

Contribution to the Identification and Quantitation of Aroclor Mixtures by Least-Squares Analysis of Gas Chromatographic Data

R. Corbella, M.A. Rodríguez-Delgado, and F.J. García Montelongo*

Department of Analytical Chemistry, Nutrition and Food Science, University of La Laguna, 38071 - Tenerife, Spain

Abstract

A procedure is proposed for the qualitative and/or quantitative determination of different Aroclor technical formulations in complex mixtures by analysis of gas chromatographic data. The method is based on the reconstruction of a time-continuous Gaussian function of the gas chromatographic data and the application of least-squares to the reconstructed functions. The results are compared with those obtained when least-squares regression is applied directly to discrete chromatographic data.

Introduction

Polychlorinated biphenyls (PCBs), which are formed by extensive chlorination of biphenyl, were commercially marketed by numerous manufacturers throughout the world and widely distributed because of their high applicability. They have been used for many years as liquid dielectrics and coolants in large transformers and capacitors. Because of their high stability, their effect on the environment, and their harmful effects on human health, PCBs are among the most frequently investigated analytes in environmental analytical chemistry, and many papers have been published about them (1–10).

The most common method for determining PCBs is gas chromatography (GC) using an electron capture detector (ECD) with capillary or packed columns (11–17). The second most frequently used detection system is mass spectrometry (MS), which permits the confirmation of identification and also the use of labelled compounds as recovery surrogates (18–23). A major disadvantage of this detection system is the relatively high minimum detectability, which is 2–3 orders of magnitude higher than that of ECD. An exception is when GC–MS in selected ion monitoring mode (SIM) is applied, in which case the relative detectability is inversely proportionate to the extent of chlorination, and in some cases, less-chlorinated congeners are more easily quantitated.

The accuracy of PCB determination is critical for evaluating contamination by Aroclor compounds. Unfortunately, the rigorous determination of all components is extremely expensive and time-consuming. It requires the complete separation of all congeners and the application of pure standards. The most common approach in PCB identification is to compare the patterns produced by the sample with those produced by mixtures of commercial preparations, such as Clophen (Bayer AG, Leverkusen, Germany) or Aroclor (Monsanto, St. Louis, MO). The comparison is generally carried out by visual inspection after the analysis of numerous Aroclor standards, and it relies solely on the judgment of an experienced analyst. The PCB contents of the samples are often expressed in terms of these commercial mixtures (24–28).

However, the complexity of certain samples requires methods that offer the possibility of determining the individual congeners in the sample. Chemometric methods represent an alternative to the identification and quantitation of PCBs in complex samples (29–30). These methods can be used to characterize sample patterns and classify the unknown as an Aroclor mixture. Several authors have demonstrated that least-squares and partial least-squares methods (31–33) are suitable for determining the composition of Aroclor mixtures in samples composed of or derived from technical Aroclor mixtures.

Two numerical methods for the identification and quantitation of Aroclor mixtures based on capillary column chromatographic data are presented. A comparative study of the methods was carried out, and even though good results were obtained in both cases, one method is preferred because of its rapidity and simplicity when applied to synthetic samples.

Experimental

GC analysis

A Varian model 3400 GC (Varian Instruments, Palo Alto, CA) equipped with a model 8200 autosampler and a ^{63}Ni ECD was used for sample analysis. The GC operation program was con-

* Author to whom correspondence should be addressed.

trolled by a Varian Star Work Station Rev-A2. The same chromatographic conditions were used for the analysis of all samples: temperature program, 90°C initial temperature (1 min) programmed 6°C/min to a final temperature of 280°C; detector temperature, 300°C; injector temperature, 250°C. A Supelco (Bellefonte, PA) SPB-5 (5% diphenyl-, 94% dimethyl-, and 1% vinyl-poly-siloxane) fused-silica capillary column (15 m × 0.32-mm i.d., 0.25-µm film thickness) was used. Helium was used as the carrier gas at a flow rate of 1.26 mL/min, and nitrogen was used as the make-up gas at a flow rate of 30 mL/min.

Chemicals and samples

Stock solutions of four Aroclor standards (1242, 1248, 1254, and 1260) were supplied by Supelco. The PCB ampoule concentration was 200 µg/mL in methanol. Ampoules were diluted with *n*-hexane to a final concentration of 4 µg/mL, and standards of 1 µg/mL were prepared. Three replicate analyses of each standard and synthetic sample were obtained in all cases. Table I contains the retention times and peak areas for the four standards used.

