PHOTONIC SENSORS / Vol. 5, No. 2, 2015: 109–115

Ammonia Sensing System Based on Wavelength Modulation Spectroscopy

Duarte VIVEIROS[1*], João FERREIRA[1], Susana O. SILVA[1], Joana RIBEIRO[2],
Deolinda FLORES[2], José L. SANTOS[1,3], Orlando FRAZÃO[1,3], and
José M. BAPTISTA[1,4]

[1]*INESC Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal*

[2]*Geology Center of the University of Porto and Department of Geosciences, Environment and Spatial Plannings, Faculty of Science at University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal*

[3]*Department of Physics and Astronomy, Faculty of Science at University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal*

[4]*Competence Center of Exact Sciences and Engineering, University of Madeira, Campus da Penteada, 9000-390 Funchal, Portugal*

[*]Corresponding author: Duarte VIVEIROS E-mail: carlos.d.viveiros@inescporto.pt

Abstract: A sensing system in the near infrared region has been developed for ammonia sensing based on the wavelength modulation spectroscopy (WMS) principle. The WMS is a rather sensitive technique for detecting atomic/molecular species, presenting the advantage that it can be used in the near-infrared region by using the optical telecommunications technology. In this technique, the laser wavelength and intensity were modulated by applying a sine wave signal through the injection current, which allowed the shift of the detection bandwidth to higher frequencies where laser intensity noise was typically lower. Two multi-pass cells based on free space light propagation with 160 cm and 16 cm of optical path length were used, allowing the redundancy operation and technology validation. This system used a diode laser with an emission wavelength at 1512.21 nm, where NH_3 has a strong absorption line. The control of the NH_3 gas sensing system, as well as acquisition, processing and data presentation was performed.

Keywords: Ammonia sensing, fiber optic system, near infrared region, wavelength modulation spectroscopy, environment

Citation: Duarte VIVEIROS, João FERREIRA, Susana O. SILVA, Joana RIBEIRO, Deolinda FLORES, José L. SANTOS, *et al.*, "Ammonia Sensing System Based on Wavelength Modulation Spectroscopy," *Photonic Sensors*, 2015, 5(2): 109–115.

1. Introduction

Ammonia (NH_3) is a colourless gas composed of nitrogen and hydrogen with a sharp, penetrating odour. Sensitive and continuous monitoring of NH_3 is relevant in several applications such as environment monitoring to quantify NH_3 emissions from coal waste piles in combustion [1], $DeNO_x$ processes, which are widely used in power plants and incinerators to reduce NO_x emissions [2], or in medicine to analyse breath NH_3 levels as a diagnostic tool [3].

Received: 20 January 2015 / Revised version: 16 March 2015

DOI: 10.1007/s13320-015-0242-3
Article type: Regular

The main optical gas sensor technologies are based on absorption spectroscopy of fundamental bands in the 3 µm–25 µm spectral region, near infrared vibrational overtone, and combination bands from 1 µm–3 µm [4, 5]. Various NH_3 analysers and measuring methods have been developed, including the differential optical absorption spectrometer [6], tuneable diode laser absorption spectrometer [7], photo acoustic spectroscopy [8], cavity ring-down spectroscopy [9], Fourier transform infrared spectroscopy [10], and others [11–15]. NH_3 has a rich spectrum in the near infrared region, in the spectral range from 1450 nm to 1560 nm. Recently, several works have been developed which use the absorption lines at 1532 nm and 1512 nm as the operating wavelength for NH_3 sensing [16]. The wavelength modulation spectroscopy (WMS) technique has also been demonstrated in a system using a distributed feedback (DFB) laser diode with an emission wavelength at 1532 nm in conjunction with hollow optical waveguides [17]. Such waveguides were used as long-path sample cells (optical path length of 3 m) which were coiled to reduce the physical extent of the system. A portable diode-laser-based sensor for NH_3 detection, using vibrational overtone absorption spectroscopy at 1532 nm (optical path length of 36 m), was described using a fiber-coupled optical element that made a trace gas sensor rugged and easy to align [16]. The gas sensor was used primarily for NH_3 concentration measurements. An NH_3 sensor based on the combination of resonant photo acoustic spectroscopy and direct absorption spectroscopy techniques with a DFB laser diode operating at 1532 nm, was also described [18]. Another photo acoustic spectroscopy sensor using a laser diode emitting near 1532 nm, combined with an erbium-doped fiber amplifier, was developed for NH_3 trace gas analysis at atmospheric pressure [19]. An instrument based on off-axis integrated cavity output spectroscopy and room-temperature near infrared diode lasers, with an emission wavelength at 1532 nm, was applied for measurement of several gas species [20]. In this case, the combination of high-finesse optical cavities with the simplicity of a direct-absorption-spectroscopy technique results in fast, sensitive, and absolute gas measurement. A compact cavity ring-down spectroscopy was reported for the measurement of atmospheric toxic industrial compounds such as hydrides and hydrazine's derivate of NH_3 [21]. The system used a DFB laser diode with an emission wavelength at 1527 nm, and it was directly modulated to produce the ring-down waveforms.

