

**AMC monitoring by laser spectroscopy:
Introduction and Recommendations**

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Scope

This document shall serve as an introduction to optical detection methods for AMC monitoring and shall discuss their strengths and weaknesses. It shall thus facilitate the selection of a suitable detection method by clean room operators and furthermore provide recommendations on the usage of these methods. Specifically, commercially available laser spectroscopic analysers based on optical cavity enhancement spectroscopy and photoacoustic spectroscopy will be discussed.

Abbreviations

(OA)-ICOS	(Off-axis) integrated cavity output spectroscopy
AMC	Airborne molecular contamination
CEAS	Cavity-enhanced absorption spectroscopy
CRDS	Cavity ring-down spectroscopy
DI	Designated institute
GC	Gas chromatography
HITRAN	High-resolution transmission molecular absorption database
IMS	Ion mobility spectrometry
ITRS	International Technology Roadmap for Semiconductors
NDIR	Non-dispersive infrared sensor
NMI	National metrology institute
PAS	Photoacoustic spectroscopy
ppb	Parts-per-billion, used here synonymous for nmol mol^{-1} as a measure of amount fraction
TDLAS	Tunable diode laser absorption spectroscopy
UV	Ultra violet (light)
VOC	Volatile organic compound

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1 Introduction

Airborne molecular contamination (AMC) is a collective term for chemical contaminants which can be harmful to a variety of processes running in clean rooms. AMC covers a wide range of different chemical compounds like inorganic acids, inorganic bases, or volatile organic compounds (VOCs), which can harm manufacturing processes for example by corrosion, or the formation of haze on optics. Yield loss and low product quality can follow from elevated AMC levels in clean room air, such that sometimes high efforts to control and monitor AMC are profitable. Control of AMC may be accomplished by the use of specialized filters or use of mini-environments. Monitoring the clean room air quality is necessary to identify source of AMC and ultimately eliminate these sources, as well as assessing whether AMC control measures meet the required performance. A well controlled and well characterized environment also helps to more easily reproduce processes from site to site and to push boundaries to smaller scale fabrication.

Several monitoring techniques for clean room air exist, the most interesting ones probably being the “real-time” or “online” techniques which enable immediate corrective action in case of a contamination. Here, we consider a technique to be online or in real-time when it provides measurement results at least every few minutes. This excludes techniques which trap the AMC that shall be monitored (e.g. impingers) over time for later offline analysis, for example by ion chromatography or mass spectrometry. Online techniques may be based on chemiluminescence, UV fluorescence, cavity-ring-down spectroscopy, or ion mobility spectrometry, to name a few common techniques.

Depending on the user requirements, one of these techniques may be better suited than the others. In this Guide, we focus on techniques based on laser spectroscopy (such as cavity-ring-down spectroscopy). We want to shortly introduce these techniques to readers which are not familiar with laser spectroscopy and to explain why it may be preferred over other techniques. Also, we provide recommendations what should be considered when purchasing and running a laser spectroscopy-based analyser.

The outline of this Guide is as follows. We start with a description of the measurement capabilities of laser spectroscopic analysers, followed by a short and very basic theoretical description of laser absorption spectroscopy and three common and more advanced spectroscopic detection techniques: Cavity-enhanced absorption spectroscopy (CEAS), cavity-ring-down spectroscopy (CRDS) and photoacoustic spectroscopy (PAS). We believe that a basic understanding of the main concepts will greatly enhance the reader’s ability to judge whether optical detection is a good option for his measurement needs and also helps to make better use of

spectroscopic devices. Based on these discussions we conclude recommendations what to consider when purchasing and using a spectroscopic instrument.

2 What laser-spectroscopic analysers can and cannot do

AMC monitoring using laser spectroscopy provides many features which are sought by the user: Fast measurements, high sensitivity and selectivity, high dynamic range, accuracy in the low percent-range, low cost of ownership and little maintenance (we discuss how these benefits come about later in the text). Special sample preparation is not required and the AMC concentration is measured from air samples without in between steps like catalytic conversion (e.g. chemiluminescence measurements of ammonia) or mixture with a doped carrier gas (ion mobility spectrometry) which lowers the probability of malfunction and erroneous measurements. Even sampling-free measurements of air not contained in a gas cell using an open-path configuration (Miller et al., 2014) are possible. In some cases, absolute laser-spectroscopic measurements can be done which do not require the calibration of the analyser using a calibration gas (calibration-free operation). Easy-to-operate, mobile spectrometers are now widely available.

