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SUB-FEMTOGRAM DETECTION OF DIOXINS AND FURANS USING A NEW TANDEM QUADRUPOLE MASS SPECTROMETER

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Introduction:

A new tandem quadrupole mass spectrometer has been developed with improvements to both sensitivity and dynamic range. Using an atmospheric pressure chemical ionisation source, the instrument's sensitivity for a dioxin and furan analysis was evaluated and found to have a detection limit of around 100 attograms on column.

Materials and methods:

The tandem quadrupole used was a Waters Xevo TQ-XS. This was fitted with a sample cone that has a 0.90mm orifice and a high displacement backing pump (Ebara EV-SA30). The ion guide assembly between the sample cone and the first analytical quadrupole was of a new design and a new detection system with increased dynamic range was used. The ionisation source was an atmospheric pressure gas chromatography (APGC) chemical ionisation source using a revised design of heated transfer line with improved thermal continuity.

The gas chromatography oven was an Agilent 7890A with a 7693B autosampler. The GC column was an Agilent DB-5MS (30m x 0.25mm x 0.25 μ m). All injections were performed on a split/splitless injector operating in the pulsed splitless mode, with an injection volume of 1.0 μ L. Samples analysed were an EPA1613 dioxin and furan standard (Wellington Laboratories, Canada), a single component 2,3,7,8 Tetrachlorodibenzo-p-dioxin standard (Supleco, USA) and extracts from various matrices (kindly supplied by LABERCA, France). All analyses were conducted using the multiple reaction monitoring (MRM) mode of acquisition, with the quadrupoles operating at 0.7Da resolution.

Results and discussion:

Initial optimisation of the system was performed using the single component 2,3,7,8 TCDD sample. A dilution series was made from its original concentration of 10ng/ μ L to a limit of detection (LOD) of 100ag/ μ L. Once the optimal conditions for the ionisation source, gas chromatograph and mass spectrometer has been determined for best sensitivity, various studies were conducted to explore the linearity, robustness and ultimate sensitivity of the system.

The sensitivity of the system was found to be a significant improvement on the previous design. The recorded peak intensities were approximately five times greater than had previously been observed on the previous instrument. While investigating the lower limits of detection for the system it was soon realised that the greatest challenge of the analysis was to obtain a true blank. Various measures were taken to reduce the TCDD signal from the injection system and eventually the background from the injection of a blank solvent was reduced to the low tens of attograms.

Example chromatograms of a 250ag/ μ L and 100ag/ μ L injection are shown in Figure 1. The lower trace in Figure 1 is a blank injection, with the vertical scaled normalised between the three traces.

The reproducibility at a sample concentration of 500ag/ μ L was assessed. Table 1 gives the peak areas of the primary TCDD MRM transition, along with the isotope ratio error, for twelve successive injections. All isotope ratio errors were within the $\pm 15\%$ of the theoretical value, the tolerance permitted by relevant legislation^{1,2}, with an average absolute error of 3.7%. The average signal to noise, using the peak-to-peak definition over a signal-free noise period of ten peak widths, was 38:1.

The linearity of the system was assessed by running the 2,3,7,8 TCDD dilution series, with 22 concentrations over the range of 100ag/ μ L to 1ng/ μ L, with intermediate concentrations of 250ag/ μ L, 500ag/ μ L, 1fg/ μ L, 2.5fg/ μ L etc. The calibration curve is shown in Figure 2, demonstrating linearity within $\pm 8\%$ over the range of 100ag/ μ L to 100pg/ μ L with an r^2 value of 0.998. Data above this upper

concentration started to show saturation effects. All isotope ratios were within $\pm 15\%$ of the theoretical expected value.

The stability of the system was assessed by repeatedly injecting a 1000:1 dilution of an EPA1613 CS3 dioxin and furan standard. Analyte concentrations within this sample varied from 10fg/ μL to 200fg/ μL , with the majority of the $^{13}\text{C}_{12}$ labelled components being of a concentration of 100fg/ μL . Analysis was performed with the collision energies for the dioxins at 30V and for the furans at 40V. 100 acquisitions were performed, and the 6800 peaks obtained were quantified and found to have an average standard deviation of 7.71%. The average absolute isotope ratio error of the 3400 ratios assessed was 3.22% with respect to the theoretical values, with only one measurement exceeding the $\pm 15\%$ legislative criteria.

