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Short communication

Determination of carbonyl compounds in pool water with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyamine hydrochloride and gas chromatographic–tandem mass spectrometric analysis

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Abstract

To avoid microbiological decay pool water is disinfected, a procedure which results into a lot of disinfection by-products, like carbonyl compounds, as well as a large number of others. The carbonyl compounds dissolved in pool water were derivatisized with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyamine hydrochloride (PFBHA) and extracted using *n*-hexane. Measuring with the help of GC–electron-capture detection is hardly possible because of interferents like halogenated organics. Another method to detect the PFBHA derivates is the use of tandem mass spectrometry. Calibration ranges and precision are applicable and sufficient to determine carbonyl compounds in pool water.

Keywords: Water analysis; Disinfection by-products; Carbonyl compounds; Pentafluorobenzylhydroxyamine hydrochloride

1. Introduction

Measuring carbonyl compounds in water was already described in [1,2]. In particular, the EPA (US Environmental Protection Agency) method 556 [1] describe how to measure carbonyl compounds in different sources of water. Other methods [4,5] describes how to determine carbonyl compounds with 2,4-dinitrophenylhydrazine (DNPH) and liquid chromatography (LC). Using DNPH to determine the variety of carbonyl compounds with GC is not trivial and has not been reported widely so far [7]. The use of *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxyamine hydrochloride (PFBHA) is a possible replacement for DNPH. Interferents from other halogenated organic compounds are problematic with PFBHA methods, because of the unspecific electron-capture detection (ECD). Using GC–MS is another possibility to detect the carbonyl compounds. To increase sensitivity, a method using tandem mass spectrometry was developed. The MS–MS method decreases background noise and facilitates measuring carbonyl compounds in the μg/l range without sample preconcentration

There are a lot of short chain aldehydes and ketones, so it was useful and practical to pick a few compounds as representatives. The chosen compounds were the homologous series methanal to decanal, 2-propanone to 2-decanone, as well as isobutanal, benzaldehyde, glyoxal and methylglyoxal. These compounds gave an overview to the strain with short chain carbonyl compounds in pool water.

2. Experimental

2.1. Samples

The samples were taken headspace free from the pool water surface in 100 ml brown glass bottles, with a screw cap and PTFE septum. Prior to the sampling, 15 mg of ammonium chloride – to absorb active chlorine – and 15 mg copper sulfate – to prevent the sample from microbiological decay – were added. Between the sampling and the procedure the samples were stored at 4 °C, maximum 14 days. The stability of the analytes was demonstrated in [1].

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2.2. Materials and reagents

PFBHA, propanal, butanal, octanal, nonanal, 2-nonanone, 2-decanone, isobutanol, benzaldehyde and methylglyoxal were purchased from Aldrich (Steinheim, Germany), *n*-hexane from Promochem (Wesel, Germany) and methanal, ethanal, pentanal, hexanal, heptanal, decanal and glyoxal from Merck (Darmstadt, Germany). 2-Butanone, 2-heptanone and 2-octanone was obtained from Fluka (Deisenhofen, Germany) and 2-hexanone from Riedel-de Haën (Seelze, Germany). All analytes were in GC grade, *n*-hexane and methanol were in trace analysis grade.

2.3. Preparation of the PFBHA solution

For derivatization the PFBHA solution was prepared freshly each day with fresh and untreated bidistilled water and at a concentration of 6 mg/ml.

2.4. Preparation of standard solutions

From each aldehyde and each ketone a solution in methanol, with a concentration of about 8 mg/l, was prepared. The standard solution was made from the component solutions. The mixture contains 22 compounds, each at approximately 30 mg/l (Fig. 1). Another solution was prepared containing 3 mg/l of each compound. As internal standard tetrafluorobenzaldehyde was used, prepared as a solution of about 160 mg/l.

2.5. Sample processing

30 ml of the sample water was placed in a 40 ml vial with a screw cap and a PTFE septum. A few milligram of potassium hydrogenphthalate (to adjust the pH value to approximately 4), 100 μl of fresh prepared derivatization solution and also 100 μl of the internal standard solution was added. After at least 12 h at room temperature and in the dark, 50 μl of concentrated sulfuric acid were added. The derivatization time and conditions were taken from [2], because the ketones require a longer reaction time. The extraction followed with 4 ml *n*-hexane on an automatic agitator for about 1 h. Afterwards 3 ml of the *n*-hexane layer were put into a 12 ml vial containing 5 ml of a 0.05 mol/l sulfuric acid, to wash interferents from the PFBHA. 2 ml of the *n*-hexane was dried with sodium sulfate. 1 ml was put in a 2 ml vial and 1.3 μl were injected into the GC.

