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A new fast method for field screening of polychlorinated biphenyls in air

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Abstract

A new fast method for the detection of a sum parameter for polychlorinated biphenyls in air is presented. Air pollutants are sampled on a thermodesorbable silicone-coated glass fibre filter. Analysis is carried out by a mobile GC–MS system with short GC columns. Total time for analysis in the field is about 10 min. A novel data evaluation is used for quantification. To evaluate the GC run, signals of the characteristic ion traces of each degree of chlorination are integrated. Superposition of ion fragments in the low-resolution GC run are eliminated by a special algorithm.

Keywords: Air analysis; Environmental analysis; Field screening; Polychlorinated biphenyls; Volatile organic compounds

1. Introduction

Polychlorinated biphenyl (PCB) analyses generally requires tedious and time-consuming procedures [1,2] starting with air sampling, several cleanup steps, separation on high-resolution gas chromatographic (GC) columns and most sensitive detection by electron-capture detection (ECD) or mass spectrometry (MS). Quantification is based on a few congeners each being the representative of one entire degree of chlorination [3]. For field analysis multicomponent mixtures tend to be a problem in quantification. Experiences in mobile analysis with GC–MS have been aquired in Hamburg (Germany) in measurement campaigns during the last decade producing a vast number of GC–MS runs of contaminants in air, water, soil and surfaces [4–7]. Often PCBs have been detected. The demand on quantitative results with the help of high-speed GC runs with low resolution has challenged us to develop a new procedure to calculate the sum concentration of PCBs. The new method is presented together with a fast air sampling procedure to detect semivolatile organic compounds (SOCs) in air.

2. Experimental

For fast compound enrichment from air we first compared uncoated to silicone-coated glass fibre filters (Schleicher and Schüll No. 6, Dassel, Germany). In contrast to uncoated material, silicone-coated filters (Dräger type III, Lübeck, Germany) work as adsorbant and as well as filter: The silicone coating adsorbs volatile PCB while lower volatile particle bound PCB are retained by the filter gauze itself. 250 L of sample gas are sucked through a 3 layer filter sheet cartridge (see Fig. 1) within 60 min at ambient temperature (pump: ASF Thomas Type 2737, Puchheim, Germany).

No breakthrough of SOCs at sample volumes up to 1000 L has been obeserved. After sampling the

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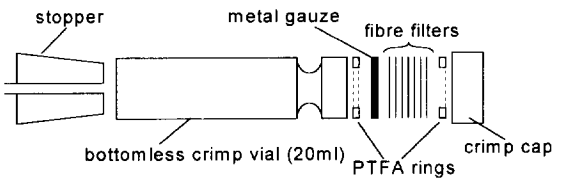

Fig. 1. Sampling device with fibre filter.

cartridge is opened and filter sheets are then placed in a desorption tube and heated at 300°C for 1 min. Desorbed compounds are sucked onto the GC column and separated by means of high speed temperature program (40–240°C, 1 C°/s).

The analysis is performed with a mobile GC–MS system (MEM, Bruker Franzen, Bremen, Germany). The GC is equipped with a short capillary column (DB5, 3m×0.25μm, I.D. 0.32mm).

Reference compounds were purchased by Promochem, Wesel, Germany and Dr. Ehrensdorfer, Augsburg, Germany.

3. Results and Discussion

Low resolution GC runs are obtained (see Fig. 2).

The mass spectra of the PCB congeners differ only slightly, thus superposition between the mass signals takes place. Especially signals of molecules with a difference of 2 chlorine atoms interfere strongly with each other (see Fig. 3).

The only compound that is free of superposition is the latest eluting peak of the highest chlorination grade present in the sample. With knowledge of the fragmentation pattern of PCBs the calculation of

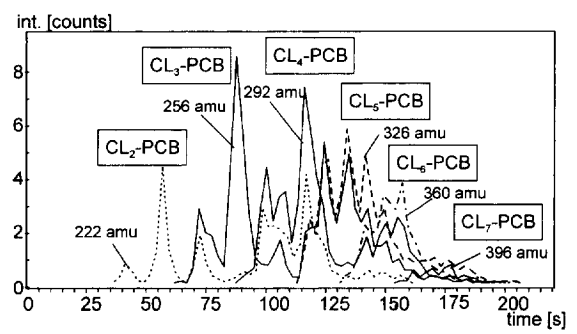

Fig. 2. Selected ions of PCBs in a low-resolution high-speed GC run.

