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COMPARISON OF ATMOSPHERIC PRESSURE IONIZATION GAS CHROMATOGRAPHY-TRIPLE QUADRUPOLE MASS SPECTROMETRY TO TRADITIONAL HIGH-RESOLUTION MASS SPECTROMETRY FOR THE IDENTIFICATION AND QUANTIFICATION OF HALOGENATED DIOXINS AND FURANS

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) have been important compounds for decades, with the first publications describing analytical techniques for their identification appearing in the 1970s.¹⁻⁵ The universally accepted detection technique for this analysis typically requires the use of a mass spectrometer that is both highly selective and sensitive. A minimum resolving power of 10 000 is generally needed for mass spectral resolution of the dioxin compounds from other halogenated organic pollutants that are common interferences.⁶ The mass spectrometer also needs to be highly sensitive to be able to detect trace levels of dioxins in samples. Due to these requirements, most validated and accepted regulatory methods require GC-HRMS as the analytical technique used for dioxin analysis, including U.S. EPA methods 1613 and 8290, EN 1948, MOE 3418, and JIS methods K0311 and K0312.⁷⁻¹² While HRMS analysis has proven to have the sensitivity and selectivity required for dioxin analysis, it has some disadvantages. The instruments are fairly expensive to maintain and require a skilled user to operate, making dioxin analysis impractical for most laboratories. Additionally, when operating HRMS systems in selected ion recording (SIR) mode, the number of masses monitored is inversely related to sensitivity. This effectively limits the number of different compounds that can be monitored at any given time. Increasing the list of target compounds analyzed in a single run to include other potentially toxic halogenated dioxins is highly desirable but would significantly reduce the sensitivity of the instrument.

A new approach to dioxin analysis is proposed through this research that does not utilize a high resolution-mass spectrometer. The new approach utilizes a triple quadrupole mass spectrometer coupled with an atmospheric pressure ionization GC source. Atmospheric pressure ionization (API) is an ionization technique that has been around since the 1970s.^{13,14} The current instrumentation utilizes a plasma discharge from a corona pin to induce ionization under atmospheric pressure. The largest benefit to using this ionization technique is that it is a soft ionization process creating more molecular ion than would be present from the more classically used electron ionization. Increased molecular ion allows for enhanced sensitivity when using multiple reaction monitoring (MRM) transitions for detection. Added benefits from the use of an API source include less GC method restrictions in the case of flow rate since the column effluent is not exiting into a vacuum outlet. Coupling to a triple quadrupole also increases sensitivity by using MRMs to monitor for specific precursor and product ions. Switching between MRM transitions is fast, making it possible to monitor for upward of hundreds of MRMs in a single run without sacrificing sensitivity.¹⁵ This is extremely useful for dioxin analysis with the increasing desire to expand methods to include additional compounds. The goal of this research is to directly compare the performance of APGC-MS/MS to GC-HRMS in an effort to validate the technology as one that is equal in performance for the analysis of dioxins in environmental samples.

Methods and Materials

Standards and Chemicals. All standards used were obtained from Wellington Laboratories, Inc. (Guelph, Ontario, Canada). Polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) identification was performed using a mixture of 17 regulated tetra- through octachloro dioxins and furans (EPA-1613CVS). This standard is a five point calibration set used to create the calibration curves used for quantification. A low level tetrachloro dibenzo-p-dioxin mix containing six different TCDD isomers ranging from 2 to 100 fg/ μ L (TF-TCDDMXB) was used for determining the sensitivity of the APGC-MS/MS instrument. A mix of 13-C labeled PCDD/Fs (EPA-1613LCS) was spiked into samples prior to extraction to use for isotope dilution quantification. Toluene was obtained from Avantor Performance

materials (formerly JT Baker, Center Valley, PA) and was ultra resianalyzed grade. Nonane was obtained from Acros Organics (New Jersey) and was 99% pure.

Reference Samples. Reference sample extracts were provided by the Ontario Ministry of the Environment and Climate Change (MOECC). These were samples that had previously been extracted at the MOECC for analysis on a GCHRMS instrument.¹⁰ Samples used for the determination of method detection limit (MDL) included two matrixes, sediment and fish. A variety of reference sample extracts were tested for instrumental comparison including WMS-01 Reference Lake Sediment for Organic Contaminant Analysis (Wellington Laboratories Inc.), WMF-01 Reference Freeze-dried Fish Tissue for Organic Contaminant Analysis (Wellington Laboratories Inc.), EDF-2524 Clean Fish Reference Material (Cambridge Isotope Laboratories Inc., Tewksbury, MA), EDF-2525 Contaminated Fish Reference Material (Cambridge Isotope Laboratories Inc.), and NIST 1944 New York/New Jersey Waterway Sediment.

