A rapid and easily applicable procedure for the quantitative determination of polychlorinated biphenyls (PCB) in fuel oils

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Schnelles und leicht anwendbares Verfahren zur quantitativen Bestimmung von polychlorierten Biphenylen in Heizölen

Nowadays routine clean-up procedures for GC-analysis of organochlorine contaminants, especially PCB, in mineral oils are most frequently carried out by means of a combination of two polypropylene bodied microcolumns filled with bonded benzosulfonic-acid and silica gel adsorbents (Brenk [3]; DIN [4]). Even on highly complex matrices such as waste oils this method will result in extracts clean enough for electron-capture analysis. Nevertheless, one of the major disadvantages is the relatively high price for disposable extract-clean columns. Therefore, an adequate method for simpler, easy-to-prepare matrices like fuel oils, gasoil, transmission fluids and similar products is highly desirable.

The proposed sample preparation comprises a miniaturized column-chromatographic clean-up including a dilution step of 1 to 50 and followed by capillary gas-chromatography with electron capture detection.

The mini-columns are made by pushing a small plug of cotton into the barrel of a pasture pipet and filling it with 0.40 to 0.45 g of activated Florisil. The adsorbent is covered by about 0.30 g (i.e., 1 cm) of anhydrous sodium sulfate. The entire packing will fill the body of the pipet up to two thirds, whereas the remaining volume acts as reservoir for the elution solvent. Prior to use, the tubes are partially wrapped with a strip of filter paper (to prevent accidentally spilled solvent from running down) and are then fixed in an appropriate holder. These mini-columns may be loaded with up to 0.2 ml mineral oil which is eluted with 10 ml cyclohexane into a 10 ml volumetric flask. Beside the particulate matter the column will remove polar accompaniments e.g., marking dyes providing an extract suitable for gas-chromatographic analysis without any further manipulations. The activity of the sorbent has to be checked in regular intervals. If some of the lower chlorinated biphenyls should not be eluted quantitatively as pointed out by Zell and Ballschmiter [9] the amount of the sorbent has to be adjusted.

Similar to other column-chromatographic preparations the apolar hydrocarbon matrix will not be separated from the organochlorine fraction but will be suppressed by the specific electron capture detector, at least in the important sections of the chromatogram. On the other hand, it has to be kept in mind that the injected extract containing 1–2% high-boiling hydrocarbons will develop a quite different evaporation profile in the chromatograph's injector than the reference cocktail consisting only of the spiked solvent. Thus as pointed out by Tuinstra et al. [8], the quantitative evaluation by peak height is biassed by a systematic error and poor recovery rates may occur. The addition of 2% demonstrably incontaminated fuel oil to the reference solution eliminated these adverse effects and established reasonable recovery rates for the selected compounds.

The quantitative evaluation of the PCB-content is hampered by the complex nature of this multicomponent contaminant. To handle this wellknown problem many quantitation procedures and arithmetic routines have been worked out in food and agricultural chemistry. Most of them are based on the comparison of the sample pattern and a best fitting reference mixture either of genuine or blended industrial PCB-fractions. But even in technical matrices where no metabolism occurs the patterns exhibited by gas-chromatography rarely match exactly, resulting in a more approximative character of these methods. High resolution congener-specific PCB-analysis is now by means of fused silica capillaries a feasible option for identification and quantification. To obtain comparable data, six individual chlorinated biphenyls (No. 28, 52, 101, 138, 153, 180 according

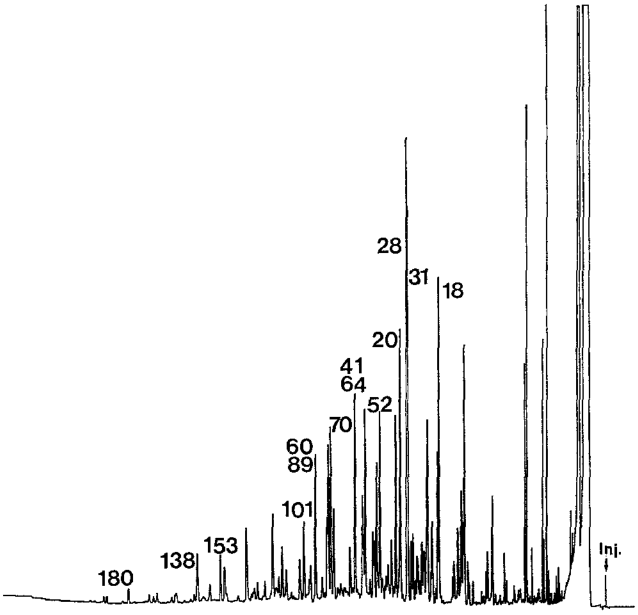

Fig. 1. Extract of a heavily contaminated oil (90 mg/kg)

