

Deliverable 2.3.4:

Guidance in spectroscopy techniques others than PAS and CES applied to AMC monitoring

EMRP
European Metrology Research Programme
■ Programme of EURAMET



The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

NPL
National Physical Laboratory

PTB
Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

Document information

Owner

Lead Name:	Geoffrey Barwood
Lead Organisation:	National Physical Laboratory
E-mail:	geoffrey.barwood@npl.co.uk

Context

Author(s):	<u>National Physical Laboratory (NPL):</u> Geoffrey Barwood, Anne Curtis, Guilong Huang, Christopher Edwards and Helen Margolis <u>Physikalisch-Technische Bundesanstalt (PTB):</u> Nils Lüttschwager, Olav Werhahn and Volker Ebert
Work Package:	2
Task:	
Deliverable Number	2.3.4
Deliverable Name	Guidance in spectroscopy techniques others than PAS and CES applied to AMC monitoring

Guide Information

What is it about?

This guide discusses advanced AMC detection methods that are alternatives to cavity enhanced (CES) and photo-acoustic spectroscopy (PAS). We discuss the circumstances under which these alternatives might be considered and compare them with NICE-OHMS which is being developed within WP2 of MetAMC and has the best reported concentration measurement sensitivities when only one known AMC is present.

Who is it for?

This guide is intended for researchers, scientists and engineers who need to understand the basis behind techniques for AMC detection that are alternatives to photo-acoustic and cavity enhanced spectroscopy (PAS and CES). In particular, it should help clean room operators understand different options available for AMC detection.

What is its purpose?

The purpose of the guide is to provide technical information for those who need to understand why a particular AMC detection method might be preferred. Issues to consider are whether the concentration of only one AMC (which has already been identified) needs to be measured with a low uncertainty, and whether AMC composition is largely unknown and could comprise several molecular species. Typically, the most sensitive commercial systems available are based on cavity ring-down technology and can detect selected AMCs at the ~ppb level; this can require signal averaging over timescales of up to a few minutes. For sensitivities approaching the ppt level or where several AMCs are present, alternative techniques are being developed and we discuss their advantages.

What is the prerequisite knowledge?

The guide assumes that the reader has some familiarity and experience in AMC detection using spectroscopic methods, as only a brief introduction will be given. Advanced high sensitivity methods such as NICE-OHMS will be described, together with femtosecond comb spectroscopy. Some prior knowledge of these methods will be assumed although references (including reviews) are provided. We recommend reading the report prepared for MetAMC deliverable 1.4.4 for a general introduction on laser spectroscopy applied to AMC monitoring.

Abbreviations

AMC	Airborne molecular contaminants
CRDS	Cavity ring-down spectroscopy
CES	Cavity enhanced spectroscopy
EOM	Electro-optic modulator
FSR	Free spectral range (of an optical cavity)
FTIR	Fourier transform infrared (spectroscopy)
HITRAN	<i>High-resolution transmission</i> molecular absorption database
NICE-OHMS	Noise-immune cavity enhanced optical heterodyne molecular spectroscopy
PAS	Photo-acoustic spectroscopy
PDH	Pound-Drever-Hall

CONTENTS

1	Introduction	7
2	Laser absorption spectroscopy	7
3	AMC detection using NICE-OHMS	11
4	Comb Spectroscopy	13
5	Summary	15
6	References	16

Foreword

This Guide gives a brief introduction to AMC detection using laser spectroscopy and contrasts well-established methods of CES (such as CDRS) and PAS with the latest techniques being reported in the scientific literature with potential for AMC monitoring, NICE-OHMS and spectroscopy based on femtosecond combs.

Acknowledgement

This work was funded by the UK Department for Business, Innovation and Skills, as part of the National Measurement System IRD programme and also by the European Metrology Research Programme (EMRP). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

1 Introduction

The MetAMC project proposal identified a clear demand from industry for continuous measurement and control of airborne molecular contamination (AMC). It was found that more detailed information on AMCs was required to optimise industrial microfabrication processes, especially when migrating to new techniques with smaller scale objectives. The primary source of airborne molecular contaminants in manufacturing environments are chemicals used in the manufacturing process. These molecules are often reactive and adsorb easily to surfaces, consequently being difficult to measure while being disruptive to the microfabrication process. Recent progress in quantitative molecular spectroscopy has brought the detection limits of typical contaminants to a level that meets the industrial need for AMC measurements. In particular, laser-based techniques have reached such technical maturity that their use in industrial environment has become realistic.

