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IMPROVING THE CHROMATOGRAPHIC CAPABILITIES OF AN ATMOSPHERIC PRESSURE CHEMICAL IONISATION SOURCE

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Introduction:

Maintaining chromatographic performance when coupling a gas chromatography system to an atmospheric pressure source on a mass spectrometer can present many challenges that are not present, or are vastly reduced, when compared to using a high vacuum source. The increased use of atmospheric pressure gas chromatography (APGC) chemical ionisation for the analysis of dioxins^[1], furans and brominated flame retardants^[2], in addition to other persistent organic pollutants, has placed a great emphasis on the performance capabilities of such sources and interface devices, specifically the maintenance of chromatographic fidelity over extended periods of time. A new design of APGC interface has been devised in order to enhance the chromatographic capabilities of the technique.

Materials and methods:

Analyses were performed on a Waters Xevo TQ-XS tandem quadrupole mass spectrometer and a Waters Synapt G2-S Q-IMS-ToF. The GC Oven used was an Agilent Technologies A7890, with a 7693B autosampler. The GC columns used were a Restek RT-1614 15m x 0.25m x 0.10 μ m, a Restek Rxi-HT1 30m x 0.32mm x 0.10 μ m and an Agilent DB-5MS 30m x 0.25m x 0.25 μ m. Samples analysed were a Polywax 655 hydrocarbon series (Restek, USA), a PBDE Window Defining Mixture (BDE-WD) and an EPA1613 CS3 dioxin and furan standard (Wellington Laboratories, Canada). The Computational Fluid Dynamic (CFD) modelling software used was Autodesk Simulation 2013 and 2016.

Results and discussion:

Operating the outlet of a GC column at atmospheric pressure results in a vastly reduced exit velocity for the analytes when compared to a more traditional high vacuum source on an electron impact mass spectrometer^[3]. A plot of the carrier gas velocity as a function of the fractional distance along a GC column, under typical flow conditions (with a mean velocity of 38cm.s⁻¹), is shown in Figure 1, for both an atmospheric outlet and high vacuum one. The average velocities in the last half meter of the column, which resides in the interface between the GC oven and the mass spectrometer, were calculated to be 77cm.s⁻¹ and 281cm.s⁻¹ for these two systems respectively.

With an atmospheric outlet, analytes have an increased residence time within the interface to the mass spectrometer and this places far more exacting demands on its thermal continuity. Cold or hot spots within the interface can result in loss of signal, increased background, irreproducibility, broadening of chromatographic peaks, decomposition of analytes and accelerated column deterioration. Achieving acceptable thermal continuity is also more difficult with an atmospheric source as convective effects can play a major role in heat loss.

In order to improve the design of the APGC interface, it was first modelled using CFD software, as shown in Figure 2. The model was developed until the predicted thermal continuity matched that determined empirically under typical operating conditions. This exercise highlighted the main causes of thermal discontinuity and focused design efforts towards its minimisation. A new design was conceived with alternative material selection, heater spacing and a number of other alterations. This new design was manufactured and tested extensively.

One of the more chromatographically demanding analyses routinely performed using APGC is that of polybrominated diphenyl ethers. In particular, the highly brominated compounds, such as BDE209, require that the interface is at a relatively high temperature in order to prevent loss of chromatographic resolution. A comparative test was performed with both the standard and the new design of APGC interface, using a RT-1614 15m x 0.25m x 0.10 μ m column and a BDE-WD standard. It was found that not only was the chromatographic resolution higher with the new interface but it could also achieve this at a set regulation temperature 60°C lower, as shown in Figure 3.

A further, more extreme test was conducted using a Polywax 655 sample containing straight chained alkanes from C₂₀ up to C₈₀. This sample was dissolved in hexane and analysed using a Rxi-HT1 30m x 0.32mm x 0.10µm GC column. The interfaces were set to regulate at 380°C for this test. Using the standard design of interface, peak broadening was observed for carbon numbers above C₄₀. The revised design was capable of maintaining chromatographic fidelity up C₆₂, as shown in Figure 4. Furthermore, it was possible to increase this upper detection limit to C₇₀ by ramping up the helium GC carrier gas flow to 10mL.min⁻¹ towards the end of the run, resulting in a 6 second wide peak.

In order to test the robustness of the interface, 100 pulsed splitless injections of an EPA1613 CS3 dioxin and furan standard were made using a DB-5MS 30m x 0.25m x 0.25µm column with the revised design interface held at a temperature of 280°C. Figure 5 shows the chromatograms of OCDD and OCDF at the start and at the end of the analysis. No appreciable change in chromatography was noted over the 62 hour run time.

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References:

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3. Poole, Colin, et al. (2012) "Gas Chromatography", Elsevier.

