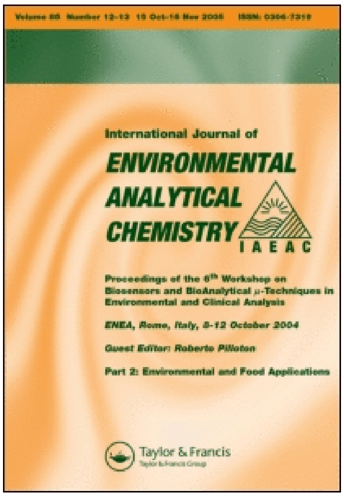

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A PROFICIENCY TESTING SYSTEM FOR THE DETERMINATION OF VOLATILE HALOGENATED HYDROCARBONS AT μg/L CONCENTRATION LEVEL IN WATER

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Fourteen laboratories participated in the Austrian proficiency testing scheme (PTS) for monitoring of volatile halogenated hydrocarbons in ground water from July 1996 to January 1998. The PTS enabled to supervise the analytical performance in the μg/L range and revealed that the participating laboratories analysed with average recoveries ranging from 91% to 98%. The inter-laboratory standard deviation was found to range from 10% to 30%. Accompanying quality assurance measures showed that both, stock solutions in methanol and artificially prepared aqueous samples containing halogenated hydrocarbons are stable for at least 111 days and 81 days, respectively. As far as storage conditions are concerned, 60 mL of head space of air above 600 mL of sample solution had only a minimal impact on the concentration of six most volatile halogenated hydrocarbons after 63 days. The sample preparation procedure was found to be well suited for the operation of the PTS.

It was possible to prepare homogeneous synthetic samples with known concentration within a bandwidth of ±10%. Moreover, the batch-wise sample preparation procedure was designed in such a way that no compound could evaporate despite its volatility. The present study revealed that permanent proficiency testing is a useful and powerful tool to make environmental monitoring more reliable and effective.

Keywords: Proficiency testing; Volatile halogenated hydrocarbons; Water analysis; Quality assurance; Environmental monitoring

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INTRODUCTION

Halogenated hydrocarbons are a group of contaminants that attract more and more attention in environmental monitoring. The increasing interest in these substances emerges from their distribution in the natural environment and from the potential health risk they pose to humans and the ecosystem. Some of the halogenated hydrocarbons are known to be carcinogenic agents and many of them are suspected to induce malign tumors in humans [1–8]. Anthropogenic sources appear to represent the major source for halogenated hydrocarbons [9], although indications exist that some of them occur naturally as well [10]. Through volatilization they reach ground and surface water along with other environmental compartments. Humans are exposed to halogenated hydrocarbons through the intake of water, which leads to a potential health risk. Most countries have therefore put halogenated hydrocarbons on top of their priority lists for environmental monitoring.

For monitoring purposes the comparability of results from different laboratories is of utmost importance. Proficiency testing systems (PTS) represent feasible tools to evaluate the reliability of data produced. The Austrian Federal Ministry for Agriculture and Forestry therefore charged the Institute for Agrobiotechnology in Tulln (IFA-Tulln) with the establishment of a PTS for trace determination of halogenated hydrocarbons in water. It is to be operated on a continuous basis within the framework of Austria's legislation on the quantitative assessment of the quality of groundwater and streams [11]. Moreover, participation in the PTS was open to any laboratory.

Although now there are about 40 PTS for water analysis in Europe, only few of them offer volatile halogenated hydrocarbons. To our knowledge, this PTS for volatile halogenated hydrocarbons is the first so far published, which is based on ready-to-analyse water samples, containing only small traces of solvent (< 10 mg/l methanol).

The goal of the PTS was a close supervision of the quality of analysis of those laboratories that perform routine analyses on the basis of a government contract. The system involved the periodical distribution of water samples spiked with known traces of halogenated hydrocarbons. The laboratories were asked to analyse these synthetic samples under routine conditions. By statistic evaluation of the analytical results an assessment of the laboratories' performance was possible. The commissioner thus obtained a tool to supervise the quality of their subcontracting laboratories. Substances investigated in this study were trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, trichloromethane, tetrachloromethane, 1,1-dichloroethylene, dichloromethane, dibromochloromethane, bromodichloromethane, 1,2-dichloroethane, and tribromomethane.

