CONFIRMATION OF DIOXINS AND DIOXIN-LIKE SUBSTANCES AT SUB-FEMTOGRAM LEVELS USING ATMOSPHERIC PRESSURE GAS CHROMATOGRAPHY (APGC) MS/MS

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INTRODUCTION

Polychlorinated dibenzo-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of chemically related compounds that are toxic and persistent organic pollutants (POPs). These compounds are restricted internationally under the Stockholm Convention[1] and due to the bioaccumlative nature of these compounds, it is essential to monitor them at ultra trace levels in food and environmental samples. Traditionally these compounds have been analyzed using magnetic sectors with electron ionization sources which require expert users to obtain consistent results. As there is a growing concern for the analysis of these compounds, more user-friendly technology is essential to analyze potentially contaminated samples. Atmospheric Pressure Gas Chromatography (APGC), coupled with a highly sensitive tandem quadrupole mass spectrometer (Xevo™ TQ-S), has already been demonstrated to be a sensitive and robust option for confirmatory analysis of PCDDs and PCDFs by GC-MS/MS in compliance with 644/2017/EU (Replaces 589/2014/EU).[2] The recent introduction of the Xevo TQ-XS from Waters has allowed lower limits of detection to be reached. This may help reduce time spent on sample preparation/preconcentration as well as reducing the cost of analysis as diluted standards can be utilized. One must however, adhere to any Regulatory guidelines.

The objective of this work was to determine the limits of detection for dioxins and furans in solvent standards, and to confirm their presence and accurate quantitation in a QC fly ash sample.

APGC coupled to a Xevo TQ-XS takes sensitivity to the next level - Confirm dioxins in complex samples at concentrations that are un-achievable by traditional magnetic sector GC systems.

METHODS

GC Method for TCDD assessment

Column: Agilent DB-5MS, 30 m x 0.25 mm I.D. x 0.25 µm film
He Flow: 1.0 mL/min
Injector: Split / splitless, 290 °C, pulsed splitless (32 psi for 0.5 min)
Inj. Vol.: 1.0 µL
Progam: Initial Temp at 130 °C, hold 1.2 min, ramp 20 °C/min to 320 °C, hold for 3.3 min.

GC Method for PCDD and PCDF assessment

Column: Zebron ZB-5MS, 60 m x 0.25 mm I.D. x 0.25 µm film
He Flow: 1.0 mL/min
Injector: Split / splitless, 290 °C, pulsed splitless (50 psi for 1.8 min)
Inj. Vol.: 1.0 µL
Progam: Initial Temp at 130 °C, hold 1.8 min, ramp 40 °C/min to 200 °C; ramp 2 at 2 °C/min to 235 °C; ramp 3 at 3 °C/min to 305 °C; ramp 4 at 20 °C/min to 320 °C, hold for 5.0 min.

MS Parameters for all assessments

Corona Pin: 2.0 µA Cone Gas: 250 L/hr
Aux Gas: 200 L/hr Makeup Gas: 300 mL/min

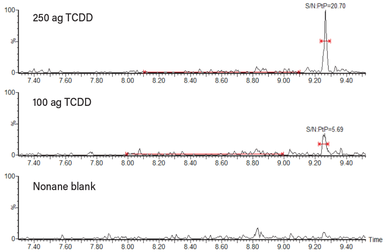

Figure 1. 2,3,7,8 TCDD at 100 & 250 ag on-column.

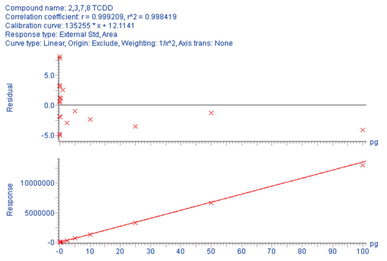

Figure 2. Linearity of 2,3,7,8 TCDD between 100 ag to 100 pg.

RESULTS & DISCUSSION

In order to assess the sensitivity of the APGC coupled with the Xevo TQ-XS, a standard of 2,3,7,8-TCDD was diluted in nonane giving a calibration range between 100 ag to 100 pg on column. At 100 ag on-column for TCDD, the signal to noise was calculated at 5.7 while at 250 ag the signal to noise was 20.7. See Figure 1. In order to perform this test, two MRM transitions for TCDD were utilized. Figure 2 shows the linearity of 2,3,7,8 TCDD, which was excellent with an R^2 of 0.998.

An on-column standard concentration of 100 fg was injected over 20 days in order to assess the reproducibility of the system. Figure 3 shows the outstanding reproducibility of the response, and Figure 4 shows the stability of the isotopic measurements over this series of injections.