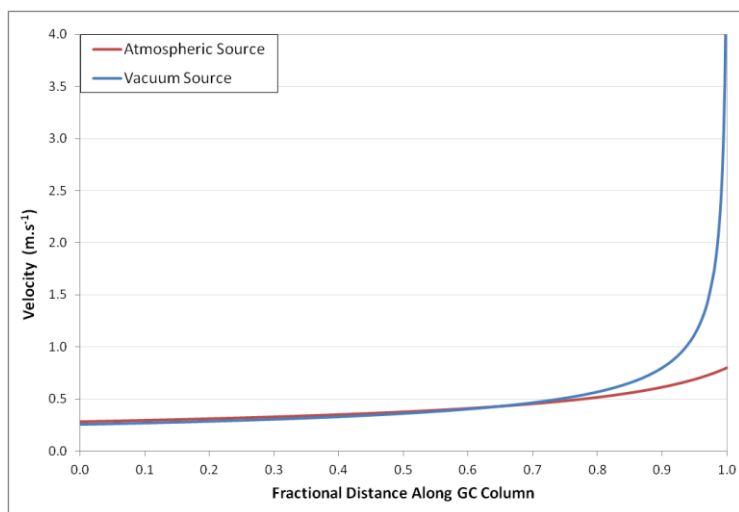


Figure 1: Gas velocity as a function of distance through a column for atmospheric and vacuum sources

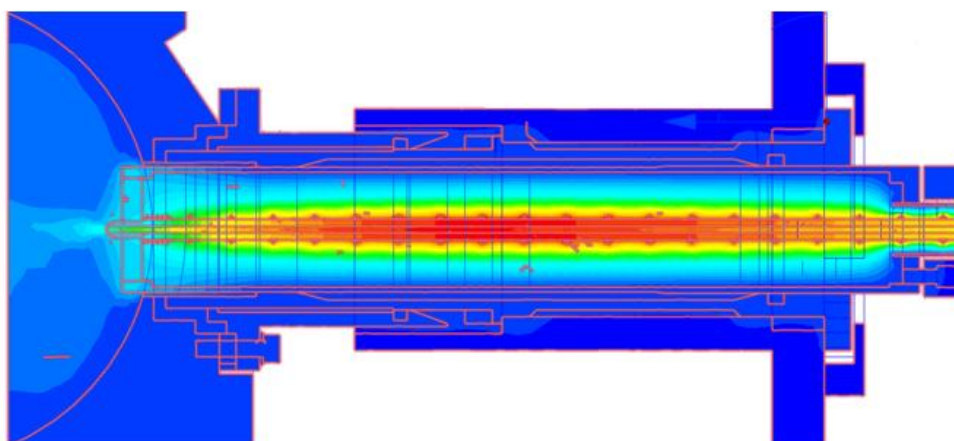


Figure 2: A CFD model of the APGC interface

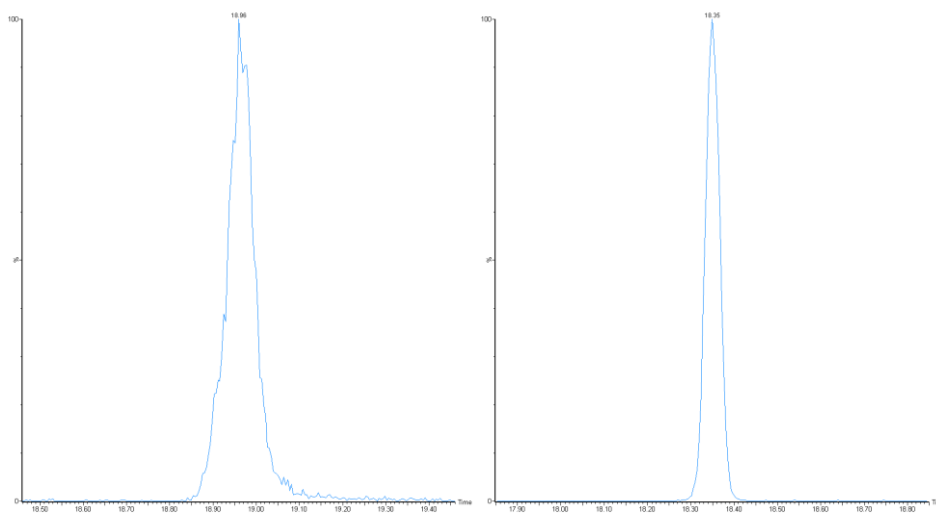


Figure 3: On the left, BDE209 with using the standard APGC interface at 360°C and the revised design at 300°C on the right. The time axes are equivalent with each showing one minute of the chromatographic trace