Besides all these positive properties, laser spectroscopy is not the universal solution to AMC monitoring. The analysers we discuss here work best only for small molecules composed of up to about 5 atoms, which excludes most VOCs and other larger AMCs. What is left are the small (but important) typical AMCs like ammonia (NH_3), hydrogen chloride (HCl) or hydrogen fluoride (HF), which are well suited for laser spectroscopic detection.

Laser spectrometers often detect only a single species. The price for multi-species analysers is considerably higher because they include several lasers (lasers for gas sensing can be expensive). Laser spectroscopy is technically more demanding than, for example, NDIR, chemiluminescence, or UV fluorescence, and the price for a spectroscopic analyser may be in the range of several 10k EUR, which can be too high for a point-of-use device.

To provide an orientation on the *approximate* performance of laser-spectroscopic analysers, we summarize specifications which were collected from overall 18 commercial instruments in Table 1. (Note that response time and accuracy of HCl and HF analysers was often not specified.)

Table 1: Typical specifications of commercial laser-spectroscopic analysers, currently available on the market (based on a web-search yielding 18 instruments)

AMC	ammonia	hydrogen chloride	hydrogen fluoride
	NH ₃	HCl	HF
detection limit / ppb	0.1–10	0.1–2.5	0.1–1
dynamic range	1:10000	1:10000	1:10000
time resolution / s	<1–5	1–5	1–5
response time / min	0.2–5	n/a	n/a
accuracy / %	1–10	n/a	n/a
dimensions / cm ³	30 x 40 x 60	30 x 40 x 60	30 x 40 x 60

3 Measurement principle of laser absorption spectroscopy

3.1 What is measured?

The laser-based analysers we are discussing in this Guide measure, in various ways, how much infrared light from a laser is absorbed when the light passes through a gas sample. The light that is passed through the gas sample excites gas molecules to vibrate if the light frequency (wavelength) matches very precisely one of the molecule-specific vibration frequencies. Light with a frequency that matches a molecular vibration frequency is partly absorbed, depending on the concentration of the excited species, and the resulting light attenuation can be measured. Figure 1 shows the schematic of a basic laser absorption spectrometer which consists of a laser, a gas cell that holds the gas sample and provides stable measurement conditions, a photodetector which measures the intensity of the laser light that passes through the sample, and electronics to analyse the signal generated by the photodetector, e.g. an os-

cilloscope. The laser is repeatedly scanned in a small wavelength interval and absorption of light is seen as a drop in the detector signal. Since the laser wavelength can be scanned very rapidly, measurements with a time resolution well below a second are possible.