THE PROCEEDINGS OF THE PROFICIENCY TESTING SYSTEM

Six laboratories that routinely perform analyses within the assessment of water quality in Austria organised by the Federal Ministry for Agriculture and Forestry were obliged to participate. The evaluation of their performance over the entire course of operation was disclosed to the commissioner. Including laboratories taking part voluntarily the number of participants was 14 on average. The names of the participants cannot be published in this study, due to confidentiality reason.

The PTS is designed as an external quality assurance tool to periodically check the quality of analysis of a number of laboratories. This is achieved by producing at certain intervals synthetic water samples spiked with known traces of halogenated hydrocarbons. The samples are distributed to the participants after a one-week's in-advance warning. The organising institution (IFA-Tulln) knows the target concentrations of the samples, which are calculated from the masses of substances weighed in. Once the samples were received by the laboratories they were asked to perform their analysis as soon as possible, but under routine conditions ensuring that no additional precautions were taken for analysing the IFA-control samples. The analytical results have to be submitted within five weeks after sample dispatch. They are statistically assessed and one week after the dead-line, a final report is produced involving an analyte-oriented and a laboratory-oriented evaluation of the results. The evaluation contained a listing and a graphic depiction of the target values along with individual recoveries and the results of the stability tests performed five weeks after sample dispatch; moreover the average concentrations [μg/L] and the average recoveries of the target values [%] were calculated on the basis of all results and of the results within the tolerance limits (of 45%) and given in the reports as well.

EXPERIMENTAL

The synthetic samples distributed were 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 *MilliQ* PF device from Millipore.

The analyses for quality assurance purpose 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 of vials filled with 10 ml of sample.

PREPARATION OF PROFICIENCY TESTING SAMPLES

Prior to sample preparation all vessels were cleaned by rinsing 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 3.5 h. Aluminium bottles were heated up to 105°C.

For each PTS cycle, 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 a 10 L volumetric flask. 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 a gravimetrically exactly determined volume 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 substances to the methanol solution. 100 µL of the thus prepared solutions were then added to each of the 10 L sample batch 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 target concentrations were calculated on the basis of the masses of halogenated compounds actually weighed in. The combined uncertainty of the target values of samples A and B were experimentally determined to be approximately 10% 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 10 L batches was achieved by using a U-shaped glass tube [12].

The entire sample preparation procedure was accompanied by a system of quality assurance (QA) measures to ensure traceability; moreover, the QA measurers revealed important facts about head space analysis of halogenated hydrocarbons in general and the stability of samples and standards in particular.

