Validation of Five Gas Analysers for Application in Ammonia Emission Measurements at Livestock Houses According to the VERA Test Protocol

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Abstract: Ammonia emissions are an important issue in livestock production. Many mitigation measures have been proposed in order to reduce the environmental impact of livestock farms, and reliable field measurements are required to evaluate the amount of released or reduced ammonia while applying these measures. Following the guideline of the Verification of Environmental Technologies for Agricultural Production test protocol, five commercially available gas analysers, i.e., INNOVA 1314, Picarro G2103, Rosemount CT5100, Gasmet CX4000, and Axetris LGD F200-A, were validated as alternative methods to the wet-chemistry method (reference method) for measuring ammonia in livestock houses. High correlations (r > 0.99) were found between the analysers and the reference method. The measurement errors of the tested analysers were below 2 ppmv or 10%. Equivalence to the wet-chemistry method was demonstrated for the INNOVA and Rosemount analysers without a recalibration and for the Picarro and Axetris analysers with a recalibration. The Gasmet analyser was seemingly subjected to an interference from carbon-dioxide and, after compensating for the cross-sensitivity, the equivalence to the wet-chemistry method could also be demonstrated. Calibration curves that were based on a certified gas cylinder were inconsistent with that based on wet-chemistry measurements, which suggested that field calibration might be necessary for optimal measurement accuracy.

Keywords: ammonia; evaluation; analyser; poultry; pig; emission; VERA

1. Introduction

Ammonia (NH₃) is one of the major pollutants emitted from livestock production. It was estimated that agriculture contributed 93.6% to the total NH₃ emissions in European countries [1]. The gas is not only harmful to human health, but also closely related to acidification and eutrophication of soil and water. Because of the substantial environmental impact, member states of the European Union are required to limit the emission level according to the National Emissions Ceilings Directive (2016/2284/EU). Moreover, excessive NH₃ emissions are prohibited in nature reserves under the Habitats Directive (92/43/EEC). In Belgium, starting up or continuing high-emission livestock production near Natura 2000 sites is no longer permitted. On the other hand, various systems have been proposed to reduce NH₃ emissions from livestock farms [2]. Several relevant aspects of these measures were investigated in early studies, such as the theoretical effectiveness on emission reductions [3–5].
energy use efficiency [6,7], and economic impact to the farms [8]. However, information on the NH$_3$ reduction efficiency of these systems in practice is still limited due to insufficient or unreliable monitoring. Field assessment methods are developed in order to evaluate the environmental performance of livestock farms and operational stability of the abatement techniques. One of the guidelines is the Verification of Environmental Technologies for Agricultural Production (VERA) test protocol for livestock housing and management systems [9]. In this protocol, a wet-chemistry method in accordance with ISO/DIS 21877 [10], NEN 2826 [11], and VDI 3496 Blatt 1 [12] is regarded as the reference method for quantifying airborne NH$_3$. Although wet-chemistry is relatively low-cost, the requirement for laboratory analysis after sample collections is practically inconvenient. This type of measurement cannot provide instantaneous concentrations either and it is thereby unsuitable for monitoring emission processes at high time resolutions. In addition, the method is sensitive to human errors, because the sampling and laboratory analysis involve complex manual procedures. As an alternative, the VERA test protocol allows for the use of automated measuring systems such as gas analysers, provided that sufficient equivalence with the reference methods is demonstrated according to the EN 14793 standard.

In the past decades, an increasing number of gas analysers applying advanced sensing technologies have become commercially available. These systems are designed to perform continuous concentration measurement of one or more gases of interest including NH$_3$. Still, measuring NH$_3$ in livestock barns is practically challenging due to the “sticky” nature of the gas and the high load of dust particles in livestock houses. Moreover, as the accuracies of these analysers are often matrix dependent, laboratory evaluation using certified gas cylinders do not always reflect their field performance. In this study, five commercially available gas analysers are compared and validated in a poultry barn and a pig barn following the procedure of EN 14793 [13], as prescribed by the VERA test protocol.