In this guide, we outline different measurement methods available for trace AMC detection, other than those based on cavity enhanced (CES) and photo-acoustic spectroscopy (PAS) which are discussed in the report for MetAMC deliverable 1.4.4. We outline the different alternative methods and suggest references for further reading. We also suggest factors to consider when selecting one method over another in particular measurement situations. In particular, we discuss the problem of AMC detection in the presence of other molecular absorbers such as CO₂ and water. Levels of these gases will ultimately limit the uncertainty achievable with any spectroscopy-based instrument.

2 Laser absorption spectroscopy

To explain the advantages of advanced spectroscopic techniques, we give a brief introduction to basic laser linear absorption spectroscopy. A simple laser spectroscopy experimental arrangement is shown in figure 1. In this system, light from a diode laser at 1527 nm is scanned in frequency by tuning either the operating temperature or current. The light is transmitted through a linear absorption cell filled with the gas being analysed (in this case, ammonia). The change in linear absorption (i.e. the absorbance) with frequency is observed, as shown.

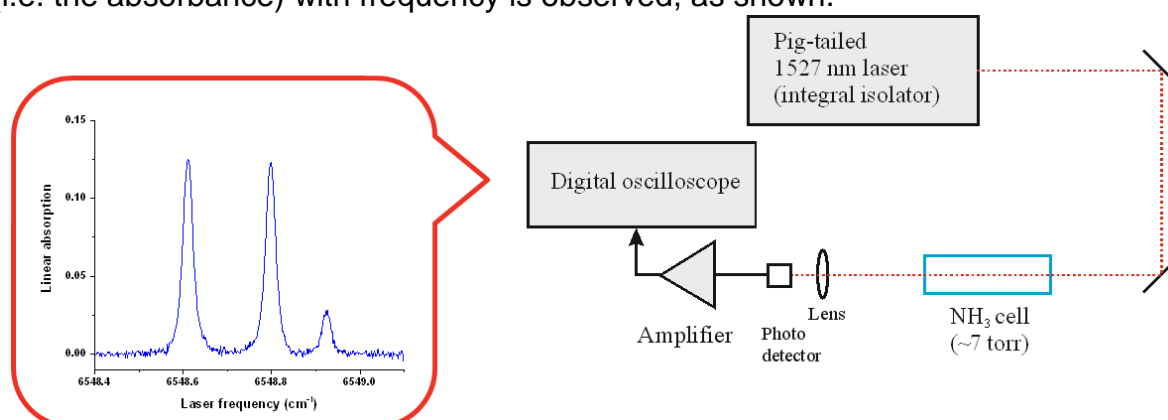


Figure 1: Experimental arrangement to measure the linear absorption through a gas cell as a function of laser frequency.

The transmitted laser intensity (I) through the cell of length L is given by the well-known Beer law which connects the light attenuation to the concentration of the light-absorbing gas:

$$I = I_0 \exp(-N\sigma L)$$

$$\rightarrow \ln\left(\frac{I_0}{I}\right) \equiv A = N\sigma L$$

Here, N is the number of molecules per unit volume, I_0 is the incident light intensity, σ is the molecule specific absorption cross section which is a function of laser frequency and A is the absorbance. The integrated cross section over all frequencies for a single absorption line is termed the line strength (S); this parameter is tabulated for many smaller molecules in a publicly accessible database, HITRAN (www.hitran.org) [Rothman12].

As a specific example, consider the case where the shape of the analysed absorption line is dominated by pressure broadening (this is often the case for gas samples close to atmospheric pressure); in this case the line-shape will approximate to a Lorentzian and we can write:

$$\sigma = \frac{S\gamma}{\pi(\gamma^2 + (\nu - \nu_0)^2)}$$

Note that, in the above equation, the integrated cross section over all frequencies for

the associated absorption line is given by $S = \int_0^{\infty} \sigma d\nu$. The transition half-width at half

maximum is denoted by γ and ν_0 is the line centre frequency. The cross-section at line centre (where we observe the peak absorption) is given by:

$$\sigma(\nu_0) = \frac{S}{\pi\gamma}$$

The relationship between cross section at line centre and line-strength will depend on the assumed profile; for a discussion of the different profiles possible, see [Wang14]. Using the HITRAN tabulated parameters allows us to determine concentration (N) from the measured linear absorption, assuming a specific model for the spectral profile. In the above example (for a Lorentzian line profile) we find that:

$$N = \frac{A(\nu_0)}{\sigma(\nu_0)L} = A(\nu_0) \frac{\pi\gamma}{SL}$$

Thus, laser absorption spectroscopy provides a straightforward method to determine concentration but has a number of potential disadvantages:

