Use of Nitrogen as an Alternative Carrier Gas to Helium for GC-MS/MS with APGC Technology for the Determination of Pesticide Residues in Food

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INTRODUCTION

Helium (He) is becoming a costly choice for a carrier gas for gas chromatography-mass spectrometry (GC-MS) as supplies have been restricted resulting in shortages. Chromatographers have found that He is much more expensive and is not always available when needed. Many have considered switching from He to hydrogen as an alternative. However, there are perceived concerns about its safety, reactivity on older instruments, reduced performance compared to He, and the length and cost of the transition process.

Another alternative to He as a carrier gas is nitrogen (N_2). While N_2 is relatively inexpensive and readily available, it significantly reduces the sensitivity of GC-MS instruments when using Electron Ionisation (EI). This is attributed to a decrease in the ionisation efficiency due to the consumption of electrons emitted by the filament through reaction with the N_2 gas, which has lower ionisation energy and larger molecular size than He. One advantage of GC-MS using atmospheric pressure ionization is that ionization does not take place under vacuum. The design of the APGC™ source already incorporates multiple uses of N_2 gas and ionization takes place around a corona pin which induces a N_2 plasma, so sensitivity is not compromised by the switch to N2 as a carrier gas.

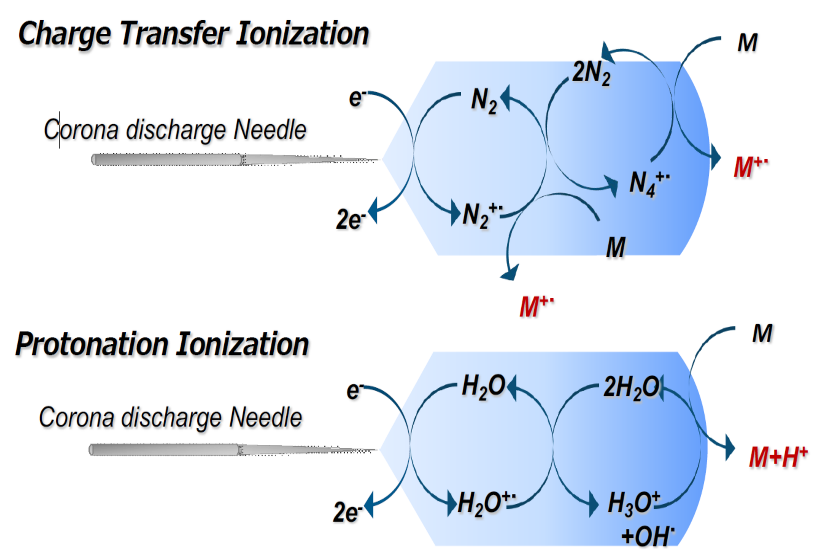


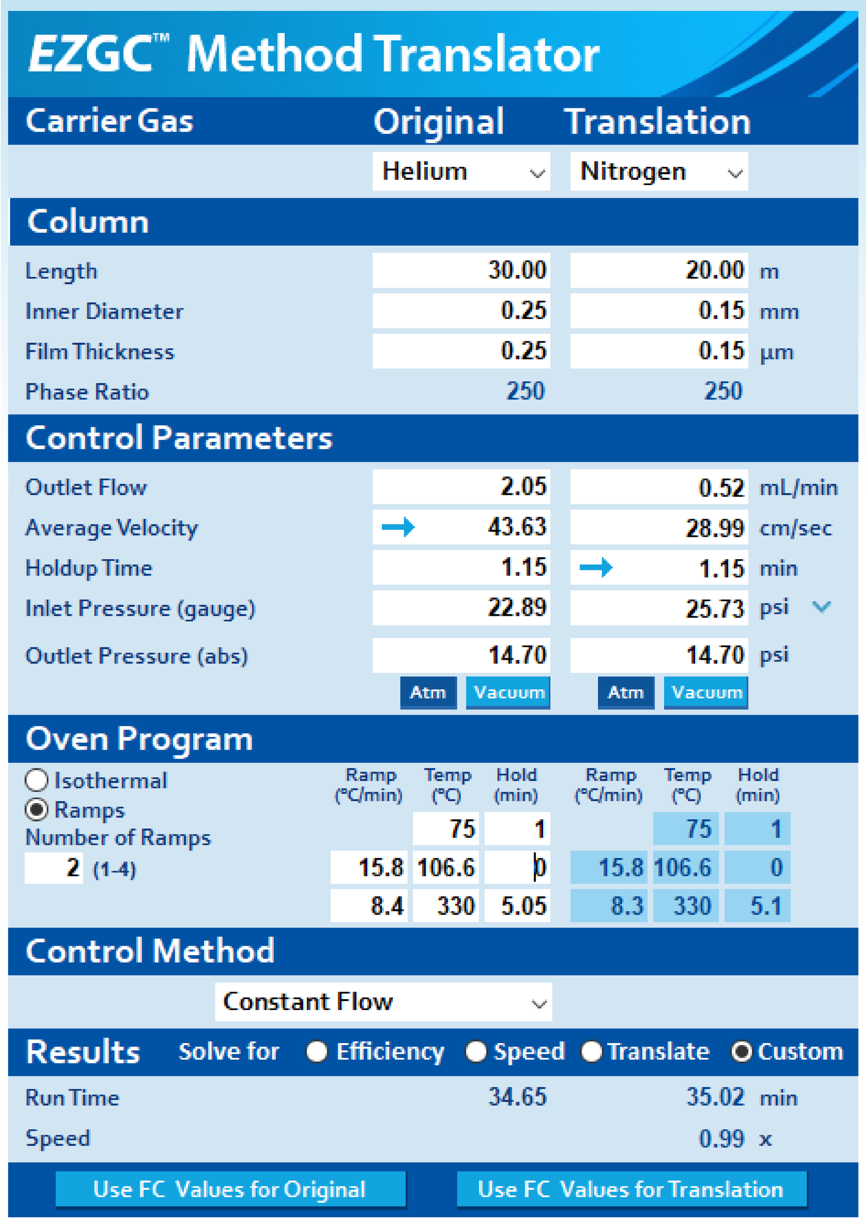
Figure 1. The two ionization mechanisms of the APGC source.

EXPERIMENTAL CONSIDERATIONS

