

## USER NOTES:

Within each class, the compounds are ordered by retention time.

The following terms are used to specify the type of mass spectral identification:

- **Authentic MS RT:** matched to both the spectrum and retention time of an authentic material.
- **Authentic MS:** matched to the spectrum of an authentic material; compound is an isomer with a different retention time.
- **Reference Database MS:** matched to a spectrum in the NIST 2008 electron impact database.
- **Literature MS:** matched to a spectrum reported in the literature.
- **Manual - Congener Group:** manually identified and belonging to a family of observed congeners. At least one congener within the family was identified with Authentic MS RT criteria.
- **Manual:** spectrum identified through manual interpretation.
- **Unknown:** spectrum could not be identified.

Fragment Ions:

- The blue m/z values printed within the spectrum generally indicate the most abundant ion in the cluster.
- The m/z values within the identity table generally refer to the monoisotopic fragment ion.
- The marks printed above the spectrum indicate peaks described in the identity table: red for those belonging to named fragments and grey for interferences due to coeluting compounds.

Chemical Formulas: If there is only one element, the number is placed first (3Br is three bromines). If there are two or more elements, the number is placed second (Br<sub>3</sub>Cl is three bromines and one chlorine).

The retention times of the identified PCBs are described in the metadata, but the spectra are not included because of space considerations. Fifty-five PCB congeners were identified and they are commonly observed contaminants with known mass spectra.

## **INSTRUMENTAL METHOD:**

The literature reference includes a description of the study goals, sample, extraction method, direct sample introduction method, GCxGC/TOF-MS method, the purpose and basic design of the software, and results. The instrumental method is repeated below:

A Pegasus 4D (LECO, St. Joseph, MI, USA) GCxGC/TOF-MS was used with a Restek (Bellefonte, PA, USA) Siltek deactivated column (5 m length, 0.25 mm i.d.) attached to the inlet as a guard column, a Restek Rtx5Sil-MS (15 m length, 0.25 mm i.d., 0.25  $\mu$ m film thickness) as the first dimension of separation, and a J&W Scientific (Folsom, CA, USA) DB-17MS (2 m length, 0.18 mm, 0.18  $\mu$ m thickness) as the second dimension of separation. Ultrahigh-purity helium (Airgas, Radnor, PA, USA) was used as the carrier gas. The primary oven temperature was held at 60 °C for 7.5 min, then ramped at 10 °C/min to 300 °C and held for 20 min. The secondary oven temperature was programmed to be 20 °C higher than the primary oven. For GCxGC, the modulation period was set to 3.5 sec, with a 0.9 sec hot pulse duration and a 35 °C modulator temperature offset vs. the primary oven temperature. The MS transfer line and the ion source temperatures were at 270 °C and 250 °C, respectively. The electron energy was -80 eV and the detector voltage was 1850 V. The data acquisition rate was 100 spectra/sec.