

# focus on Chromatography

## Automated Analysis of Canister Air and Gas – A Cryogen-free Solution

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With growing concern over the harmful effects of long-term exposure to low levels of hazardous air pollutants, there is increasing demand for analytical laboratories to detect ever-lower levels of analyte concentrations in canister air. At the same time, canisters are increasingly used for applications other than ambient air analysis, such as soil gas and vapour intrusion studies. Traditional canister analytical technologies are challenged by the ever-wider range of analytes and concentrations of interest. For example, high-concentration samples have typically required dilution before analysis, increasing analytical uncertainty and risking introduction of contaminants. Conventionally, systems have also had to be dedicated to either high- or low-concentration analysis.

The CIA Advantage has been designed to overcome the limitations of traditional cryogen-cooled technology for canister air analysis and provide compatibility with both high- and low-concentration samples on a single analytical platform, even in a single automated sequence. Two CIA Advantage models are available. The CIA Advantage-T uses a mass-flow controller for accurate sampling of large volumes, making it ideal for analysing trace-level components. The CIA Advantage-HL model has the added capability of loop (low-volume) sampling, giving it the versatility to handle both high- and low-concentration samples (and for screening unknowns). These sampling options, together with the ability to split sample flows, mean that CIA Advantage systems can accommodate component concentrations ranging from ppt to low-percent levels. This is achieved while retaining the robust cryogen-free operation and outstanding analytical performance inherent to all Markes' systems. In this article, we use four case studies to demonstrate the power and versatility of the CIA Advantage for canister analysis.

### Case Study 1 – CIA Advantage analysis of 'air toxics' in accordance with US EPA Method TO-15

'Air toxics' comprise hazardous air pollutants ranging in volatility from freons to hexachlorobutadiene. They are usually present at sub-ppb or low ppb concentrations in air, requiring that the whole sample be transferred to the GC (a 'splitless' analysis), to ensure sufficient sensitivity.

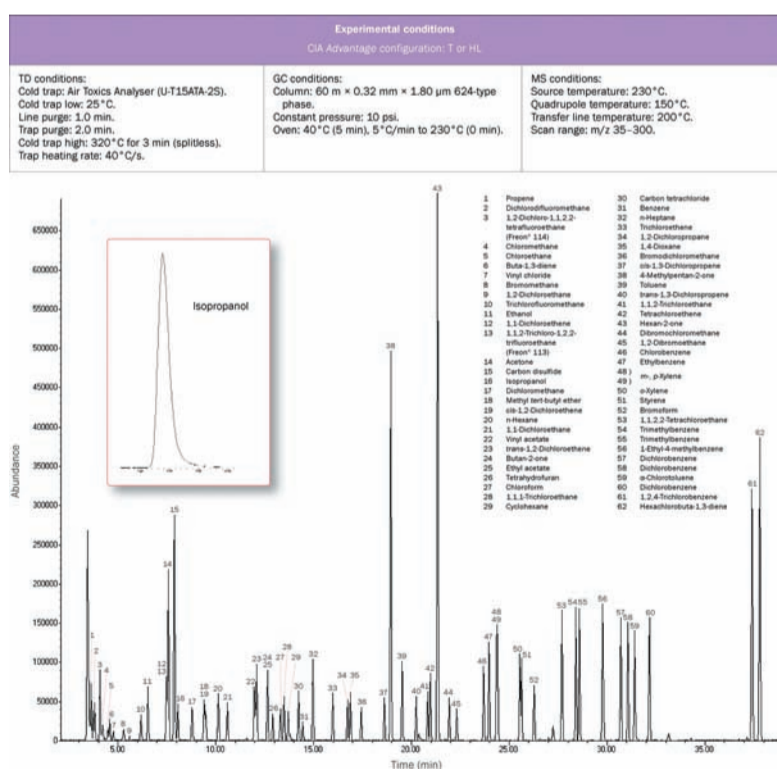


Figure 1. Total ion chromatogram for a 1 L standard containing 1 ppb air toxics, analysed splitless, cryogen-free and in full-scan mode using CIA Advantage with GC/MS (quad), according to US EPA Method TO-15. The inset shows the excellent Gaussian peak shape in an extracted-ion chromatogram of isopropanol (m/z 45)

Figure 1 shows the total ion chromatogram obtained from analysis of 1 L of a 1 ppb 'air toxics' standard using the CIA Advantage with GC and quadrupole MS in full-scan mode. The trap desorption efficiency is illustrated by the excellent peak shape of early-eluting components such as isopropanol.

A further benefit of the CIA Advantage for the analysis of these challenging samples is 'backflush' desorption of the focusing trap (for example, the direction of gas flow through the focusing trap during sampling is reversed during desorption). This makes it possible to use more than one sorbent in the focusing trap, allowing a wide volatility range of compounds to be quantitatively retained and efficiently desorbed/analysed.

In applications requiring analysis of both high- and low-concentration analytes in the same sample, it is important that both low-volume (loop-sampled) and high-volume (mass-flow-controlled) samples can be compared. To illustrate this, the CIA Advantage-HL was used to sample different volumes of the air toxics standard, and Figure 2 shows the response for each sample volume for eight representative compounds.