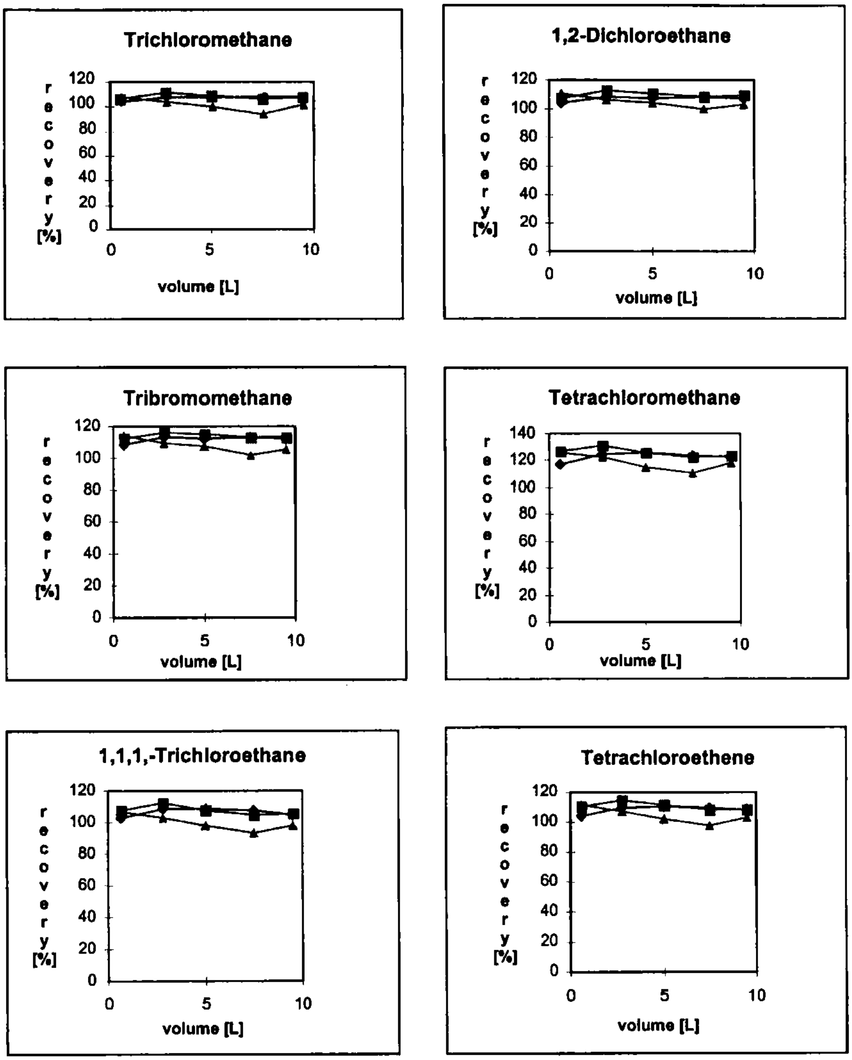
RESULTS AND DISCUSSION

Quality Assurance for the Preparation and Distribution of the Samples

Due to the volatile nature of halogenated hydrocarbons it was deemed necessary to monitor concentration profiles during the transferring process of the aqueous solution into the 600 mL aluminium bottles before the actual launching of the PTS to ensure that the analytes do not get lost. During routine operation of the PTS the concentration levels of the synthetic samples were checked by in-house analysis before each sample dispatch. Moreover, blank samples and stability tests were carried out as QA measures.

Concentration Profiles

After spiking with the stock solutions the 10 L of sample solution were transferred into the aluminium bottles by using a U-shaped glass tube, which was already successfully used by Landvoigt [12]. The whole transfer process usually took about 45 min to 60 min per batch. During this time period the concentration of the halogenated compounds was closely monitored, firstly, to ensure that the analyte substances do not get lost and, secondly, to ensure homogeneity. In a separate experimental set up which was carried out as a preliminary study, five samples of 100 mL each were taken during the transfer process using 100 mL Erlenmeyer flasks with glass stoppers that were consecutively analysed by head space GC-ECD. The results of the analyses are graphically depicted in Fig. 1 for three different batches.



Trichloromethane

1,2-Dichloroethane

Tribromomethane

Tetrachloromethane

1,1,1,-Trichloroethane

Tetrachloroethene

FIGURE 1 Concentration profiles of halogenated hydrocarbons during the transfer process as a function of volume [L]. Three different batches are indicated by the symbols ◆, ■ and ▲ respectively.

The diagrams show the concentration profile of the substances found with head space GC-ECD analysis as a function of the volume (litres) of aqueous sample already transferred into the aluminium bottles. It was revealed that even the most volatile compound trichloromethane exhibited no significant decrease in concentration during the almost one hour lasting transfer process. A non-significant trend is assumed when the concentrations do not vary more than ±20%, which is estimated to be the uncertainty of the analytical procedure applied in this study. The unexpected high recoveries for tetrachloromethane could be traced back to an error in the preparation of the calibration standard. These recoveries were not corrected, because the only aim of this experiment was to investigate concentration changes caused by the transfer process. Concluding for all eleven compounds from this investigation on six compounds – due to their similar vapour pressures – homogeneity was proven and one unique concentration level could be guaranteed for the halogenated compounds in the different aluminium bottles that were filled during the transfer process and consecutively dispatched to the participants.

Blank Samples

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. During the 2 years' operation of the proficiency testing system, no batch had to be discharged because of a discovered blank value.

