



University of Stuttgart
Germany



Analytische Qualitätssicherung Baden-Württemberg

PT-WFD

Proficiency Test Volatile organic compounds

Benzene , 1,2-Dichloroethane, Dichloromethane
Trichloromethane, Carbon tetrachloride, Tetrachloroethene,
Trichloroethene

provided by
AQS Baden-Württemberg at
Institute for Sanitary Engineering, Water Quality and Solid Waste Management,
University of Stuttgart
Bandtäle 2, 70569 Stuttgart-Büsnau, Germany



in cooperation with other European PT providers

Stuttgart, in February 2010

Responsibilities:

Scientific director AQS: Dr.-Ing. Dipl.-Chem. Michael Koch

PT manager: Dr.-Ing. Frank Baumeister

AQS Baden-Württemberg at
Institute of Sanitary Engineering,
Water Quality and Solid Waste Management
at University of Stuttgart

Bandtäle 2

70569 Stuttgart-Büsnau

Germany

<http://www.aqsbw.de>

Tel.: +49 (0)711 / 685-65446

Fax: +49 (0)711 / 685-63769

E-Mail: info@aqsbw.de

INDEX OF CONTENTS

GENERAL	2
PT DESIGN	3
SAMPLE PREPARATION	3
SAMPLE DISTRIBUTION	3
ANALYTICAL METHODS	3
SUBMISSION OF RESULTS	4
EVALUATION AND ASSESSMENT	4
PARTICIPATION	4
EXPLANATION OF THE PT REPORT DETAILS	5
MEASUREMENT UNCERTAINTY	8
TRACEABLE REFERENCE VALUES	8
INTERNET	10
Benzene	11
1,2-Dichloroethane	18
Dichloromethane	25
Trichloromethane	32
Carbontetrachloride	39
Tetrachloroethene	46
Trichloroethene	52
SINGLE LEVELS	58
BENZENE	A-1
1,2-DICHLOROETHANE	A-28
DICHLOROMETHANE	A-55
TRICHLOROMETHANE	A-82
CARBONTETRACHLORIDE	A-109
TETRACHLOROETHENE	A-136
TRICHLOROETHENE	A-163

General

This PT was provided by AQS Baden-Württemberg in the context of the "PT-WFD" network of European PT providers founded in 2008 for the determination of benzene, 1,2-dichloroethane, dichloromethane, trichloromethane, carbontetrachloride, tetrachloroethene and trichloroethene. The PT met the requirements of the water framework directive and the related environmental quality standards for the determination of priority substances in surface water. More information about this network can be found on the webpage <http://www.pt-wfd.eu>.

The PT was organized in collaboration with the following other PT providers in Europe:

- **LGC Standards Proficiency Testing**, Europa Business Park, Barcroft Street, Bury, Lancashire, BL9 5BT, UK, Telephone: +44 (0) 161 762 2500, Fax: +44 (0) 161 762 2501, Email: customerservices@lqcpt.com
- **Kemijski inštitut** Ljubljana Slovenija, SI-1001 Ljubljana, Hajdrihova 19, p.p.660, Tel.: 01/476 02 00, Faks: 01/476 03 00, mail: info@ki.si
- **QualityConsult**, Via G. Bettolo 4, (00195) Rome Italy, Tel.: +39 320-6905464, Fax: +39 0697840718, qualityconsult@aqc.it
- **VITUKI Nonprofit Ltd.**, Quality Assurance and Control, 1095 Budapest, Kvaszay J. 1., HUNGARY, Tel: +36 1 215-6140/ext. 2199, Fax: +36 1 215-6046, mecs@vituki.hu
- **SYKE Finnish Environment Institute**, Laboratories, Hakuninmaantie 6, 004300 Helsinki, FINLAND, Tel: +358 20 610 123, Fax: +358 9 448 320, proftest@environment.fi

The PT was executed and evaluated due to the requirements of the PT-WFD network.

PT design

Each participant received the following samples:

- 3 x 2 samples for the determination of benzene, 1,2-dichloroethane, dichloromethane, trichloromethane, carbontetrachloride, tetrachloroethene, trichloroethene in 250 ml amber ground bottles. The samples were stabilised by acidification with sulphuric acid (pH 2.1) and by cooling.

9 different concentration levels/batches were produced. The concentration levels were randomly allocated to the participants. It was ensured that each participant received one concentration level from the lower concentration range (level 1–3).

Sample preparation

The samples were based on a real surface water.

The surface water was filtered by using 5 µm and 1 µm filter cartridges to eliminate particles. To reduce germs, the surface water was irradiated with ultraviolet light and was pasteurised at 80 °C in a stainless steel vessel overnight. During pasteurisation the surface water was aerated with a mixture of carbon dioxide and nitrogen to prevent deposition of calcium carbonate.

The concentrations of the analytes of the spiked samples were chosen according to the Environmental Quality Standard (Directive 2008/105/EG on environmental quality standards in the field of water policy):

parameter	AA-EQS [µg/l]	MAC-EQS [µg/l]
benzene	10	50
1,2-dichloroethane	10	-
dichloromethane	20	-
trichloromethane	2.5	-
carbontetrachloride	12	-
tetrachloroethene	10	-
trichloroethene	10	-

AA: annual average

MAC: maximum allowable concentration

The samples were cooled directly after preparation. The samples were dispatched with freezer packs added to the packages.

Sample distribution

The samples were dispatched on 14th October 2009 by express service. Laboratories outside Germany received their samples from one of the cooperating PT provider.

Analytical methods

The participants were free to choose a suitable method, but following limits of quantifications were required:

parameter	limit of quantification [µg/l]
benzene	3
1,2-dichlorethane	3
dichloromethane	6
trichloromethane	0,75
carbontetrachloride	3,6
tetrachloroethene	3
trichloroethene	3

The samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to submit the results as average values in µg/l with four significant digits.

Submission of results

The deadline for the submission of results was on 13th November 2009.

Evaluation and assessment

According to the agreements in the PT-WFD network the following procedure was used for the evaluation and assessment of the PT round: The consensus mean of all participants was used as assigned value X . The mean was calculated using the "Algorithm A", a robust statistical method, described in ISO 5725-5 and in ISO 13528. A fixed value of 25% of the assigned value was used as standard deviation for proficiency assessment $\hat{\sigma}$. For each measurement result of the participant a z-score was calculated using the following formula:

$$z = \frac{x - X}{\hat{\sigma}}$$

for the assessment the following criteria were used:

	$ z \leq 2,0$	satisfactory
2,0 <	$ z < 3,0$	questionable
	$ z \geq 3,0$	unsatisfactory

Participation

Number of participants (total): 127

Registration via:

AQS Baden-Württemberg, Germany:	108
LGC Standards, UK:	6
Kemijski inštitut, Slowenien:	2
QualityConsult, Italien:	4
VITUKI, Ungarn:	6
SYKE, Finland:	1

Table 1 shows the number of satisfactory, questionable and unsatisfactory results for each parameter. Figure 1 shows the percentage of satisfactory, questionable and unsatisfactory results.

Table 1: Number of values per parameter assessed as satisfactory, questionable and unsatisfactory

	satisfactory	questionable	unsatisfactory
benzene	331	15	7
1,2-dichloroethane	329	5	22
dichloromethane	317	19	19
trichloromethane	342	7	9
carbontetrachloride	324	13	13
tetrachloroethene	333	9	20
trichloroethene	339	11	12

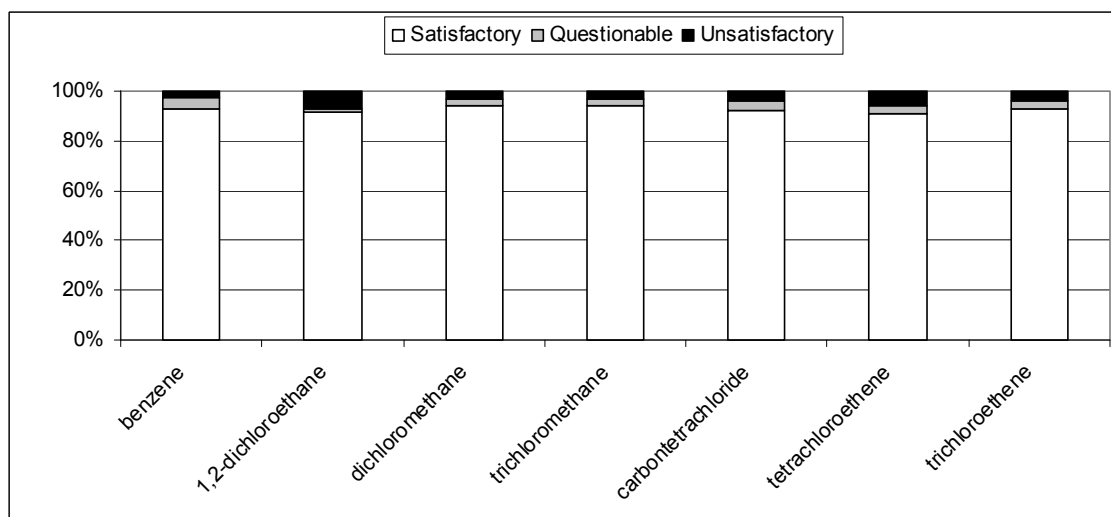


Figure 1: Percentage of satisfactory, questionable and unsatisfactory results

Explanation of the PT report details

The results for each parameter are summarized on the following pages. In the last part details for each parameter level combination are compiled.

Parameter tables

In these tables the following values are listed:

- assigned value
- expanded uncertainty of the assigned value in %, calculated according to ISO 13528 with the formula

$$U = 2 \cdot 1.25 \cdot \frac{\text{rel. standard deviation}}{\sqrt{\text{number of values}}}$$

- standard deviation, calculated with robust statistical method (algorithm A)
- standard deviation for proficiency assessment (25% of the assigned value; from PT-WFD requirements)
- rel. standard deviation for proficiency assessment
- tolerance limits (for satisfactory results) in $\mu\text{g/l}$ and in %
- number of values in this level
- number of not satisfactory values below and above the assigned value
- percentage of values that are not satisfactory

Determination of recovery rate

In the diagrams of assigned values versus the spiked amount of analyte a linear regression line was calculated. From these values the recovery rate for each parameter

was determined (see diagrams). The slope of the line indicates the average recovery over all 4 levels.

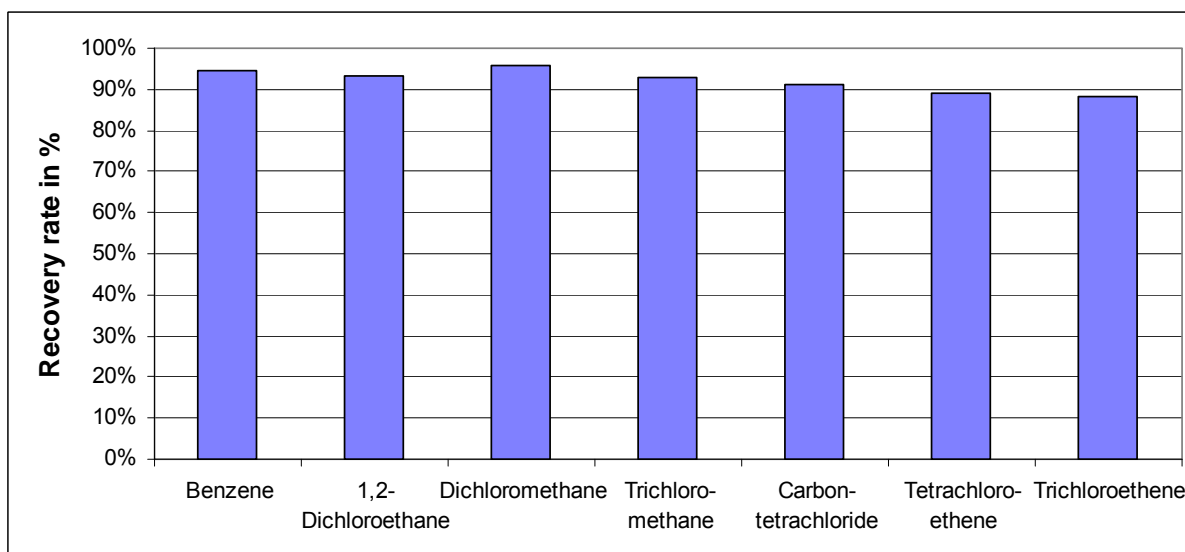


Figure 2: Average recovery rates for all parameters

Relative standard deviation

The diagrams for the rel. standard deviation vs. the assigned value show the values compared to the fixed standard deviation for proficiency assessment (horizontal line at 25%) and the concentration dependence.

Method specific evaluation

For each parameter the methods used by the participants are shown in a diagram. In a second diagram for each method values are sorted in 5 categories:

too low	results with z-score < -2
low	results with $-2 \leq \text{z-score} < -1$
correct	results with $-1 \leq \text{z-score} \leq +1$
high	results with $+1 < \text{z-score} \leq +2$
too high	results with z-score > +2

Finally the mean value calculated from all results (used as assigned value) is compared with mean values calculated for all methods separately (in this case using the Hampel estimator described in ISO/TS 20612). Mean values were calculated only, if more than 7 results were within a z-score-range of ± 2 . The means are reported with their expanded uncertainty calculated according to ISO 13528.

Measurement uncertainty

Participants were asked to report expanded uncertainties of their results on a voluntary basis. In this diagram for each parameter the reported uncertainties for all concentration levels with the reproducibility standard deviation (horizontal line) are displayed. Values which deviate from the reproducibility standard deviation with a factor more than 2 are usually not realistic.

Comparison of means and reference values

In these diagrams for each parameter and each concentration level the assigned value, the reference value and the mean values for the applied methods as well as the expanded uncertainties are illustrated. The determination of the means for each

method was calculated by using the Hampel estimator, if more than seven values were within the tolerance limits.

Single levels

In the last part of the report, for all concentration levels the results of all participants are illustrated. The participants are anonymised by using lab codes. The lab codes were sent to participants with the certificates. The assigned value with the expanded uncertainty and the tolerance limits for the concentration level is illustrated in the table. For each participant following data are given:

- lab code
- reported result
- measurement uncertainty of the value (if reported)
- ζ -Score for this value, calculated with the following formula

$$\zeta = \frac{x - \bar{x}}{\sqrt{u_{lab}^2 + u_{ref}^2}}, \text{ with}$$

$x - \bar{x}$ = difference from the measured value and the assigned

value

- u_{lab} = standard uncertainty of the value, reported by the participant
- u_{ref} = standard uncertainty of the assigned value
- z-score for proficiency assessment
- assessment of the value according to its z-score

Meaning of ζ -scores:

The assessment of ζ -scores is similar to that of z-scores. If the data are normally distributed and the uncertainties are well estimated, ζ -scores will lie between -2 and +2 with a probability of around 95 %.

ζ -scores are mainly influenced by the measurement uncertainties reported by the laboratory. Therefore ζ -scores are usually not appropriate for the assessment of the reported results, unless the reported measurement uncertainty is checked for fitness-for-purpose.

Therefore we do not use the ζ -scores for the assessment of the laboratories.

Nevertheless ζ -scores are appropriate to check the plausibility of the reported measurement uncertainty:

☐ If the z-score of a result is within the tolerance limit and the ζ -score is outside, then the measurement uncertainty is underestimated.

☐ If the z-score is outside the tolerance limits and the absolute value of the ζ -score is lower than two, then the requirements of the proficiency test were stronger compared with the reported measurement uncertainty.

Figures

In the first figure for all lab codes the measurement uncertainty (together with the reproducibility standard deviation) is illustrated. The second figure shows the associated ζ -scores.

Measurement uncertainty

41 (33,9%) out of 121 laboratories with valid values reported measurement uncertainties. In total 844 (33,8%) out of 2496 valid values were given with the measurement uncertainty.

The following table displays the number of values with measurement uncertainty against the accreditation status.

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	1801	664 (36,9%)
not accredited	276	96 (34,8%)
not specified	419	84 (20%)

In many cases the reported uncertainties are probably too low. For 284 out of 664 values the z-score (which compares the deviation from the assigned value with the requirements of the PT provider) was in the satisfactory range whereas the ζ -score, which compares the deviation from the assigned value with the reported uncertainty for this value was out of the satisfactory range.

Traceable reference values

Traceability of analytical results to national and international references is of increasing importance in all laboratories. This is not easy to realise for chemical analyses and often can only be done by analysing certified reference materials. But availability of these reference materials in the water sector is very limited. Therefore we try to provide reference values for the proficiency test samples, traceable to national and international references.

Since our PT samples without exception are spiked, real water samples, reference values can be calculated from the sum of matrix content and spiked amount of analyte. For both summands traceable values and their uncertainty have to be determined. Thereby we assume that no unrecognised bias resulting from sample preparation and transport is present and that we recognise all uncertainty components. Unfortunately this cannot absolutely be assured for samples for the analysis of highly volatile compounds. We have to accept that a small part of the analyte is lost during sample preparation leading to reduced recovery rate. The trueness of the reference values reported here therefore cannot absolutely be guaranteed. Please consider that in the interpretation of these values and your deviation from the reference values.

Determination of the spiked amount and its uncertainty

All spiking of samples was controlled gravimetrically. Conversion to concentration was done by measuring the density of the resulting samples using a pycnometer. This procedure allows the preparation of a complete uncertainty budget. The first step is the specification of the measurand with a formula. This shows the links between the result and all influence quantities

$$c_{lot} = \frac{m_{subst_ss} \cdot P \cdot m_{ss_dilA} \cdot m_{dilA_lot} \cdot \rho_{lot}}{m_{ss} \cdot m_{dilA} \cdot m_{lot}}$$

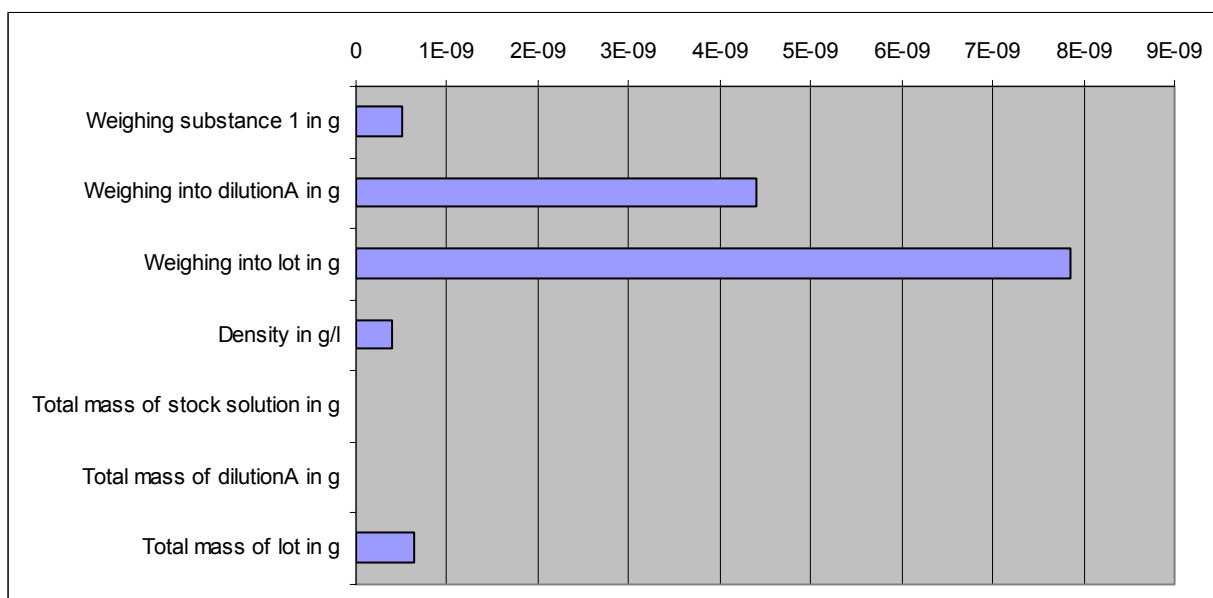
with:

c_{lot} concentration of the analyte in the lot resulting from the spike in g/l
 m_{subst_ss} mass of substance added for preparation of the stock solution in g

m_{ds_dilA}	mass of stock solution added for preparation of dilution A in g
m_{dilA_lot}	mass of dilution A added for preparation of the lot in g
m_{ss}	total mass of stock solution in g
m_{dilA}	total mass of dilution A in g
m_{lot}	total mass of the lot in g
ρ_{lot}	density of the lot in g/l
P	purity of the used substance

Based on this formula the uncertainty budget can be prepared and all components be quantified. The following figure shows a typical distribution of the contributions, here for benzene as an example.

The main contribution results from the mass of dilution A added to the lot. This addition was done by using pipettes that were “in”-calibrated with pure DMF (dimethyl formamide) using a 20fold measurement. From the standard deviation of these 20 measurements the uncertainty of this calibration was calculated.



All weighings were done as difference weighings. The precision of these weighings was determined in experiments by multiple (20fold) measurements of mass pieces with similar masses as a type A uncertainty. The trueness of the weighing, that has to be considered twice for each weighing, was taken from the calibration certificate of the balance. Maintaining of these tolerances is assured by regular maintenance of the balances by a calibration laboratory and by supervision with our mass pieces (calibrated by an accredited calibration laboratory).

The determination of the density was also made using weighings (of the pycnometer). The above said also applies here.

Temperature measurement was made with a calibrated thermometer.

The purity of the used benzene was taken from the certificate of the manufacturer.

With all these uncertainty components the combined uncertainty, as described in the EURACHEM/CITAC-Guide „Quantifying Uncertainty in Analytical Measurement“, was calculated using the sensitivity coefficients determined by partial derivation of the formula to the respective influence quantities.

So traceability was assured by using calibrated balances and thermometers.

Determination of the matrix content

Because the same matrix was used for preparation of all samples, the matrix content could be calculated from the mean values of the participants and the spiked amounts in a standard-addition-like way^{1,2}.

The uncertainties of the spiked amounts were known from the uncertainty budgets. The expanded uncertainties of the mean values of participants' result were calculated according to ISO 13528 (Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons) as

$$u_{mean} = 2 \cdot 1,25 \cdot \frac{s_R}{\sqrt{n}}$$

with:

s_R reproducibility standard deviation

n number of data for this level

2 coverage factor for the expanded uncertainty

1,25 correction factor (according to ISO 13528 to be used for robust methods)

The content of the matrix can be derived from a linear regression of means vs. spiked amounts. Since uncertainties of all data points were available for x- as well as y-direction a generalised least square regression was used as described in DIN EN 6143. The computer program B_LEAST (from BAM) was used for this purpose. With this method a value for matrix and its uncertainty are obtained.

Because of statistical variation of the input values the calculated matrix content might result in a negative value. From a scientific point of view this of course is nonsense. In those cases the matrix content is set to zero.

The lower end of the uncertainty range of the matrix content also might be negative. Therefore the expanded uncertainty of the matrix content was set to the matrix content itself in this case.

The matrix content is not directly traceable to national or international references, but it does not considerably compromise the traceability of the final content due to its comparably low contribution.

Internet

Diese Informationen sind auch im Internet erhältlich:

<http://www.aqsbw/pdf/report509.pdf>

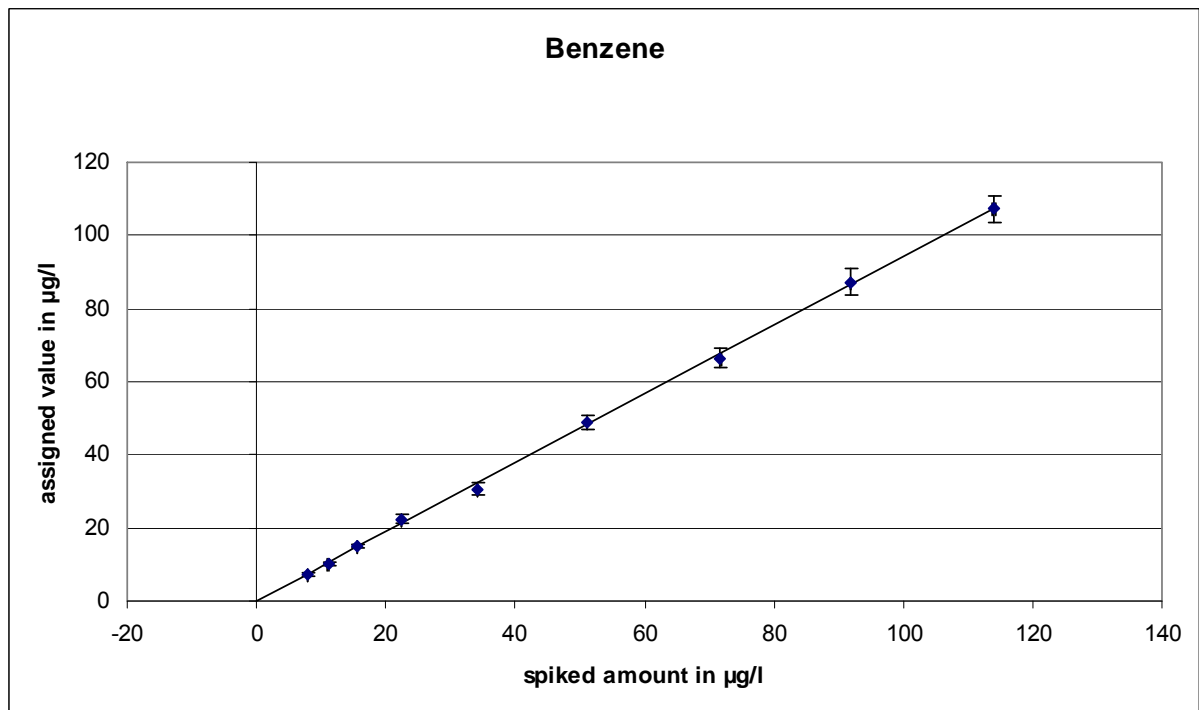
¹ Rienitz, O., Schiel, D., Güttler, B., Koch, M., Borchers, U.: A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons. *Accred Qual Assur* (2007) 12: 615-622.

² Koch, M., Baumeister, F.: Traceable reference values for routine drinking water proficiency testing: first experiences. *Accred Qual Assur* (2008) 13: 77-82.

Benzene

level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	7,338	9,68	1,7291	1,8345	25,00	11,007	3,669	50,00	-50,00	40	1	1	7,7
2	10,399	9,31	2,2245	2,5997	25,00	15,598	5,199	50,00	-50,00	38	0	3	7,9
3	15,030	8,54	3,1662	3,7575	25,00	22,545	7,515	50,00	-50,00	40	2	0	7,5
4	22,495	9,05	4,8873	5,6238	25,00	33,743	11,248	50,00	-50,00	41	2	1	7,5
5	30,707	9,89	7,3907	7,6767	25,00	46,060	15,353	50,00	-50,00	39	2	4	17,9
6	48,843	8,54	10,1448	12,2108	25,00	73,265	24,422	50,00	-50,00	39	1	2	10,3
7	66,496	8,14	13,5167	16,6241	25,00	99,744	33,248	50,00	-50,00	39	1	0	2,6
8	87,256	8,04	16,1114	21,8141	25,00	130,884	43,628	50,00	-50,00	38	1	1	5,3
9	107,347	6,89	17,5152	26,8369	25,00	161,021	53,674	50,00	-50,00	39	0	0	0,0
sum										353	10	12	6,2

Recovery rate and matrix content:

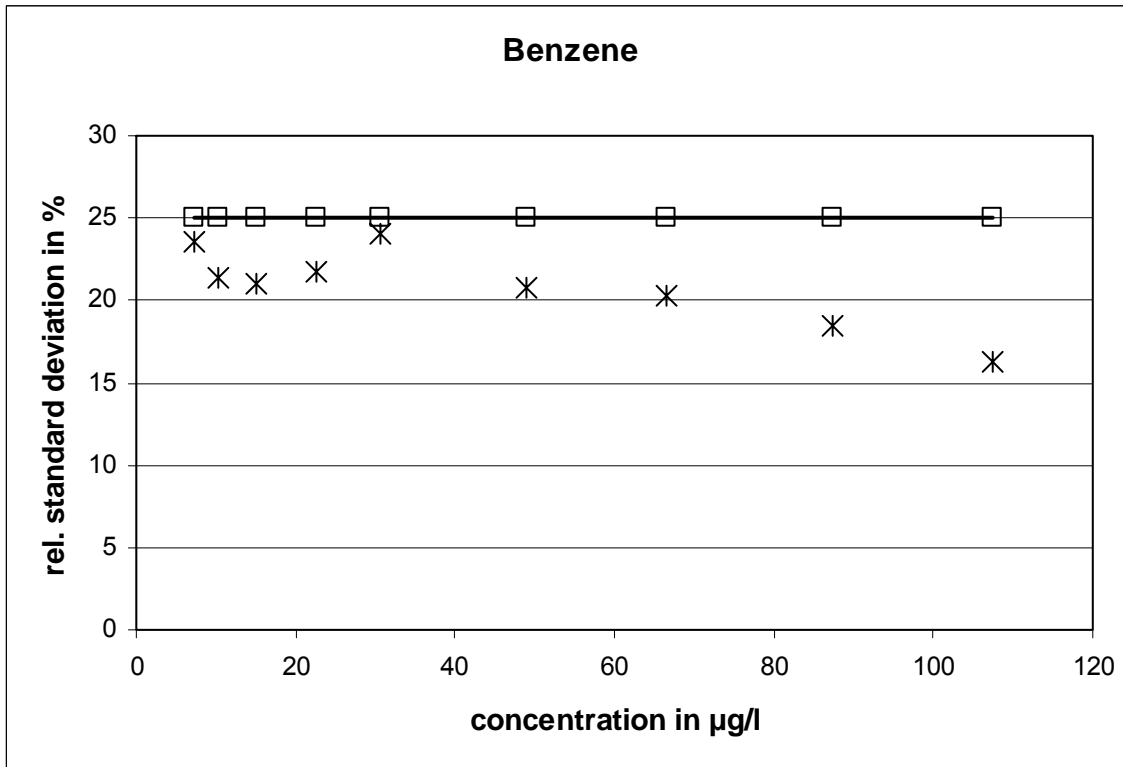


Slope of the line: 0,9442, recovery rate: 94,4 %;

neg. x-axis intercept corresponds to the matrix content: 0,02679µg/l;

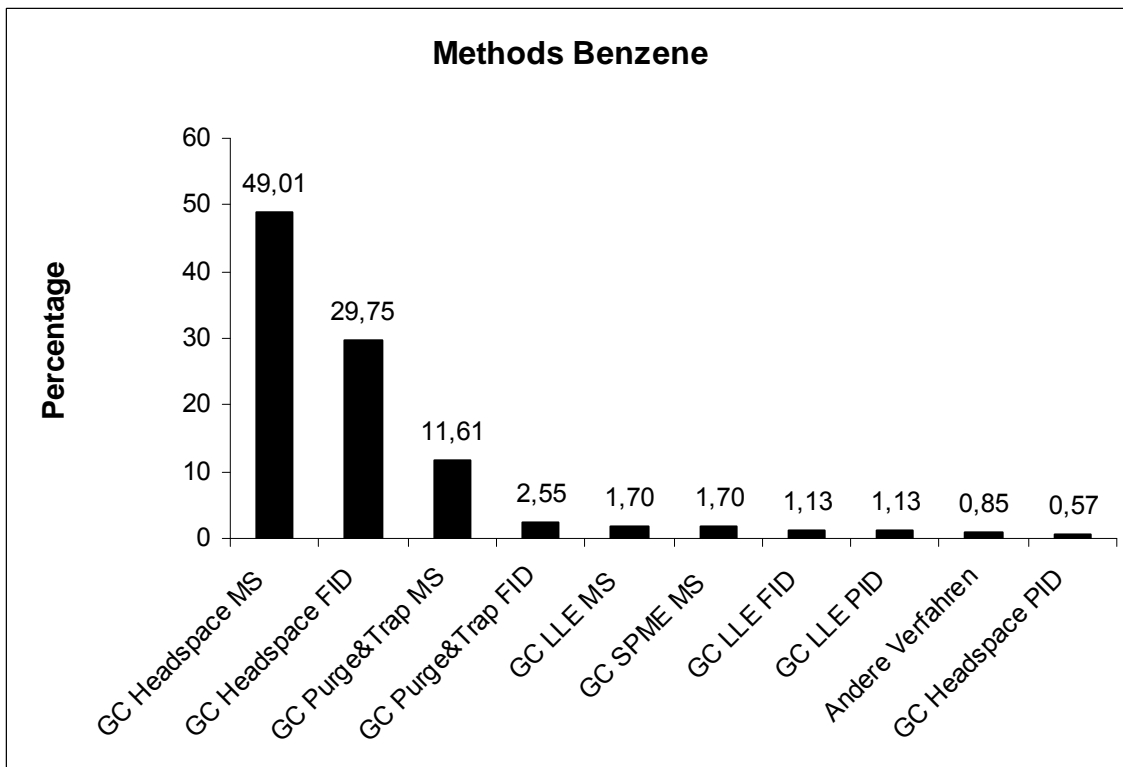
expanded uncertainty of the matrix content: 0,02679 µg/l = 100 %

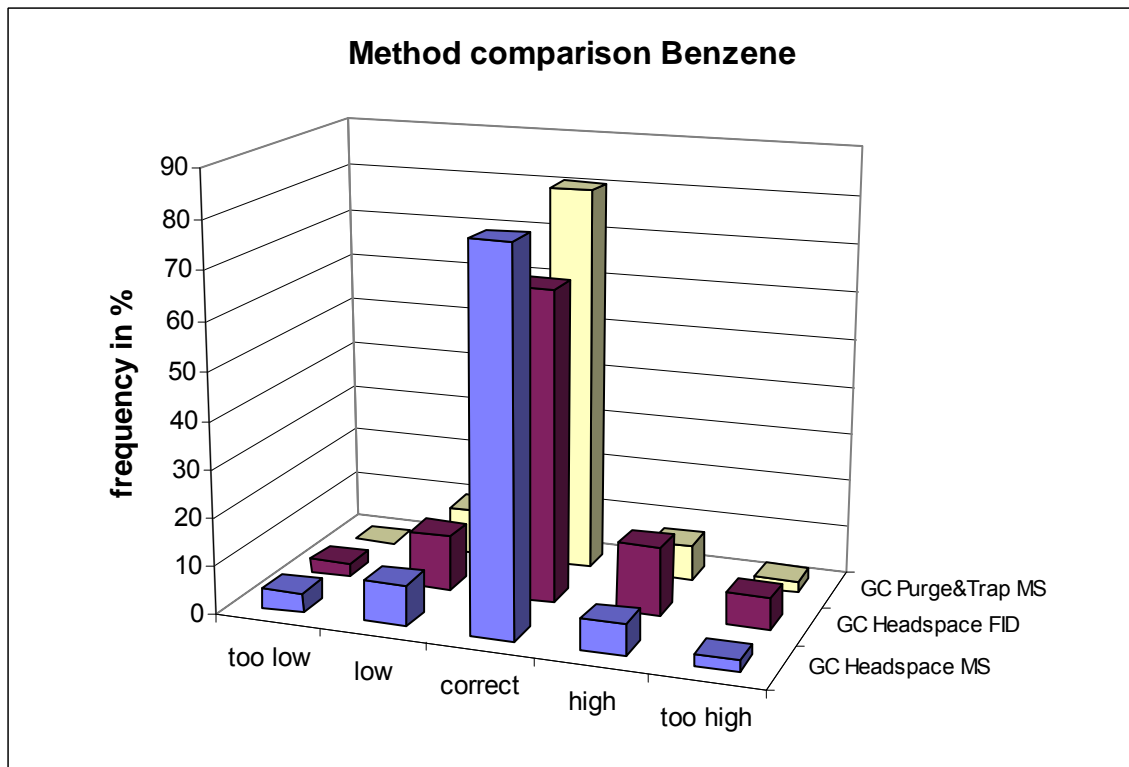
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, did not reach in any concentration level the standard deviation for proficiency assessment of 25 %.

