Hessisches Landesamt
für Naturschutz,
Umwelt und Geologie

Hessian Agency
for Nature Conservation,
Environment and Geology

HESSEN

Annual Report 2018

Results of proficiency tests for substance ranges P, G, and O on the emission simulation apparatus for quality assurance in stack emission measurements in the year 2018

HLNUG Department I3 is accredited for performing testing services
according to DIN EN ISO/IEC 17043.
The accreditation is valid for the testing procedures listed in the certificate.

DAkkS Deutsche Akkreditierungsstelle D-EP-14551-01-00

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0. About this Report

This report is a translation of *„Jahresbericht 2018 – Ergebnisse der Ringversuche der Stoffbereiche P, G und O an der Emissionssimulationsanlage zur Qualitätssicherung von Emissionsmessungen im Jahr 2018"* and was prepared with best care and attention. Nevertheless, the German version of this report shall be taken as authoritative. No guarantee can be given with respect to the English translation.

1. Summary

A total of 44 measuring institutes took part in HLNUG's dust emission proficiency tests (substance range P) in 2018, 36 of which were §29b measuring bodies and 8 volunteers. As in the past, the success rate of the §29b measuring bodies (94%) was significantly higher than that of the volunteers (75%).

A total of 47 measuring institutes took part in the gas emission proficiency tests (substance range G) in 2018, 40 of which were §29b measuring bodies and 7 volunteers. As in previous years, the success rate for the §29b measuring bodies (63%) was significantly higher than for the volunteers (43%).

A total of 21 measuring bodies took part in the odour emission proficiency tests (substance range O) in 2018, 15 of them on the basis of an authorisation in accordance with §29b BImSchG and 6 voluntarily. Here 73% of the authorised participants were successful and 33% of the volunteers.

2. Introduction

2.1 Legal Background

The stack emission proficiency tests offered at the Emission Simulation Apparatus (ESA) of Hessisches Landesamt für Naturschutz, Umwelt und Geologie (HLNUG, Hessian Agency for Nature Conservation, Environment and Geology) in Kassel were developed for the quality control of measuring bodies authorised to perform measurements in accordance with §29b Bundes-Immissionsschutzgesetz (BImSchG, Federal Immission Control Act) in Germany. The proficiency tests presented in this annual report are accredited according to DIN EN ISO/IEC 17043 (1) and are recognised by all authorizing authorities in Germany within the meaning of §16 Para. 4 No. 7a of the 41. Bundes-Immissionsschutz-verordnung (41. BImSchV (2), 41st Federal Immission Control Ordinance). Regular successful participation in these stack emission proficiency tests is therefore a prerequisite for maintaining an authorisation in accordance with §29b BImSchG (3).

Consequently, about 80-90% of the participants are laboratories authorised to perform measurements in accordance with §29b BImSchG (Federal Immission Control Act), or applicants for authorisation in accordance with BImSchG. Nevertheless, other measuring institutes can also participate in the HLNUG stack emission proficiency tests, e.g. laboratories that do not perform measurements in the regulated sector in Germany but still want to check the quality of their emission measurements.

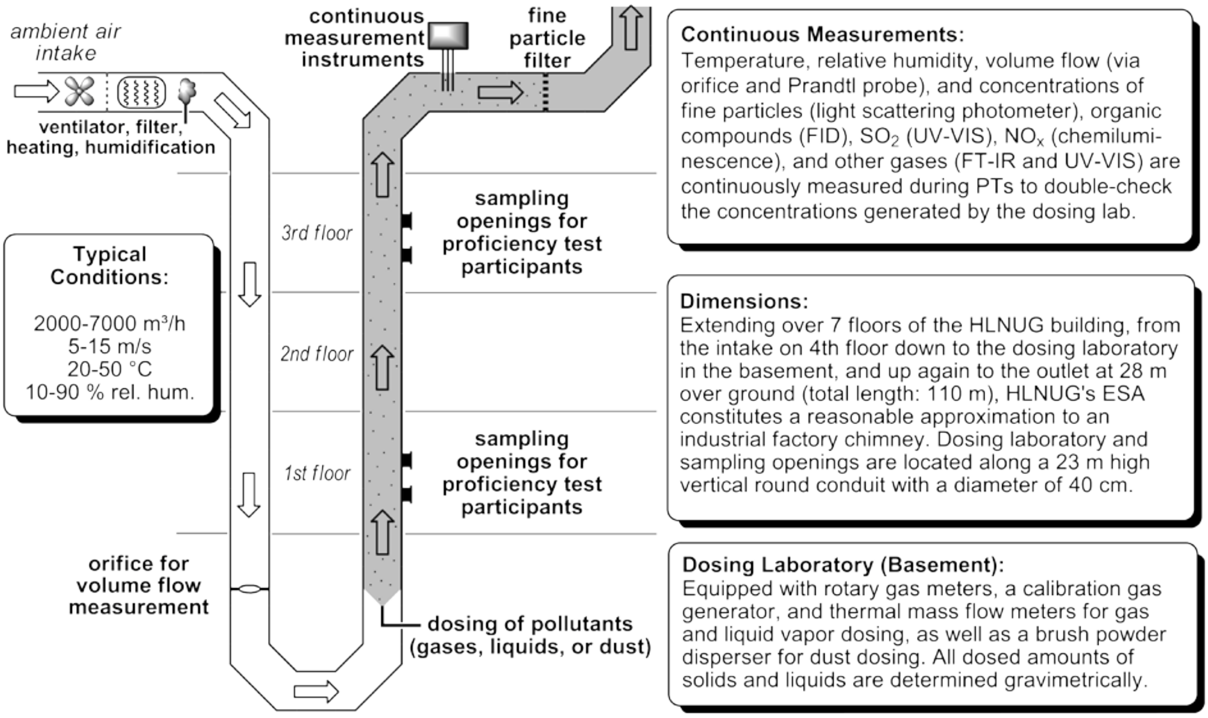
2.2 The Emission Simulation Apparatus

The prerequisite for carrying out stack emission proficiency tests is the ability to provide all participants at the same time with a stable and clearly defined simulated exhaust gas. For this purpose, HLNUG operates the Emission Simulation Apparatus (ESA, see scheme 1). It was designed as a model for an industrial flue gas chimney. It serves not only to carry out emission proficiency tests but also to carry out model investigations in the field of emission measurement technology.

The ESA has a total length of 110 m and extends over all seven floors of the HLNUG building in Kassel. The heart of this system is a vertical, 23 m high round stainless steel conduit with an inner diameter of 40 cm. This part of the ESA is the actual chimney substitute at which there are measuring openings for taking samples for emission measurements.

The test atmosphere in the form of simulated exhaust gas is created by drawing in ambient air, pumping it through the system, heating it and adding precisely metered quantities of pollutants. The exhaust gas typically flows through the ESA at approx. 5 – 11 m/s, moving a volume of approx. 2200 – 5000 m³/h through the system.

The air pollutants to be measured by the participants in the proficiency test are dispensed into the air flow in the dosing laboratory in the basement. For this purpose, the dosing laboratory is equipped with various drum gas meters and coriolis mass flow meters for dosing different gases, a calibration gas generator for dosing liquids and a brush dosing unit for dosing dusts. Various measuring instruments continuously measure volume flow, pressure, temperature and humidity as well as the concentrations of organic compounds (as TOC) and various other components in order to constantly check the concentrations generated by the dosing laboratory.



Scheme 1: Scheme of HLNUG's emission simulation apparatus (simplified and not true to scale)

3. Organisational Information

In 2018, the following proficiency tests of the substance ranges P, G, and O were carried out:

Table 1: Proficiency Tests organised by HLNUG

proficiency test	substance range	start	end	participants
RV 501S	particulate emissions (substance range P)	29.01.2018	30.01.2018	8
RV 502G	gaseous emissions (substance range G)	31.01.2018	02.02.2018	8
RV 503S	particulate emissions (substance range P)	19.02.2018	20.02.2018	7
RV 504G	gaseous emissions (substance range G)	21.02.2018	23.02.2018	7
RV 505S	particulate emissions (substance range P)	05.03.2018	06.03.2018	8
RV 506G	gaseous emissions (substance range G)	07.03.2018	09.03.2018	8
RV 507S	particulate emissions (substance range P)	19.03.2018	20.03.2018	5
RV 508G	gaseous emissions (substance range G)	21.03.2018	23.03.2018	7
RV 509S	particulate emissions (substance range P)	16.04.2018	17.04.2018	8
RV 510G	gaseous emissions (substance range G)	18.04.2018	20.04.2018	8
RV 511O	odour emissions (substance range O)	16.10.2018	16.10.2018	7
RV 512O	odour emissions (substance range O)	18.10.2018	18.10.2018	8
RV 513O	odour emissions (substance range O)	24.10.2018	24.10.2018	6
RV 515S	particulate emissions (substance range P)	05.11.2018	06.11.2018	5
RV 516G	gaseous emissions (substance range G)	07.11.2018	09.11.2018	6
RV 519S	particulate emissions (substance range P)	19.11.2018	20.11.2018	3
RV 520G	gaseous emissions (substance range G)	21.11.2018	23.11.2018	4

These proficiency tests were organised and carried out under the following conditions (see specifications for the respective substance ranges for details):

Table 2: Characteristics of HLNUG's stack emission proficiency tests

	substance range P	substance range G
duration of each sampling	30 min	30 min (dicontinuous samplings and TOC), 15 min (cont. measurements C_3H_8, CO, NO_x, SO_2)
number of samplings	for each component 10 including introductory measurement	
sampling	simultaneously for all participants (1st and 3rd floor)	
basic conditions	not detailed in specifications	2000 … 3500 m³/h 20 … 40 °C
concentrations	1 … 12 mg/m³ in the following ranges: 1: 1 … 4 mg/m³ 2: 4 … 7 mg/m³ 3: 7 … 12 mg/m³	SO_2: 20 … 150 mg/m³ NO_x as NO_2: 60 … 450 mg/m³ CO: 10 … 100 mg/m³ sum ETX: 4 … 100 mg/m³ formaldeyhde: 4 … 40 mg/m³ TOC: 4 … 100 mg/m³ (ETX/propane) TOC: 5 … 100 mg/m³ (propane only)

	substance range P	substance range G
result submission	within six weeks after the end of the proficiency test, in mg/m³ for dust concentrations and µg/m³ for heavy metal concentrations respectively, relating to normal conditions (dry) and with one digit after decimal point.	within four weeks after the end of the proficiency test, in mg/m³ relating to normal conditions (dry) and with one (components G1-3, G8, G9, see table 6) or two (G4-7 and G10, see table 6) digits after decimal point.
submission procedure	results are entered into an Excel-file provided by HLNUG and handed in via e-mail.	
	substance range O	
duration of each sampling	10 min	
number of samplings	for each component 3	
sampling	simultaneously for all participants (1st and 3rd floor)	
basic conditions	2000 … 6000 m³/h, flow velocity > 4 m/s, water vapour up to 50 g/m³	
concentrations	approx. 50 … 50000 ou_E/m³	
result submission	on the day of the proficiency test, until 19:00 Uhr	

The proficiency tests were organised by:

Hessisches Landesamt für Naturschutz, Umwelt und Geologie
(*Hessian Agency for Nature Conservation, Environment and Geology*)

Dezernat I3 – Luftreinhaltung: Emissionen
(*Department I3 – Air Pollution Control: Emission*)

The location of the proficiency tests was:

Hessisches Landesamt für Naturschutz, Umwelt und Geologie
Ludwig-Mond-Str. 33
34121 Kassel
- GERMANY -

Tel.: +49 – 561 – 2000 137
Fax: +49 – 561 – 2000 225
E-Mail: pt@hlnug.hessen.de

Technically responsible for the execution of the proficiency tests are currently:

Dr. Jens Cordes, Dr. Dominik Wildanger and Benno Stoffels.

4. Execution of the Proficiency Tests

4.1 Particulate Standards

In contrast to the use of pure substances in gas and odour proficiency tests, no reference materials for particulate substances in sufficient quantities are commercially available. For this reason, the certified reference materials produced by HLNUG according to DIN EN ISO 17034 (4) are used for proficiency tests in the substance range P.

The matrix is an industrial dust which is optimised by specific heavy metal doping, grinding, sieving and drying steps. Intensive mixing of the batch finally achieves complete homogenisation of the dust standard.

The determination of the conventionally correct value ("assigned value") of the heavy metal concentration of a doped dust sample is based on the data from interlaboratory comparisons carried out by laboratories of various state authorities. The robust mean value from the individual values of the interlaboratory comparisons is regarded as the assigned heavy metal content value of the dust standard. The dust is subject to a homogeneity and stability test and verification, which is repeated at certain intervals. Homogeneity and stability of the test dusts are tested according to DIN ISO 13528 (5).

4.2 Execution of the Measurements

Each participant determines the mass concentration of the emission components in accordance with (DIN) EN 15259 (6). In addition, the metrological boundary conditions must be recorded before the actual sampling begins. This includes exhaust gas velocity/flow rate, exhaust gas temperature and humidity as well as the air pressure in the system.

Table 3: Sequence of a stack emission proficiency test of substance range P

day of the test	component	compulsory measurement procedure
day 1 and 2	dust	(DIN) EN 13284-1 (7) / VDI 2066 Part 1 (8)
	heavy metals	Not specified

Table 4: Sequence of a stack emission proficiency test of substance range G

day of the test	component	compulsory measurement procedure
day 1	formaldehyde	VDI 3862 part 2 (9), part 3 (10) or part 4 (11)
day 2	SO_2	(DIN) EN 14791 (12)
	TOC	(DIN) EN 12619 (13)
	ETX	(DIN) EN 13649 (14)
day 3	SO_2	using a suitability tested device
	TOC	(DIN) EN 12619 (13)
	NO_x as NO_2	(DIN) EN 14792 (15)
	CO	(DIN) EN 15058 (16)

Table 5: Sequence of a stack emission proficiency test of substance range O

day of the test	component	compulsory measurement procedure
day 1	four odours	(DIN) EN 13725 (17)

4.3 Evaluation of the Proficiency Tests

4.3.1 Calculation of z-Scores

Substance range P and G

The evaluation of the proficiency test is carried out in accordance with the respective specifications (for substance range P and G) on the basis of the z-score procedure. For the measurement value x_{ijk}, which is the result of measurement *i* of concentration level *j* of component *k*, a z-score value z_{ijk} is determined:

$$z_{ijk} = \frac{x_{ijk} - X_{ijk}}{\sigma_k \cdot X_{ijk}}$$

In this equation, X_{ijk} is the assigned value of the measurement, and σ_k is the precision criterion for component *k*. The assigned value is calculated from measurement data of the dosing devices and the volume flow.

Substance range O

For odour emission proficiency tests, the evaluation is carried out on the basis of the z-score procedure, using logarithmised values:

$$z_{ik} = \frac{1}{\sigma_k} \cdot \log_{10}\left(\frac{x_{ik}}{X_{ik}}\right)$$

In this equation, X_{ik} is the assigned value of the measurement, and σ_k is the precision criterion for component *k*. The assigned value X_{ijk} is calculated from the mass concentration c_{ik} and the odour threshold $c_{0,k}$ of the component:

$$X_{ik} = \frac{c_{ik}}{c_{0,k}} \ \mathrm{ou_E/m^3}$$

The dosed mass concentration c_{ik} is determined for each measurement based on the measurement data of the dosing device and the volume flow. The odour threshold $c_{0,k}$ of *n*-butanol is $c_0 = 123\ \mathrm{\mu g/m^3}$. The thresholds of all other components are deduced from results of proficiency test participants according to the following procedure:

a) A consensus value is calculated from the measurement results reported by at least 20 participants in at least two different proficiency tests previously run by HLNUG. Here, solely results of participants are taken into account, who achieved the result ‘passed’ for the component *n*-butanol in the respective proficiency test. The consensus value is obtained by the robust mean of the logarithmic values according the standard DIN ISO 13528 (5) and is updated on a regular basis by including new results. This calculation is restricted to measurements of the past five years as long as the above mentioned requirements are met.

b) If not enough measurement results of former proficiency tests are available to determine the consensus value of a component by means of the procedure described under a), an alternative method is used: Here, the consensus value of a component offered during a proficiency test is subsequently calculated from the participants' measurement results. Provided that the sampling was carried out within 14 days, results of several proficiency tests can be taken into account. Solely results of those participants are considered, who achieved the result 'passed' for the component *n*-butanol in the respective proficiency test. The consensus value is obtained by the robust mean of the logarithmic values according the standard DIN ISO 13528 (5). If less than nine measurement results for one particular component are available that fulfil the above mentioned criteria, neither a z-score-based evaluation nor a performance rating are possible.

If the uncertainty of a true value u_k determined in compliance with DIN ISO 13528 (5) results in a value for which with $\sigma_k = 0{,}10$ the following condition is not met:

$$\sigma_k \geq \frac{1}{0{,}3} \cdot \log_{10}(1 + u_k)$$

Then σ_k is adjusted in accordance with DIN ISO 13528 (5). In doing so, σ_k is recalculated precisely to two decimal places, so that the condition above is fulfilled. Participants are informed about the increase of the precision criterion at the latest when the evaluation is communicated by HLNUG.

The precision criteria for the different components are listed in the following table:

Table 6: Precision criteria

No.	component	measurement mode	short designation	precision criterion σ_k in % of true value
		substance range P		
P1	dust	discontinuous	St	7,0
P2	Cadmium	discontinuous	Cd	8,0
P3	Cobalt	discontinuous	Co	8,0
P4	Chromium	discontinuous	Cr	12,0
P5	Copper	discontinuous	Cu	8,0
P6	Manganese	discontinuous	Mn	10,0
P7	Nickel	discontinuous	Ni	8,0
P8	Lead	discontinuous	Pb	8,0
P9	Vanadium	discontinuous	V	10,0
		substance range G		
G1	SO_2	discontinuous	Sd	3,1
G2	SO_2	continuous	Sk	3,9
G3	NO_x as NO_2	continuous	Nk	3,1
G4	toluene	discontinuous	Td	5,6
G5	ethylbenzene	discontinuous	Ed	5,8
G6	sum of *o*-, *m*-, *p*-xylene	discontinuous	Xd	5,3
G7	formaldehyde	discontinuous	Fd	3,5
G8	TOC (propane, ETX)	continuous	Ck	3,3
		substance range G – components not required for passing		
G9	TOC (propane)	continuous	Pk	3,3
G10	CO	continuous	Kk	3,6

No.	component	measurement mode	short designation	precision criterion σ_k in % of true value
G11	toluene (standard)	laboratory analysis	STDT	4,5
G12	ethylbenzene (standard)	laboratory analysis	STDE	4,5
G13	sum of *o*-, *m*-, *p*-xylene (standard)	laboratory analysis	STDX	4,5
		Stoffbereich O		
-	all odours	discontinuous	e.g. NBU, AAC, …	0,1[†]

[†] In proficiency test O the precision criterion is not expressed in % of true value (see section 4.3.1)

4.3.2 Evaluation of z-Scores

The z-scores can be interpreted using the following scheme:

$\lvert z_{ijk} \rvert \leq 2$	satisfactory
$2 < \lvert z_{ijk} \rvert < 3$	questionable
$\lvert z_{ijk} \rvert \geq 3$	unsatisfactory

Generally, for each measurement resulting in a z-score of more than two, a causal research is advised.

