

1 The application of a Cavity Ring-Down 2 Spectrometer to measurements of ambient ammonia 3 using traceable Primary Standard Gas Mixtures

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11
12 **ABSTRACT.** A correction for the undesirable effects of direct and indirect cross-interference
13 from water vapour on ammonia (NH₃) measurements was developed using an optical laser
14 sensor based on cavity ring-down spectroscopy (CRDS). This correction relied on new
15 measurements of the collisional broadening due to water vapour of two NH₃ spectral lines in the
16 near infra-red (6548.6 and 6548.8 cm⁻¹), and on the development of novel stable Primary
17 Standard Gas Mixtures (PSMs) of ammonia prepared by gravimetry in passivated gas cylinders
18 at 100 μmol mol⁻¹. The PSMs were diluted dynamically to provide calibration mixtures of dry
19 and humidified ammonia atmospheres of known composition in the nmol mol⁻¹ range, and were
20 employed as part of establishing a metrological traceability chain to improve the reliability and
21 accuracy of ambient ammonia measurements. The successful implementation of this correction
22 will allow the extension of this rapid on-line spectroscopic technique to exposure chamber
23 validation tests under controlled conditions and ambient monitoring in the field.

24

25 1. Introduction

26 Over the last century modern intensive farming practices, the increased use of nitrogen-based
27 fertilisers, and certain industrial processes are believed to be responsible for increases in the
28 ambient amount fraction of ammonia (NH₃) found in Europe [1, 2]. Emission and deposition of
29 NH₃ both contribute to eutrophication and acidification of land and freshwater, and may lead to a

30 loss of biodiversity and undesirable changes to the ecosystem. Ammonia also affects the long
31 range transportation of acidic pollutants such as sulfur dioxide and the oxides of nitrogen, and
32 contributes to the production of secondary particulate matter (PM).

33 In the European Union (EU), NH₃ emissions are regulated by legislation on national emissions
34 ceilings [3, 4, 5], which also set emission targets for individual member states. Abatement of
35 NH₃ emissions in the pig and poultry industry is covered in the EU by Integrated Pollution
36 Prevention and Control (IPPC) and in some European countries, including the UK, there are
37 dedicated NH₃ monitoring networks. In Germany, the Federal Immission Control Act [6]
38 provides guidance and technical instructions on air quality control, and recommends that at any
39 assessment point the concentration of ammonia should not exceed 10 µg m⁻³ (equivalent to
40 approximately 14 nmol mol⁻¹ at ground level), thereby limiting damage to plants and
41 ecosystems. Controlling ammonia is also important for reducing particle emissions of PM_{2.5} and
42 PM₁₀. A recent study [7] employing three chemical transport models found an underestimation
43 of the formation of ammonium particles, and concluded that the role of NH₃ on PM is larger than
44 originally thought.

45 Monitoring ammonia however poses a number of challenges: there is a lack of regulation on
46 which analytical techniques to employ, the required uncertainties for the measurements, the
47 establishment of agreed quality control and quality assurance (QC/QA) procedures, or the
48 implementation of a suitable traceability infrastructure to underpin the measurements.
49 Measurements of NH₃ are often carried out using low-cost diffusive samplers and active
50 sampling with denuders [8]. Despite currently being considered an “unofficial” reference
51 method, denuders suffer from a number of limitations: not only do they not provide rapid
52 measurements in real-time, but they also require complex post-exposure analysis by wet
53 chemical techniques, must be deployed over extended periods to achieve adequate sensitivity and
54 suffer from low accuracy. These devices deliver only average amount fraction data, and their
55 validation by traceable methods is not presently extensive.

56 In recent years, a number of spectroscopic techniques have been developed to measure trace
57 gases in the atmosphere. These rapid on-line methods, such as cavity ring-down spectroscopy
58 (CRDS) [9, 10] have the potential to overcome the limitation of the techniques currently used in
59 the field. Ammonia sensors based on CRDS [11] and on multiple-pass cells with quantum-
60 cascade lasers (QCL) [12-14] have been reported in the literature: however, before these sensors

61 can be deployed routinely in the field, their potential drawbacks (such as spectral cross-
62 interference and effects of collisional broadening on the NH₃ lines of interest) must be addressed.
63 One of the goals of this work is to extend the CRDS technology to enable more accurate
64 measurements of ambient NH₃ where the sampled atmosphere contains many species over a
65 wide range of concentrations and is also humid. Water vapour influences the measurements
66 through the presence of absorption features close to those of ammonia and through differences in
67 matrix broadening effects. Conventional moisture removal devices such as NafionTM dryers are
68 known to introduce biases in the measurements as they also remove ammonia from the sampled
69 air, and are therefore not a practical sampling option. In this paper we describe the development
70 of a correction for the effects of water vapour and its application to ammonia measurements
71 using a CRDS instrument. The correction is based on a new determination of the collisional
72 broadening of the ammonia absorption lines by H₂O, which are compared with those reported
73 previously by Schilt [15], Owen *et al.* [16] and Sur *et al.* [17]. Crucially, the correction derived
74 in the present study is underpinned by the establishment of metrological traceability of the
75 measurements through the development, at NPL, of new stable ammonia Primary Standard Gas
76 Mixtures (PSMs) prepared by gravimetry. This represents a step forward in the application of
77 spectroscopic measurements and gas standard development towards improved quantification of
78 ambient ammonia.

79

80 **2. Experimental method**

81 **2.1 Description of the standard Cavity Ring-Down Spectrometer**

82 At the heart of the apparatus is a high finesse optical cavity that can be brought into resonance
83 with a laser light source, allowing an intra-cavity optical field to build up [9, 10]. The light
84 source is then abruptly turned off and the intra-cavity power decays exponentially ("rings
85 down"). The decay time constant, τ , is measured by monitoring the intensity of the light that
86 leaks through one of the cavity mirrors. The total cavity loss, L , is related to the ring-down time
87 constant and the round-trip intra-cavity optical path, ℓ , by the expression:

88

$$89 \quad L = \ell/c\tau \quad (1)$$

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91 where c is the speed of light. If a gas sample containing absorbing molecules is introduced into
92 the cavity, the molecular absorption increases the total cavity loss by the amount al , where a is
93 the molecular absorption coefficient at the frequency that is resonant with the cavity (assuming
94 linear absorption, which is valid for the conditions of the measurements described here, and also
95 assuming $al \ll 1$). Sequential ring-down measurements at different optical frequencies generate
96 a spectrogram of cavity loss as a function of frequency, and subtracting the empty-cavity loss
97 gives the contribution from molecular absorption, which is proportional to the amount fraction of
98 the absorbing species.

99 The work reported here was carried out using a standard commercial CRDS spectrometer
100 (Picarro: model G2103) originally designed for the detection of trace amounts of ammonia in dry
101 air. The light source in this instrument is a single-frequency semiconductor laser, which can be
102 tuned over a small wavelength range by changing its temperature and drive current. The laser
103 wavelength is measured by a wavelength monitor (WLM) that operates on the principle of a
104 solid etalon [18, 19]. The WLM achieves a precision of better than 10^{-4} cm^{-1} for laser
105 frequency, but has no absolute frequency reference, consequently spectroscopic feedback is used
106 to maintain long-term frequency accuracy.

107 The G2103 analyser measures absorption in the spectral interval from $6548.5\text{-}6549.2 \text{ cm}^{-1}$.
108 Figure 1 shows the pertinent molecular spectra for the conditions of our measurements,
109 computed from the HITRAN 2012 database [20] for a gas sample containing 10 nmol mol^{-1}
110 ammonia (where 1 nmol mol^{-1} is equivalent to 1 part per billion (ppb)), $400 \text{ } \mu\text{mol mol}^{-1} \text{ CO}_2$
111 (where $1 \text{ } \mu\text{mol mol}^{-1}$ is equivalent to 1 part per million (ppm)), and 10 mmol mol^{-1} water vapour
112 (where 1 mmol mol^{-1} is equivalent to 0.1%).

113 The strongly absorbing line pair at 6548.6 cm^{-1} and 6548.8 cm^{-1} is measured to determine the
114 ammonia amount fraction, while the water and CO_2 lines around 6549.1 cm^{-1} provide a
115 frequency reference for long-term stabilisation of the WLM. The water lines also deliver the
116 measurement of the water vapour amount fraction in the sample, which is used to correct for
117 systematic effects of water vapour on the ammonia measurement.

