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Interlaboratory comparison study for the determination of halogenated hydrocarbons in water

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Abstract Sixty laboratories of five different countries participated in a large-scale interlaboratory comparison test for the determination of halogenated hydrocarbons in water. Participants used their in-house method with 44 laboratories applying head space GC ECD analysis and 5 using liquid/liquid extraction. A set of two artificially produced samples was prepared; the halogenated hydrocarbons investigated were trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trichloromethane, tetrachloromethane, 1,1-dichloroethylene, dichloromethane, dibromochloromethane, bromodichloromethane, 1,2-dichloroethane and tribromomethane. The procedure of sample preparation, storage and distribution was monitored by an extensive quality assurance system including homogeneity tests, stability tests, and trend analysis of the submitted data. The analytical results submitted by the participants exhibited RSD values of up to 35% and outlier rates of up to 19%. The percentage of false positive and false negative results was at the highest 12% for selected substances. Recovery rates varying from 86% to 106% proved the correctness of the analytical results submitted by the participants and showed that the procedure developed in this study for sample preparation and distribution is well suited for the performance of large-scale interlaboratory comparison tests of halogenated hydrocarbons in water.

1 Introduction

Halogenated hydrocarbons are a group of substances used in a variety of industrial processes as multi-purpose solvents, paint removers, metal degreasing and dry-cleaning agents [1–6]. Some of them are also chemical intermedi-

ates. The quantities produced by industry in West Europe amount to several thousand tons with dichloromethane, trichloroethylene, and tetrachloroethylene being produced in quantities of 150, 68, and 92 thousand tons, respectively, in 1997 [7]. 1,1,1-Trichloroethane and tetrachloromethane may not be produced anymore under the provision of the Montreal Protocol [7]. Anthropogenic sources appear to represent the major source of production although indications exist that halogenated hydrocarbons occur naturally as well [8]. Due to their high volatility halogenated hydrocarbons are emitted into the environment by vaporization and reach the ground and surface water along with other environmental compartments. Through the intake of water humans are exposed to halogenated hydrocarbons, thus leading to a potential health risk. Countries therefore stipulate maximum concentration levels in ground and surface water by law. In order to control these concentration levels in water the Austrian Ministry of Agriculture has developed an environmental monitoring system [9].

For monitoring purposes it is of utmost importance to be able to compare analytical results of different laboratories. Interlaboratory comparison tests represent a feasible tool to evaluate the reliability of data produced. To our knowledge large-scale interlaboratory comparison tests for halogenated hydrocarbons have been published only rarely in the recent past [10–13] so that only little is known about the reliability of the analytical data.

Therefore, need was felt to organize an international interlaboratory comparison test for the determination of halogenated hydrocarbons in water. This study was carried out under the auspices of the Analytical Quality Assurance Advisory Council (AQAAC) established by EURACHEM-Austria and financially supported by the Ministry of Agriculture in Austria. Substances included in the artificially produced water samples were trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trichloromethane, tetrachloromethane, 1,1-dichloroethylene, dichloromethane, dibromochloromethane, bromodichloromethane, 1,2-dichloroethane and tribromomethane.

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2 Participants

The interlaboratory comparison test was publicly announced in the Journal of the Austrian Association of Chemists (GÖCh) five months before the beginning of the preparation of the interlaboratory comparison test; in addition potential participants and participants of the permanent proficiency testing system of the Interuniversitäres Forschungsinstitut für Agrarbiotechnologie (IFA) Tulln [14] were personally invited. Finally, 60 laboratories participated. Analytical samples were distributed to four German, one Slovak, two Czech and four Hungarian laboratories along with 49 Austrian participants. Analytical results of 49 laboratories were received with the remaining 11 participants being unable to submit analytical data due to individual problems.

