PERFORMANCE-BASED, COST- AND TIME-EFFECTIVE PCB ANALYTICAL METHODOLOGY

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ABSTRACT

Laboratory applications for the analysis of PCBs (polychlorinated biphenyls) in environmental matrices such as soil/sediment/sludge and oil/waste oil were evaluated for potential reduction in waste, source reduction, and alternative techniques for final determination. As a consequence, new procedures were studied for solvent substitution, miniaturization of extraction and cleanups, minimization of reagent consumption, reduction of cost per analysis, and reduction of time. These new procedures provide adequate data that meet all the performance requirements for the determination of PCBs. Use of the new procedures reduced costs for all sample preparation techniques. Time and cost were also reduced by combining the new sample preparation procedures with the power of fast gas chromatography. Separation of Aroclor 1254 was achieved in less than 6 min by using DB-1 and SPB-608 columns. With the greatly shortened run times, reproducibility can be tested quickly and consequently with low cost. With performance-based methodology, the applications presented here can be applied now, without waiting for regulatory approval.

INTRODUCTION

The philosophy of analytical procedures has progressed over the years from descriptive to prescriptive to performance based. Descriptive procedures tell what the researcher did, but they often leave out important details and also leave room for adaptation by others applying the procedure. Prescriptive procedures are described as "cookbook recipes"; deviations are not allowed. Performance-based procedures examine quality objectives for each sample to evaluate the performance of the procedure. Often, performance-based procedures permit greater flexibility for adaptation. The result is flexibility in conducting required environmental monitoring, expedited use of new and innovative techniques, and cheaper and faster approaches to conducting required site characterization, monitoring, and measurements.

The initial steps for acceptance of performance-based procedures appeared in October 1997 in the *Federal Register* (62, 52098) (Kinney and Caliandro, 1998); the Environmental Protection Agency (EPA) published a notice that will expand the range of acceptance monitoring technologies and procedures for use in compliance monitoring of air, soil, and water. The outcome will be an emphasis on the analytical chemistry needs of specific monitoring projects, rather than the required use of specific technologies; a consistent way of expressing method performance criteria that is independent of the type of technology or method; and increased new technology development, as well as improvement in existing methodologies.

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New cost-effective methods that meet program requirements and performance criteria are needed. The analysis of PCBs is an example of the need for development of performance-based methodologies. The PCBs are widespread, highly visible environmental pollutants. Their analysis is a very high-volume requirement across the country, and the current methods are widely acknowledged to need improvement. Too often, PCB methods are adapted from methods for chlorinated pesticides. Despite the fact that PCBs are such prominent analytes, inadequate attention is given to quality control (e.g., all matrix spike compounds are pesticides), qualitative identification, and quantitation related to PCBs. In addition, the method approved by the EPA for the determination of PCBs in transformer fluid, waste oil, and soil (Bellar and Lichtenburg, 1982) is performed on an unnecessarily large scale. The EPA methods for determination of PCBs in various matrices have not changed to accommodate the current trend toward microscale analysis and the incorporation of waste minimization, pollution prevention, solvent substitution, and new technologies.

The early analysis of PCBs was performed by packed-column gas chromatography (GC). Subsequent improvements in GC have historically emphasized separation or resolution. The research emphasis on increased resolution has largely ignored the time requirements of GC analysis. Nearly all PCB analyses take 20-60 min per run. (Extraction and cleanup procedures take considerable additional time.) Because analysis time translates directly into analysis cost, analyses completed within a few minutes by fast GC are desirable. Many articles have been published about the theory of fast GC (Hyver and Phillips, 1987; Van Es et al., 1987; Akard and Sacks, 1994), but only recently has fast GC been applied to air monitoring (Ke et al., 1992) and analysis of volatile organic compounds (Klemp et al., 1994; Sacks and Akard, 1994).

Fast GC shows potential for reducing PCB analysis time to a just a few minutes. With the greatly shortened run times, reproducibility can be tested quickly and consequently with low cost. However, the reduction in analysis time is accompanied by a significant loss in chromatographic resolution, a decrease in the number of components that can be separated, and increased probability of peak overlap.

The objective of this project was to investigate, develop, evaluate, and implement new procedures for preventing or minimizing primary and secondary waste, reducing costs, and minimizing time for the analysis of PCBs. Laboratory applications for the analysis of PCBs in environmental matrices such as soil/sediment/sludge and oil/waste oil were evaluated for potential reduction in waste, source reduction, and alternative techniques for final determination.