2.6. Standard processing

The standards were processed with 30 ml fresh bidistilled water in a 40 ml vial with a screw cap and a PTFE septum. The standards were spiked with 1 μl of the standard solution for the 1 μg/l standard, 2 μl for the 2 μg/l one and so on. For the standards, containing 0.1, 0.2 and 0.5 μg/l, the appropriate volume of the small standard solution was taken. The rest of the processing was equal to the sample processing.

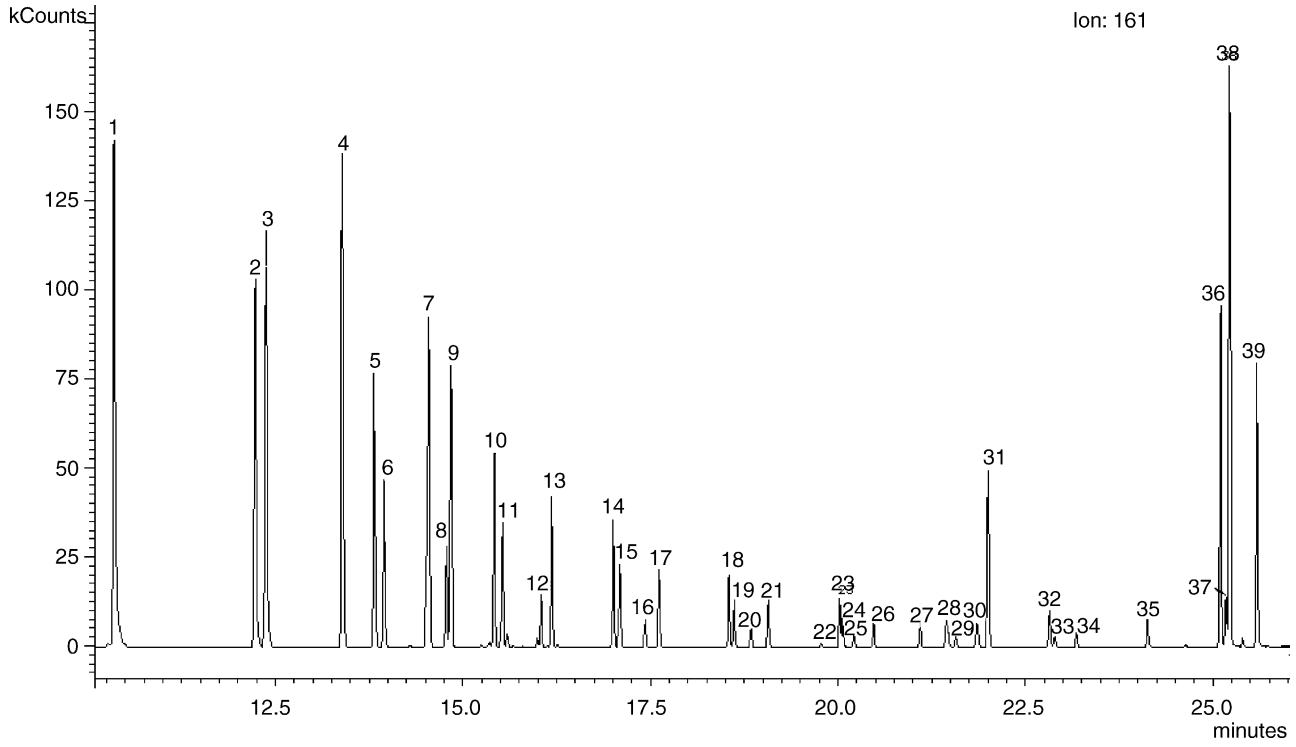

Fig. 1. Gas chromatogram of a mix standard, including 22 carbonyl compounds.

2.7. Gas chromatographic parameters

The GC analyses were performed using a CP3800 gas chromatograph directly coupled with a Saturn 2000 mass spectrometer made by Varian (Darmstadt, Germany). The column was a CP Sil 8, 50 m × 0.25 mm and a film thickness of 0.25 μm, coated with 95% dimethyl-, 5% diphenylpolysiloxane produced by Varian.

The injector was held at 280 °C, and the samples were injected in splitless mode. The column oven had an initial temperature of 50 °C for 1.5 min, followed by a rate of 8 °C/min to 250 °C held for 5 min, and a final heating rate of 25 °C/min to 300 °C for 1.5 min (35 min runtime). Helium was the carrier gas at a constant flow of 1.3 ml/min. The data processing was performed with the Saturn GC/MS Workstation 5.41 from Varian.