2. Materials and Methods

2.1. Description of Gas Analysers

The tested gas analysers for NH$_3$ in this study included an INNOVA Photoacoustic Gas Monitor (LumaSense Technologies A/S, Ballerup, Denmark), a Rosemount$^\text{TM}$ Quantum Cascade Laser Gas Analyser (Rosemount Inc., Shakopee, MN, USA), a Gasmet$^\text{TM}$ Fourier Transform Infrared Gas Analyser (Gasmet Technologies Inc., Vantaa, Finland), a Picarro Cavity Ring-down Gas Concentration Analyzer (Picarro Inc., Santa Clara, CA, USA), and an Axetris Tunable Diode Laser Gas Detector (Axetris AG, Kägiswil, Switzerland). These analysers are hereafter referred by their respective brand or trademark names. A summary of the analyser specifications is given in Table 1. Different optic gas sensing techniques are employed by the analysers, including photoacoustic spectroscopy (PAS), laser absorption spectroscopy (LAS), cavity ring-down spectroscopy (CRDS), and Fourier transform infrared spectroscopy (FTIRS). These techniques rely on a common underlying mechanism that the gas molecules of a given species are capable of absorbing electromagnetic radiation at specific wavelengths. Extensive reviews of optic sensing principle and instrumentations can be found in [14,15].

Table 1. Summary of the specifications of gas analysers for measuring ammonia (NH$_3$).

| Analyser | Model | Accuracy $^a$ | Calibration |
|----------|-------|---------------|-------------|
|          |       | Range (ppm$_v$) | Execution | Interval $^b$ |
| INNOVA   | 1314  | not specified   | 0–44       | Manufacturer | 3 |
| Picarro  | G2103 | 5% reading + 0.5 ppb$_v$ | 0–50       | Manufacturer | 18 |
| Rosemount| CT5100| 2% full-scale   | 0–52       | Manufacturer | 12 |
| Gasmet   | CX4000| 2% full-scale   | 0–150      | Manufacturer $^c$ | 9 |
| Axetris  | LGD F200-A | 2% full-scale | 0–69       | Authors      | 7 |

$^a$ Based on the product datasheet with purchase. $^b$ Number of months since the most recent calibration. $^c$ Zero-calibration with dry nitrogen gas performed daily.
All of the tested analysers are closed-path systems. That is, air samples are actively drawn to the analyser and analysed in a measurement cell to determine the NH$_3$ concentrations. INNOVA takes air samples in subsequent batches, and from each batch one concentration measurement is taken. The other analysers perform measurements from a continuous gas flow. In this study, the Picarro and Axetris analysers measured at their default frequency, which fluctuated between 0.5–1 Hz. The measurement interval of Rosemount was set to 5 s. The measurement cycle of Gasmet was set to 60 s according to the setting recommended by the manufacturer, and each measured value represented the average gas concentration in the air flow over the 60 s duration. In INNOVA, the data interval was approximately 130 s because of a more complex sampling procedure. Calibration of the gas analysers was carried out independently either by the corresponding manufacturer or the authors.

2.1.1. INNOVA

The INNOVA 1314 (LumaSense Technologies A/S, Ballerup, Denmark) is a multi-gas analyser based on PAS. The sensing principle is an application of the photoacoustic effect that is a phenomenon that the excitation of gas molecules via absorbing electromagnetic radiation generates acoustic signals, and the amplitude of which is proportional to the gas concentration [16]. INNOVA consists of a broadband infrared lamp and multiple narrowband optic filters mounted on a mechanical chopper wheel. Measurements are performed semi-continuously in three primary steps: (1) filling a built-in measurement chamber with a fixed amount of gas samples, (2) determining the concentration of each target gas in the sample based on PAS, and (3) removing the gas sample from the measurement chamber. Due to partially overlapped spectral absorption wavelength, NH$_3$ measurements can be strongly affected by water vapour applying the PAS measuring technique [17]. To overcome the issue, INNOVA integrated an algorithm to compensate for this interference. According to the calibration report provided by the manufacturer, measurement bias induced by 2 vol% water vapour concentration was negligible (NH$_3$ reading contribution <0.06 ppm$_v$).

2.1.2. Rosemount

The Rosemount CT5100 is a multi-gas analyser that is based on LAS. Gas concentrations are determined directly based on the Beer–Lambert law, where the attenuation of the laser beam after transmitting through a gas sample is described as a function of gas concentration, laser path length and absorption coefficient at the given wavelength. In Rosemount a quantum-cascade laser (QCL) module is used to emit narrowband light tuned at a desired wavelength for measuring NH$_3$. By design measurements are taken under 240 mbar and 45 °C. According to the calibration report provided by the manufacturer, the interferences from three vol% water vapour, 1000 ppm$_v$ methane and 15 ppm$_v$ nitrous oxide were negligible (NH$_3$ reading contribution <0.03 ppm$_v$).