118 The ammonia amount fractions reported by the standard analyser are derived from least-squares
119 fitting of measured absorption spectrograms to a spectral model of absorption versus frequency
120 for the three molecular species that are measured. Molecular absorption is modelled as a sum of
121 discrete spectral lines, each of which is described by a Galatry profile [21] because the Voigt

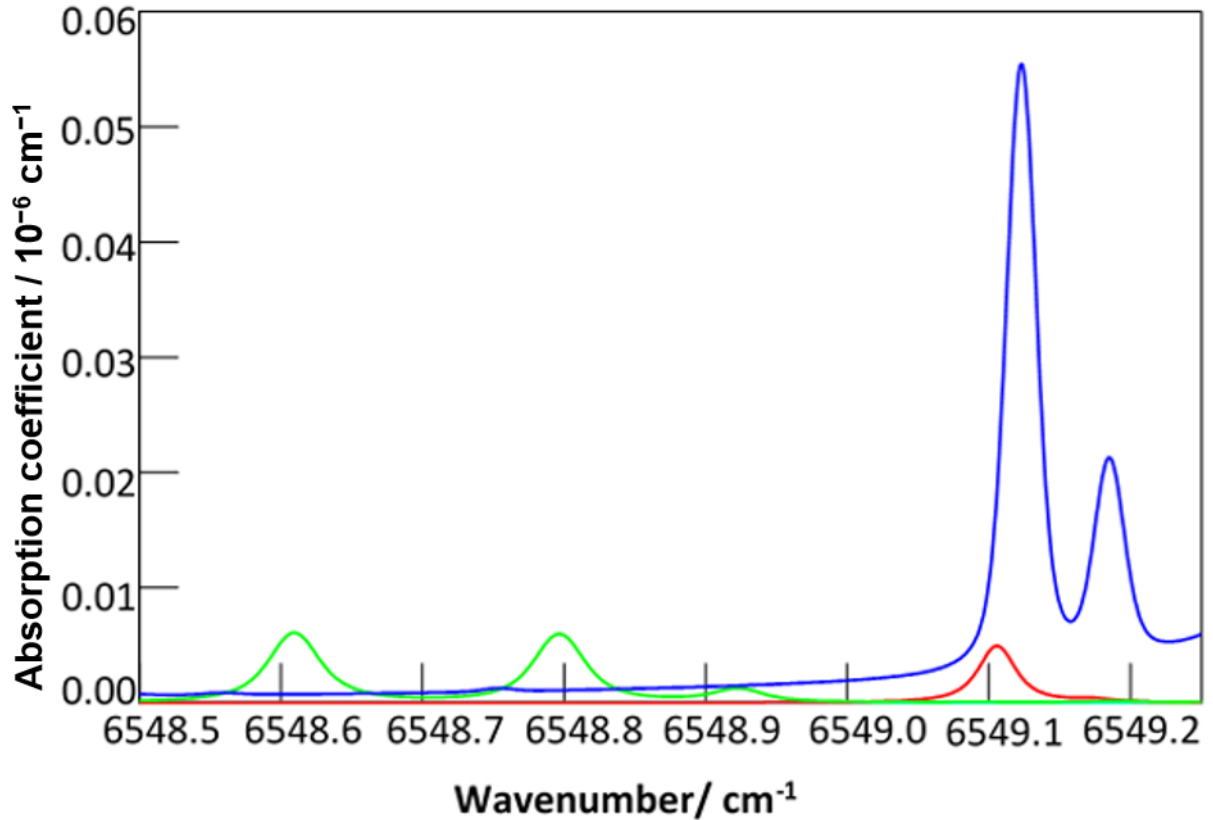


Figure 1. HITRAN simulation of absorption spectra for 10 nmol mol⁻¹ ammonia (green), 400 μmol mol⁻¹ carbon dioxide (red), and 10 mmol mol⁻¹ (1%) water vapour (blue) at 45 °C and 187 hPa.

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profile is noticeably inadequate.

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The Galatry line shape function, $G(x)$, is specified by four parameters: the line centre ν_0 (in units of cm^{-1}), the Doppler width σ (in units of cm^{-1}), and two dimensionless shape parameters, y and z . Physically, the parameter y has the same meaning as for the Voigt profile, namely the ratio of the rate of transition dipole dephasing collisions to the Doppler width, while the parameter z can be described as the rate of velocity changing collisions to the Doppler width.

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The independent variable x is the dimensionless detuning and is defined by Equation (2):

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$$x = (\nu - \nu_0)/\sigma \quad (2)$$

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and the Doppler width is given explicitly by:

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$$\sigma = \nu_0 (kT/Mc^2)^{1/2} \quad (3)$$

138

139

140 where k is Boltzmann's constant, T is the sample temperature, and M is the molecular mass. The
141 Galatry function also obeys a normalisation condition:

142

$$143 \int_{-\infty}^{\infty} G(x) dx = \pi^{1/2} \quad (4)$$

144

145 With this parameterisation, we may write the absorption coefficient as:

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$$147 \alpha(\nu) = \sum_i A_i G(x_i) \quad (5)$$

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149 where the subscript i runs over all the lines in the spectrum and the coefficients A_i (expressed in
150 units of cm^{-1}) relate the dimensionless Galatry functions to the observed absorption coefficient.
151 Here the dimensionless detunings, x_i , are given by Equation (2) evaluated with the appropriate
152 centre frequency for each individual line.

153 The spectral model used in the G2103 CRDS instrument is based on high-resolution spectra of
154 the known gases, from which the line shape parameters [22] (*i.e.* line centres and shape
155 parameters y and z , for the lines in Figure 1) were determined. The Doppler widths are not free
156 parameters since they are determined by the centre frequencies, sample temperature, and
157 molecular mass.

158 Carbon dioxide was modelled by a single absorption line and ammonia was modelled by three
159 lines. Water vapour is a more complex case, requiring six lines for an adequate description. In
160 addition to the lines at 6549.1 cm^{-1} and 6549.2 cm^{-1} , there are two much weaker lines at 6548.6
161 cm^{-1} and 6548.8 cm^{-1} that interfere with the ammonia spectral features (barely discernible in
162 Figure 1) and two very strong lines at 6547.2 cm^{-1} and 6549.8 cm^{-1} (not shown in Figure 1), the
163 off-resonant "tails" of which contribute measurably to the absorption in the ammonia region. For
164 water and ammonia, which have more than one absorption line in the spectral model, the
165 coefficients A_i in Equation (5) have fixed proportions, which are also determined from the high-
166 resolution spectra: therefore only one A coefficient is needed to specify the magnitude of the
167 molecular absorption.

168 To measure the composition of an unknown sample the CRDS analyser acquires spectra,
169 expressed as cavity loss per unit length versus frequency. To achieve the maximum data rate in

170 this analysis mode, the spectrum is sampled on a grid of adjacent cavity modes spaced by the
171 cavity free spectral range, equal to approximately 0.02 cm^{-1} in the case of this instrument.
172 Therefore no gross mechanical motion of the cavity mirrors (which would slow the data
173 acquisition) is needed. The doublet of ammonia lines at the low-frequency end of Figure 1 is
174 sampled approximately every 2 s by 160 ring-down measurements on 10 cavity modes.
175 Approximately once every 30 s the entire range of Figure 1 is sampled by 160 ring-downs on 36
176 modes; this longer scan is used only to update the water concentration and the absolute
177 frequency calibration of the wavelength monitor. In either case, the analyser performs a non-
178 linear least-squares fit (Levenberg-Marquardt algorithm) to determine the parameters in the
179 spectral model which minimize the deviation of the modelled absorption from the measured data.
180 In this fitting procedure the line centres and shape parameters are fixed.
181 There are therefore only five free parameters, namely: the magnitude of absorption for
182 ammonia, carbon dioxide, and water, an offset describing the empty-cavity absorption, and a
183 global frequency offset, due to the fact that the WLM does not provide an absolute frequency
184 scale.
185 The frequency offset is used to continually update the WLM readout software, so that the
186 reported optical frequency is always very close to the correct value. The optical absorption due
187 to ammonia is reported as the absorption coefficient at the peaks of two strong ammonia lines
188 that were measured at 6548.6 cm^{-1} and 6548.8 cm^{-1} . The two are averaged, and a linear
189 transformation is applied to convert from absorption to amount fraction. Similarly, the
190 absorption at the peak of the spectral line at 6549.1 cm^{-1} was employed for water vapour
191 measurements, together with the other five already detailed. The slope of the linear
192 transformation was derived from an in-house measurement of NH_3 by the manufacturer, which is
193 applied to all instruments. The intercept was determined for each individual analyser from a
194 measurement of air that had been scrubbed of ammonia by a chemical filter, taking into account
195 instrumental offsets, including in the absorption coefficient, due to imperfections in the empty-
196 cavity model.

