Determination of Toxaphene (Camphechlor) Residues in Foodstuff

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Toxaphene (correct ISO name: Camphechlor) is probably the most complex pesticide and more than one million tons of it have been used since 1946 [1]. Owing to its widespread use and environmental stability, predominantly chlorobornanes were identified as toxaphene residues in environmental matrices including air, fresh water/sea water and soil. The highest concentrations of these fat-soluble compounds were detected in aquatic animals, particularly dolphins, whales and fish.

On account of analytical difficulties, toxaphene residues were rarely detected by food inspection laboratories in Germany in the last years. Most analytical problems arise from the complex composition of toxaphene. According to Vetter [2], there are 16640 possible chlorobornane congeners (16128 enantiomeric pairs and 512 achiral compounds) that theoretically could be separated by achiral gas chromatographic (GC) columns. In practice, technical toxaphene could be separated into more than 300 (racemic) compounds [3]. Furthermore, substantial differences in gas chromatographic peak patterns of environmental samples as compared to those of the technical product are observed. Last, but not least peaks of toxaphene components often coelute from GC columns with PCBs and the residues of other organo-chlorinated pesticides.

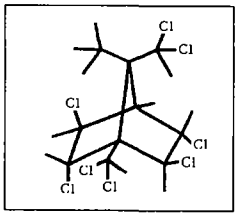
To overcome these problems, the highly selective electron capture negative ionisation mass spectrometer (ECNI-MS) was used for detection in capillary GC. This method allows the reliable identification of toxaphene components, provided that interfering signals of chlordane/nonachlor, polychlorinated diphenylethers and oxidation products of PCBs (reaction in the ion source) are known. However, in the quantification of total toxaphene, the ECNI-MS method overestimates the true residue concentration. The reason for this error is the high response of significant chlorobornanes in

samples compared to the lower mean response of technical toxaphene. Moreover, Andrews [4] have shown that reproducibility is poor even if GC/ECNI-MS is used. Some of these problems seems to result from certain ECNI-MS parameters, which have shown a remarkable influence on response in our laboratory.

Nevertheless, the chlorobornane peaks can be clearly identified with GC/ECNI-MS in samples. Provided that an open split interface is used between GC and the ion source of MS, the recorded retention times are identical to that obtained with GC/ECD (if the same column and temperature programme are used). Since ECD response factors of different chlorobornanes are nearly equal, this second ECD chromatogram allows the estimation of the concentration of identified toxaphene compounds. Using this procedure and, in addition, individual chlorobornanes which had been prepared before [5], we detected and identified three chlorobornanes that represent 25-50% of the total toxaphene residue of marine fish samples [6,7]. Two of the compounds had been identified in other marine environmental samples and human breast milk showing the general accumulation of these compounds in the food chain. Almost simultaneously a Canadian primate feeding study was carried out by Andrews [8]. The toxaphene was administered at a dose of 1mg/kg/day for one year to cynomologous monkeys. Again, those chlorobornanes that are known from fish clearly dominated in the ECD chromatograms of blood and adipose tissue. This means that in mammals treated with the whole complex mixture of toxaphene, the same chlorobornanes are found as main persistent metabolites.

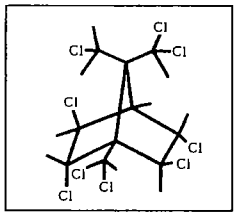
In order to obtain precise and comparable data on toxaphene residues in food, defined chlorobornanes should be used as indicators. The results above support the proposal to apply the three main persistent toxaphene components **1-3** (Figure) in such a congener specific analytical procedure as indicator compounds. This seems to be the only solution to the problems of routine toxaphene analysis.

Figure: Proposed toxaphene indicator compounds



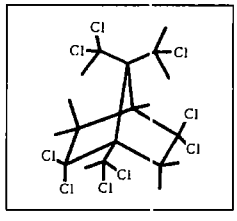
Indicator Compound 1:

2-endo,3-exo,5-endo, 6-exo,8,8,10,10-octachlorobornane = T2 = TOX 8 = Parlar's 26



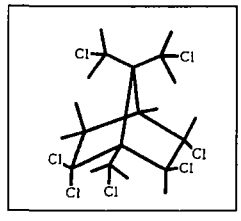
Indicator Compound 2:

2-endo,3-exo,5-endo, 6-exo, 8,8,9,10,10-nonachlorobornane = T12 = TOX 9 = Toxicant A_c= Parlar's 50



Indicator Compound 3:

2,2,5,5,8,9,9,10 10-nonachlorobornane = Parlar's 62



Indicator Compound 4:

2,2,5-endo,6-exo,8,9,10-heptachlorobornane = Toxicant B = Parlar's 32

Since toxaphene and similar products are still being in use in some countries, a contamination of foods, e.g. fruit and vegetables, with non-degraded toxaphene cannot be excluded. To be able to detect such a recent contamination routinely without permanently checking for the typical GC pattern of toxaphene, the heptachlorobornane **4** was selected. This compound seems to be less persistent, is degraded by light, and does not accumulate in fish. All four proposed indicator compounds have become commercially available.

Fish is the main source of toxaphene intake in Germany. Up to now, the toxaphene indicator compounds have been determined in more than one hundred pooled samples of fish. The investigated samples included nearly all important fish species consumed. Highest residue concentrations were found in marine fish with a high or moderate fat content, e.g. halibut, herring, redfish and mackerel. More than 60% of toxaphene intake is caused by herring. In fresh water species and marine fish with a low fat content less toxaphene was found. A significant relationship between the fishing grounds and the toxaphene residue could not be established. Differences in the contamination levels were most probably related to the age of the fish.

A considerable number of the fish samples analysed has shown high amounts of toxaphene indicator compounds. These results and the congener specific method proposed will have consequences on the establishment of a new German maximum residue limit for toxaphene.

To study the variance of toxaphene residues, a total of one hundred individual samples of herring, redfish, and halibut each from one catch were analysed [9]. Excluding 5% of the samples with the lowest and highest contamination level, respectively, the concentration range was found to be 7 - 44 ng/g, 8 - 31 ng/g and 31 - 99 ng/g based on wet weight for the sum of the three indicators in herring, redfish, and halibut, respectively. This means that in marine fish samples of one catch, the variance of the residue contents is moderate and does not significantly differ between the fish species. The graphic representation of data shows a positively skew distribution of the toxaphene content in these species.

Additionally, the residues in 30 farmed salmons from one wholesaler were investigated. The statistical examination of toxaphene concentrations found for the farmed salmon shows a slightly different picture. In this case, the data seem to be normally distributed. No correlation of residue concentration with the length of the salmons was observed. Moreover, the lowest range of toxaphene concentrations (13 - 32 ng/g wet weight) was found.

Based on these results, the error of toxaphene analysis in fish caused by the mode of sampling has been estimated. If fish from one lot is investigated, analytical data of mixed samples each consisting of five randomly collected fishes each should result in a relative standard deviation of less than 30%.

References

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