Confirmation of the Target Values

During the routine operation of the PTS, 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 to confirm the appropriate concentrations of halogenated hydrocarbons in the samples, the target values. The average value of all the analyses of the batches (usually three) was called "IFA recovery". It was taken as an indicator for the successful sample preparation reconfirming the target values. The IFA recoveries along with the average values of the participants' recoveries that were within the tolerance levels (±45%) are depicted in Fig. 2. The assessment of the IFA recoveries proved that it was possible to prepare sample with an exactly pre-defined concentration with only minor deviations of typically ±10%.

Stability Tests

Long-term stability tests were carried out of both the aqueous sample solutions and the stock solutions in methanol for all eleven investigated

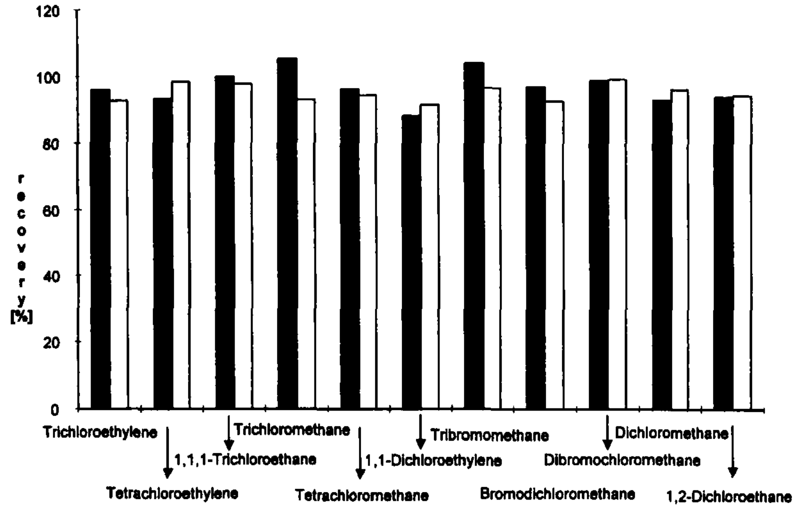


FIGURE 2 Average recoveries of 5 cycles of the proficiency testing system of IFA-Tulln and calculated on the results of participants within the tolerance limits of ±45%. Black bars are recoveries of IFA-results, white bars indicate recoveries of the participants.

halogenated hydrocarbons. To comply with the requirements of the PTS operation, stability was to be proven for a time period of at least 5 weeks (35 days), which was the deadline for data submission during the operation of the PTS. Not all compounds were investigated at the given intervals for efficiency reasons since stability test were synchronized in time with the recovery measurements for sample dispatch of future PTS rounds. The aqueous samples were analysed by head space GC-ECD at the time of sample dispatch, to confirm the target value, and 47, 81, 162, and 277 days after sample dispatch. The results of the stability test are summarised in Table I. At the time of dispatch recoveries range from 86% to 107% – with the exception of 1,1-dichloroethylene. Since the uncertainty of the analytical procedure applied in this study is estimated at about ±20%, the results of the initial recoveries at the time of sample dispatch are satisfactory. 1,1-Dichloroethylene was found at too low concentrations during the entire stability test so that it has to be assumed that stock solution B used for spiking contained a too low concentration of 1,1-dichloroethylene. As far as the results of the long-term stability tests are concerned, the recoveries after 41, 81, 162 and 277 days of sample dispatch exhibited no significant downward trends being within the limits of ±20% of the theoretical recovery of 100%.

TABLE I Recoveries of the target concentrations of halogenated hydrocarbons in aqueous sample solutions after 47, 81, 162 and 277 days; "–" indicates that the substance was not determined at the time

Substance name	*Days after dispatch*				
	At dispatch (%)	*47* (%)	*81* (%)	*162* (%)	*277* (%)
1,1-Dichloroethylene	74	83	–	78	–
Dichloromethane	86	91	–	85	–
Trichloromethane	107	–	81	–	93
1,2-Dichloroethane	92	94	–	98	–
1,1,1-Trichloroethane	98	96	89	119	119
Tetrachloromethane	93	91	96	111	123
Trichloroethylene	92	88	91	112	116
Dibromochloromethane	102	111	–	108	–
Bromodichloromethane	96	95	95	–	–
Tetrachloroethylene	90	83	87	109	122
Tribromomethane	103	100	97	94	101

The aqueous samples are therefore found to be stable: For bromodichloromethane stability could be proved for a time of up to 81 days. For all other investigated halogenated hydrocarbons a high degree of stability could be proved for a time period of up to 162 days. Some selected halogenated substances were even found to be stable for up to 277 days. The results of these tests thus exceeded by far the minimum requirement of a proven stability up to 5 weeks. As far as 1,1-dichloroethylene is concerned, the substances appeared to be stable in the long run, since the concentration – although too low on average for all analyses performed – remained constant over the entire time period.

