

Total Polychlorinated Biphenyl Quantification by Rapid Dechlorination Under Mild Conditions



The congeners of polychlorinated biphenyls (PCBs) and many of those of the chlorinated pesticides have many physical and chemical similarities. These features present a problem during chromatographic analyses of these species in the form of coeluted peaks. Reductive dechlorination of these organochlorides greatly simplifies the resulting chromatograms and allows for the quantification of total PCB content by resolving the resultant biphenyl peak by gas chromatography with flame ionization detection. The authors of this article found that they could easily accomplish rapid dechlorination of PCBs, toxaphene, chlordane, and dichlorodiphenyltrichloroethane (DDT) at room temperature and atmospheric pressure using palladium–magnesium bimetallic particles. Using this method, they obtained a 580-ppb estimated detection limit for total PCB content in the presence of the interfering species.

The analysis of polychlorinated biphenyls (PCBs) always has been a daunting task because of the problems associated with the analysis of 209 possible congeners, each of which has slightly different chemical and physical properties. Coupled with this fundamental problem is the aging process, which includes different rates of volatilization and metabolism for each congener. Finally, the problem of chemical interferences in the form of chlorinated pesticides also presents a challenge (1–8).

Figure 1 illustrates representative structures for several common chlorinated pesticide formulations. Most of these pesticides are technical mixtures of as many as 30 components, which exacerbates the overall problem. These interferences are especially troublesome in the preferred method of PCB quantification — gas chromatography (GC) with electron-capture detection (ECD). Many of these chlorinated pesticides and their metabolites are coeluted with specific PCB congeners because of similar physical characteristics (Figure 2a). Yet another complication is that the relative ECD re-

sponse of each congener varies widely, sometimes by four orders of magnitude (9). Because of these interferences, the quantification of both congener-specific and total PCBs may be grossly skewed. Several methods can separate PCBs from pesticides, but their variety adds to the complexity of PCB analysis (10,11). Therefore, continuing interest exists in alternatives to the present methods of PCB analysis.

A chemical reaction that forms a single species from PCBs and thus a single chromatographic peak would have distinct advantages in the analysis of total PCB content. A single chromatographic peak would be simple to quantify. Analysts could avoid making assumptions as to which congeners are present or the extent of aging or volatilization. A single peak also would be easy to resolve in the presence of interferences, even more so if the retention of this peak was shifted away from previously coeluted interferences. Two methods are plausible for this goal: perchlorination to decachlorobiphenyl and reductive dechlorination to biphenyl. In a previous publication, we demonstrated a rapid, simple, and

**Mark Engelmann and
I. Francis Cheng**

Department of Chemistry,
University of Idaho, Moscow,
Idaho 83844-2343, e-mail
ifcheng@uidaho.edu

Address correspondence to
I.F. Cheng.

reproducible method of total PCB quantification by reductive dechlorination to biphenyl (12), according to the following reaction.



Reaction completion under room temperature and pressure conditions requires only 5 min. Compared with other methods of PCB dechlorination, this method has several advantages, which include mild reaction conditions, inexpensive reagents, and short reaction times (8,13–15). In the previous publication we demonstrated that the biphenyl yield was 98% and that the reaction was quantitative enough to determine total PCB content (Arochlor 1221) at levels as low as 100 ppb using high performance liquid chromatography (HPLC) with UV absorbance detection at 200 nm. In this article, we will demonstrate that dechlorination of PCBs using the palladium-magnesium bimetallic system will allow for very simple and effective analyses by GC with flame ionization detection (FID) in the presence of various chlorinated pesticide interferences.

The dechlorination reaction is based on the driving force provided by the dissolution of magnesium metal, as follows.

