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Characterisation of FTIR, CRDS and OFCEAS instruments for the analysis of ammonia in biogas and biomethane

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ABSTRACT: Novel traceable analytical methods and reference gas standards were developed for the detection of trace-level ammonia in biogas and biomethane. This work focused on an ammonia amount fraction at the upper limit level of 10 mg m^{-3} (corresponding to approximately 14 μmol mol^{-1}) specified in EN 16723-1:2016. The application of spectroscopic analytical methods such as Fourier-transform infrared (FTIR) spectroscopy, cavity ring-down spectroscopy (CRDS) and optical feedback cavity enhanced absorption spectroscopy (OFCEAS), was investigated. These techniques all exhibited the necessary ammonia sensitivity at the required 14 μmol mol^{-1} amount fraction. A 29-month stability study of reference gas mixtures of 10 μmol mol^{-1} ammonia in methane and synthetic biogas, is also reported.

1. Introduction

Biogas is a renewable fuel produced from the anaerobic digestions of organic matter. Biomethane is defined as biogas that has been cleaned of impurities and upgraded to a composition similar to that of natural gas. In Europe, biomethane can be directly injected into the natural gas grid or used to fuel Compressed Natural Gas (CNG) vehicles. Use of biomethane is aligned with the RED II directive, within which the overall EU target for Renewable Energy consumption by 2030 now stands at 32 % [1].

To provide a quality framework for biomethane usage, the European Commission issued EU mandate M/475 requesting for a new CEN standard to be written that includes specifications for the quality of biomethane [2]. The limit levels of impurities within these specifications can be used as pass / fail criteria that must be met before injecting biomethane into the natural gas grid or using it as fuel in vehicles. These standards have been published by CEN TC 408 as:

- EN 16723-1:2016 - Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network – Part 1: Specifications for biomethane for injection in the natural gas network [3].
- EN 16723-2:2017 - Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network - Part 2: Automotive fuel specifications [4].

The specifications in these standards cover a wide range of impurities such as total silicon, carbon monoxide (CO), ammonia (NH_3) and dust. Research has been undertaken to investigate the measurement requirements for several of these impurities [5]. This paper will focus exclusively on NH_3. The quality specifications for NH_3 in EN 16723-1:2016 is set at a maximum level of 10 mg m^{-3} (which equates to approximately 14 μmol mol^{-1} at 20 °C) whereas in EN 16723-2:2017 (for vehicles) there is no specification for NH_3. Neither standard currently specifies an uncertainty requirement. It should be noted that both standards include an additional specification for amines (both at 10 mg m^{-3}).

A challenge in establishing these new quality specifications is that the grid networks and suppliers would not be able to use their existing natural gas analysers and natural gas calibration standards to perform these new measurements. In addition to gas analysis methods, new gas reference standards are required to ensure that the measurements are accurate and traceable. Primary Reference Materials (PRMs) establish the direct link between calibration gas standards (as used by the natural gas industry) and the SI definition of the mole. National Metrology Institutes (NMIs) such as National Physical Laboratory (NPL), Van Swinden Laboratory (VSL) and Research Institutes of Sweden (RISE) participate in international comparisons where their ability to accurately produce PRMs is assessed by analytical comparison with PRMs produced by other NMIs from around the world, which is a unique feature of reference materials produced by NMIs and designated institutes (DIs). Without these PRMs there can be no assurance that industry-produced calibration gas standards are traceable, accurate or comparable to those produced in other countries.

This paper outlines the development of novel traceable analytical methods and reference gas standards for measuring NH_3 in biogas and biomethane at amount fractions close to the maximum specified level of 10 mg m^{-3}. The limit of detection and measurement uncertainty for each analytical technique are discussed and the stability data presented for the PRMs. The range of analytical techniques presented includes Fourier-Transform Infra-red spectroscopy (FTIR), Cavity Ring-Down Spectroscopy (CRDS) and Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS). An assessment is made to whether NMIs can provide the necessary metrology infrastructure to support measurement of NH_3 impurities as specified in the EN 16723 standards or whether further development is required.

2. Experimental

2.1 Selection of analytical techniques

A range of instruments are commercially available for the measurement of NH_3 in air. The majority of these rely on monitoring NH_3 absorption in the infrared, either in regions where no significant interference arises from other infrared absorbers at their atmospheric abundance, or by measuring interfering gases (*e.g.*, water vapour) and accounting for them in the spectral fitting routine [6]. However, the measurement of NH_3 in a biogas matrix (where matrix is defined as the constituent components of the mixture other than the analyte, ammonia) by means of infrared spectroscopy is particularly challenging: while the two main components of air, N_2 and O_2, are infrared-inactive, a biogas matrix typically consists of two very strong infrared absorbers (CH_4 and CO_2) that are present at amount fractions up to five orders of magnitude higher than NH_3 and other impurities such as water. This reduces the application of infrared techniques to spectral regions in which the interference due to undesirable absorbers is minimal, but in which the NH_3 signal is still sufficiently strong to guarantee good sensitivity to trace level NH_3 (typically of the order of μmol mol^{-1}).

Three analysers were identified as suitable for the measurements of NH_3 in biogas: a Fourier-transform infrared (FTIR) spectrometer, a custom-built cavity ring-down spectrometer (CRDS) with tuneable light source, and an optical feedback cavity-enhanced absorption spectrometer (OFCEAS). A feature common to FTIR and certain OFCEAS and CRDS systems is that they allow the measurement spectral window to be adjusted carefully in order to minimise the interference of the biogas components with the NH_3 signal. A brief technical description of each instrument is given below, while a detailed account of the selection of spectral region in each case is presented in Section 3.