1. Reliance on the values given in HITRAN. The concentrations obtained using laser absorption spectroscopy can be determined from standard gas mixtures to check tabulated parameters. Also, results from laser absorption spectroscopy can be compared to results from (for example) PAS.
2. The method (as shown in figure 1) has limited sensitivity. The effective optical path length can be significantly increased by placing the sample inside an optical enhancement cavity of optical finesse F . This increases the effective path length by a factor of $2F/\pi$; this factor can be many thousands for a high finesse cavity. A commercial implementation of this idea uses cavity ring-down spectroscopy (CRDS). This method determines linear absorption from the change in cavity ring-down time observed with the laser tuned to absorption line-centre and then away from line-centre.
3. Laser availability. Strong linear absorptions are observed at telecom wavelengths (~1330 nm or 1550 nm, where the technology is widely available, mature and inexpensive) in only a limited number of AMCs. However, the demand for gas sensing means that lasers are now also manufactured specifically for this market. Also, quantum cascade lasers are now available in the 3-10 μm region where there are many strong molecular absorption lines.
4. Availability of well resolved absorption features. This will be the case for small molecules that do not have a complicated rotational-vibrational spectrum. However, with larger AMCs, the spectral lines start to overlap, forming an absorption continuum.
5. Selection of a line that is not too close to a line of another common AMC (water, for example). In most cases, the laser can be tuned to a line that is clear of absorptions arising from another AMC, even if the absorption bands overlap. With care, it is possible to use overlapping absorption bands to design an instrument capable of detecting two gas species [Pogány15]. However, often devices are specified to detect a particular AMC in dry nitrogen.
6. Ability to detect only one molecular contaminant with one system. Whilst there might be an overlap of absorption bands that allow simultaneous detection of two AMCs with a single frequency laser, this is rare.

NICE-OHMS alleviates point (2) through the use of a high-finesse cavity and enhances the signal-to-noise level via a special measurement technique to suppress noise while comb spectroscopy alleviates point (6) by using frequency combs which combine the benefits of laser light sources with a broad spectral coverage (see sections 3 and 4).

To illustrate the problem of gas sensing in a mixture of different AMCs, consider figure 2, which shows (as a logarithmic plot) the linear absorption features due to water and CO₂ that are in same spectral region as ammonia, which we are targeting. Here, we see that if the laser tuning is not carefully adjusted, linear absorption due to the ambient humidity (typically a relative humidity of 50%) can be much larger than that due to ammonia. Also, the absorption due to typical levels of 400 ppm of CO₂

can be comparable to that arising from 1 ppm of ammonia. However, by careful selection of the laser frequency, ammonia lines can be observed that are much stronger than the water and CO₂ absorptions.

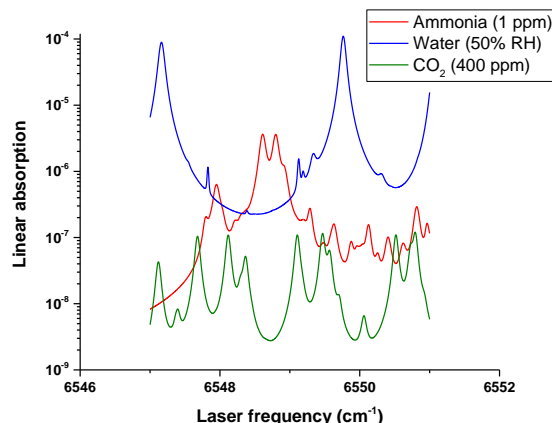


Figure 2: Plot of the linear absorption of ammonia, water and CO₂ at ~6549 cm⁻¹ (1527 nm) illustrating the problem of “cross-talk” when designing a system to detect trace levels of ammonia.

The potential problem with the detection of gas concentration of larger molecules is illustrated in figure 3. Here, we show a plot of the linear absorption of methanol at ~1390 nm. This plot shows both a few narrow features but also a slowly varying background that arises from unresolved vibrational-rotational structure. The background linear absorption will limit the achievable optical cavity finesse and so reduce the sensitivity of spectroscopic methods using single frequency laser sources.

