RAPID SCREENING TECHNIQUE FOR POLYCHLORINATED BIPHENYLS (PCBs) USING ROOM TEMPERATURE PHOSPHORESCENCE

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ABSTRACT

The analysis of Polychlorinated biphenyls (PCBs) generally requires selectivity and sensitivity. Even after cleanup, PCBs are usually at ultra-trace levels in field samples, mixed in with other halocarbons, hydrocarbons, lipids, etc. The levels of PCBs typically found in water, soil, tissue, food, biota and other matrices of interest are in the parts per billion (ppb) range. Most current measurement techniques for PCBs require chromatographic separations and are not practical for routine analysis.

There is a strong need to have rapid and simple techniques to screen for PCBs under field conditions. The use of field screening analysis allows rapid decisions in remedial actions and reduces the need for sample preparations and time consuming laboratory analyses. Field screening techniques also reduce the cost of clean-up operations.

This paper describes a screening technique room temperature phosphorescence (RTP), and provides an overview of both this analytical procedure and the instrumentation to detect trace levels of chemical pollutants and related biomarkers in complex environmental samples.

INTRODUCTION

Polychlorinated biphenyls are a class of chlorinated aromatic compounds which have found widespread applications because of their general stability and inertness as well as their excellent dielectric properties. The PCBs have been used in electrical capacitors, transformers, vacuum pumps, adhesives, plasticizers, pesticides, etc. The discovery of PCBs in environmental samples has spurred renewed concerns due to their acute and chronic toxicity, and other long-term health effects. The analysis of PCBs generally requires selectivity and sensitivity. The levels of PCBs typically found in water, soil, tissue, food, biota, and other matrices of interest are in the parts per billion (ppb) range. It is therefore important to develop simple, sensitive and rapid screening procedures for PCBs.

Most of the analytical techniques used for PCBs are not easily adapted to field measurements and generally employ chromatographic separations coupled to a specific detection scheme (e.g., flame ionization detection-FID; electron capture detection-ECD; photoionization detection-PID; thermal conductivity-TC; mass spectroscopy-MS; Fourier transform infrared-FTIR, etc.). A review of analytical techniques for PCBs has been described by Erickson (1). Packed column gas chromatography (GC), thin-layer chromatography (TLC), or high-performance liquid chromatography (HPLC) can be used to provide data on "total PCB" contents in samples. Packed column GC/ECD is the common method for quantification of PCBs as Aroclors in the American National Standards Institute (ANSI) procedures. The PCBs are quantified against an Aroclor standard using the largest peak, or a secondary peak. The GC/ECD technique was used to determine PCBs in sediments and soils (2). If congener-specific determination is required, high-resolution gas chromatography (HRGC), which uses fused silica capillary columns, would be the technique of choice (3). High-resolution gas chromatography has been used for the analysis of PCBs in transformer fluids or waste oils. Various MS techniques (electron impact MS, chemical ionization MS, coupled MS/MS, etc.) have been used to analyze complex PCB samples. Methods involving perchlorination of the biphenyl ring of the PCB congeners have been used in the determination of PCBs. One of the limitations of the perchlorination approach is due to the fact that biphenyl can also be perchlorinated, thus leading to erroneously high blank levels.

Room Temperature Phosphorimetry (RTP):

The screening technique involved in this study involve Room Temperature Phosphorimetry (4). Conventional phosphorimetry requires the use of low-temperature matrices to reduce the collisional quenching mechanisms and radiationless deactivation processes. Due to the requirement of cryogenic equipment and refrigerant, conventional phosphorimetry has limited usefulness for routine applications in field measurements.

Unlike conventional low-temperature phosphorimetry, RTP is based on detecting the phosphorescence emitted from organic compounds adsorbed on solid substrates at ambient temperatures. The general approach is to obtain a solution containing the materials to be analyzed using rapid extraction procedures (1-3 min). A few microliters of the sample solution are then spotted on a filter paper. The spot is dried for about three minutes with a heating lamp then transferred to the sample compartment of the spectrometer. Measurements can be performed with any commercial spectrofluorimeter equipped with a phosphoroscope.

The sensitivity and selectivity of RTP can be enhanced by mixing the sample or pretreating the filter paper with a heavy-atom salt solution. Salts such as thallium acetate, in lead acetate are efficient in enhancing phosphorescence quantum yields for most PCBs.

