Assessment of local HOx and ROx Measurement Techniques: Achievements, Challenges, and Future Directions

Report of the International HOx Workshop 2015
Organisers Andreas Hofzumahaus and Dwayne Heard
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Preface

Measurements of HOx and ROx radicals are an important tool for the investigation of tropospheric chemistry in field campaigns and simulation chamber experiments. The measured data allow us to test chemical models simulating the atmospheric concentrations of OH, HO_2 and RO_2, and help to improve chemical mechanisms used in regional and global models for predictions of the atmospheric chemical composition. Even after four-decades of development and application of radical measurement techniques, accurate measurement of radical species remains a highly challenging task and requires persistent care.

From March 23-25 2015, an international, IGAC-endorsed workshop took place at JUFA, Jülich, and hosted by the Forschungszentrum Jülich, Germany, to assess the performance and reliability of current HOx measurement techniques. Fifteen international groups from Germany, UK, Ireland, France, Finland, USA, China and Japan came together to discuss achievements, challenges and future directions of techniques based on laser absorption and laser-induced fluorescence spectroscopy, chemical ionisation mass spectrometry, and chemical techniques. There were 35 participants at the workshop, including Principal Investigators, Postdoctoral Fellows and Postgraduate Students, with representatives from virtually all groups world-wide undertaking field measurements of HOx and ROx. The workshop follows a number of other workshops dedicated to the measurement of HOx which were held at Leeds (2005), SRI International (1992 and 1985) and NASA (1982).

The major topic for discussion was an assessment of how well we can measure OH, HO_2 and RO_2; how instrumental performance can be improved in terms of sensitivity, calibration and artefacts; and how the reliability of HOx and ROx measurements can be demonstrated to the international community. Six invited oral presentations gave an overview of current atmospheric-radical measurement techniques and their calibrations, followed by ten contributed talks presenting new research results about potential radical measurement artefacts, and one talk about the development of a new laser-based method. There was ample of time for discussions after each talk and in dedicated sessions during the remainder of the meeting. An important feature was the presence of three rapporteurs, who although internationally leading in their own disciplines, are not practitioners of HOx measurements. Their written reports summarise the conclusions, ideas and recommendations from the discussions and have greatly assisted the writing of this report. The workshop report has been circulated among the participants before publication and their comments have been incorporated to ensure that the report reflects the consensus of all groups at the workshop.

As a major workshop outcome, a working group was established to guide the community in the near future in making progress on continued improvement in HO_x measurements. Three goals will be pursued: the development of a common calibration unit, the development of procedures to investigate and, if necessary, eliminate possible measurement artefacts, and planning for future instrumental intercomparisons.

We are very grateful to Forschungszentrum Jülich for financial support. We thank all participants who contributed to this workshop. Special thanks to Andreas Wahner and Astrid Kiendler-Scharr, heads of the Institute of Energy and Climate Research IEK-8 at Forschungszentrum Jülich, for hosting the workshop and to the rapporteurs Steven Brown of NOAA in Boulder, Jim Crawford of NASA Langley Research Centre, and Frank Keutsch of Harvard University for their session reports. We hope that the workshop report will be a useful guide for the further development of instrumental techniques and research on radicals in the field of tropospheric chemistry.

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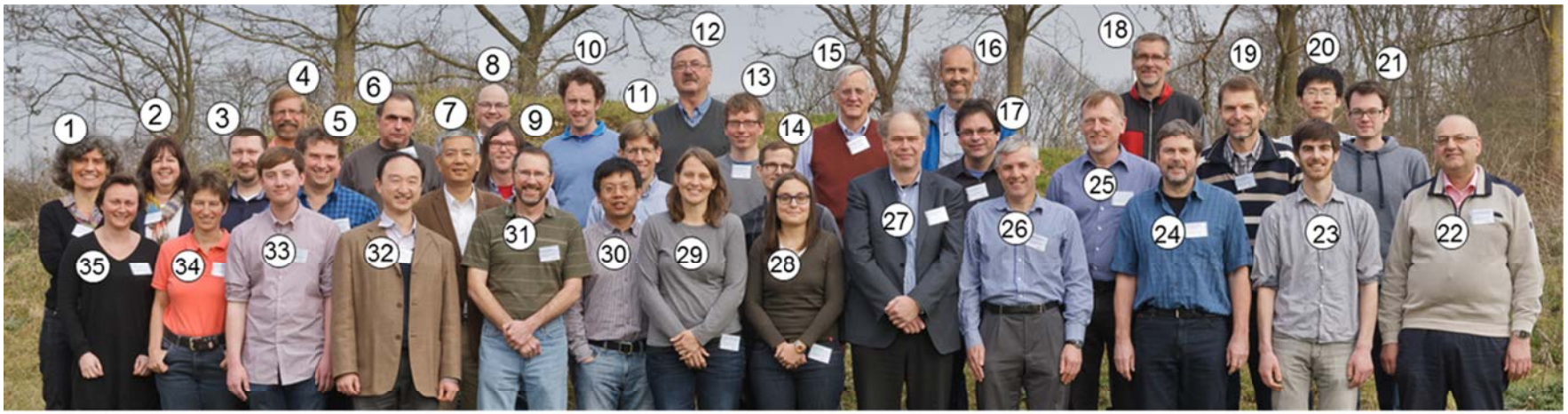

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1. HOx Workshop 2015

1.1 Introduction

The hydroxyl radical (OH) is the most important oxidant in the troposphere. It is the chemical agent that removes most trace gases from the atmosphere, for example carbon-containing compounds like methane, volatile organic compounds, hydrogen-containing CFCs, and carbon monoxide. In addition, a large fraction of atmospheric nitrogen- and sulfur-containing species is oxidised by OH forming eventually nitric and sulfuric acids. Furthermore, chemical degradation by OH contributes to the formation of secondary pollutants like ozone and secondary organic particles. Thus, exploration and understanding of the atmospheric OH chemistry is an essential part in solving air quality problems and developing strategies for mitigation of climatic impacts from non-CO_2 greenhouse gases and aerosols (Brasseur et al., 2003).

The importance of atmospheric OH became first evident when Levy II (1971) identified the photolysis of tropospheric ozone as a global source of OH driving the atmospheric removal of CO and methane. Since the very first attempts to detect OH in the atmosphere in the mid 1970's, much effort was put forward to measure reliably the extremely small concentration of the highly reactive OH radical, as well as of chemically related hydroperoxy (HO_2) and organic peroxy (RO_2) radicals. The major challenge of measuring these radicals lies in the need for very high detection-sensitivities, the demand for calibration standards with accurately known radical concentrations, and prevention of possible interferences, for example artificial radical production in the measurement instruments.

Since the beginning of the 1980's, the development of HOx measurement techniques has been accompanied by regular assessments through international expert groups consisting of experimentalists involved in radical measurements and other atmospheric chemists and physicists. Corresponding workshops were held at Leeds (2005), SRI International (1992 and 1985) and NASA (1982). The first two assessments (Crosley and Hoell, 1986; Hoell, 1984) dealt mainly with the difficulty how existing techniques could be further developed and improved to achieve sufficient sensitivity for measurement of local atmospheric OH and HO_2 concentrations. The third assessment in 1992 (Crosley, 1994) reported a major break-through in the development of several local measurement techniques that had matured and become ready for use in field studies. For OH, the techniques included low-pressure Laser-Induced Fluorescence (LIF) with 308nm excitation, long-path Differential Optical Absorption Spectroscopy (DOAS) using 308nm laser radiation, Chemical Ionisation Mass Spectrometry

(CIMS), and radiochemical ^{14}CO oxidation. Techniques for measuring HO_2 included chemical conversion to OH with subsequent OH detection by LIF, chemical amplification for measurement of the sum of HO_2 and RO_2 (Peroxy chemical amplifier, PERCA), and Matrix-Isolation Electron Spin Resonance (MIESR).

The 2005 workshop in Leeds presented and discussed considerable progress in understanding atmospheric chemistry based on field measurements of free-radicals and modelling since 1992 (Heard, 2006). The workshop covered not only results about HO_x and RO_x species, but also on atmospheric nitrate (NO_3) and halogen (X, XO_n) radicals. With respect to the measurement capabilities for HO_x and RO_x radicals, it was concluded that OH radicals could now be measured routinely by three *in-situ* techniques, namely low-pressure LIF, DOAS applying an open-multipass cell, and CIMS. Furthermore, the development of new radical measurement techniques was reported, namely CIMS-based chemical conversion techniques for measurement of HO_2 and HO_2+RO_2, and LIF-based instruments to measure atmospheric OH reactivities (inverse OH lifetimes). In the recommendations for future work, it was noted that some instruments measured nighttime OH which is not seen by other instruments, implying possible interferences that would require further investigations. Moreover, the need for speciated peroxy radical measurements and for a community radical calibration-source was pointed out.

1.2 Aims and structure of the workshop

During the last ten years, again substantial progress has been made in research and measurement of atmospheric HO_x and RO_x radicals. Atmospheric OH-reactivity measurements by different techniques are now being widely applied, for example, for the investigation of local OH budgets. Chemical conversion techniques for measurement of HO_2+RO_2 by LIF have become available. A considerable number of HO_x and RO_x measurement intercomparisons were successfully performed. One prominent test was the formal and blind HO_x intercomparison of LIF, CIMS, and DOAS instruments operated by five international groups at Forschungszentrum Jülich (HOxComp 2005). New field campaigns and atmospheric simulation chamber experiments were carried out involving comprehensive radical and trace-gas measurements. On the whole, the focus of radical research shifted from environments with clean-air towards those with complex chemical composition, for example found in densely populated areas like mega-cities, or biogenically influenced forested regions. Stimulated by field observations of OH, new chemical mechanisms related to the oxidation of biogenic VOCs have been discovered which regenerate OH from peroxy radicals without need for reaction with NO, and contribute to organic particle formation. On the other hand, measurements in VOC-rich air also gave hints to so far unrecognised chemistry that may cause interferences at least in some of the radical measurement instruments. The underlying processes are not well understood and it is not clear to what extent individual instruments may be biased. This situation causes significant uncertainty in the current exploration of the radical chemistry in urban and forest atmospheres.

In order to improve existing measurement techniques and help to remedy instrumental uncertainties, the current HOx workshop brought together representatives from virtually all groups world-wide who are directly involved in atmospheric HO_x and RO_x radical measurements. The goal was to assess the current status of radical measurement instruments, to share knowledge on possible instrumental problems, and to plan joint activities for further improvement of radical measurement techniques. For this purpose, the workshop was structured into three sessions (see detailed workshop programme in Chapter 4) each of which was chaired by participants. An important feature of the meeting was the presence of 3 rapporteurs consisting of two field scientists and one modeler, who although internationally leading in their own disciplines, are not practitioners of HO_x measurements.

Session 1: Radical measurement techniques

Here, invited speakers gave an overview about currently used measurement techniques for OH, HO_2 and RO_2, which included DOAS, LIF, CIMS, and PERCA techniques. The different technical designs used by different groups were presented and instrumental measurement performance (e.g., detection sensitivity, limit-of-detection) were compared and discussed. Furthermore, calibration procedures were reviewed and results of previous measurement intercomparisons were presented. Individual descriptions of the instruments delivered by the participating groups can be found in Chapter 3 of this report.

Session 2: Potential radical measurement artefacts

The session was targeted at collecting current knowledge of known and suspected measurement artefacts. Prior to the workshop, all participating groups had been invited to present published or unpublished results on this topic. Ten oral presentations on potential measurement artefacts were then contributed in Session 2, out of which eight were dealing with LIF techniques and two with CIMS. One additional talk presented a new laser-based method for OH detection. The presentations and the discussions following each talk are summarised in the rapporteur's report in Chapter 2.1.

Session 3: Thematic discussions

Following the presentations in Session 2 and 3, the final session provided ample of time to discuss and summarise the performance and possible problems of current measurement techniques, and discuss future directions for improvements. The plenary discussions were dedicated to 4 themes:

Theme 1: Radical detection and calibration
Theme 2: Measurement artefacts
Theme 3: Planning of future HO_x - RO_x intercomparisons
Theme 4: Future directions of atmospheric HO_x - RO_x chemistry research

The results of the discussion can be found in the rapporteur's reports (Chapter 2.2).

1.3 Participating groups

All international groups who are known to undertake field measurements of HO_x and RO_x were invited to participate in the workshop and almost all were represented during the meeting. A total of 35 participants including Principal Investigators, Postdoctoral Fellows and Postgraduate Students came from Germany, UK, Ireland, France, Finland, USA, China and Japan (see detailed list of participants in the front part of this document). A list of the participating groups together with their radical measurement techniques and measurable trace gases is given in Table 1.

Table 1. Participating groups and their measurement techniques

Group		Technique[a]	Measured Trace Gases[b]
Forschungszentrum Jülich	FZJ	DOAS	OH, SO_2, HCHO, CS_2, naphtalene, X
Forschungszentrum Jülich	FZJ	LIF - FAGE	OH, HO_2, HO_2+RO_2, k_{OH}
Max-Planck Institute for Chemistry, Mainz	MPI		OH, HO_2, naphthalene
University of Leeds	Leeds		OH, HO_2, HO_2+RO_2, k_{OH}
Université de Lille	Lille		OH, HO_2, k_{OH}
Pennsylvania State University	PSU		OH, HO_2, k_{OH}, naphthalene
Indiana University	Indiana		OH, HO_2
Japan Agency for Marine-Earth Science and Technology	JAMSTEC		OH, HO_2
Peking University	PKU		OH, HO_2
German Meteorological Service, Hohenpeissenberg	DWD	CIMS	OH, HO_2+RO_2, k_{OH}, H_2SO_4
National University of Ireland Galway	NUIG		OH, H_2SO_4, CH_3SO_3H
University of Helsinki	Helsinki		OH, H_2SO_4, CH_3SO_3H, HO_2+RO_2, ELVOC, SO_2 oxidants
CNRS Orleans	CNRS		OH, HO_2+RO_2, H_2SO_4
University of Colorado	Colorado		OH, HO_2, HO_2+RO_2, H_2SO_4, sCIs
Hong Kong Polytechnic University	Hong Kong		HO_2+RO_2
University of Bremen	Bremen	PERCA	HO_2+RO_2

[a] DOAS - Differential Optical Absorption Spectroscopy; LIF - Laser Induced Fluorescence; FAGE - Fluorescence Assay with Gas Expansion; CIMS - Chemical Ionisation Mass Spectrometry; PERCA - PEroxy Radical Chemical Amplifier

[b] X - unknown absorber; k_{OH} - inverse OH lifetime (OH reactivity); ELVOC - Extremely Low-Volatile Organic Compounds; sCIs - stabilised Criegee Intermediates

1.4 Measurement techniques

Four different techniques are currently applied for atmospheric HO_x and RO_x radical measurements. There is one instrument world-wide that is capable of measuring atmospheric OH concentrations by optical absorption (DOAS). Two PERCA groups are

currently known to measure atmospheric peroxy radicals, one of which was represented at the workshop. The most widely applied measurement techniques are CIMS and low-pressure LIF. The LIF technique is also known as Fluorescence Assay with Gas Expansion (FAGE). It is noteworthy that most techniques nowadays measure a range of substances.

An overview of individual instruments and their performances (limit-of-detection, time resolution, accuracy, applications) for measurement of OH, HO_2 and RO_2 is given in Tables 2 and 3. Although instruments of the same category (e.g., LIF, CIMS) are based on the same fundamental principles, their technical designs and operating conditions can be quite different, as indicated by footmarks in Table 2 and 3. LIF instruments, for example, may use single- or multi-pass excitation of OH, some apply wavelength modulation and others are now using chemical modulation in order to discriminate ambient OH from background signals and possible interferences. There are also major differences in the chemical conversion schemes for measuring HO_2 and HO_2+RO_2. Details of the instruments and references to original papers can be found in the descriptions provided by the participating groups (Chapter 3).

Table 2. OH measurement instruments

OH Method	Group	LOD (SNR=2)	Measurement Time	Accuracy (2σ)	Comments
DOAS (open path)	FZJ	1.6×10^6 cm^{-3}	3 min	14%	installed at SAPHIR chamber
FAGE-LIF (SP, λ)	FZJ	6×10^5 cm^{-3}	50 s	20%	ground based (field, SAPHIR chamber) and airship (Zeppelin NT)
FAGE-LIF (MP, λ, C)	MPI	8×10^5 cm^{-3}	4 min	42%	HORUS: ground based
FAGE-LIF (SP, λ)	Leeds	4.5×10^5 cm^{-3}	3 min	26%	ground based
		6.4×10^5 cm^{-3}	3 min	15%	aircraft (BAe 146-301)
FAGE-LIF (MP, λ)	Lille	$(4\text{-}6) \times 10^5$ cm^{-3}	1 min	30%	ground based; indoor; combustion
FAGE-LIF (MP, λ, C)	PSU	2.5×10^5 cm^{-3}	1 min	32%	GTHOS: ground based; ATHOS: aircraft (NASA DC8)
FAGE-LIF (MP, λ, C)	Indiana	6×10^5 cm^{-3}	15 min	36%	ground based
FAGE-LIF (SP, λ)	JAMSTEC	2×10^5 cm^{-3}	1 min	40%	ground based
FAGE-LIF (SP, λ)	PKU	1.4×10^6 cm^{-3}	30 s	28%	ground based
CIMS ({SO_2, NO_3^-}, C)	DWD	1.4×10^5 cm^{-3}	5 min	40% + 1.4×10^5 cm^{-3}	ground based
CIMS ({SO_2, NO_3^-}, C)	NUIG	1.3×10^5 cm^{-3}	5 min	40%	ground based
CIMS ({SO_2, NO_3^-}, C)	Helsinki	3×10^5 cm^{-3}	30 s	45%	ground based, laboratory
CIMS ({SO_2, NO_3^-}, C)	CNRS	3.3×10^5 cm^{-3}	2 min	30%	ground based
CIMS ({SO_2, NO_3^-}, C)	Colorado	3×10^5 cm^{-3}	30 s	40%	ground based and aircraft

SP, single-path laser excitation; MP, multi-pass laser excitation; λ, laser-wavelength modulation; C, chemical modulation by OH scavenger; {SO_2, NO_3^-}, chemical conversion by SO_2 to H_2SO_4 and ionisation by NO_3^- .

Table 3. HO_2 and RO_2 measurement instruments

HO_2 Method	Group	LOD (SNR=2)	Measurement Time	Accuracy (2σ)	Comments
FAGE-LIF (SP, λ, LNO)	FZJ	3×10^7 cm^{-3}	50 s	20%	ground based (field, SAPHIR chamber); airship (Zeppelin NT)
FAGE-LIF (MP, λ, LNO)	MPI	8.5×10^6 cm^{-3}	15 s	35%	HORUS: ground based
FAGE-LIF (SP, λ, LNO)	Leeds	2.1×10^6 cm^{-3}	3 min	26%	ground based
		5.9×10^5 cm^{-3}	3 min	20%	aircraft (BAe 146-301)
FAGE-LIF (MP, λ, LNO)	Lille	$(3.7\text{-}5) \times 10^6$ cm^{-3}	1 min	30%	ground based; indoor; combustion
FAGE-LIF (MP, λ, NO)	PSU	2.5×10^6 cm^{-3}	1 min	32%	GTHOS: ground based; ATHOS: aircraft (NASA DC8)
FAGE-LIF (MP, λ, LNO)	Indiana	4×10^7 cm^{-3}	30 s	36%	ground based
FAGE-LIF (SP, λ, NO)	JAMSTEC	2×10^5 cm^{-3}	1 min	48%	ground based
FAGE-LIF (SP, λ, LNO)	PKU	3.4×10^7 cm^{-3}	30 s	44%	ground based
CIMS ({SO_2, NO_3^-}, CM1)	Colorado	5×10^7 cm^{-3}	1 min	35%	ground based and aircraft
RO_2+HO_2 Method					
FAGE-LIF (SP, λ; CM2)	FZJ	3×10^7 cm^{-3}	50 s	20%	ground based (field, SAPHIR chamber)
FAGE-LIF (SP, λ; CM2)	Leeds	1.4×10^7 cm^{-3}	3 min	26%	ground based
CIMS ({SO_2, NO_3^-}, NO, C)	DWD	3×10^5 cm^{-3}	5 min	80% + 3×10^5 cm^{-3}	ground based
CIMS ({SO_2, NO_3^-}, NO, C)	Helsinki	5×10^5 cm^{-3}	90 s	45%	ground based, laboratory
CIMS ({SO_2, NO_3^-}, NO, C)	CNRS	1.2×10^6 cm^{-3}	2 min	≥30%	ground based
CIMS ({SO_2, NO_3^-}, CM1)	Colorado	5×10^7 cm^{-3}	1 min	35%	ground based and aircraft
CIMS ({SO_2, NO_3^-}, NO, C)	Hong Kong	$< 3 \times 10^6$ cm^{-3}	1 min	30%	ground based
PERCA (CM3)	Bremen	$(2.5\text{-}7.5) \times 10^7$ cm^{-3}	20 s	25-45%	DUALER: ground based and aircraft

SP, single-path laser excitation; MP, multi-pass laser excitation; λ, wavelength modulation;

{SO_2, NO_3^-}, chemical conversion by SO_2 to H_2SO_4 and ionisation by NO_3^-; C, chemical modulation by OH scavenger;

NO, chemical conversion by NO; LNO, chemical conversion by NO with low efficiency to suppress alkene-RO_2 interference;

CM1, chemical conversion by NO with modulation of $RO \rightarrow HO_2$ conversion by dilution with N_2/O_2 to distinguish between RO_2 and HO_2;

CM2, chemical conversion by NO with modulation of $RO_2 \rightarrow HO_2$ conversion to distinguish between RO_2 and HO_2.

CM3, chemical conversion by NO and amplification into NO_2.

1.5 Summary and recommendations

The key findings and recommendations of the workshop with respect to current and future HO_x and RO_x radical measurement techniques can be summarised as follows.

OH measurement techniques

1. Detection sensitivity and calibration

- DOAS employing an open multi-pass absorption cell is the only absolute, direct technique currently available for *in-situ* measurement of atmospheric OH. It has a limit-of-detection of 1.6 x 10^6 cm^{-3} (SNR=2) and is considered to be the gold standard with 14% accuracy (2σ).
- LIF (direct) and CIMS (indirect) measurements require calibration and are known to about 20-40% at 2σ. Current detection limits (a few 10^5 cm^{-3}) and time resolutions (typ. 1-5min.) are adequate for many environments. There was agreement that higher detection sensitivities allowing for lower detection limits (5 x 10^4 cm^{-3}) are needed to enable measurements at higher temporal resolution (e.g., on aircraft with rapidly changing conditions), or in environments with lower radical levels.
- Independent calibration methods (i.e., H_2O photolysis and species decay) agree within 10-20%. There was a consensus that H_2O photolysis should be the primary method, but instabilities in the calibration setups can be a problem in harsh environments in field applications.
- A calibration source for OH and HO_2 that can be circulated throughout the community would be extremely useful to assure consistency among field measurements by different groups. The source could be cross-calibrated to DOAS and aim for a 10% accuracy for CIMS and LIF.