2.2 Instruments

The FTIR instrument used in this work was a commercial benchtop spectrometer (Nicolet 6700, Thermo Fisher Scientific) housed in a sealed stainless steel box that was continuously purged by a flow of 99.999% purity N_2 gas of approximately 9 L min^{-1}, in order to minimise carbon dioxide and water background absorptions. The spectrometer was equipped with N_2 purged optics, a KBr beamsplitter and a liquid N_2 cooled MCT-A detector. The gas mixtures were analysed within a commercial White-type gas cell (Cyclone C5, Specac), having a path length of (8.0 ± 0.25) m and volume of 2 L. Spectra of biogas reference materials (see section 2.3) and background spectra (obtained using BIP N_2, Air Products) were made at $T = (300 \pm 2)$ K, $p = (1054 \pm 5)$ mbar, with a sample flow rate of (0.5 ± 0.1) L min^{-1}, an instrumental spectral resolution of 0.5 cm^{-1} and over a spectral window ranging from 4000 to 640 cm^{-1}. The limit of detection for NH_3 with FTIR under these experimental conditions was determined as (0.73 ± 0.62) μmol mol^{-1}, with $k = 2$ and a 95% confidence level.

A custom-built cavity ring-down spectrometer (CRDS) was developed using a mid-infrared optical parametric oscillator as light source [7]. The light source could be tuned from 2.4 to 5.1 μm (4170 – 1960 cm^{-1}). The measurement cell consisted of a stainless steel chamber of 150 mL internal volume. Gas samples were flowed into the measurement cell using mass flow controllers (Bronkhorst) at flow rates in the range of 110 - 220 mL min^{-1}. The pressure within the measurement cell was regulated at either 200 mbar (for low pressure measurements) or 1050 mbar (for ambient pressure measurements). All wetted parts, (*i.e.*, the pressure regulator, stainless steel tubing, the mass-flow controller and the measurement cell) were coated in SilcoNert©2000 (SilcoTek) to minimise the surface adsorption of NH_3. This shortened the analysis time (and therefore the gas consumption) considerably, consistent with the findings of Vaittinen *et al* [8] and Pogány *et al* [9,10] The CRDS instrument was calibrated using two mixtures of NH_3 in N_2 (both with nominal gravimetric value of 10.02 μmol mol^{-1}), previously certified against dynamic dilutions of standards at higher amount fraction using a Photo Acoustic IR analyser (Innova 1412).

A custom-built optical feedback cavity enhanced absorption spectrometer (OFCEAS) was also developed for measurements of NH_3 in biogas (ProCeas from AP2E). Gas samples were drawn into the measurement cell at a flow rate of 25 mL min^{-1} through a stainless steel restrictor using an internal pump. The measurement cell consisted of a multipath cavity equipped with highly reflective mirrors, allowing path lengths up to 10 km. The cell was kept at a pressure of 50 mbar and at a temperature of 40 °C. To minimise ingress of particulate matter and H_2O vapour into the instrument, a stainless steel particle filter with 7 μm pore size and a moisture trap were installed at the inlet. The moisture trap was only used in standby mode, during which air was continuously introduced into the system by the internal pump. The samples did not pass through the moisture trap. The instrument was calibrated with NH_3 concentrations from 1 μmol mol^{-1} to 100 μmol mol^{-1}.

2.3 Reference materials

Accurate and stable gas mixtures of NH_3 in biogas were required in order to characterise the measurement techniques described above. As the main components of biogas

(CH_4, CO_2 and N_2) can be present at different amount fractions depending on the source feedstock, a set of biogas-type matrices was defined for the preparation of the reference mixtures. Water content was not included within the mixtures due to lack of stability data, though it should be noted that water and other trace-level impurities (e.g. hydrogen sulfide) are expected to be present in real biogases. This work focused on three matrix types: pure CH_4, "Biogas 20" (20 cmol mol^{-1} CO_2, 77 cmol mol^{-1} CH_4, 3 cmol mol^{-1} N_2) and "Biogas 40" (40 cmol mol^{-1} CO_2, 45 cmol mol^{-1} CH_4, 15 cmol mol^{-1} N_2). All reference mixtures were prepared gravimetrically from the pure components in accordance with ISO 6142-1 [11] at a nominal ammonia amount fraction of 10 µmol mol^{-1}. The mixtures were validated using mixtures traceable to international comparison CCQM-K46 [12].

Commercially available mixtures of NH_3 in methane (63.0 ± 1.9 µmol mol^{-1} and 20.57 ± 0.62 µmol mol^{-1}, Air Liquide) in 5 L cylinders were used to test the OFCEAS instrument.

The gravimetric composition of the reference mixtures used in the FTIR measurements is reported in Table 1. The composition of the mixtures employed in the CRDS measurements are given in Table 2.