The test Rosemount analyser only offered the basic functionality for concentration measurement and automated temperature regulation in the measurement chamber. Prior to field deployment, the device was assembled with additional accessories. A stainless needle valve was mounted at the inlet of the analyser unit that was connected through a stainless tube coated with SilcoNert®2000 (SilcoTek GmbH, Bad Homburg vor der Höhe, Germany). The driving force of air stream was provided by a vacuum pump attached to the outlet of the Rosemount. The pressure in the measurement cell during operation was manually adjusted to 240 mbar via the needle valve. The default analyser outputs were 4–20 mA current, corresponding to 0–55 ppm$_v$, NH$_3$, updated at 1 Hz. The measured gas concentrations were also displayed on a digital readout, but no interface was provided to enable logging. The analogue outputs were read and logged with an Industruino IND.I/O microcontroller unit (ES Gear Ltd., Hong Kong, China) every 5 s.

2.1.3. Picarro

The Picarro G2103 is a dual-gas analyser for NH$_3$ and water vapour based on CRDS. During measurement a narrowband laser pulse tuned at 6548.5 to 6549.2 cm$^{-1}$ wave number is induced into
a cavity containing the gas sample. While the laser beam is reflected back and forth between two highly reflective mirrors, the light intensity decays over time due to absorption by the cavity wall, scattering and reflectivity losses. The presence of NH$_3$ molecules will lead to a faster decay governed by the Beer–Lambert law. The NH$_3$ concentration is then determined based on the shortened decay time with respect to the NH$_3$-free condition. In Picarro, measurements are taken under 187 mbar and 45 °C regulated automatically by an embedded controller. It was reported that the presence of 1.6 vol% water vapour could induce up to 3% bias in the raw NH$_3$ measurements, and to compensate for this interference a correction equation is implemented in the Picarro analyser software [18].

2.1.4. Gasmet

The Gasmet CX4000 is a multi-gas analyser based on FTIRS. The analyser performs interferometry using a narrowband laser to construct transmittance and absorption spectra over the 900–4200 cm$^{-1}$ mid-infrared region, and the 910–1150 cm$^{-1}$ region is used to estimate NH$_3$ concentrations that are based on the Beer–Lambert law. Measurements were taken at 180 °C around atmospheric pressure regulated automatically by the instrument. The Gasmet system consisted of two separate units. During measurement, the air samples sequentially flowed through a sampler unit and an analysing unit. In order to minimize the temperature difference between the incoming air samples and the analyser measurement cell, a 10 m heated hose was attached to the inlet of the sampler unit. An automated zero-calibration was performed daily while using a dry nitrogen gas. Interference from water vapour and carbon-dioxide were known to the manufacturer and were compensated in the Calcmet™ Analysis and Controlling Software offered by the manufacturer.

2.1.5. Axetris

The Axetris LGD F200-A NH3 is a single gas analyser based on LAS. The device uses a narrowband tunable diode laser (TDL) as the light source, and NH$_3$ concentration is determined based on the attenuation of the incident light according to the Beer–Lambert law. The Axetris was not a stand-alone measuring device and, thus, it was firstly integrated into a compact system as described in [19] prior to field deployment. The measured NH$_3$ concentrations were logged by a laptop using the LGD F200 Data Logger software provided by the manufacturer.

Calibration of the Axetris on NH$_3$ measurement was performed by the authors based on a degree-1 polynomial fitted with ordinary least squares. The reference values were the offered concentrations of four certified cylinders (Air Liquide Benelux, Liege, Belgium), respectively, containing 0, 5, 14.5, and 68.8 ppm$_v$ NH$_3$ mixed in dry nitrogen (±3% uncertainty). The gases were supplied around atmospheric pressure. The measurement accuracy of the Axetris was known to depend on the supply gas pressures [19]. Therefore, the measured NH$_3$ in the field were corrected for pressure by multiplying the raw ppm$_v$ readings with a correction factor $\lambda$, with $\lambda = \left( -4.032 \cdot P^{1.242} + (1 + 4.032) \cdot P \right)^{-1}$, where $P$ is the absolute pressure in bar. The manufacturer stated that water vapour could be an interfering species for NH$_3$, but no quantitative information about the effect or compensation measures were available.

