

Dioxins and Furans Analysis

ADVANCING TECHNOLOGIES FOR
GREATER EFFICIENCY AND QUALITY



Waters

THE SCIENCE OF WHAT'S POSSIBLE.™

Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of chemically related compounds that are considered highly toxic. They may cause cancer, reproductive and developmental problems, damage the immune system, and interfere with the endocrine system. They persist in the environment and are found throughout the world. These compounds are restricted internationally under the Stockholm Convention, and due to their bio-accumulative nature, it is essential to monitor them at ultra-trace levels in food and environmental samples.

Current Challenges for Laboratories

Traditionally, these compounds have been analyzed using gas chromatography (GC) coupled to magnetic sector high resolution mass spectrometers (HRMS) with electron ionization (EI) sources.

While these instruments have been the Gold Standard and work horses to date, there are some operational challenges for labs and researchers using them.



AGING INSTRUMENTS

Maintenance requirements are increasing while vendor support is decreasing.



EXPERTISE REQUIRED

HRMS are more complicated to operate than standard GC-MS platforms, and require specialized operators.



FACILITIES ISSUES

HRMS are large and need specialized facility space for optimum operation.

Evolving Regulations

Technical developments in GC-MS/MS analyzers have prompted the revision of European Commission specific criteria and the United States Environmental Protection Agency (US EPA) interest to recognize the performance similarities of this method with GC-HRMS for the analysis of dioxins/furans.

Atmospheric Pressure Gas Chromatography (APGC)-MS/MS technology is already in use by Canadian, US, and European researchers, commercial labs and government agencies for dioxin/furan analysis, as well as for other POPs analyses.

The US EPA has given interim approval (pending the standard public comment/response period) for use of the APGC-MS/MS methodology, and signifies it meets all the quality control criteria of magnetic sector-based methods.

Approval and recognition by the US EPA also opens the door to updating many other dioxin/furan and POPs testing protocols to a modern platform like Waters APGC-MS/MS.

FEBRUARY 1984

EPA released the Ambient Water Quality Criteria for 2,3,7,8-Tetrachlorodibenzo-P-Dioxin validated on Waters magnetic sector instrument

SEPTEMBER 1984

EPA released the final report, Health Effects Assessment for 2,3,7,8-Tetrachlorodibenzo-P-Dioxin

OCTOBER 1994

EPA Method 1613 Revision B released

MAY 2004

Stockholm Convention on Persistent Organic Pollutants was signed in 2001 and entered into force on May 17, 2004

OCTOBER 2004

EPA Releases ERD of Exposure and Human Health Reassessment of 2,3,7,8-TCDD

JUNE 2014

Commission Regulation (EU 589/2014) references the first acceptance of Tandem quadrupoles for use in Dioxin Confirmation, with any ionization technique which produces the molecular ion

JULY 2015

First publication on APGC-MS/MS as an alternative to HRMS¹

AUGUST 2015

ACS Publication from MTM Research Centre (Sweden), IDAEA-CSIC (Spain), EURL Reference Lab (Freiburg, Germany), RIKILT (The Netherlands) in collaboration with Waters²

SEPTEMBER 2020

SGS AXYS Method 16130 using Waters APGC-MS/MS approved by the EPA

1980s

1990s

2000s

2010s

2020s

¹ Kari L. Organtini et al.: <https://pubs.acs.org/doi/10.1021/acs.analchem.5b01705>

² Rhys Jones et al.: <https://pubs.acs.org/doi/abs/10.1021/acs.analchem.5b02264>

Innovation in Dioxin Analysis Technology – a Shift to Tandem Mass Spectrometry



“This is one of my favorite instruments, it’s highly sensitive and selective due to the soft ionization with APGC. It is easy to operate, and low-maintenance compared to the magnetic sector, which is a big benefit to routine analysis. Also I am able to switch between methods without any difficulty.”

MR. XINHUI XIE

Senior Instrument Chemist, SGS AXYS



GC with tandem MS (MS/MS) has gained popularity as a simpler, yet more sensitive alternative for high resolution mass spectrometry applications, and testing for Dioxins/ Furans has been shifting to GC-MS/MS where regulations allow for its adoption.

The Waters Atmospheric Pressure Gas Chromatography system with the Xevo™ TQ-XS (APGC-MS/MS) platform allows for successful identification and quantitation of dioxin/furans.