An additional assessment of the instrument performance was made using a number of extracts from a variety of matrices. The results were in good agreement with previous analyses on a tandem quadrupole. An example of the detection of 2.6fg of 1,2,3,4,6,7,8 HpCDF in pork fat is shown in Figure 3, with an isotope ratio error of $<4\%$ when compared to the expected theoretical value.

Acknowledgements:

Emmanuelle Bichon of LABERCA, France, for supplying sample extracts.

Jack Cochran of Restek, USA, for advice on how to minimise sample carryover and maintain a clean injection system.

References:

1. EPA Method 1613 (Revision B), U.S. Environmental Protection Agency (USEPA), Washington, DC, Sept. 1994.
2. Commission Regulation (EU) 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.

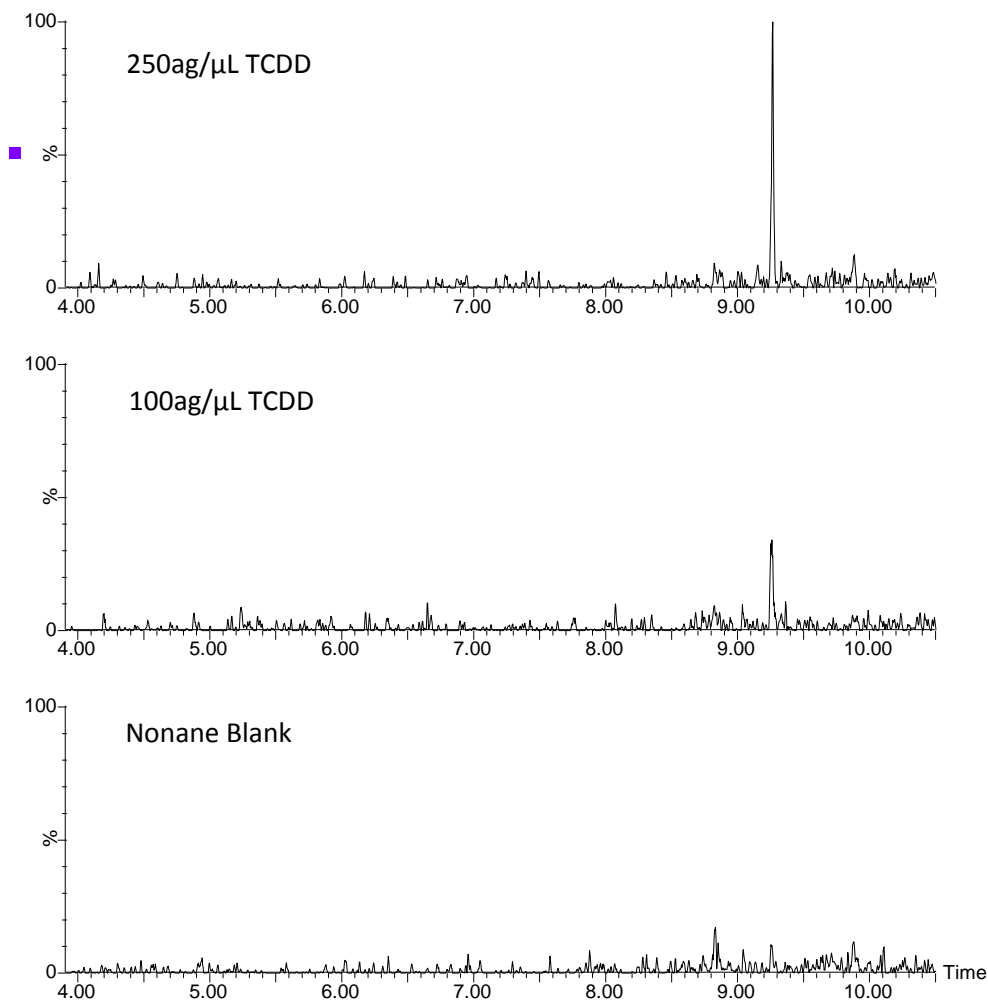


Figure 1: 250ag of TCDD (upper trace), 100ag (middle) and a nonane blank (lower)

Injection number	Peak Area	Ion Ratio Error (%)	Signal to Noise
1	73.1	-6.2	13
2	85.3	-2.1	41
3	84.1	-3.2	56
4	81.5	-4.3	43
5	79.1	2.3	27
6	82.5	-0.7	43
7	74.0	2.9	27
8	80.5	-2.2	53
9	74.1	2.7	35
10	74.6	6.3	32
11	71.0	-7.2	44
12	82.4	-4.7	37
Mean	78.5		
%RSD	6.2		

