Report for validation of ammonia testing methods as supplement to EN 16516 developed by CEN/TC 351/WG 2

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by

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1 Introduction

Document N 242 of CEN/TC 351/WG 2 regarding the validation of ammonia testing methods as supplement to EN 16516 is following a request to expand the scope of EN 16516 'Construction products – Assessment of release of dangerous substances – Determination of emissions into indoor air'. To include the determination of emissions of ammonia into indoor air, CEN/TC 351/WG 2 decided to survey existing available and published test methods for determination of ammonia in air and to validate preferably those that are in use already by concerned testing laboratories under the testing conditions specified in EN 16516. As robustness validation of the emissions testing method had already been performed earlier, see document N 0174 of CEN/TC 351/WG 2, this validation shall cover only reproducibility validation for ammonia measurements and the comparison of different analytical methods by a round robin test.

2 Goal and Execution

In order to facilitate the mandated activities in CEN/TC 351/WG 2, this report includes a reproducibility validation of available and published test methods for determination of ammonia in air, when performed in combination with chamber emissions testing as described and under the testing conditions specified in EN 16516.

Information on which methodology is in use today, or is intended to be used in the future, was collected from participants in earlier round robin tests on VOC emissions. A material suitable as homogeneous source of ammonia emissions was identified and verified. This material will be distributed to all selected testing laboratories for a round-robin test.

The obtained data shall be analysed to show which methods for determination of ammonia can be accepted for the purpose. A report will be delivered to CEN TC 351 and its WG 2, along with a first proposal of a text to amend EN 16516 to include determination of emissions of ammonia, providing pairs of test results for statistical reproducibility evaluation.

3 Work packages

3.1 Work package 1: Selection of methods for Ammonia determination

Goal:

Specification of the required sensitivity, comparison and selection of the methods for ammonia determination.

Document N231, N232, N233, and N236 of CEN/TC 351/WG 2 presented existing methods that could be used for determination of emissions of ammonia from construction products under the testing conditions of EN 16516:

N232 Dynamic photo-acoustic analysis

The advantages of the method are:

- Easy to apply and sensitive.
- On-line analytical method.

It was noted that special care shall be taken due to interferences with the filter. Detection limit for ammonia is expected to be 0.2 ppm (0.15 mg/m³ and 150 µg/m³) according to the technical documentation.

N236 Colorimetric method after adsorption of air on solid sampling tubes - NIOSH 6015

It was noted that no interference has been detected except if there is a high level of sodium. It was noted that it could be possible to meet problems with this method, if amines are present.

The working range of NIOSH 6015 is specified as 0.2 to 400 ppm (0.15 to 300 mg/m³) for a 10-L air sample. Max sampling volume is given as 96-L air, meaning a decreased sensitivity down to 0.02 ppm (0.015 mg/m³, corresponding to 15 µg/m³).

N233 Ion Chromatographic method, OSHA ID-188

Ion chromatographic method is considered as an alternative to the colorimetric method, without interferences with amines.
The quantitative detection limit (the determination or quantification limit) of OSHA ID-188 is specified as 1.5 ppm (with a 24-L air sample), corresponding to 1.1 mg/m³ and 1100 µg/m³. This can certainly be decreased by sampling a higher air volume.

N231 Draeger tubes

Working range for ammonia was reported as up from 0.25 ppm (0.19 mg/m³ and 190 µg/m³).

The reported test method applying static Draeger tubes on insulation material, after these have been locked in a sealed bag, was not included, because CEN/TC 351/WG 2 rated this method as applicable only to insulation products. Consequently it could not be considered as a horizontal method. WG 2 considered that it is an appropriate method for a quality check but not for the problem raised. In addition, it was noted that the test described does not correspond to the intended conditions of use of the products as stated in the mandate (see the minutes of the meeting on 18 June 2015, document N239).
This test method was therefore not considered to be included into this validation.

Determination by using an ammonium specific electrode

Sampling of chamber air can be done with impingers containing a solution of sulfuric acid followed by analyses using an ammonium specific electrode. This test method is analogous to EPA 350.1, APHA 4500-NH3 F, ISO 7150-1, and DIN 38406-5.

