A STUDY IN LABORATORY AUTOMATION

Analysis of PCBs in transformer oils

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POLYCHLORINATED biphenyls (PCBs) have been commercially manufactured since 1929. They were, until recently, widely used throughout industry because of their chemical and thermal stability, low or nonflammability, and good electrical insulating properties. But the very properties that have made PCBs so useful have resulted in a ban on their manufacture and strict regulation of their disposal by the Environmental Protection Agency (EPA). PCBs are so chemically inert that they persist in nature long after many other organic chemicals have broken down. Most of the biosphere is contaminated, although no natural source of PCBs exists. Not only are PCBs environmental pollutants, but they are suspected carcinogens as well.

When the EPA announced the regulations on disposal of PCBs in 1978, the technical personnel at Consolidated Edison were faced with a major problem. It was necessary to determine which of the 23,000 transformers in the Consolidated Edison systems contained PCB-contaminated transformer oil, and at what levels. The oils were almost certainly contaminated because at one time Consolidated Edison had used PCBs as transformer oil. When the switch was made, the new oil introduced became contaminated by PCB residues. This meant that a method for handling thousands of samples per year had to be developed.

The system that was finally developed has been in use for more than three years. More than 8000 samples have been assayed with it. The three-part method consists of gas chromatography, sample preparation, and automation, both instrumental and data reduction. These were integrated into one efficient system for speedy handling of many samples and rapid analysis of data.

Sample tracking

Sample preparation consists of four discrete tasks, allowing for assembly-line work and minimum critical path planning. The first task was to log in an identification number for each sample. Next, each sample was prepared and its weight entered into the log. The sample was then loaded into the autosampler for injection into the gas chromatograph. The last task was to enter the sample's i.d. and weight into the computer. Two technician-days were required for 50 samples, at a rate of about three samples per technician hour.

Gas chromatography

Two Perkin-Elmer Sigma series gas chromatographs were used. Each was equipped with a Perkin-Elmer autosampler. The Sigma 3 gas chromatograph used is a single-channel unit, equipped with an Ni^{63} electron capture detector and capable of temperature programming. The Sigma 4 is a dual channel, isothermal GC.

The chromatography was carried out under the following conditions: column packing, Chromosorb W HP; column load, 4% OV-225; mesh size, 60–80; column material, glass; column size: 1.8 m × 4 mm; carrier gas, argon: methane, 95:5; carrier flow, 30 mL/min; oven temperature, 225°C; auxiliary temperature, 375°C; standing current of electron capture detector, 0.5.

No data reduction was performed on the gas chromatographs. The output signals were fed directly into a computer.

Sample cleanup and preparation

Rapid analysis was required for the large numbers of samples. For the first analyses, sample cleanup was performed on a packed Florosil column. But, because using Florosil packing is a very laborious procedure, at this time only dirty or high samples (greater than 500 ppm of PCB) or samples giving poor chromatograms were cleaned. This procedure was changed for later PCB samples. All later analyses were performed using Sep-Paks (Waters Associates) which are Florosil units in small disposable packets. This eliminated the need for column preparation.

The preparation procedure was as follows: 100 μL of sample were dispensed on a previously weighed Sep-Pak. The loaded Sep-Pak was then reweighed. Next the sample was eluted with 25 mL of hexane, using a syringe, directly into a 25-mL volumetric flask.

Table 1

% Recovery from Sep-Pak

mL Hexane	% in aliquot	Total %
5	93.8	93.8
10	4.9	98.7
15	0.7	99.4
20	0.3	99.7
25	0.2	99.9

continued

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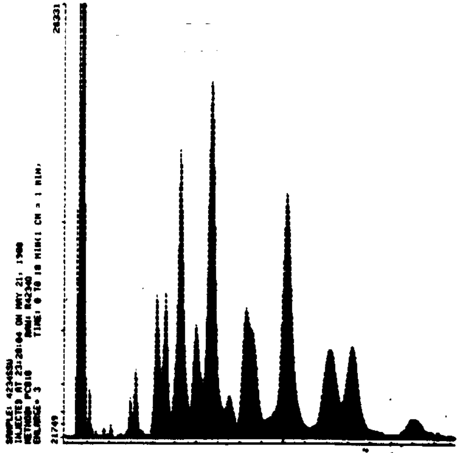

