ENVIRONMENTAL APPLICATIONS OF MASS SPECTROMETRY: A BRIEF HISTORY

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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 previously unsuspected pollutants and that mass spectrometry was the way to go. In fact, GC/MS was perfectly suited for this work because of its sensitivity and selectivity.

It is not an exaggeration to say that the entire field of organic environmental chemistry was made possible by commercially available, reasonably priced GC/MS and LC/MS instruments.

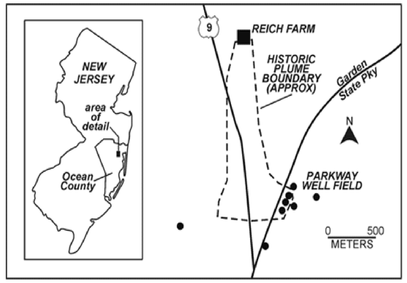
ENVIRONMENTAL MASS SPECTROMETRY EVOLVED ALONG TWO PATHS

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

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 soot from all sorts of combustion sources into the river.[1]

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 $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$. These became known as the trihalomethanes (THMs),[2,3] and it was soon recognized that the disinfection of drinking water by chlorination could produce these and other compounds, some of which were toxic.

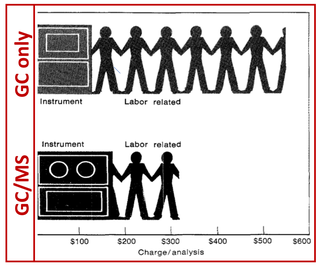
HAZARDOUS WASTE IDENTIFICATION. Dozens of abandoned hazardous waste sites came to the public's attention in 1970-1980. For example, at the Reich Farm, near Tom's River, NJ, many 55-gallon drums were found. Samples from these drums and surrounding soil were analyzed by GC/MS (low- and high-resolution) to identify several tetrahydro-cyano-naphthalenes. These were waste products traced back to Union Carbide, who was making a co-polymer of styrene and acrylonitrile.[4]



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."[5] The issue: How could the concentrations of these chemicals in water be measured cost-effectively?

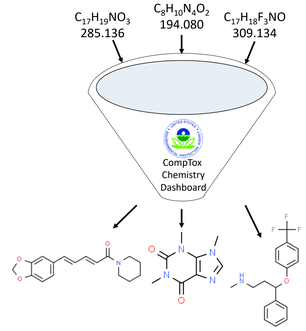
THE GC-ONLY VS. GC/MS CONTROVERSY. There was considerable uncertainty about how to measure the priority pollutants. One side believed that GC was the only cost-effective way to go. The other countered that GC/MS was not as expensive as the GC-only folks thought. Finnigan Corp. was in the latter group and published a convincing article making this point.[6] 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.



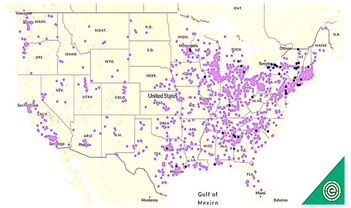
DIOXIN ! The most toxic congener is 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin with an LD-50 in male guinea pigs of 0.6 µg/kg. Measuring the concentrations of this specific isomer require the utmost in sensitivity and selectivity. The analytical solution was high-resolution MS coupled to capillary GC columns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

HOT TOPICS IN 2020

"NON-TARGET" SCREENING. The long-term goal is a set of informatic tools into which one enters 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.[7,8] We are not there yet.



PFAS ARE THE NEW PCBs. The classic polyfluorinated alkyl substance example is "PFOS" or $CF_3CF_2CF_2CF_2CH_2CF_2CF_2CF_2SO_3^-$. Widely used as surfactants, PFAS are a problem in ground-water and are measured by LC/MS/MS. This map shows where PFAS have been found in drinking water; note the northeastern United States.



1960 | 1970 | 1980 | 1990 | 2000 | 2010 | 2020

1962 *Silent Spring* by Rachel Carson
1965 Mercury poisoning in Japan
1968 Dioxin in Agent Orange in Vietnam
1969 PCBs in the Hudson River, NY
1970 United States EPA opens shop

1971 Contamination of Missouri by dioxin dumping
1973 Flame retardant contamination of Michigan's milk
1976 Dioxin explosion in Seveso, Italy
1976 Love Canal hazardous waste site
1976 Toxic Substances Control Act (ToSCA) passed

1980 Super Fund Act to clean up hazardous waste sites
1989 *Exxon Valdez* oil spill in Alaska

2001 Stockholm Convention signed to control persistent organic pollutants

2010 *Deepwater Horizon* oil spill in the Gulf of Mexico
2014 Minamata Convention signed to control Hg
2015 Lead in Flint, Michigan, drinking water