2.2. Field Test Set-up

Field measurements were conducted in a poultry (560 m$^2$, containing 3056 finisher broilers) and a pig barn (57 m$^2$, containing 48 finisher pigs) at Flanders Research Institute for Agriculture, Fisheries, and Food (ILVO, Merelbeke, Belgium). Polytetrafluoroethylene (PTFE) tubes of 4 mm inner-diameter were used to transport air samples from the sampling locations to measuring devices. A two-micron PTFE particle filter (Model SP53-T-2T, M&C TechGroup GmbH, Ratingen, Germany) was equipped at the inlet of each tube.

In the poultry barn, one sampling tube was allocated to each measurement device. The tube inlets were tightened closely together one metre above the litter. A total of ten measurement trials were carried out on the fifth and fourth day before slaughter, and three other trials on the second
day after removing all chickens from the barn. Axetris measurements were unavailable during the poultry barn test due to a technical issue. In the pig barn, in total seventeen measurement trials were performed during the first two days after removing the pigs for slaughter. The air samples were taken at a ventilation exhaust 3.2 m above the floor. Two sampling tubes were installed between the measurement point and the measuring devices. T-shaped tube connectors were used at the end of the sampling tubes to split the gas stream. One sampling tube was shared by INNOVA, Picarro, and Gasmet, and the other by Rosemount, Axetris, and the reference method.

2.3. Reference Method

The reference NH$_3$ concentration was acquired using the wet-chemistry method that was prescribed by the VERA test protocol. Airborne NH$_3$ was captured by a sampling system adapted from ISO/DIS 21877 [10] and the VITO Flemish reference method [20]. The acid trap consisted of two sequentially connected impingers filled with 100 mL 0.1 molar H$_2$SO$_4$. Both of the impingers were immersed in ice chips until being brought to a laboratory for analysis. The outlet gas from the acid trap was dehumidified with silica gel. A vacuum pump was used to provide suction force after the dehumidifier. Two floating ball flow meters (Model AFM103, Ankersmid, Wilrijk, Belgium) were respectively installed at the inlet and outlet of the pump for monitoring instantaneous flow. Accumulative volumetric flows and pressures were measured at the end of the measurement line with a dry gas meter (Model Gallus G1.6, ITRON GmbH, Karlsruhe, Germany) and a pressure sensor (Eltek GD81, Eltek Ltd., Cambridge, UK), respectively. The ambient temperature was recorded with a temperature sensor probe (Model TC type K, S.A. Testo N.V., Ternat, Belgium).

The acid trap set-up was deployed in duplicate for all field measurements. Before starting collecting samples, airtightness of both acid traps was verified by testing the flow rate while the acid trap inlet was seal. The leakage, if any, was considered insignificant if the average flow rate over 5 min. measured by the gas meter was $\leq 2\%$ of the intended sampling flow rate. The leak test was performed in a van to avoid potential sample contaminations due to non-negligible background NH$_3$ near agriculture areas. During gas sample collection, air from the measurement location was continuously drawn through the impingers at a constant flow rate, 4 L min$^{-1}$ in the poultry barn and 1.5 L min$^{-1}$ in the pig barn, determined according to the expected concentration levels. The sampling duration was 30 min. for all of the tests in the pig barn and for the tests in the poultry barn before slaughter. The duration was raised to 60 min. in the poultry barn after the birds were removed. After sample collection, the amount of dissolved NH$_3$ was analysed by an accredited laboratory at ILVO while using continuous flow analysis, flow injection analysis, and spectrophotometric detection according to [21]. The obtained NH$_3$ concentration in air were resented in mg Nm$^{-3}$ normalized for 101.325 kPa and 273.15 K.

2.4. Analyser Performance Assessment

The concentrations obtained from the wet-chemistry method were firstly converted to ppm$_v$ before further analysis. The duplicates that had large within-trial differences were detected and discarded according to a two-sided Grubb’s test at 95% confidence level [13]. The mean of each remaining duplicate was taken to represent the measured concentration of the corresponding trial. The simultaneously acquired measurements from each analyser were averaged over the same period.

