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Investigations for the improvement of the measurement of volatile organic compounds from floor coverings within the health-related evaluation of construction products

by

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Table of contents

List of figures

List of tables

Abbreviations and explanations

Anzahl Labore	number of participants
BAM	BAM Federal Institute for Materials Research and Testing
BHT	2,6-di-tert-butyl-4-methylphenol
CAS-Nr.	Chemical Abstracts Service Number
CEN	European Committee for Standardisation
DIBt	German Institute for Construction Technology
DIN	German Institute for Standardisation
GC	Gaschromatograph
GUM	Guide to the Expression of Uncertainty in Measurement
h	hour
ILS	interlaboratory study/interlaboratory comparison
ISO	International Organisation for Standardisation
Korrelationskoeffizient	coefficient of correlation
Lsg	solution
m	metre
MBO	Model Building Regulation
MIBK	methyl isobutyl ketone
min	minute
ml	millilitre
MS	mass spectrometer
MW	mean
ng	nanogram
normiertSollwert	standardised related to the target value
n.p.	not participated
RF	target value
SVOC	semivolatile organic compounds
Stabw.	standard deviation
TENAX	2,6-diphenyl-p-phenylene oxide polymer
TDS	thermodesorption system
TVOC	total volatile organic compounds
VOC	volatile organic compounds
µg	microgram
µl	microlitre

1. Introduction

In the German Institute for Construction Technology's (DIBt) principles on the health-related evaluation of building products in indoor spaces, the evaluation procedure of the Committee for Health-related Evaluation of Building Products (AgBB Scheme) is contained as a substantial base[1]. This scheme evaluates the emissions of volatile and semivolatile organic compounds (VOC and SVOC), determined by test chamber measurements. The test chamber ensures standardised climate conditions (temperature 23°C, relative air humidity 50 %) are maintained as well as providing the ability to adjust certain test parameters such as air exchange rate and product loading factor. The specifications for a test chamber are described in DIN EN ISO 16000-9. The analysis and quantification of VOCs are carried out by Tenax-thermodesorption and subsequent gas chromatography coupled with mass spectrometry and is described in DIN ISO 16000-6.

Sampling is performed on days 3 and 28 of the test chamber measurement. On the third day an assessment of the emissions from the building product takes place based on the TVOC value and the sum of the detected carcinogenic materials (according to 67/548/EWG, classification as carcinogenic of category 1 and 2). A product fulfils the criteria if the TVOC value after 3 days is not greater than 10 mg/m³ and the sum the carcinogens does not exceed 10 µg/m³. On the 28th day, in addition to the TVOC value and the carcinogens, the emission of SVOCs is considered and an individual material evaluation based on the LCI (NIK) values is made. The TVOC value after 28 days must not be greater than 1 mg/m³, the sum of the carcinogens not greater than 1 µg/m³. The sum of SVOCs may not exceed a concentration of 0.1 mg/m³. The so-called R value, the sum of all quotients of individual material concentration to the LCI (NIK) value of the individual material, must not exceed a value of 1. In addition, the sum of substances that do not possess LCI (NIK) value, must not be greater than 0.1 mg/m³.

The interlaboratory comparison, which was performed within the search for the improvement of test chamber measurements had, above all else, the purpose of determining the influence of various method parameters used for test chamber measurement across different test laboratories. Based on the results, investigation into the cause for the large deviations of the interlaboratory comparisons performed so far should take place. The three consecutive steps are supposed to clarify the influence of the analysis, the sampling and the test chamber.
The interlaboratory comparison was not designed to recognise the participating test laboratories in the field of the building product testing for a DIBt approval.

Starting from the test laboratories that cooperated in the project group "Test and Measurement Methods for the Health-related Evaluation of Building Products" of the DIBt, the circle was extended to cover European test laboratories which also deal with test chamber measurements on building products. For this purpose an invitation letter was issued to all known participants from preceding interlaboratory comparisons. Eventually a participant circle of 29 institutes was established with 16 partners from Germany, two each from Austria, Belgium, Sweden, Denmark and one each from Finland, Great Britain, France, Italy and Portugal. Before beginning the interlaboratory test, 11 of them were active in the field of approvals.

[1] http://www.dibt.de/en/323.html

To manage the process, a scientific committee was set up by the DIBt. The current results were presented and discussed in two meetings (April and November 2007) and the further proceeding discussed. A final meeting took place in April 2008 after the evaluation of the third step of the interlaboratory test in the DIBt to which all participants were invited.

For the measurement of emissions of volatile organic compounds (VOC) from materials in emission test chambers, only few interlaboratory comparisons have been performed so far (De Bortoli et al. 1999; Jann et al. 2000; Hansen et al. 2000; Oppl and Winkels 2002; Windhövel and Oppl 2005; Kirchner 2007; Oppl 2008). It was usual to find a large scattering of the results.

A major problem for the execution of such interlaboratory comparisons is the lack of reference materials with known emission rates of target substances. Therefore one takes the mean of all results as a guideline for the evaluation of such interlaboratory comparisons. However, the homogeneity of the test material is of the greatest importance and had not been properly guaranteed in earlier interlaboratory comparisons.

In the research project described here, special emphasis was placed on the homogeneity of the sample material.

The entire interlaboratory comparison was divided into three steps. The individual steps became increasingly more complex from step to step. In the first step the analysis of liquid solutions took place, in the second, VOCs were determined in test chamber air and in the third step a complete emission test chamber measurement was carried out by the participants.

1.1. Objectives

In order to grant general building authority approvals it is necessary to possess reliable measurement methods.

The research project is aimed at improving the existing measurement method for the health-related evaluation of building products concerning deviation in the procedural standards. In view of the future European harmonisation of test methods within the Building Product Directive, test institutes of other European countries should also be included.

The investigations to be performed can serve simultaneously as a base for validation of the harmonised test method, which is being compiled by CEN and required by the European mandate M/366. Findings from the research project are therefore also of importance for the relevant committees at CEN.

Another objective is the production of a catalogue of criteria to demonstrate the specialist competence of test laboratories for approving emission tests of floor coverings. DIBt can require an expert body in each individual case of approval according to § 18 the MBO.

Another goal for the interlaboratory comparison was to determine the state of the art in test chamber measurements. For this purpose questionnaires were sent to the participants for each of the individual steps, in order to obtain the most precise specification of the test chamber parameters and analysis methods as possible. Based on the questionnaires the cause of possible wide deviations of the results should also be established.

2. Interlaboratory comparison, Step 1

The interlaboratory comparison described here was performed according to DIN ISO 5725-2 (2002) using the interlaboratory test evaluation program "ProLab"[2]. Three different outlier types can be routinely determined (Funk et al., 2005):

- within-laboratory outliers (type A) *„based on the Grubbs test"*
- outliers in the mean values (type B) *„based on the Grubbs test"*
- outliers in laboratory precision (type C) *„based on the Cochran test"*

The elimination of outliers is legitimate because one of the key goals of this study was to assist the improvement of the analysis of emission chamber investigations using Tenax sampling and the subsequent thermodesorption of these sampling tubes, in view of the fact that the medium performance standard of the laboratories should be illustrated (see also Kemmlein 2005 for the calculation according to Grubbs or Cochran).

In this part of the interlaboratory comparison the actual analytical procedure (GC-MS using thermodesorption) was tested. For this purpose, various solutions were dispatched to the participants where a small amount was to be injected into the Tenax tubes. According to DIN ISO 5725-2, in which interlaboratory comparisons are described for procedure standardisation, four solutions of different concentrations were dispatched: A1, A2, B1, B2. Solution B1 contained the lowest (approx. 15 ng/µl) and B2 the highest concentration (approx. 90 ng/µl). The two A-solutions had very similar concentrations (A1 approx. 55 ng/µl; A2 approx. 60 ng/µl), which were selected with the intention of evaluating the results using Youden plots. For the practical use of Youden plots the solutions were supposed to have a broadly comparable concentration. Evaluation of these analytical results enables a statement on the precision and bias errors to be made at low cost. This method enables the determination of the trueness (when a reference value and standardised values are available) and precision of individual laboratories and to establish the procedural quality of the measurement method. In the following the key parameters accuracy, trueness and precision will be defined briefly (Eurolab 2006).

Accuracy: The closeness of agreement between a test result and the accepted reference value of the measurand.

Trueness: The closeness of agreement between the mean value obtained from a large number of independent tests and an accepted reference value of the measurand.

Precision: The closeness of agreement between independent test results obtained under stipulated conditions.

[2] HTTP:// www.quodata.de

2.1. Selection of substances, Step 1

Within the approval principles of DIBt, initially floor coverings were tested for emission of volatile organic components. The range of floor coverings tested included textile and flexible floor coverings, coatings, parquets and laminate floor mats. Since rubber floor coverings let expect good homogeneity and a characteristic emission profile, this type floor covering was first selected for the comparative tests. This practical consideration determined the choice of solutions to be used in Step 1. The following typical substances were used: styrene, benzothiazole, BHT and longifolene.

Further, because of the high standard deviations found in an earlier interlaboratory comparison (Kirchner 2007), the substances 1,3-dichloro-2-propanol, 1,2,3-trimethylbenzene and caprolactam were also tested. In order to extend the emission spectrum by some of the more typical VOCs, dodecane, 2-ethyl-1-hexanol, diethylene glycol monobutyl ether (butyl diglycol) and methyl isobutyl ketone were added.

Table 1: Weighed-in concentrations of four different solutions in µg/ml

Compound	**CAS No.:**	**Sol. A1**	**Sol. A2**	**Sol. B1**	**Sol. B2**
Methyl isobutyl ketone (MIBK)	108-10-1	53,7	58,6	14,7	88,4
Styrene	100-42-5	52,1	56,9	15,4	92,1
1,3-Dichloro-2-propanol	96-23-1	64,2	70,1	15,3	91,7
1,2,3-Trimethylbenzene	526-73-8	54,8	59,8	14,5	86,7
2-Ethyl-1-hexanol	104-76-7	53,9	58,8	14,7	88,2
Butyl diglycol	112-34-5	54,6	59,5	15,1	90,7
Dodecane	112-40-3	57,0	62,2	15,2	91,3
Benzothiazole	95-16-9	55,2	60,2	14,1	84,9
Caprolactam	105-60-2	54,3	59,3	14,7	88,0
Longifolene	475-20-7	54,6	59,5	15,2	91,0
BHT	128-37-0	55,4	60,5	15,2	94,1

2.2. Test implementation

For Step 1, 1 to 10 µl of the solutions were injected using a µl-syringe into the Tenax tubes. The usual quantity was 1 µl of solution but if this was not sufficient for a quantification, some of the participants injected up to 10 µl into the Tenax tubes. The solvent methanol was then dispersed by an inert gas flow (e.g. nitrogen or helium with a flow rate of 100 ml/min) over 10 minutes. Afterwards the injected substances were then thermodesorbed.

2.3. Quality assurance, Step 1

Homogeneity tests of the solutions for Step 1:

From each filling of the four different solutions (A1, A2, B1, B2) 4 solutions were selected by BAM from the 33 bottles. The selection pattern is displayed in Figure 1. Starting from top left, every eighth bottle was selected and tested three times. Table 2 illustrates the results obtained. For most compounds the relative standard deviation was under or around 2 %, which proves that there are hardly any differences in the solutions. Those components which exhibited higher deviations (up to a max. of 7.4 %), such as dichloropropanol, required a very thorough analysis. The elevated standard deviations were attributed to analytical fluctuations.

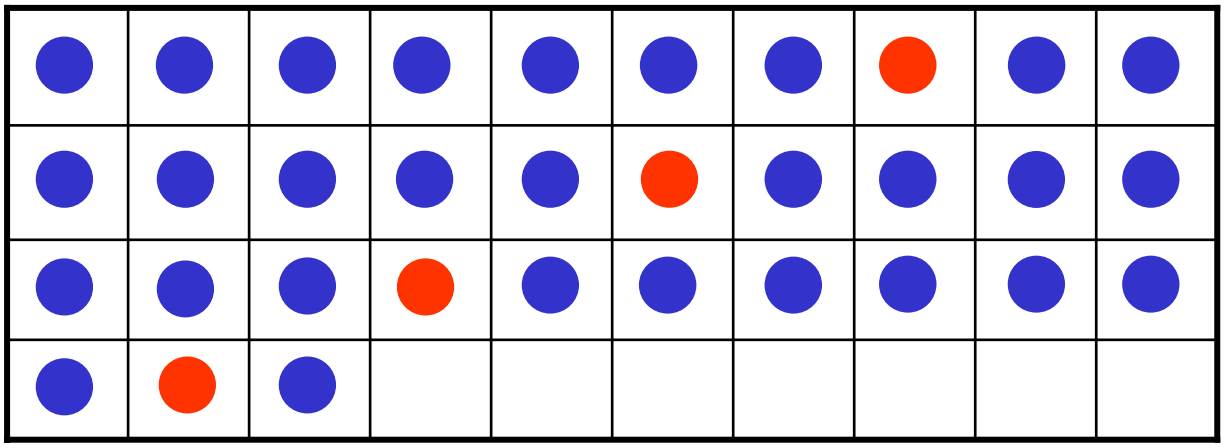

Figure 1: Selection of four solutions (red dots) from each of the four total fillings of the samples for dispatch, evenly distributed over all bottles.

Table 2: Homogeneity of solutions (BAM tests)

Solution	**A1**		**A2**		**B1**		**B2**	
	MW	StAb%	MW	StAb%	MW	StAb%	MW	StAb%
Methyl isobutyl ketone	54,3	**2,3**	60,4	**1,9**	16,0	**2,0**	85,0	**1,5**
Styrene	49,6	**2,0**	56,4	**1,7**	16,1	**1,8**	87,1	**1,4**
1,3 Dichloro-2-propanol	72,2	**5,8**	83,6	**3,4**	19,7	**7,4**	96,7	**3,5**
1,2,3 Trimetylbenzene	52,5	**2,2**	59,8	**3,1**	15,5	**1,7**	82,1	**1,3**
2-Ethyl-1-hexanol	56,2	**2,4**	61,8	**4,2**	18,9	**2,4**	84,7	**1,8**
Butyl diglycol	58,4	**1,8**	64,5	**1,6**	13,4	**5,4**	88,0	**1,2**
Dodecane	57,6	**2,2**	64,5	**3,5**	15,9	**2,1**	86,3	**2,1**
Benzothiazole	54,3	**3,7**	62,3	**3,3**	16,1	**2,6**	79,1	**1,3**
Caprolactam	55,2	**1,5**	62,1	**1,0**	15,5	**5,2**	80,7	**2,1**
Longifolene	50,3	**3,7**	58,0	**4,1**	17,1	**1,2**	83,7	**1,2**
BHT	52,4	**1,9**	59,8	**1,7**	16,5	**1,6**	87,5	**1,1**

2.4. Results, Step 1

2.4.1. Results for solutions

The following tables (3 to 10) illustrate reference value (index value), mean value, standard deviation of the mean values, median and number of participants, or the number of those participants considered for the evaluation of the individual substances of the solutions A1, A2, B1 and B2 after being injected into the thermal desorption tubes and subsequent analysis. Here all results received from the participants were considered; thus the values in the first table for each solution are not outlier-cleaned. The second tables of each solution are outlier-cleaned (Grubbs and Cochran).

Table 3: Results for solution A1 (thermodesorption).

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	54	45	6	**14**	46	29
Styrene	52	49	6	**12**	51	29
1,3-Dichloro-2-propanol	64	62	13	**20**	62	28
1,2,3-Trimetylbenzene	55	51	6	**12**	51	29
2-Ethyl-1-hexanol	54	54	8	**14**	53	28
Butyl diglycol	55	52	19	**36**	50	28
Dodecane	56	56	8	**14**	57	29
Benzothiazole	55	51	8	**16**	52	29
Caprolactam	54	55	20	**36**	52	27
Longifolene	55	50	8	**15**	52	29
BHT	55	54	9	**16**	54	29

Table 4: Results for solution A1 (after outlier cleaning).

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	54	45	5	**11**	46	27
Styrene	52	50	6	**11**	51	27
1,3-Dichloro-2-propanol	64	60	13	**22**	61	25
1,2,3-Trimetylbenzene	55	51	7	**13**	51	28
2-Ethyl-1-hexanol	54	53	8	**14**	53	26
Butyl diglycol	55	49	11	**23**	50	27
Dodecane	56	56	8	**15**	56	26
Benzothiazole	55	53	5	**10**	53	26
Caprolactam	54	52	10	**18**	52	26
Longifolene	55	52	6	**11**	52	26
BHT	55	55	9	**17**	54	26

For the non-outlier-cleaned results of solutions A1, A2 and B2 the standard deviations are under 20 % for all substances with the exception of dichloropropanol (20-24%), caprolactam (32-36 %) and butyl diglycol (33-36 %). Solution B1 exhibits somewhat higher standard deviations, which can be explained with the low concentrations of the substances. For the outlier-cleaned data both the Grubbs and the Cochran outliers have been removed. This can lead in certain cases to the fact that the standard deviations of the outlier-cleaned data do not improve compared to the non-cleaned data records. If the outlier-cleaned data are considered (4, 6, 8 and 10), standard deviations of less than 26 % are obtained for the three components mentioned. The median is also indicated for all tests. The closer this is to the mean value, the more can it be assumed that the available data exhibit a single-peak symmetry, i.e. normal distribution. In the last column of the tables the number of available measured values is indicated. A comparison of the numbers in the two tables then easily provides the number of outliers for any solution.

Table 5: Results for solution A2.

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	59	50	8	**15**	51	29
Styrene	57	56	6	**10**	57	29
1,3-Dichloro-2-propanol	70	68	15	**22**	68	28
1,2,3-Trimetylbenzene	60	57	7	**12**	57	29
2-Ethyl-1-hexanol	62	61	7	**12**	61	28
Butyl diglycol	60	58	19	**33**	55	28
Dodecane	59	64	9	**14**	65	29
Benzothiazole	60	59	10	**17**	58	29
Caprolactam	59	61	20	**32**	59	27
Longifolene	60	58	9	**15**	59	29
BHT	60	60	9	**14**	60	29

Table 6: Results for solution A2 (after outlier cleaning).

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	59	51	7	**13**	51	28
Styrene	57	56	6	**11**	57	28
1,3-Dichloro-2-propanol	70	68	15	**23**	68	26
1,2,3-Trimetylbenzene	60	56	7	**13**	56	27
2-Ethyl-1-hexanol	62	61	8	**13**	61	27
Butyl diglycol	60	56	12	**21**	55	26
Dodecane	59	63	9	**14**	64	27
Benzothiazole	60	58	7	**12**	57	26
Caprolactam	59	59	7	**11**	58	25
Longifolene	60	58	7	**11**	59	26
BHT	60	60	10	**16**	60	29

Table 7: Results for solution B1.

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	15	13	3	**21**	12	29
Styrene	14	14	2	**12**	14	29
1,3-Dichloro-2-propanol	16	14	3	**24**	13	25
1,2,3-Trimetylbenzene	15	14	2	**11**	14	29
2-Ethyl-1-hexanol	15	14	3	**24**	14	27
Butyl diglycol	14	15	6	**40**	15	26
Dodecane	15	15	3	**20**	15	29
Benzothiazole	15	14	4	**26**	14	29
Caprolactam	15	15	7	**46**	15	23
Longifolene	15	13	3	**19**	14	29
BHT	15	14	3	**18**	14	29

Table 8: Results for solution B1 (after outlier cleaning).

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	15	12	2	**16**	12	28
Styrene	14	14	2	**12**	14	27
1,3-Dichloro-2-propanol	16	14	2	**25**	13	24
1,2,3-Trimetylbenzene	15	14	4	**11**	14	27
2-Ethyl-1-hexanol	15	15	2	**14**	14	26
Butyl diglycol	14	15	5	**33**	15	24
Dodecane	15	15	2	**14**	15	24
Benzothiazole	15	14	4	**27**	14	29
Caprolactam	15	14	5	**34**	15	21
Longifolene	15	13	3	**20**	14	29
BHT	15	14	3	**20**	14	29

The concentrations in solution B1 with approx. 15 ng/µl per compound are relatively close to the range that may represent the determination limit for some components. Therefore, the resulting standard deviations are also slightly increased compared with the values of more highly concentrated solutions. Therefore it shows that not all laboratories were able to determine butyl diglycol at this concentration. Some participants injected several µl of this solution into the tubes in order to improve detectability.

Table 9: Results for solution B2.

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	88	74	9	**13**	74	29
Styrene	92	86	9	**11**	87	29
1,3-Dichloro-2-propanol	92	84	18	**22**	87	27
1,2,3-Trimetylbenzene	87	85	10	**12**	85	29
2-Ethyl-1-hexanol	88	85	9	**11**	84	28
Butyl diglycol	90	87	28	**33**	81	28
Dodecane	91	87	19	**22**	87	29
Benzothiazole	85	79	14	**17**	81	29
Caprolactam	88	85	31	**36**	84	27
Longifolene	91	82	12	**15**	86	29
BHT	94	88	13	**15**	90	29

Table 10: Results for solution B2 (after outlier cleaning).

Compound	target value	Mean	SD	SD	Median	Number
	ng/µl	ng/µl	ng/µl	%	ng/µl	n
Methyl isobutyl ketone	88	75	8	**10**	74	26
Styrene	92	85	7	**8**	87	26
1,3-Dichloro-2-propanol	92	83	20	**24**	85	21
1,2,3-Trimetylbenzene	87	84	10	**12**	85	28
2-Ethyl-1-hexanol	88	83	8	**9**	83	24
Butyl diglycol	90	83	15	**19**	81	26
Dodecane	91	85	16	**19**	87	24
Benzothiazole	85	79	15	**19**	81	22
Caprolactam	88	83	11	**13**	84	24
Longifolene	91	83	9	**11**	86	26
BHT	94	88	15	**17**	90	29

Generally, it has been found that target and mean values fit relatively well to each other, the deviation is for most components around 5 %. Only for the MIBK component of all four solutions were the results 15 % lower. The quality of the standard compounds was controlled later in the programme using standard solutions made from pure substances from other manufacturers. These tests produced deviations within the range of the respective standard deviations of the components, as are usually found in multi-laboratory measurement deviations of standard solutions. Thus no significant difference has been found. Therefore it can be assumed that the solutions have been manufactured to a high accuracy.

2.4.2. Evaluation according to Youden

In this section the standardised results (the measured values from an institute in relation to the reference value) of the two solutions A1 and A2 in form of a Youden plot are illustrated (Funk et al., 2005). The results for solution A1 vs. those for solution A2 are plotted in a coordinate system and a bivariate confidence interval with

the borders of 3 sigma are calculated. In these diagrams, the form is not always circular because the standard deviations for solutions A1 and A2 of some components are different. Laboratories, whose results lie far from the bisector and outside the circle (ellipse), exhibit biased errors. The perpendicular distance from the bisector corresponds to non-precision, i.e. the laboratory finds different results for almost the same values. The distance along the bisector from point (1,1) corresponds to the bias. Results outside the circle mean considerably worse values than the average of the participants. The more the results approach the bisector, the more precisely the laboratory is working. If the values are close to point (1,1), this indicates that the determination of the tested components is precise and true. If the distribution is coincidental and the value pairs differ more obviously from the bisector, then this indicates a component which is difficult to determine analytically.

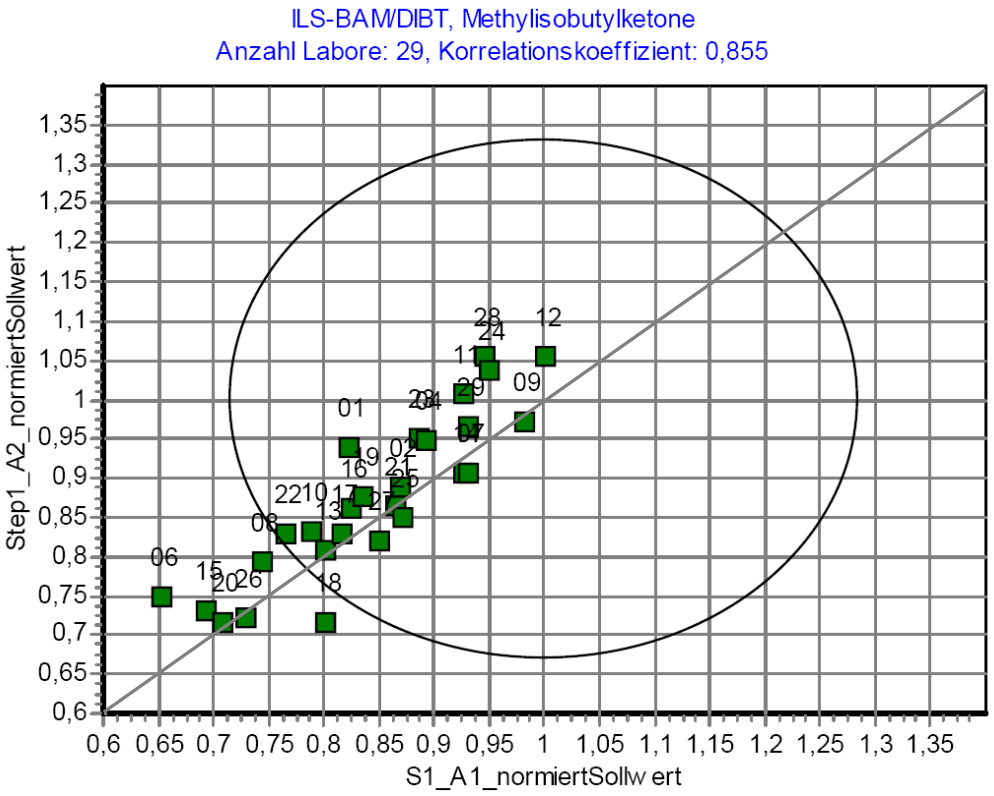

Figure 2: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, methyl isobutyl ketone

2 to 12 illustrate the results for each individual component. This representation is based on standardised values, which result from the quotient of the current measured value to the existing target value for the component, thus the point of intersection of the two axes is at (1,1) (the bisector is drawn in grey). Furthermore the limiting values of the 3-sigma circle are based on the outlier-cleaned values for the respective components. For the component MIBK (Figure 2) quite a good distribution can be recognised along the bisector, however the value 1/1 (meeting the respective reference value) is heavily shifted to the right. This may be due to the volatility of the component and consequent losses resulting from this.

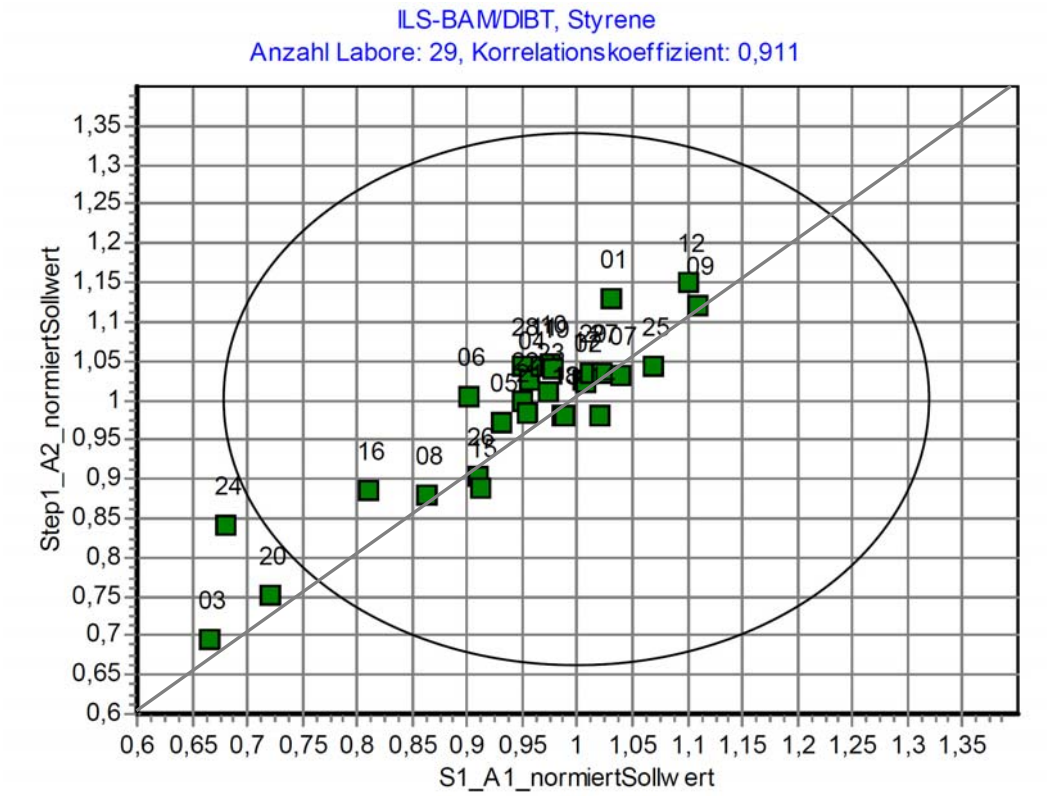

Figure 3: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, styrene

Figure 3 illustrates the results for the component styrene. A slight tendency can also be recognised around rather smaller values, even if the mean value of this component generally comes rather close to the selected reference value (3 and 10). Analytically, this relatively simple component has been determined by most participants with a high degree of accuracy. A view at the axis scaling shows that the limits of the 3-sigma circle are at 1 ± 0.3. The same also applies to trimethylbenzene (Figure 5), which exhibits a very similar behaviour to styrene. The component dichloropropanol (Figure 4) or butyl diglycol (Figure 7) however exhibits a considerably wider dispersion of the values and the 3-sigma circle is between the values of 1 ± 0.6. Therefore, the greater the standard deviation of the results, the greater the radius of the "circle". Thus it follows that in such a case an increasing number of laboratories are within the borders of the circle, even if the two values provided by the laboratory differ more noticeably.

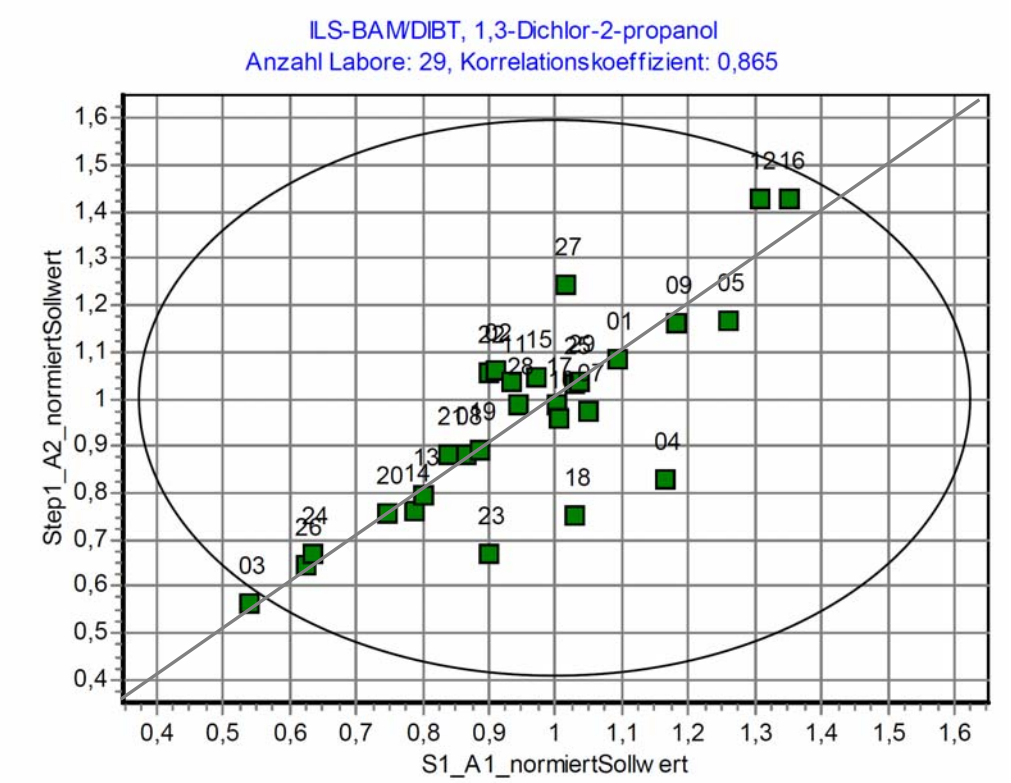

Figure 4: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, dichloropropanol

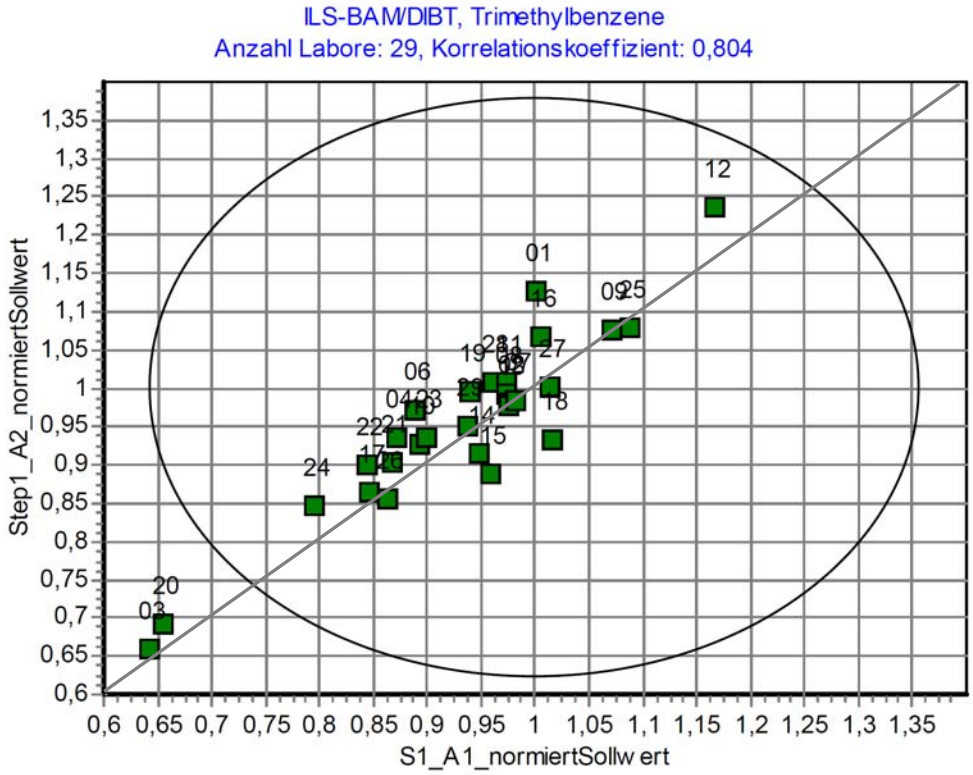

Figure 5: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, 1,2,3-trimethylbenzene

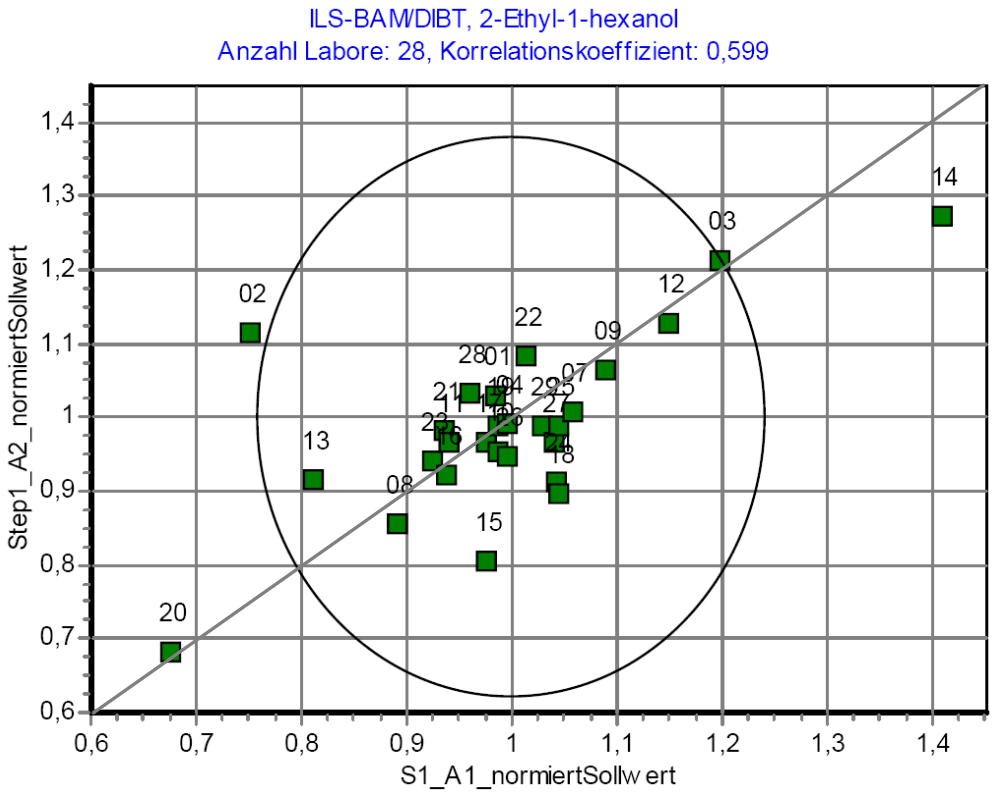

Figure 6: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, ethylhexanol

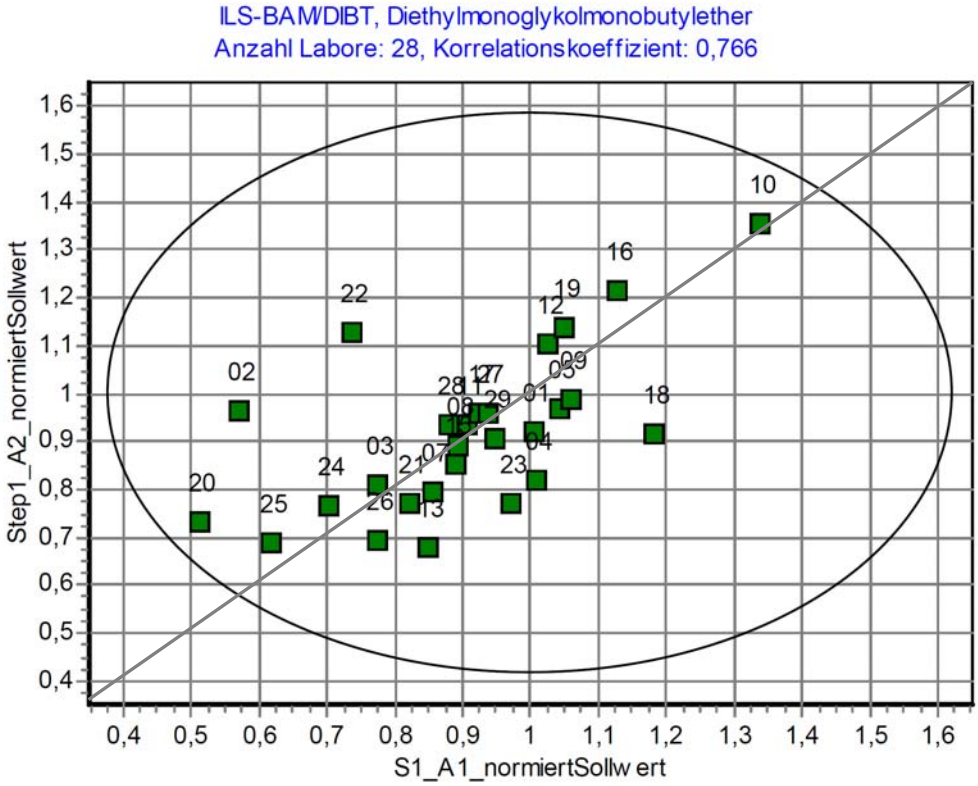

Figure 7: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, butyl diglycol

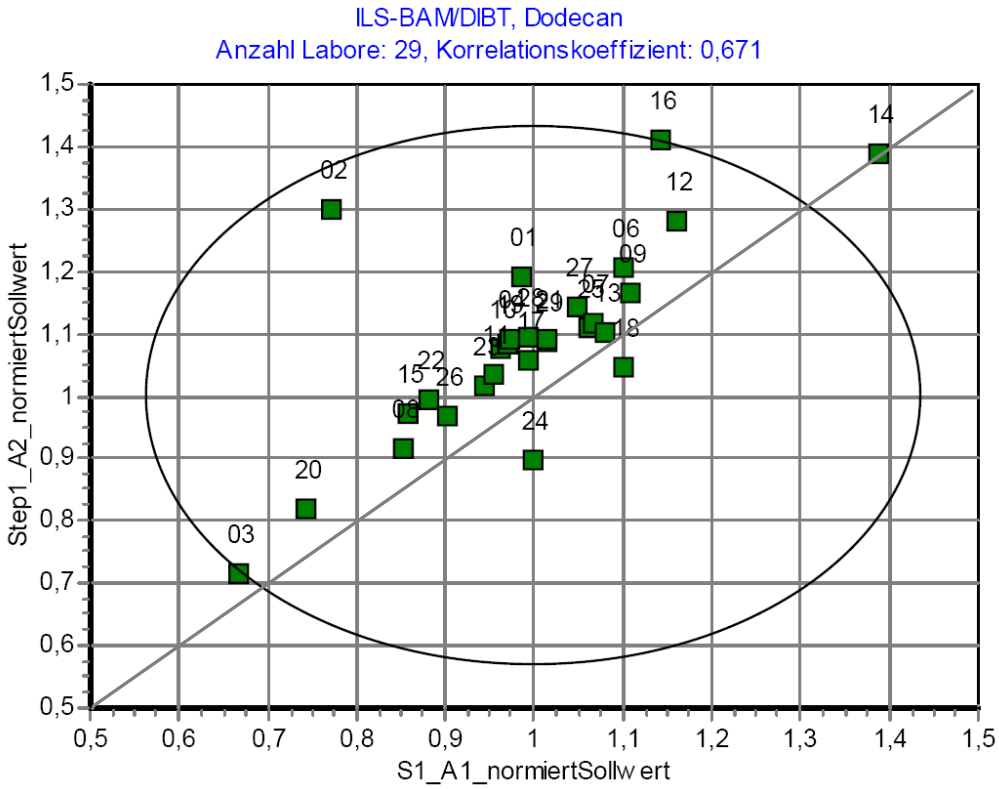

Figure 8: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, dodecane

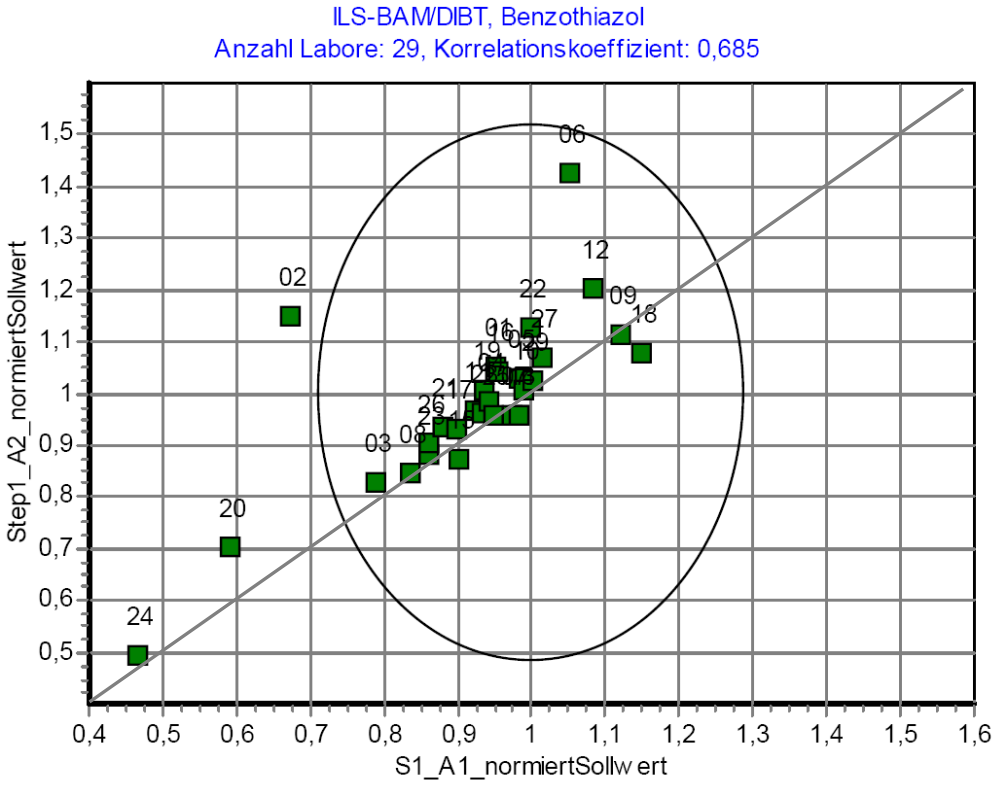

Figure 9: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, benzothiazole

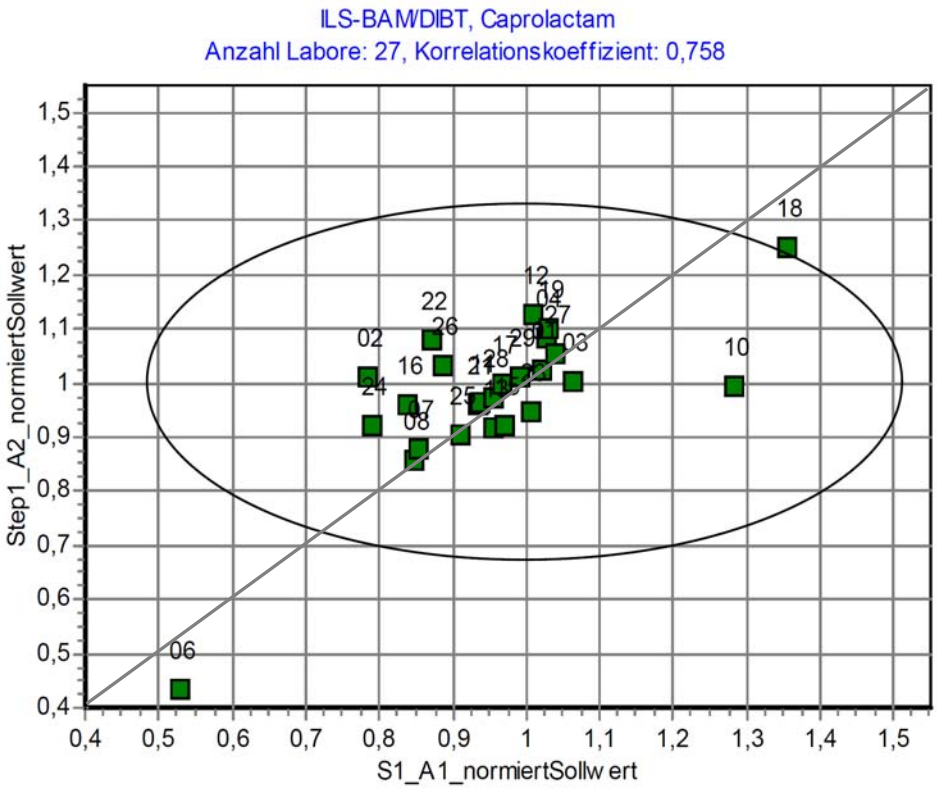

Figure 10: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, caprolactam

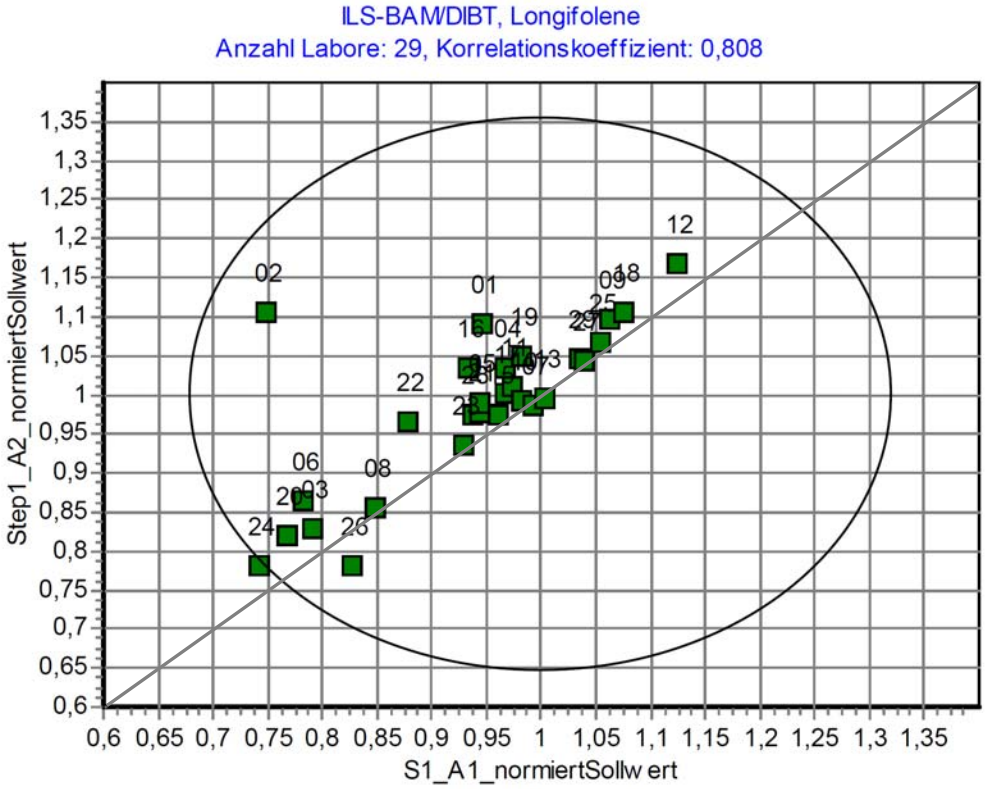

Figure 11: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, longifolene

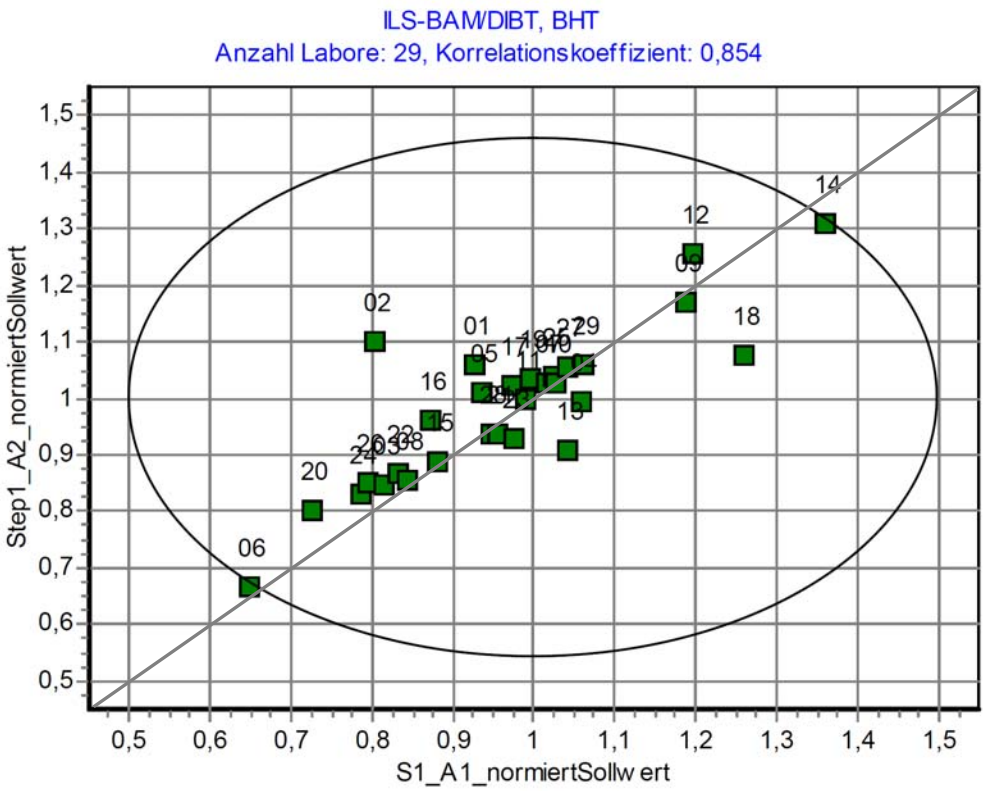

Figure 12: Youden plot, standardised and related to the target value, solution A1 vs. solution A2, BHT

2.5. Z score Step 1

One of the basic elements of all interlaboratory comparisons is the use of success indicators to evaluate the analytical performance of all participants in the interlaboratory comparison. An evaluation of interlaboratory comparisons can be made by calculating z scores. The pattern of this interlaboratory comparison however corresponds to an interlaboratory comparison for method validation according to ISO 5725. In order to use z scores the interlaboratory comparison would have had to be performed as described by ISO 13528. Nevertheless, since the establishment of a catalogue of criteria should result from the results of the interlaboratory comparison, a z score evaluation was performed.

The z score is calculated from the standard deviation and the result data of the individual laboratories for each analyte according to the following formula:

$$z = \frac{x - x_R}{s_R}$$ Formula 1

x: Laboratory mean value
x_R: mean value of all laboratories (or reference value)
s_R: Standard deviation of the mean values of all laboratories (or uncertainty of the reference value)

s_R is the "standard deviation for the suitability assessment". As described in DIN ISO 13528, s_R can be determined in various kinds:

i. by a purpose-oriented target, determined by expert evaluation or an official mandate;
ii. by an estimate based on previous suitability test rounds or expectations based on experience;
iii. by an estimate from a statistical model;
iv. by a classical or robust standard deviation.

The calculated z scores are divided into three groups: $|z| \leq 2$, $2 < |z| \leq 3$ and $|z| > 3$. If an interlaboratory test participant obtains a z score of less than two ($|z| \leq 2$), his data are considered reliable. If the z scores are between two and three ($2 < |z| \leq 3$), the data are classified as doubtful and with z scores greater than three ($|z| > 3$) the data are judged as unreliable.

The advantage of using z scores is the capability to compare the results within an interlaboratory test. The z scores can be compared between different interlaboratory tests regardless the concentration of the analyte, but one must be careful to ensure the proper standard deviation is chosen, i.e. the s_R value to calculate the z scores.

The standard deviation normally used for z score calculation is the standard deviation after expunging the outliers. Alternatively, after applying robust statistics, all values are considered. Using certified reference materials, the actual value of the reference material, previously determined in the analyses for the characterisation of the reference material, can be used instead of the mean value. Conventional expunging of outliers using statistical tests is described in DIN 38402, Part 41 and 42 and DIN ISO 5725-2 for the calculation of z scores from data with a normal distribution. For interlaboratory test data with no normal distribution, i.e. robust calculation, the corrected arithmetic mean value can be used.

In the following sections the z scores for Step 1 of the interlaboratory test are plotted, the evaluation having taken place under consideration of the target value since directly weighed concentrations were compared in this step of the laboratory comparison.

The diagram illustrates values in the range between -2 and 2 by blue tags, values up to 3 or -3 by yellow tags and larger values by red tags. Thus it is easy to see from the diagram how frequently the results of a laboratory migrate from the range between 2 and -2. Section 5 gives a relevant assessment.

In calculating the z scores the value s_R was limited to a maximum of 30 %. This limit has been established by Horwitz (Horwitz, 1982 and 2006) based on maximally accept/expected dispersions of numerous interlaboratory comparisons as a function of analyte concentration. The expected/usual relative standard deviation under reproducibility conditions is denoted for certain analyte concentrations in a table (Kromidas, 1999). It is 31.34 % for an analyte concentration of 10 ppb (22.39 % for 100 ppb, and 44.78 % for 1 ppb).

However, the relative standard deviation of caprolactam and butyl diglycol was only set to 30 % in Step 1 for solution B1 in the z score calculation because the calculated standard deviation was higher. The mean values, standard deviations and the relative standard deviations for Step 1 are shown in 4, 6, 8 and 10. For the z score calculation the mean values and the relative standard deviations are taken into account after expunging the outliers (DIN ISO 5725-2). For this reason the relative

standard deviations did not have to be limited to 30 % for the z score determination for solutions A1, A2 and B2 because these values were lower for all substances. The relative standard deviations were only set at 31.7 % and 32.8 % to 30.0 % for butyl diglycol and caprolactam in solution B1.

The participants' z scores in this interlaboratory test for the solutions A1, A2, B1 and B2 of the first step are illustrated in tables 13 to 16. Results highlighted in blue are reliable ($z \leq 2$), the results in yellow are doubtful ($2 < z \leq 3$) and those in red with $z > 3$ are unreliable.

3 out of 29 laboratories had problems with the quantification of benzothiazole in solution A1. Furthermore, only one of the 29 laboratories produced an unreliable quantification of BHT, MIBK, butyl diglycol, caprolactam and longifolene in each case. All in all, nearly all laboratories supplied reliable results. An exception is laboratory 14. This laboratory had produced unreliable results for four out of eleven substances.

For solution A2 two different laboratories had benzothiazole and caprolactam z scores greater than 3. In each case one laboratory had difficulties with the quantification of MIBK, butyl diglycol and longifolene. Laboratory 14 had z scores greater than 3 for three substances and laboratory 6 provided unreliable results for two substances.

Three laboratories supplied unreliable results for dodecane in solution B1. In each case one laboratory had z scores, greater than 3, for caprolactam, butyl diglycol and MIBK. Laboratory 14 had two z scores which exceeded 3.

Two laboratories calculated two z scores exceeding 3 in each case for dodecane and caprolactam in solution by B2. For styrene, MIBK, ethylhexanol, butyl diglycol or longifolene five laboratories had a z score exceeding 3 in each case.

The concentrations of the substances are on average 56 ng/µl in solution A1, 60 ng/µl in solution A2, 15 ng/µl in solution B1 and 90 ng/µl in B2. It is remarkable that most unreliable results occurred in solution B2, the one with the highest concentration. This can probably be traced back to the smaller dispersion of the individual results of the laboratories and thus smaller standard deviation, which plays a major role in the calculation of the z scores (see Formula 1). Solution B1 with the lowest concentration (approx. 15 ng/µl) obtained the smallest number of unreliable results since the standard deviation was here the greatest.

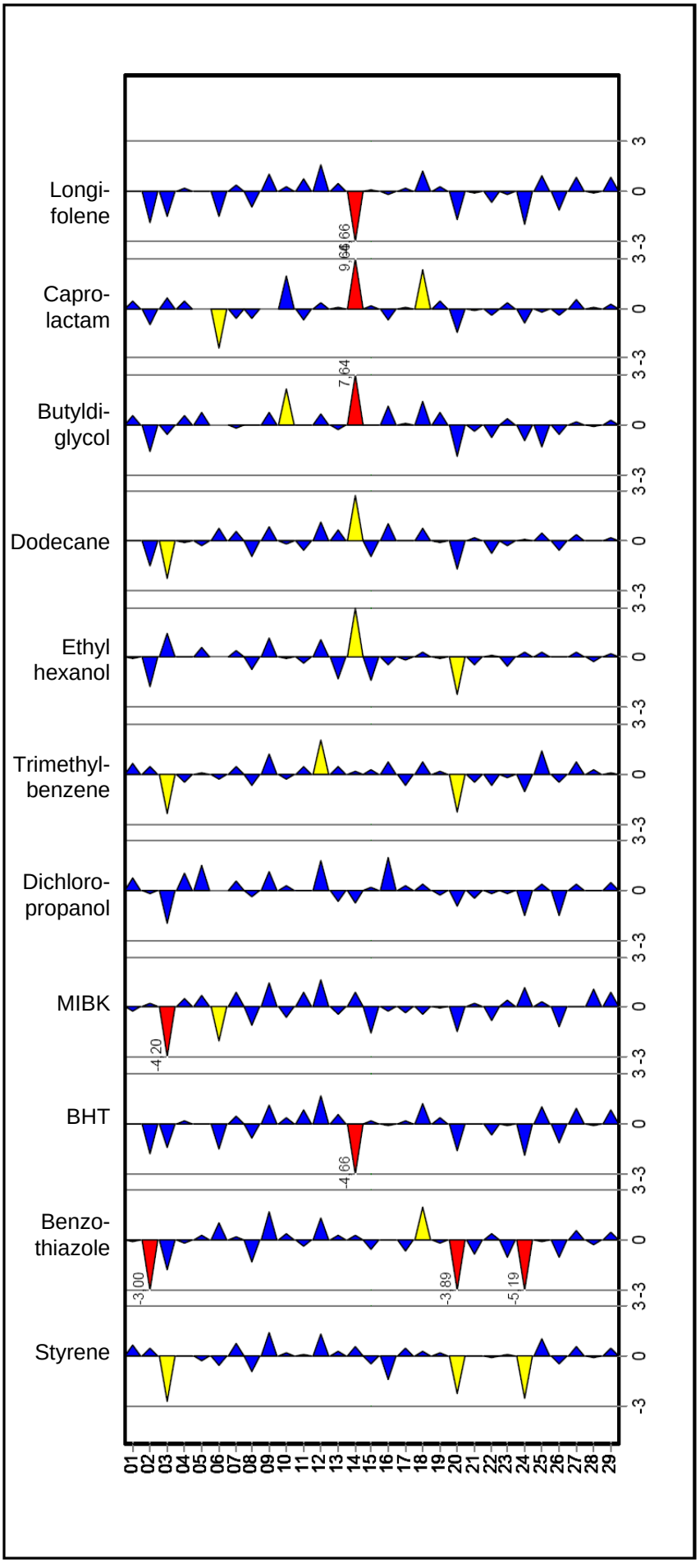

Figure 13: Z scores of the results for solution A1 after injection to Tenax and subsequent thermodesorption

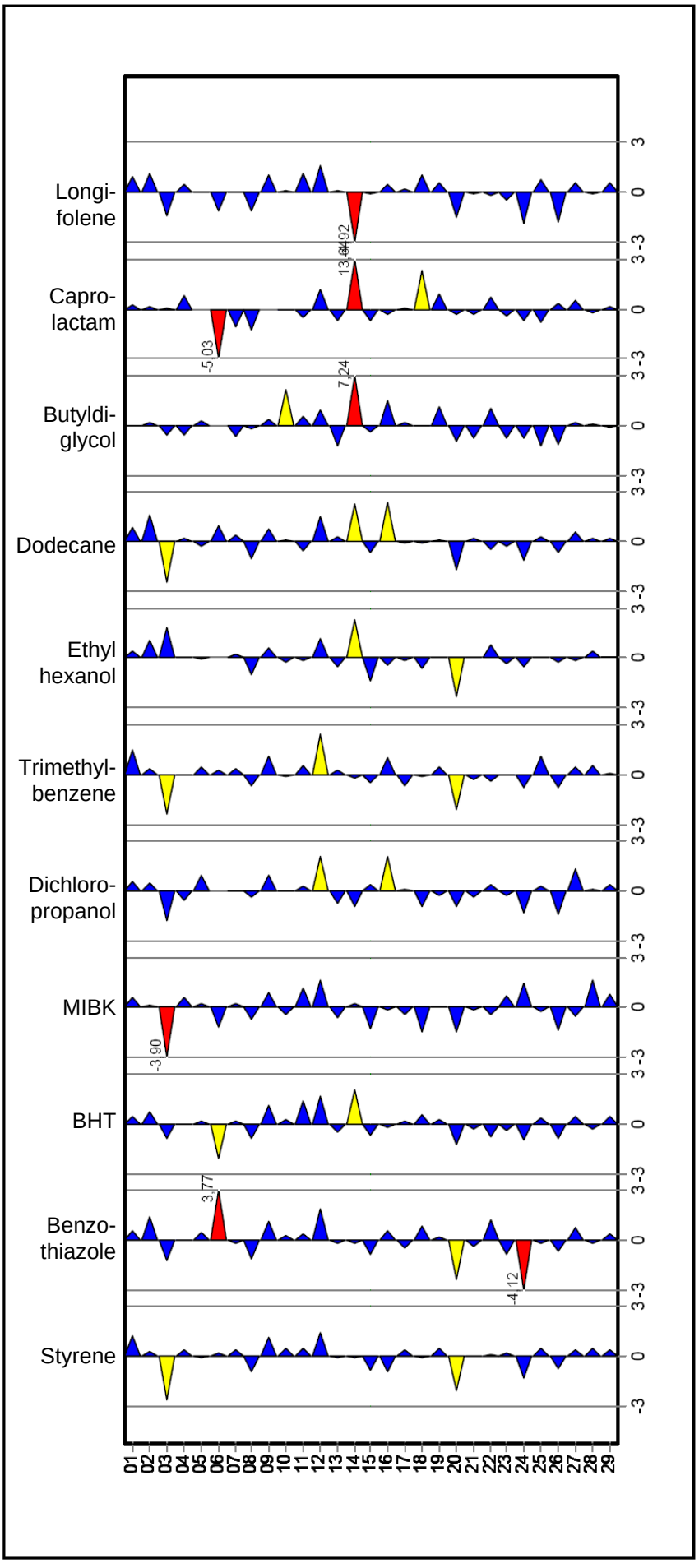

Figure 14: Z scores of the results for solution A2 after injection to Tenax and subsequent thermodesorption

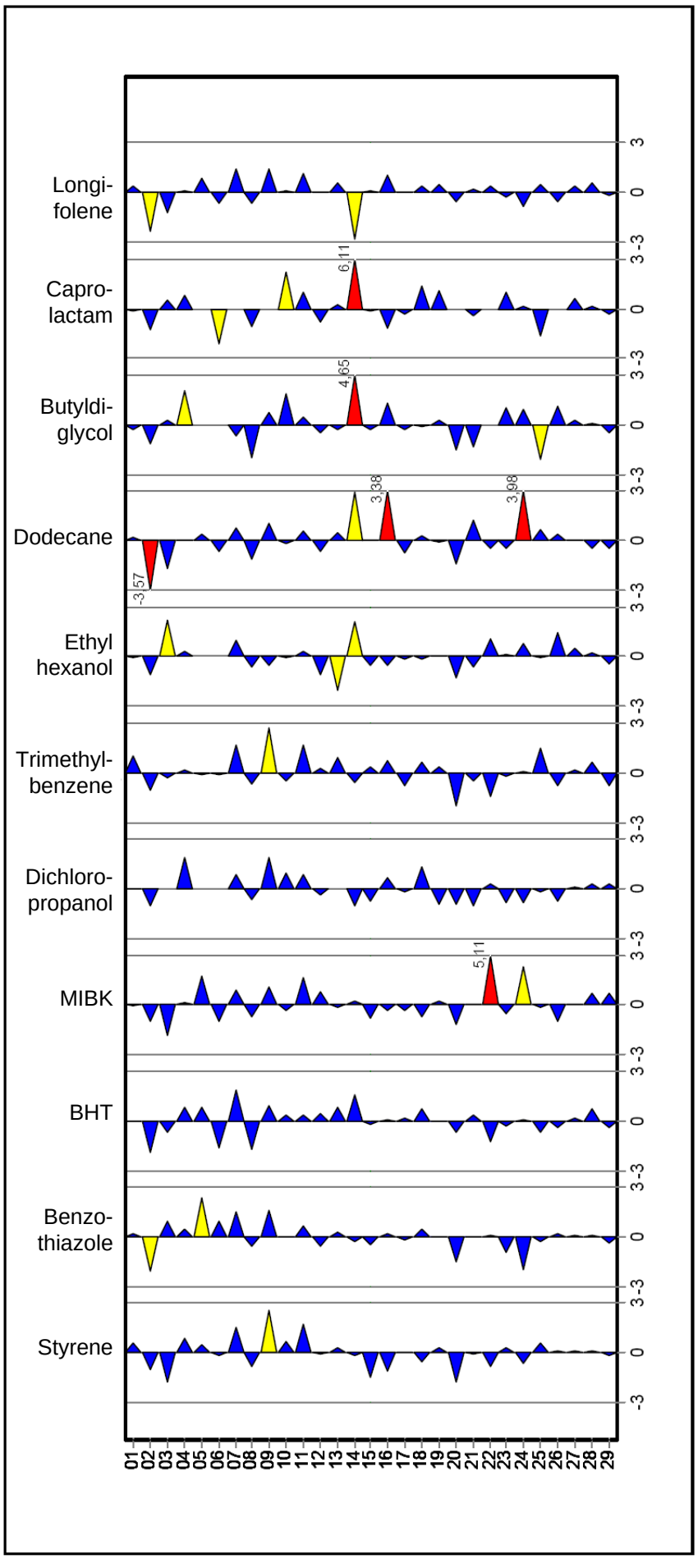

Figure 15: Z scores of the results for solution B1 after injection to Tenax and subsequent thermodesorption

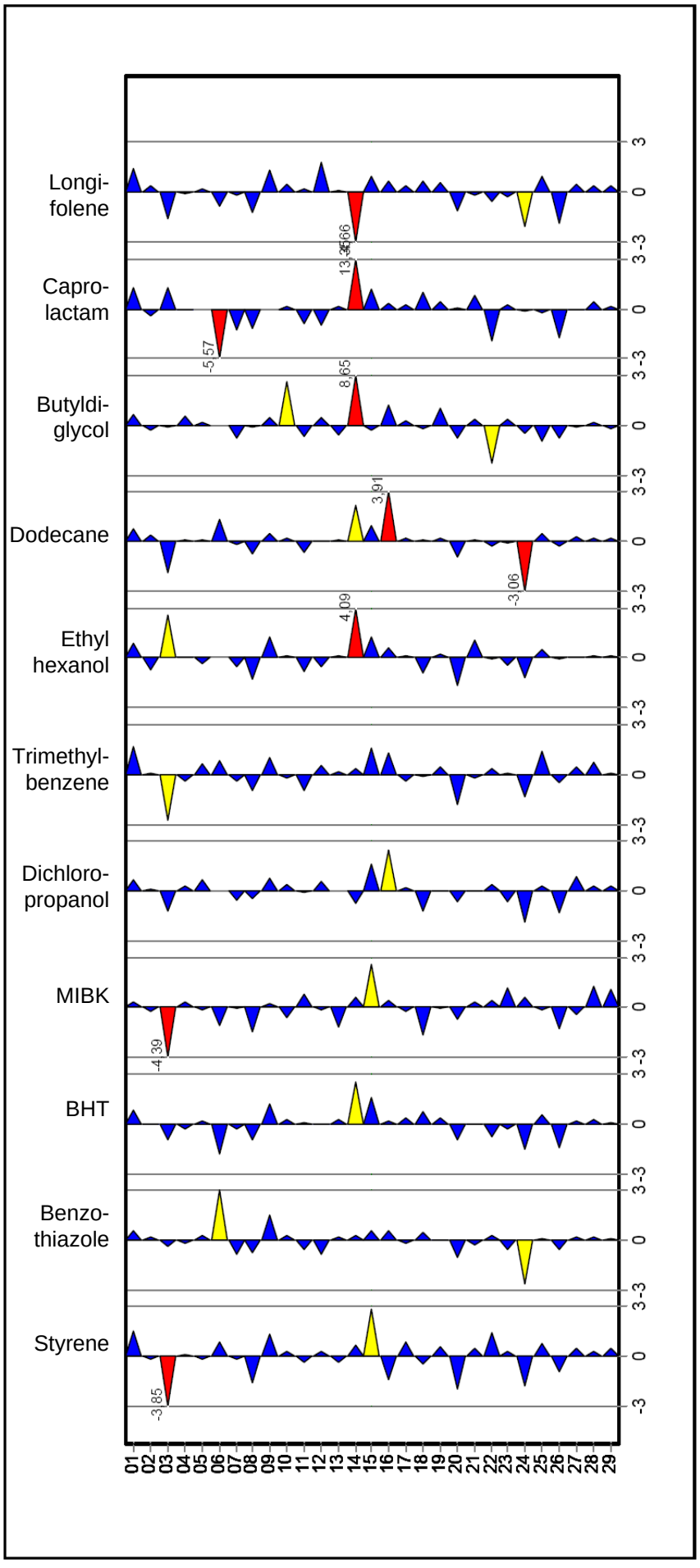

Figure 16: Z scores of the results for solution B2 after injection to Tenax and subsequent thermodesorption

2.6. Measurement uncertainty, Step 1

Measurement uncertainty characterises the dispersion of the size of a measurand. In the simplest case it can be a standard deviation (or a certain multiple of it) or the half width of an interval with a stated probability of overlap.

