Interference in the Electron-Capture Technique for Determination of Polychlorinated Biphenyls by Sulfur-Containing Compounds in Petroleum Products

by
R. A. Hofstader
Esso Research and Engineering Co.
Analytical and Information Division
P.O. Box 121, Linden, N. J. 07036

and
C. A. Bache and D. J. Lisk
Pesticide Residue Laboratory
Department of Food Science
New York State College of Agriculture and Life Sciences
Cornell University, Ithaca, N. Y. 14850

Polychlorinated biphenyls (PCB's) or Aroclors have been widely used as electrical insulating liquids, plasticizers, dye carriers and flame retardants. The resulting widespread environmental contamination by these compounds has been amply reviewed (PEAKALL and LINCER 1970). Recently electron capture gas chromatographic analysis of certain oils by a commercial laboratory resulted in a series of anomalous peaks which were attributed to the presence of PCB-type compounds even though the peak retention times did not precisely match those of four of the common Aroclors. It was suspected, however, that sulfur compounds known to be present in petroleum and having appreciable electron affinity may have been responsible. This investigation was undertaken to learn if PCB's were truly present.

Experimental

A solvent-refined neutral oil designated as "1365 C" and asserted to be contaminated with PCB's was studied. A second highly purified oil designated Marcol 72 (FN 2917) was used as a control. The oils were extracted and possible PCB's isolated by a standard procedure (PESTICIDE ANALYTICAL MANUAL 1971a) involving extraction with petroleum ether, selective solvent extraction with acetonitrile and column chromatography on Florisil. Gas chromatographic analysis followed using the following detection systems: electron capture, electrolytic conductivity (chlorine mode), flame photometric and microcoulometric (both in the sulfur mode). Table 1 lists the gas chromatographic operating parameters.

Results and Discussion

Figure 1 shows gas chromatograms developed using electron capture detection. It is evident that whereas the purified (control) oil (D) is quite free of electron capturing compounds, the 1365 C oil (C) contains numerous constituents which respond. Chromatograms A and B which illustrate the recovery of Aroclors 1254 and 1242 added to the control oil, show that the Aroclor constituents elute over the same time range as the electron-capturing compounds in 1365 C oil (Chromatogram C). Gas chromatographic analysis of 1365 C oil using both the flame photometric (Figure 2A) and microcoulometric (Figure 2C) detectors for sulfur compounds showed the presence of several peaks with retention times in the same range as Aroclors 1242 and 1254. Little response occurred when the control oil was

Bulletin of Environmental Contamination & Toxicology,
Vol. 11, No. 2

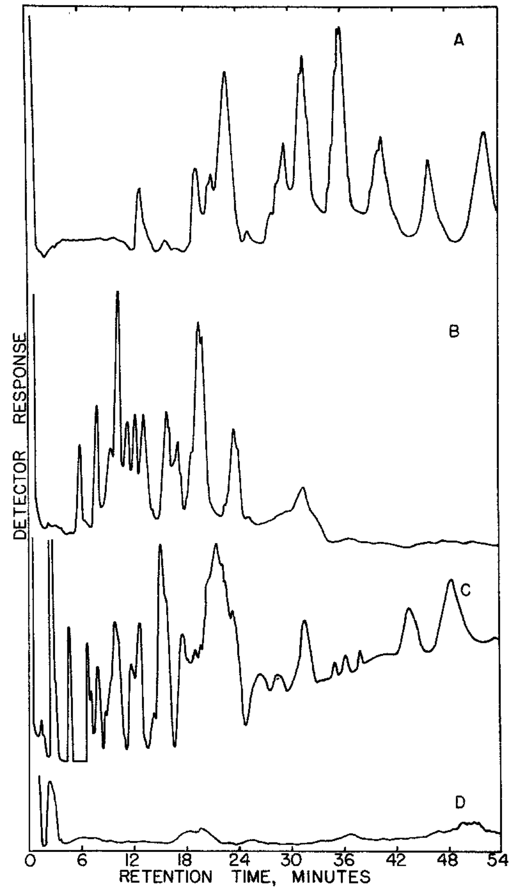

Figure 1. Electron capture gas chromatograms of control oil with 5 ppm of Aroclor 1254 added (A), control oil with 5 ppm of Aroclor 1242 added (B), 1365 C oil (C) and control oil alone (D).

