

Short Communication

False results in headspace–gas chromatographic analysis of trihalomethanes in swimming pool water due to elevated headspace temperatures

Karl Cammann and Karl Hübner*

Chair for Analytical Chemistry, University of Münster, Wilhelm Klemm Strasse 8, W-4400 Münster (Germany)

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ABSTRACT

The application of a headspace GC method for the determination of trihalomethanes (THMs) in water is described for the case of swimming pool water. As a consequence of chlorination, swimming pool water contains, besides THMs, many other halogenated compounds. Among these, the trihaloacetic acids may interfere with THM determination because they are decarboxylated to the related THMs at the usually applied headspace temperatures. This disturbing effect was investigated at different temperatures for real swimming pool water samples. It occurs down to 40°C and was found to be avoidable at a headspace temperature of 33°C or less.

INTRODUCTION

Headspace GC (HS-GC) is a common method for the determination of volatile species in water. Since 1991 HS-GC has been a standardized method for the analysis of volatile halogenated hydrocarbons (VHCs) in water in Germany [1]. It is a cleaner and less time-consuming method than, for example, liquid–liquid extraction. Because of the Clausius–Clapeyron equation most applications recommend a HS temperature of 60–80°C to achieve good sensitivity. Higher temperatures should be avoided to keep the amount of vaporized water coming onto the column low (water can destroy the stationary phase of non-polar columns).

The application of this method to water samples from swimming pools can lead to false results in the determination of trichloromethane, which is usually the most interesting VHC in chlorinated swimming pool water [2]. In addition to the trihalomethanes (THMs, including trichloro-, bromodichloro-, dibromochloro- and tribromomethane), which are the most discussed products of water chlorination, more than 100 other halogenated compounds have been identified so far [3]. The brominated species are a consequence of the bromide concentration in the water used [4]. One type of species that occurs is the trihaloacetic acids (THAs). So far mainly the presence of trichloroacetic acid (TCA) has been reported [5,6]. TCA can undergo decarboxylation to trichloromethane and carbon dioxide at high temperature. This fact is used for the determination of TCA in urine by keeping the

* Corresponding author.

urine sample at 90°C for, *e.g.*, 90 min followed by an HS analysis to quantify the trichloromethane formed, which can be used to determine the original TCA concentration in the urine [7,8]. So far, the temperature above which TCA begins to be decarboxylated has not been reported. Decarboxylation starting at lower temperatures could cause problems in THM determination.

In this paper the influence of the HS temperature on the decarboxylation of TCA will be reported, as well as the maximum temperature that can be applied for the HS analysis to determine trichloromethane in swimming pool water without any interference by trichloromethane formed from TCA. The found concentrations of different THMs and THAs for an investigated swimming pool water will be given.

EXPERIMENTAL

The HS temperature dependence of the THM peak areas of real swimming pool water samples was investigated by measuring at three different temperatures (33, 40 and 60°C) and different dwell times at these temperatures. The results were compared with an aqueous THM standard measured at 60°C HS temperature.

Instrumentation

The gas chromatograph (5890 series II) and HS sampler (19395 A) were from Hewlett Packard. The vial pressure prior to injection was set at 1.1 bar, the sample loop volume was 1 ml and the injection time was 15 s. The vials had a volume of 13 ml, contained 2 ml of sample and were capped with butylgum septa coated with PTFE. The GC injection port temperature was 250°C. The column was an SE 52 (50 m × 0.32 mm I.D.; film thickness = 0.25 μm). The temperature programme was 11 min at 40°C, 8°C/min to 80°C. Detection was accomplished by electron-capture detection at 320°C.

RESULTS AND DISCUSSION

Fig. 1 shows the peak areas of trichloromethane found for the three temperatures and the different equilibration times. It can be seen

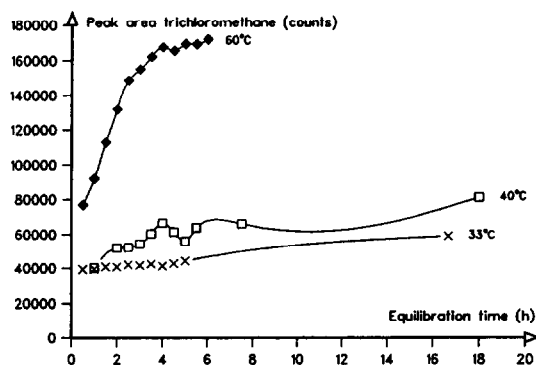


Fig. 1. Influence of HS temperature and equilibration time on the additional formation of trichloromethane in a swimming pool water sample.