EXPERIMENTAL DESIGN

Instrumentation

The fast GC used in these experiments was a Varian 3600 Star system (Sugar Land, Texas) with a cryointegrator from Chromatofast™, Inc. (Ann Arbor, Michigan). High-purity hydrogen (AGA, Hammond, Indiana) was used as carrier gas, and high-purity nitrogen (AGA) was the make-up gas for the electron capture detector (ECD). Typical carrier gas velocities ranged from 95 to 250 cm/s.

DISCLAIMER

The first injector in the two-injector system was a regular split/splitless injector set at 250°C, followed by a cold trap cooled by a continuous flow of liquid nitrogen at -90°C and resistively heated by a current pulse from a capacitor discharge power supply. The two injectors were connected by a fused-silica transfer line. To control analysis time, preconcentration, injection mode, and desorption time, the instrument has a build-in series of relays (standby, sample, purge, and analyze) for each function. For each of these relays, conditions were optimized for the final analysis.

The ECD was set at 300°C and a frequency of 40 Hz to detect fast transient signals from the analytes. Initial and final column temperature and rate of increase were optimized in each case. Two different columns were used. The initial experiments were carried out with a DB-1 column (Varian; 3 m long, 0.25 mm I.D.). Later experiments used an SPB-608 column from Supelco (Bellefonte, Pennsylvania; 3 m, 6 m, or 10 m long and 0.25 mm I.D.).

Reagents

Aroclor standards were from ULTRA Scientific (North Kingston, Rhode Island). The standard mixture came in 1-mL ampules at an Aroclor 1254 concentration of 100 µg/mL in hexane. Other standards and solutions used for the dilution and cleaning were Ultra Resi-Analyzed from J.T. Baker (Phillipsburg, New Jersey).

RESULTS AND DISCUSSION

Separation of PCBs from the matrix is generally accomplished by solvent extraction. For water samples, the solvent of choice has for decades been methylene chloride (dichloromethane), because it has good extraction properties and is heavier than water, making separatory funnel extraction mechanically easy. Methylene chloride, other chlorinated solvents, and selected nonchlorinated solvents are under increasing scrutiny because of their potential health hazards to workers and because of concerns about environmental pollution. Although solvent substitution and elimination have been aggressively addressed by industries involving semiconductor manufacturing and coatings, analytical laboratories have been far slower to confront the issue.

Once extraction has eliminated the bulk matrix, additional interfering chemicals are separated from the PCBs by a variety of cleanup techniques, including chemical degradation and column chromatography. The column chromatographic techniques continue to use large, wasteful columns that are unnecessary even with the present large sample volumes. Major improvements in time savings and reagent minimization can be realized by appropriate scaling of the cleanup adsorbent and solvent volumes; further improvements can be realized by application of more specific separations using appropriate sorbent-solvent combinations.

Improvements in GC are needed to minimize the time of analysis without detriment to the quality of the results. Typically, separation times for PCBs approach 40-60 min. To save time and minimize cost, duplicates and confirmation injections are usually omitted during standard analyses. Fast GC presents an option to minimize time without adverse results and to improve data quality objectives.

Solvent Substitution

Solvent substitution has been studied for the determination of PCBs in soils. Solvent substitution can achieve results comparable to standard methods and can eliminate environmentally less desirable solvents, as illustrated in Table 1. Widely varying solvents were used as extractants, generally without significant comparative evaluations among potential solvent systems. Technically acceptable solvents are those that yield quantitative extractions of the analyte (as measured by the spiked sample). Solubility of the PCBs and wetting of the soil matrix are contributing factors to the efficacy of the solvent. Our results indicate that many common solvents and solvent mixtures can yield quantitative extractions. Hexane is the solvent of choice for our future work.