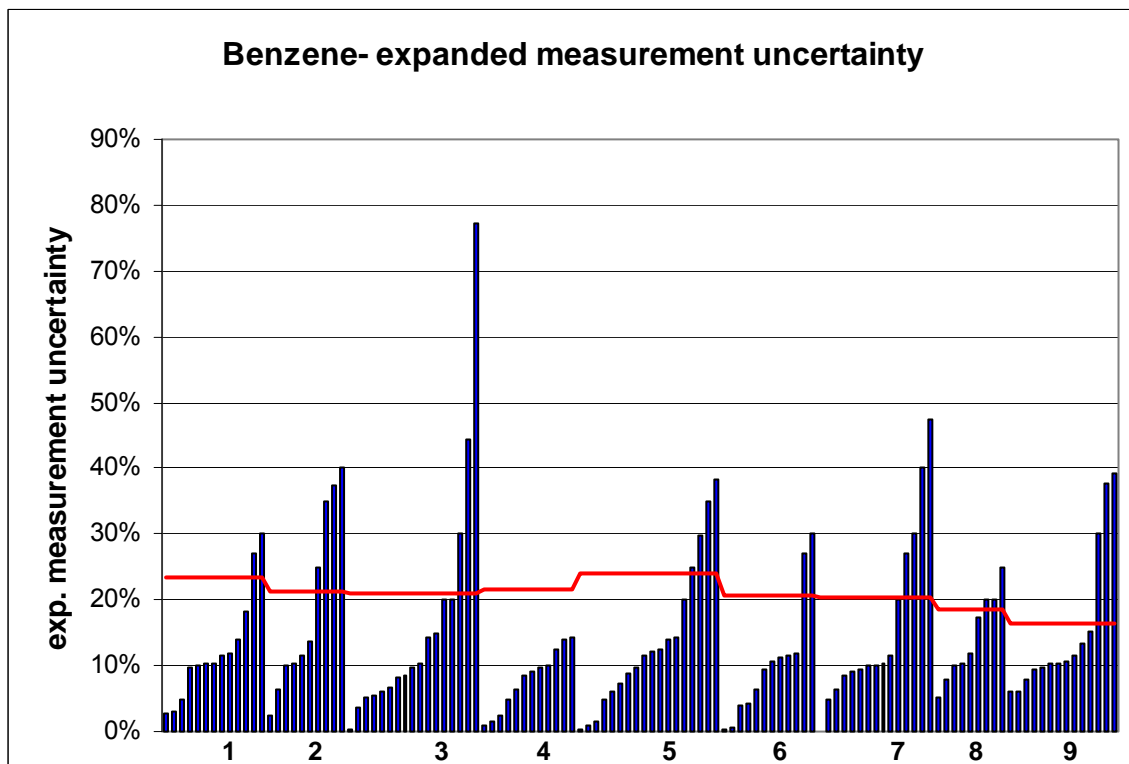
Method specific evaluation:





The differences between the methods were not significant.

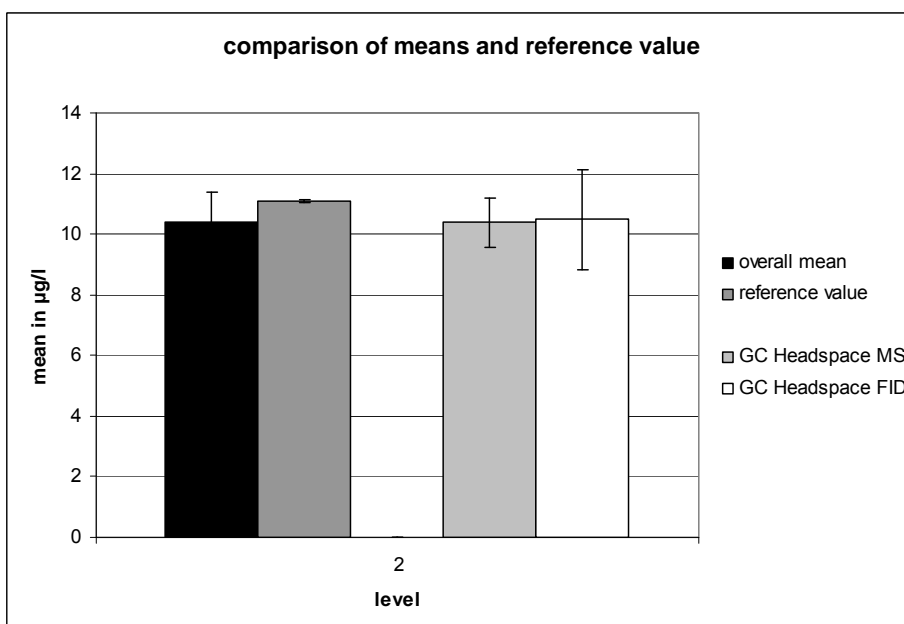
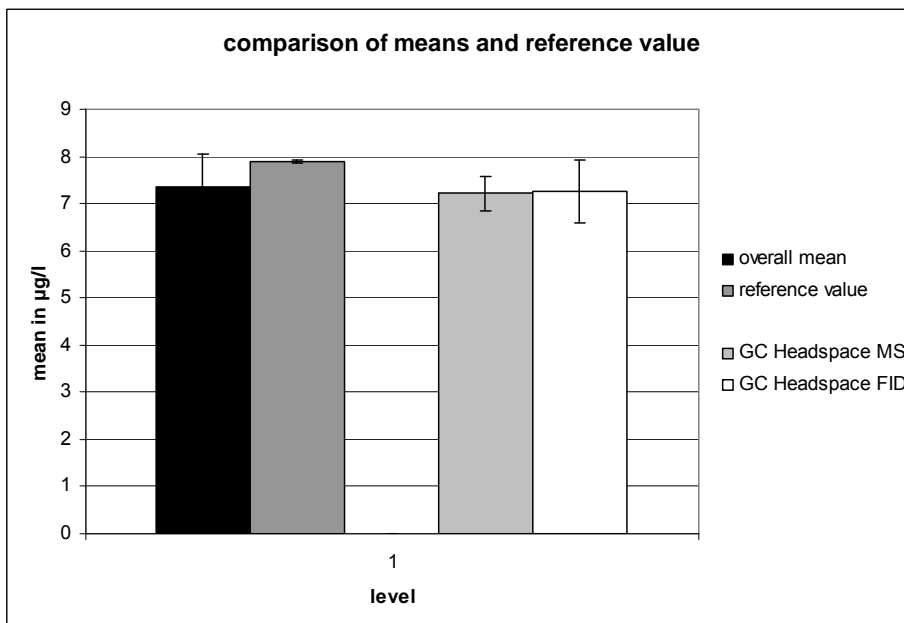
Measurement uncertainty:

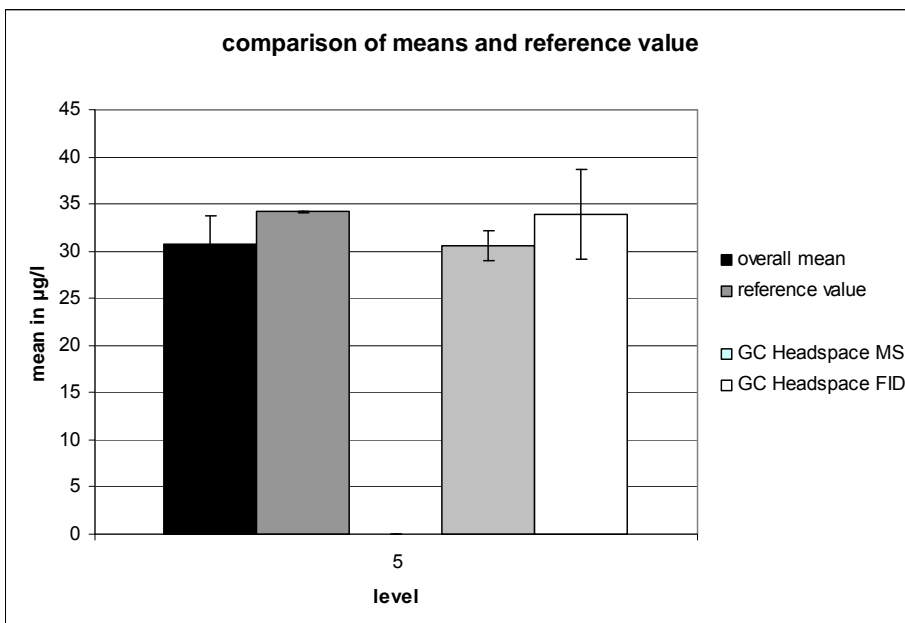
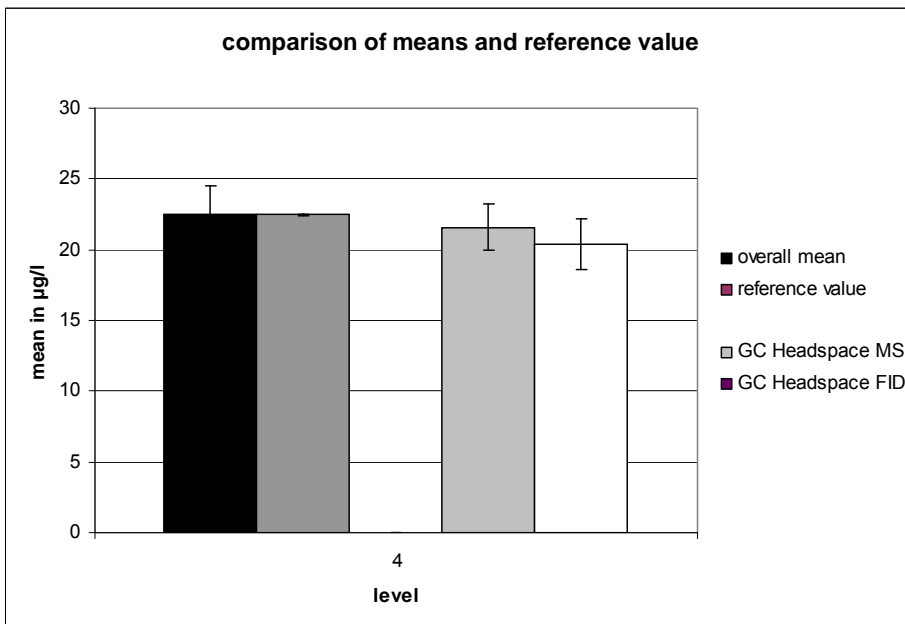
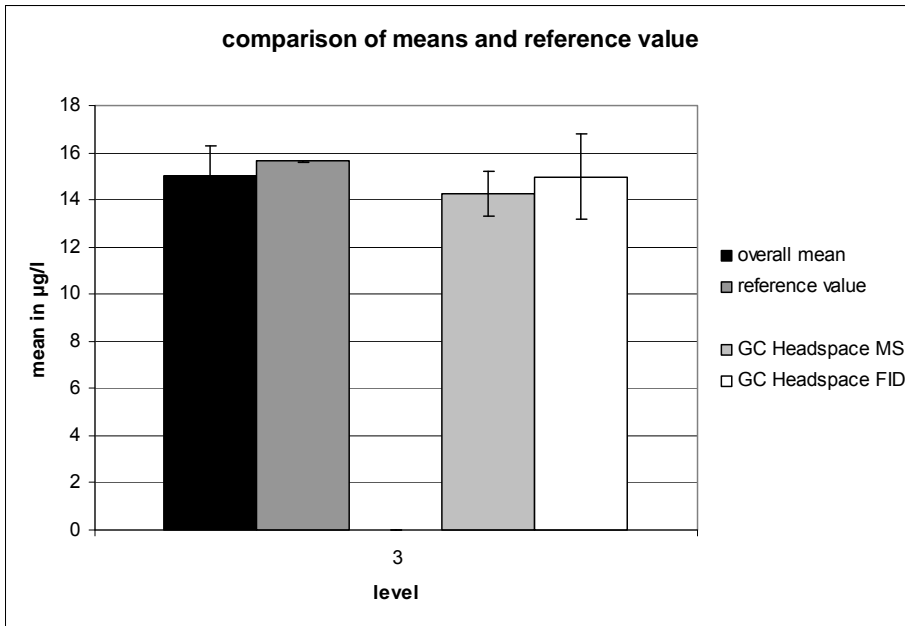


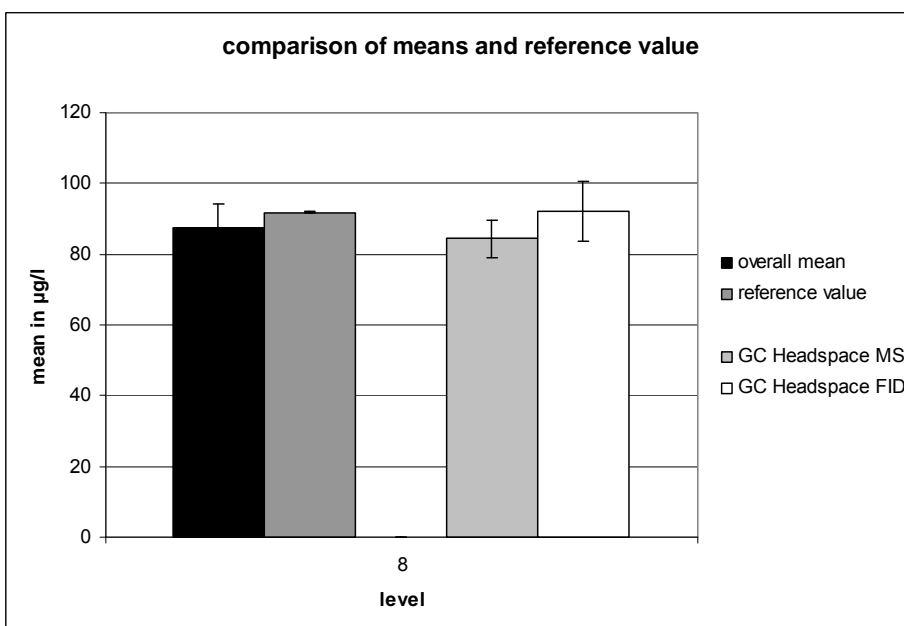
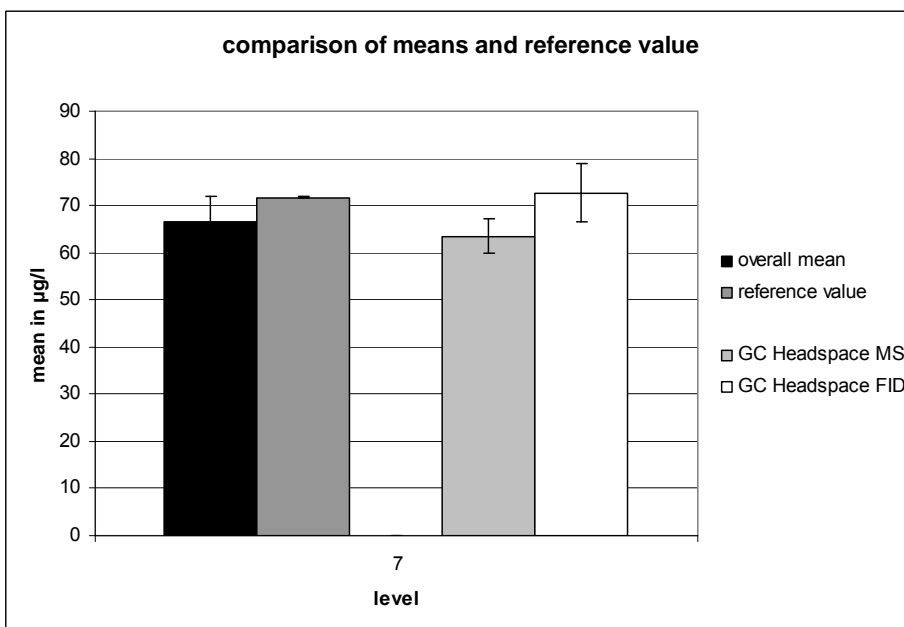
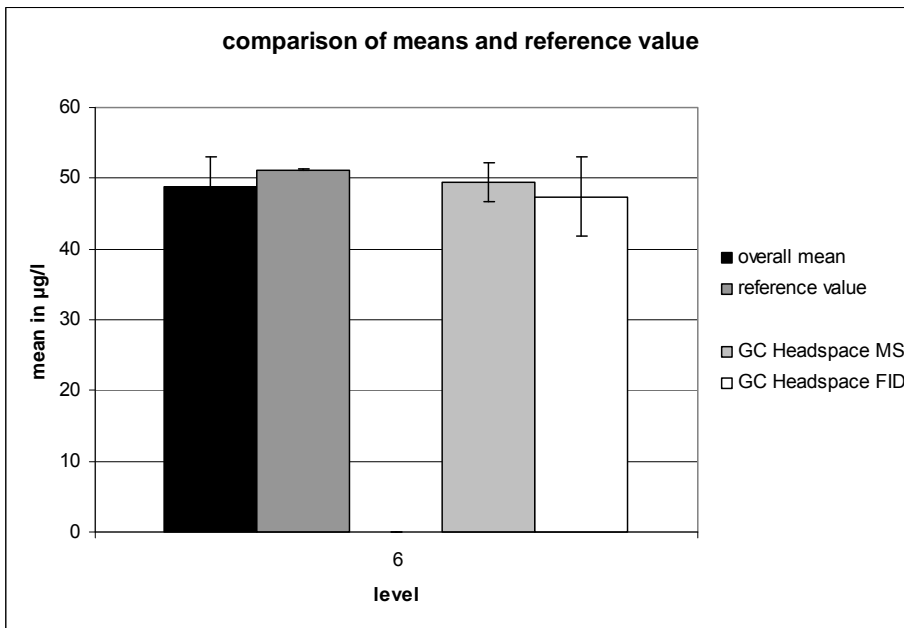
Reference values:

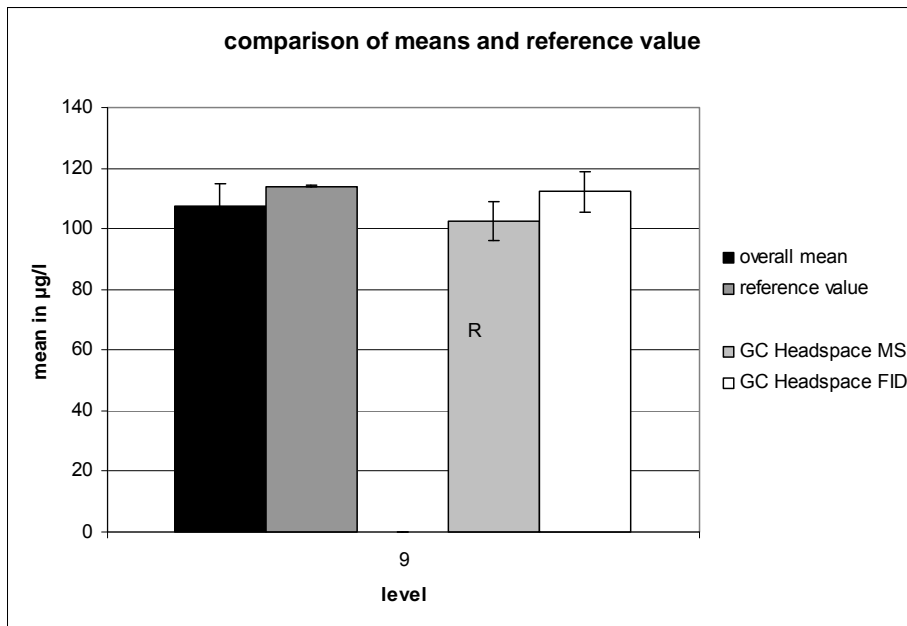
Level	assigned value	exp. uncertainty.		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]	[µg/l]	[µg/l]	[%]
1	7,338	0,7107	9,68	7,891	0,0324	0,41
2	10,399	0,9681	9,31	11,08	0,0720	0,65
3	15,03	1,2841	8,54	15,63	0,0523	0,33
4	22,495	2,0364	9,05	22,46	0,0541	0,24
5	30,71	3,038	9,89	34,17	0,0756	0,22
6	48,84	4,1695	8,54	51,18	0,1162	0,23
7	66,496	5,411	8,14	71,73	0,1385	0,19
8	87,26	7,012	8,04	91,87	0,1253	0,14
9	107,35	7,402	6,9	114,00	0,699	0,61

Comparison of the means und reference values





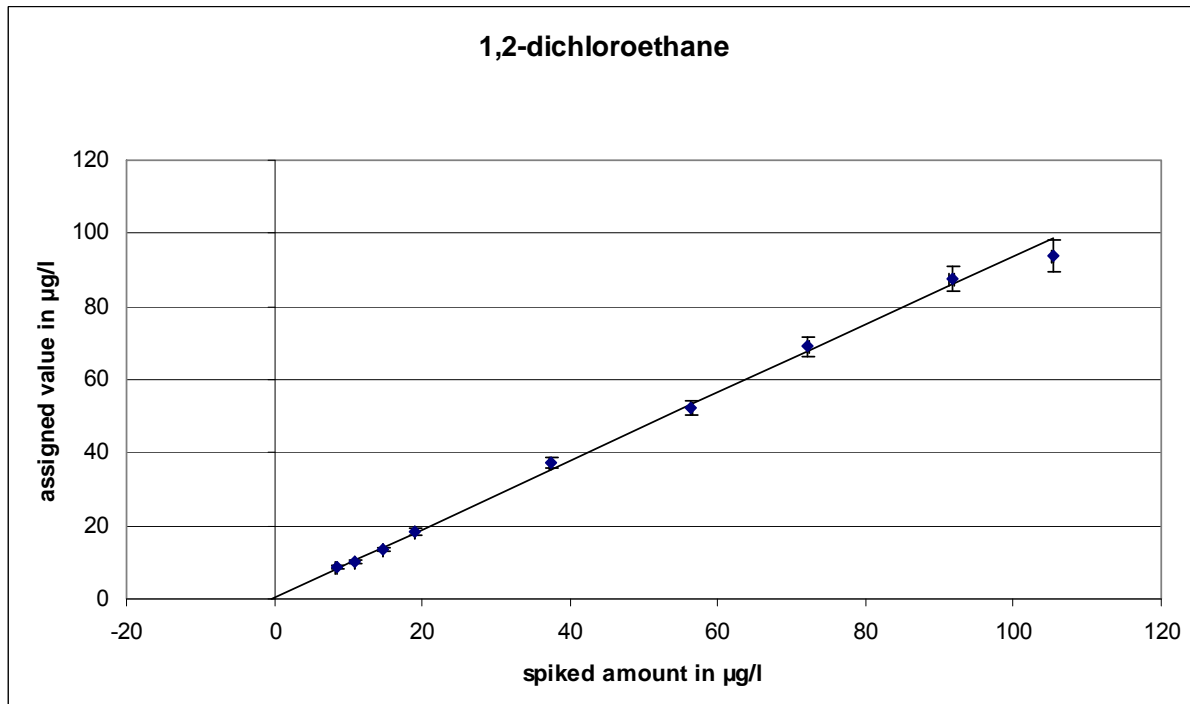




1,2-Dichloroethane

level	assigned value [$\mu\text{g/l}$]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [$\mu\text{g/l}$]	standard deviation for proficiency assessment [$\mu\text{g/l}$]	standard deviation for proficiency assessment [%]	upper tolerance limit [$\mu\text{g/l}$]	lower tolerance limit [$\mu\text{g/l}$]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	8,879	10,85	2,2802	2,2197	25,00	13,318	4,439	50,00	-50,00	39	1	5	15,4
2	10,108	8,51	2,0921	2,5270	25,00	15,162	5,054	50,00	-50,00	39	0	2	5,1
3	13,560	9,62	3,2601	3,3899	25,00	20,339	6,780	50,00	-50,00	41	1	1	7,3
4	18,338	10,87	4,8500	4,5845	25,00	27,507	9,169	50,00	-50,00	38	1	2	7,9
5	37,250	8,47	7,7839	9,3126	25,00	55,875	18,625	50,00	-50,00	42	3	2	9,5
6	52,330	7,77	9,6203	13,0826	25,00	78,495	26,165	50,00	-50,00	39	0	3	7,7
7	68,985	7,82	13,1317	17,2464	25,00	103,478	34,493	50,00	-50,00	39	1	2	10,3
8	87,747	7,56	16,1474	21,9369	25,00	131,621	43,874	50,00	-50,00	39	1	1	7,7
9	93,809	9,16	21,7459	23,4523	25,00	140,714	46,905	50,00	-50,00	40	1	2	7,5
sum										356	9	20	8,1

Recovery rate and matrix content:

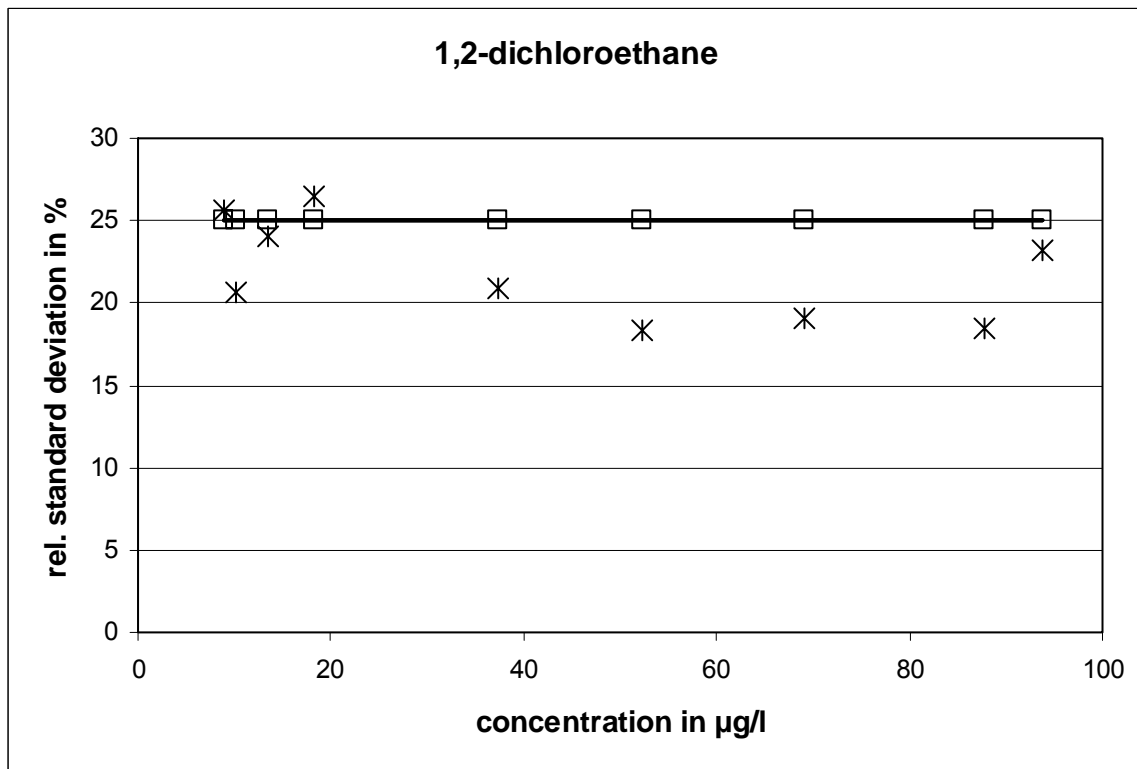


Slope of the line: 0,93396, recovery rate: 93,4 %;

neg. x-axis intercept corresponds to the matrix content: 0,4189 $\mu\text{g/l}$;