Table 1 – Gravimetric composition of the four reference gas mixtures used in the FTIR study

	Cylinder NPL 1794	**Cylinder NPL NG565**	**Cylinder NPL NG558**	**Cylinder NPL A583**
Matrix →	CH_4	Biogas 20	Biogas 40	Biogas 20
Cylinder type →	Spectra-Seal with NPL proprietary treatment	Spectra-Seal with NPL proprietary treatment	Spectra-Seal with NPL proprietary treatment	Spectra-Seal with NPL proprietary treatment
Component ↓	**Gravimetric amount fraction (cmol mol^{-1})**	**Gravimetric amount fraction (cmol mol^{-1})**	**Gravimetric amount fraction (cmol mol^{-1})**	**Gravimetric amount fraction (cmol mol^{-1})**
N_2	-	3.01	15.00	3.32
CH_4	balance	76.94	45.03	75.66
CO_2	-	20.04	39.98	21.0
NH_3	$10.0 \cdot 10^{-4}$	$10.0 \cdot 10^{-4}$	$9.99 \cdot 10^{-5}$	$10.0 \cdot 10^{-4}$
Volume / pressure →	10 L / 100 bar	10 L / 100 bar	10 L / 100 bar	10 L / 100 bar

Table 2 – Gravimetric composition of the three reference gas mixtures used in the CRDS study.

	Cylinder VSL249217	**Cylinder VSL243546**	**Cylinder VSL143730**
Matrix→	Other	Biogas 40	Biogas 20
Cylinder type→	Aculife IV	Spectra-Seal	Aculife IV
Component ↓	**Gravimetric amount fraction (10^{-2} mol mol^{-1})**	**Gravimetric amount fraction (10^{-2} mol mol^{-1})**	**Gravimetric amount fraction (10^{-2} mol mol^{-1})**
N_2	3.34	14.98	3.34
CH_4	96.66	44.95	76.68
CO_2	0.00	40.07	19.98
NH_3	$10.00 \cdot 10^{-4}$	$10.01 \cdot 10^{-4}$	$10.00 \cdot 10^{-4}$
Volume / pressure →	5 L / <> bar	5 L / <> bar	5 L / <> bar

2.3.1 Stability measurement of PRMs

When measured via FTIR, selecting individual spectral peaks is not without complications since they are affected by instrumental resolution and by collisional broadening, which is pressure and matrix gas dependent. Consequently, measuring the stability of a given gas mixture by making quantitative measurements based on calibration spectra and/or comparative measurements of standard mixtures that differ in gas matrix, introduces uncertainty in the final result that may obscure any trends within the stability data.

However, if there are components within a given mixture that are known to be stable, for instance CH_4 in biogas mixtures, then the stability of NH_3 can be measured relatively to a given CH_4 peak by integrating the baseline-corrected absorbance of each peak and then considering the ratio between the NH_3 absorbance peak area, $A_{\mathrm{NH_3}}$, and the CH_4 absorbance peak area, $A_{\mathrm{CH_4}}$. Measuring the potentially unstable trace NH_3 against the stable CH_4 matrix offers the advantage of using CH_4 as an internal standard, simultaneously measured with the "unknown". This serves to cancel out effects of pressure, temperature and optical path length, which are identical under this measurement method for both the "unknown" and the internal standard, so that any significant changes in the relative concentrations of NH_3 and CH_4 over time are assumed to arise from a change in the NH_3 concentration.

3. Results

3.1 Stability of reference materials

A study was carried out to assess the long-term stability of the three 10 µmol mol^{-1} NH_3 in CH_4 and synthetic biogas reference gas mixtures (NPL 1794, NPL NG565 and NPL NG558, described in Table 1). The integrated absorbance peak areas used to determine $A_{\mathrm{NH_3}}$ and $A_{\mathrm{CH_4}}$ are shown in Figure 1. In the case of NH_3 (Figure 1a), the integrated area corresponded to the peak at 868 cm^{-1}, which was identified as the NH_3 absorption line least suffering from overlap with CO_2 and CH_4 absorbance in the spectral analysis described in 3.2.1. A similar analysis was performed to identify a suitable range of CH_4 absorbance not affected by CO_2 or NH_3 interferences.

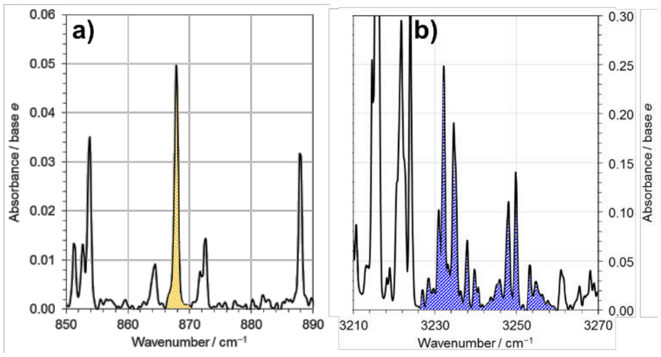

Figure 1 – FTIR spectra of trace ammonia in Biogas 20 at 0.5 cm^{-1} resolution, highlighting the integrated absorbance areas of a) NH_3 and b) CH_4.

The results of the stability study over a period of 29 months are shown in Figure 2 as change relative to the first measurement of the $A_{\mathrm{NH_3}}/A_{\mathrm{CH_4}}$ ratio (performed immediately after preparation of the mixtures). The NH_3 content of the three mixtures appears stable over the time period studied within the measurement uncertainty, with the exception of the measurement around the 15 months mark for the NPL NG565 and NPL 1794 mixtures. In this case, the $A_{\mathrm{NH_3}}/A_{\mathrm{CH_4}}$ ratio for both mixtures was considerably lower than on other dates. This is attributed to insufficient purging of the FTIR gas cell prior to measurements, which might have left traces of NH_3 in the cell when the background spectrum was recorded, and/or to insufficient conditioning of the internal surface of the gas cell with NH_3 before recording the spectra: both cases would lead to an underestimate of the $A_{\mathrm{NH_3}}/A_{\mathrm{CH_4}}$ ratio. In addition, the lack of stabilisation of the atmosphere within the measurement cell also accounts for the large uncertainty associated with the data recorded on that date (*i.e.* larger standard deviation), making this result anomalous, especially in the light of the two subsequent measurements.

