A 1024 element diode array (Spectroscopy Instruments) is used as a detector. The signal is digitized by a 14 bit ADC.

The ultimate aim is a detection limit of 10^5 molec cm^{-3} of OH. However the measurements in 1991 allowed only the recognition of OH absorptions corresponding to $3 \cdot 10^6$ OH cm^{-3} with a signal to noise ratio of 2. Improvements of the instrument are under way.

The advantages of the DOAS method are:

- The accuracy of detection is guaranteed because
 - loss of OH radicals within the device is avoided.
 - the rate of OH production by the device is negligible
 - absorptions of other trace gases could be corrected for.
- The calibration procedure for the device is fast and easy.

The disadvantages of our system are:

- Time resolution is about minutes because about ten spectra had to be added to keep the noise level down.
- The OH concentration is averaged along the whole lightpath
- Weight (500kg) and size (4*4m) of the device
- Approximately 10 l/min of coolant and supply of 8kW electrical power are necessary.

Reference:

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Measurement of Tropospheric OH Concentrations: A comparison of Field Data with Model Predictions

Journal of Atmospheric Chemistry 5 (1987) 185-216

On the possibility of measuring atmospheric OH using
intracavity laser spectroscopy

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Intracavity laser spectroscopy (ILS)^{1,2} has been demonstrated to be useful for measuring extremely weak absorption produced by gases in air. ILS is based on the observation that when there are spectrally narrow losses within the cavity of a broadband laser, the laser output has corresponding spectral holes where the laser oscillation is partially quenched. The depth of the laser output dips can be enhanced by a factor of 10^5 over the depth of the initial cavity loss, and absorptivities of 10^{-8} cm^{-1} have been measured in lasers only one meter long. With ILS, one can achieve in a compact space, a spectral contrast that would otherwise require kilometers of pathlength.

ILS systems typically use quasi-cw dye lasers operating close to threshold. The pump laser is modulated from just below to just above the threshold level for the dye laser, and the dye laser output is spectroscopically observed during a well defined time interval after the onset of lasing (the generation time). The spectral contrast of an intracavity absorber is equivalent to that produced by absorption through a path length equal to the generation time multiplied by the speed of light (assuming the cavity is completely filled with the absorber) up to some limiting time. Thus, if one measures the spectrum after 33 microseconds, the effective path length is 10,000 meters.

The OH radical has a (daylight) level that ranges from 0.02 to 0.7 ppt (5×10^5 to $2 \times 10^7 \text{ cm}^{-3}$) With an absorption cross section of $1.5 \times 10^{-16} \text{ cm}^2$ in the 308 nm band, pathlengths of 620 to 12400 meters are needed to achieve a spectral contrast of 10^{-4} . To achieve the same spectral contrast via ILS, the generation time required is 2 to 41 μs . If we use a relaxed spectral contrast of 10^{-2} , the generation times are 0.2 to 4.1 ms. This range of generation time has been demonstrated in the laboratory, so the basic sensitivity needed for point measurements of OH via ILS already exists.

There are several practical problems that must be overcome in order to demonstrate OH measurements via ILS, the foremost of which is to extend the range of UV laser dyes to reach 308 nm. This should be possible by modifying existing dye molecules, for which lasing has been demonstrated out to 311 nm at room temperature. A moderately powerful (1 to 10 W) quasi-CW UV (250-270 nm) pump laser also will be needed. With recent advances in frequency doubling of lasers, such pump lasers should be available soon.

An ILS system for measuring OH will use long generation times (on the order of 1 ms), and there are several problems which occur in this range. While the spectral contrast for absorption lines grows with time, the overall spectral envelope width decreases, so the laser output should be centered on the line of interest. Parasitic cavity effects or etalons will be amplified in the same way as atmospheric absorption lines, so etalons must be avoided or averaged. Under some circumstances, the spectrum becomes distorted near deep absorption lines, so spectral regions without strong interference must be selected. The growth in spectral contrast will become limited at some late generation time. The reason for the leveling off of the sensitivity for long generation times has been a subject of much discussion in the literature, with various fundamental and practical effects being considered. The limiting generation time in a UV ILS system would need to be determined.

We have begun to investigate the behavior of an ILS system at long generation times, as appropriate to the measurement of atmospheric trace gases³. We also have begun research on rapidly pulsing the pump laser during the generation time, which should improve the efficiency of UV pump generation via nonlinear frequency doubling.

- 1) T.D. Harris, in *Ultrasensitive Laser Spectroscopy*, [Academic, 1983], pg. 343.
- 2) S.J. Harris, "Intracavity laser spectroscopy: an old field with new prospects for combustion diagnostics," *Appl. Opt.* **23**, 1311 (1984).
- 3) J. B. McManus, C. E. Kolb, *Proc. SPIE* **1433**, 340 (1991).