Two training sets of binary (50:50), ternary (33.3:33.3:33.3), and quaternary (0.25:0.25:0.25:0.25) mixtures of different Aroclor samples (three replicates for each sample) were prepared from the standards in concentrations ranging from 0.4 to 2.0 µg/mL. Data set 1 included all combinations of binary component mixtures (six total), all combinations of ternary component mixtures (four total), and the single quaternary component mixture, for a total of eleven experiments (34). Data set 2 included varying binary mixtures of Aroclor 1254 and 1260 (4:1, 2:1, 1:1, 1:2, 1:3, and 1:4).

Data analysis

Reports from the Varian Star Work Station were processed by a computer program written in BASIC to obtain the function $G(t)$ for each data set. Statgraphics V5.0 (STSC, Rockville, MD) was used to develop the multiple regression analyses based on the least-squares method.

Method A

Data for the relative retention time of chromatographic peaks and their corresponding peak areas and widths (Table I) were used to construct a continuous multiple Gaussian curve function of time for Aroclor standards and unknown samples according to the function

$$G(t') = \sum_{i=1}^N a_i e^{-(t' - t'_i)/w_i)^2} \quad \text{Eq 1}$$

where N is the number of peaks, t' is the relative

Table I. Data of Selected Peaks of Aroclor Mixtures

| n° | RRT | A1242 | | A1248 | | A1254 | | A1260 | |
|------------------|-------|--------|-----|--------|-----|--------|-----|--------|-----|
| | | A* | W | A | W | A | W | A | W |
| 01 | 0.370 | 4689 | 3.9 | | | | | | |
| 02 | 0.384 | 4883 | 3.8 | | | | | | |
| 03 | 0.390 | 28035 | 3.8 | | | | | | |
| 04 | 0.414 | 2255 | 3.4 | | | | | | |
| 05 | 0.442 | 50705 | 6.0 | 21493 | 5.4 | | | | |
| 06 | 0.455 | 5665 | 4.1 | | | | | | |
| 07 | 0.464 | 34885 | 3.6 | 15015 | 3.7 | | | | |
| 08 | 0.489 | 6431 | 6.1 | | | | | | |
| 09 | 0.496 | 107271 | 4.3 | 80294 | 4.3 | | | | |
| 10 | 0.508 | 44881 | 4.0 | 23451 | 5.1 | | | | |
| 11 | 0.517 | 31856 | 3.9 | 18065 | 4.3 | | | | |
| 12 | 0.523 | 7959 | 4.7 | 8320 | 4.1 | | | | |
| 13 | 0.532 | 1651 | 3.1 | 2703 | 4.1 | | | | |
| 14 | 0.539 | 17829 | 3.3 | 28797 | 3.4 | 29658 | 3.4 | 1160 | 3.3 |
| 15 | 0.543 | | | | | 9764 | 4.2 | | |
| 16 | 0.547 | 19430 | 6.6 | 30803 | 6.4 | | | | |
| 17 | 0.562 | 27535 | 3.8 | 41147 | 3.5 | 19450 | 3.4 | | |
| 18 | 0.565 | | | 25704 | 5.2 | | | | |
| 19 | 0.569 | 4534 | 6.4 | | | | | | |
| 20 | 0.575 | 43910 | 3.6 | 64578 | 3.7 | 7397 | 3.6 | | |
| 21 | 0.584 | 8713 | 3.7 | 11903 | 3.7 | | | | |