NPL's XLGENLINE software [12] was used to perform weighted linear fits on the stability data. For each mixture, two linear fits were carried out: one for the complete dataset and one excluding the data point for the 15th month measurements. In the first case, the gradient was statistically significant (at the k = 2 level) in only one case (NPL NG565); in the latter, it was not significant in any of the mixtures. This is consistent with the stability of mixtures of 10 μmol mol^{-1} ammonia in nitrogen in the same cylinder type observed by Martin et al. [14].

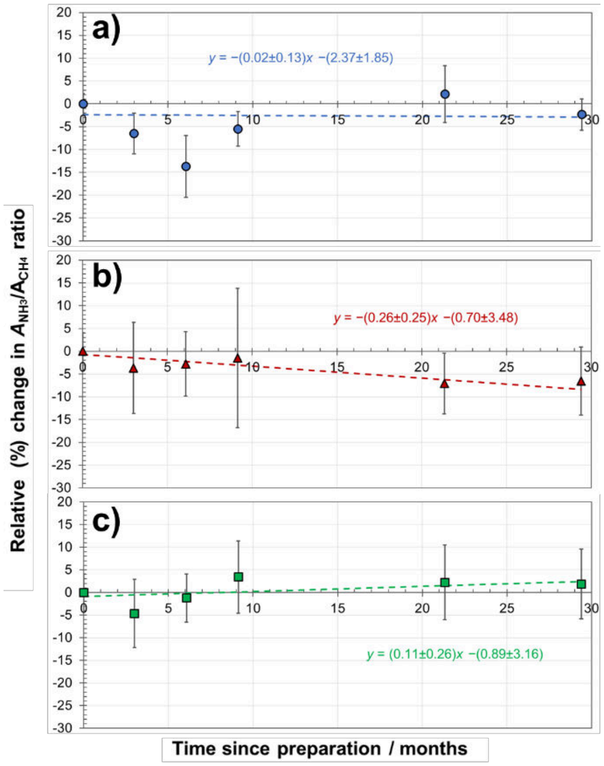

Figure 2 – Stability of 10 μmol mol^{-1} NH_3 mixtures in: a) CH_4 (NPL1794), b) Biogas 20 (NPL NG565) and c) Biogas 40 (NPL NG558). Also shown are the XLGENLINE linear fits (dashed lines) to the datasets excluding the measurements performed 15 months after preparation. Uncertainty in the gradients and intercepts are at the k = 2 level.

As a further test of the stability of NH_3 in biogas, at the end of the 29-month stability study the three mixtures (NPL 1794, NPL NG565 and NPL NG558) were certified against a newly prepared reference mixture (NPL A583), the composition of which is provided in Table 1. The NH_3 amount fraction in each of the three original mixtures ($x_{\mathrm{NH_3},unknown}$) was determined from the integrated absorbance of the NH_3 peak at 868 cm^{-1} for the original mixtures ($A_{\mathrm{NH_3},unknown}$), that for the newly prepared mixture ($A_{\mathrm{NH_3,NPL\ A583}}$), and its gravimetric amount fraction ($x_{\mathrm{NH_3,NPL\ A583}}$) according to the relationship:

$$\boldsymbol{x_{\mathrm{NH_3},unknown} = A_{\mathrm{NH_3},unknown} \times \frac{A_{\mathrm{NH_3,NPL\ A583}}}{x_{\mathrm{NH_3,NPL\ A583}}}} \qquad (1)$$

The NH_3 amount fractions in the original three reference gas mixtures, as certified by the new gas standard NPL A583, are shown in Figure 3, with error bars representing the expanded uncertainty (k = 2). In this case, the certified values are derived from the gravimetric NH_3 amount fractions, without a correction for potential NH_3 adsorption to the cylinder wall (all mixtures were prepared using the same technique and materials). For each certified value, the uncertainty budget comprises of the measurement uncertainty in the integrated absorbances of NPL A583 and in that of the mixture to be certified (both taken from the standard deviation of the integrated absorbances from the recorded spectra of each standard measured), the gravimetric uncertainty of NPL A583 and the uncertainty in the experimental temperature and pressure. The final uncertainty in the certified NH_3 amount fractions was found to be dominated by the uncertainties in the integrated absorbances from experimental spectra. These results indicate that the certified NH_3 amount fractions agree with the gravimetric NH_3 amount fractions (represented by the dashed line in Figure 3) within the measurement uncertainties (~5%), and also that the 10 μmol mol^{-1} NH_3 mixtures in biogas are stable within ~5 % over a period of 29 months.

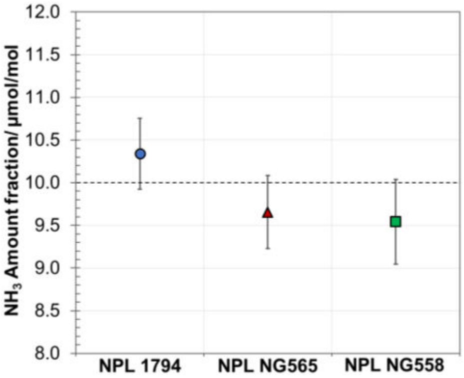

Figure 3 – Certified NH_3 amount fraction in the three 10 μmol mol^{-1} NH_3 in biogas mixtures used in the stability study. The error bars represent an expanded uncertainty with coverage factor k = 2 The dashed line indicates the gravimetric NH_3 amount fraction in the three mixtures.