Figure 1 *PCB sample before cleanup.*

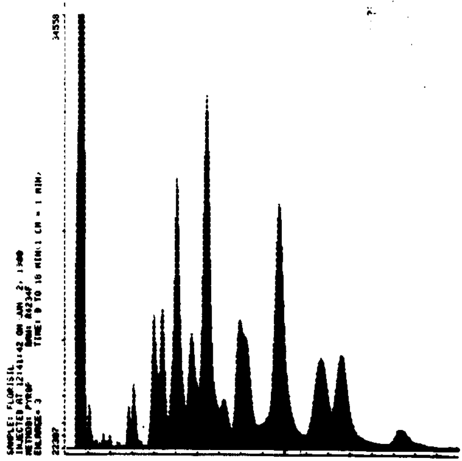

Figure 2 *Sample in Figure 1 after cleanup. Note that there is no loss of peaks, and the chromatograms are the same, indicating no loss of PCB material from the clean-up procedure.*

The recovery was found to be excellent (*Table 1*). A sample known to be clean gave the same chromatogram both before and after cleanup. It was concluded, therefore, that no PCBs were lost. A known dirty sample gave a well-resolved chromatogram after cleanup (*Figures 1–4*).

Standards

Originally the transformer oils were identified by trade name, using as standards Askarel, Inerteen, and Pyranol, which are different mixtures of PCBs but all contain about 30% trichlorobenzene. Later, for

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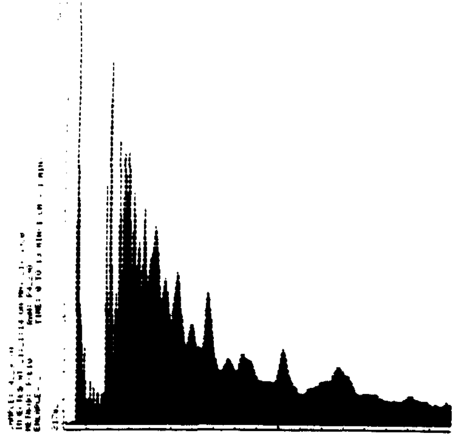

Figure 3 A very poor chromatogram before sample cleanup.

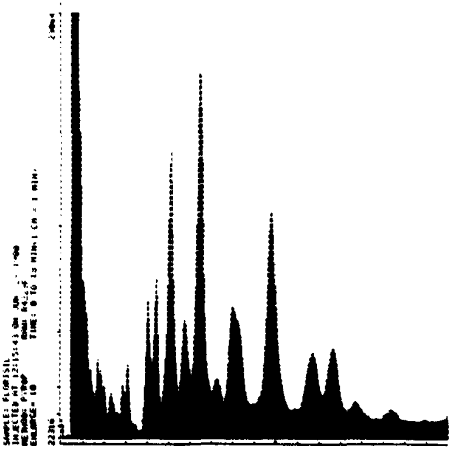

Figure 4 Sample in Figure 3 after cleanup. Note the highly improved resolution, and much cleaner chromatogram as a result of the cleanup procedure.

consistency in reporting, the Aroclors 1242, 1254, and 1260 were used. Recently Aroclors 1016 and 1221 were added. Now commercial Aroclor standards of 1000 ppm in isoctane are used.

The standards were prepared by diluting to 2 ppm PCB in hexane. This is equivalent to taking 0.1 g of oil containing 500 ppm PCB, and diluting to 25 mL with hexane. Five microliters of the standard, containing 20 ng PCB, were injected into the chromatograph. Standardization was performed, and the standard usually held with very little drift.

continued

Data reduction

An HP 3354 LAS computer was used for data reduction. The computer is a real-time on-line system with instrument and autosampler control and is compatible with any 1-volt analog instrument output. In this case, it received data directly from the gas chromatographs.

The computer was programmable in BASIC, allowing for individual data analysis. The system-level language was a user-oriented conversational language for peak-integration analysis.

Calculation and Aroclor selection were done as follows. The computer searched for 5 key standard peaks for each Aroclor of interest. It also calculated a concentration for each Aroclor based on total peak area. Each standard peak was calibrated at total concentration, all 5 peaks averaged, and a relative standard deviation (RSD) calculated. An error factor was calculated using both the RSD and the total-area value. The Aroclor with the lowest error factor was chosen. The computer then looked at the % RSD. If it was below 40%, the mean value was reported. If it was above 40%, the total-area value was reported (*Figures 5 and 6, Table 2*).

There are several reasons why this software is so significant. The program is not complex. It is merely a simple statistical process written in BASIC. The computer program was limited to identifying recognizable Aroclor chromatograms, e.g., transformer oils. The data were still reviewed by a technician, who used the printouts to write reports and troubleshoot the instrumentation.

The results of all analyses were stored in a data file, and specific runs (standards and pertinent runs) could be stored in their entirety. Numerous utility programs were also available. For example, files could be manipulated for system operation and error correction. There were also programs for calculation and other purposes.