| 22 | 0.597 | 1383 | 3.4 | 2044 | 3.3 | | | | |
| 23 | 0.601 | 17860 | 3.6 | 33243 | 3.5 | 5345 | 3.8 | | |
| 24 | 0.606 | 31831 | 3.6 | 54559 | 3.6 | 27844 | 3.7 | | |
| 25 | 0.610 | 48806 | 4.7 | 73702 | 4.9 | 71448 | 3.7 | 19674 | 3.4 |
| 26 | 0.618 | | | 7424 | 5.3 | 10704 | 4.0 | | |
| 27 | 0.628 | 43212 | 3.6 | 70262 | 3.7 | | | | |
| 28 | 0.631 | | | | | | | 2814 | 3.1 |
| 29 | 0.638 | 9457 | 3.9 | 18136 | 3.8 | 88691 | 3.4 | 29034 | 3.3 |
| 30 | 0.643 | 5637 | 3.9 | 12937 | 3.7 | 35770 | 3.5 | | |
| 31 | 0.655 | | | 1140 | 2.9 | 4790 | 3.5 | | |
| 32 | 0.661 | 4710 | 3.7 | 9211 | 3.6 | 28026 | 3.5 | | |
| 33 | 0.666 | 9688 | 3.6 | 18101 | 3.6 | 72338 | 3.5 | 5878 | 3.4 |
| 34 | 0.671 | 5388 | 3.7 | 13359 | 3.8 | 21550 | 4.2 | | |
| 35 | 0.674 | | | | | | | 10045 | 3.4 |
| 36 | 0.677 | 14469 | 3.6 | 31844 | 3.7 | 140195 | 3.5 | 19444 | 3.7 |
| 37 | 0.689 | 4070 | 3.5 | 9009 | 3.7 | 18851 | 5.0 | 44482 | 3.4 |
| 38 | 0.697 | | | 1371 | 3.7 | 20886 | 3.9 | 27845 | 3.5 |
| 39 | 0.706 | 12342 | 3.6 | 32338 | 3.8 | 186989 | 4.1 | 93442 | 3.6 |
| 40 | 0.717 | | | 1703 | 3.1 | | | | |
| 41 | 0.725 | | | | | 18286 | 3.5 | 21448 | 3.4 |
| 42 | 0.733 | 12272 | 4.0 | 32350 | 4.1 | 106850 | 5.8 | 189935 | 3.8 |
| 43 | 0.745 | | | 3078 | 4.2 | 39458 | 3.7 | 90778 | 5.1 |
| 44 | 0.755 | | | | | 13045 | 4.8 | 16231 | 3.8 |
| 45 | 0.760 | 3295 | 4.0 | 9952 | 3.9 | 198137 | 3.8 | 182283 | 3.8 |
| 46 | 0.771 | | | | | | | 27486 | 3.7 |
| 47 | 0.780 | | | 2948 | 3.2 | 17638 | 3.5 | 118301 | 3.4 |
| 48 | 0.785 | | | 1744 | 3.2 | 10026 | 3.6 | 66428 | 3.5 |
| 49 | 0.789 | | | | | 48419 | 3.9 | 19230 | 8.2 |
| 50 | 0.796 | | | | | | | 22357 | 3.7 |
| 51 | 0.804 | | | 2765 | 3.4 | 15266 | 3.6 | 94879 | 3.5 |
| 52 | 0.809 | | | 1648 | 3.4 | 9129 | 3.8 | 57370 | 3.5 |
| 53 | 0.814 | | | 2446 | 4.2 | 38321 | 3.8 | 53867 | 3.9 |
| 54 | 0.822 | | | | | 8949 | 6.0 | 12288 | 7.5 |
| 55 | 0.827 | | | | | 4451 | 4.9 | 24742 | 3.6 |
| 56 | 0.834 | 990 | 2.8 | 12996 | 3.5 | 47216 | 3.6 | 306749 | 3.5 |
| 57 | 0.864 | | | 7425 | 3.6 | 31160 | 3.6 | 145978 | 3.7 |
| 58 | 0.874 | | | 2039 | 3.1 | 5692 | 3.3 | 62392 | 3.5 |
| 59 | 0.879 | | | 3225 | 3.7 | 6326 | 3.7 | 75557 | 3.9 |
| 60 | 0.894 | | | | | | | 3903 | 3.4 |
| 61 | 0.909 | | | 1970 | 3.2 | 2983 | 3.5 | 35656 | 3.4 |
| 62 | 0.931 | | | 4951 | 3.5 | 6218 | 3.3 | 75080 | 3.4 |
| 63 | 0.969 | 1624 | 3.2 | 2153 | 3.3 | 2816 | 3.2 | 22870 | 3.3 |
| DCB [†] | 1.000 | 121607 | 3.4 | 104194 | 3.5 | 111997 | 3.5 | 151507 | 3.4 |

* A, peak area; W, peak width.