Once the initial sensitivity of the system had been verified, a full suite of TCDDs and TCDFs was acquired on the system. A series of EPA 1613 standards were used from CSL to CS5, diluted 1 in 10 with nonane. Figure 5 shows that the isotope ratio assessment for each congener was consistent at all concentrations. This is essential for the confirmation of dioxins and furans in a sample. Legislation states that these ratios are required to be <15%.[3,4,5]

The final assessment was the analysis of a QC fly ash sample. These types of samples are very complex and often used as proficiency tests for dioxin labs in order to ensure that they are producing accurate results. Figure 6 shows the complexity of the samples and demonstrates the ability of APGC and Xevo TQ-XS to quantify the compound of interest, as highlighted in Figure 6. Figure 7 shows that the value obtained with APGC coupled with the Xevo TQ-XS were consistent with that of the QC sample.

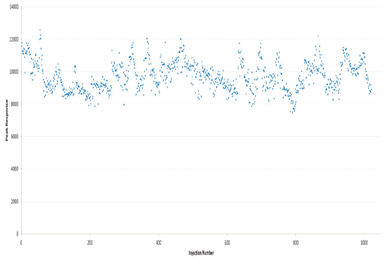

Figure 3. Stability of the response of 100 fg of 2,3,7,8 TCDD over 1000 injections with an RSD of 9.2% (no internal standard correction).

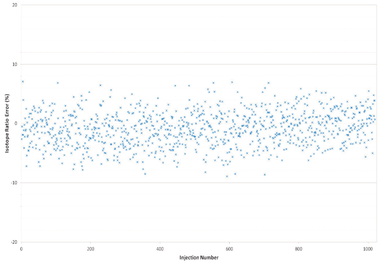

Figure 4. Stability of the isotope ratio of 100 fg of 2,3,7,8 TCDD over 1000 injections.

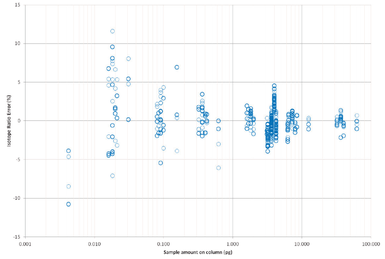

Figure 5. Consistency of the isotope ratio for 1 in 10 dilution of CSL to CS5.

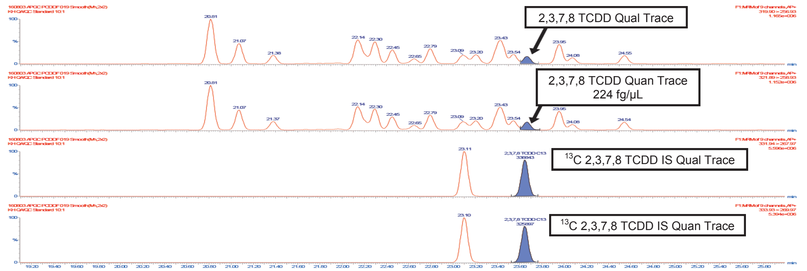

Figure 6. Complex fly ash sample chromatogram showing the identification of 2,3,7,8 TCDD.

CONCLUSION

- **Utilizing APGC coupled with the Xevo TQ-XS allows sub-femtogram levels of dioxins and furans to be analyzed in complex samples.**
- **The added sensitivity of the analysis enables the dilution of expensive dioxin standards, reduces the need for preconcentraton of sample extracts, and minimizes the amount of sample required for testing.**
- **The system is robust and produces consistent results over thousands of injections**
- **APGC coupled with the Xevo TQ-XS far surpasses the regulatory requirements for dioxin testing**

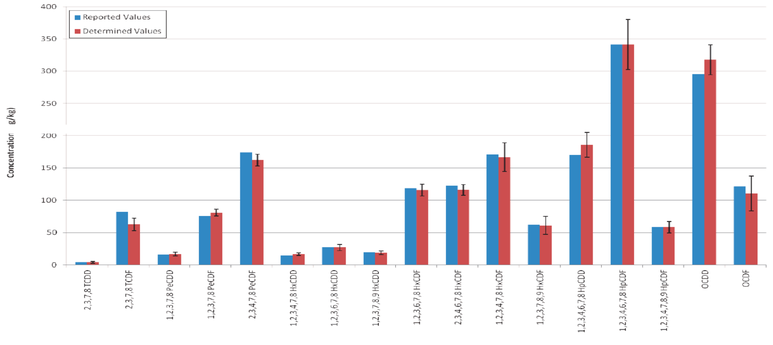

Figure 7. Results from fly ash QC sample.

REFERENCES

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4. EU Commission Regulation 589/2014: Laying down methods of sampling and analysis for the control of levels of dioxins, dioxin-like PCBs and non-dioxin-like PCBs in certain foodstuffs.
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