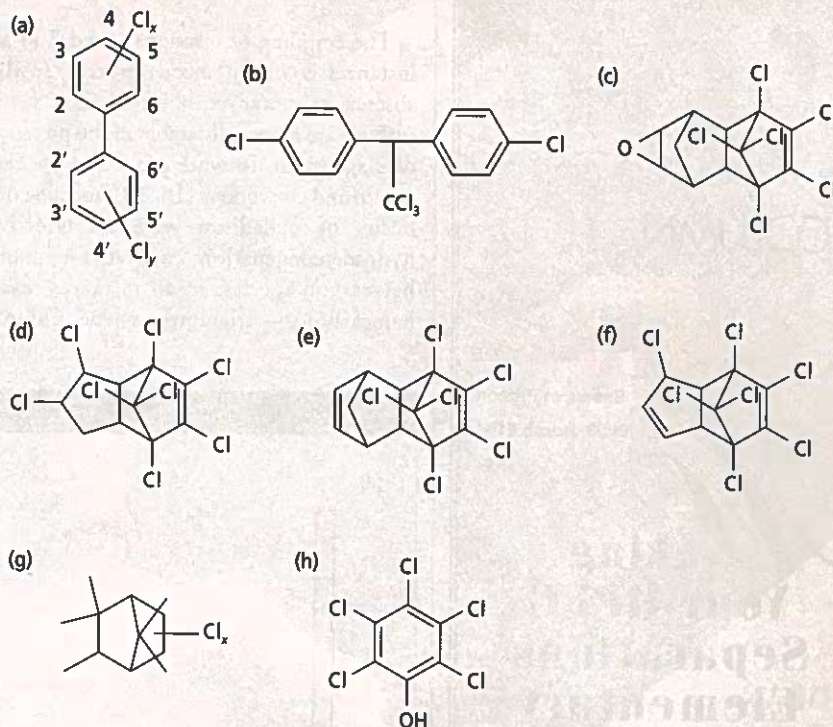


Figure 1: Structures of (a) PCBs and common PCB interferences (b) DDT, (c) dieldrin-endrin, (d) chlordane, (e) aldrin, (f) heptachlor, (g) toxaphene, and (h) pentachlorophenol.

You're *Open* for Business on the Web



\$31.25
Item#DMGB100
Over 300 Pages
Soft Cover

Written by internet specialist and leading author, Joe Tracy

...What's Your Next Move?

Web Marketing Applied, Web Marketing Strategies for the New Millennium, is the must-have book for Webmasters, Web marketers, Web developers...or anyone involved in the marketing or promotion of a Website. Every chapter is filled with powerful ideas to help you drive traffic to your site. Excellent for any industry, business or profession.

Master Your Next Move with Success!

Call 1-800-598-6008

Fax: 218-723-9146 • Outside the U.S. call 218-723-9180

Please mention code 950918LCGC when ordering

Visit our Website and order online at

www.advantstarbooks.com/webmarketing/

Z E T A L I F D E T E C T O R

Far Greater Sensitivity For Your System

The ZETALIF Laser Induced Fluorescence detector:

- Detects low zeptomole levels (10⁻²¹)
- Connects to all HPLC, Capillary LC, micro and nano-HPLC and almost all CE and CEC systems – thanks to its modular design
- Reproduces the same results without the need to recalibrate each time
- Offers the broadest range of laser wavelengths from 325 to 800 nm
- Is ideal for Pharmacokinetics, Neurochemistry, CE-SDS, Molecular Biology, Immunology, Trace Analysis and more



Picometrics
Sensitive to a Changing World

For further information, contact us by phone, fax or e-mail:

Tel (508) 528-3948

Fax (508) 528-6145

info@picometrics.com P.O. Box 190, Franklin, MA 02038

or alternatively visit our website: www.picometrics.com

COLUMN
ENGINEERING

See us at Pittcon
2000, Booth 2184

Making Your HPLC Separations Elementary

HYPERSIL®

INERTSIL®

KROMASIL®

LICHROSPHER®

LICHROSORB®

MONITOR®

NUCLEOSIL®

RELIASIL®

WATERS SPHERISORB®



UPCHURCH

JORDI ASSOCIATES

OHIO VALLEY

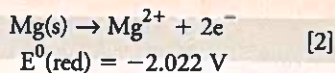
SPECIALTY CHEMICAL

HYPERQUAN

Manufacturers of Reliable HPLC
Columns and Silica Gels

www.column-engineering.com

1.800.707.HPLC (4752)



