TDAS 2000
UPGRADE Your PAL

Application Note T201E

Measuring Trihalogenmethanes (THM) in air of swimming halls using a thermal desorption system

Basics

Due to the income of micro organisms caused by customers to indoor swimming-baths, desinfection of the pool water is absolutely necessary. Most of the baths are desinfected with chlorine or hypochlorit, and in a small number of cases with substances containing bromine. Sometimes an oxidation step with ozone precedes desinfection. Organic compounds which got into the water from e.g. cosmetics, urine, sweat and many more react with chlorine, bromine or ozone, resulting into a lot of different desinfection byproducts. Lower boiling compounds that occur most often are the trihalogen methanes (THM). The four THMs are trichloromethane (chloroform), bromodichloromethane, dichlorobromomethane and tribromomethane. Considerable parts of them go into the air. The contamination with THMs in the air of baths is a very serious problem, because the THMs are inhaled by swimmers and the staff of the baths. The inhalation of higher amounts of THMs is problematic. Therefore monitoring and measuring of THMs in the air of indoor baths is very important due to health reasons. To measure the THMs, they have to be absorbed on suitable absorbents. For the following analyses with gaschromatography, the samples have to be eluted with e.g. a mixture of toluene/methanol from the absorbents. A simpler possibility and more elegant is the use of a thermal desorption method. The first option is measuring by using headspace analyses after adding a high boiling solvent (e.g. 3-Phenoxybenzyl-alcohol). It's also possible to measure the sample directly. The second option will be described in the following part.

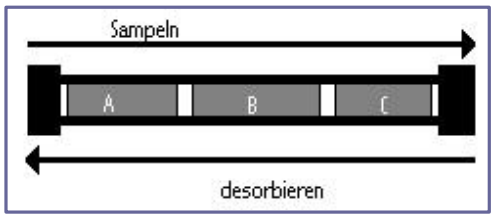

Fig. 1: TDS sampling tube
A: Carbotrap C; B: Carbotrap B; C: Carbosieve

Fig. 2: TDAS 2000 desorption unit with GC 6890 and PTV.

The THMs are sampled on three-bed charcoal tubes from Supelco. Immediately after sampling, the tubes are endcapped with PTFE/silicon septums and an aluminum cap. Afterwards the samples are desorbed directly in the gas chromatograph, while the tubes are inside the desorption oven. The analyts are freezed out, refocused and analysed by using a trap.

Chromatographic working conditions

Temperature program:
-50°C (5.67 min), with 10 °C/min up to 200°C (0 min), with 50 °C/min up to 300°C (2.33 min)
Runtime:35 min.
Injector temperature: 200°C
Detectors: ECD (at 300°C), MS
Sampling system: Combi PAL (Chromtech)
with TDAS-option

Method

The Combi-PAL (CTC Analytics) transports the sample tube from the tray into the desorption oven. Inside the oven the downside septum is penetrated as well as of a double sided needle from one side, the downside of the needle is penetrated through the septum of the injector. Then the upper septum of the sample tube is penetrated by the needle of the auto sampler. The flow goes through an automatic three-way vent, the needle of the auto sampler and the sample tube. At the same time the thermal desorption oven is heated up to 250 °C. The analyts are refocused in the injector, or even better on the column. On column focusing has the advantage, that splitting during desorption is possible. This is necessary for high ranges of THM- concentrations and so maybe the detector is expected to be out of linearity, like e.g. an ECD. A side effect is that the (high) air humidity in the sample cannot freeze out. During the desorption process the split is 1:25, the column flow is 3.3 mL/min. The desorption takes place at a flow about 75 ml/min and at a desorption oven temperature of 250°C.
The column oven (column temperature) during desorption is -50°C. After 5 minutes desorption time the auto sampler puts the tube out of the desorption oven, the double sided needle is pulled out of the injector. The column flow is shifted directly through the injector again. Afterwards the sample tube is conditioned 10 minutes at 350°C, with a flow of about 30 mL/min.

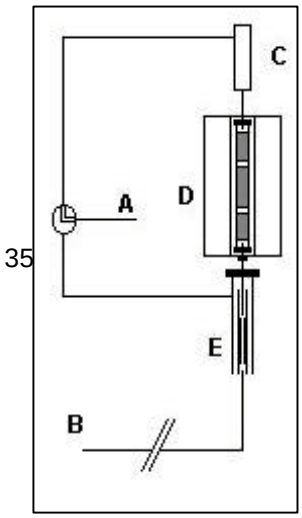

Fig. 3
Shematic drawing of TDS System

Focusing inside the injector, possibly filled (e.g. with charcoal), can cause a very low detection limit. Usually this option of measuring THMs is not used for indoor air of baths, because of the very high amounts.