[†] Decachlorobiphenyl.

retention time, t_i' is the relative retention time for i th peak, a_i is the area of i th peak, and w_i is the half-height width of i th peak. The variable time (t) of the original chromatogram was substituted with the relative retention time (t') using decachlorobiphenyl (DCB) as a reference peak in Equation 1, so that the time range in the Gaussian function curve was between 0 and 1, where

$t' = 1$ is the relative retention time of DCB. The Gaussian functions were calculated from tabulated data for each identified chromatographic peak. For severely overlapping peaks, a constant value for the width at half-height was used. The curve was reconstituted to 500 discrete points, which seemed to be dense enough. The quantitation was performed by least-squares multiple

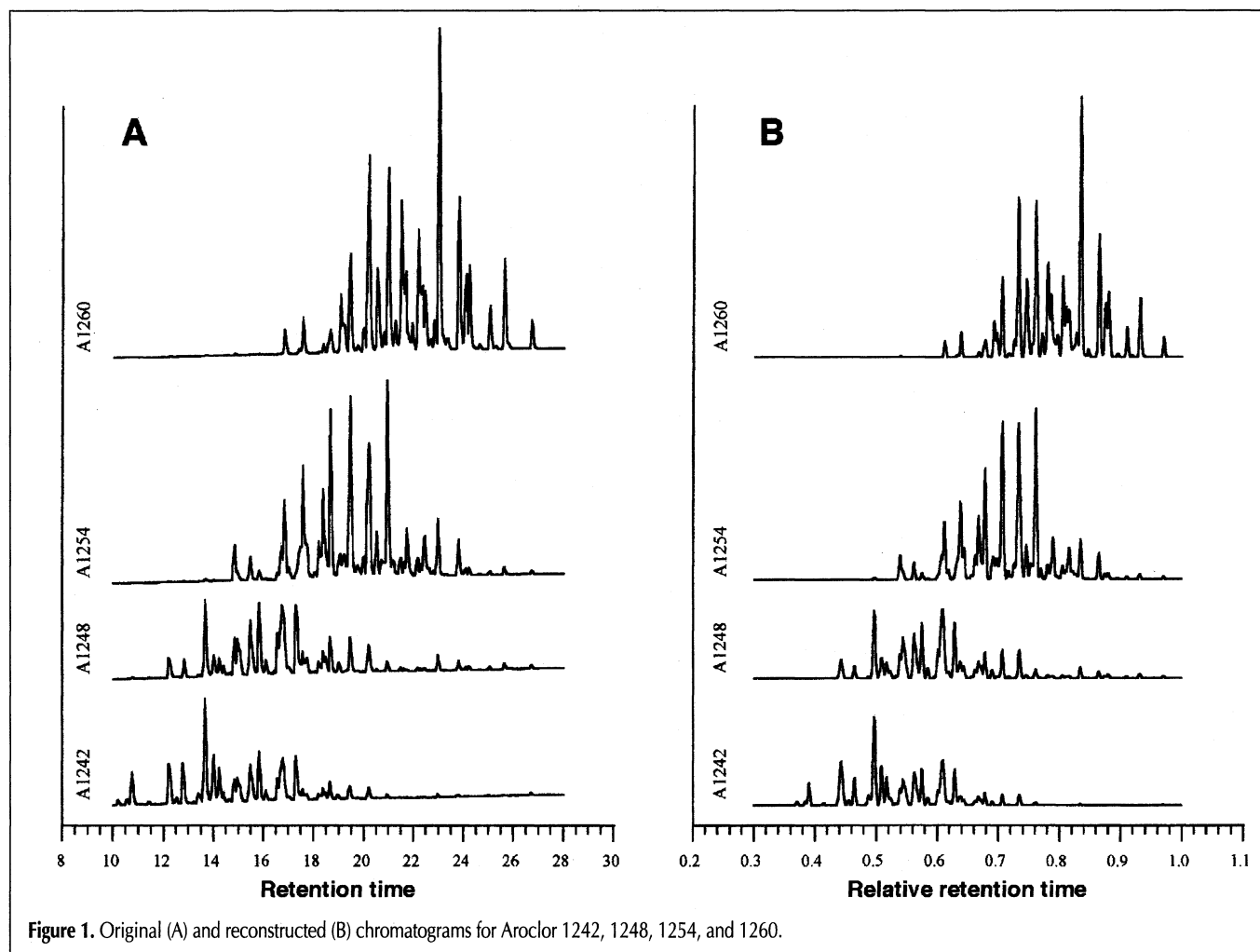


Figure 1. Original (A) and reconstructed (B) chromatograms for Aroclor 1242, 1248, 1254, and 1260.