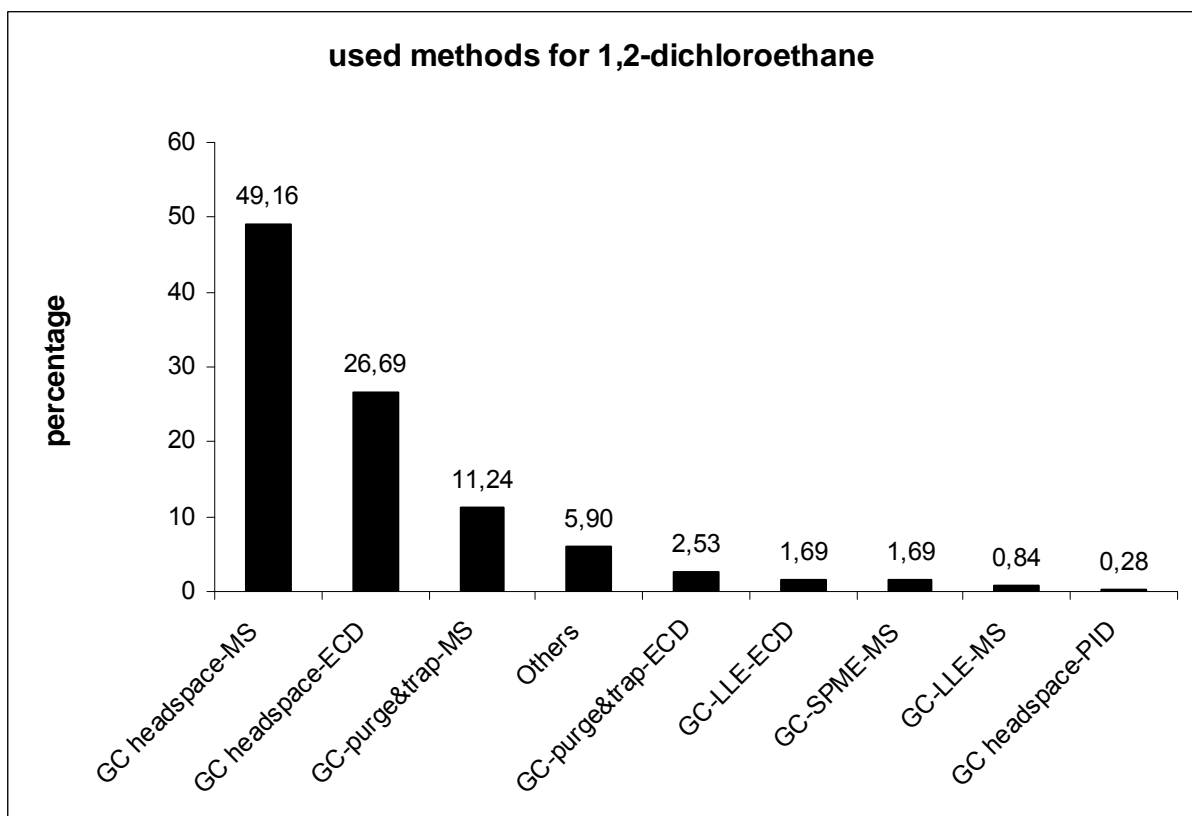
expanded uncertainty of the matrix content: 0,4189 $\mu\text{g/l}$ = 100 %

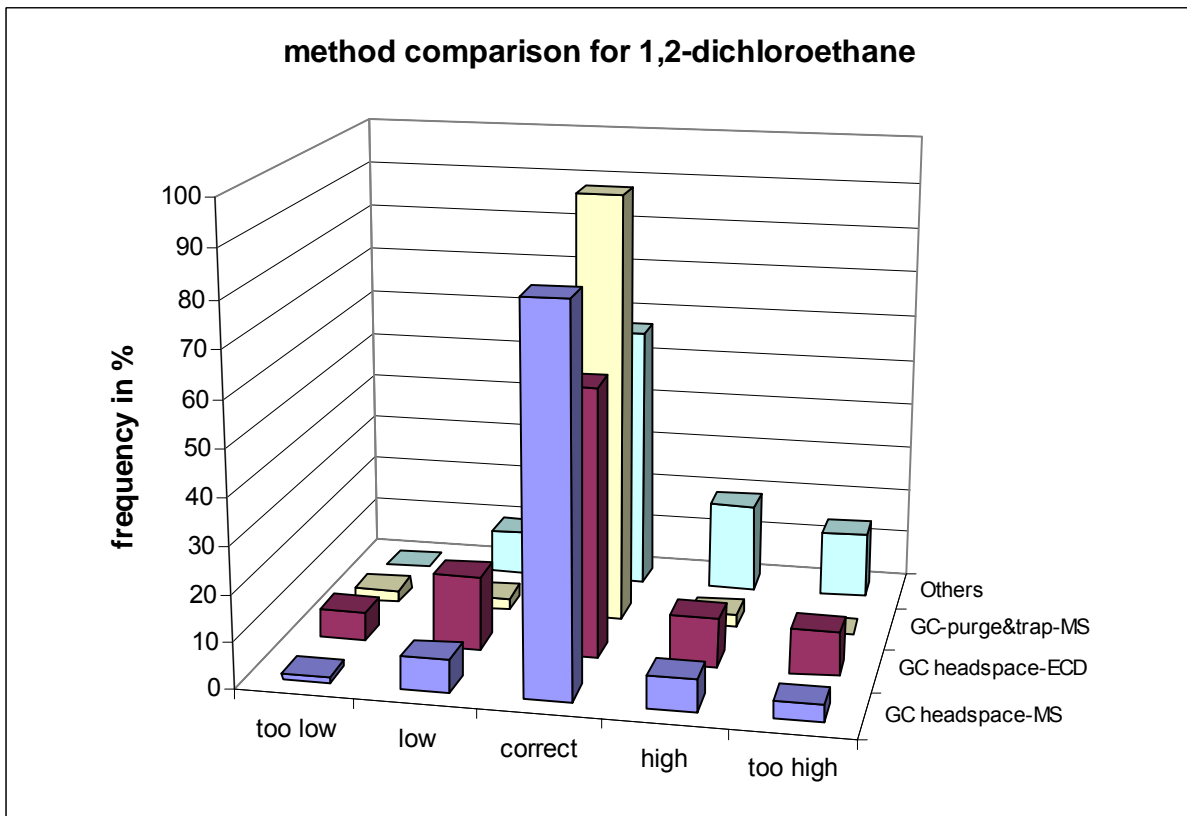
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, exceeded at two concentration levels the standard deviation for proficiency assessment of 25 %.

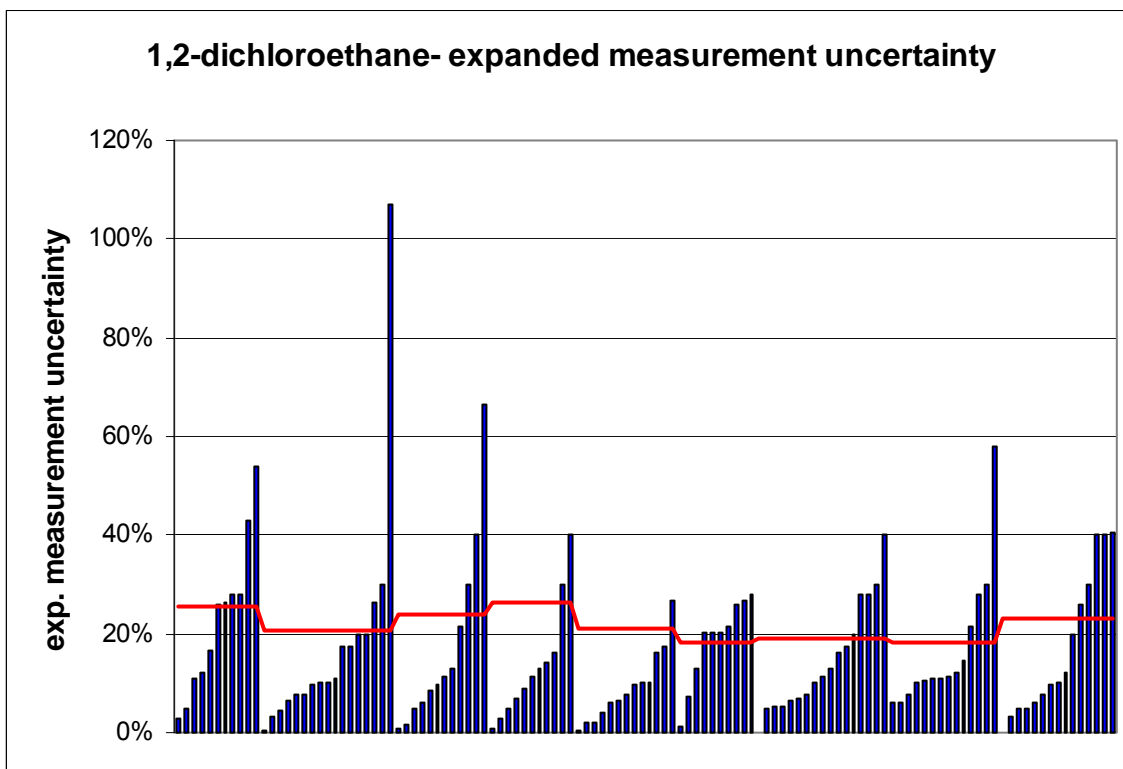
Method specific evaluation:





The values, determined with GC purge&trap-MS method showed the lowest distribution.

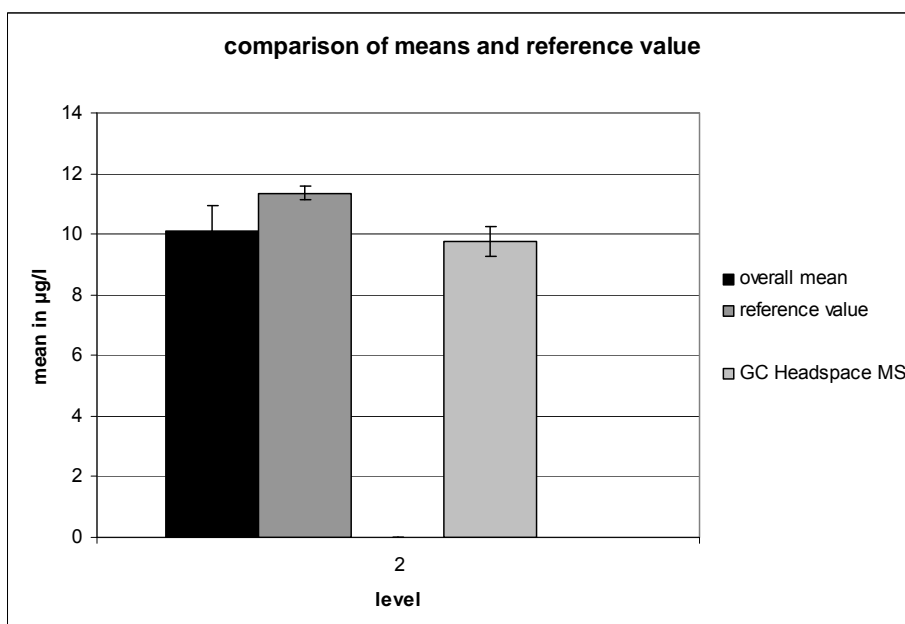
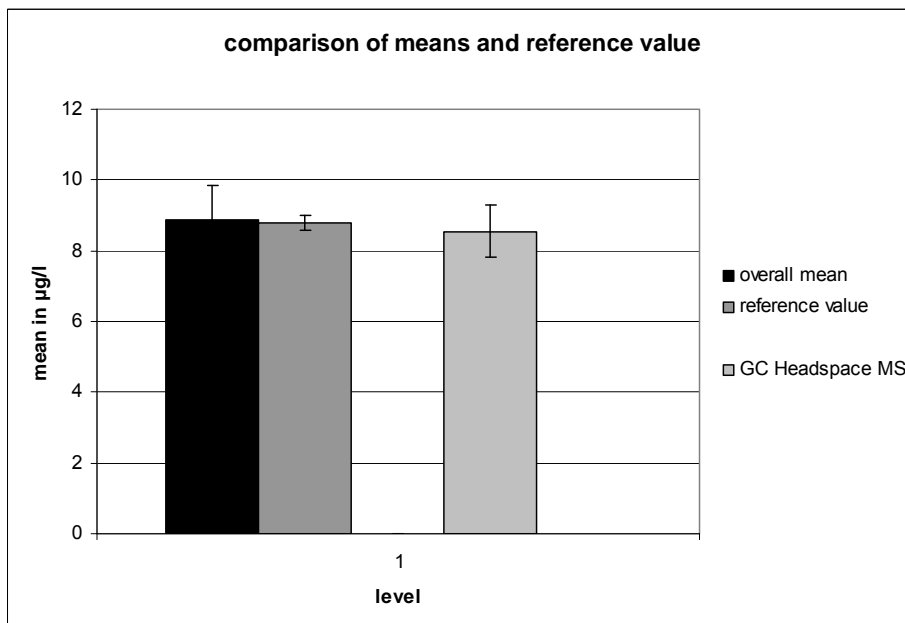
Measurement uncertainty:

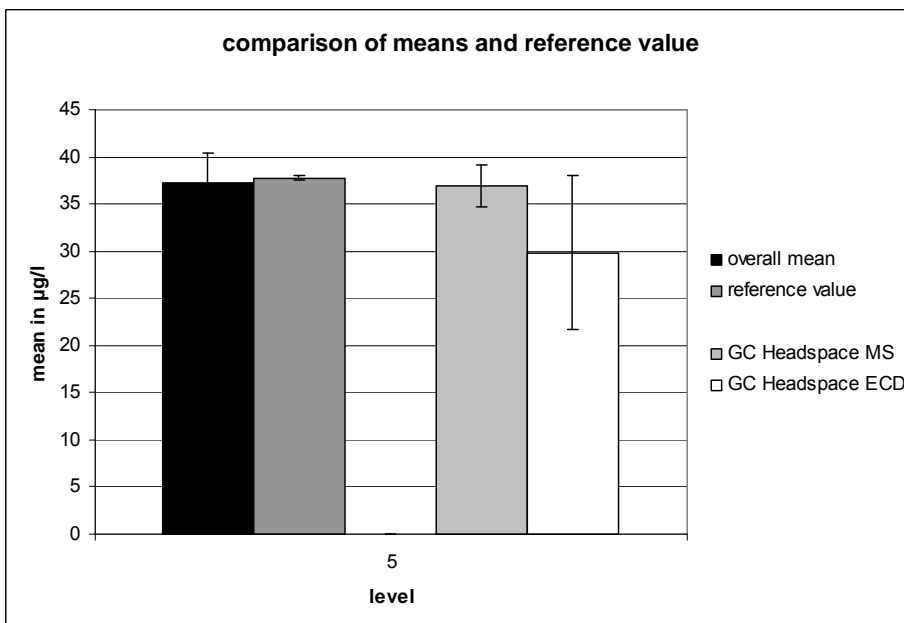
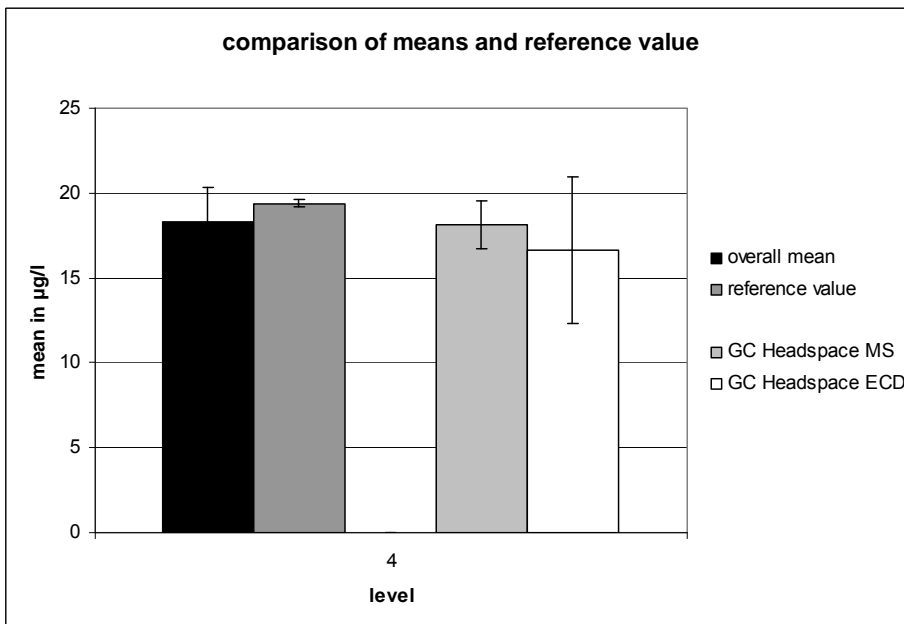
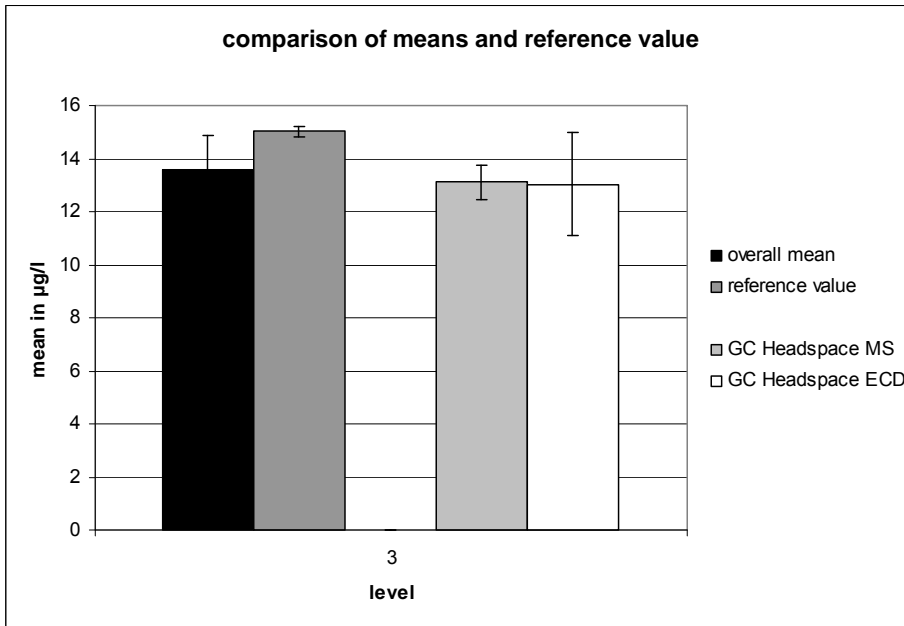


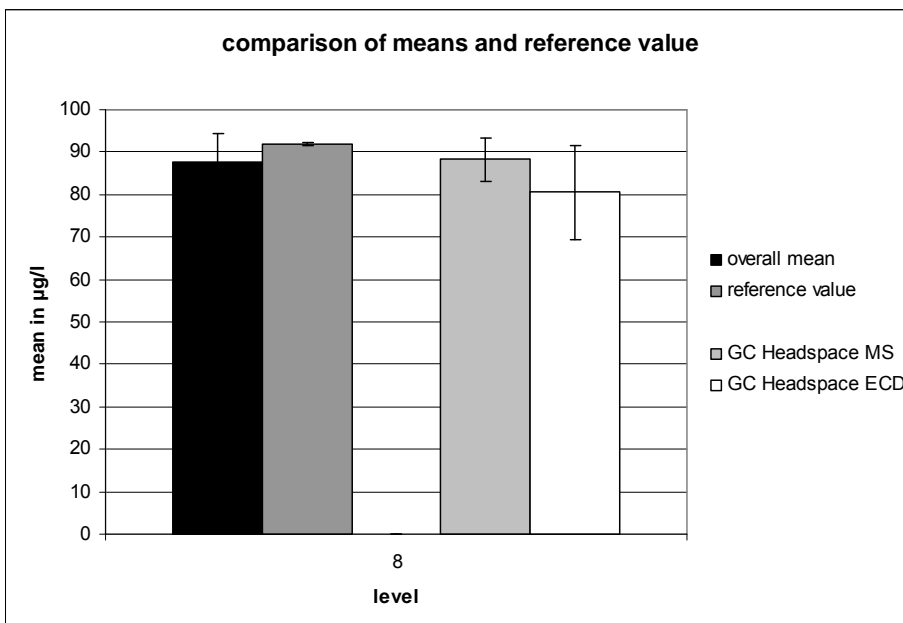
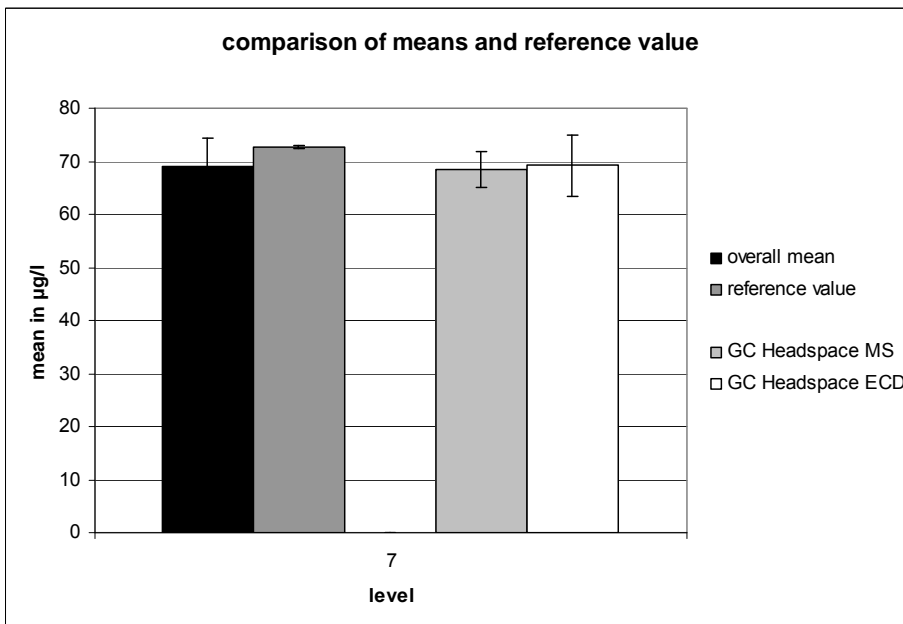
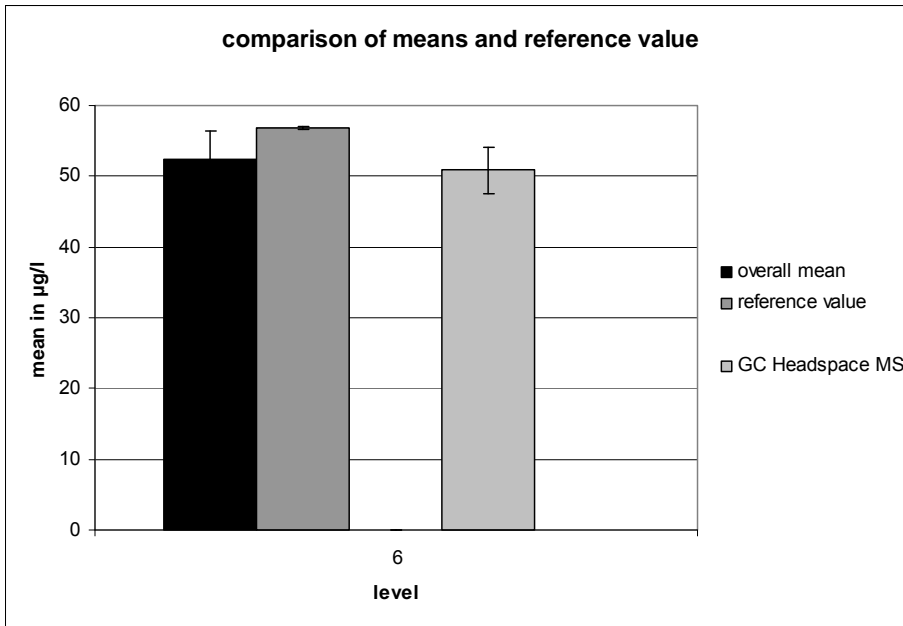
Reference values:

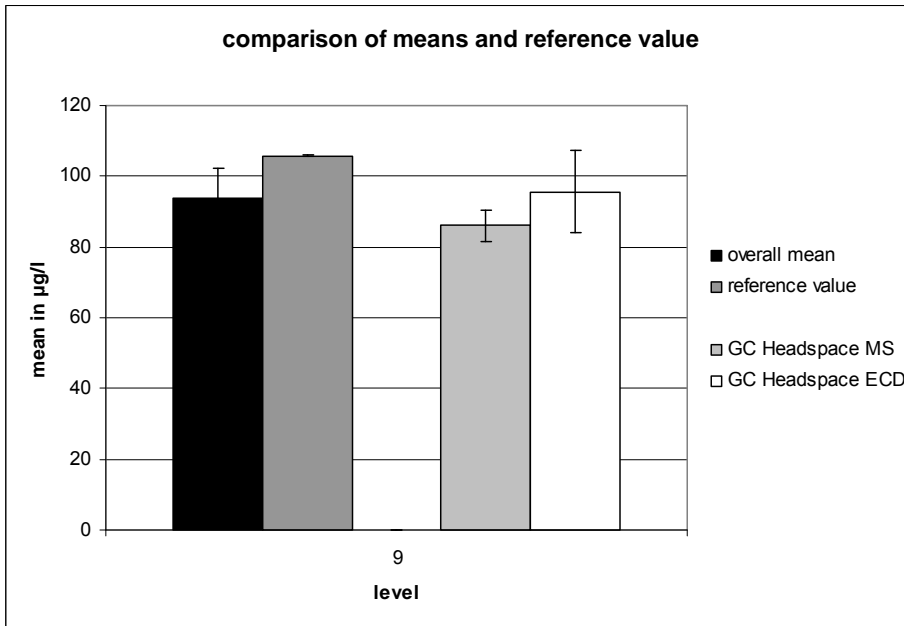
Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]	[µg/l]	[µg/l]	[%]
1	8,879	0,4818	5,43	8,778	0,4220	4,81
2	10,11	0,8599	8,51	11,36	0,4202	3,70
3	13,56	1,3051	9,62	15,03	0,4201	2,80
4	18,34	1,9934	10,87	19,39	0,4211	2,17
5	37,25	3,1568	8,47	37,75	0,4260	1,13
6	52,33	4,0653	7,77	56,86	0,4258	0,75
7	68,99	5,3971	7,82	72,61	0,4443	0,61
8	87,75	6,6365	7,56	92,07	0,7007	0,76
9	93,81	8,5958	9,16	105,78	0,4638	0,44

Comparison of the means und reference values





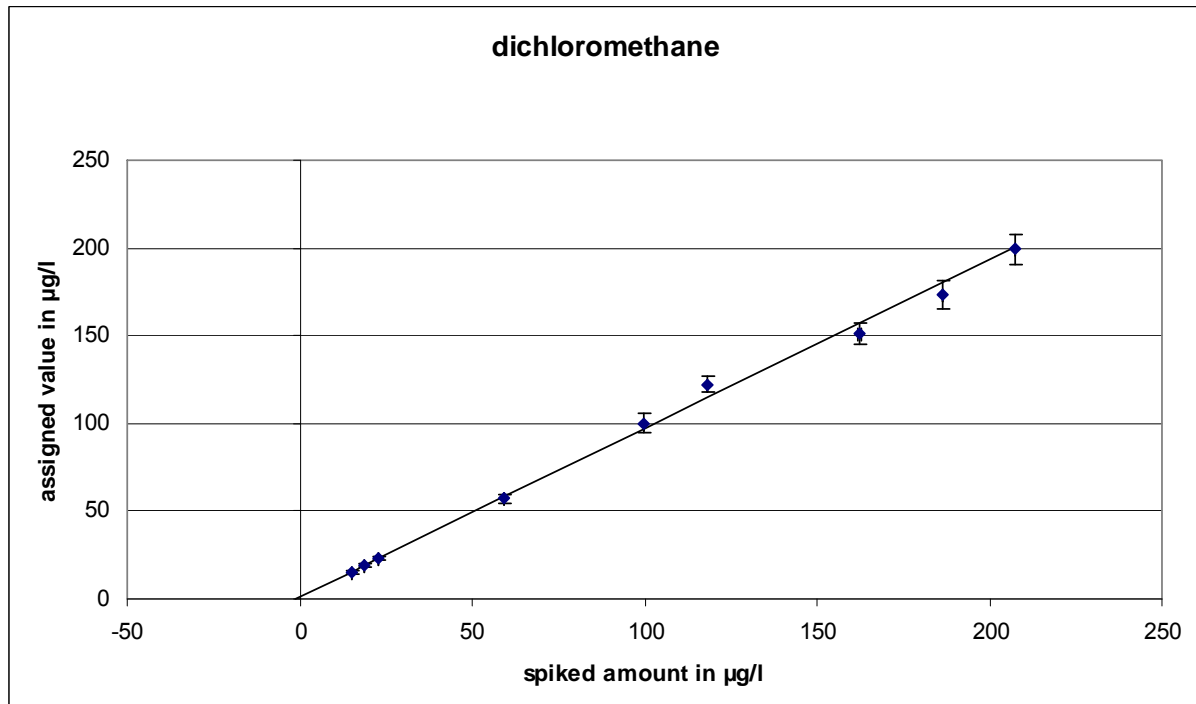




Dichloromethane

level	assigned value [$\mu\text{g/l}$]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [$\mu\text{g/l}$]	standard deviation for proficiency assessment [$\mu\text{g/l}$]	standard deviation for proficiency assessment [%]	upper tolerance limit [$\mu\text{g/l}$]	lower tolerance limit [$\mu\text{g/l}$]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	15,206	10,46	3,7625	3,8016	25,00	22,810	7,603	50,00	-50,00	37	0	3	8,1
2	19,225	10,15	4,9374	4,8062	25,00	28,837	9,612	50,00	-50,00	41	3	2	14,6
3	23,217	9,37	5,2233	5,8042	25,00	34,825	11,608	50,00	-50,00	40	3	6	22,5
4	57,343	9,02	13,0781	14,3358	25,00	86,015	28,672	50,00	-50,00	40	2	3	12,5
5	100,213	10,46	25,8572	25,0533	25,00	150,320	50,107	50,00	-50,00	39	3	1	10,3
6	122,415	7,95	23,6761	30,6037	25,00	183,622	61,207	50,00	-50,00	41	4	3	14,6
7	151,608	7,97	28,9971	37,9021	25,00	227,413	75,804	50,00	-50,00	38	1	1	5,3
8	173,503	9,29	39,7369	43,3758	25,00	260,255	86,752	50,00	-50,00	40	2	1	10,0
9	199,425	8,67	40,8971	49,8562	25,00	299,137	99,712	50,00	-50,00	39	1	0	2,6
sum										355	19	20	11,0

Recovery rate and matrix content:

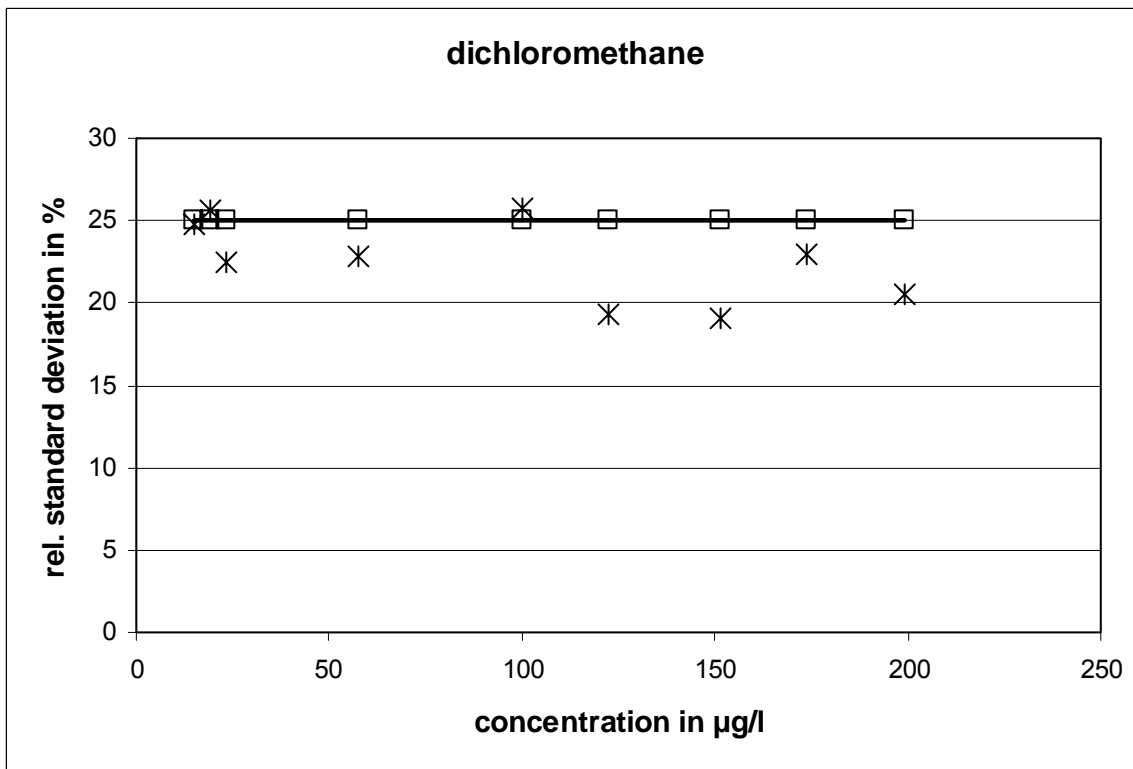


Slope of the line: 0,9593, recovery rate: 95,9 %;

neg. x-axis intercept corresponds to the matrix content: 1,2905 $\mu\text{g/l}$;

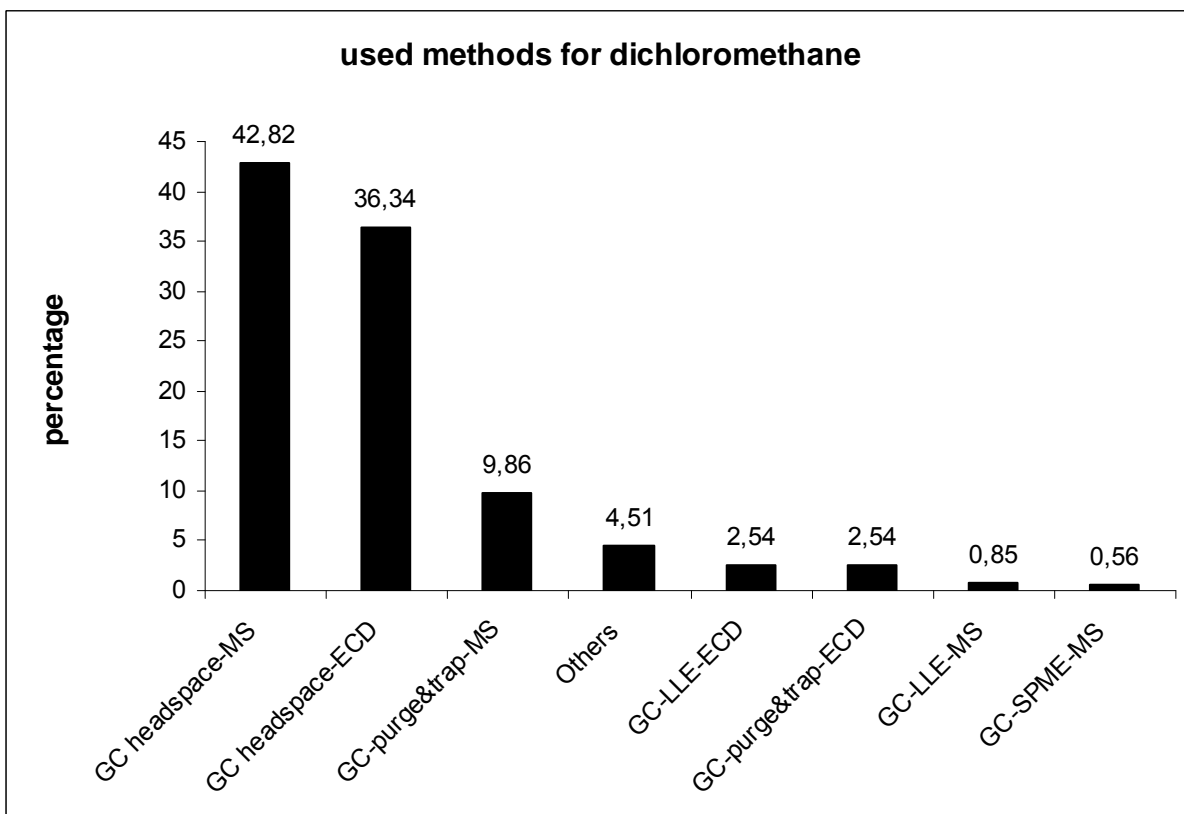
expanded uncertainty of the matrix content: 1,2905 $\mu\text{g/l}$ = 100 %

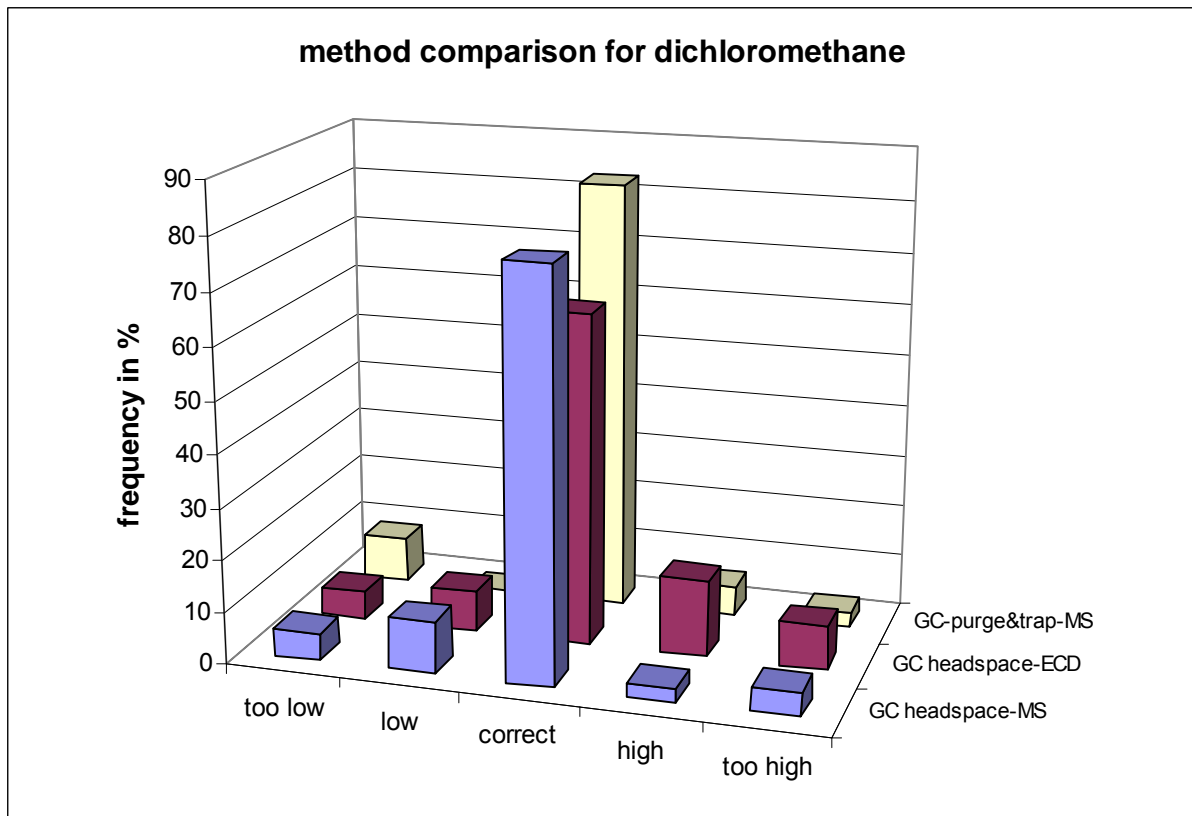
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, exceeded at two concentration levels the standard deviation for proficiency assessment of 25 %.

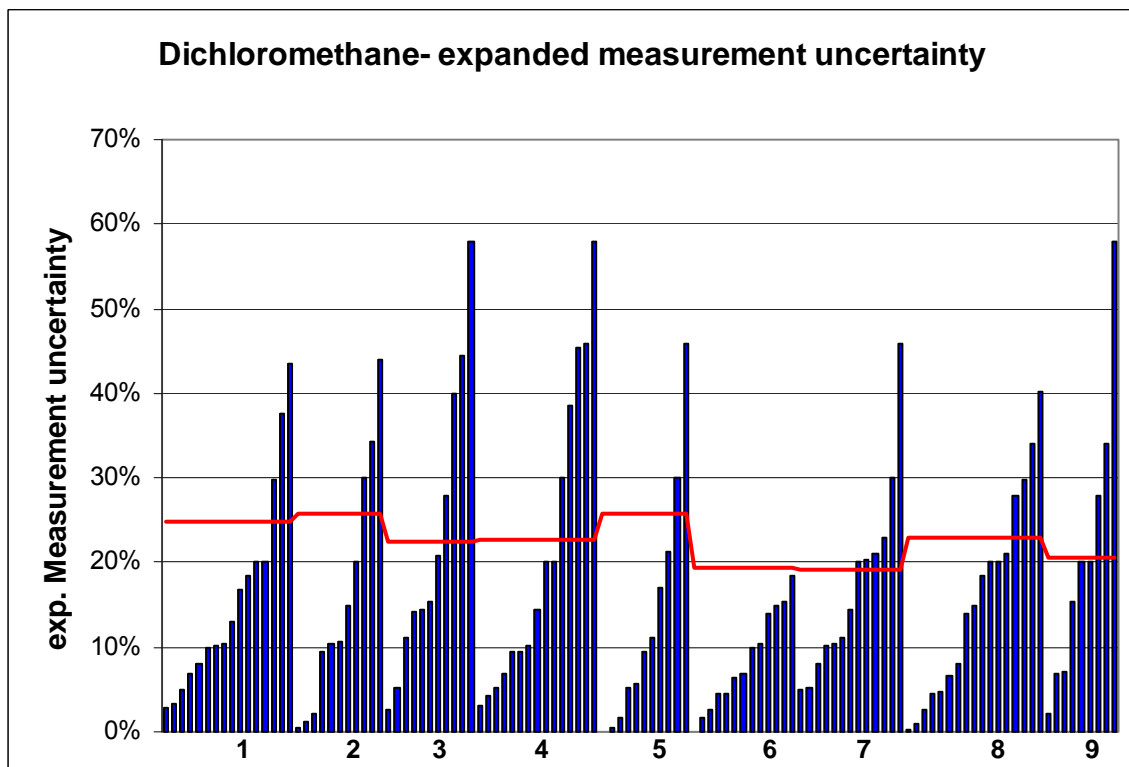
Method specific evaluation:





The differences between the methods were not significant.

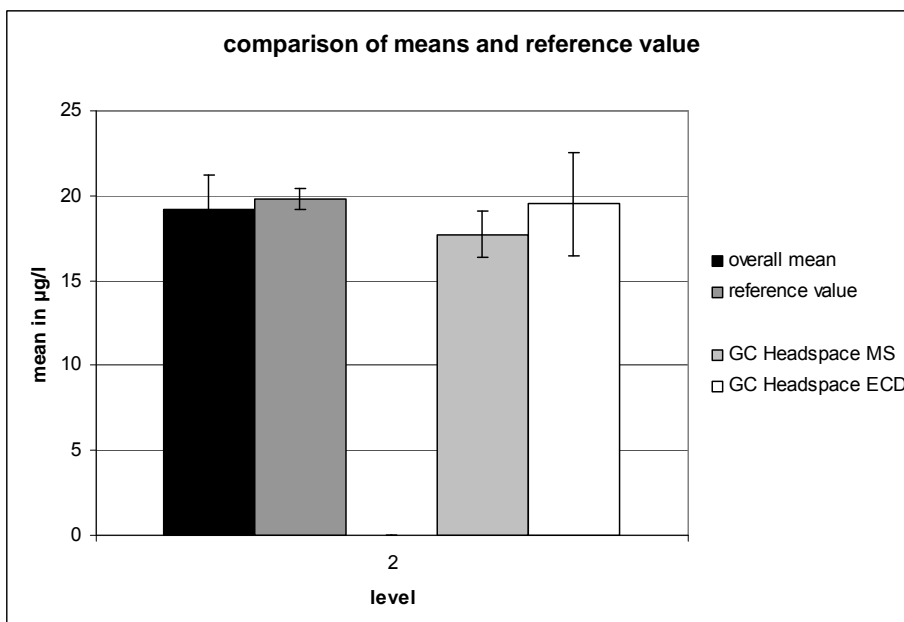
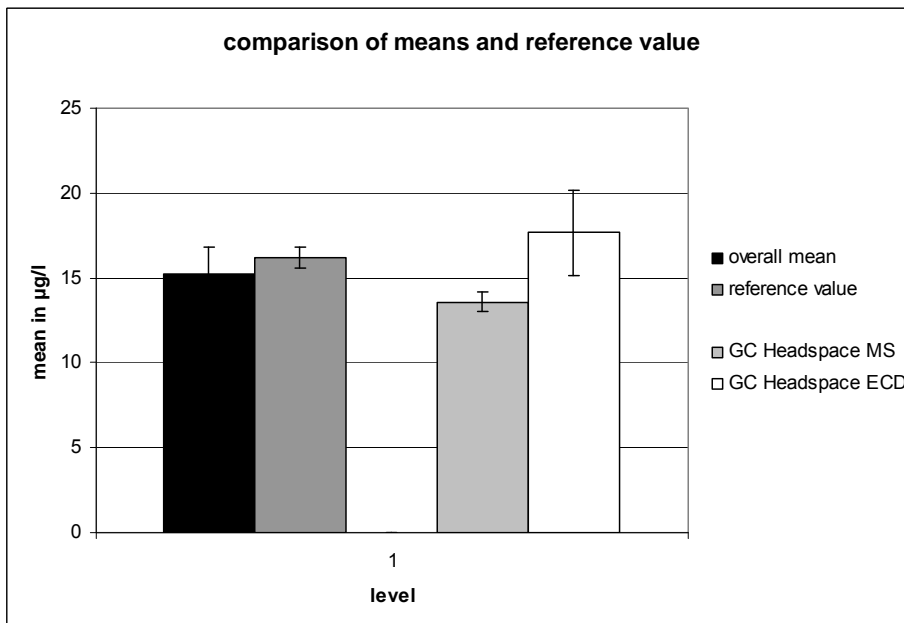
Measurement uncertainty:

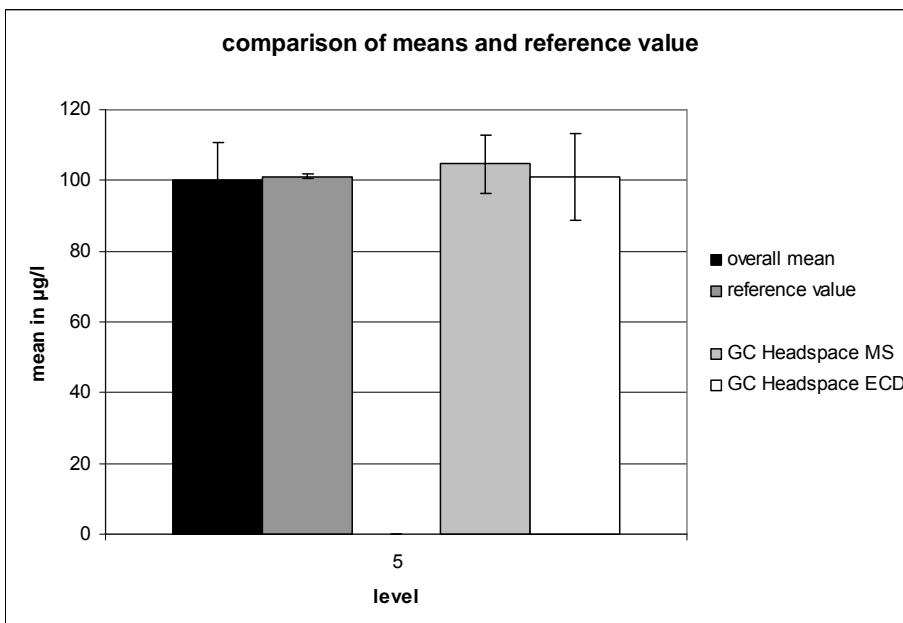
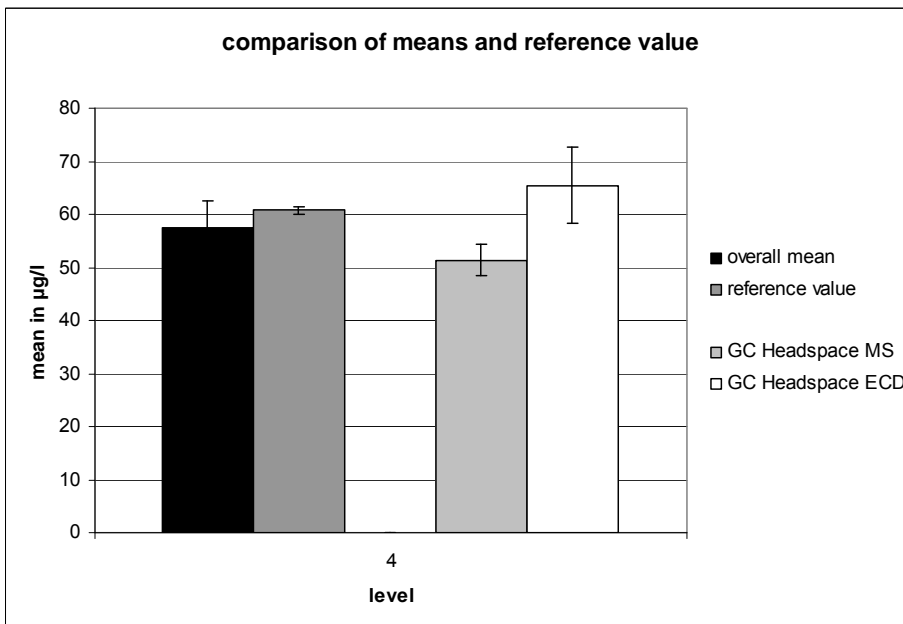
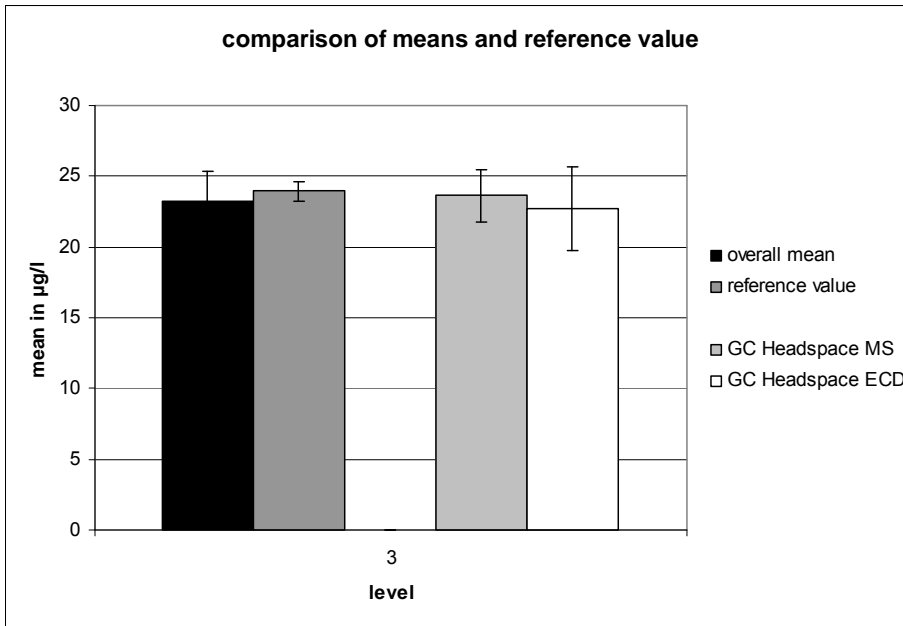


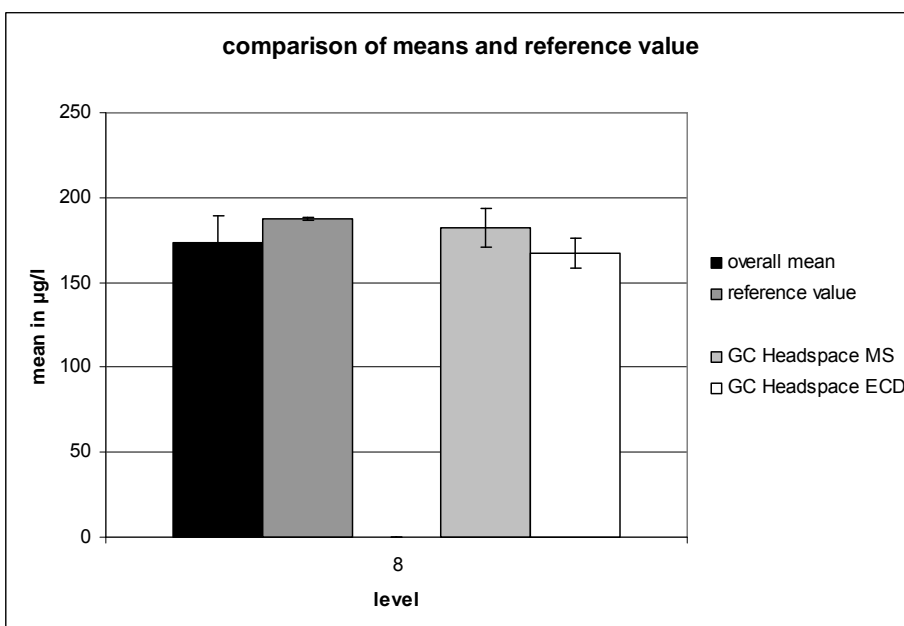
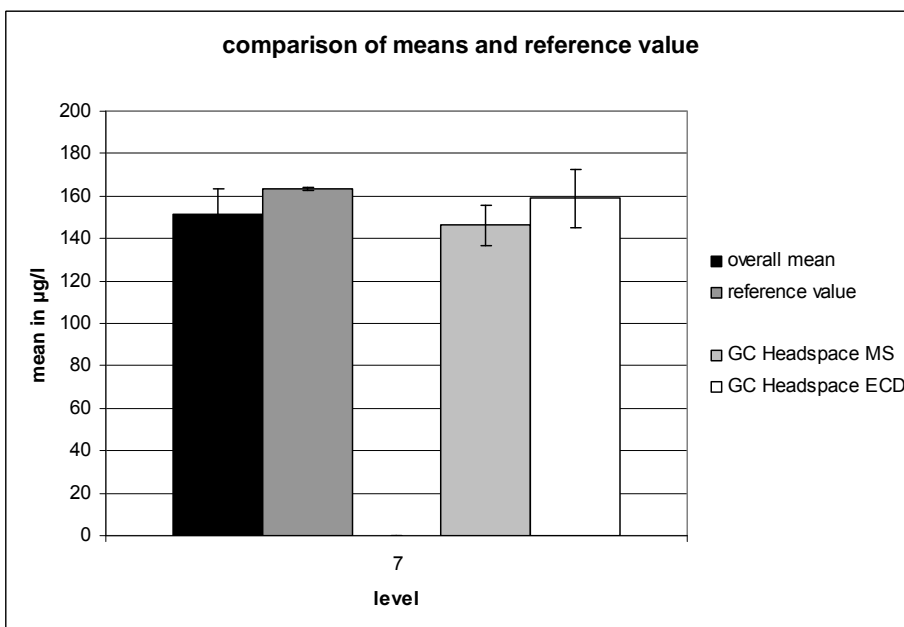
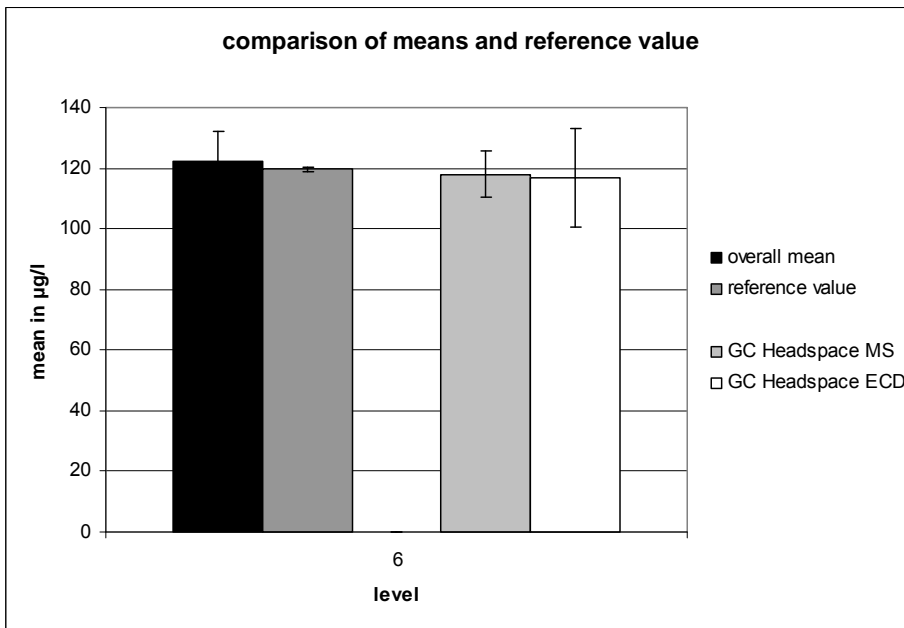
Reference values:

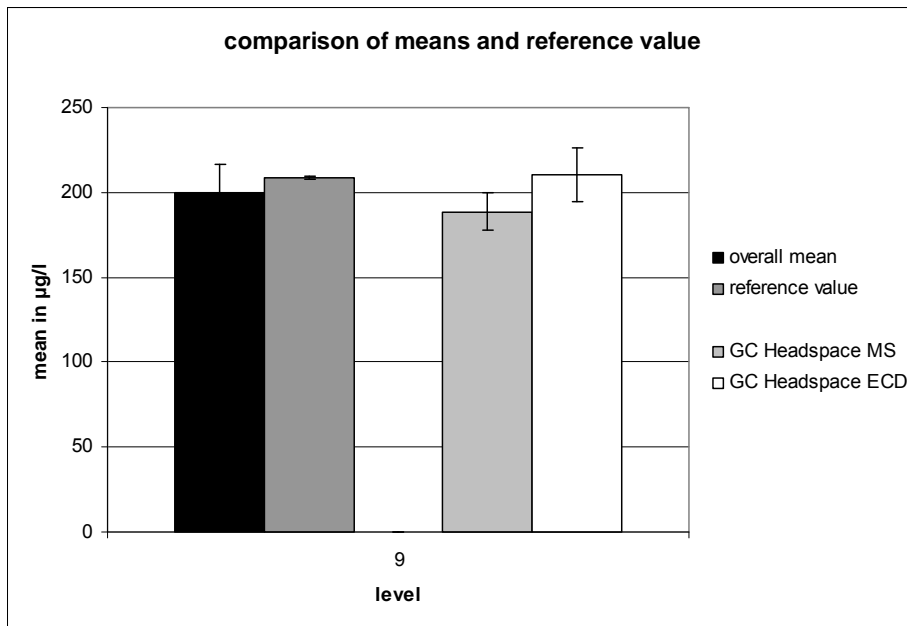
Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]		[µg/l]	[µg/l]
1	15,21	1,5900	10,46	16,19	1,2912	7,97
2	19,23	1,9517	10,15	19,79	1,2911	6,52
3	23,22	2,1764	9,37	23,94	1,2976	5,42
4	57,34	5,1696	9,02	60,72	1,2954	2,13
5	100,2	10,487	10,47	101,02	1,3090	1,30
6	122,4	9,7308	7,95	119,6	1,3129	1,10
7	151,6	12,082	7,97	163,5	1,6287	1,00
8	173,5	16,115	9,29	187,7	1,3454	0,72
9	199,4	17,282	8,67	208,7	1,3195	0,63

Comparison of the means und reference values:





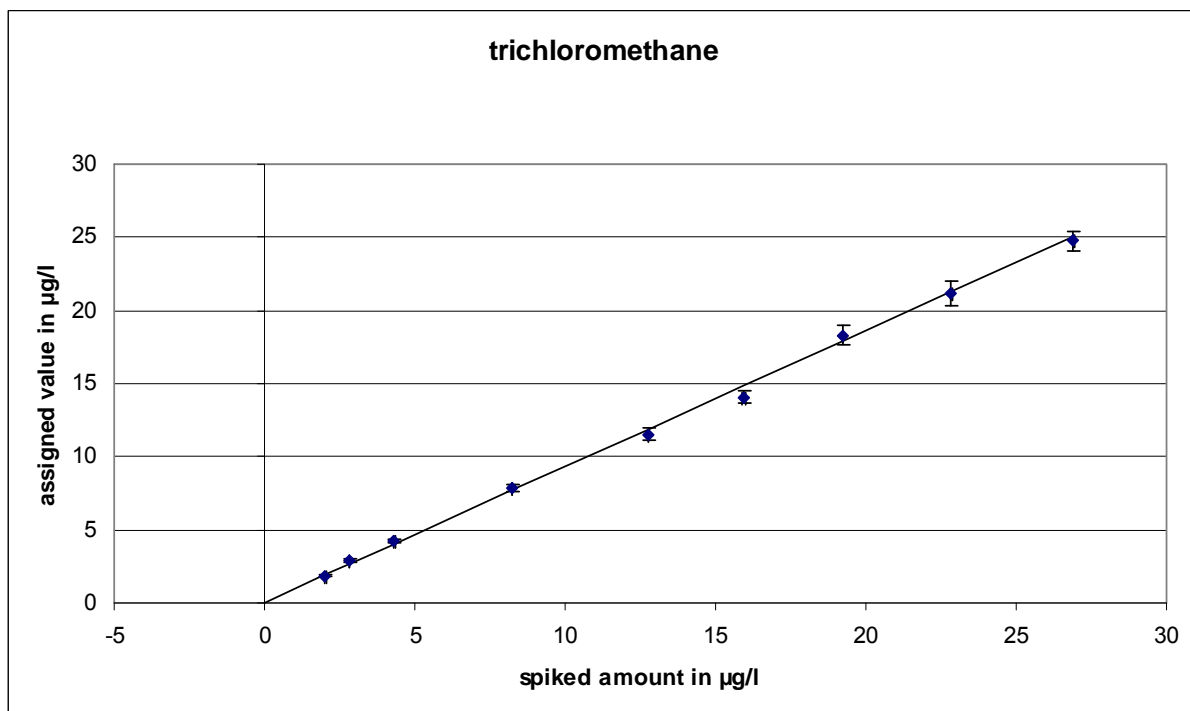




Trichloromethane

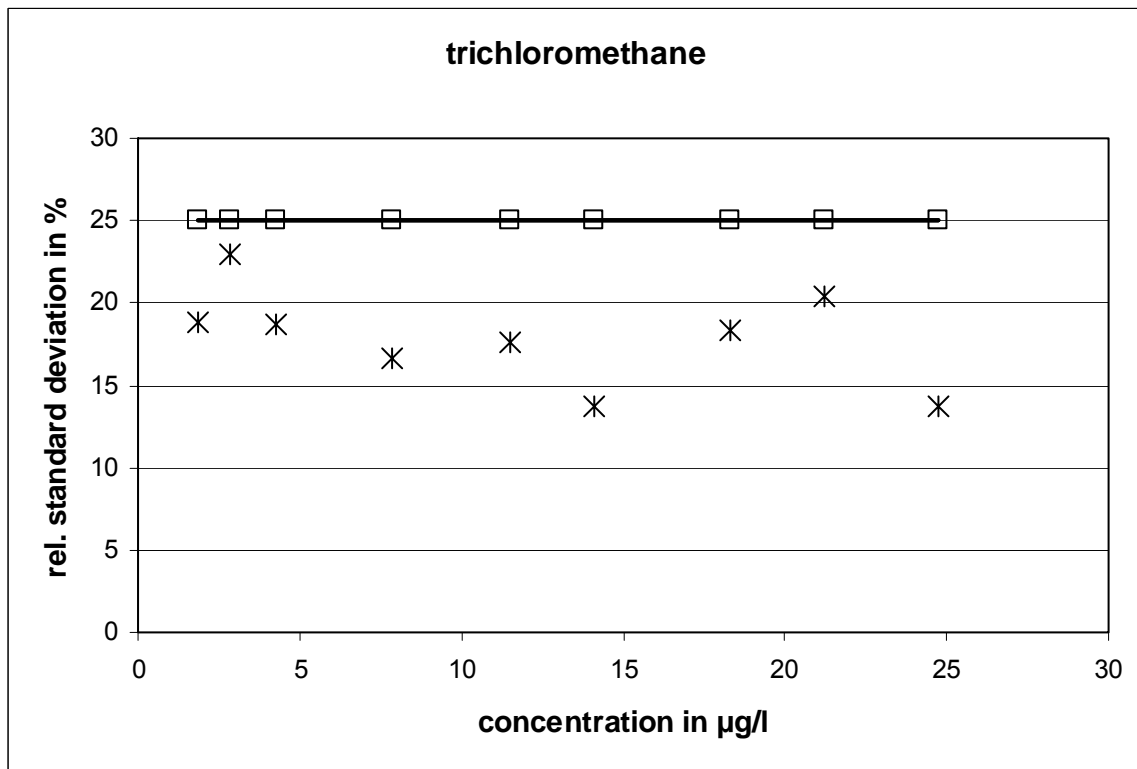
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	1,836	7,52	0,3449	0,4589	25,00	2,753	0,918	50,00	-50,00	41	1	1	7,3
2	2,863	9,31	0,6573	0,7158	25,00	4,295	1,432	50,00	-50,00	39	1	2	10,3
3	4,245	7,78	0,7925	1,0612	25,00	6,367	2,122	50,00	-50,00	39	0	2	5,1
4	7,839	7,02	1,3016	1,9598	25,00	11,759	3,920	50,00	-50,00	39	1	2	7,7
5	11,518	6,95	2,0248	2,8794	25,00	17,277	5,759	50,00	-50,00	40	0	2	5,0
6	14,077	5,63	1,9278	3,5192	25,00	21,115	7,038	50,00	-50,00	39	0	0	0,0
7	18,284	7,44	3,3527	4,5710	25,00	27,426	9,142	50,00	-50,00	41	1	1	4,9
8	21,194	8,18	4,3288	5,2986	25,00	31,791	10,597	50,00	-50,00	40	0	2	7,5
9	24,747	5,52	3,4102	6,1868	25,00	37,121	12,374	50,00	-50,00	40	0	0	2,5
sum										358	4	12	4,5

Recovery rate and matrix content:



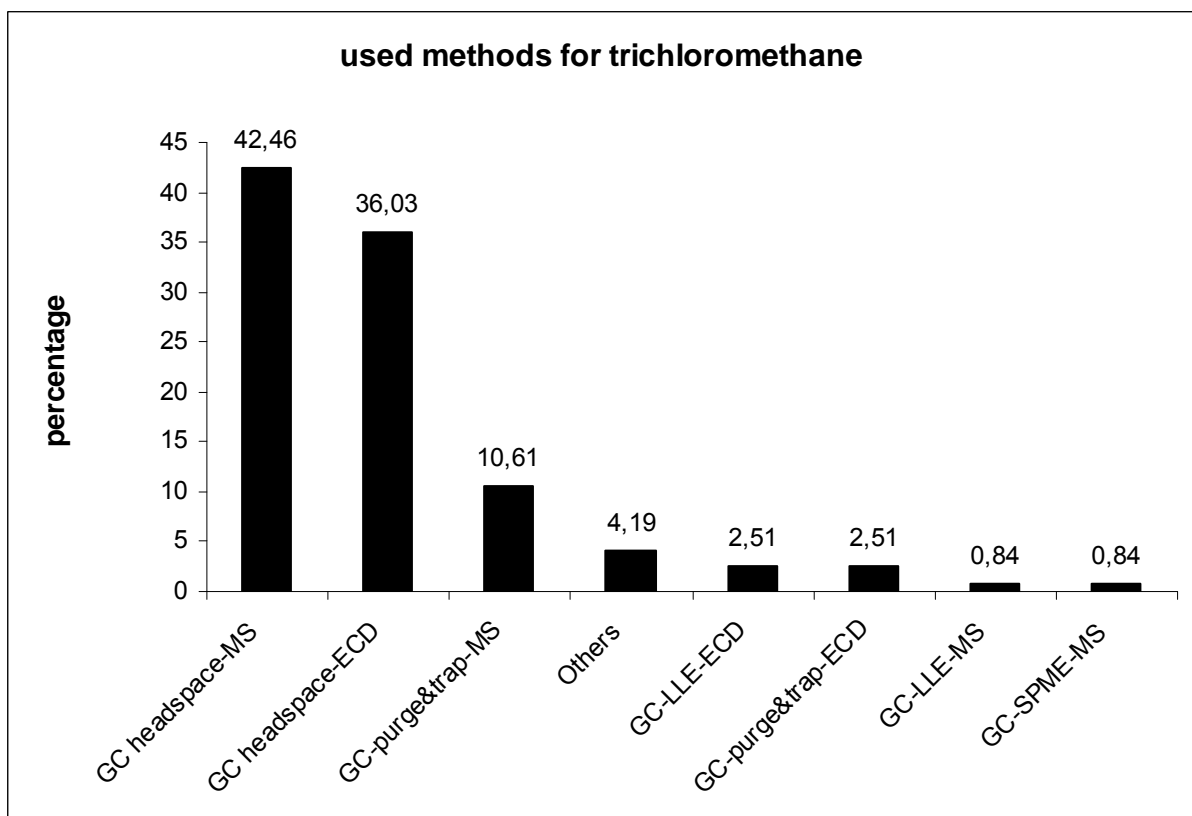
Slope of the line: 0,9303, recovery rate: 93 %;
 neg. x-axis intercept corresponds to the matrix content: 0,01712 µg/l;
 expanded uncertainty of the matrix content: 0,007021 µg/l = 41 %

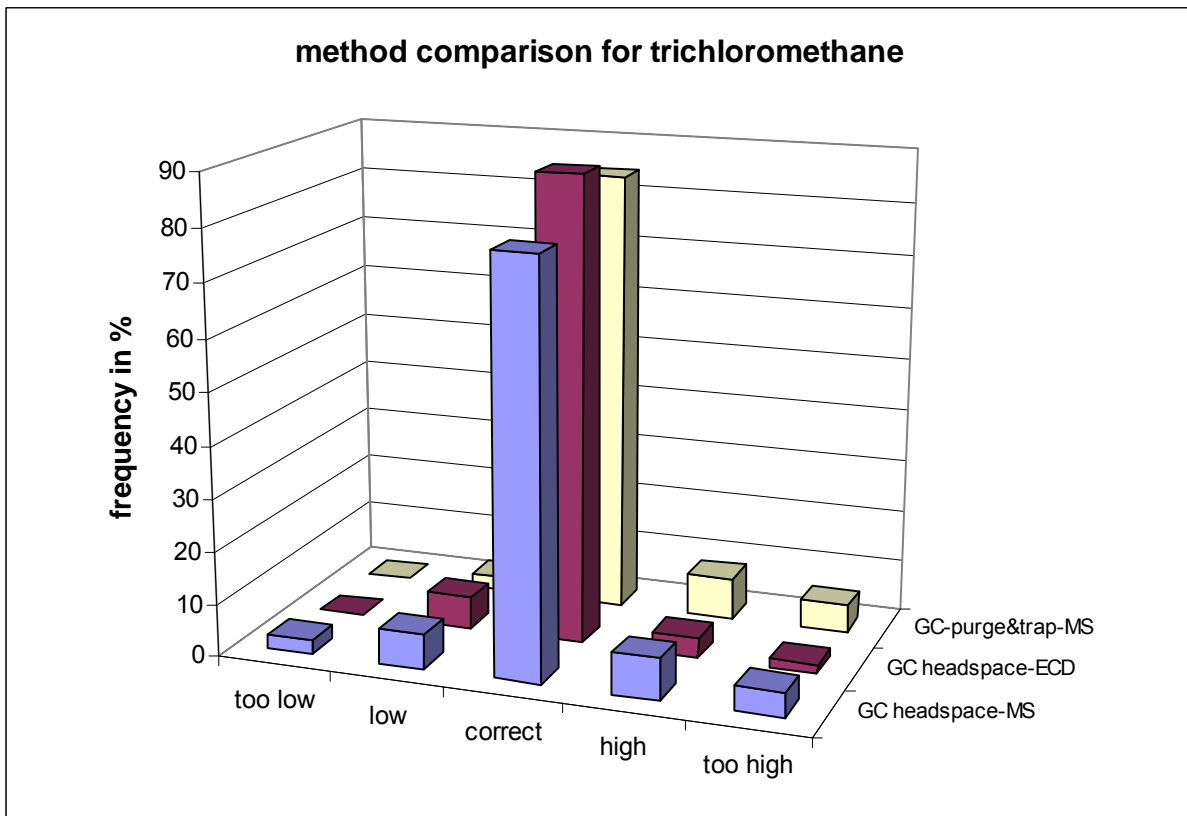
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, did not reach in any concentration level the standard deviation for proficiency assessment of 25 %.

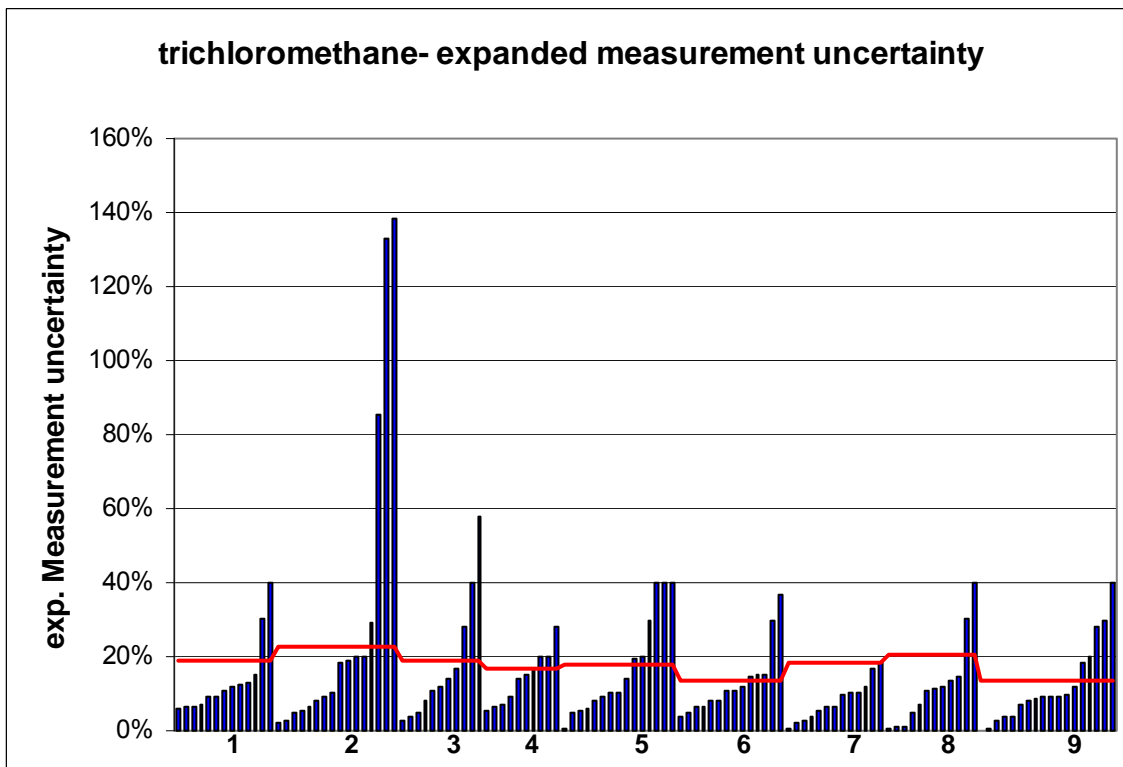
Method specific evaluation:





The differences between the methods were not significant.

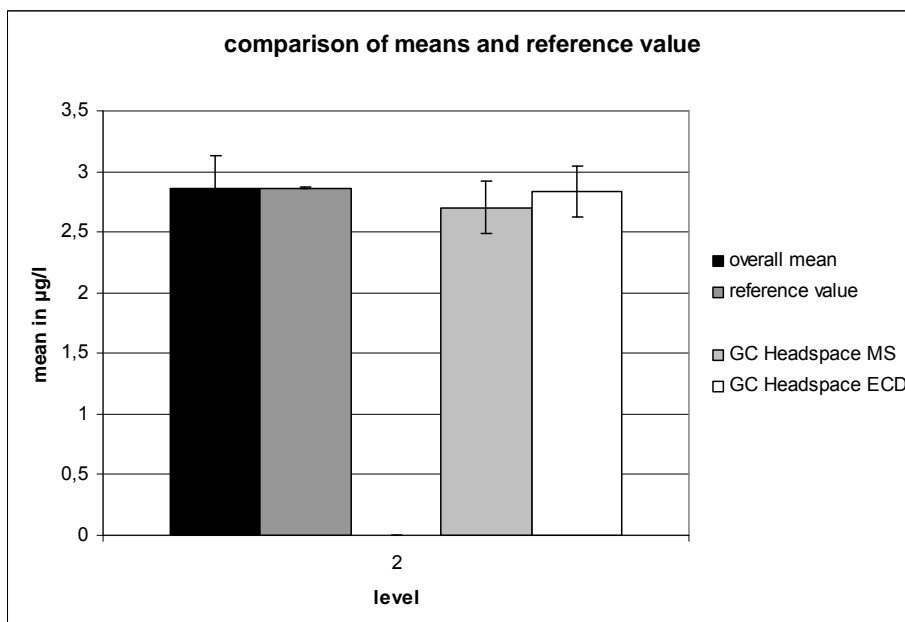
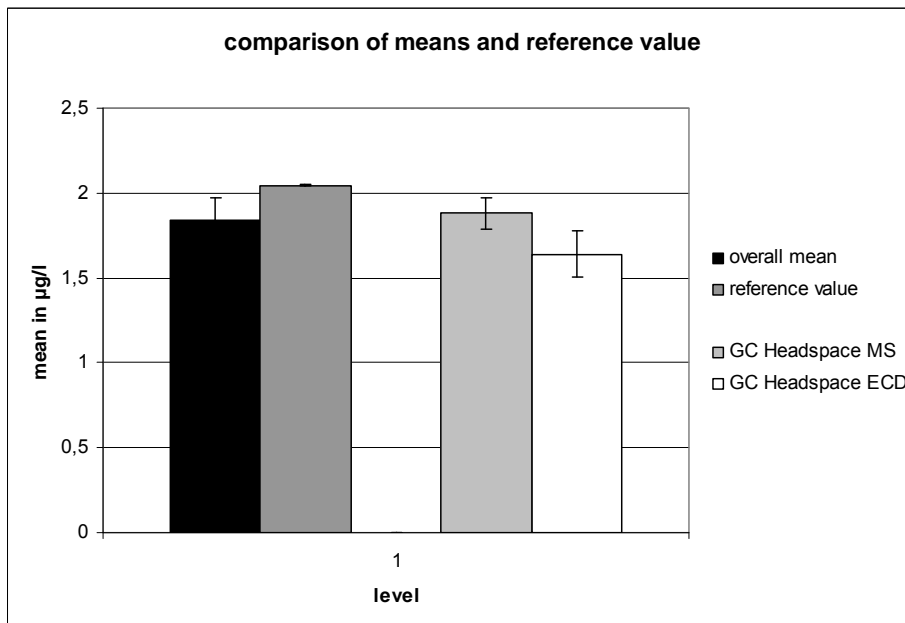
Measurement uncertainty:

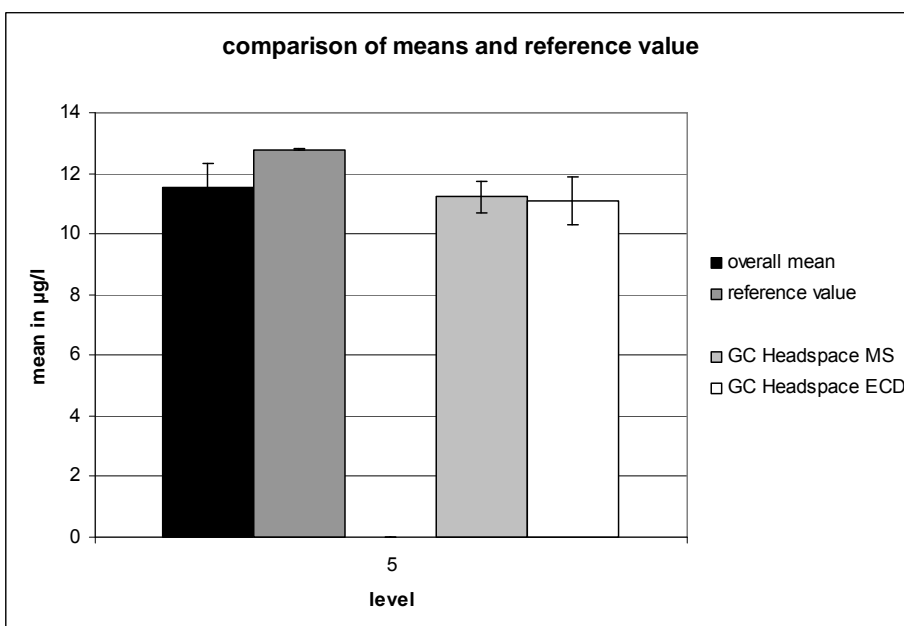
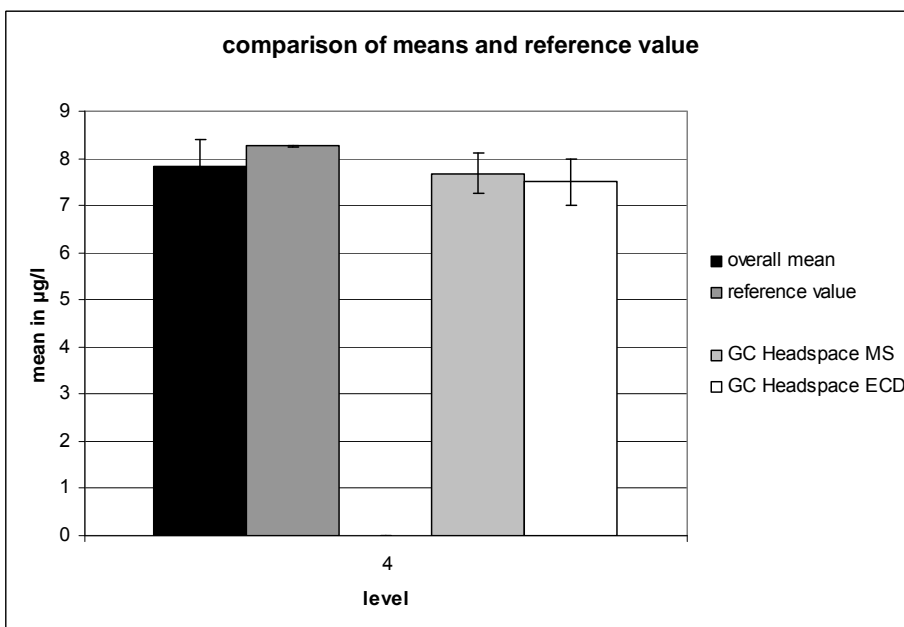
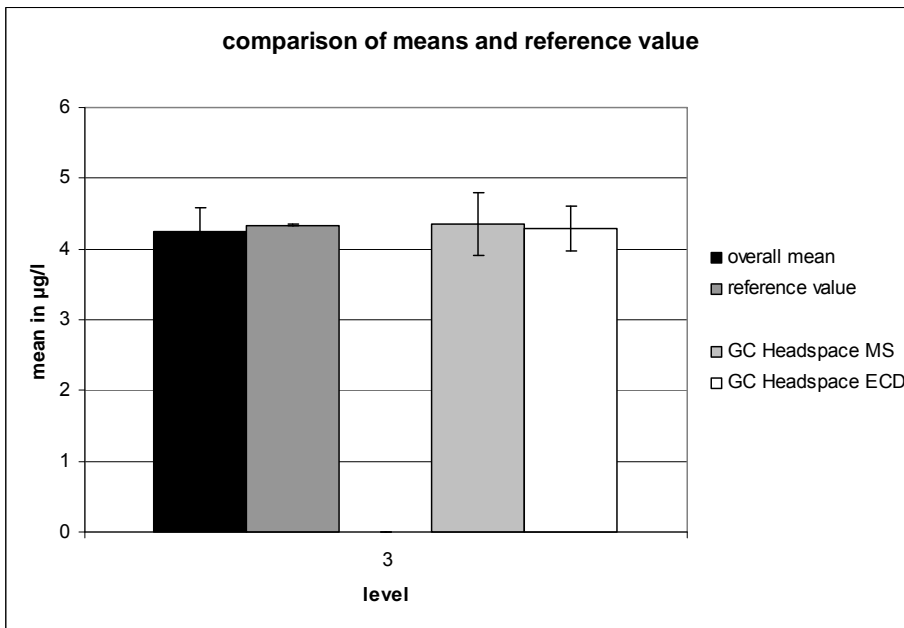


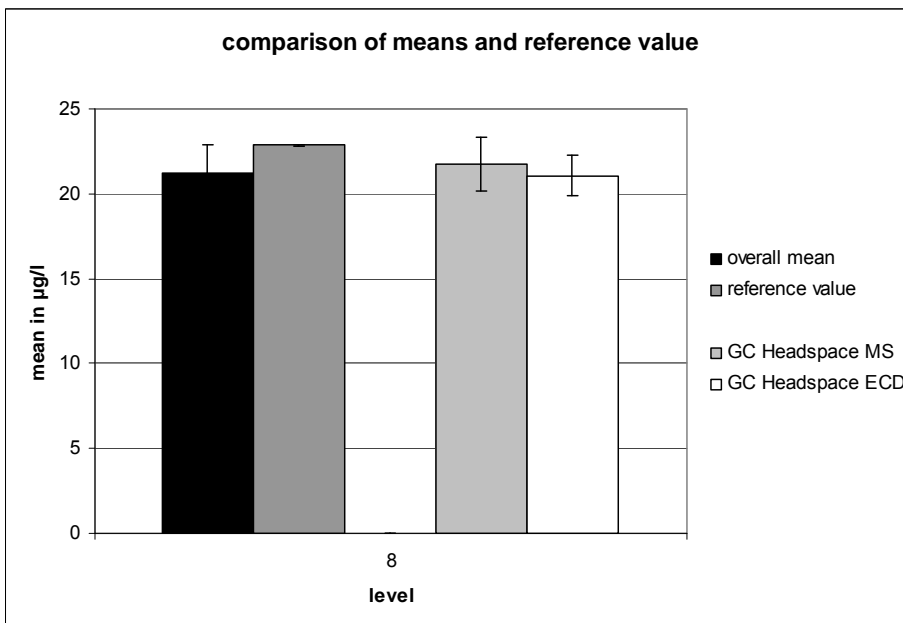
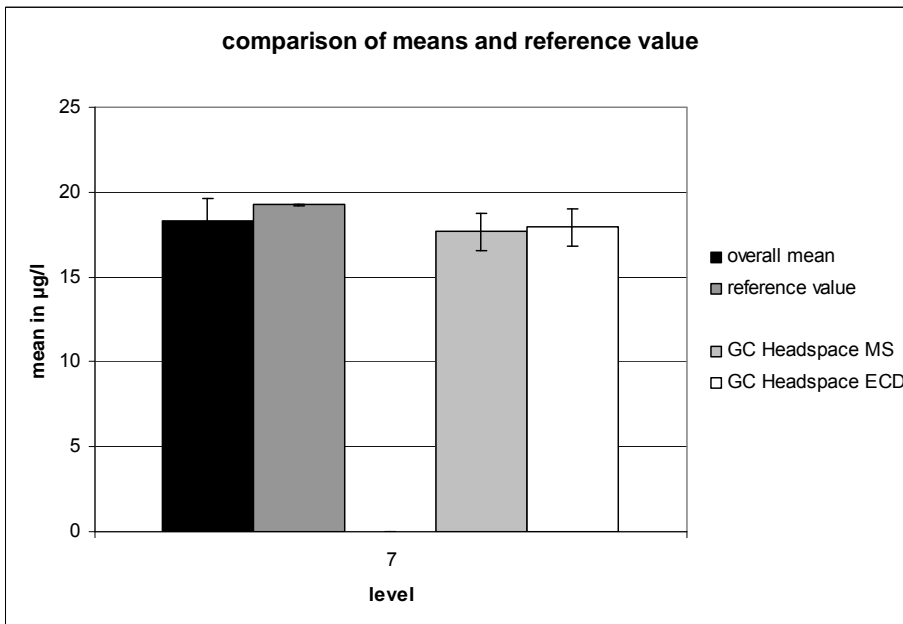
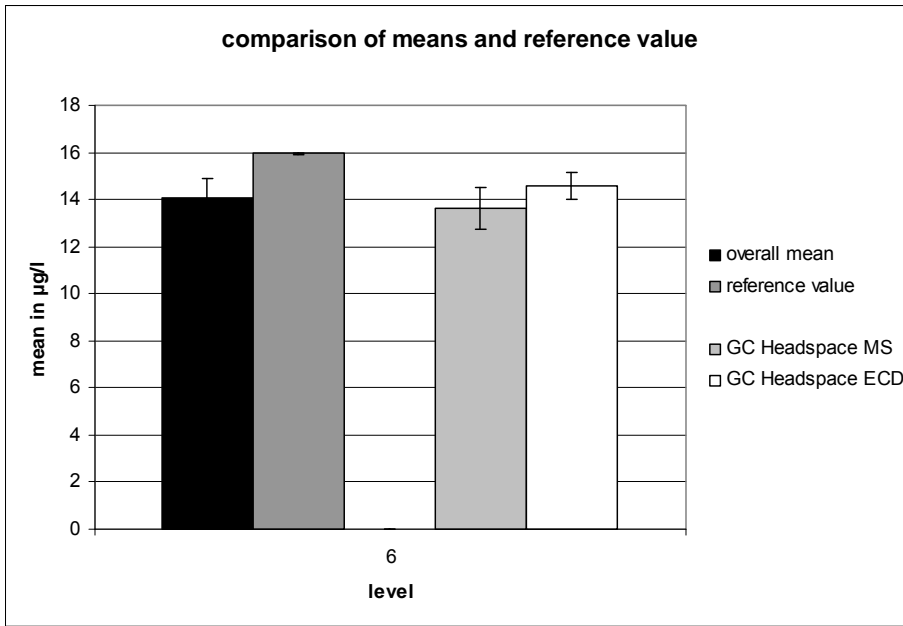
Reference values:

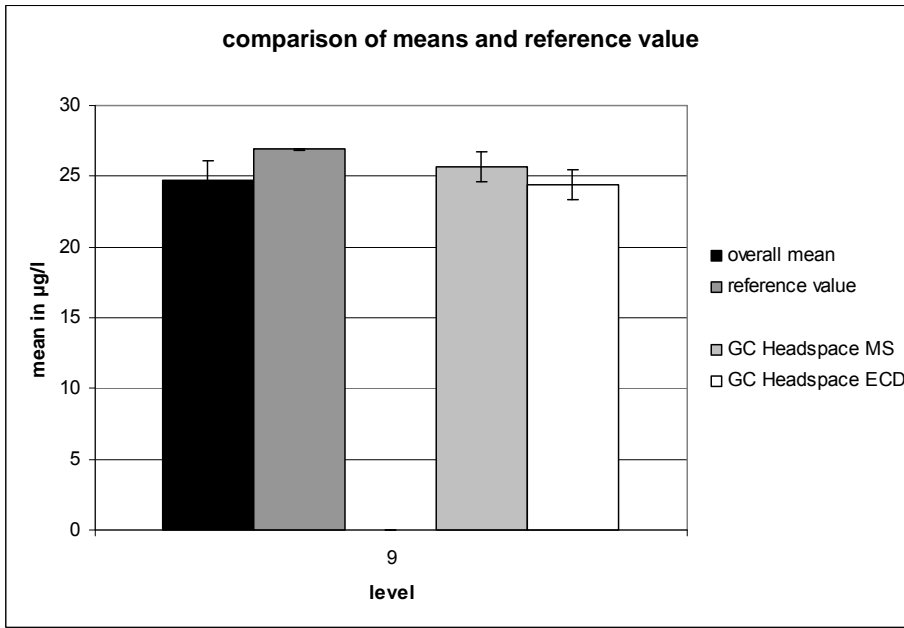
Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]		[µg/l]	[µg/l]
1	1,836	0,1381	7,52	2,046	0,0085	0,42
2	2,863	0,2666	9,31	2,865	0,0110	0,38
3	4,245	0,3302	7,78	4,337	0,0270	0,62
4	7,839	0,5500	7,02	8,257	0,0136	0,17
5	11,52	0,8004	6,95	12,79	0,0257	0,20
6	14,08	0,7923	5,63	15,95	0,0981	0,61
7	18,28	1,3597	7,44	19,25	0,0405	0,21
8	21,19	1,7329	8,18	22,85	0,0513	0,22
9	24,75	1,3652	5,52	26,91	0,0561	0,21

Comparison of the means und reference values:





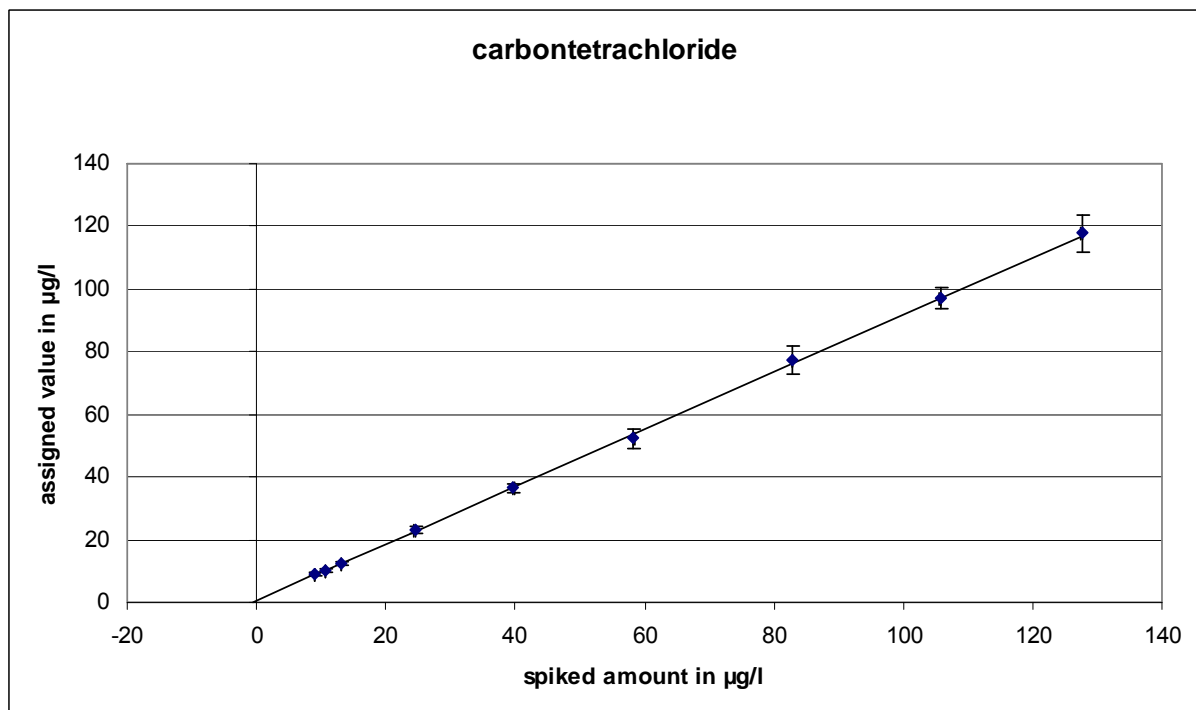




Carbontetrachloride

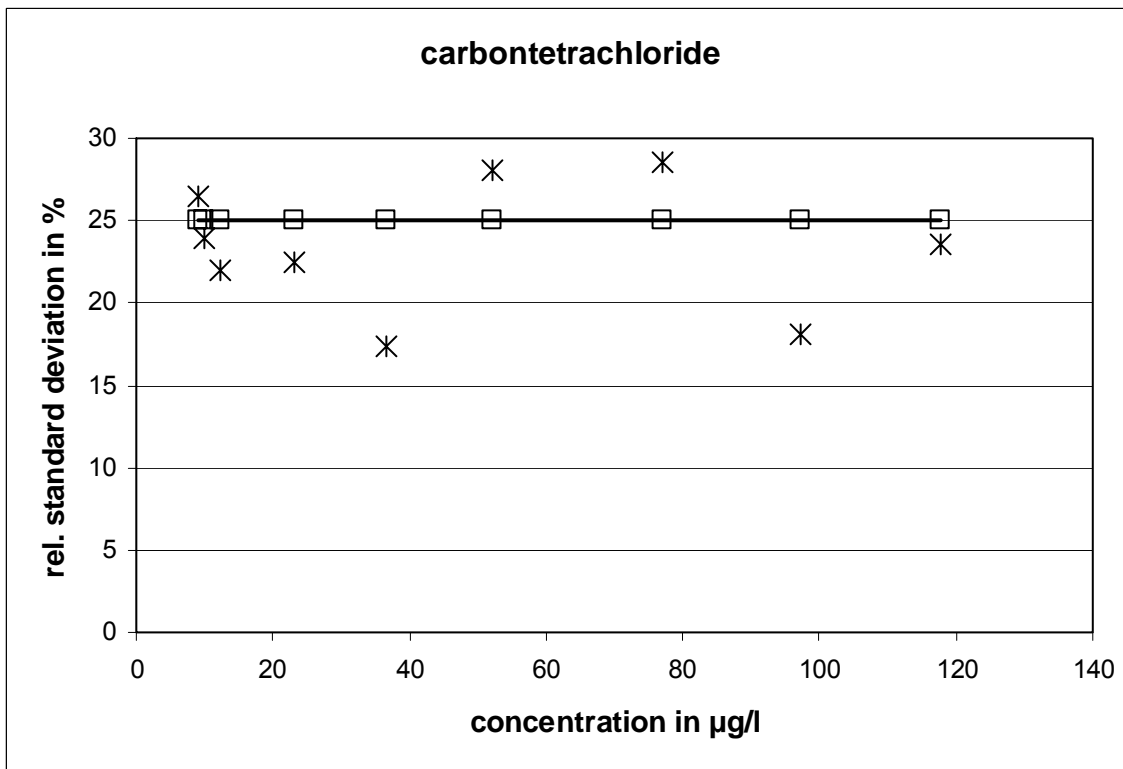
level	assigned value [$\mu\text{g/l}$]	expanded uncertainty of the assigned value [%]	standard deviation, calculated with robust statistics [$\mu\text{g/l}$]	standard deviation for proficiency assessment [$\mu\text{g/l}$]	rel. [%]	tolerance limit high [$\mu\text{g/l}$]	tolerance limit low [$\mu\text{g/l}$]	tolerance limit high [%]	tolerance limit low [%]	number of values	out high	out low	out [%]
1	8,985	11,04	2,3799	2,2463	25,00	13,478	4,493	50,00	-50,00	39	1	5	15,4
2	9,976	9,44	2,3832	2,4940	25,00	14,964	4,988	50,00	-50,00	41	1	1	7,3
3	12,352	9,31	2,7225	3,0880	25,00	18,528	6,176	50,00	-50,00	37	0	0	0,0
4	23,175	9,51	5,2131	5,7936	25,00	34,762	11,587	50,00	-50,00	37	1	2	8,1
5	36,518	7,35	6,3509	9,1295	25,00	54,777	18,259	50,00	-50,00	39	0	1	2,6
6	52,275	11,37	14,6572	13,0687	25,00	78,412	26,137	50,00	-50,00	39	0	3	10,3
7	77,157	11,73	22,0238	19,2892	25,00	115,735	38,578	50,00	-50,00	38	2	3	13,2
8	97,222	7,13	17,5401	24,3056	25,00	145,834	48,611	50,00	-50,00	40	0	1	2,5
9	117,744	9,67	27,6991	29,4361	25,00	176,617	58,872	50,00	-50,00	40	4	1	12,5
Summe										350	9	17	7,4

Recovery rate and matrix content:



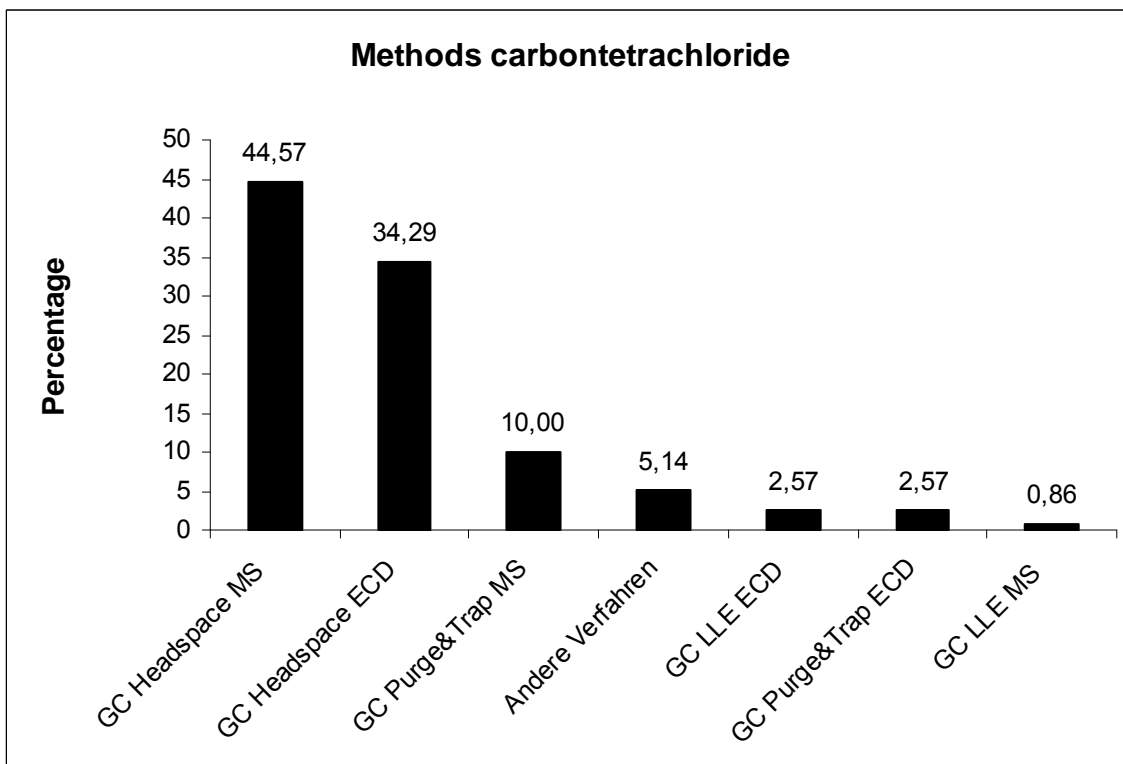
Slope of the line: 0,9121, recovery rate: 91,2 %;
 neg. x-axis intercept corresponds to the matrix content: 0,54072 $\mu\text{g/l}$;
 expanded uncertainty of the matrix content: 0,54072 $\mu\text{g/l}$ = 100 %

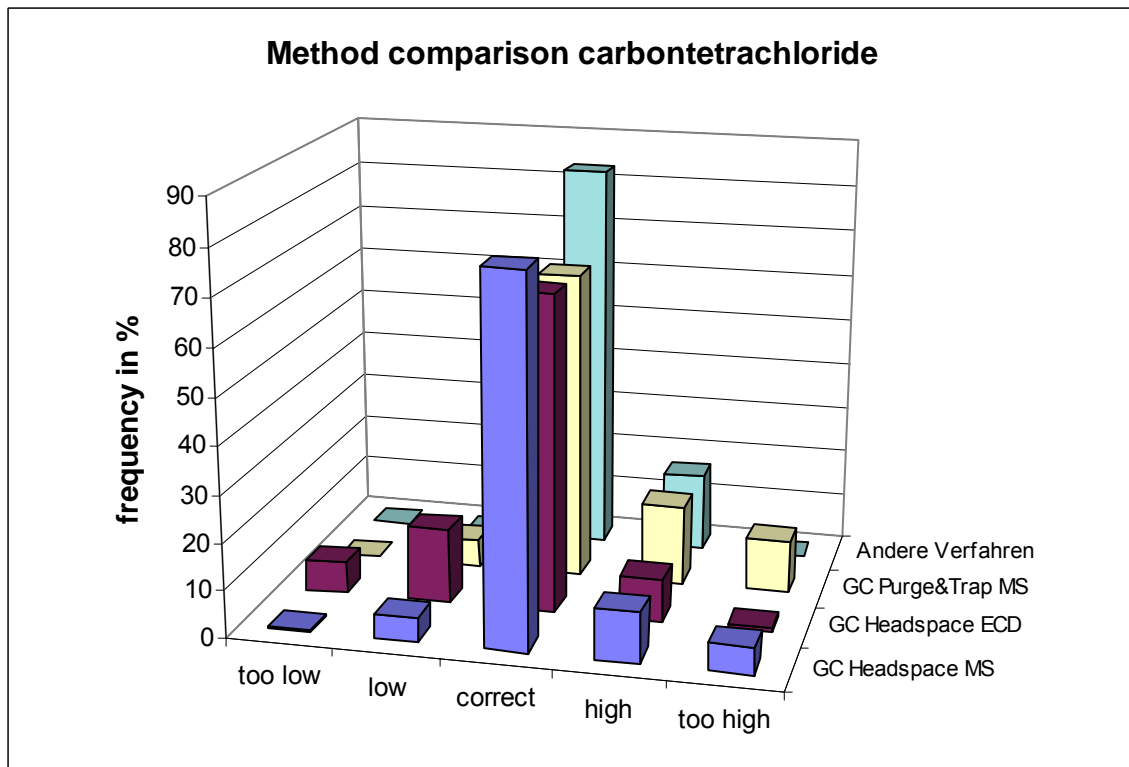
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, exceeded at three concentration levels the standard deviation for proficiency assessment of 25 %.

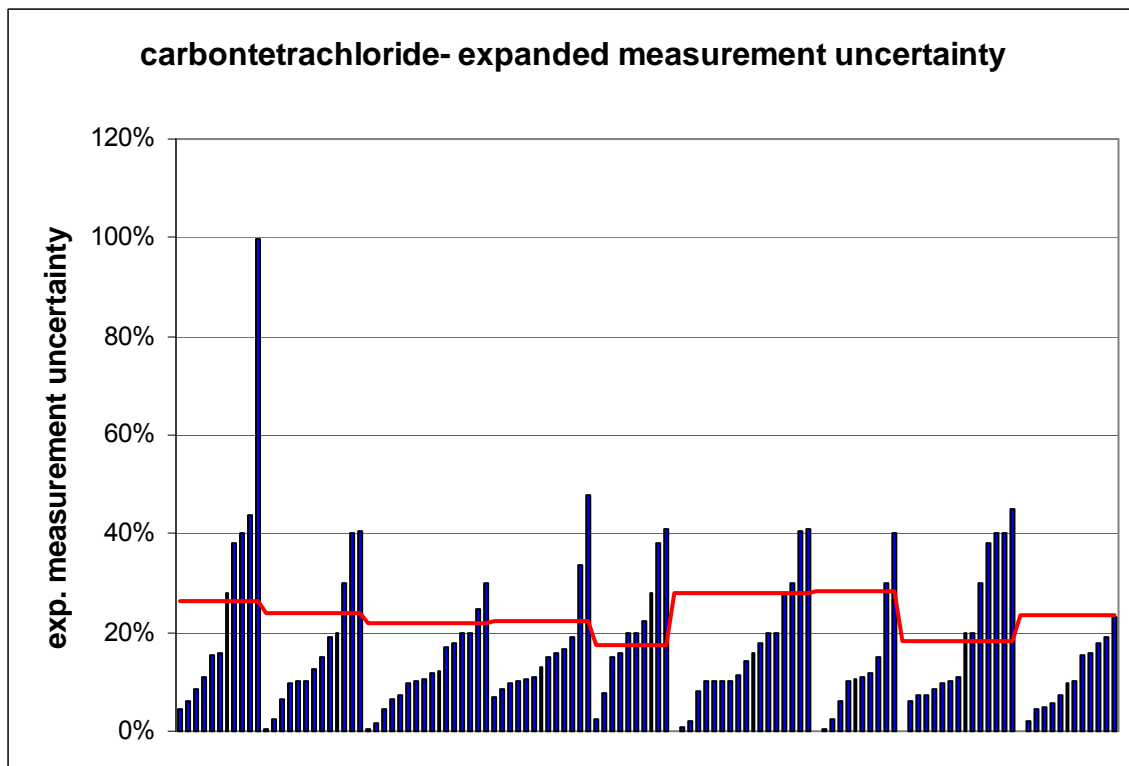
Method specific evaluation:





The difference between the methods were not significant.

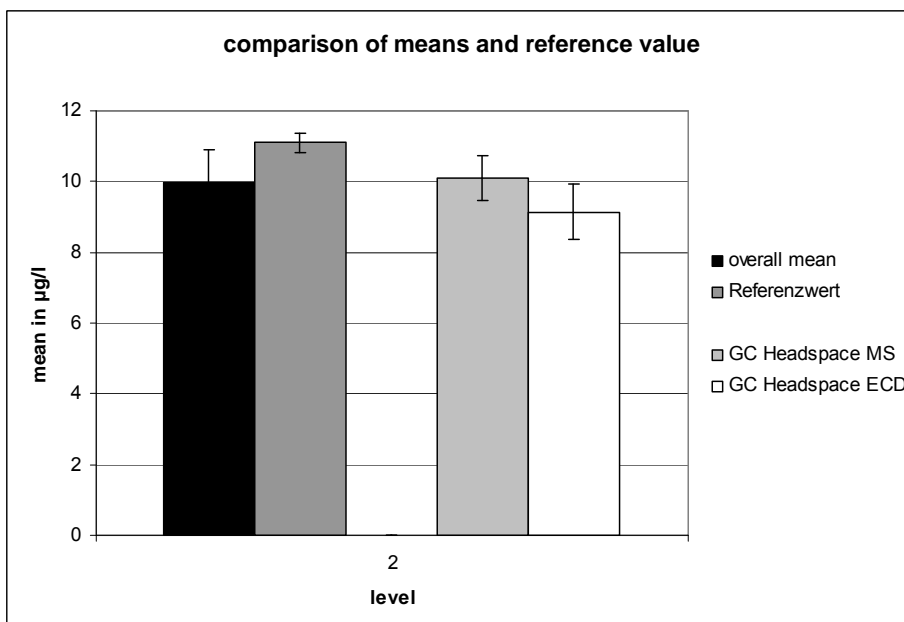
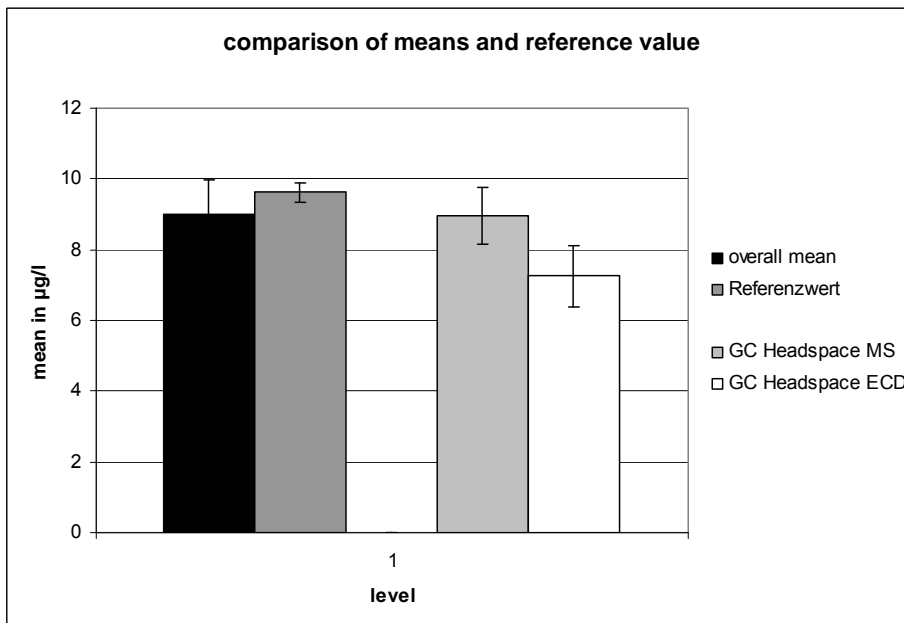
Measurement uncertainty:

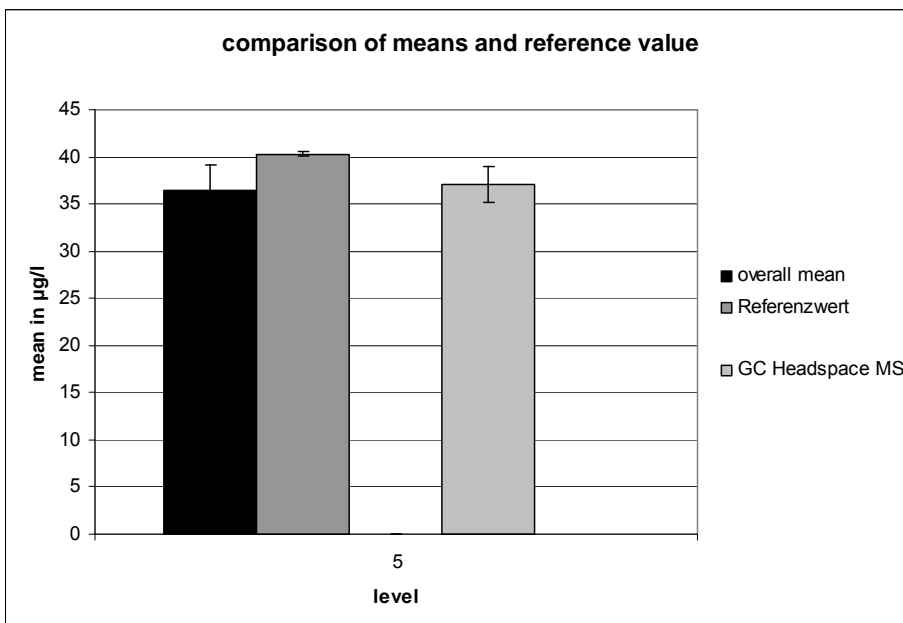
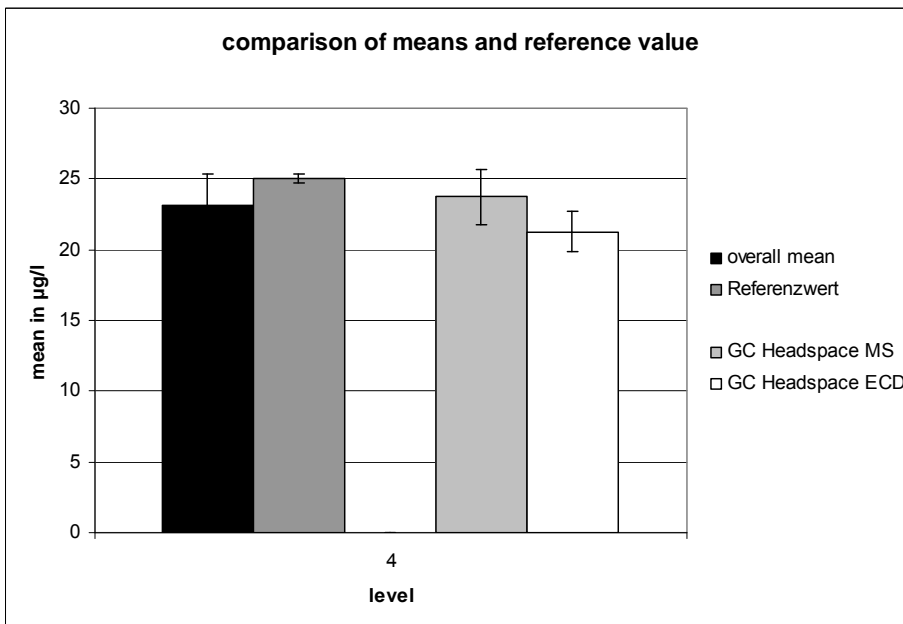
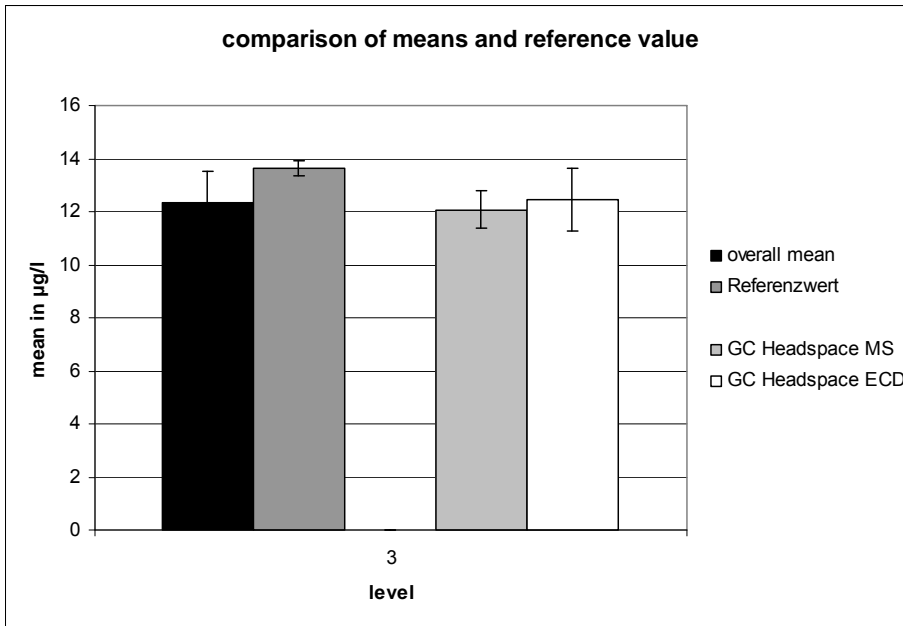


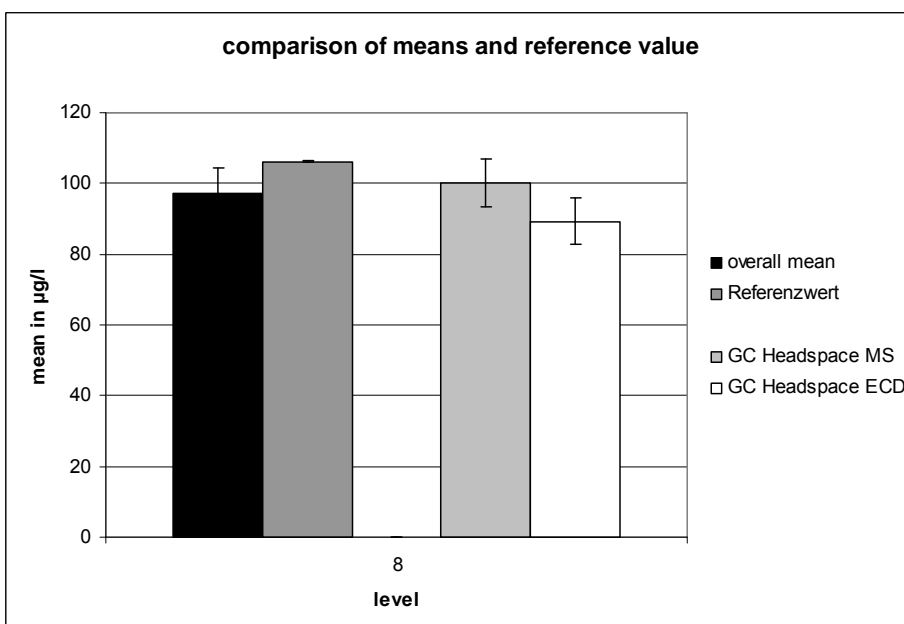
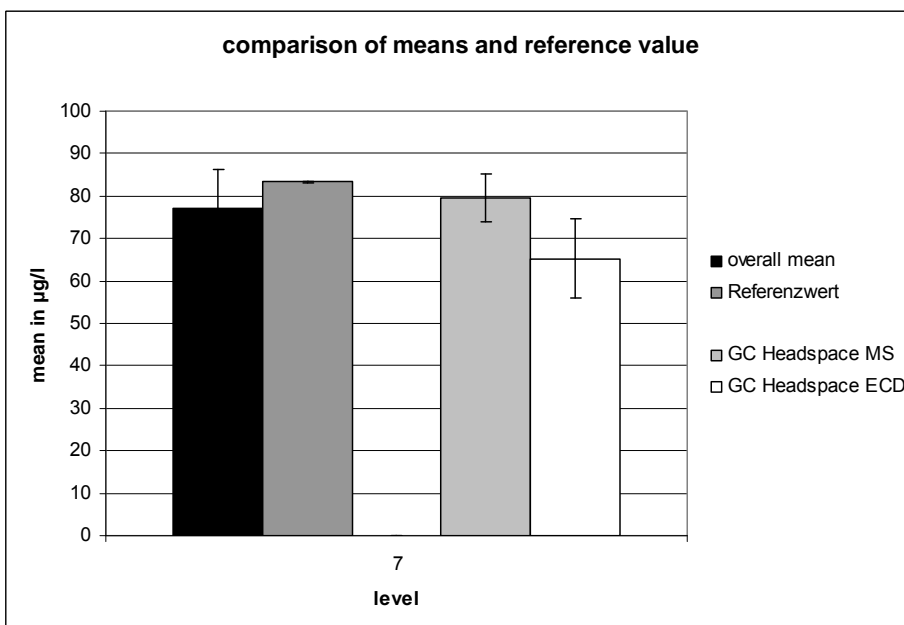
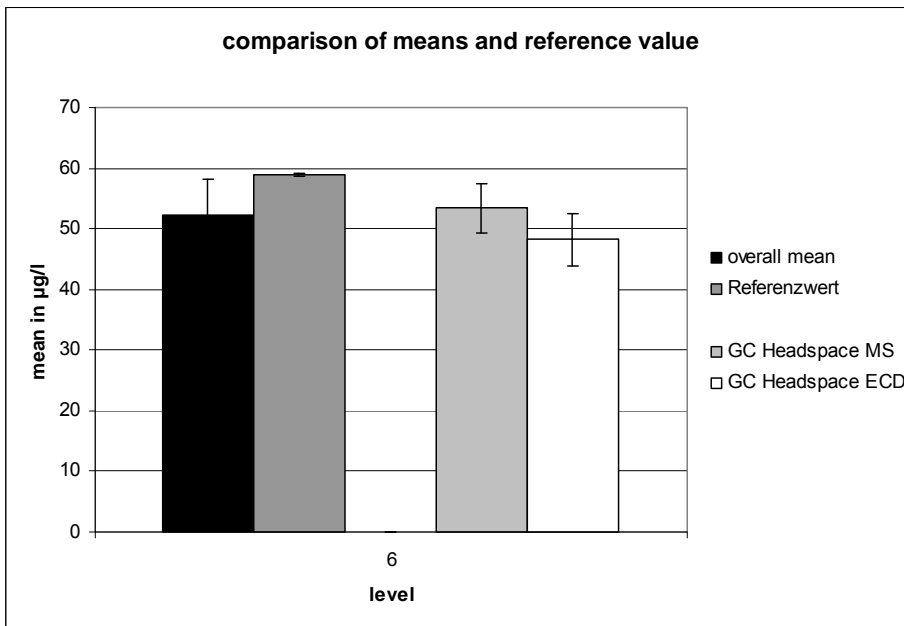
Reference values:

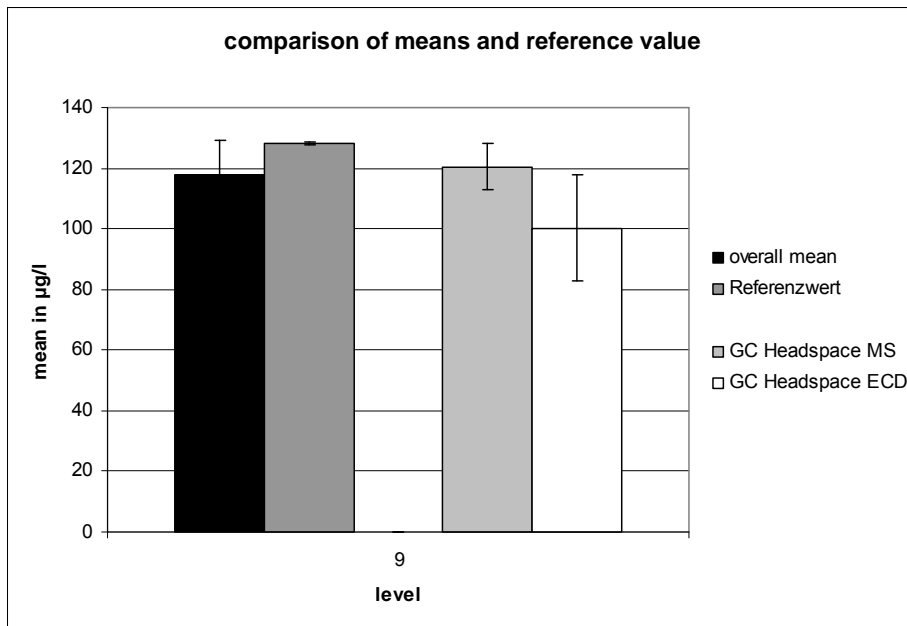
Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]		[µg/l]	[µg/l]
1	8,985	0,9916	11,04	9,617	0,5435	5,65
2	9,976	0,9420	9,44	11,10	0,5412	4,87
3	12,35	1,1505	9,31	13,65	0,5420	3,97
4	23,18	2,2030	9,51	25,05	0,5613	2,24
5	36,52	2,6837	7,35	40,29	0,5434	1,35
6	52,28	5,9443	11,37	58,87	0,5538	0,94
7	77,16	9,0517	11,73	83,34	0,5707	0,68
8	97,22	6,9333	7,13	106,3	0,5764	0,54
9	117,7	33,384	28,35	128,1	0,6001	0,47