In method-specific interlaboratory comparisons, which are evaluated according to DIN ISO 5725-2, the reproducibility standard deviation can be used under suitable conditions directly as an estimate for measurement uncertainty. It contains both random and systematic influences if they are due to different functions of the laboratories involved and not to systematic deviations determined by the method. If only the standard deviation of the mean values of all participants is available, this can be combined with the standard deviation determined in the laboratory under reproducible laboratory conditions.

The exact conditions under which a laboratory can use the reproducibility standard deviation s_R as an estimate for the measurement of uncertainty of the results obtained using the established methodologies, are specified in ISO/DIS 21748 "Guide to the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation" of January 2009. Principally, the laboratory must verify

a) that its work conforms to the standards,

b) that the test conditions and measurement objects agree with those in the interlaboratory comparison,

c) that in its implementation of the measurement procedure, trueness and precision are compatible with the interlaboratory comparison data.

In this interlaboratory comparison the measurement uncertainty of a laboratory for testing an analyte will be estimated by the medium systematic deviation δ_S' using the following formula:

$$\delta_S' = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}_{MW}\right)^2}{n}} \qquad \text{Formula 2}$$

(δ_S': medium systematic deviation = measurement uncertainty of a laboratory; $\bar{x}_{MW}$: arithmetic mean value of all values of all laboratories; x_i: value of the *i*th measurement (individual measured value, no laboratory mean value); n: number of measurements, n > 1)

The relative medium systematic deviation will be calculated according to Formula 3.

$$\delta_S = \delta_S' \times 100\,\% \qquad \text{Formula 3}$$

The mean value of the mean values of all laboratories for a specific substance $\bar{x}_{MW}$ is calcualted according to the following formula:

$$\bar{x}_{MW} = \frac{1}{m}\sum_{p=1}^{m} x_p$$ Formula 4

($\bar{x}_{MW}$: arithmetic mean value of the mean values of all laboratories; x_p: value of the *p*th mean value; m: number of the mean values of the laboratories, m >1)

A repeatability standard deviation (no reproducibility standard deviation), which has been determined in the interlaboratory comparison (s_R) or within the laboratory under as identical conditions as possible, is normally an unsuitable estimate for a measurement uncertainty because it fails to take into account key uncertainty components.

Table 11, Table 12, Table 13 and Table 14 illustrate the calculated results of the medium systematic deviation δ_S for the individual laboratories (the relative medium systematic deviation or measurement uncertainty of one laboratory for all substances $\bar{S}_{Lab}$), those for the substances used in the interlaboratory comparison (the relative medium systematic deviation or measurement uncertainty of all laboratories for one substance $\bar{S}_{sub}$)) and the relative medium method standard deviation (the relative medium systematic deviation or measurement uncertainty of all laboratories for all substances $\bar{S}'_{Sub}$) in Step 1.

To calculate the measurement uncertainty of all participating laboratories in the interlaboratory comparison, the medium systematic deviation δ_S was calculated using up to four individual values of the respective laboratory for each substance and/or component (each analyte) in the four individual steps (A1, A2, B1 and B2) using Formulas 2 and 3. From the individual values of each laboratory, the relative medium systematic deviation or measurement uncertainty of one laboratory for all substances $\bar{S}_{Lab}$ was calculated (according to Formula 6) on the one hand. On the other, the relative medium systematic deviation or measurement uncertainty of all laboratories for one substance $\bar{S}_{sub}$ of the individual tested substances from all laboratory measurement uncertainties was also determined (according to Formula 5).

$$\bar{S}_{sub} = \sqrt{\frac{\sum_{i=1}^{n} {\delta_S}^2}{n}}$$ Formula 5

(relative medium systematic deviation or measurement uncertainty of all laboratories for one substance $\bar{S}_{sub}$)

$$\bar{S}_{Lab} = \sqrt{\frac{\sum_{i=1}^{K} {\delta_S}^2}{K}}$$ Formula 6

(relative medium systematic deviation or measurement uncertainty of one laboratory for all substances $\bar{S}_{Lab}$)

In order to calculate the medium systematic deviation (δ_S) the mean value and/or target value was first determined. Since target values are only available in the first step, the mean value (for Step 1, the target value too) was used to calculate the measurement uncertainty because of the reproducibility of the measurement uncertainty of the individual steps. For each substance a general mean was calculated ($\bar{x}_{MW}$ and/or $\bar{x}_{RF}$: target value), which was cleaned of outliers (Cochran and Grubb's tests) and used to calculate the medium systematic deviation (δ_S).

Furthermore, the mean value for each laboratory (from up to four laboratory values) and the respective relative medium systematic deviation or measurement uncertainty of one laboratory for all substances ($\bar{S}_{Lab}$) were determined. These two values (laboratory mean value and relative medium systematic deviation or measurement uncertainty of a laboratory for all substances ($\bar{S}_{Lab}$)) were outlier-cleaned (see Table 11) and not outlier-cleaned (see Table 12). Thus each laboratory obtains a mean value and relative standard deviation for each substance.

In Step 1 the relative medium systematic deviations or measurement uncertainties of one laboratory for all substances were calculated according to Formula 6 for solutions A1, A2, B1 and B2 for the individual laboratories from 11 substances (MIBK, styrene, dichloro propanol, trimetylbenzene, ethylhexanol, dodecane, butyl diglycol, benzothiazole, caprolactam, longifolene, BHT) and shown in Table 11. The relative medium systematic deviations or measurement uncertainties of one laboratory for all substances are between 5 and 30 %. One laboratory exhibited a relative medium systematic deviation or measurement uncertainty of up to 65 % (B1; Laboratory 9) and another one 60 % (B1; Laboratory 21), which are, however, exceptions.

As already indicated, both the mean value and the target value were used in Step 1 to calculate the relative medium systematic deviation or measurement uncertainty of one laboratory for all substances. The target value is the directly weighed quantity. Table 11 shows the results of both calculations for the four solutions (A1, A2, B1 and B2). The participants can recognise the differences between the relative medium systematic deviations or measurement uncertainties calculated using the mean value or the target value. These differences between the weighed quantities (target value) and the actually measured values (mean values) are probably based on the high volatility of the analytes. Also, more values can be recognised as outliers in view of the target value, which were not then used in the calculation of the mean value for the measurement uncertainty.

In our further considerations (Step 2 and Step 3) the mean value will only be used for calculating the systematic deviations or measurement uncertainties.

The standard deviation and thus the measurement uncertainty depend on the analysis method, the analyte and its concentration. Measurement uncertainty increases with decreasing concentrations of the analyte. Any data from the measurement uncertainty are thus related to the quantified substance (analyte and its concentration) (DIN EN ISO/IEC 17043).

For method estimation it is important to know the medium relative method standard deviation (relative medium systematic deviation or measurement uncertainty of all laboratories for all substances $\bar{S}'_{Sub,Lab}$). This enables a comparison between the individual Steps 1 to 3 and thus to analyse the increasing degree of analytical difficulty from Step 1 toward Step 3. The analytes were selected in the three steps in

such a way that both "easy-" and "difficult-to-analyse" substances were included. The concentrations were between 5 and 500 µg/m^3. Thus it was guaranteed that the relative medium systematic deviation or measurement uncertainty of all laboratories for all substances (calculated according to Formula 7) also reflects the estimate of the medium relative standard deviation of the individual steps. Table 13 displays these values for Step 1.

$$\overline{s}'_{Sub,Lab} = \sqrt{\frac{\sum_{i=1}^{n} \overline{s}_{Lab}{}^2}{n}}$$ Formula 7

(relative medium systematic deviation or measurement uncertainty of all laboratories for all substances $\overline{s}'_{Sub,Lab}$, i.e. the relative medium measurement uncertainty of the method)

The relative medium systematic deviations or measurement uncertainties of all laboratories for one substance, shown in Table 14, were calculated in such a way as to include measurements by all laboratories for the individual tested substances (using Formula 5). The calculated relative medium systematic deviations or measurement uncertainties of all laboratories for one substance depend on both the concentration (A1, A2, B1 and B2) and the substance. The greatest relative medium systematic deviations or measurement uncertainties of all laboratories for one substance were obtained at low concentrations (B1, approx. 15 µg/ml). The largest differences between the systematic deviations or measurement uncertainties, related to the mean value or the target value, were obtained for MIBK, which is probably due to the volatility of these compounds.

Table 13 shows the relative medium systematic deviation or measurement uncertainty of all laboratories for all substances, i.e. the total standard deviation of the method for Step 1 which is 15 % to 31 % depending on the concentrations of the analytes. A relative medium measurement uncertainty of 21 % is thus obtained for Step 1, related to all analytes and laboratories. This is the standard deviation and/or measurement uncertainty for liquid feed of the substances of four solutions at different concentrations, but the same analyte.

Table 11: Relative medium systematic deviation or measurement uncertainty; one laboratory, all substances, Step 1, without outliers

	calculated with mean value								calculated with target value							
	Step_1_A1		Step_1_A2		Step_1_B1		Step_1_B2		Step_1_A1		Step_1_A2		Step_1_B1		Step_1_B2	
	ca. 50 ng/µl		ca. 60 ng/µl		ca. 15 ng/µl		ca. 80 ng/µl		ca. 50 ng/µl		ca. 60 ng/µl		ca. 15 ng/µl		ca. 80 ng/µl	
	11 compounds		11 compounds		11 compounds		11 compounds		11 compounds		11 compounds		11 compounds		11 compounds	
Laboratory	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory)	Number
1	11	11	16	11	15	11	19	11	18	11	14	11	16	11	15	11
2	25	10	15	11	35	10	17	11	31	10	18	11	39	10	18	11
3	26	10	34	10	25	10	23	9	32	9	26	10	26	9	24	8
4	15	11	30	11	27	11	12	11	19	11	24	11	23	11	13	11
5		0	10	10	27	7	7	10		0	7	10	23	7	8	10
6	23	8	11	6	27	8	25	7	29	7	20	6	32	8	25	7
7	12	11	8	11	27	10	13	11	18	11	11	11	20	10	17	11
8	10	11	11	11	26	11	13	11	20	11	14	11	30	11	19	10
9	19	10	14	10	65	10	15	10	18	10	12	10	62	10	9	10
10	19	11	7	11	42	11	16	11	20	11	13	11	40	11	14	11
11	11	11	15	11	20	11	13	11	17	11	14	11	12	11	13	11
12	23	11	30	11	15	11	11	11	20	11	24	11	17	11	11	11
13	11	11	10	11	19	10	10	10	17	11	16	11	20	10	14	10
14	24	7	20	8	54	9	24	7	23	7	23	8	26	8	17	7
15	10	11	13	11	38	11	21	11	16	10	22	11	40	11	14	11
16	19	11	30	11	26	11	22	10	20	11	27	11	22	10	17	10
17	5	11	5	11	7	11	7	11	14	11	8	11	12	11	9	11
18	22	11	17	11	20	11	13	11	20	11	19	11	18	11	14	10
19	7	11	6	11	13	11	7	11	12	11	8	11	14	11	7	11
20	29	10	24	11	30	10	16	11	34	8	25	11	34	10	22	11
21	7	11	6	11	60	11	6	11	15	11	11	11	61	11	8	11
22	10	11	8	11	19	8	17	11	18	11	12	11	19	8	20	11
23	9	11	26	11	19	11	9	11	13	11	21	11	21	11	12	11
24	25	11	18	10	45	10	25	10	25	10	18	10	44	10	25	10
25	14	11	10	11	26	11	10	11	17	11	14	11	27	11	11	11
26	14	11	17	11	22	10	18	11	21	11	20	11	23	10	23	10
27	11	11	18	11	13	11	11	11	12	11	14	11	13	11	11	11
28	7	11	11	11	9	11	7	11	11	11	8	11	6	11	5	11
29	8	11	6	11	10	11	5	11	9	11	5	11	14	11	6	11

Table 12: Relative medium systematic deviation or measurement uncertainty; one laboratory, all substances, Step 1, with outliers

	calculated with mean value								calculated with target value							
	Step_1_A1		Step_1_A2		Step_1_B1		Step_1_B2		Step_1_A1		Step_1_A2		Step_1_B1		Step_1_B2	
	ca. 50 ng/µl		ca. 60 ng/µl		ca. 15 ng/µl		ca. 80 ng/µl		ca. 50 ng/µl		ca. 60 ng/µl		ca. 15 ng/µl		ca. 80 ng/µl	
	11 Compounds		11 Compounds		11 Compounds		11 Compounds		11 Compounds		11 Compounds		11 Compounds		11 Compounds	
Laboratory	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number	$\overline{S}_{Lab}$ [%] (all compounds, Laboratory)	Number
1	11	11	16	11	15	11	19	11	18	11	14	11	16	11	15	11
2	25	10	15	11	35	10	17	11	31	10	18	11	39	10	18	11
3	26	10	34	10	25	10	23	9	32	9	26	10	26	9	24	8
4	15	11	30	11	27	11	12	11	19	11	24	11	23	11	13	11
5		0	10	10	27	7	7	10		0	7	10	23	7	8	10
6	23	8	11	6	27	8	25	7	29	7	20	6	32	8	25	7
7	12	11	8	11	27	10	13	11	18	11	11	11	20	10	17	11
8	10	11	11	11	26	11	13	11	20	11	14	11	30	11	19	10
9	19	10	14	10	65	10	15	10	18	10	12	10	62	10	9	10
10	19	11	7	11	42	11	16	11	20	11	13	11	40	11	14	11
11	11	11	15	11	20	11	13	11	17	11	14	11	12	11	13	11
12	23	11	30	11	15	11	11	11	20	11	24	11	17	11	11	11
13	11	11	10	11	19	10	10	10	17	11	16	11	20	10	14	10
14	24	7	20	8	54	9	24	7	23	7	23	8	26	8	17	7
15	10	11	13	11	38	11	21	11	16	10	22	11	40	11	14	11
16	19	11	30	11	26	11	22	10	20	11	27	11	22	10	17	10
17	5	11	5	11	7	11	7	11	14	11	8	11	12	11	9	11
18	22	11	17	11	20	11	13	11	20	11	19	11	18	11	14	10
19	7	11	6	11	13	11	7	11	12	11	8	11	14	11	7	11
20	29	10	24	11	30	10	16	11	34	8	25	11	34	10	22	11
21	7	11	6	11	60	11	6	11	15	11	11	11	61	11	8	11
22	10	11	8	11	19	8	17	11	18	11	12	11	19	8	20	11
23	9	11	26	11	19	11	9	11	13	11	21	11	21	11	12	11
24	25	11	18	10	45	10	25	10	25	10	18	10	44	10	25	10
25	14	11	10	11	26	11	10	11	17	11	14	11	27	11	11	11
26	14	11	17	11	22	10	18	11	21	11	20	11	23	10	23	10
27	11	11	18	11	13	11	11	11	12	11	14	11	13	11	11	11
28	7	11	11	11	9	11	7	11	11	11	8	11	6	11	5	11
29	8	11	6	11	10	11	5	11	9	11	5	11	14	11	6	11

Table 13: Relative medium systematic deviation or measurement uncertainty; all laboratories, all substances, Step 1

	$\overline{s}'_{Sub,Lab}$ calculated with mean value				$\overline{s}'_{Sub,Lab}$ calculated with target value				**total-mean**	**total-target**
	Step 1 A1	**Step 1 A2**	**Step 1 B1**	**Step 1 B2**	**Step 1 A1**	**Step 1 A2**	**Step1 B1**	**Step 1 B2**	**Step 1**	**Step 1**
Standard deviation in %:	17	17	31	15	20	17	29	16	21	21
Number of results	297	299	291	296	291	307	296	300	1183	1194

Table 14: Relative medium systematic deviation or measurement uncertainty of all laboratories for one substance in each case in Step 1

		calculated with mean value			calculated with mean value		
solution:	**Compound:**	**Mean:**	**Standard deviation**	$\overline{S}_{sub}$ **rel. Std. Dev.**	**Mean**	**Standard deviation**	$\overline{S}_{sub}$ **rel. Std. Dev.**
A1	MIBK	45,5	5,2	11	46,5	8,5	16
	Styrene	49,4	6,3	13	49,9	6,1	12
	Dichloropropanol	61,5	13,8	23	61,5	14,2	22
	Trimetylbenzene	50,7	6,4	13	50,7	7,6	14
	Ethylhexanol	53,5	8,4	16	53,5	8,4	16
	Dodecane	56,3	8,9	16	56,3	8,9	16
	Butyldiglycol	49,3	11,2	23	49,3	12,5	23
	Benzothiazole	51,3	8,3	16	53,0	5,7	10
	Caprolactam	51,3	9,5	18	51,3	9,8	18
	Longifolene	51,1	6,5	13	51,1	7,3	13
	BHT	52,7	8,7	17	52,7	22,1	40
A2	MIBK	51,2	6,4	12	51,2	9,7	17
	Styrene	55,8	6,4	12	55,8	6,5	11
	Dichloropropanol	67,4	19,3	29	67,4	19,6	28
	Trimetylbenzene	56,8	7,4	13	56,8	8,0	13
	Ethylhexanol	61,1	8,2	13	61,1	8,3	13
	Dodecane	64,2	11,6	18	64,2	12,5	21
	Butyldiglycol	50,3	8,0	16	55,0	14,7	24
	Benzothiazole	56,1	6,5	12	58,5	7,5	13
	Caprolactam	67,9	19,4	29	59,1	6,4	11
	Longifolene	56,8	7,5	13	58,6	7,1	12
	BHT	61,1	8,2	13	59,4	9,2	15
B1	MIBK	12,3	2,8	22	12,5	3,7	25
	Styrene	14,2	2,8	20	14,2	3,2	21
	Dichloropropanol	13,9	4,6	31	13,9	5,0	33
	Trimetylbenzene	14,2	2,7	19	14,2	2,8	19
	Ethylhexanol	14,0	4,2	30	14,0	4,3	29
	Dodecane	14,9	3,3	23	14,7	3,2	21
	Butyldiglycol	15,4	8,3	57	14,4	7,6	50
	Benzothiazole	13,6	4,2	31	13,6	4,3	30
	Caprolactam	14,1	5,2	37	14,1	5,3	36
	Longifolene	13,4	3,3	24	13,7	3,5	23
	BHT	14,3	3,6	25	14,3	3,9	25
B2	MIBK	75,0	7,6	10	76,3	13,9	16
	Styrene	86,6	8,3	10	86,6	9,9	11
	Dichloropropanol	83,9	19,4	23	83,9	20,9	23
	Trimetylbenzene	84,9	10,5	12	85,9	9,1	11
	Ethylhexanol	84,0	8,9	11	84,0	9,8	11
	Dodecane	87,2	12,7	15	87,2	13,2	14
	Butyldiglycol	82,9	15,3	18	82,9	16,9	19
	Benzothiazole	79,4	14,3	18	80,7	13,1	15
	Caprolactam	82,6	11,4	14	82,6	12,7	14
	Longifolene	83,5	10,0	12	83,5	12,5	14
	BHT	88,1	14,4	16	86,8	14,7	16

2.7. Findings, Step 1

In addition to the analytical results, detailed information on the analysis method that each participant use was queried. This included data on the capillary separation column (length, polarity), thermodesorption method (temperature, equipment manufacturer), calibration and GC method. The questionnaires can be found in the Annex. This abundant data pool was used to discover the reasons for the deviations in laboratories which lie outside the circle in the Youden evaluation (2.4.2 page 10) or whose results were frequently identified as outliers. The influence on the results will be discussed for different parameters in the following pages.

Figure 17 shows the comparison of the results using the example of butyl diglycol on a non-polar column (Type DB1) and with a moderately polar column (Type DB5). It shows that the dispersion of the results obtained by the non-polar column is markedly larger and the mean value of the results (red line) of the moderately polar column is in better agreement with the target value (54.5 ng). The polarity of the column is currently widely debated. DIN ISO 16000-6 describes the employment of a non-polar column, however, an increasing number of polar compounds (e.g. glycols) have been found in building products in the last few years, which can only be poorly chromatographed using a non-polar column. However, less polar components such as styrene (Figure 18) show a slight tendency for reaching the target value easier than using the somewhat more polar column.

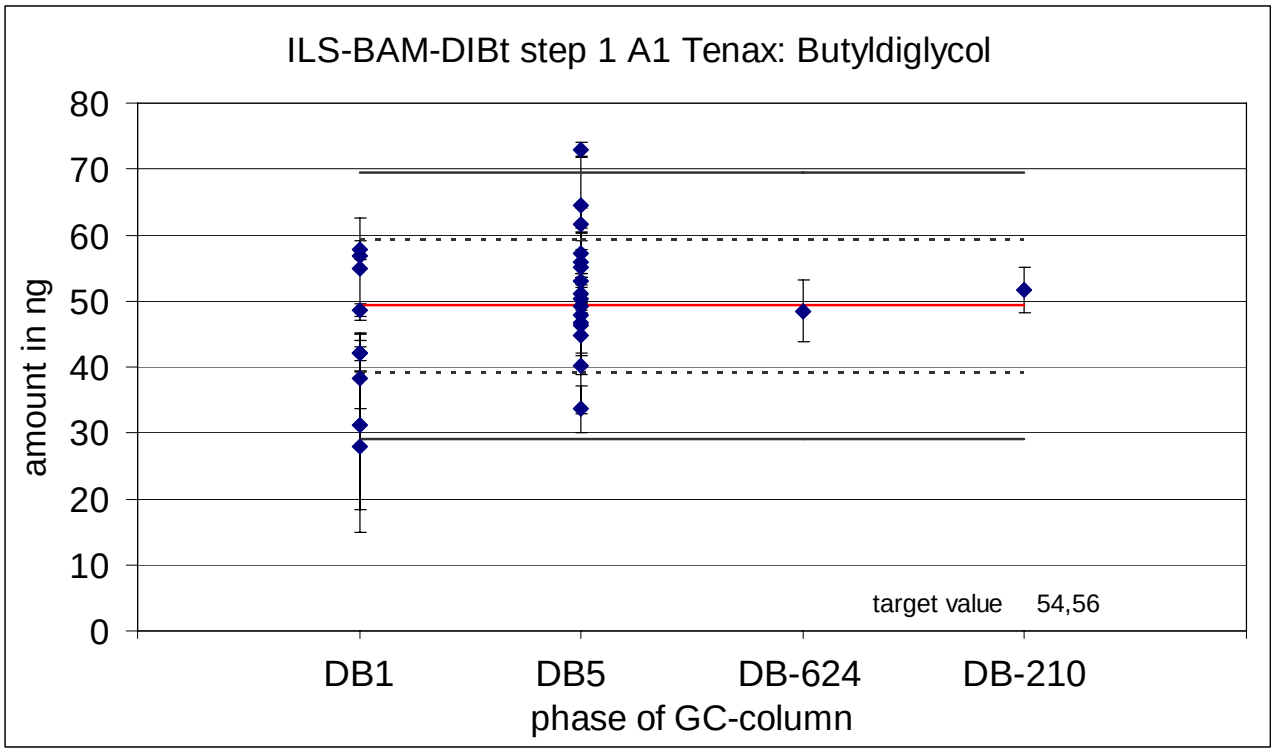

Figure 17: Results of the participants for butyl diglycol depending on the GC column used (DB1: non-polar type column, DB5: moderately polar type column). Red line: general mean value, dashed and solid lines: 1 and 2 sigma (standard deviation of the mean value).

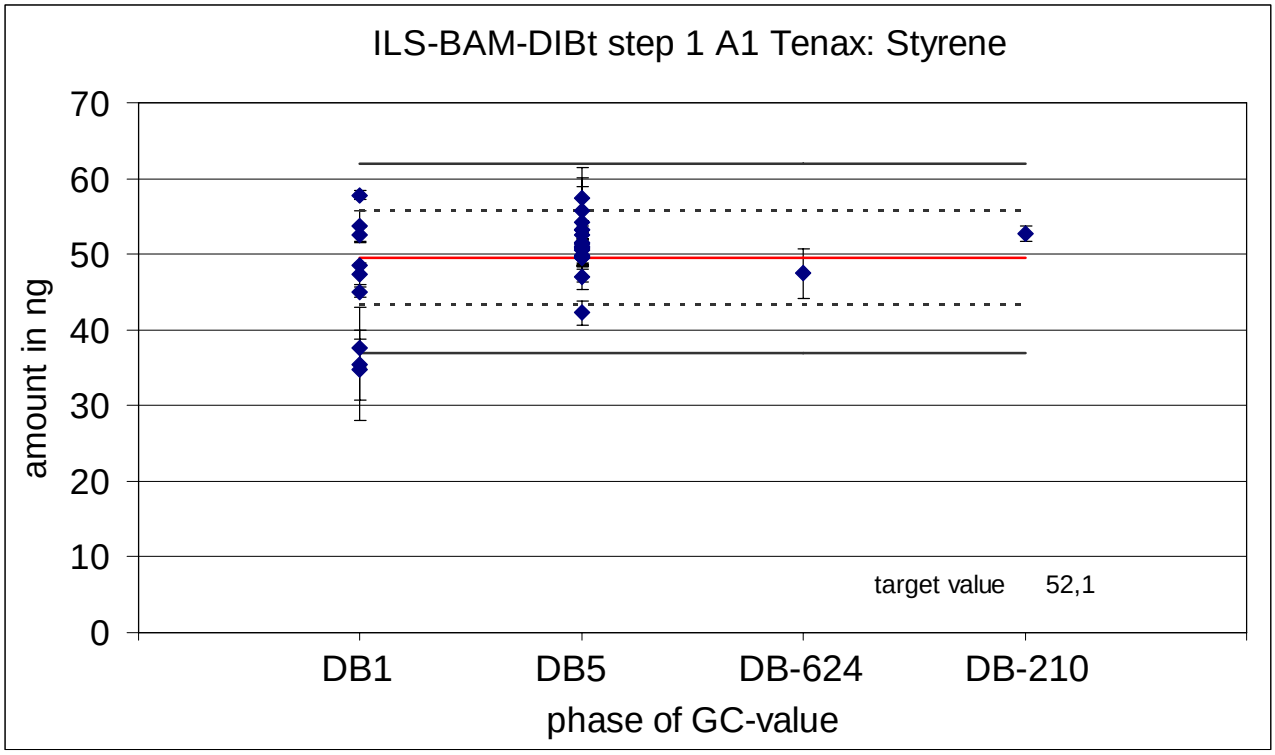

Figure 18: Results of the participants for styrene depending on the GC column used (DB1: non-polar column type, DB5: moderately polar column type). Red line: general mean value, dashed and solid lines: 1 and 2 sigma (standard deviation of the mean value).

The better suitability of the moderately polar column can easily be seen in Figure 19, which contains the standardised values (contents related to the respective target value) for the two main column types. The mean values of the results of the DB-5 type columns marked by pink squares show a good agreement with the respective target values and nearly all are close to 1. The values of the non-polar column are on average markedly lower at approx. 0.85 and thus considerably further from the target value. A comparable picture has also been obtained for the relative standard deviations: the results provided by the DB-1 type columns exhibit higher fluctuations than those by the DB-5 type (Figure 20). Since 9 participants have used DB-1 type columns and 18 DB-5 type ones, a fairly high confidence level in the statement can be assumed, although there were laboratories that used DB-1 type columns and nevertheless provided results near the target value. Obviously, several factors affect the results, whose effect is however, difficult to extract from the results.

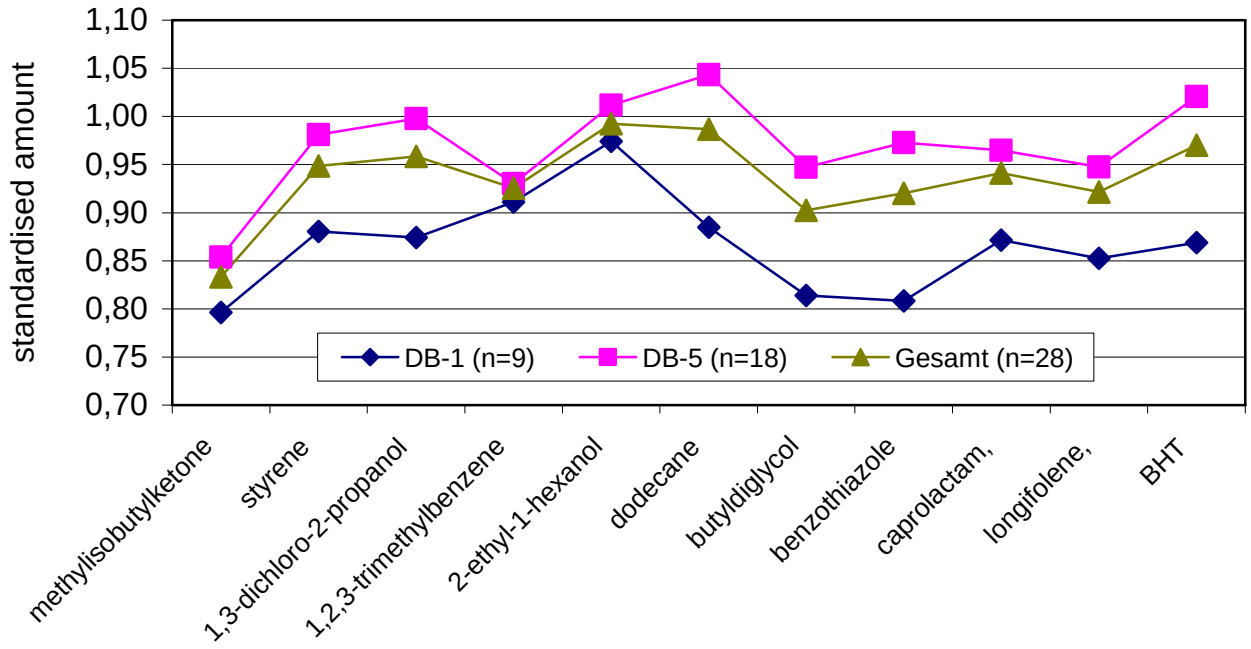

Figure 19: Overview of the results of the participants depending on the GC column used (DB1: non-polar type column, DB5: moderately polar type column); the values are standardised to the target value.

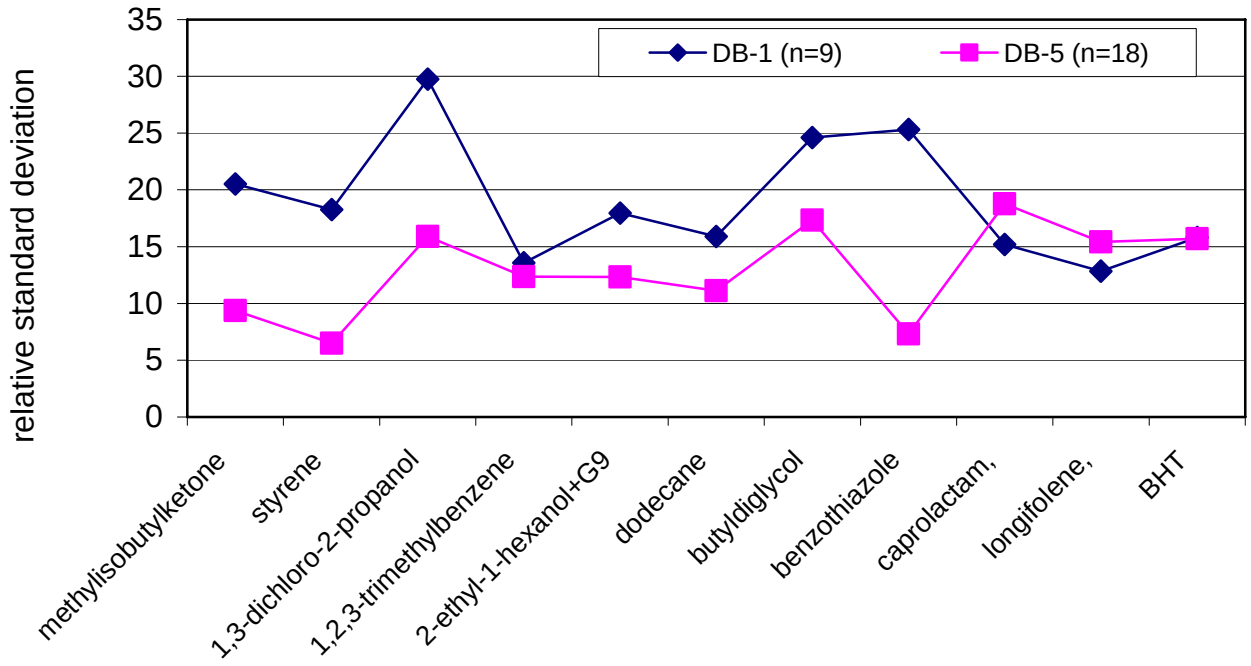

Figure 20: Standard deviation of the participant results depending on the GC column used (DB1: non-polar type column, DB5: moderately polar type column).

Another graphic test of data analysis for the different thermodesorption systems is illustrated in Figures 21 and 22. They show the standardised contents related once to the mean value (Figure 21) and once to the target value (Figure 22). The representation of the

mean values shows a good approximation of the results with the Perkin Elmer type thermodesorber, which are closer to the mean value. However, 18 participants used a Perkin Elmer device, while only participants six and four used a Gerstel and Markes device, respectively. Thus it is obvious that the mean value does not provide good information on the reliability of any particular type of device since about 60 % of the tests that the mean value is based on were determined using identical devices.

But even Figure 22 standardised to the target value does not show a clear advantage of one particular type of thermodesorber. All types vary markedly, perhaps the Gerstel version has a slight tendency for getting closer to the target value better, but this finding is rather insignificant because of the strongly shifted distribution favouring one type of thermodesorber. All in all, no particular type can be distinguished as being more suitable based on the results for the TDS systems in comparison to the evaluation of the various column types.

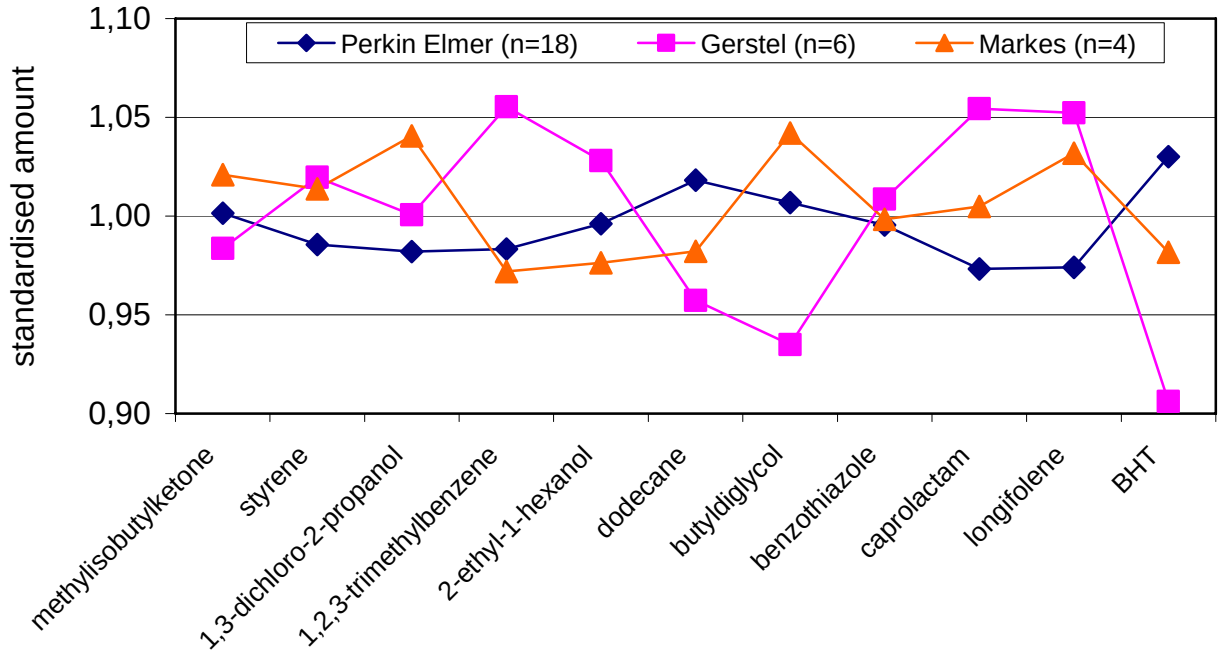

Figure 21: Overview of the thermodesorption devices used in relation to the standardised contents related to the mean value.

In addition to the assessment of column type and thermodesorber, the parameters for column diameter or length were also tested. However, just as in the case of thermodesorber, the result of the comparison does not show any tendency toward a special combination. Unfortunately, relatively few data are available about the parameters for injected volume or syringe size, so this parameter cannot reasonably be used for a comparison, although, without any doubt, it should show a clear influence, e.g. at the lower concentration of solution B1. An attempt has been made to establish further influencing factors in this relationship with the help of a cluster analysis. In addition to the column types, the thermodesorbers used, thermodesorption temperatures, column length and diameter as well as other parameters have been considered. Unfortunately, this method has not been able to provide findings of unambiguous quality.

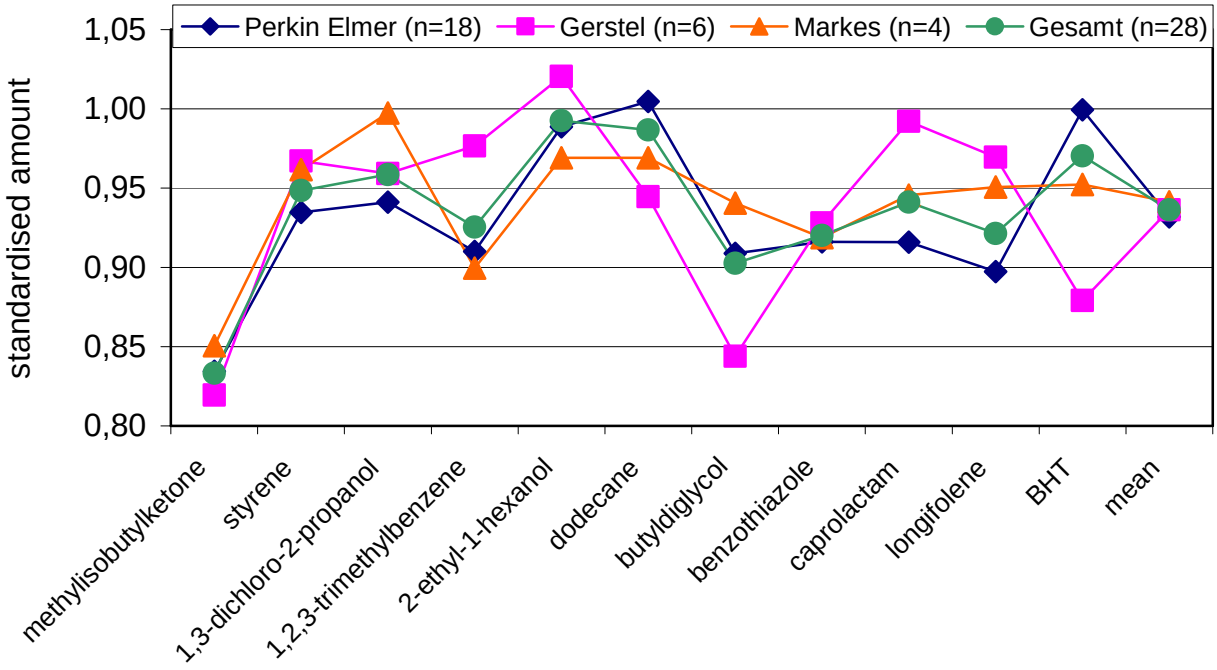

Figure 22: Overview of the thermodesorption devices used in relation to the standardised contents related to the target value.

3. Interlaboratory comparison, Step 2

3.1. Test implementation, Step 2

For Step 2 of the interlaboratory comparison a BAM 1-m³ emission test chamber was loaded with a rubber floor covering. The product loading factor was 1.5 m²/m³ and the air exchange rate was set at 0.5 h^{-1}. The temperature was 23°C and the relative air humidity 50%.

Air sampling by BAM for the participants was started on the 20th day after loading the chamber and extended over 4 days. Air sampling took place with BAM's pumps using the same sample flow rates and sample volumes as required from the individual participants. One of the participants' tubes was used to check adherence to the sampling parameters of the pumps used and another served as a transportation blank value. 23 shows the sampling of the 1-m³ chamber and 24 shows the participants' sorted sampling tubes.

In addition, a VICI AG International permeation tube was applied to the test chamber, which emitted deuterated toluene. This permeation tube was removed from the chamber at the end of the third day of sampling. On the fourth day, two participants carried out further sampling without the permeation tube, since they use deuterated toluene as an internal standard for quantification.

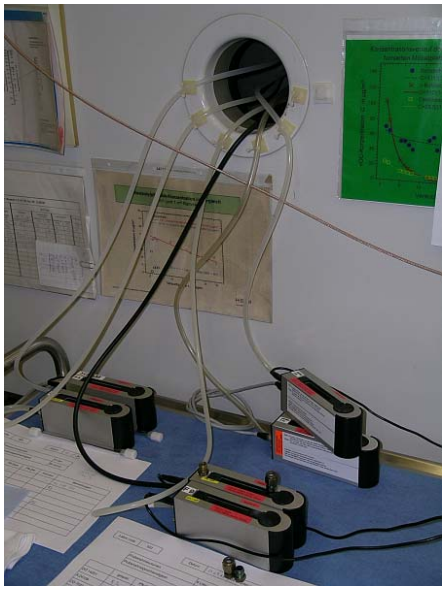

Figure 23: Sampling using six tubes simultaneously in a 1-m³ chamber

Figure 24: Sorting the sampling tubes before and after sampling.

3.2. Quality assurance, Step 2

In order to guarantee that the test chamber concentration was the same for all participants, BAM took and analysed three additional samples in the morning, at noon and in the evening. Figure 25 shows the concentrations for some of the substances to be analysed. It can be seen that the concentrations only show a moderate decrease over the four days, therefore the respective mean value over the four-day test time will be used in the following sections (regression not significant).

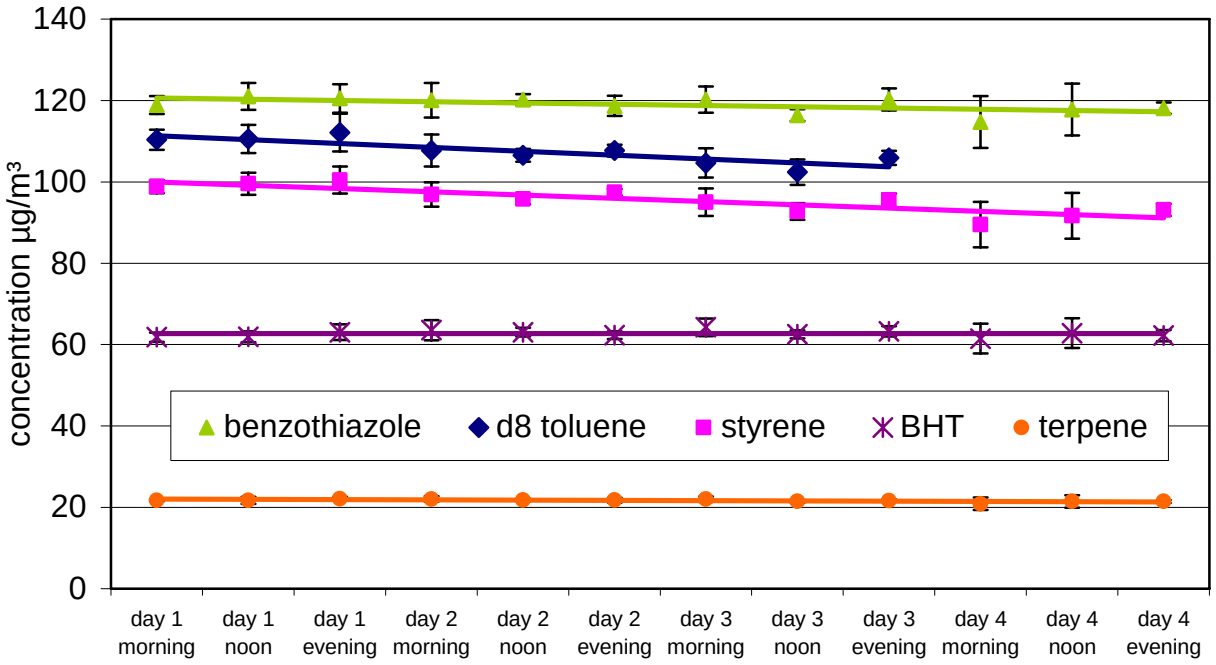

Figure 25: Concentrations measured during the 4-day sampling period simultaneously to the sampling for the participants.

Table 15: Mean values and standard deviations of the mean values of the BAM control measurements for Step 2 during the four measurement days.

compound	**mean value**	**sta dev**	**% sta dev**
toluene-d_8	107,5	4,0	**3,7**
styrene	95,4	4,2	**4,4**
cyclohexanone	13,6	0,6	**4,7**
benzaldehyde	14,2	0,8	**5,9**
benzothiazole	118,7	3,7	**3,1**
BHT	62,5	2,1	**3,3**

The standard deviations of the control measurements for the key substances show less than 6 % deviation. Although the curves in Figure 25 for two components decline slightly, a

largely constant value can be assumed over the four-day sampling period in terms of measurement accuracy and standard deviations of the results, which are shown in the form of error bars in Figure 25.

3.3. Results, Step 2

The following tables 16 and 17 show the mean values, standard deviation of the mean values, medians and the number of participants considered for the individual substances from the test chamber, as reported by the participants. Table 16 contains all results of the participants, the outlier-cleaned values can be found in Table 17.

Table 16: Results for Step 2; mean value, standard deviation of mean values, median and number of participants considered.

compound	**mean value**	**sta dev**	**rel sta dev**	**median**	**number**
	µg/m³	µg/m³	**%**	µg/m³	n
toluene-d_8	114	26	**23**	113	24
styrene	117	13	**11**	116	26
cyclohexanone	14	4	**24**	14	26
benzaldehyde	18	4	**20**	17	26
benzothiazole	113	37	**33**	107	26
BHT	57	21	**36**	56	26
cyclodecane (added)	22 ng	8	**35**	22	25

Table 17: Outlier-cleaned results for Step 2; mean value, standard deviation of mean values, median and number of participants considered.

compound	**mean value**	**sta dev**	**rel sta dev**	**median**	**number**
	µg/m³	µg/m³	**%**	µg/m³	n
toluene-d_8	109	15	**14**	110	22
styrene	116	13	**11**	116	24
cyclohexanone	14	3	**23**	13	21
benzaldehyde	17	3	**19**	17	22
benzothiazole	106	17	**16**	107	21
BHT	54	12	**22**	57	21
cyclodecane (added)	21 ng	6	**30**	23	23

The delivery rate of toluene-d_8 was gravimetrically determined. Unfortunately, during the three-week loading period the delivery rate changed continuously. For the period of the sampling a target value of 122 µg/m³ was determined for toluene-d_8.

20.0 ng cyclodecane was injected in liquid form into all the participants' tubes by BAM's personnel before sampling.

3.4. Z scores, Step 2

As for Step 1, a z score evaluation was carried out for Step 2 and is shown in Figure 26. It should be noted that the standard deviation for the calculation of the z scores (see Formula 1) must be limited to a maximum of 30 % (see Section 2.5). However, as Table 17 indicates, this is not necessary because the relative standard deviation is less than 30% after expunging the outliers for all seven substances (toluene-d_8, styrene, cyclohexanone, benzaldehyde, benzothiazole, BHT, cyclodecane).

In Step 2, Laboratory 26 has z scores exceeding 3 for three substances (benzaldehyde, benzothiazole and BHT) out of seven. Another laboratory delivered unreliable values for toluene-d_8.

As far as styrene, cyclohexanone, benzothiazole and cyclodecane are concerned, reliable to doubtful z scores have been calculated for all participants.

It is noticeable that z scores greater than 3 do not depend on the concentration of the analytes, i.e. unreliable values have been delivered by the participants both at high (100 µg/m³ to 120 µg/m³), medium (50 to 60 µg/m³) and low (10 µg/m³ to 20 µg/m³) concentrations.

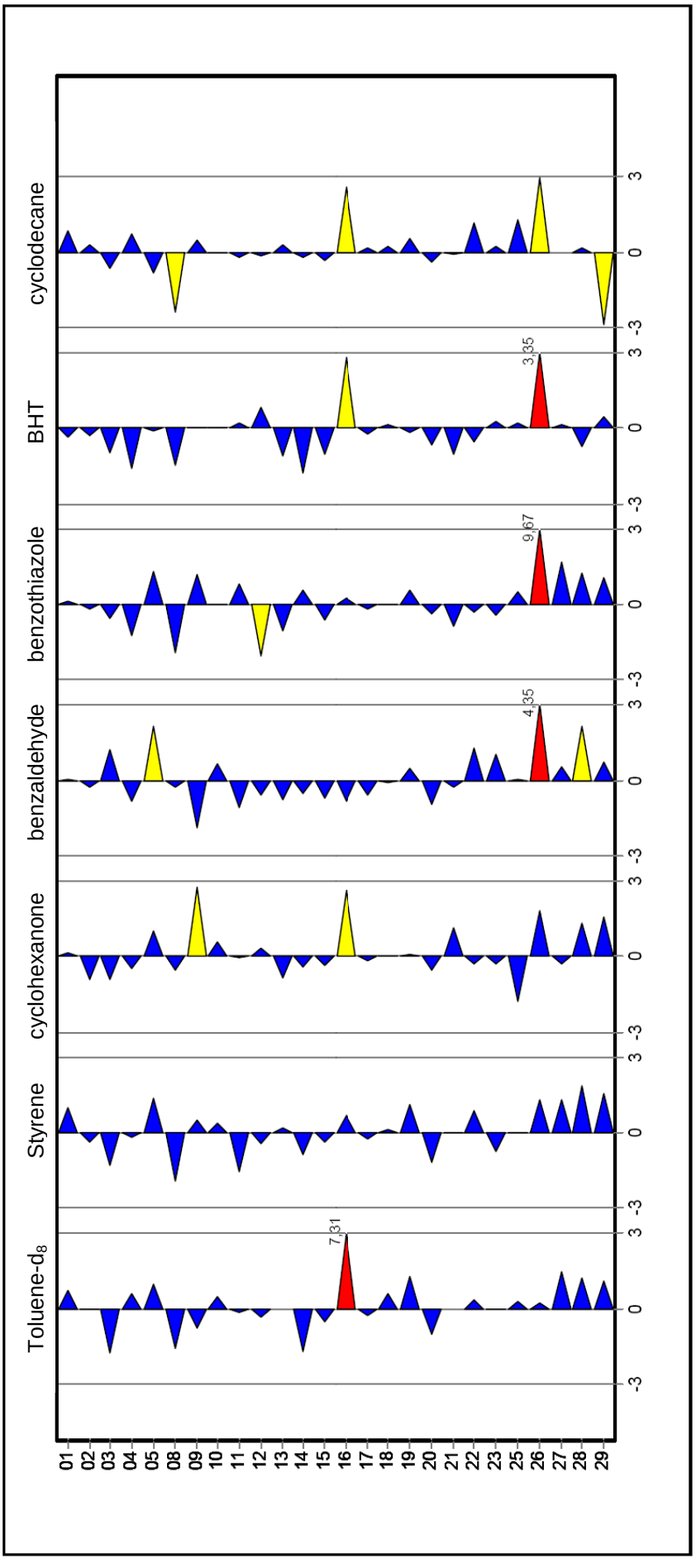

Figure 26: Z scores of the results for Step 2, standard deviation maximum 30 %

3.5. Measurement uncertainty, Step 2

Table 18 and Table 19 show the relative medium systematic deviation or measurement uncertainty of one laboratory for all substances before and after expunging the outliers. The measurement uncertainties for the individual laboratories have been calculated. The seven substances are: styrene, cyclohexanone, benzaldehyde, benzothiazole, BHT, cyclodecane and toluene-d_8.

Table 18: Relative medium systematic deviation or measurement uncertainty of each laboratory for all substances in Step 2 related to mean value without outliers

	7 Compounds	
Lab.	$\overline{S}_{Lab}$ [%] (all compounds, laboratory) **Konc. 15 to 120 µg/m^3**	Number
1	16	7
2	11	7
3	22	7
4	30	7
5	32	7
6		0
7		0
8	36	7
9	29	7
10	8	7
11	12	7
12	22	7
13	19	6
14	23	7
15	15	7
16	53	6
17	6	7
18	9	7
19	11	7
20	15	7
21	24	6
22	18	7
23	10	7
24		0
25	22	7
26	59	4
27	16	6
28	29	7
29	37	7

Differences in the medium systematic deviations or measurement uncertainties of all laboratories for all substances calculated before and after expunging the outliers are barely or not available for nearly all laboratories, except for Laboratory 26. This exception with approx. 35 % difference (reduction from approx. 94 % to 59 %) is high. In view of the measurement uncertainty of this laboratory these deviations can

be traced back to high standard deviations for the substances benzaldehyde, benzothiazole, BHT and cyclodecane.

Table 19: Relative medium systematic deviation or measurement uncertainty of each laboratory for all substances in Step 2 related to mean value with outliers

	7 compounds	
Lab.	$\overline{S}_{Lab}$ [%] (all compounds, laboratory) **Konc. 15 to 120 µg/m^3**	Number
1	16	7
2	11	7
3	22	7
4	30	7
5	32	7
6		0
7		0
8	36	7
9	29	7
10	8	7
11	12	7
12	22	7
13	19	6
14	23	7
15	15	7
16	62	7
17	6	7
18	9	7
19	11	7
20	15	7
21	24	6
22	18	7
23	10	7
24		0
25	22	7
26	94	7
27	16	6
28	29	7
29	37	7

The relative medium systematic deviation or measurement uncertainty of all laboratories for one substance and thus the measurement uncertainty of the tested substances or compounds depend, as in Step 1, on their concentration and rises with a decreasing concentration. Furthermore, the relative medium systematic deviation or measurement uncertainty of all laboratories for one substance is higher for substances for which this existing analytical method is not optimal, for example benzothiazole and BHT. Benzothiazole has a relative medium systematic deviation or measurement uncertainty of all laboratories of 38 % at approx. 112 µg/m^3 and BHT of 38 % at approx. 57 µg/m^3.

Table 20: Relative medium systematic deviation or measurement uncertainty of all laboratories in each case for one substance in Step 2

Compound:	Mean:	Std. Dev.	$\overline{S}_{sub}$ rel. Std. Dev.
Styrene	117,0	13,7	12
Cyclohexanone	14,4	3,7	27
Benzaldehyde	18,1	5,3	30
Benzothiazole	112,6	38,0	36
BHT	57,0	22,4	38
Cyclodecane	22,2	8,0	38
Toluene-d_8	113,9	26,6	24

As already explained, the largest relative standard deviation of an analyte must be chosen to estimate the total measurement uncertainty of the method because this includes the remaining ones. This means that the systematic deviation or measurement uncertainty would be 38 % for Step 2.

The relative medium systematic deviation or measurement uncertainty of the laboratories and thus the measurement uncertainty of the method is 26 % for all seven substances and all participants (calculated after expunging the outliers).

Table 21: Relative medium systematic deviation or measurement uncertainty of all laboratories for all substances in Step 2

Step 2	7 Compounds
$\overline{S}'_{Sub,Lab}$ **Standard deviation in %:**	26
Number of results	175

3.6. Findings

An evaluation of the questionnaires took place for the sampling relating to the parameters sample flow rate and sample volume. For most participants the sample flow rate was l00 ml/min, its smallest value being 40 ml/min and the highest value 200 ml/min.

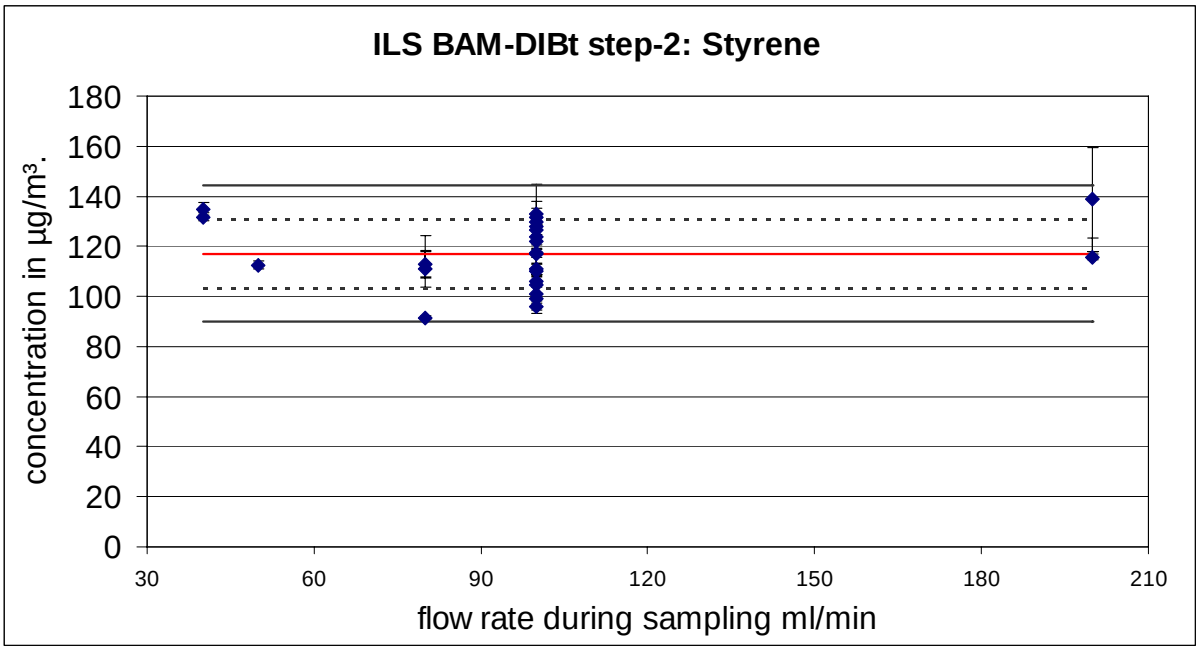

Figure 27: Measured value as a function of sample flow rate

No influence of the sample flow rate can be established from Figure 27 within this range. The same procedure has been applied as in Chapter 2.7 to show the potential dependence on the flow rate in sampling for all sampled components. The relevant mean values of the concentrations were standardised (quotient of group mean value of the considered parameter to general mean). Figure 28 provides a comparative picture of sample flow rates. However, just as in Chapter 2.3 for the comparison of TDS systems, regrettably too many laboratories used the same rate. Thus the statement that the sample flow rates of 100 ml/min are the closest to the mean value, cannot be proved because about 55 % of the data are united and thus potential dispersions are less visible.

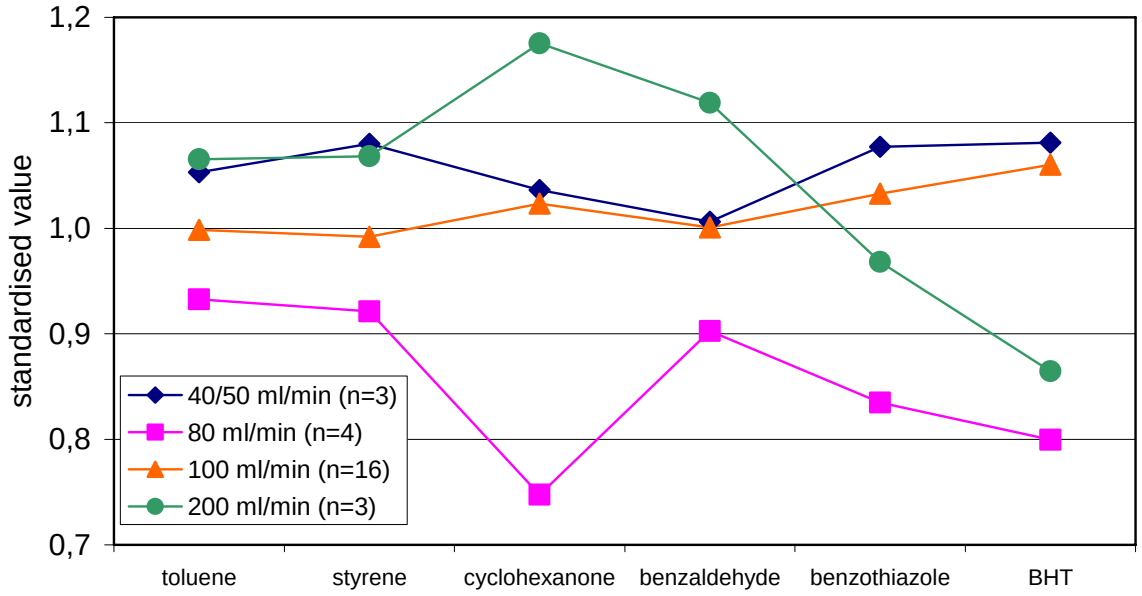

Figure 28: Standardised measured value as a function of flow rate at sampling

With the sample volume collected, there was a greater variance in the range between 1 and 9 litres. Figure 29 has not provided any tendency for a dependence of the measured value on the sampling volume either. It should be noted, however, that the measured value was smallest for the greatest sample volume (9 litres).