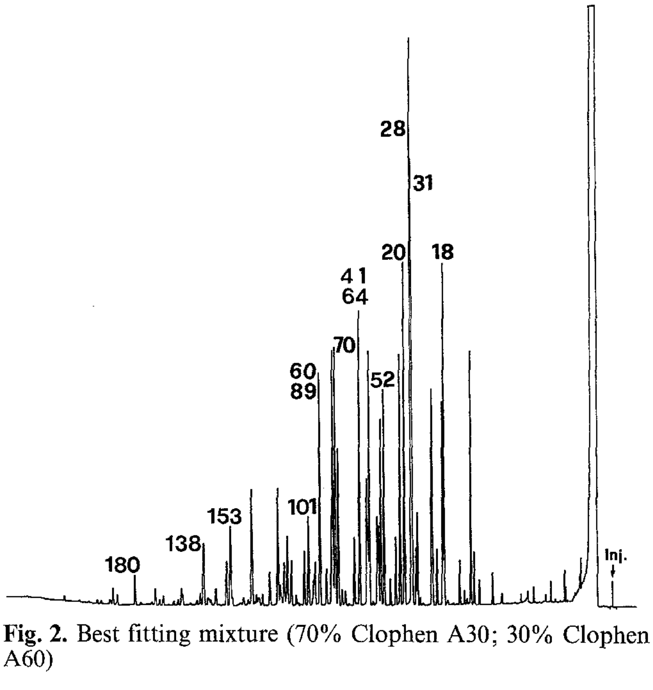

Fig. 2. Best fitting mixture (70% Clophen A30; 30% Clophen A60)

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to Ballschmiter and Zell [1]) are evaluated separately. Their fraction in the different PCB-specialities is documented by several authors (Duinker and Hillebrand [5]; Schulte and Malisch [7]) thus beside the exact quantitation of these congeners an estimation of the total PCB content is possible e.g., by multiplying the sum of the six components by five as it is proposed by the LAGA [6]. Being intended mainly for the use in food analysis the higher chlorinated and more recalcitrant congeners are dominant in this selection, whereas in technical formulations the lower chlorinated congeners are frequently emphasized. Therefore the standard set (Beck and Mathar [2]) should be extended by at least one of the lower chlorinated individuals i.e., No. 18. Like the ones previously mentioned this component can be easily separated in GC and is also commercially available as pure chemical.

Experimental

Reagents

Sodium sulfate: anhydrous, heated at 500 °C, 5 h. Florisil: activated at 650 °C, 3 h. Cyclohexane: suitable for pesticide residue analysis (PR-grade). Cotton wool: extracted with light petroleum (Soxhlet extractor).

GC-parameters

Packard-Chrompack, system 438 with automatic liquid sampler. Fused silica capillary column 30 m/0.25 mm ID, DB-1, H_2 pressure controlled at 100 kPA.

Column temperature: hold 1 min at 85 °C, then to 150 °C at 40 °C/min, then to 265 °C at 3 °C/min and hold for 10 min. Injector: 250 °C. Detector: 300 °C (ECD, range 3, attenuation 4, 35 ml/min N_2 make-up gas).

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Perspex as sample carrier in TXRF

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Plexiglas als Probenträgermaterial in der TRFA

TXRF is a rather new variant of XRF utilizing total reflection of the exciting X-ray beam at the sample carrier to reduce the background [1, 2]. In order to enable reflection the sample carrier has to be very even and plane. Commonly, polished quartz slices are used. They have, however, some decisive disadvantages: The fluorescence radiation from the silicon of the quartz makes a quantitative determination of silicon in the sample impossible. Furthermore, quartz carriers are rather expensive, because they have to be polished very accurately. The residues of the abrasive (e.g., Ce) often cause disturbing signals. So the cleaning of new carriers is rather troublesome as well as the cleaning of used carriers. If they are not cleaned very carefully contaminations of Fe, Cu and Zn may remain. Therefore, it is desirable to have sample carriers that can be used without precleaning and which are cheap enough to be used only once.

Some materials have already been tested to avoid these disadvantages, e.g., germanium [2] or glassy carbon.

A new material for sample carriers is perspex. Perspex contains only the elements H, C and O which are, in general, not determined by TXRF, and it is scarcely contaminated by other elements [3]. Perspex may be produced in form of sheets with very even surfaces which need no further polishing. This reduces the costs and the danger of contamination. The even surfaces of perspex are protected with a thin foil against scratches and contamination during handling, transport and storage.

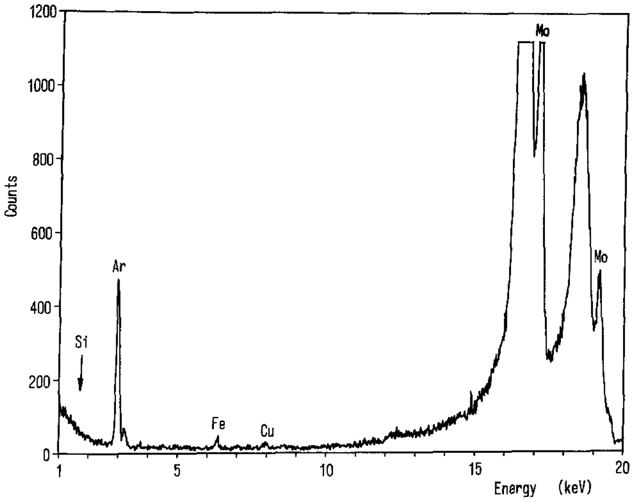

Fig. 1. Blank spectrum of a perspex sample carrier without precleaning (500 s)

The sample carriers are cut from perspex sheets of adequate thickness. They can be used without precleaning immediately after the removal of the foil.

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