3 Materials and methods

The analytical samples distributed were artificially produced using pure substances for preparation. The halogenated compounds used were trichloroethylene (Aldrich, 99%); tetrachloroethylene (Aldrich, > 99%); 1,1,1-trichloroethane (Aldrich, 99%); trichloromethane (Aldrich, 99.8%); tetrachloromethane (Fluka, > 99.5%, p.a.); 1,1-dichloroethylene (Aldrich, 99%); tribromomethane, (Aldrich, > 99%); bromodichloromethane (Aldrich, > 98%); dichloromethane (Aldrich, 99.6%); 1,2-dichloroethane (Aldrich, > 99%); dibromochloromethane (FLUKA, purum > 97%). For the preparation of standard solutions methanol (HPLC grade, MERCK) was used as a solvent. The artificial water samples were prepared with water purified by a *MiliQ PF* (pyrogen free) device.

3.1 Preparation of analytical samples

Two samples (A and B) were produced with two different sets of halogenated substances at different concentration levels. The preparation was carried out in batches of 10 L each using 10 L volumetric flasks. To yield the appropriate concentration level in water spiking of the batches was done by adding 100 µL of the standard solutions A or B, respectively.

The standard solutions (A and B) were prepared in 500 mL Erlenmeyer flasks filled with an exactly gravimetrically determined amount of methanol. Under permanent cooling at 4 °C the pure halogenated substances were weighed in the Erlenmeyer flasks by using 50 µL and 100 µL Hamilton syringes; the amount of the halogenated compound was determined by weighing the syringe before and after adding the respective substance to the methanol solution. 100 µL of

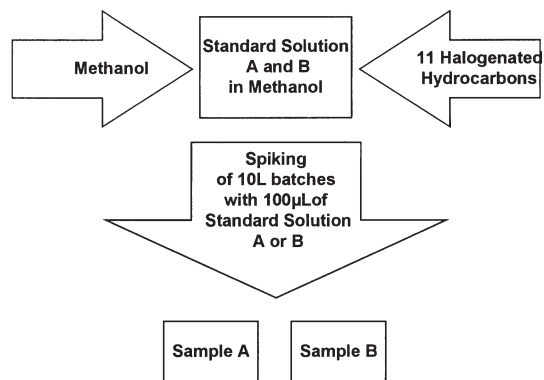


Fig. 1 Preparation procedure for samples A and B

the thus prepared solutions were then added to each of the 10 L sample batches followed by two hours of stirring at 4 °C. The preparation of the standards and the spiking was carried out in separate areas of the building to avoid any contamination of the analytical samples. The sample preparation procedure is graphically depicted in Fig. 1.

The final concentrations calculated on the basis of the amounts of halogenated compounds actually weighed in (referred to as theoretical concentrations) are listed in Tables 1 and 2. The combined uncertainty of the theoretical concentration of sample A and B was experimentally determined to be 9.8% with a confidence level of 95% covering the entire preparation procedure including the difference weighing and dilution steps.

For distribution the water samples were finally transferred into 600 mL aluminium bottles sealed with aluminium coated caps; the transfer of the liquid was achieved by using a u-shaped glass tube [13].

Prior to sample preparation all vessels used were cleaned by rinsing them thoroughly with methanol (HPLC grade, MERCK) and pentane (HPLC grade, 99+%, Sigma Aldrich), each followed by heating periods at temperatures of up to 150 °C for a total period of time of 3.5 h; aluminium bottles were heated only up to 105 °C.

3.2 Quality assurance for the preparation and distribution of the samples

Blank samples, homogeneity tests, and stability tests were carried out as measures of quality assurance. In addition trend analysis of the incoming results was performed (see results and discussion).

Blank samples were taken from both air and water. Water blanks were drawn from the 10 L batches directly; air blank samples were taken from the areas where the head space vials were filled for analysis. One batch out of nine had to be discharged because of a discovered blank value.

