

## The Occurrence and Analytical Chemistry of the Halogenated Methyl-phenyl-ethers (Halogenated Anisoles) in Air

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### 1. Introduction

The halogenated methyl-phenyl-ethers (anisoles) appear to be ubiquitous organics in the environment. Various members of the three groups of 19 chloroanisoles, 19 bromoanisoles and 96 bromo-chloroanisoles, have been detected in the marine atmosphere <sup>1)</sup>, in oysters <sup>2)</sup> and in effluents of municipal waste water treatment plants <sup>3)</sup>. Up to now no definite primary anthropogenic sources for the halogenated anisoles are known as chlorinated anisoles are not produced and/or used in technical quantities. However, methyl-phenyl-ethers are formed by many microorganisms by biomethylation of the respective phenols <sup>4)</sup>. The chlorophenols can either be direct anthropogenic emissions like the tetrachlorophenols, the pentachlorophenol and the chloromethylphenols (cresols) that are used as fungicides and bacteriocides or they are enzymatically formed by monooxygenases from other anthropogenic precursors like chlorobenzenes. The air chemistry of chlorobenzenes may also lead to chlorophenols. A further enzymatic pathway to the chlorophenols is the halogenation of phenols and halophenols by haloperoxidase enzymes <sup>5)</sup>.

This paper describes the basic analytical methodology of sampling, separation and determination of halogenated anisoles as a complex group of volatile biogenic organohalogenes in air and their occurrence in the atmosphere above a waste water treatment plant and in the troposphere of the North and South Atlantic.

### 2. Experimental

#### 2.1 Sampling of high volumes (300 - 600 m<sup>3</sup>) of air

In terms of high volume sampling the halogenated anisoles have to be regarded as volatiles. The boiling points of the halogenated anisoles are close to those of the halogenated benzenes, counting the methoxy group as equivalent to one halogen substituent. The capacity and the activity of silica gel 60, which can be used to sample the polychlorinated biphenyls and the hexachlorocyclohexanes in the picogram m<sup>-3</sup> range, is not efficient enough for the sampling of most of the halogenated anisoles at a concentration level found in ambient air. Therefore specific measures are required in high volume sampling of halogenated anisoles in the picogram m<sup>-3</sup> range.

Instead of silica gel 60 alone, we use a mixture of silica gel 60 and ENVI-Carb, a charcoal available from Supelco (Bad Homburg, Germany). In the first adsorbent layer (100 g) the charcoal content was 5 weight-% and in the second layer, which monitors the breakthrough, it was 1 weight-%. In order to control the sampling efficiency, the glass fiber filter on top of the upper layer of the adsorbent was spiked with 9.8 ng 1,2,3,4-tetrachloronaphthalene (TCN). 200 - 550 m<sup>3</sup> air were sampled with a flow between 15 - 20 m<sup>3</sup> per hour. After the sampling the adsorbent mixture was filled into glass flasks, which were flame sealed so that the samples can be stored air-tight for a long period.

Prior to the extraction each adsorbent layer was spiked with 10.0 ng  $\epsilon$ -HCH or 5.0 ng 2,4-trichlorophenyl-ethyl-ether (TCPE-C2) and 5.0 ng 2,4,6-trichlorophenyl-octyl-ether (TCPE-C8) as internal standards and retention time markers. The adsorbents were soxhlet extracted with 200 ml diethylether for 24 hours. Next the extract was concentrated to approximately 0.5 ml on a rotary evaporator at atmospheric pressure. By adding 2 ml pentane and subsequent concentrating to 0.5 ml three times, the solution was transferred to pentane, which is necessary for the following group preseparation. Recoveries between 65-105% are achieved by soxhlet extraction.

## 2.2 Sample clean-up and group preseparation by NP-LC

The clean-up of the extract and a group preseparation were performed using activated Florisil. Before use it was kept for 12 hours at 130 °C and used directly after it was taken out of the oven. A column (volume 6 ml, water cooled) was packed with 3 g Florisil in pentane, topped with 0.6 g Na<sub>2</sub>SO<sub>4</sub> and cleaned with about 50 ml pentane. Then the sample solution was added to the top. First a 19 ml pentane fraction (LC 1) was eluted, which includes most of the polychlorobiphenyls (PCB). In a second fraction (36 ml pentane + diethylether, 3:1, LC 2) the halogenated anisoles were eluted. The more polar compounds, like the chlorinated dimethoxybenzenes, were eluted in a third fraction (20 ml diethylether, LC 3). The second fraction was concentrated on a rotary evaporator using 200  $\mu$ l hexane as keeper. The concentrate was analyzed by HRGC-ECD (stationary phases: CP-Sil 2.5, Chrompack 55 m, 0.25 mm i.d., film thickness 0.25  $\mu$ m and DB 1701, J & W Scientific, 30 m, 0.25 mm i.d., film thickness 0.25  $\mu$ m) and HRGC-MSD-SIM (stationary phase: HP Ultra 2, Hewlett Packard, 50 m, 0.2 mm i.d, film thickness 0.33  $\mu$ m).