Figure 1 illustrates the characterization of Aroclor 1254, a PCB mixture commonly found in environmental samples, using the RTP technique. This figure shows the RTP spectra of Aroclor 1254 using thallium acetate as the heavy-atom perturber. The efficacy and cost-effectiveness of the RTP technique for screening complex environmental samples have been demonstrated in previous studies (4). Figure 2 shows the improved selectivity of the RTP technique by using the second-derivative method. The precision of the RTP measurements is of the order of 15%.

The RTP technique approach offers several advantages: (a) rapid analysis, (b) simple set-up, (c) field applicable, (d) low per-analysis cost. These features of merit make RTP suitable for screening where a rapid estimation for specific PCBs is needed. The use of field screening analysis allows rapid decisions in a cleanup operation and reduces the need for either return visits to a site by a cleanup crew, or extensive and costly laboratory analyses of samples that contain no detectable levels of PCBs. Field screening techniques also reduce the cost of remedial actions by preventing unnecessary excavation of uncontaminated soil.

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REFERENCES

1. Erickson, M. D., Analytical Chemistry of PCBs, Butterworth Publishers, Boston, 1986.
2. Spittler, T. M., in Environmental Sampling for Hazardous Wastes, G. E. Sweitzer and J. A. Santolucito, Eds., ACS Symposium Series 267, ACS, Washington, D.C., 1984.
3. Safe, S., M. Mullin, L. Safe, C. Pochini, S. McCrindle and M. Romkes, in Physical Behaviour of PCBs in the Great Lakes, D. MacKay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds., Ann Arbor Publishers Inc., Ann Arbor, MI 1983.
4. Vo-Dinh, T., Room Temperature Phosphorimetry for Chemical Analysis, Wiley, New York, 1984.