Table 1 Concentrations of halogenated compounds in sample A

Halogenated compound	Theoretical concentration ± uncertainty ($P = 95\%$) [$\mu\text{g/L}$]	Outlier-corrected average ± RSD found by participants [$\mu\text{g/L}$]	Stability tests: concentration ± standard deviation found by IFA Tulln [$\mu\text{g/L}$]		
			At time of dispatch ($n = 30$)	5 weeks after dispatch ($n = 9$)	Change in concentration
Tetrachloroethylene	1.46 ± 0.15	1.28 ± 0.32	1.29 ± 0.06	1.36 ± 0.14	+0.07
1,1,1-Trichloroethane	0.85 ± 0.09	0.84 ± 0.30	0.82 ± 0.03	0.84 ± 0.08	+0.02
Tetrachloromethane	1.22 ± 0.12	1.14 ± 0.30	1.10 ± 0.03	1.12 ± 0.10	+0.02
1,1-Dichloroethylene	5.28 ± 0.5	4.62 ± 1.41	4.79 ± 0.20	5.15 ± 0.36	+0.36
Bromodichloromethane	0.35 ± 0.04	0.31 ± 0.03	0.32 ± 0.02	0.33 ± 0.04	+0.01
Tribromomethane	1.54 ± 0.15	1.40 ± 0.22	1.37 ± 0.02	1.47 ± 0.10	+0.10

Table 2 Concentrations of halogenated compounds in sample B

Halogenated compound	Theoretical concentration \pm uncertainty ($P = 95\%$) [$\mu\text{g/L}$]	Outlier-corrected average \pm RSD found by participants [$\mu\text{g/L}$]	Stability test: concentration \pm standard deviation found by IFA Tulln [$\mu\text{g/L}$]		
			At time of dispatch ($n = 30$)	5 weeks after dispatch ($n = 9$)	Change in concentration
Trichloroethylene	0.88 ± 0.09	0.77 ± 0.28	0.72 ± 0.01	0.79 ± 0.03	+0.07
Tetrachloroethylene	0.89 ± 0.09	0.81 ± 0.22	0.83 ± 0.04	0.78 ± 0.04	-0.05
1,1,1-Trichloroethane	1.53 ± 0.15	1.53 ± 0.39	1.55 ± 0.05	1.41 ± 0.05	-0.14
Trichloromethane	1.56 ± 0.16	1.39 ± 0.25	1.47 ± 0.05	1.49 ± 0.05	+0.02
Tetrachloromethane	0.69 ± 0.07	0.70 ± 0.17	0.67 ± 0.02	0.63 ± 0.02	-0.04
Dichloromethane	23.1 ± 2.3	21.0 ± 4.25	19.3 ± 1.03	20.9 ± 3.2	+1.6
Dibromochloromethane	2.12 ± 0.21	2.02 ± 0.33	2.01 ± 0.04	1.87 ± 0.04	-0.14
1,2-Dichloroethane	10.5 ± 1.1	10.1 ± 1.8	10.3 ± 0.13	9.4 ± 0.40	-0.9
Tribromomethane	0.50 ± 0.05	0.49 ± 0.08	0.51 ± 0.01	0.47 ± 0.01	-0.4

To test the homogeneity two 100 mL samples of each batch were drawn during the filling of the samples into the aluminium bottles for subsequent head space GC-ECD analysis. In addition to monitoring the homogeneity of the batches, these tests also allowed to confirm the appropriate concentrations. The average value of all the analyses of the batches was taken as an indicator for the successful sample preparation, but was not taken as target value for the evaluation of the interlaboratory comparison test. The concentrations found by the IFA Tulln at the time of sample dispatch and 5 weeks after are listed in Tables 1 and 2 along with the concentrations found by the participants (outlier corrected) and the theoretical concentrations calculated based on the volumes weighed in the standard solutions.

Homogeneity criteria were set prior to the sample preparation by the advisory council (AQAAC) at 8%; any batch had to be discharged if the concentration of one single halogenated compound was found to deviate more than $\pm 8\%$ of the average concentration of the respective compound in all batches produced. One batch had to be disposed off because one single value was found not to meet the specified homogeneity criteria. All remaining substances exhibited maximum deviations of -6% to $+7\%$ with RSD values of 2.2% to 6.3% for sample A and 1.8% to 5.3% for sample B.

