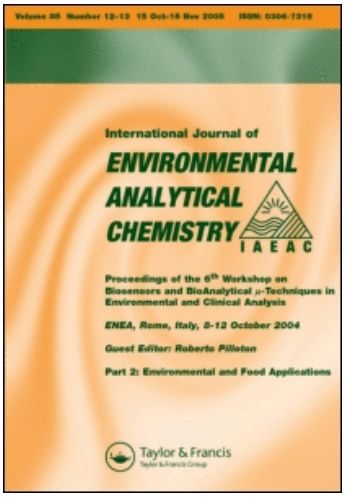


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# PROBLEMS ENCOUNTERED IN THE DETERMINATION OF 2,3,4-2'4'5' HEXACHLOROBIPHENYL (CB 138) IN ENVIRONMENTAL SAMPLES

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Selected individual chlorobiphenyls (CB) used for monitoring and tolerance purposes are checked on interferences using negative chemical ionization (NCI) mass spectrometry. An interference at the retention time of CB 138 (2,3,4-2'4'5' hexachlorobiphenyl) was found. Quantitative results reported up till now and maximum residue limits (MRL) set for this compound are at least questionable.

KEY WORDS: Chemical ionization, mass spectrometry, individual chlorobiphenyls, CB 138.



## INTRODUCTION

Since the discovery of the polychorinated biphenyls (PCBs) in environmental samples[1] high-resolution gas cromatography has replaced the analysis of PCBs on packed columns. In an early stage the Netherlands selected specified chlorobiphenyl congeners (CBs) for monitoring and tolerance purposes[2] to eliminate the problems arising during quantification when using packed columns.[3] It is a flexible concept in which other chlorobiphenyls, e.g., the toxic coplanar congeners can be included. This concept is nowadays used in Finland and West Germany[4,5] and by several international organizations such as the Community Bureau of Reference (BCR), the International Council for the Exploration of the Sea (ICES), the Verband Deutscher Landwirtschaftlicher Untersuchungs- and Forschungsanstalten (VDLUFA) and the International Union of Pure and Applied Chemistry (IUPAC).

In the Netherlands tolerances have been established for seven CBs, i.e., 28 (2,4-4'trichlorobiphenyl), 52 (2,5-2'5'tetrachlorobiphenyl), 101 (2,4,5-2'5'pentachlorobiphenyl), 118 (2,4,5-3'4'pentachlorobiphenyl), 138 (2,3,4-2'4'5'hexachlorobiphenyl), 153 (2,4,5-2'4'5'hexachlorobiphenyl) and 180 (2,3,4,5-2'4'5'heptachlorobiphenyl) in fish and milk (products).[6] Tolerances for meat (products) are under discussion. In the Netherlands, experience exists now for more than ten years with the above mentioned concept, in particular with the

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control of food and feed. During this time exceeding of tolerances was mainly due to CB 153 and, also, to CB 138 or 52.

Chromatography is a tool to prove the absence, not the presence of known compounds. This was recognized at an early stage of BCR activities when developing reference materials for specified chlorobiphenyls in fish oils. Therefore, in a BCR working group it was decided to identify and quantify specified chlorophenyls in environmental samples using at least two capillary columns with a different polarity.[7] The development of the concept and the confirmation of positive results with mass spectrometry (electron impact (EI) mode) indicated that in matrices at the end of the food chain, no interfering compounds were present. In the field of capillary columns in the last 10 years progress was made with respect to the coating efficiency, inertness, longevity, bleed and reproducibility of the column.