Table II. Results Obtained by Application of both Method A and Method B

| Sample | Composition of Aroclor mixtures in mass percent | | | | Calculated composition in mass percent | | | | | | | | | | | | | | | |
|--------|---|-------|-------|-------|--|-------|-------|-------|-------|-------|-------|-------|----------|--------|-------|--------|-------|--------|-------|-------|
| | | | | | Method A | | | | | | | | Method B | | | | | | | |
| | A1242 | A1248 | A1254 | A1260 | A1242 | %RE* | A1248 | %RE | A1254 | %RE | A1260 | %RE | A1242 | %RE | A1248 | %RE | A1254 | %RE | A1260 | %RE |
| 1 | 50.00 | 50.00 | - | - | 50.24 | -0.48 | 48.58 | 2.84 | 0.37 | - | 0.82 | - | 45.84 | 8.32 | 53.08 | -6.16 | 0.27 | - | 0.81 | - |
| 2 | 50.00 | - | 50.00 | - | 44.41 | 11.18 | 6.99 | - | 47.69 | 4.62 | 0.91 | - | 48.93 | 2.14 | 0.40 | - | 50.66 | -1.32 | 0.00 | - |
| 3 | 50.00 | - | - | 50.00 | 46.62 | 6.76 | 1.91 | - | 1.65 | - | 49.82 | 0.36 | 45.36 | 9.28 | 3.63 | - | 0.00 | - | 51.01 | -2.02 |
| 4 | - | 50.00 | 50.00 | - | 0.00 | - | 50.77 | -1.54 | 47.95 | 4.10 | 1.28 | - | 4.94 | - | 45.35 | 9.30 | 49.71 | 0.58 | 0.00 | - |
| 5 | - | 50.00 | - | 50.00 | 0.00 | - | 49.90 | 0.20 | 2.26 | - | 47.84 | 4.32 | 0.00 | - | 49.46 | 1.08 | 0.61 | - | 49.93 | 0.14 |
| 6 | - | - | 50.00 | 50.00 | 1.52 | - | 0.00 | - | 49.54 | 0.92 | 48.94 | 2.12 | 0.00 | - | 6.29 | - | 44.61 | 10.78 | 49.10 | 1.80 |
| 7 | 33.33 | 33.33 | 33.33 | - | 32.27 | 3.18 | 32.76 | 1.71 | 34.48 | -3.45 | 0.49 | - | 43.48 | -30.45 | 17.84 | 46.47 | 36.77 | -10.32 | 1.92 | - |
| 8 | 33.33 | 33.33 | - | 33.33 | 27.65 | 17.04 | 35.50 | -6.51 | 2.45 | - | 34.40 | -3.21 | 28.23 | 15.30 | 36.23 | -8.70 | 0.23 | - | 35.32 | -5.97 |
| 9 | 33.33 | - | 33.33 | 33.33 | 29.95 | 10.14 | 0.00 | - | 36.09 | -8.28 | 33.96 | -1.89 | 23.19 | 30.42 | 8.84 | - | 32.18 | 3.45 | 35.80 | -7.41 |
| 10 | - | 33.33 | 33.33 | 33.33 | 2.54 | - | 29.75 | 10.74 | 33.99 | -1.98 | 33.72 | -1.17 | 0.00 | - | 36.48 | -9.45 | 28.71 | 13.86 | 34.81 | -4.44 |
| 11 | 25.00 | 25.00 | 25.00 | 25.00 | 23.65 | 5.40 | 24.09 | 3.64 | 26.04 | -4.16 | 26.22 | -4.88 | 19.94 | 20.24 | 29.70 | -18.80 | 22.88 | 8.48 | 27.48 | -9.92 |

* Relative error.

regression, assuming that the detector operated in the linear range. The least-squares quantitation of each unknown sample was done by converting its reconstructed gas chromatogram data to a vector. The results were arranged in a data matrix (X):

$$X = \begin{bmatrix} 1 & x_{11} & \dots & x_{i1} \\ 1 & x_{12} & \dots & x_{i2} \\ \vdots & \vdots & \dots & \vdots \\ 1 & x_{1j} & \dots & x_{ij} \end{bmatrix} \quad \text{Eq 2}$$

where j refers to the discrete point chosen (1 through 500) and i is the Aroclor standard index (1 through 4; Aroclor 1242, 1248, 1254, and 1260).