In addition to the stability tests of the aqueous samples, the concentrations of the various halogenated hydrocarbons in the methanolic stock solutions were determined over a period of 111 days. For this purpose, the stock solutions were stocked in a dark environment at a temperature of 4°C in 500 mL glass Erlenmeyer flasks. After certain intervals, aqueous solutions were freshly prepared and analysed by head space GC-ECD. Calibration was always done with newly prepared standards. The results are depicted in Table II. Even after 111 days, the stock solutions were found to be stable with recoveries ranging from 94% to 109%.

Impact of Head Space above Samples Solution

Due to their high vapour pressure halogenated hydrocarbons are prone to volatilisation. This is why standard methods or standard operation procedures recommend that no head space be left above the liquid sample into which the analyte could evaporate. Only Ho [13] reported that partially filled bottles could be stored for two days without significant losses. In the present study the influence of a 60 mL head space of air was investigated by analysing samples that were stored at 4°C in aluminium bottles over a period of 63 days. The samples investigated had concentrations ranging from 0.64 µg/L to 0.77 µg/L. The results of the analyses are listed in Table III. It reveals that 82% to 103% of the theoretical concentration that was originally weighed in could be recovered in the aqueous sample solution after 63 days. When comparing these findings with the recoveries yielded from the stability tests of aluminium bottles sealed without head space (Table I) which ranged from 83% to 100% after 47 days and from 81% to 97% after 81 days it can be concluded that concentrations tend to

TABLE II Recoveries of concentrations of methanolic standard stock solutions 63, 67, and 111 days after preparation; "–" indicates that the substance was not determined

Substance name	*Days after preparation*		
	63 (%)	*67* (%)	*111* (%)
1,1-Dichloroethylene	–	–	98
Dichloromethane	–	–	96
Trichloromethane	98	–	94
1,2-Dichloroethane	–	–	94
1,1,1-Trichloroethane	94	103	105
Tetrachloromethane	103	100	106
Trichloroethylene	107	–	101
Dibromochloromethane	–	–	99
Bromochloromethane	–	100	100
Tetrachloroethylene	102	–	97
Tribromomethane	107	111	109

TABLE III Recoveries of target concentrations after 63 days of storage at 4°C with head space of 60 ml above sample solution of three different samples (1–3)

Substance name	*Sample #*		
	1 (%)	*2* (%)	*3* (%)
Trichloromethane	84	82	84
1,1,1-Trichloroethane	82	80	85
Tetrachloromethane	86	80	88
Trichloroethylene	92	90	92
Tetrachloroethylene	86	82	88
Tribromomethane	100	103	100

decrease slightly when samples are stored with a high-volume head space, but it proves that a possible head space above a water sample containing volatile halogenated hydrocarbons is not as important as had previously been assumed. This is a fairly unexpected result. It appears that stability is rather a question of perfectly sealed sample containers than a question of head space left above the sample.

EVALUATION OF THE PARTICIPANTS' PERFORMANCE

Average Recovery of Participants

Over a time period of approximately two years, on average 14 laboratories took part in the five cycles of the PTS for halogenated hydrocarbons. The participants' average recovery was chosen as a performance indicator. It was calculated on the basis of the results submitted that were within the exclusion criteria of ±45%. The concentrations of the halogenated hydrocarbons in the individual proficiency testing samples of cycle 1–5 are summarised in Table IV. Over the first five cycles the average recovery for the eleven compounds ranged from 91% to 98%. By this the outcome of the first five cycles of the PTS for the determination of volatile substances in the μg/L range in water, can be judged excellent. This provided that the participating laboratories are capable of analysing at the low concentration levels investigated.