NOAA Aeronomy Laboratory Long Path OH Experiment
 Fritz Peak Observatory, Colorado
 George H Mount

207583
 P-1

references: G.H. Mount: 1992, J. Geophys. Res., 97, 2427. *The Measurement of Tropospheric Hydroxyl by Long Path Absorption. I. Instrumentation*; G. H. Mount and F. L. Eisele: 1992, Science, Accepted. *An Intercomparison of Tropospheric OH Measurements at Fritz Peak Observatory, Colorado 15 July - 24 August 1991*

method: long path absorption of laser light over a 20.6km path at Fritz Peak Observatory 17 km west of Boulder; elevation 2800m; average beam height above terrain approx 250m; operational since March 1991. System runs at maximum signal to noise with integration times longer than 64 sec. Most of the data obtained to date have been 15-min averages due to lengthy data analysis required.

Basic components:

laser system

commercial XeCl excimer laser which produces a broadband output [100mj/pulse] near 308 nm spectral output covers several OH rotational lines for simultaneous determination of [OH] output beam is split so one beam goes into atmosphere and one to spectrograph for determination of both atmospheric absorption and laser baseline

mirror system

one square meter retroreflector array of 121 6cm retroreflectors
 returns any light beam to its source with spatial size approx 1m on return to FPO
 no alignment required - several experiments can run simultaneously on the long path

spectrograph/telescope

standard Cassegrain telescope feed to spectrograph
 f/13 2-m offset dual channel Czerny-Turner design built in our instrument shop
 measured spectral resolution 500,000 which easily resolves the 0.002nm FWHM OH lines
 two channel for simultaneous measurement of the absorbed beam and laser baseline
 spectral coverage less than 1nm, but covers 4 useful OH lines
 hollow cathode lamp produces OH spectral lines for accurate wavelength determination

detector

dual reticon array each 1 x 1024 pixels of size 25 μ m x 2500 μ m
 cooled to -90°C ---> leakage current of 4 e-/pix/sec
 S/N 7300 per read with 70x10⁶ electron saturation charge and read noise 2000 e-

Instrument sensitivity as currently operating: 5 x 10⁵/cc in 64sec

error: approximately 25-50% below 2 x 10⁶/cc; perhaps 25% above 3 x 10⁶/cc

ancillary measurements: N₂ O₃, CH₂O, SO₂, H₂O, HONO (upper limit), solar uv flux (both scattered and direct - cutoff to 320nm), meteorological parameters

advantages: spectral measurement gives a unique identification, abundance is determined from measured absorption depth and well known spectroscopic parameters and easily measurable factors such as path length, absorption features are spectrally resolved for maximum depth, laser power can be increased at night to look for laser generated OH, contribution of Rayleigh scattered laser and sunlight can be determined by closing the retroreflector and is <10⁻⁵ of the laser beam intensity, the derived OH abundances do not depend on chemical inferences, normally clean path but definite periods of pollution episodes from Denver metropolitan area which are of great interest, spectra of other molecules are always present and can be used to measure other species, predicted laser generated OH is < 5 x 10⁴/cc (using a beam expander)

disadvantages: spectra of other molecules are present in the spectrum and this sometimes masks some of the OH lines and *always* make the determination of a baseline to measure absorption depths from difficult, measurement averages over a 20.6 km path, the derived absorption line depths are not always consistent in derived OH (as they all should be) due to problems with the baseline continuum determination, coincident spatial sampling of the laser between the two channels is critical due to spectral inhomogeneities in the laser output, measurement depends on reasonable transmission along path, quantification of solar shadowing and multiple scattering of sunlight on the path is difficult,

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**MEASUREMENT OF ATMOSPHERIC OH BY TITRATION OF
NEAR-IR FLUORESCENT DYES**

"Local Measurement Techniques for Tropospheric OH and HO₂"
SRI International
Menlo Park, CA. March 23-26, 1992

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Background

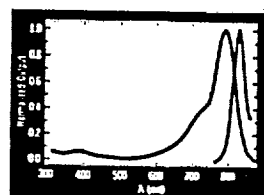
Recent research has shown that certain polymethine dyes can be detected at ultra trace levels ($\geq 6 \times 10^{-14}$ M) in solution by fluorimetry (1). These detection limits are possible a) because of the inherent sensitivity of fluorescence techniques, b) because the dyes fluoresce in the near infra-red region where background interference is negligible, and c) because powerful infra-red diode lasers are now available to improve the signal to noise ratio. Other work has shown that the hydroxyl radical destroys the ability of polymethine dyes to fluoresce (2). These observations form the basis for a new hydroxyl radical detector that is essentially a fluorometric titrator.

Theoretically the detector should show an acceptable sensitivity and response time. Assuming that the atmospheric HO· concentration is about 10^{-11} moles m⁻³ (i.e. 10^6 molecules cm⁻³), then 10 L of air "titrated" with 20 mL of 10^{-11} M dye solution (an easily detected concentration) should result in a drop in the fluorescent signal of 50% - a readily detectable change. At a flow rate of 3 L min⁻¹ the sampling time would be 3 minutes.

The biggest potential problem is selectivity: other oxidants may also cause the fluorescence signal to be lost. The chemistry of polymethine dyes has not been studied in detail and so no quantitative data are available. However, a survey of the literature suggests that in general HO· should react up to 6 orders of magnitude faster than HO₂· and other radicals such as RO₂· and RO·. It should also react much more rapidly than H₂O₂ and O₃. Thus it may be possible to discriminate kinetically against potential interfering substances.