The inter-device agreement was quantified by pair-wise Pearson’s correlation coefficients $r$ and root-mean-square error (RMSE). The RMSE were also calculated for each analyser with respect to the mean of all analysers. The equivalence between the analysers and the wet-chemistry method was assessed based on three criteria according to EN 14793: (1) $r < 0.97$, (2) orthogonal regression intercept $|\beta_0| \leq \sigma_{rm}$, and (3) orthogonal regression slope $|\beta_1 - 1| \leq \frac{\mu}{\sigma_{rm}}$, where $\sigma_{rm}$ and $\mu$ are, respectively, the documented standard deviation of the wet-chemistry method and the grand mean of claimed measurement range. To get an indication of margin for accuracy improvement, median absolute
deviations (MAD) of the absolute and relative residuals were estimated from the calibration of the analysers using the wet-chemistry measurement data.

3. Results and Discussion

3.1. Reference Measurement

Over the 30 trials, the observed concentration levels in the poultry and the pig barn ranged between 0.98 and 19.1 ppm_v. One trial from the poultry barn test failed to pass the Grubbs test for outlier and was discarded. The remaining acid trap duplicates agreed well. The mean absolute difference was 0.19 ppm_v, or 4.3%. To demonstrate performance equivalence, EN 14793 requires that more than 30% of the total number of measurements are below 20% and more than 30% of the total number of measurements are above 67% of the full concentration range. In the obtained dataset, 43% were lower than 4 ppm_v, and 57% were higher than 13.4 ppm_v. The obtained dataset complied with the test requirement for 0 to 20 ppm_v range, though no observation was available between 4 and 13.4 ppm_v.

3.2. Comparison between Analysers

The analysers agreed well with each other on the measured NH3 concentrations (Table 2). Among the total of 30 trials, six trial-measurements from the Rosemount analyser and two from the Gasmet analyser were unavailable due to system malfunction. Because of the different observation ranges and uneven weighting of error in the root-mean-squared estimation, the obtained r and RMSE estimates of Axetris will be discussed separately. Excluding Axetris, the pair-wise correlation coefficients were >0.998. The RMSE among the analysers varied between 0.27 and 1.85 ppm_v. The smallest difference was found between Picarro and Gasmet, and the largest difference between INNOVA and Gasmet. Picarro had the lowest error with respect to the mean of all the analysers, and INNOVA error was the highest.

Table 2. Pair-wise correlation coefficients (r, low-left diagonal) and root-mean-square errors (RMSE, upper-right diagonal) among five tested gas analysers and the mean on measuring ammonia (NH3) (ranged between 0.98 and 19.1 ppm_v) in the field over 30 trials. The mean represents the unweighted average of available analyser measurements per trial.

|       | INNOVA | Picarro | Rosemount | Axetris | Gasmet | Mean |
|-------|--------|---------|-----------|---------|--------|------|
| INNOVA| -      | 1.078   | 0.646     | 1.846   | 1.216  | 0.872|
| Picarro| 0.999 | -       | 0.637     | 0.542   | 0.462  | 0.300|
| Rosemount| 0.999 | 1.000   | -         | 1.205   | 0.562  | 0.327|
| Axetris| 0.889 | 0.971   | 0.976     | -       | 0.272  | 0.750|
| Gasmet| 0.998 | 0.999   | 1.000     | 0.991   | -      | 0.424|
| Mean  | 0.999 | 0.999   | 0.999     | 0.936   | 0.999  | -    |

The analysers also agreed well on the temporal pattern of the NH3 concentration. An example of the measured NH3 with 130-second time resolution in the pig barn is given in Figure 1. During this measuring period, the barn was neither actively ventilated nor heated, and the indoor temperature followed the typical sinusoid diurnal pattern where the peak appeared around 15:00. Despite the absence of pigs, the NH3 concentration fluctuated between 15–27 ppm_v and the details were captured by all of the analysers. Noticeable relative biases among the analysers can be clearly seen on the time series plot, but the offsets were moderately consistent during the test period. The measured NH3 values from INNOVA remained the lowest and Axetris the highest.
Figure 1. Time series of the measured ammonia (NH$_3$) by five gas analysers and the temperature in the pig barn. For better comparability and clarity, the data from Picarro, Rosemount and Axetris are downscaled to every 130 s based on moving averages. INNOVA and Gasmet are presented at 130 and 60 s measurement interval, respectively.

While the Pearson’s correlation coefficient values are very high (Table 2), the estimates are insufficient for representing agreement because systematic biases are not accounted for [22]. More comprehensive tools may be the concordance correlation coefficient [23] and Bland–Altman analysis [24]. Still, high linearity is a crucial basis for linear calibration. Because the Pearson’s correlation coefficient is one of the assessment criteria in EN 14793, the $r$ values are calculated to allow for direct comparisons to the results from the equivalence test.