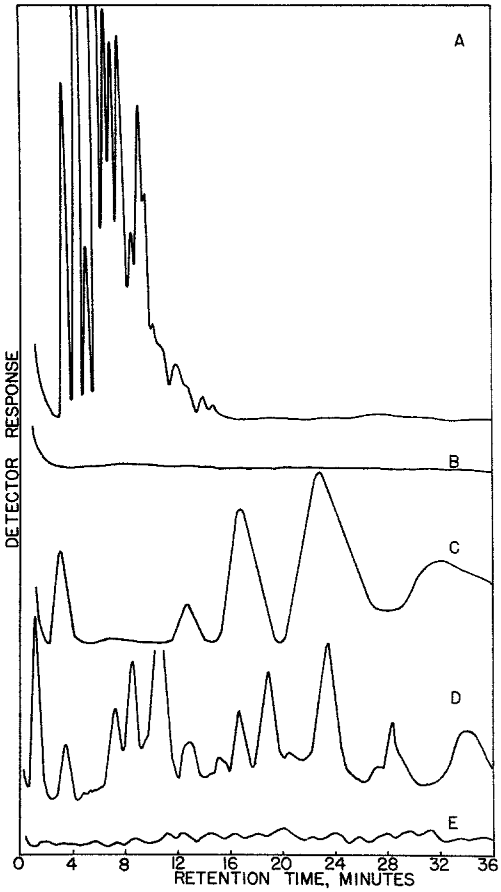

Figure 2. Sulfur flame photometric gas chromatograms of 1365 C oil (A) and control oil (B): sulfur microcoulometric gas chromatograms of 1365 C oil (C): chlorine electrolytic conductivity gas chromatograms of Arochlor 1254 standard (D) and 1365 C oil (E).

Table 1. Gas Chromatographic Operating Parameters

Detection System	Column Packing	Column dimensions, cm i.d.	lgth.	Column temp. °C.	Flow rate cc/min	Chart speed cm/hr
electron capture	5% OV-17 on 80-100 mesh, acid-washed Chromosorb W.	0.6	183	210	80	25.4
flame photometric	5% OV-17 on 80-100 mesh, acid-washed Chromosorb W.	0.4	183	210	80	38
electrolytic conductivity	5% OV-17 on 80-100 mesh, acid-washed Chromosorb W.	0.4	183	210	60	38
micro coulometric	10% DC-200 on Gas Chrom Q	0.2	122	200	35	76

analyzed using the sulfur flame photometric detector (Figure 2B). Analysis of total sulfur in 1365 C oil showed 1900 ppm. Conversely analysis of 1365 C oil using the electrolytic conductivity detector for organic chlorine compounds showed the absence of responding constituents, the chromatographic recorder tracing representing essentially detector noise (Figure 2E). The retention times of specific constituents in 1365 C oil as determined by the various detection systems in Figure 2 are not necessarily alike since varying gas chromatographic operating parameters were used (see Table 1). Also the number of sulfur compounds responding to microcoulometric detection are fewer than those detected by the flame photometric mode since the latter detector is more sensitive. When comparing the electron capture response of 1365 C oil (Figure 1C) with that using the other detection systems (Figure 2), it is obvious that certain constituents such as sulfur compounds which may respond to electron capture would not respond to the other detection modes specific for chlorine compounds. Thin layer chromatographic analysis of 1365 C oil for PCB's using the method of the Food and Drug Administration (PESTICIDE ANALYTICAL MANUAL 1971b) showed their absence. These data indicate that the electron capture response of constituents in 1365 C oil may be due at least in part to the presence of relatively high levels of natural sulfur compounds of moderate electron affinity.

References

PEAKALL, D. B. and J. L. LINCER: BioSci. 20, 958 (1970).
PESTICIDE ANALYTICAL MANUAL: Vol. 1, Sections 211.14a, b and d, J. A. Burke and J. A. Gaul, eds., Food and Drug Admin., Washington, D. C. (1971a).
PESTICIDE ANALYTICAL MANUAL: Vol. 1, Section 411, Method I, J. A. Burke and J. A. Gaul, eds., Food and Drug Admin., Washington, D. C. (1971b).