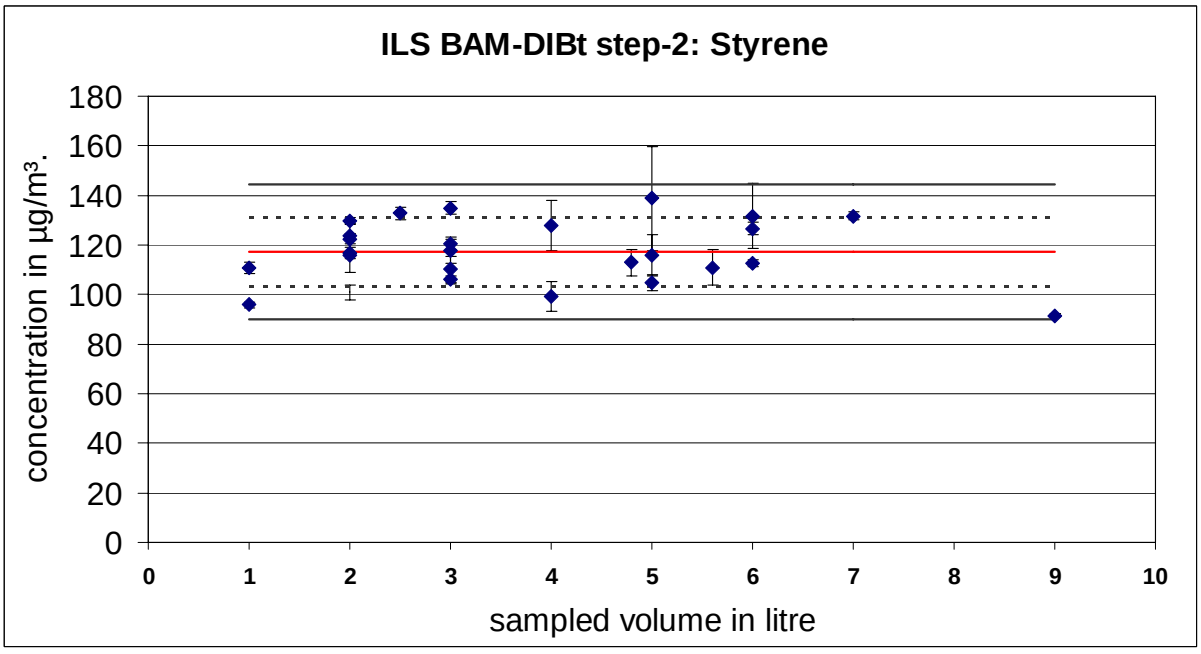

Figure 29: Measured value as a function of sample volume

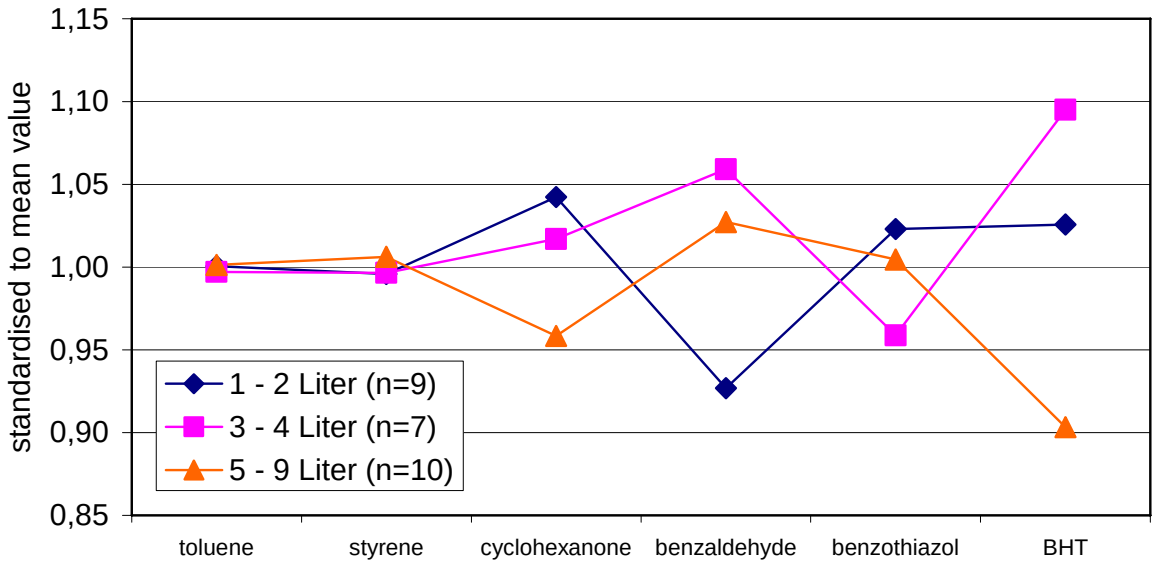

Figure 30: Measured value as a function of the total injected volume at sampling (values standardised to mean value).

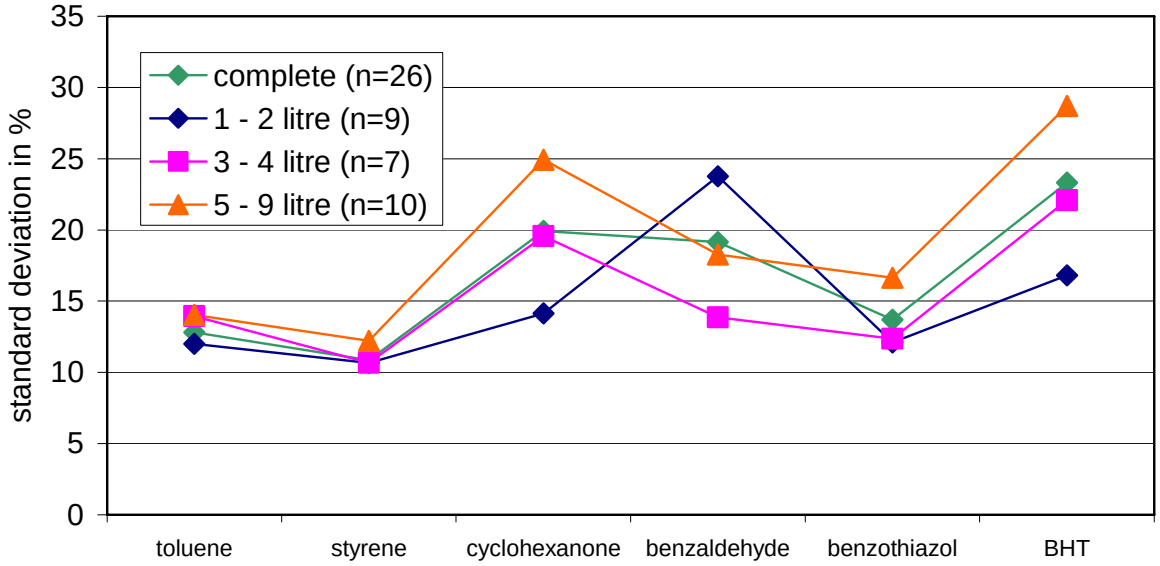

Figure 31: Relative standard deviations of the measured values as functions of the total injected sample volume.

The mean values for different groups of the total sample volume are summarised in figures 30 and 31. It can nevertheless happen that very volatile components break through over-proportionally if the sample volume is too large and this might result in markedly decreased values. Figure 30 shows the standardised concentrations for all key components. However, the most volatile component, i.e. toluene-d_8 fails to exhibit such relationship. But no proof can be established for the other components that either a high or low sample volume may lead to greater deviations. The diagram of the standard deviations for this group (Figure 31) also fails to show distinctive features. It can be concluded that neither sampling speed nor sample volume have a measurable influence on the results if work is performed within the ranges used here.

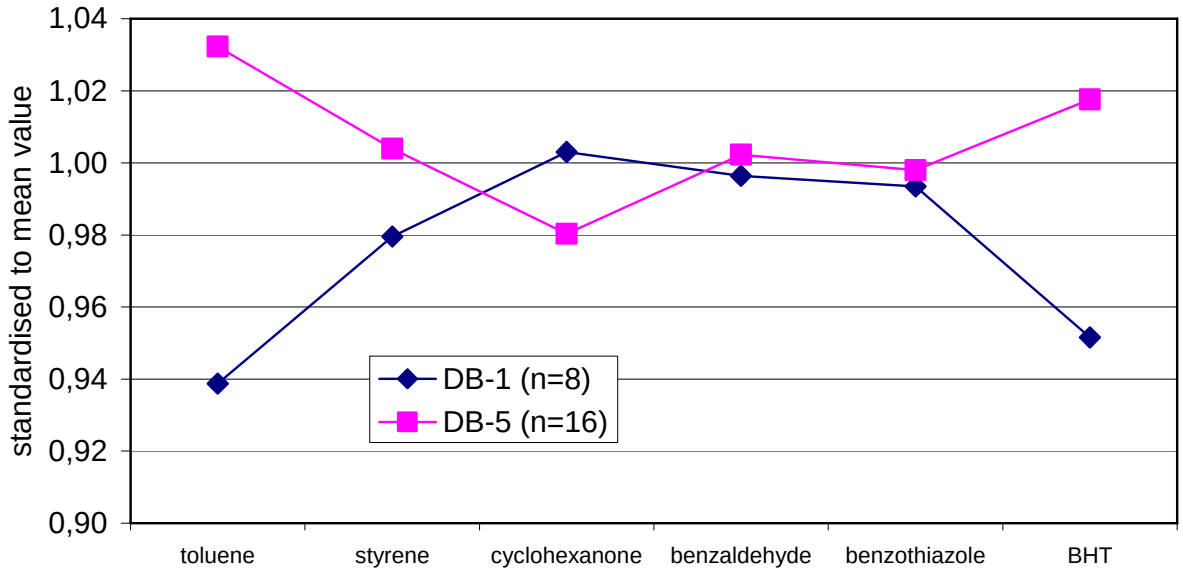

Figure 32: Overview of standardised results of Step 2 of the participants as functions of the GC column used (DB1: non-polar type column, DB5: moderately polar type column).

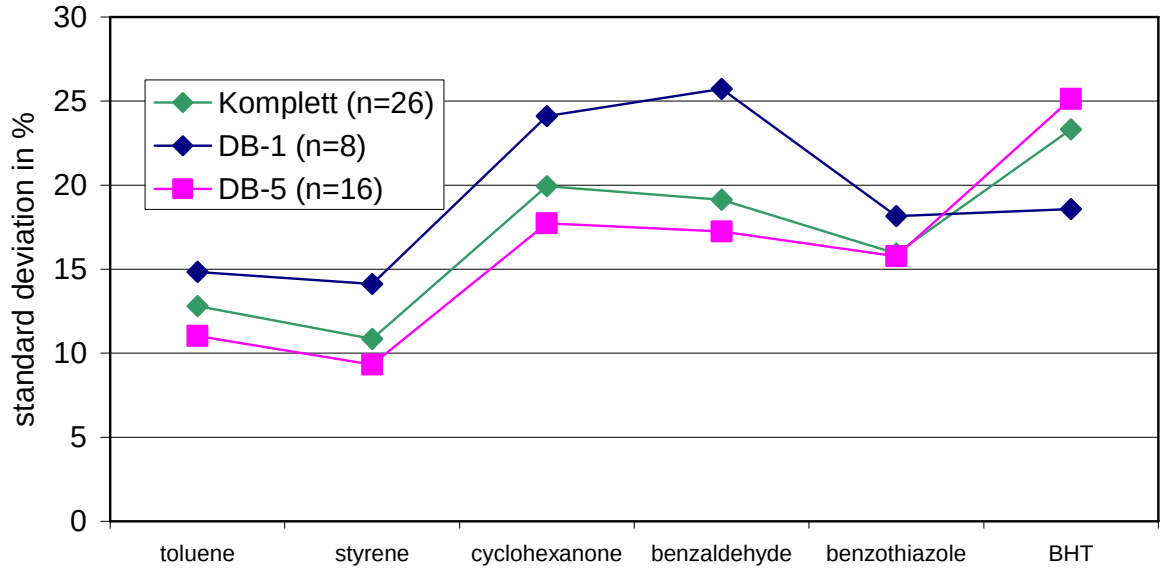

Figure 33: Relative standard deviations of the measured values as functions of the GC column used (DB1: non-polar type column, DB5: moderately polar type column).

Figures 32 and 33 also show the results of the participants for Step 2 as functions of the GC column used. In this case the difference is less marked than in Step 1 (Section 2.7). Since further parameters affect the result in this step (sampling, only 4 loaded tubes measured, transportation, storage time), this could have been expected.

4. Interlaboratory comparison, Step 3

4.1. Preliminary tests, Step 3

The third step of this laboratory comparison was planned using a rubber floor covering. In the preceding steps the target components such as benzothiazole, styrene etc. were selected accordingly. In the phase before dispatching the material to the participants, homogeneity of the material was checked on a number of samples selected from a larger batch of rubber floor tiles from amongst all the packages of the pallets. This test was performed using three different methods. Small disks were taken from the material and tested using a µ-chamber made by Markes, UK (Figure 34). The samples were allowed to emit continuously over 22 hours by flushing the chambers with clean air. Afterwards 2 samples of about 1 litre volume were taken from the air. Figures 36 and 37 show the results of these tests. 4 cells were concurrently placed on two floor covering tiles over two seven-day periods (Figure 35) and 12 chamber measurements were performed on 12 different tiles from different packages. Sampling took place simultaneously after 7 days according to the procedure specified to the participants for the interlaboratory comparison. The initial concentration had subsided markedly by the time the 7th day measurement was taken and the values are highly reproducible.

Figure 34: µ-chamber for disks of floor coverings

Figure 35: Four emission cells placed on a floor covering to test inhomogeneities within the sample.

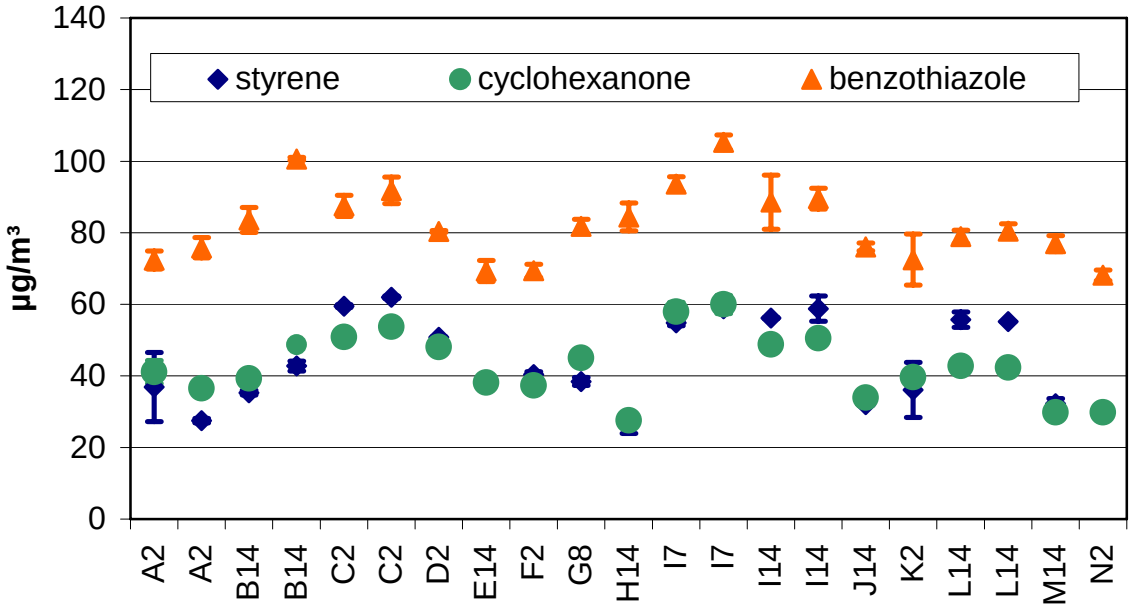

Figure 36: 21 tests from three different emittents 22 h after loading the µ-chamber of 15 disk samples from 14 packing units, results based on double tests.

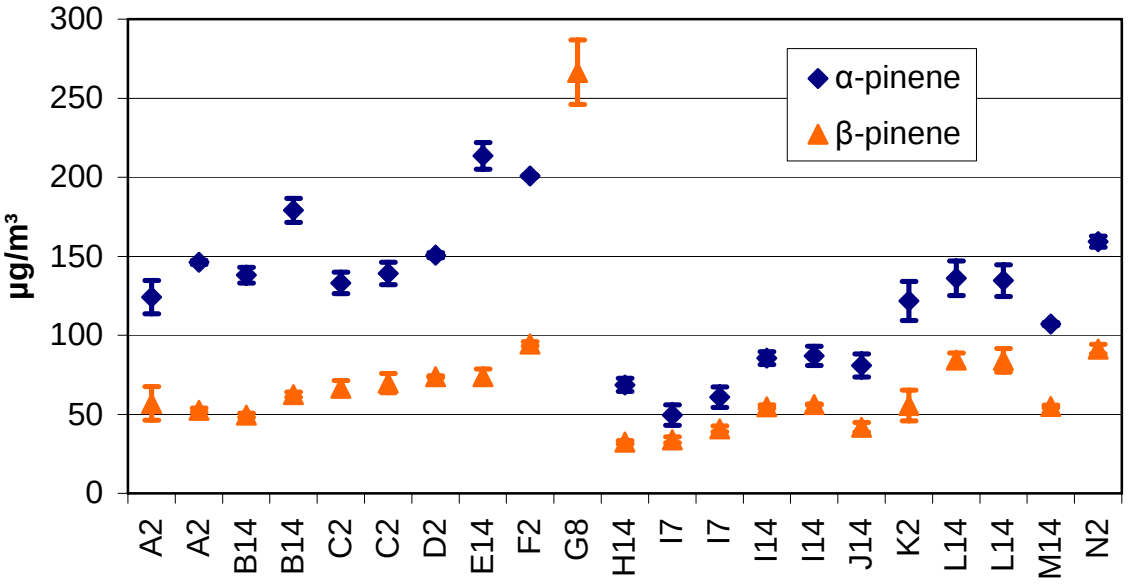

Figure 37: 21 tests on terpene emissions 22 h after loading the µ-chamber of 15 disk samples from 14 packing units, results based on double tests.

The results of the tests illustrated in figures 36 to 39 show a relatively high fluctuation among the tiles. In addition, there was only one compound (benzothiazole, Figure 39) that was detected in a target concentration of approx. 50 µg/m³ after the planned measurement time of 7 days.

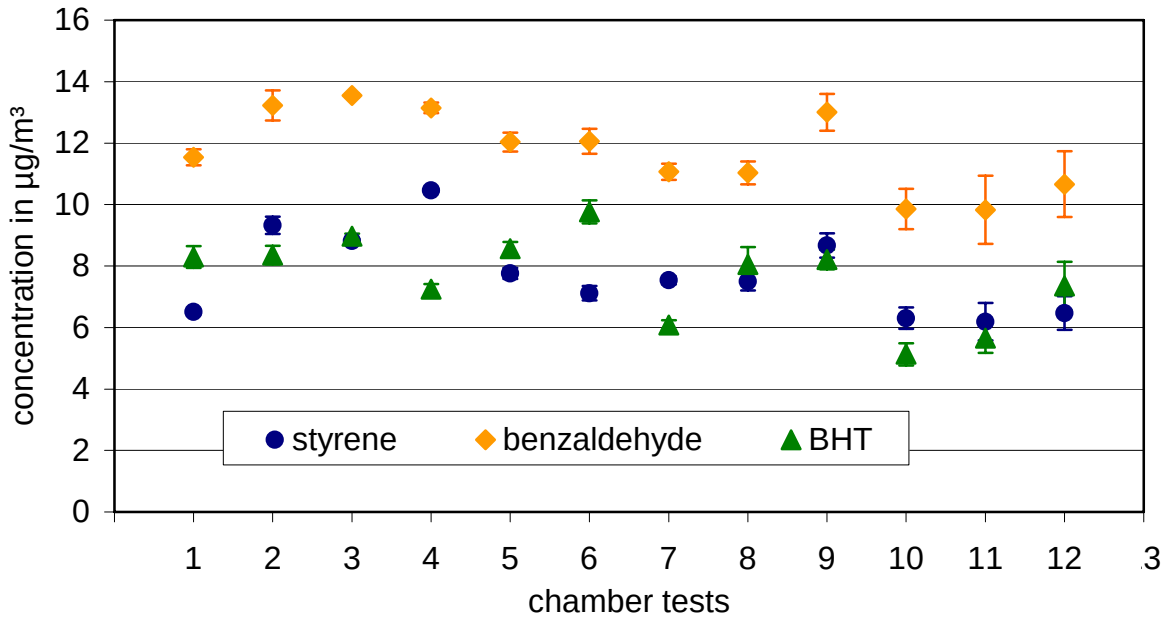

Figure 38: Emission of three different components in 12 chamber measurements, sampling after 7 days.

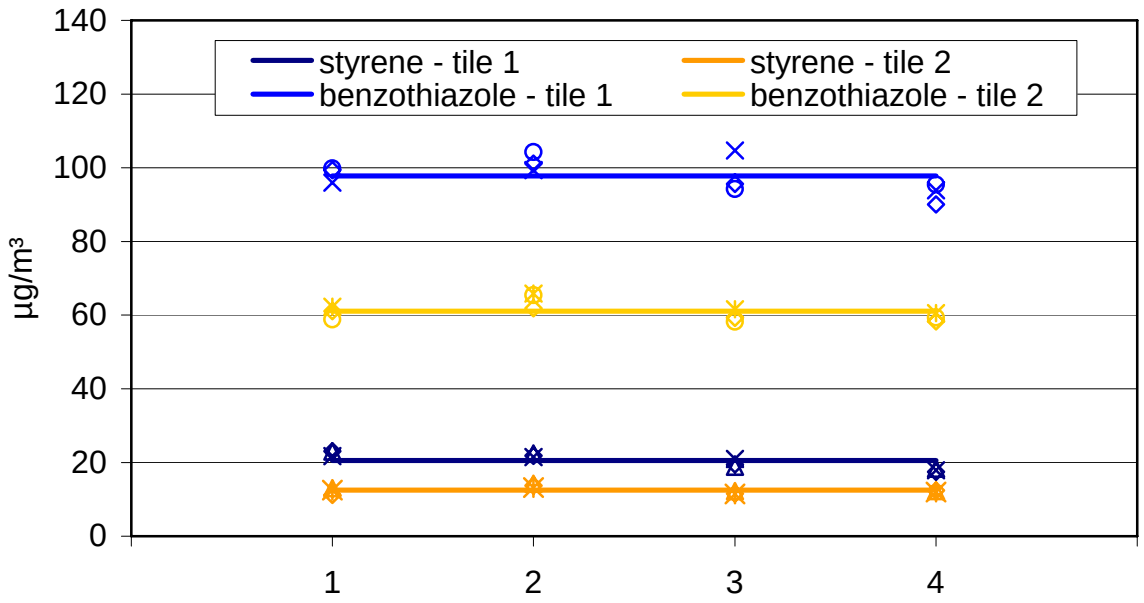

Figure 39: Two different components of two four-fold measurements by placing 4 emission cells (measuring point 1 to 4) on a floor tile, measurement after 7 days.

Components shown in Figure 38 also give a comparable picture. In addition, it can be seen that all other emissions are in the order of magnitude of 10 µg/m³, which is approximately within the range of solution B1 of Step 1 of this interlaboratory comparison. Thus it can be expected that the results are accompanied by a relatively high deviation from the beginning. Figure 39 shows the emissions of two tiles over a period of 7 days. 4 cells were simultaneously placed on a floor covering sample. The 4 measurements of a tile show relatively good agreement, i.e. the tile is largely

homogeneous. The two tiles (one tile has yellow, another blue markings), however, deviate very strongly from each other. By including all these results of homogeneity testing, it was found that the rubber floor covering was not suitable for Step 3 of the interlaboratory comparison. Therefore, it was replaced by another material at short notice which was found very consistent in another small interlaboratory comparison. Thus various acryl sealing compounds were measured in 20-litre chambers, then one species was chosen and procured in sufficient amount.

4.2. Test implementation, Step 3

Since the floor covering designated for the implementation of test chamber measurements exhibited insufficient homogeneity (see 4.1), a sealing compound was selected as a sample material. Each participant received two cartridges of it and a sufficient length of an aluminium standard channel (6 mm flank height and 10 mm breadth).

An area-specific air flow rate of 44 m^3/m^2h was adjusted for the tests. Two 7-day tests took place, either successively in the same chamber or in identically constructed chambers simultaneously. Sampling took place on the 7th day in the form of a four-fold test.

4.3. Quality assurance, Step 3

4.3.1. Homogeneity

To test the homogeneity of the sample material, 12 test chamber measurements were performed by BAM on 12 cartridges from a batch of 100 cartridges in total several weeks before they were dispatched. Figure 40 shows the results for three main components, Table 22 shows the standard deviations of the mean values for all components.

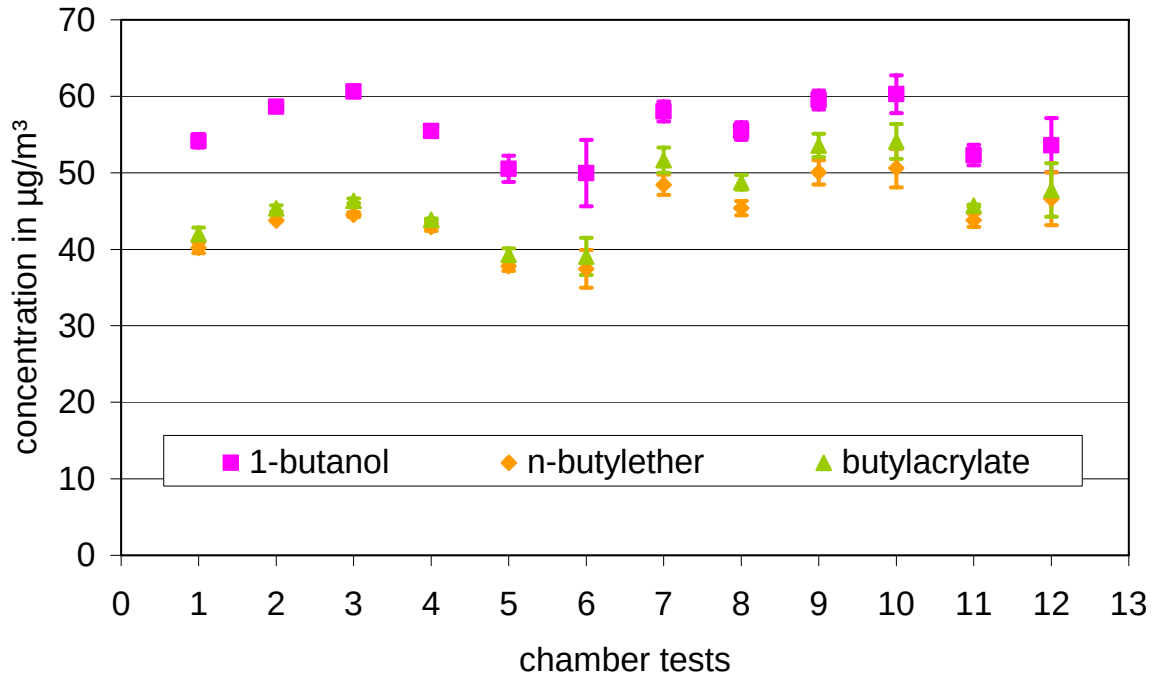

Figure 40: 12-fold measurement of the sealing compounds in 2 x 6 simultaneous test chamber measurements after 7 days

Table 22: Mean value, standard deviation and relative standard deviation of the mean values of 12 test chamber measurements for the sealing compound

Concentration in µg/m³	**Mean**	**Std. Dev..**	**Std. Dev.**	**Median**
	µg/m³	µg/m³	**%**	µg/m³
1-Butanol	56,2	3,4	**6,1**	55,5
1,2-Ethane diol	612,7	52,0	**8,5**	584,5
Butyl acetate	17,7	2,2	**12,3**	17,6
n-Butyl ether	44,9	3,9	**8,7**	44,5
Acrylic acid butyl ester	47,1	4,7	**9,9**	46,3
Propanoic acid butyl ester	9,5	0,8	**7,9**	9,5
Butanoic acid butyl ester	5,6	0,5	**8,5**	5,6

Using variance analysis according to DIN ISO 13528, the results were split into one dispersion group determined by the analysis method and another by potential non-homogeneities among the samples. The estimator for the inhomogeneity component u_{bb} was obtained from these two groups, i.e. estimated according to ISO Guide 35. This has been done in those cases where the medium method dispersion exceeded the dispersion component among the samples. The estimators for the relative inhomogeneity components u_{bb} for the analytes are listed in following table.

Table 23: Relative inhomogeneity components u_{bb} obtained from the homogeneity test under repeatability conditions, and u_{inhom} obtained from the interlaboratory comparison

	1-Butanol	1,2-Ethane diol	Butylacetate	n-Butylester	Acrylic acid butyl ester
u_bb	0,0535	0,0245	0,0568	0,0511	0,0631
u_inhom	0,0535	0,1045	0,0505	0,0641	0,0494

Using the interlaboratory comparison (after carefully expunging the unreliable laboratory results), estimators for the medium repeat dispersion s_r of the laboratories were established from the individual values of the repeat measurements and estimators for the medium intermediate sample dispersion s_{bw} of the laboratories were determined from the sample mean values. From this, based on double determinations of each sample, a post hoc estimator for the inhomogeneity contribution u_{inhom} can be obtained according to

$$u_{in\,\mathrm{hom}}^2 = \frac{2 \cdot s_{bw}^2 - s_r^2}{2}$$

The values are also contained in the table and show good agreement with the results of the homogeneity test (exception is 1,2-ethanediol, due to the extraordinarily large repeat dispersion for this analyte). On average, the uncertainty component due to potential inhomogeneity does not exceed 5-6 %.

The DIN ISO 13528 criterion that potential sample inhomogeneity must not constitute more than 1/3 of total uncertainty, is thus fulfilled.

4.3.2. Control tubes for the chamber test

In addition to their own tubes, the participants sampled two tubes during one of the two chamber tests. These tubes were sent to BAM and analysed and quantified by BAM.

Table 24: Results for BAM's control tubes (measurement in the participants' test chambers): mean value, standard deviation of the mean values, median and number of participants considered

Compound	**Mean**	**Std. Dev.**	**Std. Dev.**	**Median**	**Number**
	µg/m³	µg/m³	**%**	µg/m³	
1-Butanol	63	11	**17**	61	27
1,2 Ethane diol	656	182	**28**	652	27
Butyl acetate	20	3	**17**	20	27
Dibutyl ether	54	9	**16**	54	27
Acrylic acid butyl ester	53	9	**17**	51	27
Propanoic acid butyl ester	12	2	**17**	12	27
Butanoic acid butyl ester	7	1	**19**	7	27

4.4. Results, Step 3

4.4.1. Results of the test chamber measurements

Table 25 shows the mean value, standard deviation of the mean values and median for the individual substances of the sealing compound. Here all results provided by the participants were considered, the values are thus not outlier-cleaned.

Table 25: Results of Step 3, 1st chamber measurement; mean value, standard deviation of the mean values, median and number of participants considered.

Compound	**Mean**	**Std. Dev..**	**Std. Dev.**	**Median**	**Number**
	µg/m³	µg/m³	**%**	µg/m³	
1-Butanol	58	10	**18**	58	28
1,2 Ethane diol	499	324	**65**	475	27
Butyl acetate	17	4	**21**	18	28
Dibutyl ether	42	8	**18**	41	28
Acrylic acid butyl ester	41	8	**19**	40	28
Propanoic acid butyl ester	7	3	**47**	5	27
Butanoic acid butyl ester	4	2	**39**	4	25

Table 26: Outlier-cleaned results of Step 3, 1st chamber measurement; mean value, standard deviation of the mean values, median and number of participants considered.

Compound	**Mean**	**Std. Dev..**	**Std. Dev.**	**Median**	**Number**
	µg/m³	µg/m³	**%**	µg/m³	
1-Butanol	58	11	**19**	58	28
1,2 Ethane diol	429	175	**41**	452	25
Butyl acetate	18	4	**22**	18	28
Dibutyl ether	42	8	**19**	41	28
Acrylic acid butyl ester	41	8	**19**	40	28
Propanoic acid butyl ester	6	3	**47**	5	26
Butanoic acid butyl ester	4	2	**41**	4	24

Table 27: Results for Step 3, 2nd chamber measurement; mean value, standard deviation of mean values, median and number of participants considered.

Compound	Mean	Std. Dev..	Std. Dev.	Median	Number
	µg/m³	µg/m³	%	µg/m³	
1-Butanol	60	12	**20**	58	28
1,2 Ethane diol	482	281	**58**	495	27
Butyl acetate	17	3	**19**	17	28
Dibutyl ether	43	9	**20**	42	28
Acrylic acid butyl ester	42	8	**20**	41	28
Propanoic acid butyl ester	6	3	**48**	5	27
Butanoic acid butyl ester	4	2	**44**	4	25

Table 28: Outlier-cleaned results for Step 3, 2nd chamber measurement; mean value, standard deviation of mean values, median and number of participants considered.

Compound	Mean	Std. Dev..	Std. Dev.	Median	Number
	µg/m³	µg/m³	%	µg/m³	
1-Butanol	59	12	**20**	58	26
1,2 Ethane diol	452	136	**30**	492	26
Butyl acetate	17	3	**19**	17	26
Dibutyl ether	43	9	**21**	42	26
Acrylic acid butyl ester	42	8	**20**	41	26
Propanoic acid butyl ester	6	2	**30**	5	23
Butanoic acid butyl ester	4	1	**30**	4	23

Table 29: Results for Step 3, both chamber measurements; mean value, standard deviation of mean values, median and number of participants considered.

Compound	Mean	Std. Dev..	Std. Dev.	Median	Number
	µg/m³	µg/m³	%	µg/m³	
1-Butanol	59	10	**17**	58	28
1,2 Ethane diol	492	298	**61**	486	27
Butyl acetate	17	3	**19**	18	28
Dibutyl ether	42	8	**18**	43	28
Acrylic acid butyl ester	41	8	**19**	42	28
Propanoic acid butyl ester	6	3	**46**	5	27
Butanoic acid butyl ester	4	2	**43**	4	25

Table 30: Outlier-cleaned results for Step 3, both chamber measurements; mean value, standard deviation of mean values, median and number of participants considered.

Compound	Mean	Std. Dev..	Std. Dev.	Median	Number
	µg/m³	µg/m³	%	µg/m³	
1-Butanol	58	10	**18**	56	24
1,2 Ethane diol	424	167	**39**	472	22
Butyl acetate	17	4	**20**	18	26
Dibutyl ether	40	5	**14**	41	21
Acrylic acid butyl ester	41	8	**19**	40	25
Propanoic acid butyl ester	6	3	**46**	5	24
Butanoic acid butyl ester	4	2	**39**	4	19

The test chamber measurements show a low standard deviation of the mean values for the four key substances which lie in the concentration range between 17 µg/m^3 and 60 µg/m^3. The relative standard deviation for butanol, butyl acetate, butyl ether and acrylic acid butylester is between 14 % and 22 % and there is hardly any difference with and without outlier-cleaning.

For ethanediol the relative standard deviation of the mean values with up to 65 % is high, as expected, since this substance shows a poorly formed peak in gas chromatography on the one hand and on the other, using Tenax for sampling this polar substance is not optimal. After expunging the outliers the relative standard deviation is about 40 %.

Two substances, propanoic acid and butanoic acid butylester, with low concentrations of between 4 and 6 µg/m³, exhibit standard deviations between 39 and 46 %. They are standard deviations that in principle can be expected at such low concentrations, also according to Kromidas (Section 2.5).

4.4.2. Evaluation according to Youden

In this section the results of Step 3 from two test chamber measurements of each participant are illustrated in the form of a Youden plot (Funk et al., 2005). The results for Chamber 1 are plotted against those of Chamber 2 in a coordinate system. The values generally lie on the bisector, i.e. they show good reproducibility of the chamber measurements in one laboratory. Unfortunately, since no reference value is available, the deviations of the laboratories can only be considered in relation to the results of all participants. Nor can the precision of the participants be determined as in the first step evaluation. Generally, it cannot also be assumed that exactly the same material was tested in all cases in both chamber tests. A high degree of homogeneity was obtained, but differences between two sealing compounds with one participant cannot be excluded.

Laboratory 9 is conspicuous because it lies outside the ellipse for 4 of the 5 key substances (three-fold standard deviation), which means it is an outlier.

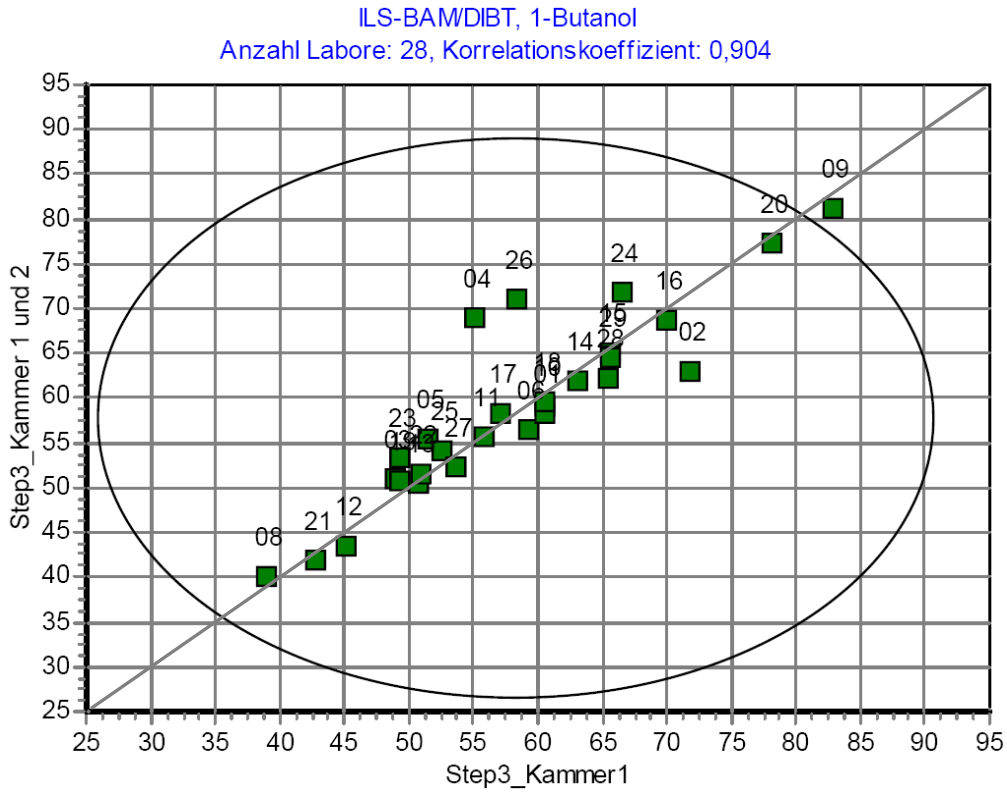

Figure 41: Youden plot, Chamber 1 against 2, butanol

Figure 42 shows the measured concentration values for the component ethanediol. The values look as though they approach the bisector well. However, it can be also seen that the range covered goes from 0 to 700 µg/m^3, thus lateral outliers are less conspicuous.

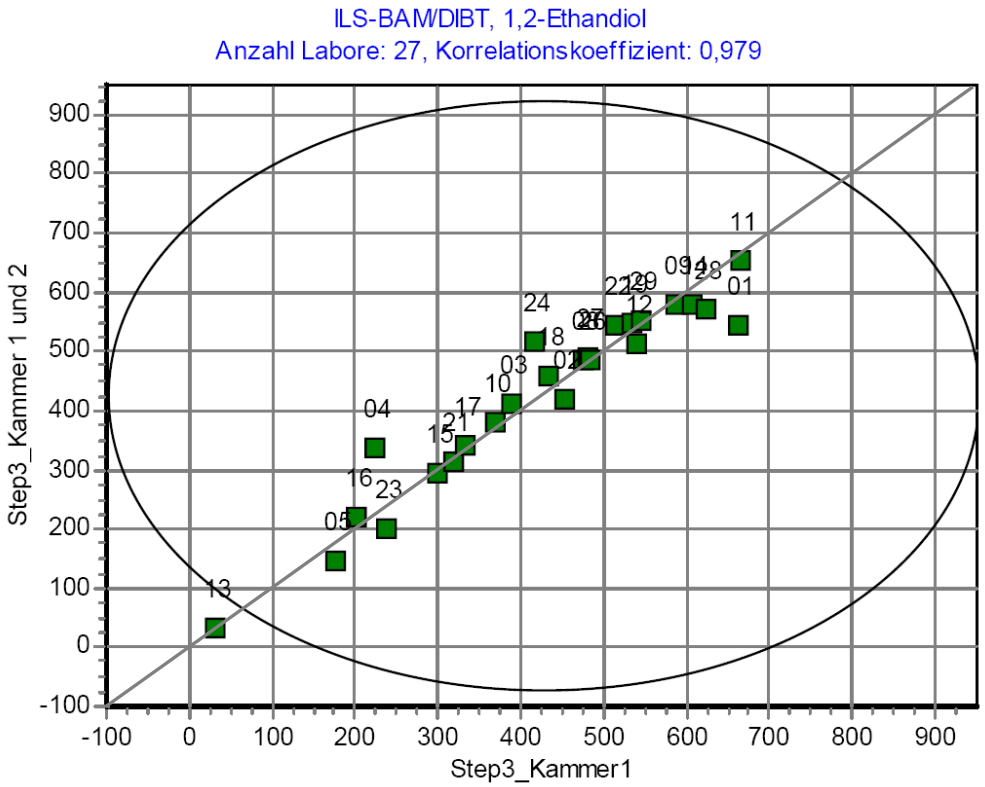

Figure 42: Youden plot, Chamber 1 against 2, ethanediol

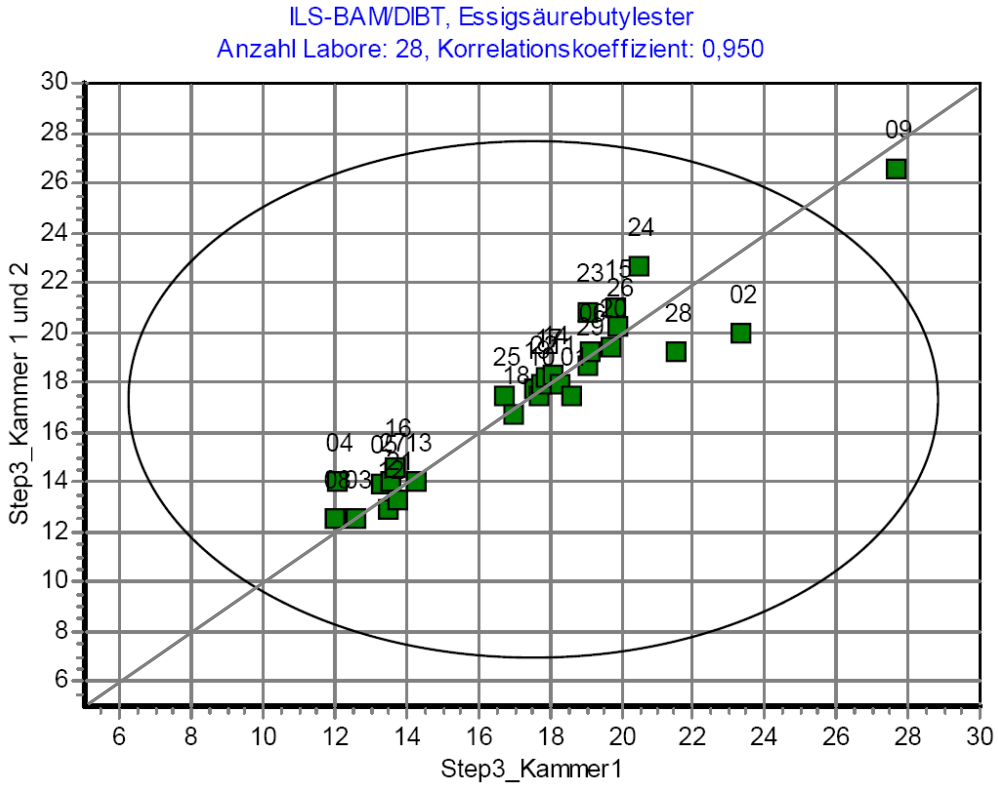

Figure 43: Youden plot, Chamber 1 against 2, acetic acid butylester

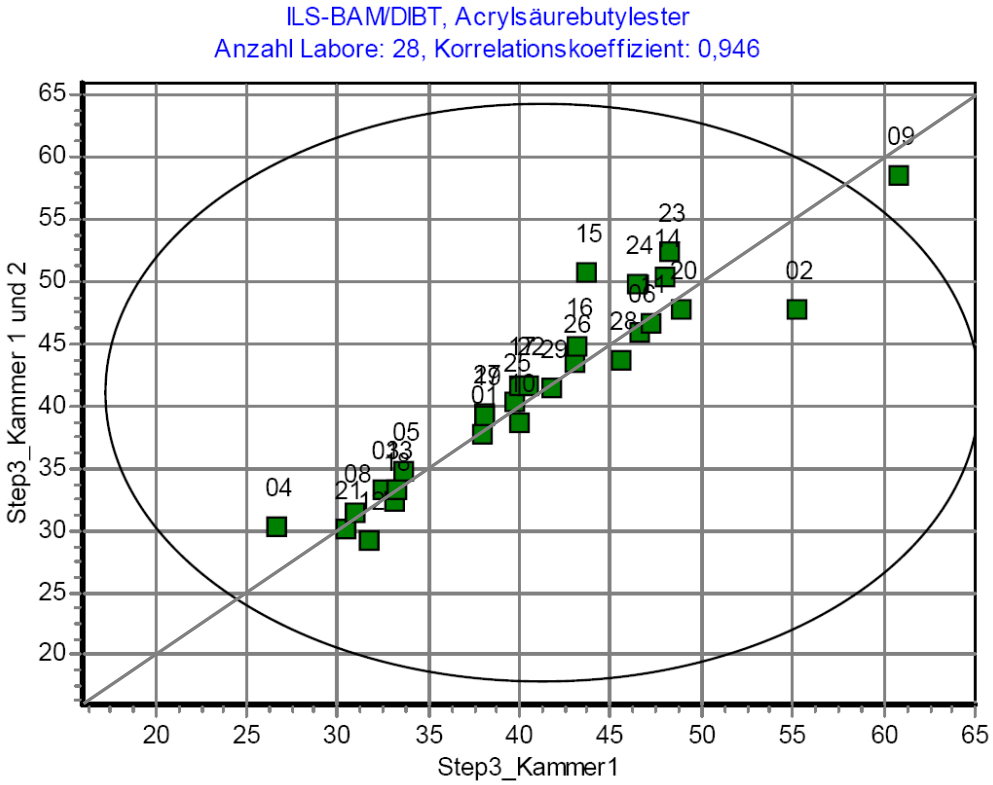

Figure 44: Youden plot, Chamber 1 against 2, acrylic acid butylester

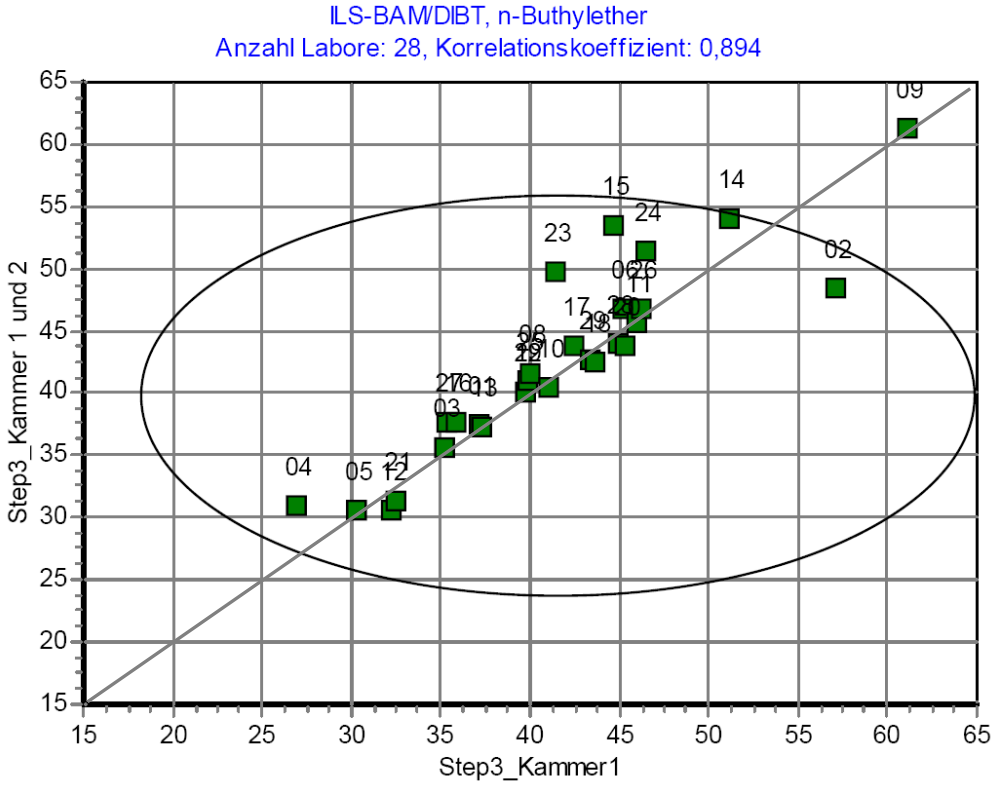

Figure 45: Youden Plot, Chamber 1 against 2, n-butyl ether

4.5. Z scores, Step 3

As for Steps 1 and 2, z score evaluations were also carried out for Step 3. They are illustrated in 46 to 48 and indicate that the standard deviation for the calculation of z scores (see Formula 1) was limited to a maximum of 30 % (see Section 2.5). The limitation had to be carried out for ethanediol (from 39 to 30 %), propionic acid butylester (from 46 to 30 %) and butanoic acid butylester (from 39 to 30 %).

Only three laboratories out of 25 provided unreliable values in Step 3 individually for Chambers 1 and 2 and for the sum of Chambers 1 and 2 for ethanediol, this is however, a "difficult" substance to quantify (using the stipulated method). One laboratory's z score exceeded 3, but only in the calculation of the z scores for Chamber 1 and 2 together, which is probably due to the differences in the results between the chambers. These were not exceeded individually considering the z scores for Chamber 1 and 2.

The z scores were calculated for Chamber 1 and 2 together (see Figure 48) for propionic acid butylester and for butanoic acid butylester, whose concentration is around 5 µg/m^3, Despite the very low concentration and considerably more difficult quantification, only three laboratories out of 26 provided unreliable values for butanoic acid butylester and one laboratory for propionic acid butylester.

Summing up, it should be emphasised that most z scores that exceeded 3 occurred in the case of the "difficult-to-quantify" ethanediol and the two substances present in a low concentration range (butanoic acid butylester and propionic acid butylester).

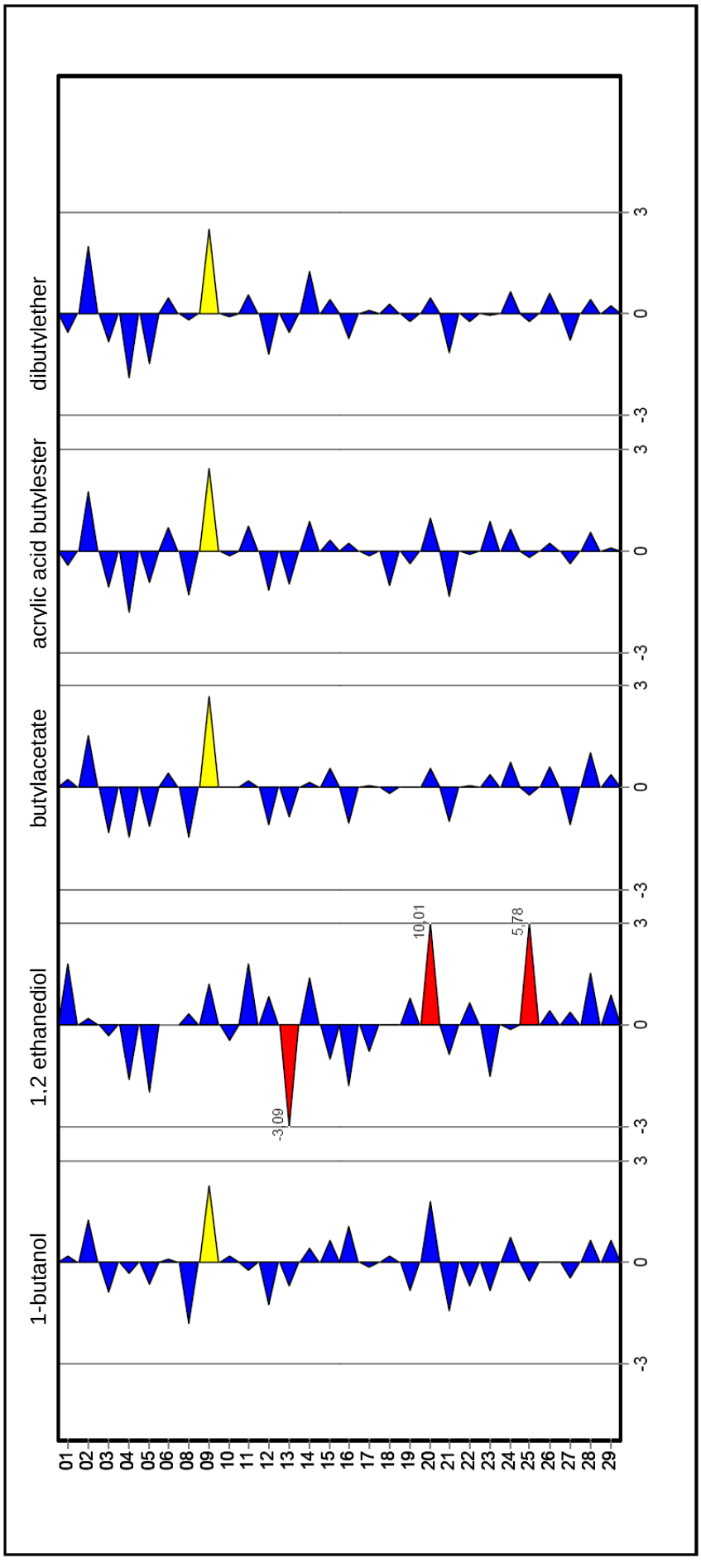

Figure 46: Z scores for Step 3 (Chamber 1, five key substances), standard deviation maximum 30 %

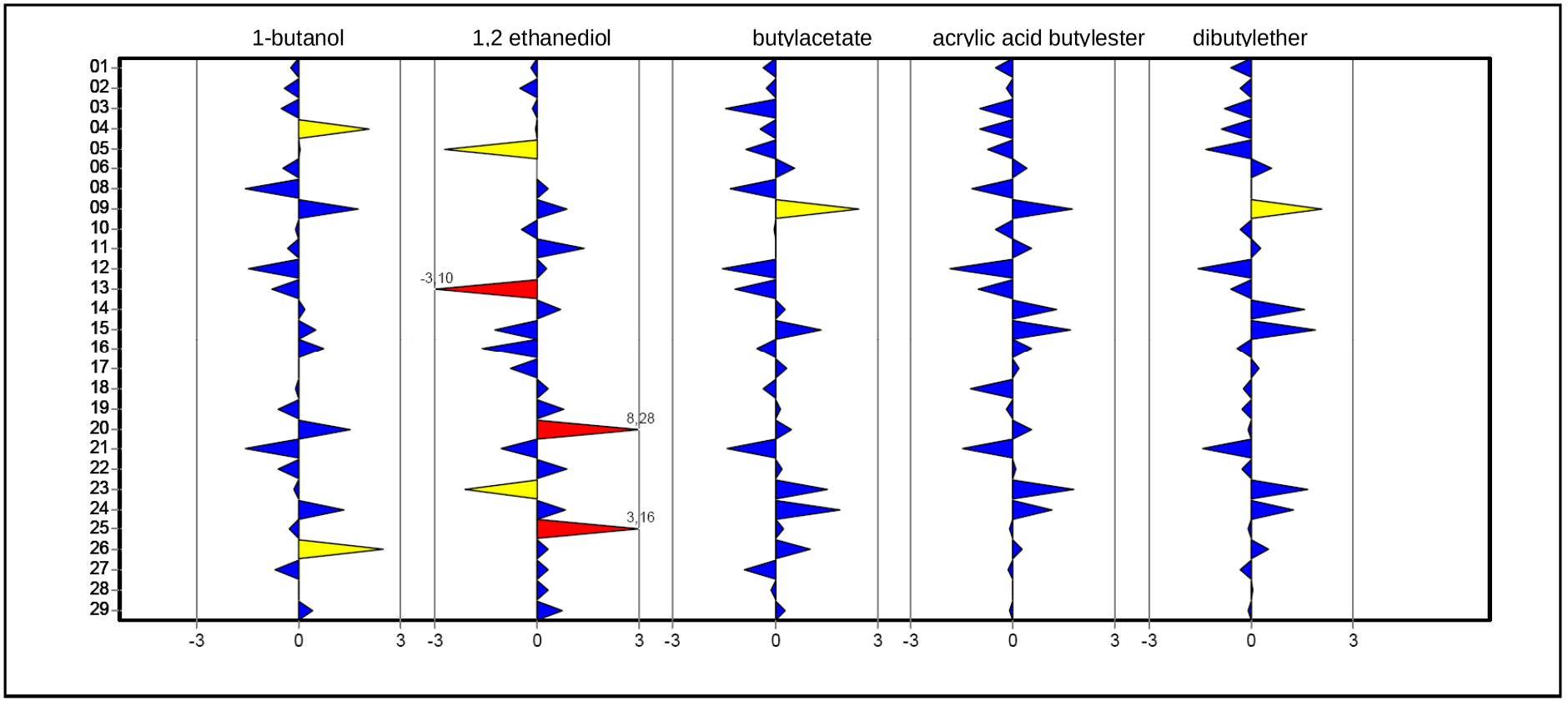

Figure 47: Z scores for Step 3 (Chamber 2, five key substances), standard deviation maximum 30 %

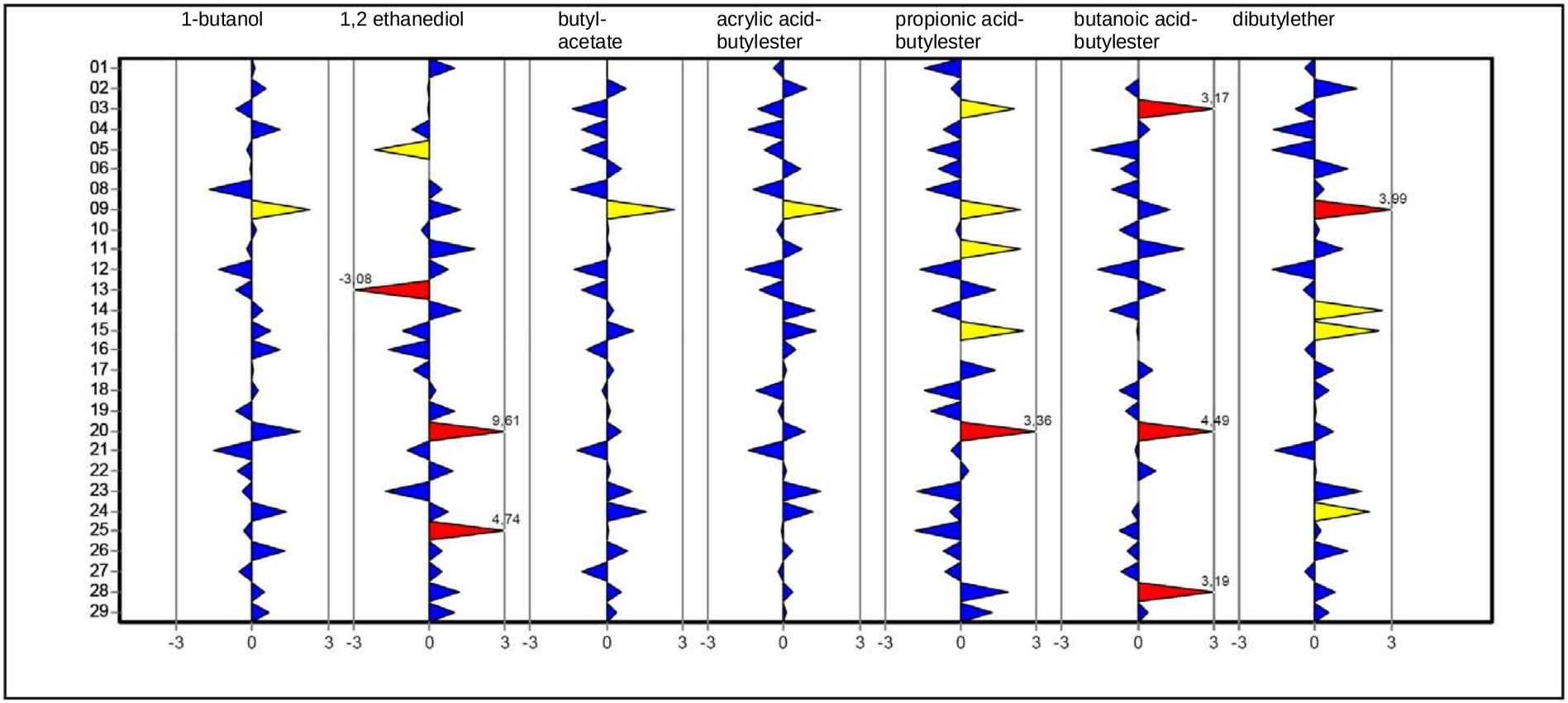

Figure 48: Z scores for Step 3 (Chambers 1+2, seven substances), standard deviation maximum 30 %

4.6. Measurement uncertainty, Step 3

Table 31 and Table 32 illustrate the differences in considering the relative medium systematic deviations or measurement uncertainties of the laboratories for all substances before and after expunging the outliers and are likewise low as in Step 1 and Step 2. The large relative medium systematic deviation or measurement uncertainty of Laboratory 9 is due to very large fluctuations and deviations in the mean value for nearly all analytes.

Table 31: Relative medium systematic deviation or measurement uncertainty of one laboratory for all substances in Step 3 related to the mean value with outliers

Laboratory	7 Compounds		5 Compounds		2 Compounds	
	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 20 bis 440 µg**	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 5 bis 440 µg**	Anzahl	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 20 bis 440 µg**	Number
1	65	6	58	5	90	1
2	70	6	75	5	39	1
3	81	7	37	5	140	2
4	46	7	50	5	36	2
5	69	7	67	5	73	2
6	37	6	28	4	50	2
7						
8	42	7	34	5	56	2
9	122	2	109	1	146	1
10	26	7	17	5	40	2
11	74	6	60	5	120	1
12	68	7	52	5	96	2
13	53	6	28	4	84	2
14	63	7	59	5	72	2
15	46	6	42	5	60	1
16	59	5	59	5		0
17	43	7	26	5	69	2
18	38	7	21	5	63	2
19	39	7	29	5	56	2
20	53	4	53	4		0
21	43	7	49	5	19	2
22	31	7	28	5	38	2
23	69	7	58	5	89	2
24	39	7	41	5	31	2
25	41	6	18	4	67	2
26	33	7	33	5	34	2
27	33	7	26	5	47	2
28	76	6	55	5	141	1
29	47	7	36	5	68	2

Table 32: Relative medium systematic deviation or measurement uncertainty of one laboratory for all substances in Step 3 related to the mean value without outliers

Laboratory	7 Compounds		5 Compounds		2 Compounds	
	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 20 bis 440 µg**	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 5 bis 440 µg**	Number	$\overline{s}_{Lab}$ [%] (all compounds, Laboratory) **Konc. 5 µg**	Number
1	65	6	58	5	90	1
2	70	6	75	5	39	1
3	81	7	37	5	140	2
4	46	7	50	5	36	2
5	69	7	67	5	73	2
6	37	6	28	4	50	2
7						
8	42	7	34	5	56	2
9	122	2	109	1	146	1
10	26	7	17	5	40	2
11	74	6	60	5	120	1
12	68	7	52	5	96	2
13	53	6	28	4	84	2
14	63	7	59	5	72	2
15	46	6	42	5	60	1
16	59	5	59	5		0
17	43	7	26	5	69	2
18	38	7	21	5	63	2
19	39	7	29	5	56	2
20	53	4	53	4		0
21	43	7	49	5	19	2
22	31	7	28	5	38	2
23	69	7	58	5	89	2
24	39	7	41	5	31	2
25	41	6	18	4	67	2
26	33	7	33	5	34	2
27	33	7	26	5	47	2
28	76	6	55	5	141	1
29	47	7	36	5	68	2

Table 33: Relative medium systematic deviation or measurement uncertainty of all laboratories for one substance in Step 3

Compound:	**Mean:**	**Std. dev.:**	$\overline{s}_{sub}$ **rel. Std. dev.:**
1-Butanol	59,8	22,8	41
1,2-Ethane diol	436,8	310,2	73
Butyl acetate	17,9	7,7	46
n-Butyl ether	42,3	14,3	36
Acrylic acid butyl ester	42,0	16,6	42
Propionic acid butyl ester	5,8	5,4	87
Butanoic acid butyl ester	3,9	2,6	62

The high relative medium systematic deviation or measurement uncertainty of 73 % in all laboratories for ethanediol is due to it being a "difficult substance", i.e. this analysis method is not optimal for this substance, but which could be improved using another GC column and similar corrections.