The available measurements of the Axetris were between 15–19 ppm$_v$, which was evidently smaller than the 0.8–20.9 ppm$_v$ observation range of the other analysers. This lead to an issue that the estimated $r$ values for Axetris tended to be smaller than the $r$ values for the other analysers. To cope with the range difference and obtain indicative estimates, Thorndike’s Case 2 [25] was applied to calculate correlation coefficients of the Axetris measurements over 0.8–20.9 ppm$_v$. After expending the observation range, the $r$ values were significantly improved, and the lowest correlation was found between Axetris and INNOVA ($r = 0.997$). For the high concentration range observed in the pig barn, the RMSE between analysers other than Axetris was 0.98 ± 0.78 ppm$_v$. This was comparable to the 0.92 ± 1.21 ppm$_v$ RMSE for Axetris (Table 2).

3.3. Comparison between Reference Method and Analysers

The analysers exhibited reasonable precisions, but the accuracy varied at different NH$_3$ levels (Figures 2 and 3). Over the complete observed concentration range, INNOVA had the lowest RMSE (0.46 ppm$_v$) as compared to the wet-chemistry method. In the poultry barn and pig barn tests, the lowest RMSE was, respectively, 0.24 ppm$_v$ with Picarro and 0.56 ppm$_v$ with INNOVA. At 0.8 ppm$_v$ in the poultry barn without chickens the analyser RMSE varied between 0.14–0.21 ppm$_v$, whereas Gasmet was the lowest and INNOVA the highest. For 2.4–3.4 ppm$_v$ in the poultry barn with chickens, Picarro, Rosemount, and INNOVA had RMSE <0.29 ppm$_v$. Gasmet overestimated the NH$_3$ concentration by 0.64 ppm$_v$. For 14–19 ppm$_v$ NH$_3$ in the pig barn, all of the analysers, except INNOVA tended to overestimate the concentrations by 1–2 ppm$_v$. 
Figure 2. The scatter plot (left) and relative bias (right) between the wet-chemistry method and five gas analyser (◦ INNOVA, △ Picarro, + Rosemount, × Axetris, ◊ Gasmet) measurements on ammonia (NH₃) in a poultry barn. The dashed line denotes 1:1 regression.

Figure 3. The scatter plot (left) and relative bias (right) between the wet-chemistry method and five gas analyser (◦ INNOVA, △ Picarro, + Rosemount, × Axetris, ◊ Gasmet) measurements on ammonia (NH₃) in a pig barn. The dashed line denotes 1:1 regression.

Table 3 provides a summary of the criteria and results of the equivalence assessment. The minimum acceptance level of the correlation coefficients is $r > 0.97$ for the method equivalence assessment. This criterion was compliant by all analysers, including Axetris after correcting for the expended observation range. The acceptable range of the regression intercept ($|\beta_0| < 0.535$) and slope ($|1 - \beta_1| < 0.056$) were determined based on the 11.2% maximum uncertainty of the wet-chemistry method found under laboratory conditions [26]. For these two parameters, INNOVA and Rosemount were both below the acceptance threshold. Picarro, Axetris, and Gasmet did not pass the slope criterion likely due to suboptimally executed calibrations or a lack of maintenance. For Axetris, although the device tended to underestimate the NH₃ concentration under sub-atmospheric pressures and was compensated accordingly, the correction was insufficient to explain the 12.2% positive bias...
with respect to the wet-chemistry method; the observed pressure remained at 846 ± 3 mbar throughout the test period, which only accounted for −1.8% expected bias.

Table 3. Compliance of equivalence between the wet-chemistry method and five gas analysers on measuring ammonia (NH₃) concentrations in air. The assessment criteria on the correlation coefficients, intercept, and slope are determined according to EN 14793 [13].

| Analyser | Correlation Coefficient (r) | Intercept (β₀) | Slope (β₁) | Variability a |
|----------|-----------------------------|----------------|-------------|---------------|
| INNOVA   | 0.998                       | −0.282         | 1.032       | 0.16          |
| Picarro  | 0.999                       | −0.194         | 1.105       | 0.16          |
| Rosemount| 0.999                       | −0.370         | 1.052       | 0.17          |
| Axetris  | 0.998 b                     | −0.063         | 1.122       | 0.22          |
| Gasmet   | 0.999                       | 0.187          | 1.096       | 0.29          |
| Criteria | r > 0.97                    | | | N/A |

a Median absolute deviation (MAD) of the residuals in ppm. b Corrected for the full observation range applying Thorndike’s Case 2.