Stability tests were carried out 5 weeks after sample distribution by analyzing three aluminium bottles of each batch after storage at 4°C . Three head space analyses were performed per bottle. The stability tests produced satisfactory results as can be seen from Tables 1 and 2; none of the halogenated compound substances exhibited a significant decrease in concentration. Analytical results revealed deviations after 5 weeks of -9% to $+10\%$ with negative deviations equalling the positive deviations. These deviations were well within the limits of $\pm 15\%$ which is the standard deviation of the analytical method used at the IFA Tulln.

3.3 Analytical methods

3.3.1 Instructions. Participating laboratories were asked to apply their routinely used method of analysis. Preparation of calibration standards was also up to the laboratories. All participants provided information on their method of analysis along with the analytical results: 44 laboratories used head space gas chromatography with electron capture detection (ECD) with a great majority applying method DIN 38407/F5 [15], 5 laboratories chose extraction techniques based on liquid/liquid extraction. Three participants used mass spectrometry for peak identification in addition.

3.3.2 Analytical methods for quality assurance. The analysis of the IFA Tulln for the quality assurance purposes were carried out on a Hewlett Packard 5890 II GC ECD with a head space sampler, Hewlett Packard 7694, using a GC column, Hewlett Packard Ultra 1

(25 m, 0.32 mm, 0.52 μm), with a temperature gradient ranging from 25°C to 85°C . Head space sampling was done in 20 mL vials filled with 10 mL of sample solution.

3.4 Evaluation of results

Identification of outliers was carried out by the Hampel test. This test is recommended for the statistical evaluation of interlaboratory comparison tests by Davies [16]. The Hampel test takes into account the specific deviation of the incoming results of the participants thus producing individual exclusion criteria for each halogenated substance [17].

As had been stipulated by the advisory council AQAAC, the "true values" of the samples were defined as the outlier corrected averages of the results submitted by the participants. False negative results were defined taking into consideration the limit of detection (LOD) of each individual participants. Negative results for halogenated compounds present in the sample at concentration levels below the individual LOD of the respective participant were not counted as false negative. False positive values were all those results where halogenated components were reported to be found by the participants although these substances were not added to the sample; this definition was applied irrespective of the concentration reported or the individual LOD of the participating laboratory.

Recovery rates of the outlier-corrected average of the participants were calculated on the basis of the theoretical concentration levels using the volumes actually weighed in. These recovery rates were used as a mean to confirm the successful sample preparation and distribution, but were not taken into account for the evaluation of a participant's performance.

As performance criteria for the individual laboratories, recovery rates of the results submitted were calculated on the basis of the outlier corrected average.

The organizing institution (IFA Tulln) did not carry out any performance evaluation of the individual participants; laboratories were not classified into successful and not successful participants. Any performance evaluation was left to the participants. This procedure was chosen by the advisory council, AQAAC, considering the large variety of laboratories with their individual motivations for participation.

A detailed trend analysis of the submitted results was performed as well. For this purpose the outlier corrected analytical data were transformed into functions of a depending variable (concentration) and an independent variable (the data of analysis of the submitting laboratory). In order to demonstrate that the incoming results showed no significant tendency in the level of concentration, regression analysis was carried out along with F-test statistics. The trend analysis can also be regarded as a further quality assurance measure in view of its power to assess the stability of the samples

independently from the organizer over the entire time period between sample distribution and deadline for submission of analytical results.