The high relative medium systematic deviation or measurement uncertainty of all laboratories for propionic acid butylester and butanoic acid butylester can be justified because of the very small concentrations of approx. 5 µg/m^3 as in Step 1 and Step 2.

Table 34 shows the standard deviation of the entire method, i.e. for different chambers, different laboratory personnel and with different laboratory equipment for analysis. Its value for all seven substances in the concentration range of 5 µg/m^3 to 440 µg/m^3 is 57 %. The measurement uncertainty of those five substances at higher concentrations (17 µg/m^3 to 440 µg/m^3) is 49 %. For the two analytes in small concentrations (approx. 5 µg/m^3) a measurement uncertainty of 78 % was found.

Table 34: Relative medium systematic deviation or measurement uncertainty of all laboratories for all substances in Step 3

Step 3	**7 Compounds Konc. ca. 20 bis 440 µg/m^3**	**5 Compounds Konc. ca. 20 bis 440 µg/m^3**	**2 Compounds Konc. ca. 5 µg/m^3**
$\overline{S}'_{Sub,Lab}$ **Standard deviation in %:**	57	49	78
Number of results	178	132	46

On expunging the standard deviations of Laboratory 9 (because of excessively high deviations), the total measurement uncertainty of the method decreases from 57 % to 53 % for all seven analytes, from 49 % to 45 % for the five substances at higher concentrations and from 78 % to 74 % for the two substances at low concentrations.

Table 35: Relative medium systematic deviation or measurement uncertainty of all laboratories for all substances in Step 3 without Laboratory 9

Step 3	**7 Compounds Konc. ca. 20 bis 440 µg/m^3**	**5 Compounds Konc. ca. 20 bis 440 µg/m^3**	**2 Compounds Konc. ca. 5 µg/m^3**
$\overline{S}'_{Sub,Lab}$ **Standard deviation in %:**	53	45	74
Number of results	176	131	45

4.7. Findings, Step 3

An important finding from the interlaboratory comparison is that the equipment used exhibits a very large bandwidth both concerning the analytical devices and the test chambers. Table 36 shows a list of the gas chromatographs, thermodesorption units and capillary columns used by the participants. Table 37 shows the different chamber parameters of the participants. Although the area-specific air flow rate is q = 44 m^2/m^3h in nearly all cases, loading factor and air flow rate vary extensively. The chamber volume ranges from 20 to 1000 litres.

Table 36: Overview of analytical devices and capillary columns of the participants in Step 3 (equipment not sorted according to participant number)

GC	TDS	Column	Length	Diameter.	Thickness.
Agilent	Perkin Elmer	DB-1	50 m	0,2 mm	0,5 µm
Agilent	Perkin Elmer	DB-1	30 m	0,25 mm	0,25 µm
Agilent	Markes	DB-1	25 m	0,32 mm	3,0 µm
Agilent	Perkin Elmer	DB-1	50 m	0,2 mm	0,33 µm
Agilent	Dani	DB-1	50 m	0,2 mm	0,5 µm
Agilent	Gerstel	DB-1	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	1 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	1 µm
Agilent	Markes	DB-5	50 m	0,32 mm	1 µm
Agilent	Gerstel	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	50 m	0,2 mm	0,33 µm
Shimadzu	Perkin Elmer	DB-5	60 m	0,25 mm	1,0 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	0,5 µm
Agilent	Perkin Elmer	DB-5	50 m	0,32 mm	0,52 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	50 m	0,2 mm	0,33 µm
Agilent	Perkin Elmer	DB-5	60 m	0,32 mm	0,5 µm
Shimadzu	Markes	DB-5	60 m	0,25 mm	0,25 µm
Shimadzu	Perkin Elmer	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	1 µm
Agilent	Perkin Elmer	DB-200	60 m	0,32 mm	1 µm
Perkin Elmer	Perkin Elmer	DB-1701	50 m	0,22 mm	0,25 µm
Agilent	Gerstel	DB-624	60 m	0,32 mm	1,8 µm
Varian	Perkin Elmer	DB-624	30 m	0,25 mm	1 µm

Table 37: Chamber parameters of the participants for Step 3 (not sorted according to participant number)

Chamber-volume	Sample-surface	air change-rate	Loading-factor	Area specific air flow rate q
Liter	cm^2	h^{-1}	m^2/m^3	m^3/m^2h
20	28	6,25	0,14	44
20	3	0,60	0,01	44
21	6	1,25	0,03	43
22	15	3,00	0,07	44
23	15	3,00	0,07	44
51	50	4,34	0,10	44
85	68	3,53	0,08	44
100	11	0,50	0,01	44
119	14	0,50	0,01	44
125	14	0,50	0,01	44
200	100	2,20	0,05	44
225	50	0,86	0,02	38
225	51	1,00	0,02	44
225	26	0,50	0,01	44
250	28	0,50	0,01	44
250	28	0,50	0,01	44
450	52	0,50	0,01	43
980	227	1,00	0,02	43
1000	114	0,50	0,01	44
1000	227	1,00	0,02	44
1000	208	0,91	0,02	44
1000	227	1,00	0,02	44
1000	227	1,00	0,02	44
1000	114	0,50	0,01	44
1000	227	1,00	0,02	44
1000	114	0,50	0,01	44
1000	227	1,00	0,02	44
1000	227	1,00	0,02	44

An attempt was made to characterise the possible important parameters using the respective results of the institutes based on the measurement parameters summarised in Tables 35 and 36. The potential influences are described below using the example of GC columns, TDS systems and sample volume.

Figure 49 shows the potential influence of GC columns as in the preceding sections for Steps 1 and 2. It can be seen that columns of type DB5 provide values that are somewhat closer to the general mean, while nearly all columns of type DB1 exhibit higher values. However, the statement in this case is not as clear as in Step 1, since there is no reference value, only the mean value being available. The columns used more frequently thus had greater influence on the mean value. No difference can be observed in the case of the component ethanediol, the relative standard deviation of this compound for both column types is equally high as indicated by Figure 50. For the other compounds the standard deviation is somewhat smaller for the DB-5 columns.

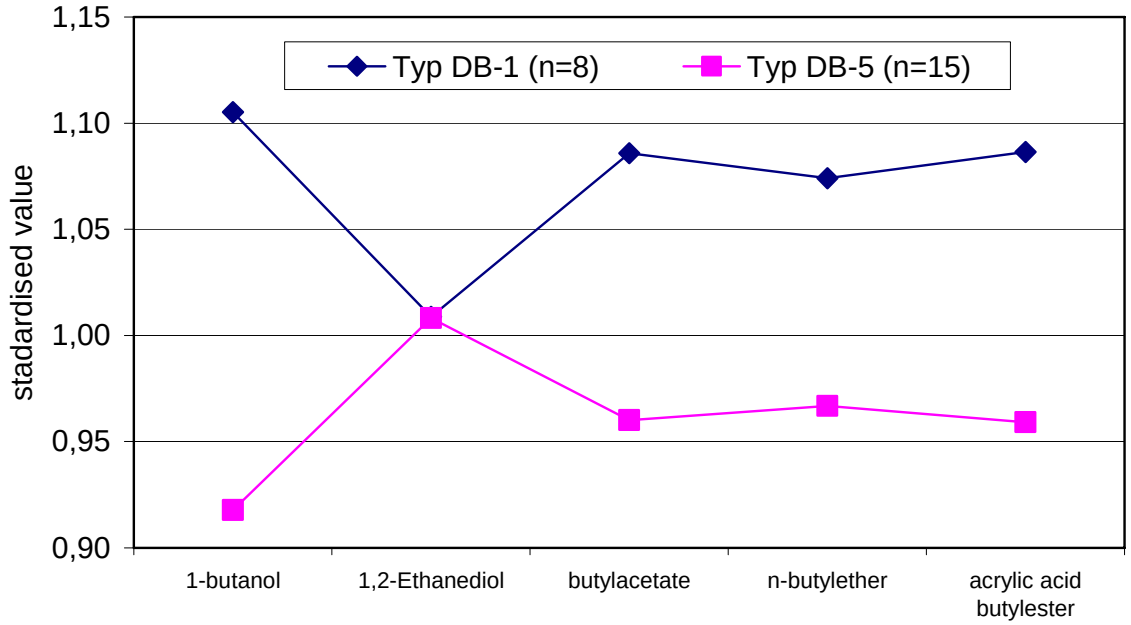

Figure 49: Measured values (standardised) as functions of column types used: DB-1 and DB-5.

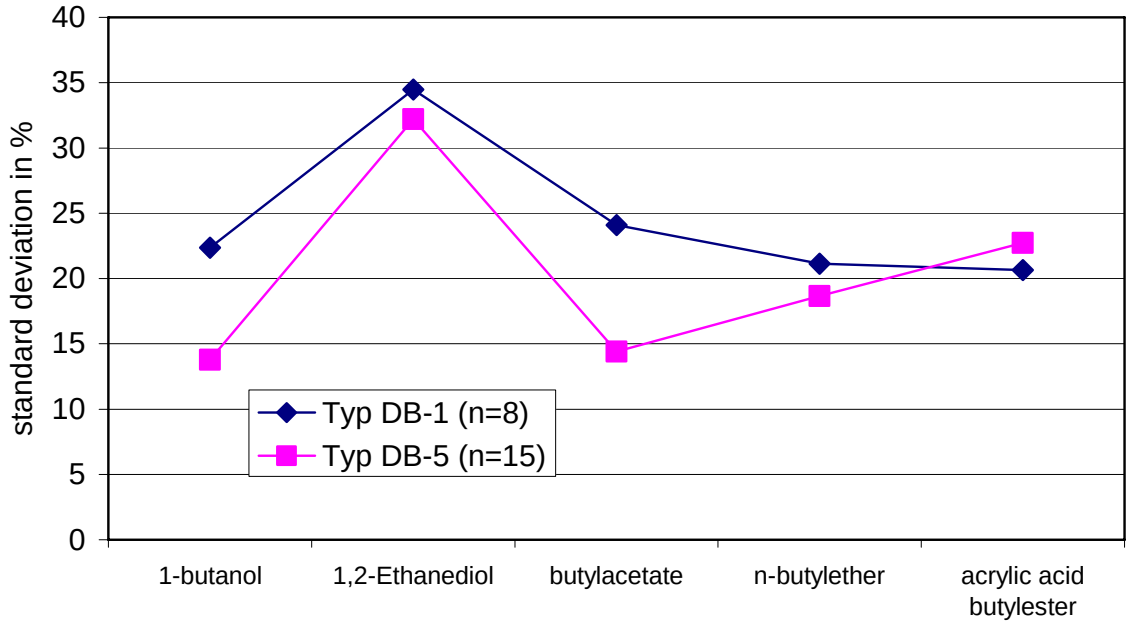

Figure 50: Differences of the relative standard deviation in % for the column types used: DB-1 and DB-5.

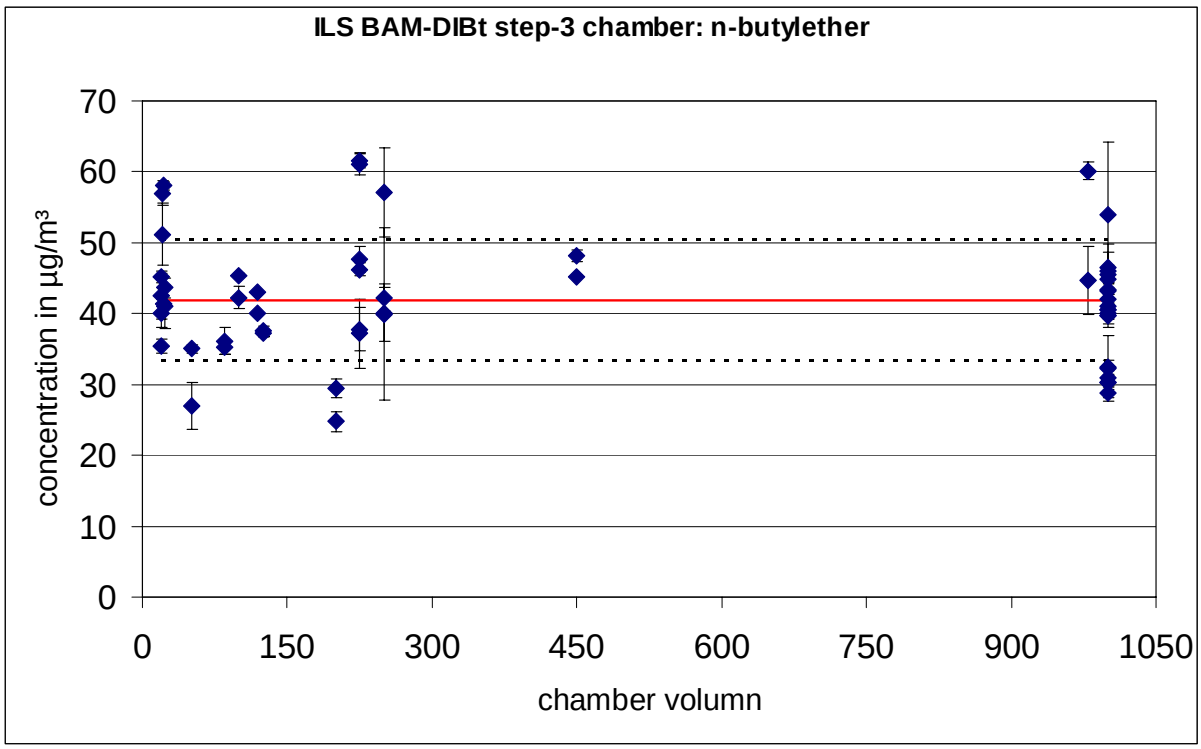

Figure 51: Measured values as functions of test chamber size (volume between 0.02 m³ and 1.0 m³)

Figure 51 shows the measured values as functions of chamber size using the example of butyl ether. An influence due to test chamber size cannot be recognised. Figure 52 displays the results for all 5 key components, standardised to the mean value and taking account of the chamber size. Except for the component ethanediol, all values are near the mean value (1.0). However, as indicated, this compound exhibits the greatest standard deviations, and the great difference between the results for different chamber sizes might be due to the measurement uncertainty of ethanediol.

Standard deviations shown in Figure 53 are the lowest for all results of the 1-m³ chambers on average. However, the data pool is nowhere near large enough to draw further conclusions, e.g. about greater sample homogeneity, better mixing within the chambers, higher flow rates at the chamber exit etc.

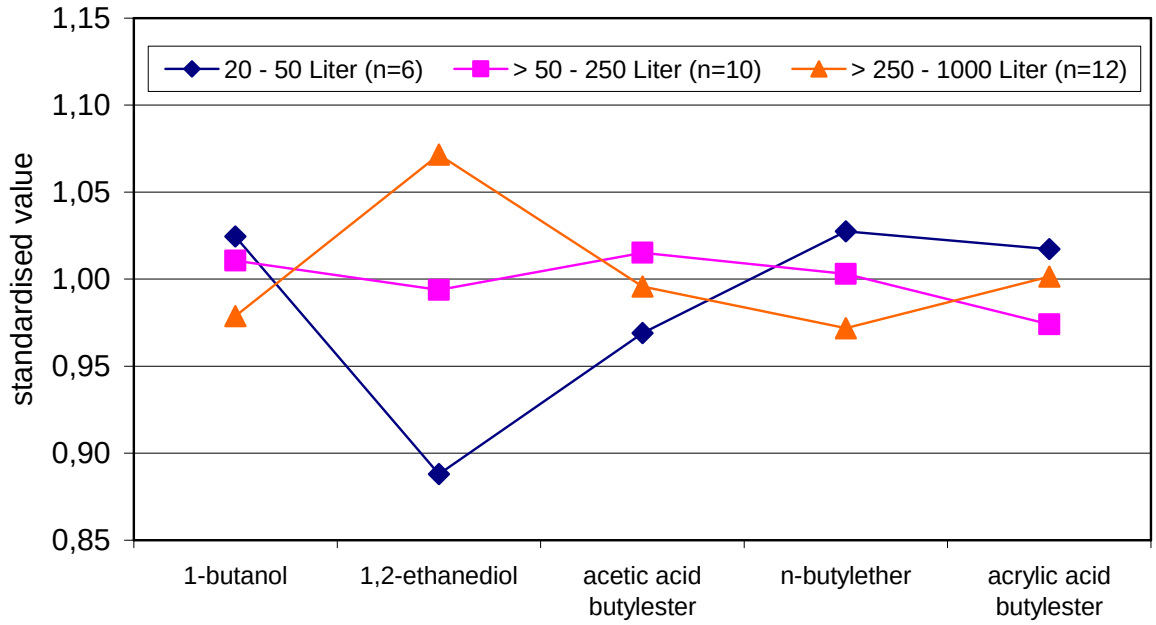

Figure 52: Measured values (standardised) as functions of the chamber size used for the tests.

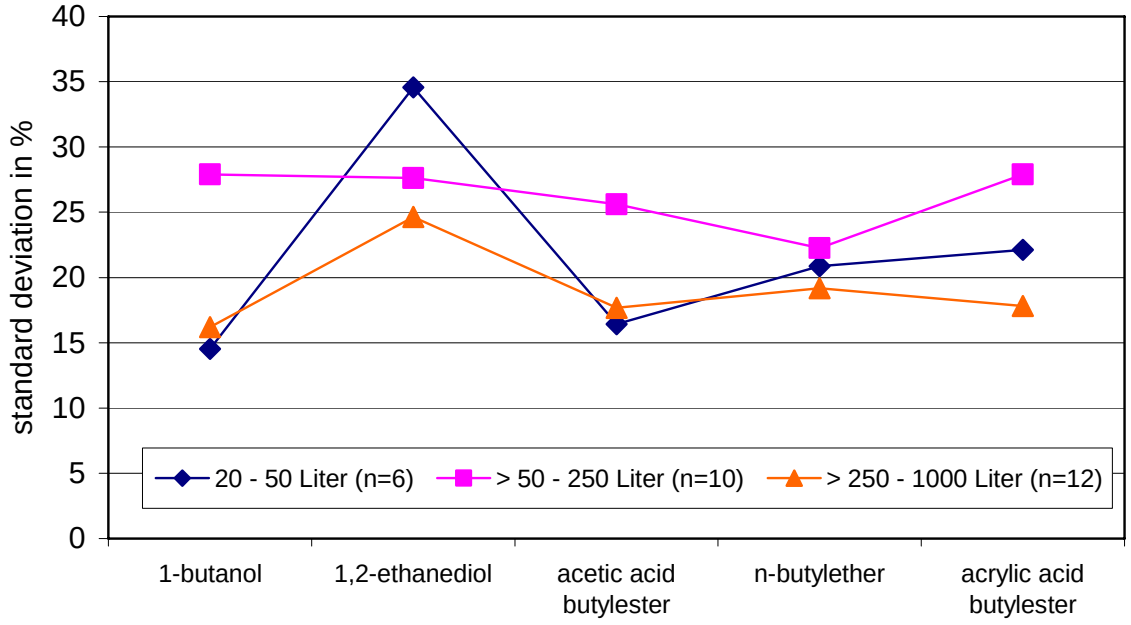

Figure 53: Differences of the relative standard deviations in % as functions of chamber size.

The following figures 54 and 55 show the evaluation of the results taking account of the sample volume, standardised to the mean value. In complete contrast to the effect of this parameter in Section 2.7, the influence of different sample volumes of 3 litres and greater than 5 litres can be seen. The results obtained using 1- to 2-litre samples are closer to the mean value than the others. However, the standard deviations show no difference between the sample quantities.

It can be seen that the data pool, apart from the column type, does not enable clear identification of any parameter that would influence the result positively or negatively. In order to determine this influence at a higher reliability, perhaps one institute alone would have to carry out as many different variations as possible in order to at least exclude the parameter analysis method and so obtain clearer results. However, these results would then have to be verified again by being compared with the results of other test institutes.

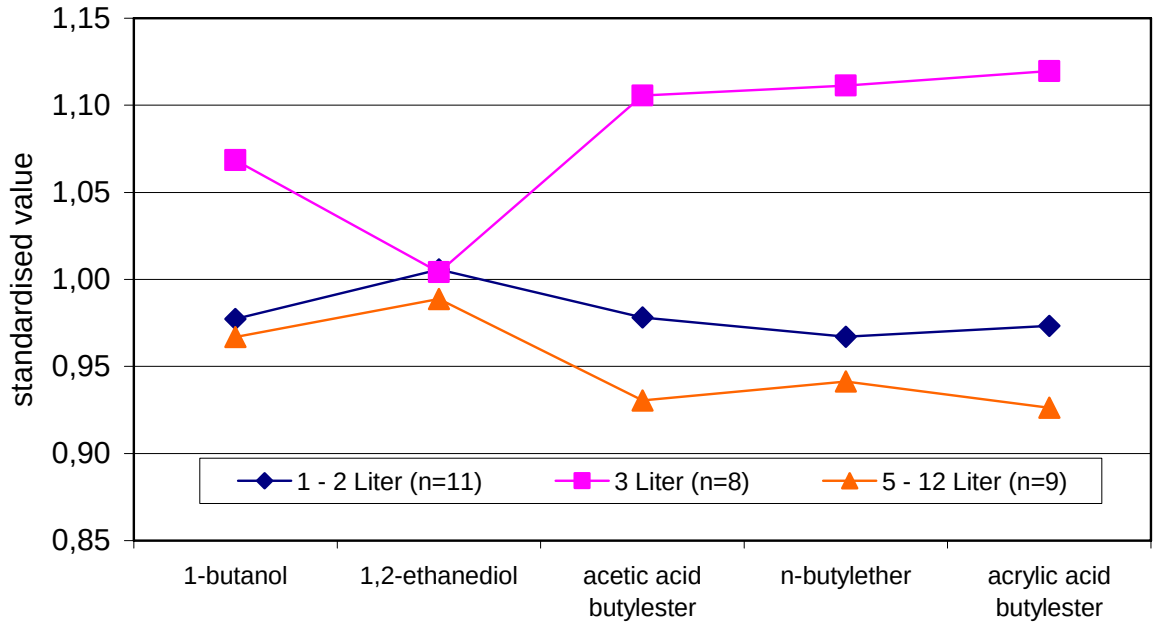

Figure 54: Measured values (standardised) as functions of volume injected into the Tenax tubes.

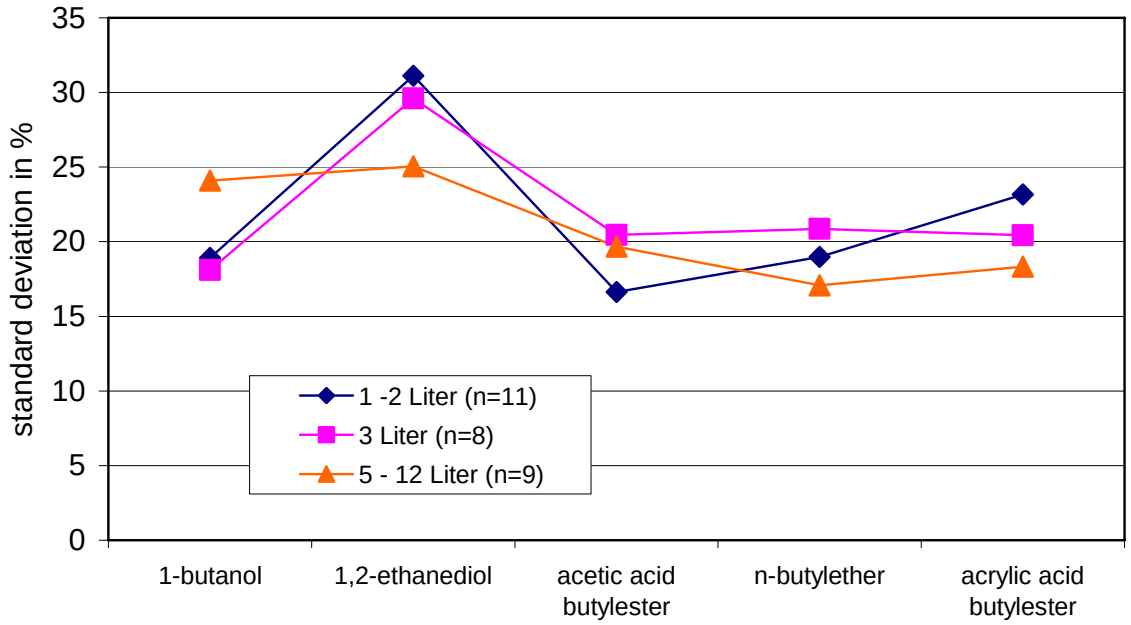

Figure 55: Differences of relative standard deviations in % as functions of the volume injected into the Tenax tubes.

Figure 56 to 60 show the comparison between the participants' and BAM's results for the five key substances. BAM's results were obtained by an analysis of two Tenax tubes which were sampled by the participants and then sent to BAM. A z score calculation based on BAM's values indicates that participants 14 and 20 stand out with two and three values > |2| and participant 22 with three values > |2|.

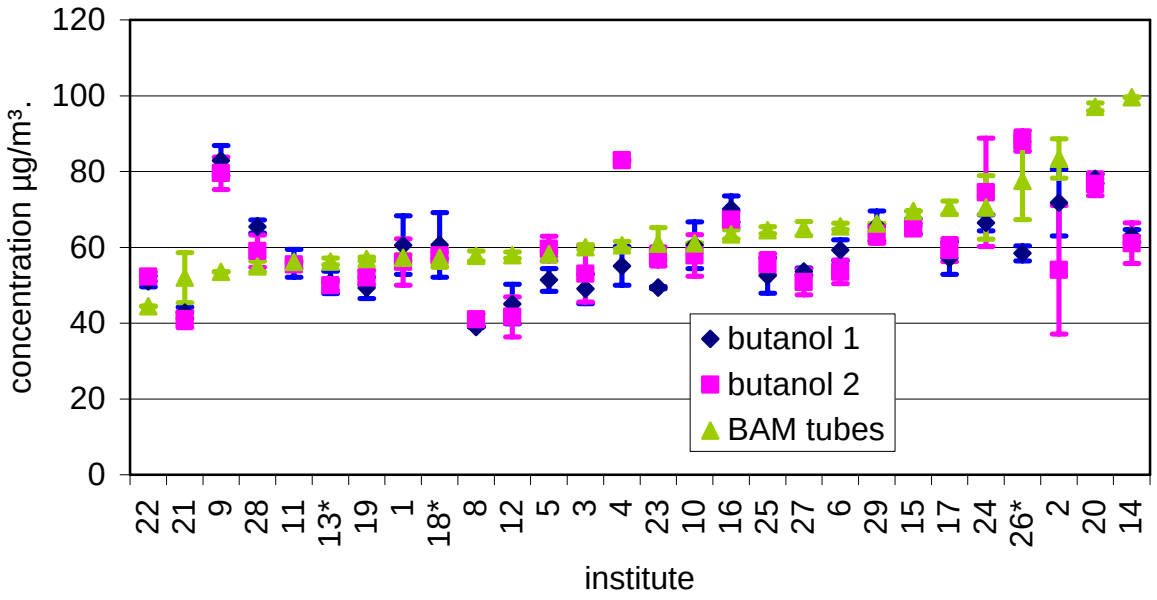

Figure 56: Comparison of the results of butanol between participant's value for both chambers and BAM's value in Step 3

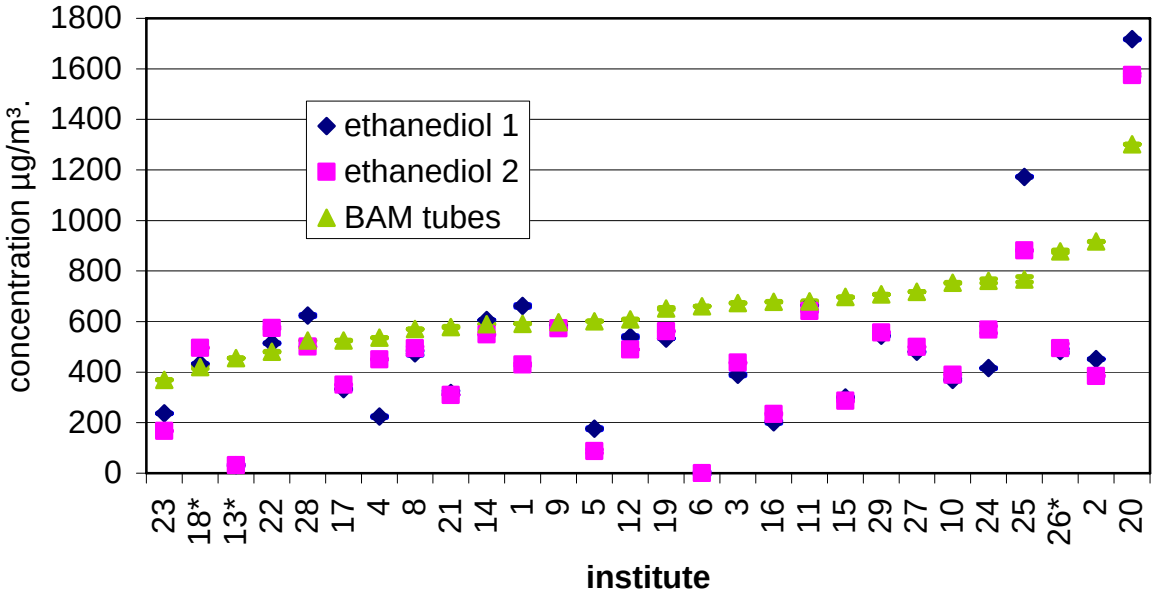

Figure 57: Comparison of the results of ethanediol between participant's value for both chambers and BAM's value in Step 3

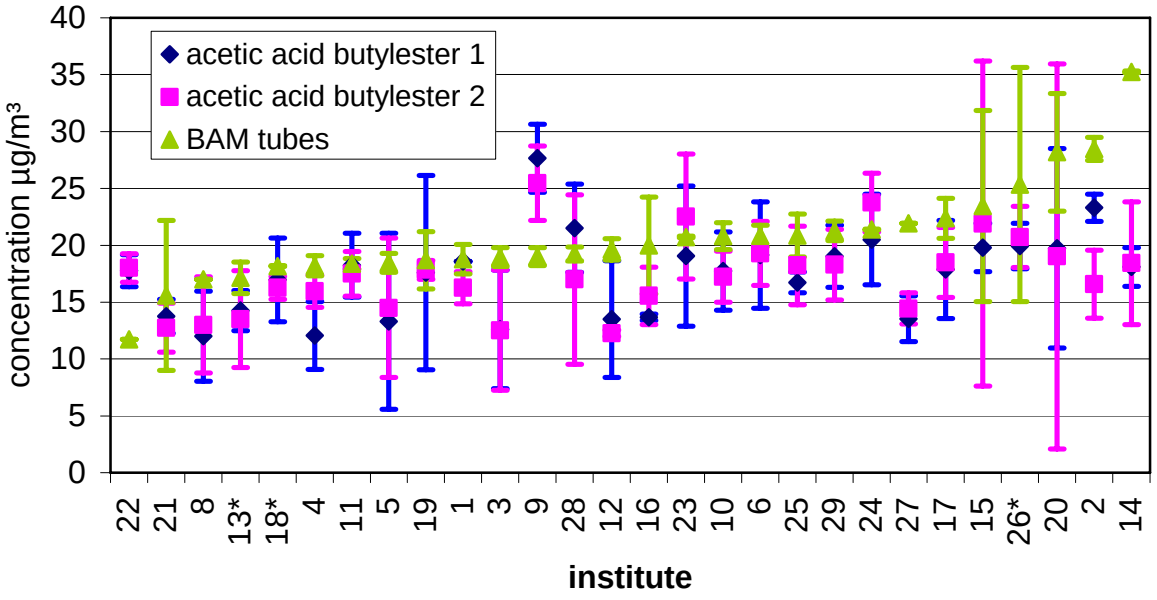

Figure 58: Comparison of the results of acetic acid butylester between participant's value for both chambers and BAM's value in Step 3

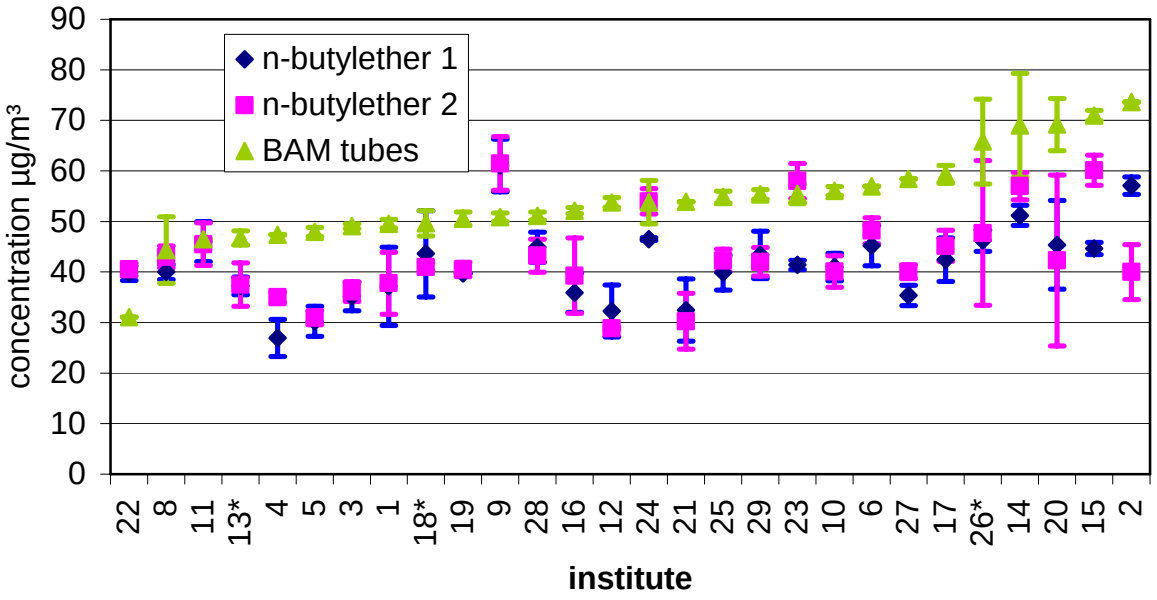

Figure 59: Comparison of the results of butyl ether between participant's value for both chambers and BAM's value in Step 3

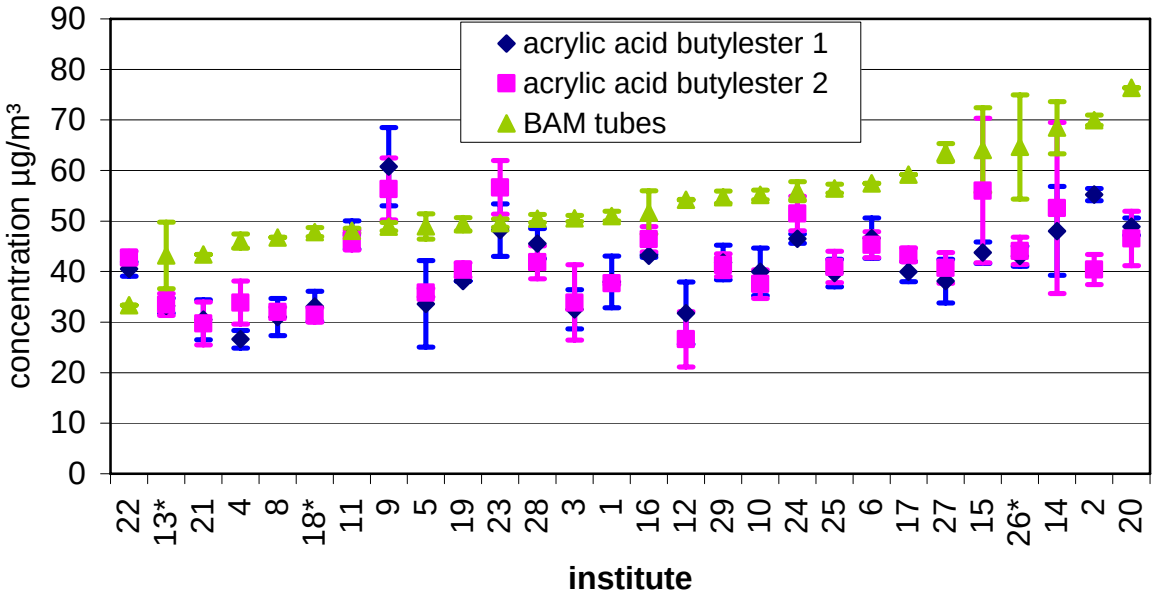

Figure 60: Comparison of the results of acrylic acid butyl ether between participant's value for both chambers and BAM's value in Step 3

5. Summary

5.1. Checking the emission chamber test

Within the interlaboratory comparison, which was divided into three steps, the emission test method from building products was checked against the principles of health-related evaluation of building products in indoor spaces (based on DIN EN ISO 16000-9 together with DIN ISO 16000-6) with the co-operation of 29 European test institutes. The objective was to assess the reproducibility of the test method carried out in different test chambers and using different thermodesorption devices. Based on the results and the relevant data on the analysis method used by the participants, possibilities for improvement were established in order to ensure reproducibility of the measurements.

As a result of the first step (analysis of 4 liquid solutions) a standard deviation of less than 20 % for 8 out of 11 substances tested was obtained. The standard deviations for dichloropropanol, caprolactam and butyl diglycol ranged up to 36 % (Section 2.4.1).

The second step, which included air sampling at a BAM test chamber, resulted in only one standard deviation value less than 20 % (11 % for styrene). The standard deviations for the other six substances were between 20 % and 36 % (Chapter 3.3).

In the third step, two test chamber measurements were carried out on a sealing compound in the participants' test chambers. Although a number of different test chambers (volumes between 20 and 1000 litres) with different loading factors and different air exchange rates (at the same area-specific air flow rate q = 44 m^3/m^2h) were used, the standard deviations for 4 of the 7 measured VOC concentrations were between 17 % and 19 % and thus within the same range as in Step 1 and even better than for most substances in Step 2. A standard deviation of 60 % was found for the key component ethanediol, but this can be explained with the difficult analysis method for this substance. Two other substances with very low concentrations (4 $\mu g/m^3$ and 6 $\mu g/m^3$) exhibited standard deviations of 43 % and 46 % (Section 4.4.1).

Table 38 to Table 40 show the results of all steps of the interlaboratory comparison after expunging the outliers.
The standard deviations for the solutions from Step 1 are in the range between 8 % (styrene, solution B2) and 34 % (caprolactam, solution B1). The results for solution B1 show somewhat higher standard deviations, which can be explained by the low concentrations of the analytes. The substances dichloropropanol, butylglycol and caprolactam always exhibit the highest standard deviations for all four solutions. For these polar substances analytical problems (e.g. peak form) must surely play a role.

For Step 2 the standard deviations of the individual substances are between 11 % (styrene) and 23 % (BHT). For styrene no change can be observed toward Step 1. Also for benzothiazole a 16 % standard deviation from Step 2 is in the range of the standard deviations for solutions A1, A2 and B2 (10 % to 19 %). Step 2 shows a somewhat higher standard deviation only for BHT (22 %) than Step 1 (16 % to 20 %).

Table 38: Outlier-cleaned results for Step 1; mean value and standard deviation of the mean values of the four solutions.

Solution	**B1**		**A1**		**A2**		**B2**		
Compound	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean SD**
	ng/µl	%	ng/µl	%	ng/µl	%	ng/µl	%	%
Methylisobutylketone	12	**16**	45	**11**	51	**13**	75	**10**	***13***
Styrene	14	**12**	50	**11**	56	**11**	85	**8**	***11***
1,3-Dichloro-2-propanol	14	**11**	60	**22**	68	**23**	83	**24**	***20***
1,2,3-Trimethylbenzene	14	**25**	51	**13**	56	**13**	84	**12**	***16***
2-Ethyl-1-hexanol	15	**14**	53	**14**	61	**13**	83	**9**	***13***
Butyldiglykol	15	**33**	49	**23**	56	**21**	83	**19**	***24***
Dodecane	15	**14**	56	**15**	63	**14**	85	**19**	***16***
Benzothiazole	14	**27**	53	**10**	58	**12**	79	**19**	***17***
Caprolactam	14	**34**	52	**18**	59	**11**	83	**13**	***19***
Longifolene	13	**20**	52	**11**	58	**11**	83	**11**	***13***
BHT	14	**20**	55	**17**	60	**16**	88	**17**	***18***

Unfortunately, because of a change in the test material, no comparisons with standard deviations from Step 1 and 2 can be made for the substances from Step 3. The standard deviations from Step 3 are between 14 % and 39 % after expunging the outliers. Ethanediol being the most difficult substance to analyse exhibited the highest standard deviation, i.e. 39 %. Standard deviations less than 20 % for other key substances are very good in comparison to earlier interlaboratory comparisons (see Literature, Section 6). Standard deviations of up to 46 % were obtained for the two substances with very small concentrations even after outlier-clearing.

Table 39: Outlier-cleaned results for Step 2; mean value, standard deviation of the mean values, median and number of participants considered.

Compound	**Mean**	**Std. Dev.**	**Std. Dev.**	**Median**	**Number**
	µg/m³	µg/m³	**%**	µg/m³	n
Toluene-d_8	109	15	**14**	110	22
Styrene	116	13	**11**	116	24
Cyclohexanone	14	3	**23**	13	21
Benzaldehyde	17	3	**19**	17	22
Benzothiazole	106	17	**16**	107	21
BHT	54	12	**22**	57	21
Cyclodecane (spiked)	21 ng	6 ng	**30**	23	23

Table 40: Outlier-cleaned results for Step 3, both chamber tests; mean value, standard deviation of mean values, median and number of participants considered.

Compound	**Mean**	**Std. Dev..**	**Std. Dev.**	**Median**	**Number**
	µg/m³	µg/m³	**%**	µg/m³	
1-Butanol	58	10	**18**	56	24
1,2 Ethane diol	424	167	**39**	472	22
Butylacetate	17	4	**20**	18	26
Dibutyl ether	40	5	**14**	41	21
Acrylic acid butyl ester	41	8	**19**	40	25
Propanoic acid butyl ester	6	3	**46**	5	24
Butanoic acid butyl ester	4	2	**39**	4	19

Interestingly enough, the standard deviations for all three steps are within the expected/acceptable range according to Horwitz (see Section 2.5). This is with high probability, in particular in Step 3, due to the homogeneity of the sample material.

Therefore, the important conclusion is that the emission test chamber method is, in principle, suitable to perform an assessment of the emissions from building products. However, based on the findings obtained, measurement uncertainty should be considered in the assessment pattern in an appropriate way. For this purpose the in-house laboratory measurement uncertainty of the respective testing institute, determined by the regular interlaboratory comparisons, can be consulted.

The bandwidth of the test chamber parameters (volume, air exchange rate, loading factor) is very great. Perhaps a more exact regulation (like the one being compiled in TC 351, WG 2) could lead to more reproducible values.

The same applies to the use of a moderately polar separating column (DB 5) for gas chromatography. Although this contradicts ISO 16000-6, but provides advantages for the analysis and quantification of polar substances such as glycol compounds that nowadays replace the non-polar solvents in most building products.

A further step toward better reproducibility of emission measurement could be the application of a uniform temperature programme for gas chromatography. Thus it would also standardise the evaluation of chromatograms since the isolation of substance peaks would become more reproducible.

The relatively small standard deviation for the third step of the interlaboratory test is also certainly due to improvements in the analytical methods of some laboratories by participating in the first two steps. Therefore, regular participation in interlaboratory comparisons for emission tests is very important to maintain this quality.

5.2. Criteria for approval as a test institute

A second objective of the project was to formulate criteria against which the specialist competence of the test institutes for emission tests can be checked and based on the principles of the health-related evaluation of building products in indoor spaces. For this purpose a catalogue of criteria (see Annex) has been developed, which is divided into three parts.

In the first part, basic requirements are formulated such as impartiality, accreditation for test chamber measurements, verification of experience by participation in earlier interlaboratory comparisons and the laboratory equipment.

The second part requires the test-specific proof in the form of successful participation in interlaboratory comparisons organised by BAM bi-annually.

The third part instructs the laboratories that they must ensure they are always up-to-date both in terms of their knowledge and the available equipment. The quality assurance for the knowledge is ensured by regular participation in the exchanging of experience between the test laboratories. In terms of technical requirements the test institutes must be willing to successfully participate in at least one interlaboratory comparison per year.

The evaluation of interlaboratory comparisons usually takes place based on z scores.

The z score calculation using the "ProLab" software can provide an automatic assessment of the interlaboratory test for each individual participant concerning their total results and decide whether or not is has been successful. For this purpose different evaluation parameters are available. A potential evaluation parameter is the "LAWA criterion" which evaluates the participation in an interlaboratory comparison as successful if 80 % of all required results exhibit a z score between -2 and 2 (i.e. $|z| \leq 2$).

The "LAWA criterion" has been specified by the Government/States (Länder) Water Working Group and has already been applied in the evaluation of interlaboratory comparisons for drinking water analysis for the approval of test institutes.

If one evaluates the three steps of the performed interlaboratory test within this research project under the latter criterion, one could judge the competence of the test laboratories using the z score on the basis of this criterion (see Tables 41 to 44):

Step 1: 4 out of 29 laboratories would not fulfil the LAWA criterion.

Step 2: 2 out of 26 laboratories would not fulfil the LAWA criterion.

Step 3: 1 out of 28 laboratories would not fulfil the LAWA criterion.

During a summing up evaluation of Steps 1, 2 and 3 with a weighting of 25 % (Step 1) to 25 % (Step 2) to 50 % (Step 3), 4 of 29 laboratories would not fulfil the LAWA criterion; however, three of them have not participated in all 3 steps.

The end result is that only about 10 % of the laboratories would not fulfil the LAWA criterion. In Step 3, which contained the complete method of test chamber measurement, only one participant would not meet the requirements. This positive result can be explained by the improvement of the analytical method due to the participation in the first two steps.

It is important to emphasise the importance of the standard deviation in the calculation of z scores. It was in the range of 11 to 47 % for Step 1, in the range of 12 to 38 % for Step 2 and in the range of 21 to 62 % for Step 3.

In the application of the LAWA criterion (subsequent evaluations) a maximum standard deviation of 30% has been used, i.e. when it exceeded 30%, the standard deviation was set to 30% and this value was used to calculate the z scores (see Section 2.5).

It should also be pointed out that the identification of the substances was not an objective of the interlaboratory comparison. The substances had been known in advance to the participants in all three steps.

Therefore, it would be of great interest to learn whether or not this good result can be achieved if the composition of the sample material is unknown.

The next routine interlaboratory comparisons, required within the catalogue of criteria, will provide the answer.

Table 41: Z score evaluation for Step 1 based on the target values (BAM weighed portion) (all four solutions)

Laboratory	Results	Results ok	Percentage	successful
1	44	44	100	Yes
2	44	40	90,91	Yes
3	44	30	68,18	No
4	44	43	97,73	Yes
5	44	36	81,82	Yes
6	44	24	54,54	No
7	44	43	97,73	Yes
8	44	44	100	Yes
9	44	38	86,36	Yes
10	44	40	90,91	Yes
11	44	44	100	Yes
12	44	41	93,18	Yes
13	44	41	93,18	Yes
14	44	21	47,73	No
15	44	42	95,45	Yes
16	44	39	88,64	Yes
17	44	44	100	Yes
18	44	41	93,18	Yes
19	44	44	100	Yes
20	44	35	79,55	No
21	44	44	100	Yes
22	44	40	90,91	Yes
23	44	44	100	Yes
24	44	36	81,82	Yes
25	44	43	97,73	Yes
26	44	43	97,73	Yes
27	44	44	100	Yes
28	44	44	100	Yes
29	44	44	100	Yes

Measured values ok: z score ≤|2|
Successful: fraction (%) > 80

Table 42: Z score evaluation for Step 2 based on the mean values and a maximum standard deviation of 30 %

Laboratory	Results	Results ok	Percentage	successful
1	7	7	100	Yes
2	7	7	100	Yes
3	7	7	100	Yes
4	7	7	100	Yes
5	7	6	85,71	Yes
6	7	0	0	No
7	7	0	0	No
8	7	6	85,71	Yes
9	7	6	85,71	Yes
10	7	7	100	Yes
11	7	7	100	Yes
12	7	6	85,71	Yes
13	7	6	85,71	Yes
14	7	7	100	Yes
15	7	7	100	Yes
16	7	3	42,86	No
17	7	7	100	Yes
18	7	7	100	Yes
19	7	7	100	Yes
20	7	7	100	Yes
21	7	6	85,71	Yes
22	7	7	100	Yes
23	7	7	100	Yes
24	7	0	0	No
25	7	7	100	Yes
26	7	3	42,86	No
27	7	6	85,71	Yes
28	7	6	85,71	Yes
29	7	6	85,71	Yes

Measured values ok: z score ≤|2|
Successful: fraction (%) > 80

Table 43: Z score evaluation for Step 3 based on the mean values and a maximum standard deviation of 30 %

Laboratory	Results	Results ok	Percentage	successful
1	10	10	100	Yes
2	10	10	100	Yes
3	10	10	100	Yes
4	10	9	90	Yes
5	10	9	90	Yes
6	10	8	80	Yes
7	10	0	0	No
8	10	10	100	Yes
9	10	4	40	No
10	10	10	100	Yes
11	10	10	100	Yes
12	10	10	100	Yes
13	10	8	80	Yes
14	10	10	100	Yes
15	10	10	100	Yes
16	10	10	100	Yes
17	10	10	100	Yes
18	10	10	100	Yes
19	10	10	100	Yes
20	10	8	80	Yes
21	10	10	100	Yes
22	10	10	100	Yes
23	10	9	90	Yes
24	10	10	100	Yes
25	10	8	80	Yes
26	10	9	90	Yes
27	10	10	100	Yes
28	10	10	100	Yes
29	10	10	100	Yes

Measured values ok: z score ≤|2|
Successful: fraction (%) > 80

Table 44: Z score evaluation for Steps 1, 2 and 3 with weightings 25 %, 25 % and 50 %

Laboratory	Results	Results ok	Percentage	successful
1	176	176,0	100,0	Yes
2	176	172,0	97,7	Yes
3	176	162,0	92,0	Yes
4	176	159,9	90,9	Yes
5	176	152,9	86,9	Yes
6	176	94,4	53,6	No
7	176	43,0	24,4	No
8	176	169,7	96,4	Yes
9	176	117,2	66,6	No
10	176	172,0	97,7	Yes
11	176	176,0	100,0	Yes
12	176	166,7	94,7	Yes
13	176	149,1	84,7	Yes
14	176	153,0	86,9	Yes
15	176	174,0	98,9	Yes
16	176	145,9	82,9	Yes
17	176	176,0	100,0	Yes
18	176	173,0	98,3	Yes
19	176	176,0	100,0	Yes
20	176	149,4	84,9	Yes
21	176	169,7	96,4	Yes
22	176	172,0	97,7	Yes
23	176	167,2	95,0	Yes
24	176	124,0	70,5	No
25	176	157,4	89,4	Yes
26	176	141,1	80,2	Yes
27	176	169,7	96,4	Yes
28	176	169,7	96,4	Yes
29	176	168,7	95,9	Yes

Measured values ok: z score ≤|2|
Successful: fraction (%) > 80

6. Literature

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7. Annex

7.1. List of Tables Annex

7.2. List of Figures Annex

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7.4. Overview results of step 1, 2 und 3 (details)

Table 1: In the different stepps of the ILS following compounds were measured or asked for:

Compound	CAS-RN
benzaldehyde	100-52-7
benzothiazole	95-16-9
BHT (2,6-di-tert-butyl-4-methylphenol)	128-37-0
1-butanol	71-36-3
butanoic acid butylester	109-21-7
butyl diglycol	112-34-5
caprolactam	105-60-2
cyclodecane	293-96-9
cyclohexanone	108-94-1
1,3-dichloropropanol	96-23-1
dodecane	112-40-3
butylacetat	123-86-4
1,2-ethanediol	107-21-1
2-ethyl-1-hexanol	104-76-7
longifolene	475-20-7
Methylisobutylketon (MIBK)	108-10-1
n-butylether	142-96-1
propanoic acid butylester	590-01-2
propenoic acid butylester	141-32-2
styrene	100-42-5
toluene-d8	2037-26-5
1,2,3-trimetylbenzene	526-73-8

7.4.1. Results of ILS BAM/DIBt step 1

7.4.1.1. Solution A1

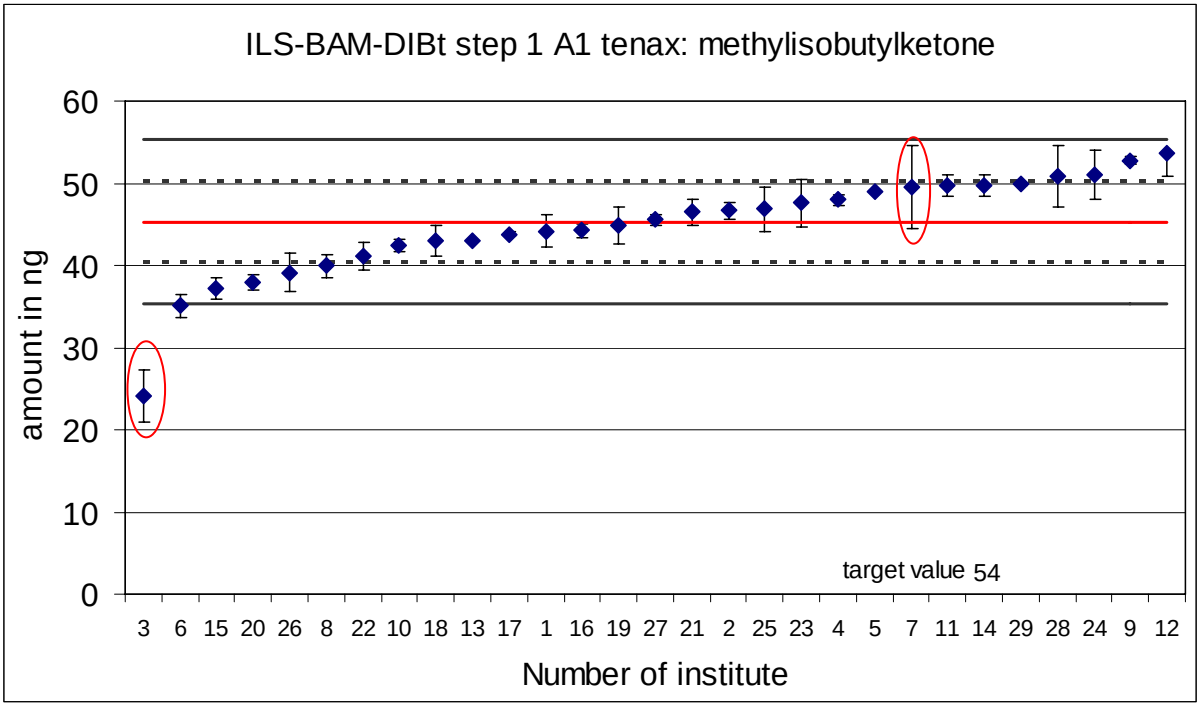


Figure 1: Results MIBK solution A1 injected on Tenax (outlier marked)

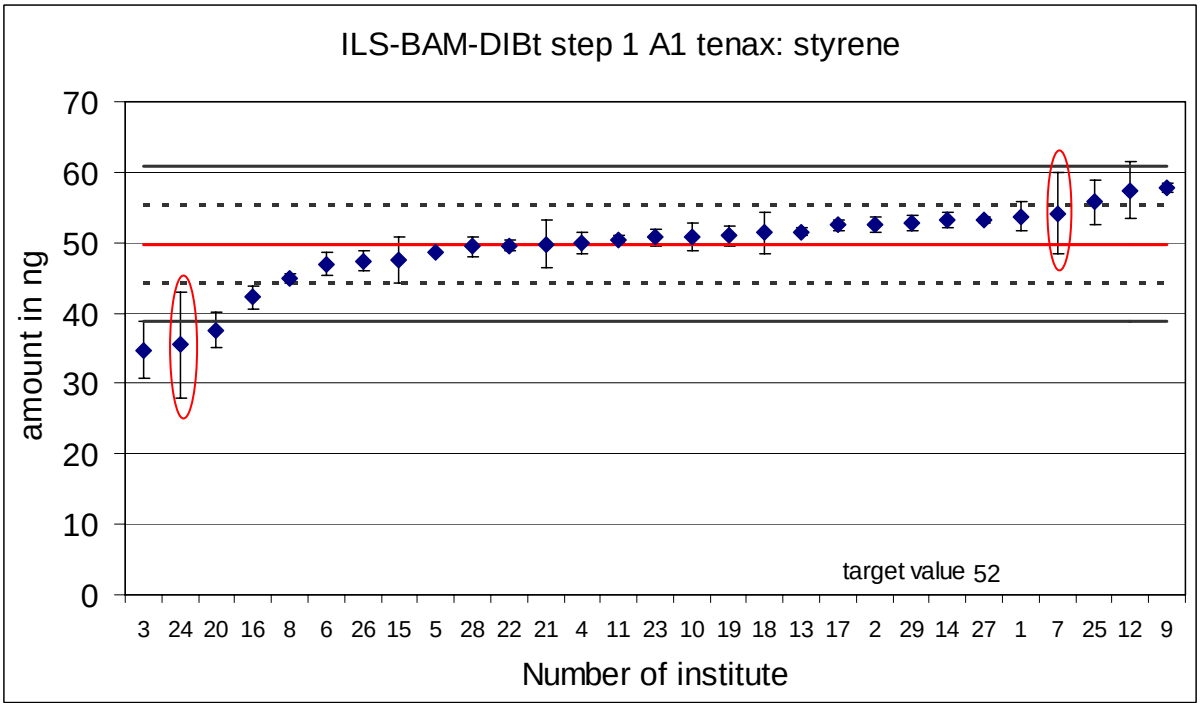


Figure 2: Results styrene solution A1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

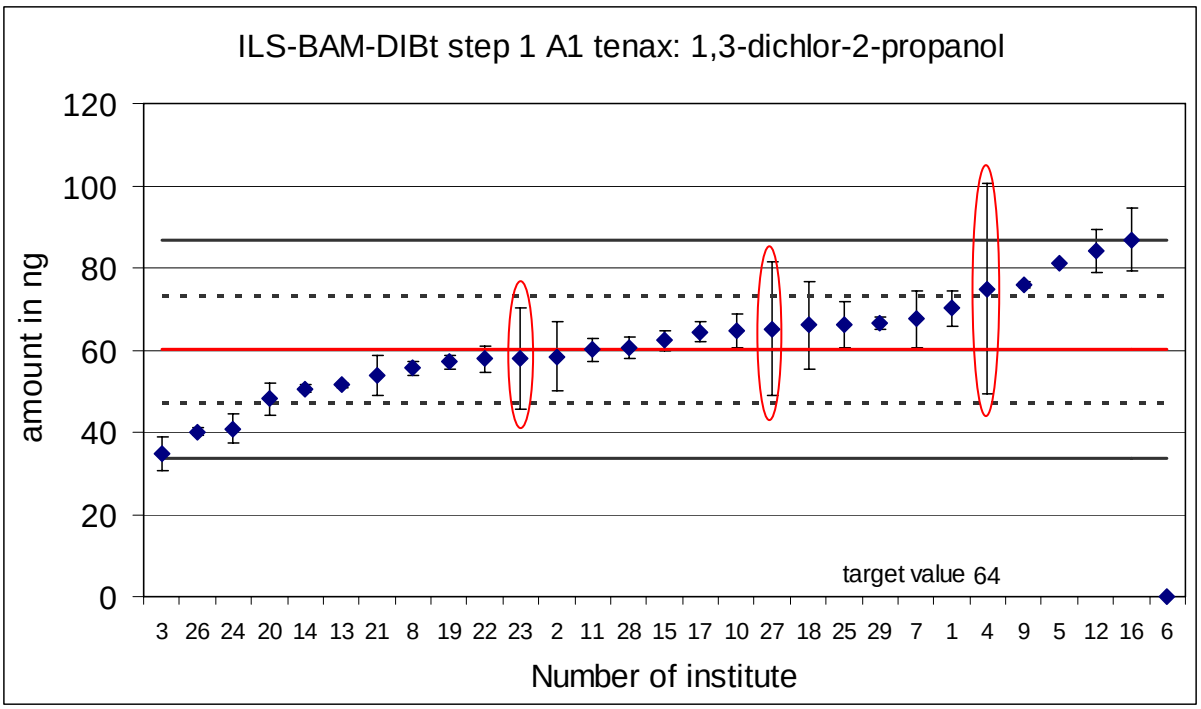


Figure 3: Results 1,3-dichloro-2-propanol solution A1 injected on Tenax (outlier marked)

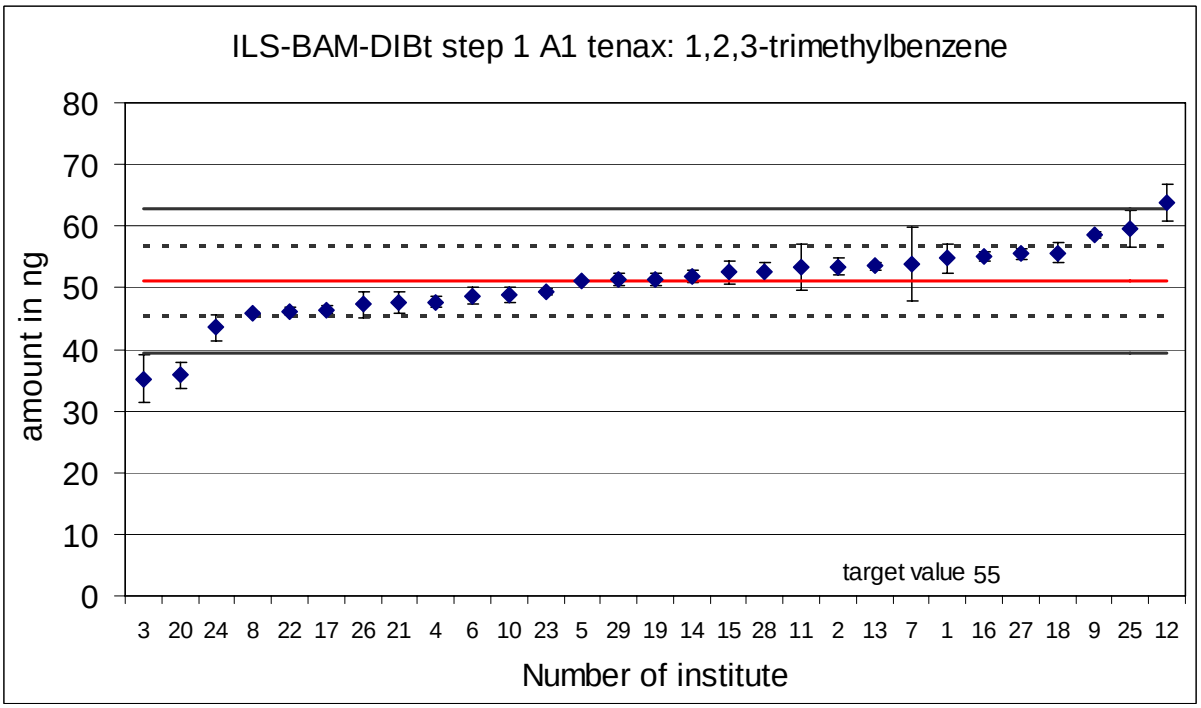


Figure 4: Results 1,2,3-Trimethylbenzol Solution A1 nach Aufgabe sampled on Tenax (no outlier)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

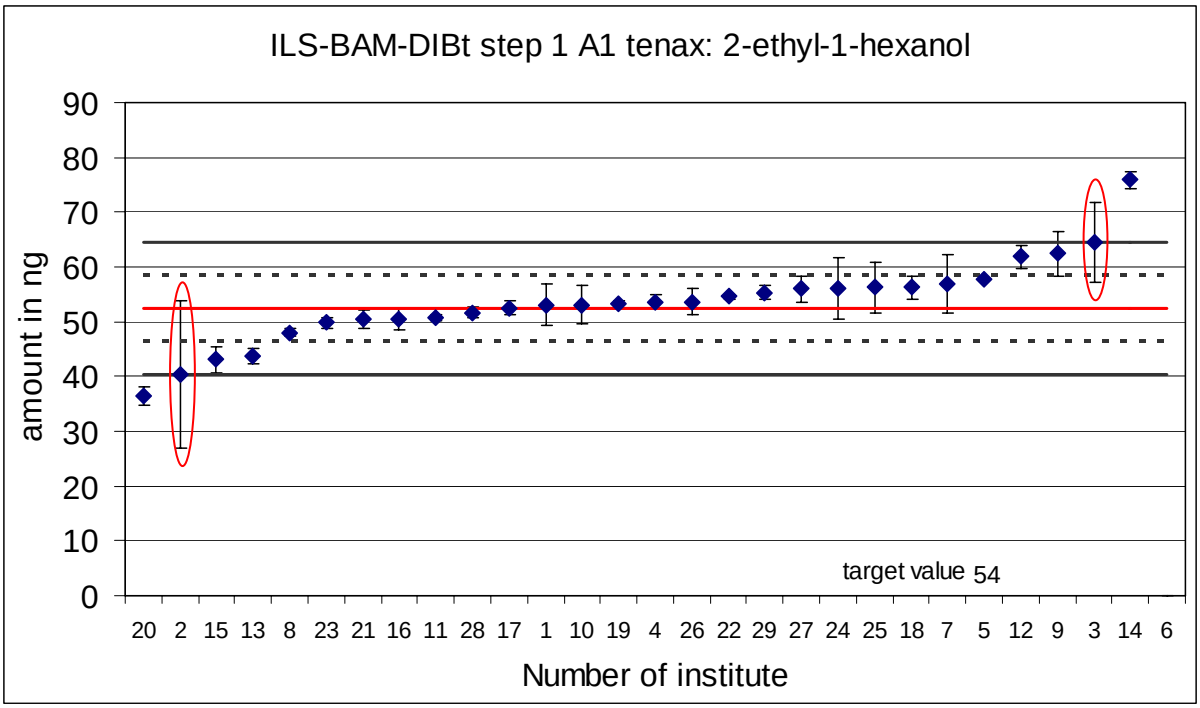


Figure 5: Results 2-ethyl-1-hexanol solution A1 injected on Tenax (outlier marked)