Data matrix X can be correlated with a matrix Y of the unknown sample according to the equation

$$Y = XB + R \quad \text{Eq 3}$$

where B is the matrix of parameters and R is the matrix of residuals. Matrix Y is a column vector of 500-row length. The matrix of parameter estimates \hat{B} is obtained using the equation

$$\hat{B} = (X'X)^{-1}(X'Y) \quad \text{Eq 4}$$

The prime (') indicates the transposition of a matrix, and the superscript reciprocal ($^{-1}$) indicates the inverse of a matrix. The estimation of the responses at the original data can be calculated using the equation

$$\hat{Y} = X\hat{B} \quad \text{Eq 5}$$

where \hat{Y} is the matrix of estimated responses. Finally, the residuals in the measured response can be expressed as the equation

$$R = Y - \hat{Y} \quad \text{Eq 6}$$

Method B

After selecting only 63 peaks, present or absent, in the chromatograms of every Aroclor standard (Table I), these peaks were identified in the samples and their quantitation was carried out using least-squares multiple regression method, where j referred to the chosen peak (1–63) and i referred to the Aroclor standard index (1–4; Aroclor 1242, 1248, 1254, and 1260). Therefore, matrix Y became a column vector of 63-row length.

Results and Discussion

Gas chromatograms of the four commercial Aroclor standards are shown in Figure 1. As can

be seen, there are significant differences in their chromatographic profile as the percentage of chlorine increases. Because generally unknown samples are mixtures of Aroclors, it could be possible to deconvolute the sample signal into the relative

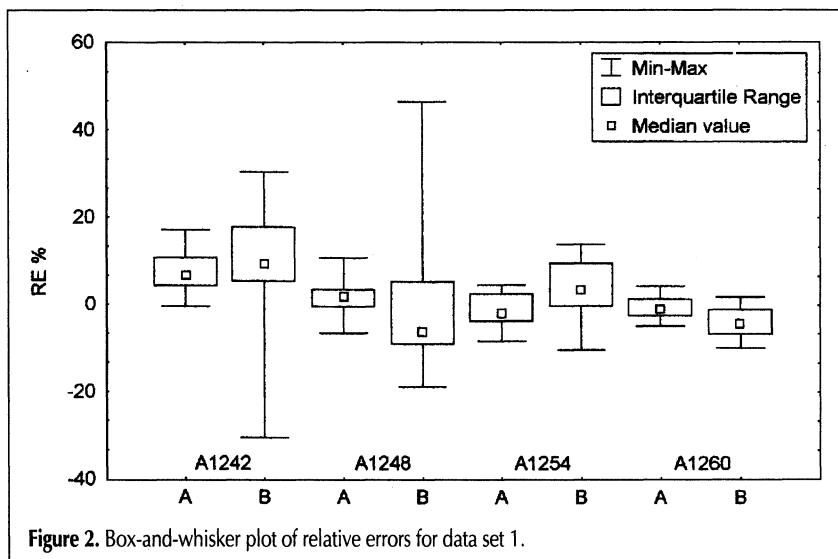


Figure 2. Box-and-whisker plot of relative errors for data set 1.