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198 **2.2 Description of the modified Cavity Ring-Down Spectral Analysis**

199 The G2103 CRDS instrument was originally conceived to measure trace ammonia in well-
200 controlled environments, such as clean rooms. Environmental monitoring encounters a much

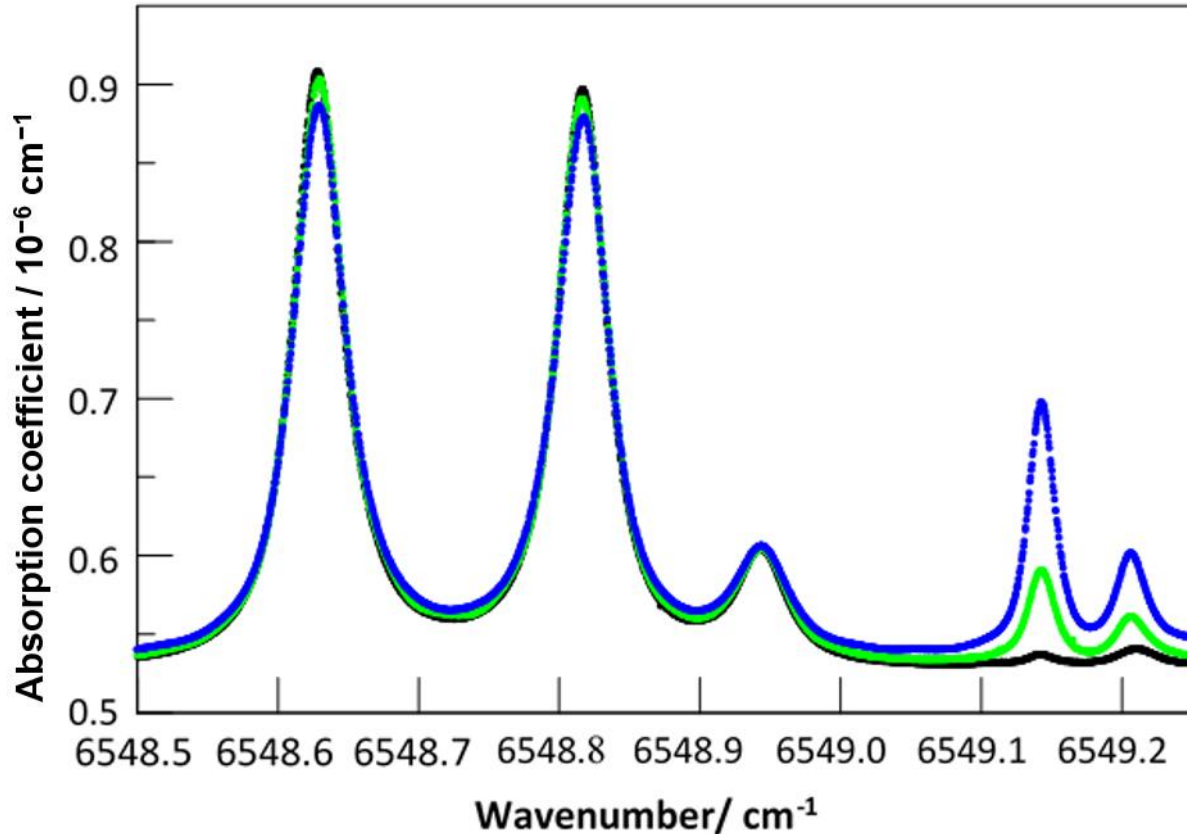
201 wider range of conditions. Consequently, the effects of water vapour on the ammonia
202 spectroscopy, which could be neglected in the original instrument, have to be addressed for the
203 present application.

204 Water affects the measured ammonia spectra in two ways, which can be called direct and indirect
205 interference. A direct interference arises from absorption by water molecules at the same optical
206 frequency where ammonia molecules absorb. The instrument software was modified at the
207 factory to apply an empirical, linear correction to the ammonia amount fraction, based on
208 measurements of ammonia-free air with varying water amount fraction.

209 Indirect interference is a result of the contribution of water molecules to the collisional
210 broadening of the ammonia spectral lines. The cross-section for spectral broadening is different
211 (typically larger) for H₂O than for air. Therefore, the ammonia lines are broader, and the peak
212 absorption is smaller when measured in humid air than when measured in dry air at the same
213 amount fraction.

214 Since the analyser reports amount fraction based on peak absorption, it systematically under
215 reports the ammonia amount fraction measured in a humid environment. This indirect
216 interference manifests itself, to lowest order, as an error in the coefficient relating peak
217 absorption to amount fraction; this error is in general a non-linear function of the water amount
218 fraction. To illustrate the effect, Figure 2 shows raw high-resolution spectra, acquired from
219 samples of 3 $\mu\text{mol mol}^{-1}$ NH₃ in dry air, to which humidified air was added to generate water
220 vapour amount fractions of 1.0 mmol mol^{-1} , 10 mmol mol^{-1} and 25 mmol mol^{-1} . As expected
221 there is a clear drop observed in NH₃ peak absorption and an increase in line width at higher
222 humidity.

223 Close to 100 spectra were collected for the three water vapour amount fractions listed and then
224 individually fitted with Galatry profiles, allowing the y parameter to be adjusted to deliver the
225 best-fit value. For completeness, an example spectrum with its fitted model and fit residuals is
226 shown in Figure 3. The simplified model made use of three spectroscopic lines for ammonia,
227 neglecting several of the very weak lines. This is adequate to ensure that the agreement between
228 the recorded ammonia absorption and the model is considerably better than $\pm 1\%$, and also to
229 quantify the variation of NH₃ line width with water vapour concentration. A commonly used
230 figure of merit for the fitting procedure is the ratio of the peak absorption to the root-mean-
231 square residuals, designated as “signal-to-noise ratio” by Cygan *et al.* [23] and as “quality of fit”