The coupling of reactions 1 and 2 in all instances is a spontaneous process. In the absence of a catalyst, however, most halocarbons are kinetically stable in the presence of magnesium. In work pioneered by Fernando and co-workers (16–18), metallic deposits of palladium were an effective hydrodehalogenation catalyst for many halocarbon species. In all instances, each halocarbon — trichloroethylene, chloro-

phenol, and PCB — was rapidly dechlorinated to the hydrocarbon skeleton under mild conditions.

Experimental

Materials: All organic solvents, acetonitrile, acetone, and 2-propanol were of HPLC grade and were obtained from Fisher Scientific (Pittsburgh, Pennsylvania). Water was purified to 18 MΩ using a Millipore-Q reagent water system (Bedford, Massachusetts). Arochlor 1260, toxaphene, dichlorodiphenyltrichloroethane (DDT), and chloro-

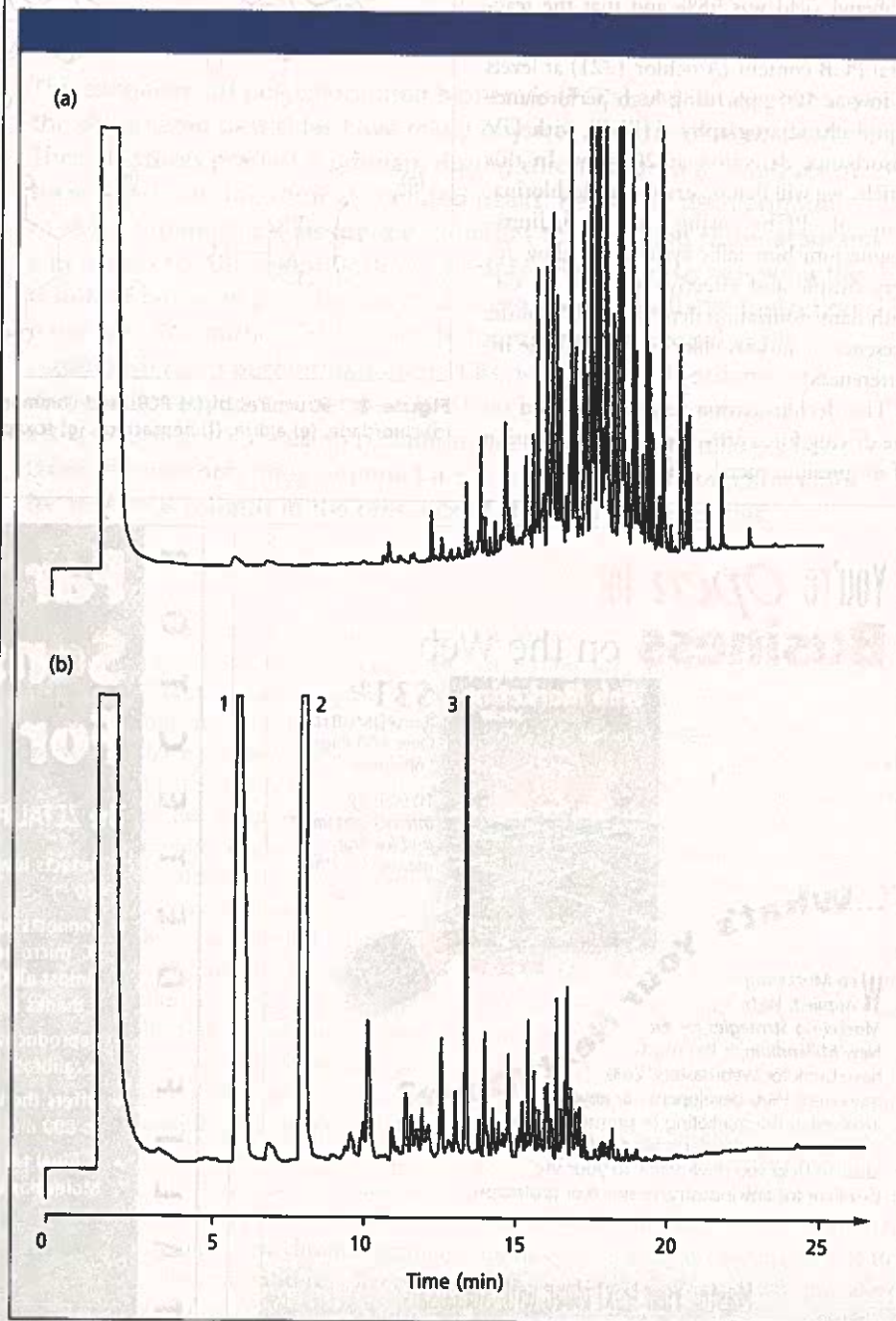


Figure 2: GC-FID chromatograms of (a) 100 ppm each Arochlor 1260, DDT, chlordane, and toxaphene and (b) the same mixture after dechlorination by the magnesium-palladium bimetallic system. Peaks: 1 = biphenyl from dechlorinated PCBs, 2 = 1,1-diphenylethane from DDT, 3 = 1,1,4,4-tetraphenylbutane from DDT. Minor peaks are partially dechlorinated byproducts of chlordane and toxaphene.

dane (technical standards) were obtained from Supelco (Bellefonte, Pennsylvania). We purchased magnesium (20 mesh, 98%) and potassium hexachloropalladate(IV) (K_2PdCl_6) from Aldrich Chemical Co. (Milwaukee, Wisconsin). Before use in dechlorination reactions, we washed the magnesium with HPLC-grade acetone, dried it with argon, and stored it in an airtight container.