Following test methods were identified and included into this validation:

Number	Sampling method	Analytical method	Reference method
1	Solution of sulfuric acid	spectrophotometric determination by indophenol complex	SFS 3032
2	Solution of sulfuric acid	ion chromatography	OSHA ID-188
3	Solution of sulfuric acid	ammonium specific electrode	analogous to EPA 350.1, APHA 4500-NH3 F, ISO 7150-1, and DIN 38406-5
4	Silica gel coated with sulfuric acid (SKC tubes)	spectrophotometric determination by indophenol complex	NIOSH 6015-1994; SFS 3032
5	Online	photo acoustic monitoring	INNOVA 1412i, LumaSense Technologies

Table 1: Overview of analytical test methods

3.2 Work package 2: Selection of suitable material for a round robin test

Goal:
Selection and characterization (homogeneity over surface and over time) of a material suitable as source of ammonia emissions for use in a round robin test.
First intention was to use a cellulose based insulation material for the round robin tests. This type of material is rather inhomogeneous and the ammonia salt has the tendency to trickle down the inside the insulation material. Sample preparation in the laboratories with adjusting a defined thickness and density would result in additional possible deviations. Use of cellulose insulation material for the round robin test was therefore dismissed.

Three different types of test specimen were examined afterwards:

- Ammonium phosphate solution
- Ammonium phosphate crystals
- Fire retardant coating

Several pre-tests were performed by eco-INSTITUT Germany GmbH.

The ammonium phosphate solution was not practicable because of generating high rel. humidity inside the test chambers, which could not be controlled to 50%.

The ammonium phosphate crystals were not easy to handle during sample preparation in terms of reproducible thickness and density. The test chamber concentrations after 3 days at 50% rel. humidity inside the chamber were in the range of 1800 µg/m^3 and therefore in a reasonable high range and seemed to be not as good reproducible compared to the fire retardant coating.

The fire retardant coating showed very stable and homogeneous ammonia emissions:

1st test run	**50 % rH inside the chamber**				**Deviation, %**
Reference number, test specimen	A009	A010	A011	A012	-
Concentration after 3 days, µg/m³	330	370	320	340	6
Concentration after 6 days, µg/m³	230	210	190	190	9

Table 2: Results of first pre-test for the fire retardant coating

2nd test run	**50 % rH inside the chamber**				**Deviation, %**
Reference number, test specimen	A009	A010	A011	A012	-
Concentration after 3 days, µg/m³	380	320	470	420	16
Concentration after 6 days, µg/m³	210	210	230	190	8

Table 3: Results of second pre-test for the fire retardant coating

3rd test run	**90 % rH inside the chamber**				**Deviation, %**
Reference number, test specimen	B011	B012	-	-	-
Concentration after 6 days, µg/m³	980	1270	-	-	18

Table 4: Results of third pre-test for the fire retardant coating at elevated rel. humidity

Decision was made to use the fire retardant coating for the round robin test, because the other materials were deemed unsuitable. For minimising deviations from test specimen preparation, BAM performed test specimen preparation and pre-conditioning.

The effect of that pre-conditioning and way of dispatching the test specimen was determined in a test trial by eco-INSTITUT Germany GmbH. Emissions were tested after a pre-conditioning period. Then the test specimen were wrapped and stored for 7 days at 23°C simulating the transport. After this period the test specimen was again transferred into a test chamber and the emissions of ammonia were tested. The results of the test before and after the storing period had a deviation of < 5 % from the average. With this test it was proven that the transport does not have an impact on the results of the ammonia emissions.
All prepared test specimen were shipped to the participating laboratories on the same day and testing should start at the same day in the laboratories. The time between wrapping the sample for transport and start of the round robin test was lower than the 7 days of above described trial.

3.3 Work package 3: Identification of participating laboratories

Goal:
Identification of laboratories interested in participation in a round robin test, negotiation of conditions to participate.
Following testing laboratories were selected to participate in the round robin test:
WKI, VTT, VITO, Saint-Gobain ISOVER, Eurofins, eco-INSTITUT, DTI, CSTB.