that at 60°C the area is increasing continuously. To a lesser extent this pattern was also found at 40°C, whereas at 33°C the peak area was almost constant for several hours. A temperature lower than 33°C was not always practicable and reliably constant owing to the high laboratory ambient temperatures during the summer. The increasing areas at higher HS temperatures were found not to be a consequence of a slow reaching of the equilibrium state between the gaseous and the liquid phase. This is shown in Fig. 2, in which the peak area of trichloromethane in a THM standard in distilled water is plotted against the equilibration time at 60°C. Fig. 2 shows that the equilibrium state in an aqueous matrix is reached after 60 min or even after 30 min. This leads to the assumption of an additional formation of trichloromethane in the pool water sample dur-

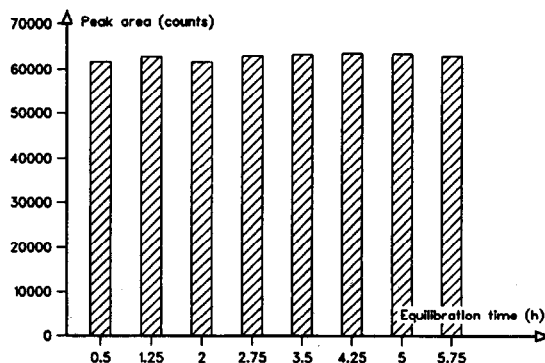


Fig. 2. Influence of the equilibration time at 60°C on the peak area of trichloromethane in an aqueous standard.

ing the equilibration in the HS sampler. Since the chlorine was reduced by sodium thiosulphate at the moment of sampling, the formation of trichloromethane by chlorine could be excluded. Thus, most likely, the presence of TCA in the sample was the reason for the trichloromethane formation. Temperatures of 40 and 60°C seem to be high enough to allow TCA to be decarboxylated to trichloromethane. Fig. 3 shows the decarboxylation rate of TCA at four different temperatures and various dwell times at these temperatures. This experiment was carried out with a TCA standard containing 142 $\mu\text{g/l}$ TCA. Thus 104 $\mu\text{g/l}$ trichloromethane would have meant 100% decarboxylation. At 70 and 90°C, after 1 or 2 h decarboxylation, rates of 80% (90°C) or more than 10% (70°C), respectively, were found. More than 10% can mean tens of $\mu\text{g/l}$ of additional trichloromethane in the case of hundreds of $\mu\text{g/l}$ TCA. This would lead to much increased and therefore false results in the determination of trichloromethane. An investigation at 60°C is missing, but Fig. 1 shows that the contribution of TCA to the formation of trichloromethane cannot be neglected at 60°C. At 50 and 40°C the increase in peak areas was still measurable but not very high. Thus, the error would be smaller but not negligible depending on the quantity of TCA. Even 48 h at 30°C had no influence on the peak area of trichloromethane.

Fig. 4 shows the results for bromodichloro-

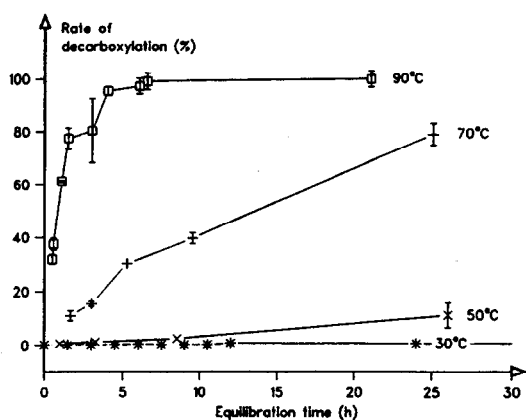


Fig. 3. Influence of temperature and dwell time on the decarboxylation rate of TCA.