In the next step of the evaluation, the mean value z_{jk} of the absolute values of the *n* z-scores of one concentration level (usually *n* = 3) is calculated:

$$z_{jk} = \sum_{i=1}^{n} \frac{\lvert z_{ijk} \rvert}{n}$$

Based on z_{jk}, to each concentration level a class number K_{jk} is assigned according to the following scheme:

$z_{jk} \leq 2$	results in $K_{jk} = 1$
$2 < z_{jk} < 3$	results in $K_{jk} = 2$
$z_{jk} \geq 3$	results in $K_{jk} = 3$

For each component in gas and dust emission proficiency tests, at least 6 measurement results must be submitted, otherwise the respective component is automaticalle evaluated as „failed“.

The evaluation of single components as well as the overall assessment differs between substance ranges P, G, and O.

Dust emission proficiency test

A component was determined successfully, if the respective sum of class numbers does not exceed 5. If in justified single cases only values for two concentration levels were submitted, the component was determined successfully if the sum of class numbers does not exceed 4 and the sum of absolute z-scores does not exceed 5.2. Successful determinations are labelled “passed”, unsuccessful determinations are labelled “failed”.

The overall result of the proficiency test is “passed”, if the component total dust (no. P1) and at least 5 of the 6 mandatory heavy metal components (no. P2 to P5, no. P7, and no. P8) are rated “passed“, otherwise the overall result is “failed”.

Gas emission proficiency test

A component was determined successfully, if the respective sum of class numbers does not exceed 6. If in justified single cases only values for two concentration levels were submitted, the component was determined successfully if the sum of class numbers does not exceed 4. Successful determinations are labelled "passed", unsuccessful determinations are labelled "failed".

The overall result of the proficiency test is "passed", if all compulsory components (no. G1 to G8) are "passed", otherwise the overall result is "failed". With the publication of the new version of the guideline VDI 4220 (18), the component G2 (SO_2 continuous) became a voluntary component in November 2018. From this point on, the proficiency test was successfully passed if the components no. G1 and G3 to G8 were successfully determined.

For the analytical part of the proficiency test (which does not include sampling), z-scores are calculated following the scheme described above. A component was here determined successfully, if

$$|z_k| < 3$$

The overall result of the analytical part is "passed", if all 3 components of the standard are "passed", otherwise the overall result is "failed".

Odour emission proficiency test

For the evaluation of odour measurements, the mean value z_k of the absolute values of the n z-scores (usually n = 3) of one component is calculated:

$$z_k = \sum_{i=1}^{n} \frac{|z_{ik}|}{n}$$

A component was determined successfully, if

$$z_k < 3$$

is fulfilled. In this case, the component is rated "passed". If this criterion is not met or if no measurement result was submitted in due time, the component is rated "failed". The overall result of the proficiency test is "passed", if all components were determined successfully. If one or more components are rated "failed", the overall result is "failed".

4.3.3 Communication of the Evaluation Result

Communication of the evaluation of the participants' results by HLNUG is done within six weeks after the last day for submission of results for the respective proficiency test. This evaluation is given to the participants in form of a general survey, including tables and diagrammes, and quoting their unique ID-code.

5. Results

5.1 z-Scores

A compact overview of the z-scores achieved by the participants can be found in the following box whisker plots. The rectangle indicates values between the 25th and 75th percentile (interquartile distance), the continuous line in the rectangle indicates the median of the values. The "antennas" reach from the upper edge of the rectangle to the highest and from the lower edge to the lowest value, which is still within 1.5 times the interquartile distance. Values outside this range are entered separately as points in the diagram.

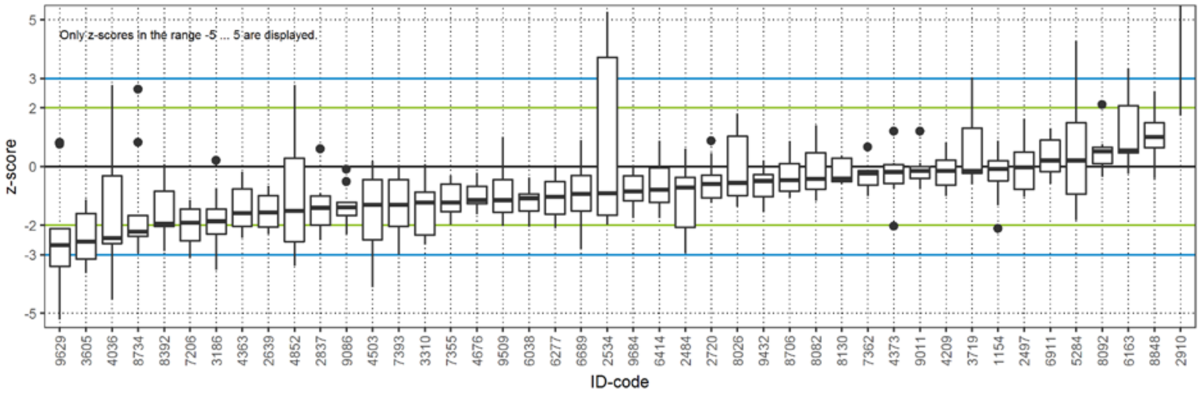
In order to be able to assess the performance of individual participants across all components and to get an impression of the quality of measurements for individual components, the diagrams are available in two different sorts; on the one hand as an overview on one page, on the other hand sorted according to the respective median of the achieved z-scores.

A list of the individual measurements of all participants can be found in a separate document (appendix to the annual report).

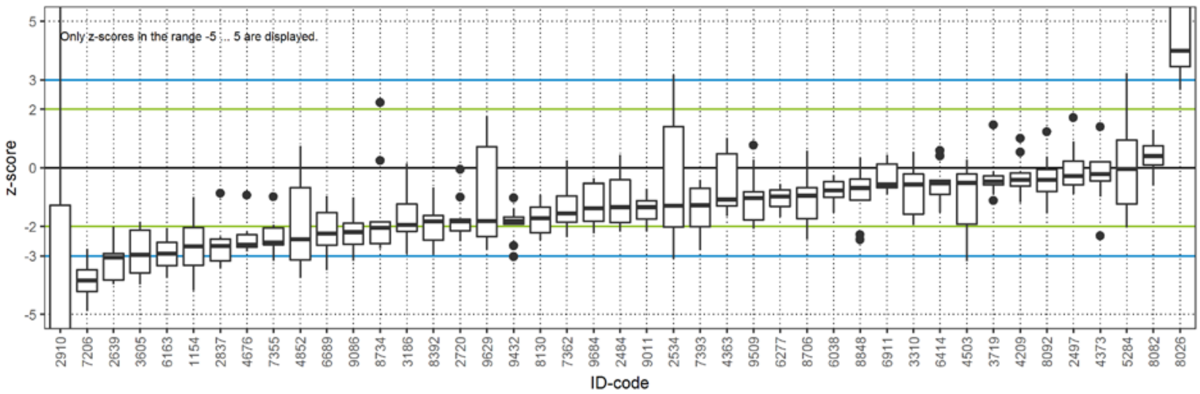
5.1.1 Substance range P

Scheme 2: Achieved z-scores dust proficiency test (only values in the range -5 … 5 are shown)

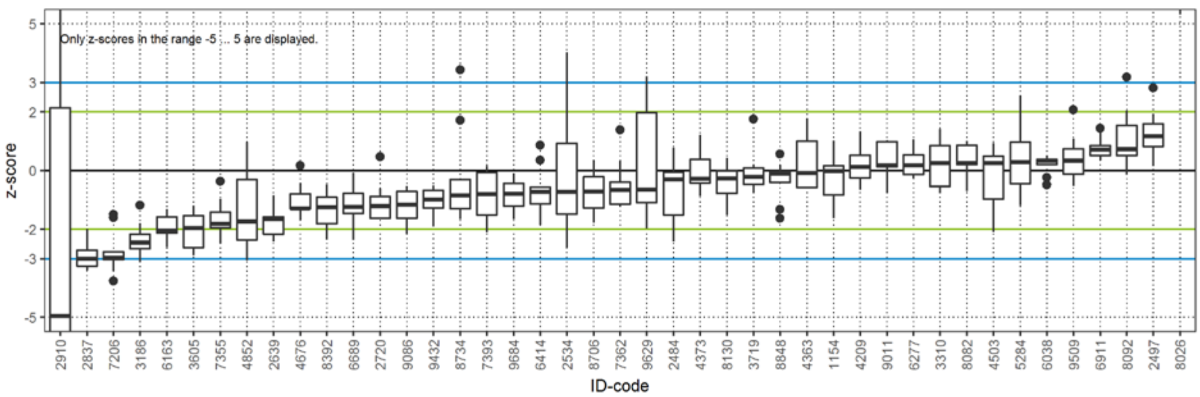
z-scores for component dust concentration (St)



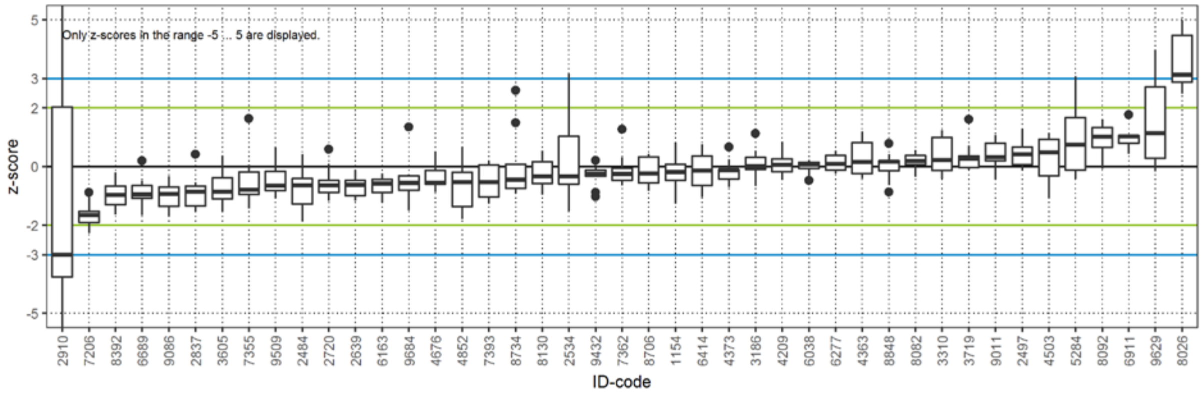
z-scores for component Cadmium (Cd)



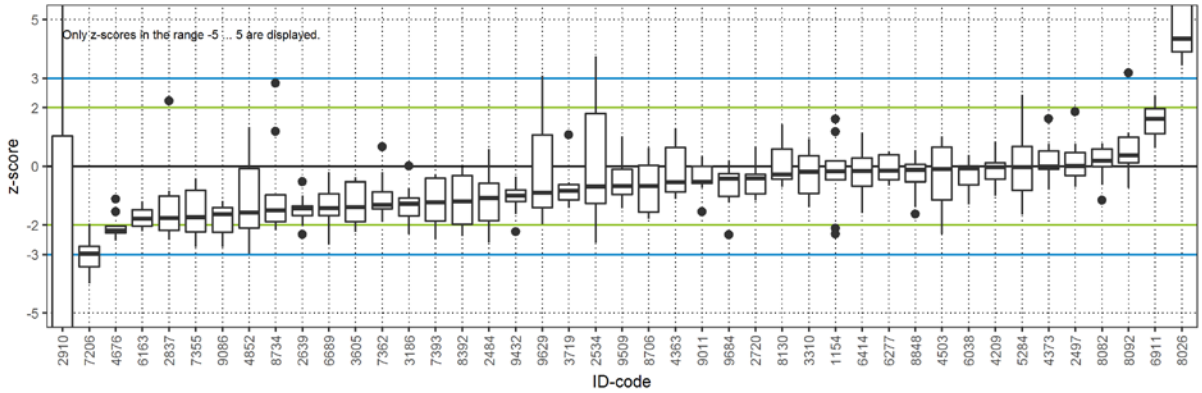
z-scores for component Cobalt (Co)



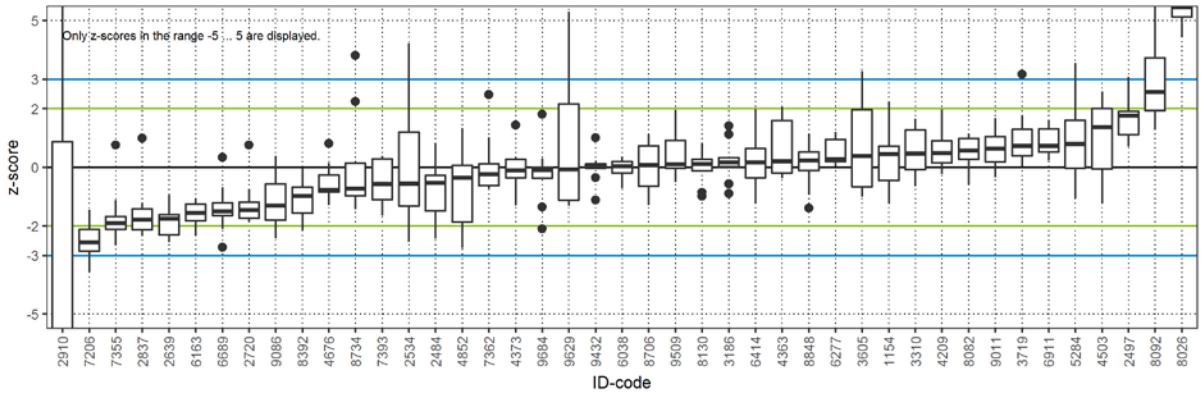
z-scores for component Chromium (Cr)



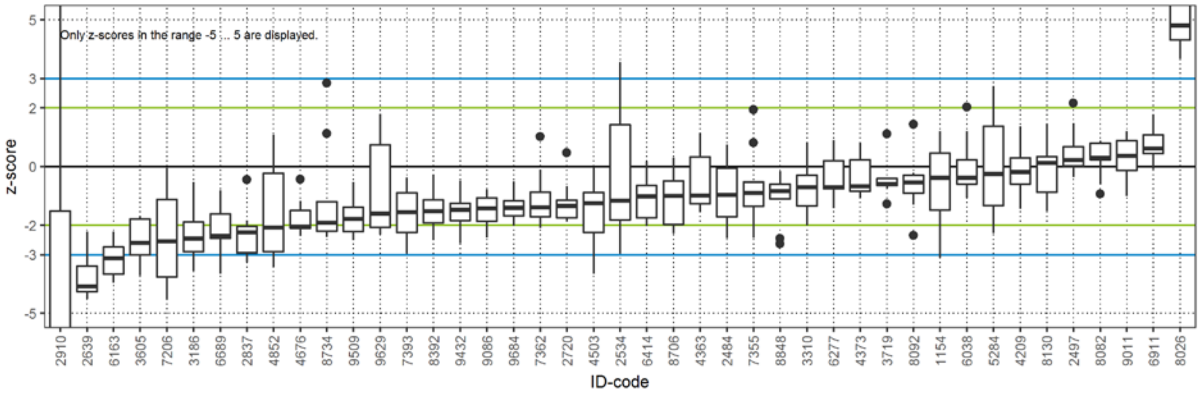
z-scores for component Copper (Cu)



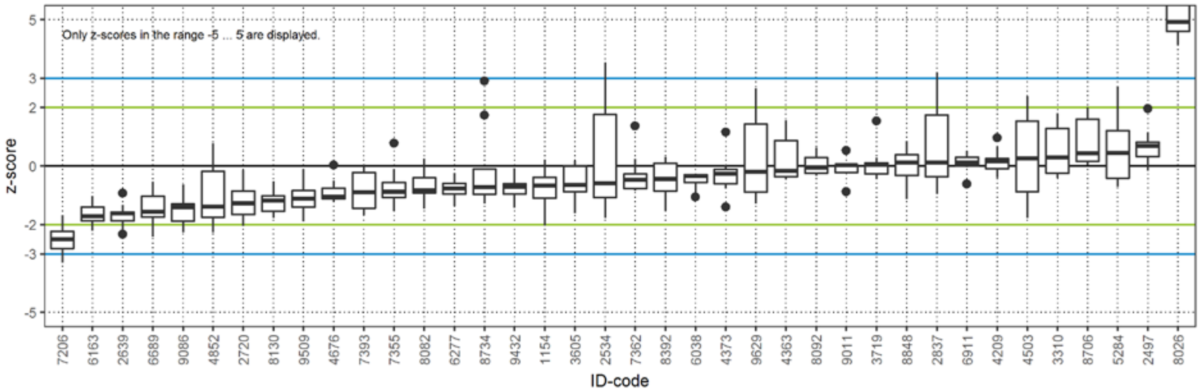
z-scores for component Nickel (Ni)



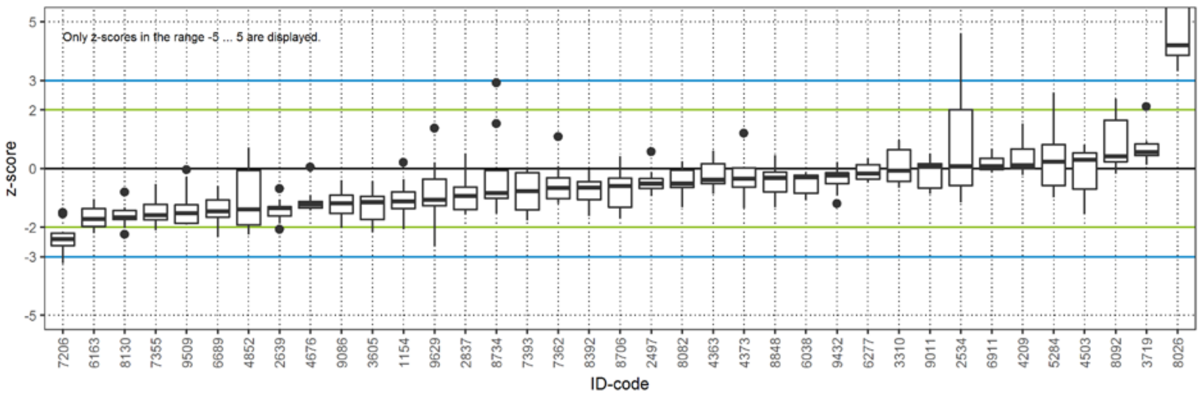
z-scores for component Lead (Pb)