Macroscale Extractions

Macroscale and microscale extractions were performed for samples of oil, waste oil, and soils. For macroscale extractions, EPA method 600/4-81-045 and method 8080 were used for the determination of PCBs in transformer fluid and waste oils and in soil samples, respectively. The chromatographic columns used for the macroscale procedure for the analysis of oil samples were 50 cm long with 250-mL reservoirs. The columns were filled with approximately 20 g of Florisil™ heated overnight at 160°C, as described in the EPA method. The loaded column was preeluted with 75-100 mL of hexane. The 2-mL aliquot of sample was placed on top of a sodium sulfate layer. The sample was eluted with 280 mL of hexane, as shown in Table 2. For extraction of soils, the

TABLE 1 Solvent Recoveries for Soxhlet Extraction of Soil Samples

Extraction Solvent	Recovery of Aroclor 1254 (%)
Hexane	101
Acetone	101
1:1 Hexane:acetone	105
3:1 Hexane:acetone	109
3:1 Acetone:hexane	94
Methylene chloride	89
1:1 Methylene chloride:acetone	104
9:1 Hexane:methylene chloride	99
10:1 Toluene:methanol	101

TABLE 2 Macroscale and Microscale (SPE) Florisil™ Extraction of PCBs from Motor Oil

Parameter	Macroscale	Microscale
Reagent		
Florisil™ (g)	20	1
Hexane (mL)	280	25
Oil sample (g)	1.5	0.2
Total Waste (mL)[a]	~ 300	~ 26
Time (min)		
Dilution/cleanup	120	20
Eluate concentration[b]	50	50
GC analysis time	45	45
Total	215	115
Cost ($)		
Florisil™	2.61	2.37 (SPE syringe)
Hexane	3.28	0.29
Apparatus[c]	0.52	-
Total[d]	6.41	2.66
Yield (%)	100	100

[a] Assumes no recycling; does not include gloves and other ancillary waste.

[b] Nitrogen blowdown technique used for concentration of eluate. Time required is based on volume of solvent evaporated.

[c] Glass chromatography column with reservoir amortized over 100 uses (i.e., column investment of $52) for the macroscale procedure. Microscale procedure requires no comparable apparatus.

[d] Based on manufacturers' catalog prices or actual purchase requisitions; assumes complete consumption of amount purchased.

sample was dried over anhydrous sodium sulfate. The amount of sample used was relative to the percent humidity of the sample. The sample was extracted with approximately 300 mL of a hexane-methylene chloride mixture.

Microscale Extractions

Two different approaches were used for the determination of PCBs in oil matrices: solid-phase extraction (SPE) and disk extraction. The SPE Florisil™ (activated Mg_2SiO_3) columns were used as specified in J.T. Baker Bakerbond Application Note EN-014. SPE sulfonic acid ($C_6H_5SO_3H$) and SPE silica gel (SiOH) microscale columns were used, as described in J.T. Baker Bakerbond Application Note EN-015. For soil matrices, a microscale Soxhlet system was used, decreasing solvent consumption and extraction time. Microscale extractions can cut the scale of the analysis by at least a factor of ten, as illustrated in Tables 2-4.

TABLE 3 Comparisons of Soxhlet, Micro-Soxhlet, and Shakeout Extractions

Parameter	Soxhlet	Micro-Soxhlet	Shakeout
Sample size (g)	10	1	0.5
Sodium sulfate used (g)	10	1	0.5
Extraction solvent volume (mL)	300	15	15[a]
Extraction time (hr)	16-24	5	0.25
Concentration technique	Kuderna-Danish	Nitrogen blowdown	Nitrogen blowdown
Concentration time (min)	10-20	10-20	10-20
Florisil™ used for cleanup (g)	20	1	1
Solvent used for cleanup	Methylene chloride	Hexane	Hexane
Final concentration volume (mL)	10	1	1
Waste volume (mL)[b]	610	25	24
Apparatus cost ($)[c]	2.50	1.40	0.19
Reagent cost ($)[d]	12.76	2.76	2.76

[a] The 15 mL was in three 5-mL extractions, each lasting 5 min.

[b] Assumes no recycling at this point; does not include gloves and other ancillary waste.

[c] Based on manufacturers' catalog prices or actual purchase requisitions. Soxhlet and micro-Soxhlet were amortized over 100 uses (with a Soxhlet investment of $250).

[d] Based on manufacturers' catalog prices or actual purchase requisitions; assumes complete consumption of amount purchased for sodium sulfate, Florisil™, and solvent.

TABLE 4 Scale and Costs of Sulfonic Acid and Silica Gel Microscale Extraction

Parameter	Quantity	Cost ($)	Time (min)
Reagent			
Sulfonic acid SPE column	1	1.64	
Silica gel SPE column	1	1.56	
Hexane	11 mL[a]	0.19	
Connectors	1[b]	0.23	
Dilution/cleanup			20
Eluate concentration[c]			20
GC analysis			45 (6 min for fast GC)
Total Waste	6 mL and 2 columns		
Total Cost		3.62	
Total Time			85 (46 min for fast GC)

[a] The method calls for dissolving 1.5-2.0 g of oil sample in 50 mL of hexane. However, such a scale is unnecessary, and both of the figures can be cut by a factor of ten. The data in the table are calculated for this methodology.