The current work reports the development of an NH_3 gas sensing system based on the WMS principle. This system uses a diode laser with an emission wavelength at 1512.21 nm, where the absorption coefficient of NH_3 is approximately twice its value at 1532 nm [22]. The proposed sensing system also allows the selection of two multi-pass cells based on free space light propagation with 160 cm and 16 cm of the optical path length.

2. Wavelength modulation spectroscopy

Absorption spectroscopy is based on a unique signature attenuation of spectral intensity caused by the gas to be monitored. It happens when light radiation interacts with molecular species and it is represented by the Beer-Lambert Law [23, 24]:

$$I_t(\lambda)=I_0(\lambda)e^{-\alpha(\lambda)L} \tag{1}$$

where $I_t(\lambda)$ and $I_0(\lambda)$ are the transmitted and incident light intensities at wavelength λ of the laser diode, respectively, and L is the interaction length or path length that the light has to pass through the gas. The absorption coefficient $\alpha(\lambda)$ is that by [23, 24]

$$\alpha(\lambda)=C\times\varepsilon(\lambda) \tag{2}$$

where C is the gas concentration, and $\varepsilon(\lambda)$ is the specific absorptivity of the gas. The WMS is a rather sensitive technique based on absorption spectroscopy for atomic/molecular species detection, presenting the advantage that can be used in the near-infrared region [23, 24]. A typical experimental configuration of WMS is composed by a wavelength-tuneable DFB laser diode, a function generator, a gas chamber, a photodetector, and a lock-in amplifier, as illustrated in Fig. 1.

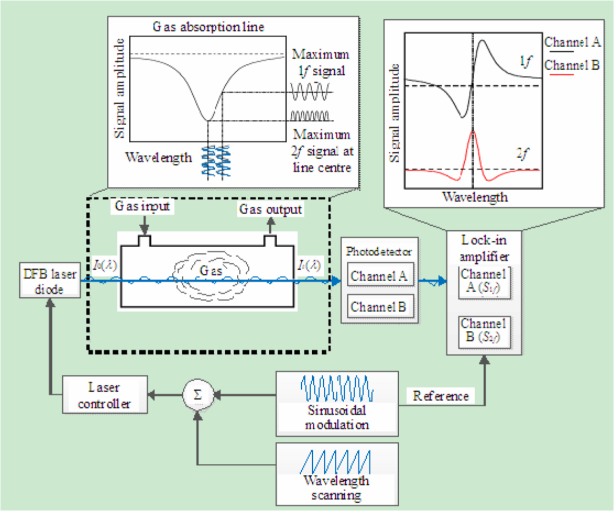

Fig. 1 Generic configuration for WMS showing detected signals: laser scan through a single gas absorption line (left side wavelength spectrum). Synchronous detection of the first and the second harmonic of the laser modulation through a lock-in amplifier (right side wavelength dependent responses of the measurement setup).

This technique consists in applying a sine wave modulation signal, at a frequency of a few kHz, superimposed on the laser bias current, which in turn modulates both the wavelength and the intensity of the laser light. A ramp signal is added to sweep the laser frequency across the gas absorption line. The sinusoidal modulation in the operational kHz range shifts the detection bandwidth to higher frequencies where laser intensity noise is lower [23, 24].