2. Measurement artefacts and interferences

DOAS instrumentation

- No significant interference is known for atmospheric OH measurement by open-path DOAS. Other absorbers (SO_2, HCHO, naphthalene) at 308nm can be spectroscopically identified and discriminated against OH by a spectral multicomponent analysis. In principle, OH self-generation by laser photolysis of O_3 in humid air is possible, however, accumulation of significant laser-generated OH is avoided by wind-driven air exchange in the open-path cell and by keeping the power of the probe-laser sufficiently small.

LIF instrumentation

- Artefacts producing OH radicals in the instrument via laser photolysis (e.g., O_3) are fully understood and subtracted if they contribute a signal above the limit-of-detection.

- Non-photolytic ozone artefacts had been reported previously for some LIF instrumentation with magnitudes at current detection limits. If the detection limits are improved below 10^5 cm^{-3}, the artefacts will require further investigation.
- Chemical artefacts have been reported recently in field studies in the presence of biogenic VOCs for two LIF instruments (PSU, MPI). OH interference signals were detected when a chemical scavenger for removal of ambient OH was applied. The interference is apparently caused by OH formed inside the measurement instruments, but the responsible species and formation mechanism is not clear. Two other LIF instruments (Indiana, PKU) have implemented scavenging of ambient OH in field measurements for test purposes but have found no clear evidence for an artefact. The inconsistent field observations may be caused by different air-composition at the measurement sites and/or different instrumental designs.
- Laboratory experiments suggest that chemical artefacts may be caused by products from the ozonolysis of alkenes, e.g., Criegee radicals. Extensive laboratory tests with ozone and different alkenes by several LIF groups yield the following preliminary results:
    - the interference signal seen in laboratory tests should be insignificant at ambient levels of ozone and biogenic VOCs;
    - the magnitude of artefact depends on instrument and chemical conditions;
    - the OH artefact is not caused by laser photolysis.

  It is recommended that the LIF groups continue their investigations under standardised conditions to allow for easier comparison of their results and to determine the influence of instrumental designs.
- An OH interference signal from simple addition of NO_3 to synthetic air has been discovered in the LIF instrument of FZJ. 10 pptv of NO_3 gave an OH signal equivalent to 10^5 molecules cm^{-3}. Laboratory experiments point to possible involvement of heterogeneous reactions in the gas expansion or at wall surfaces of the instruments, but the mechanism is not clear. No other instruments have been tested for this artefact so far. Further studies of this interference may provide an important clue for generation of artefacts in OH LIF instruments.
- Chemical modulation with periodic use of scavengers (e.g., propane, C_3F_6) for ambient OH in all LIF field measurements is currently recommended until the origin of observed artefacts will have been identified and eliminated. This method is currently being applied or developed by several groups.

CIMS instrumentation

- Current CIMS instruments are designed for clean air conditions. Operation in polluted air is more difficult due to OH recycling in the titration zone. It was noted that recycling effects are about 10-15% at 2 ppb NO_x and can reach 50% in polluted urban air. This artefact and its model-assisted correction in data evaluation, and the residual error were not further discussed at the workshop. It was pointed out that

the recycling effects could be reduced by shortening the titration zone for measurements in polluted air.

- CIMS has operational problems if gas tank purity is not high enough. It is recommended to use standards for gas purity.
- CIMS instruments detect sulfuric acid which is formed in the instrument by oxidation of SO_2 via reaction with OH and other oxidants. Ambient OH is discriminated against other oxidants by chemical modulation, using a reactant like propane or NO_2 for titration of OH. Since the nature of the other oxidants (e.g. Criegee radicals) is not fully understood, the choice of scavenger is important to ensure interference-free OH measurements.

3. General recommendations

- The need for absolute OH methods applicable in the field was identified. Although open multi-pass DOAS is an absolute standard and has been used for ground-based measurements in the past, it is not currently practical for deployment to the field. Investigation of the feasibility of cavity-based absorption-spectroscopy techniques is recommended.

HO_2 measurement techniques

1. Detection sensitivity and calibration

- Current atmospheric HO_2 measurement techniques (LIF, CIMS) are all indirect and rely on chemical conversion of HO_2 to OH. The majority of HO_2 instruments uses LIF for subsequent OH detection. There is one CIMS (Colorado) instrument which is capable of discriminating HO_2 from RO_2 radicals. Though PERCA instruments are sensitive to HO_2, they do not distinguish between HO_2 and RO_2 in atmospheric measurements.
- Detection limits and time resolution of current instruments are sufficient for HO_2 field measurements. This is even the case for LIF instruments that are being operated with reduced conversion efficiencies to suppress RO_2 interferences.
- 185nm photolysis of H_2O in air is a useful HO_2 radical source as accurate as for OH.

2. Measurement artefacts and interferences

- Since the last HO_x workshop in 2005, a significant interference in HO_2 measurements was identified, which results from fast conversion of certain large RO_2 and β-hydroxy RO_2 radicals to HO_2 by the reactant NO needed for HO_2 to OH conversion. The interference has been eliminated in most instruments by adjusting the chemical conversion conditions, reducing the interference below the limit-of-detection.
- The artifical OH signal from NO_3 reported for the OH LIF instrument (FZJ) was also observed in the HO_2 measurement mode, resulting in an interference equivalent to 10^7 HO_2 molecules cm^{-3} at 10 ppt of NO_3. Further studies are recommended to understand the underlying production mechanism.

3. General recommendations

- The need for direct, and if possible absolute HO_2 methods applicable in the field was identified. The only direct, absolute HO_2 method in the past was Matrix-Isolation Electron Spin Resonance (MI-ESR) formerly used by FZJ. It is no more available because of its cumbersome handling and poor time resolution. Investigation of alternative measurement techniques using, for example, HO_2-ion detection by CIMS, or cavity-based absorption-spectroscopy is recommended.

RO_2 measurement techniques

- All current RO_2 measurement techniques (LIF, CIMS, PERCA) rely on the chemical conversion of RO_2 to HO_2 and subsequent conversion of HO_2 to OH by reaction sequences involving NO as reactant. As a result, the techniques are sensitive to the sum of RO_2 and HO_2. Three instruments (FZJ-LIF, Leeds-LIF, CIMS-Colorado) are capable to distinguish between RO_2 and HO_2 by modulating the chemical conversion conditions.
- The RO_2 measurements are non-selective. Though the initial reaction with NO is similar for most RO_2, subsequent conversion chemistry may differ for certain RO_2 leading to different detection efficiencies which cannot be corrected for without knowledge of the RO_2 speciation.
- The sensitivity of HO_2 measurements to particular RO_2 species can be used to determine the concentration of the sum of large RO_2 and β-hydroxy RO_2 radicals. The method uses alternatingly small and large amounts of NO for chemical conversion, producing HO_2 data without and with interference, respectively. The difference is an estimate for the concentration of the particular RO_2 species.
- Detection limits and time resolution of the instruments are generally sufficient for field measurements.
- Photolysis of H_2O at 185nm and conversion of the resulting OH to RO_2 by addition of a corresponding VOC is recommended for calibration. The alternative RO_2 production by reaction of e.g., Cl atoms with VOCs is not recommended for unsaturated VOCs, since the resulting RO_2 will be chemically different from RO_2 formed by OH reactions in the atmosphere.
- Measurement artefacts can potentially arise from reactions such as thermal decomposition of peroxy nitrates. PERCA instruments, which determine HO_2+RO_2 from the measured NO-to-NO_2 conversion, have a significant water-vapour dependence that can be calibrated. In PERCA and RO_2 CIMS instruments halogens can be interferences, although this is only important in some locations.

General recommendations

- The need for more specificity in RO_2 measurements was underlined during the workshop. A specific measurement of CH_3O_2 would be very valuable as it comprises a

large fraction of RO_2 in many environments. Spectroscopic techniques for direct detection of CH_3O_2 (e.g., by LIF, CEAS) or direct RO_2 detection by CIMS techniques are encouraged.

1.6 Future directions

At the workshop it was decided to form a working group to be led by the organisers of the workshop (Dwayne Heard and Andreas Hofzumahaus) to guide the community through the next three years. The group would be expected to communicate regularly to make progress on three tasks.

- Task 1- Development of a community radical calibration unit
  (Lead: Bill Brune, PSU)
- Task 2- Development of protocols/procedures for testing of artefacts and instrument behaviour that can be quantitatively compared
  (Lead: Hartwig Harder, MPI)
- Task 3- Development of plans for future measurement intercomparisons
  (Lead: Andreas Hofzumahaus, FZJ)

The working group is open to the community, and each interested measurement group should have a representative. The group is not intended to take the place of continued collaboration or direct communication between specific groups.

The idea of the first task is to provide a common reference for OH, HO_2, and RO_2 calibration which can be circulated in the community. This would help each group to test their individual radical calibration source and harmonise data calibrations throughout the community. The source should be cross-calibrated to an absolute technique. For that purpose, the DOAS instrument at the atmosphere simulation chamber in Jülich would be available.

The second task is expected to help identifying and eliminating possible artefacts in existing radical measurement instruments, especially for OH. Test experiments (field, laboratory, chambers) so far indicate that products from VOC oxidation or NO_3 reactions may interfere with radical measurements under certain conditions, but the mechanisms are not clear. It is apparent that different instrumental designs exhibit different magnitudes of interferences, but a quantitative comparison is missing. The development of standardised test protocols should help to assess to what extent different instrument designs are affected by different interferences. Thereafter, side-by-side instrument tests may help to identify which instrumental parameters (e.g., flow speeds, wall materials, gas inlets etc.) have a critical influence in order to eliminate the interferences. Independent of these efforts, it is recommended for all LIF field measurements to apply chemical modulation with scavengers for atmospheric OH measurements until the origin of artefacts observed in some instruments has been identified and eliminated. For CIMS instruments, further

characterisation of the inlet chemistry is recommended especially for chemically complex and polluted environments.

Intercomparison studies (Task 3) are vital to establishing the credibility of radical measurement methods. While a number of successful HOx measurement comparisons were performed in the last two decades, it was proposed at the current workshop to perform new intercomparisons specifically under conditions where instruments observed artefacts (e.g., at high concentrations of biogenic VOCs). There was consensus that a new formal comparison should aim for a test of improved instruments after Tasks 1 and 2 will have been accomplished, and/or of novel techniques.

It was generally recommended to continue efforts to explore new technologies such as optical cavity-based absorption techniques and CIMS-based direct methods for radical measurements. Despite successful applications of current techniques in the last two decades, there is ongoing demand for highly sensitive, direct and absolute techniques which can be deployed in ground-based and airborne field campaigns, as well as in atmospheric simulation experiments.

1.7 References

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2. Session Reports

Prepared by Steven Brown, Jim Crawford, and Frank Keutsch (Rapporteurs)

Session 2: Potential radical measurement artefacts

Report prepared by Steven S. Brown

Session 2 contained 11 contributed talks representing many of the research groups conducting OH, HO_2 and RO_2 measurements. The majority of the talks (9) were from groups using the LIF technique, with 2 talks from CIMS groups. There were no talks in this session from the PERCA community. Additionally, there was one talk on alternative methods for two-photon OH LIF that is not summarized below since it is not as directly relevant to the theme of the session. As the title suggests, the focus of the discussion was on artefacts in OH, HO_2 and RO_2 measurements. For the LIF instruments, these artefacts can be broadly sorted into two categories, those affecting OH measurements and those affecting HO_2 measurements. These are outlined further below. For the CIMS instruments, there was little discussion of OH artefacts, but there was some discussion of the accuracy of the OH measurements. The CIMS instruments also have a separate category of artefact in that they have a background signal that they subtract, and this background signal may or may not have atmospheric significance depending on the environment in which it is measured.

1. Artefacts in LIF measurements of OH

The common theme from this set of talks is that many groups can generate an artefact OH signal from reactions of O_3 with biogenic hydrocarbons. This OH signal is not present in ambient air, but spectroscopic measurements show it to be real OH within the instrument. There is some evidence that this signal is related to stabilized Criegee intermediates (SCIs), which are species formed in O_3-alkene reactions. However, there was also some counter-evidence and some disagreement in results from different groups on the potential for SCIs to interfere with OH measurements. Regardless, most of the laboratory experiments suggest that the interference signal seen in O_3 + alkene laboratory tests should be insignificant at ambient ozone and BVOC levels. The amount of interference signal in field environments varies with the site and, potentially, with the configuration of the instrument itself, with some groups reporting large interference signals and others reporting small ones, all at different sites and times. There is currently no clear identification of the source of the interference, nor agreement about the extent to which it affects different instruments. Observations of OH interference signal from simple addition of NO_3 to one of the LIF instruments may provide an important clue to the mechanism for generation of artefacts in OH LIF instruments, but even for this experiment no mechanism for OH generation within the instrument has been identified.

Bill Brune discussed OH measurement artefacts in the Penn State LIF instrument. His group sees a difference between chemical titration of OH and wavelength modulation. They regard the chemical titration as the actual, ambient OH measurement, and the difference between chemical titration and wavelength modulation as the interference signal, which they refer to as OH_int. His group participated in a set of 32 experiments at the CalTech FIXCIT chamber study in 2013. The instrument sampled alternately from 2 separate bags, one with and one

without NO. FIXCIT experiments may find the cause of the interference signal once the data has all been analyzed. There are no final, quantitative conclusions yet, but preliminary observations are as follows.

- O_3+isoprene make OH_int, but not at sufficient levels to be important to the ambient measurements.
- IsopOOH makes very little OH_int.
- NO_x + "slow cooking" (meaning long exposure time at low light levels) make the largest OH_int signal, although there is no isoprene in these experiments.
- NO injection kills both the real OH signal and OH_int.
- OH_int behaves similarly to real OH, but not identically (e.g. of OH_int in the dark).
- OH_int showed correlation with HO_2+O_3 although observations were not definitive.

Anna Novelli discussed recent results from the MPI LIF instrument. Their group has been performing similar experiments to the Penn State group using an OH scavenger to measure ambient OH. In their case, the scavenger is propane rather than perfluoro propene. They add enough scavenger to remove 90% of the atmospheric OH to avoid titration of the background, or interference, OH. They conclude that their interference signal is not due to a bimolecular reaction, not due to a spectral interference (it is really OH), not dependent on laser power (so not laser generated) and not dependent on multipass vs single pass cell configuration (although they did not vary the beam diameter but went to a single pass that swept out the entire multipass detection volume in consecutive experiments). They used a combination of field and laboratory data to test the hypothesis that their interference signal is due to stabilized Criegee intermediates (SCIs). Field data from Finland, similar to the Mauldin *et al.*, Nature (2012), shows a correlation between the interference signal and the missing oxidant needed to convert SO_2 to H_2SO_4. The interference signal also scaled with temperature, suggestive of a source from monoterpenes. Finally, SO_2 also functions as a scavenger for OH_int, even though it should not be an efficient scavenger for real OH. These observations suggest a role for SCIs in creating the interference signal. However, the observations do not prove this result, and the discussion following the talk revealed considerable skepticism about the SCI hypothesis, especially from other LIF measurement groups. The suggestion was that even if SCIs create an OH interference signal, the characteristics of this interference may vary from instrument to instrument depending on the characteristics of the expansion, residence time, etc. Several questions were raised about the potential role of water vapor as well, since it may scavenge SCIs.

Phil Stevens presented recent tests of the Indiana University OH LIF instrument using a flow tube reactor with biogenic hydrocarbons and ozone. All experiments were done under dry conditions, and the instrument used both wavelength modulation and chemical titration to determine an interference signal. The O_3 reactions conclusively produced interference signals, with a large number of biogenic hydrocarbons, mainly monoterpenes, tested. The interference signal was affected by inlet length but was insensitive to laser power and reaction/residence time. There was evidence again that the source of the interference signal was SCIs, supported by tests with different types of scavengers. However, these experiments

were done at very large ozone and biogenic VOC levels, and there was no attempt to scale them to atmospheric conditions, where they are expected to be much smaller. These interference signals have not been observed in a field setting. There was some discussion about differences in PSU and Indiana measurements at the PROPHET site in different years. Bill Brune commented that there were cooler temps and potentially lower BVOC levels when the Indiana group was there.

Hendrik Fuchs discussed OH interference in the FZJ LIF instrument. Here there were two key experiments. 1) Ozone + alkene experiments, similar to the previous three presentations; and 2) Additions of NO_3 to the LIF inlet. Ozonolysis experiments were done in a flow tube and in the SAPHIR chamber. There was a clear signal observed using a propane scavenger relative to the wavelength modulation measurement. Their signal cannot be titrated by H_2O, CO or SO_2, arguing against SCI as the source of the signal and contrary to results from other groups. Importantly, they further conclude that there is no measureable interference at relevant atmospheric O_3 and alkene levels. The NO_3 experiments were also done in a flow tube and in the SAPHIR chamber. Addition of NO_3 produced a clear OH signal that could not be removed by an OH scavenger but that could be removed by an NO_3 scavenger. The mechanism for the OH signal is completely unknown, but it did not depend on laser power, cell pressure or H_2O. 10 pptv of NO_3 gave an OH signal of 10^5 molecules cm^{-3}. These experiments may give some clue to the interference signals observed in other instruments if its mechanism can be identified. For example, where does the hydrogen come from if NO_3 is to be the source of OH?

Zhaofeng Tan of PKU presented a preliminary analysis of OH interferences in their LIF instrument (essentially the same as the FZJ instrument) at recent field campaigns in China. Periodic tests were done with an OH scavenger vs. wavelength modulation. At Wangdu in the summer of 2014, ambient OH was on average 6×10^6 molecules cm^{-3}, and the "unaccounted OH" was (10±20)% of that signal, with the interference signal due to O_3 estimated at no more than 6% of the measured signal.

Rob Woodward Massey presented data from the University of Leeds instrument, showing results similar to those of the other groups for reactions of O_3 with alkenes. With part per million levels of ozone and 100's of ppbv of isoprene, they observed a difference between wavelength modulation and scavenging (using perfluoro propene). The signal was not laser generated. It would also be insignificant if extrapolated to the conditions typical of ambient biogenic and ozone levels. However, the Leeds group expects to do more extensive experiments since they were not satisfied with the performance of the scavenger in their initial experiments. For example, the O_3 + isoprene interference signal could be fully removed by propane scavenging, but that C_3F_6 was not fully effective.

2. Artefacts in LIF measurements of HO_2

Several groups discussed the potential for interferences in HO_2 instruments based on conversion of HO_2 to OH via reaction with NO, followed by LIF measurement of OH. The

recent paper by Fuchs *et al*., AMT (2011) quantified an interference in the FZJ LIF instrument arising from the unintended conversion of certain RO_2 species to HO_2 on the same time scale as the HO_2 to OH conversion. A paper reporting similar findings for the Leeds instruments was also published recently by Whalley et al., AMT 2013. RO_2 derived from small alkanes were shown to present a negligible or at most small interference, while RO_2 derived from larger alkanes, and especially β-hydroxy peroxy radicals derived from oxidation of alkenes, is a far more significant HO_2 interference. Talks in this session followed on the details of these papers and quantified the effect in specific instruments and for specific campaigns.

All groups (Indiana, FZJ, Leeds) show that the RO_2 interference in HO_2 measurement can be mitigated by reducing the NO addition, which reduces the RO_2 conversion faster than the HO_2 conversion, resulting in lower overall HO_2 sensitivity but much less interference from RO_2. In other words, the HO_2 derived from RO_2 must undergo two or more conversion steps and so has a stronger dependence on added NO than does ambient HO_2.

Sebastian Dusanter discussed the quantification of the HO_2 interference in the University of Indiana LIF instrument. They performed laboratory experiments to quantify the conversion efficiencies of $RO_2 \rightarrow HO_2$, then used these results to correct measured HO_2 from several recent campaigns. They determined:

- CABINEX 2009: 20-130% interference, dominated by isoprene and MVK + MACR RO_2.
- MCMA 2006: 20-35% interference derived from a wide variety of RO_2.
- CalNex 2010: 40% daytime, 100% nighttime interference, again from a variety of RO_2.

All of these results were derived from a model of the composition of the RO_2 pool, such that the model to measurement comparison now provides less information than it would have if the HO_2 measurements were not affected by interferences. In other words, the HO_2 measurement for these past campaigns is now not fully independent of the model that it is intended to test.

Rob Woodward Massey quantified the same set of interferences in the Leeds LIF instrument. They derived $\alpha(RO_2) < 0.1$ for all RO_2 in a ground based instrument that had a short residence time, but $\alpha(RO_2) = 0.46$ in an aircraft instrument with a longer expansion and residence time (Whalley et al., AMT, 2013). For correction of HO_2 from recent field campaigns, they derive:

- ClearFlo: interference of 3%.
- Borneo: interference of 23%.

Yugo Kanaya discussed evidence for an HO_2 interference from RO_2 during the 2005 HOxComp campaign. He made the key recommendation that a separate standard for HO_2 ought to be developed based on its direct measurement rather than on conversion to OH.

3. CIMS OH, HO_2 and RO_2 measurements

There were fewer presentations and much less discussion about the accuracy of OH measurements by CIMS. The major issue discussed is the background signal in the CIMS

instruments, which is the signal remaining after the OH is removed via chemical scavenging, in much the same way that some LIF groups are now measuring their zero. It is not clear if the background in the CIMS instruments is the same as that in the LIF instruments that use chemical titration, or if the two signals are even related.

Thomas Elste discussed the factors that lead to uncertainty in the calibration of the long term OH CIMS measurements at Hohenpeissenberg station. Overall uncertainty is ±20%, and is dominated by drift in the OH calibration source, which in turn is dominated by drift in the photon flux measurement that is done using a photocathode. Interferences by inlet chemistry (OH recycling) are in the order of 20% for conditions at Hohenpeissenberg (kOH < 6s-1). The instrument is not appropriate for higher OH reactivities. By contrast, the calibration uncertainty for ROx measurements is much larger, on the order of a factor of 2, and quite variable.

Harald Berresheim gave Franz Rohrer's presentation on the OH conversion and ionization scheme used in the CIMS instruments. Data from Mace Head, Ireland were discussed in terms of the background OH signal. As with the similar recent report from Finland (Mauldin, Nature (2012)), the measured H_2SO_4 signal was not consistent with the calculation of H_2SO_4 based on measured SO_2, OH and aerosol surface area (condensational sink for H_2SO_4). The result suggests another oxidant for SO_2, but at Mace Head, SCI is an unlikely candidate. There was some discussion about potential sources of SCI other than biogenic hydrocarbon ozonolysis, but no conclusive explanation for the result. The clear point of this talk in the context of this workshop is that the background signals in the CIMS instruments may not always be interpretable as something that is occurring in the atmosphere, such as an SCI. It leaves open the question as to the identity of this signal and its relationship, if any, to OH artefacts discussed for other instruments.

Session 3 - Theme 1:

Radical detection and calibration

Report prepared by Jim Crawford

The discussion focused on the adequacy of current methods for instrument calibration and associated detection limits. The resulting accuracy and precision in radical observations was discussed without consideration for the known artefact issues (which was the subject of a separate theme). While discussion centered primarily on ground-based instruments, it was noted that airborne uncertainties are essentially the same, although instruments must be calibrated over a wide range of pressures (not in flight, but in the lab).