## 3. Results and discussion

### 3.1 Halogenated anisoles as emission in the air of a waste water treatment plant

The improved sampling method, based on silica gel 60/ENVI-Carb, was tested by analyzing air of the biological waste water treatment plant at Ulm. Three air samples were taken above the well aired biological treatment basins. Only few anisoles have been found as breakthrough in the second adsorbent layer, if ENVI-Carb is added to the first silica gel layer. Sampling was more effective adding 5 weight-% instead of 1 weight-% of ENVI-Carb to the silica gel. The breakthrough of anisoles is in this case smaller than 5 percent. This adsorbent mixture also retains the dichloroanisoles. The samples were analyzed and quantified against the internal standard described above.

In HRGC-ECD analysis the limits of detection of the chlorinated anisoles, using aliquots of 1 m<sup>3</sup> air, range from 10 pg m<sup>-3</sup> (dichloroanisoles) to 0.6 pg m<sup>-3</sup> (pentachloroanisole). Monochloroanisoles can not be analyzed by the ECD. Monobromoanisoles can be detected by ECD, although the limit of detection is quite high with 100 pg m<sup>-3</sup>. The limits of detection of

the bromoanisoles are between 2 pg m<sup>-3</sup> (dibromoanisoles) and 1.2 pg m<sup>-3</sup> (pentabromoanisole). In HRGC-MS-SIM analysis the limits of detection of the chloroanisoles, using aliquots of 15 m<sup>3</sup> air, range from 6 pg m<sup>-3</sup> (dichloroanisoles) to 15 pg m<sup>-3</sup> (pentachloroanisole). The limits of detection of the bromoanisoles range from 7 pg m<sup>-3</sup> (monobromoanisoles) to 18 pg m<sup>-3</sup> (pentabromoanisole).

The following chloroanisoles were detected: 2,6-dichloroanisole, 2,3,4-trichloroanisole, 2,4,6-trichloroanisole, 3,4,5-trichloroanisole, 2,3,4,5-tetrachloroanisole, 2,3,5,6-tetrachloroanisole and pentachloroanisole. Pentachloroanisole, 2,4,5-trichloroanisole and 2,4,6-trichloroanisole are the major components detected. They were present in the 200 pg m<sup>-3</sup> range. Furthermore 2,4-dibromoanisole, 2,6-dibromoanisole, 2,4,6-tribromoanisole and tetrachloro-1,4-dimethoxybenzene were detected.

### 3.2 Halogenated anisoles in marine air

On cruise leg ANT XI/1 of the German research vessel "Polarstern", from Bremerhaven (Germany) to Capetown (South Africa), in October/November 1993 high volume air samples were taken with the method described above.

The pattern of the congeners and the concentrations of halogenated anisoles in the marine atmosphere, differ remarkably in correspondence to the region, where the sample was taken. In regions, known for their high rate of primary production halogenated anisoles can be found in high concentrations. But also in regions with a relatively low rate of primary production halogenated anisoles can be detected.

The atmospheric concentrations of the chlorinated anisoles in marine air of the tropic eastern North Atlantic (12 °N 22 °W), a region known for its high rate of primary production, ranged from 44 pg m<sup>-3</sup> (2,4,6-trichloroanisole) to 99 ng m<sup>-3</sup> (3,4,5-trichloroanisole). The concentrations of the bromoanisoles were somewhat lower and ranged from 28 pg m<sup>-3</sup> (4-bromoanisole) to 2.3 ng m<sup>-3</sup> (2,4-dibromoanisole). Moreover, there were detected 2-bromo- and 4-bromoanisole and three of the six theoretically possible dibromoanisoles by GC-MS-SIM. Also, all existing tribromoanisoles (six isomers), as well as the three possible tetrabromoanisoles and pentabromoanisole were found.

In marine air, sampled near Benguela (14°S 7°E), a zone of nutrient rich, upwelling water with a high rate of bioproductivity, only few chlorinated anisoles (2,4,6-trichloroanisole and pentachloroanisole) were detected. Besides 2,4,6-tribromoanisole we also found by GC-ECD another tribromoanisole and two bromodichloroanisoles.

In marine air of the South Atlantic, originating from a region with a relatively low rate of primary production (45°S 13°E) only 2,4,6-trichloroanisole, pentachloroanisole and 2,4,6-tribromoanisole were found. The atmospheric concentrations ranged from 1 to 10 pg m<sup>-3</sup>. No further brominated or mixed halogenated anisoles could be detected by GC-ECD.

Compared with the halogenated anisoles, detected in the air above the waste water treatment plant, the marine air samples differ remarkably in the pattern of the congeners and in the concentrations. Whereas, pentachloroanisole is the compound with the highest atmospheric concentration above the waste water treatment basin, it is among the congeners with medium concentrations in the marine air. While 3,4,5-trichloroanisole and 2,3,4,5-tetrachloroanisole are present in concentrations in ng m<sup>-3</sup> in a single marine air sample, collected at 12 °N 22 °W, they are only present in the pg m<sup>-3</sup> range in the air above the waste water treatment plant. This result is surprising. Other samples of marine air did not give the extraordinary high levels of these two specific chloroanisoles.

## 4. Conclusions

The differences of the pattern of the congeners detected in marine air and in air above a waste water treatment plant indicate that there must be different precursors. Probably, the main source for halogenated anisoles in the waste water treatment plant is the methylation of anthropogenic chlorinated phenols, especially of pentachlorophenol. Whereas, in the marine environment the brominated and mixed halogenated anisoles will be synthesized by biohalogenation. Especially the occurrence of brominated anisoles is a signal for a biogenic input, as no anthropogenic brominated precursor molecules are known.

## 5. References

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