[b] Connectors may be used repeatedly. The price of one connector is amortized over 10 uses.

[c] Eluate concentration time is reduced over both of the Florisil™ procedures because the analyte is eluted in a total volume of only 5 mL, whereas the analyte from the Florisil™ procedures is concentrated from 25 mL.

Waste Volume Reduction

Microscale extraction can cut the volume of waste generated by at least a factor of ten, as shown in Tables 2 and 3. This reduction is increasingly important as we move toward full cost accounting, including waste disposal costs, in the analytical chemistry laboratory.

Fast Gas Chromatography

Figure 1 shows the fast gas chromatogram of Aroclor 1254. Initial studies used a 3-m DB-1 column (0.25 mm I.D.) programmed from 100 to 150°C at 12.5°C/min. A 1-µL sample (0.5 µg/mL), injected into a split/splitless injector in the splitless mode at 250°C, flowed to a cryogenic trap at -90°C prior to introduction into the column. The preconcentration time was 30 s. Although results were very promising, total separation of the PCB congeners was not achieved.

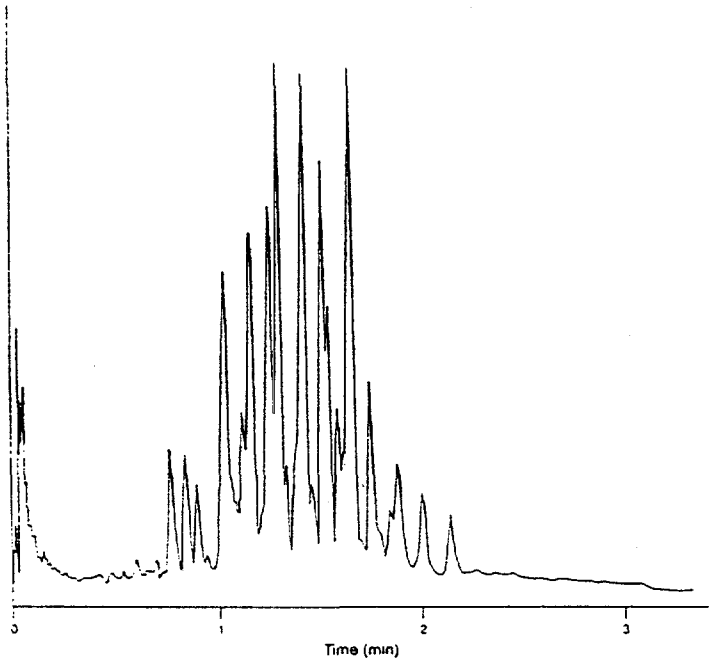

FIGURE 1 Fast Gas Chromatogram of Aroclor 1254 with a DB-1 column (3 m, 0.25 mm I.D.) Programmed from 100°C to 150°C at 12.5°C/min (Hydrogen carrier gas velocity was 100 cm/s. A 1-µL sample at 0.5 µg/mL was injected into a splitless injector.)

Figure 2 shows the fast gas chromatogram of Aroclor 1254 for a run using a 10-m SPB-608 column (0.25 mm I.D.) and temperature programming starting at 190°C and finishing at 260°C. The initial temperature was kept at 190°C to accommodate the separation of congeners from other Aroclors (e.g., Aroclor 1248) with early elutions. Similarly, the final time was increased to allow the separation of high-molecular-weight congeners such as Aroclor 1260.

The application to PCBs is an excellent illustration of the power of fast GC, because the separation of an identifiable Aroclor pattern without full resolution of congeners often provides adequate data without the typical GC turnaround time of 20-40 min. Further, PCBs represent a different analytical challenge to the fast GC than do gases and volatile organic compounds, which have often been used to illustrate the inherent power of the technique. Separations, as shown in the figures, took less than 6 min, and the chromatograms met all requirements for the analysis of PCBs in environmental samples.