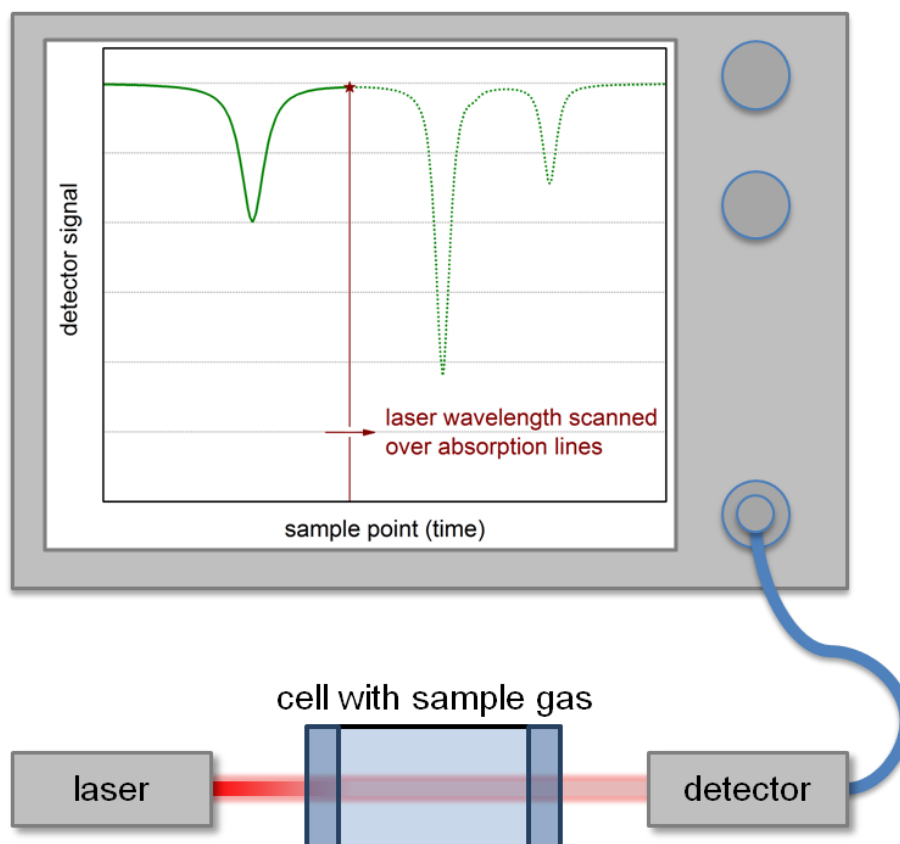


Figure 1: Illustration of a laser absorption experiment.

Typically, light absorption is measured in terms of the absorbance, which is the logarithm of the ratio of the light intensity before (I_0) and after it passes through the gas sample (I):

$$A = \ln(I_0/I).$$

Figure 2 shows how a laser absorbance spectrum of air could look like under typical measurement conditions if it would contain a trace of hydrogen fluoride. One sees different peaks, commonly called *absorption lines*, each belonging to a particular molecular vibration excitation from one of the species present in the sampled air. Most of the absorption lines belong to water from the air humidity, but the peak highlighted in blue is caused by the excitation of hydrogen fluoride molecules. The peak absorbance of the HF line is proportional to the amount of HF in the measured gas sample over a wide range of concentrations (which is the basis for the high dynamic range of laser spectrometry). A basic analyzer for HF could thus be realized by using a laser which is tuned to an emission wavelength of about 2475.88 nm (4038.9 cm^{-1}),

the peak centre of the HF absorption line in our example, measuring the absorbance at this single wavelength and calibrating against known HF concentrations. However, more often the laser will be scanned repeatedly in a small wavelength window to measure not only the height but also the shape of the absorption line. This allows a more sophisticated data evaluation that will be more robust to potential cross interference which may result from overlapping absorption lines.

Through their use in telecommunications, tunable diode lasers have reached particular technical maturity and are often employed as light sources, not least because their emission wavelength can conveniently be controlled by varying the laser temperature and/or supply current. Spectroscopy which uses a diode laser as light source is often termed TDLAS, for tunable diode laser absorption spectroscopy. While TDLAS is simple, robust and well developed, detection limits are commonly in the range of several parts-per-million (ppm) which is not sensitive enough for use in clean room AMC monitoring.