Laboratory	Used testing method *
Lab 1	1, 5
Lab 2	4
Lab 3	1, 3
Lab 4	1, 4
Lab 5	2
Lab 6	1
Lab 7	3
Lab 8	2

Table 5: Participating laboratories and used test methods
* see test method number in 3.1 Work package 1, table 1

3.4 Work package 4: Round robin test

Goal:
Dispatch of the selected material to the participating laboratories, testing in the participating laboratories and reporting to the consortium.

Each testing laboratory received test specimen of the fire retardant coating prepared by BAM. Each laboratory performed analyses of ammonia emissions according to Table 4 under following conditions:

2 tests in 2 separate chambers with sampling after 7 days at 50% rel. hum. inside the test chamber.
2 tests in 2 separate chambers with sampling after 7 days at 90% rel. hum. inside the test chamber

Sample preparation was done by BAM in September 2017 followed by dispatch of samples to the participating laboratories and the round robin test itself.

3.4.1 Round robin test at 50% relative humidity

First round of the round robin test was done at a relative humidity of 50% with a tolerance of ± 5%. The exact rel. humidity was determined during sampling. The results from the different test methods were compared as well as the influence of the variation of the relative humidity.

3.4.2 Test results comparing the different test methods

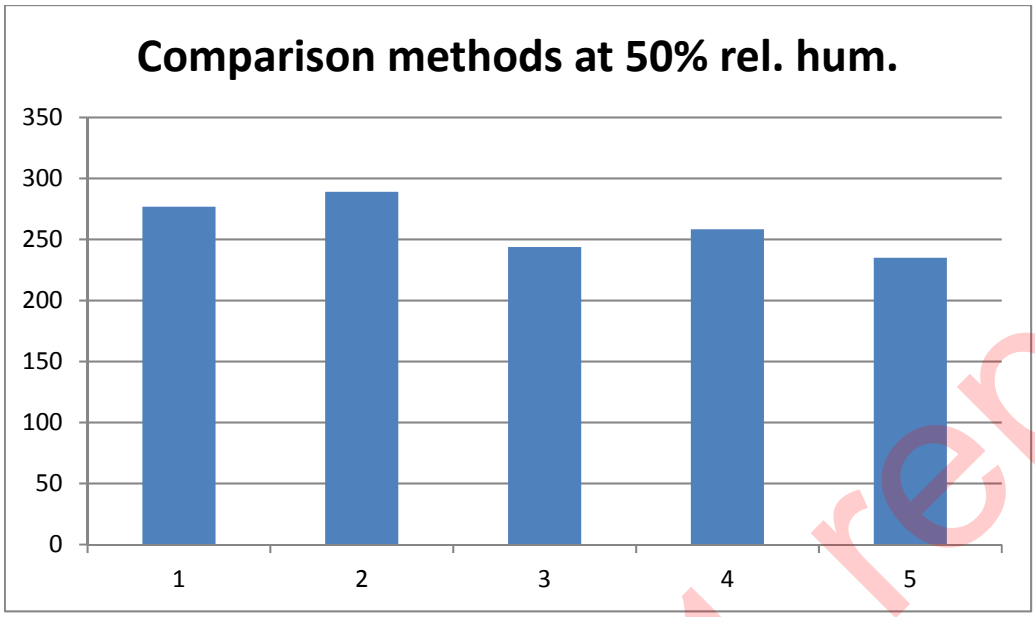
Test results depending on the used test methods were compared in Table 6. The results given in the table are an average of double sampling at each test chamber after 7 days.

Method number:	**1**	**2**	**3**	**4**	**5**
Sampling method:	**Solution of sulfuric acid**	**Solution of sulfuric acid**	**Solution of sulfuric acid**	**Silica gel coated with sulfuric acid (SKC tubes)**	**Online**
Analytical method:	**Spectrophotometric determination by indophenol complex**	**Ion chromatography**	**Ammonium specific electrode**	**Spectrophotometric determination by indophenol complex**	**Photo acoustic monitoring**
Chamber concentration:	**µg/m3**	**µg/m3**	**µg/m3**	**µg/m3**	**µg/m3**
Lab 1 - chamber 1	108*				240
Lab 1 - chamber 2	77*				230
Lab 2 - chamber 1				304	
Lab 2 - chamber 2				264	
Lab 3 - chamber 1	295		267		
Lab 3 - chamber 2	265		239		
Lab 4 - chamber 1	253			207	
Lab 5 - chamber 1		263			
Lab 5 - chamber 2		303			
Lab 6 - chamber 1	249				
Lab 6 - chamber 2	322				
Lab 7 - chamber 1			275		
Lab 7 - chamber 2			194		
Lab 8 - chamber 1		301			
Average	277	289	244	258	235
Standard deviation, %	**11**	**8**	**15**	**19**	**3**
Total average	263				
Total standard deviation, %	13				

