Analytical Measurement Advances Over 25 Years: POPs and PAHs

Donald Patterson Jr.[1]

[1]Centers For Disease Control

Over the past 25 years of Dioxin and Polynuclear Aromatic Hydrocarbon Symposia there have been spectacular advances in all areas related to the measurement of PAHs and POPs in both environmental and biological matrices. These advances have followed a life-cycle common to most systems of advancing technology.

Many times depending on the length of dead time, the "Early Birds" are forgotten or not given the credit for their early contributions. In fact, without the early contributions to build upon there may not even be applications or at the very least, they would have been much delayed. Both the PAH and POPs community of Scientists have seen great advances in all areas of the analytical process. A brief discussion of some of these advances will be presented here and will be discussed at greater length in the presentation. The work of the "Early Birds" and the "New Early Birds" will be emphasized.

CHEMICALS AND CHEMICAL CLASSES. Twenty five years ago the methods available were limited to TCDD and 1-OHPyrene. Today the PAHs have been expanded to include a large list of PAHs, NO2-PAHs, and metabolites and adducts. The POPs methods now include nearly all of the congeners of the PCDDs, PCDFs, PCBs, persistent and non-persistent pesticides, PCNs, PBDEs, halogenated alkanes, fluorinated compounds, as well as metabolites of some of these classes, and others.

SAMPLE PREPARATION. Today in many methods the sample extraction and cleanup steps have been combined and automated. Methods have been developed that utilize SPE//ASE//SOX//SEC//LLE//HPLC. The numbers of matrices that are amenable to analysis have increased to include adipose tissue, urine, blood, milk, amniotic fluid, meconium, feces, semen, as well as large number of environmental sample types.

ANALYTE SEPARATION. Gas chromatography and liquid chromatography continue to be developed with new GC column types with smaller column IDs and micro-liquid chromatography columns. The new technique of multidimensional comprehensive GCxGC continues to attract new researchers taking advantage of the techniques increase in peak capacity and sensitivity enhancement.

ANALYTE DETECTION AND SENSITIVITY. New detection schemes continue to be developed that provide more sensitivity for the halogenated POPs as well as PAHs. In addition to the FID detector there is now available ECD and mass spectrometric detection. High resolution, quadrapole, ion trap, and time-of-flight mass spectrometers are becoming more routine in the laboratory. Techniques such as MS/MS with electrospray ionization, negative ion chemical ionization, and EI are now available.

In 1974, Baughman and Meselson were able to achieve a detection limit of 100 pg for TCDD by repetitive scanning of a HRMS over a mass to charge ratio range of 310 to 330 (see Figure 1). These same authors were able to measure 0.5 pg of TCDD by time averaged repetitive scanning over a 0.300 m/z range. However, the S/N ratio was very low for this measurement (see Figure 2). By 1980, Facchetti was able to measure TCDD from 10g of human blood with a S/N ratio of 15 and this same blood (3.4g) was measured for TCDD again in 1988 at the Centers for Disease Control and Prevention with a S/N ratio of 333 (see Figure 3). By 2005, using a combination of comprehensive GCxGC and HRMS (10,000 RP), detection is possible for 313 attograms of TCDD with a S/N ratio of 890 to 1 (see Figure 4). This measurement represents about 595,000 molecules of TCDD. The analysis of an extract from a human serum sample diluted to contain ~540 attograms of TCDD produces a S/N ratio of 479 to 1 using the GCxGC-ID-HRMS SIM technique. This new use of GCxGC will be discussed in more detail in another presentation in the special session on GCxGC. The sensitivity of the measurement for PAH metabolites has steadily increased over the years. Figure 5 illustrates the high S/N ratio attainable for a series of OH-PAH and amino-PAH metabolites using high resolution mass spectrometry. This highly sensitive method can be used to measure PAH metabolites in urine of a statistically designed sampling of the U.S. population as shown in Figure 6. These reference ranges provide useful information with which to compare levels found during various exposure investigations and epidemiologic studies.

Figure 1. Repetitive Scanning of m/z 310-330 Range.