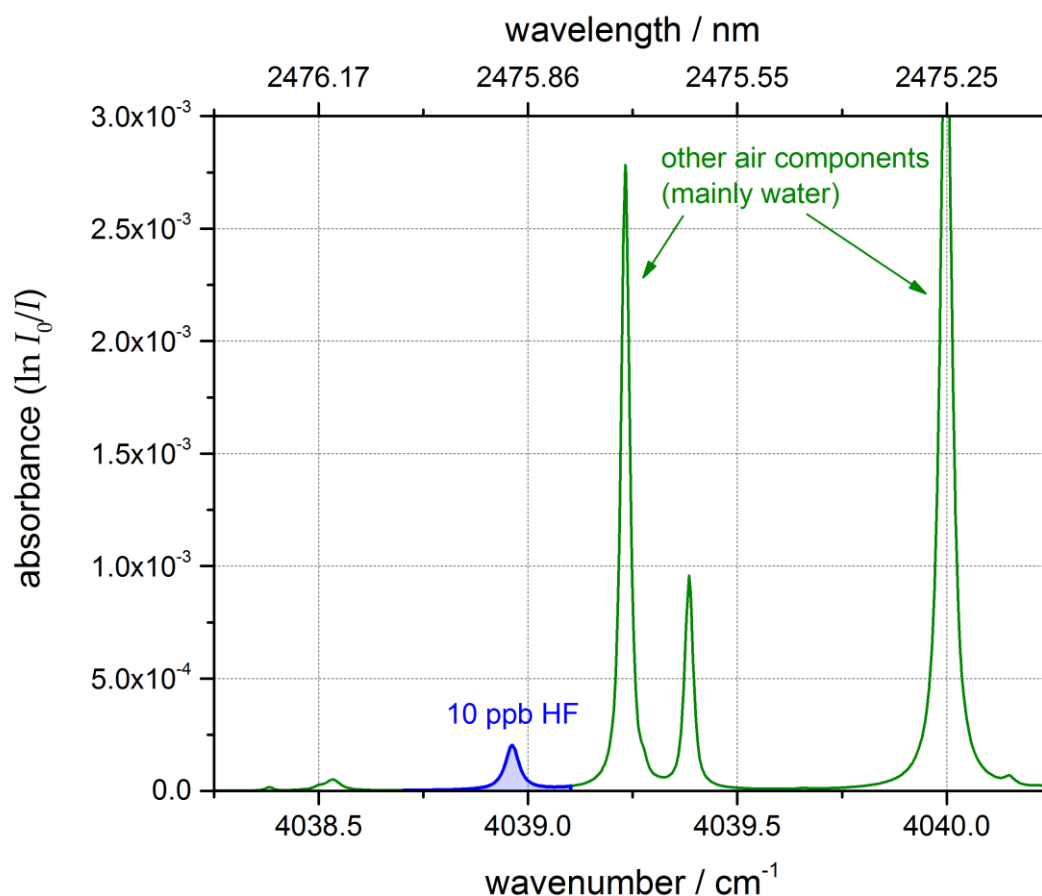


Figure 2: Absorption spectrum of hydrogen fluoride in air (HITRAN simulation, see below)

3.2 Cavity-enhancement and photoacoustic detection

The sensitivity of a laser absorption spectrometer can be improved by increasing the *absorption path length*, that is, the distance the laser light travels through the absorbing medium. A longer absorption path length leads to stronger absorbance and a better signal-to-noise ratio.

An effective way to enhance the absorption path length is the use of optical resonators where the light is reflected back and forth between two or more highly reflective mirrors. Under certain conditions, light can effectively travel distances up to several kilometres between the mirrors and pass through a gas sample contained between the mirrors many times. At each round trip, a small portion of the light is transmitted through the mirrors and can be measured with a photodetector as a function of wavelength. This allows to record spectra similar to an ordinary TDLAS experiment but with much enhanced absorption path length and thus sensitivity. This technique is called cavity-enhanced absorption spectroscopy (CEAS) or sometimes integrated cavity output spectroscopy (ICOS). The variant “off-axis ICOS” (OA-ICOS) was reported to be particularly robust and suitable for field measurements (Sayres et al., 2009).

Cavity-ring-down spectroscopy (CRDS) is the technically somewhat more complex predecessor of CEAS. In CRDS one measures the time it takes for the light in the cavity to vanish after the laser is abruptly switched off (Berden et al., 2000). This is done with a fast photodetector that measures the intensity decay of light that leaks out through the output (back) mirror of the cavity. The so-called ring-down time is retrieved from fitting an exponential decay to the photodetector signal. It depends (upon other things) on the concentration of absorbing gas in the cavity. CRDS allows performing absolute measurements, which means that the measured signal is translated to compound amount fraction (concentration) using tabulated absorption line parameters and not a calibration with reference gas (Nwaboh et al., 2012; Werhahn, 2011). This can be advantageous for reactive and/or sticky molecules (see below).

Photoacoustic spectroscopy (PAS) is another spectroscopic technique with enhanced sensitivity compared to plain laser absorption measurements. In PAS, the light absorption is not quantified by the attenuation of light after it travelled through a gas sample, but the effect of the laser light on the gas sample itself is probed. When light is absorbed by the gas, the absorbed energy is partly transferred to heat such that the pressure of the gas sample rises if it is contained in a gas cell. If the laser light is modulated, e.g. by repeatedly switching the laser on and off, periodic pressure fluctuations can be measured as sound using a microphone. This technique stands out by granting relatively high sensitivity at low complexity and costs. The optical path length does not limit PAS measurements such that very small systems are possible (Bauer et al., 2014). A disadvantage of PAS is the higher susceptibility to cross-interference because of changes in the efficiency of heat dissipation if the gas matrix changes,

which determines how much laser light is translated into an acoustic signal (Gillis et al., 2010; Kosterev et al., 2006). Also, flow rates cannot be as high as in case of absorption-based techniques because the microphone starts to pick up flow noise, and PAS is generally sensitive to acoustic background noise and vibrations (Bozóki et al., 2011).