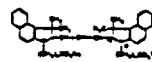
We have shown in the laboratory that 10^{-4} M H₂O₂ has little effect on the absorption spectrum of the dye IR125 over a period of hours but that the band at 780 nm is slowly lost in water over a period of days even under argon in the dark. By contrast, DMSO solutions of IR125 are stable.

IR-125



— Absorption max. 780 nm
ε_{max} = 2.6×10^4 L mol⁻¹ cm⁻¹
ε₇₈₀ = 1.7×10^4 L mol⁻¹ cm⁻¹
ε₆₈₀ = 1.1×10^4 L mol⁻¹ cm⁻¹
— Fluorescence max. 832 nm
Solute: DMSO
Dioxetane

Excitation Laser
818 nm
818 nm
818 nm



CAS No. 599-32-4

Application References

1. Determination of Protein in Human Serum by High Performance Liquid Chromatography with Semiconductor Laser Fluorimetric Detection. K. Saito, Y. Imazaki and S. Ishibashi, *Anal. Chem.*, 58(7): 2549(1986).
2. Laser Properties of Several Near-IR Dyes for a Ringed Laser Pumped Dye Laser with an Optical Isolator. S. Purts and R. Bruns, *IEEE J. Quantum Electron.*, QE-18, 1164(1982).
3. Solvent Free Ringed Laser Dyes Excited by a Simple Laser Oscillator. J. Bruns, *IEEE J. Quantum Electron.*, QE-11, 1143(1975).
4. Lifetime State Absorption and Laser Emission from Infrared Dye Detectors Pumped at 832 nm. C. Drexler, *Appl. Phys. Lett.*, 57(1), 67(1978).

A prototype fluorimeter is under development. It consists of a pulsed 200 mW diode laser (≈ 795 nm), a monochromator set at ≈ 818 nm and a photomultiplier connected to a lock-in amplifier. We are currently attempting to duplicate the dye detection limits reported in the literature.

Acknowledgements

We gratefully acknowledge funding from EPRI (contract # 8004-11).

Selected References

1. Johnson, P. A.; Barber, T. E.; Smith, B. W.; Winefordner, J. D. "Ultralow detection limits for an organic dye determined by fluorescence spectroscopy with laser diode excitation", *Anal. Chem.* 1989, 61, 861.
2. Imasaka, T.; Okazaki, T.; Ishibashi, N. "Semiconductor laser fluorimetry for enzymatic assays", *Anal. Chim. Acta* 1988, 208, 325.

THE RADIOCARBON HYDROXYL TECHNIQUE

207585
P-1

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The Radiocarbon Technique depends upon measuring the rate of oxidation of CO in an essentially unperturbed sample of air. (The airborne technique is slightly different.) Hydroxyl concentrations can be calculated directly; peroxy concentrations can be obtained by NO doping.

GROUND INSTRUMENT: We pioneered the interfacing of a flow reactor to the (turbulent) atmosphere and have devoted much effort to testing to eliminate wall effects. The reactor uses a sheath of air to insulate the reaction volume with plans to monitor isolated turbulent events. Extreme-purity ^{14}C CO is added to the flowing sample (typically 10-20 ppb) and the product ^{14}C CO₂ after a ten-second reaction time is physically separated and counted.

STATUS: Manual version well tested, imprecision established ($\approx 16\%$ SD); requires highly trained operators. Automated modules partly tested, completion due 1992.

AIRCRAFT INSTRUMENT: Uses a titration technique with a different reactor and shorter (~1s) reaction time. Other modules are mostly interchangeable with ground instrument. Wall-less inlet and reactor tested on NASA Convair and met specifications for wall loss despite mounting problem. Complete system has not yet functioned in aircraft.

SPECIFICATIONS (Ground Instrument):

Sample flow:	3 L s ⁻¹
Integration time:	30s at 3 x 10 ⁶ cm ⁻³ , 300s at less than 10 ⁵ cm ⁻³
Repetition rate:	Currently 2 hr ⁻¹ , soon 12 hr ⁻¹
Detection limit:	Currently 2 x 10 ⁵ cm ⁻³ (1 SD) or better; objective 5 x 10 ⁴ cm ⁻³ , in 1992.
Counting time (lab):	Depends on desired counting precision and ambient HO concentration; typically 20 min per sample for 10% (SD) precision. (Counting equipment can be replicated.)
Imprecision:	Measured at better than ~16% SD
Accuracy:	Technique is absolute for CO oxidation rate and accuracy is limited in most cases by precision. Errors in rate constant must be added (but adjustment can be made at later date).

ADVANTAGES: Ground instrument:

1. Adequate sensitivity.
2. Established precision and accuracy.
3. Short integration time.
4. Absolute---no calibration required.
5. No identified interferences except CH₃O, etc., believed rare.
6. Readily portable, sets up in 3 hr., travels by air.
7. Perfectly adapted to a variety of *in situ* photochemical experiments of diagnostic importance.
8. Replicable at relatively low cost and cost per measurement low.
9. Power requirements modest (~1 kW peak).