3.2 FTIR

Fourier-Transform infrared (FTIR) spectroscopy is a quantitative spectroscopic method that has been widely used in gas analysis [12-15]. In FTIR spectroscopy, broadband measurements are made as a function of wavenumber, enabling the collection of complete absorption spectra of a sample. This allows the interrogation of different spectral regions and can minimise the effects of overlapping absorptions by multiple components within the sample mixture by selecting absorption peaks or bands that originate from a single target component.

3.2.1 Selection of spectral range for FTIR

Individual absorbances originating from a single component may be identified and measured in complex biogas mixtures, regardless of the concentration of the other IR absorbing compounds in the mixture, provided that a region with no overlapping absorptions exists within the recorded spectrum. This principle is illustrated in Figure 4 by comparing the FTIR spectrum of a mixture containing 10 µmol mol^{-1} NH_3 in nitrogen (which is IR-inactive) with those of mixtures of similar amount fractions of NH_3 in IR-absorbing matrices (CH_4 and Biogas 20). Figure 4 highlights the effect of the matrix gas on the recorded absorption spectra when measuring a target component, in particular when the matrix gas absorbs in the IR and especially over the same region. In the case shown in Figure 4a, the characteristic spectrum of NH_3 is significantly obscured by the CH_4 matrix at wavenumbers greater than 1000 cm^{-1}, thus limiting the spectral region suitable for NH_3 detection to the range 800-1000 cm^{-1}.

The inclusion of another strong IR absorber such as CO_2 in the biogas matrix adds further complexity to the FTIR spectra, as shown in Figure 4b. In this case the spectral region with minimal cross-interference (overlap) between the desired NH_3 signal and the matrix components is limited to the range 867-890 cm^{-1}.

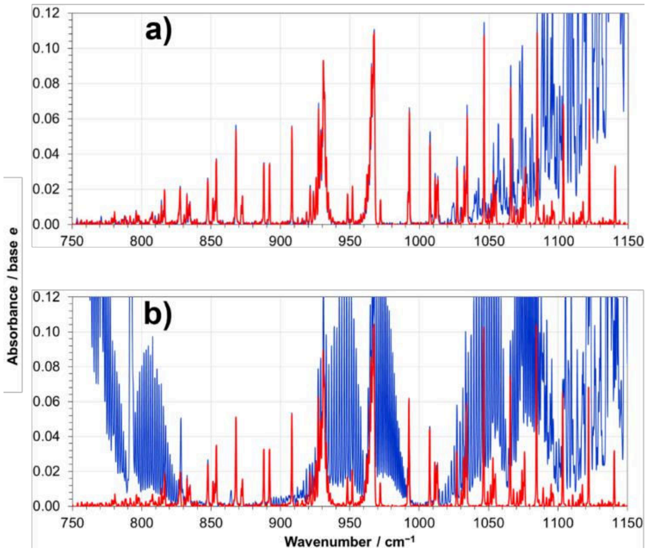

Figure 4 – FTIR spectra of 10 µmol mol^{-1} NH_3 mixtures in a variety of gas matrices. a) NH_3 in N_2 (red) and in CH_4 (blue), highlighting the strong CH_4 absorption at wavenumbers greater than 1000 cm^{-1}. b) NH_3 in N_2 (red) and in Biogas 20 (blue), showing additional CO_2 absorption in the 900 - 1100 cm-1 range as well as below 850 cm^{-1}.

3.3 CRDS

3.3.1 Selection of spectral range for CRDS

To find wavelength regions suitable for the analysis of NH_3 in biogas, spectral simulations were carried out using reference spectra from the HITRAN [16] and PNNL [17] databases. As with the FTIR set-up, the aim was to find a region with strong NH_3 absorption (sufficient for the technique to be sensitive to µmol mol^{-1} NH_3 amount fractions) where the interference from the overlapping absorbance of the CH_4 and CO_2 in the biogas matrix was minimal. To reduce the interference further, simulations (and later on the measurements) were made at a pressure of 200 mbar.

The ammonia absorption feature at 3414.7 cm^{-1} (2928.5 nm) was selected (see

Figure 5), as it has relatively low interference from overlapping CH_4 and CO_2 absorbances (also shown in (Figure 5).

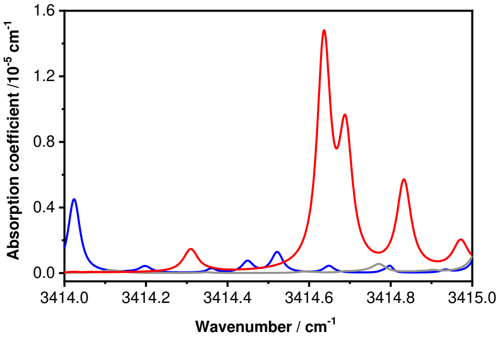

Figure 5 - Simulated absorption spectra at 200 mbar of 10 µmol mol^{-1} NH_3 (red) and 45 cmol mol^{-1} CH_4 (blue) and 40 cmol mol^{-1} CO_2 (gray) corresponding to the CH_4 and CO_2 amount fractions found in in Biogas 40.