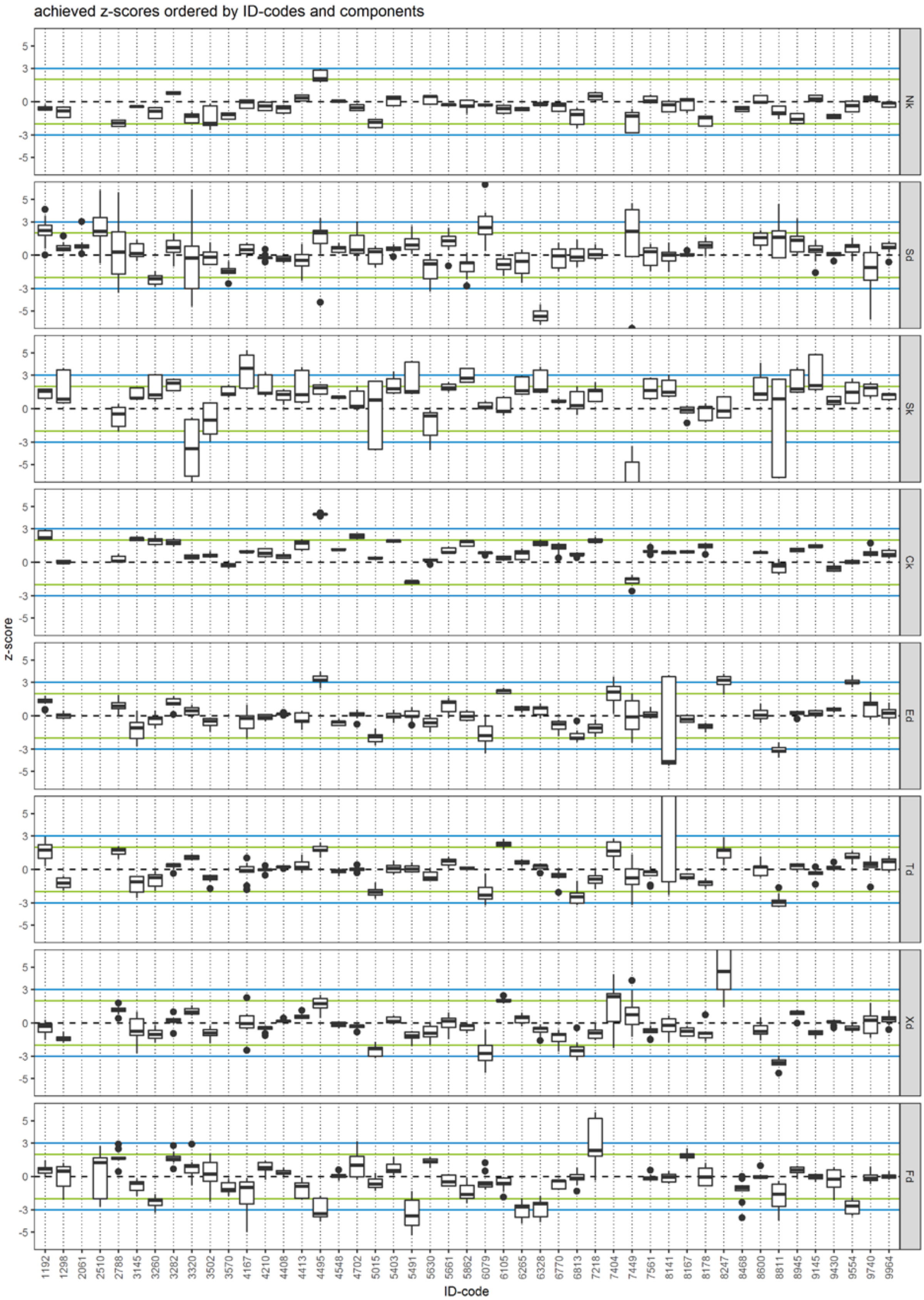
z-scores for component Manganese (Mn)



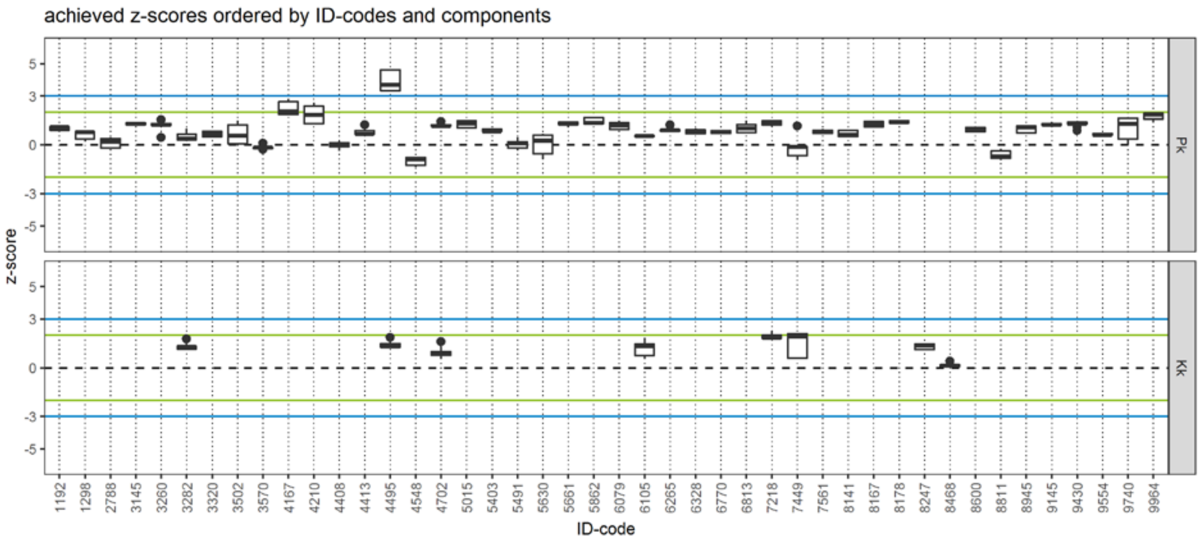
z-scores for component Vanadium (V)



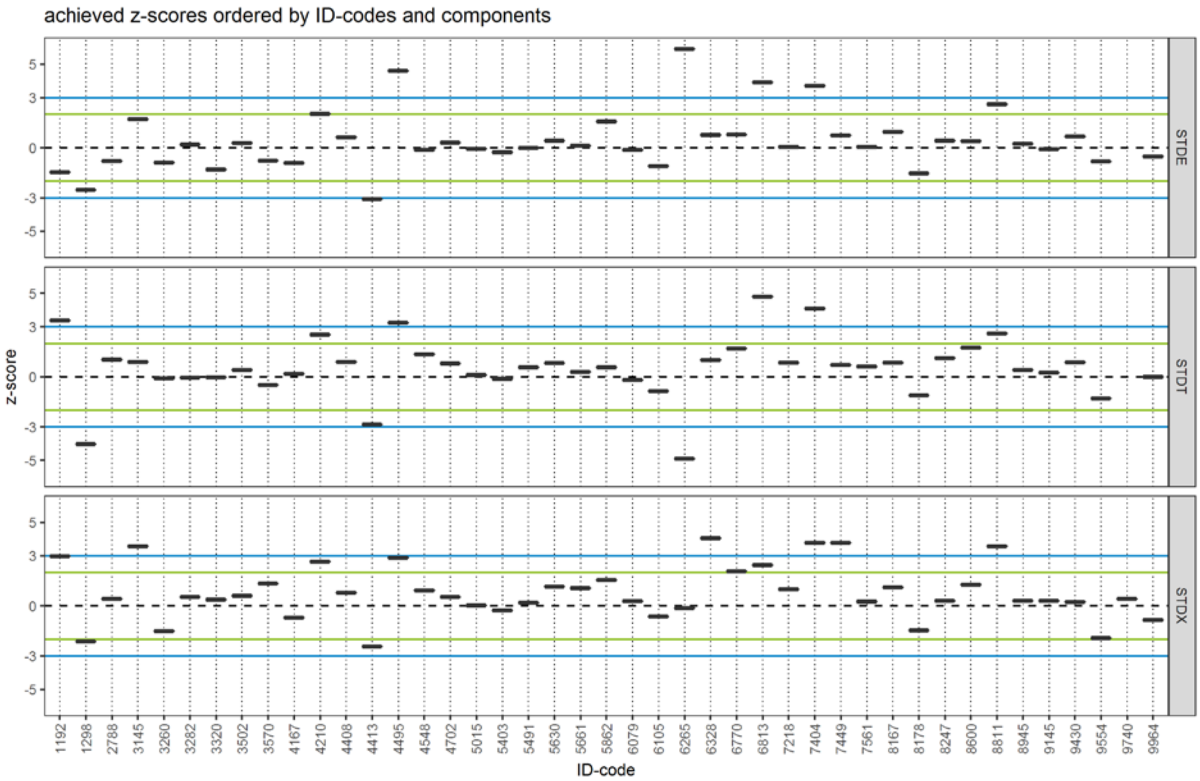
5.1.2 Substance range G



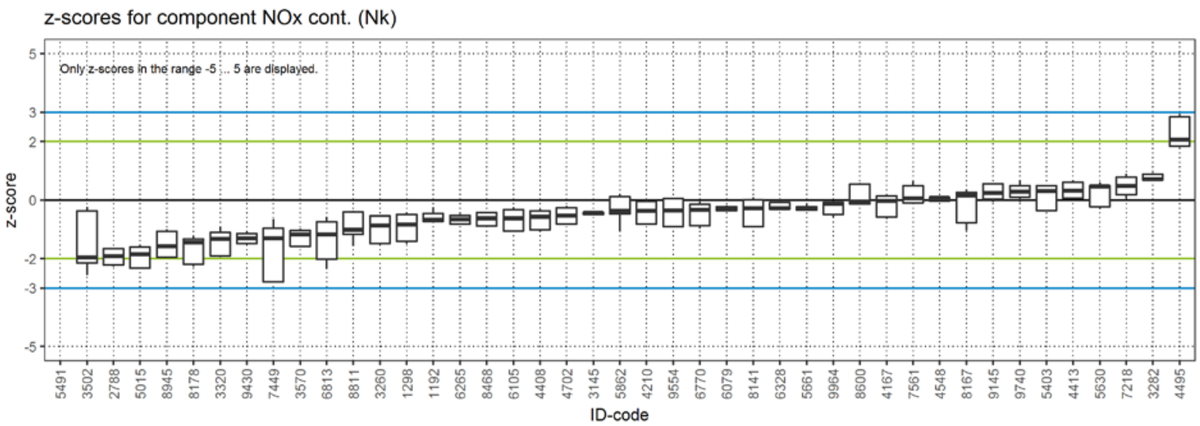
Scheme 3: Achieved z-scores gas proficiency test (only values in the range -5 … 5 are shown)

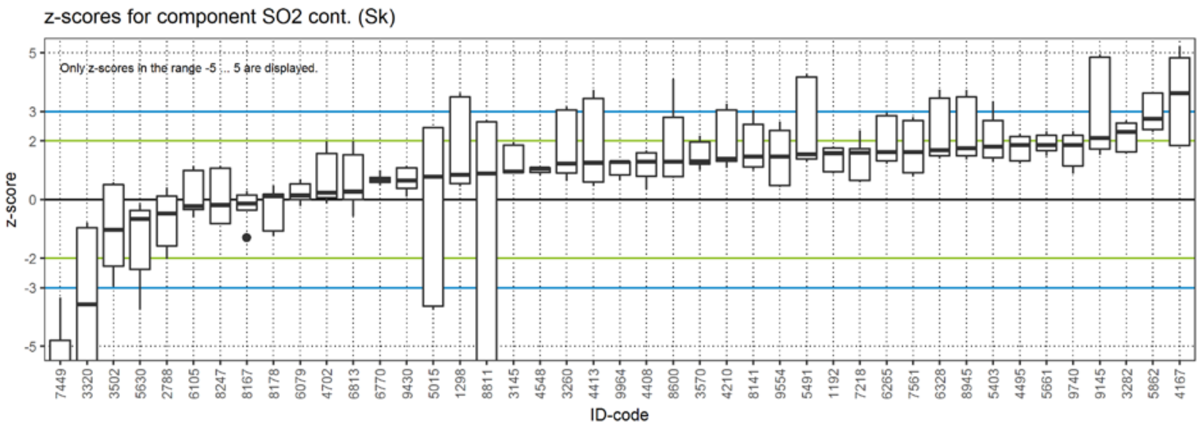


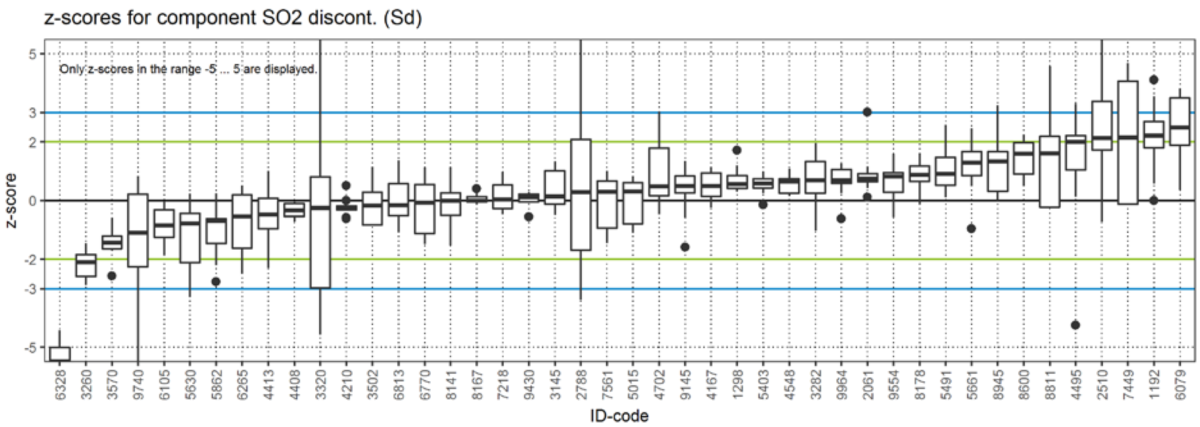
Scheme 4: Achieved z-scores gas proficiency test, components not required for passing (only values in the range -5 … 5 are shown)



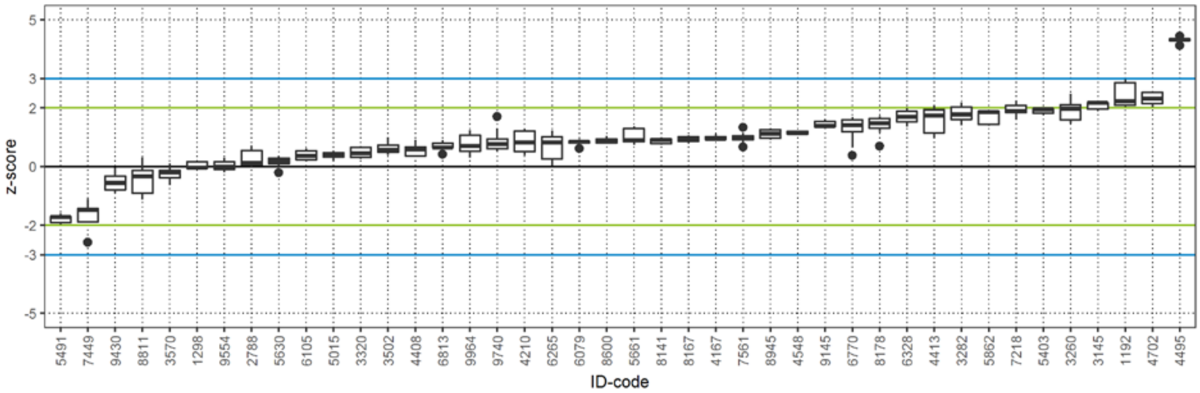
Scheme 5: Achieved z-scores gas proficiency test, ETX standard (only values in the range -5 … 5 are shown)


z-scores for component NOx cont. (Nk)
Only z-scores in the range -5 ... 5 are displayed.
z-score
5
3
2
0
-2
-3
-5
5491 3502 2788 5015 8945 8178 3320 9430 7449 3570 6813 8811 3260 1298 1192 6265 8468 6105 4408 4702 3145 5862 4210 9554 6770 6079 8141 6328 5661 9964 8600 4167 7561 4548 8167 9145 9740 5403 4413 5630 7218 3282 4495
ID-code

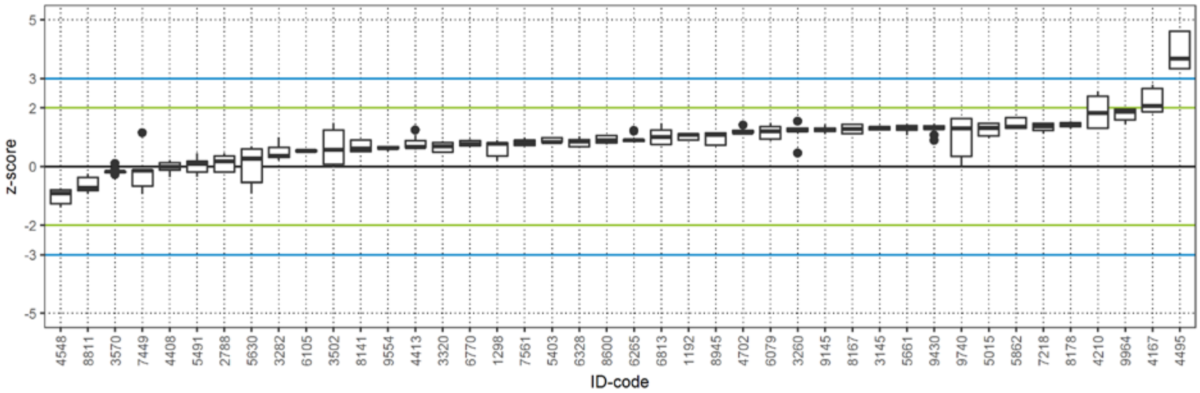

z-scores for component SO2 cont. (Sk)
Only z-scores in the range -5 ... 5 are displayed.
z-score
5
3
2
0
-2
-3
-5
7449 3320 3502 5630 2788 6105 8247 8167 8178 6079 4702 6813 6770 9430 5015 1298 8811 3145 4548 3260 4413 9964 4408 8600 3570 4210 8141 9554 5491 1192 7218 6265 7561 6328 8945 5403 4495 5661 9740 9145 3282 5862 4167
ID-code


z-scores for component SO2 discont. (Sd)
Only z-scores in the range -5 ... 5 are displayed.
z-score
5
3
2
0
-2
-3
-5
6328 3260 3570 9740 6105 5630 5862 6265 4413 4408 3320 4210 3502 6813 6770 8141 8167 7218 9430 3145 2788 7561 5015 4702 9145 4167 1298 5403 4548 3282 9964 2061 9554 8178 5491 5661 8945 8600 8811 4495 2510 7449 1192 6079
ID-code

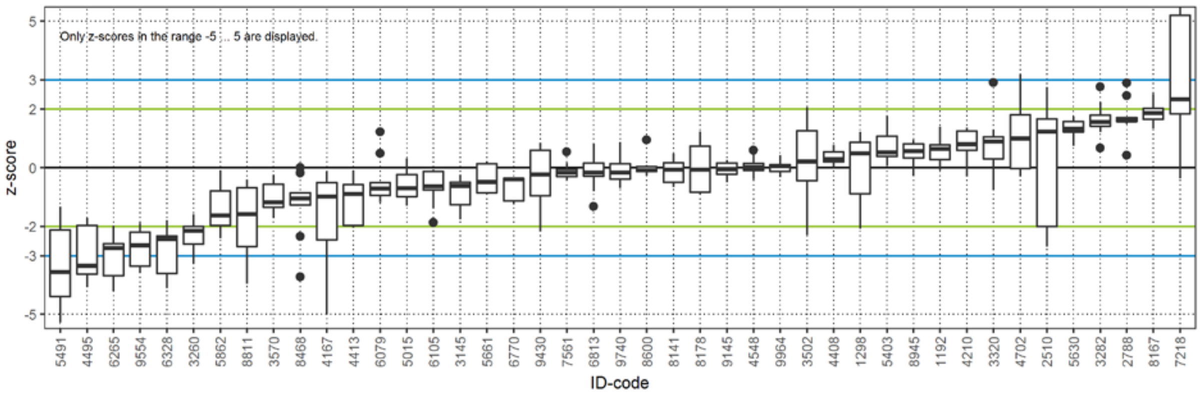
z-scores for component TOC (Ck)