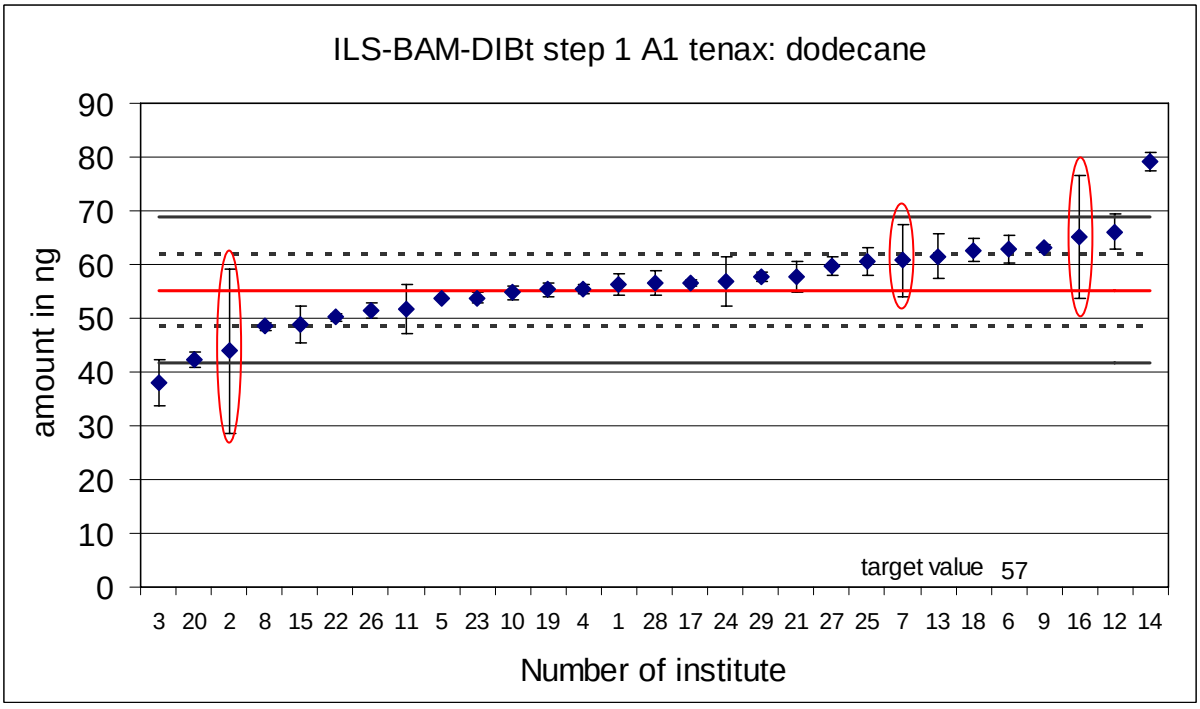


Figure 6: Results dodecane solution A1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

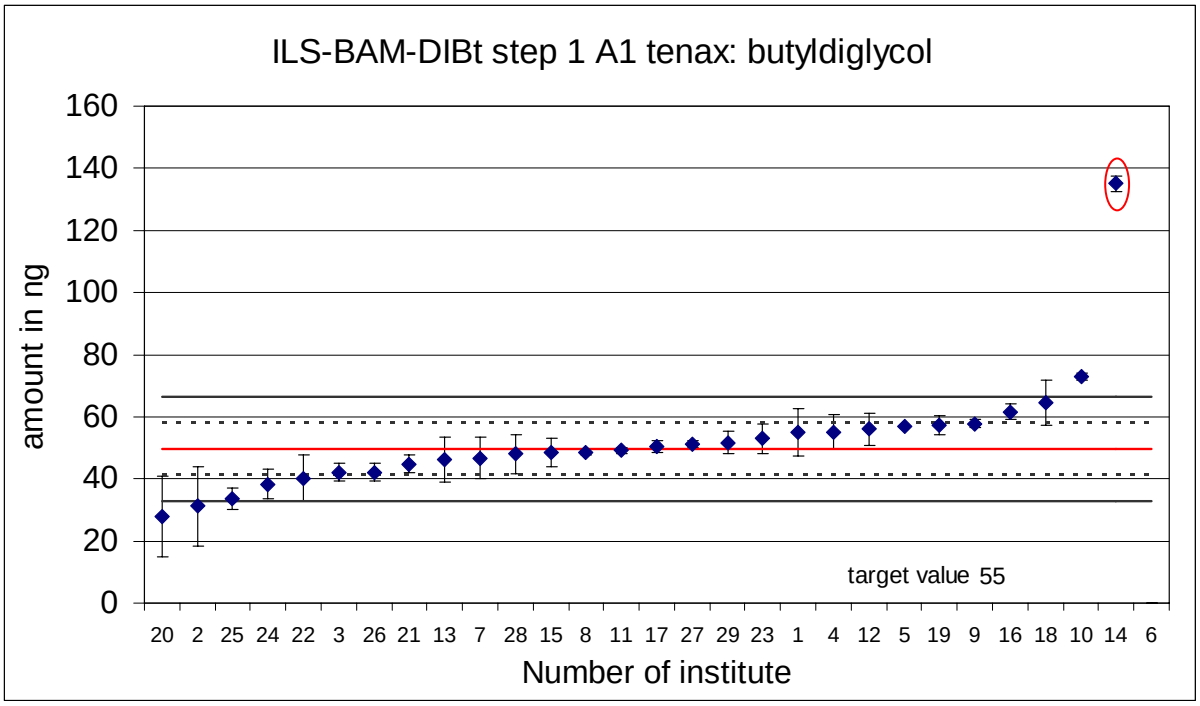


Figure 7: Results butyl diglycol solution A1 injected on Tenax (outlier marked)

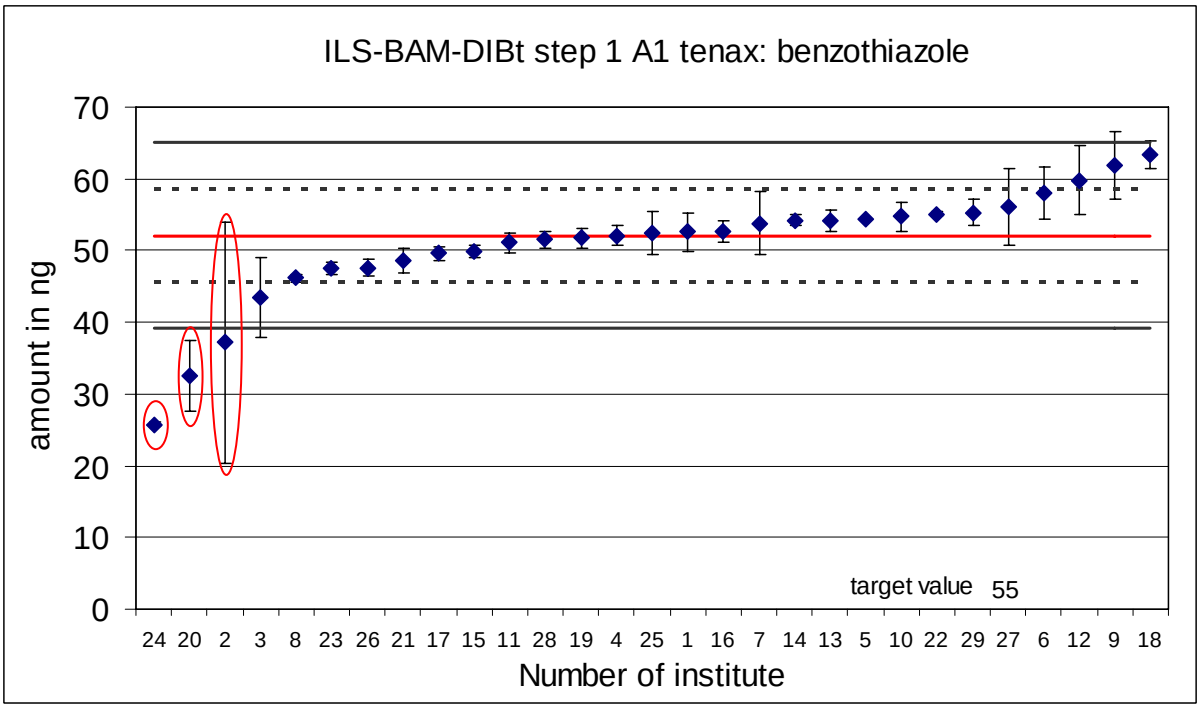


Figure 8: Results benzothiazole solution A1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

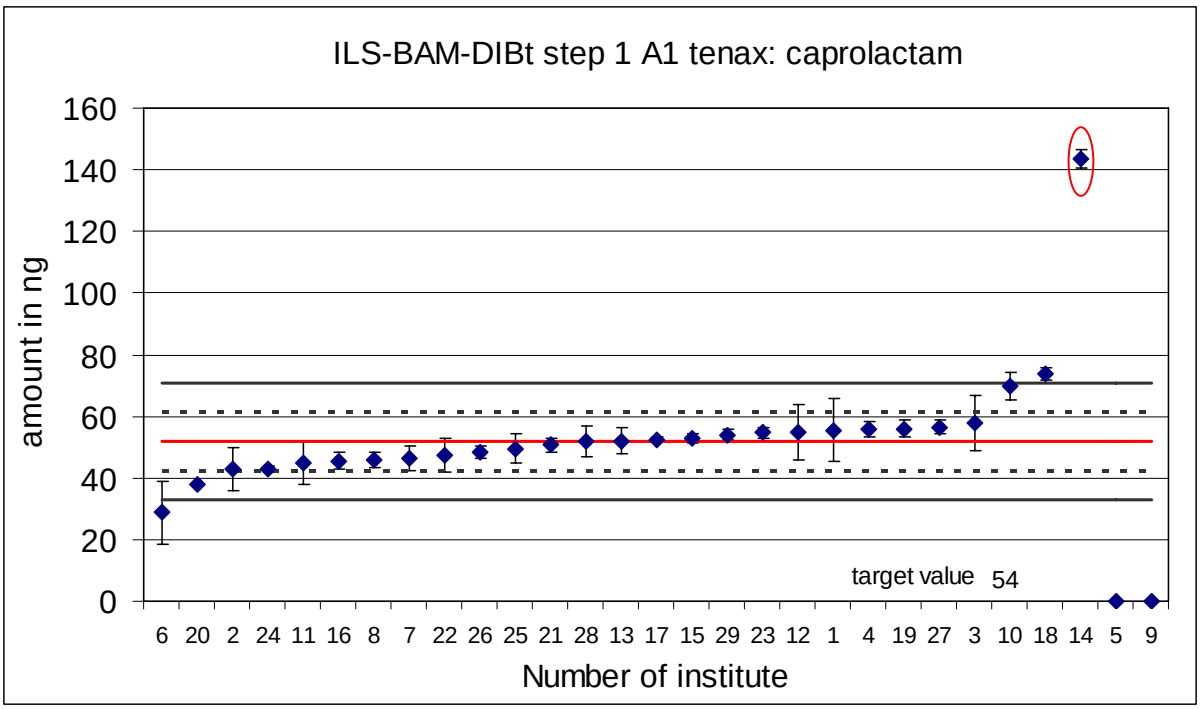


Figure 9: Results caprolactam solution A1 injected on Tenax (outlier marked)

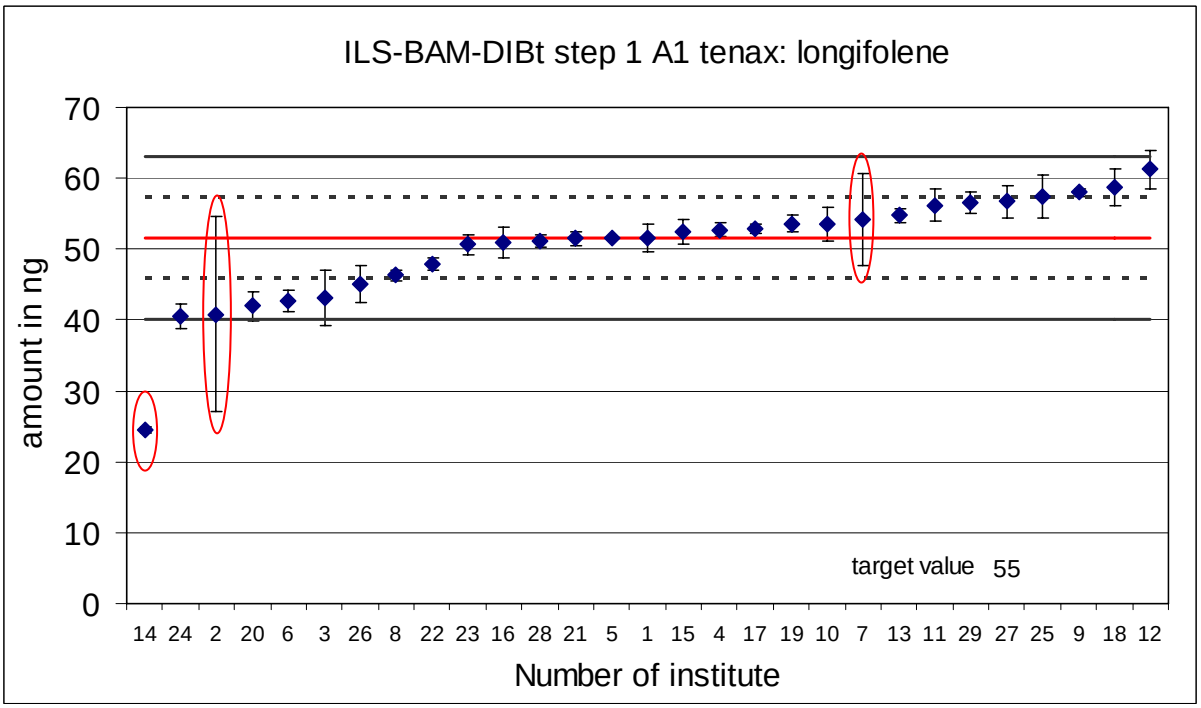


Figure 10: Results longifolene solution A1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

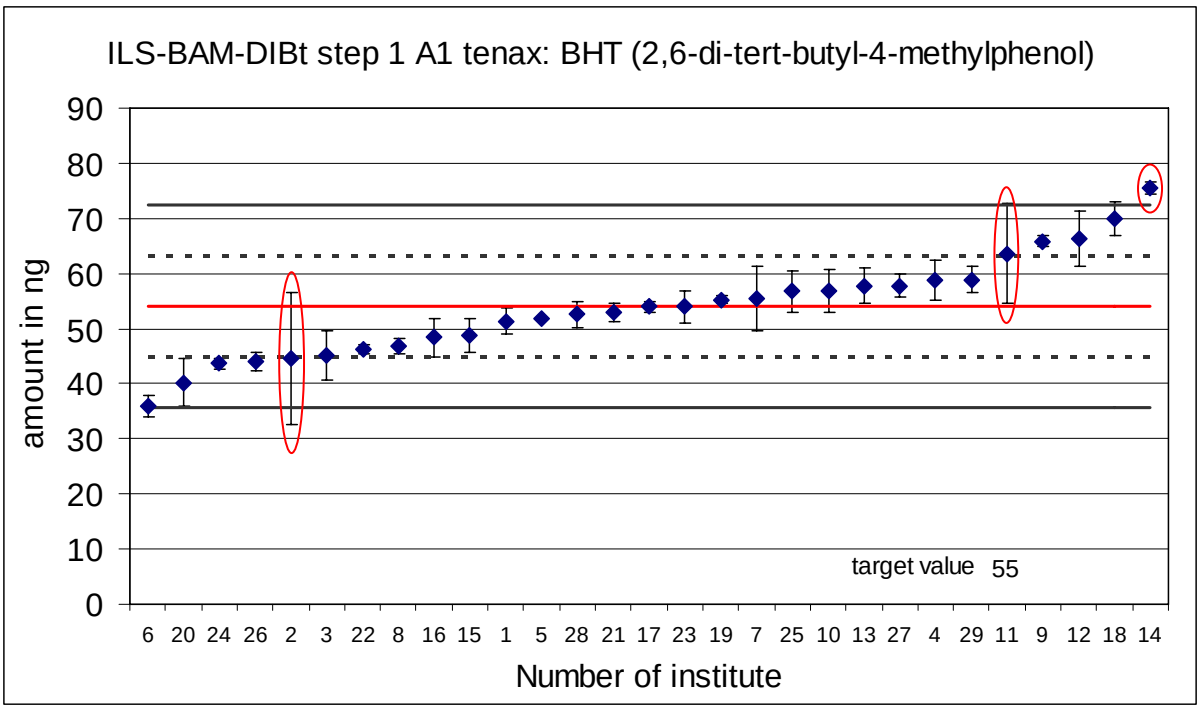


Figure 11: Results BHT (2,6-Di-tert-butyl-4-methylphenol) solution A1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

7.4.1.2. Solution A2

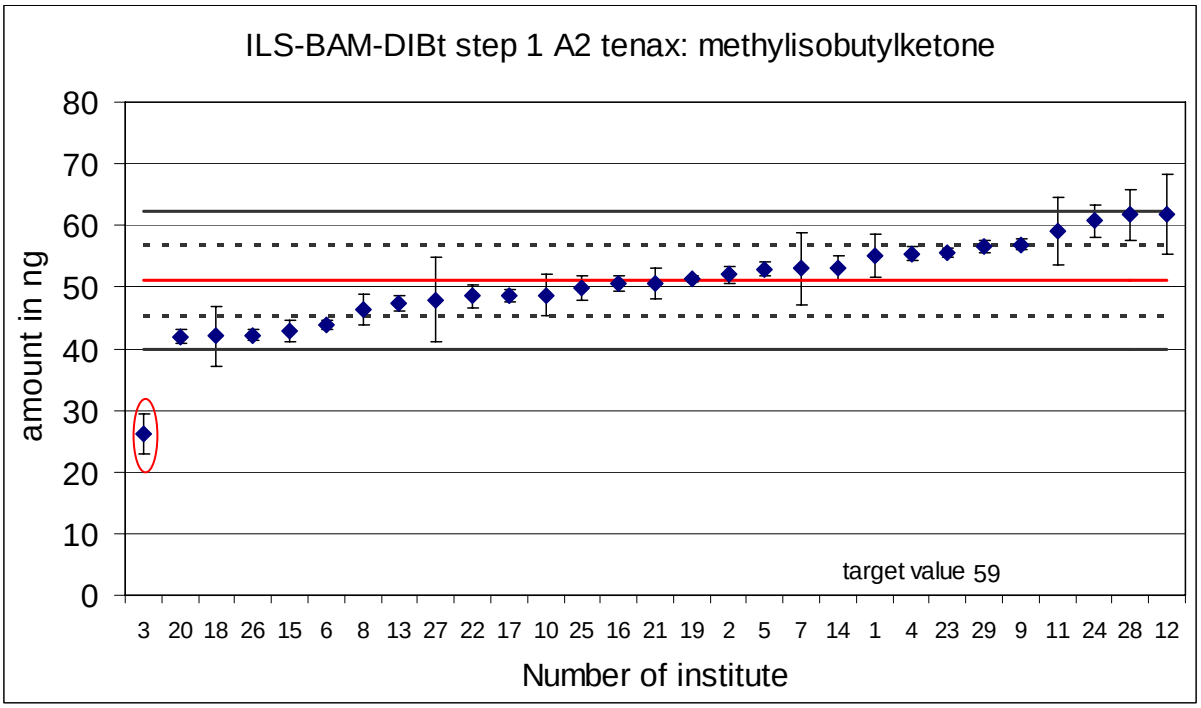


Figure 12: Results MIBK solution A2 injected on Tenax (outlier marked)

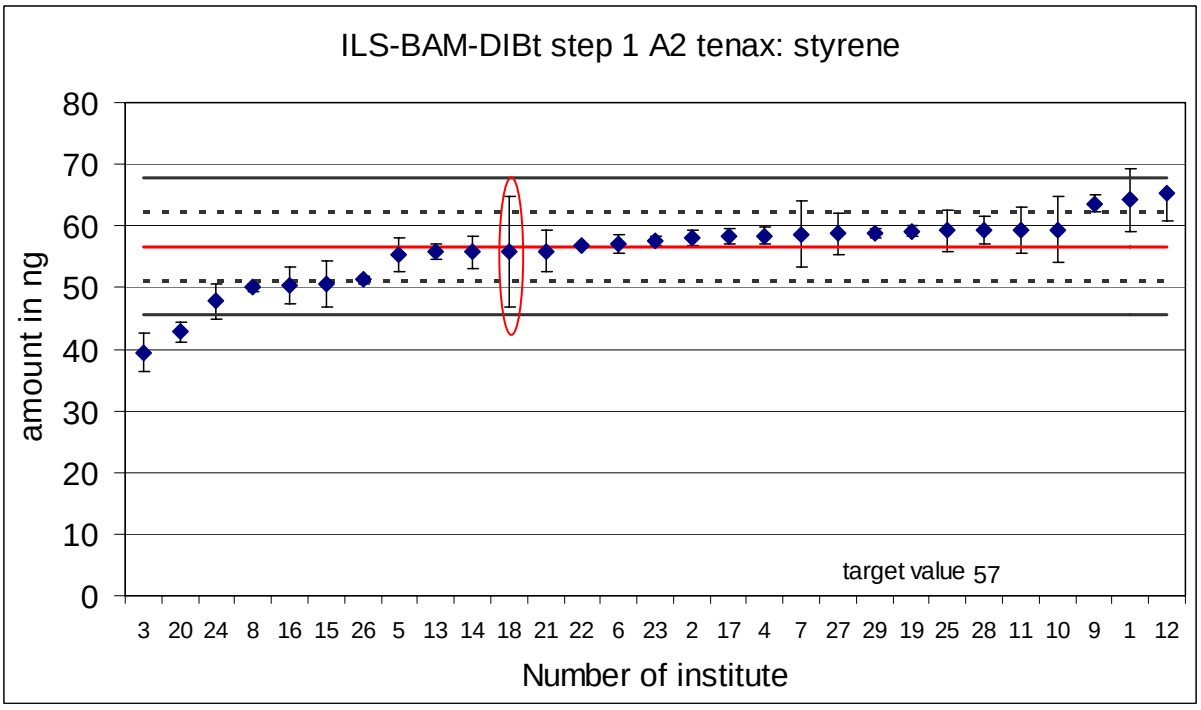


Figure 13: Results styrene solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

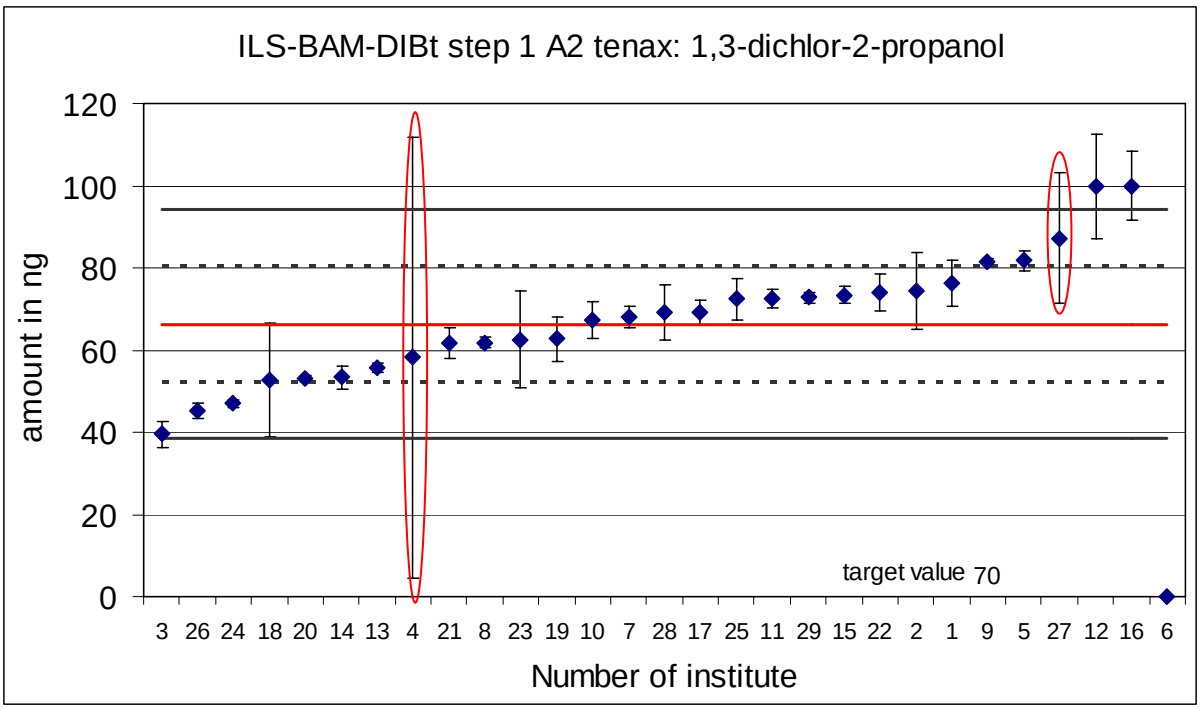


Figure 14: Results 1,3-dichloro-2-propanol solution A2 injected on Tenax (outlier marked)

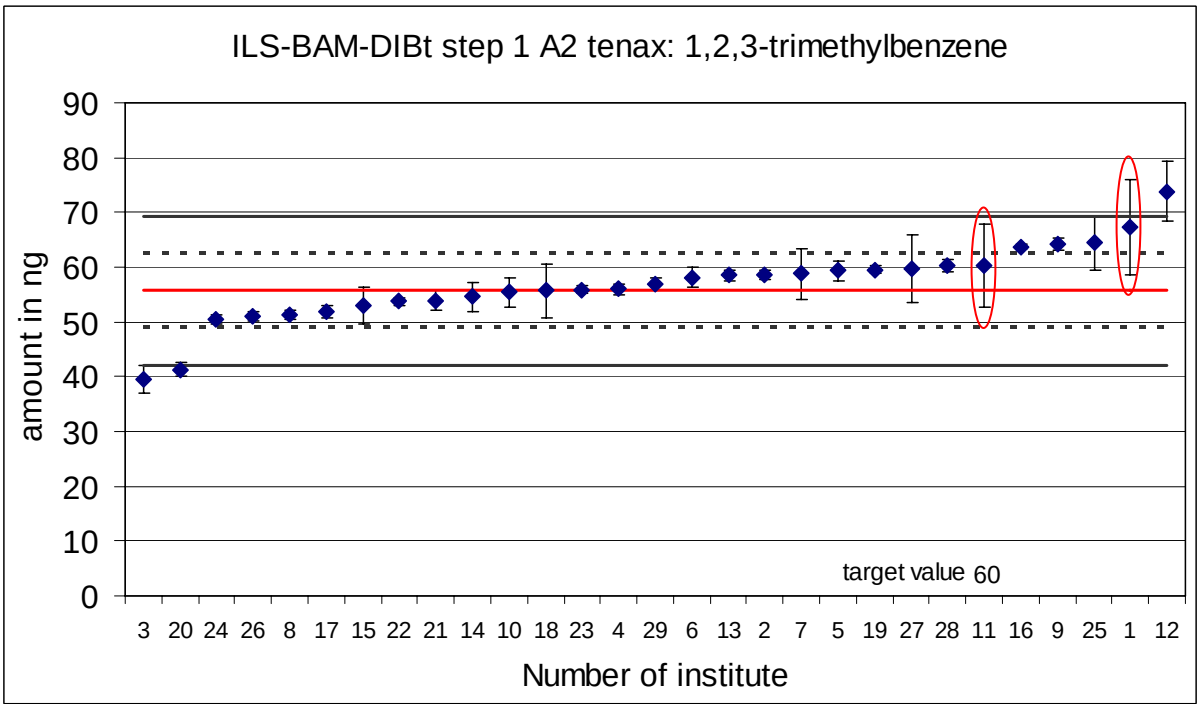


Figure 15: Results 1,2,3-trimethylbenzene solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

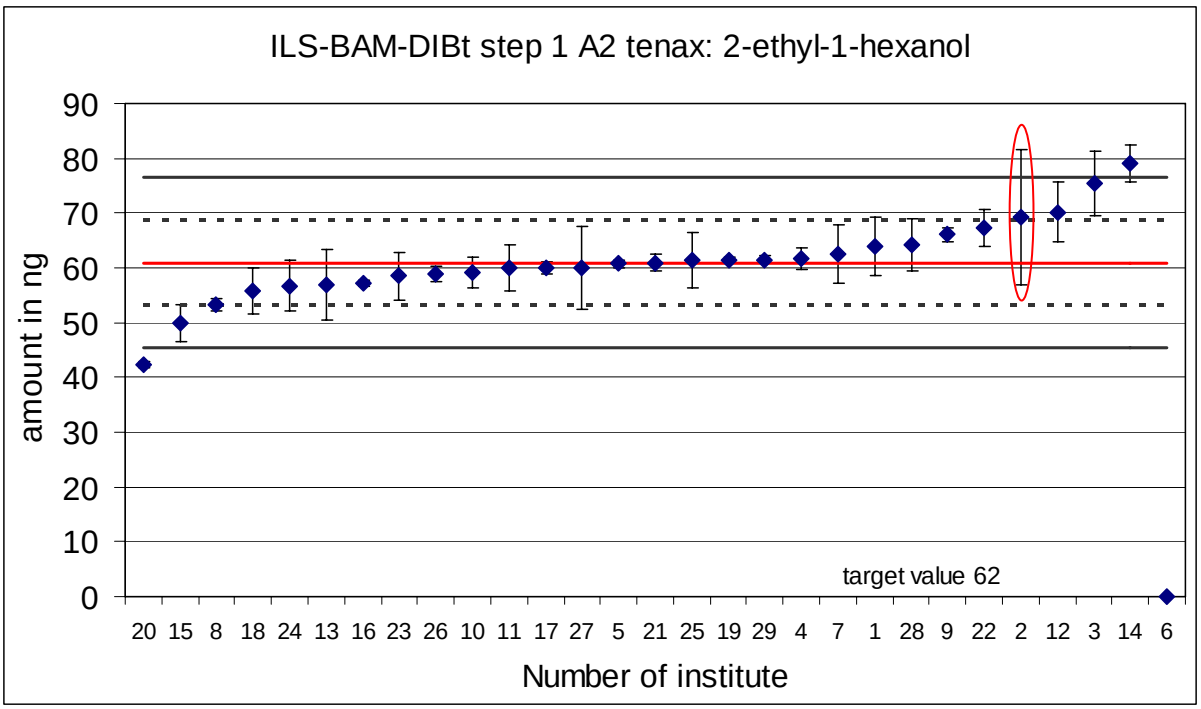


Figure 16: Results 2-ethyl-1-hexanol solution A2 injected on Tenax (outlier marked)

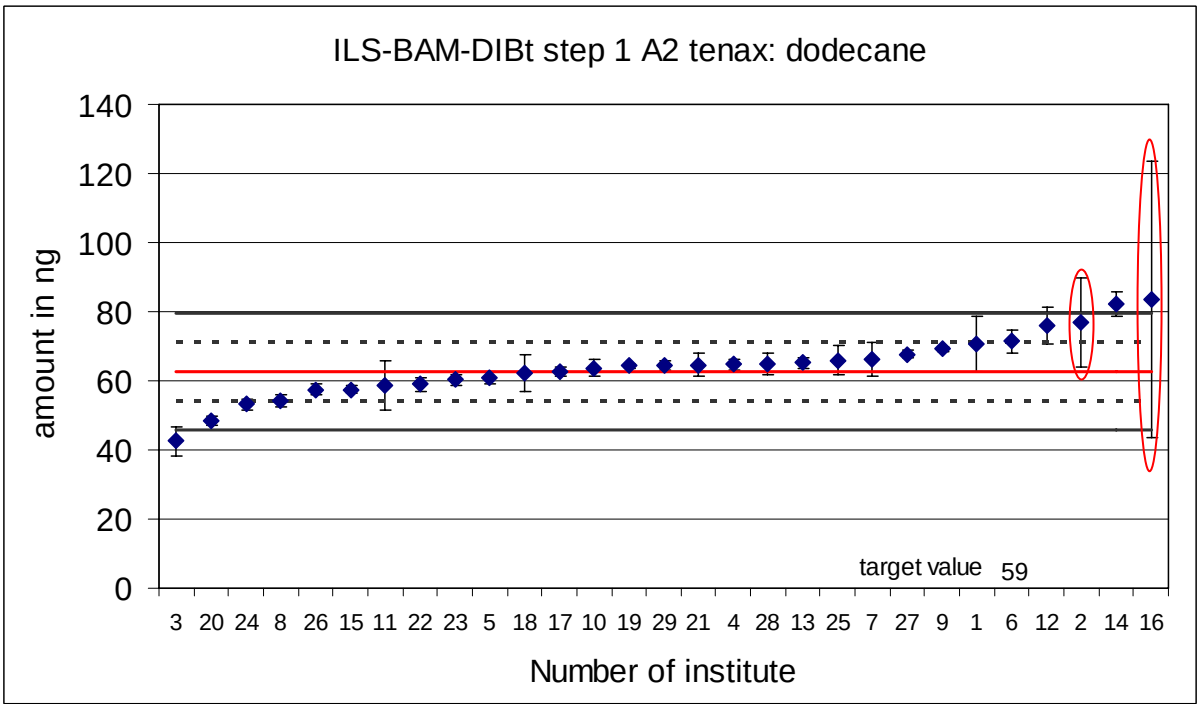


Figure 17: Results dodecane solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

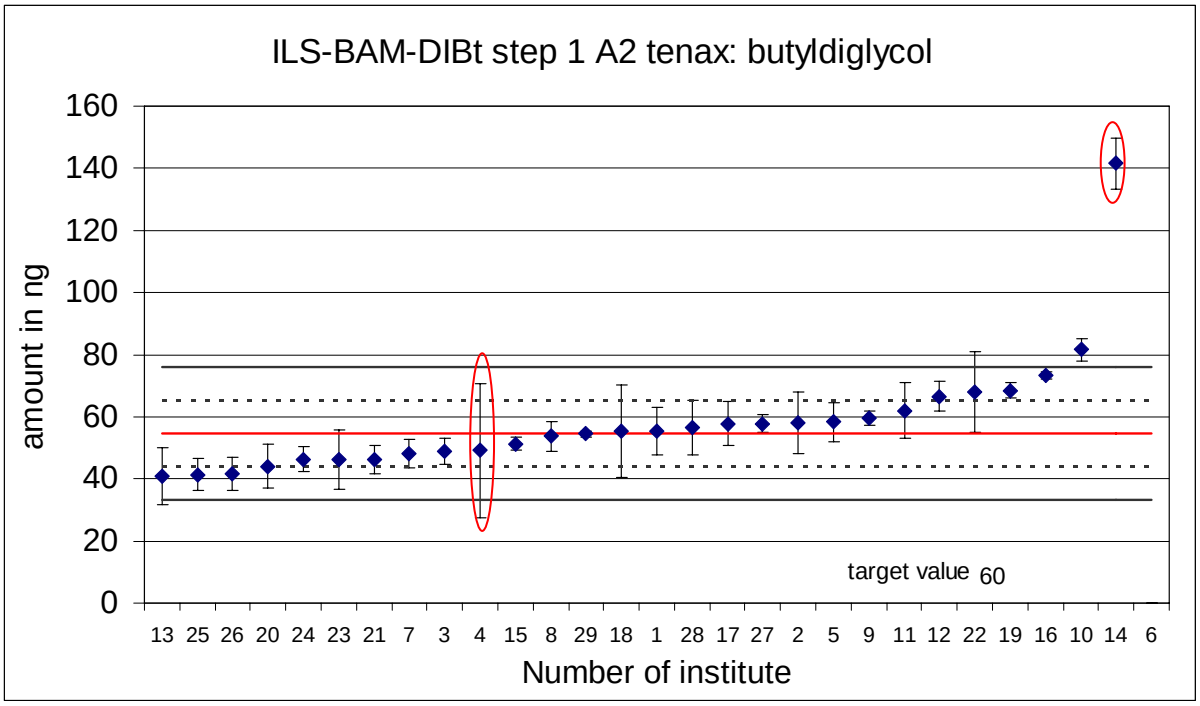


Figure 18: Results butyl diglycol solution A2 injected on Tenax (outlier marked)

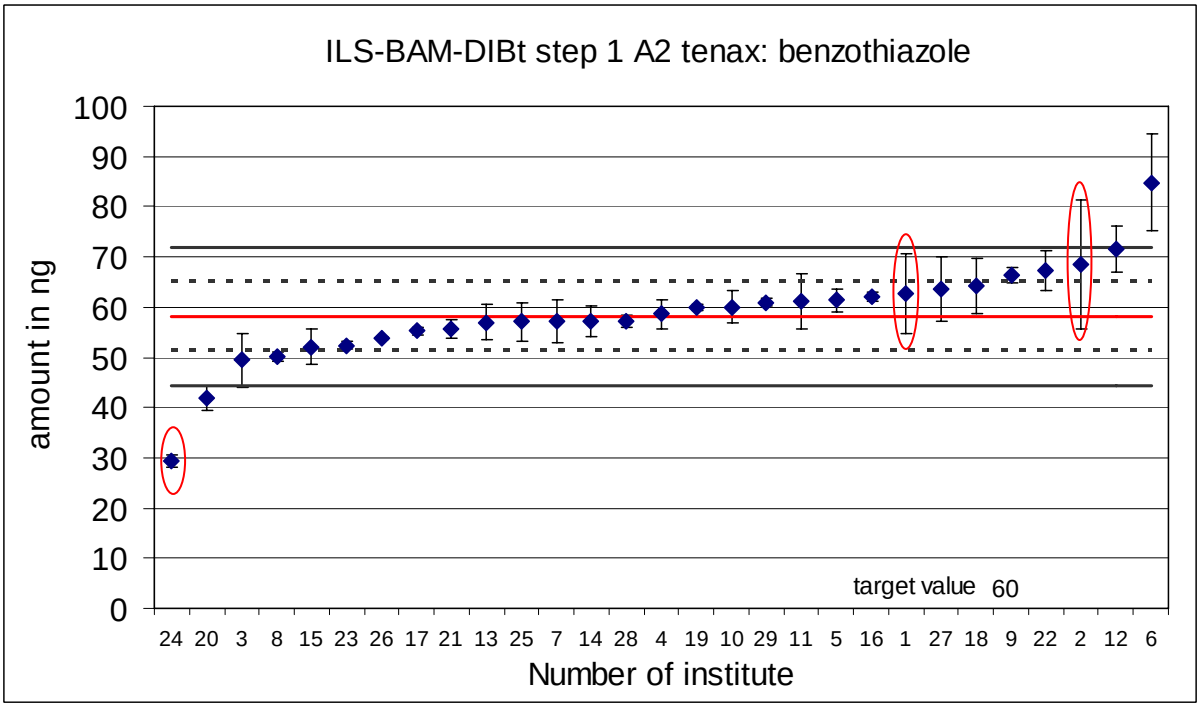


Figure 19: Results benzothiazole solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

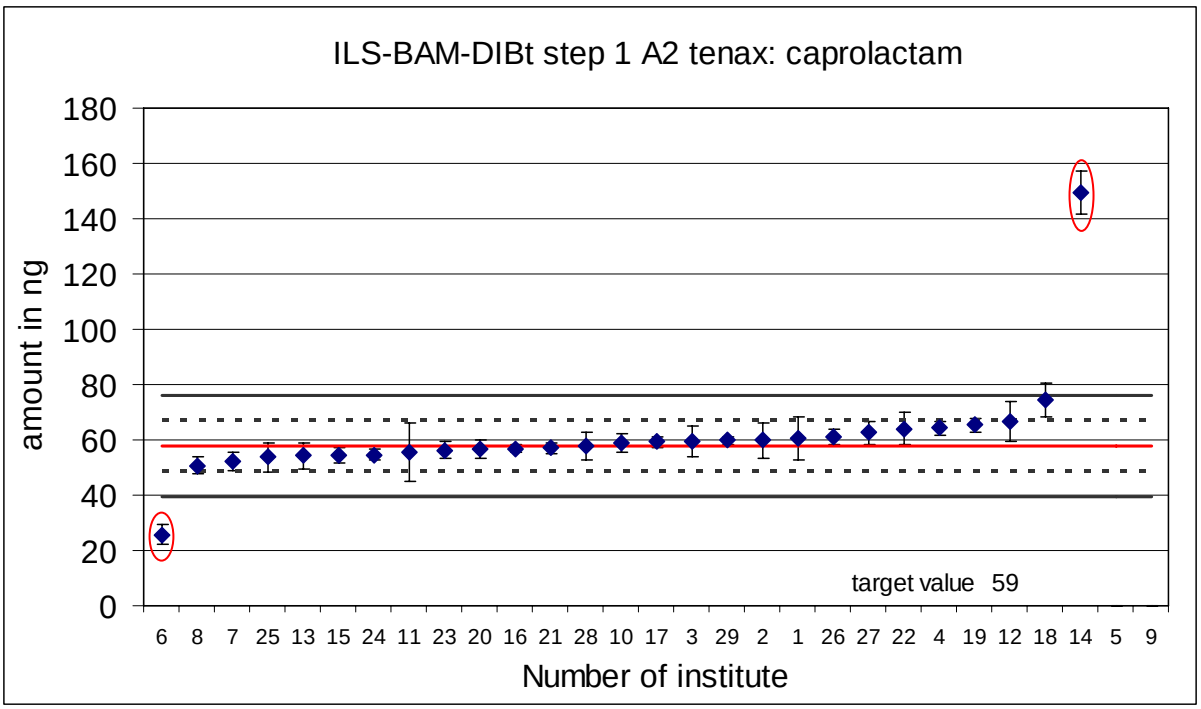


Figure 20: Results caprolactam solution A2 injected on Tenax (outlier marked)

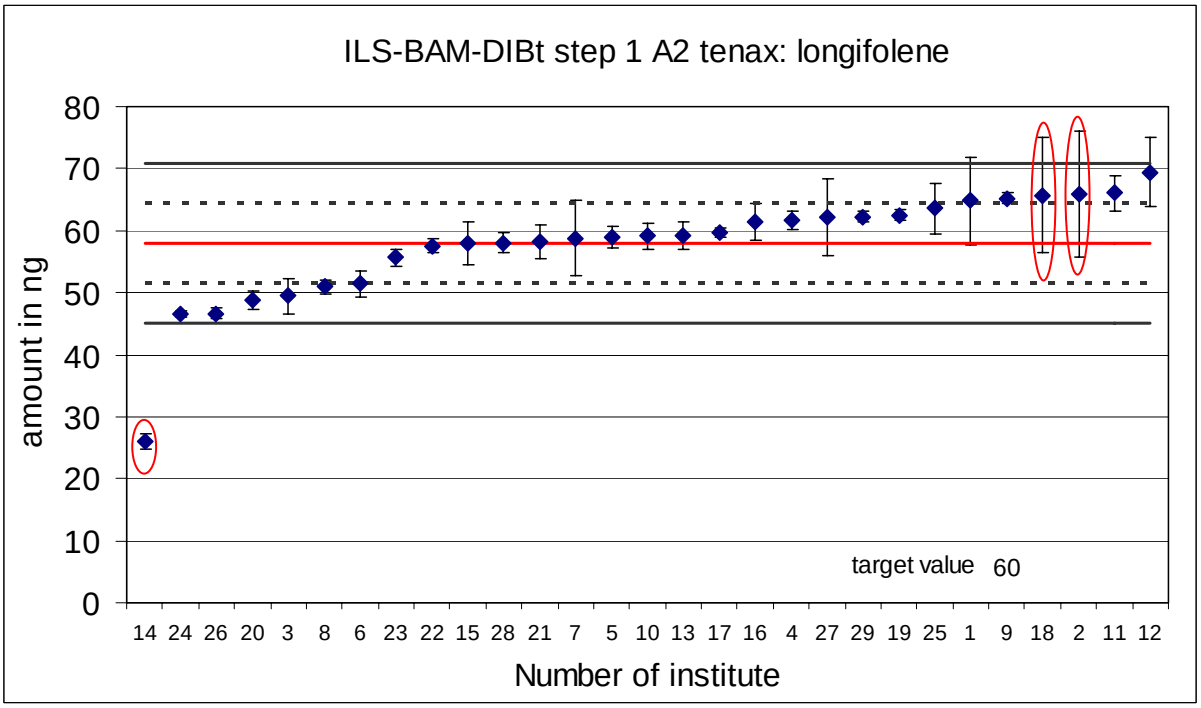


Figure 21: Results longifolene solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

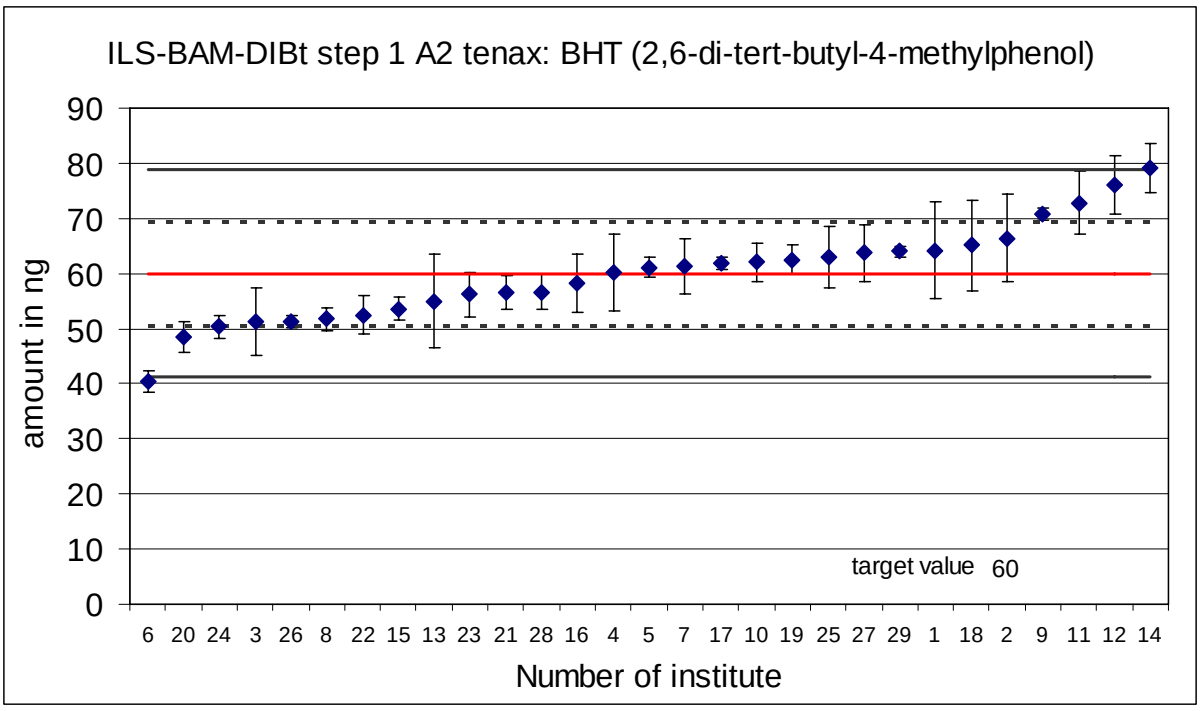


Figure 22: Results BHT (2,6-Di-tert-butyl-4-methylphenol) solution A2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

7.4.1.3. Solution B1

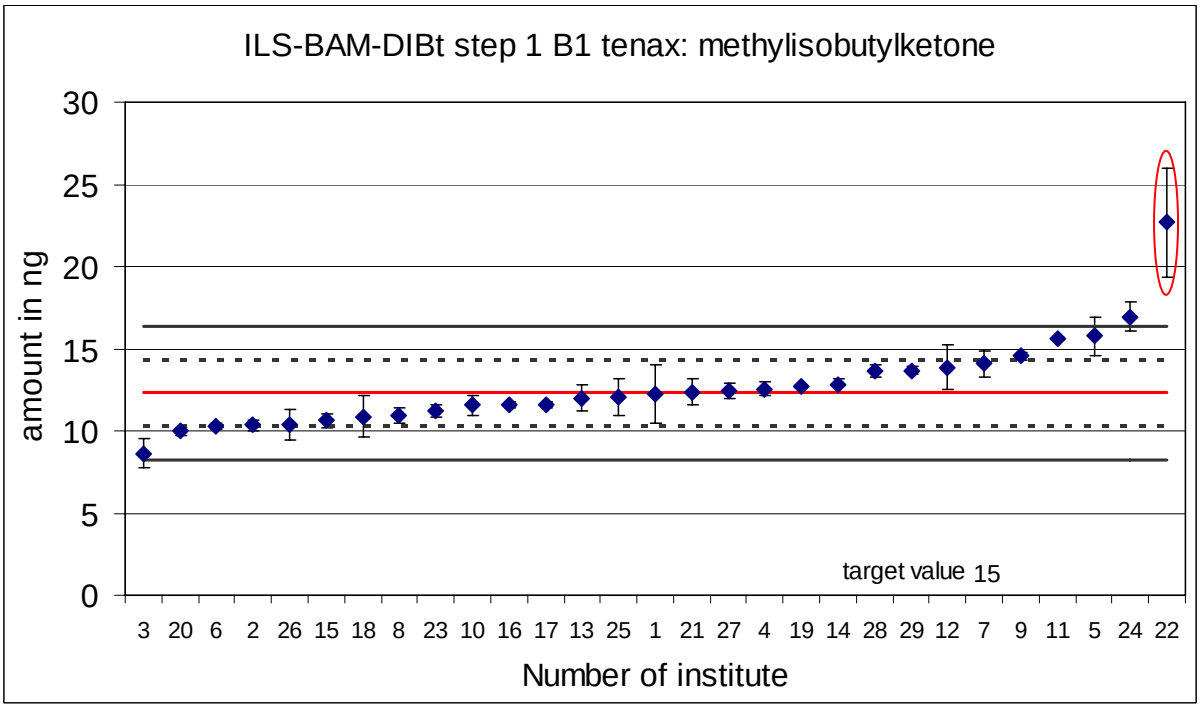


Figure 23: Results MIBK solution B1 injected on Tenax (outlier marked)

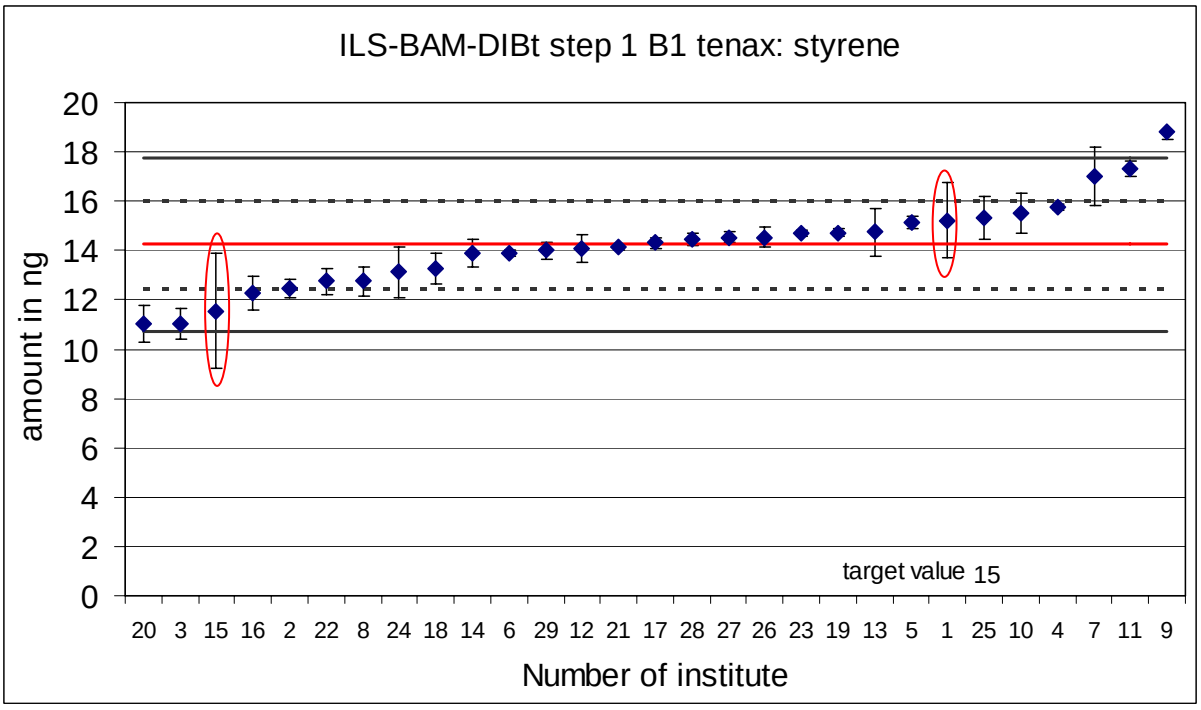


Figure 24: Results styrene solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

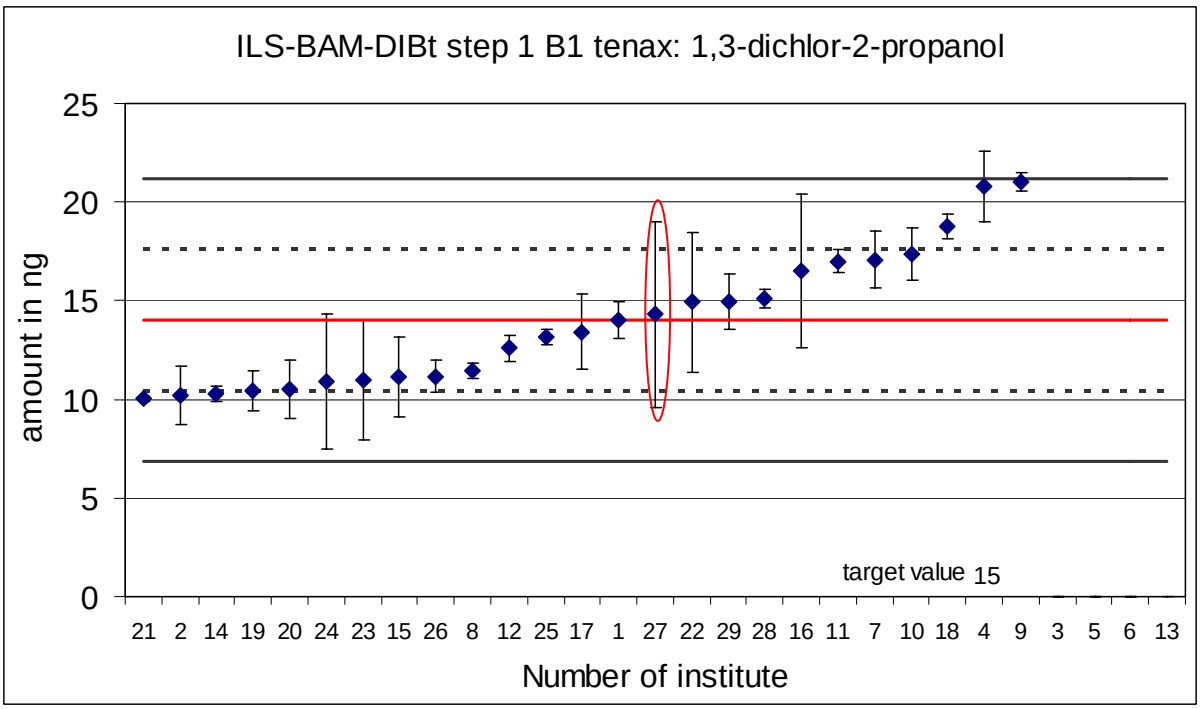


Figure 25: Results 1,3-dichloro-2-propanol solution B1 injected on Tenax (outlier marked)

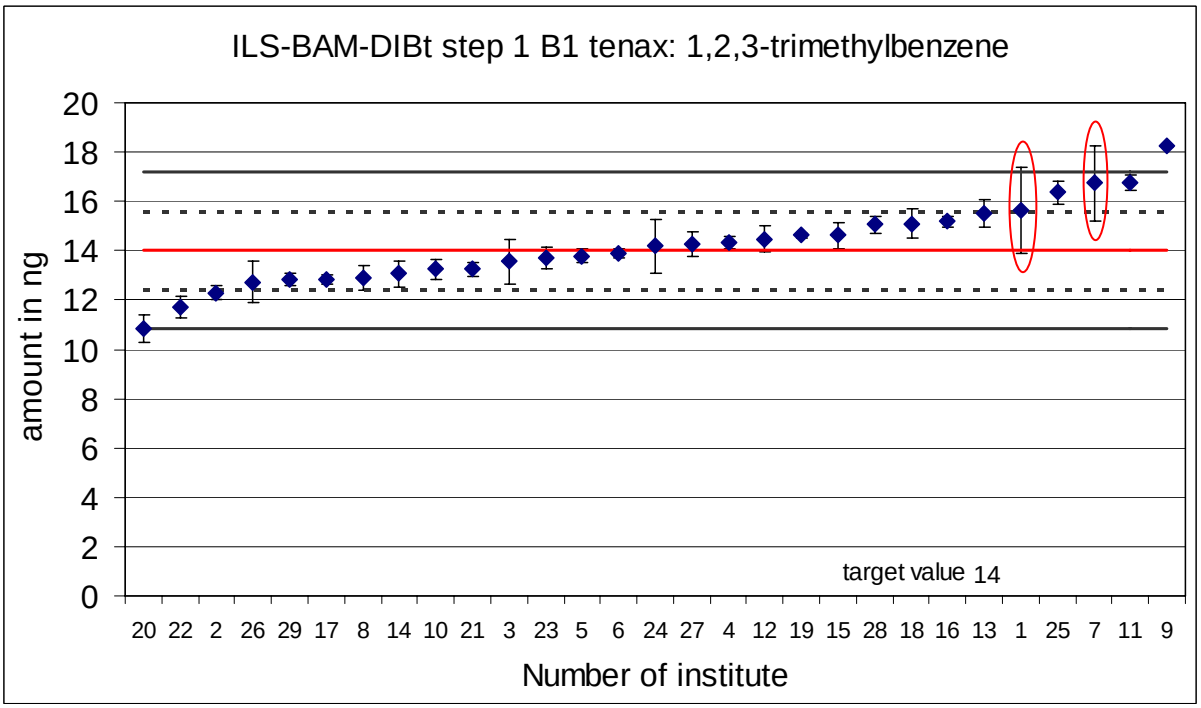


Figure 26: Results 1,2,3-trimethylbenzene solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

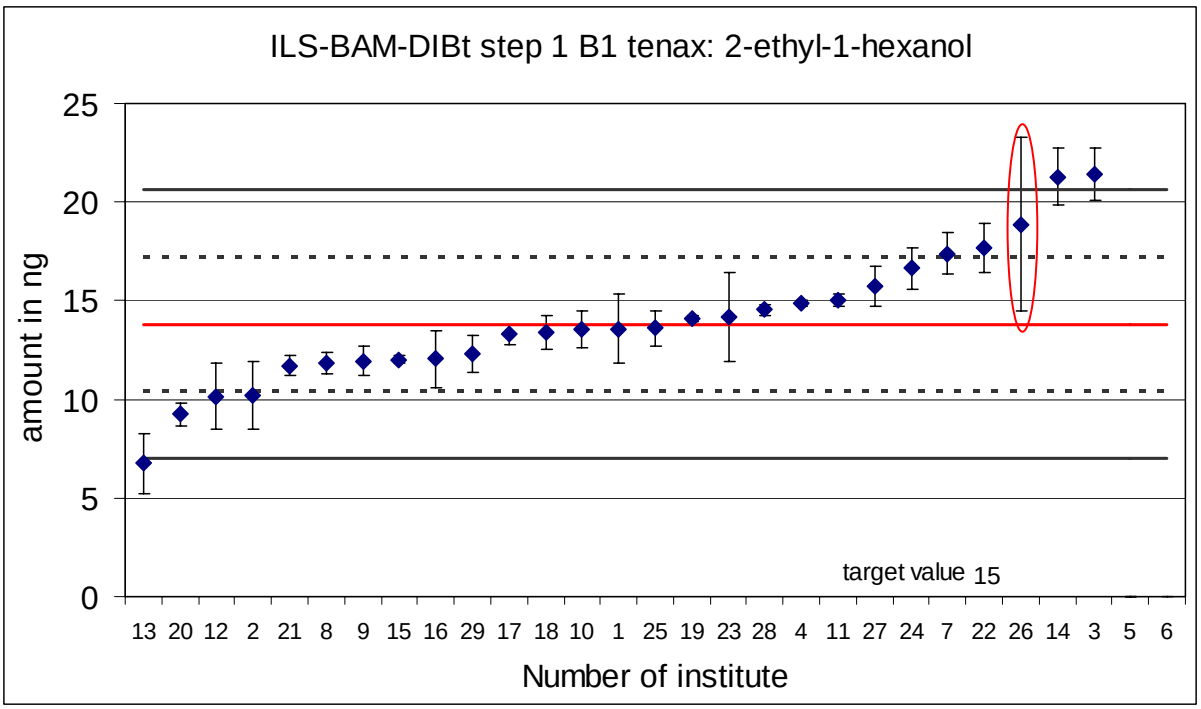


Figure 27: Results 2-ethyl-1-hexanol solution B1 injected on Tenax (outlier marked)

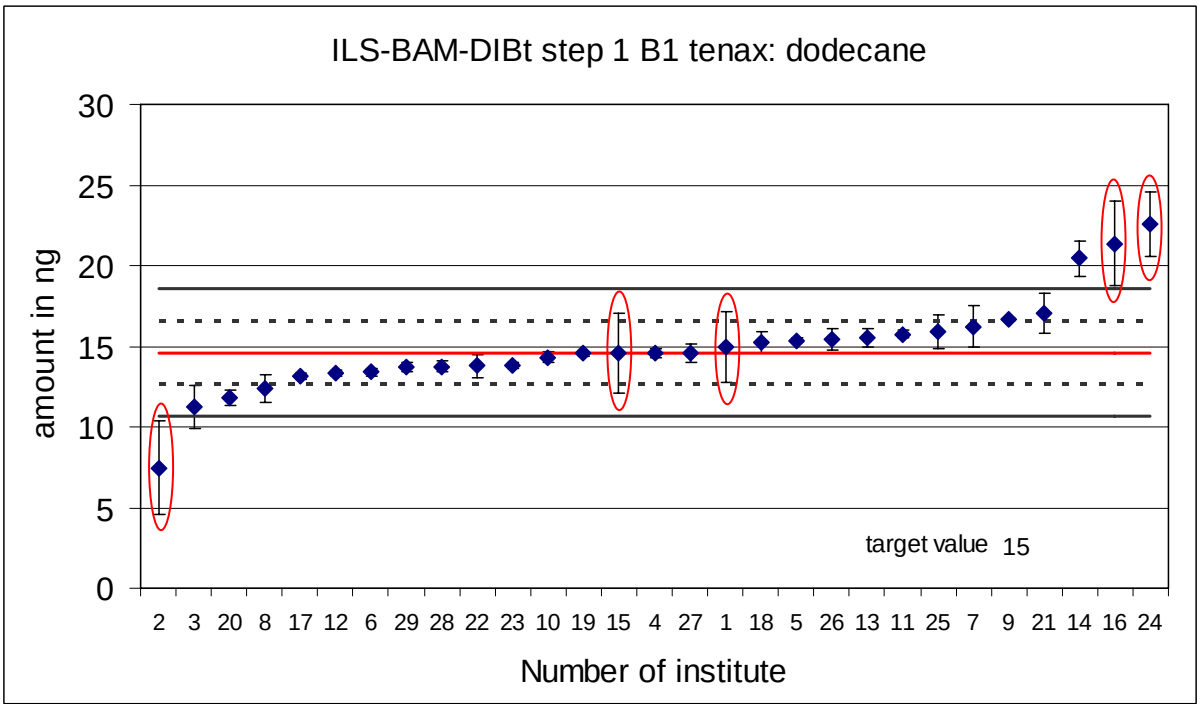


Figure 28: Results dodecane solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

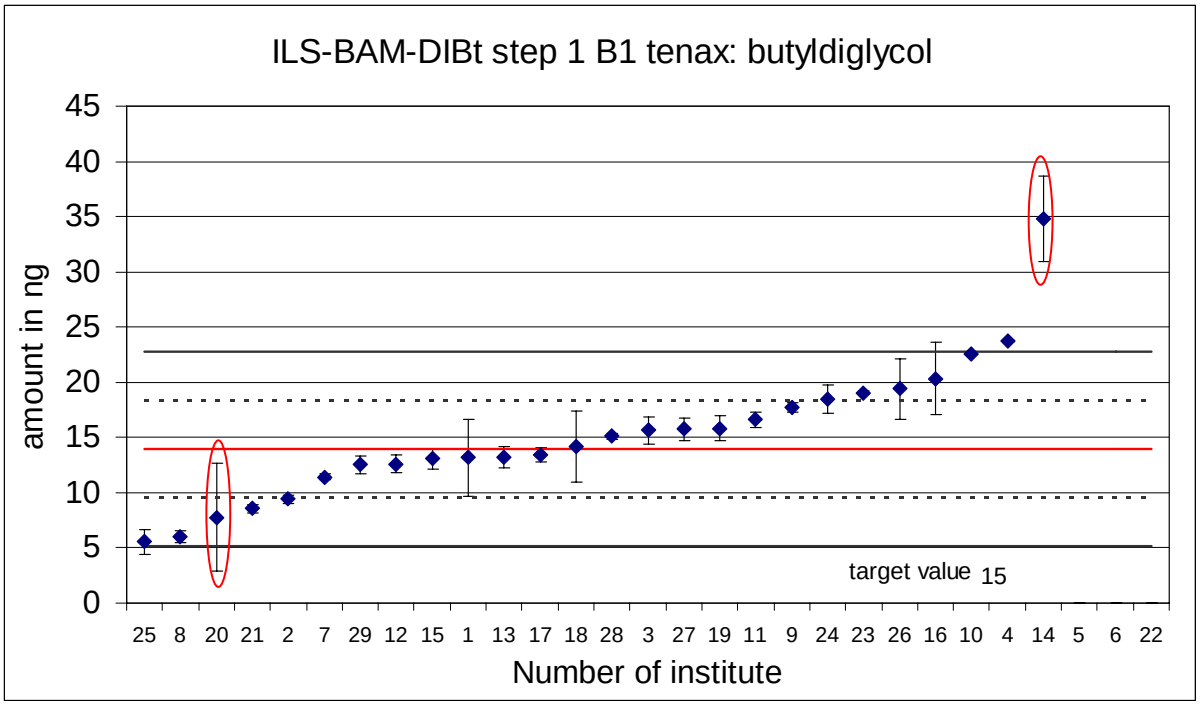


Figure 29: Results butyl diglycol solution B1 injected on Tenax (outlier marked)