The mechanism of the APGC technique is gas-phase ion molecule reactions by charge or proton transfer (Figure 1). For pesticide residue analysis, source conditions are adjusted to have just enough water present in the ionization chamber to give sufficient sensitivity for compounds that prefer either charge or proton transfer. The instrument setup has very dry conditions, achieved by using appropriate quality nitrogen gas and filtration. Water is then added vials in a holding tray which is placed within the source enclosure.

Due to N_2 having a lower optimum linear velocity than He, the optimum gas flow rate is much lower, so a shorter column is used to avoid lengthy run times. Matching the phase ratio of the column to the one used with He ensures the same chromatographic performance is maintained. Restek's *EZ*GC method translator tool (see right) was utilized to move the GC method from He to N_2 carrier gas by scaling the Restek Rxi 5Sil MS column dimensions and parameters. The goal was to match retention times from one carrier gas to another. Poor peak shape was observed for early eluting peaks using acetonitrile as the injection solvent. Reducing the initial oven temperature to provide solvent focusing improved matters.

The performance of the methods were compared using matrix-matched standards prepared with 203 pesticides in QuEChERS (CEN) extracts of cucumber and cottage pie baby food.



RESULTS AND DISCUSSION

The translated method for use with N_2 carrier gas on the scaled column dimensions of 20m x 0.15mm gave a comparable analysis time even with a much lower carrier gas flow rate. By matching the holdup time, the retention times of the compounds from the shorter column were comparable to those observed with He carrier gas on a 30m x 0.25mm column so only minor changes had to be made to the MRM acquisition and processing methods for the 203 pesticides after switching to N_2. Figure 2 shows a comparison of the chromatograms for the early and late eluting compounds from the two different configurations, whereas Figure 3 shows separation of a critical pair.