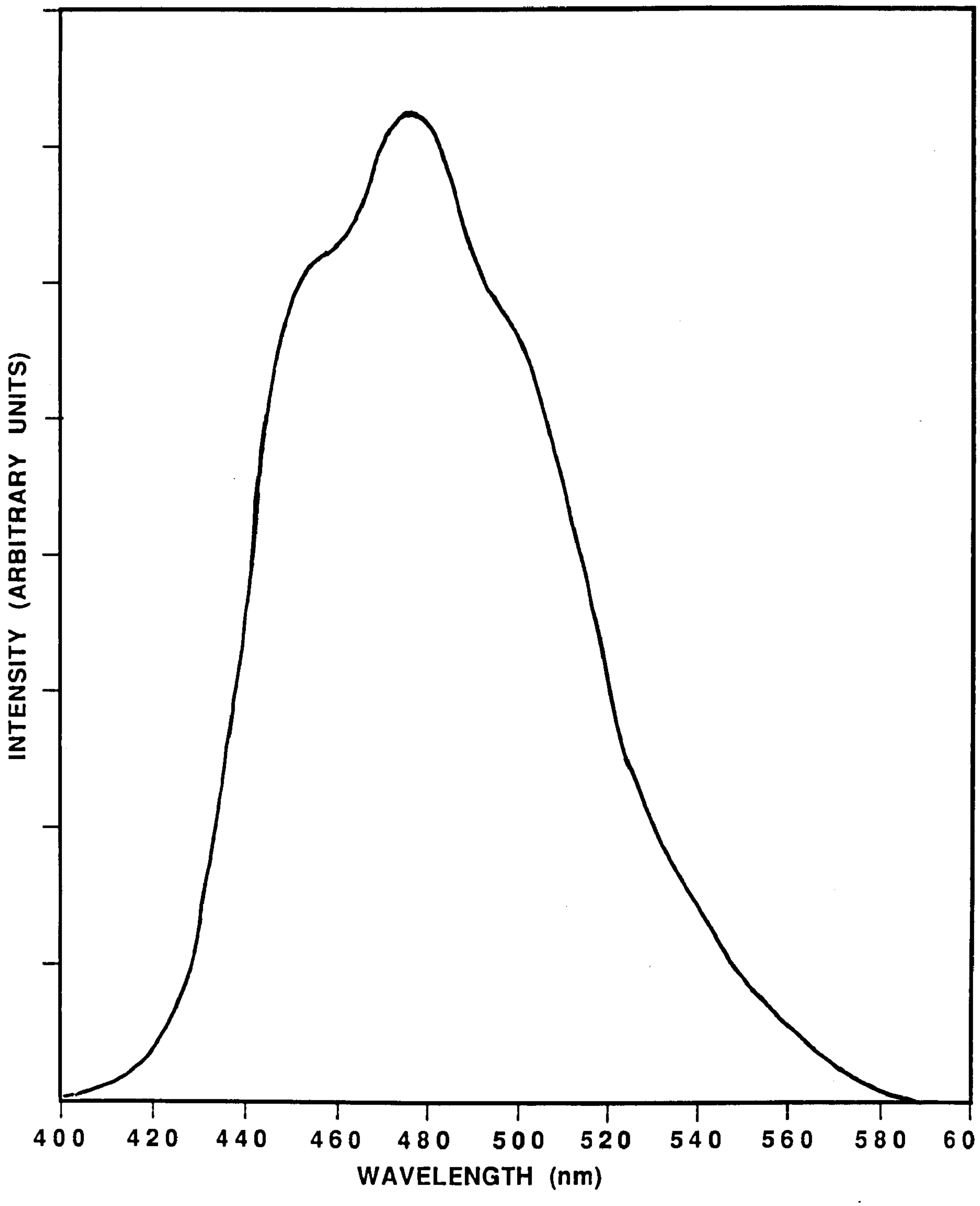

Figure 1

Example of RTP Spectrum of Aroclor 1254

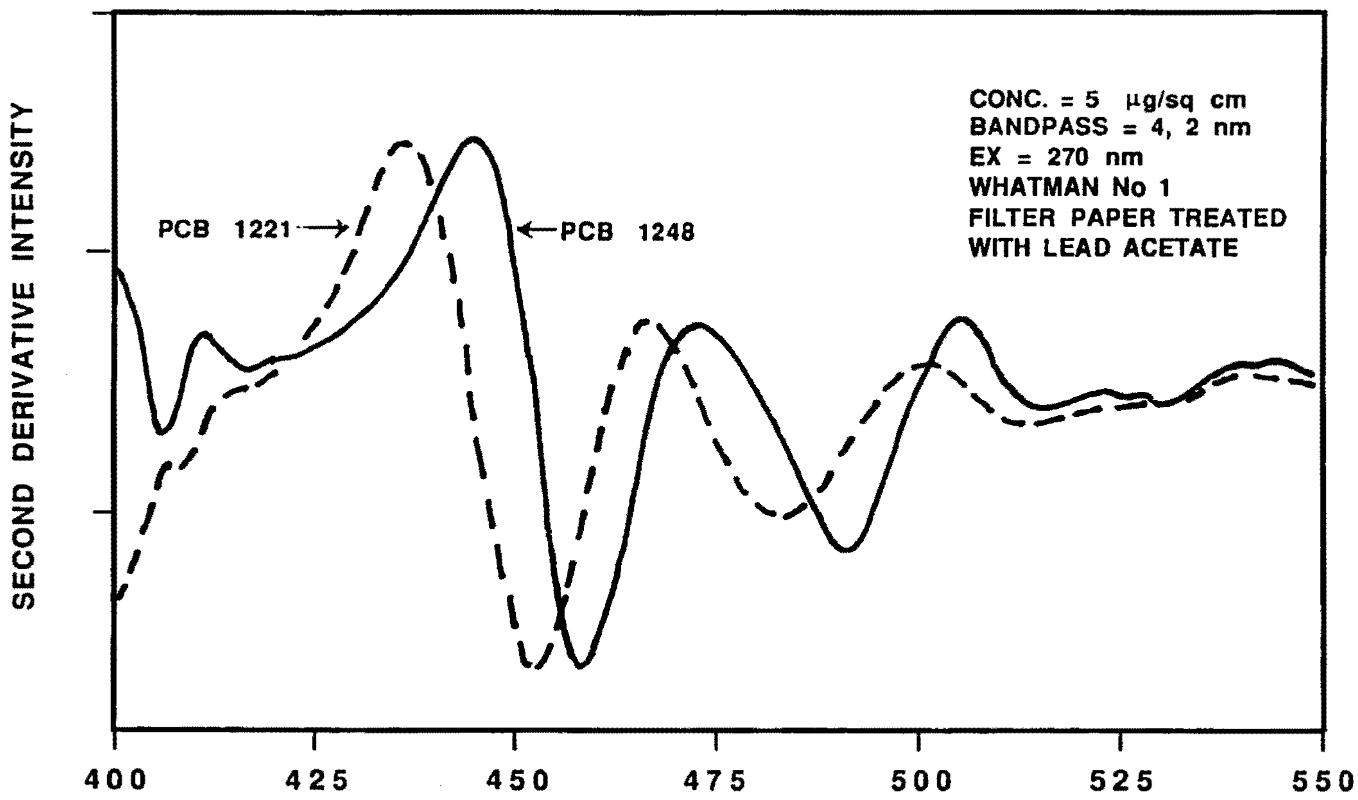

Figure 2

SECOND DERIVATIVE RTP EMISSION OF POLYCHLORINATED BIPHENYLS

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