Dechlorination reactions: Dechlorination reactions began with the addition of premixed stock solutions of PCB, DDT, chlordane, or toxaphene or a combination of all four compounds in a vial containing preweighed portions of 1.0 g of 20-mesh magnesium particles and 10 mg of potassium hexachloropalladate(IV). To this vial, we added methanol, acetone, 2-propanol, and water to achieve the desired concentration of chlorinated hydrocarbon in 5 mL of 10:20:30:40 (v/v/v/v) methanol-acetone-2-propanol-water. The water, which was added last, spontaneously initiated the palladization of the magnesium and also the dechlorination reaction. Finally, we added one drop of acetic acid to speed up the reaction. The vial then was capped, shaken vigorously for 5 s, and vented with a syringe to allow evolved hydrogen gas to escape.

After 30 min of reaction time, the products were extracted into hexanes by adding 1 mL of the solution to a reaction vial and agitating the vial for 2 min on a rotator set at 20 rpm. The extract then was analyzed immediately by GC-FID. All concentrations were calculated before extraction. We made no attempts to quantify the extraction efficiency; however, we made every attempt to perform the extractions in a reproducible manner.

Chromatography: All chromatograms were produced using a model 5890 gas chromatograph (Agilent Technologies, Wilmington, Delaware) equipped with a flame ionization detector. We used a 30 m \times 320 μ m, 0.25- μ m d_f AT-5 column (Alltech Associates Inc., Deerfield, Illinois). The carrier and makeup gases were ultra-high-purity helium at flow rates of 3.5 and 30 mL/min, respectively. The injection mode was splitless with a 30-s purge delay. The inlet and detector temperatures were 270 °C and 290 °C, respectively. The initial oven temperature was held at 125 °C for 5 min, after which it was increased at 10 °C/min to 275 °C and held for 5 min.