A few years ago the chromatographic properties of all 209 PCB congeners were described and it was claimed that under optimum conditions, all congeners with the exception of eleven pairs of compounds, could be separated on a 50 m narrow bore fused silica capillary SE-54 column.[8] No separation problems were mentioned for the above mentioned seven CBs. Recently[9] two-dimensional gas chromatography was used. The first column was a 25 m SE-54 capillary column, the second a 30 m OV-210 capillary column. With this short SE-54 column and under the GC conditions used, distinct separation problems were now encountered for CB 28, CB 138 and CB 153; possible interferences were mentioned for CB 52 and 101. The conflicting results of both publications[8,9] initiated a new evaluation concerning the choice of the seven CBs, using mass spectrometry (GC-MS) under negative chemical ionization (NCI) conditions; to our knowledge GC-MS in the NCI mode is hardly used for confirmation purposes.[10,11] It is known that mass spectrometry does not easily discriminate between CB isomers. In general it can be said that CB isomers give the same fragmentation pattern. The abundance of the fragments indeed will often more or less differ, but in mixtures of isomers it is difficult to identify the compounds by using GC-MS. Differentiation is possible when retention times of the isomers differ in the GC analysis, but identification is never conclusive.

Therefore, if the spectrum of a chlorobiphenyl compound in a sample does not completely fit with that of a standard, the conclusion should be that the peak in the sample comprises one or more other compounds.

In this report we describe the results of NCI-MS analysis of some selected samples with special attention to CB 138 (2,3,4-2'4'5' hexachlorobiphenyl).

## EXPERIMENTAL

### *Apparatus*

Analysis were performed with a Finnigan 4500 quadrupole mass spectrometer and an INCOS data system. Methane was used for the NCI at a pressure of 1.0 Torr and a source of temperature of 190°C. The quadrupole was linearly scanned every

0.25 sec from 230 to 400 m/z. The emission current was 0.25 mA and the electron energy 70 eV.

A Finnigan 9610 gas chromatograph was equipped with a 50 m x 0.15 mm fused silica capillary column coated with CP Sil 8 CB. The film thickness was 0.14 $\mu$m.

The following conditions were used: injector temperature, 250°C; linear helium gas velocity, about 40 cm/s; temperature programme, 3 min 90 °C–15 °C/min–250 °C, final hold 20 min.

### *Chemicals*

Glassware, solvents and chemicals used for chlorobiphenyl determinations were redistilled or cleaned as is usual for this type of analyses. The technical PCB mixtures Aroclor 1242, 1254 and 1260 and the individual chlorobiphenyls CB 28, 52, 101, 118, 138, 153 and 180 were obtained from Analabs (North Haven, Conn., USA) or Promochem (Wesel, FRG). Hexachlorobenzene was used as internal standard.



### *Samples*

Extraction and major clean-up of a cod-liver oil, mackerel oil, milk fat, sheep fat and sludge were carried out by saponification.[2,12] After final clean-up using a basic alumina column the concentrated extract was injected splitless on the CP Sil 8 CB capillary column (Chrompack, Middelburg, The Netherlands).

## RESULTS AND DISCUSSION

Standard solutions of the technical Aroclor mixtures, the individual chlorobiphenyls CB 28, 52, 101, 118, 138, 153 and 180, and extracts of the above mentioned samples were injected as indicated under Experimental, in the GC-MS. The present paper deals primarily with CB 138. The results of the other chlorobiphenyls will be published in the near future.

In Figure 1 the full NCI spectrum of the standard CB 138 is given, eluting at a retention time (RT) of 23.52 min, and with a scan number of 5727. Figure 2 shows the reconstructed ion current and extracted ion profiles of the molecular ion (m/z 360) and $(M\text{-}2Cl)^-$ (m/z 290) of the peaks in the cod-liver oil with an RT around that of CB 138. It is obvious that the profiles are not symmetric; that is, an interference may be present. Therefore scans were also made at the front and the back of the peak. Figure 3 shows the spectrum of scan 5738 (back of the peak) of cod-liver oil extract, which is identical with the spectrum of CB 138 and confirms its presence.