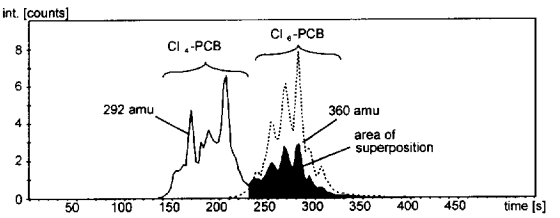

Fig. 3. Superposition of ions from different degree of chlorination (fast GC run on short column).

each PCB congenere group with the same number of chlorine atoms can be carried out. It starts with the integration of one selected ion of the non-influenced spectra and continues with reducing all superimposed GC peaks which elute before. This procedure follows the calculation scheme shown in Table 1.

The concentration is calculated by using calibration curves [8] of each chlorination grade (see Fig. 4). The calibration curves have been produced with solutions of clean compounds in 10 different concentrations per calibration decade. The solution is applied onto a clean filter sheet and thermally desorbed. Each calibration point was been measured four times.

The limit of detection lies in the range of 2–5 ng per compound taking full scan spectra (45–400 amu, 1 scan/s).

Good agreement exists between the absolute amount injected and the calculated data from the measurement of spiked solution applied onto clean filter sheets. Air samples analysed by the new GC–MS method and standard procedures have resulted in comparable PCB sum concentrations. More parallel tests and round robin tests for PCBs and other groups of semivolatile and low volatile organic compounds are planned.

4. Conclusion

The calculation of PCB concentrations analysed by low-resolution high-speed GC–MS runs is needed for the evaluation of field screening analyses. This can be done, e.g. for samples taken on hazardous waste dumps or for indoor air analysis. Besides the detection of single toxic compounds, this calculation procedure for multicomponent mixtures like PCBs

Table 1
Calculation table for the elimination of PCB-signal superposition to get 'reduced integrals'

Reduced integral[a]	M^+ {subtraction: reduction factor×intensity of ion=superposition of PCB with higher degree of chlorination}
Cl_1-PCB=	$I_{188}-[0.044\times I_{222}]-[0.318\times I_{256}]-[0.018\times I_{292}]-[0.0002\times I_{326}]-[0.0008\times I_{360}]-[0.001\times I_{396}]-[0.002\times I_{430}]$ $-[0.013\times I_{464}]-[0.015\times I_{498}]$
Cl_2-PCB=	$I_{222}-[0.037\times I_{256}]-[o.557\times I_{292}]-[0.009\times I_{326}]-[0.033\times I_{360}]-[0.004\times 396]-[0\times I_{430}]-[0.0007\times I_{464}]-[0\times I_{498}]$
Cl_3-PCB=	$I_{256}-[0.083\times I_{292}]-[0.623\times I_{326}]-[0.024\times I_{360}]-[0.122\times I_{396}]-[0.003\times I_{430}]-[0.005\times I_{464}]-[0\times I_{498}]$
Cl_4-PCB=	$I_{292}-[0.035\times I_{326}]-[0.344\times I_{360}]-[0.017\times I_{396}]-[0.021\times I_{430}]-[0.005\times I_{464}]-[0\times I_{498}]$
Cl_5-PCB=	$I_{326}-[0.044\times I_{360}]-[0.522\times I_{396}]-[0.012\times I_{430}]-[0.100\times I_{464}]-[0\times I_{498}]$
Cl_6-PCB=	$I_{360}-[0.032\times I_{396}]-[0.482\times I_{430}]-[0.060\times I_{464}]-[0.156\times I_{498}]$
Cl_7-PCB=	$I_{396}-[0.019\times I_{430}]-[0.349\times I_{464}]-[0.008\times I_{498}]$
Cl_8-PCB=	$I_{430}-[0.017\times I_{464}]-[0.390\times I_{498}]$
Cl_9-PCB=	$I_{464}-[0.015\times I_{498}]$ ⇑most interfering ions
Cl_{10}-PCB=	I_{498}

[a] Reduced integral= sum of Cl_{1-10}-PCB.

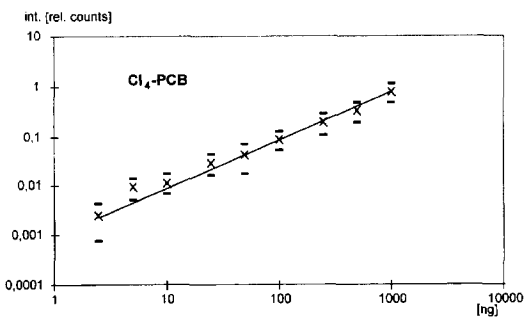

Fig. 4. One of ten calibration curves of each degree of chlorination (Cl_4 congeners), 4 measurements per calibration point.

enables the analyst to get data of high reliability even by fast unresolved GC–MS runs.

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