TABLE IV Target concentrations of analyte compounds of sample A/B for the first five cycles; "–" indicates that the respective substance was not added to the sample

Substance name	*1. cycle* [μg/L]	*2. cycle* [μg/L]	*3. cycle* [μg/L]	*4. cycle* [μg/L]	*5. cycle* [μg/L]
Trichloroethylene	–	0.69/1.38	0.88/1.32	0.56/0.83	0.40/1.36
Tetrachloroethylene	–	0.69/1.38	0.90/1.35	1.0/0.63	0.53/1.52
1,1,1-Trichloroethane	0.46/0.46	0.73/1.45	0.94/1.41	0.61/0.92	0.35/0.73
Trichloromethane	–	0.64/1.27	–	2.6/1.84	1.0/0.55
Tetrachloromethane	0.44/0.43	0.72/1.43	0.91/1.37	0.92/0.61	0.47/1.0
1,1-Dichloroethylene	–	–	5.12/7.68	2.8/4.8	–
Tribromomethane	0.49/0.49	0.77/1.54	1.06/1.58	0.52/0.54	0.25/0.74
Bromodichloromethane	0.37/0.37	–	–	–	1.15/0.65
Dibromochloromethane	–	–	1.96/2.94	2.3/1.9	–
Dichloromethane	–	–	24.5/36.8	–	0.86/2.6
1,2-Dichloroethane	–	–	23.2/34.7	12.0/15.0	0.70/4.3

TABLE V Inter-laboratory relative standard deviations [%], averaged for results of sample A and B for each cycle

Substance name	*Between-lab. RSD*				
	1. cycle (%)	*2. cycle* (%)	*3. cycle* (%)	*4. cycle* (%)	*5. cycle* (%)
Trichloroethylene	–	25	22	15	17
Tetrachloroethylene	–	17	24	15	16
1,1,1-Trichloroethane	20	16	24	19	26
Trichloromethane	–	17	–	14	17
Tetrachloromethane	19	15	26	20	25
1,1-Dichloroethylene	–	–	20	43	–
Tribromomethane	16	10	26	11	11
Bromodichloromethane	19	–	–	–	26
Dibromochloromethane	–	–	13	11	–
Dichloromethane	–	–	21	–	14
1,2-Dichloroethane	–	–	16	14	33

Inter-laboratory Standard Deviations

The inter-laboratory relative standard deviation (RSD) [%] is analysed to assess how far the analytical results of different laboratories are spread. It is calculated per parameter based on the analytical data submitted. In Table V all inter-laboratory RSD are listed per parameter and per cycle.

The values for the inter-laboratory RSD vary between 10% and 33%. The results for the two compounds tribromomethane and dibromochloromethane are spread to a lesser extent than for the remaining compounds. For all other compounds, 20% approximately can be taken as an estimate for the interlaboratory RSD. Only for 1,1-dichloroethylene the value is higher and reaches even 30%. These results correspond well to the findings of the international inter-laboratory comparison test for halogenated hydrocarbons previously published [14,15].

CONCLUSION

The present study showed the feasibility of successfully operating a permanent proficiency testing scheme (PTS) for the difficult to handle halogenated hydrocarbons at the µg/L concentration level in water. It revealed important facts relevant for the analysis of halogenated hydrocarbons in general. QA measures showed that both, stock solutions in methanol and artificially prepared aqueous samples containing halogenated hydrocarbons are stable for at least 111 days and 162 days, respectively. As far as storage conditions are concerned, 60 mL of head space of air above the sample solution had only a minimal impact on the concentration of the halogenated hydrocarbons after 63 days. The sample preparation procedure was found to be well suited for the operation of the PTS. It was possible to prepare homogeneous synthetic water samples with known concentrations of halogenated hydrocarbons within a bandwidth of ±10%. Moreover, the batch-wise sample preparation procedure was designed in such a way that no analyte compound could evaporate despite its volatility. The assessment of the participants' performance by means of average recovery values yielded very good results and proved that the participants analysed well within the concentration ranges investigated. The present study thus revealed that permanent proficiency testing make environmental monitoring more reliable and effective.

Acknowledgement

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