1. OH limits of detection

The workshop participants agreed that the current capability for detection limits (1-5min, SNR=2) is (3-9)$\times 10^5$ cm^{-3} for LIF and (1-3)$\times 10^5$ cm^{-3} for CIMS. These detection limits are adequate for many environments; however, improvements to reach lower detection limits (~$5x10^4 cm^{-3}$) are needed to enable measurements at higher temporal resolution and environments with lower radical levels, e.g., forests. Drivers for higher temporal resolution include complex chemical environments, nonlinear chemistry, and aircraft observations with rapidly changing conditions. Some complex environments (e.g., highly polluted conditions) do not require improved detection limits. Current capabilities have also provided important answers and advanced tropospheric chemistry in other environments, such as the need for improved understanding of chemistry in pristine conditions with high BVOC emissions.

The barriers to improving detection limits differ depending on the measurement technique and even the specific instrument. For instance, background stability and gating speed (i.e., how quickly detectors can be switched back on) affect all LIF instruments. Laser power is also a consideration for LIF instruments, with the exception of FZJ. FZJ and JAMSTEC improvements are challenged by a solar scattering background signal. Though the solar background is accurately measured and subtracted, it contributes shot noise and increases the LOD.

For CIMS, improvement could be accomplished by shortening the titration period to limit interference by secondary chemistry. The ion chemistry, however, requires ~1s, placing a limit on how short the titration period can be. Another strategy would be to implement dual channels to measure signal and background simultaneously. While a stronger ion source would not be helpful, it was agreed that improved transmission of ions into the detector would improve sensitivity, but there was no immediate ideas on how that might be accomplished.

2. OH accuracy

Open-path DOAS is the gold standard with 7% accuracy, but although it has been used at ground sites and on a ship in the past, it is not currently practical for deployment to the field.

For other methods, current measurements are known to ~20-40% at 2-sigma. It was also noted that current errors in model calculations are not dramatically different. Model errors, however, have a dominant component from missing chemistry and kinetic uncertainties which are systematic rather than random. Thus, comparisons are still valuable to expose biases and chemical trends between measurements and model calculations for the purpose of identifying possible gaps in current chemical mechanisms.

While it was agreed that 10% accuracy is the goal for CIMS and LIF, it would require a huge advance in capability. It was also noted that precision is already at ~10% when OH is well above the limit of detection.

3. Improving OH calibrations

Independent calibration methods (i.e., H_2O photolysis and species decay) agree within 10-20%. There was a consensus that H_2O photolysis should be the primary method, but results from HO_xComp showed that this method is still not as good as it could be, potentially due to instabilities in the calibration setups. Improving H_2O photolysis calibration is most limited by the radiation measurements. It was noted that a pure OH source, i.e., without HO_2, from H_2O photolysis would be useful.

Discussion also focused on the need for a standard calibration for all (LIF and CIMS) instruments. Such a method would require consensus design, which Bill Brune volunteered to initiate. The design would have to consider the differences between the instruments. For instance, it was noted that the calibration unit would have to be separate from the detection cell given the range of nozzle designs for LIF instruments. While the angle of flow from the calibrator was discussed, it was not considered critical to the calibration method. For CIMS, it was noted that turbulence from the calibrator could pose a problem.

4. Limit of detection and calibration for HO_2 measurements

Ambient signals for HO2 are always well above the detection limit, even when reducing conversion to limit RO2 interference. The stability of the instrumental detection sensitivity, however, needs improvement.

<u>Areas of attention</u> include the following:

1. NO injection and mixing, which differ between instruments.
2. With the same calibration source, HO_2 has an uncertainty that is twice as large as OH. It is assumed that this is from instability in the instrument and is not due to the calibration source.
3. Quality of NO gas cylinders and potential impurities, e.g., NO_2 and HONO.
4. Small wall losses (1-2%) in the calibrator.
5. Temperature effects for field calibrations.

Measurement of second order decay of HO_2 could in principle be used as a calibration source for this species, but would not very likely improve the current accuracy of HO_2 calibrations.

5. Limit of detection and calibration for RO_2 measurement

Conversation focused on the need for more specificity in this measurement. For instance, information on speciation is needed since many species have similar NO reactivity, but subsequent chemistry differs widely. The first critical step is to separate HO_2 and RO_2 cleanly. This appears to be possible through NO variations to estimate the RO_2 contribution to the total signal. An absolute method for HO_2 would also work, but there are no current ideas on how it might be done.

Once the RO_2 signal is isolated, further interpretation is necessary since not all RO_2 are measured. It is necessary to know the VOC parent mixture and the resulting RO_2 products and detection sensitivities for each. A specific measurement of CH_3O_2 would be very valuable. It was speculated that the CIMS technique might be the fastest path to such a measurement, but how to calibrate it would be an issue.

Session 3 - Theme 2:

OH, HO_2 and RO_2 Measurement Artefacts

Report prepared by Frank Keutsch

The discussion focused on addressing concerns by experimentalists and modelers that HO_x measurements may be unreliable. Substantial progress has been made in the last years and the current state of knowledge, in particular with respect to OH artefacts, was discussed in great detail by all groups as presented below. The outcome of discussions has laid the foundation for planning intercomparison campaigns that require accompanying measurements, such as OH reactivity and ozone production potential, in order to provide meaningful context for the HO_x measurements. The need for absolute methods, such as DOAS for OH, was identified; however, currently no such methods exist for the environments in which they are most needed, e.g., in the field at low OH mixing ratios. Investigation of the feasibility of open-cavity CEAS for OH was recommended.

OH Artefacts

Substantial progress has been made in studying artefacts in OH measurements and a strategy for addressing remaining questions was formulated.

1. OH produced via laser photolysis

- All artefacts that produce OH radicals via photolysis from the UV laser are fully understood and subtracted if they contribute a signal above the LOD. OH radicals formed within the detection cell via photolysis of ozone followed by reaction with water are subtracted in the FZJ and Indiana University LIF instruments. In other instruments laser power is limited to suppress this effect, as is the case for the DOAS system used in the SAPHIR chamber.

- Photolysis of photolabile oxidation products with high OH yield, such as HPALDs, has not been investigated for the DOAS system, but is unlikely. This effect has also been ruled out as an explanation of the OH artefact observed in some instruments (see point 3) as no laser-power dependence has been observed.

2. Non-photolytic ozone artefacts

Non-photolytic ozone artefacts had been reported previously for some LIF instrumentation. These need not be taken into account, as their magnitudes are not significant in any currently used instrumentation. However, if detection limits are improved below 10^5 molecules cm^{-3}, this needs to be considered (for one instrument this artefact was quantified as 2×10^3 per ppbv of ozone). This artefact is distinct from that discussed under point 4).

3. Operation of CIMS in polluted air or with impure gas lines

The discussion noted that CIMS has operational problems if gas tank purity is not high enough. Additionally, current CIMS instruments are designed for clean conditions, making

their operation in polluted air more difficult. As a result of the discussion the *workshop recommends the use of standards for gas purity*. No recommendation was given regarding CIMS operation in polluted air. It was noted that recycling effects are ~ 10-15% at 2 ppb_v of NO_2 and can reach 50% in polluted urban air. Details of the interference in current instruments and model-assisted corrections were not discussed. It was pointed out that for operation in polluted air the recycling effects can be reduced by adjusting the reaction time/shortening the titration zone.

4. Chemical artefacts identified with OH scavengers

4.1. OH scavenging in CIMS

CIMS instrumentation implements scavenging of ambient OH, commonly with propane, to allow subtraction of a background signal that corresponds to compounds other than OH oxidizing SO_2 to sulfuric acid as well as other compounds resulting in a signal at the corresponding mass-to-charge ratio.
The corresponding oxidants leading to this background have not been identified, although Criegee radicals have been proposed to contribute. It was noted that scavenging of ambient OH with NO_2 would also remove ambient Criegee radicals and not just ambient OH. Thus, the choice of scavenger is important.

4.2. OH scavenging in LIF—ambient

Recently, two LIF groups—PSU and MPI—have implemented scrubbing ambient OH with hexafluoropropene or propane and found an artefact OH signal corresponding to OH being generated in their instruments via an unknown mechanism. The magnitude of the artefact OH varies with environment and instrument. Under some ambient conditions, the artefact can correspond to the majority of the OH signal measured without the scavenger. Both the nature and the significance of the background OH artefact for different LIF instruments were extensively discussed. *The discussion highlighted that it is desirable to both identify the identity/cause of the artefact and to modify all LIF instruments so that they can make OH measurements with negligible artefact signal.* It was further discussed that if the artefact is determined to measure a compound or class of compounds of atmospheric interest (e.g., Criegee), it may be worth developing a method to measure the "artefact" in the field. In response to the findings of the PSU and MPI instruments, artefact OH subtraction via use of scavengers is being implemented in all OH LIF instrumentation.
The Indiana and PKU LIF instruments have implemented scavenging of ambient OH in field measurements for test purposes but have found no clear evidence for an artefact. However, more work may be necessary. The Indiana field measurements took place at two locations, but it is unclear whether a considerable artefact signal should be expected under the conditions of the measurements. The PKU field measurements took place with an under-development scavenger injector that resulted in measurements statistically consistent with zero artefact, but with a relatively large uncertainty.

It was noted that the OH scavenger approach now being used by LIF groups could be considered similar to the OH scavenger technique used by CIMS groups to quantify their background, in that both subtract off a signal whose origin is not well-characterized. However, unlike for the LIF instrumental artefact, CIMS instruments have not been recommended to identify the source of their background OH with the same urgency. The CIMS background has only recently received more attention, primarily due to the proposed contribution of stabilized Criegee intermediates (SCI) in some environments. It is presently unclear whether the CIMS background is related to the artefact identified in LIF instruments using external OH scavengers. It may be helpful for the community if the background in both LIF and CIMs instruments can be identified and compared.

4.3. OH scavenging in LIF—laboratory

All LIF groups are conducting extensive laboratory tests to evaluate the magnitude of the artefact in their respective instruments and to identify the nature of the artefact. The main findings of the laboratory work completed so far are:

a. In the laboratory an OH artefact has been observed from alkene ozonolysis conditions by the PSU, MPI, FZJ and IU LIF instruments, but this can require extreme conditions, i.e., concentrations of precursors that exceed ambient ones by orders of magnitude. For the University of Leeds ground-based instrument, similar alkene ozonolysis experiments are underway, again with no artefact observed except under extreme conditions, but more work is necessary before a definitive conclusion can be reached. The University of Leeds airborne instrument, as well as the instruments of the University of Lille and JAMSTEC have not been tested.

b. Although the laboratory studies mentioned above are not quantitatively comparable due to differences in experimental setup and procedures, it is clear that magnitude of artefact depends on instrument and chemical conditions. Further work is needed to make experimental procedures comparable, in order to quantitatively evaluate the magnitude of the differences in artefact between different instrumentation.

c. All laboratory (and field) studies reporting the presence of an OH artefact have definitively shown that the OH artefact in question is not caused by photolysis from the UV laser.

d. Different chemical systems that can produce an OH artefact in the laboratory have been identified.

i. Introduction of ozone + alkene. Criegee radicals were suggested, and are consistent with the result of MPI experiments. However, experiments at FZJ are not consistent with Criegee radicals, or with the full set of MPI experiments, and suggest reaction products with a longer life-time than Criegee radicals. Thus, the contribution of Criegee radicals remains unclear.
ii. Introduction of NO_3. This interference has only been studied by the FZJ LIF group. The size of the interference scaled to ambient conditions appears negligible for the FZJ

instrument under typical surface level mixing ratios of NO_3. However, it may be important at high NO_3 concentrations (ca. 10^6 OH cm^{-3} at 100 ppt_v NO_3) and is expected to be important for (nighttime) aircraft measurements. In addition, there is the possibility that other instruments may be more sensitive to this interference, and the discrepancy of the MPI OH measurements during HOxComp in the dark may be suggestive of NO_3 interference. Non-FZJ LIF groups expressed the desire to study the effect of this interference on their instruments and the use of D_2O was suggested as helping in interpretation of such experiments.

iii. During FIXCIT a large suite of experiments in the Caltech chamber were performed with the PSU LIF instrument and an extensive suite of supporting measurements, and multiple chemical systems resulted in an artefact. The largest artefact signal was detected during an experiment with low-light conditions in the NO_x-containing bag. Correlations with HO_2 *and* O_3 were observed but neither correlation was sufficient to account for the entirety of the artefact signal. Further analysis of this rich dataset is planned.

4.4. OH scavenging in LIF—recommendations

The discussion resulted in the following recommendations by the workshop:

a. Periodic use of scavengers for ambient OH in all LIF field measurements is recommended.

b. All instruments should be tested for the artefact at multiple field sites.

Regarding these two recommendations two considerations were noted. First, current instrument calibration procedures are designed for instrument configurations without the use of the scrubbers. Thus, routine implementation of the scavengers requires new calibration designs, a considerable effort. Second, when the artefact can correspond to a large fraction of the total OH signal, as sometimes observed in the PSU and MPI instruments, the subtraction method lowers the precision of OH measurements.

c. Identification of the fundamental mechanism of the chemical artefact formation, e.g., a cluster mechanism, Criegee decomposition, is desirable.

A common protocol is needed for experiments and experimental setups to quantify the OH artefact under conditions where some instruments see it. These protocols should be applied to all instruments, including CIMS.

d. Instrument design aspects relating to artefact formation should be studied.

i. The nozzles of the MPI and the FZJ instruments should be tested on other instruments. This comparison is of interest because based on the studies done to date, the magnitude of the OH artefact in these two instruments is different, even if experiments are not yet quantitatively comparable. Additionally, a comparison of nozzle design may provide insight to the hypothesis that the artefact may be related

to low-temperature clusters transiently formed in the low-pressure expansion region directly after the nozzle.

ii. Side by side comparisons of different instruments should be implemented. A short-term visit of one group's instrument to another group's lab or field site may be a cost-effective way to carry this out. These tests do not correspond to a full intercomparison campaign (discussed in Theme 3), but rather to improve understanding of how instrumental differences may affect the formation/magnitude of the OH artefact under different conditions.

iii. Technical details of instruments should be compared in a standardized and complete way, including:
   - laser bandwidth, laser power density per pulse, repetition rate, single-pass versus multi-pass design
   - imaging volume, detector quantum efficiency
   - comparing characteristics of the flow after nozzle (temperature, residence time, etc.) are desirable, as these are expected to differ between instruments. However, the accuracy and cost of the flow modeling are concerns.

5. Final note

The broader atmospheric community is unaware of the design differences of the various LIF instruments, and perhaps not even sensitive to the fundamental differences between CIMS and LIF instruments. The opinion was expressed that only identifying and eliminating the artefact will address current concerns, even if the chemical modulation technique now implemented by LIF groups that see a large artefact is an adequate solution for obtaining a reliable OH measurement. Large differences in the magnitude of the artefact being corrected for, and a diversity of ways of addressing it, will raise skepticism, particularly without any fundamental understanding of the artefact's origin.

HO_2 Artefacts

The discussion highlighted that great advances have been made in understanding artefacts in HO_2 measurements since the last HO_x workshop in 2005. Specifically, it was discovered that certain large or unsaturated RO_2 radicals can rapidly convert to HO_2 in the presence of NO. Thus, these RO_2 can be measured together with HO_2. The opinion of the workshop is that detailed studies of this artefact have resulted in changes to HO_2 measurement procedures to make any $RO_2 \rightarrow HO_2$ conversion interference smaller than the accuracy of the instrument. Thus, the confidence in current HO_2 measurements is high.

In addition, previously obtained data may be corrected if RO_2 conversions are quantified under the previous experimental conditions. That is, the contribution of RO_2 can be subtracted from (HO_2 + RO_2) with knowledge of the sensitivity of the instrument to the relevant RO_2 interferences together with model-derived knowledge of RO_2 radical concentrations.

HOxCOMP HO_2 measurement comparisons showed an effect of ozone on HO_2 measurements in the MPI instrument, and linear variation between all instruments in chamber HO_2 measurements at low humidity alone, despite using calibration factors corrected for the water vapor mixing ratio. The workshop discussed these results with no clear answers. The consensus was that follow-up work is needed to address these discrepancies.

ESR instruments, as a direct measurement of HO_2 radicals in past campaigns, was discussed. This technique is cumbersome, involving cryogenic collection and sample transfer, and has not been used recently. However, its major value was in providing a direct HO_2 measurement rather than one based on conversion of HO_2 to OH, as is the standard in all current LIF, CIMS (and in principle, even PERCA) instruments. It is unlikely that this technique will be employed again in the near future. That said, there may be developing, alternative methods, such as I^- cluster CIMS, that are sensitive enough to HO_2 to provide a direct measurement. The community should stay abreast of such developments in order to provide best possible cross calibrations and intercomparisons with such developing methods.

RO_2 Artefacts

RO_2 measurements are not as developed as those of OH and HO_2. As a result instrumentation is not yet at a stage that allows reliable quantification of artefacts. However, limitations in current RO_2 instrument capabilities were clearly identified:

- Currently, many tertiary RO_2 cannot be observed, as the alkoxy radicals resulting from reaction with NO often decompose to form an organic peroxy radical and not HO_2.
- RO_2 concentrations are obtained only as a difference measurement between RO_2+HO_2 and HO_2. However, this disadvantage has been alleviated to some degree as mentioned in the previous section, HO_2 measurements without interference from RO_2 are now available.
- In PERCA and PER-CIMS instruments halogens can be interferences, although this is only important in some locations.
- Methods with a smaller chain length are less sensitive to uncertainties in the chain length. PERCA has a chain length of 100-200, PER-CIMS of 5-10 and RO_X-LIF of 1.

Overall the discussion of artefacts in RO_2 measurements were not as conclusive as those for OH and HO_2, and further method development, in particular for speciated RO_2, are highly desirable, as mentioned in theme 1.

As with the discussion of HO_2, there is potential for emerging methods to provide more direct measurements of RO_2, or potentially even speciated measurements of RO_2. The current HO_x measurement community should stay abreast of and participate in such developments.

Session 3 - Theme 3:

Planning of future HO_x-ROx intercomparisons

Report prepared by Steven S. Brown

1. Statement of the goal of any future HO_x intercomparison activity

If all groups agree that there are problems with instruments currently, then nothing would be achieved through a blind comparison. A blind comparison is intended to compare best instrument against best instrument, not to determine or understand artefacts that are already suspected. Furthermore, the groups do not currently all understand or agree about which experiments are the most important. While there is broad agreement that a formal intercomparison is valuable, it must be approached deliberately and carefully.

2. Discussion of principles for HO_x comparisons

- The scale of intercomparison activities will be important. Comparisons designed or occurring at [OH] = 10^7 molecules cm^{-3} will mask issues that occur at 10^6 molecules cm^{-3}, where much of the controversy and potentially important science occurs.
- Some groups that have already identified artefacts feel that it is their burden to identify the origin of these artefacts. However, there is consensus within the community that all groups will benefit from such an inquiry, even if individual instruments show greater or lesser sensitivities to specific, well understood artefacts.
- There is a clear need for direct, side by side comparisons where artefacts have been seen already. Planning of large or small activities should focus on measuring in or attempting to reproduce such environments.
- A common calibration unit for OH and HO_2, transferable to all instruments, should be developed prior to any large intercomparison activity.
- Every group in the LIF community should apply the scavenging technique on a regular basis.
- Any intercomparison activity must have sufficient supporting measurements to interpret all of the data and provide best understanding of any observed artefacts.
- Field campaigns are ongoing. Groups can more easily take advantage of already planned opportunities to undertake small intercomparisons by joining together with existing activities. The community should make every effort to incorporate multiple HO_x measurements into existing or planned campaigns.

3. Proposed approach to a set of intercomparisons

- An early set of informal comparisons or measurements to determine the specific origin of artefacts and the structure for laboratory experiments and protocols to best identify or test interferences and artefacts.

- A period of instrument modification and development with clear and timely communication and exchange of methods and parts between groups to make all instruments more robust and their artefacts better understood or suppressed.
- A formal, blind, best instrument to best instrument comparison at the end of this period.

4. Guidelines for intercomparison campaign structure

- The process should lead to a formal comparison activity within 3 years.
- There is further consensus that both a field and chamber comparison are valuable, but that the location of a field intercomparison, if attempted, must be carefully selected. The essential characteristics of such a field site have not yet been defined.
- Field comparisons in more than one environment would be valuable, but would also be expensive and difficult to organize.
- Further discussion is needed to define the role of models in a field or chamber comparison, as well as the level of detail and completeness of ancillary measurements needed to support a model component.
- The DOAS instrument or its equivalent should participate in future comparisons if it is feasible.

5. Final note:

In the United States, the NSF has encouraged, but failed to fund, a similar activity in the U.S. The outcome and report of this workshop may provide NSF with further motivation to fund such an activity, together with guidance about how it should be structured.

Session 3 - Theme 4:

Future Directions of Atmospheric HOx-ROx Chemistry Research

Report prepared by Jim Crawford

The meeting concluded with discussion of future directions to aid in making progress on continued improvement in HO_x measurements and addressing questions concerning the scavenging process and the associated background signal. Specific steps in community organization, priorities, and leadership responsibilities were formulated as detailed below.

1. It was decided to form a working group to be led by the organizers of the workshop (Dwayne Heard and Andreas Hofzumahaus) to guide the community through the next three years. The group would be expected to meet regularly to make progress on the three tasks described below.

- Task 1- Development of a common community calibration unit (Lead: Brune)
- Task 2- Development of protocols/procedures for testing (lab, chamber, and field) of artifacts and instrument behavior that can be quantitatively compared (Lead: Harder)
- Task 3- Development of plans for a future intercomparison (Lead: Hofzumahaus)

The working group is open to the community, and each measurement group should have a representative in the working group. The group is not intended to take the place of continued collaboration or direct communication between specific groups.

2. A wiki will be established by Frank Holland at FZJ to facilitate working group communication. It was also agreed that AGU, EGU, and other conferences should be leveraged to enable face-to-face meetings of the working group.

3. FZJ also extends an open invitation for visitors since ongoing experiments take place regularly at the SAPHIR chamber.

4. In addition to continued investigation of the instruments and their behavior, it was agreed that better kinetic information on Criegee intermediates and cluster chemistry would be useful to the group.

5. A discussion of environments where continued HO_x measurements would be of value resulted in the extensive list shown below. This list demonstrates ongoing knowledge gaps and uncertainties in atmospheric oxidation that further demonstrate the importance of improving HO_x measurements.

- Urban environments (e.g., HONO generation and impacts on HO_x)
- Forested environments (e.g., improving mechanistic understanding for complex degradation of BVOCs)
- Urban-rural interface (e.g., wide range of NO_x-VOC combinations)
- Upper troposphere (e.g., NO_x dependence, convective perturbations)

- Tropospheric ozone studies (e.g., HO_x is fundamental to understanding local ozone production, however, scale matters. When evaluating ozone on larger regional scales, emissions and meteorology become equally important.)
- Lower atmosphere/near-surface gradients (this is a difficult sampling problem that is still being explored. Zeppelin may be the most effective method.)