By producing and monitoring for specific product ions generated by fragmenting the precursor ions of interest, the selectivity and sensitivity of APGC-MS/MS is typically better than that of GC-HRMS without modification to sample preparation procedures.

Reasons to Adopt APGC-MS/MS

Customers adopting Waters APGC coupled to Xevo TQ-XS will see their operational efficiency and analytical quality improved as they experience:

SUPERIOR SENSITIVITY

With the APGC source and StepWave technology, regulatory detection limits can easily be achieved, and typically exceeded.

ENHANCED SAMPLE PREPARATION EFFICIENCY

Using the gains in sensitivity, sample prep can be simplified by reducing the initial sample aliquot size, or by decreasing amount of sample extract concentration required. These strategies can decrease overall sample preparation time, reduce matrix effects, and/or decrease solvent usage, saving time and reducing costs. More diluted samples also increase the lifetime of consumables such as injection port liners and GC columns.

IMPROVED TURN AROUND TIMES

The APGC-MS/MS instrument will be up and running samples steadily and consistently for much longer intervals than the traditional HRMS systems, keeping the lab on schedule. Annual preventative maintenance cycles are completed for tandem quadrupole systems in about one-third the time compared to HRMS, and other maintenance/cleaning events are much less frequent than those required of HRMS.

STRAIGHTFORWARD IMPLEMENTATION

The Xevo TQ-XS with APGC sits on a bench top, with no need for a chiller, and uses 230V power supply for easy set-up in a standard laboratory setting.

USER FRIENDLY TECHNOLOGY

Operation of MS/MS platforms is uncomplicated. Training personnel is simplified, making it accessible to a broader range of lab chemists, especially those familiar with routine MS testing.

REDUCED OPERATIONAL COSTS

APGC-MS/MS uses fewer consumable parts. Combined with savings of reagents during modified sample preparation workflows, laboratories will reduce the materials needed to perform routine testing.



Comparison of MS/MS to HRMS

Laboratory managers and data users can be assured there is no data shift in moving from detection and quantification using HRMS to tandem mass spectrometry. The sample extraction and gas chromatography procedures are unchanged from the current method.

Analysis of GC column effluent is now analyzed using a tandem quadrupole mass spectrometer rather than a magnetic sector HRMS. Here is a quick comparison of core mass spectrometer performance metrics:

Attribute	HRMS	TQ-MS
Identification	Detection of precursor ions within a narrow mass window of 100 ppm. Ion ratios meet $\pm 15\%$ specifications as in 1613B.	Precursor and Product Ions via MRMs 2 MRM transitions per analyte and labeled compound. Product ion ratios meet $\pm 15\%$ specifications as in 1613B. Two masses from molecular ion cluster as precursor masses. Product ions are from loss of $[\text{CO}^{35}\text{Cl}]$.
Ionization	EI	Atmospheric Pressure Chemical Ionization (APCI)
Quantification <i>Internal Standard Calibration established using Isotope Dilution, with ^{13}C labeled dioxins/furans, and concentration range as outlined in 1613B</i>	Yes	Yes
Lock Mass	Yes	Not required
Source suppression check	Yes	Yes
12 hr mass resolution and accuracy check	Yes	Yes
Interference by chlorodiphenyl ethers established and monitored	Yes	Yes



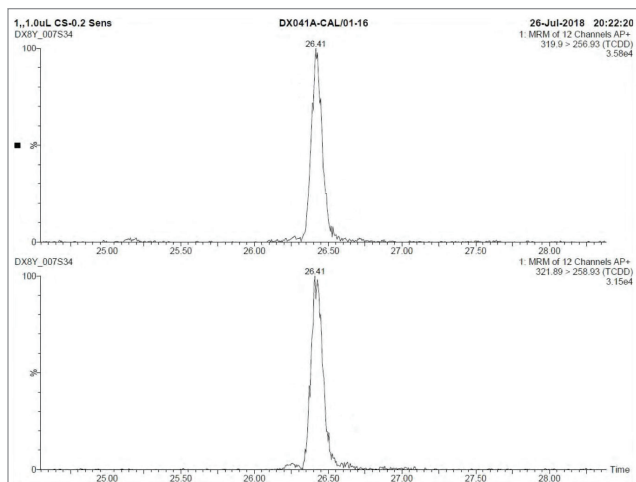
A Comprehensive Study – Old Versus New

SGS AXYS Analytical Services (Sidney, British Columbia) led a two-year effort to evaluate and confirm the efficacy of tandem quadrupole MS applied to Dioxin/Furan testing. This work resulted in the US EPA's approval of an alternative test procedure (ATP) - the SGS AXYS Method 16130.