DISADVANTAGES:

1. Takes one day or more to obtain data.
2. Frequency of measurements limited to ~12 hr⁻¹.
3. Requires (ground instrument) 1 to 5 m s⁻¹ wind, not excessively turbulent.
4. Currently requires skilled staff, automation not complete.
5. Counting times long (hours) for low concentrations of HO.
6. Relies on CO-HO rate constant measured value.
7. Aircraft version not yet tested.
8. Requires LN₂, (non-toxic) gases, "excepted" quantities of radioactivity.

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- Felton, C.C., Sheppard, J.C., Campbell, M.J. (1990) The Radiochemical hydroxyl radical measurement method, *Environ. Sci. Technol.* 24, 1841-1847.
- Felton, C.C., Sheppard, J.C., Campbell, M.J. (1992) Precision of the radiochemical OH method. To appear in *Atmos. Environ.*

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P-1

ION-ASSISTED TROPOSPHERIC OH MEASUREMENT TECHNIQUE

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The present technique measures atmospheric OH concentrations by first titrating OH into isotopically labeled $\text{H}_2^{34}\text{SO}_4$ by a series of gas phase reactions in an effectively wall-less flow tube reactor on a time-scale which is short in comparison to the OH lifetime. The gas phase H_2SO_4 concentration is then determined by reacting it with $\text{NO}_3^- \cdot \text{HNO}_3$ ions in a flow tube, and subsequently measuring the resulting $[\text{HSO}_4^-]/[\text{NO}_3^-]$ ion ratio. Since the determination of H_2SO_4 concentration does not depend on the measurement of an absolute photon flux or chemical concentration but rather only on the relative concentration measurement of two fairly similar mass ions in conjunction with a fixed reaction time and reaction rate coefficient, no in-field calibration technique should be required. The ion-assisted OH measurement technique provides a concentration measurement about once each 10 to 20 seconds and had a detection sensitivity $\leq 1 \times 10^5$ molecules/cm³ (2 standard deviations) with an integration time of 5 minutes during the past field study. Typically, the total background signal level is in the low 10^6 molecule/cm³ range with the scatter in this background (or background noise in 5 minutes) in the mid 10^4 molecules/cm³ range. A more detailed discussion of this technique, potential measurement problems, and the results of two OH field studies are contained in reference 1. A second paper² discusses a very successful inter-comparison of the present technique with a NOAA long path absorption OH measurement technique which was performed at Fritz Peak Observatory, Colorado in July and August of 1991.

Since last summer, OH signal levels have been increased slightly and background levels have hopefully been significantly decreased. Also, two potential measurement interferences have been investigated in the laboratory: 1) the possible effect of NH_3 on the OH titration scheme, and 2) the effect of H_2O clusters on the $\text{NO}_3^- \cdot \text{HNO}_3/\text{H}_2\text{SO}_4$ reaction rate. Neither potential interference appears to pose a practical measurement problem for the present technique. An additional quasi-continuous OH field calibration technique using ambient air is planned for upcoming measurements at Mauna Loa Observatory in April thru August 1992, as is an extension of the present measurement capability to include HO_2 .

The major disadvantages of the present technique and apparatus include: 1) measurement depends on several different chemical reactions, 2) it is not an instantaneous measurement of OH; the HO_2 which cycles into OH in 70 milliseconds is presently included in OH measurement, 3) the use of diffusion pumps on the present analysis system prevents mobile operation, and 4) background interferences from ambient $\text{H}_2^{34}\text{SO}_4$ and reactions with non- NO_3^- ion species.

References

1. F. L. Eisele and D. J. Tanner, Ion-Assisted Tropospheric OH Measurements, *J. Geophys. Res.* **96**, 9295 (1991).
2. G. H. Mount and F. L. Eisele, An Intercomparison of Tropospheric OH Measurements at Fritz Peak Observatory, Colorado, 15 July to 24 August 1991, submitted to *Science*.

The Active Titration Method for Measuring
Local Hydroxyl Radical Concentration

1185 0117
207587
P.1

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Massachusetts Institute of Technology
Cambridge, MA 02139

We are developing a method for measuring ambient OH by monitoring its rate of reaction with a chemical species. Our technique involves the local, instantaneous release of a mixture of saturated cyclic hydrocarbons (titrants) and perfluorocarbons (dispersants). These species must not normally be present in ambient air above the part per trillion concentration. We then track the mixture downwind using a real-time portable ECD tracer instrument. We collect air samples in canisters every few minutes for roughly one hour. We then return to the laboratory and analyze our air samples to determine the ratios of the titrant to dispersant concentrations. The trends in these ratios give us the ambient OH concentration from the relation: $d\ln R/dt = -k[OH]$.

A successful measurement of OH requires that the trends in these ratios be measurable. We must not perturb ambient OH concentrations. The titrant to dispersant ratio must be spatially invariant. Finally, heterogeneous reactions of our titrant and dispersant species must be negligible relative to the titrant reaction with OH. (See Prinn, 1985 for a more detailed discussion.)