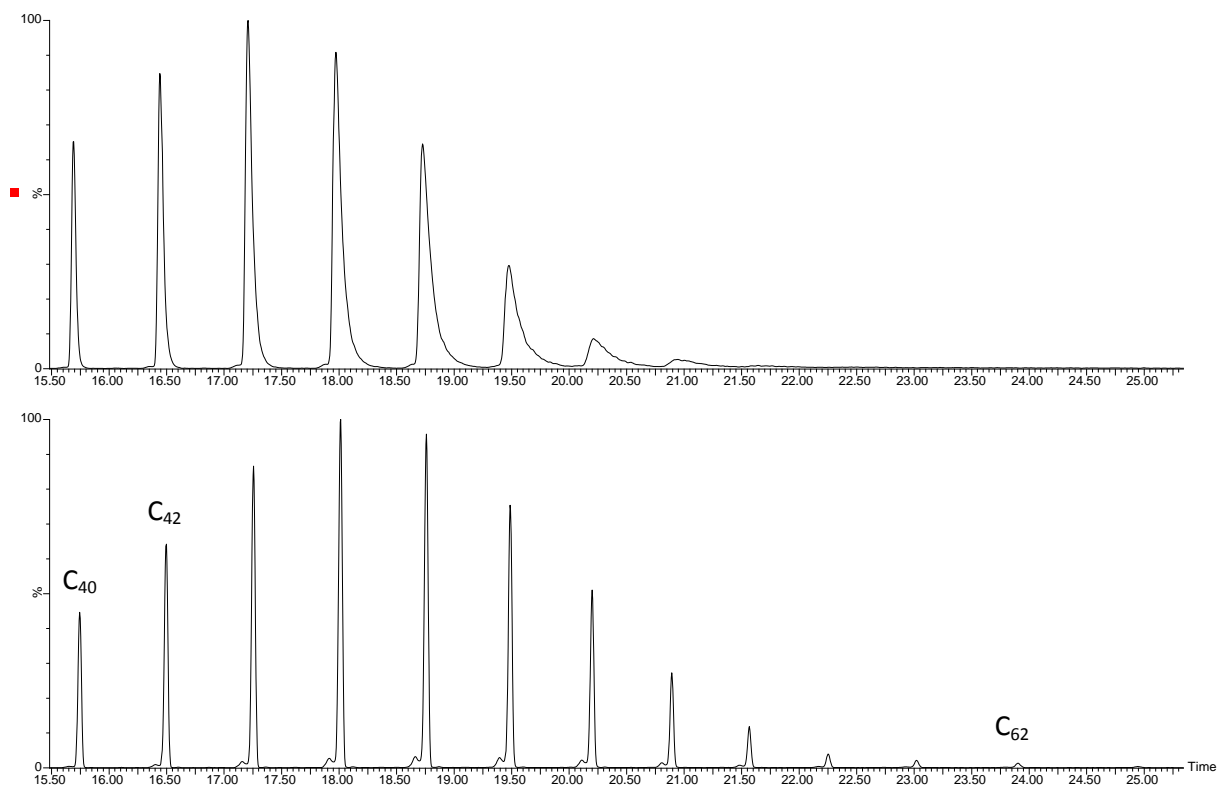


Figure 4: Polywax 655 analysed using the standard APGC interface (upper trace) and the revised design (lower trace)

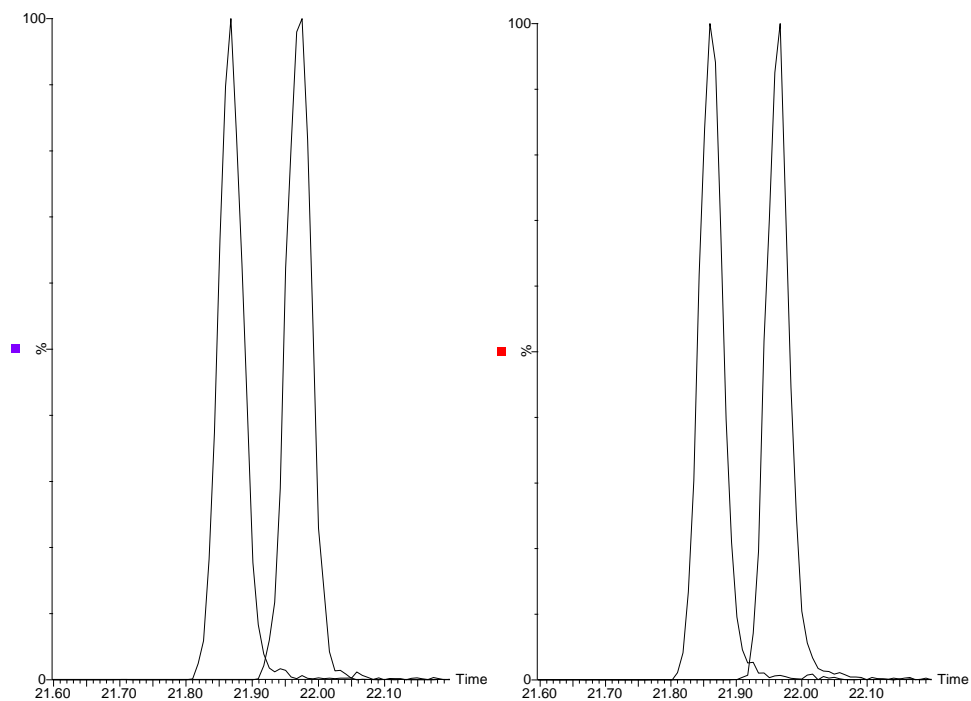


Figure 5: Chromatography of OCDD and OCDF at the start and end of a 62 hour, 100 acquisition study