When this project began, PCBs were classified into two significant concentration levels. Samples with concentrations of less than 50 ppm were considered clean regarding disposal, except for environmental reentry. Any samples greater than 50 ppm were classified as PCB material.

Due to the enormous amount of

Table 2

Aroclor algorithm

Aroclor	1242	1254	1260
All peaks?	Yes	Yes	Yes
Mean	37.8	58.8	36.4
% RSD	108.8	78.8	25.4
Total area	92.0	69.2	60.4
Mean-total area	54.2	11.4	26
% Diff.[a]	41.8	9.1	26.1
(% RSD) × (% Diff.)	4538	726	663

Sample is Aroclor 1260.
Use mean value.

[a](Mean − total area)/(mean + total area).

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0                2

RET TIME         PPM              NAME
9.17044          53.4?67          #1260-1
10.7465          20.6187          #1260-2

AROCLOR          MEAN             # PEAKS          % RSD
1260             47.0???          2                54.234.

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0                2

RET TIME         PPM              NAME
1.5              171.229          #1260-T

AROCLOR          MEAN             # PEAKS          % RSD
1260             171.229          1                53.335?

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ERROR SCORE = 31.64?6

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0                2

RET TIME         PPM              NAME
1.68635          500              #1242-1
2.0478           500              #1242-2
2.60157          500              #1242-3
3.13204          500.             #1242-4
4.72365          500              #1242-5

AROCLOR          MEAN             # PEAKS          % RSD
1242             500              5                4.47214E-02

--------------------------------------------------------------
0                2

RET TIME         PPM              NAME
1                500              #1242-T

AROCLOR          MEAN             # PEAKS          % RSD
1242             500              1                0

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ERROR SCORE = 0

**************************************************************
0                2

RET TIME         PPM              NAME
3.13204          1?45.6           #1254-1
4.72365          ?9?.?14          #1254-2
5.04944          81.0?65          #1254-3
9.17044          44.4445          #1254-4
10.7465          23.8113          #1254-5

AROCLOR          MEAN             # PEAKS          % RSD
1254             3??.?14          5                133.044

--------------------------------------------------------------
0                2

RET TIME         PPM              NAME
1.5              21?.?35          #1254-T

AROCLOR          MEAN             # PEAKS          % RSD
1254             213.?35          1                27.765?

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ERROR SCORE = 36.94?1

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Figure 5 Printout for a 1242 standard. Note that the error factor would be 0 for 1242, as expected.

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0                  2

RET TIME           PPM                NAME

AROCLOR            MEAN               # PEAKS           % RSD
1260               0                  0                 0

------------------------------------------------------------
0                  2

RET TIME           PPM                NAME
1.5                138.431            #1260-T

AROCLOR            MEAN               # PEAKS           % RSD
1260               138.431            1                 100

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ERROR SCORE = 0

------------------------------------------------------------
0                  2

RET TIME           PPM                NAME
1.54386            15.5958            #1242-1
2.16024            8.90514            #1242-2
2.7592             14.3326            #1242-3
3.33462            13.5122            #1242-4
5.05479            46.2421            #1242-5

AROCLOR            MEAN               # PEAKS           % RSD
1242               19.7176            5                 60.2290

------------------------------------------------------------
0                  2

RET TIME           PPM                NAME
1                  183.3              #1242-T

AROCLOR            MEAN               # PEAKS           % RSD
1242               183.3              1                 80.5755

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ERROR SCORE = 54.9765

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0                  2

RET TIME           PPM                NAME
3.33462            36.5069            #1254-1
5.05479            40.1813            #1254-3
8.03097            64.9035            #1254-4
10.6215            50.1655            #1254-5

AROCLOR            MEAN               # PEAKS           % RSD
1254               47.9143            4                 22.8603

------------------------------------------------------------
0                  2

RET TIME           PPM                NAME
1.5                147.977            #1254-T

AROCLOR            MEAN               # PEAKS           % RSD
1254               147.977            1                 51.0007

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ERROR SCORE = 11.6013

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Figure 6 *Printout for a sample.*

oils with over 50 ppm PCB, a third class of concentration had to be established. Samples with concentrations greater than 500 ppm were referred to as PCB material. Samples that were between 50 and 500 ppm are now labeled PCB-contaminated.

In terms of disposal, this classification of the samples meant that non-PCB material was disposed of as waste oil, PCB-contaminated material required some restrictions regarding disposal, and PCB material required severe restrictions.

Conclusion

Analytical systems designed for very large numbers of samples must be carefully designed. All aspects of analysis, sample preparation, instrument automation, and data reduction must be considered, both separately and as a system. Even where large capital investments are necessary, the savings in labor alone make such a system profitable.

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