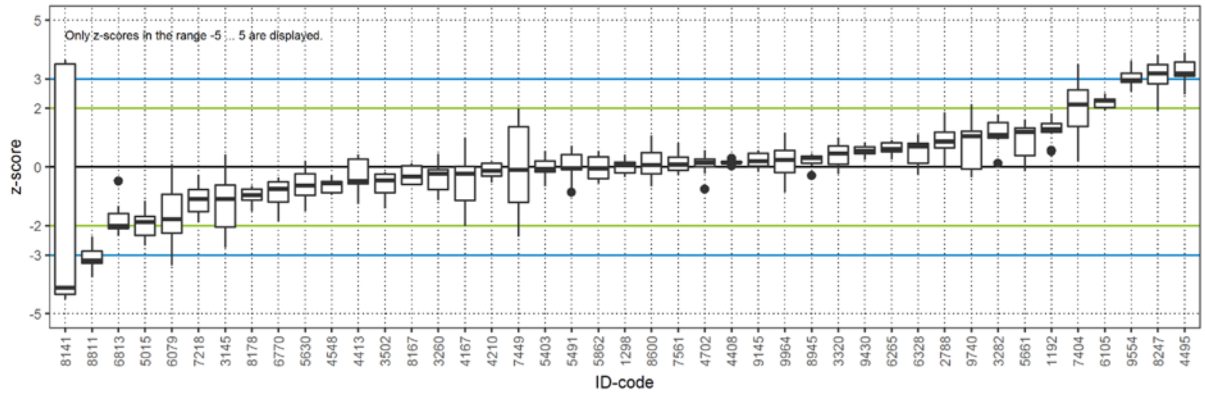
z-scores for component propane (Pk)



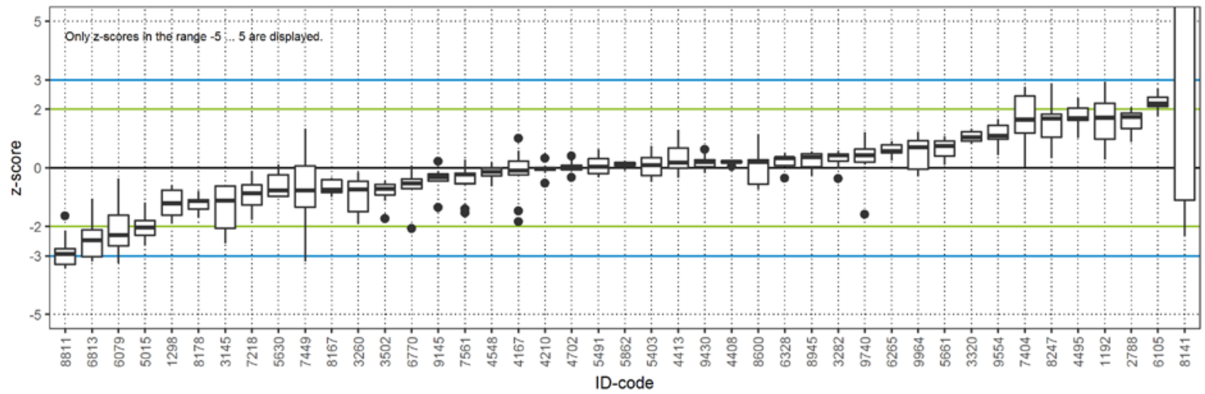
z-scores for component formaldehyde (Fd)



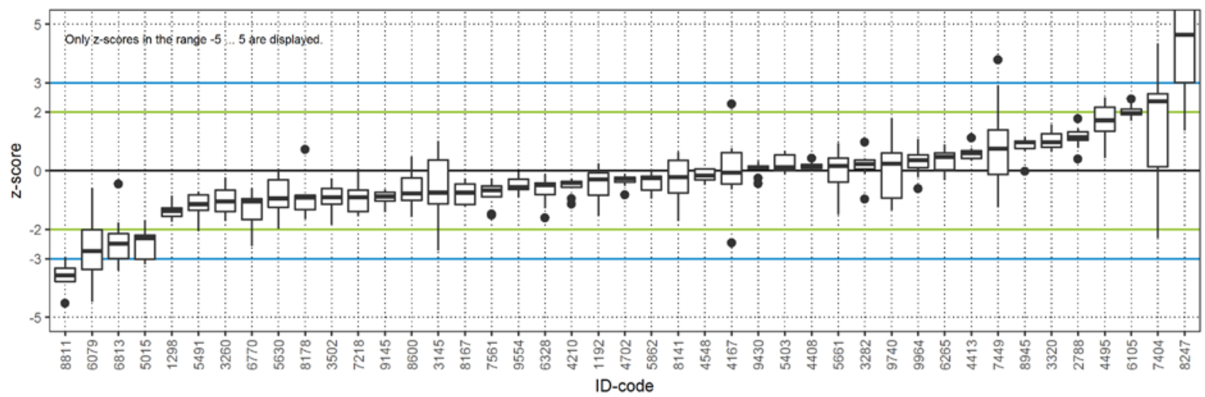
z-scores for component ethylbenzene (Ed)



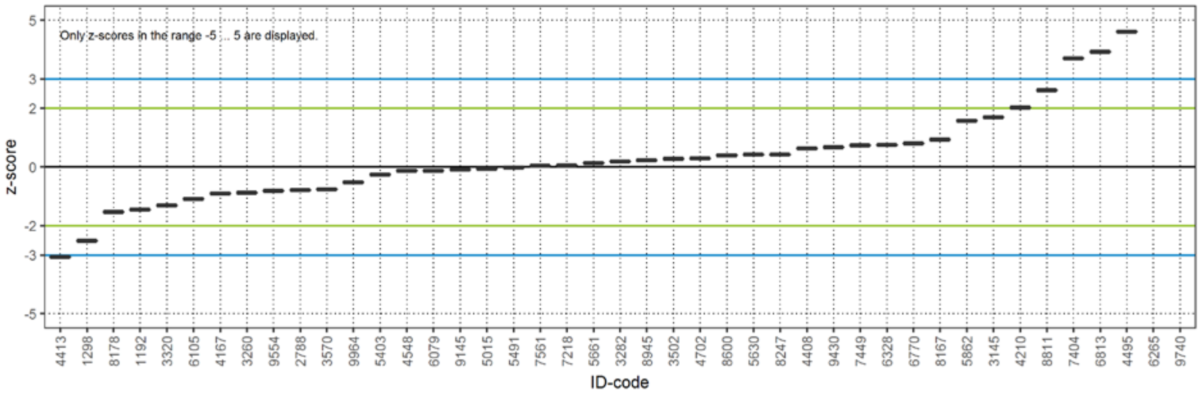
z-scores for component toluene (Td)



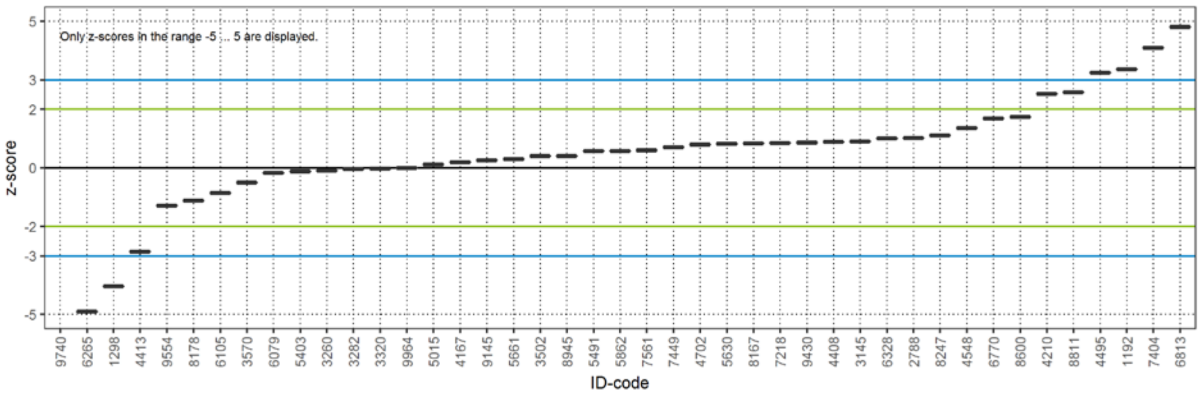
z-scores for component xylene (sum) (Xd)



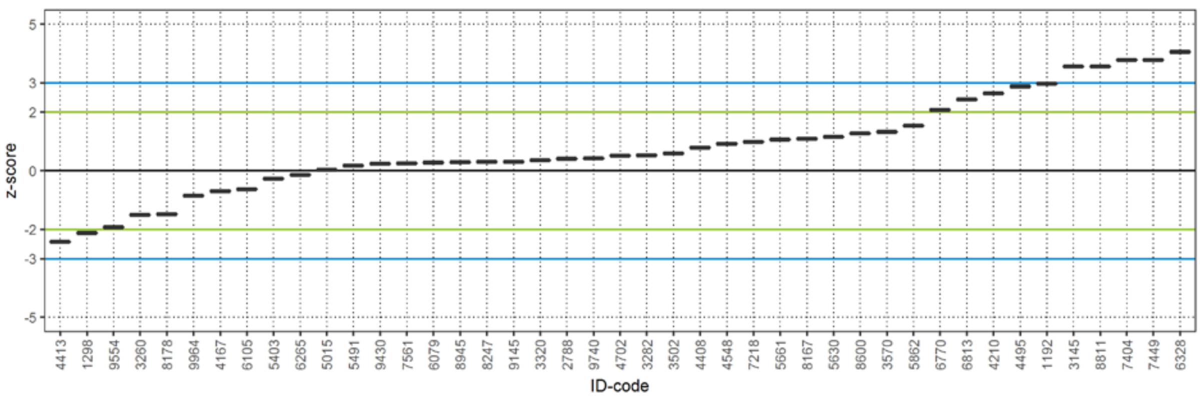
z-scores for component ethylbenzene (standard) (STDE)



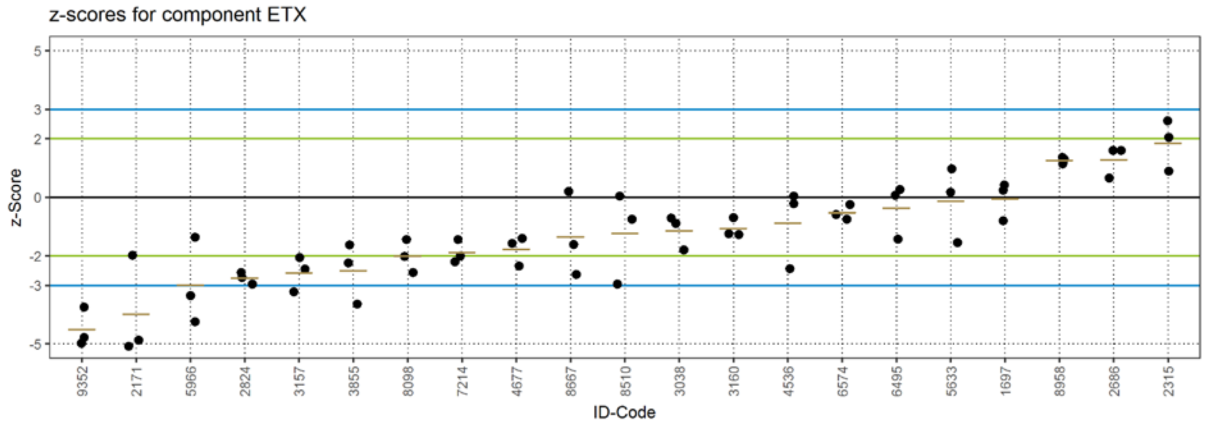
z-scores for component toluene (standard) (STDT)

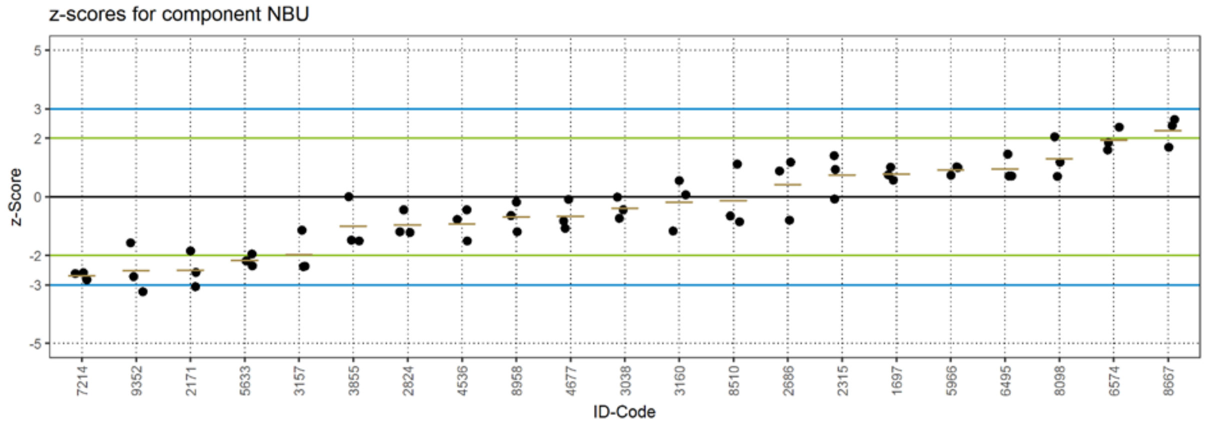


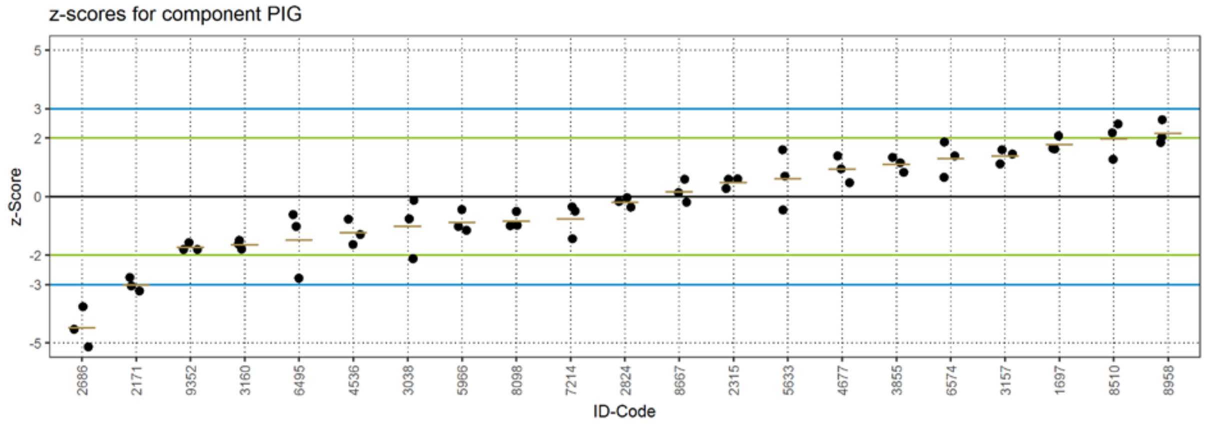
z-scores for component xylene (standard) (STDX)

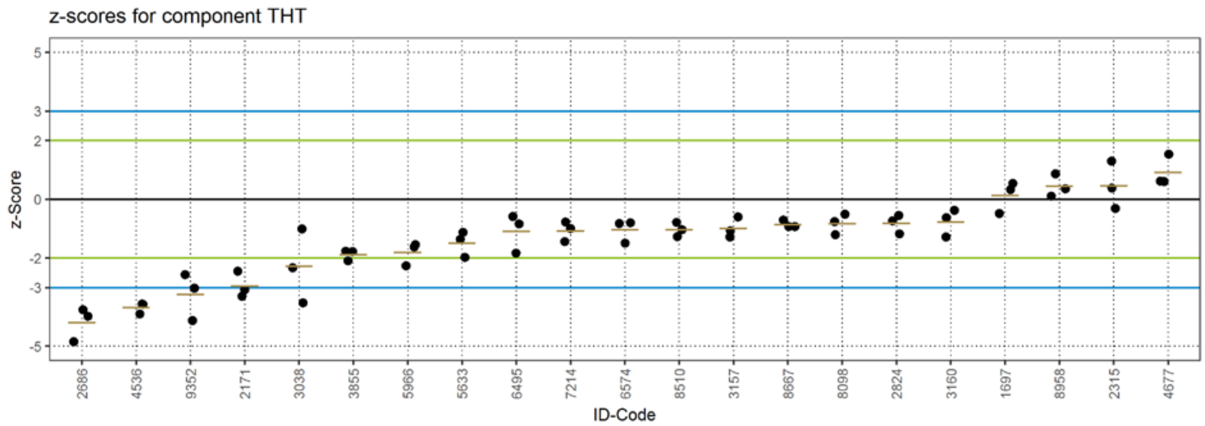


5.1.3 Substance range O





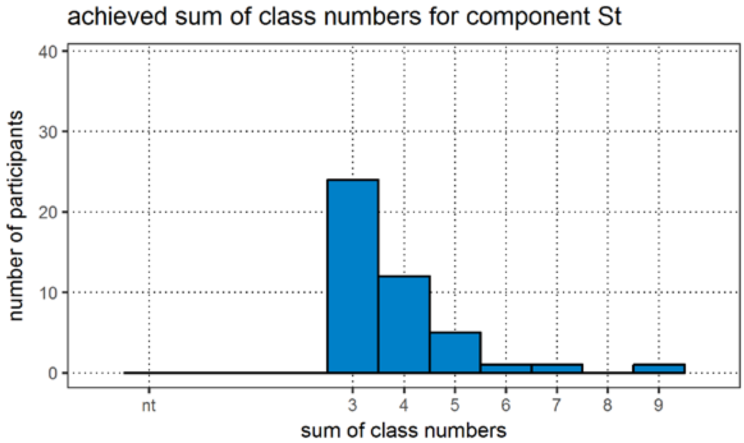


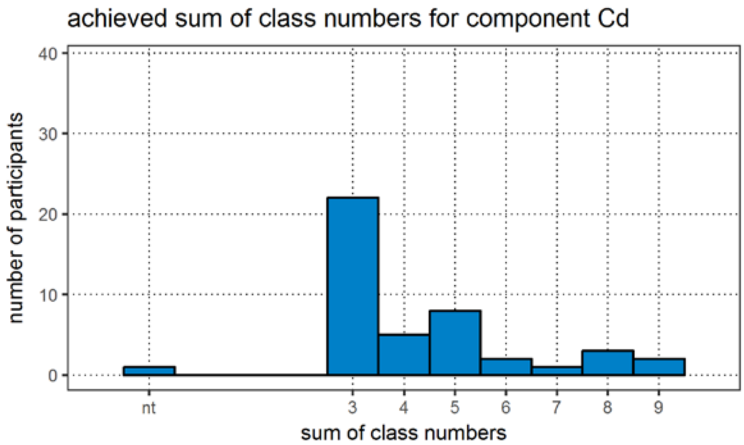


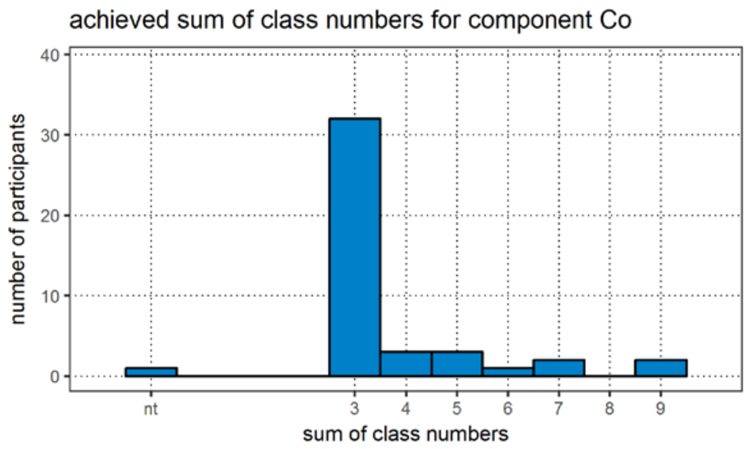
5.2 Acheived Sums of Class Numbers

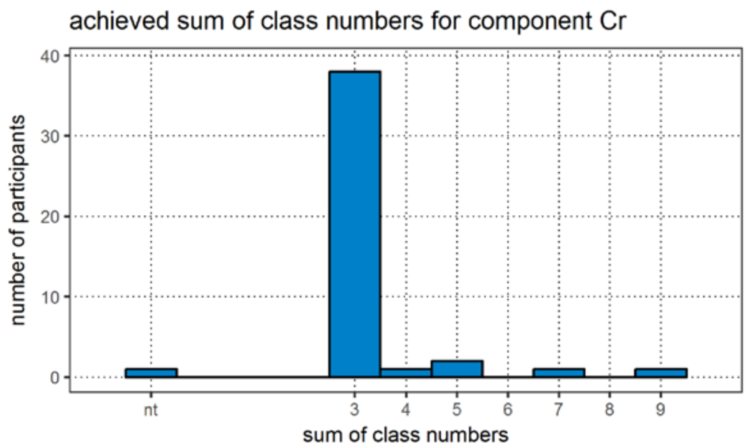
The following schemes show the sum of class numbers that the participants achieved for the different components in form of histogramme charts. For the interpretation of the sums of class numbers, please see section 4.3.2. Participants that did not hand in results for a component are listed as “nt”.