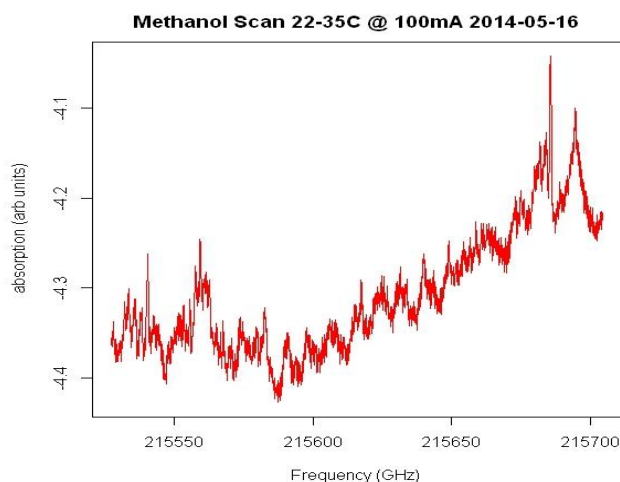


Figure 3: Observed linear absorption spectrum of methanol at ~1390 nm. This illustrates the problem of trace detection of larger molecules where rotational-vibrational bands can overlap. However, some well-resolved features are also observed.

3 AMC detection using NICE-OHMS

The highest reported sensitivity of all laser spectroscopy techniques for AMC detection uses a method first developed at JILA [Ye98] that combines the advantages of increased sensitivity via cavity enhancement with signal recovery using FM techniques [Hall81] to give shot noise-limited signal recovery. The technique is termed “noise immune cavity enhanced optical heterodyne molecular spectroscopy” and hence given the acronym NICE-OHMS. The development of a NICE-OHMS system at NPL for the trace detection of ammonia and formaldehyde was part of the MetAMC project. JILA [Ye98] reported a detection sensitivity of 10^{-14} cm⁻¹ using a 1064 nm laser in a 47-cm cavity (finesse = 100,000) for a 1-s averaging time. The technique was later used for oxygen detection [Gianfrani99] at 776 nm and water [Dinesan14] at 1390 nm. However, the most extensive NICE-OHMS studies have probably been undertaken by a group at Umeå University in Sweden [for example, see Silander15]. A recent review of cavity-enhanced spectroscopy has been published [Gagliardi14] covering, for example, cavity ring-down spectroscopy and NICE-OHMS (chapter 6). Commercial ring-down spectrometers claim 600 ppt (1 σ) for a 2 s averaging time¹ for the measurement of acetylene; other manufactures² offer similarly low sensitivities for a small number of other AMCs. This contrasts with the detection sensitivity of 5×10^{-13} (0.5 ppt) at 1 s reported at JILA for C₂H₂, C₂HD, and CO₂.