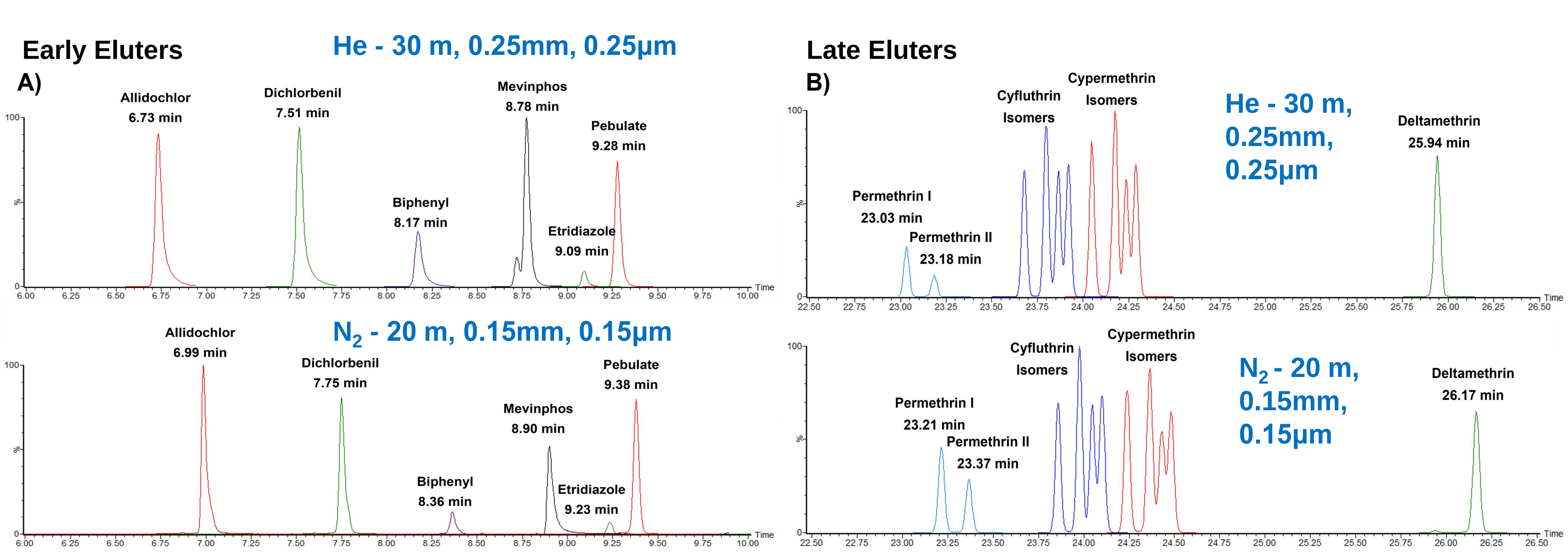


Figure 2. Comparison of the chromatographic performance from the He and N_2 methods.

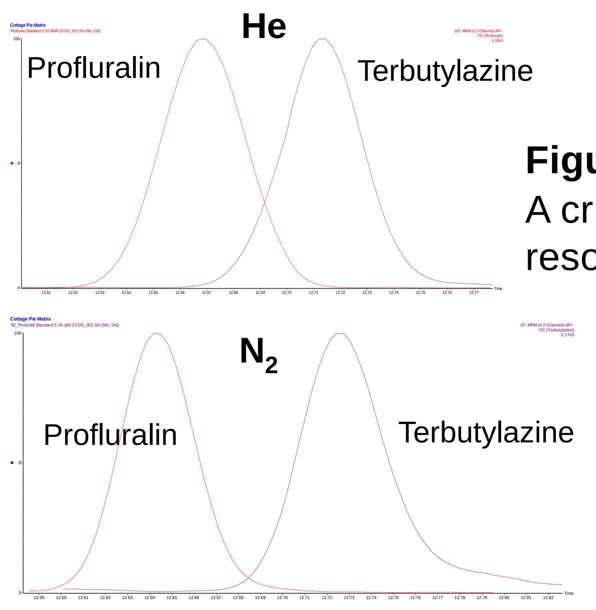


Figure 3. A critical pair with improved resolution using N_2.