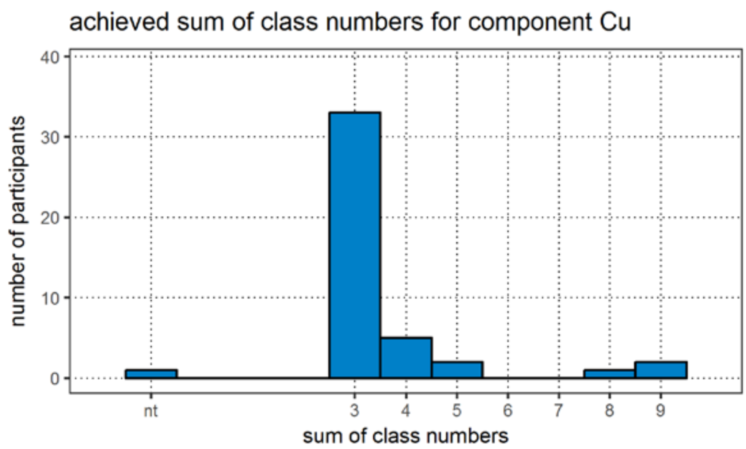
5.2.1 Substance range P

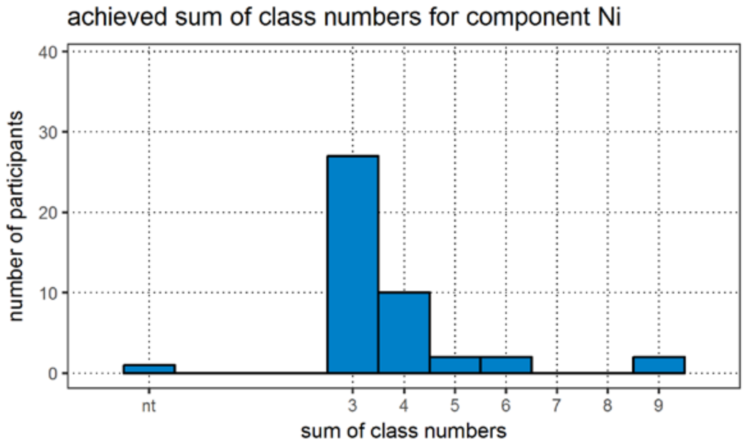


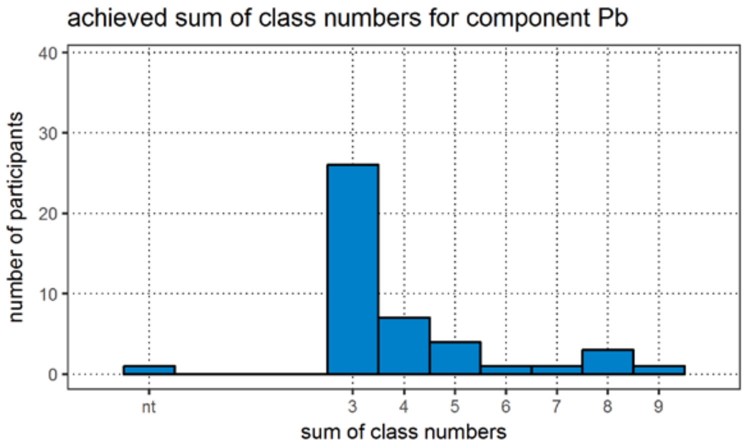


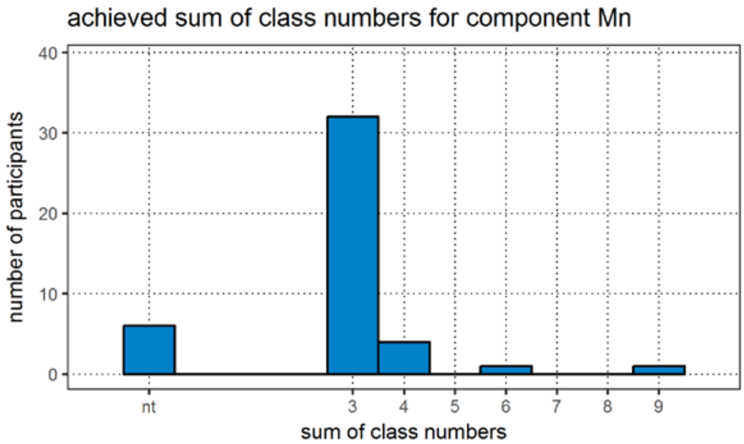

achieved sum of class numbers for component Co
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers

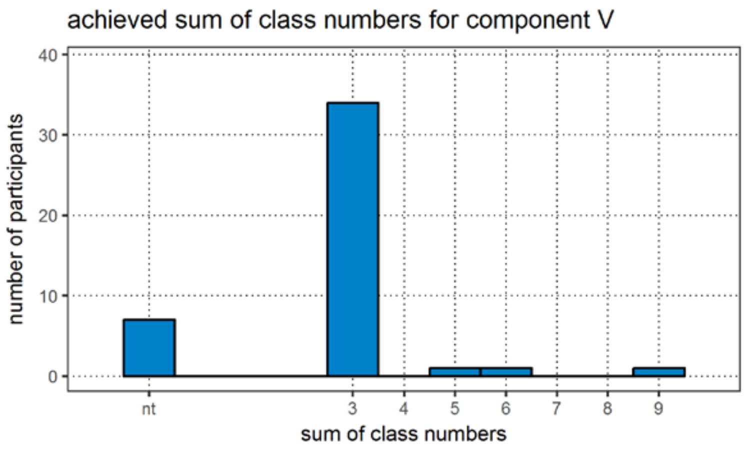

achieved sum of class numbers for component Cr
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers


achieved sum of class numbers for component Cu
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers

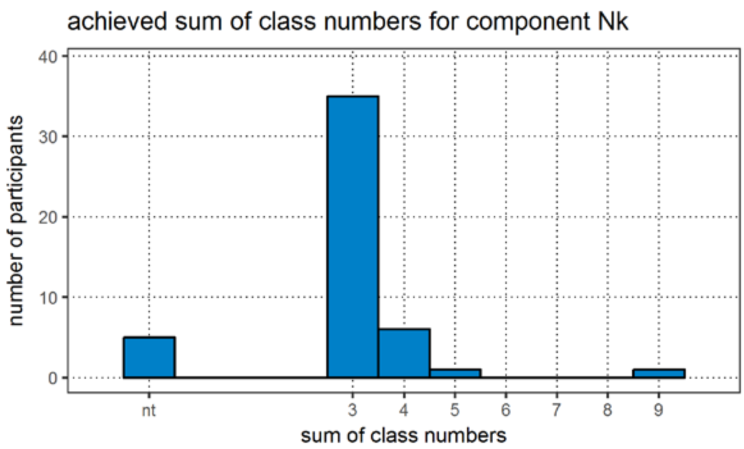

achieved sum of class numbers for component Ni
number of participants
0
10
20
30
40
nt
3
4
5
6
7
8
9
sum of class numbers

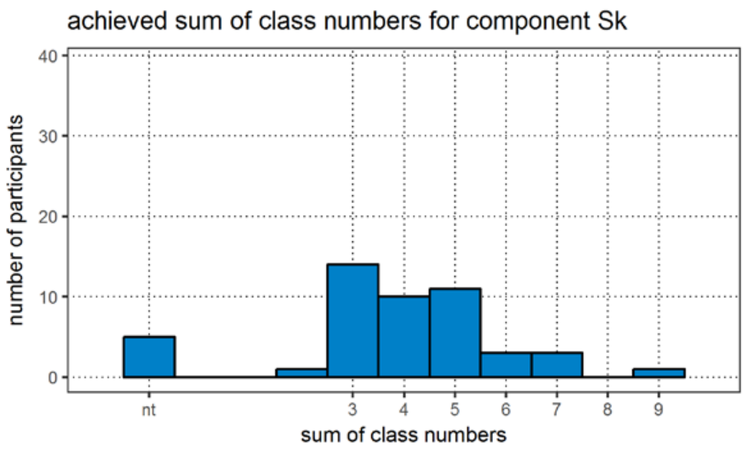

achieved sum of class numbers for component Pb
number of participants
0
10
20
30
40
nt
3
4
5
6
7
8
9
sum of class numbers

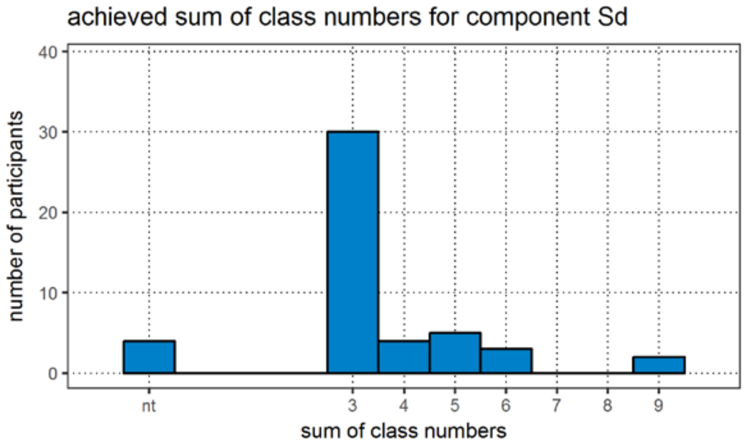

achieved sum of class numbers for component Mn
number of participants
0
10
20
30
40
nt
3
4
5
6
7
8
9
sum of class numbers

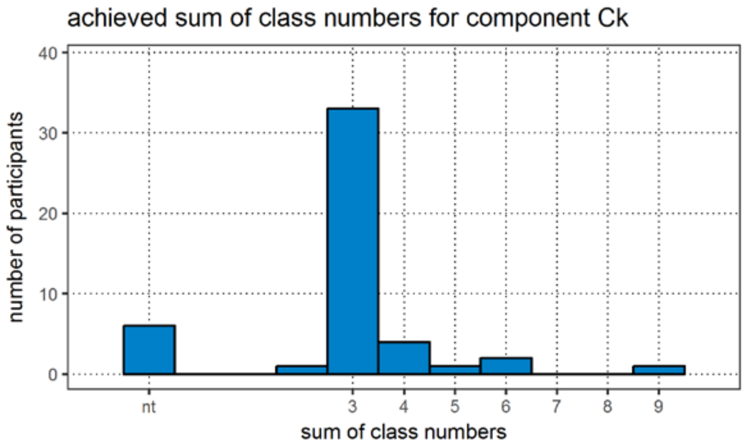


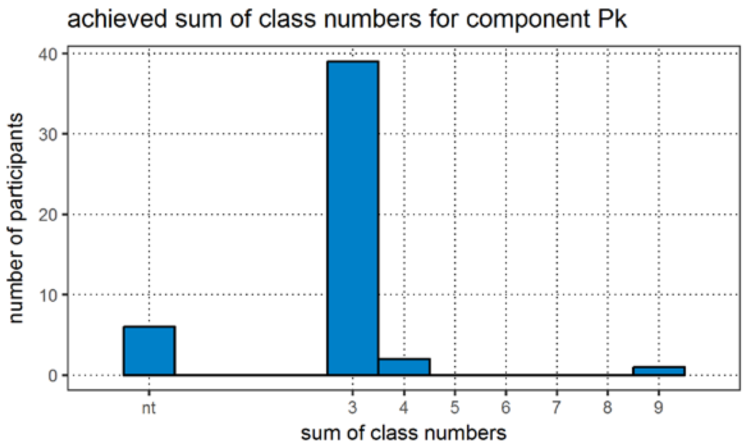
5.2.2 Substance range G

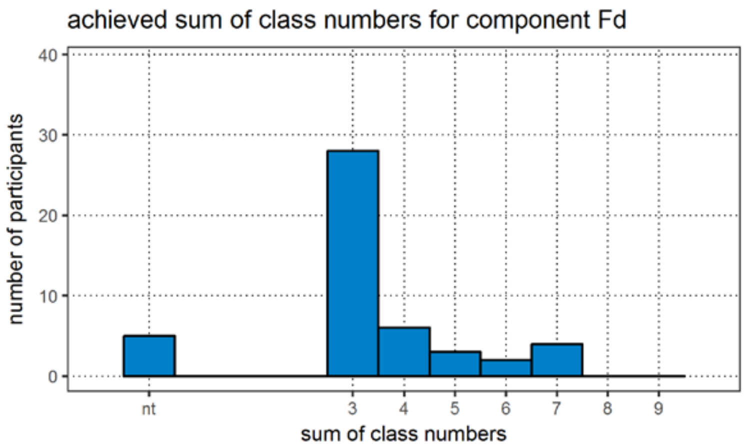


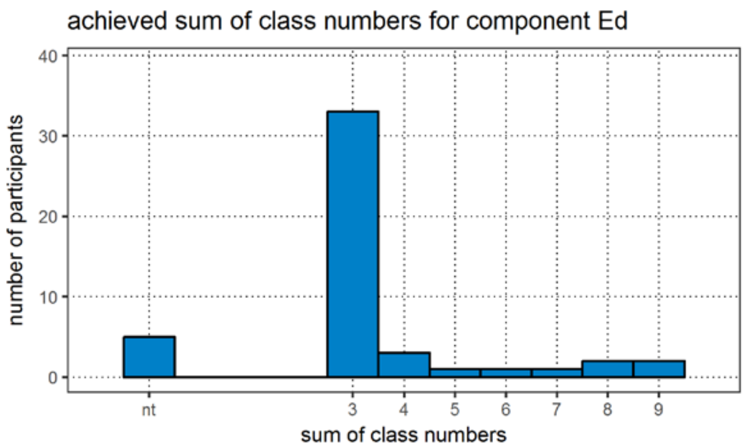


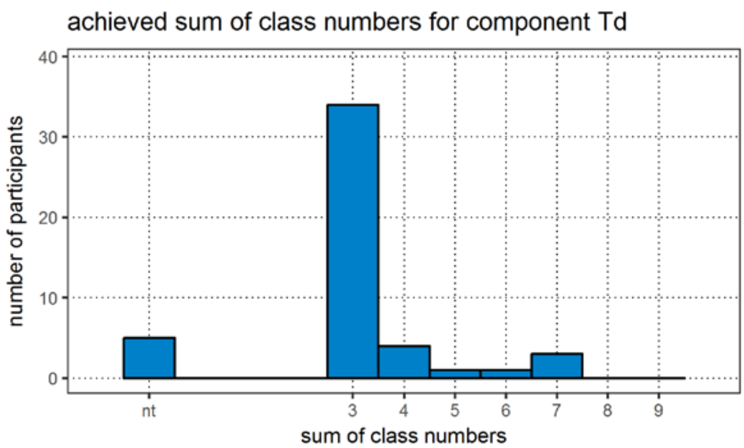

achieved sum of class numbers for component Sd
number of participants
sum of class numbers
nt
3
4
5
6
7
8
9
0
10
20
30
40

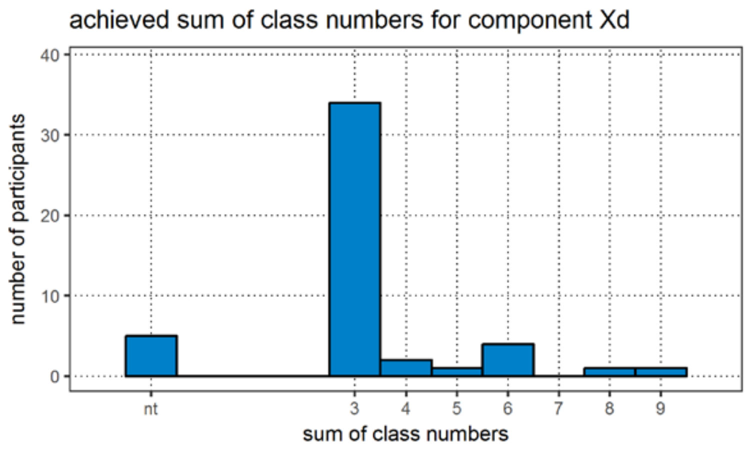

achieved sum of class numbers for component Ck
number of participants
sum of class numbers
nt
3
4
5
6
7
8
9
0
10
20
30
40


achieved sum of class numbers for component Pk
number of participants
sum of class numbers
nt
3
4
5
6
7
8
9
0
10
20
30
40


achieved sum of class numbers for component Fd
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers

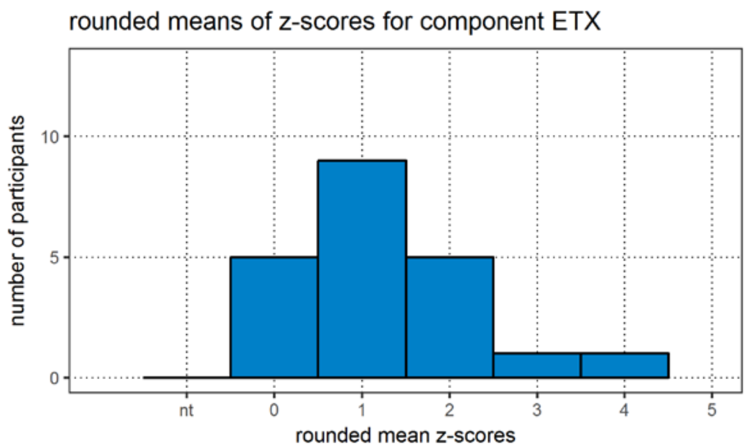

achieved sum of class numbers for component Ed
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers

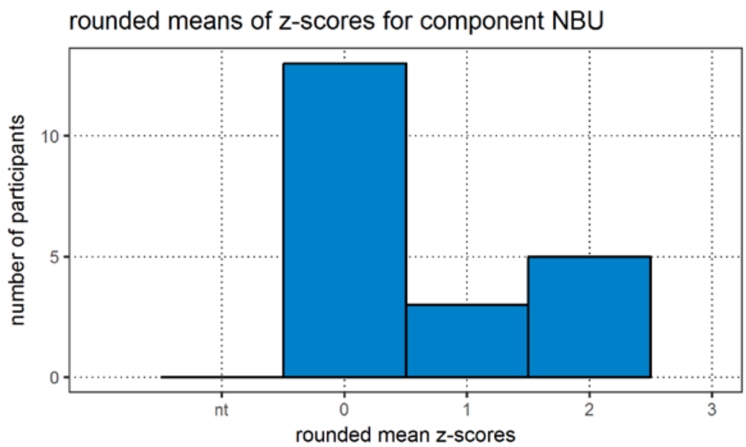

achieved sum of class numbers for component Td
number of participants
40
30
20
10
0
nt
3
4
5
6
7
8
9
sum of class numbers