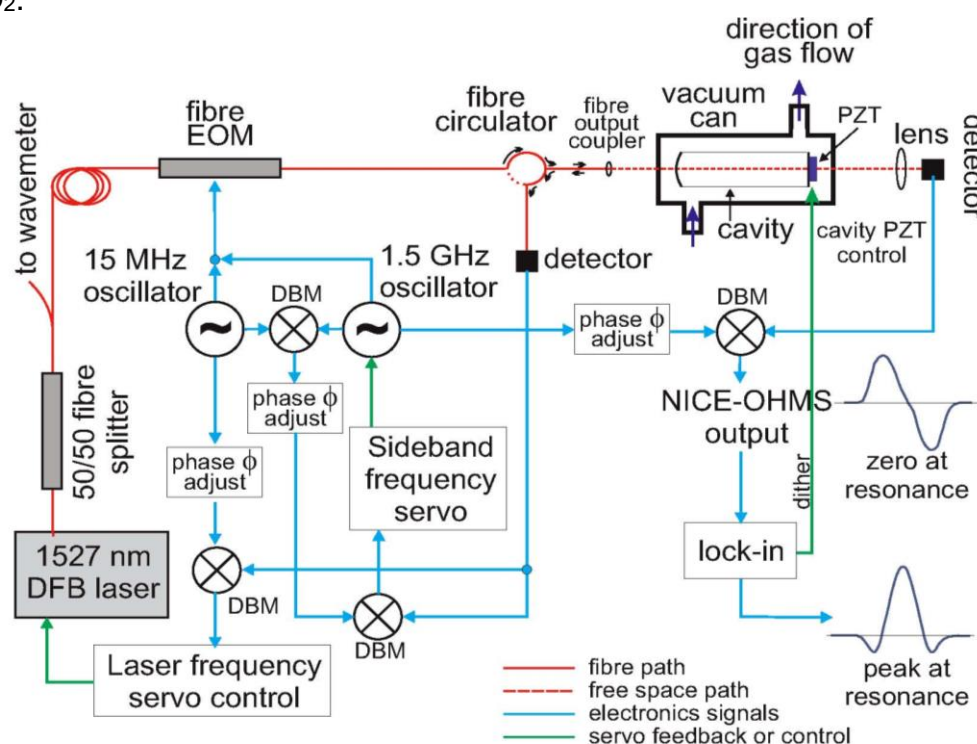


Figure 4: Overall schematic of the NPL NICE-OHMS system

¹ See, for example, <https://picarro.app.box.com/s/hflyqti3iz3xsgi0wi8k9ifkk2b325t6>

² See, for example, <http://www.tigeroptics.com/app/tigeroptics/>; other manufacturers may offer similar specifications.

The system developed within WP2 comprises prototype analogue electronics, lasers at 1527 nm and 1531 nm (for ammonia), phase modulator and an optical cavity. A third laser at 1512 nm (for formaldehyde detection) is also available. This system is currently undergoing evaluation within the final stage of MetAMC. However, the system will need further development to produce a user-friendly package for commercial exploitation.

A schematic of the NICE-OHMS system being developed at NPL is shown in figure 4. The EOM modulates the laser output at two frequencies; the lower frequency (~ 15 MHz) is used for locking of the laser to a cavity resonance using Pound-Drever-Hall servoing [Drever83; Hall81] and a second modulation is at the cavity free spectral range (FSR) frequency of ~ 1500 MHz. A servo is used to keep this frequency centred on the cavity FSR [DeVoe84]. With both servos active, the laser carrier and 1500 MHz sidebands all resonate within the cavity. The signal transmitted through the cavity is demodulated at 1500 MHz and a Pound-Drever-Hall (PDH) output signal observed [Drever83; Hall81]. A modulation of the cavity piezo at a frequency of a few hundred Hz can additionally be used, as shown in figure 4. Detecting this modulated signal with a phase sensitive detector gives an output that is the first derivative of the PDH profile; this has a maximum output rather than a zero crossing at line centre which can be more convenient for gas sensing applications.

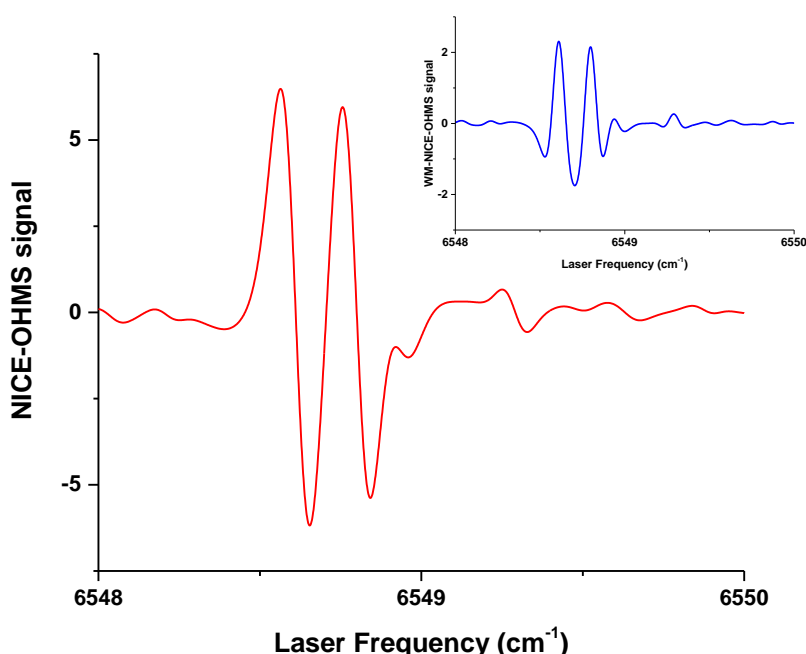


Figure 5: Calculated NICE-OHMS at ~ 1527 nm (see figure 1 for the linear absorption profile) from the experimental arrangement of figure 4. A WM-NICE-OHMS signal (see text) can also be obtained and this is shown in the inset figure.