From Fig. 1 (see left side wavelength spectrum), the modulated laser light interacts with the absorption line of the target gas and two possible situations may be observed: (1) the modulated frequency is doubled when the laser light is tuned to the center of absorption line and (2) the frequency remains unchanged when the laser is tuned out of the center of the absorption line. Therefore, this interaction between the modulated laser light and absorption line of the target gas generates signals at different harmonics of the applied modulation frequency—see the wavelength dependent responses of the measurement setup at the right side of Fig. 1 [23, 24].

Gas concentration is typically detected by the recovery of the second harmonic (2*f*) of the laser modulation frequency through a synchronous detection, using a lock-in amplifier and reading its amplitude [23, 24]. The forms of the first and the second demodulated harmonics are shown in Fig. 1 (see the wavelength dependent responses of the measurement setup at the right side), where the amplitude of the second harmonic (2*f*) of the laser modulation frequency is proportional to the gas concentration. The first harmonic (*f*) is proportional to the first derivative of the gas absorption line and equals zero when the wavelength modulated laser light is centered at the NH_3 gas absorption line, therefore providing a rather sensitive mechanism to tune the central laser wavelength to this line [23, 24].

3. Sensing system design

The NH_3 gas sensing system proposed in this experiment was based on the WMS principle (Section 2) and it was composed by two free-space light-propagation multi-pass cells. Such cells, with distinct optical path lengths, namely, 160 cm and 16 cm, (see Fig. 2) were selected through an optical switch.

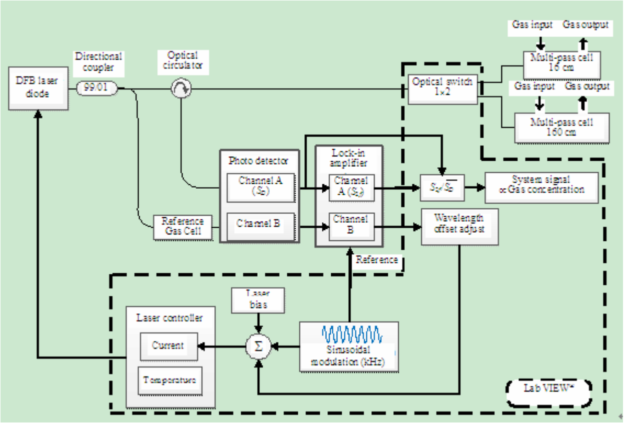

Fig. 2 Schematic diagram of sensing system for NH_3 gas sensing using WMS.

A reference gas cell in order to fine tune the wavelength emission of the DFB laser diode was also used, with an optical path length of 5.5 cm and a pressure of 0.263 atm at room temperature.

The control of the NH_3 gas sensing system presented in Fig. 2, as well as acquisition, processing, and data presentation was performed using a LabVIEW® application.

The DFB laser diode provided 7 mW at 1512.21 nm with a specified line-width < 2 MHz. The fiber was spliced to a 99/1(%) directional coupler with the 99% power arm sent to the optical switch. The 1% power arm was used as the reference beam passing through the reference NH_3 gas cell.

Figure 3 shows the NH_3 gas absorption line for a concentration of 100% in the 1511.2 nm–1513.6 nm region, a temperature range of 16.1 ºC–27.4 ºC, and for the current range of 27.5 mA–103 mA. As a result, the NH_3 absorption line detected had a central wavelength of 1512.21 nm and a full width at half maximum (FWHM) of 59 pm.

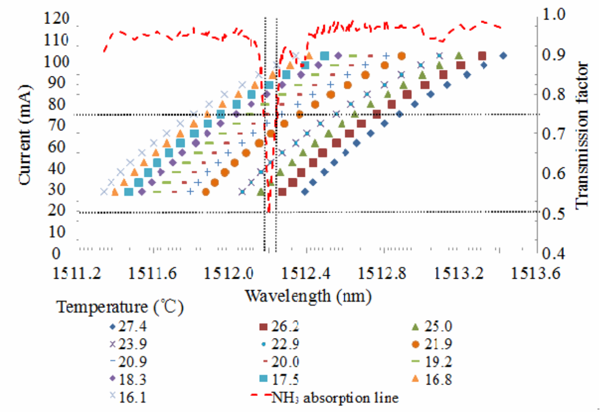

Fig. 3 DFB laser emission wavelength shift as function of the bias current, for a specific temperature, of the detected absorption line at 1512.21 nm.