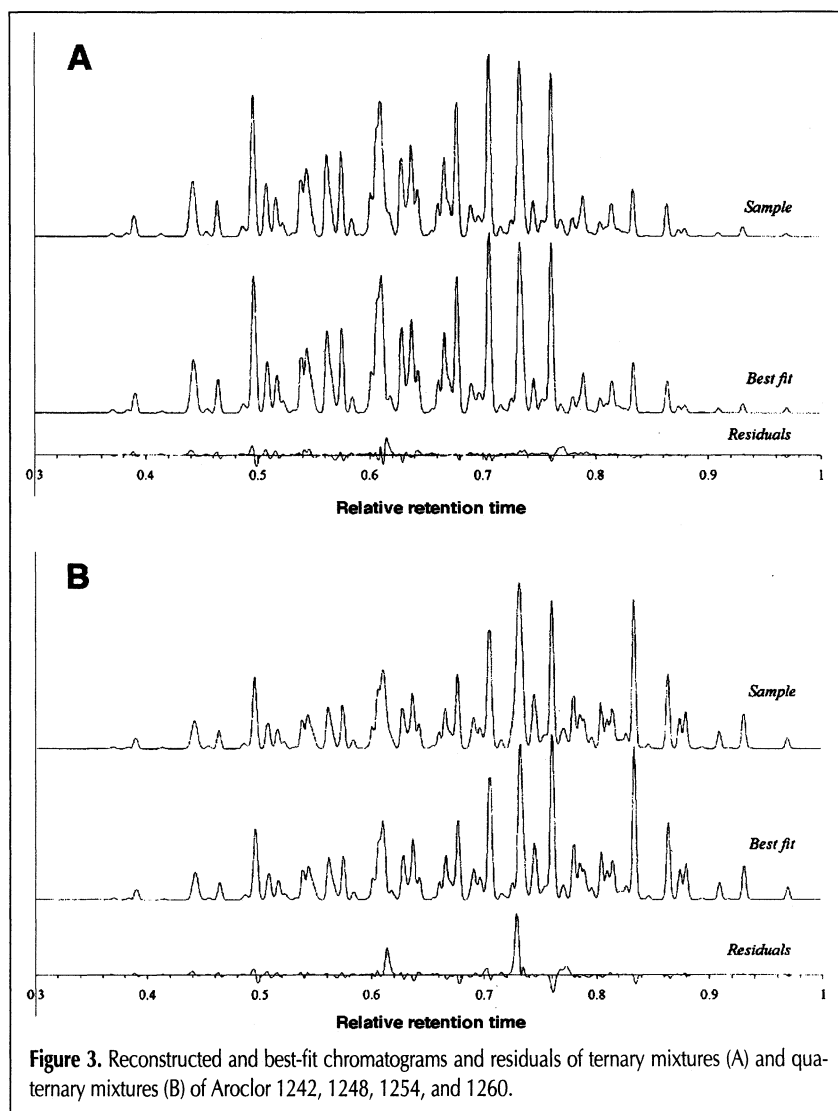


Figure 3. Reconstructed and best-fit chromatograms and residuals of ternary mixtures (A) and quaternary mixtures (B) of Aroclor 1242, 1248, 1254, and 1260.

Table III. Calculated Compositions in Mass Percent for Different Aroclor 1254 and Aroclor 1260 Mixtures

| Sample | Composition* | | Method A | | | | | | Method B | | | | | |
|--------|--------------|-------|----------|-------|-------|------------------|-------|-------|----------|-------|-------|-------|-------|-------|
| | A1254 | A1260 | A1242 | A1248 | A1254 | RE% [†] | A1260 | RE% | A1242 | A1248 | A1254 | RE% | A1260 | RE% |
| 1 | 50.00 | 50.00 | 1.09 | 0.00 | 48.44 | 3.12 | 50.46 | -0.92 | 0.00 | 9.23 | 40.52 | 18.96 | 50.25 | -0.50 |
| 2 | 33.33 | 66.67 | 0.17 | 0.72 | 32.58 | 2.25 | 66.52 | 0.22 | 0.00 | 7.00 | 28.63 | 14.10 | 64.38 | 3.43 |
| 3 | 25.00 | 75.00 | 0.45 | 0.22 | 23.06 | 7.76 | 76.27 | -1.69 | 0.00 | 5.19 | 21.02 | 15.92 | 73.79 | 1.61 |
| 4 | 16.67 | 83.33 | 2.05 | 0.88 | 19.16 | -14.94 | 77.91 | 6.50 | 0.00 | 4.34 | 17.52 | -5.10 | 78.14 | 6.23 |
| 5 | 83.33 | 16.67 | 0.00 | 2.82 | 79.05 | 5.14 | 18.14 | -8.82 | 0.00 | 6.15 | 75.93 | 8.88 | 17.92 | -7.50 |
| 6 | 66.67 | 33.33 | 0.76 | 0.00 | 64.56 | 3.16 | 34.68 | -4.05 | 0.00 | 11.81 | 54.18 | 18.73 | 34.02 | -2.07 |

* A1242 and A1248 were not added to the mixtures.
[†] Relative error.