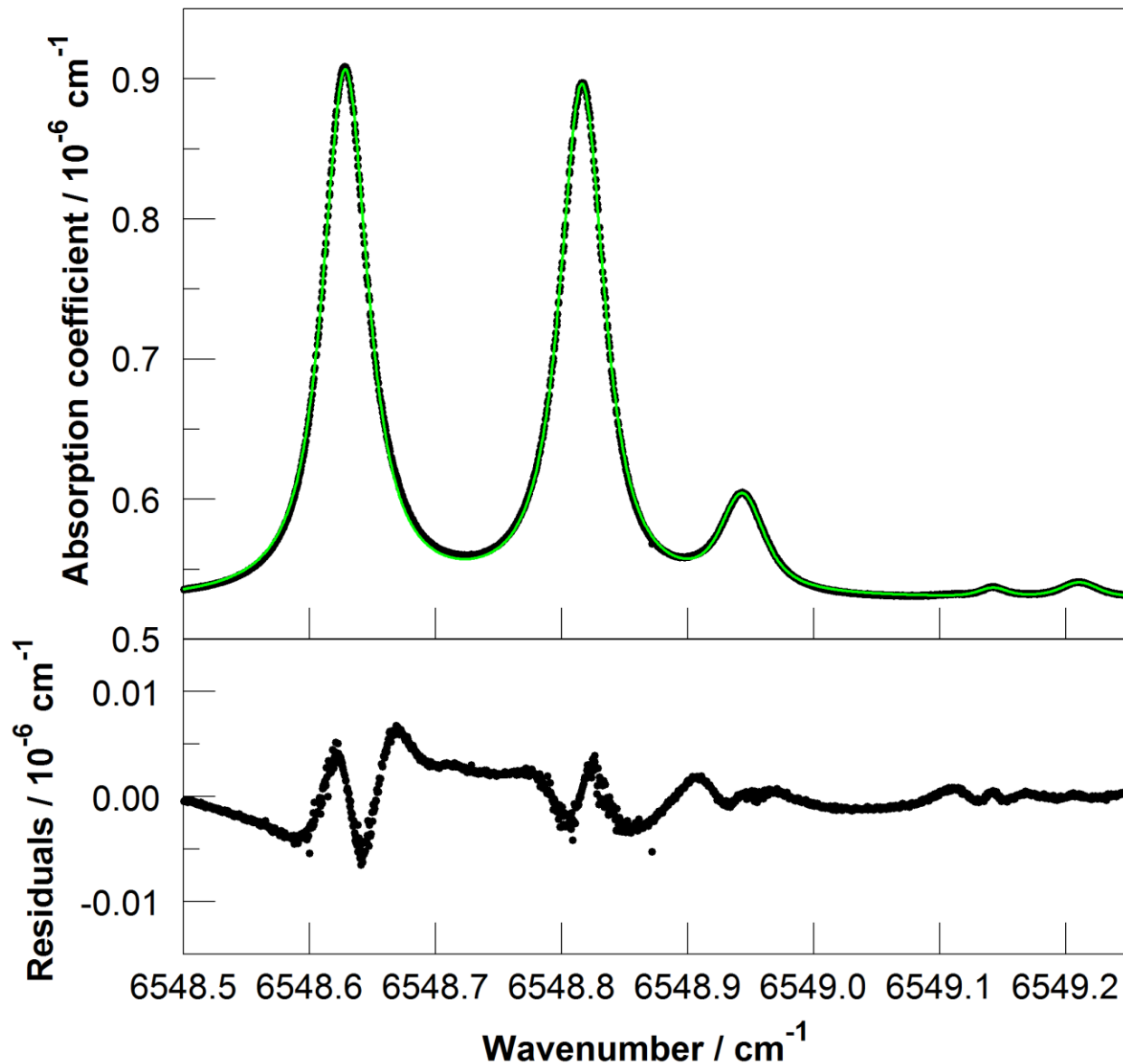


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Figure 2. Raw spectra for ammonia ($3 \mu\text{mol mol}^{-1}$) in air with varying water vapour amount fractions: 1 mmol mol^{-1} (black points), 10 mmol mol^{-1} (green points), and 25 mmol mol^{-1} (blue points). Sample conditions are $45 \text{ }^\circ\text{C}$ and 187 hPa . Each individual spectral point is the result of one ring-down measurement, with the x -axis being the wavenumber measured by the instrument’s wavelength monitor and the y -axis being the reciprocal of the speed of light times the ring-down time constant, which we treat as an “absorption coefficient”. Between ring-downs the cavity length was adjusted so as to change the resonant frequency in steps of 0.0005 cm^{-1} by moving a piezoelectric transducer, with the laser temperature and current adjusted accordingly to change the laser frequency by the same amount.

243 by Lisak *et al.* [24] For the data provided in Figure 3, where the spectrum is complex because the
244 lines are not completely isolated, this measure is approximately 160. This is sufficient for this
245 application, but is not as high as could be achieved with very well isolated lines that can serve as
246 much better tests of spectral line shape theory.

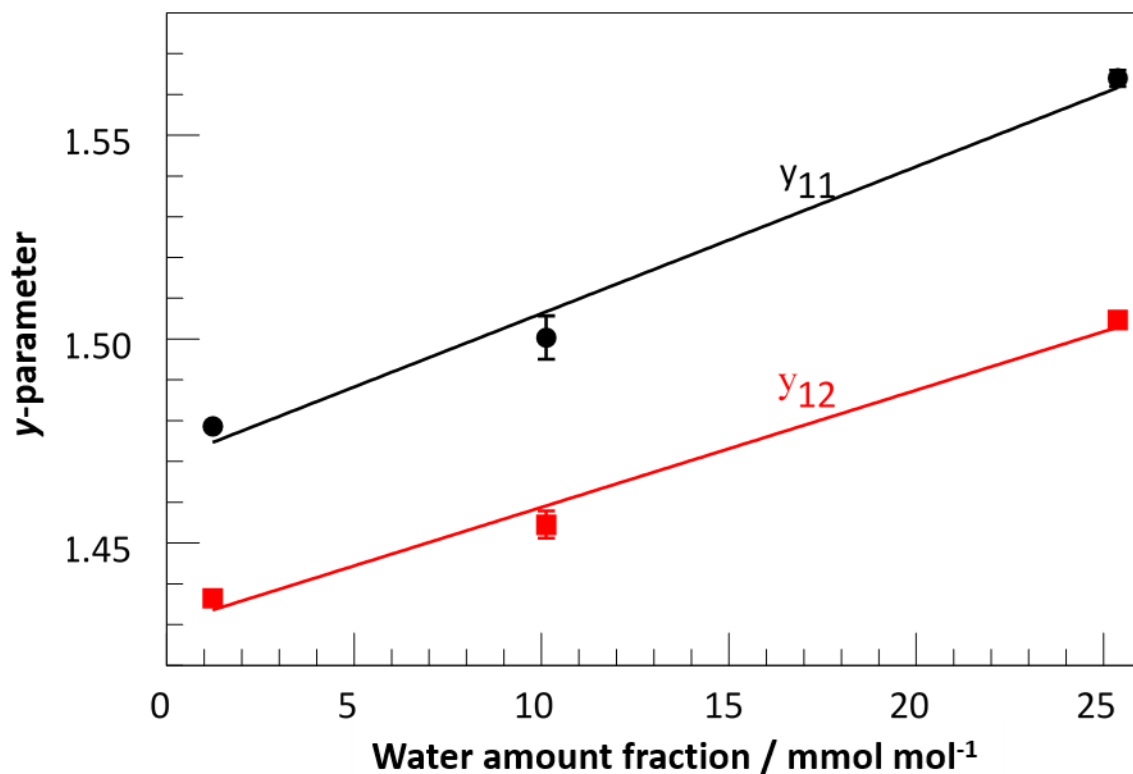
247 The use of a Galatry profile led to an improvement (+35 %) in the quality of the spectral fit
248 compared to using a Voigt profile; in addition, the quality of fit was essentially found to be the
249 same for all three humidity conditions considered here. These validation tests enabled us to



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 251 **Figure 3.** CRDS spectrum of ammonia ($3 \mu\text{mol mol}^{-1}$) in air with 1 mmol mol^{-1} water vapour
 252 (black points), together with the best-fit model (green curve), as described in the text. The lower
 253 panel shows the residuals of the fit,

254
 255 establish the systematic effect of water vapour on line width, in the selected spectral window,
 256 well enough to make accurate absorption-based measurements of ammonia in both dry and
 257 humidified atmospheres.

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 259 The average values of the y parameters show a linear dependence with water amount fraction, as
 260 illustrated in Figure 4. Converting the water amount fraction to partial pressure, and multiplying



261
 262 **Figure 4.** Dependence of the line broadening parameter y on water amount fraction. The upper
 263 points (black circles) refer to the ammonia line at 6548.6 cm^{-1} and the lower points (red squares)
 264 refer to the line at 6548.8 cm^{-1} . The points are average values from fitting of experimental spectra,
 265 with error bars corresponding to the standard error of the mean, and the straight lines are linear fits.

266
 267 the y parameter by the ammonia Doppler width, the slope of the fitted lines can be converted to a
 268 broadening parameter of the form tabulated in the HITRAN database [20], indicated here as
 269 γ_{water} . The average value obtained this way is $\gamma_{\text{water}} = (0.31 \pm 0.04)\text{ cm}^{-1}\text{atm}^{-1}$, which is
 270 intermediate between the HITRAN values for air- and self-broadening, $0.0957\text{ cm}^{-1}\text{atm}^{-1}$ and
 271 $0.486\text{ cm}^{-1}\text{atm}^{-1}$, respectively. The only other study of ammonia lines broadened by water
 272 vapour in the near infra-red is that of Schilt [15], who found $\gamma_{\text{water}} = 0.148\text{ cm}^{-1}\text{atm}^{-1}$ for an
 273 absorption feature at 6612.7 cm^{-1} and $\gamma_{\text{water}} = 0.24\text{ cm}^{-1}\text{atm}^{-1}$ for a feature at 6596.4 cm^{-1} . It
 274 should be noted, however, that Schilt measured absorption from multiple, unresolved lines at
 275 atmospheric pressure, so that the Lorentzian line width reported in their study arises from a
 276 combination of collisional broadening and the smearing of unresolved lines with different centre
 277 frequencies and is therefore not directly comparable to our measurement of the widths of
 278 resolved lines. Owen *et al.* [16] measured an absorption feature consisting of six partially

279 resolved transitions near 1103.46 cm^{-1} and reported broadening coefficients for all of them. The
 280 reported values for γ_{water} range from $0.276 \text{ cm}^{-1}\text{atm}^{-1}$ to $0.336 \text{ cm}^{-1}\text{atm}^{-1}$, depending on the
 281 transition and the choice of line shape model (both Voigt or Galatry were considered), in fairly
 282 close agreement with our observations. Similarly, Sur *et al.* [17] reported values for γ_{water} for nine
 283 ammonia lines in the frequency range $961.5\text{-}965.5 \text{ cm}^{-1}$: they observed broadening coefficients
 284 ranging from $0.257 \text{ cm}^{-1}\text{atm}^{-1}$ to $0.486 \text{ cm}^{-1}\text{atm}^{-1}$, in good agreement with the findings of Owen
 285 *et al.* [16] and those from this study. However it must be noted that Sur *et al.* [17] only used
 286 Voigt line shapes in their analysis.