The laser wavelength and intensity was modulated by applying a sine wave signal with a frequency of 5 kHz. The initial injection DC current (laser bias) and temperature were set in the laser controller to 61.3 mA and 21.58 ºC, respectively, in order to tune the emission wavelength DFB laser diode to the desired wavelength of the NH_3 absorption line (1512.21 nm).

To lock the laser wavelength to the NH_3 gas absorption central line, the experimental setup had a feedback-loop that consisted in part of the emitted light passing through the reference gas cell. This means that, on Channel B of the lock-in amplifier (Fig. 2), the amplitude of the first harmonic must equal zero, thus tuning the laser wavelength to the targeted gas.

The amplitude of the second harmonic (channel A of lock-in amplifier), which was proportional to the gas concentration, was normalised by the average laser intensity read by the photodetector, therefore providing compensation for undesirable optical power fluctuations.

4. Ammonia sensing

Real-time concentration measurement was performed by introducing NH_3 gas inside the multi-pass cells, with 16 cm and 160 cm of optical path length, and sealed at the room temperature and atmospheric pressure (1 atm). The different NH_3 gas concentrations were achieved by mixing a calibrated NH_3 sample in an N_2 environment. Figure 4 illustrates the obtained results.

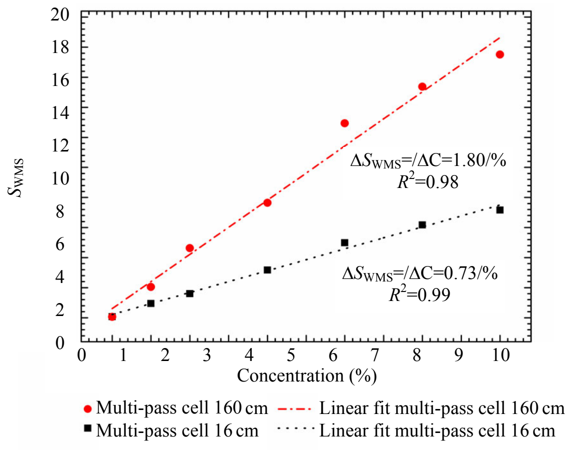

Fig. 4 Output of the sensing system versus ammonia concentration using the multi-pass cells of 16 cm and 160 cm.

The proposed sensing system shows linear responses in the ammonia concentration range from 0 to 10%. The limit of detection (LOD) was 0.12% and 0.06%, for the multi-pass cells with 16 cm and

160 cm, respectively. The limit of detection was defined according to [25]:

$$\mathrm{LOD} = \mu_b + k_D \frac{\sigma_b}{S_S} \tag{3}$$

where μ_b and σ_b are the mean and the standard deviations of the blank measures (0% of concentration), respectively, and k_D is a factor chosen according to the confidence level desired (k_D was chosen to equal 3 that corresponds to a confidence level of about 90%). The sensitivity of the proposed system S_S is the slope ($\Delta S_{\mathrm{WMS}}/\Delta C$) of the calibration curve, where C is the NH_3 concentration and S_{WMS} is the normalized signal measured by the sensing system that is proportional to gas concentration. This signal (S_{WMS}) was obtained through division of the lock-in amplifier signal by the average value of the photodetector signal. In this case, the sensitivity obtained was 0.73/% and 1.8/%, for the multi-pass cells with 16 cm and 160 cm, respectively. The interaction of light with gas in the optical path length is higher for the multi-pass cell with 160 cm, thus causing an increase in sensitivity.

The resolution of the system was also measured for each multi-pass cell. The results are depicted in Fig. 5.

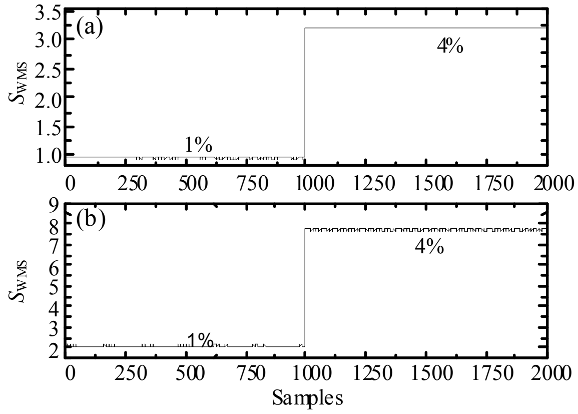

Fig. 5 Resolution of the system obtained using the multi-pass cells of (a) 16 cm and (b) 160 cm of optical path-length.