We have conducted laboratory studies of our ability to measure the titrant to dispersant ratios as a function of concentration down to the few part per trillion concentration. We have subsequently used these results in a gaussian puff model to estimate our expected uncertainty in a field measurement of OH. Our results indicate that under a range of atmospheric conditions we expect to be able to measure OH with a sensitivity of $3 \times 10^5 \text{ cm}^{-3}$. In our most optimistic scenarios, we obtain a sensitivity of $1 \times 10^5 \text{ cm}^{-3}$. These sensitivity values reflect our anticipated ability to measure the ratio trend. However, because we are also using a rate constant to obtain our [OH] from this ratio trend, our accuracy cannot be better than that of the rate constant, which we expect to be about 20%.

Two feasibility questions remain which we are in the process of assessing. The requirement that we not perturb ambient [OH] forces us to work at titrant concentrations at or below the part per billion level. We do not yet know how readily we will be able to track such low concentration puff releases. In addition, we are in the process of testing the integrity of our stored air samples with low concentrations of these species.

This technique provides a measurement of ambient [OH] averaged over a time scale of roughly one hour and over a spatial scale of a few kilometers. Its advantages are that it is fairly inexpensive and it offers a measurement completely independent of spectroscopic methods.

The method's disadvantages arise from the need to track an instantaneous puff over roughly an hour. Successful measurements require calm meteorological conditions, so weather conditions will restrict measurement times. Also, the local terrain must be such that one could track the puff as it moves with the mean wind.

Prinn, Ronald G., On the Feasibility of Quantitative Analysis of Atmospheric OH by Titration, *Geophys. Res. Lett.*, 12, 597-600, 1985.

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P-1

PEROXY RADICAL MEASUREMENTS WITH NCAR'S "CHEMICAL AMPLIFIER"

by Christopher Cantrell, Richard Shetter and Jack Calvert

The present NCAR instrument for HO₂/RO₂ measurements has been described previously by Cantrell et al. (1991) and is an improved version of that first reported by reported by Cantrell and Stedman (1982) and Cantrell et al. (1984). It is based on the reactions involving HO₂, RO₂, and HO radicals with CO and NO. Since [HO₂] + [RO₂] + [HO] >> [HO] for most atmospheres, it is useful as a peroxy radical detector. Operation of the instrument depends on the creation of a chemical chain reaction which is initiated as HO₂ and RO₂ radicals in ambient air encounter added NO gas; this forms an NO₂ molecule and an HO or RO radical: HO₂(RO₂) + NO → HO(RO) + NO₂. RO radicals react relatively efficiently with O₂ to form an HO₂ radical, and subsequently an HO-radical, by reaction with NO. CO gas added to the reaction chamber during part of the operating cycle, recycles the HO to HO₂; HO + CO (+O₂) → HO₂ + CO₂. The reaction sequence may form several hundred NO₂ molecules per HO₂ (RO₂) originally present, before chain termination occurs. The added CO is replaced by N₂ addition periodically so that the chain reaction is suppressed, and a "blank" signal resulting from NO₂, O₃ and possibly other NO₂-forming species (non-chain processes) in ambient air is recorded. The difference between the signal with and without CO is proportional to the peroxy radical concentration. The NO₂ produced is monitored using a sensitive luminol chemiluminescence detector system. In the NCAR instrument the length of the amplification chain is determined using a stable source of HO₂ radicals (H₂O₂ thermal decomposition); the ratio of the signal seen with CO present to that with N₂ present gives the sensitivity of the instrument to HO₂ (molecules of NO₂ formed/peroxy radical). The instrument is automated to carry out in hourly repeated cycles: 1) chain length determination; 2) NO₂ calibration; 3) linearity check on the response of the detector to NO₂; and 4) during most of the cycle, CO/N₂ gas modulation to determine the peroxy radical signals. One minute averages of signals are normally recorded. The sensitivity of the instrument to detect peroxy radicals is in the pptv range. The present instrument has operated continuously (24 hr/day) in field studies which extended over a period of several weeks. The major advantages of this instrument are: 1) its relative simplicity; 2) low power requirements; and 3) its rapid response to all types of peroxy radicals: HO₂, CH₃O₂ and the higher alkyl and acyl peroxy radicals; however not all RO₂ species generate HO₂ radicals with perfect efficiency and hence have somewhat lower response/molecule than HO₂ radicals.

Potential problems: 1) *Interferences.* Both peroxyacetyl nitrate (PAN) and peroxyntic acid (HO₂NO₂) are potential interferences in the instrument, since these can generate peroxy radicals in the reactor of the instrument. The extent of interference is determined by: the temperature of the reactor region of the instrument, the concentrations of the PAN and HO₂NO₂, and the residence time of the air mass in the reactor region. For operation of the instrument in clean or rural ambient air masses, this interference is normally small (less than a few percent), but in highly polluted air masses a significant artifact radical signal may be generated. Modification of the instrument to eliminate this potential problem is desirable (Hastie, et al., 1991) for use in PAN-rich environments. 2) *Variation of background NO₂ and NO_x precursors.* If ambient NO₂, or O₃ (through the NO + O₃ → NO₂ + O₂ reaction) and other non-chain sources of NO₂ vary rapidly in the air mass monitored during an RO₂-measurement cycle, then this can lead to background shift and contribute to noise in the "radical" signal.