Although a recent comparison of research grade spectrometers concludes a higher sensitivity of CEAS and CRDS (both comparable) compared to PAS (Hodgkinson and Tatam, 2013), specifications of current commercial instruments do not reflect this finding.

3.3 Interpretation of absorption spectra

So far, we put little focus on the actual absorption spectra which are probed by laser spectrometers. In fact, the absorption spectrum shown in Figure 2 bares much resemblance with spectra obtained from a GC or IMS analysis. However, there are quite fundamental differences: While in GC or IMS analysis, the position and shape of the peaks depend on the instruments themselves, the position, line shape, and intrinsic intensity (so-called *line strength*, the intensity per unit concentration) of absorption lines are universal, molecule specific properties, which do not depend on the measurement instrument. Absorption line parameters can be collected in a database and be used to identify molecule species which are measured with any laser-spectroscopic analyser. Line parameters can also enable quantification of gases without the need of a calibration gas of known concentration (see next section). Scientists have measured absorption line parameters of numerous compounds over many years. Millions of these parameters are freely available from databases like HITRAN (Rothman et al., 2013), e.g. via [HITRAN on the web](#) or the [HITRAN Python programming interface](#) and can be used to interpret and model absorption spectra.

The many, well resolvable and unique absorption lines of small molecules in the gas phase are responsible for the exceptional selectivity of techniques based on spectroscopy: For many gas matrices it is possible to find an “isolated” absorption line, i.e. one which does not overlap with other absorption lines from the same or other compounds. This leads to minimal cross-interference. In case one encounters cross-interference through an overlapping line nevertheless, the line may be assigned by comparison to the HITRAN database to identify the interfering compound. This can be accomplished even by less experienced users.

As an example, consider Figure 3, which shows a comparison of an absorption spectrum of ammonia (about 200 ppb) in humid air measured with a commercial CRDS spectrometer (top panel) to a HITRAN simulation (bottom panel). Using HITRAN line data, the absorption lines of the experimental spectrum can readily be assigned to ammonia (three smaller peaks on the

left side) and water (two stronger peaks on the right side). Such a simulation can be prepared, for example, by using the [HITRAN Python programming interface](#).

Clean room operators should use the rich information encoded in absorption spectra to their advantage and pay attention that commercial spectrometers that shall be purchased grant access to spectra. In many cases, the origin of erroneous measurement results of a spectrometer can be identified by looking at the spectra.