4 Results and discussion

4.1 Evaluation of the procedure used for sample preparation and distribution

The recovery rates of the theoretical concentration calculated on the basis of the outlier corrected average values submitted by the participants represent the most appropriate tool to evaluate the sample preparation and distribu-

Table 3 Recovery rates of the outlier-corrected average of the participants' results calculated on the basis of the theoretical concentration

Halogenated compound	Recovery sample A \pm confidence interval	Recovery sample B \pm confidence interval
Trichloroethylene	–	89 \pm 13%
Tetrachloroethylene	88 \pm 9%	92 \pm 10%
1,1,1-Trichloroethane	99 \pm 14%	98 \pm 10%
Trichloromethane	–	89 \pm 7%
Tetrachloromethane	93 \pm 9%	106 \pm 10%
1,1-Dichloroethylene	88 \pm 13%	–
Dichloromethane	–	91 \pm 8%
Dibromochloromethane	–	95 \pm 7%
Bromodichloromethane	89 \pm 4%	–
1,2-Dichloroethane	–	95 \pm 8%
Tribromomethane	91 \pm 15%	98 \pm 7%

Remark: "–" Substance was not added to the water sample

Table 4 Results of regression analysis and F-test statistics for sample A and B

Halogenated compound	Regression analysis of sample A			
	Sample A	F-value calculated	F (95%)	F (99%)
Tetrachloroethylene	$y = 1.15 + 0.009 x$	1.30	3.22	5.15
1,1,1-Trichloroethane	$y = 0.85 - 0.001 x$	0.01	3.21	5.14
Tetrachloromethane	$y = 1.07 + 0.005 x$	0.39	3.23	5.16
1,1-Dichloroethylene	$y = 4.38 + 0.019 x$	0.19	3.34	5.45
Bromodichloromethane	$y = 0.33 - 0.001 x$	2.78	3.32	5.39
Tribromomethane	$y = 1.25 + 0.011 x$	3.42	3.26	5.25
Halogenated compound	Regression analysis of sample B			
	Sample B	F-value calculated	F (95%)	F (99%)
Trichloroethylene	$y = 0.79 + 0.001 x$	0.068	3.22	5.15
Tetrachloroethylene	$y = 0.75 + 0.009 x$	1.23	3.23	5.18
1,1,1-Trichloroethane	$y = 1.49 + 0.003 x$	0.08	3.25	5.23
Trichloromethane	$y = 1.39 + 0.001 x$	0.06	3.27	5.27
Tetrachloromethane	$y = 0.66 + 0.002 x$	0.41	3.29	5.34
Dichloromethane	$y = 21.4 - 0.005 x$	0.003	3.26	5.31
Dibromochloromethane	$y = 2.16 - 0.006 x$	0.32	3.24	5.19
1,2-Dichloroethane	$y = 9.37 + 0.045 x$	0.82	3.28	5.31
Tribromomethane	$y = 0.48 + 0.001 x$	0.03	3.29	5.34

Remark: $y = d + k x$ represents a linear correlation between y (the concentration of the compound found in the sample [$\mu\text{g/L}$]) and the time of analysis x (days after sample distribution) with k being the slope of the linear trend. F-values are calculated on the basis of the results submitted and compared to those given for certain levels of probability. F (95%) and F (99%)

tion. The results are listed in Table 3. All recovery rates ranged between 87% and 106%.

The results for the recovery rates are highly satisfactory in view of the low concentration of most of the halogenated compounds in the samples and the high number of analytes. It has to be stressed at this point that only recovery rates calculated on the same basis can be compared. The fact that the Hampel outlier test was used as a selection criterion for acceptance of analytical results makes these results only comparable to other results of interlaboratory comparison tests that used the same selection criterion. To our best knowledge no such data have yet been published.

4.2 Trend analysis

The submitted results were transformed into functions of the concentration depending on time. To assess any possible trend in the level of concentration, regression analysis was carried out assuming a linear relationship between time and concentration. F-test statistics was applied to find out whether any possible trend in concentration was significant. If the F-value calculated on the basis of the analytical results is inferior to the statistical F-value given for certain probabilities (usually 95% and 99%) and numbers of values, the slope of the regression analysis is not significantly superior to zero; in other terms, if the calculated F-value is below the given F-value for a certain probability, there is no significant shift in the level of concentration.

In Table 4, the results of both, the regression analysis and the F-test statistics are depicted.