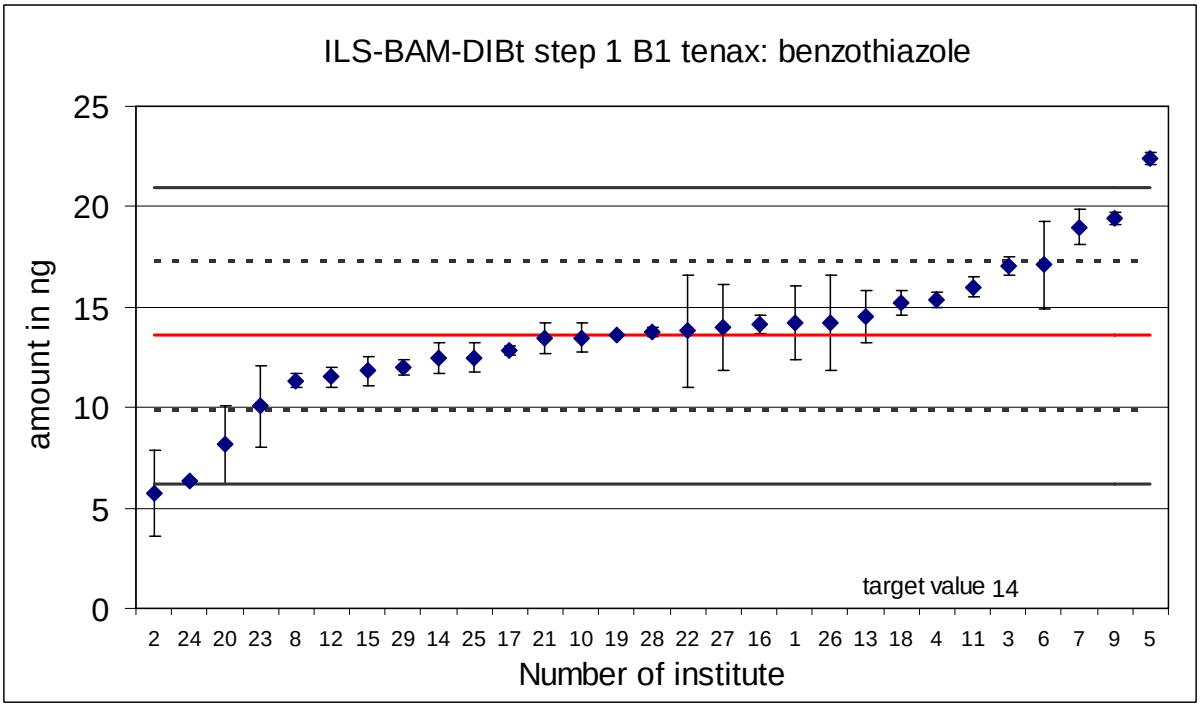


Figure 30: Results benzothiazole solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

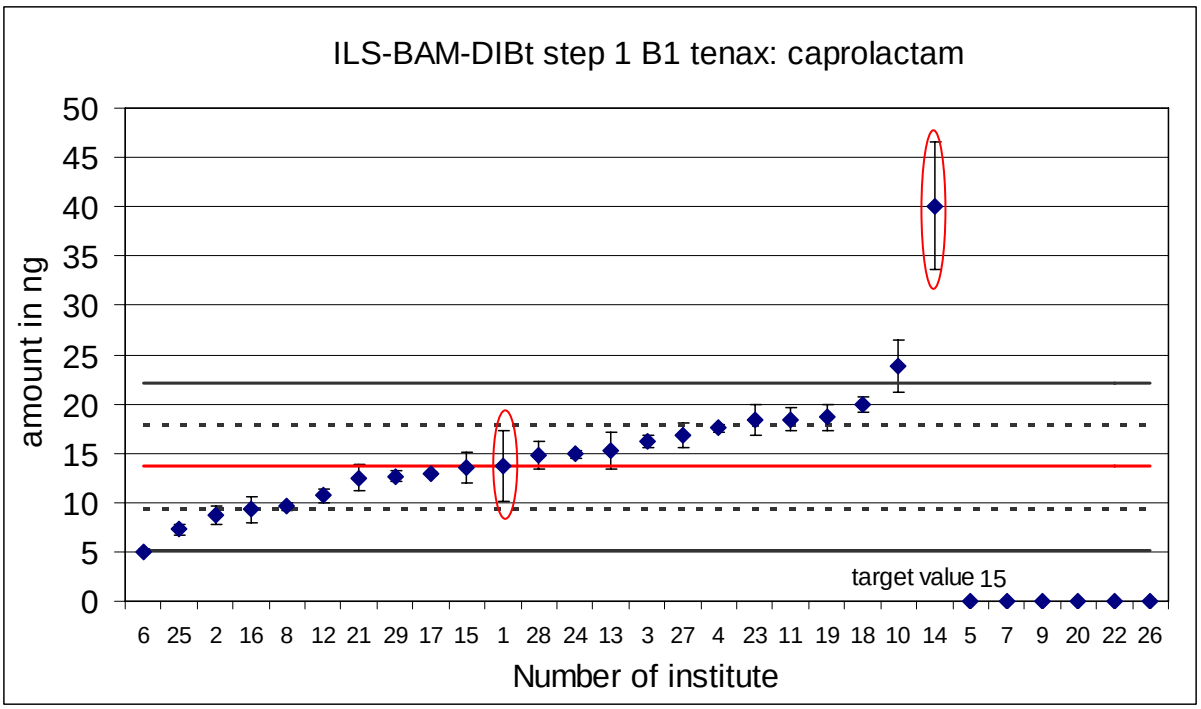


Figure 31: Results caprolactam solution B1 injected on Tenax (outlier marked)

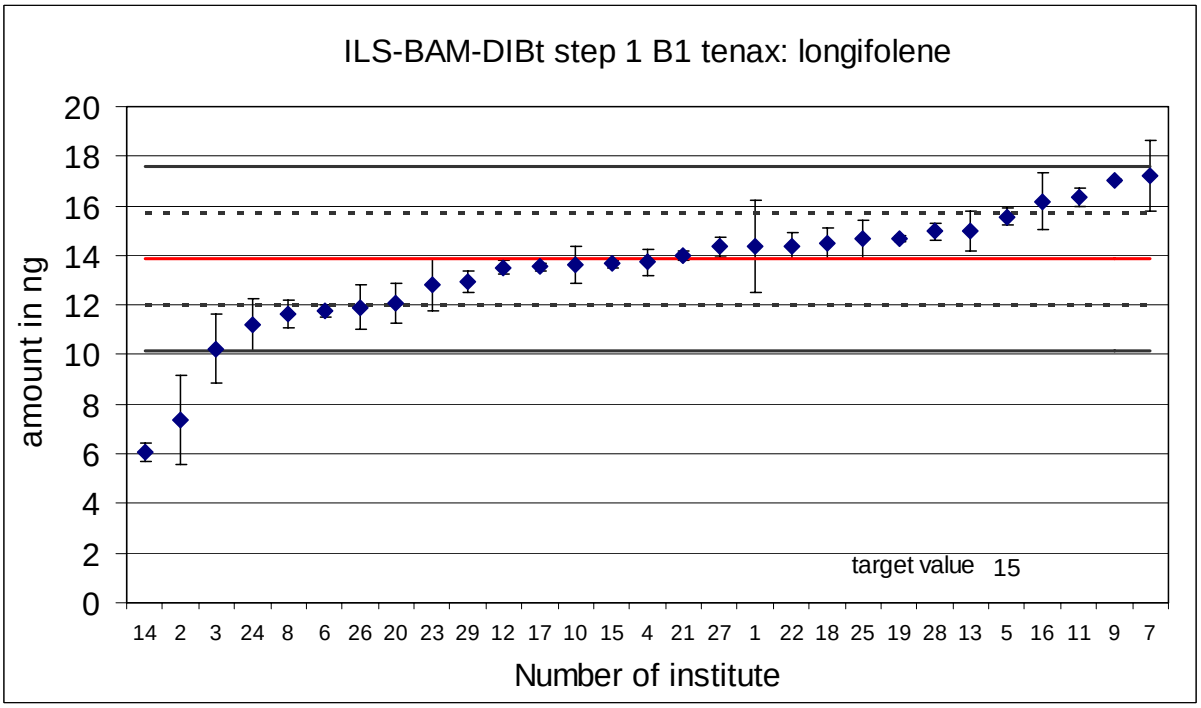


Figure 32: Results longifolene solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

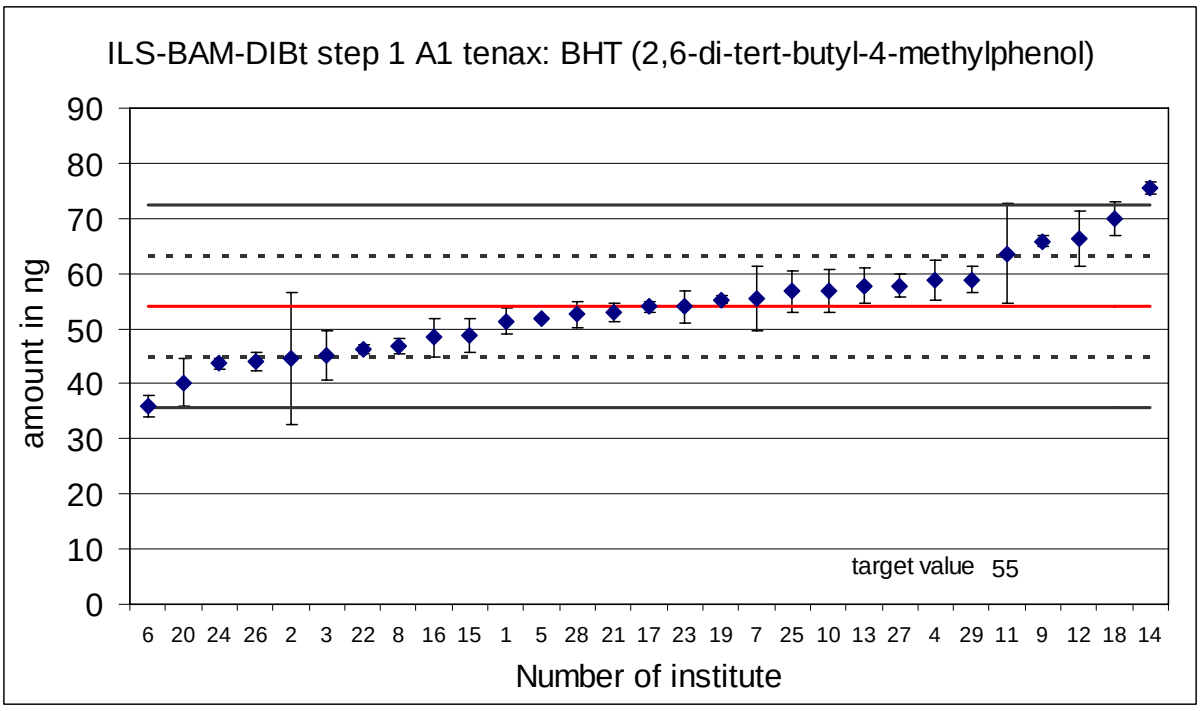


Figure 33: Results BHT (2,6-Di-tert-butyl-4-methylphenol) solution B1 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

7.4.1.4. Solution B2

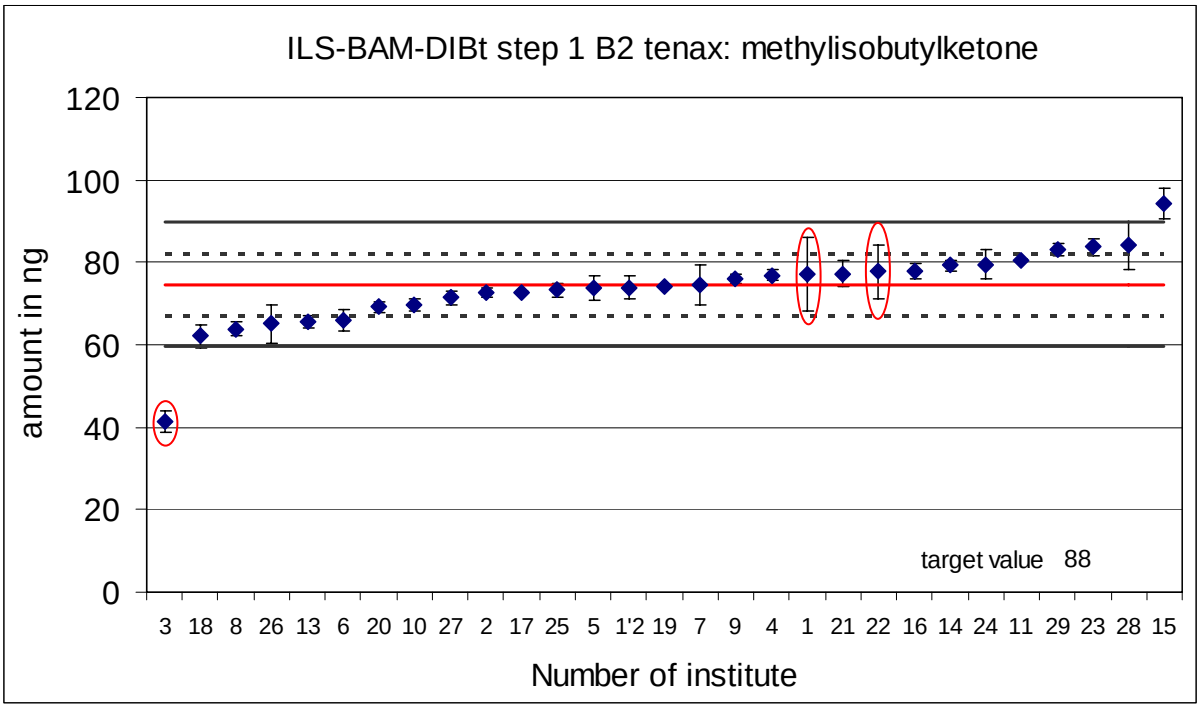


Figure 34: Results MIBK solution B2 injected on Tenax (outlier marked)

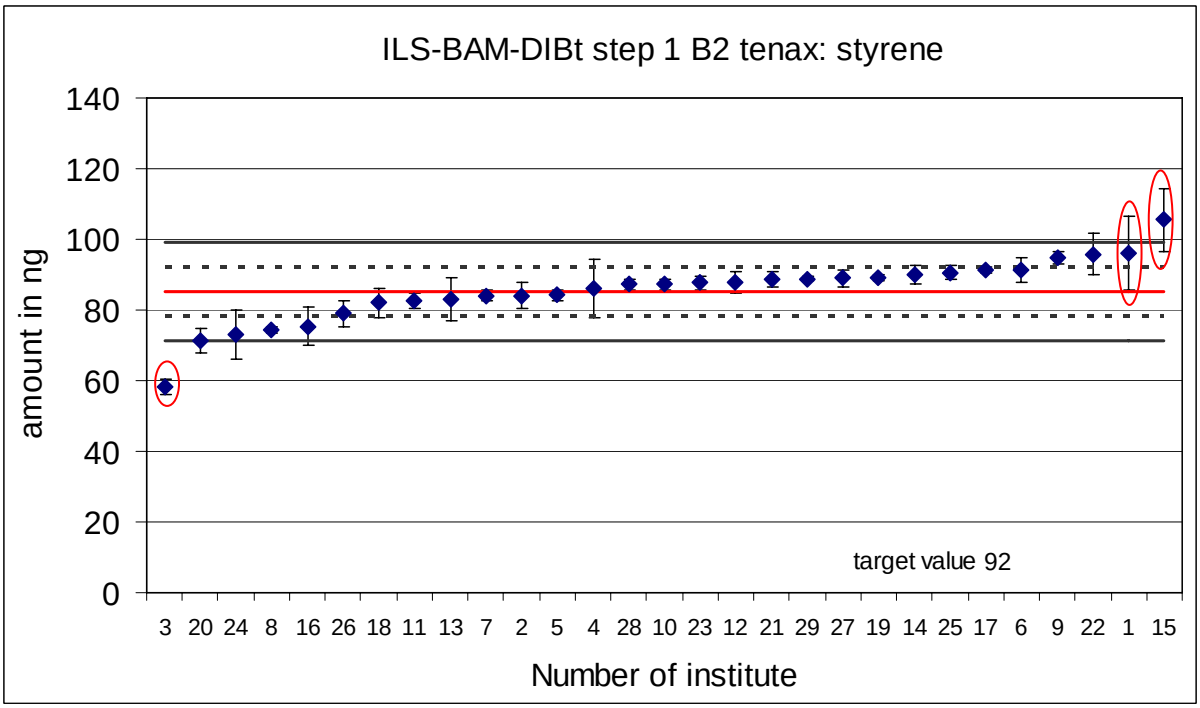


Figure 35: Results styrene solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

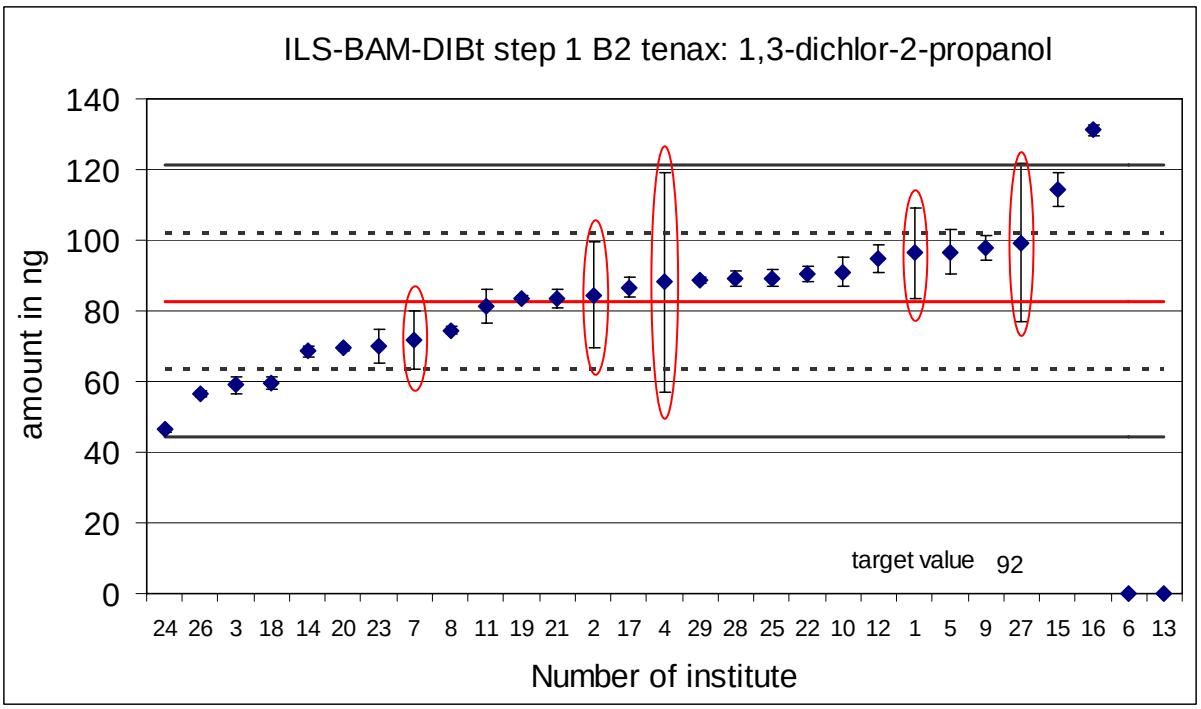


Figure 36: Results 1,3-dichloro-2-propanol solution B2 injected on Tenax (outlier marked)

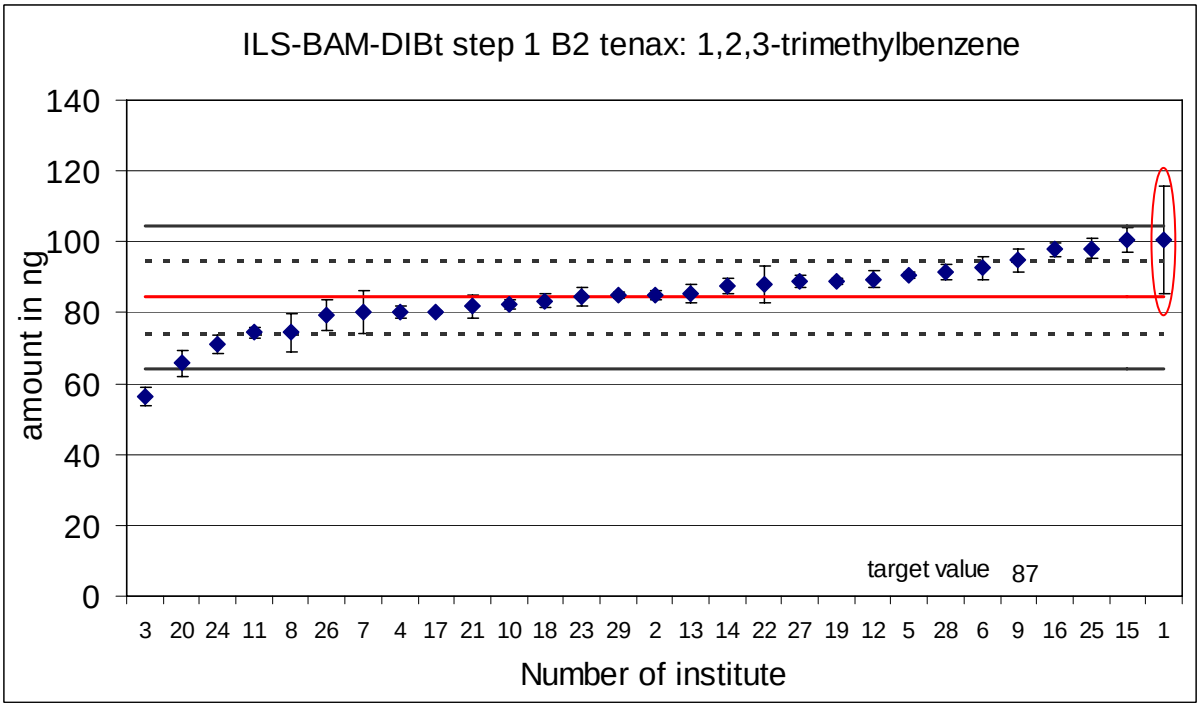


Figure 37: Results 1,2,3-trimethylbenzene solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

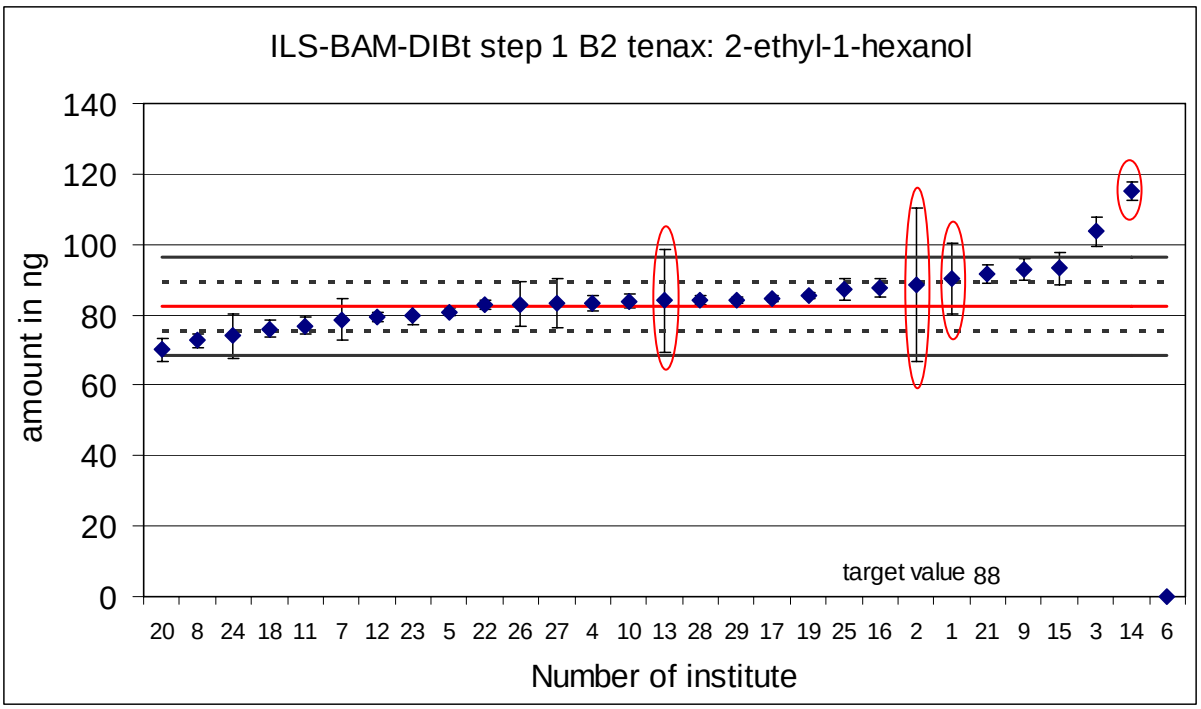


Figure 38: Results 2-ethyl-1-hexanol solution B2 injected on Tenax (outlier marked)

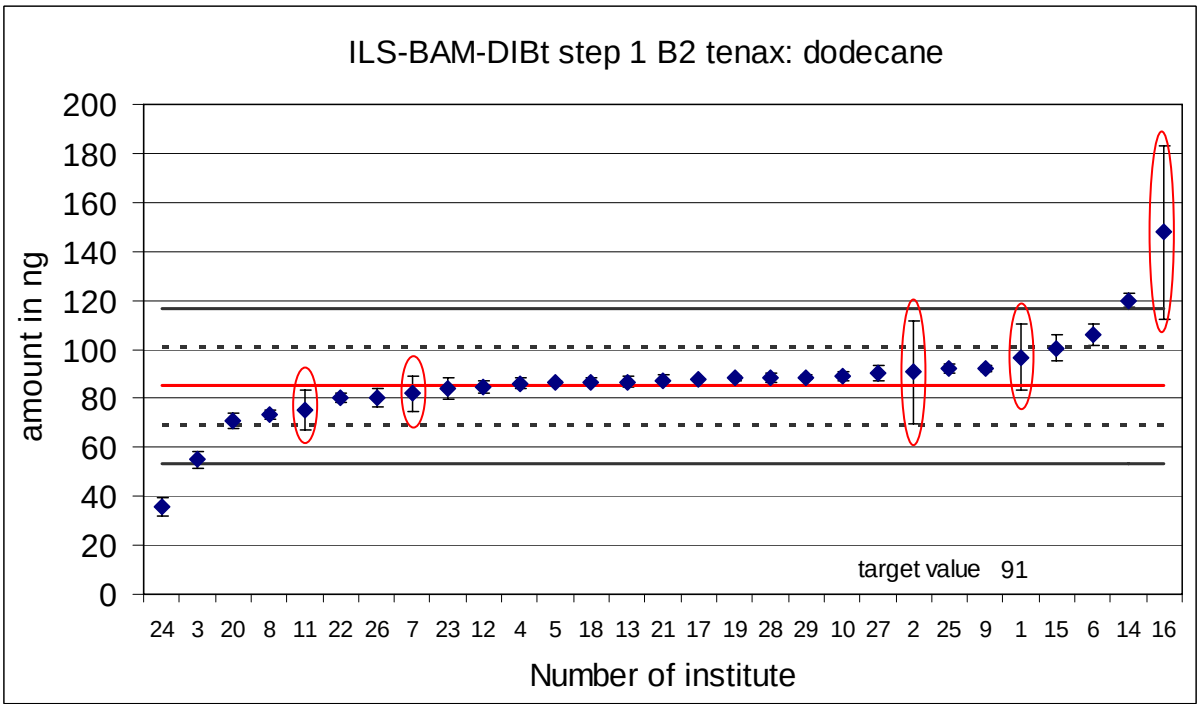


Figure 39: Results dodecane solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

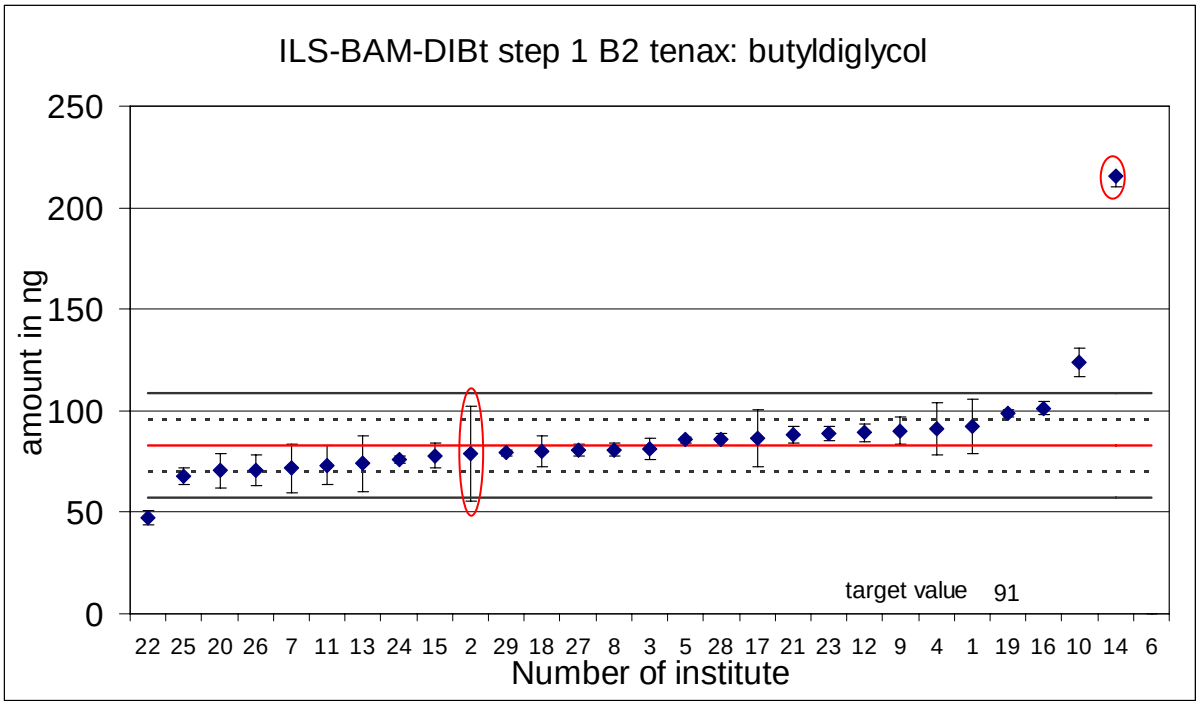


Figure 40: Results butyl diglycol solution B2 injected on Tenax (outlier marked)

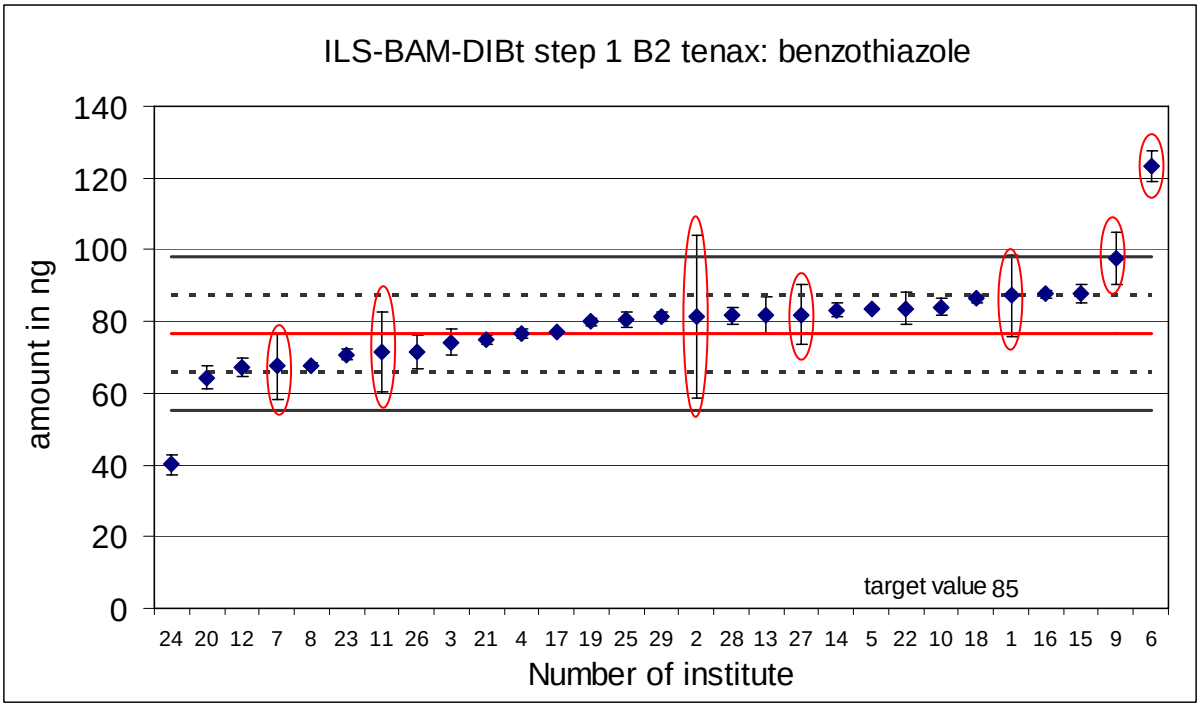


Figure 41: Results benzothiazole solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

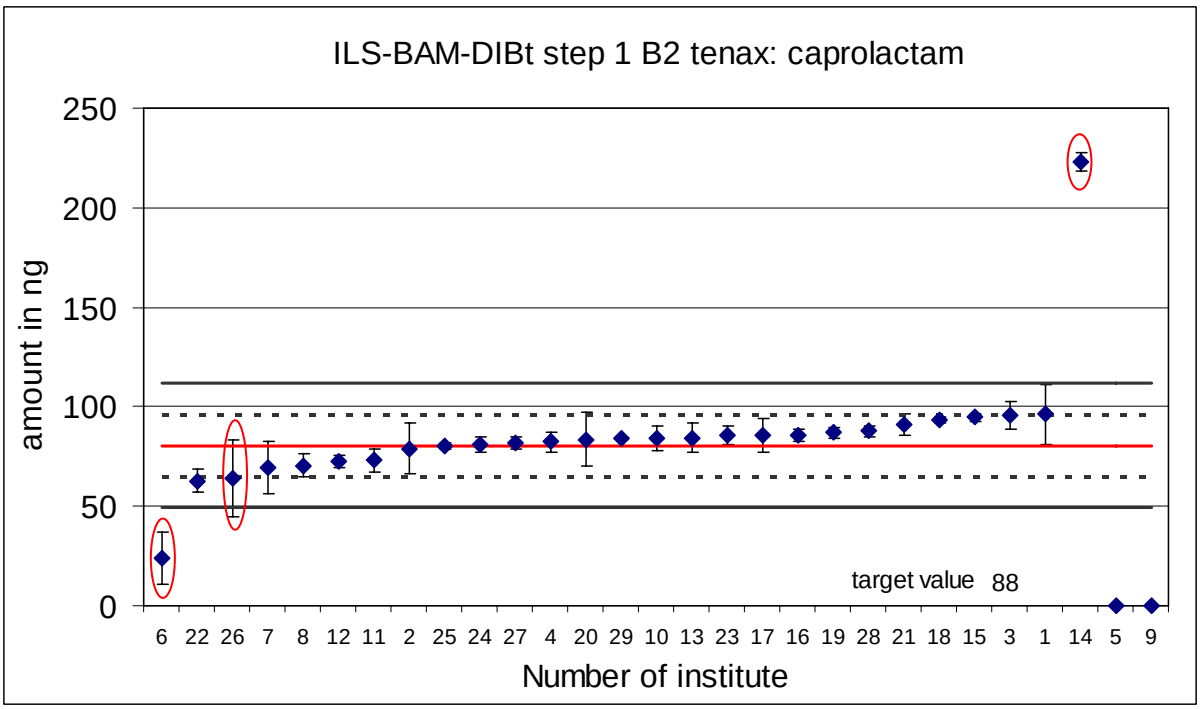


Figure 42: Results caprolactam solution B2 injected on Tenax (outlier marked)

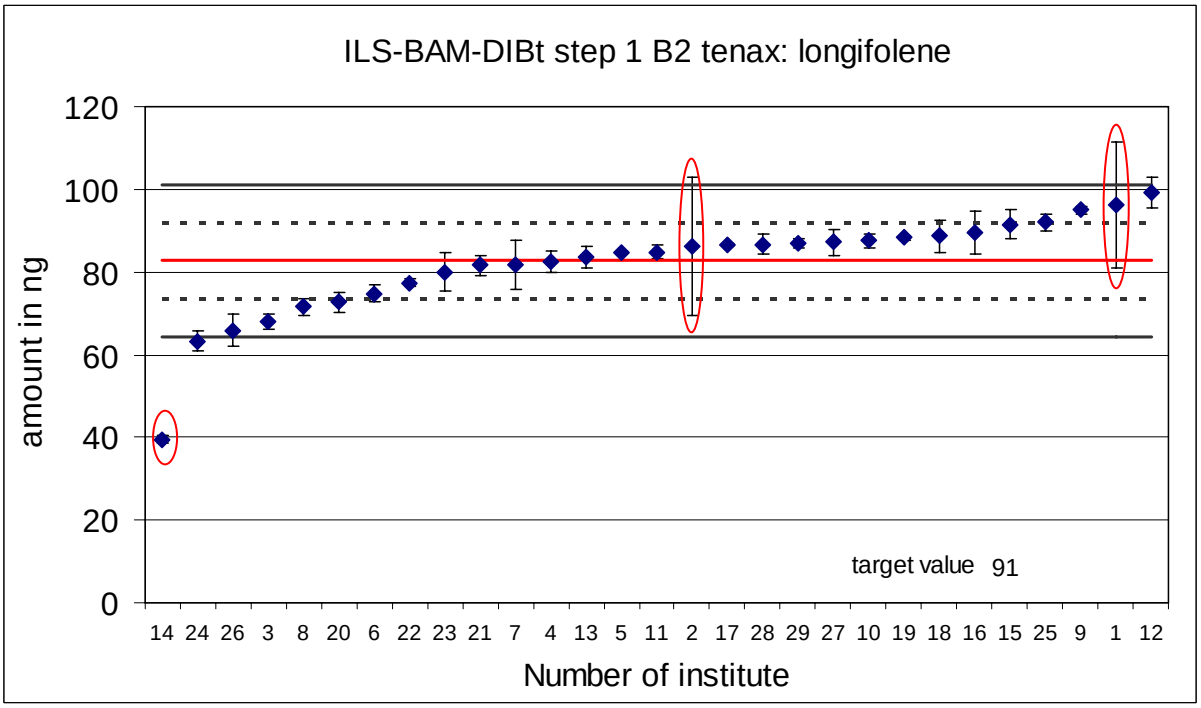


Figure 43: Results longifolene solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

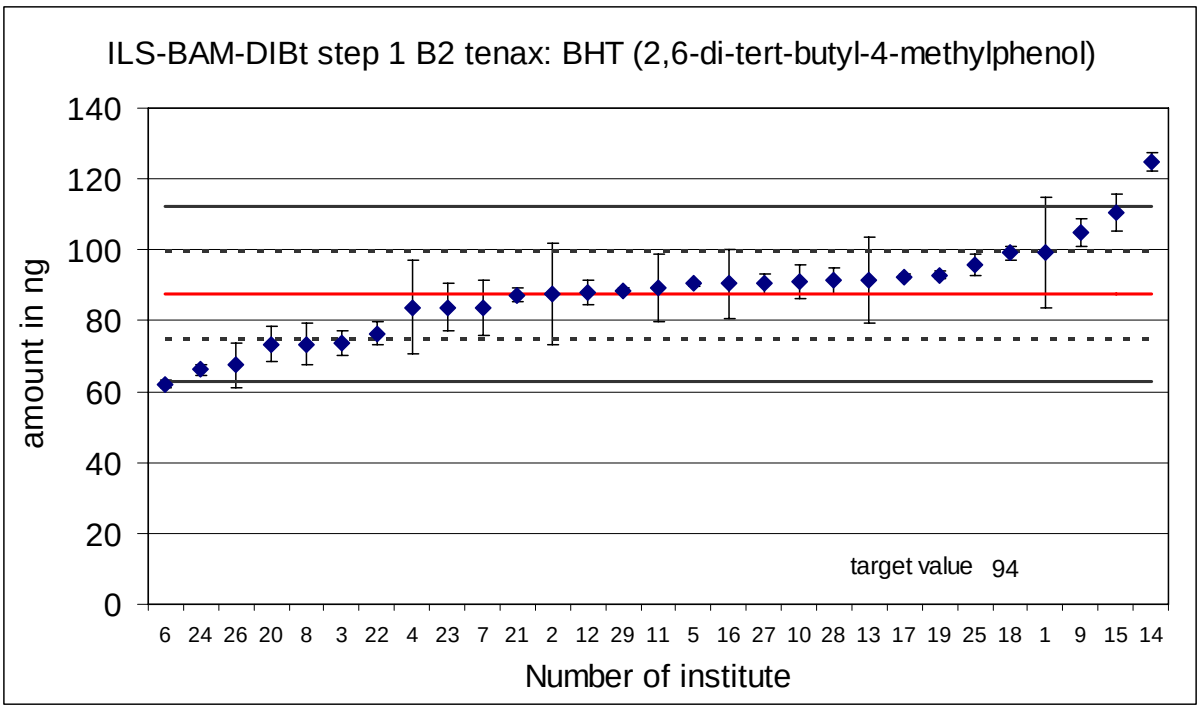


Figure 44: Results BHT (2,6-Di-tert-butyl-4-methylphenol) solution B2 injected on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

7.4.2. Results of ILS BAM/DIBt step 2

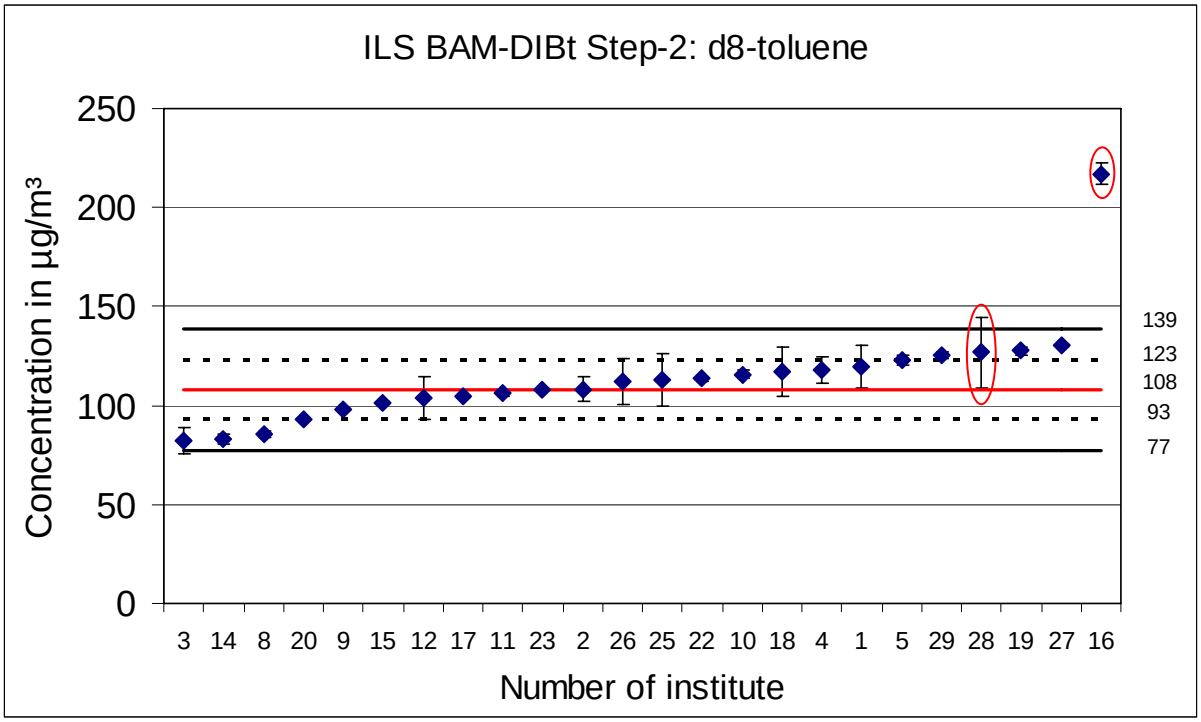


Figure 45: Results d_8-toluene (permeatiauf tube) sampled on Tenax (outlier marked), target value: 122 µg/m³

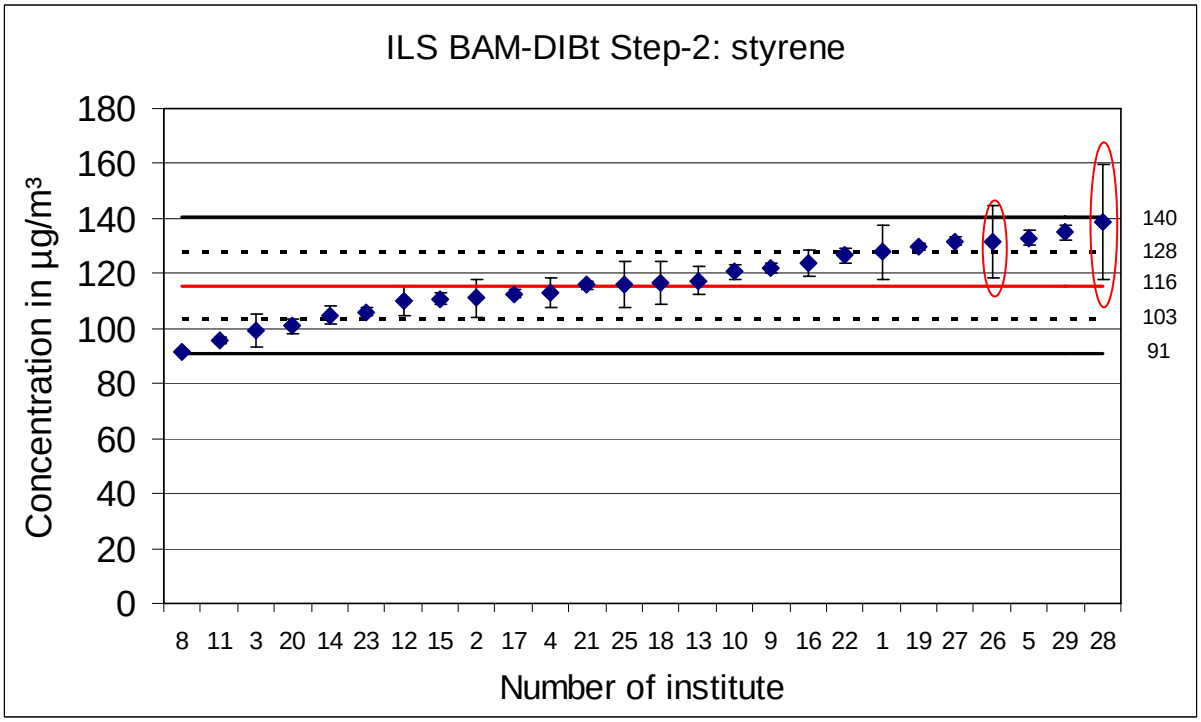


Figure 46: Results styrene sampled on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

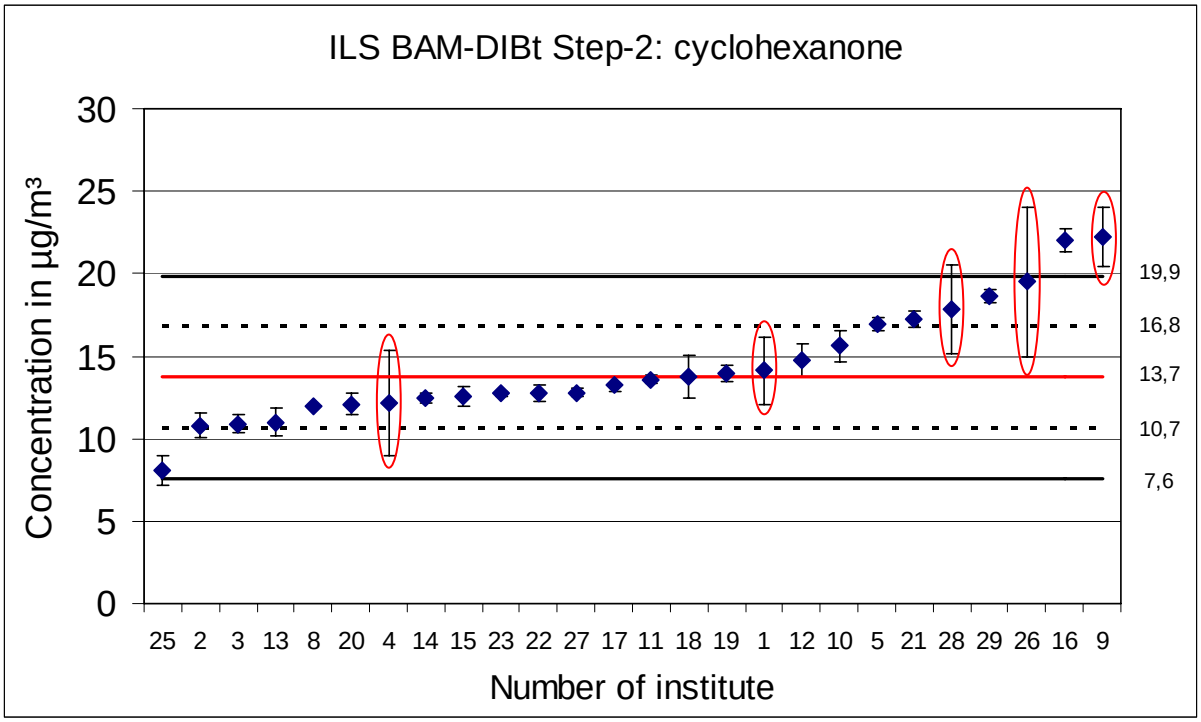


Figure 47: Results cyclohexanone sampled on Tenax (outlier marked)

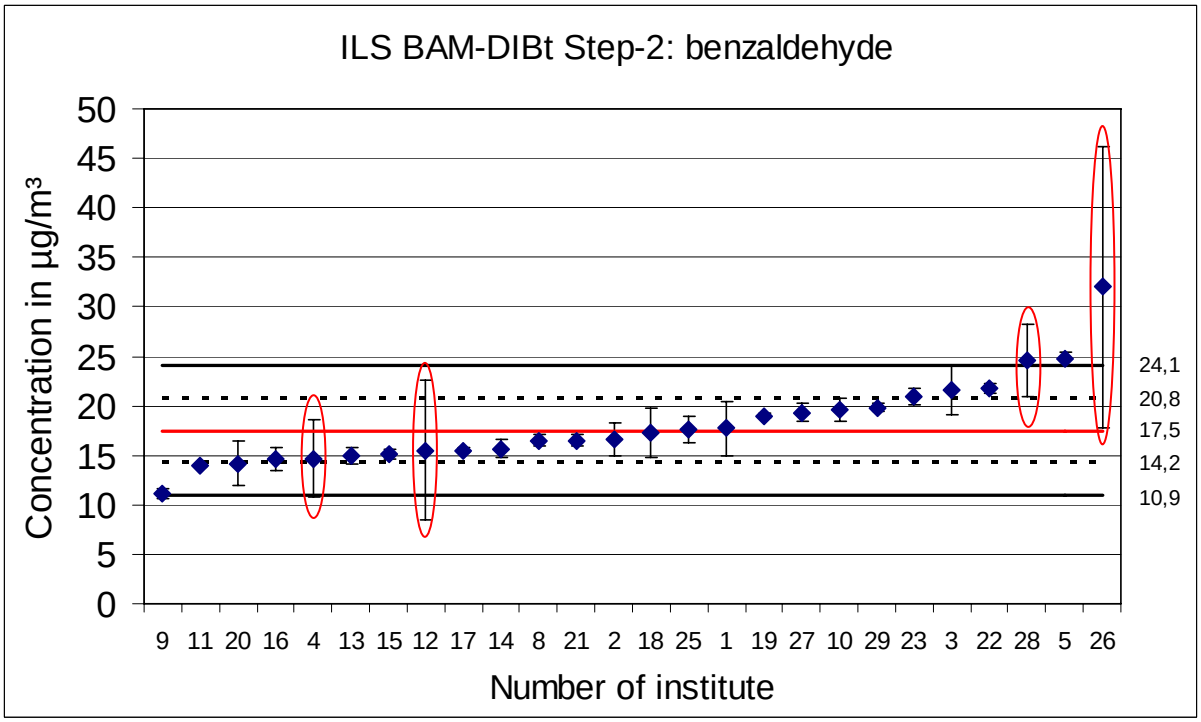


Figure 48: Results benzaldehyde sampled on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

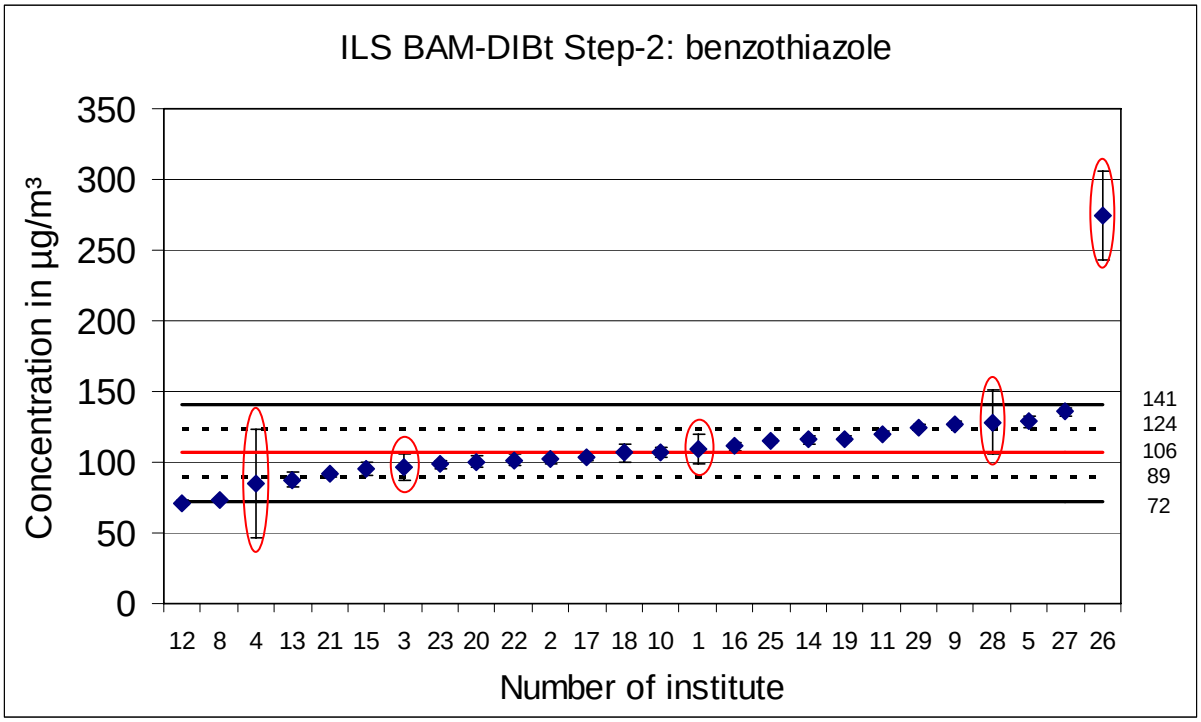


Figure 49: Results benzothiazol sampled on Tenax (outlier marked)

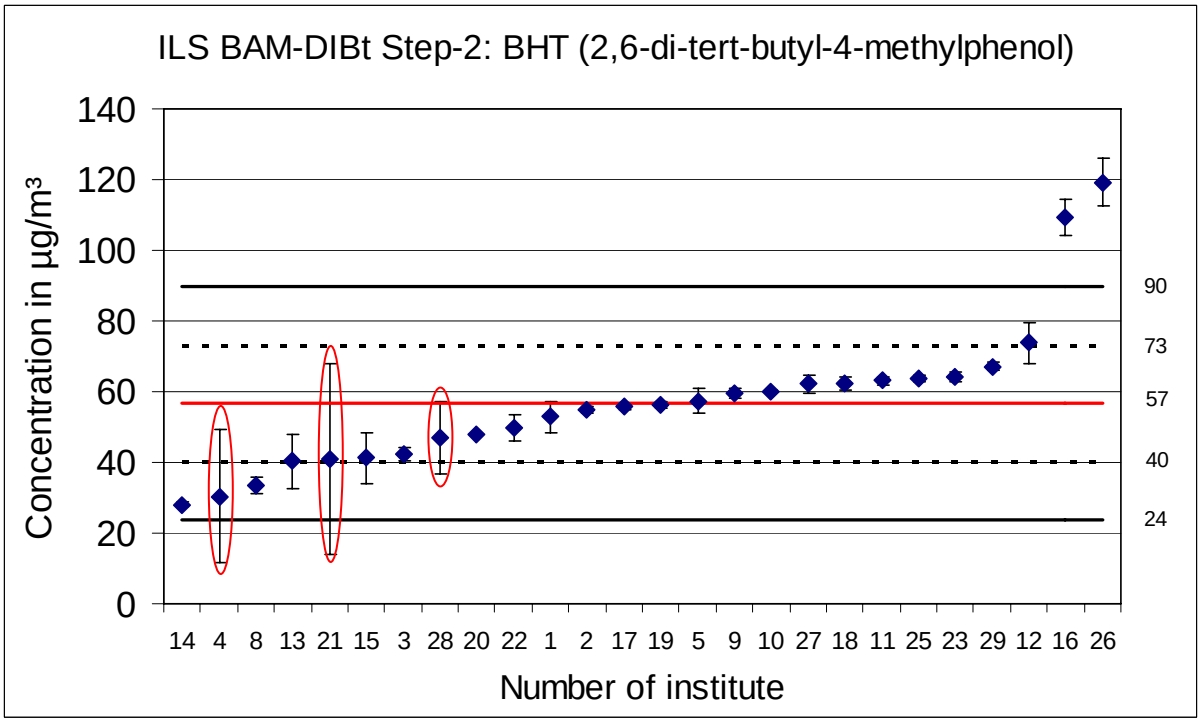


Figure 50: Results BHT sampled on Tenax (outlier marked)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

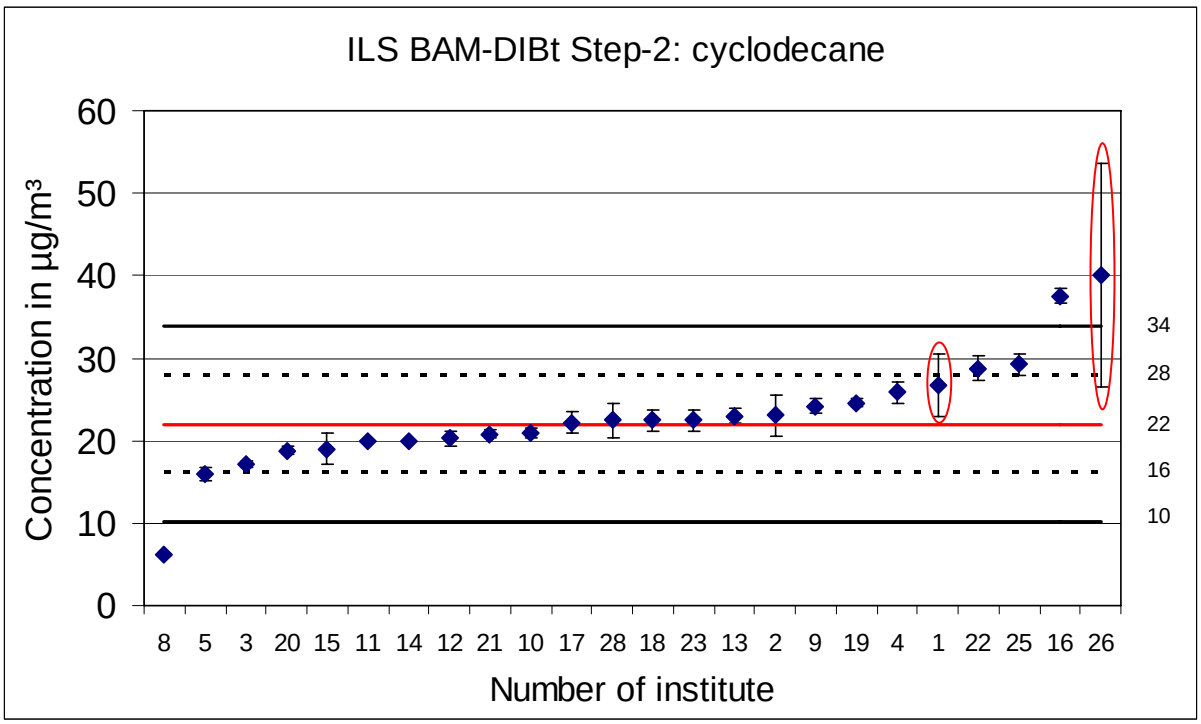


Figure 51: Results Cyclodecane sampled on Tenax (outlier marked)

The following compound is quantified with the response of native toluene.

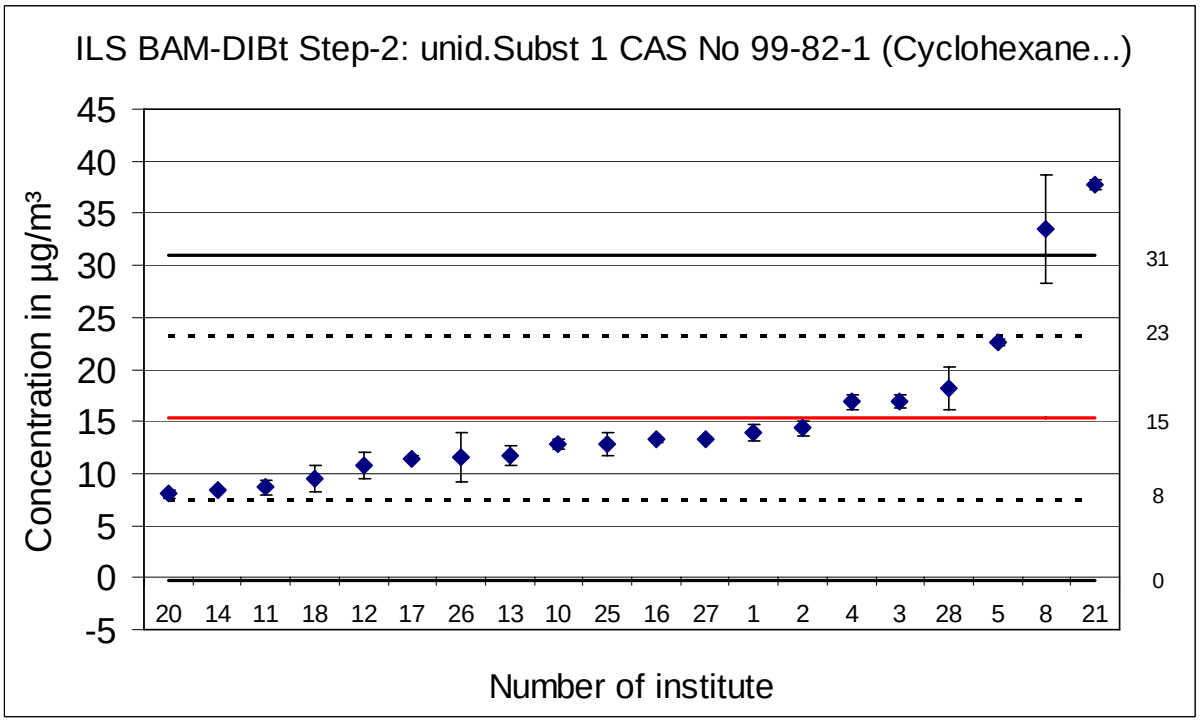


Figure 52: Results of the unidentified compound No. 1 sampled on Tenax (all data)

Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

The following compounds are quantified with the response of native toluene.