Table 6: Comparison of test results depending on analytical test method

* results are regarded as outliers and not calculated into the average and standard deviation

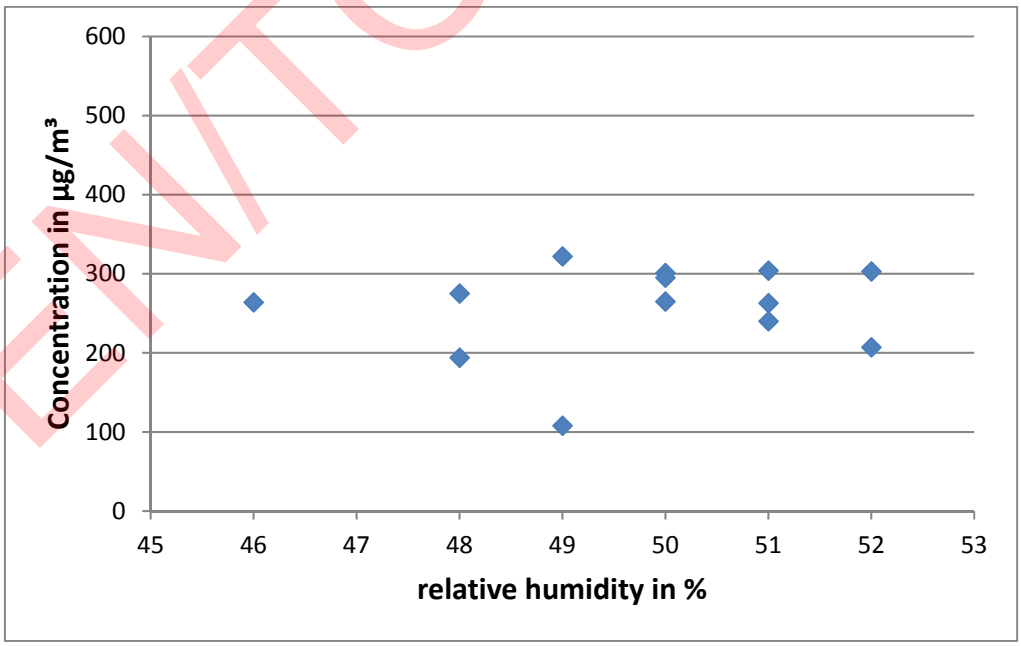
Graphic 1 shows the average of the results for each test method as given in Table 6.



Graphic 1: Comparison of test results depending on analytical test method

3.4.2.1 Influence of relative humidity on test results

Each participating laboratory recorded the relative humidity inside the test chamber during sampling. The adjusted relative humidity was supposed to be in the range of 50 ± 5%. The actual relative humidity during sampling and the respective test results were shown in Graphic 2 independently from the analytical test method.



Graphic 2: Impact of relative humidity on test results in a range of 50 ± 5%

3.4.3 Round robin test at 90% relative humidity

Second round of the round robin test was done at a relative humidity of 90%. The aim was to reach this high relative humidity as precise and stable over time as possible. The exact rel. humidity was determined during sampling. The results and deviations were compared as well as the influence of the variation of the relative humidity.

3.4.3.1 Tests results

Some laboratories used different analytical methods with sampling at the same time from the same chamber. Table 7 shows the results of these measurements and the deviation between the results within the same test chambers.