3.3.2 Quantification of spectral interference

The potential contribution of H_2O vapour to spectral interference is negligible, as H_2O absorbs very weakly over the selected spectral window. Further tests on spectral inference therefore focused on CH_4 and CO_2 alone.

Pure CH_4 and a mixture of 20% CO_2 in N_2 were measured on the CRDS at 200 mbar, and their spectra are shown in Figure 6 along with that of a certified 9.12 µmol mol^{-1} mixture of NH_3 in N_2.

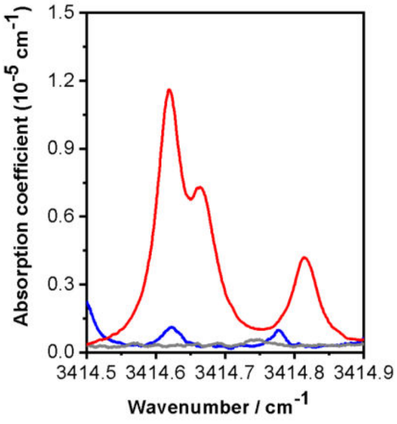

Figure 6 – Measured absorption spectra of a 9.12 µmol mol^{-1} NH_3 in N_2 mixture (red), pure CH_4 (blue) and 20% CO_2 in N_2 (gray) at 200 mbar.

These measurements show a good agreement with the simulation results (Figure 5) and helped narrowing down the spectral region for analysis to the range 3414.55 - 3414.8 cm^{-1}. Within this region, the area under the absorption curve was calculated for the interfering compounds relative to the area under the NH_3 absorption curve for the two types of biogas matrix used. These values are reported in Table 3, and show that in Biogas 20 both compounds contribute equally to the interference, while CO_2 interference dominates in Biogas 40. The values shown in this table represent an upper limit for the interference due to the matrix gases.

Table 3 - Relative interference of the biogas matrix components based on the areas determined under the absorption spectra.

	Area 10^{-6} cm^{-2}	**Area interferent / area 10 µmol mol^{-1} NH_3**	**Area Biogas40 / area 10 µmol mol^{-1} NH_3**	**Area Biogas20 / area 10 µmol mol^{-1} NH_3**
10 µmol mol^{-1} NH_3 in N_2	1.08	-	-	-
Pure CO_2	0.43	0.40	0.16	0.08
Pure CH_4	0.11	0.11	0.05	0.08

To quantify NH_3 in biogas a multiple linear regression routine was used to fit a linear combination of the spectra of NH_3, CH_4 and CO_2 to the recorded spectrum. First, the spectrum of the mixture VSL143730 (Aculife IV, nominally 10 µmol mol^{-1} NH_3 in Biogas 20) was analysed against a "pure" Biogas 20 mixture (i.e., no NH_3) and of a certified 9.36 µmol mol^{-1} mixture of NH_3 in N_2 (VSL528639). Multiple linear regression resulted in a calculated amount fraction of NH_3 of (9.32 ± 0.30) µmol/mol, with R^2 value of 0.9991. Similarly, for VSL243546 (Spectra-Seal, nominally 10 µmol mol^{-1} NH_3 in Biogas 40) the NH_3 amount of fraction was determined as (8.47 ± 0.30) µmol mol^{-1}. Residuals from the multiple linear regression analysis are small for all tested biogas matrices. The obtained NH_3 values are respectively 7% and 15% below their gravimetric value. This is in line with the results at VSL for 10 µmol mol^{-1} NH_3 in N_2 in these cylinder types: for Aculife IV 7% (range 2-13%, 10 cylinders tested) and for Spectra-Seal 11% (range 5-18%, 6 cylinders tested) below the gravimetric value.

3.3.3 Detection limits

To determine the detection limit of the CRDS instrument, a mixture of NH_3 in Biogas 40 was diluted with the pure matrix using mass flow controllers. The spectra recorded are shown in Figure 7.

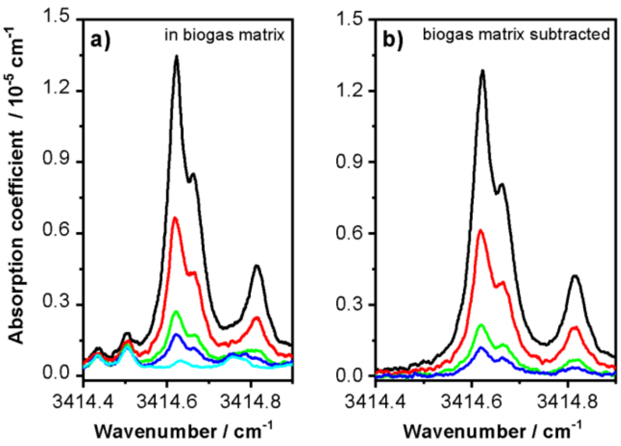

Figure 7 - Panel a) Recorded spectra of NH_3 in Biogas 40 (8.5 µmol mol^{-1} NH_3, black), 3 dilutions with Biogas 40 (4.2 µmol mol^{-1}, red), (1.4 µmol mol^{-1}, green), (0.7 µmol mol^{-1}, blue) and pure Biogas 40 (teal). Panel b) Residual spectra following subtraction of the pure Biogas 40 spectrum.