The change in the signal (S_{WMS}) associated with a step change of 3% was measured by the system. Based on the step changes and rms fluctuations, resolutions of 0.014% and 0.028% were achieved for the multi-pass cells with 16 cm and 160 cm, respectively. The shorter cell presented better resolution because the number of total internal reflections (one internal reflection) was inferior to the one with 160 cm (ten internal reflections), therefore increasing the optical loss with the associated degradation of the signal-to-noise ratio. For the system resolution to benefit from the larger length interaction of light with gas in the case of the 160 cm multipass cell, an increased level of optical power would be required, which could be achieved considering optical amplification.

This sensing system also shows a fast response and recovery time below 1 s. Table 1 summarizes the system parameters for ammonia sensing.

Table 1 Summary of the system parameters for ammonia sensing.

Gas	Ammonia (NH3)	
Optical path length (cm)	16	160
Sensitivity (1/%)	0.73	1.80
LOD (%)	0.12	0.06
Resolution (%)	0.014	0.028

5. Conclusions

In this work, an ammonia gas sensing system in the near infrared region has been developed based on the WMS principle. The sensing system was composed by two multi-pass cells sensing heads based on free space light propagation with 16 cm and 160 cm of optical path length, permitting redundancy operation and technology validation. The DFB laser diode used in the sensing system worked at the wavelength of 1512.21 nm, where the NH_3 gas has a unique absorption response and a stronger absorption line when compared to the 1532 nm region, which has been used in most systems reported in the literature, to detect ammonia in the infrared region. The experimental results showed that the best sensitivity (1.80/%) as well as the best limit of detection (0.06%), were achieved with the multi-pass cell with 160 cm of optical path length. However, the cell with 16 cm presented better resolution (0.014%) when compared with the one with 160 cm. This sensing system also showed a fast response and recovery time below 1 s allowing its use in harsh environments were concentrations between 15% and 28% by volume may be found.

Acknowledgment

This activity is supported by the project ECOAL–MGT–SOE3/P2/P714, the *Ecological Management of Coal Waste Piles in Combustion,* SUDOE–Interreg IV B.

References

[1] D. Viveiros, J. Ribeiro, J. P. Carvalho, J. Ferreira, A. M. R. Pinto, R. A. Perez-Herrera, *et al.*, "Fiber optic sensing system for monitoring of coal waste piles in combustion," in *Proc. SPIE*, vol. 9157, pp. 91573O-1–91573O-14, 2014.

[2] G. Busca, L. Lietti, G. Ramis, and F. Berti, "Chemical and mechanistic aspects of the selective catalytic reduction of NO(x) by ammonia over oxide catalysts: A review," *Applied Catalysis B: Environmental*, 1998, 18(1–2): 1–36.

[3] L. R. Narasimhan, W. Goodman, and C. K. Patel, "Correlation of breath ammonia with blood urea nitrogen and creatinine during hemodialysis," *Proceedings of the National Academy of Sciences of the United States of America*, 2001, 98(8): 4617–4621.

[4] J. Hodgkinson and R. P. Tatam, "Optical gas sensing: a review," *Measurement Science and Technology*, 2013, 24(1): 012004-1–012004-95.

[5] M. Ferm, "Method for determination of atmospheric ammonia," *Atmos. Environ (1967)*, 1979, 13(10): 1385–1393.

[6] R. Kincaid, K. Johnson, G. H. Mount, D. Yonge, J. Havig, H. Westberg, *et al.*, "Measurement of atmospheric ammonia at a dairy using differential optical absorption spectroscopy in the mid-ultraviolet," *Atmospheric Environment*, 2002, 36(11): 1799–1810.

[7] J. E. Sickles, L. L. Hodson, W. A. McClenny, R. J. Paur, T. G. Ellestad, J. D. Mulik, *et al.*, "Field comparison of methods for the measurement of gaseous and particulate contributors to acidic dry deposition," *Atmospheric Environment. Part A. General Topics*, 1990, 24(1): 155–165.