287

288 Starting from the observed linear dependence of the y parameter on water concentration shown in
 289 Figure 4, it is possible to derive a correction for the effect of water vapour on the reported
 290 ammonia amount fraction. The sample temperature and pressure are stabilised in the instrument
 291 cell to known measured values that are constant, consequently the ammonia absorption is
 292 proportional to a dimensionless Galatry function, G , as described in Equation (5). Since the
 293 ammonia in the sample is quantified using the absorption at the line centre (*i.e.*, when the
 294 dimensionless detuning x is 0), and as the instrument is calibrated with dry gas (*i.e.*, $[\text{H}_2\text{O}] = 0$
 295 mol mol^{-1}), then a Galatry function in the form $G(y = y_0; x = 0)$ is employed in Equation (5),
 296 where the expression $y = y_0$ indicates the value of the broadening parameter y in the absence of
 297 water, and $x = 0$ is the detuning at the line centre. When the same instrument is used to measure a
 298 sample with water vapour amount fraction $[\text{H}_2\text{O}] \neq 0 \text{ mol mol}^{-1}$, the plot in Figure 4 is used to
 299 determine the y parameter of the humid sample, $y_{\text{H}_2\text{O}}$, as follows:

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$$301 \quad y_{\text{H}_2\text{O}} = y_0 + s \times [\text{H}_2\text{O}] \quad (6)$$

302

303 where s is the average slope of the linear dependence in Figure 4. Therefore, whilst the standard
 304 fitting routine fixes the y parameter to y_0 , the absorption of the humid sample relative to a dry
 305 sample is obtained by $G(y = y_{\text{H}_2\text{O}}; x = 0) / G(y = y_0; x = 0)$, which can be re-written using
 306 Equation (6) as $G(y = y_0 + s \times [\text{H}_2\text{O}]; x = 0) / G(y = y_0; x = 0)$. This ratio of Galatry functions
 307 can be thought of as the systematic change in line shape introduced by the presence of water
 308 vapour. To make the evaluation of the water correction more rapid during operation, the ratio of

Galatry functions was numerically evaluated for water amount fractions from zero to 0.1 mol mol⁻¹ and then approximated (with relative accuracy better than 5×10⁻⁴) by a power series of the form 1 + a[H₂O] + b[H₂O]². In addition, we implemented a small correction for the direct interference of water vapour with the ammonia lines that was not perfectly accounted for in the original spectral model. The final result was a modified instrument with two reported ammonia outputs, both in units of nmol mol⁻¹, namely: “NH₃_raw” (no change to the original design) and “NH₃_corrected” (based on the most recent near simultaneous measurement of the amount fraction of water vapour), given by:

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$$\text{NH}_3\text{_corrected} = (\text{NH}_3\text{_raw} + \text{offset} \times [\text{H}_2\text{O}]) / (1 + a[\text{H}_2\text{O}] + b[\text{H}_2\text{O}]^2) \quad (7)$$

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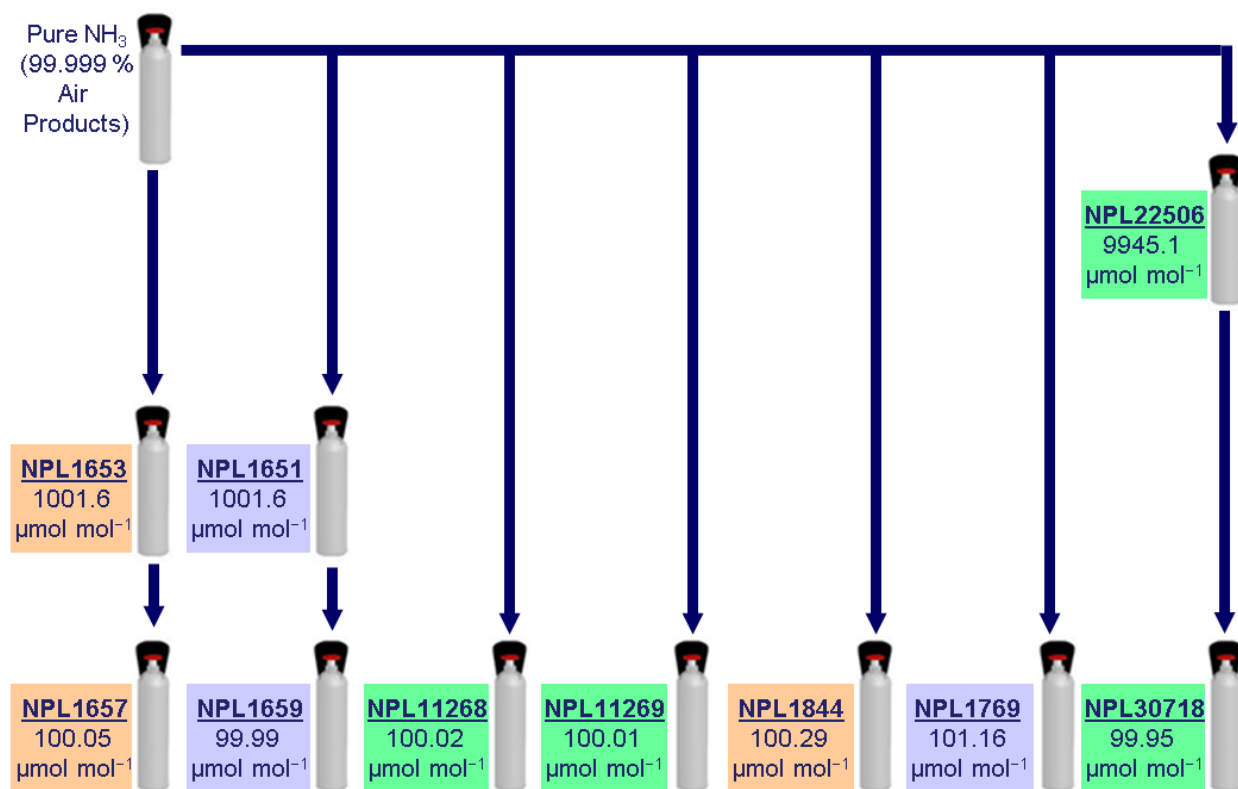
where [H₂O] is the water amount fraction in the sample in units of mol mol⁻¹, and *a* and *b* are the constants in the power series approximation to the ratio of Galatry functions as described above, with values *a* = -1.78 and *b* = +2.35. The offset coefficient has the numerical value of 1.73 × 10⁻⁸, corresponding to a 0.173 nmol mol⁻¹ correction to the ammonia amount fraction per percent amount fraction of water vapour in the sample.

325

2.3 Preparation and Validation of NH₃ Primary Standard Gas Mixtures

An accurate ammonia Primary Standard Gas Mixture (PSM) was necessary to be able to produce test atmospheres of known ammonia content. Due to the reactivity of ammonia, the preparation of gas mixtures is affected by a series of issues, including adsorption onto internal surfaces and reaction with impurities in the matrix gas used, as highlighted by the lack of consensus between National Metrology Institutes (NMIs) in an international key comparison in 2006-07, CCQM-K46 [25]. This exercise focused on the analysis of mixtures of 30-50 μmol mol⁻¹ ammonia in nitrogen; the disagreement between the results (up to 5% in some cases) was attributed to a number of reasons, including the different cylinder passivation chemistries used by the participating NMIs to produce their own reference mixtures.

In the light of these issues, a suite of seven PSMs was prepared in 10 L high-pressure aluminium gas cylinders, all of which had undergone different internal passivation treatments, which included Spectra-Seal™ (BOC plc [26]), Spectra-Seal™ with NPL's proprietary treatment (BOC plc and NPL), and Aculife IV™ (Air Liquide/Scott [27]).



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Figure 5. Hierarchy of ammonia gas mixtures prepared at NPL; mixtures prepared in Spectra-Seal™, Spectra-Seal™ with NPL’s proprietary treatment and Aculife IV™ cylinders are shown in orange, lilac and green respectively.