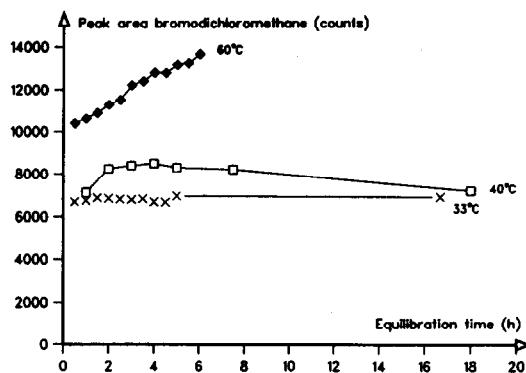


Fig. 4. Influence of HS temperature and equilibration time on the additional formation of bromodichloromethane in a swimming pool water sample.

methane of the same pool water sample. Again an increase in the peak area was found at 60°C but not at 40°C (at least not after 2 h equilibration time) or 33°C. The increase at 60°C indicated the presence of bromodichloroacetic acid in the sample.

The areas of the other trihalomethanes, dibromochloro- and tribromomethane, showed no dependence on temperature, which might be because of the absence of the corresponding THAs or because those decarboxylations only take place at even higher temperatures.

Measured concentrations

Applying a HS temperature of 33°C, the concentrations of THMs were measured by using an external calibration in distilled water. The equilibration time was 90 min, the vial pressure was set at 1.1 bar and the sample volume was 2 ml in 10-ml vials. For the determination of the THAs other vials of the same water samples were kept at 90°C for 6.5 h (less did not lead to a 100% decarboxylation rate according to Fig. 3) and afterwards analysed in the same way as the samples mentioned above. The results from the samples not treated at 90°C were subtracted from the latter ones and thus gave the amounts of THM formed by the decarboxylation of THA. These concentrations could be transformed into the original amounts of THA in the water samples. Table I shows the results for the four THMs, TCA, bromodichloroacetic acid and dibromochloroacetic acid. The concentration of

TABLE I

FOUND CONCENTRATIONS OF THMs AND THAs IN THREE DIFFERENT POOLS OF TWO GERMAN INDOOR SWIMMING POOLS

	Concentration ($\mu\text{g/l}$)		
	Bath I (swimmers' pool)	Bath I (jumpers' pool)	Bath II (swimmers' pool)
Trichloromethane	22.4 \pm 2.64	26.5 \pm 3.18	21.4 \pm 2.52
Bromodichloromethane	2.60 \pm 0.89	2.90 \pm 1.01	2.28 \pm 0.77
Dibromochloromethane	0.40 \pm 0.09	0.36 \pm 0.08	0.50 \pm 0.12
Tribromomethane	0.06 \pm 0.01	0.18 \pm 0.04	0.35 \pm 0.09
Trichloroacetic acid	199 \pm 45.9	175 \pm 37.1	245 \pm 43.9
Bromodichloroacetic acid	1.59 \pm 3.04	0.85 \pm 3.04	1.05 \pm 2.49
Dibromochloroacetic acid	0.47 \pm 0.34	0.08 \pm 0.23	0.06 \pm 0.31

tribromomethane did not change after the treatment at 90°C and thus no tribromoacetic acid was quantified. More than 6.5 h at 90°C did not lead to higher peak areas and therefore it can be assumed that for all THAs the decarboxylation was completed after 6.5 h, though this was not investigated in detail for THAs other than TCA.

The proportions of THMs are typical of chlorinated water that contains very little bromide. In the investigated pools the concentrations found were less than 0.1 mg/l. Because of this trichloromethane is the main THM and the concentrations of the other THMs decrease with increasing number of bromine atoms per molecule. The THAs behave in the same way, which means that trichloroacetic acid is the dominant representative of this group. The relatively high levels of confidence for the THAs result from the standard deviation of the results after keeping the samples at 90°C, which were quite high ($n = 3$). The confidence levels of the THAs were obtained by addition of those of the measurements before and after 90°C treatment, also making them higher.

CONCLUSIONS

Since the presence of TCA in swimming pool water seems to be common, the determination of trichloromethane (and thus also of the other VHCs, e.g. trichloroethene) by HS-GC should

be performed by using an HS temperature of 33°C or even less to avoid any interference by additional THM formation. This considered, the HS method is still a sufficient, clean and time-saving method compared with liquid-liquid extraction methods. Higher temperatures would lead to false results and thus misinterpretations.

By keeping part of the samples at 90°C for at least 6.5 h, the total amount of THM after decarboxylation of the corresponding THA can be measured. Subtracting the values found without treatment at 90°C from those after this treatment gives the amount of THAs in the water samples.

ACKNOWLEDGEMENTS

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The results of this paper will also be part of a master thesis.

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