# IMPROVING THE QUANTITATIVE REPRODUCIBILITY OF AN ATOMSPHERIC PRESSURE CHEMICAL IONISATION SOURCE FOR GC/MS AND GC MS/MS ANALYSIS

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**Introduction**

Recent studies have evaluated the use of atmospheric pressure chemical ionisation gas chromatography mass spectrometry for quantitative analysis of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans[1], as well as other persistent organic pollutants such as polyaromatic hydrocarbons[2]. Fundamental to the suitability of this ionisation technique for this purpose is the reproducibility of the ionisation efficiency and hence the recorded peak response. It has been found that one of the most significant factors in the variation of peak response from one analytical run to the next is how the coronal discharge process is affected by the elution of the diluent solvent, which precedes the elution of the analytes of interest during the GC run. This study describes the inimical effects of the solvent front for this ionisation technique and discloses methods for its mitigation.

**Materials and methods**

All data presented here were acquired using an atmospheric pressure chemical ionisation source designed for gas chromatography (APGC). Initial studies were performed on a Q-IMS-ToF mass spectrometer (Synapt G2-S) operating in MS mode, with performance optimised for sensitivity and an operating resolution of 14,000 R.P. (FWHM definition). Additional studies were performed on a tandem quadrupole mass spectrometer (Xevo TQ-S) using MRM transitions to target specific constituents of the samples, with Q1 and Q2 resolutions set to 0.7Da.

Two samples were used in these studies; a 10:1 dilution (in nonane) of a CS3 US EPA1613 dioxin/furan standard (Wellington Laboratories), with analyte concentrations ranging from 1 to 10pg/µL, and a Semivolatile Organics US EPA Method 8270 Megamix sample (from Restek) diluted in hexane to a concentration of 1pg/µL.

Separations were performed using both a Rxi-5Sil MS (Restek) and a DB-5MS (Agilent) GC column, both of 30m length, 0.25mm ID and 0.25µm film thickness, run at a flow rate of 2.0mL/min. The GC ovens used were both Agilent 7890As and a 7683 autosampler was used for sample introduction. The GC inlet was a split/splitless inlet operating in the pulsed splitless mode. Injections were of a volume of 1.0µL.

**Results and discussion**

In positive ionisation mode, the APGC source operates at optimum efficiency when in a coronal discharge mode known as "Hermstein's Glow"[3,4], characterised by a steady current and quiet operation with little or no sparking. The high potential gradient about the tip of the pin imparts sufficient energy on free electrons that they can ionise molecular nitrogen (IE = 15.6eV)[5]. This process yields a $N_2^+$ radical cation, which is repelled from the corona pin and can go on to ionise analyte species, either through direct charge exchange or through an intermediate species such as water. The process also yields an additional electron which is accelerated towards the pin and thereby initiates an electron avalanche as this reaction is repeated. High energy photons from recombination reactions within this ionisation region causes ionisation of molecular nitrogen further out in the corona pin's electric field, thus seeding further reactions and sustaining the corona. The voltage that has to be applied to the corona pin to achieve a desired current is characteristic of how efficiently this corona reaction is occurring.

Research studies into the ionisation processes occurring within an atmospheric pressure chemical ionisation source coupled to a gas chromatograph identified a significant correlation between the recorded peak response for a given compound and the corona voltage at the time the compound eluted from the gas chromatograph. The data shown in Figure 1 is from the repeated analysis of the Megamix sample on a Q-IMS-ToF MS under the same conditions. The peak response for the protonated ion of phenanthrene is shown for a number of sequential

acquisitions and plotted in conjunction with the corona voltage (at the time that the species eluted) on the secondary y-axis. There is a strong inverse correlation between gross changes in both values.

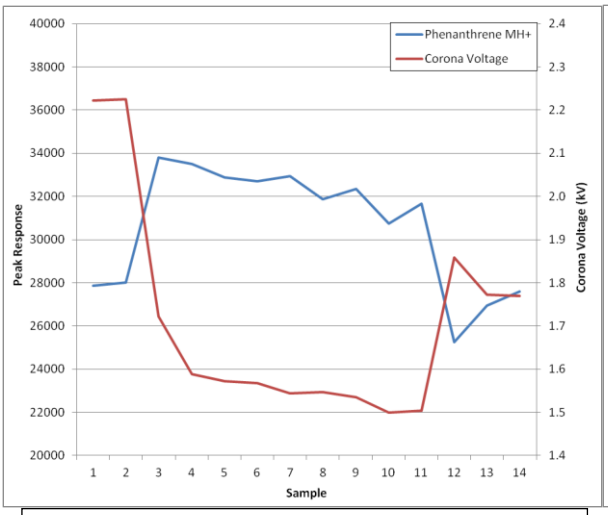


Figure 1: Variation in peak response for protonated phenanthrene and the corona voltage at its elution time