The regression analysis yielded linear correlations between the concentrations submitted by the participating laboratories [in $\mu\text{g/L}$] and the time of analysis [in days af-

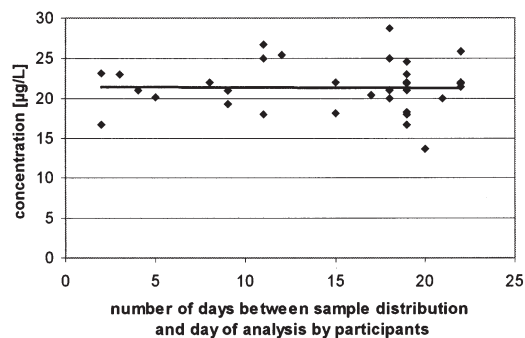


Fig. 2 Regression analysis of dichloromethane vs. time

Table 5 Number of false negative and false positive results for sample A and B

Halogenated compound	False positive results	False negative results
Trichloroethylene	Sample A: 5	0
Tetrachloroethylene	0	Sample B: 1
1,1,1-Trichloroethane	0	0
Trichloromethane	Sample A: 4	0
Tetrachloromethane	0	Sample A: 1; sample B: 2
1,1-Dichloroethylene	Sample B: 3	Sample A: 1
Dichloromethane	Sample A: 1	0
Dibromochloromethane	0	Sample B: 1
Bromodichloromethane	0	Sample A: 2
1,2-Dichloroethane	Sample A: 2	0
Tribromomethane	0	Sample A: 3

Remark: Only false positive/negative result are listed. No entry or "0" indicates that no false positive/negative results were submitted

ter sample distribution]. This correlation is graphically depicted for dichloromethane in Fig. 2.

The F-test statistics revealed that for all substances, except for tribromomethane, the slope of the linear trend (represented by the slope k of the regression analysis) is not significantly different from zero; this means that the submitted results show no trend in the concentration level. Tribromomethane, however, appears to have a positive trend in the concentration level. Due to the positive value of the linear trend, sample instability cannot be the reason for the shift in concentration.

The trend analysis as a tool of quality assurance revealed that in none of the samples a degradation of the halogenated substance could be found.

Table 6 Average values, RSD and outlier rates (in per cent of all results submitted) for sample A

Halogenated compound	Theoretical concentration \pm uncertainty [$\mu\text{g/L}$]	Outlier-corrected average \pm RSD found by participants [$\mu\text{g/L}$]	RSD [%]	Outlier rate [%]
Tetrachloroethylene	1.46 ± 0.15	1.28 ± 0.32	27	11
1,1,1-Trichloroethane	0.85 ± 0.09	0.84 ± 0.30	35	5
Tetrachloromethane	1.22 ± 0.12	1.14 ± 0.30	26	7
1,1-Dichloroethylene	5.28 ± 0.5	4.62 ± 1.41	31	10
Bromodichloromethane	0.35 ± 0.04	0.31 ± 0.03	9.7	19
Tribromomethane	1.54 ± 0.15	1.40 ± 0.22	16	3

4.3 False positive and false negative values

False negative values were defined taking into consideration the individual limit of detection (LOD) (see 3.4 Evaluation of results). False positive values were defined regardless of the concentration level.

In Table 5, the false positive and false negative results are depicted. The highest number of false positive values was found for trichloroethylene with 5 false positive results corresponding to about 12% of all results submitted. The concentrations of false positive results reported were relatively high, ranging from $0.1 \mu\text{g/L}$ to $20 \mu\text{g/L}$. It is therefore very unlikely that false positive results originate from impurities contained in the pure substances of the halogenated compounds (assuming a similar high response factor for impurities and halogenated compound). No false positive results were submitted for the compound, the pure substance of which had the lowest purity (dibromochloromethane with a purity of $> 97\%$). The highest number of false negative results was found for tribromomethane with 3 false negative results corresponding to about 7.5% of all data submitted for this halogenated compound. Overall, very few false positive and false negative results were received, revealing that the participating laboratories were well performing their analyses within their individual working range of concentration.