From the spectra shown in Figure 7b the NH_3 amount fraction was calculated using the fitting routine outlined above to within 0.1 µmol mol^{-1} from the calculated diluted values. A detection limit better than 0.2 µmol mol^{-1} of NH_3 (with k=2 and a 95% confidence level) in all types of biogas gas mixtures was estimated.

Over the selected spectral window, the CRDS instrument can detect NH_3 amount fractions in the range 0.2 - 20 µmol mol^{-1} in biogas. Higher amount fractions could in principle be measured by selecting one of the numerous weaker NH_3 absorption features, thus extending the upper limit up to a few hundred µmol mol^{-1} of NH_3 in biogas.

3.4 OFCEAS

3.4.1 Selection of spectral range

Similarly to the previous two instruments, the spectral range for the OFCEAS technique was optimised in order to avoid interferences from main biogas compounds (methane, carbon dioxide) with NH_3. The instrument operates in near IR with a resolution of $6 \cdot 10^{-3}$ cm^{-1}. The exact spectral window is proprietary information.

3.4.2 Repeatability

The intermediate precision was calculated by analysing duplicates during a period of time and pooling the standard deviation. The repeatability was calculated to be 2.49% relative.

3.4.3 Bias

The bias of the method was calculated by using two commercially available reference gas mixtures (63.0 ± 1.9) µmol mol^{-1} and (20.57 ± 0.62) µmol mol^{-1} NH_3 in CH_4. A systematic absolute error of 2 µmol mol^{-1} was observed, and therefore applied as a correction to take into account a systematic adsorption of NH_3 onto the surfaces of the instruments/sampling vessels observed even after conditioning the instrument.

3.4.4 Measurement range

Due to the propensity of NH_3 to adsorb onto surfaces, the limit of detection was estimated to be 10 µmol mol^{-1}. The range of the method was estimated to be 10-100 µmol mol^{-1}. Higher concentrations of NH_3 can be analysed but the pre-calibration of the instrument has not been assessed for concentrations above 100 µmol mol^{-1}.

3.4.5 Measurement uncertainty

The expanded uncertainties were calculated using the software MUKit (Measurement Uncertainty kit) (see annex A). Uncertainty is estimated using quality control and validation data. The expanded relative uncertainty (k = 2, with a coverage probability of approximately 95 %) for this method is 10%.

3.4.6 Parameters influencing the measurement

When analysing a gas containing low levels of NH_3 (< 100 µmol mol^{-1}) and low levels of H_2O, the measured value and the analysis time are greatly dependent upon what has been analysed before, the H_2O concentration in the instrument, the H_2O concentration in the sample, the material used in the sampling line (especially for the filter), and how long the filter has been used. In this work the measurements were all performed with dry gas (<100 µmol mol^{-1} of H_2O).

The instrument was conditioned in order to reduce the analysis time and to obtain a reliable result. This is shown in Figure 8, where a dry mixture containing 20.57 ± 0.62 µmol mol^{-1} NH_3 in CH_4 was analysed under three conditioning scenarios: without prior conditioning of the instrument, after conditioning the instrument with gas containing 20 µmol mol^{-1} NH_3 and after conditioning with gas containing 60 µmol mol^{-1} NH_3. Without any conditioning, the value of 17 µmol mol^{-1} was obtained after 40 minutes. When conditioning with 20 µmol mol^{-1} NH_3, the same value was obtained with a faster initial response increase. When conditioning with 60 µmol mol^{-1} NH_3, the value of 19 µmol mol^{-1} was obtained after 40 minutes.

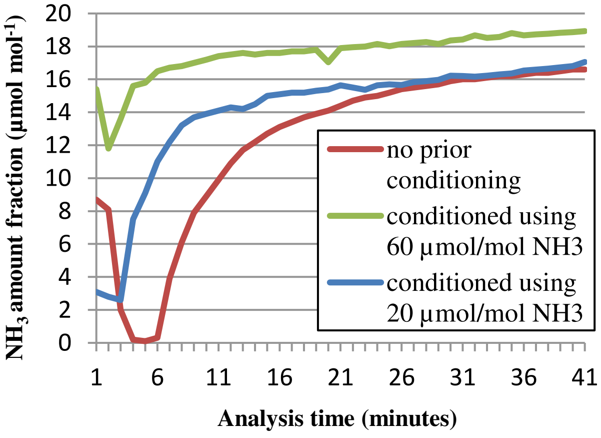

Figure 8 - Effect of conditioning the instrument prior to the analysis of biomethane for the determination of NH_3 concentration

The stainless-steel particle filter has a clear influence on the analysis time. As shown in Figure 9, when using a filter that has been exposed to gases of different compositions (referred to as a 'used' filter), the analysis time has been found to be much longer than when using a newly installed filter. On the contrary, the influence of the restrictor was not so distinct.

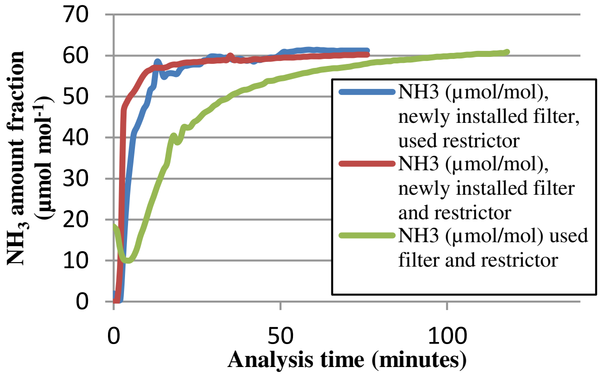

Figure 9 - Effect of filter condition when analysing biomethane for the determination of NH_3 concentration

It was found to be important to avoid any introduction of H_2O in the instrument after the conditioning, as H_2O immediately deconditions the instrument as shown in Figure 10. When a high amount of H_2O is introduced in the instrument, the amount fraction of NH_3 measured increases immediately to values higher than the targeted amount fraction (in this case 60 µmol mol^{-1}), showing that NH_3 is released from the surfaces of the instrument, which has also been observed in previous studies [17].