In Figure 4 the NCI spectrum of scan 5715 (front of the peak) shows a different spectrum, as far as the abundances of the fragments are concerned. This indicates the presence of an unknown hexachlorobiphenyl near the RT of CB 138. In the

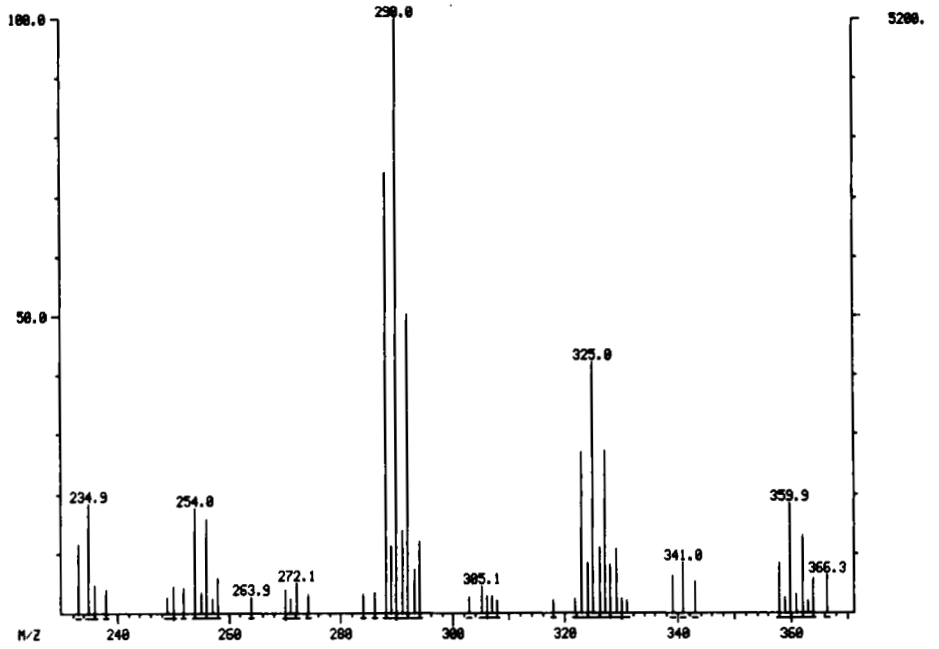


**Figure 1** NCI spectrum of the standard 2,3,4-2′4′5′ hexachlorobiphenyl (CB 138), $M = 360$.

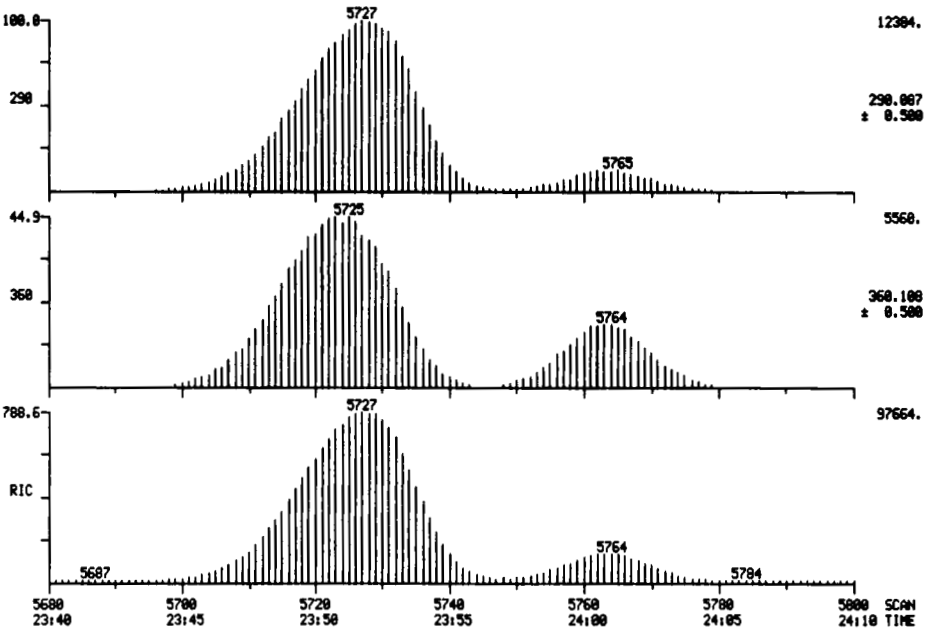


**Figure 2** Mass chromatogram of a cod-liver extract around the retention time of CB 138 for the reconstructed ion current, m/z 360, and m/z 290 (scan 5764 represents CB 158).