Sampling method:	Solution of sulfuric acid	Solution of sulfuric acid	Online	Silica gel coated with sulfuric acid (SKC tubes)	Deviation between methods
Analytical method:	Spectrophotometric	Ammonium specific electrode	Photo acoustic monitoring	Spectrophotometric	
Chamber concentration:	µg/m³	µg/m³	µg/m³	µg/m³	%
Lab 1 - Chamber 1	4670		4085		9
Lab 1 - Chamber 2	7788		6777		10
Lab 3 - Chamber 1	4500	5000			7
Lab 4 - Chamber 1	6986			7542	5
Lab 4 - Chamber 2	6677			6885	2

Table 7: Deviation of test results from different test methods from the same chambers (90% rel. hum.)

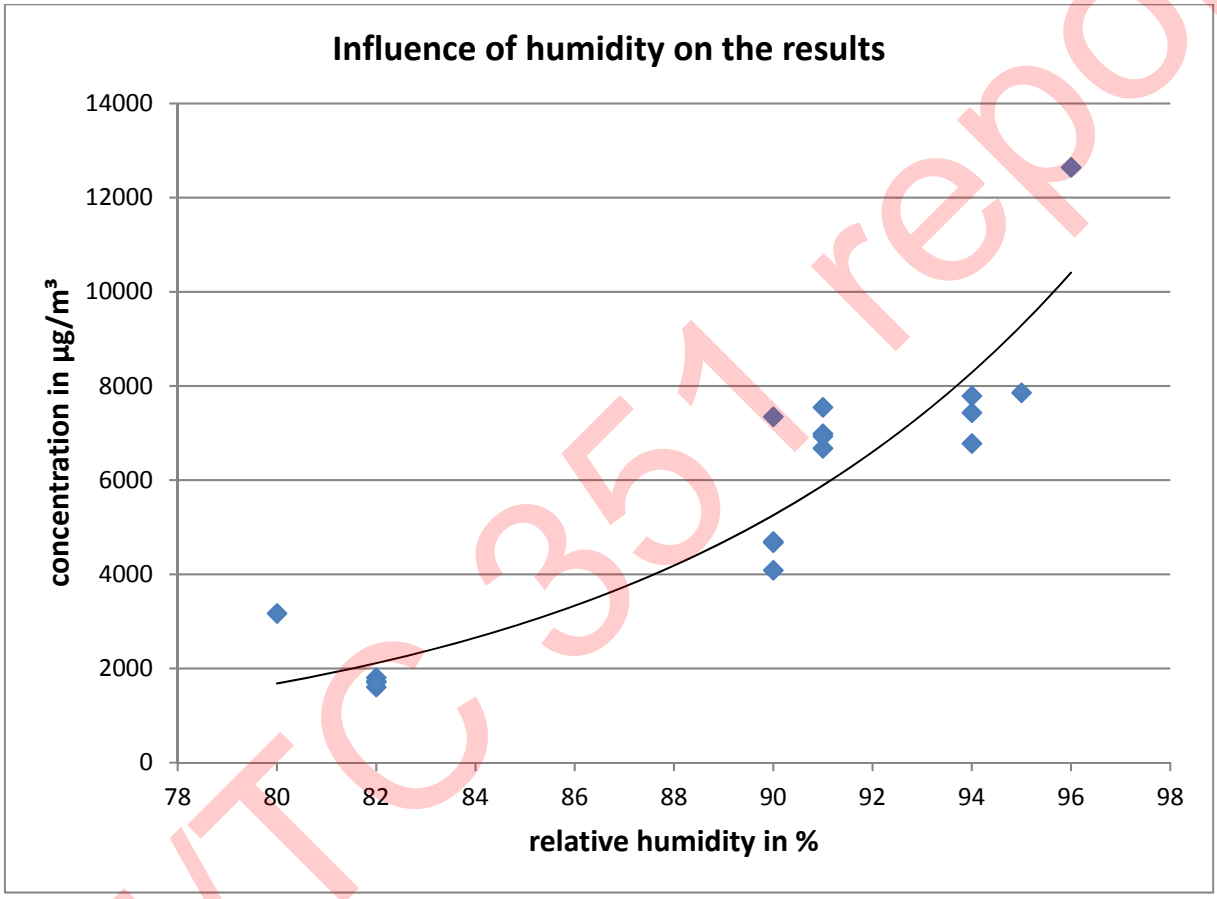
The deviation reported in Table 7 was 10% or lower. Neglecting this deviation, Table 8 shows the results of each test chamber from the participating laboratories as an average from all samplings and analyses taken at the same time. The results are sorted by the concentration in an ascending order.
Some laboratories did not reach to adjust the rel. humidity to approximately 90%, therefore only results obtained at a relative humidity between 90 and 96 % were presented here.