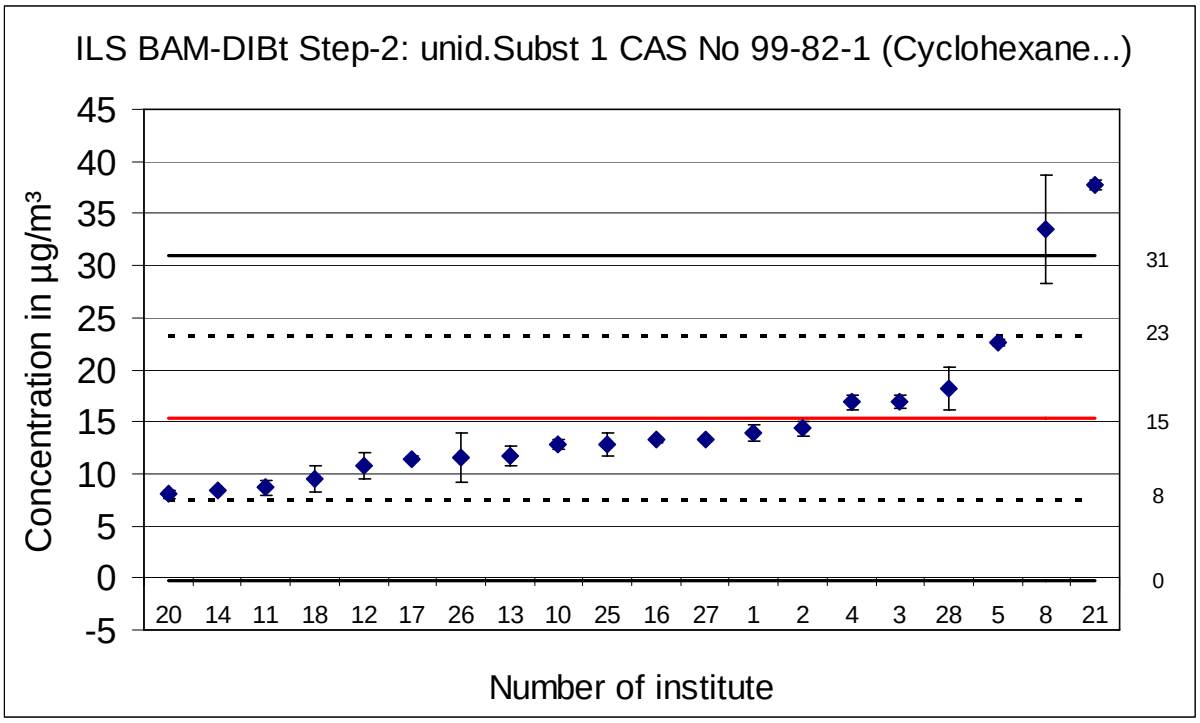


Figure 53: Results of the unidentified compound No. 1 sampled on Tenax (all data)

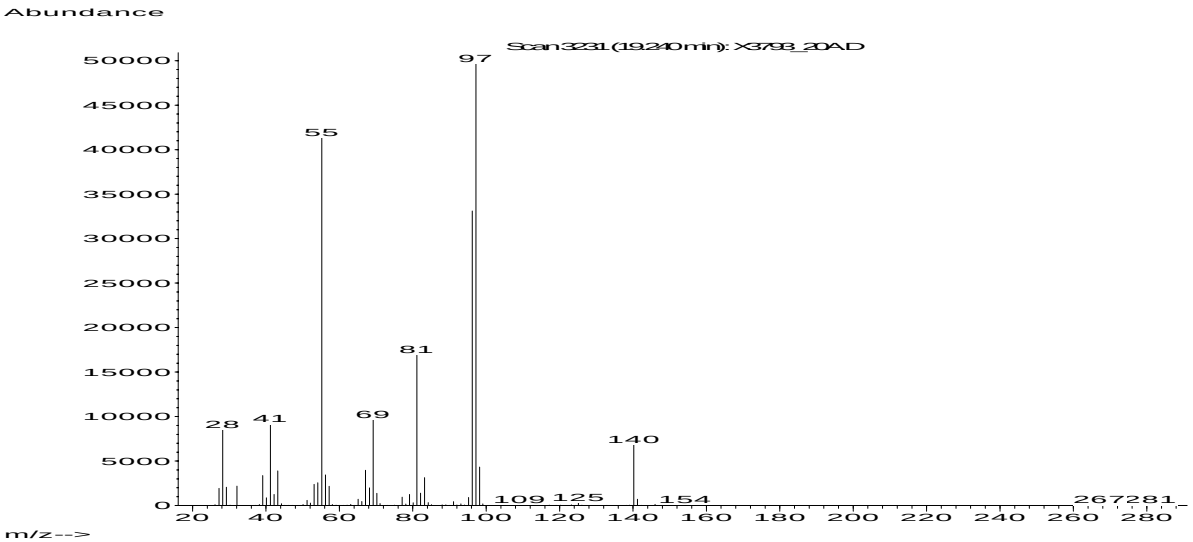


Figure 54: MS-Spectrum of the unidentified compound No. 1

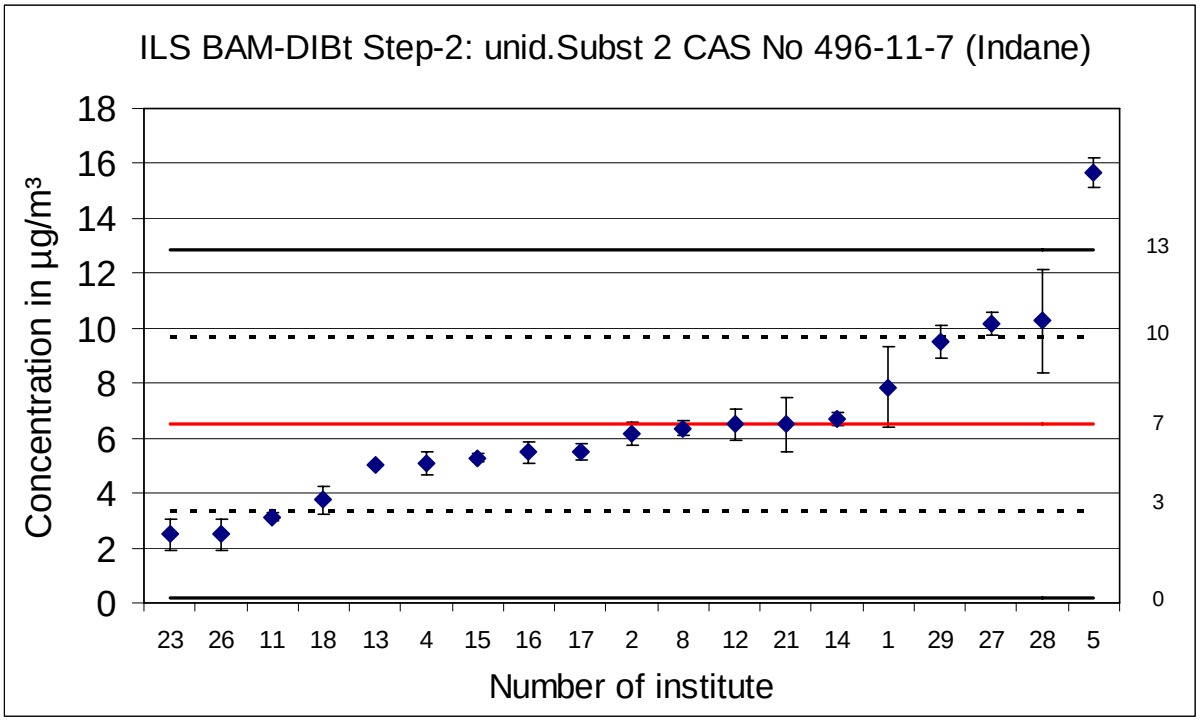


Figure 55: Results of the unidentified compound No. 2 sampled on Tenax (all data)

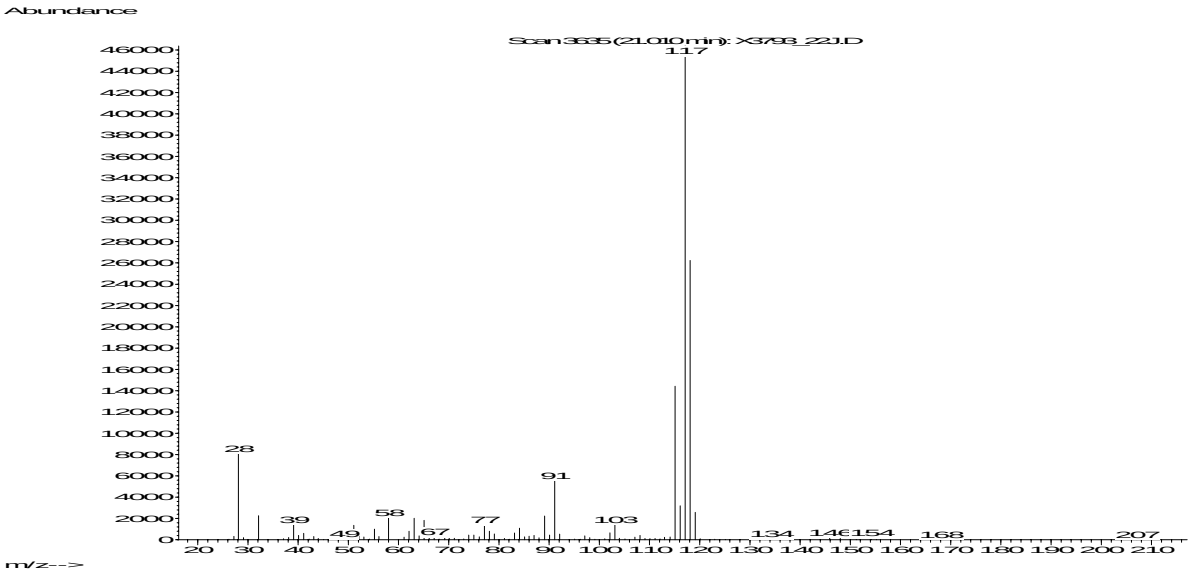


Figure 56: MS-Spectrum of the unidentified compound No. 2

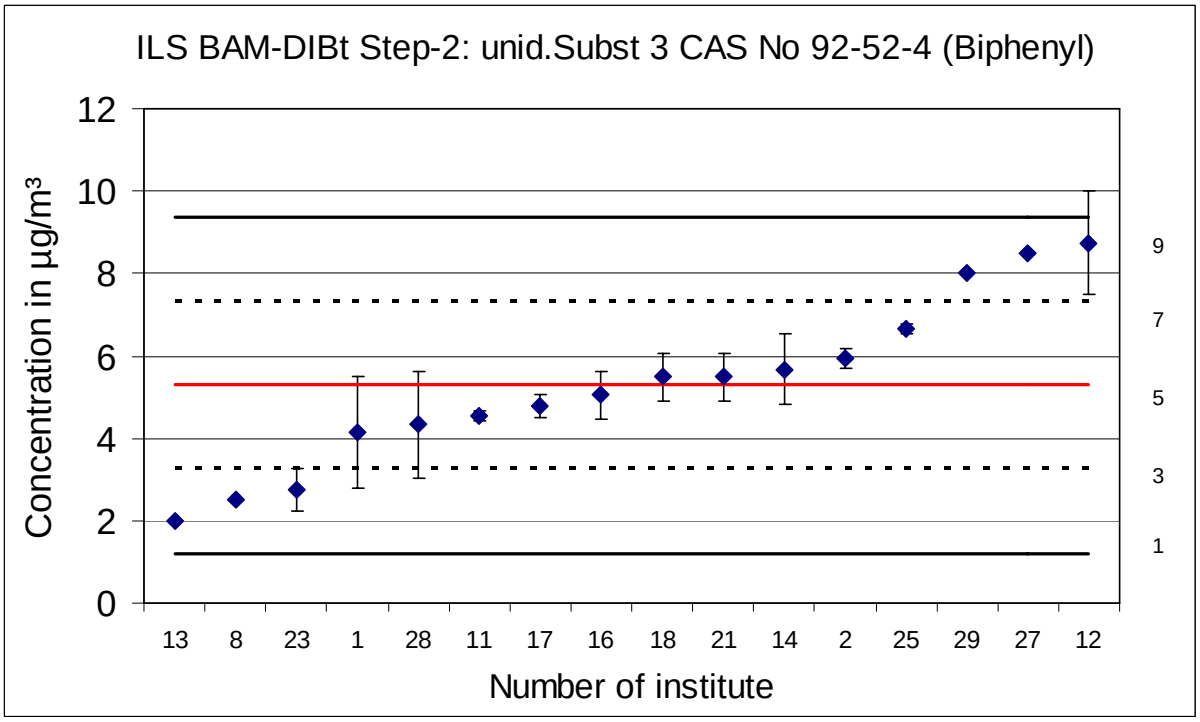


Figure 57: Results of the unidentified compound No. 3 sampled on Tenax (all data)

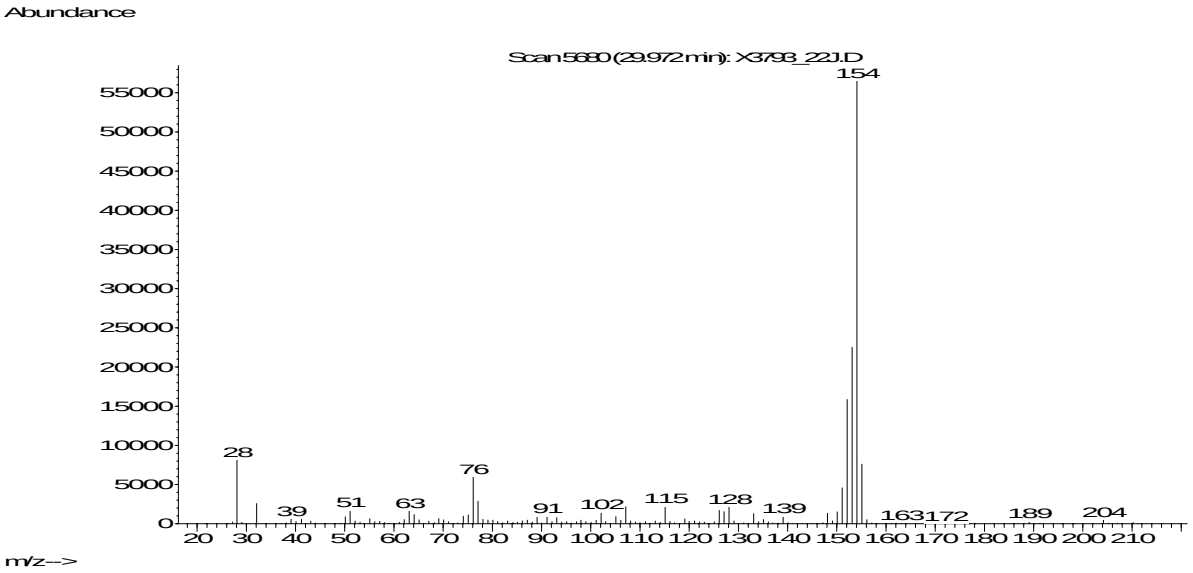


Figure 58: MS-Spectrum of the unidentified compound No. 3

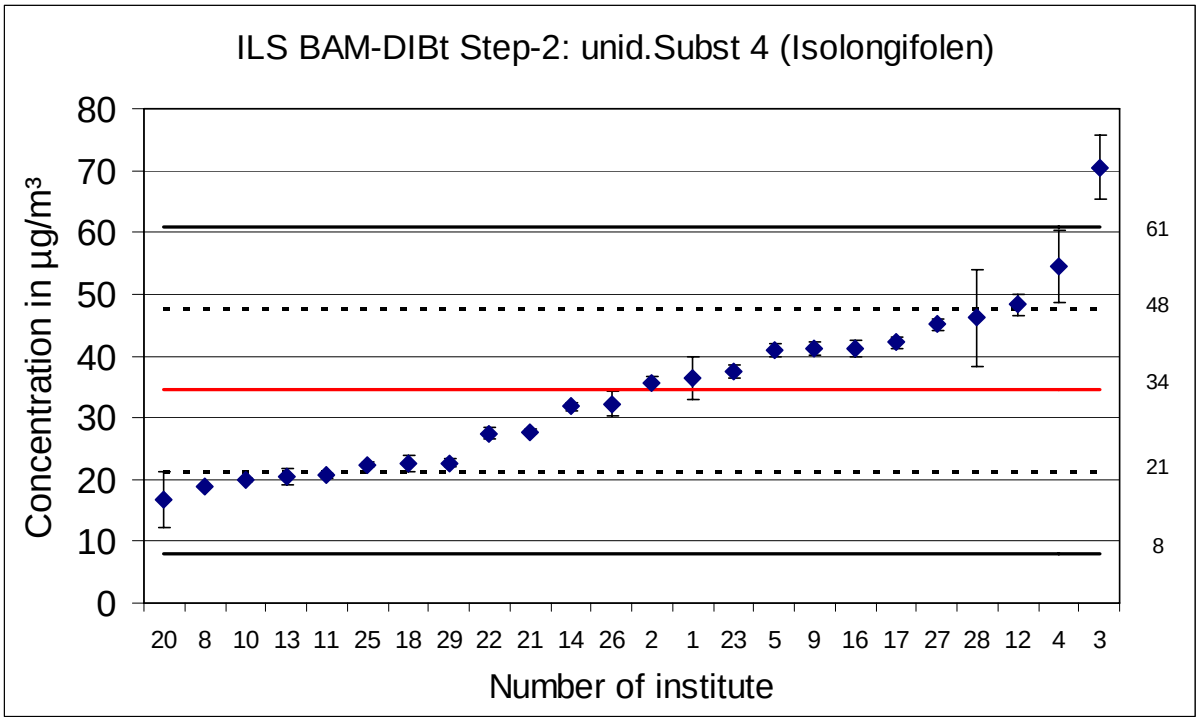


Figure 59: Results of the unidentified compound No. 4 sampled on Tenax (all data)

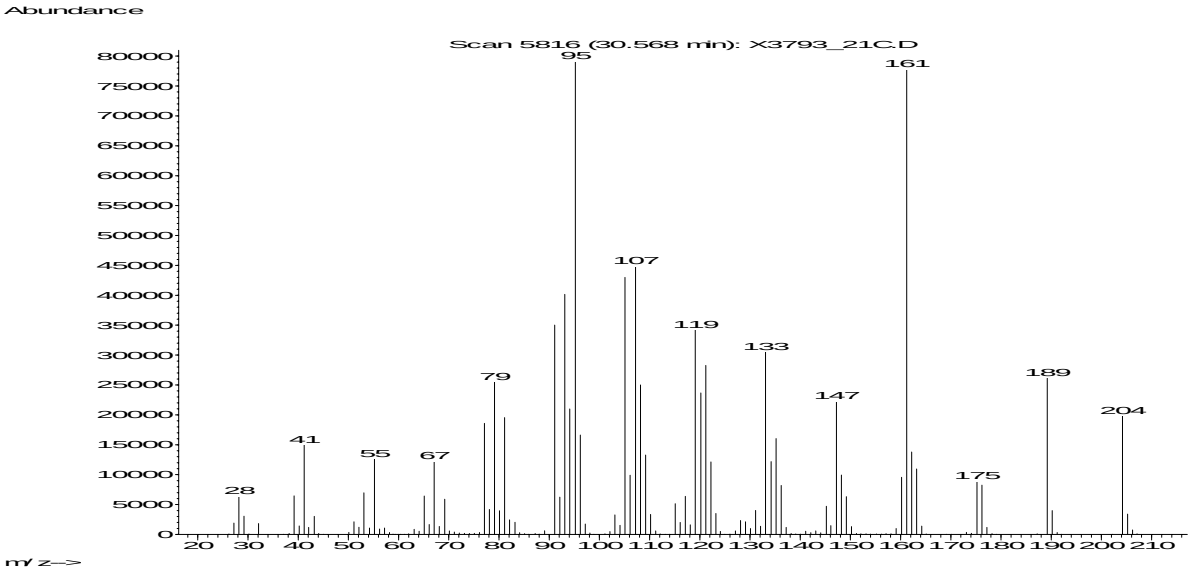


Figure 60: MS-Spectrum of the unidentified compound No. 4

7.4.3. Results of ILS BAM/DIBt step 3

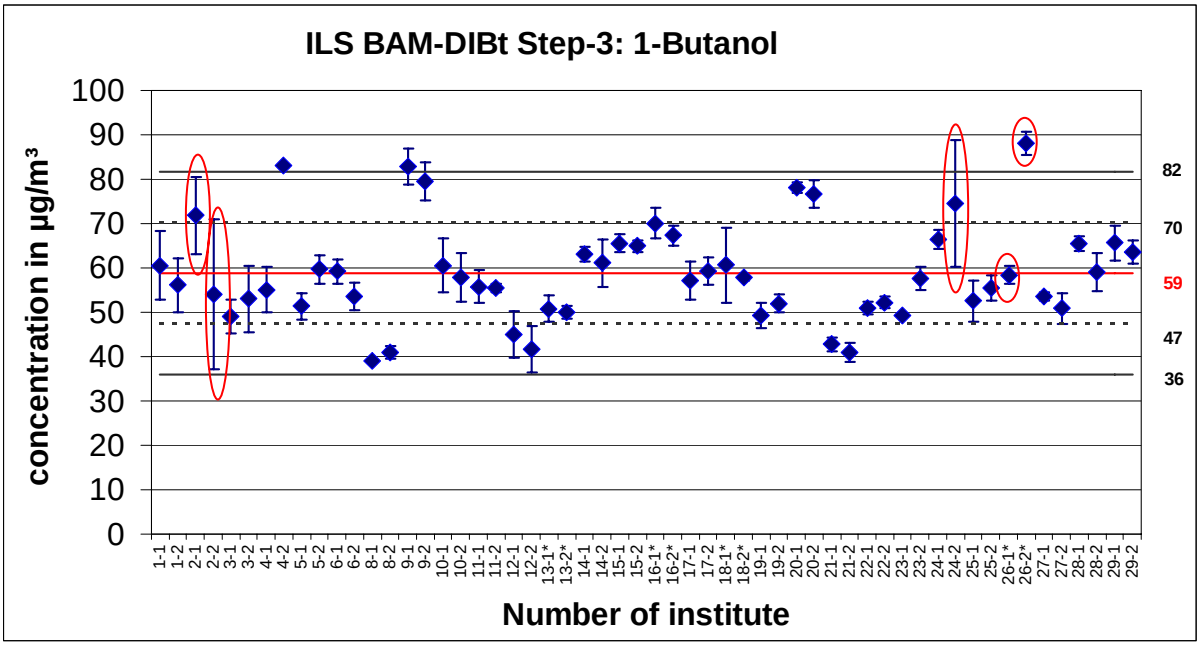


Figure 61: Results for n-Butanol (outlier marked)

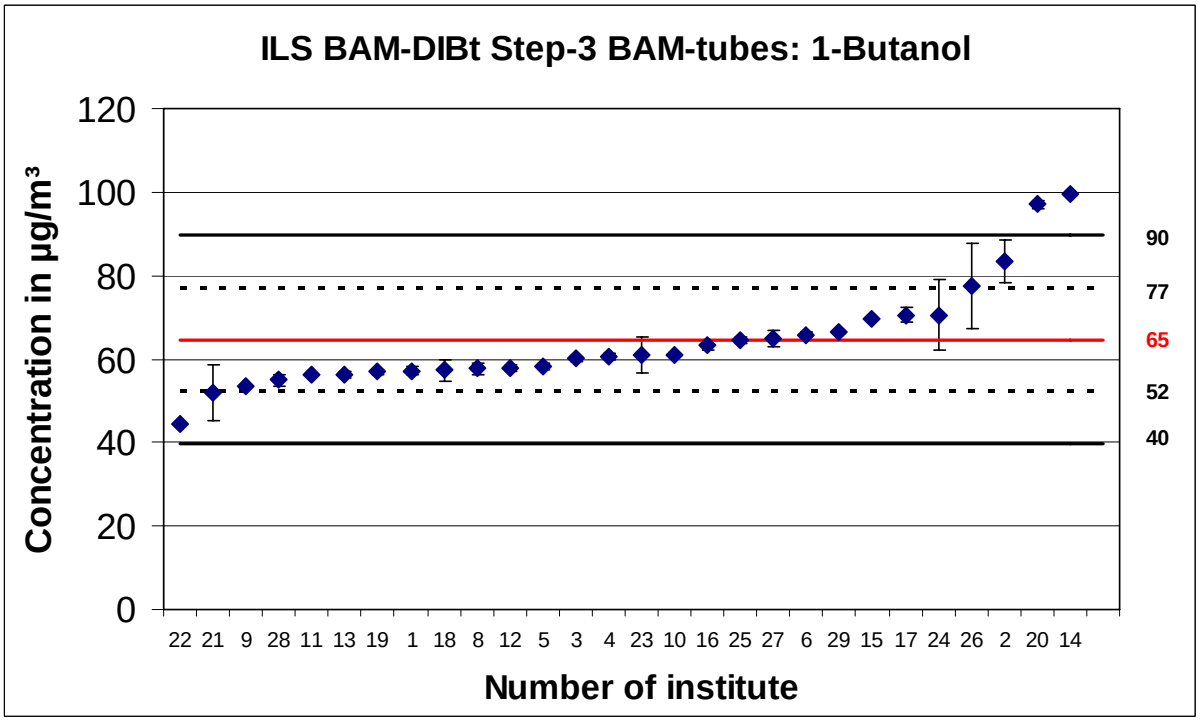


Figure 62: Results for n-Butanol received with tubes from BAM, sampled at the chambers of the participants.

** this institutes were asked to recalculate or to repeat their first test in complete*
Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

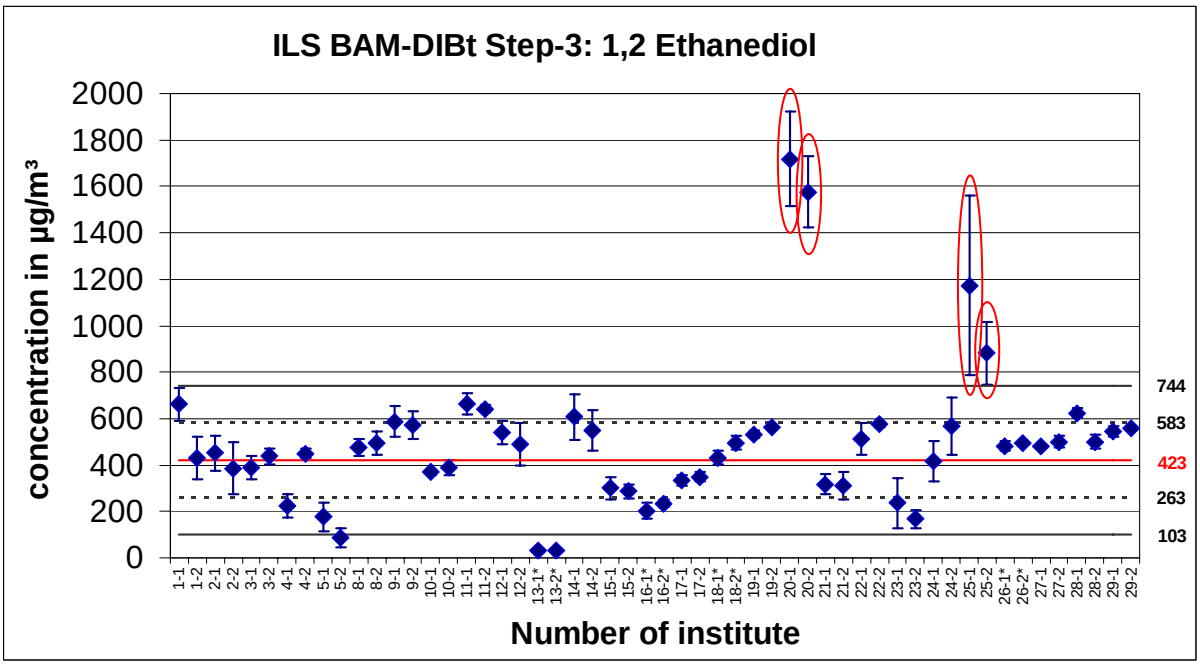


Figure 63: Results for 1,2-ethanediol (outlier marked)

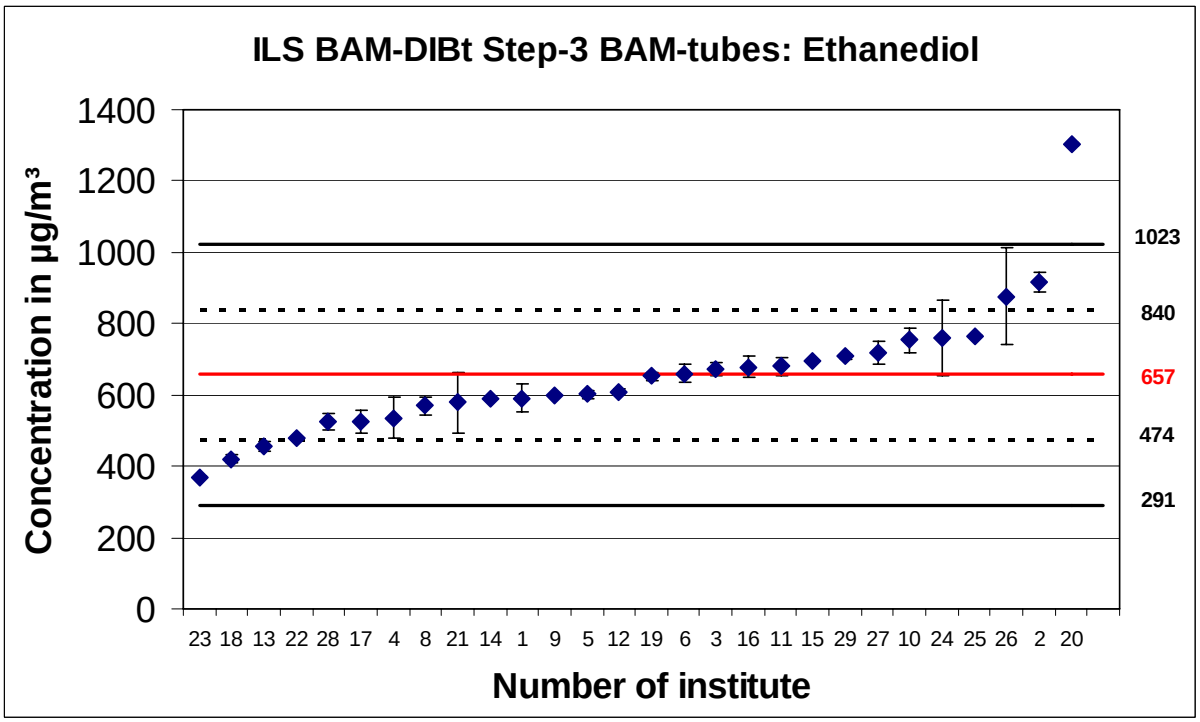


Figure 64: Results for 1,2-ethanediol received with tubes from BAM, sampled at the chambers of the participants.

** this institutes were asked to recalculate or to repeat their first test in complete*
Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

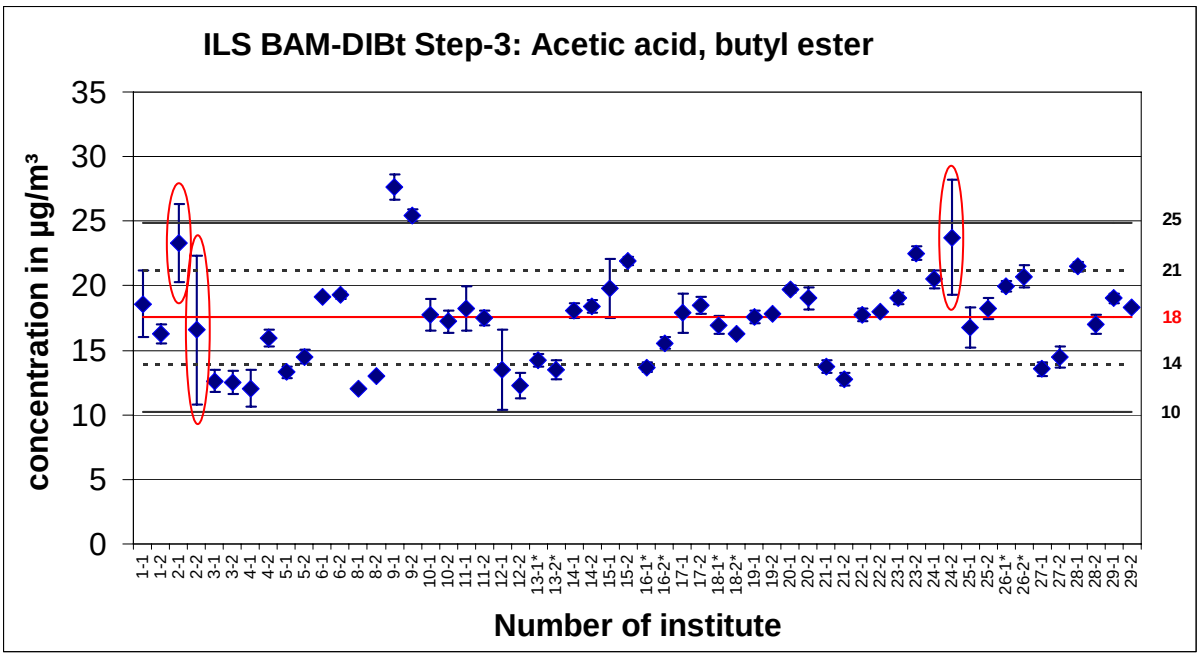


Figure 65: Results for acetic acid butylester (outlier marked)

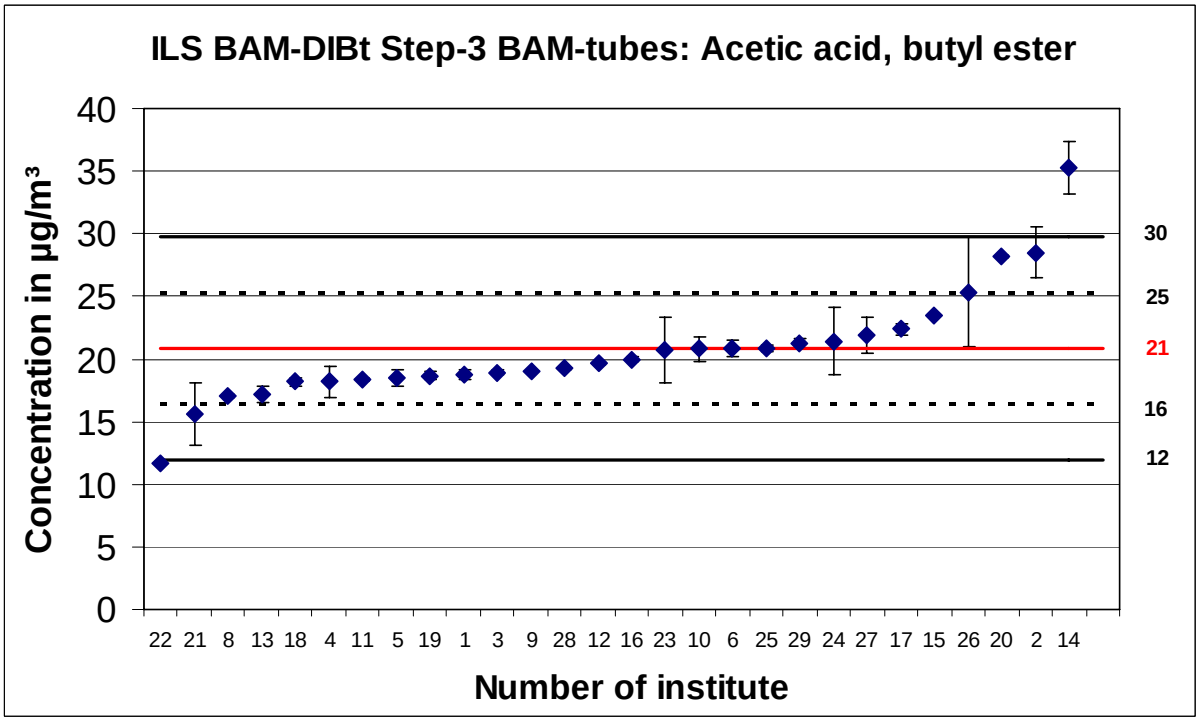


Figure 66: Results for acetic acid butylester received with tubes from BAM, sampled at the chambers of the participants.

** this institutes were asked to recalculate or to repeat their first test in complete*
Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

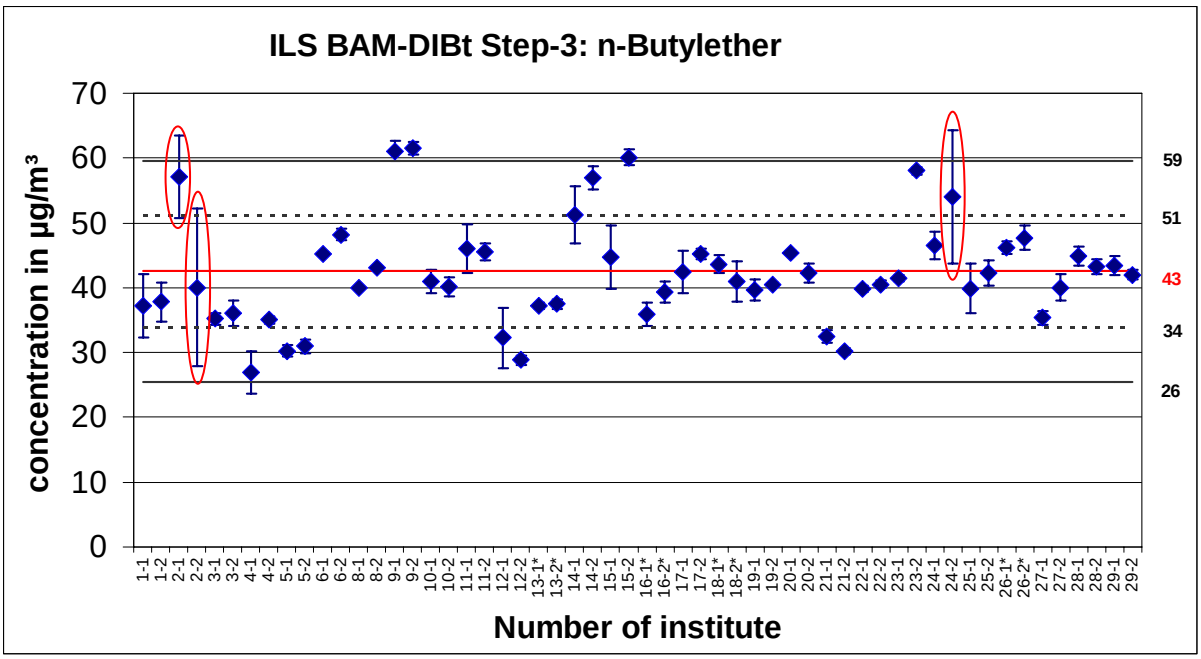


Figure 67: Results for n-butylether (outlier marked)

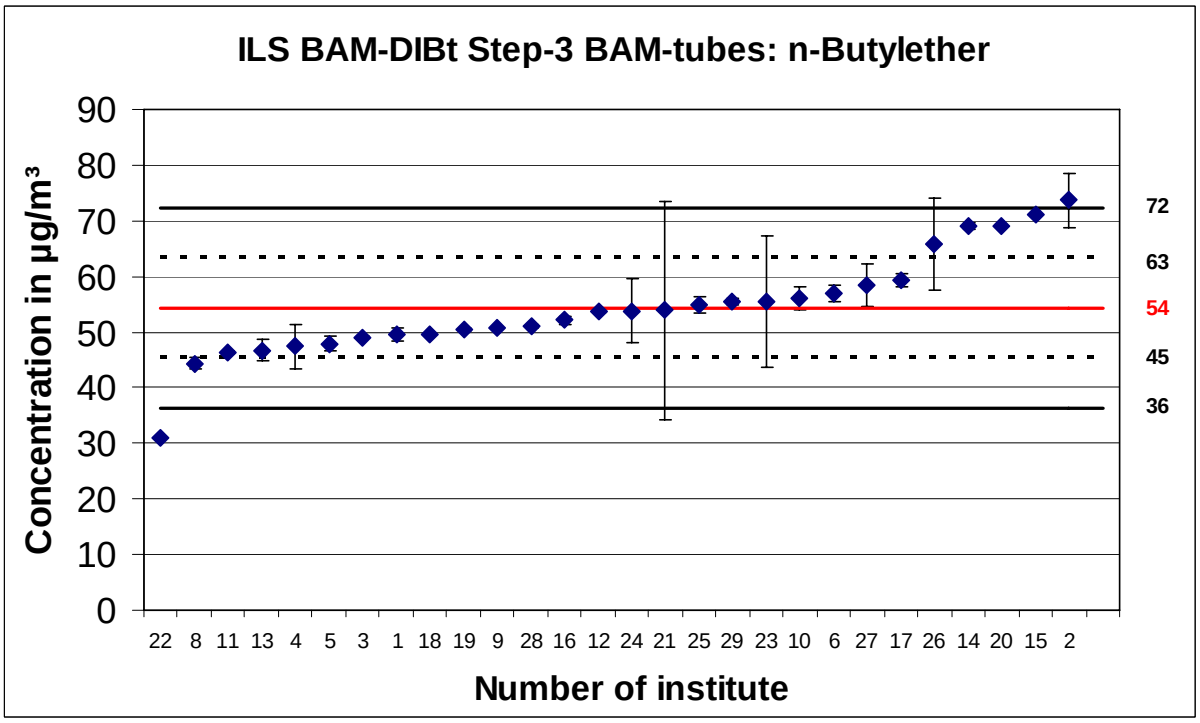


Figure 68: Results for n-butylether received with tubes from BAM, sampled at the chambers of the participants.

** this institutes were asked to recalculate or to repeat their first test in complete*
Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

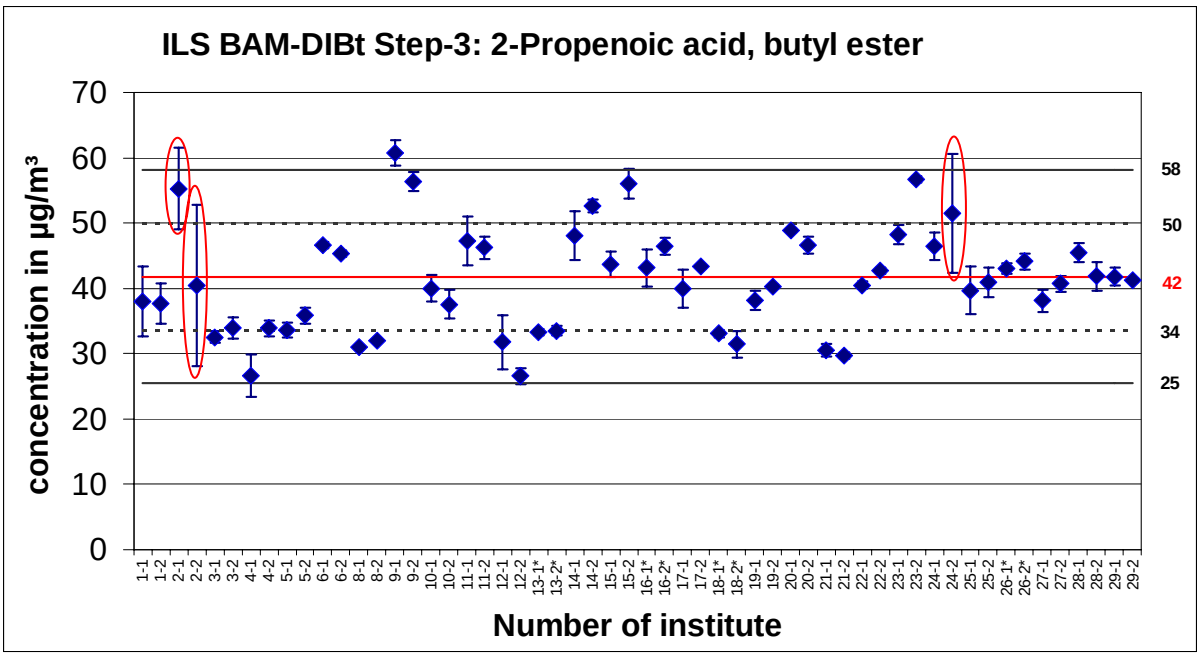


Figure 69: Results for acrylic acid butylester (outlier marked)

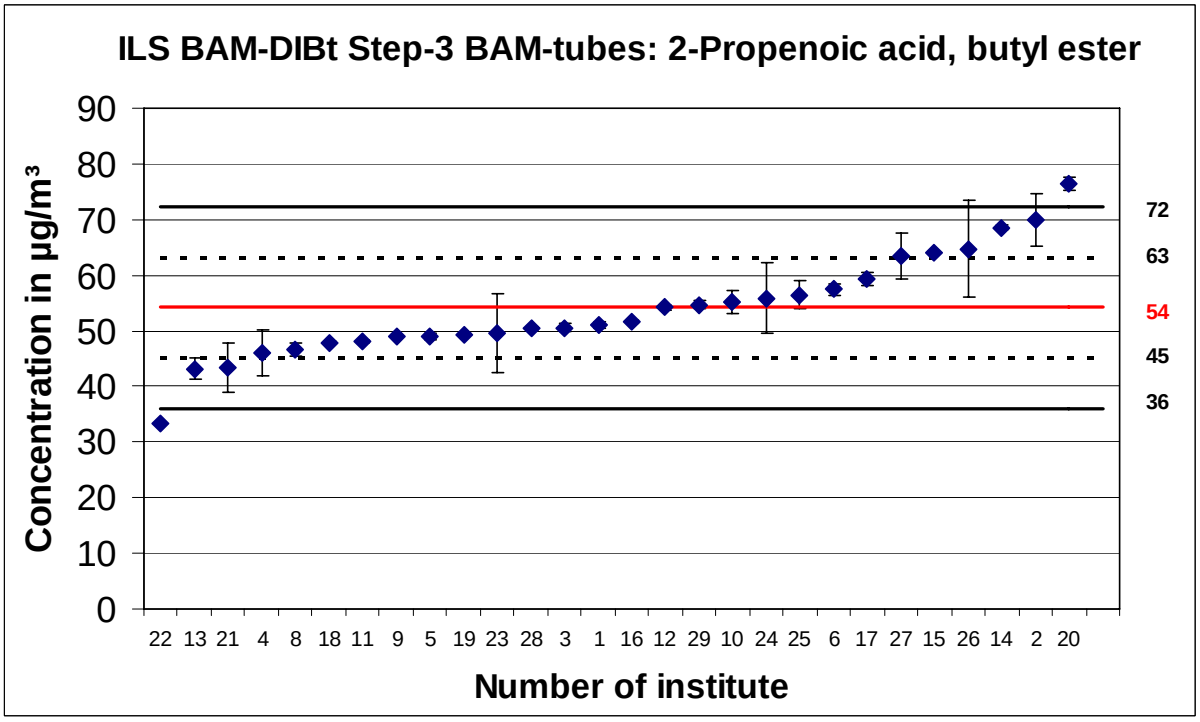
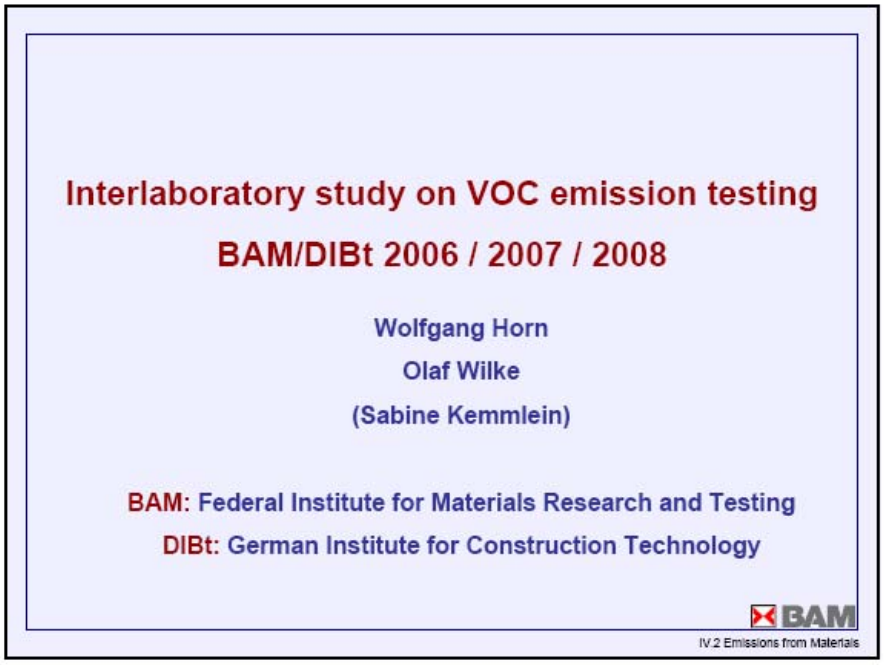


Figure 70: Results for acrylic acid butylester received with tubes from BAM, sampled at the chambers of the participants.

** this institutes were asked to recalculate or to repeat their first test in complete*
Red Ellipse: Outlier (Cochran und Grubbs test)
Red full line: mean; dashed line: one sigma; full line two sigma

7.5. Final workshop 9th of April 2008



Provenance of all participants

29 participants from Europe

BAM

Aim: Improvement of the emission chamber test method

Fundamentals:

- **ISO 16000-6**
  (Tenax thermal desorption and gas chromatography)
- **ISO 16000-9**
  (Emission test chamber method)
- **ISO 16000-11**
  (Sampling, storage, preparation of test specimen)

BAM

Interlaboratory study: statistical evaluation -1-

Interlaboratory study in accordance with ISO 5725-2

- Number of participants: min. n = 8, to be prefered n > 15!
- K = 4 parallel tests of the same solution with the same analytical procedure, less than a double test is not correct
- Test for outliers: Grubbs (arithm. mean), Cochran (variance)
- Proof of in average reachable precision of each laboratory (repeatability standard deviation)
- Comparing the arithmetic mean value of the single laboratory with the target value or the mean value -> accuracy of the mean
- Proof of the analytical procedure with repeatability standard deviation

BAM

IV.2 Emissions from Materials

Aim: Improvement of the emission chamber test method

Project classification in three steps:

Step 1 (Analytical method):

Analysis of liquid solutions by thermal desorption and liquid injection

Step 2 (Air sampling):

Sampling onto Tenax tubes at BAM-chamber, Sampling by BAM staff using BAM pumps

Step 3 (Emission test chamber):

Test of a sealant by Tenax TDS/GC-MS in the test chambers of the participants, additional sampling for BAM analysis

BAM

IV.2 Emissions from Materials

Aim: Improvement of the emission chamber test method

Questionnaire send for each step (including):

- TDS-system (temperature, flow, etc.)
- GC-MS system (column, oven program, etc.)
- Air sampling (volume, flow)
- Calibration (range, number of calibration points)
- Test chamber (size, material, climate, etc.)

BAM
IV.2 Emissions from Materials

ILS Step 1

STEP 1

Target compounds:

Relevant for rubber material:

styrene, Benzothiazol, BHT, (Iso-)Longifolene?

High standard deviation in former round robin tests:

1,3-dichloro-2-propanol, 1,2,3-trimethylbenzene, Caprolactam

Further compounds:

dodecane, 2-ethyl-1-hexanol, diethylenglycolmonobutylether, methylisobutylketone

BAM
IV.2 Emissions from Materials

ILS Step -1: Standard solutions

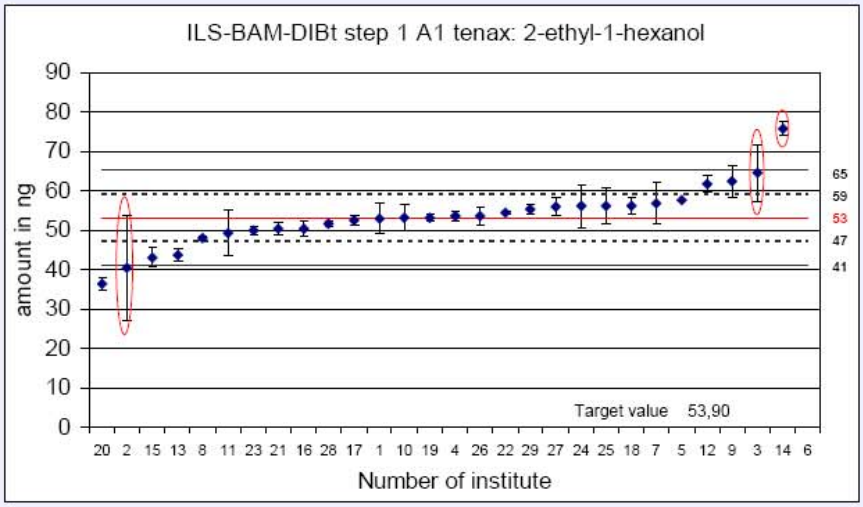
- Shipping of 4 different solutions to 29 Laboratories
- planned: shipment with parcel service and 24 h service
- shipment problems! Delay for foreign country laboratories!
- narrow deadlines <> problem for some participants (see above)

test procedure

- 4 solutions (methanol)
- analysis of each solution **4-fold** with Tenax/TDS/GC/MS
- For comparison:
  analysis of each solution **4-fold** with direct injection (GC/MS)

BAM
IV.2 Emissions from Materials

Simple statistic results of Step 1



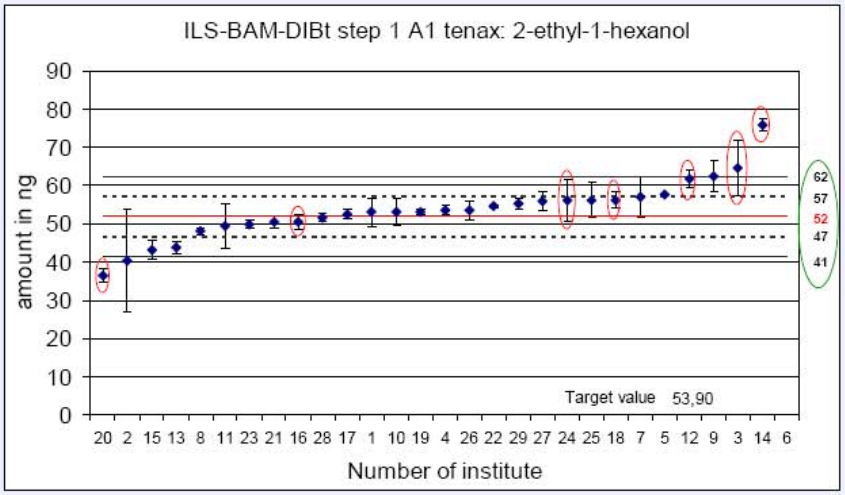
Ellipse: Outlier for Cochran or Grubbs test

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 1 - (alternative Approach)



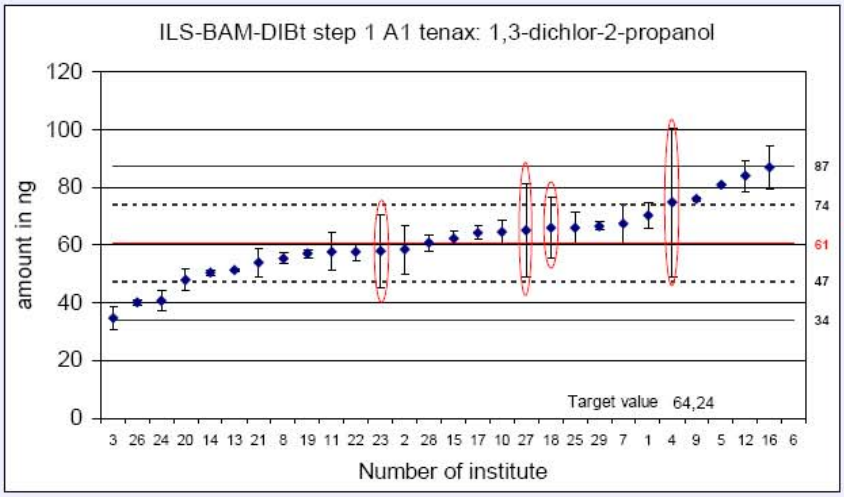
Ellipse: Outlier

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Simple statistic results of Step 1



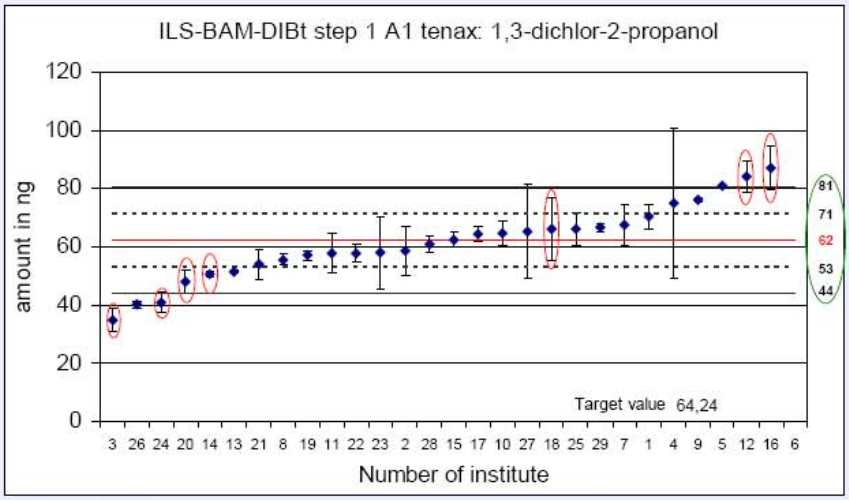
Ellipse: Outlier for Cochran or Grubbs test

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 1 - (alternative Approach)



Ellipse: Outlier

mean value ***single standard deviation***

twofold standard deviation

BAM
IV.2 Emissions from Materials

Relative standard deviation step 1

	A1	A2	B1	B2
	% Stabw	% Stabw	% Stabw	% Stabw
methylisobutylketone	11	11	16	10
styrene	11	10	12	8
1,3-dichlor-2-propanol	22	21	26	23
1,2,3-trimethylbenzene	11	12	11	12
2-ethyl-1-hexanol	11	13	25	17
dodecane	12	13	13	9
diethylenmonoglycolmonobutylether	19	21	30	19
benzothiazole	12	12	27	14
caprolactam,	18	16	31	19
longifolene,	11	11	13	11
BHT (2,6-di-tert-butyl-4-methylpheno	17	16	20	14
Mean	*14*	*14*	*21*	*14*

BAM
IV.2 Emissions from Materials

Mean Step 1 incl. TVOC *all data*

compound	A1	A2	B1	B2
methylisobutylketone	44,7	50,5	12,7	73,7
styrene	49,5	56,0	14,2	85,5
1,3-dichlor-2-propanol	61,0	67,9	13,9	83,8
1,2,3-trimethylbenzene	50,7	56,9	14,2	84,8
2-ethyl-1-hexanol	53,4	61,3	14,0	84,9
dodecane	56,3	64,2	14,9	87,3
diethylenmonoglycolmonob…	52,2	58,5	15,1	87,5
benzothiazole	50,6	58,6	13,6	79,2
caprolactam,	55,3	61,2	15,3	85,1
longifolene,	50,3	57,8	13,4	81,8
BHT	54,0	60,0	14,3	87,9
TVOC	**565**	**636**	**145**	**898**
St. dev. TVOC	**15**	**14**	**19**	**14**
mean from st. dev.	***14***	***14***	***21***	***14***

BAM

IV.2 Emissions from Materials

Standard deviation (average) in % for Step 1 *(alternative approach without outliers)*

compound	mean	st. dev.	st. dev %
	µg/ml	µg/ml	
methylisobutylketone	45,1	3,9	8,7
styrene	50,9	2,6	5,1
1,3-dichlor-2-propanol	60,8	7,7	12,7
1,2,3-trimethylbenzene	51,1	3,8	7,3
2-ethyl-1-hexanol	51,4	4,6	9,0
dodecane	54,8	4,7	8,6
Diethylenmonoglycol-monobutylether	48,7	9,0	18,4
benzothiazole	50,9	4,4	8,6
caprolactam,	52,0	6,0	11,5
longifolene,	51,9	4,3	8,3
BHT (2,6-di-tert-butyl-4-methylphenol)	53,5	5,4	10,1

BAM

IV.2 Emissions from Materials

Repeatability standard deviation and reproducibility standard deviation for Step 1 Solution A1 (*all Data*)

compound	mean	repeat. st dev	reprod. st dev
		s_r	s_R
methylisobutylketone	44,5	2,5	6,5
styrene	49,8	2,9	6,8
1,3-dichlor-2-propanol	62,5	7,9	13,8
1,2,3-trimethylbenzene	50,6	2,3	6,4
2-ethyl-1-hexanol	53,0	4,0	8,5
dodecane	56,4	4,5	8,9
Diethylenmonoglycol-monobutylether	52,4	5,8	20,0
benzothiazole	50,8	4,3	8,8
caprolactam,	54,8	4,9	20,2
longifolene,	50,5	3,5	8,5
BHT (2,6-di-tert-butyl-4-methylphenol)	53,5	3,8	9,3

BAM
IV.2 Emissions from Materials

Step 1: influence of analytical parameters

- Questionnaires were sent to participants
- some parameter can be linked with the results
- the next slides show the correlation between
  - length of the column and the
  - analytical phase in the columns

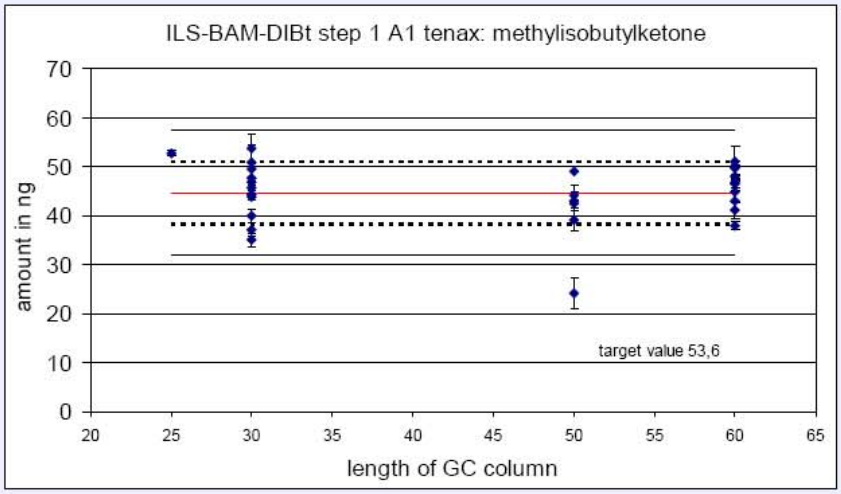
BAM
IV.2 Emissions from Materials

Influence of Parameters (GC/TDS)

GC	TDS	column			
Agilent	Gerstel	DB1	60 m	0,32 mm	1,8 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	1 µm
Agilent	Perkin Elmer	DB-1	50 m	0,2 mm	0,5 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	1 µm
Agilent	Perkin Elmer	DB-1	30 m	0,25 mm	0,25 µm
Agilent	Markes	DB-1	25 m	0,32 mm	3,0 µm
Agilent	Markes	DB-5	50 m	0,32 mm	1 µm
Agilent	Gerstel	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	50 m	0,2 mm	0,33 µm
Shimadzu	Perkin Elmer	DB-5	60 m	0,25 mm	1,0 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	0,5 µm
Varian	Perkin Elmer	DB-624	30 m	0,25 mm	1 µm
Agilent	Perkin Elmer	DB-5	50 m	0,32 mm	0,52 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	50 m	0,2 mm	0,33 µm
Agilent	Perkin Elmer	DB-5	60 m	0,32 mm	0,5 µm
Shimadzu	Markes	DB-1	60 m	0,25 mm	0,25 µm
Shimadzu	Perkin Elmer	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-1	60 m	0,25 mm	0,25 µm
Agilent	Gerstel	DB-5	60 m	0,25 mm	0,25 µm
Agilent	Perkin Elmer	DB-1	50 m	0,2 mm	0,33 µm
Agilent	Perkin Elmer	DB-5	30 m	0,25 mm	1 µm
Perkin Elmer	Perkin Elmer	DB-5	50 m	0,22 mm	0,25 µm
Agilent	Perkin Elmer	DB-210	60 m	0,32 mm	1 µm
Agilent	Dani	DB-1	50 m	0,2 mm	0,5 µm
Agilent	Gerstel	DB-1	60 m	0,25 mm	0,25 µm

BAM
IV.2 Emissions from Materials

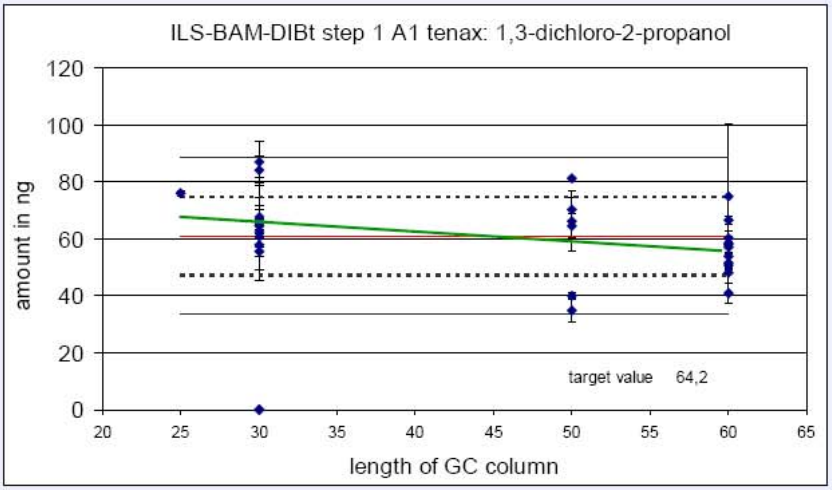
Parameters influencing results of Step 1



Results for methylisobutylketone given in amount in ng in correlation to the length of the GC column

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 1

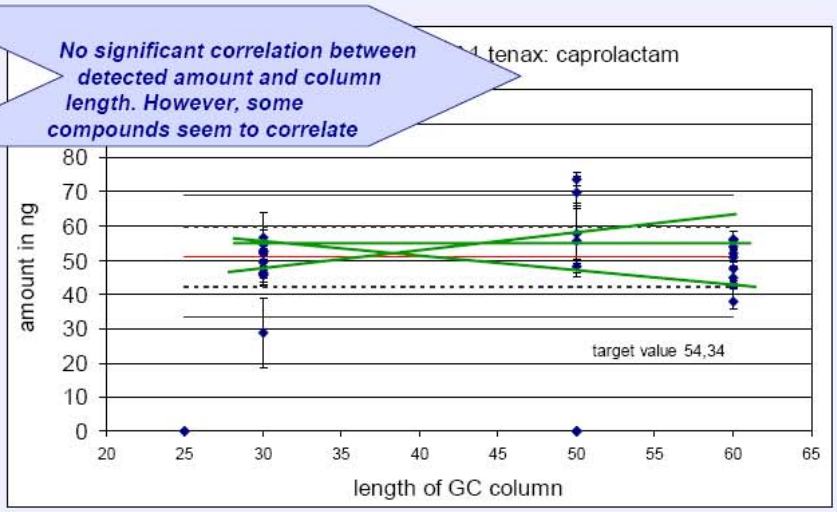


Results for dichloropropanol given in amount in ng in correlation to the length of the GC column