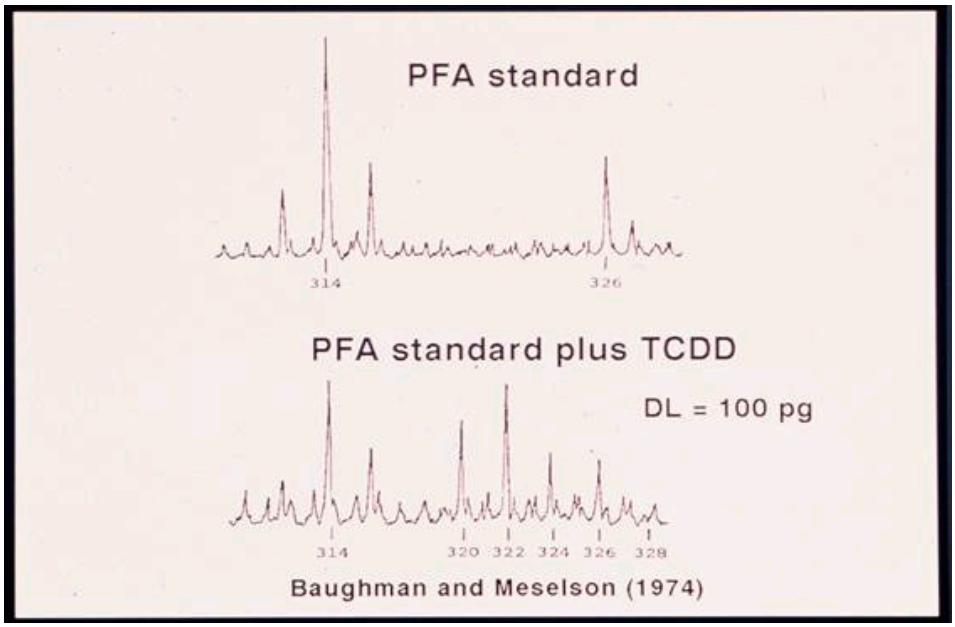

Figure 2. Time Averaged Repetitive Scanning (41 Seconds) of 0.300 m/z Range

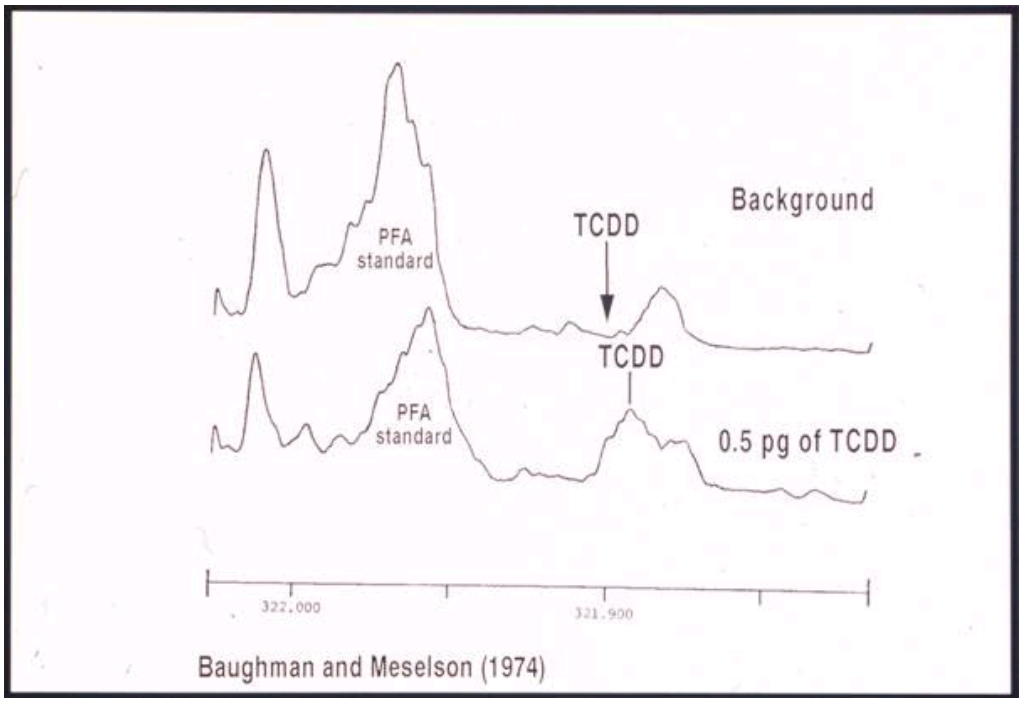

Figure 3.Measurement of TCDD in the Same Sample by Facchetti and CDC Eight Years Apart