Results and Discussion

Figures 2 and 3 demonstrate the general problem encountered in the analysis of

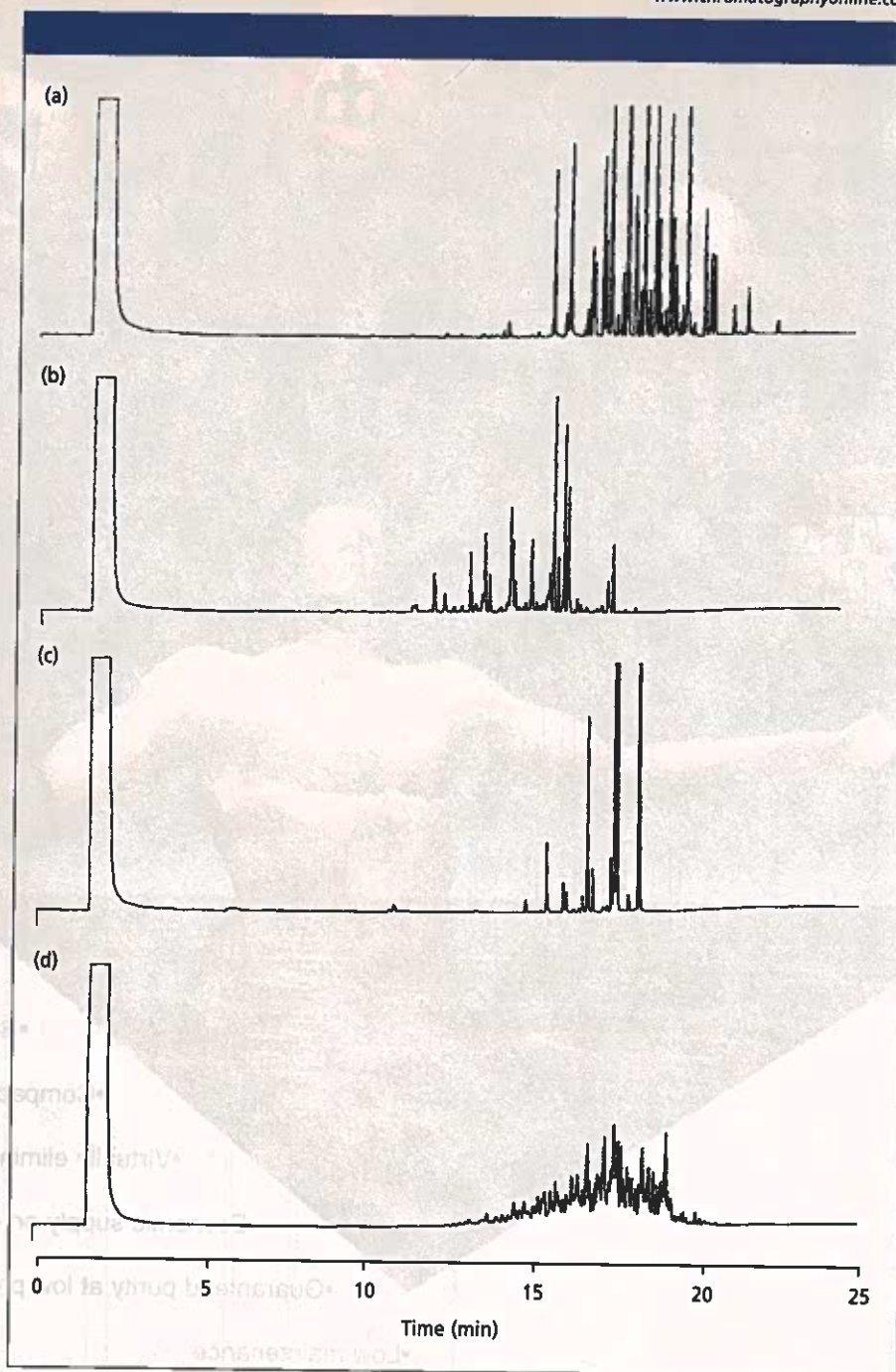


Figure 3: GC-FID chromatograms of 100 ppm each of (a) Arochlor 1260, (b) chlordane, (c) DDT, and (d) toxaphene.

