Trace Analysis of Organic Pollutants with GCMS according to the new European Drinking Water regulation

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Introduction

Since the 1st of January 2003 the new European Drinking Water regulation is effective in Germany (TVO 2001). Its aim is to protect human health from the bad influences of contaminated drinking water. All water that is used for the preparation of food as well as for cleaning of material used for the preparation of food and water that is used for personal hygiene is regulated under the European drinking water regulation. Water used for these purposes should not contain chemical substances in concentrations that could cause harm to human health. For many compounds limits are defined that have to be controlled on a regular basis and cannot be exceeded.

Analysis of Organic Pollutants in Drinking Water

The analysis of organic pollutants in drinking water is a complex task which requires a high degree of precision, know-how and modern analytical equipment. The analysis technique used has to be able to detect a large array of compounds in very low concentrations according to the specified limits. For the organic pollutants a detection limit of 25 % or 10 % (for chlorinated organic compounds) has to be achieved. The precision of the results shall not be more than 25 % of the limit.

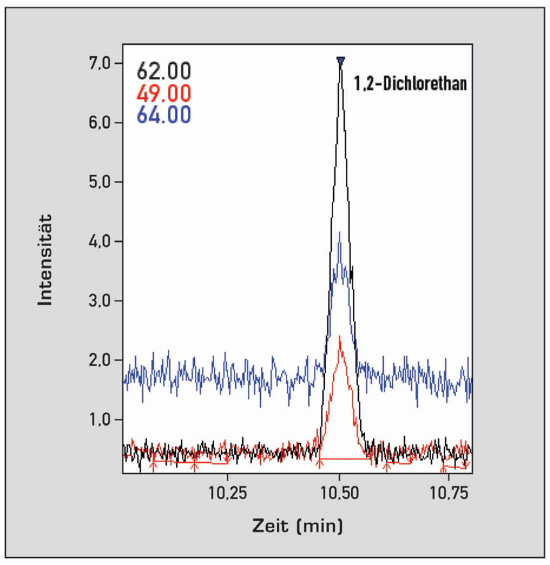

Fig. 1: Chromatogram Dichloroethane

GCMS Analysis of Drinking Water

The coupling of gas chromatography with mass spectrometry is a powerful tool for the qualitative and quantitative analysis of drinking water samples. Due to its high sensitivity it fully complies to the regulations of the drinking water directive. In scan mode organic pollutants can be identified even in low concentrations unambiguously by library search in commercially available spectral libraries like NIST or Wiley and special libraries like the Shimadzu Pesticides library which includes EI and also NCI (Negative Chemical Ionisation) spectra. NCI measurements give high sensitivity for compounds with high electronegativity like e.g. chlorinated substances. Measurements in SIM mode (Single Ion Monitoring) enhance the selectivity and increase the sensitivity of detection.

Classification of Organic Pollutants

Substances which have to be analysed according to the drinking water regulation can be classified into the following groups: volatile (chlorinated) organic hydrocarbons (VOC), polycyclic aromatic hydrocarbons (PAH) and pesticides. The limits for the different groups and

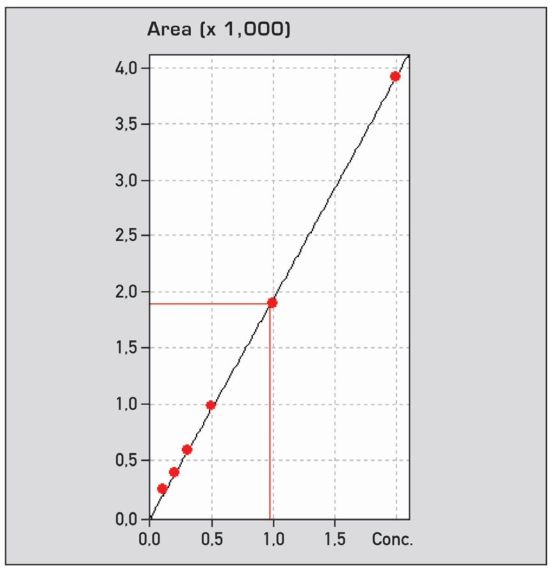

Fig. 2: Calibration curve Dichloroethane

also for the single components to be determined are given in Table 1. In this study the analysis of VOC´s including Benzene and Pesticides was studied with GCMS.

VOC Analysis by Headspace GCMS

Many VOC´s are toxic and some of them are also cancerogenic. They are soluble in fat and thus can accumulate in the natural cycles. For the analysis of VOC´s the Headspace technique is employed. In Figure 1 a chromatogram of the VOC 1,2 Dichloroethane in a concentration of 1 µg/l is shown giving a signal/noise of 65:1. Fig. 2 shows the calibration curve in the concentration range of 0.1 to 10 µg/l (correlation coefficient 0.9997). All data were acquired in SIM mode. The limit in the drinking water regulation is 3 ng/l, so the requirements are easily met.