Cantrell, C. A., R. E. Shetter, J. A. Lind, C. A. Gilliland, and J. G. Calvert, A chemical amplifier for peroxy radical measurements based on luminol chemiluminescence, *Proceedings of the Society of Photo-Optical Instrumentation Engineers, Measurement of Atmospheric Gases*, 1433, 263-268, 1991.

Cantrell, C. A., and D. H. Stedman, A possible technique for the measurement of atmospheric peroxy radicals, *Geophys. Res. Lett.*, 9, 846-849, 1982.

Cantrell, C. A., D. H. Stedman, and G. J. Wendel, Measurement of atmospheric peroxy radicals by chemical amplification, *Anal. Chem.*, 56, 1496-1502, 1984.

Hastie, D. R., M. Weissenmayer, J. P. Burrows, and G. W. Harris, Calibrated chemical amplifier for atmospheric RO_x measurements, *Anal. Chem.*, 63, 2048-2057, 1991.

THE RADICAL AMPLIFIER

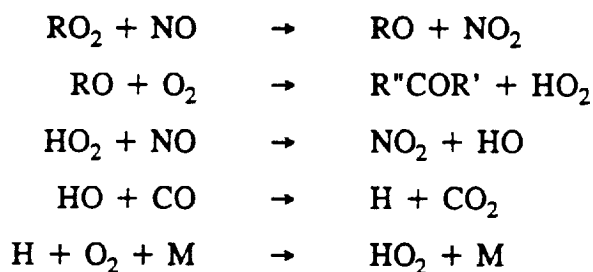
D. R. Hastie,
York University,
North York, Ontario,
CANADA

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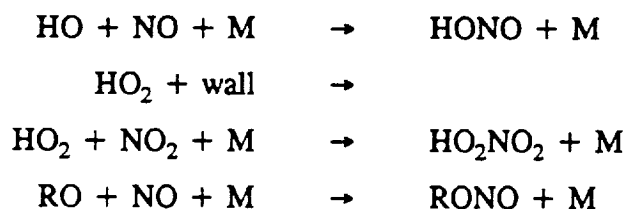
P-1

The radical amplifier as a method for measuring radical concentrations in the atmosphere has received renewed attention lately. In principle it can measure the total concentration of HO_x and RO_x radicals by reacting ambient air with high concentrations of CO (3-10%) and NO (2-6 ppmv), and measuring the NO₂ produced.

The relevant chain carrying chemistry is:



With the chain being terminated predominantly by:



The worst of the previously reported calibration difficulties seem to have been overcome, and chain lengths of up to 250 seem feasible, stable, and quantifiable.

The NO₂ produced by the radical amplifier must be detected on top of the ambient NO₂ and O₃ levels. It is the fluctuation in these concentrations that limits the radical detection limit. Rapid switching between "zero" and "measure" modes minimizes this problem, but this is limited to cycles of about 60 seconds by the need to stabilize flows. With 15 minute averaging times, detection limits of a few pptv have been demonstrated under real measurement conditions.

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207590

An Improved Method of Measuring Tropospheric NO₂, NO₃, HO₂ and RO₂ by Matrix Isolation and Electronic Spin Resonance (MIESR)

The MIESR method consists of two steps (1) collection of the radicals present in the ambient air at 77K in a polycrystalline D₂O matrix and (2) identification and quantification of the different radicals in the laboratory by Electron Spin Resonance spectroscopy. (1) The sampling efficiency for sampling NO₂ and RO₂ was determined to be $\geq 95\%$, with a measured accuracy of $\pm 5\%$ (Mihelcic et al., [1985]). (2) After collection the samples are maintained at 77K and spectra are recorded in the laboratory using a standard 9.5 GHz ESR system (Varian E-line). About 50 individual scans of each spectrum are recorded and digitally averaged in order to improve the signal-to-noise ratio. The ESR-spectra are analyzed with a recently developed numerical procedure which was demonstrated to allow speciation of NO₂, NO₃, HO₂, CH₃C(O)O₂, and the sum of the alkylperoxy radicals (Mihelcic et al., [1990]). The detection limit is 5ppt for HO₂, RO₂, and NO₂ and 3ppt for NO₃ due to its narrower ESR-linewidth.

Primary limitations of radical detection by MIESR are:

1. Sensitivity of the ESR spectrometer :

A) Varian E-line spectrometer and V-4535 cavity with a sensitivity of

$2.2 \cdot 10^{10} \cdot (\Delta H)$ [spins/Gauss linewidth] (for measurements until January 1991).

B) Bruker ESP 300E spectrometer and ER 4109 cavity with a sensitivity of $1.1 \cdot 10^{10} \cdot (\Delta H)$ [spins / Gauss linewidth] (for measurements from June 1991).