	Chamber Concentration, µg/m^3
Lab 6 - Chamber 1	3168
Lab 1 - Chamber 1	4378
Lab 8 - Chamber 1	4698
Lab 3 - Chamber 1	4750
Lab 2 - Chamber 1	6929
Lab 4 - Chamber 2	6781
Lab 4 - Chamber 1	7264
Lab 1 - Chamber 2	7283
Lab 7 - Chamber 1	7344
Lab 5 - Chamber 2	7430
Lab 6 - Chamber 2	7545
Lab 5 - Chamber 1	7855
Lab 2 - Chamber 2	12643
Average	6774
Standard deviation, %	34

Table 8: Chamber concentrations measured at rel. humidity between 90 and 96%

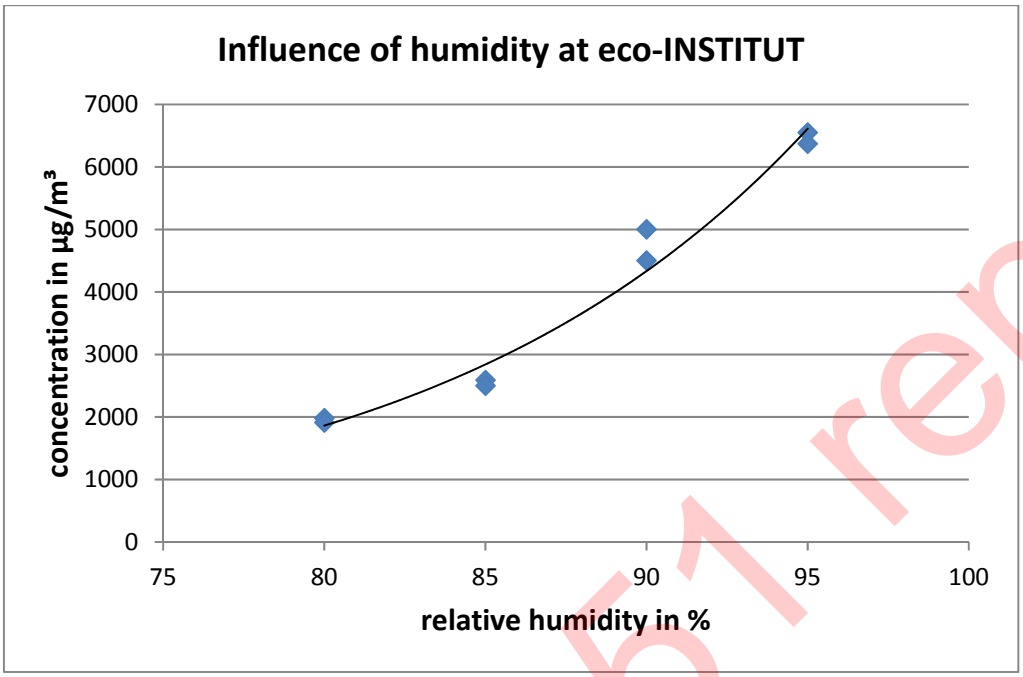
3.4.3.2 Influence of relative humidity on test results

Each participating laboratory recorded the relative humidity inside the test chamber during sampling. The adjusted relative humidity was supposed to be in the range of 90%. The actual relative humidity during sampling and the respective test results were shown in Graphic 3 independently from the analytical test method. Some laboratories had difficulties in adjusting a relative humidity of 90%.



