

Environmental Applications of
Triple Quadrupole Mass Spectrometry:
Aroclors in Industrial Oils,
Dioxin Screening and Hazardous
Waste Analysis

A.D. Sauter and L.D. Betowski
U.S. EPA, Environmental Monitoring and Systems Laboratory
Las Vegas, Nevada 89114
J.M. Ballard
Lockheed Engineering and Management Services Co., Inc.
P.O. Box 15027
Las Vegas, Nevada 89114

A recent review of MS/MS applications concluded that "there are insufficient data available to establish exactly where the quadrupole MS/MS instrument's performance fits into the analytical picture."¹ We present three examples of MS/MS applications of environmental importance and we briefly discuss the significance of the Triple Quadrupole Mass Spectrometer (TQMS) from a spectroscopic and programmatic perspective.

For the applications reported here, a moving belt LC/MS interface was employed to rapidly and directly introduce microliter quantities of sample into the ion source without chromatographic separations. Using, in most cases, stable isotopic variants of analytes of interest and this introduction approach, linear calibration curves and good to excellent sensitivity are demonstrated for a variety of molecules of environmental interest. Sample throughput rates using this introduction mode in limited objective analytical strategies of approximately 50 - 150 determinations/hour are shown.

Aroclors in Industrial Oils

Aroclor mixtures introduced into the ion source without chromatography in full scan mode under positive ion electron impact and positive/negative methane chemical ionization were found to yield readily differentiable "mixture" mass spectra, for Aroclors 1221, 1232, 1242, 1248, 1254 and 1260. However, direct analysis of low level Aroclors in transformer oils requires the scanning options provided by a TQMS. In negative CI, and parent ion scanning, we could directly analyze and distinguish the higher Aroclors 1242, 1248, 1254 and 1260 at regulatory levels of interest with effectively no sample work-up (other than addition of labelled internal standards and dilution). Using this approach, complex Aroclor mixtures produce simplified mixture mass spectra, not complex chromatograms. These data suggest that such approaches are adequate for regulatory decisions.

"Dioxin" Screening

Based on our laboratory's recent involvement in a "dioxin" monitoring program, we have reported that a TQMS based screening procedure for 2,3,7,8-tetrachlorodibenzo-p-dioxin could be employed to significantly reduce the costs and decrease the response time of programs of this nature.² Low picogram sensitivity for pure 2,3,7,8-TCDD solutions is demonstrated under oxygen Townsend discharge negative ion conditions. Detection and confirmation of pg/μl quantities of 2,3,7,8-TCDD in the presence of ng/μl amounts of Aroclor 1260 by daughter ion scanning is also shown. The combination of sensitivity (negative ion mode), specificity (daughter ion scan) and high sample throughput rate via the moving belt LC/MS interface appears to provide a viable alternative to established analytical strategies.

Hazardous Waste Extract Analysis

Results from hazardous waste extracts prepared by the National Enforcement Investigation Center at Denver, Colorado, and analyzed at our laboratory by TQMS are presented. Positive and negative ion, full scan, methane CI data for "clean" and "complex" extracts spiked with selected priority pollutants is presented. In

the former case, pseudo-molecular ions (positive or negative) for all spiked compounds were readily observed. Positive ion daughter analysis of adjacent molecular ions (M/Z 139 and 140) for isophorone and 2-nitrophenol, clearly confirm the spiked analytes in the sample without chromatography. Similar analysis of the complex extract demonstrated that many of the spiked compounds were obscured in the positive ion full scan spectra; however, negative ion full scan and daughter ion techniques qualitatively confirm the presence of nitroaromatics, chlorinated phenols and large polynuclear aromatic compounds.

Full scan QIMS positive and negative ion CI data is presented for a priority pollutant standard containing most of the extractable priority pollutants at 25 ng/ μ l/analyte to demonstrate the "best" case potential for such screening analysis, i.e., no matrix. The fact that most priority pollutants can be qualitatively confirmed down to 1 ng/ μ l/analyte and the fact that the sample volume can be significantly increased (in this introduction mode), provides the user with great flexibility in pollutant analysis of actual hazardous waste extracts.

Using a crude, but rapid, introduction technique, isotopic variants of analytes of interest, and the scanning options of a TQMS, the ability to analyze samples in limited objective analytical problems at high throughput rates is demonstrated. While instrument and sample related limitations exist, our TQMS data and our experience with large environmental monitoring programs,^{3,4} lead us to conclude that TQMS based analytical methods (for screening or confirmation) are practical. We expect that the routine application of TQMS to large environmental monitoring or testing programs will be driven both by technical and programmatic considerations.

¹Burlingame, A.L.; Dell, A.; Russell, D.H.; Anal. Chem., Vol. 54, No. 5, April 1982, 371 pp.

²Sauter, A.D.; Betowski, L.D.; Ballard, J.M.; "Rapid Analytical Methods Development, the Triple Quadrupole Mass Spectrometry Potential," presented at the Sixth Annual Symposium on Priority Pollutant Analysis, March 1983, Norfolk, VA.

³Shackleford, W.M.; Cline, D.M.; Burchfield, L.; Fass, L.; Kurth, G.; and Sauter, A.D., Computer Survey of GC/MS Data Acquired in the U.S. EPA Screening Analysis: Systems and Results, Advances in the Identification and Analysis of Organic Pollutants in Water. Chapter 33, Ann Arbor Science, 1981.

⁴Sauter, A.D., "Love Canal Study, Analytical Procedures for Organic Compounds in Soil and Sediment, June 1981.