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The gas mixtures were prepared by gravimetry in accordance with the standard procedures defined in ISO 6142 [28], using high-accuracy calibrated single pan balances and adding each component separately either by small transfer vessels or direct gas transfer. Prior to filling, the cylinders were evacuated to 1×10^{-7} mbar with an oil-free rotary pump and turbo-molecular pump combination. The PSMs were prepared from pure NH_3 (Air Products, VLSI, 99.999% purity) and purified BIP+ nitrogen (Air Products, BIP+, 99.99995% purity) *via* a number of different dilution routes, in order to minimise any potential biases that might be introduced into the method. Figure 5 summarises the hierarchy of gas mixtures prepared in the amount fraction regime of $100 \mu\text{mol mol}^{-1}$, and the internal passivation treatments employed.

Ammonia amount fractions and their stability with time were measured with a non-dispersive infra-red (NDIR) spectrometer (ABB, Uras 26), using a “standard/unknown” routine in which each mixture was in turn treated as the unknown and was certified against the other six,

358 effectively used as standards. By this method it was possible to establish that the ammonia
 359 mixtures were internally consistent and stable with respect to each other, irrespective of the
 360 preparation path employed.

361 The amount fraction of the “unknown” mixture, x_u , is given by:

$$363 \quad x_u = \frac{R_u - R_0}{(R_{st} - R_0)/x_{st}} \quad (8)$$

364
 365 where R_u is the analyser response for the “unknown” mixture, R_0 is the analyser response to the
 366 zero gas (purified BIP+ nitrogen), R_{st} is the analyser response to the standard and x_{st} is the
 367 gravimetric amount fraction of the standard. Each mixture was therefore assigned six certified
 368 values of x_u . The results obtained are summarised in Table 1 and show that, for all mixtures, the
 369 certified amount fractions are within less than 1% from the gravimetric amount fractions
 370 (calculated only from the gravimetric preparation data). This indicated that loss of ammonia was
 371 minimal, and a conservative estimate of the expanded ($k = 2$) uncertainty in the amount fraction
 372 of ± 2 % was used for further calculations.

373 The stability over time of the PSM used for the dilutions, NPL30718 (as described in Section 2.4
 374 below) was monitored by recertifying it against newly made mixtures, nominally at the same

375

376 **Table 1.** Summary of the validation of PSMs

Cylinder number	Gravimetric amount fraction/ $\mu\text{mol mol}^{-1}$	Percentage deviation from gravimetric amount fraction when certified using:						
		NPL1657	NPL1659	NPL30718	NPL1844	NPL1769	NPL11269	NPL11268
NPL1657	100.05		- 0.42	+ 0.10	+ 0.15	- 0.60	- 0.82	- 0.07
NPL1659	100.00	+ 0.42		+ 0.53	+ 0.57	- 0.18	- 0.40	+ 0.36
NPL30718	99.95	-0.10	-0.52		+ 0.05	- 0.70	- 0.92	- 0.17
NPL1844	100.29	-0.15	-0.57	-0.05		-0.75	-0.97	-0.22
NPL1769	101.16	+ 0.60	+ 0.18	+ 0.70	+ 0.75		- 0.22	+ 0.54
NPL11269	100.01	+ 0.83	+ 0.40	+ 0.93	+ 0.98	+ 0.22		+ 0.76
NPL11268	100.02	+ 0.07	- 0.36	+ 0.17	+ 0.22	- 0.53	- 0.75	

377

378 amount fraction, at regular intervals. No signs of ammonia loss were observed.

379

380 **2.4 Generation of trace ammonia amount fractions for spectroscopic measurements**

381 Tests were carried out to establish the response of the CRDS spectrometer to well-characterised
382 humidified atmospheres containing ammonia and to confirm that the changes incorporated by the
383 manufacturer into the CRDS design were successful in removing water cross interference effects
384 and delivering improved values of the NH₃ amount fraction.

385 A NH₃/N₂ Primary Standard Gas Mixture (Cylinder NPL 30718) was employed to carry out the
386 main ammonia evaluation tests. The PSM contained a certified ammonia amount fraction of
387 $99.95 \pm 2.00 \mu\text{mol mol}^{-1}$ in a cylinder treated internally with the Aculife IV™ commercial
388 passivation process.

389 The PSM was subsequently diluted with known amounts of high purity diluent air (Peak
390 Scientific) and water vapour to generate various ammonia atmospheres in the nmol mol⁻¹
391 amount fraction regime. Comparative tests with a range of diluents showed that the scrubbed air
392 supply was a cost effective source of high purity diluent gas. Mass flow controllers (MKS and
393 Brooks Instruments) were employed to deliver the gases and these were all calibrated with
394 traceable high accuracy Bios DryCal flow meters (Mesa Laboratories, base unit: ML-800 series
395 with ML-800-44 and ML-800-3 measuring cells). Water vapour was introduced from a liquid
396 water reservoir contained in a high pressure cylinder, and fed from a 4 bar back pressure of
397 helium (Air Products). The liquid H₂O was then directed into a low flow Coriolis mass flow
398 controller and liquid injection vaporizer system (Quantim Series, Brooks Instruments). Here the
399 output was combined with the relevant dry NH₃ sample in a dedicated manifold to produce the
400 required humidified atmospheres. The liquid water employed had previously been de-ionised
401 using a purifier (Elga DV 35 Purelab (Option S15 BP)).

402 The water vapour generator was calibrated by on-line measurements of the mass loss of the
403 liquid water reservoir, using a top pan balance (Mettler Toledo SG32001). With the above
404 method it was possible to generate traceable humidified NH₃ amount fractions in the nominal
405 range of $10.2 \text{ nmol mol}^{-1}$ to $215 \text{ nmol mol}^{-1}$, each set at a relative humidity of 40%, 50%, 60%,
406 and 70%. The various multi-component mixtures generated were then introduced into the CRDS
407 instrument *via* a perfluoroalkoxy (PFA) pipe fitted with an excess flow that was also directed
408 into a safe exhaust.

409

410 **2.5 Testing for CO₂ spectroscopic interference**

411 Finally, the CRDS was checked to confirm that there was not a potential problem from cross-
412 interference with carbon dioxide (CO₂). A CO₂ amount fraction of 505 μmol mol⁻¹ was
413 introduced into the dry atmosphere, which is well above the levels expected for normal ambient
414 monitoring. The spectral features of this molecule were found to be too weak to be of
415 significance to the measurements. For ambient monitoring or humidified atmospheres, Figure 1
416 shows that the absorption lines of CO₂ and H₂O overlap, but this is taken into account by
417 allowing the line strength of both molecules to adjust independently when fitting the measured
418 spectra. Consequently, this method enables the relative contributions to the absorption from CO₂
419 and H₂O to be separated.