Graphic 3: Impact of relative humidity on test results in a range of 80 – 96 %

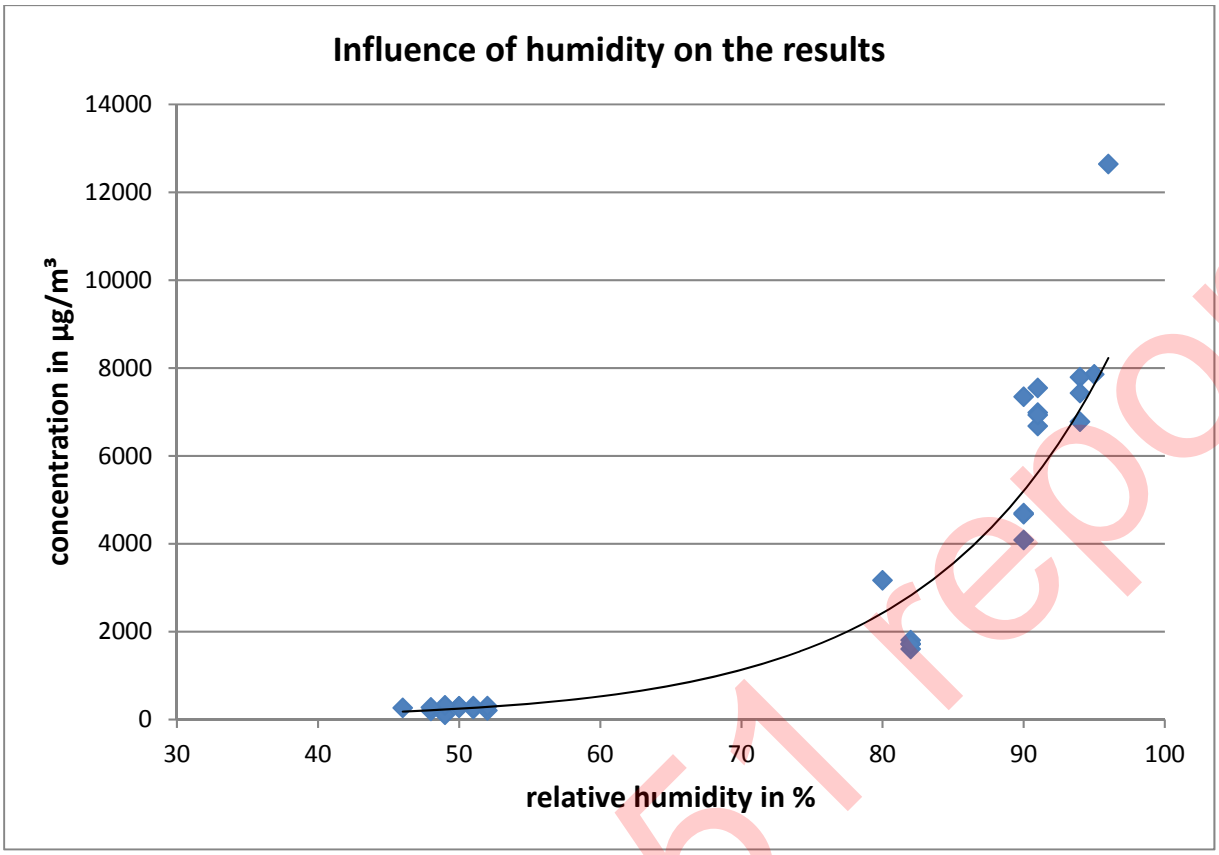
Because of high variation of results and influence of the relative humidity inside the test chamber further tests were performed at eco-INSTITUT. Four tests were performed on the same test specimen at 80%, 85%, 90% and 95% relative humidity. Graphic 4 shows these test results.



Graphic 4: Influence of relative humidity on test results in a range of 80 - 95%

3.4.4 Influence of relative humidity on test results in the range of 45 – 95%

Graphic 5 combines the results of Graphic 2 and 3 giving an overview of the influence of relative humidity on the emissions of ammonia in the range of 45 – 95%.



Graphic 5: Influence of relative humidity on test results in a range of 45 - 95%

3.5 Work package 5: Analysis of data and reporting

Goal:

Analysis of the data, comparison of the methods, conclusions, proposal for an amendment to EN 16516.

Test results reported in 3.4 “Work package 4: Round robin test” were analysed and the conclusions are documented in the following chapter.