[8] A. Schmohl, A. Miklós, and P. Hess, "Detection of ammonia by photoacoustic spectroscopy with semiconductor lasers," *Applied Optics*, 2002, 41(9): 1815–1823.

[9] A. O'Keefe and D. A. G. Deacon, "Cavity ring-down optical spectrometer for absorption measurements using pulsed laser sources," *Review of Scientific Instruments*, 1988, 59(12): 2544–2551.

[10] B. Galle, L. Klemedtsson, B. Bergqvist, M. Ferm, Kåre Törnqvist, D. W. Griffith, *et al.*, "Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques," *Atmospheric Environment*, 2000, 34(26): 4907–4915.

[11] G. P. Wyers, R. P. Otjes, and J. Slanina, "A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia," *Atmospheric Environment. Part A. General Topics*, 1993, 27(13): 2085–2090.

[12] M. P. Keuken, A. Wayers-Ijpelaan, J. J. Mols, R. P. Otjes, and J. Slanina, "The determination of ammonia in ambient air by an automated thermodenuder system," *Atmospheric Environment (1967)*, 1989, 23(10): 2177–2185.

[13] L. P. Breitenbach and M. Shelef, "Development of a method for the analysis of NO_2 and NH_3 by NO-measuring instruments," *Journal of the Air Pollution Control Association*, 1973, 23(2): 128–131.

[14] S. Schilt, L. Thévenaz, M. Niklès, L. Emmenegger, and C. Hüglin, "Ammonia monitoring at trace level using photoacoustic spectroscopy in industrial and environmental applications," *Spectrochim Acta A Mol Biomol Spectrosc*, 2004, 60(14): 3259–3268.

[15] B. Timmer, W. Olthuis, and A. V. D. Berg, "Ammonia sensors and their applications—a review," *Sensors and Actuators B: Chemical*, 2005, 107(2): 666–677.

[16] R. Claps, F. V Englich, D. P. Leleux, D. Richter, F. K. Tittel, and R. F. Curl, "Ammonia detection by use of near-Infrared diode-laser-based overtone spectroscopy," *Applied Optics*, 2001, 40(24): 4387–4394.

[17] G. J. Fetzer, A. S. Pittner, W. L. Ryder, and D. A. Brown, "Tunable diode laser absorption spectroscopy in coiled hollow optical waveguides," *Applied Optics*, 2002, 41(18): 3613–3621.

[18] H. Huszár, A. Pogány, Z. Bozóki, Á. Mohácsi, L. Horváth, and G. Szabó, "Ammonia monitoring at ppb level using photoacoustic spectroscopy for environmental application," *Sensors and Actuators,*

B: Chemical, 2008, 134(2): 1027–1033.

[19] J.-P. Besson, S. Schilt, E. Rochat, and L. Thévenaz, "Ammonia trace measurements at ppb level based on near-IR photoacoustic spectroscopy," *Applied Physics B*, 2006, 85(2–3): 323–328.

[20] D. S. Baer, J. B. Paul, M. Gupta, and A. O'Keefe, "Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy," *Applied Physics B*, 2002, 75(2–3): 261–265.

[21] B. A. Paldus, B. G. Fidric, S. S. Sanders, S. M. Tan, H. Pham, A. A. Kachanov, *et al.*, "High sensitivity detectors based on cavity ring-down spectroscopy," in *Proc. SPIE*, vol. 5617, pp. 312–322, 2004.

[22] Pacific Northwest National Laboratory, "PNNL - available compounds by CAS number." [Online]. Available at: https://secure2.pnl.gov/nsd/NSD.nsf/OrderCAS?OpenView&View=CAS&Start=1&Count=30. [Accessed: 24-Apr-2013].

[23] J. D. Ingle and S. R. Crouch, *Spectrochemical Analysis*. London, UK: Prentice Hall, 1988.

[24] S. Schilt, L. Thevenaz, and P. Robert, "Wavelength modulation spectroscopy: combined frequency and intensity laser modulation," *Applied Optics*, 2003, 42(33): 6728–673.

[25] V. Thomsen, D. Schatzlein, and D. Mercuro, "Limits of detection in spectroscopy," *Spectroscopy*, 2003, 18(12): 112–114.

.