Fast GC holds significant promise, once the operational problems that limit its reproducibility and usability are overcome. An obvious advantage of the speed of fast GC is throughput of more samples per day, eliminating the need for a whole bank of GCs in a production laboratory environment. A corollary advantage would be rapid turnaround time in a field laboratory that is supporting on-line decision making in a remediation effort. However, this is a limited-use

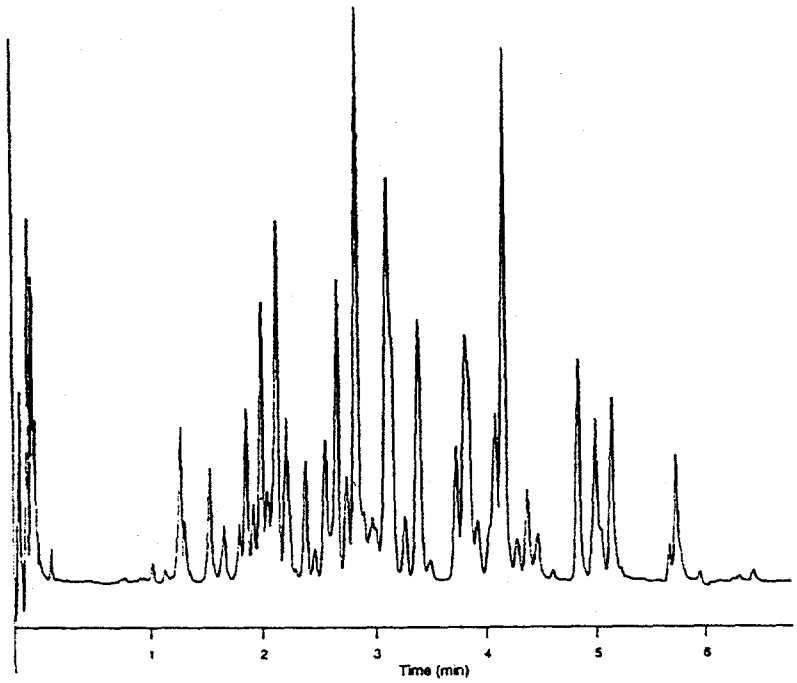

FIGURE 2 Fast Gas Chromatogram of Aroclor 1254 with a SPB-608 column (10 m, 0.25 mm I.D.) Programmed from 190°C to 260°C at 15°C/min. (Hydrogen carrier gas velocity was 125 cm/s. A 1-µL sample at 0.5 µg/mL was injected into a splitless injector.)

application, because sample preparation is often the rate-limiting factor. Where fast GC is likely to become advantageous is in improving data quality. Few laboratories will have a sample load of several hundred injections per day per instrument; rather, we can reinvent GC analysis to include more calibration replicate injections and to permit signal averaging and standard addition. These common quality control techniques, routinely practiced in other areas of analytical chemistry, have been recommended in several interlaboratory study reports on PCB analysis in environmental samples. Another area that will be facilitated by fast GC is multidimensional analysis to exploit retention-time information for improved compound identification. Thus, fast GC represents an opportunity for a paradigm shift in our approach to improving the quality of GC analysis, rather than simply a tool for increasing throughput and cutting cost.

Cost Considerations

Microscale extraction significantly reduces the costs of apparatus, reagents, and labor. The cost reduction for the apparatus and reagents are illustrated in Tables 2-4. The labor costs were not quantified but can be inferred directly from the tables. A cost impact will occur during the transition to microscale extraction, in that new glassware and instrumentation will be purchased, method

validation will require some overhead time (see below), training will require some down time, and some efficiencies will be seen only after a break-in period.

Quality Assurance

Any adaptation of a method requires some sort of internal validation and data quality objectives to demonstrate performance. The changes discussed here are no different. Any laboratory adapting its routine methods to microscale techniques and fast GC needs to validate the changes with the appropriate quality control samples to demonstrate that the laboratory is providing data of known and consistent quality. In addition, quality control measures must be modified as necessary to clearly monitor the performance of the analyses.

CONCLUSION

The application of microextraction techniques to PCB analysis is an excellent illustration of the application of new technologies in a performance-based measurement system. We investigated new extraction and cleanup procedures for the analysis of soils and oils, incorporating solvent substitution, miniaturization of extractions, minimization of reagent consumption, reduction of energy consumption, reduction of cost per analysis, and reduction of time by applying new fast GC technology.

The methods developed here have direct applicability to routine PCB analyses, such as those used by the utility industry and in environmental characterization and monitoring programs. With performance-based methods, the applications presented here can be applied now, without waiting for regulatory approval.

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