Discussion concluded by acknowledging that previous findings based on historical HO_x measurements will need to be put into context. It was agreed that there is insufficient data to make any specific statements as of yet regarding how measurement artifacts have affected previous observations. Such possibilities might arise from analysis of SOAS observations and upcoming ground-based measurements in the Amazon during the summer of 2015. The working group will provide an important forum for discussing what is learned from these datasets.

3. Instrumental Descriptions

Provided by the Participating Groups

Airborne and ground based measurement of peroxy radicals using chemical amplification and absorption spectroscopy

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The instruments developed at the Institute of Environmental Physics, University of Bremen (IUP-UB) measure the total sum of peroxy radicals, HO_2 and RO_2 (R: organic chain), hereafter called RO_2^* ($RO_2^* = HO_2 + \Sigma\ RO_2$), by using chemical conversion and amplification into NO_2, which is detected by chemiluminiscence (**DUALER** instrument: **DU**al channel **A**irborne peroxy radical chemica**L** amplifi**ER**) or by absorption spectroscopy (**PeRCEAS** instrument: **Pe**roxy **R**adical **C**hemical **E**nhancement and **A**bsorption **S**pectroscopy).

The chemical conversion and amplification takes place in the inlet whose shape and form varies according to the application (airborne or ground based). For airborne applications the inlet generally comprises a double reactor sampling from a common pre-reactor nozzle which is kept at a constant pressure below ambient (Fig.1). By addition of NO at adequate concentrations and alternatively CO and N_2, a modulation signal is generated from which the initial ambient RO_2^* concentration can be derived, provided that the chemical conversion has been adequately characterised under known and controlled laboratory conditions. In that context, the detection limit and accuracy are closely related to the relative humidity (RH) dependency of the chain length (CL) of the chemical conversion [9]. In addition, the chemical amplification has been found to be sensitive to ClOx (Cl+ClO+OClO) [8].

The CL calibration of the reactor is based on the production of radicals from the UV photolysis of water at 184.9 nm [10]. Briefly, a known water-air mixture is photolysed with a low pressure mercury lamp which intensity is attenuated by using a N_2O filter, i.e., varying the N_2O/N_2 ratio in the absorption zone to produce different radical amounts. CO or CH_4 is added to the gas mixture to convert the OH produced into HO_2 or CH_3O_2 radicals respectively [9].

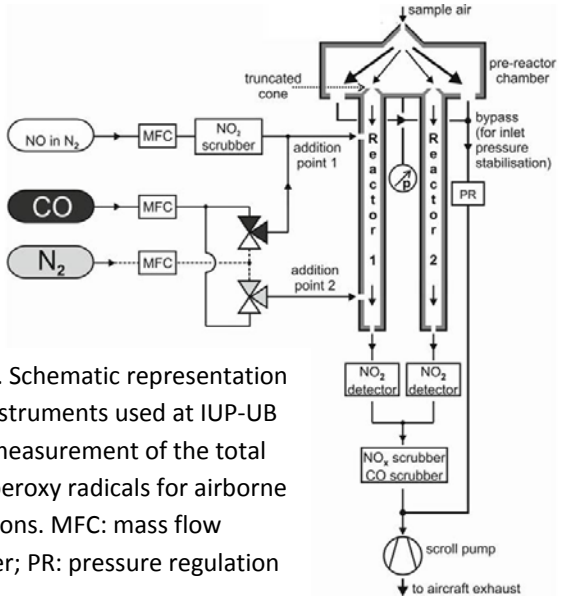

Figure 1. Schematic representation of the instruments used at IUP-UB for the measurement of the total sum of peroxy radicals for airborne applications. MFC: mass flow controller; PR: pressure regulation

Two independent detectors are connected to each reactor for the measurement of NO_2. The NO_2 detection by the **chemiluminiscence** of its reaction with luminol (3-aminophthalhydrazide: $C_8H_7N_3O_2$) is described in detail elsewhere ([1-4], [7]) and has been successfully applied in several ground based and airborne measurement campaigns. The detection limit of the NO_2 detector under laboratory conditions is calculated to be 0.13±0.05 ppb NO_2 which leads to 1-3 pptv for 20 s time resolution times at 200 mbar and RH up to 50% [7].

Concerning absorption spectroscopy, the NO_2 detectors in their current stage stem from research on optical feedback cavity-enhanced absorption spectroscopy (**OF-CEAS**) [6]. Briefly, a V-shaped

resonator consisting of three highly reflective mirrors is excited via a wavelength-scanning continuous-wave laser. Optical feedback from the resonator forces the laser to stabilize itself onto the resonator resonance, yielding broad transmission lines. Resonator optical losses can be calculated from these transmissions if their maxima are calibrated with a ring-down time measurement. OF-CEAS thus outputs absorption spectra with a wavelength resolution governed by the resonator free spectral range. The NO_2 detection limit for the detector using the OF-CEAS technique is 4ppbv approximately for 1s averages at a resonator pressure of 290hPa. As the OF-CEAS detection proved to be too susceptible to both temperature variation and vibration, the more robust cavity ring-down spectroscopy technique (**CRDS**) has been implemented for airborne applications. The use of a V-resonator allows the optical feedback to still provide high resonator transmission and bypasses the need for an optical isolator between laser and resonator.

The last configuration of the PeRCEAS instrument has been deployed on board the HALO (**H**igh **A**ltitude **LO**ng range) research aircraft January 2015 in the preparatory phase of the OMO (Oxidation Mechanisms Observations in the extratropical free troposphere) Asian campaign. Preliminary data show a ΔNO_2 in-flight S/N of ca. ± 0.5 ppbv (1-σ) for 60 s modulations measured at 200 hPa.

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CIMS OH System at the National University of Ireland Galway (NUIG)

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A new generation chemical ionization mass spectrometer (CIMS) with advanced ion guide optics and compact design was built at the National Center of Atmospheric Research (Boulder, USA) and put into operation at the NUIG Mace Head Atmospheric Research Station in 2010. Major objectives of the research programme include measurements of OH, H_2SO_4, and CH_3SO_3H concentrations in the coastal atmosphere. Similar prototype instruments have been described in detail previously [*Mauldin et al.,* 1998]. The overall system has been significantly compacted and miniaturized compared to previous instrument generations such as the one used by *Berresheim et al.* [2000]. Briefly, OH is measured as the resulting $H^{34}SO_4^-$ ion signal after addition of $^{34}SO_2$ which reacts with OH in the sample air followed by reaction of the oxidation product $H_2{}^{34}SO_4$ with NO_3^- ions. The NO_3^- ions are produced in a clean air sheath flow which passes by a radioactive alpha source (^{241}Am). Figures 1 and 2 present a schematic overview of the system and its operation principle, respectively. From the main air flow the central axis region is sampled at ca. 12 slpm through a ¾ inch diameter sample flow tube. Two pairs of oppositely arranged capillary injectors (at 5.2 cm distance from each other) protrude into the sample flow tube. Depending on the operational mode (OH signal measurement, OH background measurement, or H_2SO_4 and MSA(g) measurement) selected flows of $^{34}SO_2$, propane (C_3H_8), and N_2 (as make-up gas) are added through the injectors to the sample flow. The following reactions apply:

Conversion (titration) reactions:

$$OH + {}^{34}SO_2 + M \rightarrow HO{}^{34}SO_2$$

$$HO{}^{34}SO_2 + O_2 \rightarrow {}^{34}SO_3 + HO_2$$

$$^{34}SO_3 + H_2O \rightarrow H_2{}^{34}SO_4$$

Chemical Ionization reaction:

$$H_2{}^{34}SO_4 + NO_3^- \rightarrow H^{34}SO_4^- + HNO_3$$

The [OH] concentration is determined from the ratio of the signal counts for $H^{34}SO_4^-$ and NO_3^- ions as measured by the quadrupole mass spectrometer:

$$[OH] = \frac{(H^{34}SO_4^-}{(NO_3^-)k}$$

where k is the rate constant and t the reaction time for the chemical ionization reaction, and 1/kt represents a calibration factor C which is determined offline at least once every three months and before or after extensive field campaigns. Calibration is based on 185 nm photolysis of H_2O in ambient air generating equal concentrations of OH and HO_2 in the 10^8 cm^{-3} range and concurrent determination of [H_2O] using hygrometry. Further details have been described by *Berresheim et al.* [2000]. For the NUIG Mace Head CIMS instrument the overall detection limit for OH is estimated to be 1.3 x 10^5 cm^{-3} for 5 min signal integration with an accuracy of 40% (both 2σ). In OH measurement mode propane is added through the rear injectors to scavenge OH which may be recycled downflow via HO_2+NO reactions. For background signal measurement, propane addition is switched to the front injectors. Purity of all operational gases (propane, nitrogen, $^{34}SO_2$) is essential. More details are given in *Berresheim et al.* [2014].

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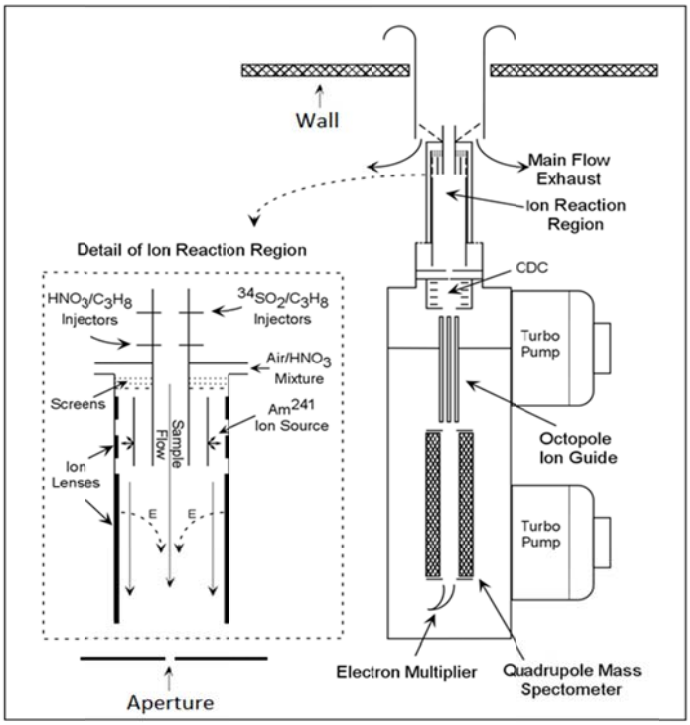

Figure 1

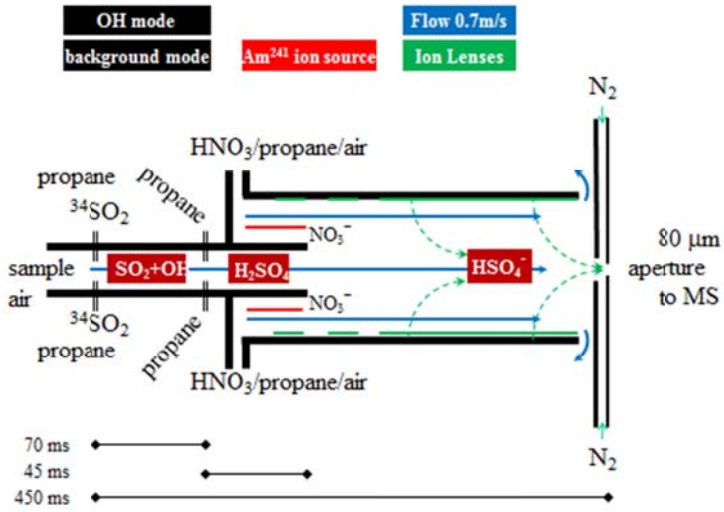

Figure 2

OH LIF using two-photon excitation: first steps towards an instrument for ambient OH measurements

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Preliminary experiments have been performed by the Keutsch group in collaboration with Forschungszentrum Jülich to start developing an instrument to measure ambient levels of OH using laser-induced fluorescence with two-photon excitation (TP-LIF). A two-photon technique for measuring ambient OH, where a fluorescing state is reached by sequentially exciting OH to a vibrationally excited state with an infrared laser and then to an electronically excited fluorescing state with an ultraviolet laser, has previously been discussed in the literature, with some groups achieving fluorescence signal in laboratory experiments[1,2]. However, due to past limitations in available laser power at the needed infrared wavelength, an instrument with the ability to measure ambient concentrations of OH using TP-LIF has never been developed. Harnessing new advances in laser technology, we aim to develop an instrument capable of detecting ambient levels of OH using TP-LIF. The advantages and drawbacks of such an instrument will not be fully understood until it is built, but it is predicted that such an instrument may not require gated detection due to the blue-shifted spectral separation of the fluorescence signal from any incident light, and may offer reduced background due to some combination of being extremely selective for OH fluorescence and minimizing the amount of solar background, depending on the particular selection of TP-LIF excitation scheme and instrumental design. Challenges with such an instrument include the requirement for high IR laser power and the experimental difficulties in operating two lasers that both must be well-aligned and tuned to the correct spectral line.

Preliminary calculations have been performed to predict the amount of signal achievable with TP-LIF compared to the Forschungzentrum Jülich OH LIF instruments now in use ('single-photon LIF', SP-LIF). Using the idler output from a Lockheed Martin Aculight Argos optical parametric oscillator (OPO) with CW output of 2-3 W at approximately 2900 nm, it is estimated that 5-10% of the population in a single rotational (and lambda-doubled) X(v"=0) quantum state can be excited to a X(v"=1) state. From this X(v"=1) state, a UV laser can be used to further excite this OH population to a fluorescing state—either within A(v'=0), with 346 nm excitation and 308 nm fluorescence, or A(v'=1), with 313 nm excitation and fluorescence detected at 282 nm (A(v'=1) → X(v"=0)) and/or 308 nm (vibrational relaxation followed by A(v'=0) → X(v"=0)). Accounting for an IR excitation efficiency of 10%, and using literature rate constants to compare the UV excitation, fluorescence, and detection efficiencies of TP-LIF and SP-LIF excitation schemes, it is predicted that a fluorescence signal equal in magnitude to 1.5% of the current SP-LIF can be obtained with TP-LIF, using 313 nm excitation and operating at 2 torr with a bath gas consisting of 2% H_2O.

Initial steps in developing a TP OH-LIF instrument along these lines have been pursued by coupling the continuous wave Argos IR OPO into an existing OH detection cell and pulsed UV laser system developed by the OH LIF group at Forschungszentrum Jülich. To minimize the dimensions of operational space that initially need to be searched, a first goal is to observe a 'depletion signal' from tuning the IR laser to a v"=1 ← v"=0 line while the UV laser is on resonance with a line at 308 nm that

produces SP-LIF signal, using OH generated from a calibration source. When the IR laser is on resonance with the v”=1 ← v”=0 transition, the depleted v”=0 population should lead to an observable dip in SP-LIF fluorescence signal, confirming the experimental set-up is correct and providing a first opportunity to quantify the extent to which the IR laser excites population to v”=1.

Future steps will include achieving TP-LIF fluorescence signal, determining optimal operational parameters for a TP-LIF instrument (line selection, pressure, gating) and investigating the utility of systems where the IR and UV lasers are either both pulsed or both CW, in order to make best use of available IR laser power.

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University of Lille FAGE (UL-FAGE):
Quantification of OH and HO_2 and OH reactivity measurements

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OH and HO_2 quantification

Instrument Description

The UL-FAGE instrument is based on the PennState design (2 white cells, a HO_2 cell downstream of an OH cell, P=1.5 Torr, Figure 1) Ambient air is pumped at 9.2 L/min through a 1 mm pinhole[1]. OH excitation (308.1541 nm/ $Q_1(3)$) is done by a 5 kHz laser (Spectra Physics Navigator+Sirah dye laser).

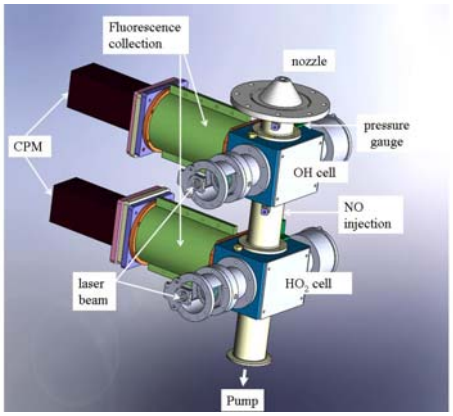

***Figure 1** : UL-FAGE instrument*

Measured species	OH and HO_2 simultaneously
time resolution	1 min
precision (1σ)	10%
LOD OH (2σ) -1 min	OH : 4.3-6.10^5 molecule.cm^{-3} HO_2 : 3.7-5.10^6 molecule.cm^{-3} ([NO]=1.4x10^{13} molecule.cm^{-3})
accuracy (2σ)	30%
sensitivity	OH : 60-100 cts s^{-1} $pptv^{-1}$ HO_2 :10-15 cts s^{-1} $pptv^{-1}$ ([NO]=1.4x10^{13} molecule.cm^{-3})
Calibration method	185nm photolysis of water + ozone actinometry
HO_2 Conversion efficiency	<20 % below [NO]=1.4x10^{13} molecule.cm^{-3}
NO concentration range	1.1x10^{12} – 3x10^{14} molecule.cm^{-3} (most often 1.4x10^{13})
Interferences	Ozone : Linear (0.6-3mW); (1.7±0.3) × 10^3 cm^{-3} [OH] /ppb of O_3 at 2mW , [H_2O]=0.3% RO_2 : estimated with MCM (i.e : isoprene α_{RO2}=0.07 with ε_{HO2}=0.15)
Type of application	Groundbased/ Indoor/ Combustion

Intercomparisons

Two intercomparison campaigns have been carried out with the UL-FAGE/quantification.The first one was on the SAPHIR chamber with the FZJ-LIF in April 2010 with conditions similar to the HOxComp campaign. The OH measurements are in good agreement (differences mainly explained by the calibration source). Differences in HO_2 are mainly due to different HO_2 conversion conditions used (ε=0.45 for Lille/0.9 for FZJ-LIF). The second one was done in July 2012 with the LATMOS-CIMS (now at ICARE). The correlation between both instruments is good ($[OH]_{CIMS}$=0.87.$[OH]_{Lille}$+5.74). No clear dependence of the ratio $[OH]_{CIMS}/[OH]_{Lille}$ with [NO], [O_3] or [H_2O] has been found. Plotting this ratio against $[OH]_{Lille}$, the ratio varies from 1.4 at low [OH] to 0.7 at high [OH].

Deployments

The UL-FAGE has been used for low temperature combustion studies of butane in a Jet Stirred Reactor [2]. Experimental profiles of OH and HO_2 are in good agreement with the model (PSR CHEMKIN/EXGAS). The instrument has also been deployed in indoor environments (a high school in the south of France [3] and recently in a low consumption building (data under analysis)). In the school, significant levels of OH and HO_2 have been measured. The radical chemistry has been found to be initiated by the nitrous acid photolysis. The UL-FAGE has also been deployed during the HCCT (October 2010) campaign (downstream site) but the lack of VOC measurements and the high conversion efficiency used for HO_2 makes the analysis and interpretation of the data difficult.

OH reactivity

Instrument Description

The UL-FAGE can be used to measure OH reactivity when coupled with a laser photolysis cell (pump-probe method). Two configurations have been tested and used depending on the purpose[4].

Configurations	ON-line (characteristics below) or 90°
Resolution time	30s-3 min (adjusted for S/N >4)
1σ accuracy	20 %
LOD (3 σ) -30 s-3 min	3.6-0.9 s^{-1}
k_{zero}	7-4.5 s^{-1} (function of zero air quality)
$k_{ambient\ max}$	150 s^{-1}

Intercomparisons

A brief intercomparison (July 2012) has been made with the CRM of the LSCE and the MPI. The same dynamic has been found but the reactivities measured with the UL-FAGE are the highest. Another reactivity intercomparison has been carried out for 2 weeks on the UL campus with the CRM of Mines Douai characterised by high NOx levels [5].

Deployments

The instrument in the 90° configuration has been used to study the potential formation of OH by the reaction of excited NO_2 (λ=565 nm) with water vapor[6] and showed that the OH formation is due to a multiphoton process. Recently, the instrument has been improved to allow the simultaneous measurement of HOx concentrations and the OH reactivity and has been used indoors (under analysis, campaign in March 2015).

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Pennsylvania State University ATHOS / GTHOS and OHR

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OH and HO_2

The instrument has two configurations: the airborne hydrogen oxides sensor (ATHOS) used on the NASA DC-8 (Figure 1) and the ground-based hydrogen oxides sensor (GTHOS) used on towers. GTHOS is now packaged in an air-conditioned box on top of the tower, with the pump on the ground and the operator in a trailer. The air sample is drawn through an orifice (~ 1.0 mm diameter) into a low-pressure chamber (p = 4-5 hPa for GTHOS; p = 3-12 hPa for ATHOS). OH is excited by the laser (~ 32 passes with a White Cell) and is detected at ~ 308 nm. The OH fluorescence is detected with a time-gated microchannel plate (MCP) detector. OH is detected in the first of two detection axes. In a second axis, HO_2 is chemically converted to OH by reaction with reagent NO; the resultant OH is detected by LIF. The laser wavelength is turned on and off resonance with an OH transition every 15 seconds. The OH fluorescence signal is the difference between on-resonance and off-resonance signals. Every two minutes, an OH reactant (perfluoropropylene) is added to remove OH and the removed signal is a second OH measurement. GTHOS is calibrated before, during, and after the study using the techniques described in Faloona *et al.* (1994) – 185 nm photolysis of water vapor, using calibration against an absolutely calibrated PMT, N_2O photolysis, and O_3 photolysis to get the absolute flux from the Hg lamp.

Table 1. *Detection Properties for OH, HO_2, and OH reactivity*	
Absolute uncertainty (2σ)	OH and HO_2: ±32% OH reactivity: ±15%
Limit-of-detection (1 minute)	OH: 0.01 pptv (~2.5×10^5 cm^{-3}) HO_2: 0.1 pptv OHR: 1 s^{-1}
Typical midday signals / backgrounds (cts s^{-1})	OH: 25 / 2 HO_2: 100 / 0.5 OHR: 200 / 2
Typical detection sensitivities (cts s^{-1} $pptv^{-1}$)	OH: 25 HO_2: 5
Data collection rate (Hz)	OH: 5 HO_2: 5 OHR: 5

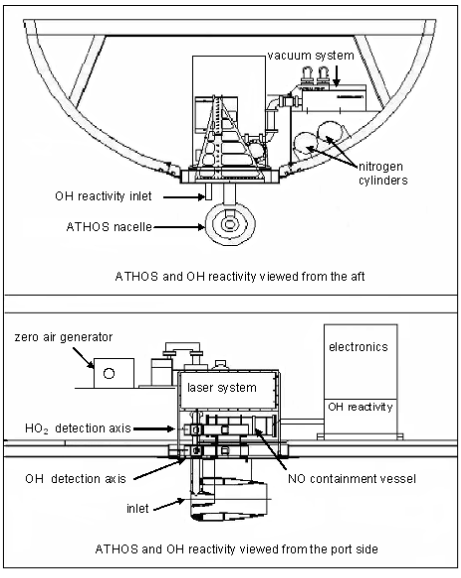

Figure 1. *ATHOS in the forward cargo bay of the NASA DC-8 aircraft. The operator sits in the cabin with a monitor, keyboard, and mouse.*

Naphthalene

Naphthalene is detected by LIF at an electronic transition at 308.002 nm, to the red side of the OH $Q_1(2)$ transition at 307.995 nm. The detection sensitivity is ~ 50 cts s^{-1} $ppbv^{-1}$, so that the limit of detection (2σ) is ~ 20 pptv in 1 minute. We have observed naphthalene in urban environments at night and behind aircraft at levels of tens to hundreds of pptv.

