ENVIRONMENTAL APPLICATIONS OF MASS SPECTROMETRY: A BRIEF HISTORY

ENVIRONMENTAL MEASUREMENTS ARE NOT EASY

Environmental analyses deal with complicated mixtures in complex samples (fish, soil, sediment, water, etc.) at very low concentrations. Before 1960, organic compounds in the environment were measured using techniques that were not compound-specific.

All this changed in 1962 with the publication of Silent Spring by Rachel Carson. This book drew attention to pesticides, such as DDT, in the environment. Soon methods for measuring pesticides using gas chromatography with electron capture detection were available.

By the 1970s, it became clear to many scientists that gas chromatography alone was not helpful in identifying potentially hazardous compounds in the environment. The issue: How much of a compound is present in an environmental sample?

QUALITATIVE
What compounds are in the environment that should not be there?

DISCOVERY OF DISINFECTION BYPRODUCTS. New Orleans drinking water is treated Mississippi River water. Similarly, Cincinnati drinking water is treated Ohio River water. In these and other cases, GC/MS helped identify relatively high levels of CHCl₃, CHBr₂Cl, CHBrCl₂, and CHBr₃. These became known as the trihalomethanes (THMs).¹,² and it was soon recognized that the disinfection of drinking water by chlorine could produce these and other compounds, some of which are toxic.

Hazardous waste identification. Dozens of abandoned hazardous waste sites came to the public’s attention in 1970-1980. For example, at the Reich Farm, near Tom’s River, NJ, many 55-gallon drums were found. Samples from these drums and surrounding soil were analyzed by GC/MS (low- and high-resolution) to identify several tetrahydroxycyanophenol ethers. These were waste products traced back to Union Carbide, who was making a co-polymer of styrene and acrylonitrile.³

AN EARLY POLLUTANT IDENTIFICATION EXPERIMENT. One of the first GC/MS experiments to identify compounds in the environment took place at the Massachusetts Institute of Technology, and it focused on water from the Charles River. This work identified polycyclic aromatic hydrocarbons, some of which are carcinogenic. These compounds were coming from street run-off, which washed off from all sorts of combustion sources into the river.

QUANTITATIVE
How much of a compound is present in an environmental sample?

PRIORITY POLLUTANTS. In 1976, a consent decree was signed settling a lawsuit between the EPA and several public interest groups, who had claimed that the EPA failed to implement significant portions of the United States Water Pollution Control Act of 1972. This settlement required the EPA to publish a list of toxic pollutants for which effluent guidelines and limitations would be required. This list eventually included 114 organic compounds that became known as the “priority pollutants.”⁴ The issue: How could the concentrations of these chemicals in water be measured cost-effectively?

The GC-only vs. GC/MS controversy. There was considerable uncertainty about how to measure the priority pollutants. One side believed that GC was the only cost-effective way to go. The other countered that GC/MS was not as expensive as the GC-only folks thought. Finnigan Corp. was in the latter group and published a convincing article making this point.⁵ Cheaper, low-resolution systems, using quadrupole mass spectrometers and driven by small computers, were becoming available. GC/MS won this argument, and several GC-MS methods are official.

Dioxin! The most toxic congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin with an LD-50 in male guinea pigs of 0.6 µg/kg. Measuring the concentrations of this specific isomer require the use of sensitive GC/MS methodology. The analytical solution was high-resolution MS coupled to capillary GC columns and isotopically labeled internal standards (EPA method 1613). Revisions to this method (1613B) allow for the use of less expensive quadrupole GC/MS systems.

HOT TOPICS IN 2020
"Non-target" screening. The long-term goal is a set of informatic tools into which one enter the complete GC or LC high-resolution mass spectral data set and out of which come the identifications of the compounds in the sample, perhaps ranked in terms of their environmental significance.⁶ We are not there yet.

PFAS ARE THE NEW PCBs. The classic polychlorinated alkyl substance example is “PFOS” or CF₃CFO(CF₂)₇CF₃. Widely used as surfactants, PFAS are a problem in ground water and are measured by LC/MS/MS. The map shows where PFAS have been found in drinking water; note the northeastern United States.

References
¹ Hites, Ronald A. Hites on History Committee. “This work shows where PFAS have been found in drinking water; note the northeastern United States.”
² See ASMS.org/About/history/history-posters for the references.