Using APGC on a Xevo™ TQ-S Micro mass spectrometer, 98% of the 203 pesticides were detected at 0.005 mg/kg in cucumber and baby food. Calibration graphs typically exhibited residuals within the ±20% SANTE tolerance. Examples of chromatograms for key pesticides at 0.01 mg/kg in baby food and associated calibration graphs are given in Figures 4 and 5, respectively.

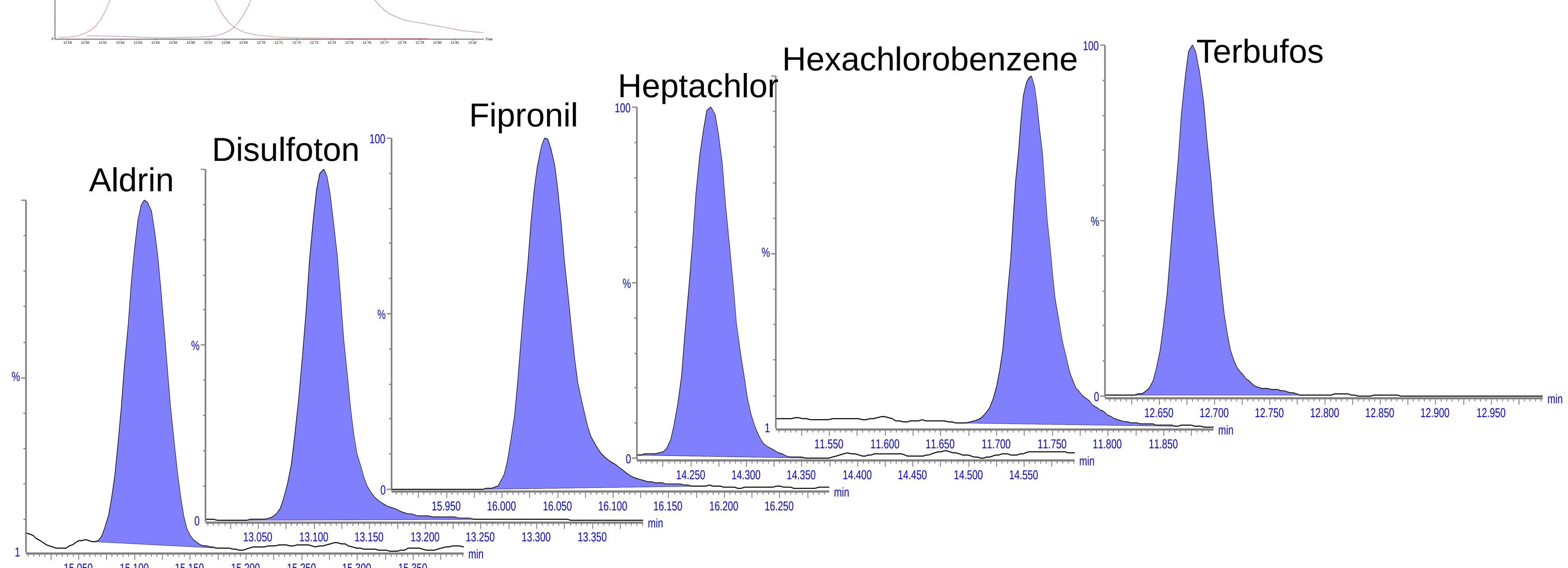


Figure 4. Chromatograms for a selection of pesticide residues in baby food at 0.01 mg/kg.