420

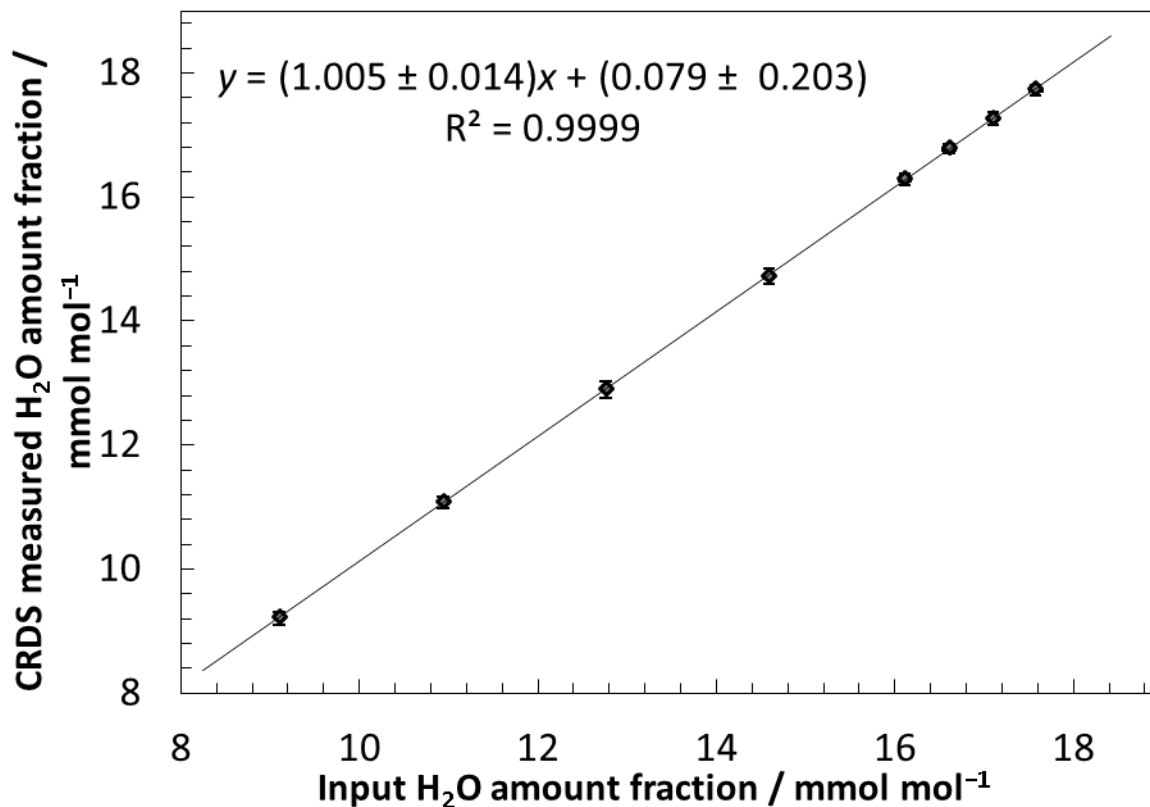
421 **3. RESULTS AND DISCUSSION**

422 The separate water and ammonia CRDS measurement ranges were evaluated by introducing
423 humidified air containing several known water vapour amount fractions into the instrument up to
424 18 mmol mol⁻¹ (corresponding to a relative humidity of approximately 70% at 20 °C). The
425 objectives here were to confirm that the factory internal water calibration was in agreement with
426 the known delivered H₂O input amount fractions generated at NPL, to check that the instrument
427 showed a linear response to water vapour, and to measure the cross sensitivity to water in the
428 ammonia measurement channel.

429

430 **3.1 Water vapour spectroscopic measurements**

431 Figure 6 is an example of a lack of fit plot showing the CRDS water response to a series of
432 known traceable H₂O input amount fractions generated at NPL, and is linear with r^2 effectively
433 equal to one. The factory internal calibration was found to be in agreement to within 1.3% with
434 the on-line mass loss calibration method. This provided further confidence that such water
435 vapour measurements could be employed by the manufacturer to verify the success of
436 modifications to the instrument. The factory water vapour calibration made use of results from
437 earlier work [29] and quadratic terms were applied to the raw data such that the reported water



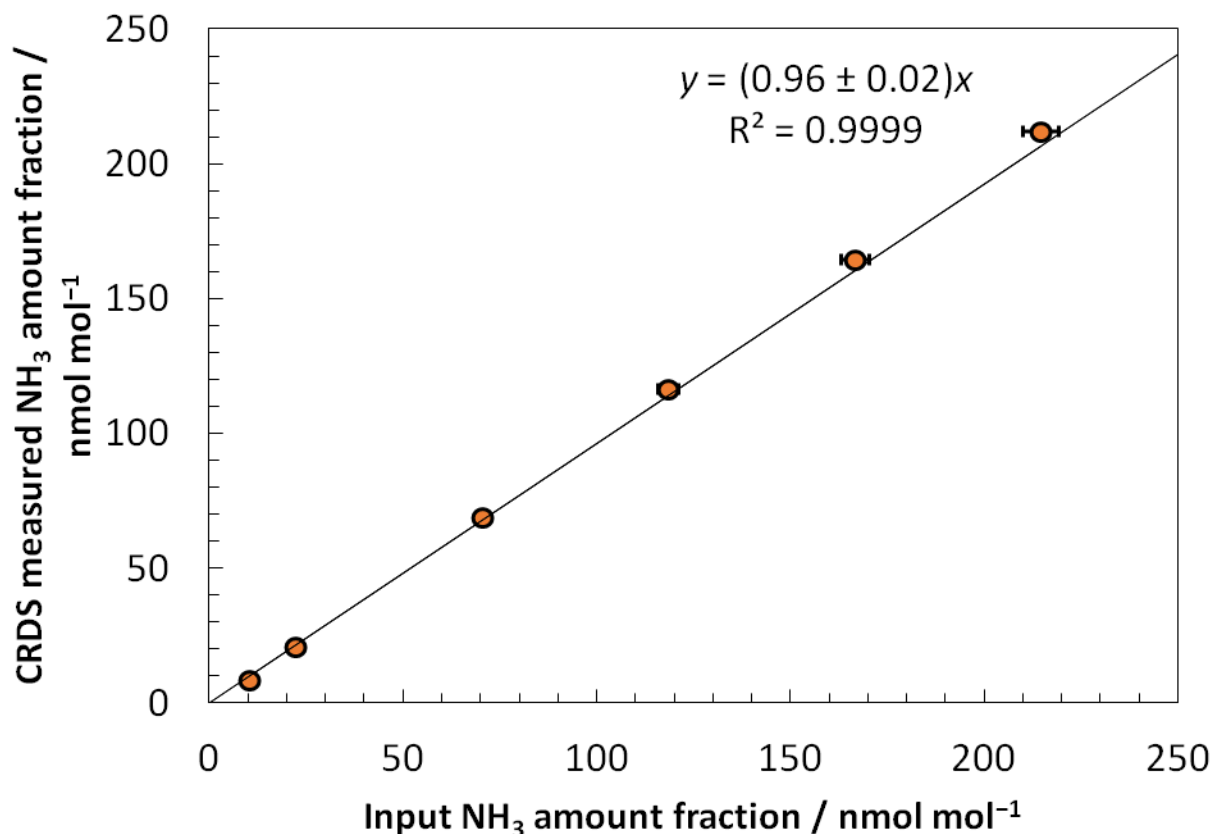
438
439 **Figure 6.** Lack of fit plot showing CRDS water response to traceable H₂O input amount fractions.
440

441 amount fraction from the present measurements at 6549.1 cm⁻¹ matched the amount fraction
442 reported by a different CRDS analyser measuring this compound at 6057.8 cm⁻¹, which was
443 calibrated against a chilled mirror hygrometer.
444

445 **3.2 NH₃ spectroscopic measurements**

446 Figure 7 is an example of a lack of fit plot showing the CRDS ammonia response (“NH₃_raw”)
447 to a series of traceable NH₃ input amount fractions at a known measured relative humidity of
448 nominally 60% at 20 °C. Figure 8 shows the corresponding modified (“NH₃_corrected”) results
449 for the same input amount fractions as transformed by Equation (7).

450 In this example each of the amount fractions reported by the CRDS were background subtracted
451 using the apparent NH₃ amount fraction obtained from a sample of humidified zero air at 60%
452 RH, and scrubbed free of ammonia. A similar subtraction procedure was carried out for the other
453 NH₃ lack of fit data, using the corresponding zero gas (either dry or humidified) applicable to a
454 relative humidity of: 0%, 40%, 50% and 70%.