Sample extracts were reconstituted with 20 μ L of injection standard containing 2000 pg of ¹³C-labeled 1,2,3,4-TCDD and ¹³C-labeled 1,2,3,7,8,9-HxCDD in order to determine the recoveries of the labeled internal standards. For this study, 7 PCDD and 10 PCDF compounds were quantified using isotope dilution. For GC-HRMS analysis, no further sample preparation was performed. For APGC-MS/MS analysis, sample extracts were diluted prior to injection due to instrument sensitivity. All samples, excluding NIST 1944, were diluted 20-fold in toluene. NIST 1944 was diluted 10-fold in toluene.

GC-HRMS Analysis. High-resolution mass spectrometry (HRMS) experiments were performed using a Micromass Autospec magnetic deflection instrument (Waters Corporation, Milford, MA) coupled to an HP 7890A gas chromatograph equipped with an Agilent 7693B autosampler (Agilent Technologies, Santa Clara, CA). The HRMS was operated in the electron ionization (EI) mode at a resolution of 10 000 (10% valley definition) across the entire mass range. Detection was achieved by selected ion monitoring (SIM) of the PCDD/PCDF molecular ions. Perfluorokerosene (PFK) was introduced via a heated septum inlet system to generate lock mass ions. Helium carrier gas was used, and the GC was operated in splitless mode at a constant flow rate of 0.8 mL/min. The injector was maintained at a temperature of 280 °C and utilized a 4.0 mm double gooseneck splitless liner (Restek, Bellefonte, PA). Samples were injected under these conditions at a volume of 1.0 μ L. A 40 m \times 0.18 mm, 0.18 μ m DB-5 column (Agilent Technologies, Santa Clara, CA) was used for the separation. The GC oven temperature program was as follows: initial oven temperature 140 °C hold 1 min, 40 °C/min to 200 °C no hold, 3 °C/min to 235 °C no hold, 2.9 °C/min to 300 °C hold until OCDD eluted. The injector, ion source, and transfer line temperatures were 280 °C.

APGC-MS/MS Analysis. Sample analysis was performed using a Xevo TQ-S equipped with atmospheric pressure ionization source (Waters Corporation, Milford, MA), an Agilent 7890A gas chromatograph, and Agilent 7693 autosampler (Agilent Technologies, Santa Clara, CA). A 60m \times 0.18 mm \times 0.10 μ m Rtx Dioxin-2 column (Restek, Bellefonte, PA) was used for the analysis. Approximately 1.0 m \times 0.32mm stainless steel Sulfinert tubing (Restek, Bellefonte, PA) was coupled to the end of the column to act as a transfer line into the ion source. Helium carrier gas was used, and the GC was operated in splitless mode at a flow rate of 1.1 mL/min. The injector was maintained at a temperature of 290 °C and utilized a 4.0 mm drilled hole Uniliner (Restek, Bellefonte, PA). Samples were injected under these conditions at a volume of 0.5 μ L. The GC oven temperature program was as follows: initial oven temperature 120 °C hold 1 min, 35 °C/min to 200°C no hold, 4.5 °C/min to 280 °C hold 8 min, 20 °C/min to 330 °C hold 15 min. The Xevo TQS triple quadrupole mass spectrometer source was run under dry conditions to promote charge transfer ionization. Nitrogen was supplied by an NM32LA nitrogen generator from Peak Scientific (Billerica, MA) and was used as the auxiliary gas, maintained at a flow rate of 400 L/h. Argon was utilized as the collision gas at a flow rate of 0.18 mL/min. Cone gas flow rate was maintained at a flow rate of 215 L/h and corona current was maintained at 4.0 μ A until the end of the analysis. Cone voltage was maintained at 30 V for all compounds. The APGC source was heated to 150 °C and the mass spectrometer transfer line was run at 360 °C. The mass spectrometer was operated using the multiple reaction monitoring (MRM) mode.

Results and Discussion

Method Detection Limits. Method detection limits (MDL) were determined for each instrument in both a soil and fish matrix. The MDL for each matrix was calculated from 10 replicates of the same set of sample extracts analyzed on both instruments. MDL was calculated by using the equation $MDL = SD \times$

t, where SD is the standard deviation of data measurement and t is the 98% confidence interval t-value for $n - 1$ samples.¹⁰ The MDL values are considerably lower on the APGC-MS/MS instrument for both the soil and fish matrix. MDL values determined on the APGC-MS/MS were 2 through 18-fold lower as compared to the GC-HRMS. On the other hand, the % RSD varied more overall on the APGC-MS/MS than the GC-HRMS, but it should be noted that the samples were run on the APGC-MS/MS instrument using a 20-fold dilution. The increased RSD values could be attributed to detection of a much smaller concentration of each compound.