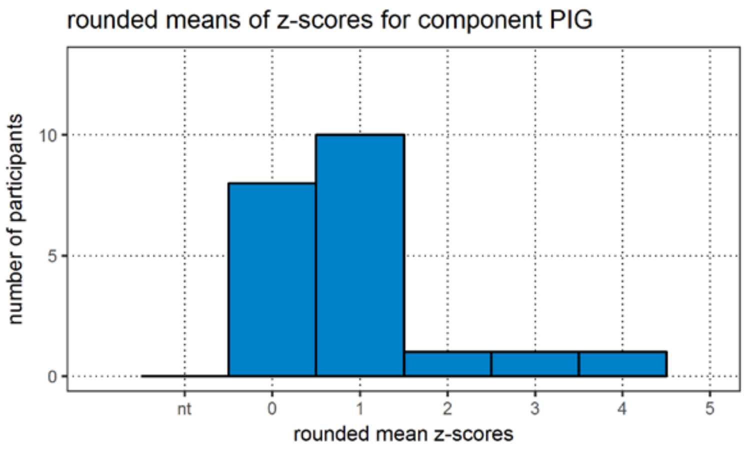


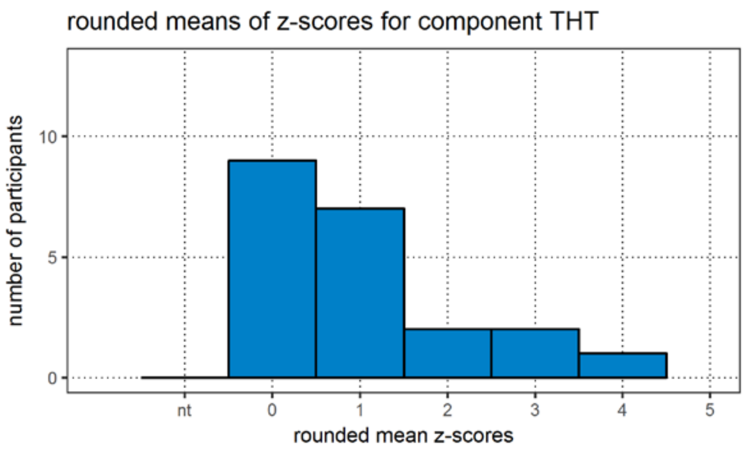
5.2.3 Substance range O

In odour emission proficiency tests, instead of sums of class numbers a mean value of z-scores is calculated. In the following histograms, the participants are allocated to a group by rounding down their mean z-score to the next lower integer.

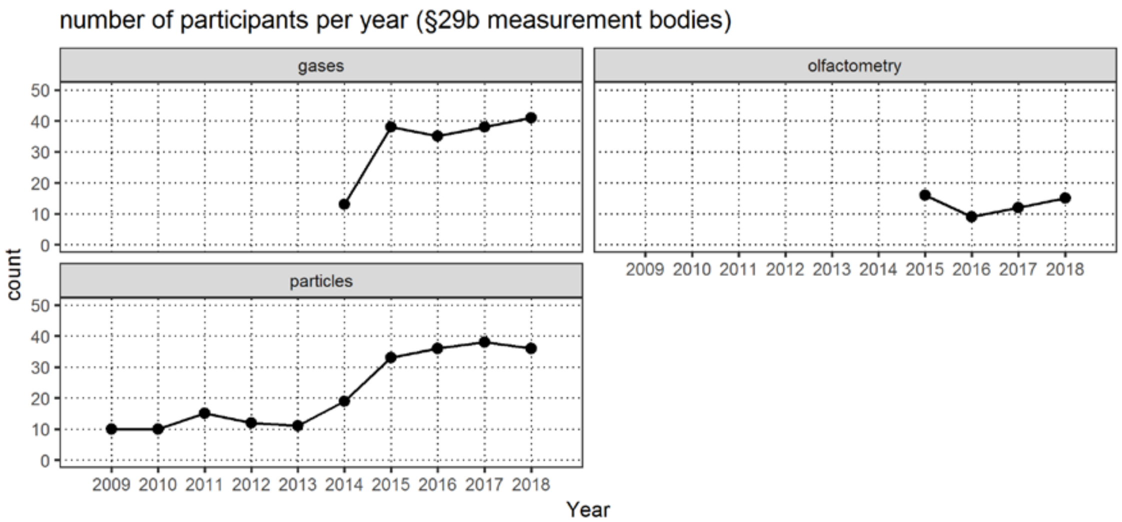


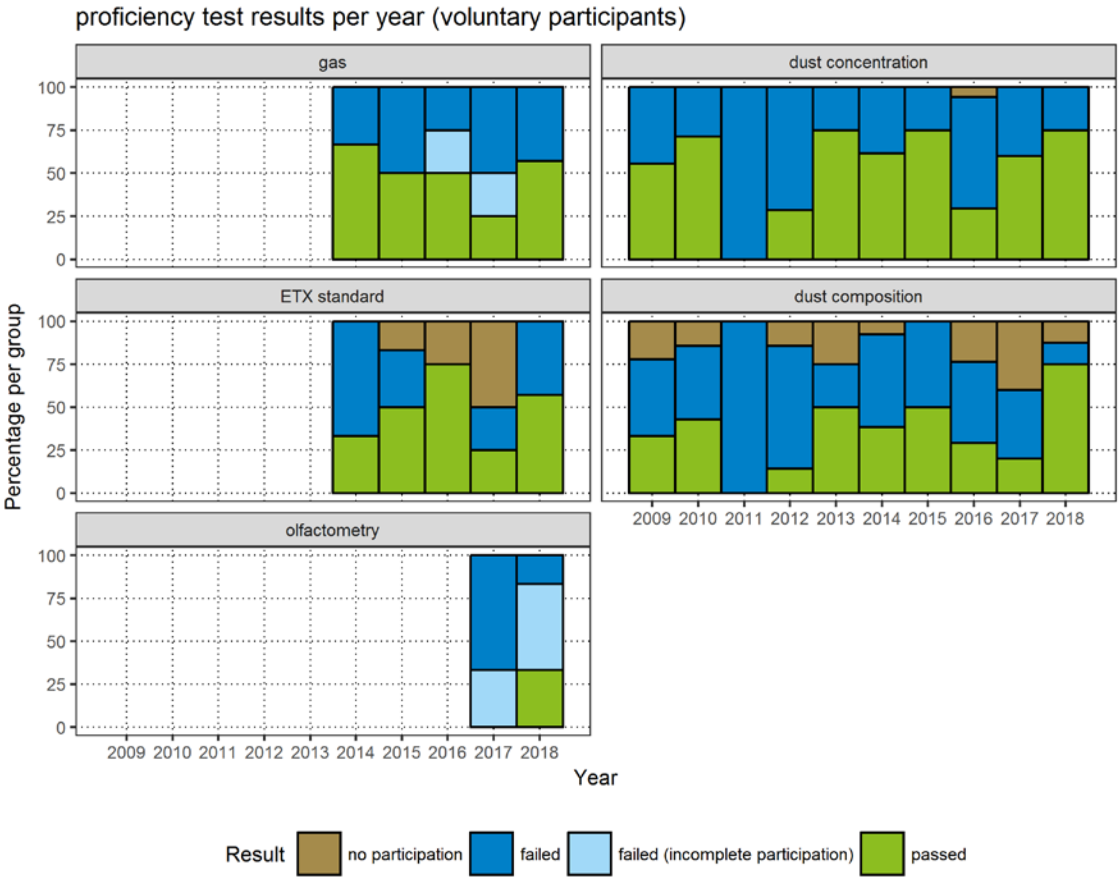



rounded means of z-scores for component PIG
number of participants
10
5
0
nt
0
1
2
3
4
5
rounded mean z-scores


rounded means of z-scores for component THT
number of participants
10
5
0
nt
0
1
2
3
4
5
rounded mean z-scores

6. Interpretation





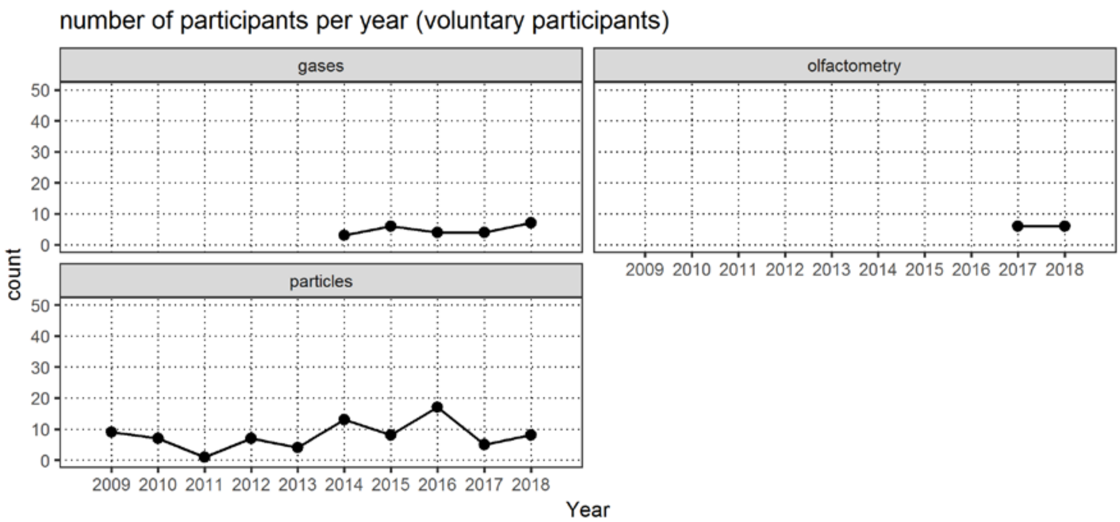


Table 7: Overview of results since 2015 (§29b-bodies)

year	components group	passed	failed	failed (incompl. participation)	no participation
2015	ETX-standard	28	8	-	2
	gas	30	6	2	-
	odour	11	5	-	-
	dust (total)	32	1	-	-
	dust composition	26	7	-	-
	dust composition (post-analysis)	6	-	-	-

year	components group	passed	failed	failed (incompl. participation)	no participation
2016	ETX-standard	26	8	-	1
	gas	30	4	1	-
	odour	7	2	-	-
	dust (total)	34	2	-	-
	dust composition	29	7	-	-
	dust composition (post-analysis)	4	1	-	-
2017	ETX-standard	32	5	-	1
	gas	35	2	1	-
	odour	10	2	-	-
	dust (total)	37	1	-	-
	dust composition	32	6	-	-
	dust composition (post-analysis)	3	2	-	-
2018	ETX-standard	27	9	-	5
	gas	25	10	5	1*
	odour	11	3	1	-
	dust (total)	35	1	-	-
	dust composition	30	6	-	-
	dust composition (post-analysis)	4	1	-	-

* One participant was absent without excuse at his proficiency test date.

Table 8: Overview since 2015 (voluntary paricipants)

year	components group	passed	failed	failed (incompl. participation)	no participation
2015	ETX-standard	3	2	-	1
	gas	3	3	-	-
	dust (total)	6	2	-	-
	dust composition	4	4	-	-
	dust composition (post-analysis)	2	-	-	-
2016	ETX-standard	3	-	-	1
	gas	2	1	1	-
	dust (total)	5	11	-	1
	dust composition	5	8	-	4
	dust composition (post-analysis)	2	-	-	-
2017	ETX-standard	1	1	-	2
	gas	1	2	1	-
	odour	-	4	2	-
	dust (total)	3	2	-	-
	dust composition	1	2	-	2
	dust composition (post-analysis)	-	1	-	-
2018	ETX-standard	4	3	-	-
	gas	4	3	-	-
	odour	2	1	3	-
	dust (total)	6	2	-	-
	dust composition	6	1	-	1

6.1 Evaluation of the Measurement Results

§29b Measuring Bodies

The number of participations of §29b measuring bodies in HLNUG's stack emission proficiency tests has approximately doubled between 2013 and 2015 and now stands at approx. 30-40 participations for gas and dust per year. The sum of all results of a year has therefore been on a much broader statistical basis since 2015 compared to the years before 2014. Failures of individual participants thus no longer distort the overall picture of a year as much as in the past.

In the dust proficiency test, the results of the §29b measuring bodies are still at a high level, 35 of 36 participants (97%) were successful in the dust (total) part of the proficiency test. The positive trend of the last years continues with regard to the dust composition measurements, here 30 of 36 participants (83%) regularly passed this part of the proficiency test, further 4 participants (11%) passed this part of the proficiency test only via the post-analysis. Altogether 94% of the participants in the dust proficiency test were successful.

In the gas proficiency test 25 of 40 (63%) of the §29b measuring bodies passed. The pass rate in 2018 was thus lower than in previous years, for various reasons:

- 5 participants (13%) did not pass only because they did not measure all mandatory components (incomplete participation), e.g. in the context of a repeat participation after a previously failed proficiency test. Formally these participations are to be evaluated as "failed", however these 5 participants passed all components measured by them in the course of their participations.
- 9 participants (23%) were not successful in a full participation, of which 3 (8%) were unsuccessful solely due to insufficient results in continuous SO_2 measurements, which stopped being a mandatory component in autumn 2018. The other unsuccessful participants mainly had problems with the correct determination of formaldehyde (4 participants, 10%) and organic single compounds (3 participants, 8%), as well as with discontinuous SO_2 measurements conforming to SRM, and with NO_x (one participant each, 3%). Of these 6 participants 4 failed 2 components, the remaining 2 failed one component each.
- One participant (3%) failed a compulsory component in an (incomplete) repeat participation. Since an unsuccessful participation was repeated here at the beginning of the year, this participant alone is responsible for 20% (2 out of 10) of all unsuccessful participations in 2018.

It is striking that almost all participants who were not successful in the gas proficiency test in 2018 already had problems with the quality of their measurements in the past. The average pass rate of the 9 authorised bodies that failed in 2018 a regular (complete) participation was only 58% in the last 10 years. These 9 participants passed only 21 of a total of 36 gas proficiency tests.

The analysis of the ETX standard was successfully performed by 27 out of 36 (75%) of the §29b measuring bodies, 5 measuring bodies did not participate in this analysis.

The results of the §29b measuring bodies at the odour proficiency tests are comparable with the results of the previous year. 11 out of 15 participants (73%) passed the odour proficiency test. The results of one participant were classified as "failed (incomplete participation)" due to deviations from the procedure specified in the implementing regulations.

Voluntary participants

The number of voluntary proficiency test participations varies from year to year, as a rule there are approx. 4 participations in the gas proficiency test and approx. 8 participations in the dust proficiency test. In 2018, there were 7 participants in the gas proficiency test and 8 voluntary participants in the dust proficiency test. Due to the usually low number of voluntary participations in many years, the results collected in one year are extremely influenced by the performance of individual laboratories; a comparison over many years is only of limited informative value.

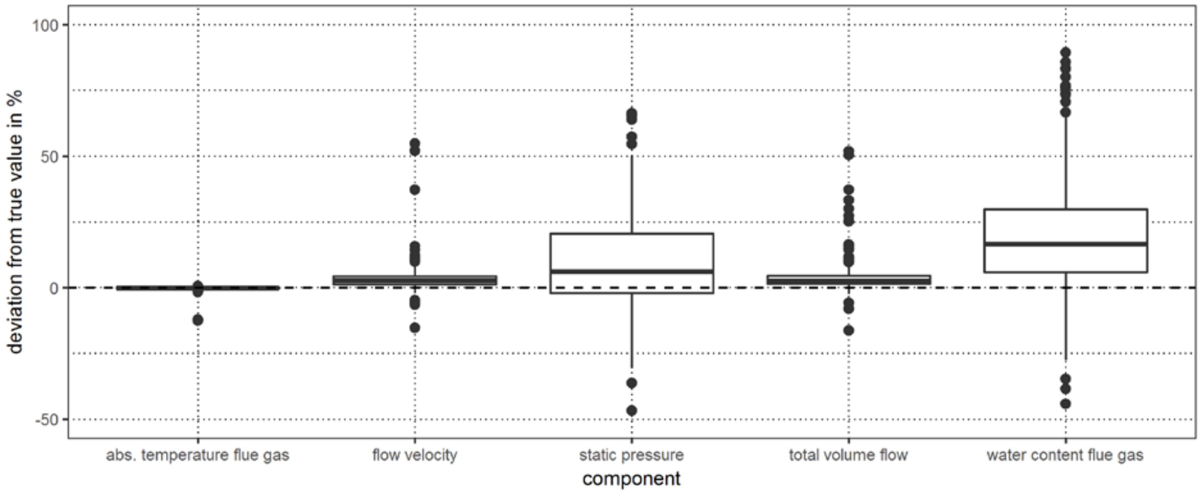
In the dust (total) part of the proficiency test, a total of 6 out of 8 participations (75%) were successful in 2018. In the case of dust composition, also 6 of the 8 participants (75%) were successful. Altogether 6 (75%) of the 8 voluntary participations in the dust proficiency test were successful. With these numbers it is to be noted that one participant determined only dust mass concentrations and did without a determination of heavy metal concentrations.

With the gas proficiency test 4 of 7 (57%) of the voluntary participants passed the proficiency test. 4 out of 7 (57%) of the voluntary participants successfully completed the analysis of the ETX standard.

In the odour proficiency tests, 2 out of 6 voluntary participants (33%) passed. 3 participants (50%) delivered correct measurements, but these were not determined within 6 hours in accordance guideline VDI 3880. The overall results were therefore classified as "failed (incomplete participation)".

6.2 Basic Flow Conditions

For each proficiency test, the participants must also determine and specify the basic flow conditions. The measured values of the participants are compared in the result communications with the target values determined by the HLNUG. The data basis for the evaluation in this report are the measured values received from proficiency test participants in 2018. A list of individual results is not given here, in the following scheme only a summary representation of the values is shown. The display is limited to relative deviations of the participant measured values from the respective setpoint value in order to be able to compare different proficiency tests with different flow conditions. Obviously incorrect measured values that deviate from the setpoint by orders of magnitude were removed from the data collective. This applies in particular to information on static pressure. Here, numerical values were often submitted that would be reasonably correct, e.g. in the unit Pa or as total pressure, but not as static pressure in the unit hPa, as asked for in the results submission.



As can be seen, the measured values for the exhaust gas temperature are always very close to the setpoint. In comparison, the measured values for the flow velocity and the volume flow show a significantly higher dispersion and many individual values that are far from the setpoint value. Even more extremely, the measured values of the participants scatter for the static pressure and the water vapour concentration.

An evaluation of the absolute values of the relative deviations (positive and negative deviations do not cancel each other out here) can be found in the following table. The median of the absolute values of the respective deviations as well as the 25th and 75th percentile are listed there. This information should be understood as follows: Only a quarter of the readings showed a deviation below the 25th percentile. Half of the measurements showed a deviation below or above the median. One quarter of the measured values had a deviation (positive or negative) greater than the 75th percentile.