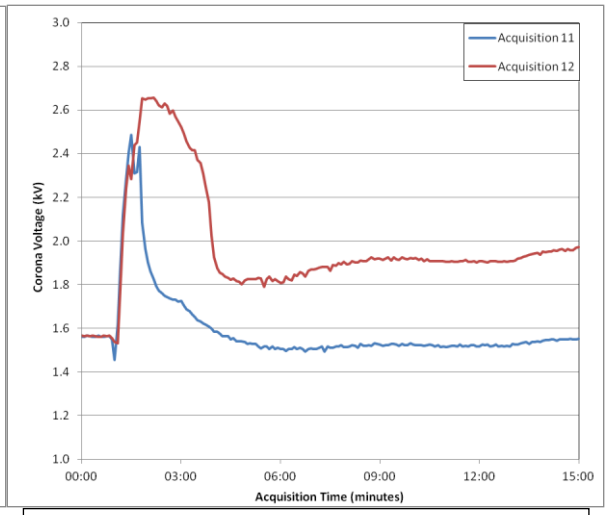


Figure 2: Variation in corona voltage during analysis for two sequential acquisitions

Further study into this variation in corona voltage from one sample to the next identified the solvent front as having a significant impact on the ionisation conditions of the source. Figure 2 shows the corona voltage during two subsequent analyses while the corona current is regulating at a value of 2.0µA. The solvent (hexane) starts to elute from the column at an acquisition time of 1.2 minutes and causes a significant rise in corona voltage. The ionisation potential of hexane (10.1eV[6]) is lower than that of molecular nitrogen, so is more readily ionised and within a larger volume about the tip of the corona pin. The sudden rise in positively charged ions about the tip of the corona pin causes a weakening of the electric potential gradient, with a corresponding reduction in current from electrons avalanches. The corona voltage increases in order to compensate for this change and thereby maintain the regulation current. As demonstrated in Figure 2, this adverse coronal form can persist long after the solvent front has passed, and in a highly irreproducible fashion.

It was found through experimentation that the corona voltage could be stabilised by maintaining the corona current at either 0µA or at an unusually high value (20µA) throughout the solvent front and then returning it to its normally optimal value of 2.0µA. The reproducibility of the corona voltage at any point within the analysis was seen to improve from having an RSD of 4.6% to 0.9% as a result of setting the current to either 0µA or 20µA for the solvent front. It is believed that it is the re-initiation of the corona discharge reaction once the source conditions have settled that provides this stability improvement.

Additional studies into the source environment determined that the solvent front can also be purged more effectively from the ionisation chamber by varying the cone gas flow. The cone gas is used to partially ballast the pumping requirements of the mass spectrometer's sampling orifice, and therefore affects the flow of gas drawn in from the source enclosure. When the cone gas flow is lowered, the amount of gas drawn through the ionisation chamber is increased. This can more effectively remove solvent vapour from the ionisation region about the corona pin and is especially beneficial when using higher boiling point solvents such as nonane.

In order to qualify the effect of the described variations in source conditions during the solvent front, a study was performed on a tandem quadrupole mass spectrometer, analysing various components of the 8270 Megamix sample. Three source conditions were compared; A) standard source conditions with a cone gas flow of 200L/Hr and corona current of 2.0µA, B) with the corona current at 20µA during the solvent front and C) with corona current at 20µA and cone gas flow at 0L/Hr during solvent front. The stability of one of the targeted components of this sample (molecular ion of pyrene) under the three sets of source conditions are shown in Figure 3, along

with the corona voltage at the time the peak eluted. A summary of the relative standard deviations of the targeted components and their corresponding corona voltages is given in Table 1. Each modification to the source conditions for the solvent front resulted in an improvement in reproducibility.