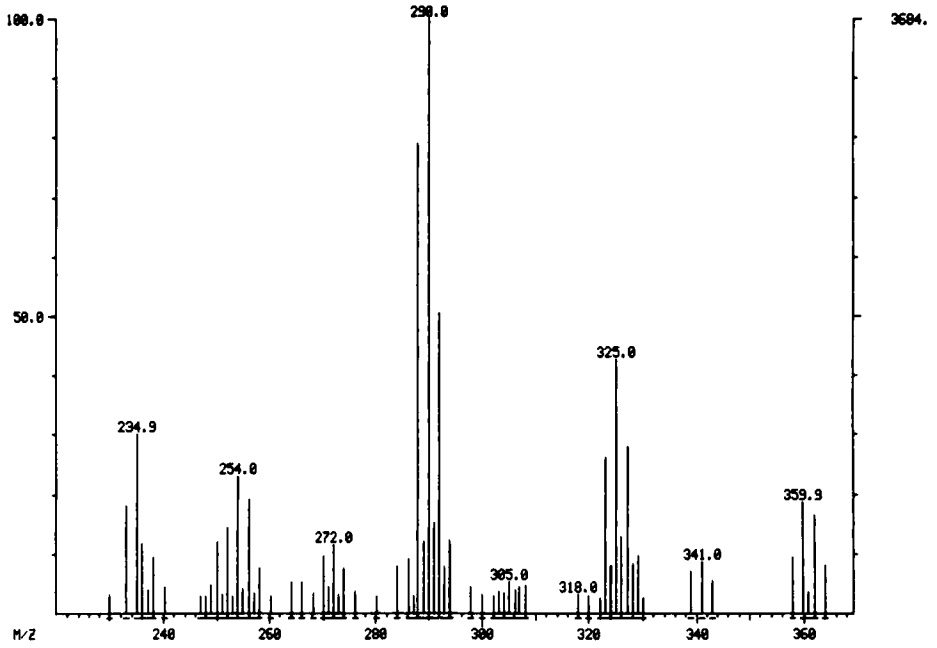


**Figure 3** Full NCI spectrum of scan 5738 of the cod-liver extract.

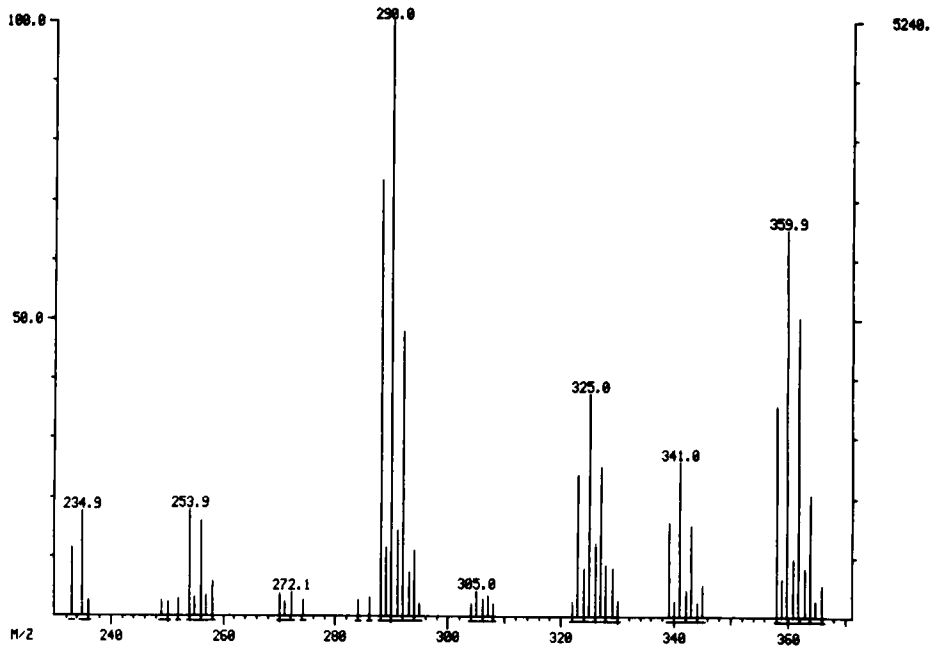


**Figure 4** Full NCI spectrum of scan 5715 of the cod-liver extract.

**Table 1** Relative intensity (%) of ion fragments of hexachlorobiphenyls obtained with negative chemical ionization

| *PCB number* | *Structure* | *RT*[a] | *Relative intensity (% of the sum of the fragments)* | | | |
|---|---|---|---|---|---|---|
| | | | $M^-$ | $(M\text{-}Cl)^-$ | $(M\text{-}2Cl)^-$ | $(MH\text{-}3Cl)^-$ |
| 155 | 246–246 | 1.343 | 1 | 45 | 36 | 18 |
| 136 | 236–236 | 1.445 | 0 | 10 | 74 | 16 |
| 154 | 245–246 | 1.447 | 1 | 24 | 63 | 12 |
| 151 | 2356–25 | 1.469 | 4 | 25 | 58 | 13 |
| 149 | 236–245 | 1.501 | 2 | 22 | 64 | 12 |
| 140 | 234–246 | 1.507 | 1 | 16 | 68 | 15 |
| 153 | 245–245 | 1.558 | 20 | 25 | 48 | 7 |
| 132 | 234–236 | 1.570 | 1 | 10 | 72 | 17 |
| 141 | 2345–25 | 1.592 | 11 | 33 | 47 | 9 |
| 137 | 2345–24 | 1.614 | 7 | 40 | 45 | 8 |
| unknown | hexa CB | (scan 5715) | 30 | 15 | 45 | 10 |
| 138 | 234–245 | 1.639 | 10 | 27 | 54 | 9 |
| 158 | 2346–34 | 1.649 | 49 | 16 | 30 | 5 |
| 129 | 2345–23 | 1.663 | 6 | 36 | 49 | 9 |
| 128 | 234–234 | 1.734 | 5 | 13 | 67 | 15 |
| 156 | 2345–34 | 1.800 | 56 | 12 | 27 | 5 |
| 169 | 345–345 | 1.952 | 95 | 1 | 3 | 1 |

[a]HCB = 1.000.



technical PCB mixtures and in the other samples scans have also been made around the RT of CB 138. In all cases just before the RT of CB 138 a deviating spectrum could be found identical with the spectrum of Figure 4. This indicates the presence of a generally occurring unknown hexachlorobiphenyl in environmental samples and technical mixtures.