PCBs in the presence of chlorinated pesticides. The complexity of the GC-FID chromatogram of Arochlor 1260 compounded by the overlap of the peaks associated with the technical pesticide mixtures of DDT, chlordane, and toxaphene. The treatment of a mixture containing 100 ppm each of Arochlor 1260, DDT, chlordane, and toxaphene by the presently described palladium-magnesium dechlorination system clearly demonstrates that biphenyl is resolvable from this mixture (Figure 2b).

Using only Arochlor 1260, it is possible to construct a calibration curve for the quantification of total PCB content from biphenyl FID response (Figure 4). The FID response for biphenyl from dechlorinated Arochlor 1260 is very linear in the 1–50 ppm range. Comparisons of biphenyl peak areas obtained from similar concentrations of Arochlor 1260 in the presence of the pesticide mixture indicate a yield of 102% with a 5.1% relative standard deviation (Tables I and II). These results are within the error

Ple

• I n

• I v

• I k

• I a

• I a

• I d

• TS

• I d

• I h

• I d

• I b

• In

• I o

• I o

• Ye

□ P

□ G

□ A

□ S

□ P

□ S

NAM

COM

DEP

BUIL

ADD

CITY

COUN

PHON

E-M

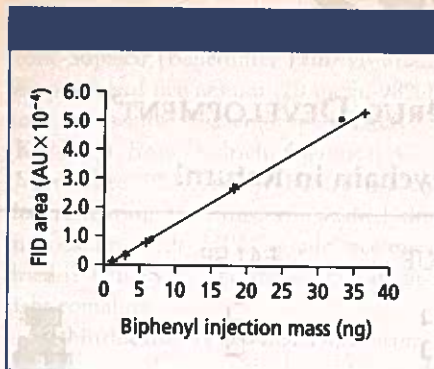


Figure 4: Calibration curve for biphenyl derived from Arochlor 1260 alone (crosses with trend line) compared with biphenyl from Arochlor 1260 obtained in the presence of the pesticide mix (squares).

allowed by the experimental procedures and do not reflect irreproducible results from the dechlorination reaction. The precision and accuracy of the injection volume is the limiting factor for error. From these data, we can conclude that this method is quite suitable for the quantification of Arochlor 1260 in the presence of certain pesticide interferences. The limit of detection for this method, as determined by the concentration of PCB that yields biphenyl at triple the background signal, is 580 ppm or 0.38 ng by GC-FID. This limit of detection takes the preconcentration extraction step into consideration.

Each chlorinated pesticide also undergoes dechlorination when treated by the palladium-magnesium bimetallic system. Mass spectral data indicate that the major product of DDT dechlorination is 1,1'-diphenylethane (Figure 2b, peak 2), which is the hydrocarbon backbone of this pesticide (Figure 1). Toxaphene and chlordane also undergo dechlorination as shown by changes in their chromatographic features, particularly a shift to shorter retention times before and after treatment with palladium-magnesium.

We have not identified the major products from the dechlorination of toxaphene and chlordane, and it may not be entirely possible to do so. The dechlorination of aliphatic compounds relative to aromatic organochlorine compounds appears to occur at a reduced rate. In addition, the dechlorination reaction most likely occurs through a radical mechanism that leads to the coupling of dechlorinated aliphatic residues. This process would be highly irreproducible and would lead to many possible products. In contrast, these radical intermediates would be stabilized by an aromatic

Table I: Biphenyl data obtained from the analysis of Arochlor 1260 alone

Injection Volume (μ L)	Concentration (ppm)	Injection Mass (ng)	FID Peak Area	Normalized Peak Area*
1.10	50	36.3	52,504	47,731
1.10	25	18.2	26,472	24,065
0.90	10	5.9	8,029	8,921
0.90	5	3.0	3,629	4,032
0.90	2	1.2	1,543	1,714

* Normalized peak areas are derived by the division of the FID peak area by the injection volume.