Results

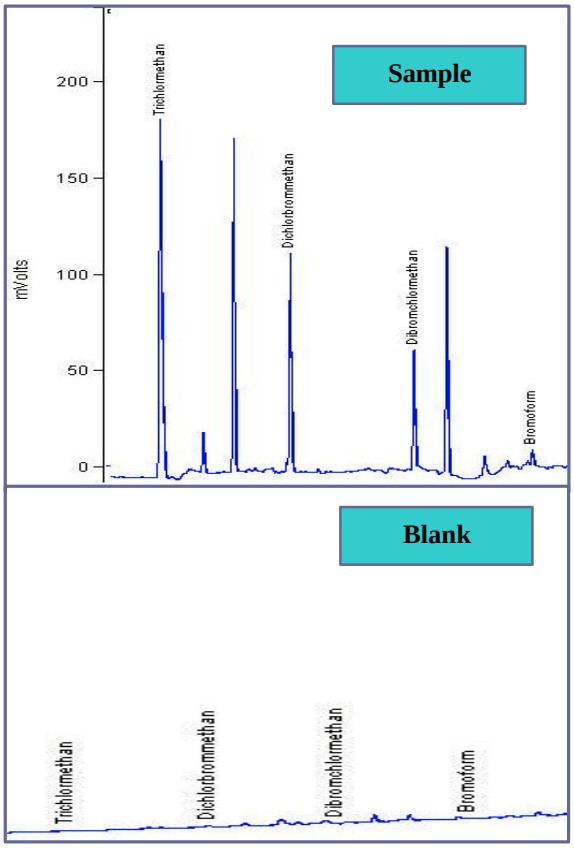

Fig. 4

Figure 4 compares chromatograms between a real sample and a conditioned sample tube (blank).

The chromatogram of a real sample shows the first big peak is an air peak. Chloroform has the highest amount in chlorine-desinfected baths using drinking water. The concentrationrates decrease from chloroform to bromoform. If baths use sole, salt water or thermal water instead of drinking water and chlor-desinfection, the brom containing desinfection byproducts are increasing. Using bromine for desinfection also causes an increasing of bromine-containing desinfection byproducts.

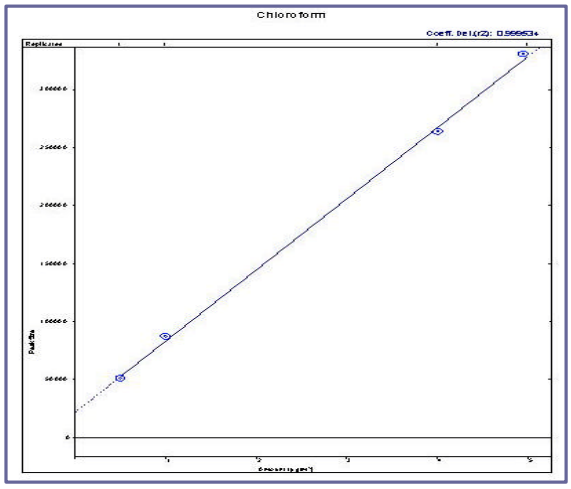

Fig. 5: Calibration of Chloroform, 0,5 – 5 µg/m³ at 10L sample volume. Correlation factor: 0,9995

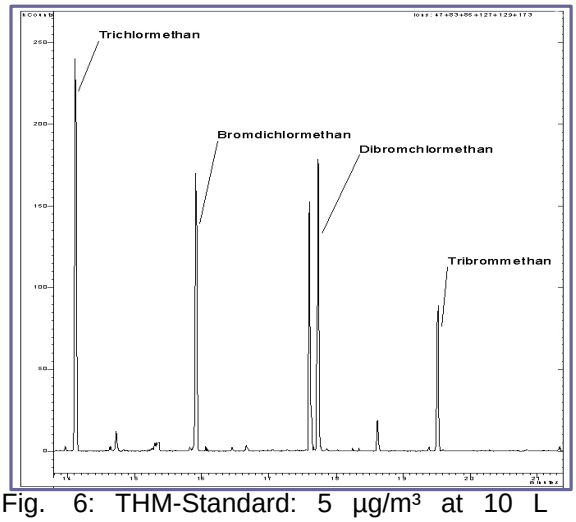

Fig. 6: THM-Standard: 5 µg/m³ at 10 L sample volume.

Discussion

The procedure described above saves time and has a low detection limit. At moderate costs, a Combi-PAL can be extended to a thermal desorber system. Then it is possible to do three jobs with one automated sampler: liquid injection, headspace analysis and thermal desorption analysis.