OH reactivity

The OH reactivity is the inverse of the OH lifetime. Comparing the measured OH reactivity to the OH reactivity calculated from the sum of the products of measured reactants and their OH reaction rate constants is a good test of missing OH reactants. OH reactivity is measured with an instrument called the OH Reactivity instrument (OHR).

OH is generated at mixing ratios of a few 10's of pptv by a 185 nm Hg lamp that dissociates water vapor in a nitrogen flow inside a 1 cm diameter movable tube. This moveable tube is in the center of a metal flow tube (7.5 cm diameter, ~25 cm long) through which ambient air is drawn by a fan. The OH is injected through radially drilled holes at the end of the movable tube, mixed turbulently into the air flow, and detected by a low pressure LIF detector at the end of the flow tube.

OH reacts with trace constituents in the air flow and, as the movable tube moves away from the detector, the observed OH signal decreases. A decay is measured every 15 seconds while the laser is on the OH absorption line, giving a measurement period of 30 seconds. The OH reactivity (s^{-1}) is determined from the slope of the logarithm of the OH signal as a function of distance between OH injector and detector divided by the velocity of the air. The absolute uncertainty is ± 15 %; the wall loss is 4.0 ± 1 s^{-1}.

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ATHOS /GTHOS

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OHR:

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Measurements of HO_x and Other Species with the University of Colorado CIMS

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The University of Colorado four-channel chemical ionization mass spectrometer (CIMS) system can be staged on ground-based and aircraft platforms. One channel or instrument is used to measure OH, H_2SO_4, and the sum of sCIs, and another channel or instrument used to measure HO_2 and HO_2+RO_2. The measurement of H_2SO_4 is based on the chemical ionization via reaction with negatively-charged nitrate ions.

$$H_2SO_4 + NO_3^- \rightarrow HSO_4^- + HNO_3 \qquad \text{(R1)}$$

In reality, the reagent ions are a mixture of bare ions and those clustered with one or two nitric acid molecules and one or more water vapor molecules. This is not a problem since the kinetics for all are very similar. The nitrate ions are produced in a flow annular to the sample flow by exposing a part-per-million (ppmv) mixture of HNO_3 in air to a radioactive Americium-241 source. The ions are directed into the sample flow using electrostatic lenses. After reaction, the ions are directed through a dry nitrogen buffer into a pinhole entrance into the mass spectrometer chamber. Clusters are dissociated by gentle acceleration with electrostatic lenses at a moderate pressure (about 100 mtorr). The ions are directed with an octopole ion guide through a 1 mtorr pressure region into the quadrupole filter region at 10^{-5} torr where the ions are separated by their mass-to-charge (m/z) ratios. The mass separated ions are counted by a channel electron multiplier configured in the pulse counting mode.

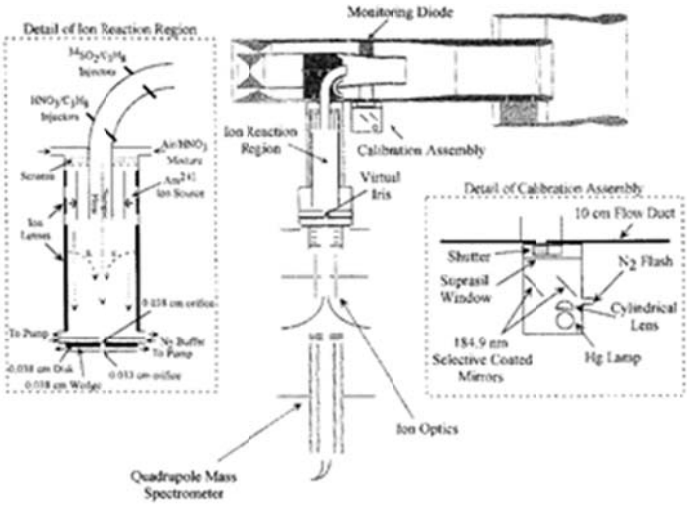

Figure 1. *Components of OH measurement channel.*

Hydroxyl radicals are measured (e.g. Mauldin et al., 2001) using an inlet that slows the ambient flow (about 150 m/s) to about 10 m/s. The flow is sampled and mixed with a small amount of sulfur-34 labeled SO_2. The reaction of hydroxyl radicals with the labeled SO_2 produces labeled H_2SO_4. The labeled sulfuric acid product is measured the same as ambient sulfuric acid, but at an m/z value of 99 rather than 97. The OH background is measured by injection of propane to the front reagent injectors (it is present

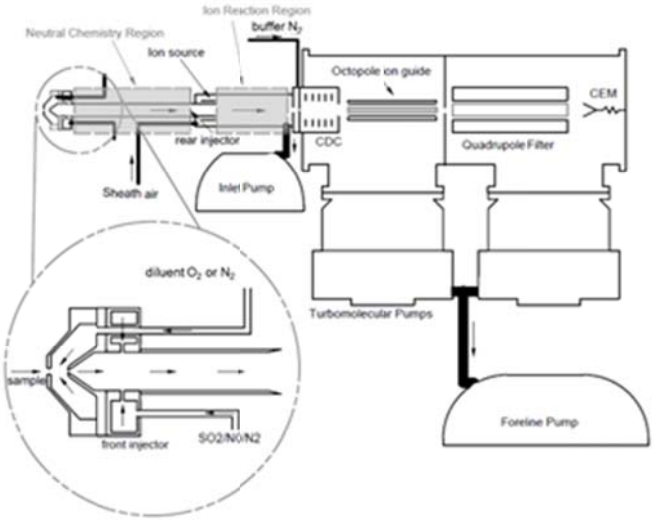

Figure 2. *Components of peroxy radical measurement channel.*

continually at the rear reagent injectors), which serves to remove ambient OH, but allows non-propane reacting species to survive. An electronic background is also measured by reversing the quadrupole filter polarity as a system check. It is typically less than 1 count per second (cps). Since sCIs do not apparently react at an appreciable rate with propane, they appear in the OH background. For those situations when the OH background has no artifacts (e.g. the artifact found when NO is very high and OH is produced from HO_2 plus NO within the instrument inlet), it may be interpreted as the sum of the concentrations of the sCIs. The OH, H_2SO_4, sCI sampling system is shown in Figure 1. Calibration is accomplished in flight by the 184.9 nm photolysis of water vapor.

Peroxy radicals are measured similarly (e.g. Hornbrook et al., 2011). The inlet samples the ambient flow in a perpendicular direction through a pinhole into a 150 torr region. The ambient air is diluted with either nitrogen or oxygen which facilitates measurement of either HO_2 or HO_2 plus RO_2. Then the reagent gases NO and SO_2 (unlabeled) are added which leads to production of unlabeled sulfuric acid with some amplification. The background is measured by changing the addition of SO_2 to the rear injector, in which case ambient peroxy radicals are converted to nitrous acid (HONO). The sulfuric acid product of the chemistry is ionized and counted as with the OH channel. Calibration is accomplished on the ground also using the 184.9 nm photolysis of water vapor. The system schematic diagram is shown in Figure 2.

The parameters of these measurements (averaging times, detection limits, precision, etc.) are summarized in Table 1.

Parameter	**OH**	**H_2SO_4**	**sCIs**	**HO_2**	**HO_2+RO_2**
Sample Frequency	30 s	15 s	30 s	60 s	60 s
Averaging Period	8 s	5 s	8 s	8 s	8 s
Precision	1 x 10^5 cm^{-3}	1 x 10^5 cm^{-3}	1 x 10^5 cm^{-3}	1 pptv	1 pptv
Accuracy (2σ)	40%	40%	50%	35%	35%
Detection Limit	3 x 10^5 cm^{-3}	3 x 10^5 cm^{-3}	3 x 10^5 cm^{-3}	2 pptv	2 pptv

Table 1. *Parameters of measurements.*

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High resolution long-path OH-Differential Optical Absorption Spectroscopy (OH-DOAS)

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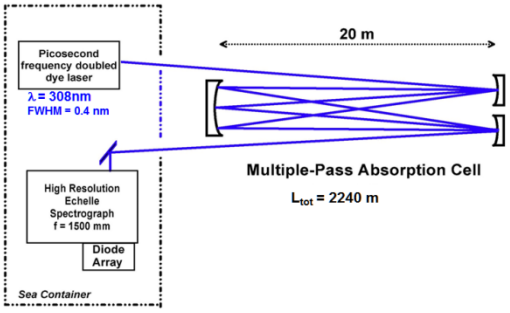
Instrumental setup

The DOAS instrument consists of a UV-laser light source, a folded detection light path, a high resolution spectrograph, and an optical multi channel detector to record the spectra. The light source is a mode-locked (repetition rate 82 MHz) frequency doubled synchronously pumped picosecond dye laser emitting a broad spectral profile with a full width at half maximum of 0.41 nm at 308 nm. The absorption light path of 2240m is realized by folding the light 112 times into an open optical multiple reflection cell having a mirror separation of 20 m. Absorption spectra are recorded with the help of a high resolution ($\Delta\lambda$=2.7 pm, $\lambda/\Delta\lambda$=114 000) Echelle grating spectrograph coupled to a linear photodiode array detector. This technique allows simultaneous recording of a spectral interval of 0.22 nm which covers 6 of the strongest atmospheric OH absorption lines [Dorn et al., 1995a]. DOAS is a specific, direct, absolute, and **calibration-free** OH detection method. It makes use of Lambert-Beer's law to calculate the concentration C from the measured optical density OD:



$$OD(\lambda) = \ln(I_0(\lambda)/I(\lambda)) = \sigma(\lambda)\, L\, C_{OH}$$

Since the light path length L is known accurately to 0.1%, the accuracy of the OH measurement only depends on the uncertainty of $\sigma(\lambda)$. The OH spectrum and its wavelength dependent absolute absorption cross section $\sigma(\lambda)$ can be calculated with an error of less than 7 % using accurately known fundamental spectroscopic constants of the OH molecule (e.g. natural radiative lifetime, Einstein coefficients, and spectral pressure broadening coefficients), the spectrograph transmission function of the instrument, atmospheric pressure, and temperature. For atmospheric measurements $\sigma(\lambda)$ can be regarded as an instrument specific constant since it changes only little (less than 2 %) with typical atmospheric pressure and temperature changes during a field campaign (Dorn et al., 1995b, Hausmann et al., 1997).

Detectable trace gases and evaluation of absorption spectra

Besides OH radicals, sulphur dioxide, formaldehyde, carbon disulfide, naphthalene and a so far unidentified absorber *X* possess spectrally well resolved absorption lines in the wavelength range observed and accordingly can be detected by high-resolution DOAS. Ozone and NO_2, fortunately, show no rotational fine structure in the UV and only contribute to the broadband background absorption. The individual concentrations of trace gases contributing to an atmospheric absorption spectrum are calculated from a least-squares fit of reference spectra.

The reference spectra of SO_2, HCHO, CS_2, and $C_{10}H_8$ are measured placing sealed quartz cells (L=10 cm) into the laser beam filled with the pure gases diluted with synthetic air at atmospheric pressure. The individual absorption cross sections are obtained from calibration measurements (Neuroth et al., 1991, Brandenburger et al., 1998). *X* was first identified during the POPCORN field

study in 1994 averaging residuals resulting from subtraction of OH and all other known trace gas spectra from the atmospheric signal (Brandenburger et al., 1998).

Integration time, detection limit, and precision

The detection limit is fundamentally determined by the shot noise of the detector signal. We are using the multi-channel scanning technique MCST which allows to discriminate between the weak trace gas absorption signals and the detector specific signatures (Brauers et al., 1995, Hausmann et al., 1997). Together with a refined technique to fit the curvature of the spectral background, the shot noise limit can almost be attained (Fuchs et al., 2012). In field campaigns **100 spectra - each with 1 s integration time – are averaged**. Typically one OH data point is measured **every 187 s**.The OH detection limit of the DOAS instrument can be determined from the frequency distribution of measurements in zero air in the Juelich simulation chamber SAPHIR measurements (see Schlosser et al., 2007). The recently observed width of the frequency distribution of **0.8x10^6 OH/cm^3** is an appropriate measure for the **1-sigma detection limit**.In order to calculate individual errors for each OH data point (the OH precision) we are using a combination of two Monte-Carlo methods in order to quantify the influence of the residual spectral background on the least-squares (LSQ) fitting process (Hausmann et al., 1999). Usually the mean of the measurement errors corresponds to the 1-sigma width of the frequency distribution of zero-air measurements (see Schlosser et al., 2007).

Potential interferences

Field and chamber measurements have demonstrated that high mixing ratios of SO_2 (15 ppb) and HCHO (>35 ppb) do not have marked influence on the OH evaluation as long as the reference spectra are accurately measured. In addition our field studies gave no hint for the existence of further atmospheric trace gases having rotational fine structures in the wavelength range monitored.

A potential interference results from OH self-production due to ozone photolysis in the laser beam. The self-production rate depends on O_3, water vapour, UV-laser power and residence time of OH within radiation field. We have never observed self-production in ambient air measurements, because atmospheric turbulence and advection 'flush' the irradiated volume sufficiently fast, preventing a build up of [OH] above the detection limit. In experiments in the SAPHIR chamber with elevated ozone mixing ratios (>100 ppbv) and in stagnant air, OH self-production could - in principle - be forced. However, SAPHIR experiments are usually conducted in well mixed air (two fans are installed inside SAPHIR) and with low laser power (<1.5 mW) and consequently OH self-production is kept well below the detection limit.

Summary of field deployments:

The OH-DOAS instrument was deployed in the past during the POPCORN field campaign in 1994 (Dorn et al., 1996, Brandenburger et al., 1998) and during the ship-based campaign ALBATROSS in the Atlantic Ocean in 1996 (Brauers et al., 2001). Since then the instrument is installed as one of the key radical detection instruments in the Juelich Atmosphere Simulation Chamber *SAPHIR* where regular OH measurements started in 2002.

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Ground-based Measurements of OH, kOH, RO_x and H_2SO_4 with CIMS

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A ground based Chemical Ionization Mass Spectrometer (CIMS) is operated at the Meteorological Observatory Hohenpeissenberg (47°48'N, 11°01'E) by the Deutscher Wetterdienst (DWD) in Germany measuring since 1998 OH and H_2SO_4 [1], since 2009 kOH [4] and since 2012 RO_x [5] concentrations in ambient air. All compounds are measured in alternating cycles of 2.5 min each with a signal resolution of 30 seconds. Our CIMS system is based on a prototype system previously developed by F. Eisele and coworkers at NCAR [2]. Measurements spanning over more than 15 year period (1999-2015) will be evaluated soon. Based on this extensive data set including progressive improvements the current detection limit, accuracy, and precision of the Hohenpeissenberg CIMS system for OH: 1.4×10^5 cm^{-3} (2-sigma), 0.7×10^5 cm^{-3} + 0.2×[OH] (1-sigma), 0.7×10^5 cm^{-3} + 0.13× [OH] (1-sigma), for RO_x about factor 2 worse, for H_2SO_4: 3×10^4 cm-3 (2-sigma), 0.39×[H_2SO_4] (1-sigma), 0.3×[H_2SO_4] (1-sigma) and for kOH 2 s^{-1}, 2 s^{-1}, 2 s^{-1} respectively; all values refer to 5 min signal integration. A schematic drawing of the CIMS system and the principle reactions used to measure OH, kOH, ROx and H_2SO_4 are depicted in Figure 1.

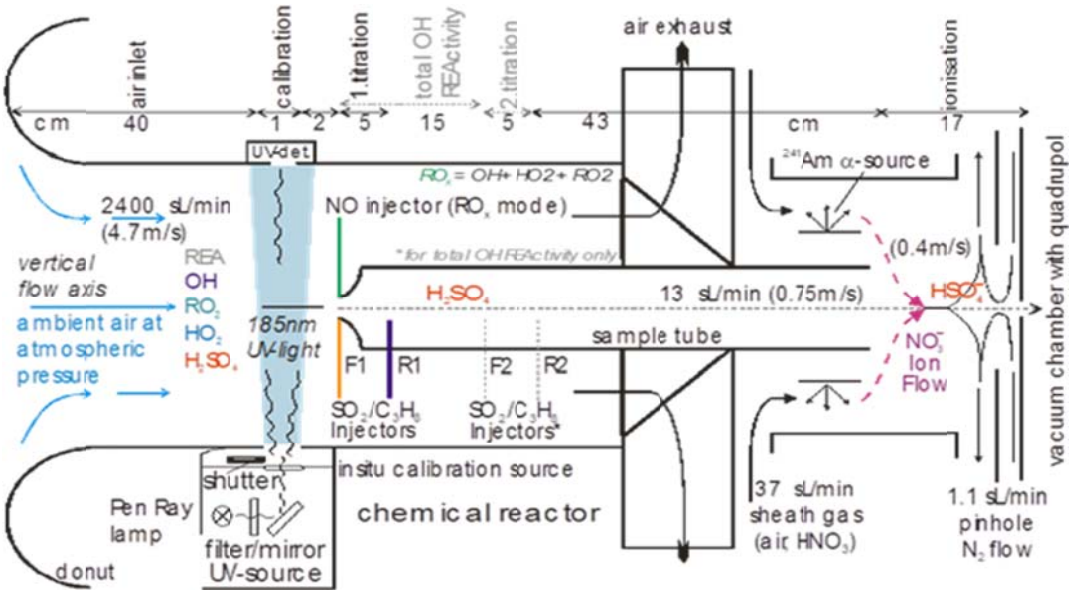

Figure 1. *CIMS system for measuring ambient OH, kOH, RO_x and H_2SO_4 operated at the Meteorological Observatory Hohenpeissenberg, Germany, and principle reaction schemes.*

The system consists of four main parts: 1. inlet and calibration section, 2. RO_x conversion and two OH titration zones, 3. ion reaction region and 4. vacuum quadrupole mass spectrometric detection region. Ambient air is continuously sampled from a 2.4 m^3 min^{-1} smoothed inlet flow at about 12 l min^{-1} through a 18 mm diameter tube into the ion reaction region of the system and vented through an exhaust line at approximately 100 m distance from the intake. In the ionization region neutral sample molecules are ionized at atmospheric pressure by charge transfer reactions with NO_3^- core ions which are produced in a separate sheath gas by a radioactive ^{241}Am source. The NO_3^- ions are concentrically focussed by electrical fields to the centre of the sample flow to ensure optimal ionization conditions. H_2SO_4 molecules directly react with NO_3^- as shown in the bottom equation of Figure 1. To measure OH, the sample flow is mixed with SO_2 through a needle injector in front of the

10mm diameter nozzle prior to reaching the ionization region which titrates all the OH in the sample flow producing H_2SO_4 molecules. These are subsequently ionized (see Figure 1) yielding HSO_4^- product ions. A fraction of the remaining NO_3^- ions and the newly formed product ions is forced by electrical fields through a 200 µm diameter synthetic air flushed aperture into the differentially pumped vacuum region where they are first stripped of neutral ligand molecules (in the collision dissociation chamber), then mass-filtered by a quadrupole (at approximately 3×10^{-5} hPa pressure), and finally detected by an electron multiplier and PC. To measure RO_x, the sample flow is mixed with NO through a needle injector yielding 400ppb NO, converting RO_2 to HO_2 and HO_2 to OH within several ms and reacting with SO_2 to form H_2SO_4. The conversion ratio for HO_2 to OH for this time period is typically 85% and for RO_2 75%, both under synthetic condition. This, however, may vary in atmospheric conditions by factor 2 for unknown reasons. To measure kOH, the decay of OH is determined from a second titration zone 15 cm downstream the sample tube. According to the reaction scheme, kOH can be calculated from the calibration minus ambient OH in the two titration zones and the wall losses determined by adding zero air. The OH concentration is equivalent to the H_2SO_4 produced, i.e. to the product between the calibration factor and the ratio of the HSO_4^-/ NO_3^- signals. Calibration is performed every 20 minutes using a calibration unit which irradiates a region in front of the sample tube by a UV-profile at 185 nm. The UV light photolyses ambient air water vapour yielding concentrations of HO_2 and OH in the 10^7 to 10^8 cm^{-3} range which are calculated based on the known absorption cross section and highly accurate measurements of $[H_2O]$ using a chilled mirror dew point hygrometer. UV flux is mapped by PTB calibrated photocathodes (R5764/6800U) monthly and continuously monitored by a cathode inside the inlet region opposite to the Pen Ray Lamp. Background measurements are made by adding propane scavenger to the front injector in such amount that 97% of OH is titrated by propane instead of SO_2. Potential measurement interferences can be inlet chemistry, e.g. recycling of OH from HO_2 in the presence of high NO levels, crosswind turbulence, and impurities in the propane. Under the rural conditions at Hohenpeissenberg, corrections for inlet chemistry are on the order of 20%, crosswind turbulence effects are significant only at wind speeds exceeding 5 m/s, and propane impurities are checked upon delivery of the gas cylinders. The Hohenpeissenberg CIMS system has been used continuously and during various campaigns for measuring OH mostly at the Observatory such that we now have recorded the first long-term data set of OH/H_2SO_4 spanning over more than 15 years and including all seasons of the year. A major result of these measurements is that more than 85 % of the variability in OH could be explained by the variability in $j(O^1D)$, i.e. solar UV, over the entire period, despite the many chemical reactions and meteorological parameters influencing OH [3]. The slope of this very simple linear relation is characteristic for the respective chemical regime. Similar strong OH/$j(O^1D)$ relations were found in other regions (marine, rural, urban) but with significantly different slopes.

$$RO_2 + NO \rightarrow RO + NO_2 \qquad HO + SO_2 \rightarrow HSO_3$$
$$RO + O_2 \rightarrow R'O + HO_2 \qquad HSO_3 + O_2 \rightarrow SO_3 + HO_2$$
$$HO_2 + NO \rightarrow HO + NO_2 \qquad SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O$$
$$H_2SO_4 + NO_3^- \rightarrow HSO_4^- + HNO_3$$

$$[RO_X] \Rightarrow [HO_2] \Rightarrow [OH] \Rightarrow [H_2SO_4] = \frac{[HSO_4^-]}{kt \bullet [NO_3^-]}$$

$$kOH = \frac{1}{dt} \times \ln\left(\frac{(OH_{UV1} - OH_1)}{(OH_{UV2} - OH_2)}\right) + k_0$$

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HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy (HORUS) with Inlet Pre-Injector (IPI)

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The HORUS instrument at the MPI for Chemistry in Mainz (Figure 1) utilizes the laser-induced fluorescence of OH molecules based on the fluorescence assay by gas expansion technique (LIF-FAGE). Air is drawn into the instrument at approximately 7 L min^{-1} through a critical orifice (1 mm diameter) and OH is selectively excited by pulsed UV light at around 308 nm on resonance with the $Q_1(2)$ transition line ($A^2\Sigma^+ - X^2\Pi$, v' = 0 ← v'' = 0). The laser pulse is directed into a multipass White Cell crossing the detection volume 32 times. The fluorescence signal from the excited OH radicals is detected at low pressure (~300-500 Pa) using time-gated micro-channel plate detectors (MCP). The UV light for excitation of the OH radicals is generated by a Nd:YAG pumped, pulsed, tunable dye laser system operating at a pulse repetition frequency of 3 kHz. The instrument has two consecutive detection cells: in the first cell OH radicals are detected, and in the second cell HO_2 radicals are measured following the conversion of HO_2 to OH by the addition of NO. Calibration of the instrument is achieved via production of a known amount of OH and HO_2 from the photolysis of water vapor at 185 nm using a mercury lamp. The fluorescence background signal of the instrument is measured by tuning the excitation laser on and off resonance with the OH transition line at 308 nm. Usually the HORUS instrument is equipped with a 14 cm inlet resulting in a residence time of the air between the pinhole and the detection cell of 2.5 ms. Laser power and pressure in the OH cell were ~4 mW and 310 Pa during HUMPPA (Finland, 2010) and DOMINO HO_x (Spain, 2010), ~9 mW and 380 Pa during HOPE2012 (Germany, 2012), and ~6 mW and 450 Pa during CYPHEX (Cyprus, 2014).