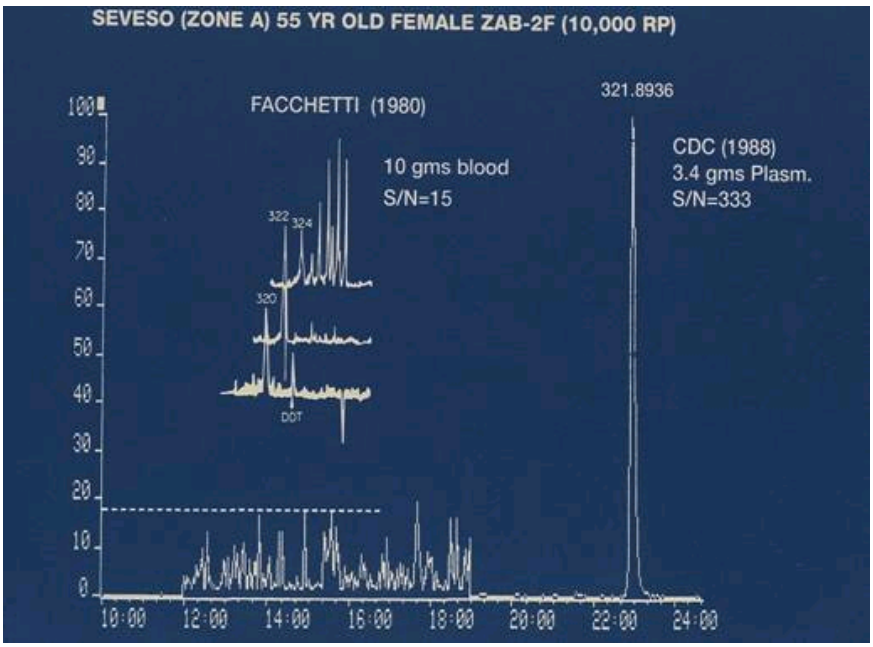

Figure 4. Three-Dimensional Plot of the GCxGC-ID-HRMS SIM Measurement of 313 Attograms (Approximately 595,000 Molecules) of 2,3,7,8-TCDD Injected On-Column (S/N Ratio of 890 To 1)

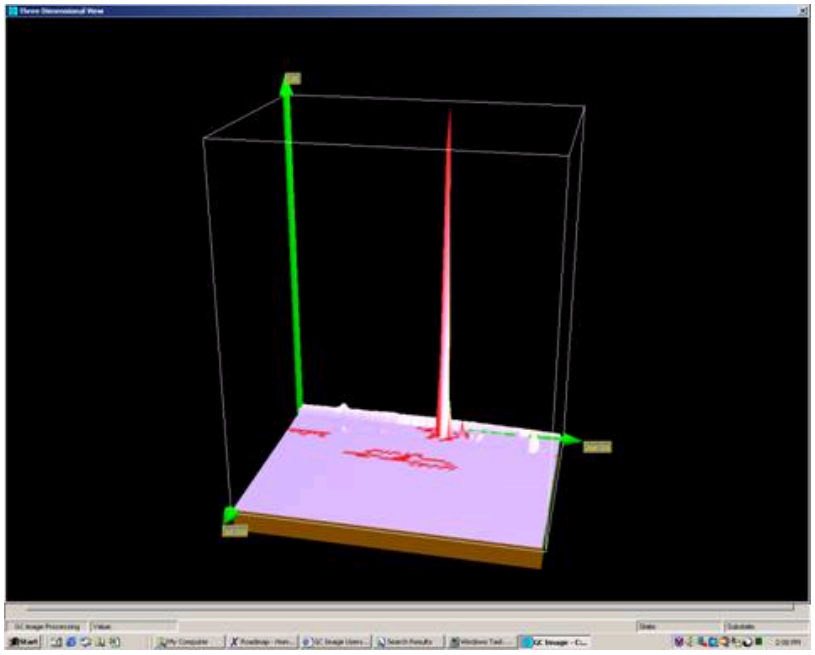

Figure 5. GC-ID-HRMS SIM measurement of 37 Derivatized Metabolites of PAHs and Nitro-PAHs in a Single GC Run (30 Picograms per Analyte Injected On-Column)

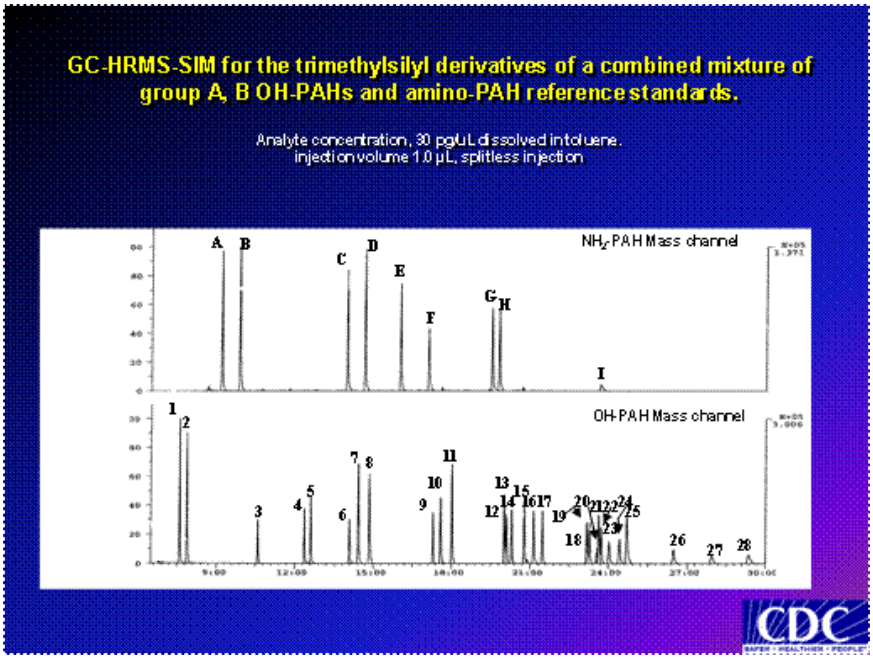

Figure 6. The U.S. Reference Range in 1999-2000 for PAH Metabolites