2. The background or "finger" signal spectrum is different for each sample holder, however maximum contribution to the HO₂, CH₃C(O)O₂, and sum of alkylperoxy radicals spectra are less than 2ppt. We found that this background spectra can be reduced by better gold-plating of the sample holder.

3. Poor speciation of the alkylperoxy radicals due to large degree of correlation amongst their ESR spectra in D₂O matrix.

4. The time resolution of 30 minutes. (maximum amount of 8 STP liter air is accumulated during 30 minutes; et higher air flow rate, the sampling efficiency decrease).

Mihelcic, D., Müsgen, P., and Ehhalt, D., 1985, An Improved Method of Measuring Tropospheric NO₂ and RO₂ by Matrix Isolation and Electron Spin Resonance, *J. Atmos. Chem.* **3**, 341-361.

Mihelcic, D., Volz-Thomas, A., Pätz, W., Kley, D., and Mihelcic, M., 1990, Numerical Analysis of ESR Spectra from Atmospheric Samples, *J. Atmos. Chem.* **11**, 271-297.

Tropospheric HO₂ Determination by FAGE
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In the present work HO₂ is determined by FAGE [Hard *et al.*, 1984, 1986; Chan *et al.*, 1990], a method which employs low-pressure laser-excited fluorescence to observe the hydroxyl radical HO, using chemical modulation to distinguish the desired signal from the background. In the HO₂ determination mode, NO is added to the low-pressure flowing sample, converting HO₂ to HO:



The efficiency of HO₂ detection as HO following R1 is limited by another reaction also driven by the NO reagent:



Thus the yield of HO from the above mechanism is pressure-dependent, and therefore low-pressure flow conditions are most effective for HO₂ determination by conversion to HO via R1.

In the present method, a constant NO flow is added to two air-sampling channels of FAGE. The signal from the HO product is turned on and off (modulated) in each sample channel by addition of isobutane (*i*-C₄H₁₀, *i*-BuH) to the flow, alternating between the two channels, via:



Earlier [Hard *et al.*, 1984] we used NO alone as the modulating reagent. The reason for the change to chemical modulation by isobutane is to avoid possible interferences associated with NO modulation. The isobutane also modulates ambient HO via R3, with somewhat higher overall efficiency, but the resulting small HO signal is comparable with the measurement uncertainty of the much more abundant HO₂.

The decay of HO₂ in the dark due to the parallel reactions



is used to calibrate the HO₂ response of FAGE. For the HO₂ + HO₂ self-calibration procedure, the initial HO₂ concentration is provided by uv irradiation of CH₂O vapor in dry air in a continuously-stirred flow reactor (CSTR), made of FEP teflon film. After steady-state HO₂ signals are observed, the uv lamps and the stirring fan are turned off, the resulting HO₂ signal decay is recorded, and the HO₂ response is obtained from the slope of the inverse of the signal vs. time plot, using literature rate coefficients for Reaction R4.

We have measured ambient HO₂ at two sites, one coastal and the other inland urban, for continuous periods of 36 to 48 hours. The coastal site sampled sea-level North Pacific air which was free from local pollution sources under suitable wind conditions. The urban site was subject largely to automotive pollutant sources.

The advantages of FAGE for HO₂ determination are its ability to provide a continuous HO₂ record with adequate sensitivity for daytime concentrations, and adequate time resolution to follow the response of HO₂ to changes in ambient irradiation and chemical composition. The disadvantages of FAGE are its need for a moderately large vacuum pump and a moderately complex laser system.

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P-1

NEAR-IR DIODE LASER ABSORPTION FOR
MEASUREMENT OF TROPOSPHERIC HO₂

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The possibility of using tunable lead salt diode lasers in the infrared for measurement of tropospheric HO₂ has been frequently considered. Although the sensitivity of diode laser absorption has been improved through the use of high frequency detection techniques, nature has been unkind in that the HO₂ absorption cross sections are weak.¹ Even using the most optimistic assumptions about attainable path length and detectable absorbance, measurement of tropospheric HO₂ by diode laser absorption in the mid-IR appears marginal.

A possible alternative method for measuring HO₂ is by absorption at near-infrared wavelengths. Several absorption bands of HO₂ occur in the wavelength region between 1.2 and 1.6 μm due to electronic transitions and overtones of the fundamental vibrational modes. InGaAsP diode lasers operate in this wavelength region and can be used for high resolution spectroscopy in a manner analogous to the lead salt lasers. A diode laser system in the near-IR offers some advantages:

- (1) No cryogenic cooling is required for either the laser or detector;
- (2) The near-IR diode lasers are 10 to 100 times more powerful than lead salt lasers, resulting in better theoretical sensitivity for measuring small absorptions;
- (3) The optical characteristics of the near-IR lasers are superior to those of the lead salt lasers, making the use of multiple pass cells with very long absorption path lengths feasible;
- (4) Detector performance and the quality of optical components and coatings (e.g. high reflectivity mirror coatings) is superior in the near-IR as compared to mid-IR counterparts.