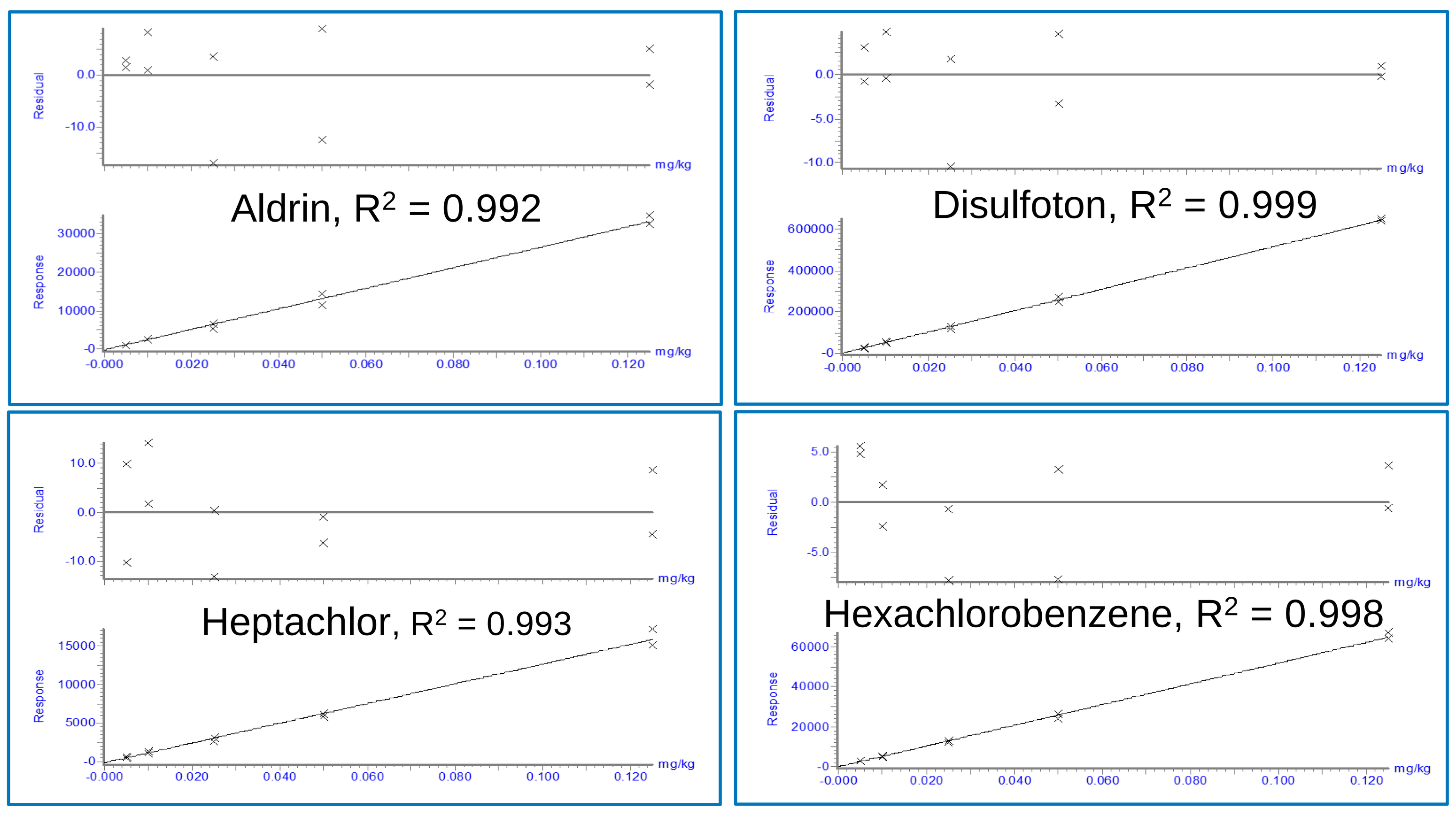


Figure 5. Bracketed calibration curves and residual plots for a selection of pesticide residues in baby food.

CONCLUSIONS

- **This poster describes the easy conversion of an existing GC method for the determination of pesticide residues from He to N_2 as a carrier gas.**
- **As the ion source is not constrained by vacuum, the APGC system is able to switch to using N_2 as a carrier gas without a loss in performance and can be returned to He at the turn of a valve.**
- **After scaling the column dimensions and adjustment of parameters, separations and run time were almost identical with no impact upon sensitivity.**
- **APGC with N_2 as a carrier gas has been shown to be reliable for the determination of pesticide residues in food and offers considerable saving on carrier gas costs with no supply issues.**