Table 9: Absolute relative deviations from true values for basic conditions

	absolute temperature [%]	water vapour concentration [%]	static pressure [%]	flow velocity [%]	volume flow [%]
75th percentile	0.22	33.50	23.08	4.62	4.78
median	0.13	18.57	11.11	2.91	2.71
25th percentile	0.07	10.97	4.17	1.44	1.42
number of values	241	219	219	236	235

The deviations from the assigned values for most components were thus relatively close to the results from 2016 and 2017. Only for the water vapour concentration were the deviations in 2018 significantly higher than in the previous years; here the medians in 2016 and 2017 were around 9% and 12% relative deviations.

6.3 Optional Information from Participants

All participants were asked to provide additional information on their measurements on a voluntary basis together with the measurement results. The data received are summarised in the following tables and presented graphically. The database is based on feedback from participants from the years 2016 to 2018.

For some components, the participants in the proficiency test have a certain freedom in the choice of various process parameters. Based on the participants' voluntary data, an attempt was made to determine correlations between the methods, equipment, etc. used and the results obtained. Since 9 measurements are always carried out at different concentrations for each component, it is difficult to make a clear statement about the quality of a procedure. For a simple and clear presentation, correlations to the mean z-scores of the participants were therefore established, with negative values also being included in the mean value. In addition, similar components such as heavy metals or organic solvents were combined to form a common mean value. This type of evaluation certainly represents a simplification of the problem and cannot show all the details. Thus, for example, different influences in different concentration ranges or high fluctuations between the individual results of a participant are completely ignored in this evaluation. However, the limitation to the mean values of the participants' z-scores allows a simple estimation of the effects of different methods on the mean deviation of the measured values from the assigned value.

For most evaluations, a certain stabilisation of the values can be observed. This is ultimately due to the fact that the data basis for the 2018 Annual Report has only increased by about one third, while the values for most evaluations hardly differ from the values of previous years. As a result, most of the findings become more and more reliable and meaningful over time.

For all correlations presented in this report, it should be kept in mind that a correlation is merely an indication of a connection, but by no means proves causality. For example, it is quite conceivable that participants who use a certain device or procedure may happen to have other similarities that actually affect the measurement results, while the identified similarity actually plays no role at all.

6.3.1 Measurement Uncertainties

The participants' data on the absolute extended measurement uncertainties of their methods used in the dust proficiency test are shown in the following scheme. The median of the respective data as well as the 25th and 75th percentile are listed in the following table. This information should be understood as follows: Only a quarter of the participants indicated an uncertainty of measurement below the 25th percentile. Half of the participants indicated an uncertainty of measurement below or above the median. A quarter of the participants indicated an uncertainty of measurement greater than the 75th percentile.

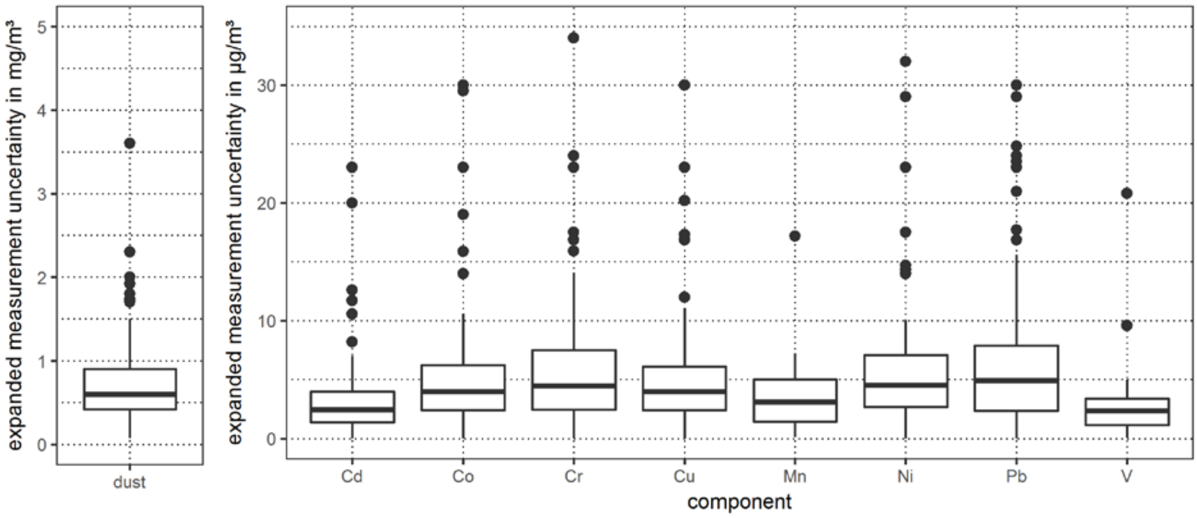


Table 10: Expanded measurement uncertainties reported by participants of the dust proficiency test

	dust [mg/m³]	Cd [µg/m³]	Co [µg/m³]	Cr [µg/m³]	Cu [µg/m³]	Mn [µg/m³]	Ni [µg/m³]	Pb [µg/m³]	V [µg/m³]
75th percentile	0.90	4.00	6.24	7.50	6.11	5.00	7.09	7.86	3.39
median	0.60	2.46	4.00	4.50	4.00	3.10	4.53	4.95	2.35
25th percentile	0.42	1.37	2.40	2.47	2.40	1.42	2.68	2.35	1.15
number of values	89	74	75	75	75	39	75	74	36

For all information on absolute expanded measurement uncertainties, it should be noted that for reasons of comparability, participants were asked to give only one value for each method. The information may therefore refer to the highest concentration measured in the proficiency test and would be lower for lower concentrations. Nevertheless, these values should enable all participants to make an approximate assessment of how their own uncertainty of measurement relates to the uncertainty of measurement of other laboratories.

For the gas emission proficiency test, the following uncertainties were reported.

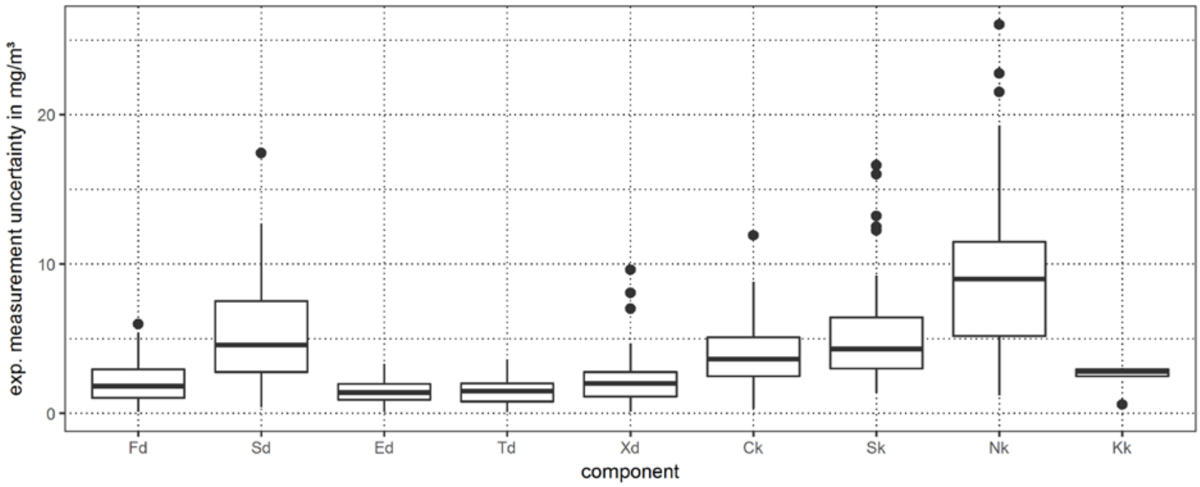


Table 11: Expanded measurement uncertainties reported by participants of the gas proficiency test

	formal-dehyde [mg/m³]	SO_2 (disc.) [mg/m³]	ethyl-benzene [mg/m³]	toluene [mg/m³]	sum of xylenes [mg/m³]	TOC [mg/m³]	SO_2 (cont.) [mg/m³]	NO_x as NO_2 [mg/m³]	CO [mg/m³]
75th percentile	2.95	7.51	1.98	2.00	2.75	5.10	6.42	11.48	2.95
median	1.83	4.58	1.40	1.48	2.00	3.65	4.31	9.00	2.80
25th percentile	1.04	2.75	0.91	0.80	1.13	2.50	3.00	5.20	2.48
number of values	76	81	77	77	77	77	72	81	7

6.3.2 Probes and Rinsing in Dust Sampling

In the correlation of probe systems and rinsing procedures, the participant field of the dust proficiency tests is essentially divided into 7 groups, depending on whether an in-stack probe with or without gooseneck is used, whether this probe is rinsed after each sampling or not, and whether the rinsed residues are taken into account in the measurement result or not. The representation here is limited to the combinations given by at least four participants.

The database in this report covers the results for the years 2016 to 2018 and is thus again larger than in the previous year. The evaluations for 4 of the 7 combinations of probe system and rinsing procedure are based on a relatively solid amount of data (13 to 35 results), the statements for the remaining 3 combinations are still uncertain in comparison (database: 4 to 10 results).

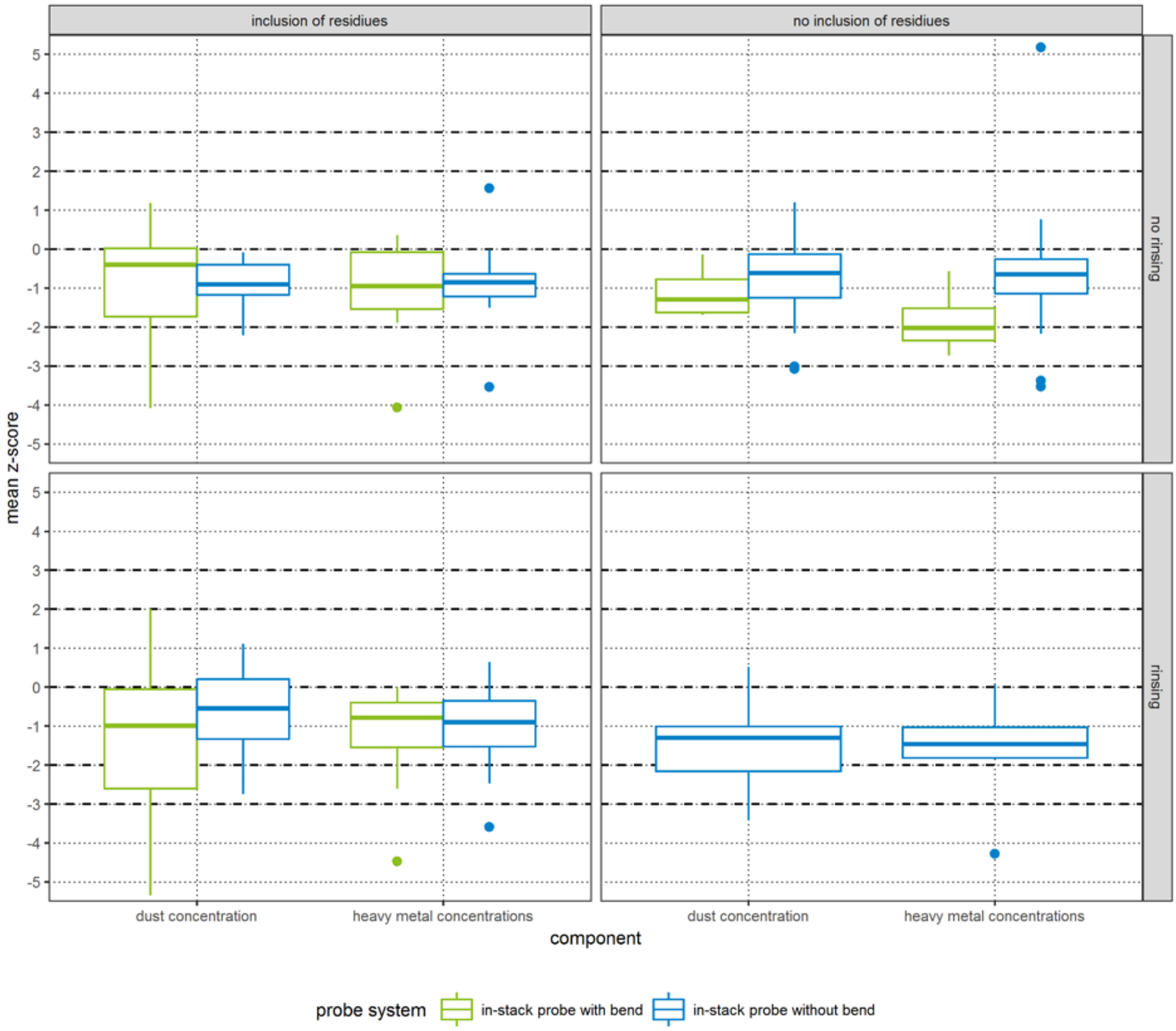


Table 12: Correlation of dust measurement results with probe systems and rinsing procedures

combi-nation	probe system and rinsing procedure	median of mean z-scores total dust results	number of participants	median of mean z-scores heavy metal results	number of participants
1	in-stack probe without bend, rinsing after each sampling, residiues included in results	–0.55	26	–0.90	24
2	in-stack probe without bend, rinsing after each sampling, residiues **not** included in results	–1.30	6	–1.46	6
3	in-stack probe without bend, **no** rinsing after each sampling, residiues included in results	–0.91	13	–0.85	14
4	in-stack probe without bend, **no** rinsing after each sampling, residiues **not** included in results	–0.61	35	–0.65	34
5	in-stack probe with goose neck, rinsing after each sampling, residiues included in results	–0.99	21	–0.78	17

combi-nation	probe system and rinsing procedure	median of mean z-scores total dust results	number of participants	median of mean z-scores heavy metal results	number of participants
6	in-stack probe with goose neck, **no** rinsing after each sampling, residiues included in results	–0.40	10	–0.95	10
7	in-stack probe with goose neck, **no** rinsing after each sampling, residiues **not** included in results	–1.30	4	–2.02	4

The information provided by the participants indicates that the best results of the dust proficiency test are obtained using one of the two combinations most frequently used by the participants. The combination of system and rinsing procedure used by most participants, the use of an in-stack probe without gooseneck and no rinsing (combination 4, in the scheme top right, blue) seems to lead to very good results overall (mean deviation of total dust: –4.3%) with comparatively low dispersion. This method shows the smallest mean deviation in the heavy metal measurements.

Comparable results with slightly higher scatter are apparently obtained using an in-stack probe without gooseneck, if the probe is rinsed after each sampling and the rinsing residues thus obtained are taken into account in the measurement result (combination 1, in the scheme bottom left, blue). This procedure also provides results for total dust that are relatively close to the target value (mean deviation total dust: –3.9%). The deviations for heavy metals are somewhat greater here.

Significantly worse results are achieved if a probe with gooseneck is used, this is rinsed after each sampling and the rinsing residues are taken into account in the measurement result (combination 5, in the scheme bottom left, green). Also, the measured values for the total dust concentrations show a very high dispersion here (mean deviation total dust: –6.9%).

Comparable results (mean deviation total dust: –6.4%) were achieved by participants with in-stack probes without gooseneck who stated that they did not rinse after each measurement, but nevertheless included rinsing residues in their results (combination 3, in the scheme top left, blue). This might mean, for example, that the rinsing was only carried out every working day and that the residues were distributed proportionately among the samples taken up to that point.

The four combinations already described were all given by 13 to 35 participants each. The following three combinations were only stated by 4 to 10 participants each, the statements on this are correspondingly less reliable.

It comes as no surprise that significantly lower results (mean deviation of total dust: –9.1%) are achieved if an in-stack probe without gooseneck is used and rinsed after each measurement, but the residues are not taken into account in the result (combination 2, in the scheme bottom right, blue).

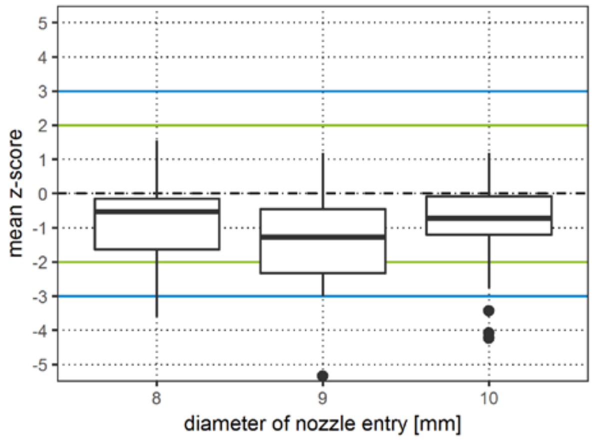
Equally poor results (mean deviation of total dust: –9.1%) were achieved by participants using an in-stack gooseneck probe without rinsing (combination 7, in the scheme top right, green). It should be noted that combinations 2 and 7 do not represent standard-compliant procedures according to EN 13284-1.

A mixed picture is obtained by users of a gooseneck probe and a (presumably) daily flushing with consideration of the residues (combination 6, in the scheme top left, green). The best average results for total dust (mean deviation total dust: –2.8%) are obviously achieved here. However, the values also scatter most strongly here, and the results for the heavy metals also tend to be below average.

In order to get a clearer picture of the influence of the rinsing routine on the measurement results, since summer 2018 the participants have been asked to choose instead of yes / no between the following options for their rinses: never / once at the end of the rinsing routine / every working day / after each measurement. The data available so far do not yet permit any statistical evaluation and have been assigned to the yes/no scheme for this annual report. A more detailed consideration of the actual rinsing procedures is planned for the annual report 2019.

6.3.3 Diameter of the Nozzle Opening in Dust Samplings

The information provided by the participants on the diameter of their probe‘s nozzle opening does not indicate a clear trend. Irrespective of the diameter, the measured values always seem to spread over a wide range.



Probe diameters mentioned by less than 6 participants are not listed here. In the following table, the values were evaluated based on the absolute values of the z scores.

Table 13: Correlation of absolute means of z-scores for total dust with nozzle opening diameters

diameter of nozzle opening	8 mm	9 mm	10 mm
75th percentile	1.63	2.32	1.20
median	0.61	1.26	0.86
25th percentile	0.26	1.21	0.35
number of values	25	7	82

A clear connection is also not recognisable here. Only the dispersion of the results seems to be somewhat lower for users of 10 mm nozzle openings than for other participants. Overall, however, the size of the nozzle opening does not seem to be decisive for the measurement results.

6.3.4 Analytical Instruments for Heavy Metals

The information provided by the participants on the analytical instrument used for heavy metal analysis reveals a certain difference between AAS and ICP users. A total of 18 participants stated that heavy metal analysis was performed using AAS equipment, while 95 participants stated that they used an ICP instrument. On average, all participants achieved comparable z scores for the heavy metals, regardless of the analytical instrument used. However, the measured values of the ICP users scatter significantly more than those of the AAS users. In addition, ICP users seem to be more prone to massive underreporting than users of AAS devices.