These considerations suggest that a near-IR diode laser system might offer improved detection sensitivity for HO₂, provided that the near-IR absorption cross sections are sufficiently large. Hunziker and Wendt² have published low resolution HO₂ absorption spectra in the near-IR. From their work, we infer integrated band strengths of 88 cm⁻² (STP atm)⁻¹ for the ²A' (000) ← ²A~ (000) electronic band near 1.43 μm and 58 cm⁻² (STP atm)⁻¹ for the 1.50 μm 2ν₁ overtone band. These estimated band strengths are comparable to the strengths of the fundamental infrared bands.¹ Recent results of Johnson *et al.*³ indeed show experimental line strengths in the 2ν₁ band that are about equal to those of the most intense lines in the ν₁ fundamental. However, these lines are weak compared to the strongest line pairs in the ν₂ fundamental.

We have proposed further high resolution studies of the near-IR HO₂ bands to prove or disprove the feasibility of near-IR diode laser detection of tropospheric HO₂. Diode laser measurements in the 1.43 μm band would be performed to measure the cross sections of the strongest features. Also, new measurements of cross sections in the 2ν₁ band would be compared with the results of Johnson *et al.*, using the same scheme for quantifying HO₂ that was used previously in measuring the strengths of the IR fundamental bands.¹ Finally, potential spectroscopic interferences at the wavelengths corresponding to promising HO₂ absorption features would be investigated.

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HO₂ DETECTION BY NEAR INFRARED ABSORPTION USING TUNABLE DIODE LASERS

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Method Overview

Strongest absorption lines are in ν_2 vibrational band around 1400 cm^{-1} ; several near-coincident line pairs in this region provide max linestrengths of $1.2 \times 10^{-20} \text{ cm}^2 \text{ molec}^{-1} \text{ cm}^{-1}$

Use high frequency (5-20 MHz) wavelength modulation coupled with sweep integration to minimize noise and maintain spectral discrimination

Reduced pressure sampling (20 Torr) using supersonic nozzle and aerodynamic flow cell to minimize residence time and wall losses of radicals

Astigmatic mirror design provides pathlengths up to 200 m in volume of 3 liters with minimal optical interference fringes; longer pathlengths are possible

Detection limit depends on pathlength and minimum fractional absorptions; 1×10^{-6} with 200 m corresponds to 30 ppt HO₂

Advantages

Specific -- spectroscopic absorption features provide fingerprint for HO₂

Selective -- low pressure sampling minimizes interferences from other species

Absolute -- calibration based on spectroscopic parameters (linestrengths and broadening coefficients) which are transferable from laboratory measurements; sampling wall losses can be assessed by cell impulse response at higher concentrations

Continuous -- response limited only by integration time for required detectivity

Instrumental simplicity -- relatively low size, weight, and hardware costs

Disadvantages

Sensitivity -- relatively weak infrared linestrengths require state of the art TDL signal processing and long pathlengths to obtain sufficient signal-to-noise ratio

TDL technology -- requires high power, single mode diodes, for specific spectral regions; diodes and detectors require liquid nitrogen cooling

Vacuum pump -- high throughput to minimize sampling losses for radicals requires large pumps

Operator expertise -- requires extensive experience at this level of detection.

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Appendix B

BIBLIOGRAPHY OF LOCAL MEASUREMENT OF ATMOSPHERIC OH



BIBLIOGRAPHY OF LOCAL MEASUREMENT OF ATMOSPHERIC OH

This listing contains papers describing local tropospheric OH measurement techniques, instrument development, or local tropospheric OH measurements themselves. It does not include papers concerned with regional or global OH measurement, modeling of OH without accompanying measurement, or ancillary laboratory measurements (e.g., quenching coefficients or ozone photolysis quantum yields) separate from development.

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Appendix C

BIBLIOGRAPHY OF LOCAL MEASUREMENT OF HO₂



BIBLIOGRAPHY OF LOCAL MEASUREMENT OF ATMOSPHERIC HO₂

This listing was compiled with the same qualifications as for the OH bibliography.

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13. ABSTRACT (Maximum 200 words) In March of 1992 a workshop sponsored by NASA and NSF was held at SRI International to assess the current ability to measure atmospheric OH and HO ₂ . The workshop participants consisted of experimentalists involved in measurements of the two radicals, atmospheric chemists, and chemical physicists familiar with the measurement techniques. The measurement techniques reviewed during the workshop for detection of OH included five laser-induced fluorescence schemes, five laser-based absorption techniques, and four non-laser methods. Six instruments or instrument concepts for HO ₂ detection, including chemical amplification, conversion to OH with subsequent OH detection, or direct spectroscopic detection of the HO ₂ were also discussed. The conclusions from the workshop identify several measurement techniques for OH and HO ₂ that are ready for field tests. These have the ability to measure the radicals with sufficient sensitivity and accuracy to form meaningful comparison with atmospheric model predictions. The workshop conclusions also include recommendations for informal and formal intercomparison protocols, including ancillary measurements, and intercomparison using measurement techniques having different sampling volumes and temporal averaging scales, as well as requirements on intercomparison sites.				
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