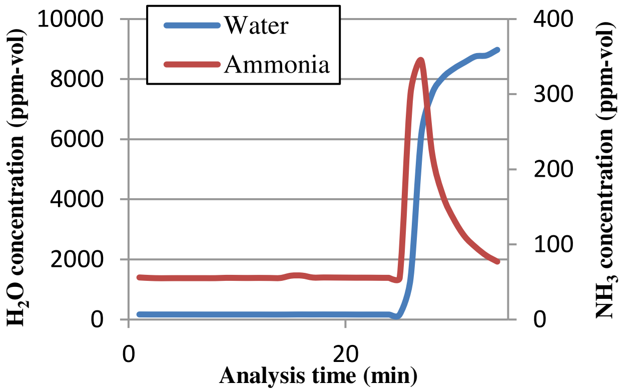

Figure 10 - Deconditioning of the instrument when H_2O is introduced into the instrument

4. Conclusions

The FTIR measurement technique was found to be capable of measuring 10 µmol mol^{-1} NH_3 amount fractions to within a 5% measurement uncertainty.

FTIR has been used to investigate the long term stability (29 months) of three reference gas mixtures of 10 µmol mol^{-1} NH_3 in CH_4 and biogas prepared in Spectra-Seal cylinders, pre-treated with an NPL proprietary treatment. In this study, the stability of NH_3 has been measured relative to a fixed CH_4 peak, to determine the relative stability. The advantage of measuring the potentially unstable trace NH_3 against the stable CH_4 matrix, is that the CH_4 acts as an internal standard which is simultaneously measured with the target component.

The stability of the NH_3 amount fraction was confirmed by a final measurement, in which a new 10 µmol mol^{-1} NH_3 in biogas 20 reference gas mixture was compared to the three older reference gas mixtures. Consequently, it is possible to claim that the 10 µmol mol^{-1} amount fraction of NH_3 within each reference gas standard is stable to within 5 % when compared against the new standard. All mixtures agree within the measurement uncertainty, which was dominated by the standard deviation of the integrated absorbances of the experimental spectra.

With regards to the measurements using laser spectroscopic methods (CRDS), the observation that the careful conditioning of the sample path is critical is less strict with the set-up developed due to the use of only coated materials and the small volume of the measurement cell. The response time of the measurement system can be further improved by reducing the cell volume (around 30 mL is feasible for the same cell length leading to an effective volume of 6 mL at a cell pressure of 200 mbar). The broadening of NH_3 in biogas is almost independent of the biogas composition for the analysed NH_3 absorption feature. This simplifies the analysis of measured spectra when using spectral fitting.

For the OFCEAS system, the careful conditioning of the sample path is a prerequisite to obtain reliable results. It also significantly reduces the time response of the system for ammonia. Another critical parameter is water; if water is introduced in the system after conditioning, it will cause a deconditioning of the system so it is very important to ensure that no water (for instance due to an introduction of air) is introduced after conditioning of the system.

Of the 3 systems presented, the CRDS system has the lowest detection limit for ammonia in biogas. A further improvement in detection limit by about a factor 3 can be obtained by replacing the relatively low reflectivity mirrors used with higher reflectivity mirrors currently available.

Based on the results obtained in this study, it can be concluded that NMIs can provide the necessary infrastructure to support measurement of NH_3 impurities as specified in EN 16723. Further development is recommended to improve the uncertainty and stability of the reference standards. It is important that end-users of the systems are aware of the effects of adsorption and moisture levels in biogas to prevent mis-reporting of data.

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ASSOCIATED CONTENT

Supporting Information

Background measurement data is provided to support the values and uncertainties supplied in section 3.4. “Supplementary information – OFCEAS background data (PDF file)

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The manuscript was written through contributions of all authors.

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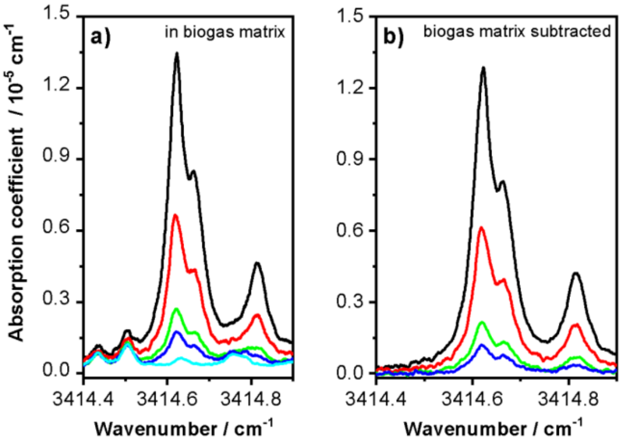
Table of contents artwork:



Characterization of Fourier transform infrared, cavity ring-down spectroscopy, and optical feedback cavity-enhanced absorption spectroscopy instruments for the analysis of ammonia in biogas and biomethane

Culleton, Lucy P.

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