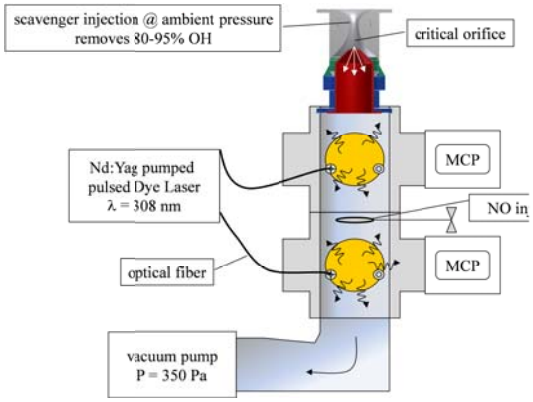

Figure 1: *HORUS instrument with IPI*

In some environments, the measurement of atmospheric OH by LIF-FAGE may be influenced by artificial OH generated within the instrument, and therefore a chemical method to remove this interference was proposed by Mao et al. (*ACP,* **12**, 8009-8020, 2012). To this end, we have developed and deployed an inlet pre-injector (IPI, Figure 2) to determine the chemical zero level in the instrument via scavenging of the ambient OH radical. The injection of the scavenger is achieved via eight 0.5 mm holes (1) positioned 5 cm above the pinhole of the inlet (2). The scavenger is carried through IPI by 4-10 L min^{-1} of synthetic air. A roots blower is used to pull 150-280 L min^{-1} through IPI (4) resulting in a residence time in IPI after the injection of the scavenger of 2.5-4

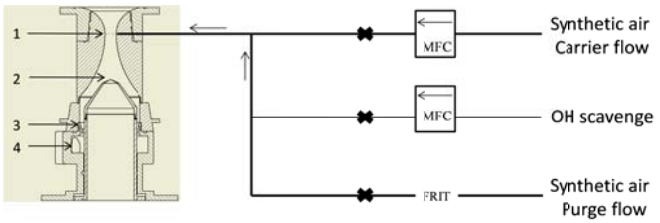

Figure 2*: Inlet pre-injector (IPI)*

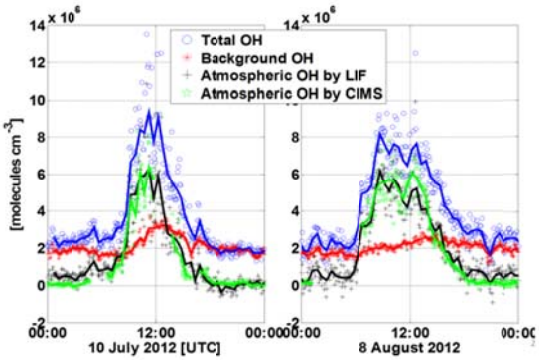

***Figure 3**: OH radical measurements by HORUS with IPI and CIMS on 2 days during HOPE2012*

ms. The scavenger concentration is such to scavenge 80-95% of the atmospheric OH. The current IPI cycle results in a minimum time resolution for the measurement of atmospheric OH of one data point every 4 min consisting of cycles of 2 min injection of OH scavenger and 2 min with no injection of OH scavenger. A thorough and careful characterization of the operational parameters was necessary to find the optimum conditions for implementing the IPI. The best results were achieved when propane was used as OH scavenger at a concentration of 2.5 x 10^{15} molecules cm^{-3} with a carrier gas flow of at least 6 L min^{-1} and a residence time after the injection of the scavenger of ~4 ms. Ambient measurements during the 4 campaigns show that the OH generated within the HORUS instrument is a non-negligible fraction of the total OH signal, and can comprise 30-80% during daytime and 60-100% during the night. The contribution of the background OH varied greatly between measurement sites and was likely related to the type and concentration of volatile organic compounds (VOCs) present at each location. Intercomparisons between the HORUS instrument and two different chemical ionization mass spectrometers (CIMS) in contrasting environments (HUMPPA – Boreal forest, HOPE2012 – rural, Figure 3) have demonstrated the efficacy of the IPI and the necessity of the chemical zeroing method for the HORUS LIF-FAGE instrument.

The chemical scavenging method will be implemented for airborne measurements for the first time in 2015. On the HALO aircraft, air will be sampled from within a shroud mounted on the underside of the aircraft. Scavenging of ambient OH radicals will take place in the IPI reactor (Figure 4) at pressures below ambient. The pressure within the reactor will be such that a residence time of ~100 ms is maintained. 1% propane will be injected to scavenge ~95% of the ambient OH. The air will then be drawn into the OH detection cell through a critical orifice where OH detection will proceed as for the ground instrument. The air then enters the second detection cell for HO_2 radical measurements as described previously.

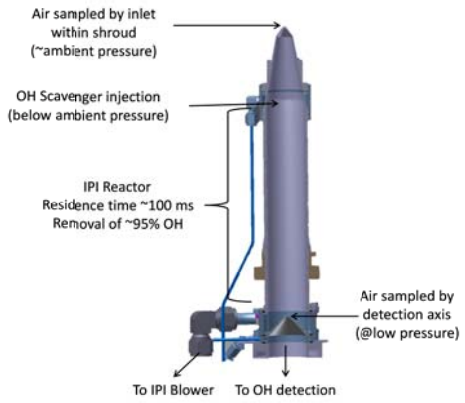

***Figure 4**: Operation of HALO IPI*

Measurement of HO_2 using the HORUS instrument utilizes chemical conversion to OH by the addition of NO. Organic peroxy radicals (RO_2) react with NO at nearly the same rate as HO_2 and one of the products of this reaction is HO_2 itself. Since RO_2 radicals are present at similar concentrations as HO_2 in ambient air, they can react with the NO injected in the detection cell, producing additional HO_2 and causing interference in ambient HO_2 measurements (Fuchs et al., *Atmos. Meas.*

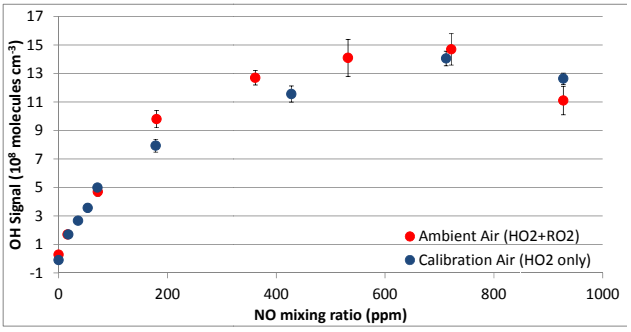

***Figure 5**: NO titrations during HOPE2012*

Tech., **4**, 1209-1225, 2011; Whalley et al., *Atmos. Meas. Tech.*, **6**, 3425-3440, 2013). This interference can be limited by reducing the amount of NO added, thus decreasing the RO_2 to HO_2 conversion efficiency. During HOPE2012, small flows of 20% NO (internal mixing ratio <50 ppm) were used to obtain ~10% conversion of HO_2 to OH. NO titrations (Figure 5) done with calibration air (HO_2 only) and ambient air (HO_2 and RO_2) can indicate the potential strength of this interference, which for HOPE2012 was negligible. Instrument performance during HOPE2012 is shown in Table 1.

***Table 1**: Instrument Performance*

Species	Time resolution	Accuracy (2σ)	Precision (1σ)	LOD
OH	4 min	42%	1.4×10^5 molec cm^{-3}	4×10^5 molec cm^{-3}
HO_2	15 s	35%	0.35 ppt	0.34 ppt

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Jülich instrumentation for measurements of atmospheric OH, HO_2, RO_2 and OH reactivity using Laser-Induced Fluorescence (LIF) detection of OH at low pressure

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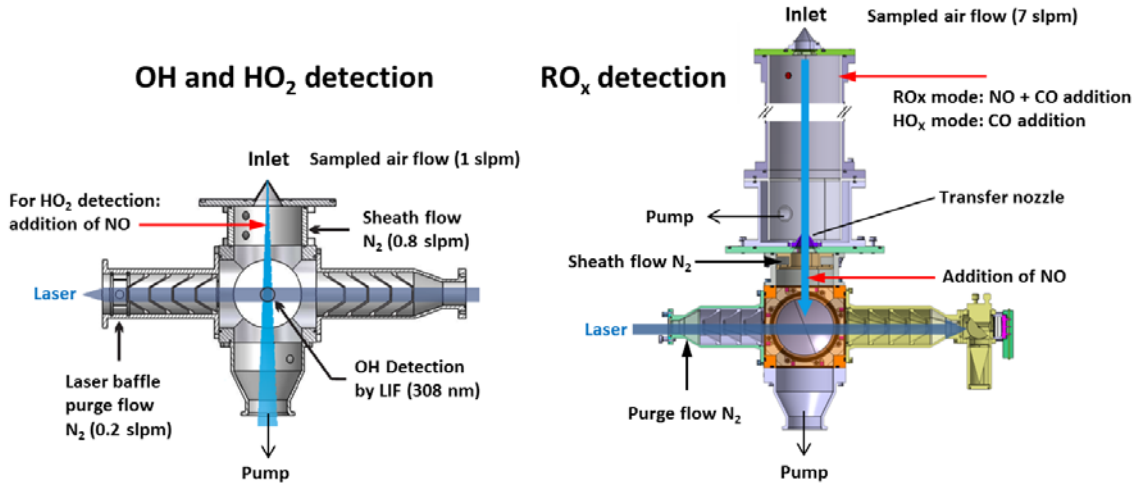
Forschungszentrum Jülich deploys two home-built radical measurement instruments based on the laser-induced OH fluorescence (LIF) technique. One of the instruments is permanently installed at the atmosphere simulation chamber SAPHIR in Jülich. The other instrument has a modular design for field operation on the ground or on airborne platforms (Zeppelin NT, HALO Gulfstream G550). Both instruments have capabilities to measure OH, HO_2, RO_2, and OH reactivity (Table 1).

	Instrument 1	Instrument 2		
	SAPHIR	Ground	Zeppelin	HALO
OH	X	X	X	X
HO_2	X	X	X	X
RO_2	X	X	-	X
k_{OH}	X	X	X	-

The LIF instruments utilise pulsed 308 nm single-photon excitation of OH at low pressure (3-5 hPa) ("FAGE" concept) with temporally delayed detection of the resonant OH fluorescence [*1,2*]. Background signals are taken into account by wavelength modulation (periodical on-off-resonance measurements). Measurement of HO_2 is accomplished by chemical conversion with NO yielding OH which is detected by LIF [*3,4*]. The conversion occurs at low pressure (3-5 hPa) to discriminate HO_2 from RO_2 by their different reaction times needed to form OH. The measurements of OH and HO_2 are performed in two independent detection cells. A third channel (ROxLIF) is used to measure ROx (RO_2 + HO_2 + OH) [*5*]. In a differentially pumped pre-reactor (25 hPa), ambient ROx is first converted into HO_2 by addition of NO and CO. The gas is then transferred into a detection cell at an even lower pressure (3.5 hPa), where HO_2 is converted with excess NO to OH for detection by LIF. Atmospheric OH reactivity (k_{OH}) is measured with Laser flash Photolysis (LP) and LIF. In a flow of sampled air, ozone is flash-photolysed to produce artificially a pulse of OH, which decays by chemical reaction with atmospheric reactants. Pseudo-first order OH decays are monitored in realtime by LIF and k_{OH} is determined as the inverse OH lifetime [*6*].



Schematic drawing of the LIF measurement channels for ground and Zeppelin based operation. Left: OH, HO_x (with NO addition). Right: ROx (with NO+CO addition in the pre-reactor), HOx (with CO addition in the pre-reactor). A single laser beam (8 mm dia.) passes the gas flow in the centre of the detection cells.The OH fluorescence is detected by a gated multichannel photomultiplier perpendicular to the laser beam.

For operation on the HALO aircraft, special OH and HO_2 (RO_2) measurement devices have been developed using extended inlet tubes (250 mm lengths) for transferring ambient air into the measurement cells inside the aircraft. For OH, a shrouded inlet reduces the air flow speed before the air is sampled. It also allows for in-flight calibration by photolysis of ambient water vapour at 185 nm. The HALO configuration is currently being tested and its first field deployment will take place during the OMO mission in summer 2015.

Both LIF instruments have been equipped with home-built frequency-doubled dye laser systems providing tunable 308 nm radiation (spectral bandwidth of 5-7 GHz, pulse duration of 30 ns, pulse repetition frequency of 3-8.5 kHz). Commercially available, frequency-doubled Nd:YAG lasers (532 nm) serve as pump lasers. The dye laser systems are suitable for operation on aircraft and Zeppelin with excellent stability and deliver about 20 mW of UV into the detection units via fibre couplings [*7*].

Calibration: the radical measurement channels are calibrated with a flow reactor, in which 185 nm photolysis of water vapour in synthetic air produces OH and HO_2 in equal amounts at ambient pressure and temperature. For RO_2 calibration, the OH is completely converted into RO_2 by reaction with added VOCs [*5*]. The intensity of the 185 nm radiation can be adjusted by means of a gas filter (N_2O/N_2 mixture) and is monitored by a solar-blind phototube which is calibrated actinometrically against ozone formation from oxygen (O_2) photolysis. OH fluorescence signals are always corrected for quenching by ambient water vapour. The accuracy of the calibration is estimated to be ±20% (2σ) and has been confirmed by measurement intercomparisons for OH against DOAS [*e.g.,Lit. 8*], and for HO_2 and RO_2 against MI-ESR [*9*].

Limit-of-Detection (LOD): the measurement channels of the ground-based instruments have typical LODs (SNR = 2) of about 6 x 10^5 cm^{-3} for OH and 3 x 10^7 cm^{-3} for HO_2 and RO_2. The LODs apply to a total measurement time of 50 s for each data point. At noon, the LOD for OH and HO_2 can be a factor of 2 higher due to increased background signals by solar radiation entering the measurement cells through the inlet nozzles.

Interferences: OH measurements are corrected for interference signals from the photolysis of ozone. The correction is typically a few 10^5 cm^{-3} @ 50ppb O_3. Measurements of HO_2 are additionally corrected for an OH signal related to the added NO. The correction is equivalent to a few 10^7 cm^{-3}. After the discovery of an HO_2 interference from the fast decomposition of alkene- and aromatic peroxy radicals [*4*], the NO concentration for HO_2 conversion has been decreased, reducing the interference to less than 20%. Ongoing work on potential interferences in the measurements of OH and HO_2 suggests that (a) interferences from the reaction of ozone with (biogenic) alkenes play no role at ambient alkene/ozone concentrations; (b) an interference from NO_3 may become important at hundreds of ppt of NO_3. Interference studies using chemical modulation of OH are underway.

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JAMSTEC LIF instrument for the measurement of OH and HO_2 radicals

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Our instrument for measuring OH/HO_2 radical concentrations is based on the laser-induced fluorescence technique using 308 nm for both excitation and detection. Always the $Q_1(2)$ transition of the OH A-X(0,0) band is used for excitation. A frequency doubled Q-switched YAG laser operated at a repetition rate of 8 kHz (QDP-100-532QS-MM, Quantronix) is used to pump a tunable dye laser (Scanmate, Lambda Physik), whose wavelength is again frequency doubled. During HOxCOMP a different pump laser (Nd:YVO_4, Photonics) operated at 10 kHz is used. Typical laser power delivered to the fluorescence detection cell via an optical fiber is 10-30 mW (5-9 mW during HOxCOMP). Periodically the laser wavelength is shifted away from the OH line to measure the background signal.

A single fluorescence detection cell is used (Fig. 1), where OH and HOx radicals are sequentially measured by switching the NO flow to titrate HO_2 into OH (conversion efficiency is typically >90 %). The total sample flow rate is 7 SLM, and the NO flow (passed through an Ascarite trap) was 3 SCCM. The cell pressure is about 2.9 hPa. The inlet nozzle size is 1 mm (in a conical shape). The distances to the detection axis are 23 cm from the nozzle and 21 cm from the point of NO addition, respectively. The NO number density is ~2.7×10^{13} cm^{-3} and the reaction time should be ~7 ms, estimated from the conversion efficiency to OH. A gated channel photomultiplier is used to minimize after pulse rate (Kanaya and Akimoto, 2006). The instrument is regularly calibrated by using a radical generator based on the simultaneous photolysis of O_2 and H_2O at 185 nm in a laminar flow. The O_3 concentration produced from the photolysis of O_2 in the center line is measured and used for the determination of the produced OH and HO_2 concentrations. The detection limit of the instrument is estimated to be 2×10^5 cm^{-3} for nighttime and 1×10^6 cm^{-3} for daytime with increased background due to solar scattering at 308 nm (S/N = 2, 1 min). The total systematic 2-sigma uncertainty in the calibration was estimated to be ±40 % and 48 % for OH and HO_2, respectively.

The instrument has a small positive sensitivity to atmospheric ozone (Kanaya et al., 2007a). The OH level equivalent to the interference is parameterized as $[OH]_{eq}$ (cm^{-3})=(1800+46 ×P(mW) ×[O_3(ppbv)], where P is the laser power in mW. The equivalent OH level is typically 6×10^4 cm^{-3} with 11 mW laser power and an ozone mixing ratio of 25 ppbv. During a SAPHIR chamber experiment when dark ozonolysis reactions occurred in the humidified condition, our instrument gave OH levels higher than the steady state level (by 8×10^5 cm^{-3}), which might be attributable to interference from some products (unspecified) of the reactions. However, considering that the total ozonolysis reaction rate in the chamber (1.4×10^9 molec cm^{-3} s^{-1}) was two or more orders of magnitude higher than that in the ambient condition, the interference in the real atmospheric condition is likely small. For HO_2 measurement mode, the relative sensitivity for $C_2H_5O_2$ to HO_2 is measured to be ~0.05 (Kanaya et al., 2001). Unfortunately measurements of the degree of interference from other RO_2 (especially those derived from alkenes) have not been tested. Analysis of SAPHIR chamber experiments during HOxCOMP indicated that RO_2 interference was likely present but quantitative assessment was not possible.

Details of the instrument are described in the references below. Only ground-based measurements were conducted: at Oki Island in 1998 (Kanaya et al., GRL 1999, JGR 2000a), at Cape Hedo, Okinawa,

in 1999 (Kanaya et al., JGR 2000b, 2001), at Rishiri Island in 2000 and 2003 (Kanaya et al., GRL 2002,

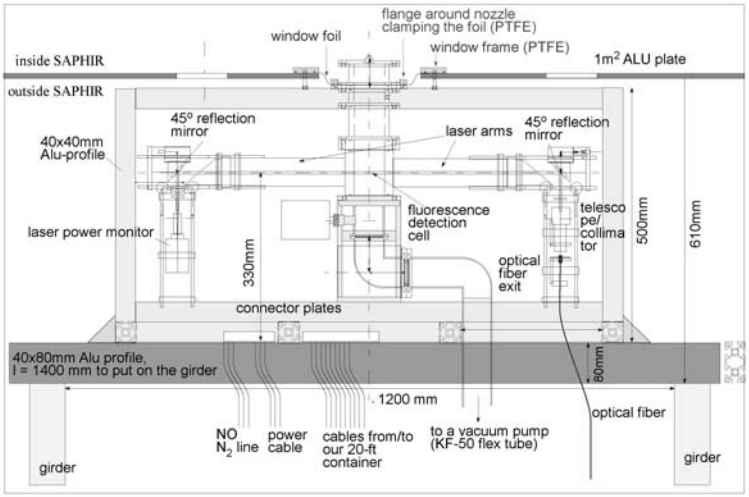

Figure. 1. *Fluorescence detection unit mounted at SAPHIR chamber during HOxCOMP 2005.*

AE2003, JGR 2007a), in Tokyo in 2004 (Kanaya et al., JGR 2007b, 2008), and HOxCOMP in 2005 (Schlosser et al., 2008; Fuchs et al., 2010; Kanaya et al., ACP 2012). After HOxCOMP in 2005, no field observations were conducted; the instrument was used for laboratory experiments of heterogeneous loss of HO_2 on the various types of aerosol surfaces (Taketani et al., JPC A, 2008 etc).

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CIMS instrument for measurements of OH, RO_2 and H_2SO_4

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The instrument was developed in LATMOS, CNRS (Paris) in the period 2004-2008 and the first version of the instrument is described in ref.[1]. Since 2013 the instrument is in the LPC2E, CNRS in Orléans.

Description of instrument

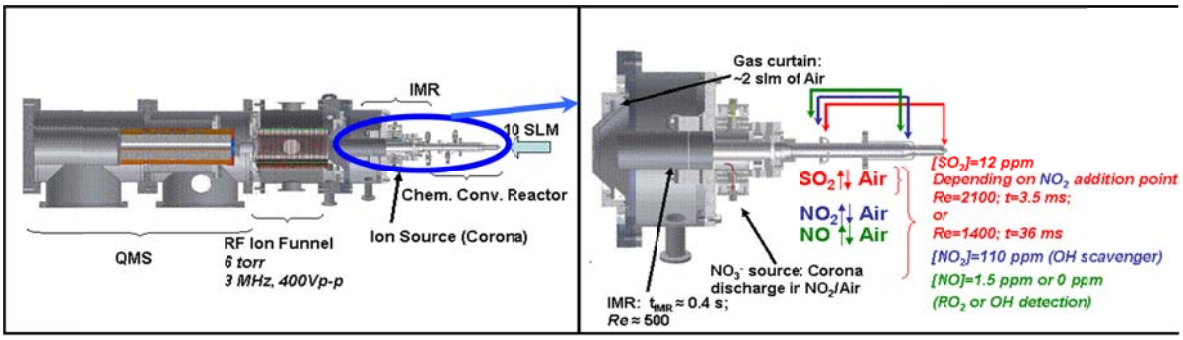


Figure 1. *General scheme of the instrument (left) and Chemical Conversion / Ion Molecular Rector section (right).*

OH radicals are measured by titrating OH radicals with SO_2 to form H_2SO_4 in a chemical conversion reactor (CRR). H_2SO_4 is detected as the HSO_4^- ion produced by chemical ionisation with NO_3^- in an ion-molecule reactor (IMR) following the CCR. To distinguish for atmospheric H_2SO_4 the chemical titration can be performed using $^{34}SO_2$. Total RO_2 are measured by converting RO_2 into OH radicals via reactions with NO injected in the CCR followed by conversion of OH into sulfuric acid.