Comparison of the means und reference values:





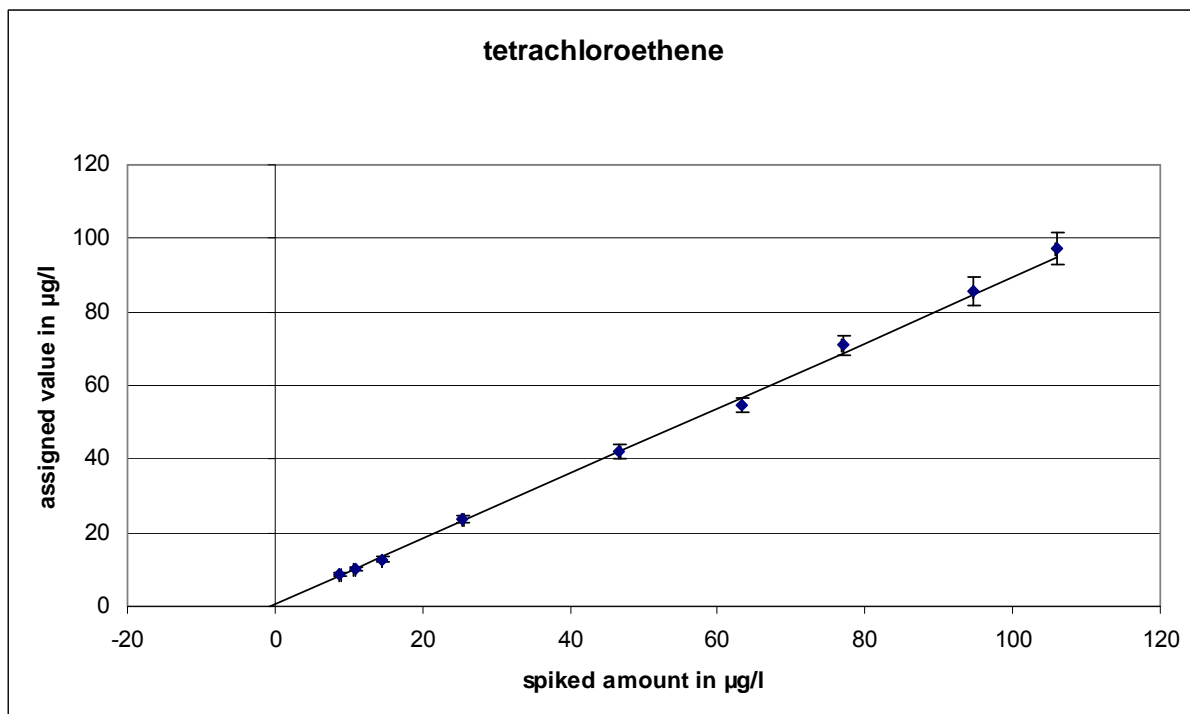




Tetrachloroethene

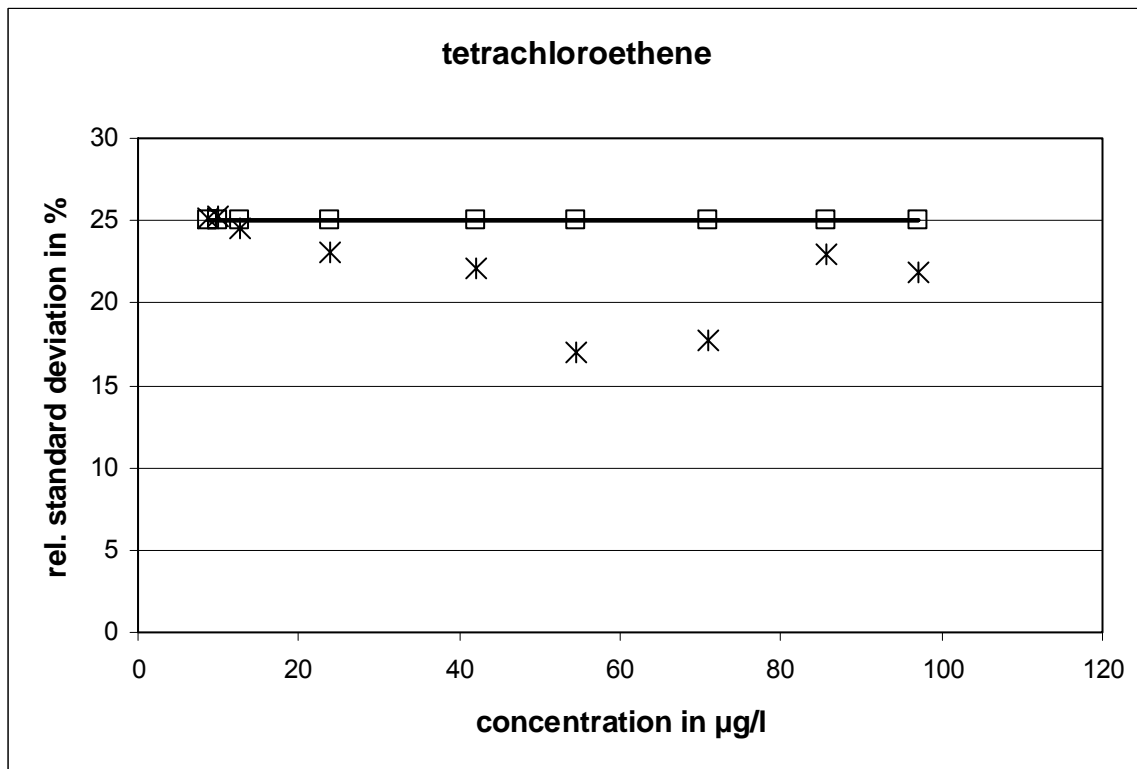
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	8,752	10,19	2,1989	2,1881	25,00	13,129	4,376	50,00	-50,00	40	1	3	12,5
2	10,070	10,52	2,5423	2,5174	25,00	15,104	5,035	50,00	-50,00	40	0	5	12,5
3	12,731	9,68	3,1191	3,1828	25,00	19,097	6,366	50,00	-50,00	41	1	0	4,9
4	23,805	9,26	5,5055	5,9513	25,00	35,708	11,903	50,00	-50,00	41	1	1	4,9
5	41,974	9,09	9,2840	10,4934	25,00	62,961	20,987	50,00	-50,00	39	1	3	10,3
6	54,634	6,71	9,2735	13,6584	25,00	81,950	27,317	50,00	-50,00	40	0	0	0,0
7	70,990	7,47	12,5491	17,7474	25,00	106,484	35,495	50,00	-50,00	39	1	1	5,1
8	85,584	9,29	19,6042	21,3961	25,00	128,377	42,792	50,00	-50,00	42	3	4	16,7
9	97,131	8,77	21,2728	24,2827	25,00	145,696	48,565	50,00	-50,00	40	1	3	12,5
sum										362	9	20	8,0

Recovery rate and matrix content:



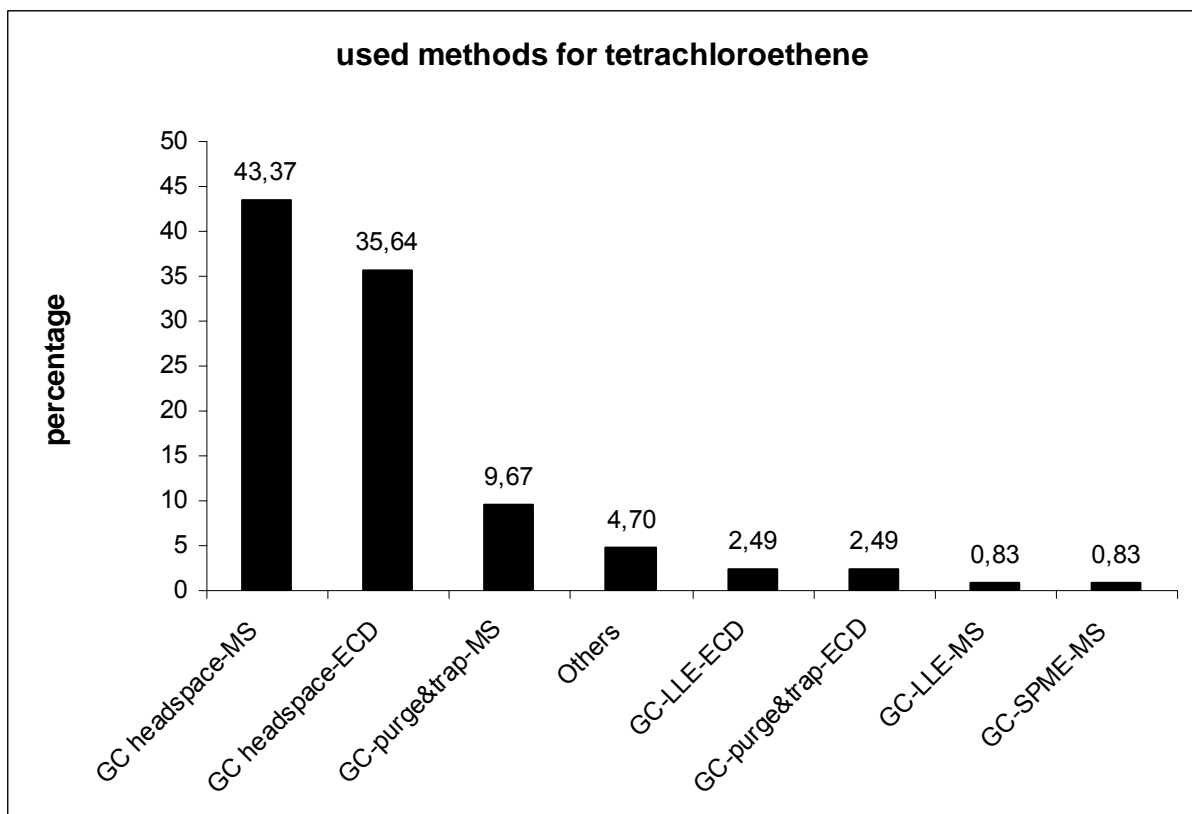
Slope of the line: 0,8886, recovery rate: 88,9 %;
 neg. x-axis intercept corresponds to the matrix content: 0,6181 µg/l;
 expanded uncertainty of the matrix content: 0,6181 µg/l = 100 %

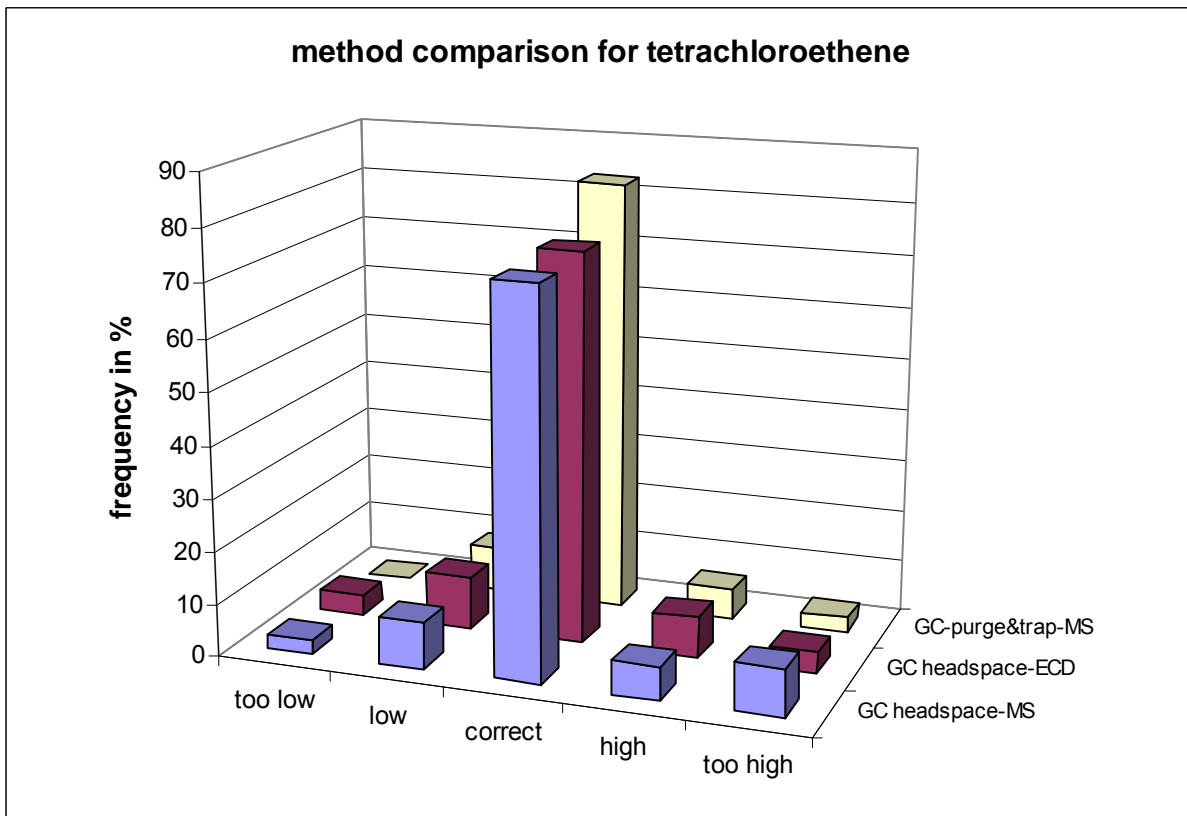
Relative standard deviation:



The relative standard deviation, calculated with the Q-method, did not reach in any concentration level the standard deviation for proficiency assessment of 25 %.

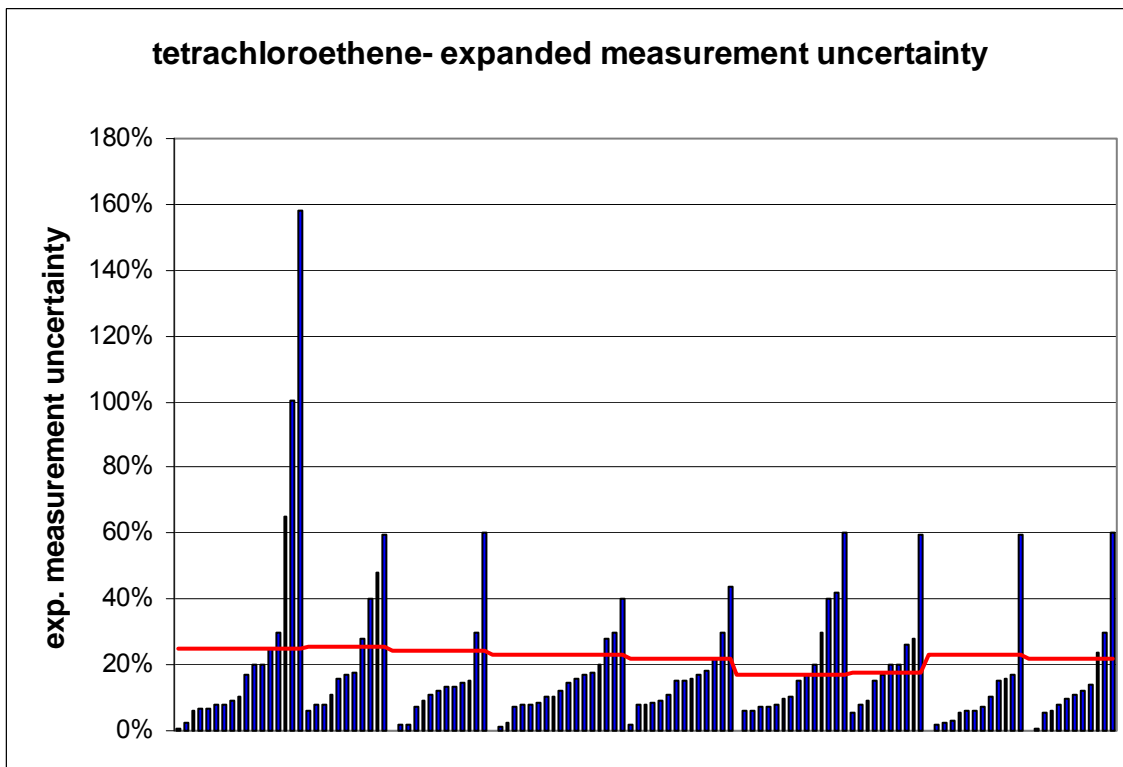
Method specific evaluation:





The differences between the methods were not significant.

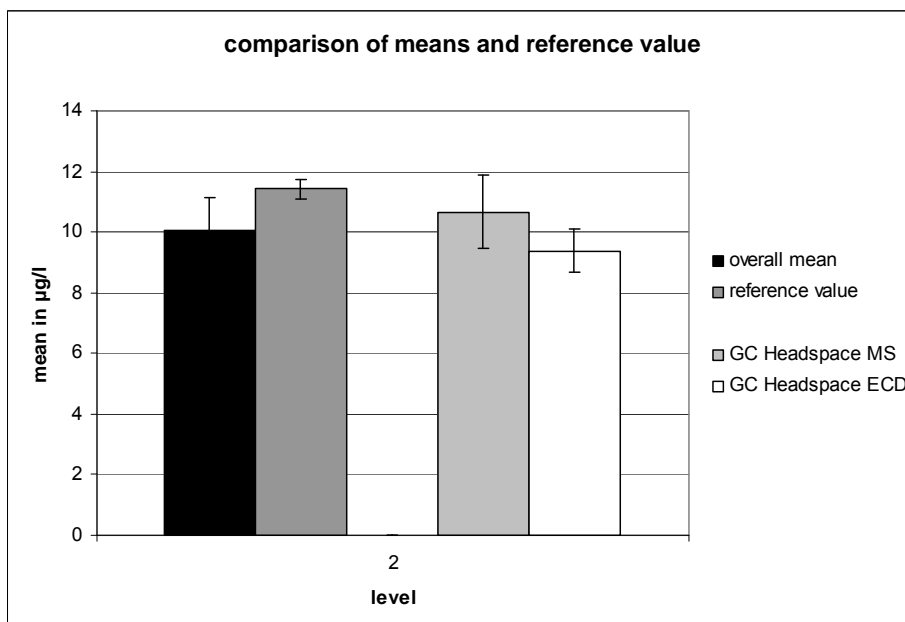
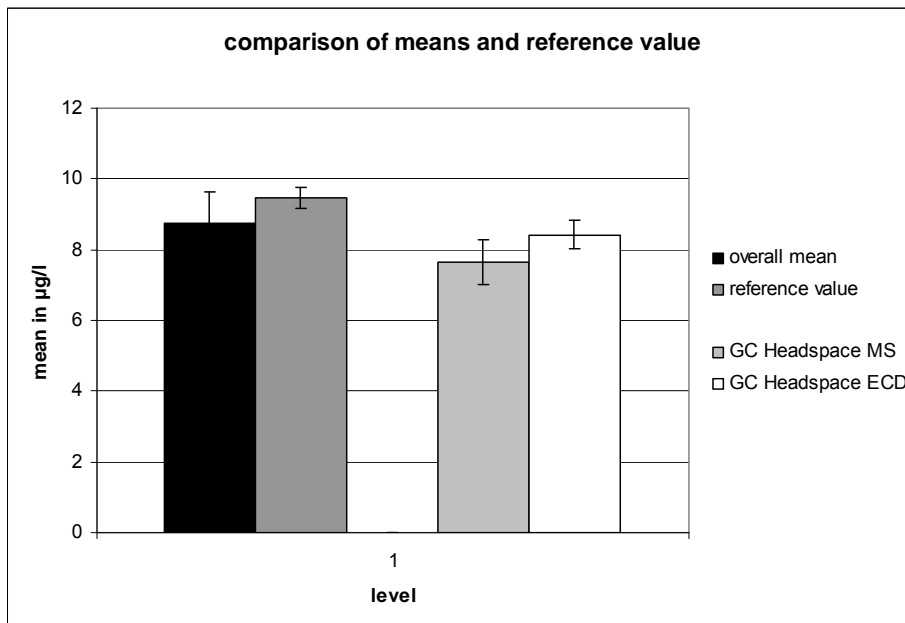
Measurement uncertainty:

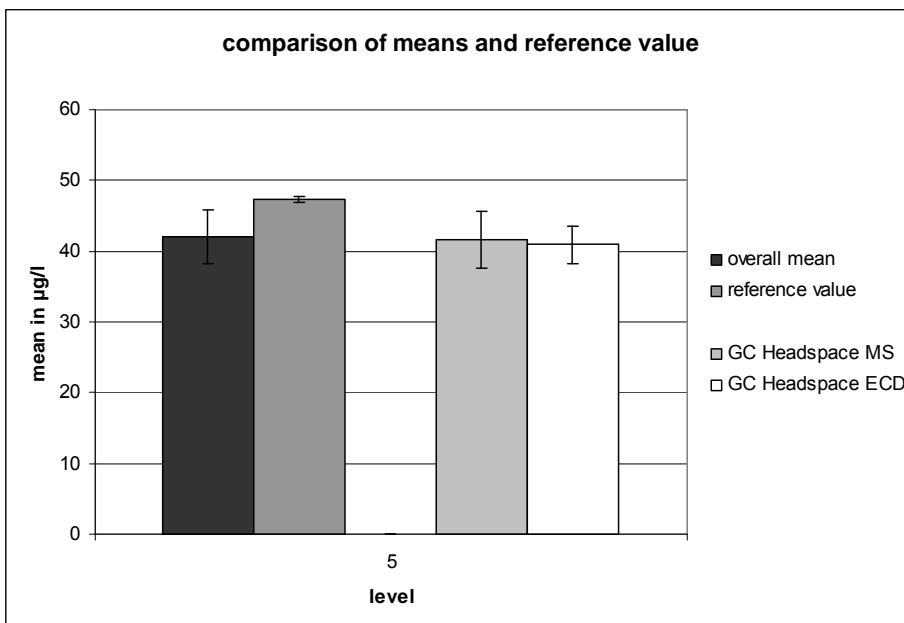
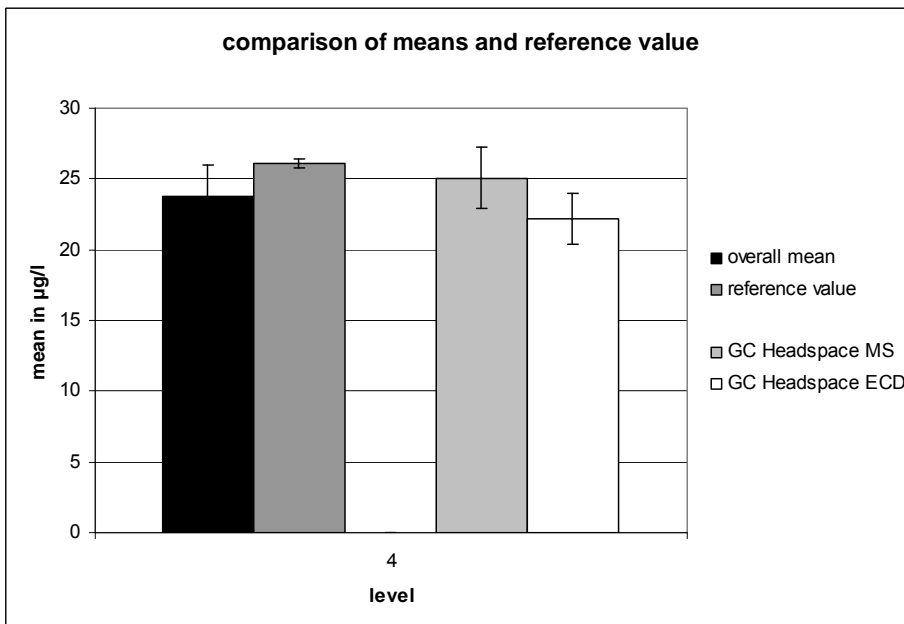
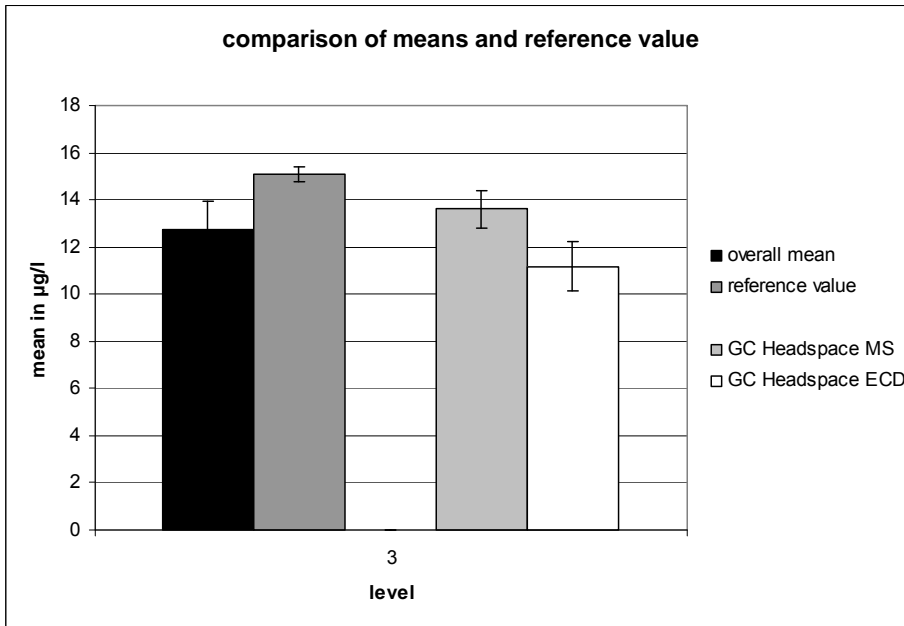


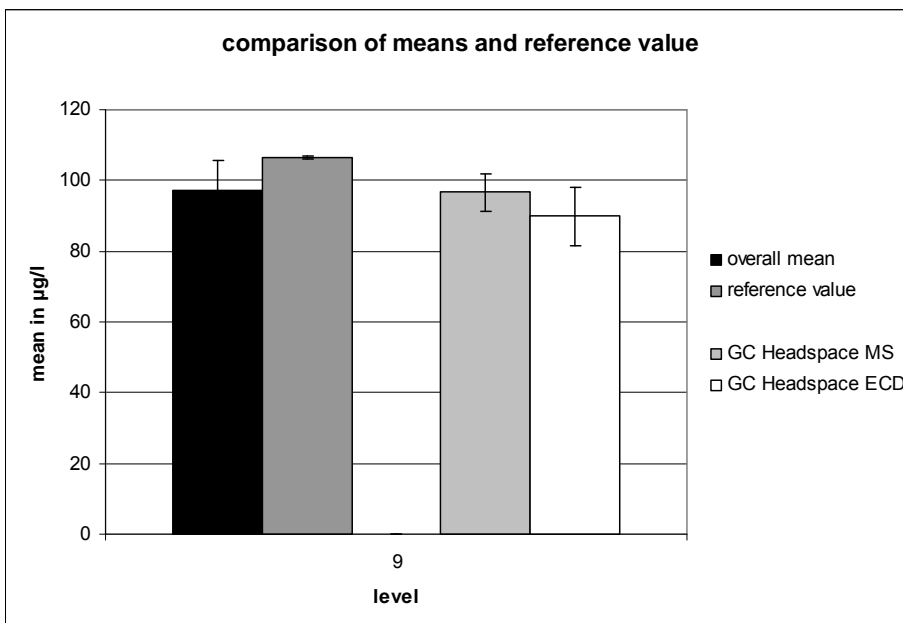
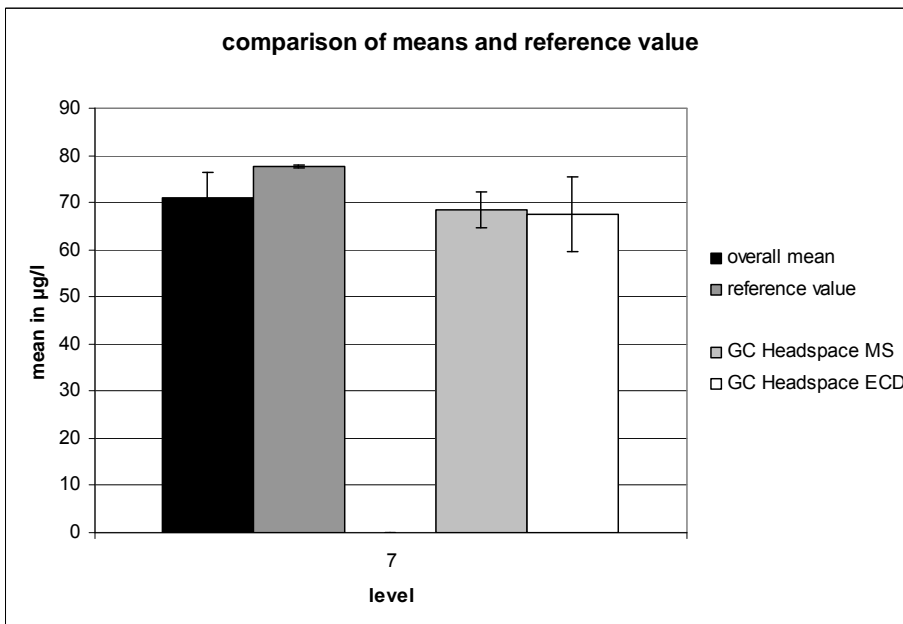
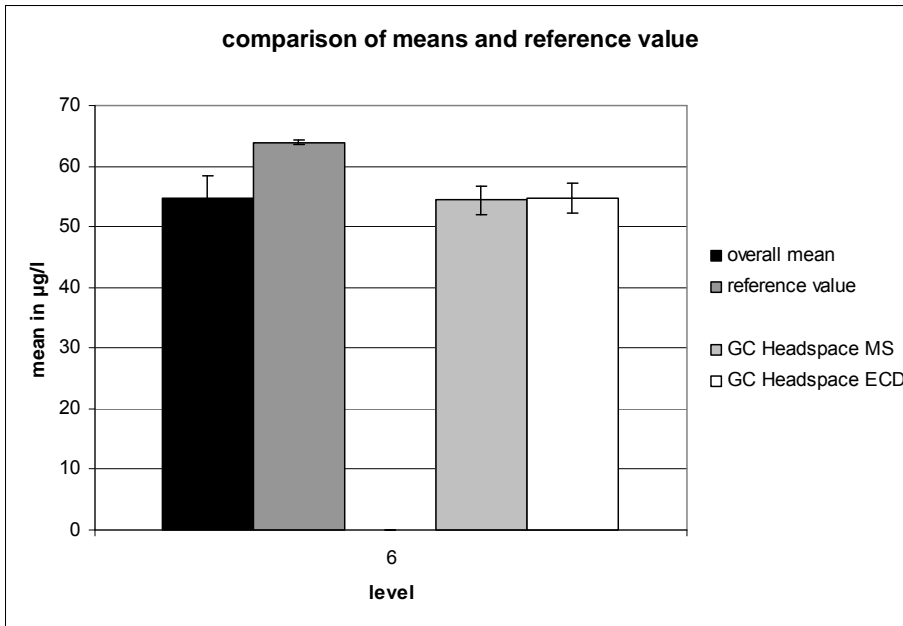
Reference values:

Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]		[µg/l]	[µg/l]
1	8,753	0,8918	10,19	9,461	0,6187	6,54
2	10,07	1,0593	10,52	11,43	0,6215	5,44
3	12,73	1,2329	9,68	15,08	0,6189	4,10
4	23,81	2,2040	9,26	26,11	0,6204	2,38
5	41,97	3,8157	9,09	47,32	0,6812	1,44
6	54,63	3,6657	6,71	63,93	0,6297	0,98
7	70,99	5,3030	7,47	77,56	0,6266	0,81
8	85,59	7,9506	9,29	95,26	0,6477	0,68
9	97,13	8,516	8,77	106,6	0,6607	0,62

Comparison of the means und reference values:



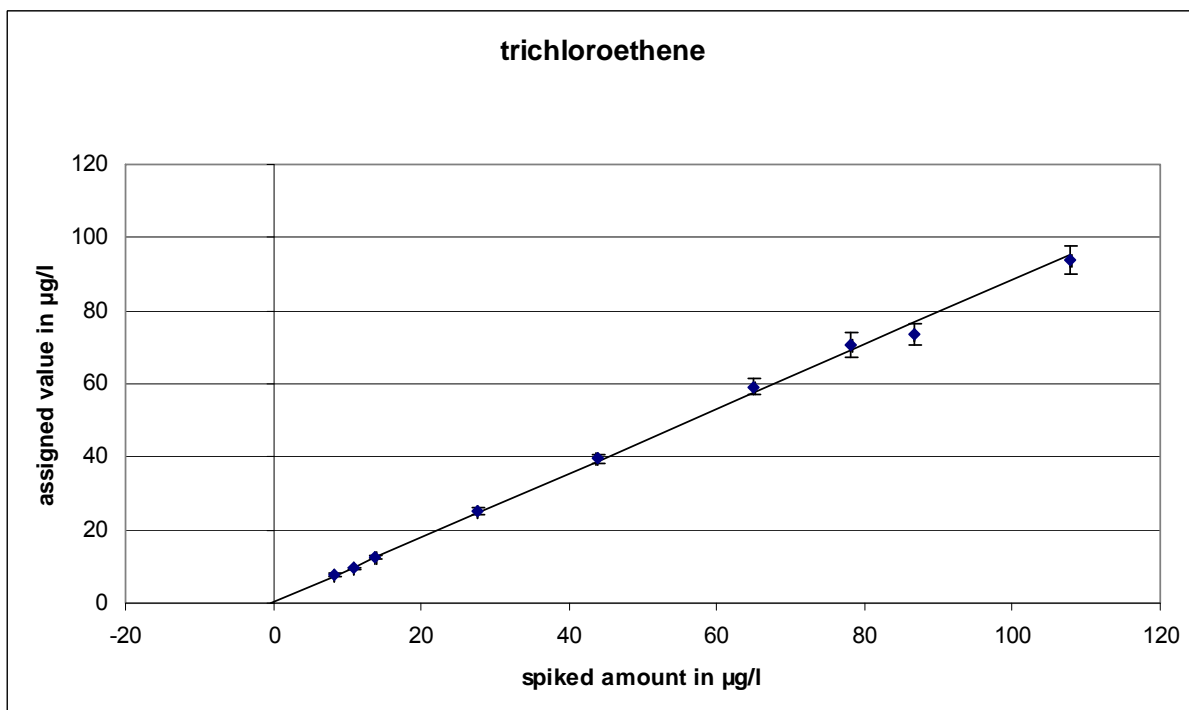




Trichloroethene

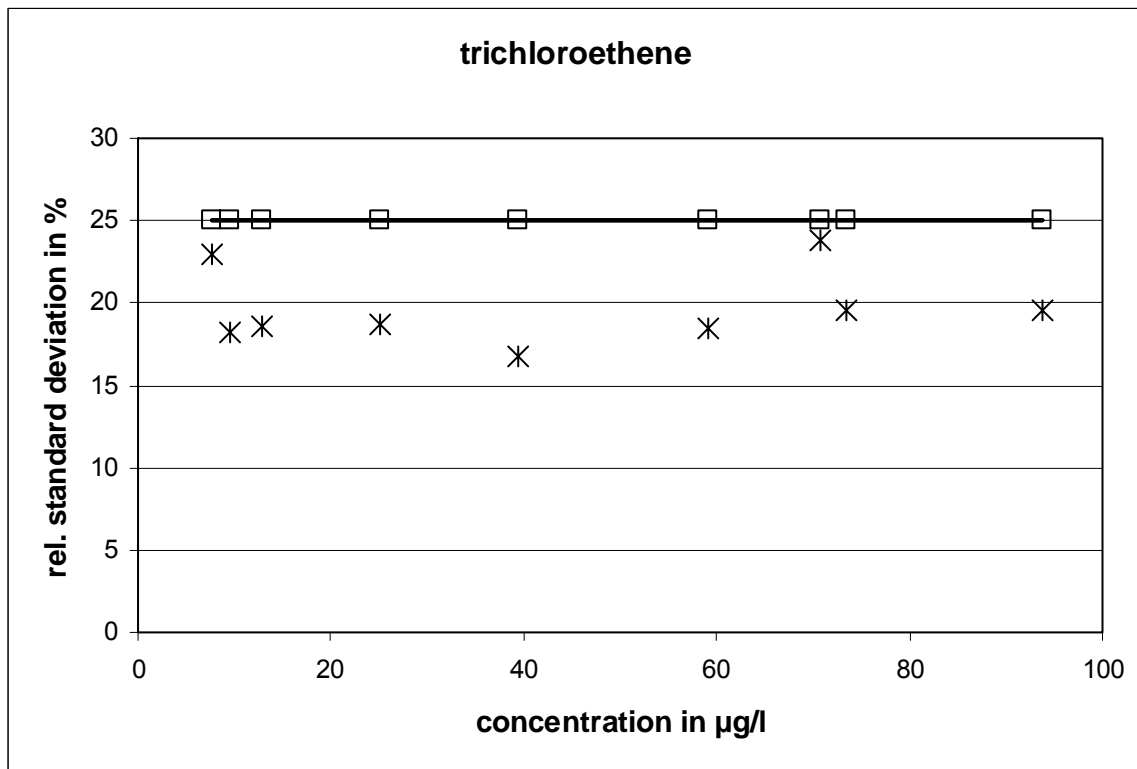
level	assigned value [$\mu\text{g/l}$]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [$\mu\text{g/l}$]	standard deviation for proficiency assessment [$\mu\text{g/l}$]	standard deviation for proficiency assessment [%]	upper tolerance limit [$\mu\text{g/l}$]	lower tolerance limit [$\mu\text{g/l}$]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	7,666	9,55	1,7568	1,9166	25,00	11,500	3,833	50,00	-50,00	40	1	5	15,0
2	9,484	7,22	1,7331	2,3710	25,00	14,226	4,742	50,00	-50,00	41	0	0	4,9
3	12,793	7,54	2,3775	3,1983	25,00	19,190	6,397	50,00	-50,00	40	1	1	7,5
4	25,119	7,51	4,7107	6,2799	25,00	37,679	12,560	50,00	-50,00	40	0	3	7,5
5	39,449	6,90	6,6234	9,8624	25,00	59,174	19,725	50,00	-50,00	39	0	1	2,6
6	59,216	7,40	10,9433	14,8040	25,00	88,824	29,608	50,00	-50,00	41	1	1	7,3
7	70,825	9,64	16,8265	17,7061	25,00	106,237	35,412	50,00	-50,00	42	3	2	11,9
8	73,487	7,74	14,3966	18,3718	25,00	110,231	36,744	50,00	-50,00	40	0	1	2,5
9	93,760	8,28	18,3752	23,4400	25,00	140,640	46,880	50,00	-50,00	39	1	1	5,1
sum										362	7	15	6,1

Recovery rate and matrix content:



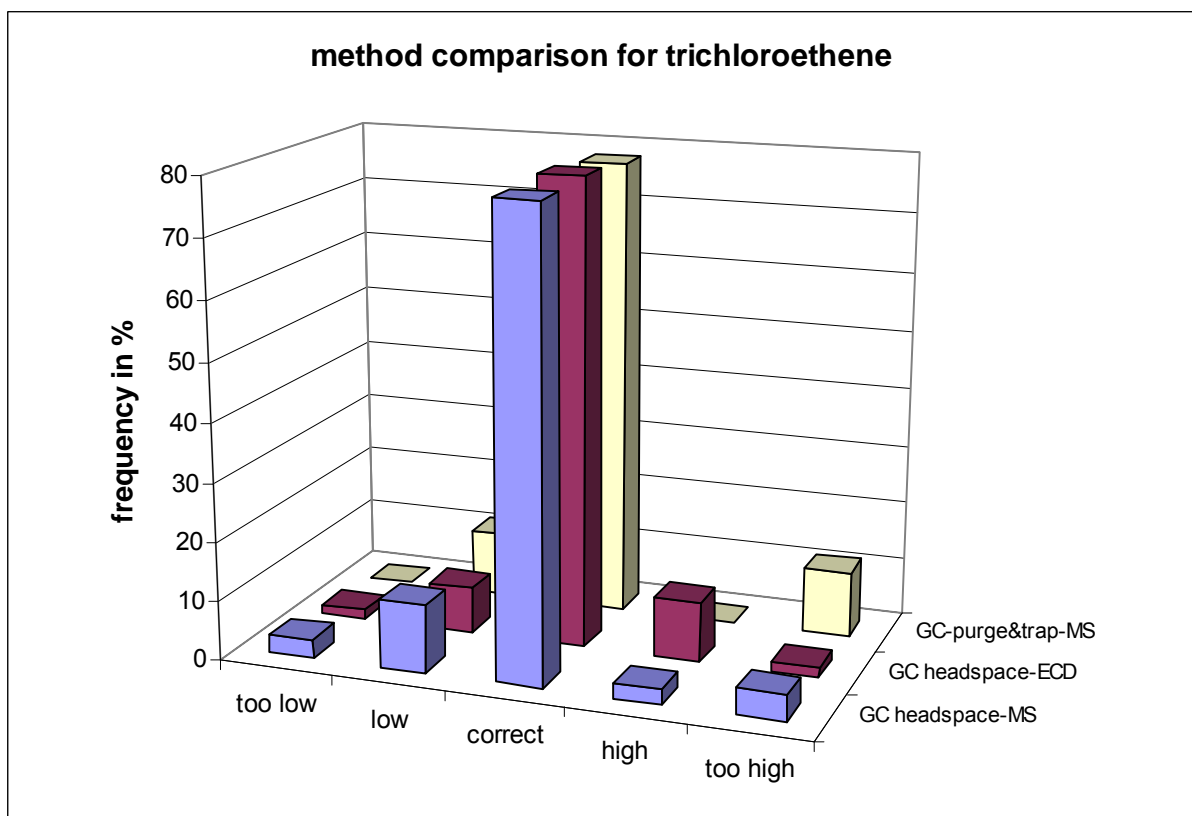
Slope of the line: 0,883, recovery rate: 88,3 %;
 neg. x-axis intercept corresponds to the matrix content: 0,296 $\mu\text{g/l}$;
 expanded uncertainty of the matrix content: 0,296 $\mu\text{g/l}$ = 100 %

Relative standard deviation:



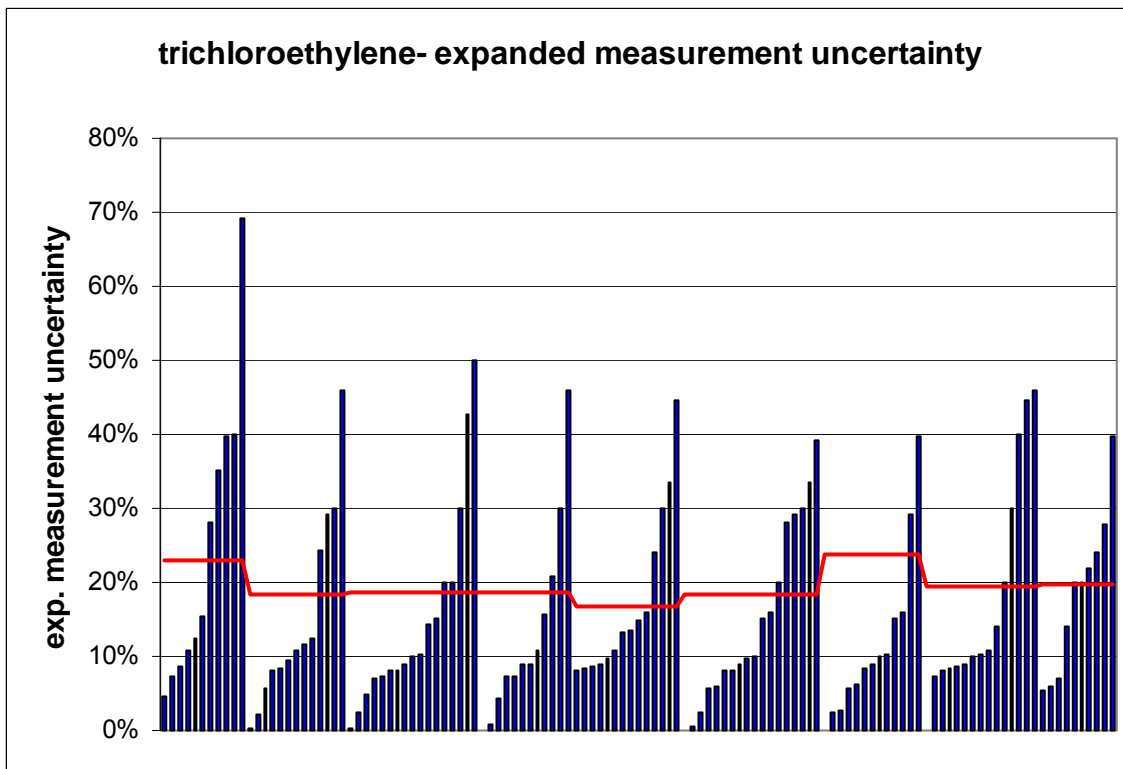
The relative standard deviation, calculated with the Q-method, did not reach in any concentration level the standard deviation for proficiency assessment of 25 %.

Method specific evaluation:



The differences between the methods were not significant.

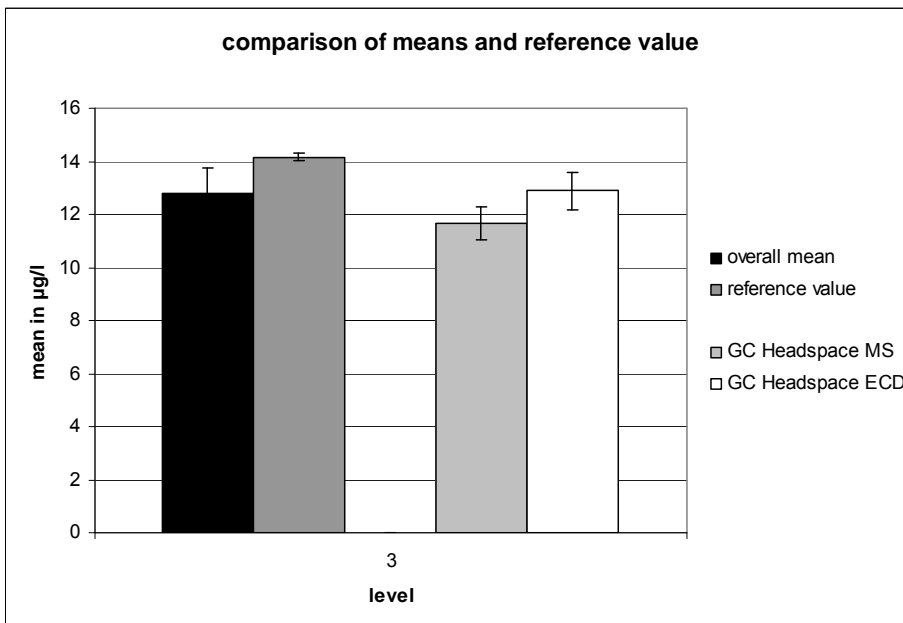
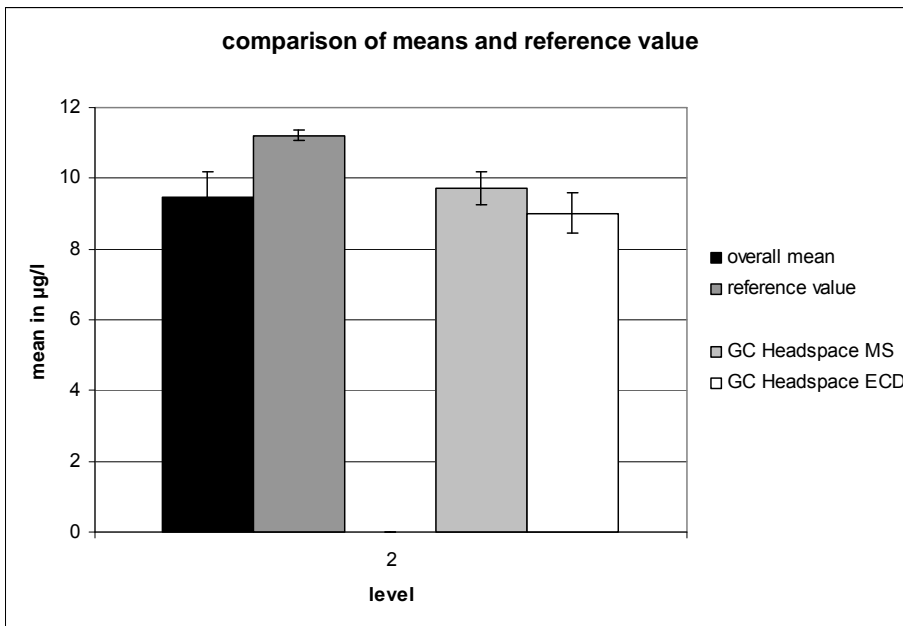
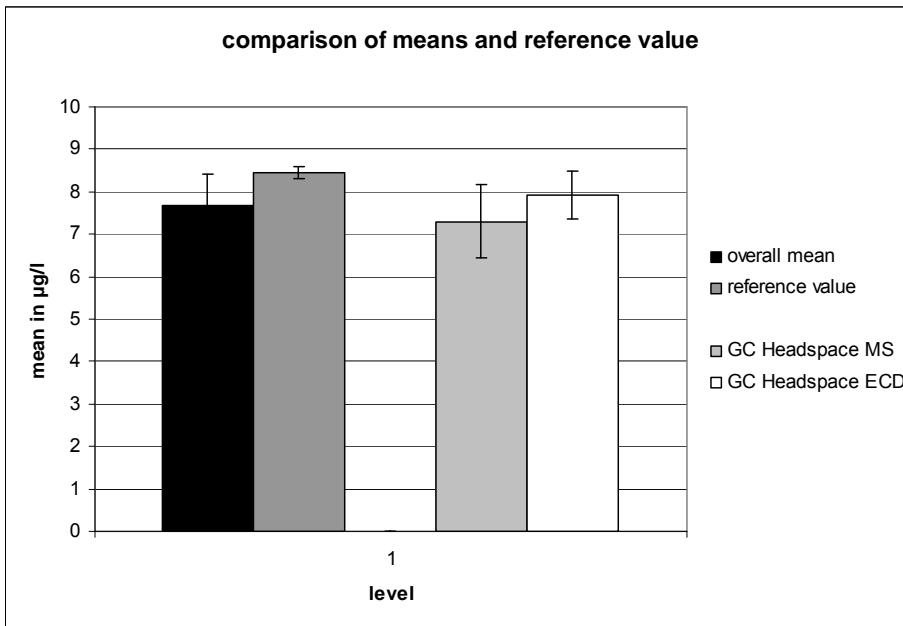
Measurement uncertainty:

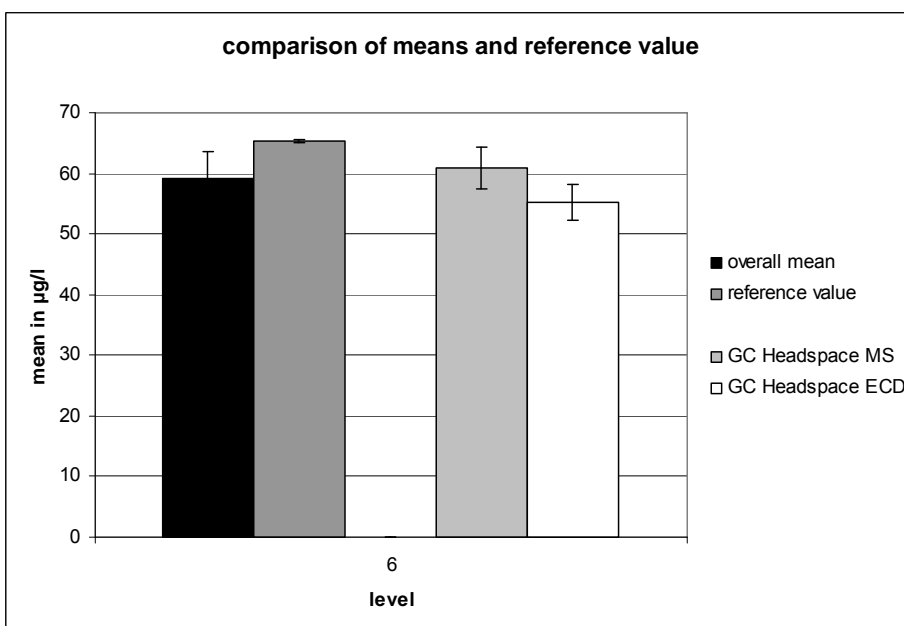
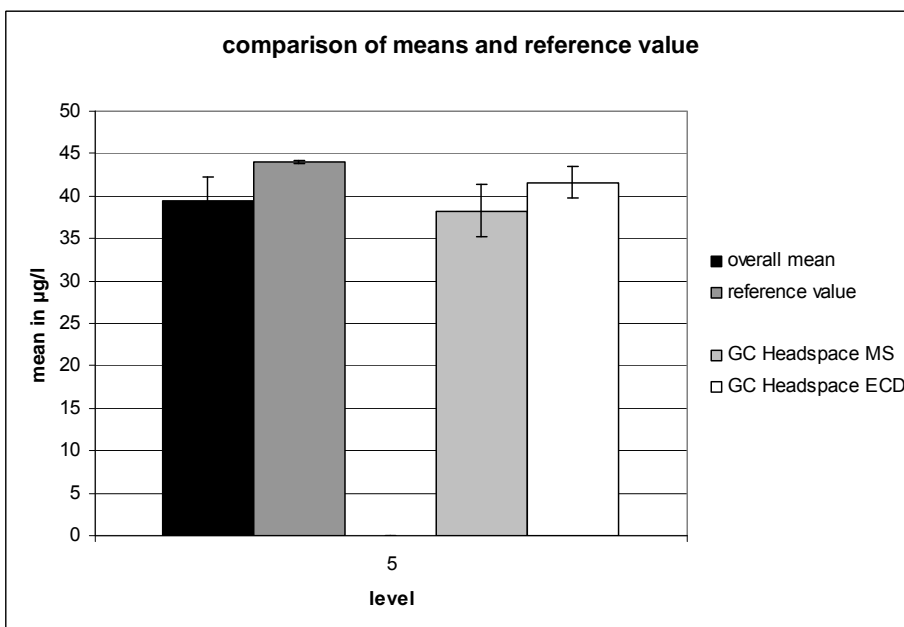
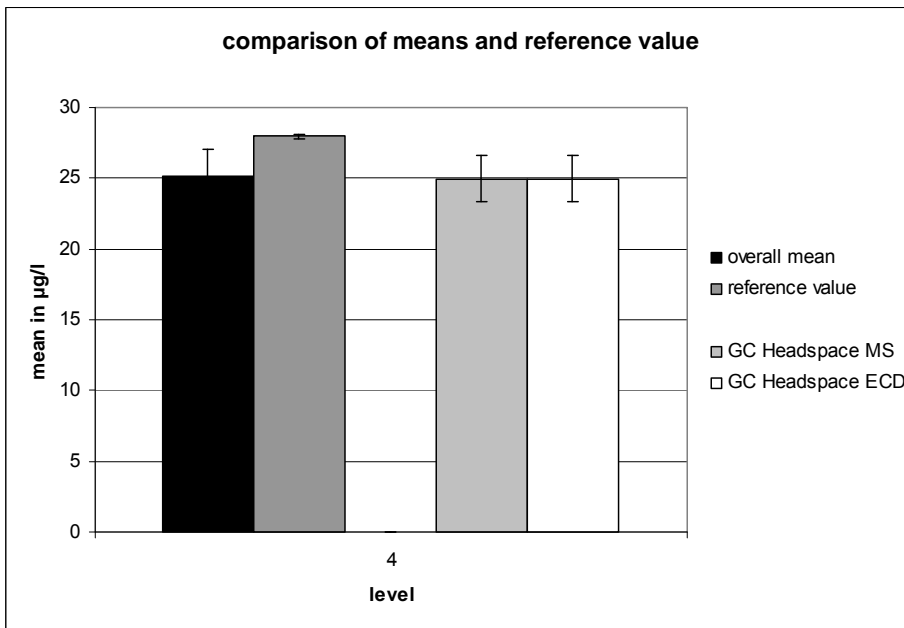


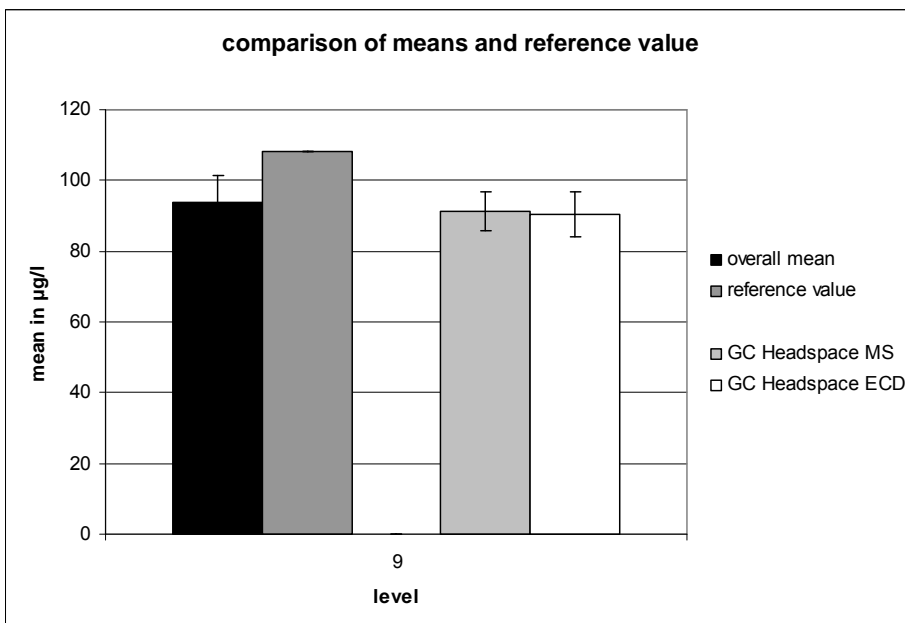
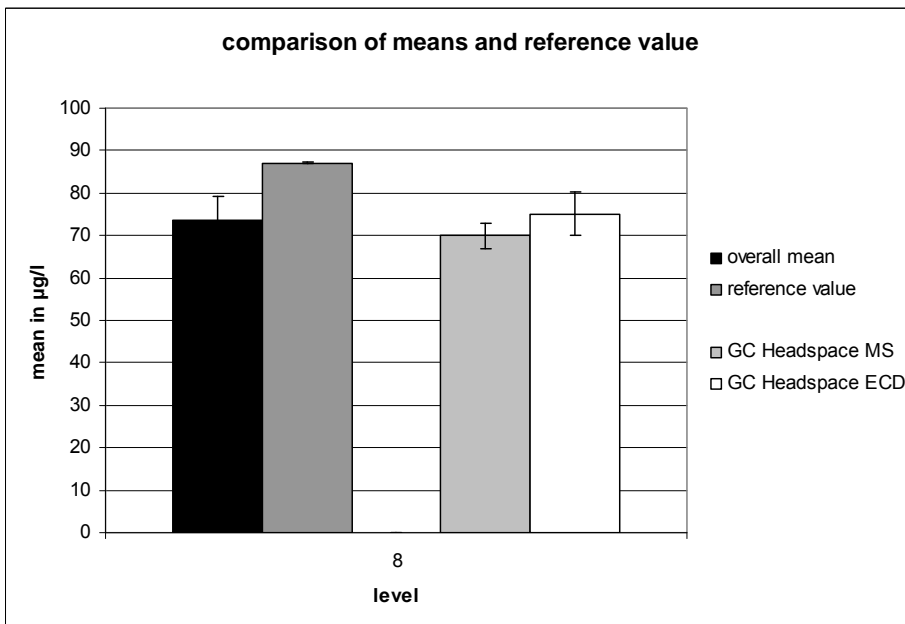
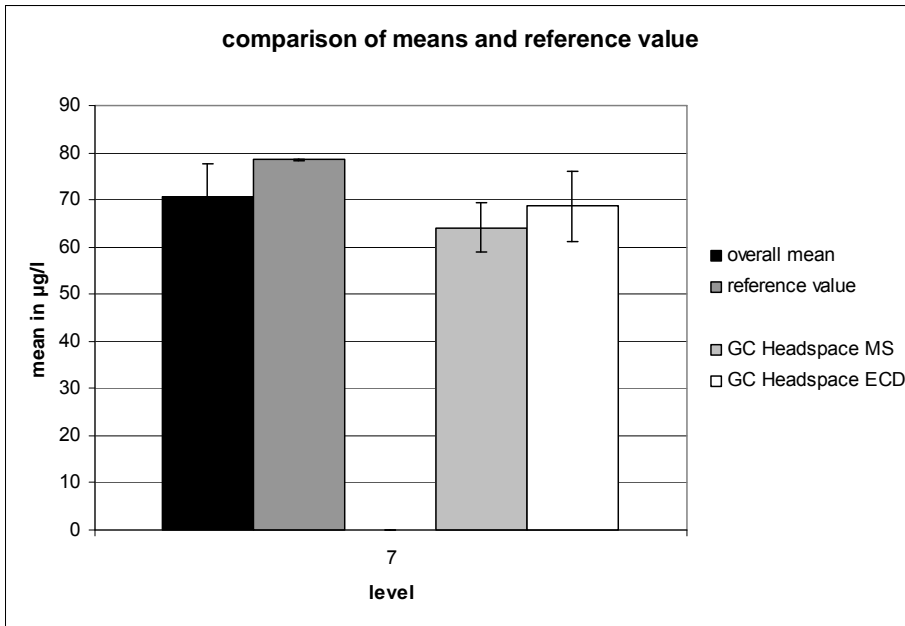
Reference values:

Level	assigned value	exp. uncertainty		reference value	exp. uncertainty.	
	[µg/l]	[µg/l]	[%]	[µg/l]	[µg/l]	[%]
1	7,666	0,7320	9,55	8,451	0,3001	3,55
2	9,484	0,6851	7,22	11,20	0,2970	2,65
3	12,79	0,9642	7,54	14,16	0,2987	2,11
4	25,12	1,8858	7,51	27,97	0,3024	1,08
5	39,45	2,7222	6,90	44,07	0,3996	0,91
6	59,22	4,3808	7,40	65,33	0,3247	0,50
7	70,83	6,824	9,64	78,495	0,3364	0,43
8	73,49	5,691	7,74	87,06	0,3385	0,39
9	93,76	7,765	8,28	108,2	0,3290	0,30

Comparison of the means und reference values:







SINGLE LEVELS

BENZENE	A-1
1,2-DICHLOROETHANE	A-28
DICHLOROMETHANE	A-55
TRICHLOROMETHANE	A-82
CARBONTETRACHLORIDE	A-109
TETRACHLOROETHENE	A-136
TRICHLOROETHENE	A-163