2.8. Mass spectrometric parameters

The mass spectrometer was the ion trap MS–MS system Saturn 2000 from Varian. The emission current of the filament was set to 70 μA. For ionization, the EI mode with automated gain control (EI AGC) was used. The target was set to 8000 with a prescan time of 1500 μs, and the preparation technique was MS–MS. The ionization storage level of the preparation was *m/z* 48.0, the ejection amplitude was set to 20.0 V. The parent ion *m/z* 181 was isolated, in a window of *m/z* 3.0, with an excitation storage level of *m/z* 79.9. The waveform type was resonant at a voltage of 1.6 V.

3. Results and discussion

Compared to other methods, this method reaches average ranges of detection for water matrices. Several problems during sample preparation can accumulate. The biggest problems are blank values of the following compounds: methanal, 2-propanone, 2-butanone, ethanal, propanal, isobutanal, 2-pentanone, butanal and pentanal in decreasing order. To prepare the calibration standards, clean water is essential. Traces should be as small as possible. The ambient laboratory air should have low amounts of solvents. Blank values should be less than half of the minimum reporting level and the blanks should not be subtracted.

The recoveries were reproduceable and acceptable. They were determined by measuring on 3 different days, 6 unspiked pool water samples, compared to 6 pool water samples spiked with 5 μg/l. The precision of the method (relative standard deviation (RSD), values in Table 1) was calculated by measuring three times (on different days) at 6 standards, spiked with 5 μg/l mixture of all aldehydes, on each day with a complete, new procedure. The confirmation of analytes was done as in [1] suggested, with GC–ECD analysis.

The tandem mass spectrometry decreases the background levels of the masses and gives a better signal-to-noise ratio. The second fragmentation step was performed after mass 181 had exclusively been stored. The mass 181 probably is a tropylium like cation consisting of 5 F, 7 C and 2 H in a C 7 ring cation, which is stabilized by mesomerism. The second fragmentation step results in a high intensity of a mass 161 cation. This is probably a 4 F, 7 C and 1 H cation, arranged in an C 7 ring also stabilized by mesomerism and

Table 1
Peak, precision, recovery and calibration data of the carbonyl compounds analyzed by GC–MS–MS

Carbonyl compound	Peak numbers	RSD (%)	R^2	Calibration range (μg/l)	Relative recoveries (%)
Methanal	1	2.9	0.995	1–50	90
Ethanal	2, 3	3.1	0.997	1–50	89
Propanal	5, 6	3.9	0.999	0.2–50	81
Butanal	10, 11	2.9	0.997	0.1–50	80
Pentanal	14, 15	4.3	0.998	0.1–50	87
Hexanal	18, 19	4.3	0.998	0.1–50	93
Heptanal	23, 24	7.1	0.997	0.5–50	87
Octanal	28	8.4	0.998	0.5–50	96
Nonanal	32	12.6	0.998	0.5–50	94
Decanal	35	10.5	0.998	0.5–50	97
2-Propanone	4	3.2	0.995	1–50	83
2-Butanone	8, 9	6.3	0.995	0.1–50	92
2-Pentanone	12, 13	4.2	0.995	0.1–50	81
2-Hexanone	16, 17	3.0	0.998	0.2–50	88
2-Heptanone	20, 21	2.9	0.998	0.2–50	84
2-Octanone	25, 26	8.1	0.998	0.5–50	82
2-Nonanone	29, 30	7.6	0.998	0.5–50	83
2-Decanone	33, 34	10.9	0.998	0.5–50	95
Isobutanal	7	2.9	0.998	0.1–50	84
Benzaldehyde	31	4.2	0.998	0.1–50	74
Glyoxal	36, 37, 38	10.4	0.997	0.1–50	102
Methylglyoxal	39	14.6	0.998	0.1–50	92
Internal standard	22, 27	5.4		50	

originated from the 181 cation by losing HF. When another fragmentation step was applied to the cation 161, the mass 141 was measured, with some likelihood of another HF loss. But using the MS–MS–MS technique was not practicable, because of the strong decrease of the signal, resulting into a bad signal-to-noise ratio.

4. Conclusion

A method which is appropriate to determine a wide range of small chain carbonyl compounds in pool water has been developed. The method allows reliable quantification in the μg/l range without sample preconcentration. The resolution of this method is very high, so most of the carbonyl compounds had two peaks to be analyzed.

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