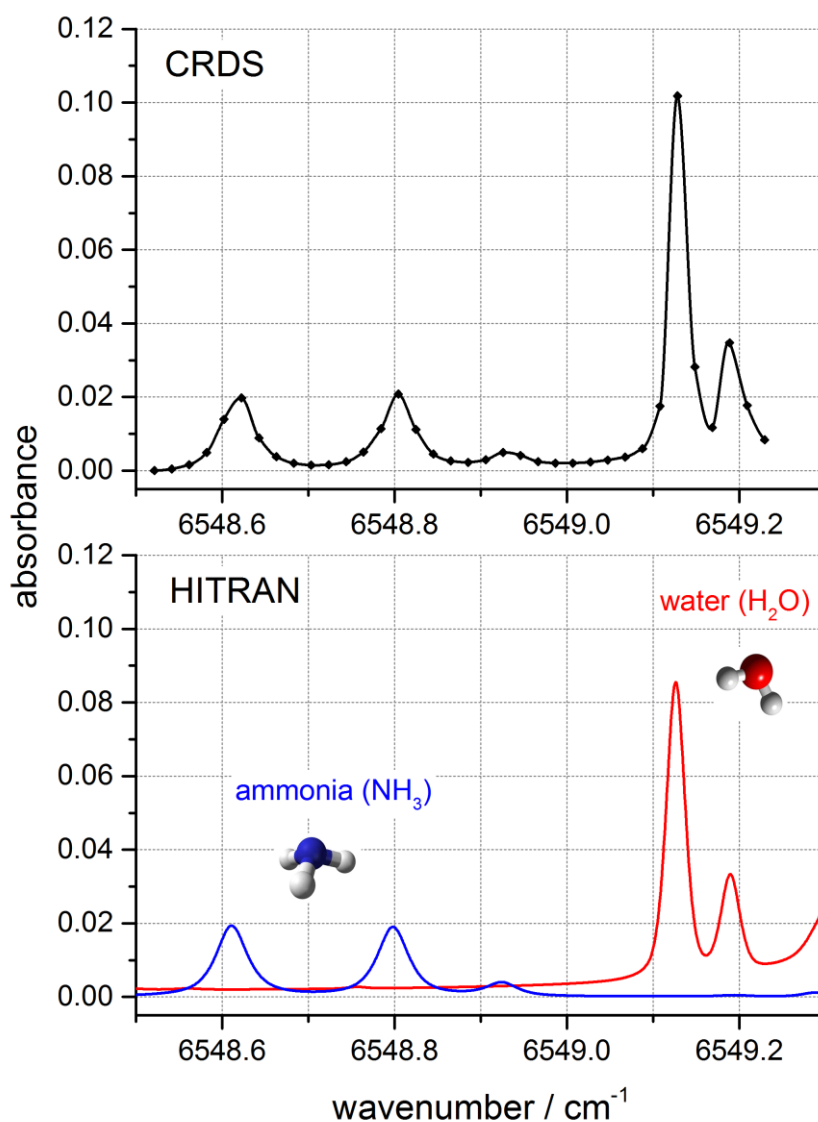


Figure 3: Comparison of a CRDS spectrum (top) to a HITRAN simulation (bottom)

3.4 From spectrum to compound amount fraction (concentration)

As mentioned in Section 3.1, the peak absorbance of an absorption line can be translated to compound concentration using a calibration. However, if a wider spectrum is available, a model based on tabulated absorption line parameters can be fitted to it, which also includes interfering analytes. This will reduce cross-interference and is preferable over measurement at a single wavelength.

It is noteworthy that it is possible to use tabulated line strengths, gas pressure, and gas temperature to derive the compound concentration without requiring a calibration of the spectrometer using a reference gas. Deriving measurement result from line parameters and a model equation is sometimes termed “absolute” or “calibration-free” spectroscopy. For more information on this topic, see references (Buchholz et al., 2014; Nwaboh et al., 2013; Pogány et al., 2015b; Werhahn, 2011). The uncertainty of absolute laser spectrometric amount fraction measurement results can be in the low percent range (Pogány et al., 2015b). Traceability of such measurements requires traceable line parameters, which are a current topic in metrological research (Pogány et al., 2015a; Werhahn et al., 2014).

4 Recommendations on instrument selection

From the discussion above, we can conclude some things to consider, when choosing a spectroscopic analyser for AMC detection:

Detection limit—Usually the user will seek a very low detection limit and manufacturers of AMC analysers will focus on detection limit as one of the main selling arguments. However, the user should not put too much weight on the detection limit alone and carefully consider other issues like dynamic range, response time, potential cross-interference, or stability.

The International Technology Roadmap for Semiconductors (ITRS 2013) lists AMC levels that should not be exceeded, for example, between 0.1 and 1 nmol mol⁻¹ (ppb) for compounds like NH₃, HCl, or HF, depending on the process that shall be protected. Detection limits of commercial CEAS, CRDS, or PAS instruments for these compounds are often specified in this range. The user should inquire an Allan deviation plot (Werle et al., 1993) which indicates what averaging time is necessary to reach the specified detection limit, and also whether it is possible to enhance the detection limit beyond the specified value (at the expense of the time resolution). The Allan deviation is also the basis for a fair comparison of analysers regarding detection limits (detection limits are reported for different averaging times).

Response time— Most spectrometers are extractive systems, meaning the gas sample is kept inside or guided through a gas cell to provide well defined measurement conditions (the less common alternative in spectroscopy are “open-path” systems (Miller et al., 2014)). The use of sampling raises the problem that the sample gas has to be delivered to the gas cell *unaltered*. It should thus not react or adsorb on surfaces of the sampling system (supply tubes, wetted parts of valves and filters) or gas cell of the spectrometer. However, some AMC's have a strong tendency to do so. This can have pronounced effects on the response time of the spectrometer and be a source of considerable measurement uncertainty. A spectrometer for reactive AMC's must thus be designed to minimize such negative effects, for example through minimizing the surface of wetted parts, through the use of proper materials for the wetted parts, and the use of a proper gas exchange procedure (e.g., a high gas flow through the system is favourable).

When purchasing a spectrometer, the user should inquire how a specific device handles the problem of “sticky” molecules. Special attention should be paid to the response time stated by the manufacturer: What was the design of the sampling system and for what magnitude of concentration change did the manufacturer specify the response time? The latter is important since the response time depends on the magnitude of the change in concentration, like shown in Figure 4 (smaller changes have longer response times). Air humidity does also influence the response time of the system by changing the rate at which the target AMC adsorbs on surfaces, because water itself is “sticky” and occupies binding sites on surfaces (Ellis et al., 2010).