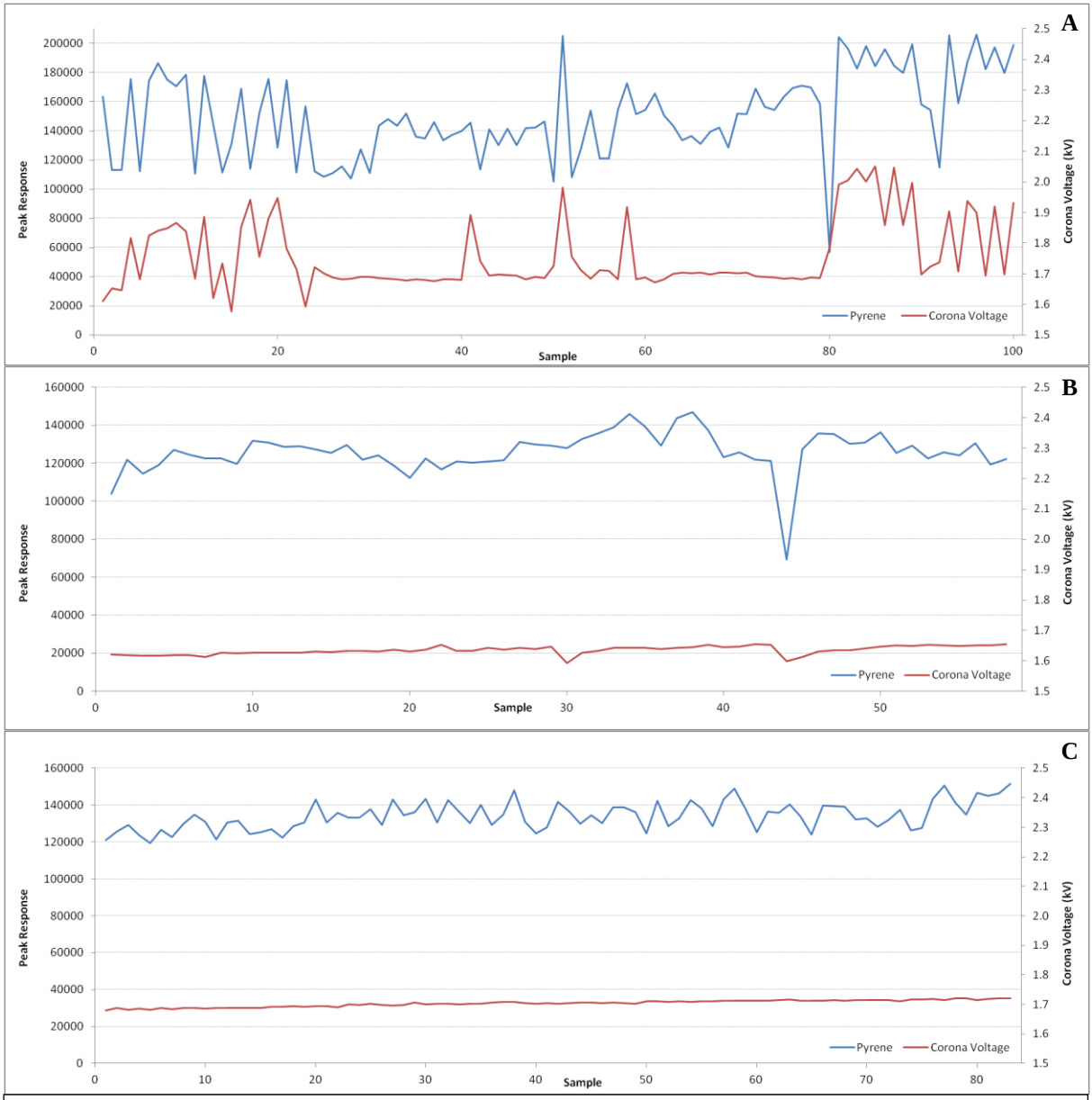


Figure 3: Variation in pyrene peak response and corona voltage on tandem quadrupole with A) no variation in source conditions, B) with the corona current at 20µA during the solvent front and C) with corona current at 20µA and cone gas flow at 0L/Hr during solvent front

A second analysis was performed using a dioxin/furan standard diluted in nonane, analysed on the Q-IMS-ToF. This analysis was undertaken to qualify the effect of lowering the cone gas during the solvent front when using a higher boiling point solvent. An additional parameter was varied, termed the auxiliary gas flow. This gas flow is used to sweep the source enclosure and prevent the build up of contamination. For this experiment, when the cone gas flow was lowered, the auxiliary gas flow was increased. This helps prevent back-streaming of gases from the exhaust port of the source enclosure by maintaining a higher combined input gas flow than the pumping

requirement of the sampling orifice of this mass spectrometer. Two sets of source conditions were tested; A) with the corona current set to 0µA during the solvent front, 2.0µA thereafter and B) with the corona current at 0µA, cone gas flow of 50L/Hr and auxiliary gas flow of 400L/Hr during the solvent front, returning to their respective optimised values of 2.0µA, 225L/Hr and 50L/Hr thereafter. The peak response for 2,3,7,8 Tetrachloro($^{13}C_{12}$)dibenzo-p-dioxin under the two conditions used is shown in Figure 4. Table 2 summaries the relative standard deviations of the peak responses, both as absolute and internal standard corrected values.