In figure 5, we show the calculated NICE-OHMS signal for ammonia in the same spectral region where the linear absorption profile is observed in figure 1. The main plot (in red) shows the NICE-OHMS profile that has a zero signal at line centre; this profile is the same as the PDH profile for a single pass system reported in [Hall81]. In order to obtain a signal with a maximum output at line centre, the cavity length (figure

4) can be modulated in length (e.g. at a rate of ~500 Hz). This modulates the laser frequency (wavelength) and hence the NICE-OHMS feature; the resulting AC signal can be recovered in a phase sensitive detector (figure 4). The output from the phase sensitive detector is termed the wavelength modulated NICE-OHMS signal (WM-NICE-OHMS) and the expected profile is shown in the inset plot (blue) of figure 5. The size of the peak WM-NICE-OHMS signal is proportional to AMC concentration; the proportionality constant will require individual instrument calibration.

Implementation of NICE-OHMS is primarily confined to research laboratories and is not easy to use for AMC detection in clean room environments. Actually, MetAMC is the first attempt to our knowledge, to implement this concept for an AMC of interest to the clean-room community (i.e. ammonia). As a follow-on activity to MetAMC, NICE-OHMS will need to be developed into a robust turn-key system.

Commercial use of NICE-OHMS will require software development (also ideally replacing analogue with digital electronics) that will allow a NICE-OHMS signal size to be readily interpreted as a concentration measurement. This instrument will require periodic recalibration against gas reference standards to ensure a traceable measurement. The optics package will also require development to provide a robust optical alignment that will be stable over years, regardless of temperature fluctuations (e.g. $\pm 5^\circ\text{C}$) and transportation to different laboratories.

4 Comb Spectroscopy

There are a wide variety of applications where trace gas detection of multiple species is required and where it is not necessarily known which gases are present. Here, femtosecond combs offer a unique advantage since the short pulse lengths result in a wide spectral coverage. As is well-documented, for example see [Diddams10], the output consists of millions of discrete output frequencies, with each frequency separated by the frequency of the repetition rate. The frequency of each comb mode (f) is given by the straightforward formula (figure 6):

$$f = f_0 + n f_{rep}$$

Here, f_0 is termed the carrier envelope offset frequency, f_{rep} is the repetition rate and n is a large integer.

The output can span a full octave, for example from 1 μm to 2 μm and this spectral region includes strong absorption bands of a number of molecules listed in HITRAN [Rothman12]. Additionally, work is underway to demonstrate frequency combs operating in the infrared using difference frequency generation or an optical parametric oscillator, to overlap with stronger molecular absorption lines [Nugent-Glandorf15; Ruehl12]. A comprehensive review of comb spectroscopy is given in [Margolis12].