3.5.1 Comparison of different analytical test methods

When determining ammonia emissions within a humidity range of 50 ± 5% relative humidity, all five examined analytical test methods showed similar results within an uncertainty of ± 13% (see Table 6). This uncertainty is regarded as acceptable and all five examined analytical test methods are considered as equivalent. It is recommended to include all five examined analytical test methods into the amendment of EN 16516 for determination of ammonia emissions.

3.5.2 Influence of relative humidity

The relative humidity has no influence on the ammonia emissions at standardized conditions of 50 ± 5% relative humidity. Graphic 2 shows that all results are stable and only deviating within the uncertainty of the measurement. There is no increase of results when comparing results from the lower end and the higher end of the range of 50 ± 5% relative humidity. This means that the defined range of 50 ± 5% relative humidity from EN 16516 is appropriate for determining ammonia emissions and does not need to be adjusted.

Determining ammonia emissions using an elevated relative humidity in the range of 80 – 95 % is clearly influenced by the humidity. Graphic 5 shows a considerable exponential correlation between ammonia emission and relative humidity. The uncertainty of testing at elevated humidity is much higher compared to tests done in the range of 50 ± 5% relative humidity. Variation of the adjusted elevated humidity inside the test chambers would result in higher uncertainty and lower reproducibility of the test results.

In case a range of 90 ± 5% relative humidity would be used for testing, graphic 4 shows that the results are a factor 2.5 larger for the test at 95% compared to the test of 85%. A tolerance of ± 5% at this high relative humidity will results in very high uncertainties and would not give reproducible results.

When testing at high humidity, it is very important to control humidity precisely at 90 % and it seems to be difficult to create such a high and stable humidity for a complete test over 7 days. Some laboratories had even difficulties to reach that level.

As a consequence it is advised not to perform product emission tests for determining ammonia at a relative humidity above the range of 50 ± 5%. If testing at elevated relative humidity is desired, further investigations are recommended in order to minimize the uncertainty in this range.

Annex I: Proposal for an amendment to EN 16516

Below proposal for an annex for EN 16516 for determination of ammonia in chamber air is based on findings described earlier in this report.

A study of ammonia testing methods delivered data for the suitability of these tests methods and for chamber parameters as defined in EN 16516. This study included a round robin test of a homogeneous test specimen under the testing conditions as defined in EN 16516 in eight different testing laboratories.

1 Suitable test methods for determination of ammonia in test chamber air

Following test methods are suitable for determination of ammonia in test chamber air.

1.1 Spectrophotometric determination by indophenol complex

Sampling of chamber air can be done with impingers containing a solution of sulfuric acid followed by spectrophotometric determination by indophenol complex. This test method is described in the Finnish standard SFS 3032.

Alternatively sampling can be done on tubes filled with silica gel coated with sulfuric acid followed by extraction and spectrophotometric determination by indophenol complex. This test method is described in NIOSH 6015-1994 and in the Finnish standard SFS 3032.

1.2 Determination by ion chromatography

Sampling of chamber air can be done with impingers containing a solution of sulfuric acid followed by analyses using ion chromatography. This test method is described in OSHA ID-188.

1.3 Determination by using an ammonium specific electrode

Sampling of chamber air can be done with impingers containing a solution of sulfuric acid followed by analyses using an ammonium specific electrode. This test method is analogous to EPA 350.1, APHA 4500-NH3 F, ISO 7150-1, and DIN 38406-5.

1.4 Determination by using photo acoustic monitoring

Sampling of chamber is done directly with the air monitor and analysis is based on the photoacoustic infrared spectroscopy.

2 Test chamber conditions – relative humidity

The emissions of ammonia are depending on the relative humidity inside the test chambers. Ammonia emissions are increasing exponentially with the humidity inside the chamber.

Therefore test chamber conditions shall be used as defined in EN 16516 with a relative humidity of 50 ± 5%. There is no significant influence of the relative humidity to ammonia emissions in this range.

It is not recommended to determine ammonia emissions above the relative humidity range of 50 ± 5%.

In case testing shall be done at higher relative humidity (for example 90%) a tolerance of ± 5% of the target value is not precise enough and would not give reproducible results of the ammonia emissions. In order to minimize the uncertainty it is very important to control humidity precisely at the target value. In practice it is very difficult to create such a high and stable humidity for a complete test over 28 days.