The response time of the instrument should not exceed a few minutes to enable fast corrective actions and to ensure that fast changes can be accurately quantified (a slow response of the instrument will effectively “blur” sharp peaks in the time series). Note that manufacturers sometimes only specify measurement rate or gas exchange rate, both of which *can* limit the system response time but are often not limiting when sticky gases are measured and adsorption/desorption processes dominate.

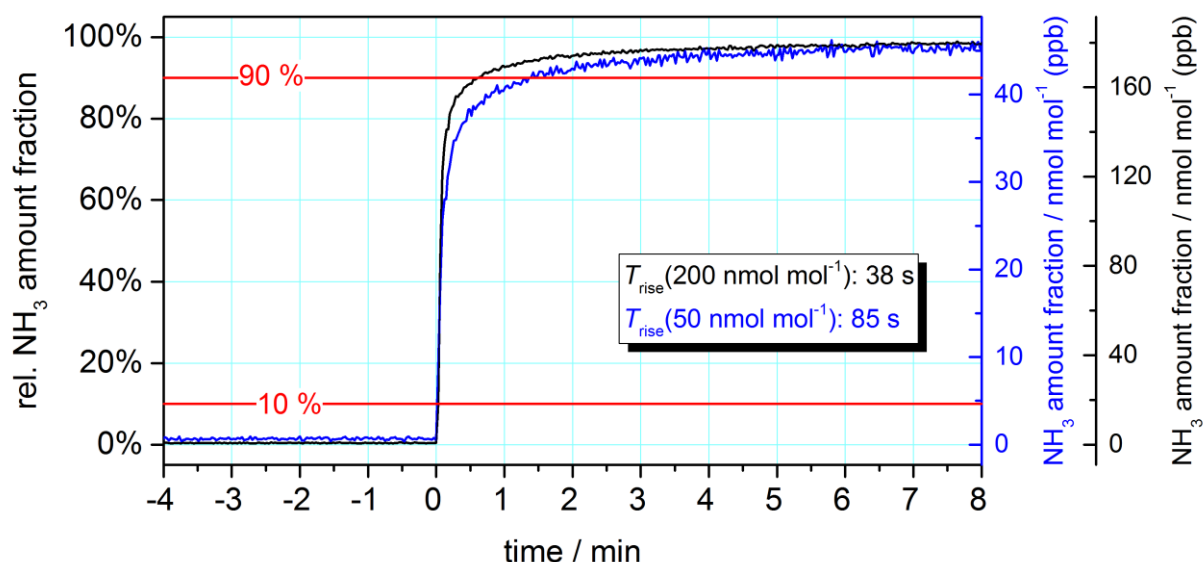


Figure 4: CRD spectrometer response to stepwise increase of ammonia concentration from 0 to 50 ppb (blue) and 0 to 200 ppb (black)

Dynamic range—A high dynamic range is important to correctly quantify spikes in the AMC concentration which considerably surpass the AMC background level. Especially IMS devices struggle with limitations in the dynamic range. The dynamic range of spectroscopic analysers usually covers 4 orders of magnitude (0.1 to several 1000 ppb), see Table 1.

Drift—The analyser's drift limits how much its sensitivity can be improved by averaging (see above, *Detection limit*) and how often recalibration is required (see below, *Maintenance*). Manufacturer's specification thus should clearly state short and long term drift, and minimal values must be sought. For those specification sheets of analysers from which we compiled Table 1, this was often not the case beyond a generic statement.

Cross-interference—The potential susceptibility of a spectrometer to cross-interference can be anticipated by the spectral absorption lines which are probed to quantify the target analyte. If there are pollutants other than the target analyte present in the clean room air which absorb light in the same wavelength interval, they may cause cross-interference (Malowany et al., 2015). Absorption line parameters, or at least positions of absorption bands (e.g. from [NIST Chemistry Webbook](#) or the [Spectral Database for Organic Compounds](#)) may be used to identify potential cross-interferences before purchasing an instrument. The manufacturer should thus specify the spectral region which is scanned by the instrument. In case the instrument scans spectra (as opposed to single-wavelength operation, see Section 3.1), the raw spectra should be easily accessible to facilitate diagnosis, and to enable “calibration-free” operation (Section 3.4), if possible.