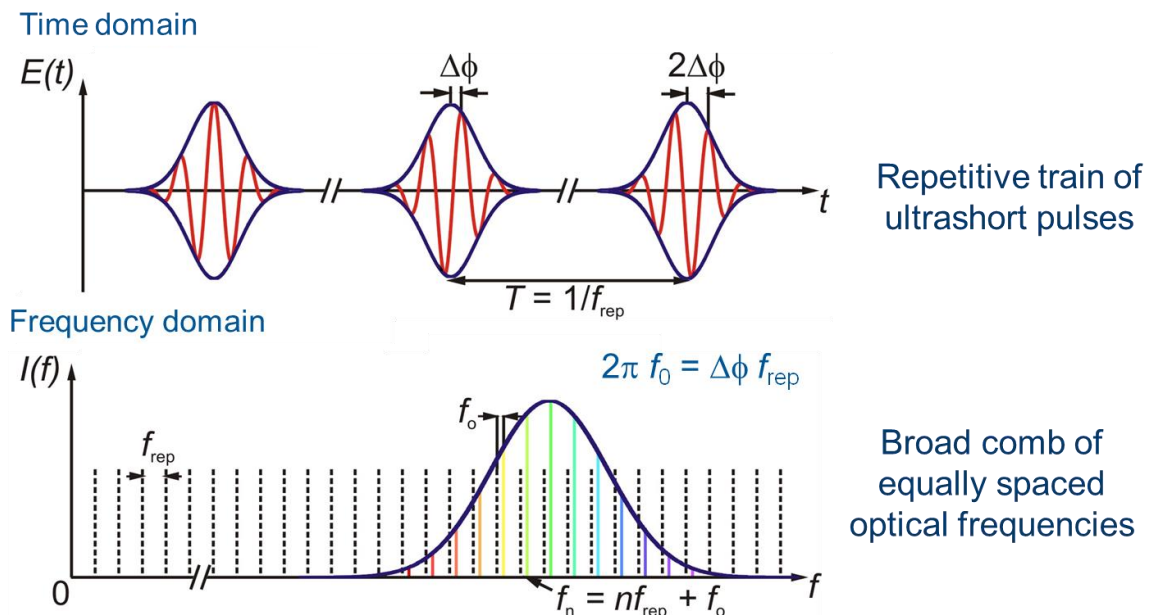


Figure 6: Output from a femtosecond comb in the time (upper plot) and frequency (lower plot) domains. In the frequency domain, the frequency f_n of each mode is given by $f_n = nf_{\text{rep}} + f_0$ (see text)

Apart from AMC detection in industrial environments, applications of comb spectroscopy also include counter-terrorism (detection of explosives or chemical warfare agents), medical diagnostics (i.e. breath analysis for disease diagnosis) and atmospheric environmental monitoring (e.g. ozone, CO, NO, CO₂ and methane).

While techniques such as CRDS, PAS or NICE-OHMS can enable very high sensitivity at high detection speed, the spectral coverage is usually very small, such that usually only a single AMC can be detected with one spectrometer. FTIR spectrometers have a large spectral coverage which enables simultaneous detection of several AMCs but the sensitivity and detection speed are not satisfactory for clean room monitoring purposes. Comb spectrometers combine the advantages of laser spectroscopy and FTIR spectroscopy and introduce the high accuracy inherent to frequency combs. The advantages of femtosecond combs include:

- Large spectral coverage (the comb spectrum spans hundreds of nanometres; the pulsed output enables efficient nonlinear frequency conversion)
- High spectral resolution (comb spectrum consists of narrow spectral lines)
- Rapid data acquisition time (intrinsically parallel detection capability; no need to scan the laser)
- Comb line positions and spacing known to high accuracy (intrinsic frequency calibration)

Rapid recording of broadband spectra has been demonstrated using dual comb spectroscopy [Coddington08, Bernhardt09 and Znakovskaya14]. Additionally, high sensitivity is possible through the development of high-finesse broadband low-dispersion enhancement cavities. For example, with application to breath analysis,

measurements of isotope ratios of CO₂, together with CO and NH₃ detection in the presence of high concentrations of H₂O was demonstrated by [Thorpe07]. A novel combination of comb spectroscopy and NICE-OHMS was recently presented that combines the advantages of both techniques [Khodabakhsh14]. The authors report sensitivities using their technique (which they term “noise immune cavity enhanced optical frequency comb spectroscopy” or NICE-OFCS) of $4.3 \times 10^{-10} \text{ cm}^{-1}\text{Hz}^{-1/2}$ for the overtone CO₂ band at 1575 nm.

However, comb spectroscopy is currently not easy to implement for on-line AMC detection in clean rooms because of cost and complexity. Use of femtosecond combs is a highly-skilled operation and is largely confined to use in research laboratories although work is underway to adapt combs to operation in different environments (for example, in space³). For on-line AMC detection, a turn-key robust comb system will need to be developed that can be marketed at a much lower cost than current systems.

5 Summary

In this guide, we have outlined advanced AMC detection methods that a user could consider as an alternative to CES and PAS technology. In selecting a methodology, a number of factors need to be considered:

- Whether the AMC is a large complex molecule with a resulting complex rotational-vibrational spectrum. A larger molecular structure might preclude the use of a spectroscopic technique; small molecules will give the best resolved spectral lines.
- Whether very low concentrations (e.g. ppt levels) are being measured. This might indicate that a novel method such as NICE-OHMS should be considered
- Whether the identity and number of the AMCs present in the clean room is known. If this is not the case, then spectroscopy with high spectral coverage (e.g. comb spectroscopy) might be required.
- Method complexity. Unusual measurement situations such as ppt gas detection or detection of many AMCs simultaneously will favour a choice of novel techniques that are necessarily expensive and complicated to implement.

