GC/MS and LC/MS Analysis of Endocrine Disruptors

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Introduction: Several chemical compounds that are widely distributed in the environment have been found to possess hormone-mimicking activities. These compounds have been found to interfere with hormonal activity through a variety of mechanisms, and they may have adverse effects on the health of animals and humans. Terms used to describe these compounds include *endocrine disruptors*, *hormone disruptors*, and *estrogen mimickers*. Classes of compounds believed to have hormone-disrupting effects include phthalates (plasticizers), alkyphenols (detergents), organochlorine pesticides, PCBs, dioxins, and food packaging chemicals such as bisphenol A (BPA) and butylated hydroxyanisole (BHA). Efforts are underway in several countries to develop analytical methods for assessing the distribution of these compounds in the environment. In the US, the Environmental Protection Agency has established the *Endocrine Disruptor Screening and Testing Advisory Committee* (*EDSTAC*)[1]*, a*nd in Japan*,* the Environment Agency has organized the *Environmental Endocrine Disruptor Group*[2].   We report the analysis of ppb-level samples of standard samples, river water and water from sewage treatment plants by both low-and high-resolution selected ion moniroting (SIM) mass spectrometry with benchtop GC/MS systems. We evaluate high- and low-resolution SIM with LC/MS methods as an alternative analytical approach that does not require derivatization.

GC/MS Analysis: GC/MS analyses were obtained by using an HP 6890 GC (Supelco SPB-5 or Frontier Labs UA-5(P) Phenol column) with a JEOL **GCmate** (high-resolution MS), or a quadrupole mass spectrometer (low-resolution MS). Classes of compounds analyzed by GC/MS included 8 phthalate esters, bisphenol A and chlorophenols, 13 alkylphenols, and 6 pesticides. Phthalates were analyzed by extraction with hexane. Contamination of laboratory glassware and solvents required special handling precautions, and high-resolution mass spectrometry did not offer any advantage for phthalate analysis. Phenols were analyzed by solid-phase extraction or liquid extraction with dichloromethane. Derivatization with TMS gave the best results, and high-resolution mass spectrometry showed a significant reduction in chemical background interferences for phenol analyses. High-resolution mass spectrometry also provided a significant reduction in background for chlorinated pesticides analyzed following liquid-liquid extraction.

1. Internet URL:*http://www.epa.gov/opptintr/opptendo/index.htm*
2. SPEED '98 - Strategic Plan to Regulate Hormone Disruptors, May 1998, Environment Agency (Japan).

LC/MS Analysis: LC/MS analyses were obtained by using an HP1100 LC system (L-column ODS, 1.5 mm) with a JEOL *LCmate* benchtop sector mass spectrometer (both high- and low-resolution MS). Compound classes studied included phenols (BPA and chlorophenols), alkylphenols, pesticides (benomyl, amitrole, and methomyl as well as phenoxyacetic acids), and 17-β-estradiol. Phenols, alkylphenols, and chlorinated pesticides gave best results with negative-ion electrospray ionization (ESI-), while the remaining pesticides gave best results by positive-ion electrospray ionization (ESI+), and the estradiol sample was best analyzed by negative-ion atmospheric pressure chemical ionization (APCI-). The LC/MS approach appears to provide comparable results to GC/MS analysis, but with simpler sample preparation because derivatization is not required. <u>An analysis of bisphenol A and chlorophenols in river water by LC/MS suggests that high-resolution can offer advantages in distinguishing these analytes from background interferences.</u>
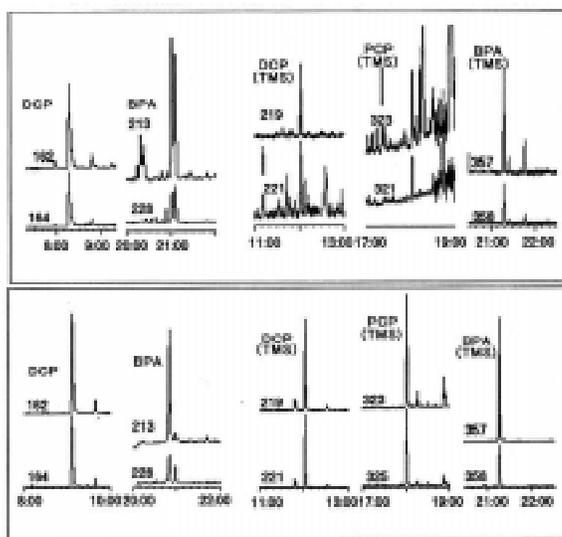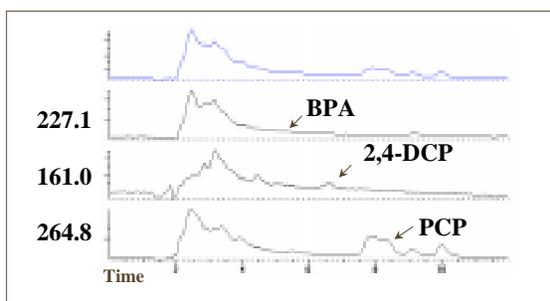

**Top:
Low-resolution
SIM
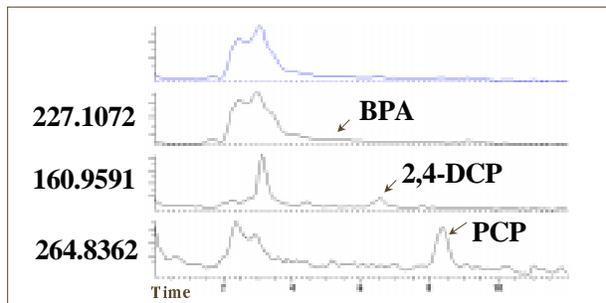Quadrupole mass
spectrometer**

**Bottom:
High-resolution SIM
GCmate mass
spectrometer,
R = 5000**

*GC/MS: Sewage treatment plant water spiked with 10 ppb phenols.
High-resolution SIM (lower figure)shows a reduction in background interferences.*

*LC/MS: River water spiked with 10 ppb phenols. High-resolution SIM
(right) shows a reduction in background interferences.*