3.4. Practical Prospects

3.4.1. Calibration and Reliability

The INNOVA that was tested in this study had the shortest interval, since the most recent calibration. It was reasonable that the instrument showed a better performance than the others. Rosemount also performed well despite the long calibration interval. The Picarro analyser exhibited satisfying performance at low concentration range in the poultry barn, but a recalibration was required for the higher range. The daily performed zero-calibration by the Gasmet analyser could prevent long-term offset drift, but this measure had no effect on correcting the slope. A recalibration also appeared to be necessary for Axetris.

The optimal performance of the analysers can be indicated by the calibration residuals while using the wet-chemistry measurements as the reference (Table 3). The variabilities of the regression residuals were all below the 11.2% uncertainty of the wet-chemistry method reported in [26]. Applying that 1σ ≈ 1.4826 · MAD, the highest optimal accuracy was ±0.46 ppmv (±6.7% uncertainty) at a 95% confidence level found on INNOVA. This value provided an indication of the best achievable performance in practice. Gasmet exhibited the lowest 0.84 ppmv (7.1% uncertainty) accuracy at a 95% confidence level. Axetris showed a 0.64 ppmv optimal accuracy, but, because this analyser was not tested for <4 ppmv, the relative error should not be compared to the other analysers.

Manufacturer recalibrations are often expensive and time-consuming due to the transportation between distant locations. Sparing a wide time slot for manufacturer calibrations is also often not feasible in practice, especially when the measurement tasks are directly related to the production stage of farm animals. In this study, high costs and time conflicts limited the possibility of having the analysers calibrated by the manufactures right before each field test. Nonetheless, the used calibration intervals provided a good indication of the long-term reliability of the analysers, while assuming that the initial manufacturer calibrations were properly carried out and valid.

Because of practical constraints, calibrations performed by the end users are usually unavoidable. In this study, only Axetris was calibrated by the authors using certified gas cylinders. To verify whether the measured biases in the field were due to suboptimal calibrations, Rosemount, Axetris and INNOVA were tested in a laboratory after the field tests. Reference concentration levels (5.8% total uncertainty in the dilution process and the gas cylinder) were generated by diluting a 52.3 ppmv certified NH₃ cylinder (Air Products N.V., Vilvoorde, Belgium) in dry nitrogen. In contrast to the field tests, the outputs from these analysers were all lower than the reference by, on average, 3.7% with Rosemount, 6.2% with Axetris and 8.3% with INNOVA (Figure 4). While the Rosemount error might be explained by the uncertainty of the reference values, attention is required to this inconsistency between the wet-chemistry based and gas cylinder based calibration curves. The representativeness and reliabilities
of certified gas cylinders should be further investigated. For the moment, the wet-chemistry method is seemingly the only reliable source of reference under field conditions if optimal accuracy is desired.

![Figure 4](image.png)

**Figure 4.** The scatter plot (left) and relative bias (right) between the generated reference concentrations (diluted from a certified 52.9 ppm$_v$ ammonia cylinder with nitrogen) and three gas analyser (○ INNOVA, + Rosemount, × Axetris) measurements on ammonia (NH$_3$). The dashed line denotes 1:1 regression.

### 3.4.2. Interference

The NH$_3$ measurement by the Gasmet analyser was known to interfere with carbon-dioxide (CO$_2$) by the manufacturer. Although CO$_2$ compensation was incorporated in the Gasmet software, still a reading contribution of 0.086 ppm$_v$ NH$_3$ per 100 ppm$_v$ CO$_2$ was found on laboratory results with the tested device (unpublished data). The apparent CO$_2$ concentrations were, respectively, 782 ± 217 ppm$_v$ in the poultry barn and 2073 ± 239 ppm$_v$ in the pig barn measured by the Gasmet. After compensating for the interference, the RMSE of Gasmet comparing to the wet-chemistry method was reduced to 0.41 ppm$_v$, and the instrument also reached sufficient equivalence to the wet-chemistry method, with $r = 0.999$, $\beta_0 = -0.306$ and $\beta_1 = 1.018$. For the Gasmet analyser, gas composition plays an equally important role as the reliability of the reference NH$_3$ values, and single-gas calibration appeared to be insufficient for achieving an optimal accuracy under field conditions. Similar interference issues could also occur on the other analysers and should be investigated.

