Cryogenic Zone Compression for the Measurement of Dioxins in Human Serum at Attogram Level by GCxGC-IDHRMS.

Donald G. Patterson, Jr.[1], Susan M. Welch[1], Wayman E. Turner[1], and Jean-François Focant[2]

[1]Division of Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, Georgia, USA; DGP Jr (donpatt@etcmail.com): current address, EnviroSolutions Consulting, Inc., 172 Camelot Way, #20198, Jasper, GA 30143.

[2]Mass Spectrometry Laboratory, Biological and Organic Analytical Chemistry, Department of Chemistry, University of Liege, Liege, Belgium. (JF.Focant@ulg.ac.be)

For the last 25 years, background levels of dioxins and related persistent organic pollutants (POPs) in humans have declined to the point that their measurement has become increasingly difficult. Improving sample preparation procedures to accommodate larger sample sizes has been carried out to a certain extent at the beginning of the last decade but these methods became of limited use because of the increasing demand to reduce the size of the specimen collected for human biomonitoring.

Gas chromatography (GC) coupled to high resolution mass spectrometry (HRMS) is a very sensitive. Isotope dilution (ID) based on ^{13}C-labelled standards in selected ion monitoring (SIM) acquisition mode is used. However, many compounds are present at levels below the limits of detection (LODs) established using stringent quality assurance/quality control (QA/QC) criteria.

Based on earlier attempts carried out at CDC to enhance GC-IDHRMS sensitivity by coupling thermal desorption modulator (TDM) to sector instruments, we revisited the GCxGC-HRMS coupling using the more robust jet-cooled loop modulator for the measurement of low levels of PCDD/Fs in human serum samples.

A simple single short length GC column set up was selected and optimized for 2,3,7,8-TCDD. The modulation period was adjusted to match the width of the unmodulated peak in order to collect and remobilize the whole peak in one modulation event. The peak width was 500-600 ms. The acquisition parameters of the MS instrument have been optimized to adequately measure narrow GC peaks (MS cycle time was decreased 40-70 ms). A 1 fg 2378-TCDD has a signal-to-noise ratio of over 400:1 (4σ definition), when only one ion is monitored. Very low matrix effects are observed with real samples because the quantity required for injection is very small. Extension to other SIM descriptors was also studied to ensure proper use of ID standards for the low concentration analytes.