

# Toxaphene, the Underestimated Pesticide

## THE APPLICATION OF STANDARD METHODS FOR THE DETERMINATION OF TOXAPHENE IN ENVIRONMENTAL MEDIA

Francis J. Carlin, Jr.<sup>\*</sup>; H. Lavon Revells<sup>#</sup>; and Danny L. Reed<sup>‡</sup>

<sup>\*</sup> Hercules Incorporated, Analytical Science Division, Research Center, 500 Hercules Road, Wilmington, Delaware 19808-1599, U.S.A.; (present address: FJC Analytical Consulting, Inc., 136 Timberline Drive, Newark, Delaware 19711, U.S.A.)

<sup>#</sup> United States Environmental Protection Agency, Region IV Laboratory, 980 College Station Road, Athens, Georgia 30605-2720, U.S.A.

<sup>‡</sup> State of Georgia Environmental Protection Division, Organic Laboratory, 455 Fourteenth Street NW, Atlanta, Georgia 30318-7900, U.S.A.

### INTRODUCTION

Toxaphene is a chlorinated camphene insecticide that may contain more than two hundred components [1]. Hercules Incorporated (Hercules) was the major producer [2] of toxaphene in the United States from the late 1940's until December 1980, when production ceased. In recent years, Hercules has been involved in environmental monitoring activities; and large numbers of samples have been analyzed as part of those activities. The progress of those programs has been followed by the determination of toxaphene using validated United States Environmental Protection Agency (EPA) methods [3] of analysis, performed in commercial analytical laboratories. Hercules has observed wide variations in the application of standard EPA methods to the detection and measurement of toxaphene.

The recent literature contains many descriptions of analytical methods [4-10] in which individual chlorobornane congeners have been detected and their concentrations estimated by gas chromatography followed by electron capture negative chemical ionization mass spectrometry detectors (GC-ECNCI-MS). While those methods demonstrate good sensitivity and reasonable specificity for the individual congeners, they have not been validated for environmental monitoring activities by the regulatory agencies that are responsible for the technical toxaphene product that was manufactured, registered for use, and regulated by statutes. Therefore, it is necessary to analyze for toxaphene using approved, validated methods acceptable to the regulatory agencies.

The determination of toxaphene by gas chromatography produces a multi-component chromatogram. Because of the complexity of this chromatogram, even experienced analysts have extreme difficulty with the detection, identification, and measurement of toxaphene in environmental samples. Matrix components may provide significant interferences. Extremely

# Toxaphene, the Underestimated Pesticide

critical is proper calibration with reliable toxaphene reference materials. Significant variations in the gas chromatography profile of toxaphene reference materials have been observed among several suppliers [11], and those differences have been shown to have significant effects on the quantitation of toxaphene [12]. EPA SW-846 Method 8081A also contains cautionary statements about variations among calibration standards for toxaphene [13].

The current guidance that is recommended for the analysis of toxaphene in environmental samples from the Brunswick, Georgia, area will be described.

## **EXPERIMENTAL**

For the analyses of environmental media for toxaphene, the methodology provided in U.S. EPA SW-846 Method 8081, "Organochlorine Pesticides, Halowaxes, and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique," [3] with a sulfuric acid clean up (SW-846 Method 3665), will be followed. To ensure consistent application of the method between laboratories, the following steps are specified in more detail.

### I.) GAS CHROMATOGRAPHY

#### 1.) GC Columns:

- a.) 30-meter DB-1701 (1.0- $\mu$ m film thickness) Megabore (J&W Scientific).
- b.) 30-meter DB-5 (1.5- $\mu$ m film thickness) Megabore (J&W Scientific).

#### 2.) GC Operating Temperatures:

The column oven temperature profile will be adjusted in each laboratory to separate the GC peaks satisfactorily and to demonstrate the performance criteria required in Method 8081.

Injector:	220° C - 250° C
Electron Capture Detector:	300° C - 350° C

- 3.) Tetrachloro-m-xylene (TCMX) and/or decachlorobiphenyl (DCB) will be used as surrogates.
- 4.) A five-point toxaphene calibration curve will be used. All laboratories must use a toxaphene reference standard that matches the GC profile of the Hercules product standard, that is, Hercules technical toxaphene X16189-49 (Lot No. 8BC25; 68.6 % Cl).

# Toxaphene, the Underestimated Pesticide

## II.) EXTRACTION OF SAMPLES:

U.S. EPA SW-846 Method 3550A, "Ultrasonic Extraction," (SW-846) will be used for the extraction of all soil and sediment samples. The extraction solvent will be a 1:1 mixture of hexane and acetone. All solvent extracts will be exchanged to hexane for analysis by GC. The extracts will be made to a final volume of 10 mL.

U.S. EPA SW-846 methods will be used for the liquid-liquid extraction of all water samples. The extraction solvent will be methylene chloride. All solvent extracts will be exchanged to hexane for analysis by GC. The extracts will be made to a final volume of 10 mL.

## III.) SULFURIC ACID CLEANUP:

After the sample extract is adjusted to final volume in hexane, in a glass vial with a Teflon-lined screw cap, add 10 mL of concentrated sulfuric acid for each 5 mL of sample extract. Shake the tube vigorously for one minute. Vent the vial carefully to relieve any pressure that may build up in the vial. Allow the layers to separate. (If excessive heat is generated during the extraction, the sample extract should be discarded and steps taken to eliminate the source of the heat generation.) If the layers are not clearly separated, centrifuge the mixture. After a clear separation is obtained, transfer the hexane layer to a GC injection vial for analysis. Store the excess extract in a clean vial with a Teflon-lined screw cap in a refrigerator at 4°C, or less.