| Species | RSD of Peak Response (%) | | | RSD of Corona Voltage (%) | | |
|---|---|---|---|---|---|---|
| | A | B | C | A | B | C |
| 4-chloro-3-methylphenol | 22.0 | 10.2 | 7.6 | 6.34 | 0.80 | 0.68 |
| Fluorene | 21.9 | 10.0 | 4.4 | 6.18 | 0.85 | 0.70 |
| Hexachlorobenzene | 18.0 | 7.9 | 6.6 | 6.12 | 0.86 | 0.66 |
| Phenanthrene | 22.0 | 9.6 | 4.1 | 6.13 | 0.82 | 0.64 |
| Fluoranthene | 19.6 | 8.6 | 5.5 | 6.39 | 0.83 | 0.65 |
| Pyrene | 19.4 | 8.7 | 5.6 | 6.43 | 0.83 | 0.64 |
| Chrysene | 21.1 | 10.7 | 6.0 | 6.67 | 0.82 | 0.68 |
| Indeno(1,2,3-cd)pyrene | 15.8 | 13.9 | 12.1 | 6.62 | 0.88 | 0.67 |
| Benzo(ghi)perylene | 16.0 | 13.2 | 11.6 | 6.58 | 0.94 | 0.68 |
| Average | 19.5 | 10.3 | 7.0 | 6.38 | 0.85 | 0.67 |

Table 1: RSDs of peak response and corona voltage for Megamix analysis on tandem quadrupole, using three source conditions

| Groups | Average Relative Standard Deviation (%) | | | |
|---|---|---|---|---|
| | Source Conditions A | | Source Conditions B | |
| | Absolute | IS corrected | Absolute | IS corrected |
| Tetrachlorodibenzo-p-dioxins | 9.3 | 4.4 | 4.3 | 3.9 |
| Tetrachlorodibenzofurans | 9.8 | 3.0 | 4.9 | 3.7 |
| Pentachlorodibenzo-p-dioxins | 9.6 | 1.7 | 4.3 | 1.8 |
| Pentachlorodibenzofurans | 9.1 | 2.1 | 4.8 | 2.2 |
| Hexachlorodibenzo-p-dioxins | 9.8 | 3.7 | 6.4 | 3.9 |
| Hexachlorodibenzofurans | 9.5 | 2.4 | 5.4 | 2.4 |
| Heptachlorodibenzo-p-dioxins | 10.2 | 1.9 | 6.0 | 2.0 |
| Heptachlorodibenzofurans | 10.1 | 2.0 | 5.6 | 2.2 |
| Octachlorodibenzo-p-dioxin | 11.6 | 1.9 | 5.8 | 2.2 |
| Octachlorodibenzofuran | 11.5 | - | 6.1 | - |
| Average | 10.0 | 2.6 | 5.4 | 2.7 |

Table 2: Comparison of RSDs of peak response for PCDD/F analysis on Q-IMS-ToF using two source conditions

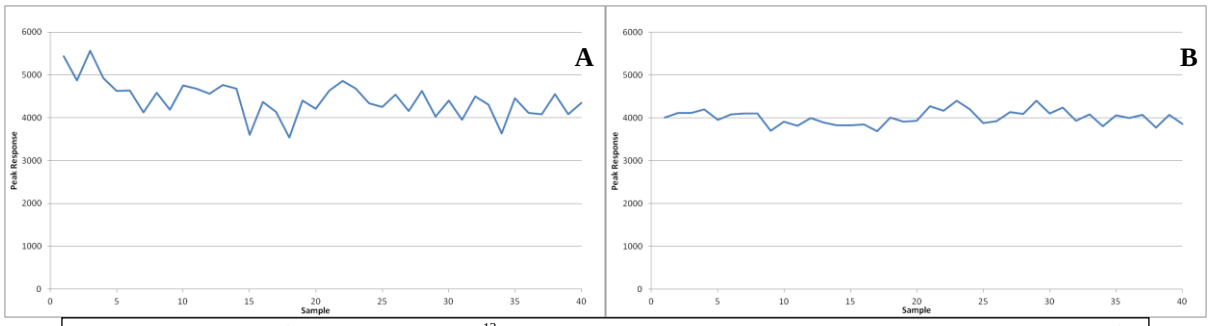


Figure 4: Peak response for 2,3,7,8 Tetrachloro($^{13}C_{12}$)dibenzo-p-dioxin on Q-IMS-ToF with A) corona current set to 0µA for solvent front and B) corona current set to 0µA, cone gas at 50L/Hr and auxiliary gas flow set to 400L/Hr for solvent front

The analysis showed a near two-fold improvement in reproducibility as a result of varying the cone and auxiliary gas flows during the solvent front. As expected, no appreciable difference was seen in the reproducibility of the internal standard corrected peak responses.

This study demonstrates that it is essential to control the corona discharge in order to maximise the quantitative reproducibility of analyses performed using an atmospheric pressure chemical ionisation source with a gas chromatograph. The dominant source of variation for this type of analysis is how the corona is affected by the elution of the solvent during the GC cycle. The techniques described result in stable and reproducible corona discharge conditions, with a corresponding benefit to the reproducibility of the analysis.

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