APGC-MS/MS vs GC-HRMS: Reference Samples. Sediment Matrix Reference Materials Comparison. Two different sediment reference materials were chosen for comparison between the two analytical systems, WMS-01 Lake Sediment and NIST 1944 Waterway Sediment. Figure 1 demonstrates a graphical representation of the quantitative comparison of the NIST 1944 Waterway Sediment reference material. Both sediment reference materials demonstrated similar trends and comparisons. The APGC-MS/MS values compare very well to the certified reference value for both sediment reference materials. In cases where the APGC-MS/MS quantification was outside of the standard error range of the certified value, the value corresponded well to the GC-HRMS quantification, indicating this was most likely due to sample preparation instead of an instrumental quantification error. Furthermore, in the NIST 1944 sample, there are some compounds where the APGC-MS/MS quantification compares well with the certified range and the GC-HRMS quantification does not.

Fish Tissue Matrix Reference Materials Comparison. Three different fish tissue reference materials were chosen for comparison between the two analytical systems; WMF-01 Freeze-dried Fish, EDF-2524 Clean Fish Tissue, and EDF-2525 Contaminated Fish Tissue. The fish reference comparisons are more difficult to identify distinct trends due to large variability of standard deviation in the certified values. For the WMF-01 reference material, the APGC-MS/MS quantified values either correlated well with the GC-HRMS quantified values or fell within the range of the certified values. The EDF-2524 reference sample provided an interesting test of system sensitivity as it was a clean fish tissue reference material with all concentrations well below 1.0 pg/g, with the exception of 2,3,7,8-TCDF. The APGC-MS/MS system performed well, reporting values below 1.0 pg/g for all relevant compounds except OCDF. The GC-HRMS quantification of OCDF was extremely high as well, correlating well to the APGC-MS/MS value, indicating a likely interference. Comparable results were seen also with the EDF-2525 Contaminated Fish reference material. There were some compounds that were quantified higher on the APGCMS/MS instrument relative to the GC-HRMS, but these either fell within, or were close to, the certified range. These typically correlated to the compounds in the reference material with the highest variance in certified reference values.

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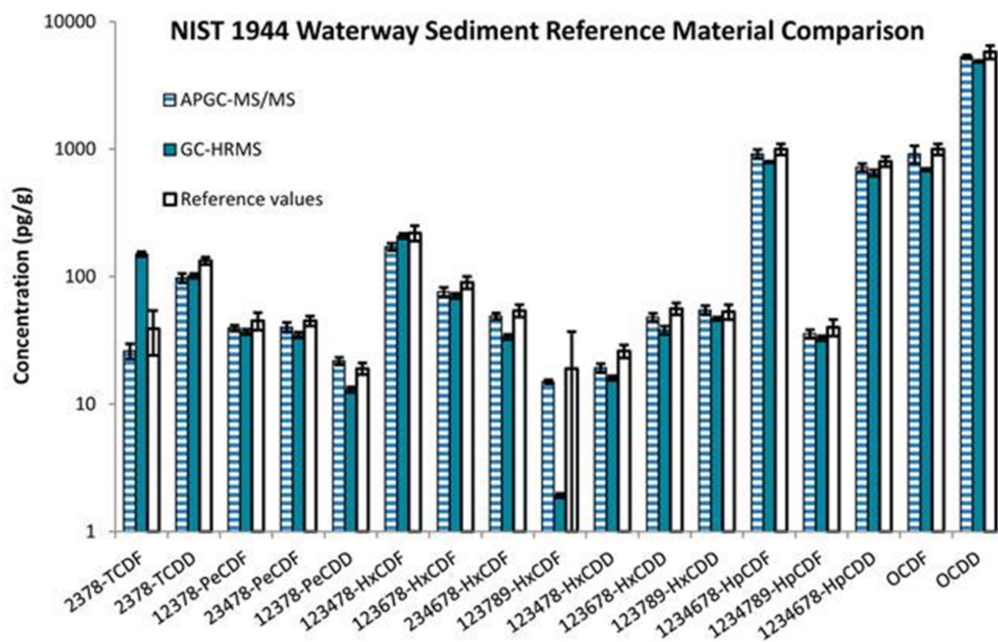


Figure 1. Graphical representation of the comparison of quantitative analysis of NIST 1944 Waterway Sediment reference material on both the APGC-MS/MS and GC-HRMS instruments.