Air humidity can be problematic in particular, since it may vary considerably and it may not be straight forward to account for this variation by a calibration. If absorption lines of the target analyte overlap with water absorption lines, the spectral evaluation will need to account for this overlap which may lead to a higher measurement uncertainty. Water can also have more subtle influence on the spectra, like changing the width of absorption lines, which can also lead to cross-interference. The accuracy of photoacoustic measurements can in particular suffer from changes in the air humidity, because water vapour changes the efficiency of heat dissipation, i.e. how much laser light is translated into an acoustic signal (Gillis et al., 2010; Kosterev et al., 2006).

5 Recommendations on instrument operation

Maintenance—Laser spectrometers exhibit few moving parts and lasers are long-lived light sources, such that continuous operation over several months with little to no maintenance other than recalibration and filter exchange (if applicable) is possible. The calibration interval depends on the maximum AMC concentration that can be tolerated and the drift of the instrument that would lead to false or missed alarm conditions. Initially a more frequent recalibration should be done which can be relaxed based on the experience regarding the drift of the instrument.

Calibration gas—Calibration gases for AMC are not always readily available at relevant concentration, such that dynamic generation by dilution (Brewer et al., 2014) from a gas cylinder, from a permeation source, or a diffusion source is necessary. The difficulties which arise when generating AMC reference gases are discussed in the Report for MetAMC deliverable 3.1.10 (“Good Practice Guide addressing the issues of generating trace level AMCs”). The challenges with AMC reference gases render the “calibration-free” operation of some spectroscopic analysers particularly beneficial. Traceability of commercial calibration gases are based on primary standards at NMIs or DIs. Information on available highest level certified reference materials can be found in the [CMC database](#) hosted by BIPM or by directly contacting NMI/DI gas metrology groups. Note that the calibration gas should provide the analyte in synthetic air, since absorption line shapes depend on the gas matrix. Calibration with reference gas in nitrogen might lead to considerable bias.

“Calibration-free” operation—Spectrometers based on direct laser absorption spectroscopy and CRDS can be operated without calibration using a calibration gas, which may reduce cost-of-ownership of analysers for some especially reactive and/or sticky AMC. Some manufacturers actively advertise this feature while others do not. If the user has access to raw spec-

tra, it is possible to perform “calibration-free” measurements even when this is not (yet) supported by the manufacturer, by a custom data evaluation. This requires, however, trained personnel. Other sensors of the spectrometer, in particular temperature and pressure sensors, still need regular calibration (which is why calibration-free is often written in quotes; strictly it means free of a calibration with a gas that represents a certain reference concentration).

Sampling-system—The user usually has some flexibility when it comes to the sampling system (e.g., supply tubes which are connected to the spectrometer) and can thereby also influence the performance of the analyser. The following should be considered.

- Material choice: The user should make sure that proper materials are chosen, such as Teflon or stainless steel with specialized coatings, which have been shown to be a good choice for some typical AMCs (Vaaitinen et al., 2014).
- Sampling tube dimensions: Sampling tubes should be kept as short as possible to minimize the wetted surface area of the sampling system. When reducing the tube diameter to further minimize the surface area, the user should be aware of the increase of the pressure drop and the limited volume flow. The spectrometer performance will suffer if target flow rate or pressure cannot be reached.
- Multi-point sampling: A multi-point sampling system reduces the cost of AMC monitoring but has several disadvantages. Longer tubing of a multi-point sampling system will increase the response time. A spectrometer using multi-point sampling provides much less usable data than a point-of-use device: Each sampling point can only be measured for a small fraction of the day, and because AMC from the measurement of the previous sampling point might be trapped in the sampling system, the user has to purge when switching between sampling points, which leads to extended dead time. Risk mitigation is another factor to be considered: The malfunction of a central analyser paralyzes the whole AMC monitoring network while a malfunction of a point-of-use device creates only a single blind spot.
- Filters: Cavity-enhancement-based spectrometers often use filters to protect the high reflectivity mirrors of their optical cavity from dust. In clean room monitoring such filters may not be necessary. The user should consult the manufacturer.
- Active passivation: Recently, the use of additives in the sampled gas was suggested to actively passivate wetted parts of spectrometers (Roscioli et al., 2015). For AMC monitoring, this technique should be considered with care, since the additive itself can potentially cause cross interference or be harmful to clean room processes if released.

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