3 For example, see a recent press release <http://www.menlosystems.com/events/news-press-releases/view/2343> from Menlo Systems

6 References

- Bernhardt09 B Bernhardt, A Ozawa, P Jacquet, M Jacquety, Y Kobayashi, T Udem, R Holzwarth, G Guelachvili, TW Hänsch and N Picqué, “Cavity-enhanced dual-comb spectroscopy”, *Nature Photon* **4**, 55 (2009)
- Coddington08 I Coddington, WC Swann, and NR Newbury “Coherent Multiheterodyne Spectroscopy Using Stabilized Optical Frequency Combs” *Phys Rev Lett* **100**, 013902 (2008)
- DeVoe84 RG DeVoe and RG Brewer, “Laser frequency division and stabilisation”, *Phys Rev A*, **30**, 2827 (1984)
- Diddams10 SA Diddams, “The evolving optical frequency comb”, *J. Opt. Soc. Am. B*, **27**, 51 (2010)
- Dinesan14 H Dinesan, E Fasci, A Castrillo, and L Gianfrani, “Absolute frequency stabilization of an extended-cavity diode laser by means of noise-immune cavity-enhanced optical heterodyne molecular spectroscopy” *Opt Lett* **39**, 2198 (2014)
- Drever83 RWP Drever, JL Hall, FV Kowalski, J Hough, GM Ford, AJ Munley and H Ward, “Laser phase and frequency stabilisation using an optical resonator” *Appl Phys B* **31**, 97 (1983)
- Gianfrani99 L Gianfrani, RW Fox and L Hollberg, “Cavity-enhanced absorption spectroscopy of molecular oxygen” *J. Opt. Soc. Am. B* **16**, 2247 (1999)
- Gagliardi14 G Gagliardi and H-P Looock (editors), “Cavity-Enhanced Spectroscopy and Sensing”, *Springer Series in Optical Sciences* (2014); see <http://link.springer.com/book/10.1007/978-3-642-40003-2>
- Hall81 JL Hall, J Hollberg, T Baer and HG Robinson, “Optical heterodyne saturation spectroscopy” *Appl Phys Lett* **39**, 680 (1981)
- Khodabakhsh14 A Khodabakhsh, C A Alrahman, and A Foltynowicz, “Noise-immune cavity-enhanced optical frequency comb spectroscopy”, *Opt Lett* **39**, 5034 (2014)
- Margolis12 HS Margolis, “Spectroscopic applications of femtosecond optical frequency combs” *Chem. Soc. Rev.*, **41**, 5174 (2012)
- Nugent-Glandorf15 L Nugent-Glandorf, FR Giorgetta, Scott A. Diddam, “Open-air, broad-bandwidth trace gas sensing with a mid-infrared optical frequency comb” *Appl. Phys. B* **119** 327 (2015)
- Pogány15 A Pogány, S Wagner, O Werhahn, and V Ebert, “Development and Metrological Characterization of a Tunable Diode Laser Absorption Spectroscopy (TDLAS) Spectrometer for Simultaneous Absolute Measurement of Carbon Dioxide and Water Vapor” *Applied Spectroscopy* **69**, 257 (2015).
- Rothman12 LS Rothman *et al*, “The HITRAN2012 molecular spectroscopic database” *J. of Quantitative Spectroscopy & Radiative Transfer* **130** 4 (2013)
- Ruehl12 A Ruehl, A Gambetta, I Hartl, ME Fermann, KSE Eikema, and M Marangoni, “Widely-tunable mid-infrared frequency comb source

- based on difference frequency generation" Opt Lett **37**, 2232 (2012)
- Silander15 I Silander, T Hausmaninger, W Ma, P Ehlers, and O Axner, "Doppler-broadened noise-immune cavity-enhanced optical heterodyne molecular spectrometry down to $4 \times 10^{-13} \text{ cm}^{-1} \text{ Hz}^{-1/2}$: implementation of a 50,000 finesse cavity" Opt Lett **40**, 2004 (2015)
- Thorpe07 MJ Thorpe, D Balslev-Clausen, MS Kirchner, and J Ye, "Cavity-enhanced optical frequency comb spectroscopy: application to human breath analysis" Opt Express **16**, 2387 (2007)
- Wang14 Junyang Wang, Patrick Ehlers, Isak Silander, and Ove Axner, "On the accuracy of the assessment of molecular concentration and spectroscopic parameters by frequency modulation spectrometry and NICE-OHMS", J Quant Spect and Rad Transf., **136** 28 (2014)
- Ye98 J Ye, L-S Ma, and JL Hall, "Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy" J. Opt. Soc. Am. B **15**, (1998)
- Znakovskaya14 I Znakovskaya, E Fill, N Forget, P Tournois M Seidel, O Pronin F. Krausz and A. Apolonski, "Dual frequency comb spectroscopy with a single laser" Opt Lett **39**, 5471 (2014)