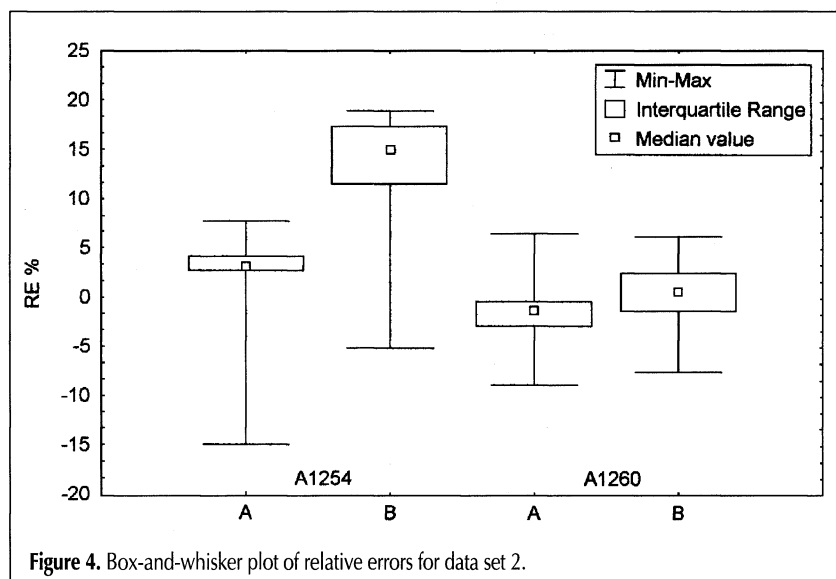


Figure 4. Box-and-whisker plot of relative errors for data set 2.

amounts of Aroclor components. This can be done by a variety of mathematical techniques, depending on the nature of the experimental data.

Two methods for identification and quantitation of different Aroclor mixtures were developed. In Method A, data for the relative retention time of chromatographic peaks and their corresponding peak areas and widths were used to construct a continuous time function according to Equation 1. In Method B, the traditional multiple regression using least-squares method was directly applied.

Figure 1 shows the original chromatograms (A) for the four Aroclor standards. The data from each chromatographic report were used to reconstruct discrete-time chromatogram vectors of dimension 500, corresponding to 500 evenly spaced points that were 0.0013 units (in relative retention time) or 0.035 min (in absolute retention time) apart, covering a 0.63-unit or 17.3-min interval, respectively. Figure 1 also shows the reconstructed chromatograms (B) for the four Aroclor standards according to Method A. From these vectors and those corresponding to the samples, the composition of each sample was calculated by least-squares multiple regression, assuming that the detector operated in the linear range. The calculated compositions (Table II) were compared with the compositions of the Aroclor mixtures. It can be seen that results obtained by Method A are very good, except for sample 2. The maximum difference between the

known and calculated data was 5.68% (average difference, 1.60%). However, the percent difference (or relative errors) for the two methods were dependent on the specific Aroclors (such as Aroclor 1242 and Aroclor 1248) and the ratio of the various Aroclors to each other (Figure 2). The calculated coefficients of multiple determination (r^2) for Method A were ≥ 0.990 in all cases, whereas for Method B they were ≥ 0.960 .

Figure 3 shows the reconstructed chromatograms for two mixtures of Aroclors, the best-fit chromatograms, and the corresponding residuals. The residuals were small in most cases, indicating that the best-fit chromatogram corresponded very well with the reconstructed chromatogram.

Table II also shows the results obtained using Method B, which applied the least-squares method directly to the experimental data corresponding to the 63 selected discrete peaks. The maximum difference between known and calculated data was 15.49% (average difference, 2.97%), higher than that obtained using Method A.

In order to establish the range of error when determining a wide range of concentrations ratios, studies were carried out on mixtures of Aroclor 1254 and 1260, which have been the standards most used in environmental concerns. The results are displayed in Table III, which shows that errors obtained applying Method A (Gaussian) are much lower than those obtained applying Method B (direct least-squares) (Figure 4). Thus, for Method A, the maximum differences between known and calculated amounts were found for the higher ratios of 1:5 and 5:1 (Aroclor 1254 to 1260) with errors of 5.4% (Aroclor 1260) and 4.3% (Aroclor 1260), respectively. For the lower ratios of 1:1, 1:2, 2:1, and 1:3, maximum error was 2.1%. When concentrations were calculated by applying Method B to the same mixtures of Aroclor in higher ratio mixtures, the errors were 5.2% (Aroclor 1260) and 7.4% (Aroclor 1254). However, for the lower ratios, maximum difference was 12.5% (Aroclor 1254) for the 2:1 ratio.

It can also be seen in Table III that errors in the quantitation of Aroclor 1248 (not present in the mixtures) using Method B were considerably higher than those using Method A. Maximum error using Method A was 2.8%, whereas with Method B it was 11.8%.

Conclusion

Two procedures have been described for the determination and quantitation of Aroclor mixtures by using capillary chromatography data and numerical calculation methods. In Method A, the transformation of the chromatographic data into a Gaussian function followed application of the least-squares method, and in Method B, the least-squares method was directly applied to the chromatographic data. The data show that the Method A is more precise and accurate than Method B. Furthermore, Method A is simpler than Method B and allows the selection of target peaks. Noise in the chromatogram was eliminated by preprocessing to form reconstructed chromatograms. Method A also takes less time than Method B (5–10 min instead of hours).

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