Air is sampled at a flow rate of 10 SLM creating turbulent flow in the CCR (*Re* = 2100). The turbulent flow conditions minimize possible influence of wind speed on the measurements and ensure fast mixing of reactants ($^{34}SO_2$ and NO) and the radical quencher (NO_2). NO_2 used as a scavenger removes not only the OH radicals, but also peroxy radicals converting them into HO_2NO_2 and RO_2NO_2. Switching the reactants between different injectors allows measurements in four different modes: background, two different OH measurement modes and RO_2 mode. The two OH modes differ by the times of chemical conversion, 3.5 and 36 ms. Ratio of the signals with the short and the long conversion times may be used as an indicator of an artificial OH formation in the reactor.

Measurements of OH, RO_2 and H_2SO_4 are performed by monitoring the peak intensities at m/z=62 (NO_3^-), m/z=99 ($H^{34}SO_4^-$) and m/z=97 ($H^{32}SO_4^-$). The detection of $H^{34}SO_4^-$ and $H^{32}SO_4^-$ corresponds to the measurement of the radicals (OH or RO_2) and H_2SO_4, respectively. The ion peak intensities are measured sequentially resulting in nine measurements of OH and one measurement of RO_2 for every 28 minutes. Every measurement of OH is derived from 1 min of OH ion signal count and two 30 s background ion signal counts before and after the OH signal measurement. RO_2 is measured at the end of the OH detection sequence by switching on the NO flow for the duration of 2 min. A time delay of 10 min is introduced after switching off the NO flow and before starting the next OH measurement sequence. Typically, the measurements of OH and RO_2 radicals are averaged to 15 minute and 30 minute time intervals, respectively. The concentration of the radicals is derived from the measured ratio of the $H^{34}SO_4^-$ and NO_3^- ion peak intensities. Calibration coefficient is determined using N_2O actinometry and OH/RO_2 generation in a turbulent flow reactor by photolysis of N_2O or

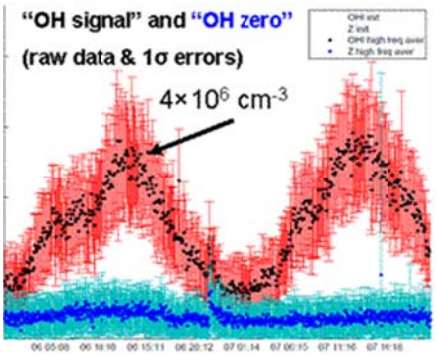
H_2O at 184.9 nm. The calibration of HO_2, CH_3O_2 and other RO_2 is performed by adding into the calibration cell photolysis reactor CO, CH_4 (or other RO_2 precursors) converting any OH radical to RO_2. The overall estimated calibration accuracy (2σ) for OH is about 25%. The uncertainty of the RO_2 measurements is typically higher due to uncertainty in RO_2 composition in air.

Usually during the field measurements the instrument is installed in a shipping container with the CCR fixed to the roof of the container via an interface cap covered with a PTFE sheet. The sampling aperture of the CCR (3 mm diameter) is positioned 50 cm above the roof and about 3 m above the ground surface.

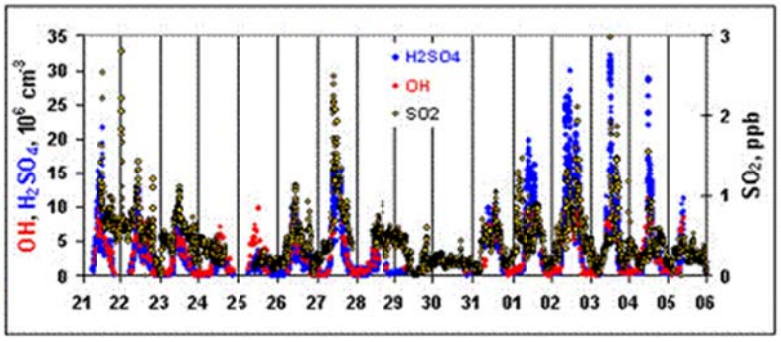
Performance data

- Accounting for the calibration uncertainties and measurement precision, the overall 2σ uncertainty of the 15 min averaged measurements of OH is estimated to be **30%**. For RO_2 the uncertainty depends on RO_2 composition in ambient air.
- The lower limits of detection for OH and RO_2 radicals at S/N=3 and a 2 minute integration time is **5×10^5** molecule cm^{-3} and **2×10^6** molecule cm^{-3}, respectively.
- Time resolution: 2 min for one point of OH (typically averaged to 15 min time steps)
- Interferences:
    - artificial OH generation in the CCR at high NO ([NO] > 5-10 ppb) (*correction can be applied*);
    - interference from H_2SO_4 formed via Criegee+SO_2 reactions (*studies in progress*);

Examples of measurements



Example of raw OH data (2min) (Dome C, 2012)



OH, H_2SO_4 and SO_2 measurements (Corsica, 2013)

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The Indiana University LIF-FAGE instrument for the detection of ambient OH and HO_2 radicals

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The Indiana University Fluorescence Assay by Gas Expansion (IU-FAGE) instrument detects ambient OH radicals by laser-induced fluorescence after expansion of ambient air into a low pressure chamber. This technique enhances the OH fluorescence lifetime, allowing temporal filtering of the OH fluorescence from laser scatter. One detection axis is typically used for ambient measurements of OH and HO_2 (Griffith et al., 2013), while a second axis is used for measurements of total OH reactivity using a flow reactor (Hansen et al., 2014). A detailed description of the instrument can be found in Dusanter et al. (2009).

A schematic of the ground-based instrument is shown in Figure 1. Briefly, the early version of this instrument employed a Spectra Physics Navigator II YHP40-532Q diode-pumped Nd:YAG laser that produced approximately 5.5 W of radiation at 532 nm at a repetition rate of 5 kHz. This laser pumped a Lambda Physik Scanmate 1 dye laser (Rhodamine 640 in isopropanol) that produced approximately 20 mW of laser power at 308 nm. Recently, the laser system was replaced by a Spectra Physics Navigator II YHP40-532Q laser that produces approximately 7.5 W of radiation at 532 nm at a repetition rate of 10 kHz. This laser pumps a Sirah Credo dye laser, producing 70-100 mW of radiation at 308 nm. OH radicals are excited using the $Q_1(3)$ transition and a reference cell where OH radicals are produced by thermal dissociation of water vapor is used to insure maximum overlap of the laser with the OH transition. After exiting the dye laser, the laser beam is focused onto an optical fiber to transmit the radiation to the sampling cell.

Ambient air is expanded into the detection cell through a 0.6-mm inlet, and the pressure in the cell is maintained at ~4.0 ± 0.1 Torr (~5.3 ± 0.1 hPa). The air stream passes through the central region of the sampling cell where the laser beam is reflected 24 times in a multi-pass White cell configuration (Figure 2). The OH fluorescence is collected at right angles to both the air stream and the laser beam and detected using a microchannel plate detector (Hamamatsu R5916U) and a gated detection scheme. The laser power entering the cell is kept at 2-3 mW and is continuously monitored by a photodiode mounted at the exit of the multi-pass cell, and nitrogen is continuously flushed through each end of the multi-pass cell to avoid contamination of the mirrors.

The net OH fluorescence signal is determined by successive modulation cycles during which the laser wavelength is successively tuned on-resonance with the OH transition to measure the OH fluorescence, and off-resonance to measure a background signal due to solar and laser scatter that is subtracted. To measure known and unknown interferences, perfluoropropylene (C_3F_6) is added through an external loop injector directly above the inlet to scavenge ambient OH concentrations. The resulting signal is a direct measurement of interferences that can be subtracted from the ambient signal. Interferences measured in ambient air using this technique have been consistent with laser-generated OH under conditions of high concentrations of ozone and water vapor, where photolysis of ambient ozone by the laser produces excited oxygen atoms that can quickly react with ambient water vapor to produce OH. However, laboratory measurements of the OH radical yield produced from the ozonolysis of several alkenes suggests that under high ozone and alkene

concentrations the IU-FAGE instrument is sensitive to an interference associated with certain alkenes, possibly from the decomposition of stabilized Creigee intermediates inside the low-pressure sampling cell. This interference has yet to be observed in ambient air.

Concentrations of HO_2 in the IU-FAGE instrument are measured indirectly after conversion to OH by addition of nitric oxide. A Teflon loop located directly below the inlet allows for the intermittent addition of NO to convert ambient HO_2 to OH through the fast HO_2 + NO → OH +NO_2 reaction. Recent studies have shown that some hydroxyalkyl peroxy radicals from the OH-initiated oxidation of alkenes and aromatics can also be detected by instruments using chemical conversion of HO_2 to OH through the addition of NO (Fuchs et al., 2011; Whalley et al., 2013). This is due to the rapid decomposition of the hydroxyalkoxy radicals produced from the RO_2 + NO reaction leading to the formation of hydroxyalkyl radicals which react quickly with O_2 forming HO_2. As a result, addition of high concentrations of NO to the sampling cell can lead to the conversion of both HO_2 and hydroxyalkyl peroxy radicals to OH. We have measured the conversion efficiency of several alkene- and alkane-based peroxy radicals and have found that with the addition of high concentrations of NO to the airstream (greater than 10^{13} cm^{-3}), the IU-FAGE instrument is sensitive to the detection of isoprene and other alkene-based peroxy radicals (α >70%, α = conversion efficiency) and less sensitive to butane and other alkane-based peroxy radicals (α <30%). This interference is minimized through the addition of lower concentrations of NO (approximately 10^{12} cm^{-3}). Depending on the concentration of NO added, the IU-FAGE instrument is capable of detecting both HO_2 and HO_2*, where HO_2* = HO_2 + αRO_2.

The IU-FAGE instrument is calibrated using the UV-water photolysis method (Dusanter et al., 2008). For these calibrations, humidified zero air is delivered at a flow rate of 50 SLPM to a calibrator where water vapor is photolyzed at 185 nm using a mercury lamp leading to the production of equal concentrations of OH radicals and H atoms. The latter are then stochiometrically converted into HO_2 by reaction with O_2. The concentration of OH (and HO_2) is determined from the known absorption cross-section of water, the unity photodissociation quantum yield, the photon flux and the photolysis time. The photon flux and photolysis time are determined by oxygen actinometry (Dusanter et al., 2008). The uncertainty associated with the UV-water photolysis calibration technique is estimated to be 36% (2σ) for both OH and HO_2. The OH detection limit for the IU-FAGE instrument is typically 6 × 10^5 cm^{-3} (S/N=2, 15-min average) when the external chemical scrubber is used to determine the background signal. The detection limit for HO_2 is approximately 4 × 10^7 cm^{-3} (S/N=2, 30 sec average).

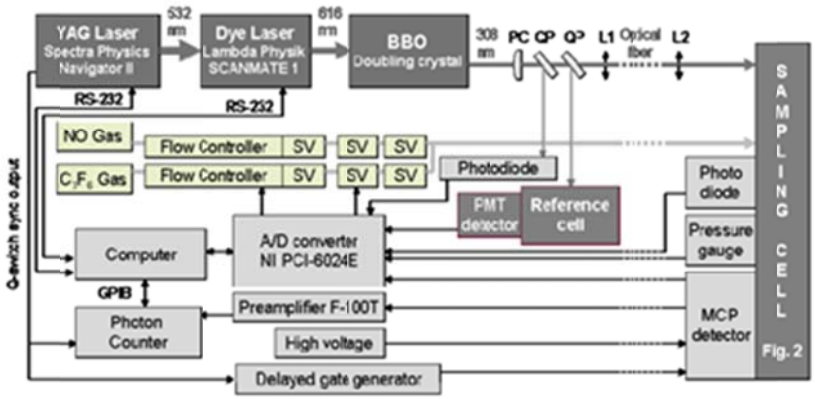

***Figure 1**: Schematic diagram of the IU-FAGE instrument. PC: planoconvex lens, QP: quartz plate, L1 and L2: optical launchers, SV: solenoid valve, MCP: microchannel plate (Dusanter et al., 2009)*

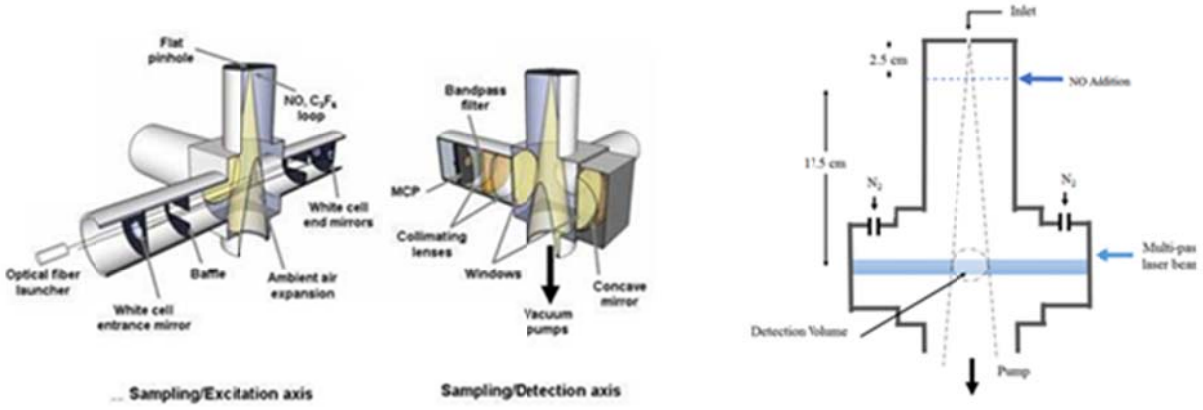

***Figure 2**: Cross-sections of the detection cell. The left figure displays the intersection between the sampled air mass and the excitation beam through the multi-pass cell. The center figure displays the detection axis (Dusanter et al., 2009). The right figure displays the dimensions of the detection cell.*

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Description of the nitrate (NO_3^-) ion based CI-APi-TOF (Chemical Ionization Atmospheric Pressure interface Time of Flight) HOxROx instrument

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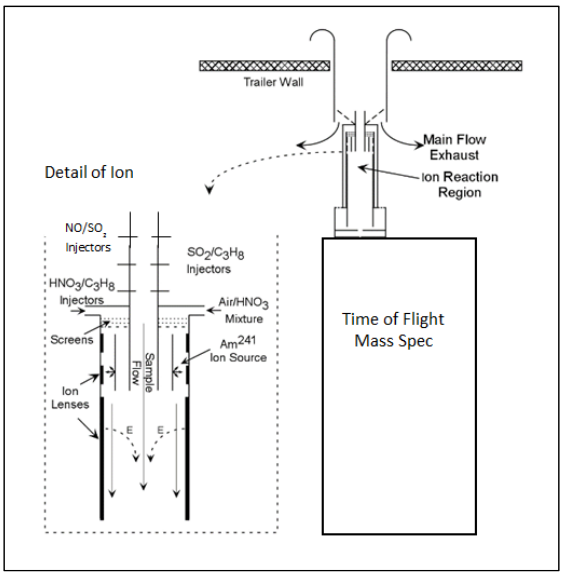
General description:

This instrument is a combination of the CIMS OH technique developed by Eisele et al. 1991, 1993 and Tanner 1997, and the HO_2+RO_2 technique developed by Cantrell et al. 2003, with the additional extension of a Time-of-Flight (ToF) mass detection. Briefly, the instrument can be operated in three different modes: One for the detection of hydroxyl radicals (OH mode), one for the detection of peroxy radicals (HO_2+RO_2 mode), and one where the sample flow is not treated with reagent compounds (NO_3 ion mode). These modes allow the sequential determination of [OH], [HO_2+RO_2], [H_2SO_4], [MSA], an upper limit to the concentration of other SO_2 oxidants as well as numerous Extremely Low Volatility Organic Compounds or ELVOCs.



***Schematic of HOxROx ToF system**. Depending upon the mode in use, different reagent gases are added through a series of injector needles whereupon either OH, or HO_2+RO_2 are converted to H_2SO_4. The sample air then enters the ion source region where reactions with NO_3 ions take place. The flow then enters the Time of Flight spectrometer through a pinhole for mass detection.*

Detection Scheme

The OH detection scheme is based on the chemical conversion of OH to H_2SO_4 via reaction with SO_2 which is added to the sample flow. Once formed, the H_2SO_4 is then detected by the well characterized NO_3^- CIMS technique (Eisele 1993, Jokinen 2012):

$OH + SO_2 \rightarrow HSO_3$ (1)

$HSO_3 + O_2 \rightarrow SO_3 + HO_2$ (2)

$SO_3 + 2H_2O \rightarrow H_2SO_4 + H_2O$ (3)

RO_2, RO and HO_2 radicals are detected by converting them to OH radicals (and subsequently to H_2SO_4) via the reactions:

$RO_2 + NO \rightarrow RO + NO_2$ (4)
$RO + O_2 \rightarrow R=O + HO_2$ (5)
$HO_2 + NO \rightarrow OH + NO_2$ (6)

It's important to note that the above reaction sequence (1-6) represents a chain reaction with an additional HO_2 being produced by reaction (2) in the conversion of OH to H_2SO_4. This chain will propagate producing H_2SO_4 until it is ultimately terminated by the formation of HONO via:

$OH + NO + M \rightarrow HONO + M$ (7)

The gain or chain length is controlled by the ratio of $[NO]/[SO_2]$. For normal operating conditions this ratio is maintained for a gain of one, or one H_2SO_4 produced for each HO_2 or RO_2.

Both the OH and HO_2+RO_2 measurements involve the addition of reagents to the sample flow. In the case of OH, SO_2 is added to the sample flow through a pair of injector needles. To prevent the interference of ambient peroxy radicals being converted to OH by ambient NO, propane (an OH scavenger) is added to the sample flow 50 msec downstream of the SO_2 addition. SO_2 is added in sufficient concentrations such that 99% of the ambient OH is converted to H_2SO_4 before the addition of the propane. To account for additional processes that can produce H_2SO_4 from SO_2 other than oxidation by OH, an additional measurement is made where propane is added to the injector along with the SO_2. This measurement is related to all species which will oxidize SO_2, but do not react with propane – currently speculated to be stabilized Criegee intermediates (sCi).

In the case of the HO_2+RO_2 measurement, both SO_2 and NO are added through a pair of injection needles at a ratio to maintain a gain of one. As in the case of the OH measurement, a second measurement is also performed to account for H_2SO_4 not produced from the conversion of HO_2. Here NO is added first, and SO_2 is added 50 msec downstream of the NO addition. NO is added in sufficient concentration such that 99% of the OH formed is converted to HONO before the addition of the SO_2.

In the case of the NO_3 ion mode, no reagents are added to the sample flow before entering the ion reaction region. In this case the instrument measures ambient H_2SO_4, MSA, as well as a host of highly-oxidized organic ELVOCs.

Performance Data

The instrument uses a Tofwerk build APi-TOF (Tofwerk AG, Switzerland) described in detail in Junninen et al. 2010. Briefly, the mass spec is operated in the lower resolution and shorter flight path mode (V-mode) with a resolution of about 4000 Th/Th, transmission around 0.2%, and mass accuracy better than 20 ppm (0.002%). The mass spectrum is recorded only for negative polarity ions and usually up to about 1500 Th.

Primary species measured with the instrument:

Species	LOD	Uncertainty (2 sigma)	Time Resolution
OH	~3 x 10^5 molecule cm^{-3}	+/- 45% for 30 sec integration	30 sec
H_2SO_4	~3 x 10^5 molecule cm^{-3}	+/- 45% for 30 sec integration	1 sec
MSA	~3 x 10^5 molecule cm^{-3}	+/- 45% for 30 sec integration	1 sec
HO_2+RO_2	~5 x 10^5 molecule cm^{-3}	+/- 45% for 90 sec integration	90 sec
Other SO_2 Oxidants	~3 x 10^5 molecule cm^{-3}	+/- 100% for 30 sec integration	30 sec
ELVOC	~3 x 10^5 molecule cm^{-3}	+/- 45% for 30 sec integration	1 sec

Applications

Presently the system has only been used for ground based and laboratory measurements.

Potential interferences (and problems)

The conversion of larger and more oxidized RO_2 radicals into corresponding nitrates by:

$RO_2 + NO \rightarrow RO_2NO$ (8)

$RO_2 + NO_2 \rightarrow RO_2NO_2$ (9)

the latter being relevant to acyl-type peroxy radicals (i.e., R-C(O)-OO*), whereas the former reaction (8) could in principle be possible for various different RO_2 radical structures. Furthermore, potentially significant fraction of RO will decompose or isomerize, which are the only options if there is no hydrogen atom available in the α-carbon.

Calibration method

Two different methods are used to calibrate the system, both of which rely on water photolysis at 185 nm.

(1) In the field, photolysis of ambient H_2O is used to produce a known amount of OH and HO_2. The photon fluence of the calibration system is mapped using a photo diode calibrated to a NIST standard photo diode.

(2) The system can also be calibrated by a system that uses H_2O photolysis followed by the addition of SO_2, to produce a known amount H_2SO_4. The fluence of the photolysis region is measured using actinometry (Kürten, A. 2012). This system offers the benefit of control of the calibrating species.

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Short introduction of the Laser Induced Fluorescence system for the detection of ambient OH and HO_2 radicals in Peking University

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The Laser Induced Fluorescence system for the detection of ambient OH and HO_2 radicals in Peking University (PKU-LIF) consists of two separate channels which measure OH and HO_2 respectively. The instrument shares similar design as FZJ-LIF and detail information can be found in previous publications (Fuchs et al., 2011; Holland et al., 2003; Hofzumahaus et al., 1996; Holland et al., 1995; Lu et al., 2012). Schematic drawing is shown in Figure 1 and here is a brief description of the instrument.

The laser module (Figure 2) is made up of a pump laser, a dye laser and a reference cell. They are set up in a temperature-controlled and vibration-isolated box for stable operation. The laser radiation (308 nm) is generated by a pulsed, frequency-doubled tuneable Nd-Yag-pumped (Spectra-Physics Navigator) dye-laser system. The pulse repetition frequency is 8.5 kHz with output power of 3.2 W. Rhodamine 101 in ethanol solution is used as dye to change the laser wavelength to 616 nm. Fine wavelength selection is achieved by the etalon and prisms in the dye laser. The 616.32 nm laser is frequency doubled by a BBO crystal to narrow bandwidth (7GHz) of UV laser. The typical laser power at 308 nm is about 150 mW.