Table 1: Reproducibility of twelve successive injections of 500ag of TCDD

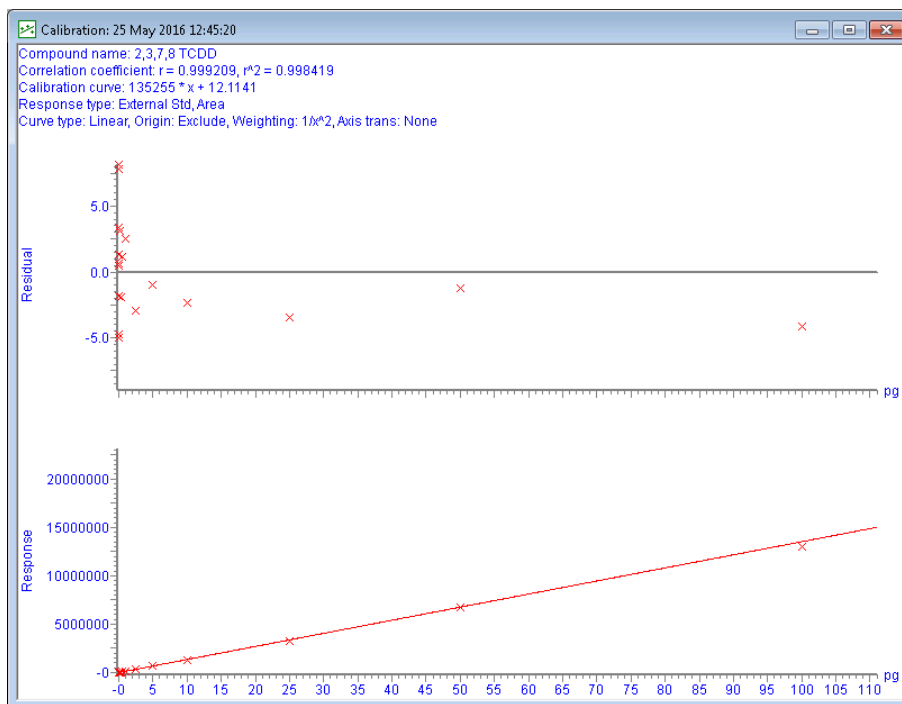


Figure 2: Linearity over 6 orders of magnitude, from 100ag/μL to 100pg/μL

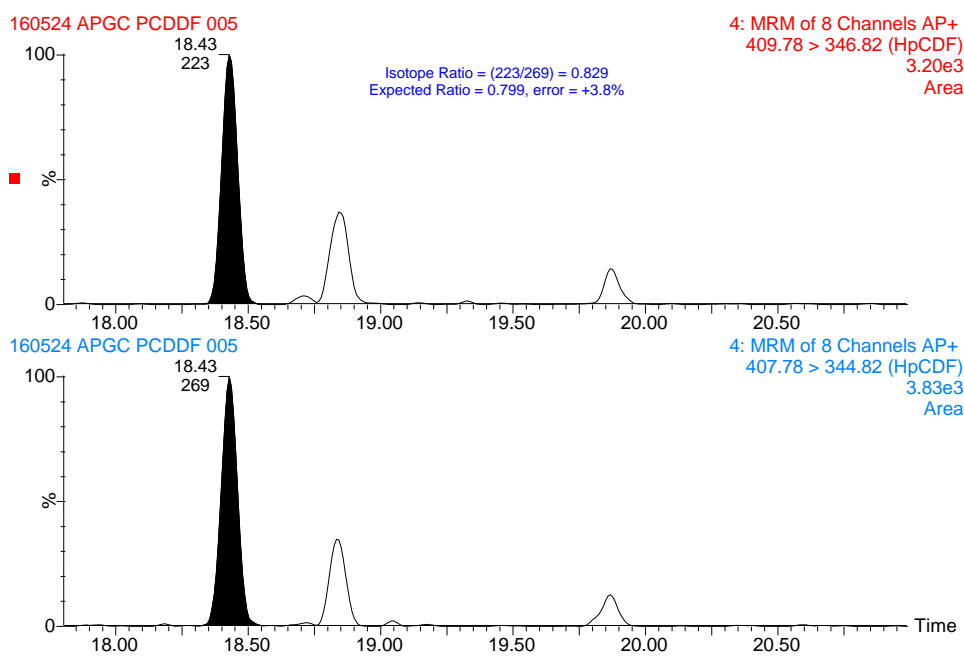


Figure 3: 2.6fg of 1,2,3,4,6,7,8 HpCDF in extract of pork fat