All hexachlorobiphenyls available to us were studied by GC-MS. Information on the relative intensity of their fragments $M^-$, $(M\text{-}Cl)^-$, $(M\text{-}2Cl)^-$ and $(MH\text{-}3Cl)^-$, together with information on the unknown CB in the cod-liver extract is given in Table 1. For the latter compound it is assumed that the spectrum at the front of the peak (scan 5715) is the spectrum of the pure unknown hexachlorobiphenyl and that no interference occurs with CB 138.

From the table it is clear that there are remarkable differences between the isomers. In our experiments we used a capillary column under GC circumstances different from those in ref. 8. The polarity of this column, however, is the same as that of SE-54. Therefore an agreement in eluting order of the CB congeners can be expected and only few compounds can be considered as unknown hexachlorobiphenyl candidates. Besides, based on the presence of the unknown CB in the samples and technical mixtures a non-degrading type of CB is expected.[13] The candidates are the CBs 160 (2,3,4,5,6-3′), 163 (2,3,5,6-3′4′) and 164 (2,3,6-3′4′5′). None of these CBs is commercial available and, until now, the identity of the unknown compound has not been established. For the time being, the only conclusion is that under the analytical circumstances presently used, quantitative

data reported for CB 138 and tolerances set for this compound are at least questionable.

Recent information from Mullin,[14] which will be published in the near future, confirms that an interfering compound is present in the CB 138 peak. Acccording to this information, the interfering compound is 2,3,5,6-3'4' hexachlorobiphenyl (CB 163).

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