## RESULTS AND DISCUSSION

Federal and state regulatory agencies and Hercules shared similar concerns regarding the proper application of analytical methods for the determination of toxaphene in environmental samples. Therefore, in 1991, chemists from the EPA Region IV Laboratory, the State of Georgia Environmental Protection Division (EPD), and Hercules Research Center performed a limited study of Method 8080. The result was a set of guiding principles to aid experienced analysts in the application of Method 8080 for the determination of toxaphene in ground water, soil, and sludge samples [14]. In subsequent years, the review and comparison of results from several sample analyses indicated that the guidance needed refinement. Through additional consultations, the guidance was modified – with the objective of developing consistent application of Methods 8080 or 8081. As a result, analysts and data reviewers can be confident that the commercial laboratories and the agency laboratories have applied the method similarly. Comparison of data from split samples could then be interpreted on a more reliable basis. The current guidance is discussed below.

All analyses will be performed according to approved EPA SW-846 Methods -- for the liquid-liquid extraction of water samples, for the ultrasonic extraction of the soil and sediment samples, and for the gas chromatography (GC) with electron capture detector (ECD) analyses of

## Toxaphene, the Underestimated Pesticide

the extracts. Because split samples will be analyzed, certain aspects of the methods have been specified in detail to assure consistent application of the methods.

All QA/QC requirements specified in the methods will be followed by the laboratories. Use the DB-1701 column for quantitation where possible, that is, when there are fewer interfering peaks on the DB-1701 column than on the DB-5 column. A continuing calibration sample will be injected after every 10 samples; and, as the final injection at the end of each injection sequence. The final volume of the sample extracts may be adjusted according to the detection limit required by the data quality objectives specified in the specific project plan.

Four to seven major peaks in the "back half" of the toxaphene chromatogram will be used for calibration and quantitation of toxaphene. The "back half" of the chromatogram is defined as the major peak in the toxaphene chromatogram and all peaks with longer retention times.

The Perkin-Elmer TurboChrom data system will be used for measurement of peak heights. Baseline parameters will be selected so that the baselines are drawn by the TurboChrom data system from valley-to-valley under the groups of peaks in the chromatogram so that the resulting baselines follow the general curve of the toxaphene baseline. Adjust the baselines with manually-selected baselines if the data system selects a peak shoulder or other erroneous baseline. The baselines in the chromatograms of the samples will be placed under the peaks exactly as in the calibration standards.

Peaks that are larger in relative proportions in the samples than in the toxaphene standard will not be used for quantitation. If fewer than four peaks are used for quantitation, the resulting values will be considered only as estimated values; and those results will be qualified as "J" (estimated) values. Any results qualified as "JN" will be interpreted as "**not detected**," or "U" values. The "N" qualifier signifies presumptive evidence of the presence of a compound, but its presence cannot be confirmed.

This guidance for the implementation of EPA SW-846 Method 8081 for the determination of toxaphene in environmental media has been applied since August 1997 for monitoring activities in the Brunswick, Georgia, area. Review and comparison of the analytical results can be made with the confidence that the laboratories are applying approved methodology in a manner that is as similar as possible.

# Toxaphene, the Underestimated Pesticide

## REFERENCES

1. Saleh, M. A., *J. Agr. Food Chem.* **31**, 748 (1983).
2. Saleh, M. A., *Rev. Environ. Contam. Toxicol.* **118**: 1-85 (1991).
3. United States Environmental Protection Agency, "Test Methods for Evaluation of Solid Waste, Volume 1B: Laboratory Manual, Physical/Chemical Methods, (SW-846)," Method 8080A, Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography, Revision 1, November 1992.
4. Buser, H.R. and Müller, M.D., *J. Agric. Food Chem.* **1994**, 42, 393-400.
5. Howdeshell, M.J. and Hites, R.A., *Env. Sci. Tech.* **1996**, 30 (1), 220-224.
6. Xu, L.; Hainzl, D.; Burhenne, J.; and Parlar, H., *Chemosphere* **1994**, 28 (2), 237.
7. Gill, U. S.; Schwartz, H.; Wheatley, B.; and Parlar, H., *Chemosphere* **1996**, 30 (2), 1021.
8. Andrews, P.; Keadrick, K.; Pilon, J-C.; Bryce, F.; and Iverson, F., *Chemosphere* 1996, 32 (6), 1043.
9. Vetter, W.; Oehme, M.; and Lukas, B., *Chemosphere* **1993**, 27, 597.
10. Kimmel, L.; Angerhöfer, D.; Gill, U.; Coelhan, M.; and Parlar, H., *Chemosphere* **1998**, 37 (3), 549.
11. Carlin, F. J., Jr. and Hoffman, J. M., Proceedings of the Twelfth Annual Water Testing & Quality Assurance Symposium, **1996**, 148.
12. Carlin, F. J., Jr. and Hoffman, J. M., *Organohalogen Compounds*, **1997**, 33, 70.
13. United States Environmental Protection Agency, "Test Methods for Evaluation of Solid Waste, Volume 1B: Laboratory Manual, Physical/Chemical Methods, (SW-846)," Method 8081A, Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography, Revision 1, Paragraph 5.6.2, December 1996.
14. Bennett, T. B., Jr., (Report) "Toxaphene Task Force," U. S. EPA, Region IV, Environmental Services Division, Athens, Georgia (June 4, 1993).

# **Toxaphene, the Underestimated Pesticide**