Benzene is one of the most prominent aromatic hydrocarbons and next to the PAH one of the most important environmental carcinogens. It is emitted mostly from fuel used in cars. In the new drinking water regulation benzene has to be determined as a single parameter in a concentration of 1 µg/l. Also for the analysis of benzene the headspace GCMS technique is used.

Analysis of Pesticides

In modern agriculture still a large number of pesticides is commonly employed. Generally pesticides are considered as harmful to human health. They can cause malfunctions of kidney and liver and some of them are also cancerogenic.

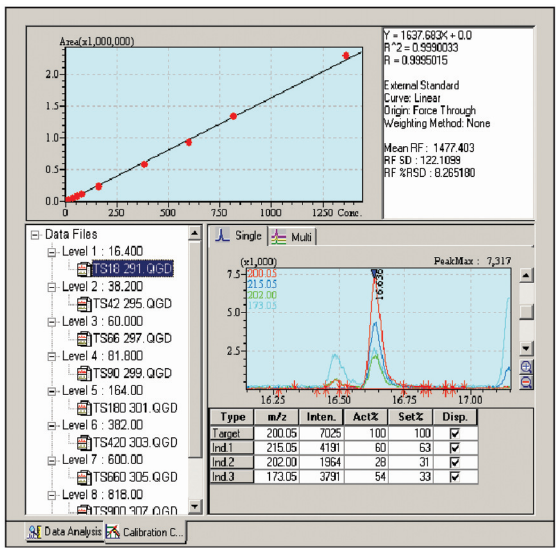

Fig. 3: Calibration curve Atrazine

Parameter	Limit (µg/l)	Detection limit in % of the limit	Precision in % of the limit
Acrylamide	0,1	-	-
Benzo[a]pyrene	0,01	25	25
Benzene	1	25	25
1,2-Dichloroethane	3	10	25
Epichlorhydrine	0,1	-	-
Pesticides (single components)	0,1	25	25
Pesticides (Sum)	0,5	25	25
PAH (4 components)	0,1	25	25
TRI / PER	10	10	25
Trihalomethanes	50	10	25
Vinylchloride	0,5	-	-

Independently of their toxicity for the pesticides in Drinking Water a limit of 0.1µg/l for single components is specified. The majority of positive determinations is due to the presence of the pesticides Atrazine and its major degradation product Desethyl-Atrazine. Atrazine has been used extensively especially in the cultivation of corn, but was also used for asparagus, potatoes and tomatoes. Atrazine is toxic for water organisms but shows only little toxicity for humans. Its deterioration in the environment is relatively slow. Atrazine and Desethyl-Atrazine have been analysed in this study, showing that the requirements of the Drinking Water regulation could be fulfilled.

In Fig. 3 the calibration curve for Atrazine in a concentration range of 0.015 to 1.5 µg/l is shown. Fig. 4 and 5 show the determination of Atrazine and Desethyl-Atrazine in a real sample. Table 2 shows the data for the concentration and standard deviation of the 3 replicates. For Atrazine a very good repro-ducibility can be achieved but for Desethyl-Atrazine the standard deviation is higher. This is due to the high polarity of the compound which leads to a tailing of the peak. A column with high polarity would be preferable for this compound, however a 5 % phenyl substituted methyl polysiloxane column was chosen for the analysis since a wide range of compounds can be analysed on this column in one run.

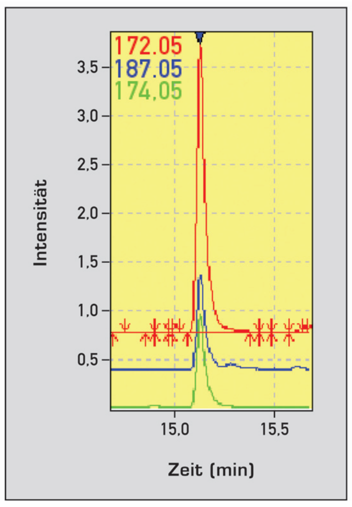

Fig. 4: Chromatogram Atrazine (real sample)

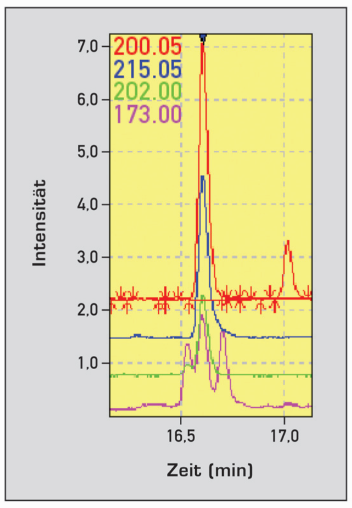

Fig. 5: Chromatogram Desethyl-Atrazine (real sample)

Triazine	MW (µg/l)	STD (µg/l)	STD (%)
Atrazine	0,121	0,002	1,7
Desethyl-Atrazine	0,292	0,013	4,4

Instrumentation

GCMS-QP2010
GCMSsolution software
AOC-5000 autosampler
Shimadzu Pesticide EI/NCI library