Table II: Biphenyl data obtained from the analysis of Arochlor 1260 in the presence of DDT, chlordane, and toxaphene

Injection Volume (μ L)	Concentration (ppm)	Injection Mass (ng)	FID Peak Area	Normalized Peak Area
1.00	50	33.0	50,261	50,261
1.10	25	18.2	27,455	24,959
1.00	10	6.6	9,137	9,137
0.90	5	3.0	3,877	4,308
0.90	2	1.2	1,425	1,583

system and would not undergo radical addition reactions. This result is evident by the 100% biphenyl yield from PCB, which is an entirely aromatic system, and the less-than-100% yield of diphenylethane from DDT, which has aliphatic as well as aromatic chlorine. The dechlorination of chlordane and toxaphene produce many products during the same time period as complete PCB dechlorination.

Conclusion

Reductive dechlorination should not be viewed a supplanting method of PCB analysis but rather a complementary tool to existing ones. Congener-specific information is lost in the dechlorination of PCBs. Also, it is important to highlight the need for a biphenyl background, because this species will skew total PCB content upward. Finally, our study does not address the application of this method to different sample matrices such as soils and industrial waste.

Regardless of these limitations, we believe there is cause to be optimistic about the use of the palladium-magnesium reductive dechlorination in the analysis of PCB and halocarbon mixtures. The procedure is a low-cost, rapid method for the complete and reproducible dechlorination of PCB to biphenyl under mild — room temperature and atmospheric pressure — conditions.

References

- (1) S.A. Chiosi, G. Evidente, G. Randazzo, and D. Scalorbi, *J. Liq. Chromatogr.* **5**, 1653-1663 (1982).

- (2) R.G. Webb and A.C. McCall, *J. Chromatogr. Sci.* **11**, 366-373 (1973).
- (3) S.C. Leung and B.Y. Giang, *Bull. Environ. Contam. Toxicol.* **50**, 528-532 (1993).
- (4) R.J. Letcher and R.J. Norstrom, *Anal. Chem.* **67**, 4155-4163 (1995).
- (5) H.-U. Meisch and H.-J. Lafontaine, *Fresenius' J. Anal. Chem.* **334**, 418-420 (1989).
- (6) L.L. Needham, A.L. Smrek, S.L. Head, V.W. Burse, and J.A. Liddle, *Anal. Chem.* **52**, 2227-2229 (1980).
- (7) G. Rimkus, L. Rexilius, and G. Heidemann, *Chemosphere* **26**, 1099-1102 (1993).
- (8) M. Cooke, G. Nickless, A.M. Prescott, and D.J. Roberts, *J. Chromatogr.* **156**, 293-299 (1979).
- (9) O. Hutzinger, S. Safe, and V. Zitko, *The Chemistry of PCBs* (CRC Press, Boca Raton, Florida, 1974), p. 269.
- (10) A.S.Y. Chau and L.J. Babjek, *J. Assoc. Off. Anal. Chem.* **62**, 107-113 (1979).
- (11) J.A. Teichman, A. Benenue, and J.W. Hylin, *J. Chromatogr.* **28**, 405-423 (1977).
- (12) J.G. Doyle, T. Miles, E. Parker, and I.F. Cheng, *Microchem. J.* **60**, 290-295 (1999).
- (13) B. Zimmerli, *J. Chromatogr.* **88**, 65-75 (1974).
- (14) M.L. Ware, M.D. Argentine, and G.W. Rice, *Anal. Chem.* **60**, 383-384 (1988).
- (15) G. Seidl and K. Ballschmiter, *Fresenius' J. Anal. Chem.* **296**, 281-284 (1979).
- (16) R. Muflikian, Q. Fernando, and N. Korte, *Water Res.* **29**, 2434 (1995).
- (17) C. Grittini, M. Malcomson, Q. Fernando, and N. Korte, *Environ. Sci. Technol.* **29**, 2898-2900 (1995).
- (18) I.F. Cheng, Q. Fernando, and N. Korte, *Environ. Sci. Technol.* **31**, 1074-1078 (1997). ■

Var
Spe

Select

Thousands
for GC, GC
UV/Vis, an
from Vari
manufact
our latest

Enjoy the
chromato
consumab
from a sin