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 1

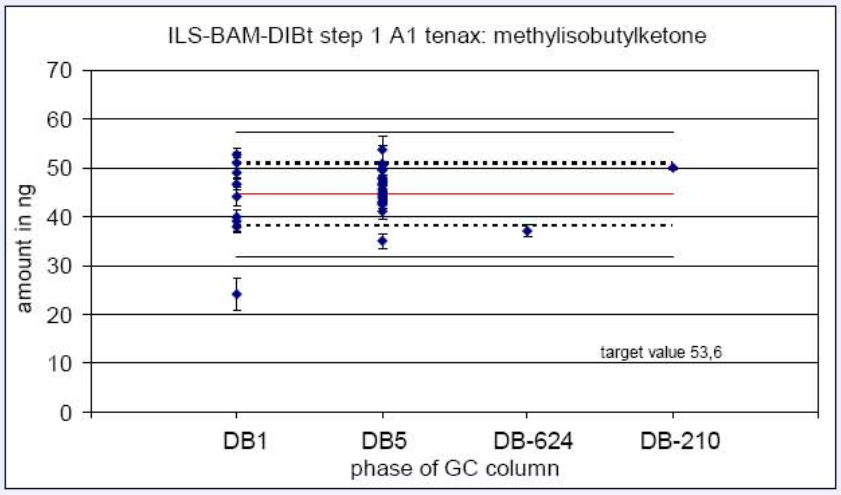
No significant correlation between detected amount and column length. However, some compounds seem to correlate



Results for caprolactam given in amount in ng in correlation to the length of the GC column

BAM
IV.2 Emissions from Materials

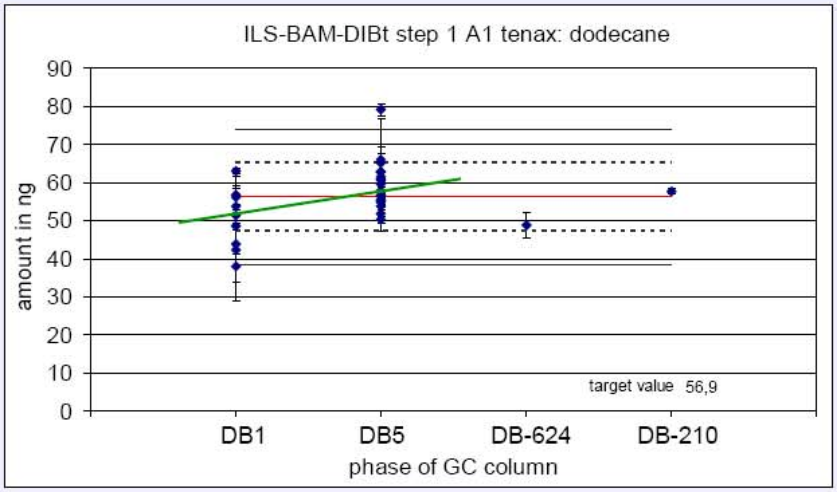
Parameters influencing results of Step 1



Results for methylisobutylketone given in amount in ng in correlation to the phase of the GC column

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 1

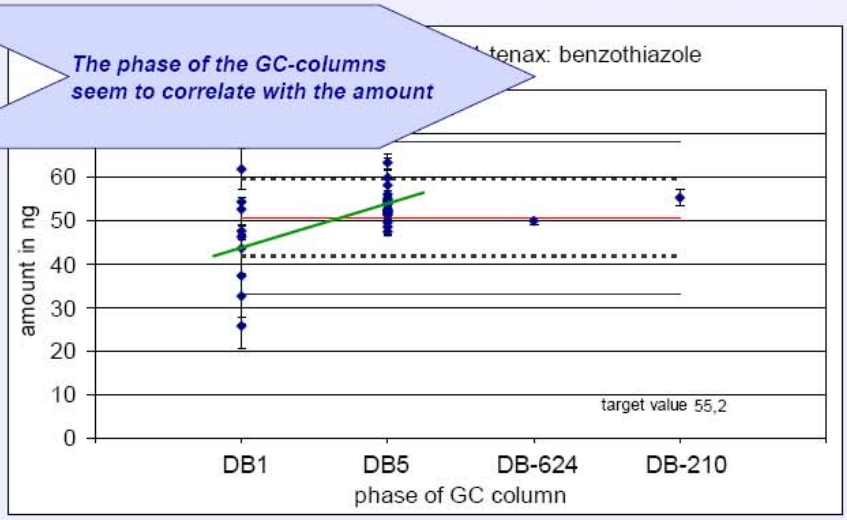


Results for dodecane given in amount in ng in correlation to the phase of the GC column

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 1

The phase of the GC-columns seem to correlate with the amount



Results for benzothiazole given in amount in ng in correlation to the phase of the GC column

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 1

	complete mean *rel. st. dev.*	DB-1 mean *rel. st. dev.*	DB-5 mean *rel. st. dev.*
methylisobutylketone *Target: 53,7*	**44,7** *13,8*	**42,8** *20,5*	**45,9** *9,4*
1,3-dichloro-2-propanol *Target: 64,2*	**61,5** *20,5*	**56,1** *29,8*	**64,1** *15,9*
1,2,3-trimethylbenzene *Target: 54,8*	**50,7** *12,1*	**49,9** *13,6*	**51,0** *12,4*
dodecane *Target: 57,0*	**56,2** *14,3*	**50,4** *15,9*	**59,5** *11,1*
benzothiazole *Target: 55,2*	**50,8** *15,8*	**44,6** *25,3*	**53,7** *7,3*

n (DB-1) = 9 *n (DB-5) = 18*

BAM
IV.2 Emissions from Materials

End Step 1

BAM
IV.2 Emissions from Materials

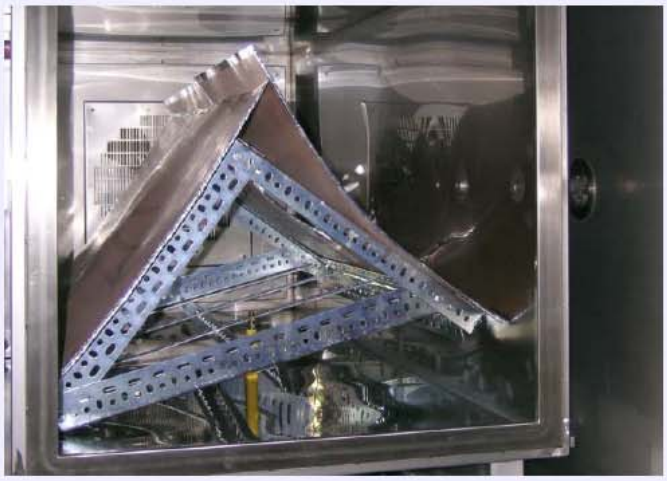
Step 2: Air sampling at BAM chamber

Procedure:

- 4-fold sampling with Tenax tubes for each participant
- Sampling with BAM pumps (flow control) by BAM staff
- Sampling over 4 days
  (sampling started 21 days after chamber loading)

BAM
IV.2 Emissions from Materials

ILS BAM/DIBt step-2



1 m³ chamber loaded with flooring and permeation tube

BAM
IV.2 Emissions from Materials

ILS BAM/DIBt step-2

Sampling tubes received from the participants

BAM
IV.2 Emissions from Materials

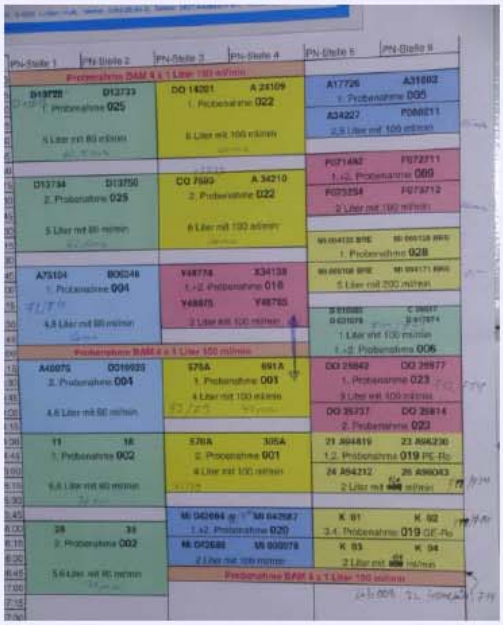
ILS BAM/DIBt step-2

Control of air flow through all different types of sampling tubes received from the participants

BAM

IV.2 Emissions from Materials

ILS BAM/DIBt step-2



Flow chart of one day of sampling

We tried to fulfill all specifications of the participants

Sampling volume between 1 and 9 Liters

Sampling air stream between 40 and 200 ml/min

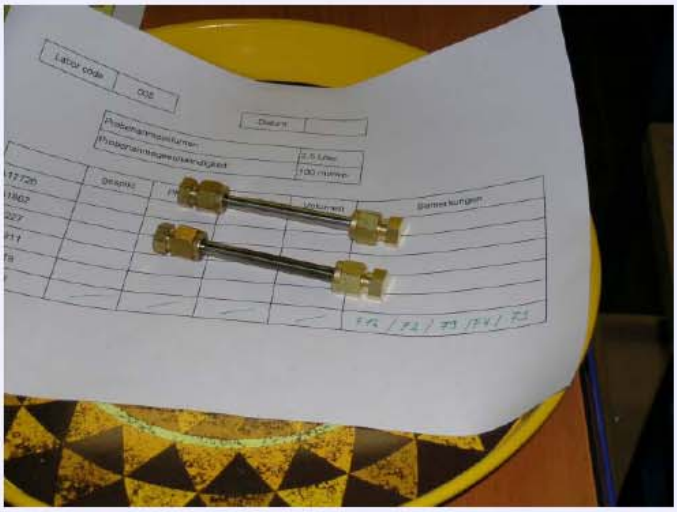
Sampling on 3 days

One further day without d_8 toluene

BAM

IV.2 Emissions from Materials

ILS BAM/DIBt step-2



Sampling protocol with two sampling tubes

BAM

IV.2 Emissions from Materials

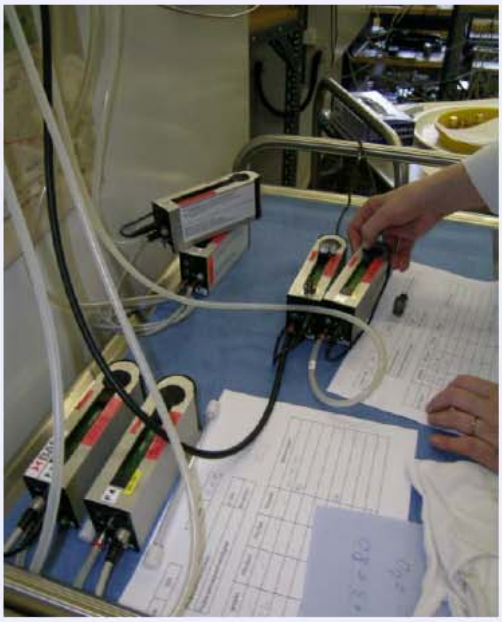
ILS BAM/DIBt step-2

Adding 20 ng cyclodecane on the sampling tubes with 5 min N_2-stream

BAM

IV.2 Emissions from Materials

ILS BAM/DIBt step-2

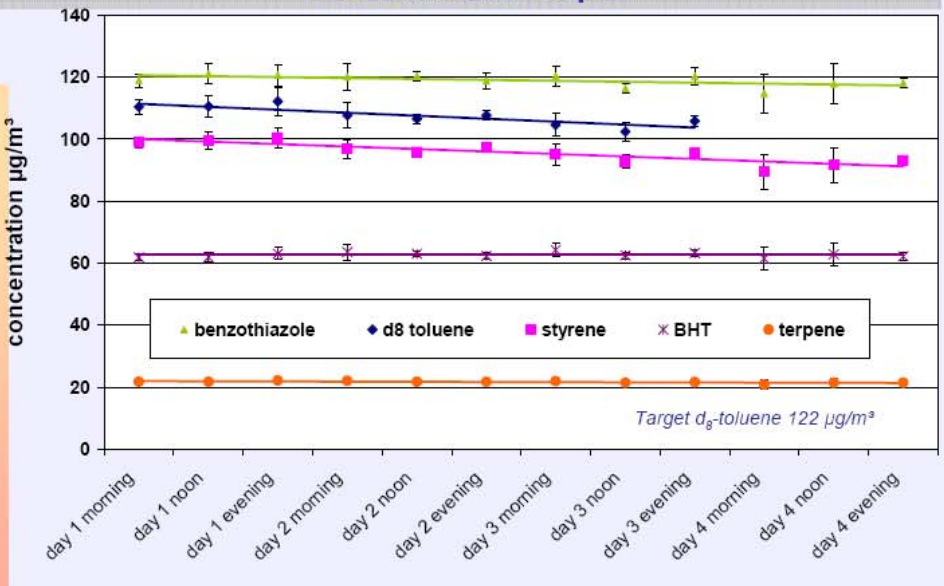


Sampling at the 1m³-chamber 6 tubes in parallel

3 sampling periods in the morning, at noon and at the evening with 4 tubes each for quality assurance

BAM
IV.2 Emissions from Materials

ILS BAM/DIBt step-2



Chamber tests at BAM 12th up to 15th of February

BAM
IV.2 Emissions from Materials

Step 2 – standard deviation for BAM control values

compound	mean	st dev	% st dev
toluene d_8	107,5	4,0	3,7
styrene	95,4	4,2	4,4
cyclohexanone	13,6	0,6	4,7
benzaldehyde	14,2	0,8	5,9
benzothiazole	118,7	3,7	3,1
BHT	62,5	2,1	3,3

BAM
IV.2 Emissions from Materials

Standard deviation (average) in % for Step 2 *(without outliers)*

compound	mean	st dev	% st dev	median
	µg/m³	µg/m³		µg/m³
d_8-toluene	108,0	15,3	**14,2**	108,2
styrene	115,1	12,2	**10,6**	113,9
cyclohexanone	13,7	3,1	**22,4**	12,8
benzaldehyd	17,5	3,3	**18,8**	17,0
benzothiazole	106,5	17,1	**16,0**	106,6
BHT (2,6-di-tert-butyl-4-methylphenol)	56,7	16,5	**29,1**	55,0
cyclodecane	22,0	6,0	**27,1**	21,0

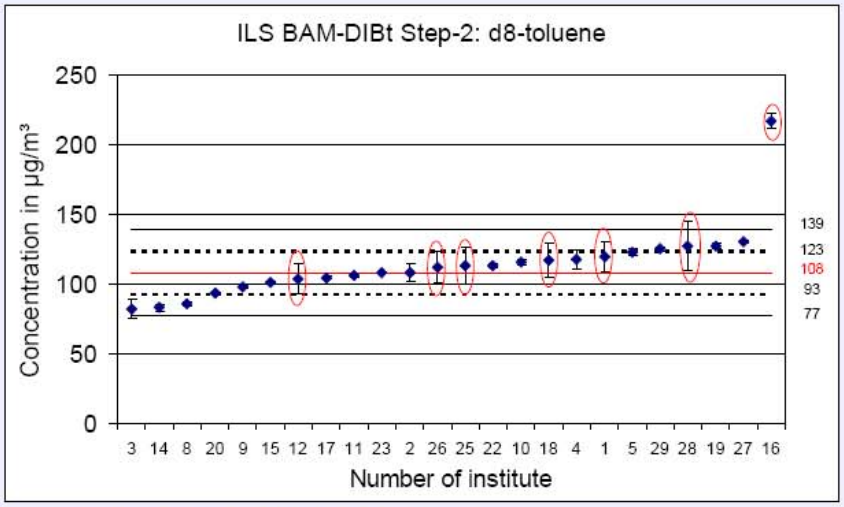
BAM
IV.2 Emissions from Materials

Standard deviation (average) in % for Step 2
(alternative approach without outliers)

compound	mean	st dev	% st dev	median
	µg/m³	µg/m³		µg/m³
d8-toluene	109,5	13,6	12,4	110,7
styrene	115,1	11,0	9,5	114,4
cyclohexanone	13,2	2,3	17,6	12,8
benzaldehyd	17,4	2,5	14,4	16,9
benzothiazole	104,3	14,9	14,3	103,0
BHT (2,6-di-tert-butyl-4-methylphenol)	52,8	12,5	23,6	55,2
cyclodecane	22,5	3,4	15,1	22,3

BAM
IV.2 Emissions from Materials

Results for Step 2



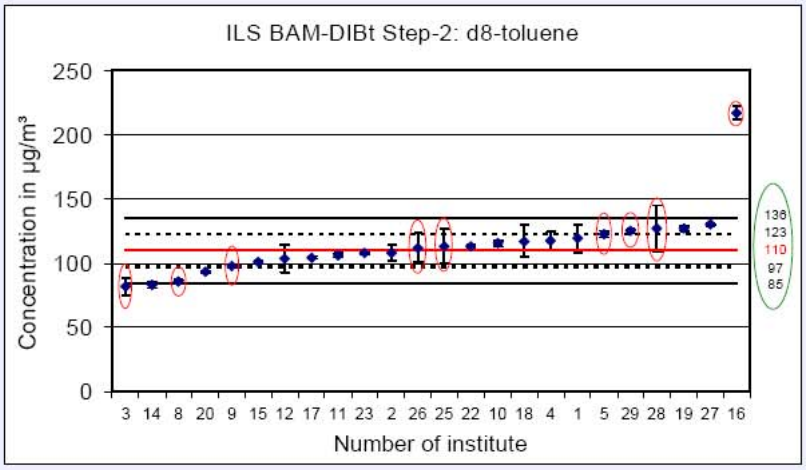
Ellipse: Outlier for Cochran or Grubbs test

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 2 - (alternative Approach)



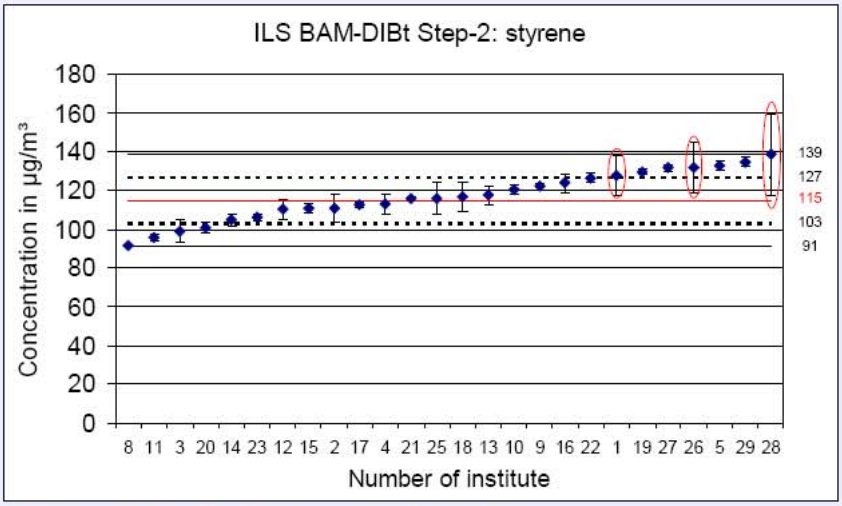
Ellipse: Outlier

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 2



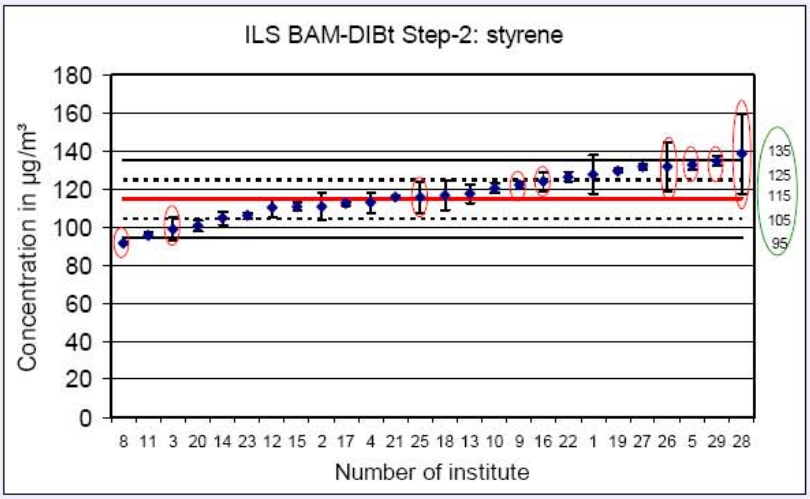
Ellipse: Outlier for Cochran or Grubbs test

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 2 - (alternative Approach)



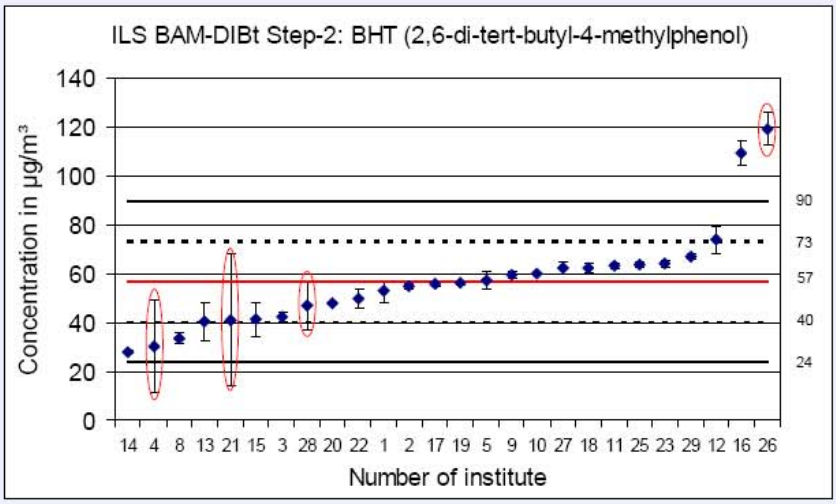
Ellipse: Outlier

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 2



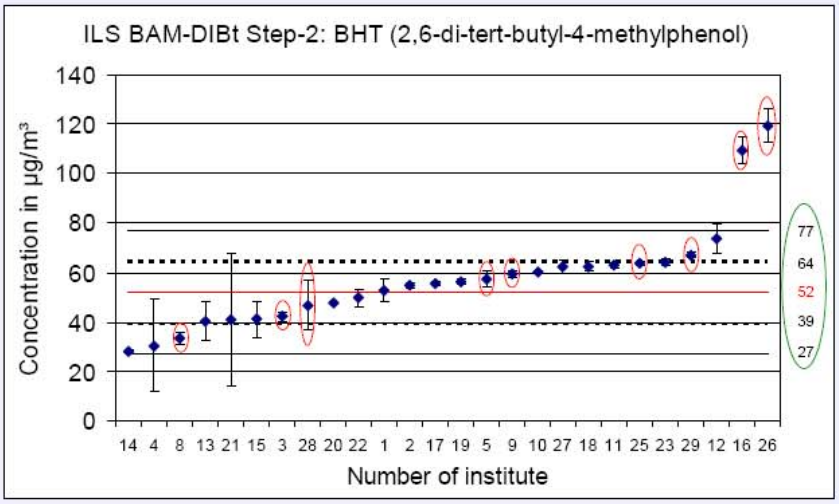
Ellipse: Outlier for Cochran or Grubbs test

mean value *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 2 - (alternative Approach)



Ellipse: Outlier

mean value *single standard deviation*

twofold standard deviation

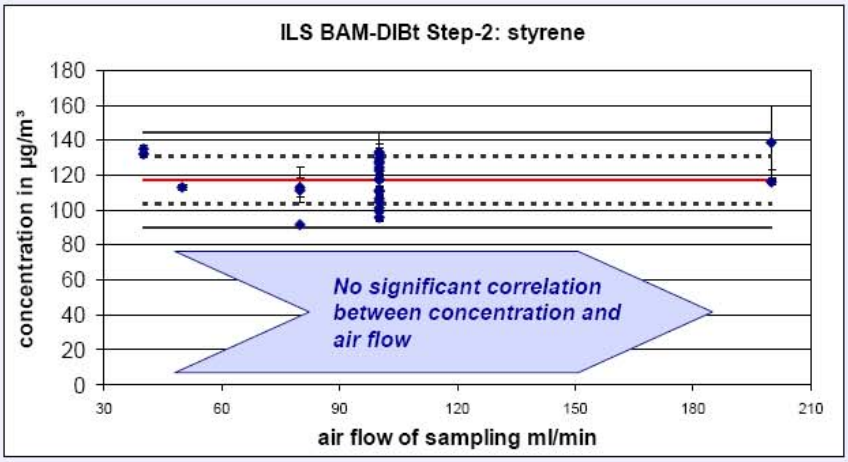
BAM
IV.2 Emissions from Materials

Repeatability standard deviation and reproducibility standard deviation for Step 2 (*all Data*)

compound	mean	repeat. st dev	reprod. st dev
		s_r	s_R
d_8-toluene	114	7,2	26,7
styrene	117	6,5	13,9
cyclohexanone	14,4	1,5	3,7
benzaldehyd	18,1	3,5	5,3
benzothiazole	113	11,5	38,4
BHT (2,6-di-tert-butyl-4-methylphenol)	57,0	7,6	21,8
cyclodecane	23,0	3,1	7,3

BAM
IV.2 Emissions from Materials

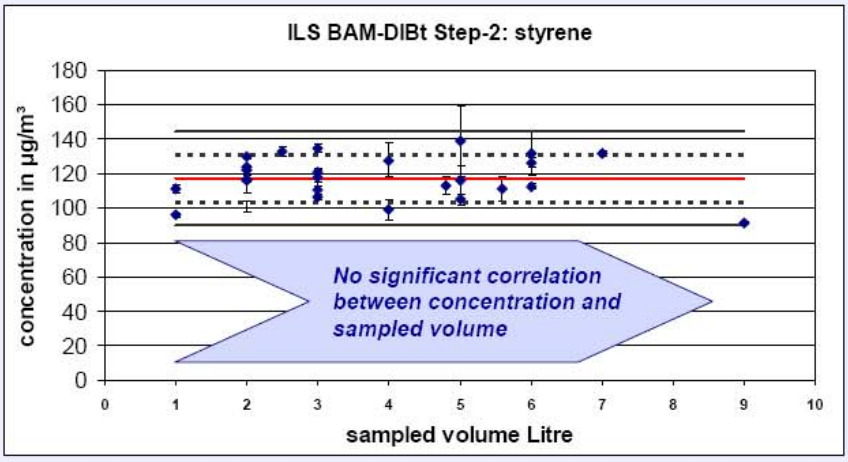
Parameters influencing results of Step 2



Results for styrene given in concentrations in the chamber in correlation to the air flow through the sampling tubes

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 2



Results for styrene given in concentrations in the chamber in correlation to the sampled volume on the sampling tubes

BAM
IV.2 Emissions from Materials

Step 2: influence of parameter

- no significant influence for sampled volume or air flow
- questionnaire unfortunately shows a broad variance of parameters

BAM
IV.2 Emissions from Materials

End Step 2

BAM
IV.2 Emissions from Materials

Step 3: Emission test chamber measurement

Emission tests in the chambers of each participant

BAM

IV.2 Emissions from Materials

ILS step 3: planned schedule

planned:

- tests in the chambers of the participants
- loading of the chamber in the week beginning with June 18
- Sampling at day 7 after loading
- Duplicate loading of two chambers
- 4-fold sampling with Tenax at each chamber

BAM

IV.2 Emissions from Materials

Step-3: material pre tests

Homogeneity of the VOC emission from the flooring material

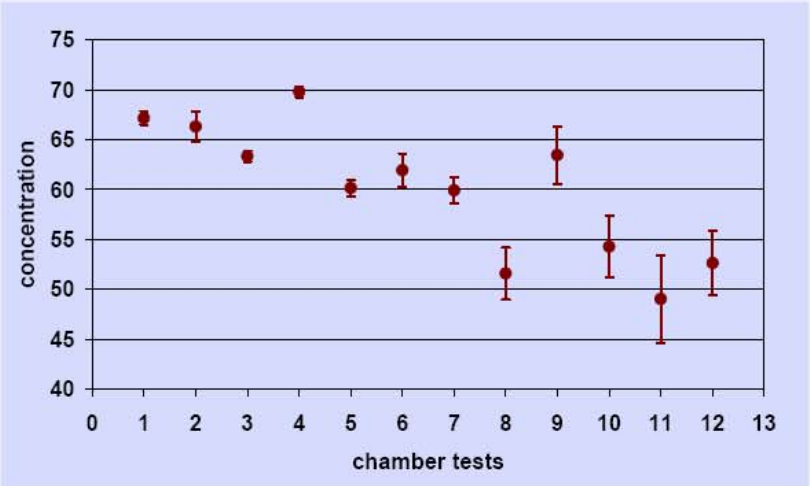
Tests in parallel:

- 12 x 0.02 m³ emission test chambers
- 3-fold analysis (Tenax TDS/GC/MS), day 7
- Markes Thermoextraktor (µ-Chamber)
  measurement 22 h after loading

BAM
IV.2 Emissions from Materials

Step-3: material pre tests

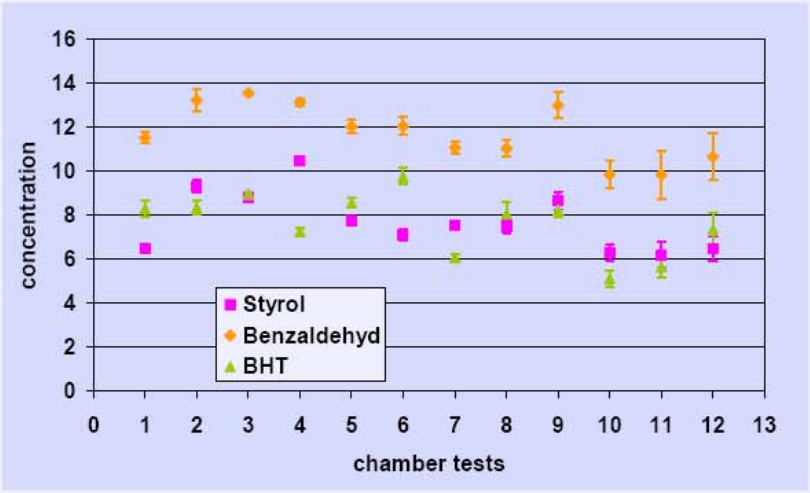
Benzothiazole



BAM
IV.2 Emissions from Materials

Step-3: material pre tests

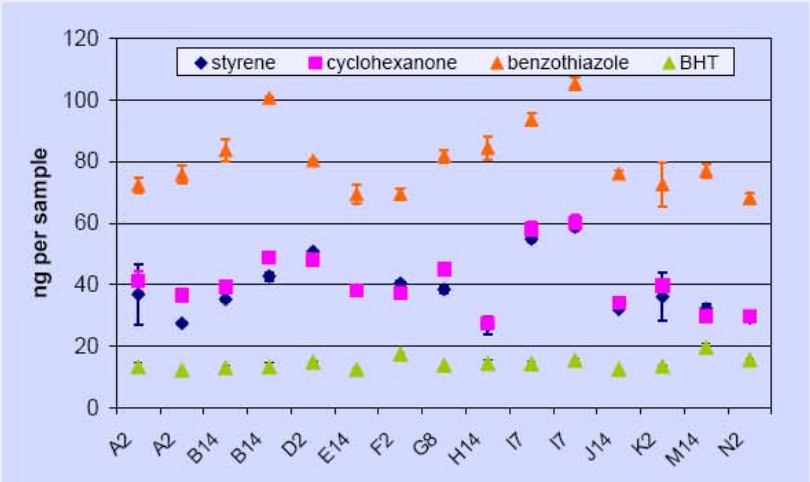
3 further compounds



BAM
IV.2 Emissions from Materials

Ringversuch -3- : µ-Chamber Untersuchungen

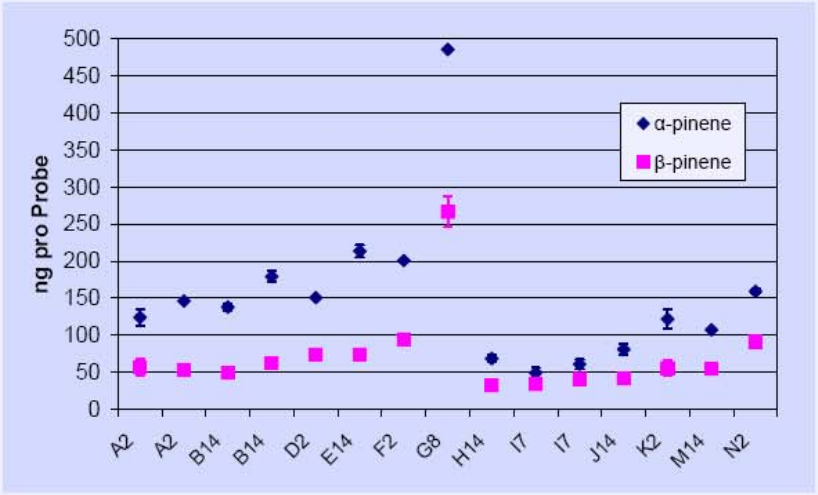
4- Komponenten



BAM
IV.2 Emissions from Materials

Ringversuch -3- : µ-Chamber Untersuchungen

Terpene



BAM

IV.2 Emissions from Materials

Step-3: second material pre tests

New Material

Homogeneity of the VOC emission from a sealant material

- **12 x 0.02 m³ emission test chambers**
- **3-fold analysis (Tenax TDS/GC/MS), day 7**

BAM

IV.2 Emissions from Materials

Step 3: Sealant pre test

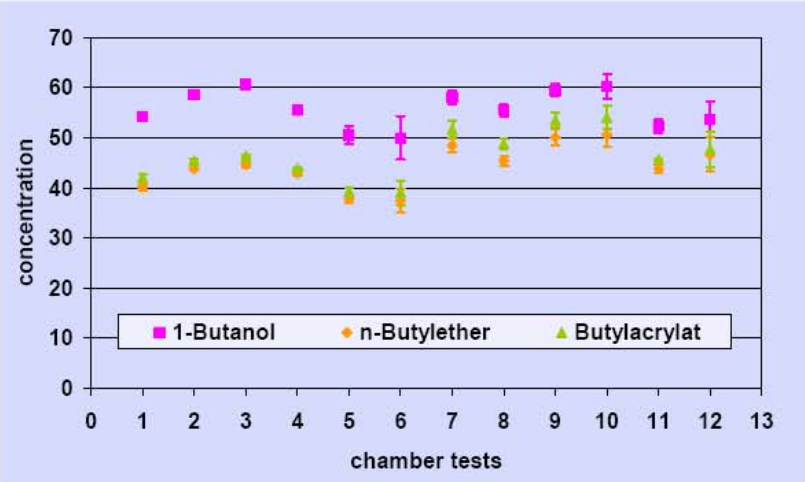
Mean, standard deviation and median of 12 fold chamber test at `BAM

	mean	st dev	st dev %	median
1-Butanol	56,2	6,1	3,4	55,5
1,2-Ethanediol	612,7	8,5	52,0	584,5
Acetic acid butyl ester	17,7	12,3	2,2	17,6
n-Butylether	44,9	8,7	3,9	44,5
Propenoic acid butyl ester	47,1	9,9	4,7	46,3
Propanoic acid butyl ester	9,5	7,9	0,8	9,5
Butanoic acid butyl ester	5,6	8,5	0,5	5,6

BAM
IV.2 Emissions from Materials

Step 3: Sealant pre test

3 compounds tested 12 – fold in emission test chambers at BAM



BAM
IV.2 Emissions from Materials

Step 3: Emission test chamber measurement

Final Plan:

- Measurement in the test chamber(s) of each participant
- Loading in the week starting on 24. Sept. 2007
- Air sampling on 7th day
- Parallel testing in two identical chambers (if possible)
- Fourfold sampling for each test
- Twofold sampling with BAM tubes for one chamber test

BAM
IV.2 Emissions from Materials

Step 3: shipment of test material

BAM
IV.2 Emissions from Materials

Step 3: preparation of test material for chamber test

BAM

IV.2 Emissions from Materials

Step 3: parallel shipment of Tenax tubes

Tenax tubes shipped by BAM

- 3 tubes send to all participants
- Loading of two tubes at 7th day
- Both tubes on one chamber
- Last tube field blank
  (no requirement / replacement tube)

BAM

IV.2 Emissions from Materials

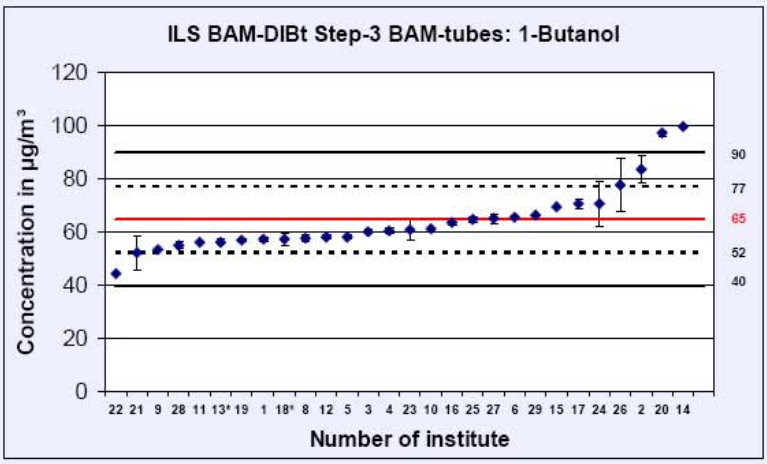
Results for step 3 - participants

Mean, standard deviation and median *all Data BAM tubes*

	mean	st dev.	% st dev	median
1-butanol	63	10	16	61
1,2 ethanediol	659	184	28	643
butyl acetate	20	4	22	20
dibutyl ether	54	9	16	52
acrylic acid butyl ester	54	9	17	52

BAM
IV.2 Emissions from Materials

Results for Step 3

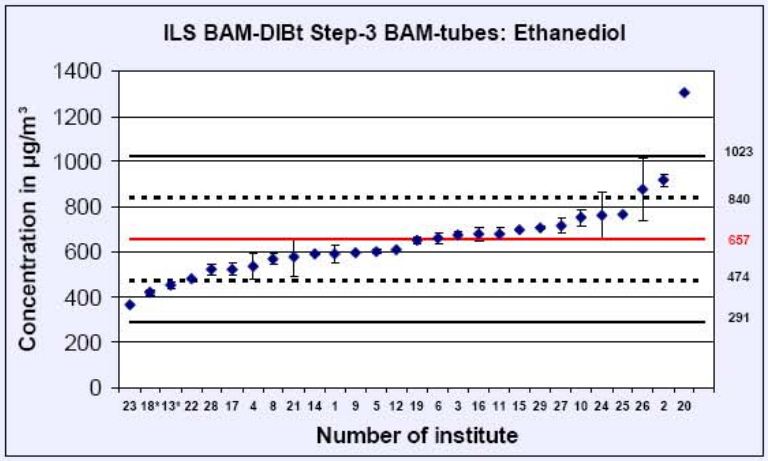


mean value ····· *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 3



mean value ····· *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Repeatability standard deviation and reproducibility standard deviation for Step 3 (*all Data BAM tubes*)

compound	mean	repeat. st dev	reprod. st dev
		s_r	s_R
1-butanol	64,83	1,28	13,04
1,2 ethanediol	641	25,13	123,91
butyl acetate	20,58	1,18	3,72
dibutyl ether	55,60	2,36	9,23
acrylic acid butyl ester	55,14	2,77	9,52

BAM
IV.2 Emissions from Materials

Results for step 3

Mean, standard deviation and median (all data)

compound	mean	st dev.	% st dev	median
	µg/m³	µg/m³		µg/m³
1-butanol	58	12,2	21	56
1,2 ethanediol	506	316	62	476
butyl acetate	17	4,5	27	18
dibutyl ether	42	9,0	21	42
acrylic acid butyl ester	41	9,3	23	41

BAM
IV.2 Emissions from Materials

Results for step 3

Mean, standard deviation and median (without outliers)

compound	mean	st dev.	% st dev	median
	µg/m³	µg/m³		µg/m³
1-butanol	56	11,3	20	55
1,2 ethanediol	431	164	38	468
butyl acetate	17	3,5	20	18
dibutyl ether	41	8,2	20	41
acrylic acid butyl ester	40	9,1	23	41

BAM
IV.2 Emissions from Materials

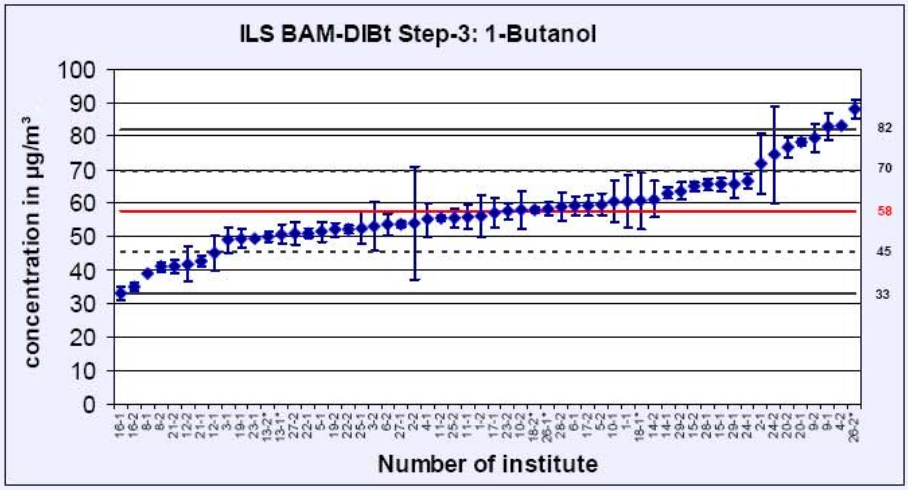
Results for step 3

Mean, standard deviation and median
(alternative approach, without outliers)

compound	mean	st dev.	% st dev	median
	µg/m³	µg/m³		µg/m³
1-butanol	58,4	8,5	14,5	58,8
1,2 ethanediol	478	123	26	492
butyl acetate	17,8	2,7	15,0	18,0
dibutyl ether	43,3	6,3	14,6	43,2
acrylic acid butyl ester	41,6	6,9	16,7	41,6

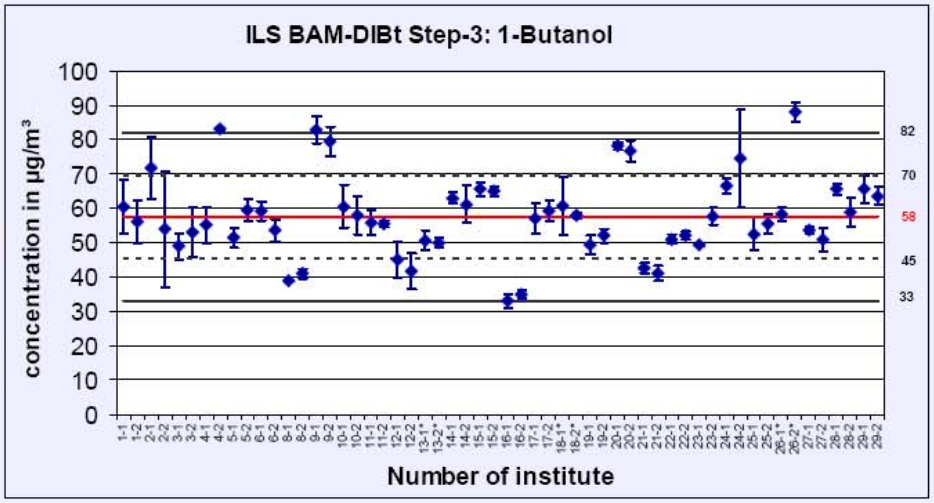
BAM
IV.2 Emissions from Materials

Results for Step 3



BAM
IV.2 Emissions from Materials

Results for Step 3



mean value ····· *single standard deviation*

twofold standard deviation

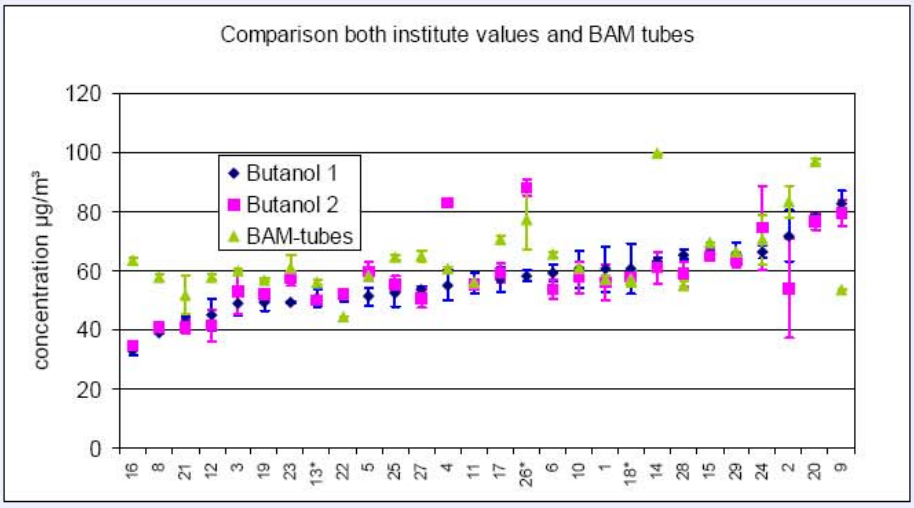
BAM
IV.2 Emissions from Materials

Repeatability standard deviation and reproducibility standard deviation for Step 3 (*all Data*)

compound	mean	repeat. st dev	reprod. st dev
		s_r	s_R
1-butanol	57,5	5,56	15,54
1,2 ethanediol	493	100,23	430,18
butyl acetate	17,0	1,57	6,08
dibutyl ether	42,0	3,38	11,60
acrylic acid butyl ester	40,4	3,28	12,35

BAM
IV.2 Emissions from Materials

Results for Step 3

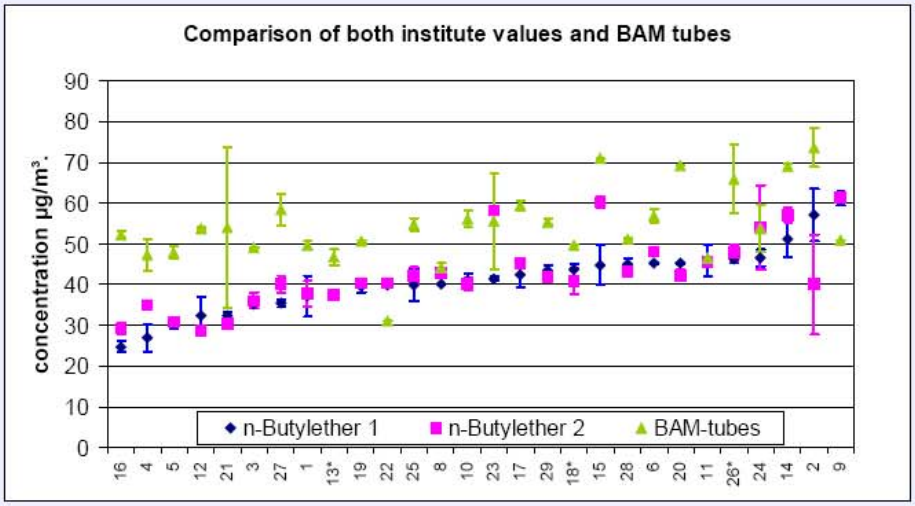


mean value ····· *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Results for Step 3

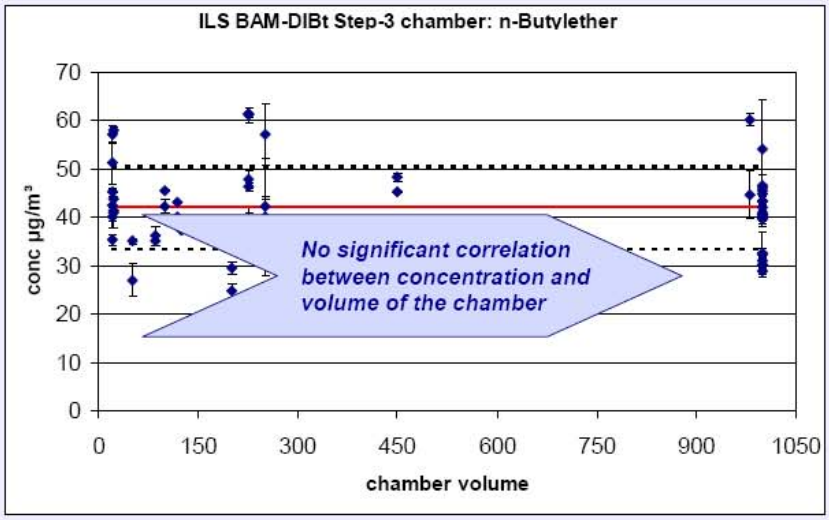


mean value ····· *single standard deviation*

twofold standard deviation

BAM
IV.2 Emissions from Materials

Parameters influencing results of Step 3



Results for n-butylether given in concentrations in the chamber in correlation to the volume of the chamber

BAM
IV.2 Emissions from Materials

Many thanks

Team of BAM for interlaboratory study

BAM
IV.2 Emissions from Materials

Thanks to all of you

For your engagement and participation in this study

For your tolerance to our requirements

For your delivery of data

Thanks to Mr. Bremser for his engagement

And to all of you for your attention

BAM

IV.2 Emissions from Materials

7.6. Questionnaires for the Steps 1, 2 and 3

7.6.1. Questionnaire for step 1

Testing Laboratory

Lab Code

Please give short particulars to your equipment and measurement conditions.

Analyses of VOC standard solutions

Tenax sorption tube preparation

o gaseous spiking with the aid of a GC injection unit

GC System :

GC injector temperature parameters:

gas flow [mL min^{-1}] ;[100 mL min^{-1}][1]:

injection volume [µL]:

type of syringe:

syringe maximum capacity [µL]:

syringe readable scale division ;[0.1 µL][1]:

time of calibration [min]:

Please report any difficulties with blank values:

o	spiking by direct fluid injection onto Tenax	
	injection volume [µL]:	
	type of syringe:	
	syringe maximum capacity [µL]:	
	syringe readable scale division [0.1 µL][1]:	

[1] ISO 16000-6

	gas flow [mL min^{-1}]:	
	Please describe how the solvent was removed:	

Please report any difficulties with blank values:

Analysis – Tenax-TDS-GC-MS

GC system

- ☐ Agilent
- ☐ Perkin Elmer
- ☐ Varian
- ☐ others:

GC Carrier Gas

- ☐ helium
- ☐ other

Thermal desorption unit

- ☐ Perkin Elmer
- ☐ Gerstel
- ☐ Markes
- ☐ other:

-	temperature programme:	
-	splitless / split	
-	split-ratios:	
-	purge time [min]:	
-	gas flow [ml min^{-1}]:	
-	transferline temperature:	

Cooling unit

-	temperature programme:	
-	purge time [min]:	
-	splitless / split	
-	split-ratios	
-	gas flow [ml min^{-1}]:	

☐	liner with filling -> type of filling:	
☐	liner without filling	

GC-Column

-	Type:	
-	Length:	
-	Internal Diameter:	
-	Film thickness:	

GC Oven

Temperature programme:

Transferline temperature [°C]:

Date of analysis:

Analysis - Fluid injection of standard solutions - GC-MS

GC system

☐ as per section 1.2
☐ other:

GC Carrier Gas

☐ helium
☐ other:

GC Injector

☐ PTV
☐ Other:

- temperature programme:
- purge time [min]:

- split-ratios
- gas flow [ml min^{-1}]:

☐ liner with filling -> type of filling:

☐ liner without filling

GC-Column

- Type:
- Length:
- Internal Diameter:
- Film thickness:

GC Oven

Temperature programme:

Transferline temperature [°C]:

Injection volume [µL]:

Date of analysis:

Manufacturer of pure standards used for the analyses:

Concentration range of target analytes in [µg mL-1]*

Lowest concentration [µg mL^{-1}]:

Highest concentration [µg mL^{-1}]:

*only should be filled in if different from the protocol instructions. Please comment any change of concentration.

Please add one chromatogram of the lowest concentration of your standard solution used for calibration (TDS-GC-MS and fluid injection,resp.). Please add also chromatograms of each analysis of the standard solution (TDS-GC-MS and fluid injection-GC-MS, respectively). Please identify all peaks you have used to calibrate and to identify the target analytes!
Please add also a print-out of your calibration curve for each target analyte.

Indicate clearly your Lab Code (LXXX) on each chromatogram and print-out.

Coefficient of variation of the calibration curve [%]:

	[%]
Methylisobutylketone	
2-ethyl-1-hexanol	
dodecanee	
Diethylenglykolmonobutylether	
caprolactam	
Styrene	
1,3-Dichloropropanol	
Benzaldehyde	
1,2,3 Trimethylbenzene	
longifolenee	
BHT	

General remarks (operator change during analyses, missing results, comments, difficulties etc.):

7.6.2. Questionnaire for step 2

Testing Laboratory

Lab Code ☐

For correct interpretation of the results of the interlaboratory study (ILS) it is very important for us, that you compare the results of your laboratory with the target and median values resulted in the ILS. We request your analysis of the data for a better interpretation of the results and especially for a better understanding of high variances and outliers.

Please give short particulars to your equipment and measurement conditions.

o Analysis – Tenax-TDS-GC-MS

- GC system

☐ Agilent
☐ Perkin Elmer
☐ Varian
☐ others:

- GC Carrier Gas

☐ helium
☐ other

- Thermal desorption unit

☐ Perkin Elmer
☐ Gerstel
☐ Markes
☐ other:

-	temperature programme:	
-	splitless / split	
-	split-ratios:	
-	purge time [min]:	
-	gas flow [ml min^{-1}]:	

-	transferline temperature:	

- Cooling unit

-	temperature programme:	
-	purge time [min]:	
-	splitless / split	
-	split-ratios	
-	gas flow [ml min^{-1}]:	

☐	liner with filling -> type of filling:	
☐	liner without filling	

- GC-Column

-	Type:	
-	Length:	
-	Internal Diameter:	
-	Film thickness:	

- GC Oven

Temperature programme:

Transferline temperature [°C]:

- Detector system

☐	mass spectrometer	Producer:
		Type:
☐	other	Producer:
		Type:

- Date of analysis:

o Manufacturer of pure standards used for the analyses:

o Concentration range of target analytes in [µg mL^{-1}]

Lowest concentration [µg mL^{-1}]:

Highest concentration [µg mL^{-1}]:

Please add one chromatogram of your analysis of each of the tubes sampled at our chamber. Please identify all compounds we asked for in your analysis. Try to identify all other compounds with approximately higher concentrations than 2 or 5 µg/m³ and quantify them with the response of toluene (native). Please send us your retention time and the mass spectrum of other compounds identified.

Please add one chromatogram of the lowest concentration of your standard solution used for calibration (TDS-GC-MS and fluid injection,resp.).
Please identify all peaks you have used to calibrate and to identify the target analytes!
Please add also a print-out of your calibration curve for each target analyte.

Indicate clearly your Lab Code (LXXX) on each chromatogram and print-out.

- Coefficient of variation of the calibration curve [%]:

	[%]
Methylisobutylketone	
2-ethyl-1-hexanol	
dodecanee	
Diethylenglykolmonobutylether	
caprolactam	
Styrene	
1,3-Dichloropropanol	
Benzaldehyde	
1,2,3 Trimethylbenzene	
longifolenee	
BHT	

- General remarks (operator change during analyses, missing results, comments, difficulties etc.):

Date: responsible person:

7.6.3. Questionnaire for step 3

Laboratory

Lab Code | 000 |

For correct interpretation we request your analysis of the data for a better interpretation of the results and especially for a better understanding of high variances and outliers.

Please give short particulars to your equipment and measurement conditions.

Sample preparation

Number of sealant cartridge(s) used

Length of aluminium profile used[2]

	cm	chamber test 1
	cm	chamber test 2
optional[3]:	cm	chamber test 3
	cm	chamber test 4

Weight of sealant used to fill profile (if available)

	g	chamber test 1
	g	chamber test 2
optional	g	chamber test 3
	g	chamber test 4

Remarks to sealant preparation

[2] can be different in relation to chamber volume and air exchange rate
[3] several participants plan to make more than 2 chamber tests, if you want you can give us your results of these tests too.

Chamber conditions

Chamber volume

Chamber 1	m3
Chamber 2	m3

optional

Chamber 3	m3

Air exchange rate

Chamber 1	h-1
Chamber 2	h-1

optional

Chamber 3	h-1

Control of air exchange rate via

- ☐ tracer gas
- ☐ inlet measurement
- ☐ inlet - outlet measurement
- ☐ calibrated mass flow controler
- ☐ other

climatic conditions

Chamber 1	temperature	°C	±	°C
	relative humidity	%	±	%
Chamber 2	temperature	°C	±	°C
	relative humidity	%	±	%

optional

Chamber 3	temperature	°C	±	°C
	elative humidity	%	±	%

Control of climatic conditions via

- ☐ internal sensor (originally installed in chamber)
- ☐ external sensor (measurement in the chamber)
- ☐ internal and external sensor
- ☐ other

Air velocity

Chamber 1	m s-1
Chamber 2	m s-1

optional
Chamber 3 m s-1

Control of air velocity via	☐	hot wire
	☐	film anemometer
	☐	other

- Sampling device

Manufacturer of air sampling pump
Used air flow for sampling mL min-1
Used volume for Tenax-sampling Litre

internal Air flow control of sampling pump via	☐	mass flow controller
	☐	needle valve
	☐	other

Additional control of air sampling volume? Yes ☐ No ☐
Which type of control unit?

- Remarks to chamber test

- Analysis – Tenax-TDS-GC-MS

  - GC system

☐ Agilent
☐ Perkin Elmer
☐ Varian
☐ others:

  - GC Carrier Gas

☐ helium
☐ other

  - Thermal desorption unit

☐ Perkin Elmer
☐ Gerstel
☐ Markes
☐ other:

temperature programme:	
temperature hold:	

valve temperature:	
flow path temperature:	
splitless / split	
split-ratios:	
purge time [min]:	
gas flow [mL min^{-1}]:	
transferline temperature:	

o Cooling unit

temperature programme:	
cooling temperature	
purge time [min]:	
splitless / split	
split-ratios	
gas flow [mL min^{-1}]:	

liner with filling	☐	type of filling:
liner without filling	☐	

o GC-Column

Type:	
Length:	m
Internal Diameter:	mm
Film thickness:	µm

o GC Oven

Temperature programme:
Transferline (GC to MS) temperature [°C]:

o Detector system

mass spectrometer	Producer:
	Type:
Temperature in MS	Source: °C; Quad: °C
	other Temp zones: with °C

o Date of analysis:

o Manufacturer of pure standards used for the analyses:

1-butanol	
1,2 ethanediol	
butyl acetate	
dibutyl ether	
acrylic acid butyl ester	
toluene	

o Concentration range of target analytes in [µg mL^{-1}]

Lowest concentration [µg mL^{-1}]:

Highest concentration [µg mL^{-1}]:

Please add one chromatogram of your analysis of each of your chamber tests.

Please identify all compounds we asked for in your chromatogram. Try to identify all other compounds with approximately higher concentrations than 2 or 5 µg/m³ and quantify them with the response of toluene (native). Please send us your retention time and the mass spectrum of other identified compounds.

Please add one chromatogram of the lowest concentration of your standard solution used for calibration.
Please identify all peaks you have used to calibrate and to identify the target analytes!
Please add also a print-out of your calibration curve for each target analyte.

Indicate clearly your Lab Code (LXXX) on each chromatogram and print-out.

- General remarks (operator change during analyses, missing results, comments, difficulties etc.):

Date: responsible person:

7.7. Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of allgemeine bauaufsichtliche Zulassungen ('national technical approvals') for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
Part I: Basic requirements				
1	**Impartiality**			
	The testing laboratories must be independent, e.g. they must act free from economic interests of individual manufacturers. (mandatory)			Please tick if applicable.
2	**Accreditations**			
	According to DIN EN ISO/IEC 17025 including test chamber analysis (mandatory)			Presentation of the accreditation certificate and annex.
3	**Verification of experience**			
3a)	Participation in round robin tests ("RRT") or interlaboratory studies ("ILS"). The successful participation in at least three of the following "rrt" or "ils" has to be proven.			Please tick if applicable and provide appropriate verifications.
	VOCEM 1997/98 / Floor coverings			Please tick if applicable and provide appropriate verifications.
	BAM RAL UZ 38, 1998 / Furnitures			Please tick if applicable and provide appropriate verifications.
	Nordic round robin test 1999 / Laquer			Please tick if applicable and provide appropriate verifications.

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
	GEV1, 2000 / Adhesives			Please tick if applicable and provide appropriate verifications.
	GEV2, 2003 / Adhesives			Please tick if applicable and provide appropriate verifications.
	BGIA 2002 / VOC in solution			Please tick if applicable and provide appropriate verifications.
	BGIA 2003 / VOC in solution			Please tick if applicable and provide appropriate verifications.
	BGIA 2004 / VOC in solution			Please tick if applicable and provide appropriate verifications.
	BGIA 2005 / VOC in solution			Please tick if applicable and provide appropriate verifications.
	BGIA 2006 / VOC in solution			Please tick if applicable and provide appropriate verifications.
	BGIA 2007-1 / VOC in gasphase			Please tick if applicable and provide appropriate verifications.
	BGIA 2007-2 / VOC in gasphase with sampling			Please tick if applicable and provide appropriate verifications.
	BGIA 2008-1 / VOC in gasphase			Bitte ankreuzen, falls zutrifft, sowie entsprechende Nachweise vorlegen.
	BGIA 2008-2 / VOC in gasphase with sampling			Bitte ankreuzen, falls zutrifft, sowie entsprechende Nachweise vorlegen.
	Regierungspräsidium Stuttgart-LGA, 2006 / Aldehydes in solution			Please tick if applicable and provide appropriate verifications.

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
	Regierungspräsidium Stuttgart-LGA, 2007 / Aldehydes in solution			Please tick if applicable and provide appropriate verifications.
	DIBt 2004 / Floor coverings in emission chamber			Please tick if applicable.
	DIBt 2005 / VOC in solution, VOC on TENAX-tubes			Please tick if applicable.
	DIBt 2006 / Aldehydes in solution			Please tick if applicable.
	BAM / DIBt ILS 2006 u. 2007 / 1) VOC in solution, 2) VOC on TENAX-tubes from chamber air, 3) Sealant in emission chamber			Please tick if applicable.
	BAM-ExQMS (2008 - 10) 1) VOC in solution, 2) VOC added to Tenax by BAM, 3) VOC on TENAX-tubes from chamber air			Please tick if applicable and provide appropriate verifications.
	others			Please tick if applicable and provide appropriate verifications.
3b)	Presentation of at least three test reports about VOC emission tests on construction products at various intervals.			Please tick if applicable and present test reports (if relevant, blacken the client).
3c)	Publications, presentations			informative

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
4	**Technical equipment**			
4a)	Testing from one source. The testing laboratory has to be technically equipped such that it can perform emission test and analysis in one laboratory at not regionally different locations. A subcontracting of the whole emission test or of the individual stages is not allowed.			Please tick if applicable.
4b)	Technical equipment for the VOC, VVOC and SVOC emission testing according to (EN) ISO 16000-3, -6, -9, -10 and -11			
	Test chamber walls made of steel			Please indicate number (quantity) and sizes.
	Test chamber walls made of glass			Please indicate number and sizes.
	Thermal desorption system			Please indicate manufacturer and number.
	GC system			Please indicate manufacturer and number.
	Type of column (slightly polar or nonpolar)			Please indicate what type of column is used for the work.
	Detector for analytics according to ISO 16000-6			Please indicate type, manufacturer and number.
	HPLC system			Please indicate manufacturer and number

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
	Detector for analytics according to ISO 16000-3			Please indicate type, manufacturer and number.
4c)	Technical equipment for short-time measurements			
	Microchamber			Please indicate type, manufacturer and number.
	Thermoextraktor			Please indicate type, manufacturer and number.
4d)	Technical equipment for formaldehyde in wood-based material according to DIN EN 717-1			
	Test chamber according to DIN EN 717-1			Please indicate type, number and size.
	Test chamber walls made of steel			Please indicate number and sizes.
	Test chamber walls made of glass			Please indicate number and sizes.
	Test chamber walls made of different material			Please indicate number, sizes and wall material.
	Analytics according to DIN EN 717-1			Please indicate manufacturer and number.
	Technical equipment for formaldehyde in wood-based material according to DIN EN 717-2			Please tick if available and fit for service. Please indicate also number, further comments, if relevant.

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
	Technical equipment for formaldehyde according to DIN EN 120			Please tick if available and fit for service. Please indicate also number, further comments, if relevant.
4e)	Presence of LCI compounds as reference standards			Please indicate number of the existing compounds.
	Presence of compounds from the C-list (red marked compounds from the "carciongeinc substances" list in the "Adam-Evaluaiton-mask")			Please indicate number of the existing compounds.
4f)	Inspection and evaluation of laboratory			Applicant's agreement relating to an evaluation either by DIBt or BAM or a third party (unless the laboratory, equipment of the laboratory and personnel are already known).
5	**Miscellaneous**			
	Is the AgBB scheme known? Is it already used?			Please tick if applicable.
	Are the "Principles for the health evaluation of construction products in interiors" known?			Please tick if applicable.
	Is ADAM known? If so, is it already used?			Please tick if applicable.
	Is DIBt-RL (RL: guideline) 100 known?			Please tick if applicable.

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
Part II: Technical verifications				
6	**Successful participation in a round robin test of BAM every two year**			Please provide verifications. For a successful participation the Z score has to be at 80% of the analytes between +2 and -2 (included). If the standard deviation is more than 30 %, then the standard deviation will be fixed at 30 % (according Horrwitz) for the calculation of the Z score. The calculation of the Z score is done by means of the software "ProLab". For the assessment the "criterion LAWA" is applied.
Part III: Continuous quality assurance				
7	**Exchange of experiences**			
	The testing laboratory commits to participate in the exchange of experience at its own expense. The relevant meetings will be convened either by DIBt or the testing laboratories.			Please tick if you agree.

Catalogue of criteria for the determination of the professional competence for emission tests of construction products within the framework of approvals for the granting of national technical approvals for floor coverings

	Requirement	*Please tick where applicable*	*Comments*	*Procedure*
8	**Regular participation in cooperative tests**			
	The testing laboratory commits to participate in round robin tests ("RRT") for VOC thermodesorption measurements. In addition to the participation in the "RRT" of BAM it is necessary to participate in at least one more "RRT" once a year. In case DIBt does not prescribe any special test, participation in "RRT" proposed by BGIA is recommended (see http://www.dguv.de/bgia/en/fac/ring/organ/index.jsp).			Please tick if you agree.
	Name of the testing laboratory:			
	Address of the testing laboratory carrying out the tests:			
	Name of the head of the testing laboratory:			***Place, date and signature***