### 3.4.3. The Sampling Line Set-up

In the field tests, the measuring devices were taking air samples from either an independent or a shared gas tube. The sampling process can be an important source of errors, and it was possible that the NH$_3$ concentration levels were inherently different between tubes due to adsorption and absorption of NH$_3$ molecules, air leakage, and spatial variability of the gas concentrations [27]. To ensure identical gas compositions and avoid sampling errors confounding the comparisons, ideally the air samples were transported to all devices via one shared sampling tube. Such a set-up was established among the Rosemount, Axetris, and acid traps in the pig barn test. Setting up a shared tube between the acid traps and the INNOVA, Picarro, and Gasmet analysers was however not accomplished, since the respective pump capacity of these gas analysers could not be smoothly tuned, risking unbalanced pressure changes in the sampling tube. This could sabotage the impinger sampling due to backflow or violent splashing of the acidic solutions. Therefore, a second sampling tube was established. Another solution would have been adding a control valve (made of low absorption materials) at each analyser inlet. Using an independent tube per device, as in the poultry barn test, would, on the other hand, ensure
representative test results to the actual work condition, in particular the air pressure and flow rate. This would be necessary in case that the accuracy of an analyser was pressure or flow rate dependent. For all field tests in this study, measures were taken to prevent sampling errors, including using PTFE-based materials for the sampling line set-up, ensuring no air leakage, and placing the sampling tube inlets closely together. In future work, it could be worthwhile to investigate the uncertainty caused by sampling from separate tubes and account for the effect accordingly in the VERA protocol.

3.4.4. Applicability of EN 14793 within the VERA Protocol

To fully qualify an analyser type for VERA, EN 14793 [13] requires that the results are reproducible across multiple devices of that type. Because only one device of each analyser type was available in this study, the reproducibility assessment could not be conducted. Nonetheless, this brings up a dilemma concerning the feasibility of proving the proficiency of an analyser instrument, as currently prescribed by the VERA test protocol. Most providers of gas analysis instruments do not have direct access to livestock test sites, whereas testing organizations in the agricultural sector are usually not in possession of multiple devices of the same type mainly because of the high costs involved. On the other hand, while the demonstrated reproducibility of an analyser type is undoubtedly helpful for the users to make an appropriate choice among the wide variety of NH₃ measurement devices, the longitudinal repeatability is arguably of the highest importance for conducting field measurements. It is, after all, impractical to perform frequent instrument checks and calibrations in the field, especially in the absence of reference alternative to the wet-chemistry method.

4. Conclusions

In this study, five gas analysers (an INNOVA 1314, a Rosemount CT5100, a Picarro G2103, a Gasmet CX4000 and an Axetris LGD F200-A) were validated under field conditions for application in ammonia emission measurements at poultry and pig houses according to the VERA test protocol, using the wet-chemistry method as the reference. The apparent ammonia concentration ranged between 0.98 and 19.1 ppmᵥ. High correlations (r > 0.99) were found between all the analysers and the reference method. The measurement errors were generally below 2 ppmᵥ or 10%. Equivalence to the wet-chemistry method was demonstrated for the INNOVA and Rosemount analyser. After recalibration, the highest achievable accuracy was ±0.46 ppmᵥ or ±6.7%. The Picarro and Axetris analyser could also achieve sufficient accuracy after a recalibration. The Gasmet analyser was subjected to an interference from carbon-dioxide, but it showed good results after correcting for this interference. The Rosemount, Axetris, and INNOVA analyser outputs based on laboratory calibrations using certified a gas cylinder were inconsistent with the wet-chemistry measurements. Further research is required in order to verify the representativeness and reliability of certified gas cylinders for calibrating gas analysers applications in the field.

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**Abbreviations**

The following abbreviations are used in this manuscript:

- CRDS: cavity ring-down spectroscopy
- FTIRS: Fourier transform infrared spectroscopy
- LAS: laser absorption spectroscopy
- MAD: median absolute deviations
- PAS: photoacoustic spectroscopy
- ppm$_v$: parts per million by volume
- PTFE: polytetrafluoroethylene
- QCL: quantum-cascade laser
- RMSE: root-mean-square error
- TDL: tunable diode laser
- VERA: Verification of Environmental Technologies for Agricultural Production

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