In collaboration with Waters Corporation and others, SGS AXYS performed comprehensive studies that compared the performance of traditional magnetic sector mass spectrometry to tandem mass spectrometry.

IMPROVED SENSITIVITY

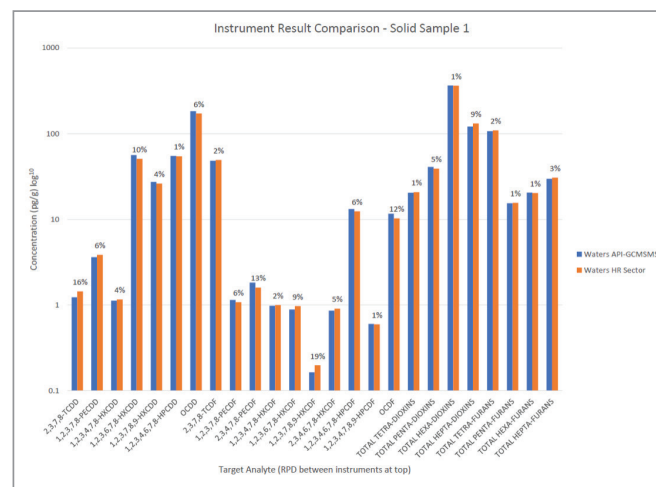
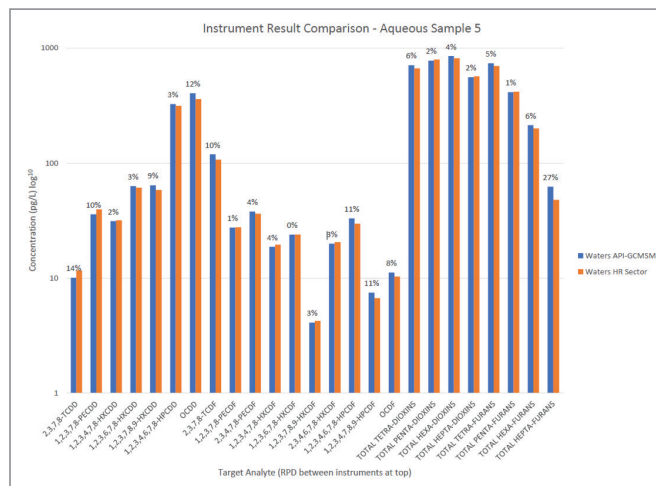
The Xevo TQ-XS with APGC showed excellent sensitivity for PCDD/PCDF analyses. The nature of tandem mass spectrometry results in little noise reaching the detector and therefore excellent S/N. Additionally, the atmospheric pressure ionization approach used in APGC is a soft ionization technique that produces less fragmentation and abundant molecular ions for use as precursor ions, also resulting in better sensitivity.



MRM Response of 2,3,7,8-TCDD for 0.1 pg injection using the Waters Xevo TQ-XS with APGC.

SURPASSING REGULATORY REQUIREMENTS

APGC coupled with the Xevo TQ-XS far surpasses the regulatory requirements for dioxin testing. Not only is this system exceptionally sensitive, it is also robust and consistent.



Wastewater sample (top) and sediment sample (bottom) showing tandem quadruple (MS/MS) compared with high resolution mass spectrometry (HRMS). RPD = Relative percent difference.

Supporting Greater Success

Waters is committed to working alongside our customers to ensure a successful transition or start-up of tandem MS methods.

Waters along with Wellington Laboratories, the leader in providing reference standards for POPs and emerging contaminants, have partnered to provide dioxin standards formulated specifically for the Xevo TQ-XS with APGC. In addition, Wellington's laboratories have adopted the Water's platform for their in-house testing of products, including their dioxin mixes.



Installation engineers specifically trained on the dioxin method and set up on the tandem MS



Experienced dioxin analysts working to ensure system and method suitability and customer success



Methods ready to load into MassLynx Software for quick start up and avoid independent development of MRM transitions



Restek GC Kits with all the columns, vials, ferrules and other chromatography supplies needed to get started



FlexChoice Service packages are customized to meet your laboratory's needs



waters.com/dioxins

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