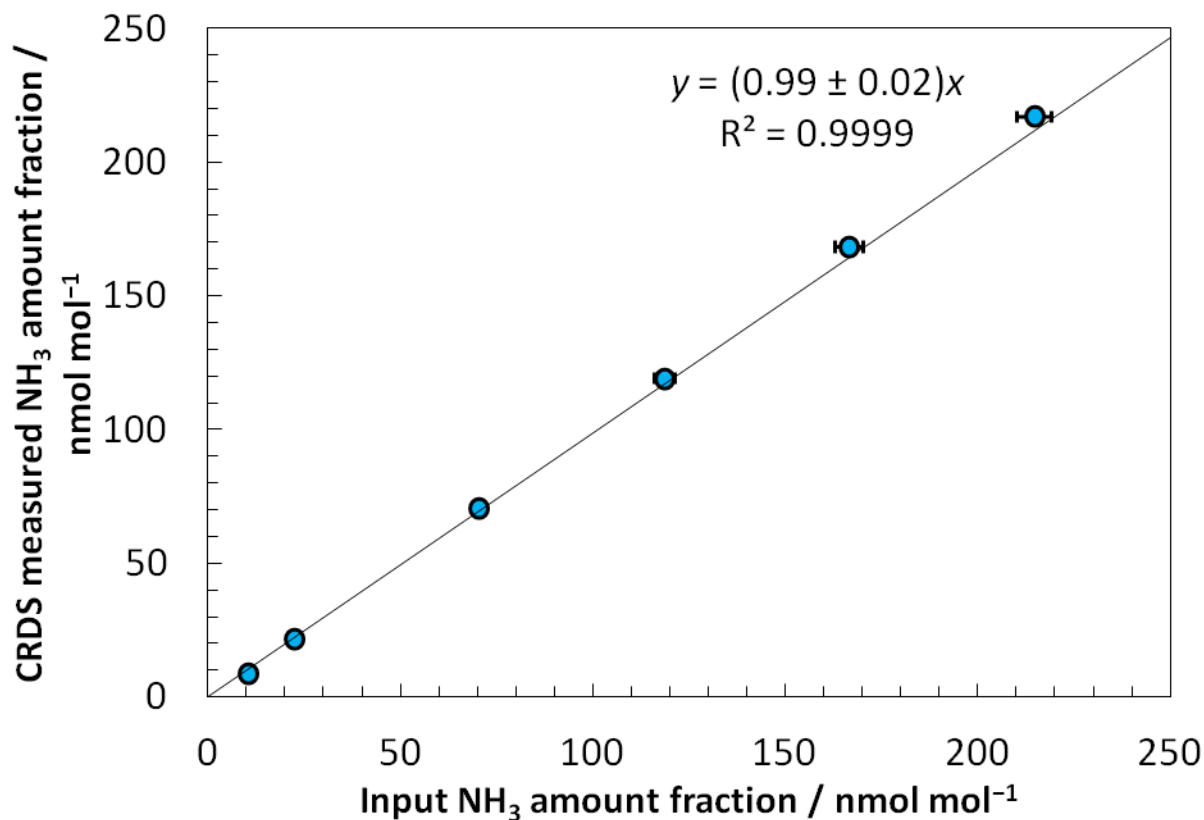


455
 456 **Figure 7.** Lack of fit plot showing mean CRDS response (“NH₃_RAW”) to traceable humidified
 457 (*RH* = 60%) ammonia input amount fractions. The solid line is the Generalised Least Squares
 458 (GLS) fit to the data, described in the text.

459
 460 To generate the lack of fit plots, uncertainties were assigned to each of the NH₃ input amount
 461 fractions, in preparation for analysis using XLGENLINE, which is a Generalised Least Squares
 462 (GLS) Microsoft Excel-based software package for low degree polynomial fitting developed at
 463 NPL [30]. This was also used in the analysis of the water vapour data detailed above.
 464 XLGENLINE employed a user-defined input file containing values of x and $u(x)$ (respectively
 465 the known NH₃ input amount fractions and combined standard uncertainty), y and $u(y)$
 466 (respectively the reported mean zero-corrected CRDS NH₃ amount fractions and repeatability
 467 standard deviation).

468 The software package was used to perform a first order polynomial GLS fit, in this case forced
 469 through zero. The fitted function automatically calculated analytical results and defined
 470 uncertainties for any number of unknown samples.

471



472

473

474

475

476

477

Figure 8. Lack of fit plot showing mean CRDS response (“NH₃_Corrected”) to traceable humidified (RH = 60%) ammonia input amount fractions. The solid line is the Generalised Least Squares (GLS) fit to the data, described in the text.

Table 2. Summary of gradients of all lack of fit plots

			NH ₃ _raw channel	NH ₃ _corrected channel
Nominal Relative Humidity /%	Water Amount Fraction /mmol mol ⁻¹	Delivered NH ₃ Amount Fraction Range /nmol mol ⁻¹	Gradient of lack of fit plots:	Gradient of lack of fit plots:
70%	15.6	10.2-215	0.96 ± 0.02	0.98 ± 0.02
60%	13.7	10.2-215	0.96 ± 0.02	0.99 ± 0.02
50%	11.7	10.2-215	0.97 ± 0.02	0.99 ± 0.02
40%	9.8	10.2-215	0.97 ± 0.02	0.99 ± 0.02
0%	0.0	10.2-215	0.98 ± 0.02	0.98 ± 0.02

478 Table 2 summarises the output gradients calculated by XLGENLINE for all the NH₃ atmosphere
479 lack of fit plots, each applicable to a relative humidity of: 0%, 40%, 50%, 60%, and 70%. The
480 column marked “NH₃_raw” shows the gradients obtained for results generated with the original
481 CRDS instrument configuration, together with their combined expanded standard uncertainties
482 (with a coverage factor $k = 2$, providing a coverage probability of approximately 95%). The
483 column marked “NH₃_corrected” shows the corresponding gradients generated using the
484 modified CRDS instrument configuration, designed to account for the influence of water vapour.
485 As expected, the gradient results obtained for the dry ammonia data are similar for both
486 “NH₃_raw” and “NH₃_corrected”. The trend for the humidified ammonia data shows a departure
487 from the supplied amount fraction in “NH₃_raw”, which within the uncertainty is rectified in
488 “NH₃_corrected” for all the conditions tested.

489

490 3.3 Error propagation and uncertainty analysis

491 In each case, the NH₃ amount fractions delivered to the CRDS (C_{Final} , in units of nmol mol⁻¹)
492 were calculated using Equation (9):

493

$$494 \quad C_{Final} = \frac{C_{Cylinder} \cdot F_{span}}{F_{Diluent1} + F_{Diluent2} + F_{Span} + F_{H_2O}} \cdot 1000 \quad (9)$$

495

496 where $C_{Cylinder}$ is the ammonia amount fraction in the cylinder (in units of $\mu\text{mol mol}^{-1}$), F_{span} is
497 the flow rate of NH₃ span gas, $F_{Diluent1}$ and $F_{Diluent2}$ are the flow rates of diluent zero gas and
498 F_{H_2O} is the flow rate of water vapour.

499 The sources of error identified include the NH₃ amount fraction of the parent cylinder, individual
500 repeatability standard deviations in the mass flow rates, mass flow controller temperature
501 dependencies, gravimetric water calibration (including balance drift), mass flow meter
502 calibrations, and time. Errors were then allocated to each term in Equation (9) that they
503 influenced.

504 Following the method outlined in ISO 6145-7:2010 [31], a ‘sensitivity’ was assigned to each
505 component in Equation (9) by differentiating the amount fraction with respect to each component
506 and summing in quadrature in accordance with Equation (10):

507

508

$$u(C_{Final}) = \left\{ \begin{array}{l} \left[\frac{\partial C_{Final}}{\partial C_{Cylinder}} \right]^2 [u(C_{Cylinder})]^2 + \left[\frac{\partial C_{Final}}{\partial F_{Span}} \right]^2 [u(F_{Span})]^2 + \\ \left[\frac{\partial C_{Final}}{\partial F_{Diluent\ 1}} \right]^2 [u(F_{Diluent\ 1})]^2 + \left[\frac{\partial C_{Final}}{\partial F_{Diluent\ 2}} \right]^2 [u(F_{Diluent\ 2})]^2 + \\ \left[\frac{\partial C_{Final}}{\partial F_{H_2O}} \right]^2 [u(F_{H_2O})]^2 \end{array} \right\}^{1/2} \quad (10)$$

510

511

512 The typical combined expanded standard uncertainties calculated for the humidified NH₃
 513 atmospheres were no greater than ± 2.3%. The relevant individual values were used as inputs
 514 into XLGENLINE, along with the corresponding values for the readings recorded for the CRDS
 515 instrument.

516

517 4. Conclusion

518 The collisional broadening due to water vapour of two ammonia (NH₃) lines in the near infra-red
 519 (6548.6 and 6548.8 cm⁻¹) was measured over a range of relative humidity by means of cavity
 520 ring-down spectroscopy (CRDS). The average value obtained for the broadening parameter, γ_{water}
 521 ($\gamma_{water} = (0.31 \pm 0.04) \text{ cm}^{-1} \text{ atm}^{-1}$) is in good agreement with previous studies. The measurement
 522 of γ_{water} allowed the implementation of a method which accounted for the cross interference of
 523 water vapour and has delivered an improved accuracy for low amount fraction measurements of
 524 NH₃ in the 10.2 nmol mol⁻¹ to 215 nmol mol⁻¹ regime with relative humidity in the range: 0%,
 525 40%, 50%, 60% and 70%. The development and validation of new stable NH₃ Primary Standard
 526 Gas Mixtures (PSMs) at 100 $\mu\text{mol mol}^{-1}$ was crucial for the further collaborative development of
 527 the CRDS sensor as part of the process of establishing traceability to measurements of ambient
 528 ammonia. The correction for the effects of water vapour on the reported ammonia amount
 529 fraction has been incorporated by the manufacturer in all new CRDS ammonia sensors. The
 530 analyser has potential use as a “spectroscopic reference instrument” for monitoring ammonia in
 531 future exposure chamber tests to validate diffusive and pumped samplers, and also for field
 532 measurements.

533

534

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542

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