4.4 Average value found, RSD and outlier rates

To identify outliers the Hampel outlier test was applied. The numbers of outliers are listed in Tables 6 and 7 for sample A and B. The highest outlier rate of about 19% was found for the detection of bromodichloromethane (6 out of 32) in sample A; for sample B the highest rate of outliers was found to be 14% for dichloromethane and dibromochloromethane (5 out of 36). Outlier rates of up to 19% appear to be high at first glance; considering the fact that there was also a considerable number of participants that do not run analysis of halogenated substances at such low concentrations on a routine basis, an outlier rate of 19% can be regarded acceptable.

After identification of the outliers, the average value of the results submitted was calculated (results listed in Tables 6 and 7). These data were then taken to calculate the recovery rates based on the theoretical concentration to assess the procedure of sample preparation and distribution

Table 7 Average values, RSD and outlier rates (in per cent of all results submitted) for sample B

Halogenated compound	Theoretical concentration \pm uncertainty [$\mu\text{g/L}$]	Outlier-corrected average \pm RSD found by participants [$\mu\text{g/L}$]	RSD [%]	Outlier rate [%]
Trichloroethylene	0.88 ± 0.09	0.77 ± 0.28	35	7
Tetrachloroethylene	0.89 ± 0.09	0.81 ± 0.22	26	12
1,1,1-Trichloroethane	1.53 ± 0.15	1.53 ± 0.39	27	12
Trichloromethane	1.56 ± 0.16	1.39 ± 0.25	18	13
Tetrachloromethane	0.69 ± 0.07	0.70 ± 0.17	24	5
Dichloromethane	23.1 ± 2.3	21.0 ± 4.25	20	14
Dibromochloromethane	2.12 ± 0.21	2.02 ± 0.33	17	14
1,2-Dichloroethane	10.5 ± 1.1	10.1 ± 1.8	18	6
Tribromomethane	0.50 ± 0.05	0.49 ± 0.08	17	5

(see 4.1). Furthermore, the outlier-corrected average together with the recovery rates can be taken to judge the correctness of the analysis of the participants. With recovery rates ranging from 86% to 106% the correctness of the data submitted is very good for organic trace analysis.

RSD values were calculated on the basis of the outlier corrected results. As is depicted in Tables 6 and 7, RSD values range from 9.7% to 35%. RSD values of up to 35% are undoubtedly high and show that the analytical results of the participants are relatively widely spread.

5 Conclusions

Homogeneity tests, stability tests and recovery rates proved that the procedure developed in this study for sample preparation and distribution is well suited for the performance of large-scale interlaboratory comparison tests of halogenated hydrocarbons in water. Trend analysis of the submitted results revealed that there was no shift in concentration in the course of time between sample dispatch and deadline for data submission for any of the halogenated compounds investigated, except for tribromomethane. For tribromomethane a positive trend of the incoming results was found. After sample dispatch, degradation of the halogenated compounds during sample storage and distribution can thus be disregarded.

The results of this interlaboratory comparison test revealed that the correctness of the analysis of halogenated hydrocarbons in artificially contaminated water samples is good with recovery rates calculated on the basis of the theoretical concentration ranging from 85% to 106%. The percentage of false positive and false negative results is at the highest 12% and 7.5%, respectively, for selected substances. Although the outlier rate appears high with values of up to 19% of the data submitted, it is still acceptable considering the participation of a certain number of laboratories that do not perform halogen analysis on a routine basis at such a low concentration level. Recovery rates

and the number of false positive and false negative values proved that the participating laboratories appear to be able to analyze well within their individual working ranges of concentration, although high RSD values of up to 35% were found indicating that the analytical data of halogenated hydrocarbons produced from different laboratories are relatively widely spread.

The results of this study show that there is further need for large-scale interlaboratory comparison tests or permanent proficiency testing systems to make analytical data of halogenated hydrocarbons more comparable.

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