The instrument is designed to be compact and adapted to field measurement. The sampling and detection system, data acquisition system as well as the gas supply units are integrated to a measurement box (see Figure 3). Inside the box, fluorescence cells are mounted on the top level. Two cells are arranged in a line and connected with baffle arms so that the laser beam can go through the cells. Also, the laser beam is detected by a photo diode at the exit window to monitor the power and the position of the laser beam. In between two cells, quartz window is set for gas segregation. One liter per minute of pure nitrogen is purged all the time to reduce gas dead volume in each cell. The orifice diameter of nozzles are 0.4mm. The measurement cells are operated at reduced pressure (typical 4 hPa) and ambient air is collected by gas expansion through inlet nozzles. OH detection is accomplished in the measurement cell by laser induced fluorescence while HO_2 are detected in a different cell as OH after chemical conversion by NO. Low pressure in the detection cells is achieved by high-performance dry vacuum pumps (Edwards XDS35). The pulsed OH fluorescence (307-311nm, 150ns lifetime) in the detection cells is monitored by UV-sensitive bialkali multi-channel plate photomultiplier detectors (PMT) which are operated in photon-counting mode. The PMTs are protected against laser stray light by gain switching and the fluorescence is measured with a time delay (50 ns) after the exciting laser pulse (FWHM 20ns). The signal detected by PMTs usually consisted of fluorescence of OH, solar stray light, laser stray light. To distinguish between fluorescence and stray lights, different strategies are applied. For solar stray light, a second detection gate(duration of 25 μs) is utilized after the OH fluorescence detection gating (duration of 500 ns) and the corresponding signal is corrected automatically. On the other hand, laser stray light reflected by gas molecules, particles and cell walls is measured in the OFF mode. In the off mode, the laser wavelength is tuned away from OH absorption line, so no OH fluorescence appears. It is assumed that the laser background is constant between ON and OFF mode. Thus, the difference between ON and OFF mode is the OH fluorescence.

The calibration of the instrument is performed by a radical source which consists of a laminar photochemical reactor. In this reactor, a flow of humidified synthetic air is exposed to VUV (185nm) radiation by a low-pressure mercury discharge lamp in order to generate well quantified concentrations of OH and HO_2. The LIF instrument and the calibration source are equipped with gas-supply units which control gas flows and monitor temperatures, pressures and humidity. The uncertainty of calibration source is estimated to be 10%.

***Table 1**. Typical sensitivity and measurement uncertainties of the PKU-LIF instrument*

	Sensitivity cts/mw/(10^6cm^{-3})	**1σ detection limit cm^{-3}**	**1σ Accuracy**
OH	4.6	0.7×10^6	14%
HO_2	0.27	1.7×10^7	22%

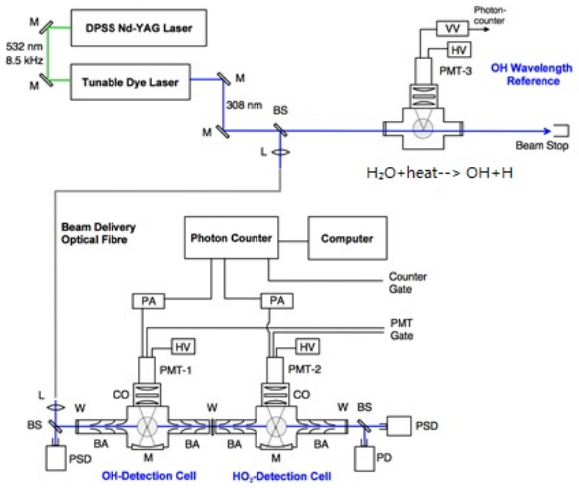

***Figure 1** Schematic drawing of the PKU-LIF system*

***Figure 2** Laser module*

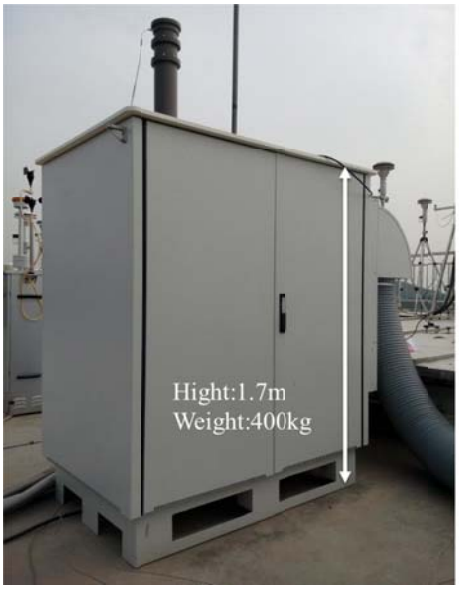

***Figure 3** Measurement module*

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Investigation of Atmospheric Radical Chemistry in Hong Kong and South China by Chemical Ionization Mass Spectrometry

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Recently, Hong Kong acquired a chemical ionization mass spectrometry (CIMS) system to measure the ambient RO_x ($OH+HO_2+RO_2$) radicals. This RO_x-CIMS instrument is developed and built by Professor Gregory Huey and Mr. David Tanner from Georgia Tech, based on the work of Tanner et al. (*1997*) and Edwards et al. (*2003*). The RO_x-CIMS instrument utilizes a detection technique based on the chemical conversion of ambient peroxy radicals (HO_2 and RO_2) into a unique ion (HSO_4^-), which is quantified by mass spectrometry. The CIMS consists of five main parts, a sampling inlet, a flow tube attached with a corona-discharge ion source, a collisional dissociation chamber (CDC), an octopole ion guide and quadrupole mass filter together with a detector.

Ambient air is continuously sampled at 5.0 LPM through a 50-μm-diameter orifice into an inlet held at ambient pressure. Peroxy radicals (HO_2 and RO_2) within this air are converted to sulfuric acid by the addition of SO_2 and NO through a front injector in the inlet (*Sjostedt et al., 2003*). Addition of an OH scavenger, hexafluoropropene C_3F_6, through the rear injectors allows termination of the radical chemistry. Nitric acid (HNO_3) is used as the primary ion reagent, and is ionized into nitrate ion (NO_3^-) by the electron generated by corona-discharge. The nitrate ions then react with the produced sulfuric acid to form HSO_4^- ion, which is then quantified by a quadrupole filter mass spectrometer at 97 amu.

Calibration is performed through photolysis of water vapor by 185-nm light generated by a mercury lamp. A calibration unit consists of a temperature controlled water bubbler, a humidity sensor, a pre calibrated mercury lamp and photolysis cell. Pure N_2 is humidified by passing through the bubbler containing deionized water held at an accurately known temperature (298K). The humidified air is diluted with dry N_2 to achieve the desired water mixing ratios, and then passed through the photolysis cell to generate a known concentration of HO_x. The calibration unit is used for multipoint calibration in the laboratory and the field. In addition, a pre-calibrated mercury lamp equipped with a 185-nm bandpass filter is mounted on a pipe in front of the sampling inlet, to serve as online calibration source of HOx radicals. The light photolyse ambient air water vapor yielding HO_x radicals which can be calculated based on the known absorption cross section and concurrent measurements of humidity. The online calibration is performed every 2 hours. The system **background** is determined by adding high concentration of C_3F_6 into the flow periodically. The time resolution of the RO_x measurements is 10 seconds, and detection limit for RO_x is less than 3×10^6 molecules·cm^{-3} (2σ) for 1 minute integration period, with estimated accuracy ~30%.

In addition to the RO_x-CIMS, we have another CIMS using iodide adduct ionization to measure the ambient **N_2O_5 and $ClNO_2$** (*Wang et al., 2014*). An intercomparison campaign with the N_2O_5-CIMS and a CRDS from US NOAA was conducted at Hong Kong, and both instruments agreed very well. With this CIMS, we have conducted several field studies in Hong Kong and North China. Overall, the results indicated relatively high abundances of N_2O_5 and $ClNO_2$ (up to ppbv level) in these regions (*Tham et al., 2013*). Moreover, we have measured ambient HONO concentrations with a long path absorption photometer (LOPAP) at several sites in Hong Kong (*Xu et al., 2014; Zha et al., 2014*). We have gained

some interesting results on HONO, including elevated daytime HONO formation related with aerosol surface, a potentially important source from air-sea interactions, etc. These results highlight unique features of atmospheric environment and chemistry of Hong Kong and PRD region, and suggested the necessities for further investigations.

At present, the RO_x-CIMS is being tested in the laboratory at HK PolyU, to optimize the system and to identify the possible interferences. We are planning to conduct intensive field campaigns with measurements of RO_x radicals and related species in Hong Kong and Pearl River Delta (PRD) region in 2015 and 2016. We aim to investigate the atmospheric radial chemistry in the highly oxidative condition of this unique region, and address some knowledge gaps on source(s) and chemistry of RO_x and other radicals such as NO_3 and Cl, as well as heterogeneous chemistry of nitrogen.

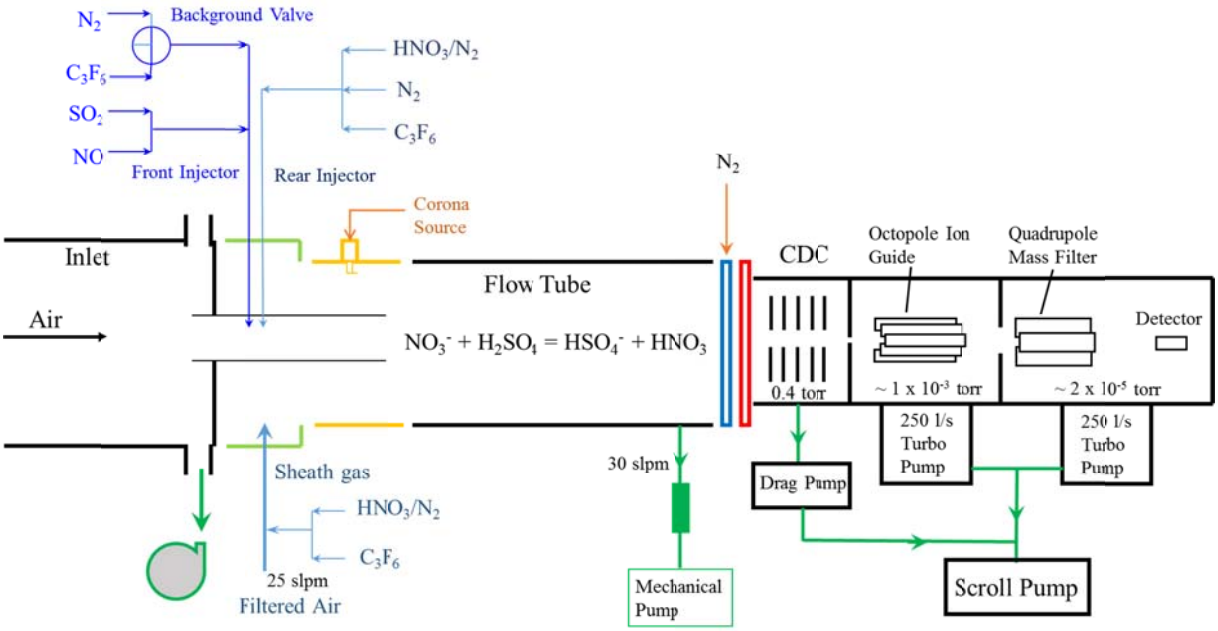

Figure 1. *Schematic diagram of ROx-CMS deployed at the Hong Kong Polythechnic University*

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The University of Leeds FAGE instruments for measurements of OH, HO_2 and RO_2 radicals

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Two instruments have been developed at Leeds for the field measurement of OH, HO_2 and RO_2 radicals. The "ground-based" instrument is housed within a standard shipping container, with fluorescence cells either located on the roof of the container or on a sampling tower. The "aircraft" instrument was designed for operation on the NERC/Met Office Bae 146-301 aircraft, where it has been deployed several times, but its smaller size has resulted in it being used on several ground-based and ship-borne campaigns where deployment of the container is more difficult.

Each instrument uses a Nd:YAG pumped tunable Ti:Sapphire laser system (manufactured by Photonics Industries) which is frequency tripled to generate the 308 nm radiation for laser-excitation of OH. The system produces up to ~80 mW of UV radiation at 308 nm, operating at a pulse repetition frequency of 5 kHz, with a typical pulse length of 35 ns, and a spectral bandwidth of 0.065 cm^{-1}. Fibre optic cables are used to transmit the laser radiation to the fluorescence cells, and a small fraction is directed into a reference cell, which uses a hot filament to dissociate water vapour, providing a convenient source of OH, fluorescence from which provides an accurate wavelength reference. The detector gain is rapidly switched during the laser pulse using a home-built gating circuit.

The ground-based system utilises two separate fluorescence cells in parallel, each with its own inlet and being independently pumped, and with the laser beam passing through both cells in turn via one optical axis (i.e. single pass excitation). Historically, OH was measured in one cell and HO_2 in the other, but following implementation of the ROxLIF method for the measurement of RO_2 radicals, how each cell is used has been changed. There are three modes of operation in Cell 1: (i) OH measurement with no NO flow added to the cell, (ii) HO_2 measurement with a low NO flow added to cell, and (iii)

HO_2^* = HO_2 + α (RO_2i) measurement with a high NO flow added to cell, where RO_2i are those RO_2 species which give an interference to HO_2, and which can be obtained from RO_2i = HO_2^* - HO_2 by subtraction. We have determined the value of α for a wide range of RO_2 by calibration, using the reaction of OH with a suitable hydrocarbon. A flow reactor (30 Torr, ~1 s residence time) is interfaced to the other Cell (Cell 2), which has two modes of operation, (i) HO_2^*, with no NO added to the reactor, (just CO which converts all OH to HO_2), and (ii) HO_2 + ΣRO_2, with NO added to reactor which converts RO_2 to HO_2 (with CO converting any OH formed immediately into HO_2). It is thus possible to measure ΣRO_2 by subtraction, and also, to distinguish short-chain alkane derived RO_2 (which provide no interference in Cell 1) from the total organic RO_2 by subtracting ΣRO_2 Cell 2 minus the alkene/aromatic derived RO_2 (RO_2i , Cell 1). We have calibrated both the sensitivity of the reactor and Cell 2 to various RO_2, and also quantified the interference towards HO_2 for various RO_2 in Cell 1 Table 1 summarises the operational parameters and performance characteristics for Cell 1 and Cell 2.

For the aircraft system, there is one common inlet, and the two fluorescence cells are in series, with NO injected between the cells, and detection of HO_2 in the second cell. Table 2 summarises the operational parameters and performance characteristics of the aircraft system.

Parameter	HOx (Cell 1)	ROx (Cell 2)
Inlet orifice / mm	1.0	1.0 (4.0, connecting pinhole)
Sample flow rate / slpm	8	7
Cell pressure / Torr	1.0	1.5
[NO] / 10^{13} cm^{-3}	0.9 (low), 9 (high)	7
Distance nozzle – detection / cm	8	8
Method of NO injection	¼" injector	¼" injector
Distance NO addition to detection / cm	5	5
Reaction time for HO_2 to OH conversion /ms	0.9	60
Laser power / mW	13	13
Laser beam diameter / mm	10	10
Accuracy of calibration (2σ) / %	± 26	± 26
Typical background signal (cts s^{-1})	25	40
Limit of detection (3 min, SNR=2) / cm^{-3}	OH=$4.5x10^5$	HO_2low=$2.1x10^6$ HO_2high=$5.5x10^5$ RO_2=$6.9x10^6$

Table 1. *Typical operational parameters and performance characteristics for the ground-based cells.*

Parameter	OH	HO_2
Inlet orifice / mm (on pylon)	0.7	0.7
Sample flow rate / slpm	4	4
Cell pressure / Torr	1 – 2 Torr (altitude dependent)	
[NO] / 10^{13} cm^{-3}		1
Distance nozzle – detection / cm	39	49
Method of NO injection	-	1/8" tube
Distance NO addition to detection / cm	-	16
Reaction time for HO_2 to OH conversion /ms		10
Laser power / mW	25	10
Laser beam diameter / mm	8	8
Accuracy of calibration (2σ) / %	± 15	± 20
Typical background signal (cts s^{-1})	15	10
Limit of detection (3 min, SNR=2) / cm^{-3}	$6.4x10^5$	$5.9x10^5$

Table 2. *Typical operational parameters and performance characteristics for the aircraft system*

For both systems the calibration is performed using the 184.9 nm photolysis of water vapour (measured using a dew point hygrometer) in a flow of synthetic air in a turbulent flow reactor. The product of the photolysis time and lamp flux is determined using an N_2O actinometer, which is photolysed at 184.9 nm to generate $O(^1D)$ atoms which react with N_2O to generate NO in a known yield, which is measured using a chemiluminescence analyser. More recently alternative methods have been developed for the calibration of OH and HO_2 as a function of pressure using the Leeds HIRAC chamber, in which a decay of a hydrocarbon is monitored (to determine [OH]), or the second-order kinetic decay of HO_2 from its self-recombination is monitored following HCHO photolysis (to determine [HO_2]). An inlet for the injection of an OH scavenger has recently been constructed and is currently being integrated/tested with the OH fluorescence cell.

Since the ACCENT Workshop on Radicals held in Leeds in 2005, the container instrument has been deployed in the following field campaigns/locations: RHAMBLE (Roscoff, France and Cape Verde), OP3 (Borneo), HCCT (Mt Schmucke, Germany), ClearFLo (London, summer and winter)) and York (UK). For the aircraft instrument: AMMA (West Africa), SHIVA (Western Pacific, ship deployment), RHAMBLE (Tropical Atlantic, ship-borne), OP3 (Borneo), Mace Head (ground-based), RONOCO (Above UK), SOS and ORC-3 (Cape Verde, ground-based), COBRA (Hudson Bay, ground-based).

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4. Workshop Programme

HOx Workshop Programme

Monday 23 March 2015

11:00 Registration

12:00 Lunch buffet

13:00 Welcome
Structure and goals of the workshop
A. Hofzumahaus, D. Heard

Session 1: Radical measurement techniques

Rapporteur: *F. Keutsch*

Overview talks about currently used measurement techniques
(detection method, technical realisation, sensitivity, limit of detection, time resolution)

13:15 OH Techniques: DOAS (30 + 10 min) Chair: *W.H. Brune*
H.-P. Dorn

13:55 OH + HO_2 Techniques: LIF (40 + 10 min)
P.S. Stevens

14:45 Coffee & Tea break (20 min) + group photo

15:05 OH Techniques: CIMS (40 + 10 min)
H. Berresheim

15:55 ROx Techniques: LIF, CIMS, Perca (40 + 10 min)
L. Whalley

16:45 Coffee & Tea break (15 min) Chair: *L. Andrés Hernández*

17:00 HOx and ROx calibration procedures (20 + 10 min)
C. Cantrell

17:30 Results from previous OH measurement intercomparisons (20 + 10 min)
H. Harder

18:00 Results from previous HO_2/RO_2 measurement intercomparisons (20 + 10 min)
H. Fuchs

18:30 End of session

19:30 Dinner at Restaurant Rossini (Jülich)

Tuesday 24 March 2015

Session 2: Potential radical measurement artefacts

Rapporteur: *S. Brown*

08:15 Introduction - *A. Hofzumahaus* (5 min)

08:20 *W.H. Brune*, Pennstate Univ. (20 + 10 min) Chair: *F. Holland*
Update on finding the GTHOS OH interference

08:50 *A. Novelli*, MPI-Mainz (20 + 10 min)
Characterization of an inlet pre-injector laser-induced fluorescence instrument for the measurements of atmospheric hydroxyl radicals

09:20 *P. Stevens*, Indiana Univ. (10 + 5 min)
Measurements of the OH radical yield from the ozonolysis of biogenic alkenes: A potential interference with laser-induced fluorescence measurements of ambient OH

09:35 *H. Fuchs*, FZJ (20 + 10 min)
Investigation of potential interferences in the detection of OH radicals by laser-induced fluorescence under dark conditions

10:05 *Z. Tan*, Peking University + FZJ (10 + 5 min)
OH interference test of a laser induced fluorescence instrument using chemical modulation in field experiments in China

10:20 Coffee & Tea (15 min) Chair: *M. Martinez*

10:35 *Y. Kanaya*, JAMSTEC (20 + 10 min)
Analysis of SAPHIR chamber data during HOxCOMP 2005 to assess the degree of interference in the JAMSTEC LIF OH/HO_2 measurements

11:05 *S. Dusanter*, Mines Douai + *P. Stevens*, Indiana Univ. (10 + 5 min)
Measurement of interferences associated with the detection of the hydroperoxy radical in the atmosphere using laser-induced fluorescence

11:20 *R. Woodward-Massey*, Univ of Leeds (10 + 5 min)
Laboratory and modelling studies of potential OH and HO_2 interferences in the Leeds FAGE instruments

11:35 *T. Elste*, DWD Hohenpeissenberg (10 + 5 min)
Individual studies of known or speculated interferences and calibration problems from long term experiences with CIMS technique

11:50 *F. Rohrer*, FZJ + *H. Berresheim*, NUIG (20 + 10 min)
Additional oxidation processes for SO_2 in a CIMS-OH instrument

Tuesday 24 March 2015

Session 2: Potential radical measurement artefacts (continued)

12:20 *A. Birdsall*, Univ. of Wisconsin (10 + 5 min)
Detection of ambient OH using a two-photon laser-induced fluorescence technique: calculated efficiency and preliminary experiments

12:35 Lunch

Session 3: Thematic discussions

Chair: *A. Wahner*

14:00 **Theme 1: Radical detection and calibration** Rapporteur: *J. Crawford*
Summary of previous day talks, conclusions, open questions,
research needs, future directions; new concepts?
a. OH techniques
b. HO_2 + RO_2 techniques

15:30 Coffee & Tea (30 min)

16:00 **Theme 2: Measurement artefacts** Rapporteur: *F. Keutsch*
Summary of talks, conclusions, open questions,
research needs, future directions; new concepts?
a. OH techniques
b. HO_2 + RO_2 techniques

17:45 End of session

19:00 Departure at JUFA (bus transfer to Burg Obbendorf)

19:30 Conference banquet at Burg Obbendorf (Niederzier)

Wednesday 23 March 2015

Session 3: Thematic discussions (continued)

Chair: *C. Plass-Dülmer*

09:00 **Summary: Measurement Techniques, Potential Artefacts and Themes 1 and 2**
Rapporteur's summaries of previous discussions
(Session 1, Session 2, Theme 1, Theme 2)

09:30 **Theme 3: Planning of future HOx - ROx intercomparisons** Rapporteur: *S. Brown*
Scientific goals, chemical environment + conditions,
possible participants, locations, time schedules, data handling

10:45 Coffee & Tea break (30 min)

11:15 **Theme 4: Future directions of atmospheric HOx - ROx chemistry research** Chair: *A. Hofzumahaus, D. Heard*

General research needs to make progress in atmospheric radical chemistry; strategies to advance chemical understanding; field vs. designer atmospheres; other topics... Rapporteur: *J. Crawford*

a. laboratory and chamber experiments

b. field experiments

12:30 Lunch

14:00 **Summary: Theme 3 + 4** Chair: *A. Hofzumahaus, D. Heard*

Rapporteur's summaries of morning discussions

14:30 **Future directions and plans**

Workshop report and possible publication (ACP, AMT, IGAC newsletter) to inform atmospheric science community, funding agencies etc.

15:00 Coffee & Tea

End of meeting