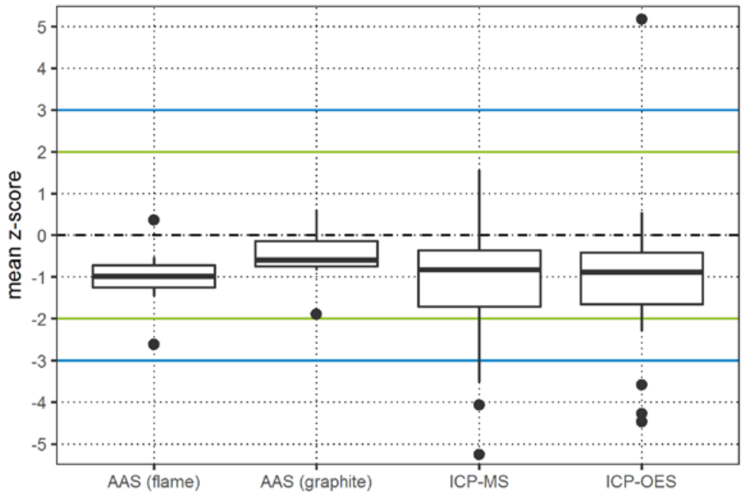


Table 14: Correlation of heavy metal results and analysis devices

analysis device	flame-AAS	graphite furnace AAS	ICP-MS	ICP-OES
75th percentile	–0.72	–0.14	–0.36	–0.42
median	–0.98	–0.59	–0.82	–0.89
25th percentile	–1.25	–0.75	–1.71	–1.66
number of values	7	11	56	39

Compared to the previous year, there has been a general reduction in the extend of underreportings for heavy metals. Only among flame AAS users did the deviations rise against the trend in 2018.

6.3.5 Formaldehyde

For the measurement of formaldehyde concentrations, participants can choose from the guidelines VDI 3862 Parts 2 (9), 3 (10) and 4 (11). The following picture emerges from the information provided by the participants:

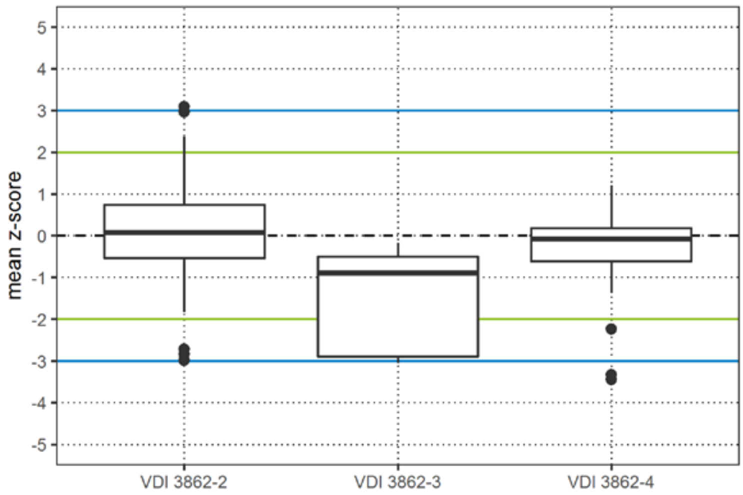


Table 15: Correlation of formaldehyde measurement results with the guidelines used

guideline	median of mean z-scores formaldehyde results	number of participants
VDI 3862 Part 2 (DNPH wash bottles)	0.07	66
VDI 3862 Part 3 (DNPH cartridges)	–0.89	5
VDI 3862 Part 4 (AHMT-procedure)	–0.08	36

The DNPH wash bottle procedure apparently delivers on average comparable good values as the AHMT procedure, but spreads over a larger area. The DNPH cartridge method was only reported by 5 participants, all had rather disappointing results.

6.3.6 Sulphur dioxide

For the discontinuous determination of sulphur dioxide concentrations, participants can choose between analysis of the samples using ion chromatography or the thorin method as part of the standard reference method. The following picture emerges from the information provided by the participants:

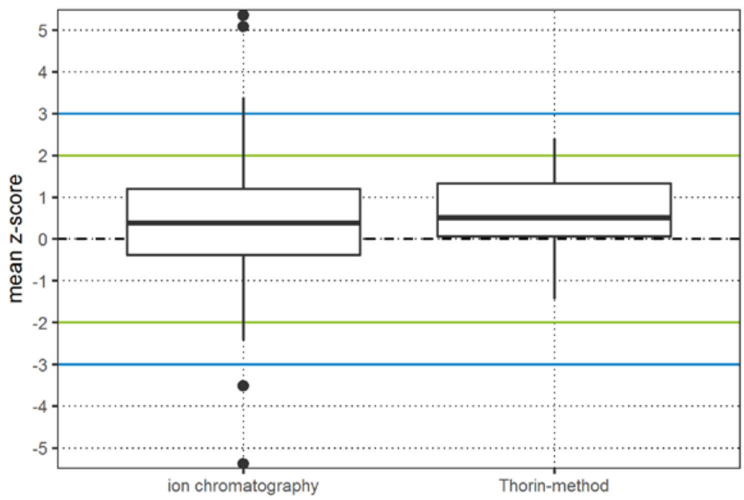


Table 16: Correlation of sulphur dioxide measurement results with the analytical method used

method used	median of mean z-scores discontinuous SO_2-results	number of participants
Ion chromatography	0.38	102
Thorin method	0.51	8

The available results do not suggest a significant difference between the two methods, but the number of participants using the Thorin method is comparatively small. The higher dispersion of the IC method with various "outliers" may be due solely to the almost 12 times higher number of participants.

6.3.7 Solvents for Desorption of ETX

For the desorption of the solvents ethylbenzene, toluene and xylene (ETX) the participants can choose between other solvents or solvent mixtures besides the usual solvent carbon disulphide (CS_2). The majority of the participants reported that they had worked with CS_2. The average results of all participants were close to the target value. The measurement results of participants using CS_2 tended to scatter slightly more than those obtained with other desorbents.

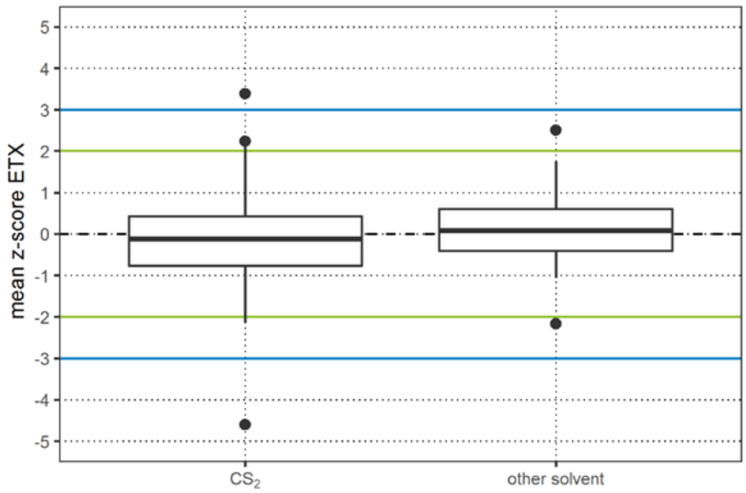


Table 17: Correlation of ETX measurement results with the desorption solvent

solvent used in desorption	median of mean z-scores ETX results	number of participants
CS_2	–0.12	90
other solvent	0.07	13

6.3.8 Gas Chromatography Detectors

Gas chromatographs with either an FID detector or a mass spectrometer are usually used for the analysis of ETX samples. The information provided by the participants results in the following picture:

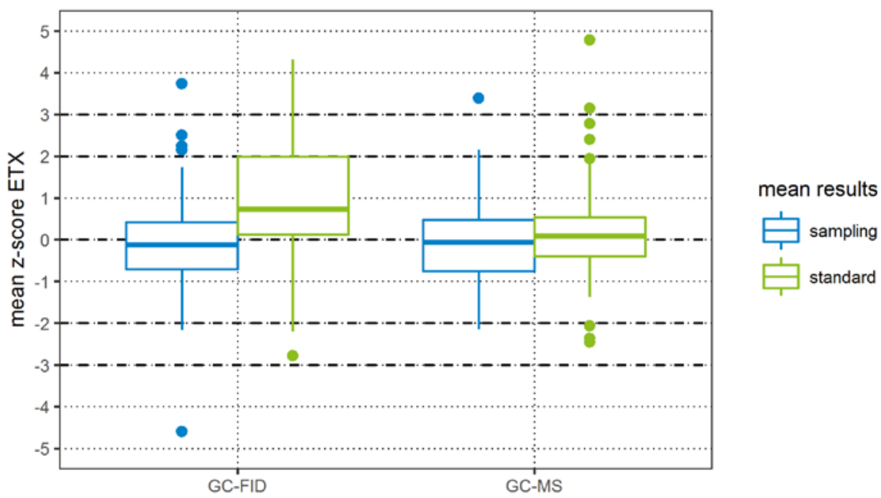
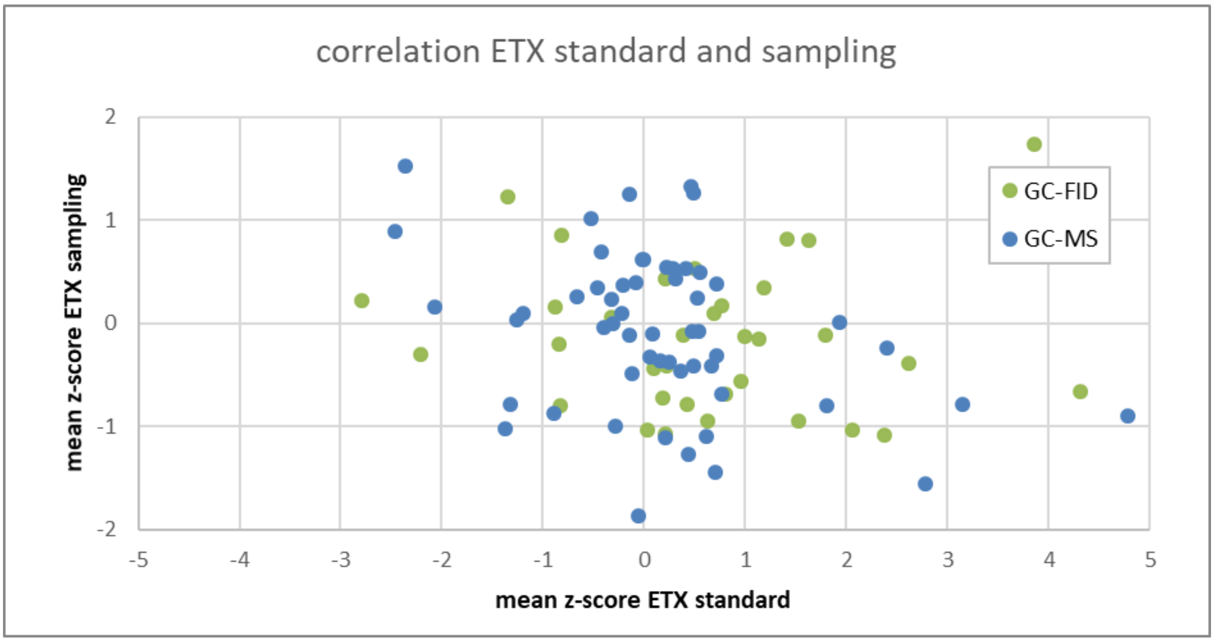


Table 18: Correlation of ETX measurement results with analytical instruments

analytical instrument	median of mean z-scores ETX including sampling	median of mean z-scores ETX standard solution	number of participants
GC-FID	–0.12	0.73	42
GC-MS	–0.06	–0.09	61

Here the results are surprisingly inconsistent. For the overall procedure of sampling and analysis, the participants achieved comparable results with both detector variants very close to the target value with comparable scattering. In the analysis of the ETX standard, the GC MS users achieve on average results equivalent to those obtained from sampling. The GC FID users, however, obviously tend to have measurement results far above the target values in some cases. It is also astonishing that there seems to be no correlation between the results of the measurements with sampling and those of the pure analytical standard, as the following scheme shows.



A high error in the results with sampling and a small error in the standard (points along the y-axis) can be explained by a combination of sampling errors and flawless analysis. The results with small errors in sampling but high errors in the standard (points along the x-axis) can only be explained by an error-free execution of the overall procedure (sampling + analysis) with simultaneous errors in the pure analysis of the standard. Here, for example, an incorrect calculation of desorption rates would be conceivable. Overall, however, all conceivable combinations of positive and negative findings can be observed in the data, relatively independent of the detector used.

7. Concluding Remark

Since the year 2015, the frequency of participation of the §29b measurement bodies has noticeably increased compared to previous years due to the systematic and regular participation of all sites that are authorised in accordance with §29b BImSchG. The results recorded since then clearly show a positive effect on the quality of the measurement results. In particular, the measurement results for total dust mass concentrations and heavy metal mass concentrations show a steady improvement in the measurement results. On the other hand, last year's proficiency test results for the measurement of various gaseous components show that there is a clear need for improvement for a number of §29b measurement bodies. The significantly higher number of unsuccessful participations in the gas proficiency test in 2018 can ultimately be traced back to sites that already had quality deficits in the measurement of gaseous air pollutants in the past. At a participation rate of once in 5 to 10 years for the respective sites, which was usual only a few years ago for measuring bodies with many branch sites, the deficits existing there would probably have remained undiscovered for a long time. This shows that the regular participation of all sites in stack emission proficiency tests is continuing to be important in order to detect faulty tendencies at an early stage and to maintain the quality of the measurement results in the legally regulated area at a consistently high level.

Kassel, 23rd April 2019

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8. References

1. DIN EN ISO/IEC 17043:2010-05 - Konformitätsbewertung - Allgemeine Anforderungen an Eignungsprüfungen (ISO/IEC 17043:2010); Deutsche und Englische Fassung EN ISO/IEC 17043:2010. *(Conformity assessment - General requirements for proficiency testing (ISO/IEC 17043:2010)*; German and English version EN ISO/IEC 17043:2010). Berlin : Beuth-Verlag.

2. Einundvierzigste Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Bekanntgabeverordnung – 41. BImSchV) vom 2. Mai 2013 (BGBl I, 2013, Nr. 21, S. 1001–1010). *(Forty-first Ordinance on the implementation of the Federal Immission Control Act (Ordinance on authorisation – 41st BImSchV) of 2 May 2013 (BGBl I, 2013, p. 973))*

3. Gesetz zum Schutz vor schädlichen Umwelteinwirkungen durch Luftverunreinigungen, Geräusche, Erschütterungen und ähnliche Vorgänge (Bundes-Immissionsschutzgesetz – BImSchG) in der Fassung der Bekanntmachung vom 17. Mai 2013 (BGBl I, 2013, Nr. 25, S. 1274–1). *(Act on the Prevention of Harmful Effects on the Environment Caused by Air Pollution, Noise Vibration and Similar Phenomena (Federal Immission Control Act – BImSchG) in the version promulgated on 17 May 2013 (BGBl I, 2002, p. 1274))*

4. DIN EN ISO 17034:2017-04 - Allgemeine Anforderungen an die Kompetenz von Referenzmaterialherstellern (ISO 17034:2016); Deutsche und Englische Fassung EN ISO 17034:2016. *(General requirements for the competence of reference material producers (ISO 17034:2016)*; German and English version EN ISO 17034:2016). Berlin : Beuth-Verlag.

5. DIN ISO 13528:2009-01 - Statistische Verfahren für Eignungsprüfungen durch Ringversuche (ISO 13528:2005); Text Deutsch und Englisch. *(Statistical methods for use in proficiency testing by interlaboratory comparisons (ISO 13528:2005); Text in German and English)*. Berlin : Beuth-Verlag.

6. DIN EN 15259:2008-01: Luftbeschaffenheit - Messung von Emissionen aus stationären Quellen - Anforderungen an Messstrecken und Messplätze und an die Messaufgabe, den Messplan und den Messbericht; Deutsche Fassung EN 15259:2007. *(Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report)*. Berlin : Beuth-Verlag.

7. DIN EN 13284-1:2002-04: Emissionen aus stationären Quellen - Ermittlung der Staubmassenkonzentration bei geringen Staubkonzentrationen - Teil 1: Manuelles gravimetrisches Verfahren; Deutsche Fassung EN 13284-1:2001. *(Stationary source emissions. Determination of low range mass concentration of dust. Manual gravimetric method)*. Berlin : Beuth-Verlag.

8. VDI 2066 Blatt 1:2006-11 - Messen von Partikeln - Staubmessungen in strömenden Gasen - Gravimetrische Bestimmung der Staubbeladung. *(Particulate matter measurement - Dust measurement in flowing gases - Gravimetric determination of dust load)*. Berlin : Beuth-Verlag.

9. VDI 3862 Blatt 2:2000-12 - Messen gasförmiger Emissionen - Messen aliphatischer und aromatischer Aldehyde und Ketone nach dem DNPH-Verfahren - Gaswaschflaschen-Methode. *(Gaseous emission measurement - Measurement of aliphatic and aromatic aldeydes and ketones by DNPH method - Impinger method)*. Berlin : Beuth-Verlag.

10. VDI 3862 Blatt 3:2000-12 - Messen gasförmiger Emissionen - Messen aliphatischer und aromatischer Aldehyde und Ketone nach dem DNPH-Verfahren - Kartuschen-Methode. *(Gaseous emission measurement - Measurement of aliphatic and aromatic aldehydes and ketones by DNPH method - Cartridges method)*. Berlin : Beuth-Verlag.

11. VDI 3862 Blatt 4:2001-05 - Messen gasförmiger Emissionen - Messen von Formaldehyd nach dem AHMT-Verfahren. *(Gaseous emission measurement - Mesurement of formaldehyde by the AHMT method)*. Berlin : Beuth-Verlag.

12. DIN EN 14791:2017-05 - Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von Schwefeloxiden - Standardreferenzverfahren; Deutsche Fassung EN 14791:2017. *(Stationary source*

emissions. Determination of mass concentration of sulphur oxides. Standard reference method). Berlin : Beuth-Verlag.

13. DIN EN 12619:2013-04: Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration des gesamten gasförmigen organisch gebundenen Kohlenstoffs – Kontinuierliches Verfahren mit dem Flammenionisationsdetektor; Deutsche Fassung EN 12619:2013. *(Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method)*. Berlin : Beuth-Verlag.
14. DIN CEN/TS 13649:2015-03 - DIN SPEC 33969:2015-03 - Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von gasförmigen organischen Einzelverbindungen - Sorptive Probenahme und Lösemittelextraktion oder thermische Desorption; Deutsche . *(Stationary source emissions. Determination of the mass concentration of individual gaseous organic compounds. Sorptive sampling method followed by solvent extraction or thermal desorption)*. Berlin : Beuth-Verlag.
15. DIN EN 14792:2017-05 - Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von Stickstoffoxiden - Standardreferenzverfahren: Chemilumineszenz; Deutsche Fassung EN 14792:2017 . *(Stationary source emissions. Determination of mass concentration of nitrogen oxides. Standard reference method. Chemiluminescence)*. Berlin : Beuth-Verlag.
16. DIN EN 15058:2017-05 - Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von Kohlenmonoxid - Standardreferenzverfahren: Nicht-dispersive Infrarotspektrometrie; Deutsche Fassung EN 15058:2017. *(Stationary source emissions. Determination of the mass concentration of carbon monoxide. Standard reference method: non-dispersive infrared spectrometry)*. Berlin : Beuth-Verlag.
17. DIN EN 13725:2003-07 Luftbeschaffenheit - Bestimmung der Geruchsstoffkonzentration mit dynamischer Olfaktometrie; Deutsche Fassung EN 13725:2003. *(Air quality - Determination of odour concentration by dynamic olfactometry; German version EN 13725:2003)*. Berlin : Beuth-Verlag.
18. VDI 4220 Blatt 1:2018-11 - Qualitätssicherung - Anforderungen an Stellen für die Ermittlung luftverunreinigender Stoffe an stationären Quellen und in der Außenluft - Allgemeine Anforderungen. *(Quality assurance - Requirements on bodies for the determination of air pollutants at stationary sources and in ambient air - General requirements)*. Berlin : Beuth-Verlag.

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