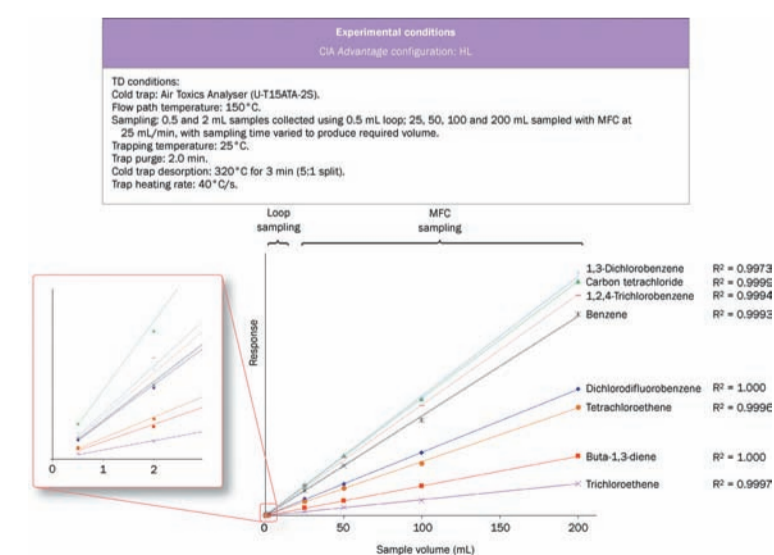


Figure 2. Responses for loop sampling (at 0.5 and 2 mL), and mass-flow-controlled sampling (at 25, 50, 100 and 200 mL) for selected compounds from an air toxics standard, showing that a single curve can be fitted to both sets of points. Vertical scaling has been applied to some of the plots to allow them all to be shown on the same axes

The RSD (relative standard deviation) for the vast majority of the 62 compounds in the air toxics standard was <15% run-to-run, despite the wide range of sample volumes used. Moreover, carryover was not detected for 82% of the compounds, and was below 0.07% in all cases. This feature of the CIA Advantage is explored in more detail in the next study.

## Case Study 2 – Running high- and low-concentration samples

If a system is to be suitable for analysing both low- and high-concentration samples, it is absolutely essential that sample carryover is minimal. Otherwise, multiple blanks will be required between samples, or, more seriously, the concentration of target compounds in low-concentration samples can be over-estimated. Figure 3 demonstrates that the CIA Advantage recovers quickly from being subjected to an overloaded sample. Taking the highest-boiling compound in the list, 1,2,4-trichlorobenzene, just 185 pg was present in the subsequent blank run, compared to 303ng in the original.

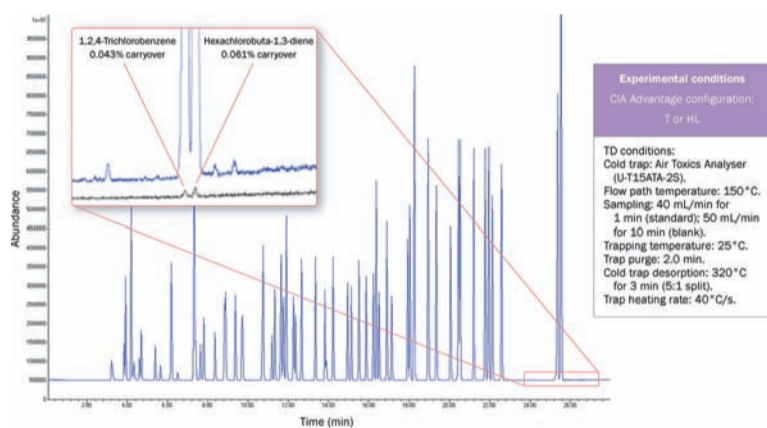


Figure 3. Main image: Low-split analysis of a 40mL sample of a 1 ppm 62-component air toxics standard (i.e. a heavily overloaded sample). Inset: Expansion of the peaks for 1,2,4-trichlorobenzene and hexachlorobuta-1,3-diene, with the subsequent low-split analysis of a 500mL nitrogen blank added in black, showing very low carryover even for these late-eluting components

It is also important to demonstrate that the system can run splitless, to guarantee maximum sensitivity for low-concentration samples. The CIA Advantage can do this without any reduction in the quality of the peak shape, as shown in Figure 4.

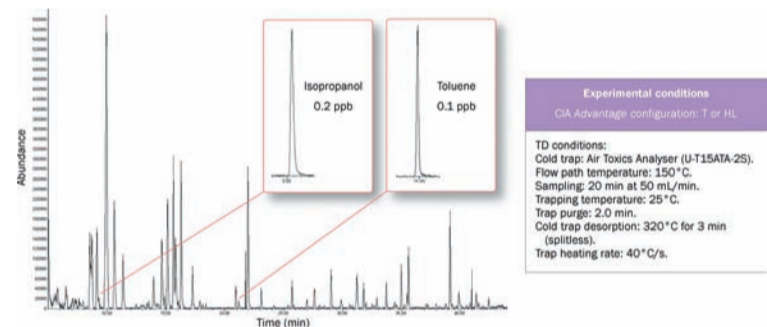


Figure 4. A low-level rural air sample, highlighting the excellent peak shape achieved in the extracted-ion chromatograms of isopropanol and toluene following splitless analysis using the CIA Advantage

## Case Study 3 – Extending the range of component quantitation ('High/Low' analysis)

To ensure quantitative measurement of trace-level components in complex matrices, a highly concentrated sample might need to be introduced to the GC/MS. However, the mass of more abundant constituents may then exceed the capacity of a highly resolving column, resulting in column and detector overload. In this situation, the CIA Advantage-HL model can first run a low-volume sample from the canister to facilitate measurement of the high-concentration components, and then run a larger volume of sample to analyse the trace-level components ('High/Low' analysis).

Figure 5 shows an example of this for a highly complex diesel sample. The black trace shows the results from a low-volume loop injection, which gives good data for high-concentration components. A higher-volume sample is then introduced using the mass flow controller (MFC), allowing measurement of the trace components (see inset).

Overall, accurate quantitation can be obtained over a concentration range spanning up to four orders of magnitude. Harnessing the added flexibility of splitting the sample flow could extend this range even further if required.

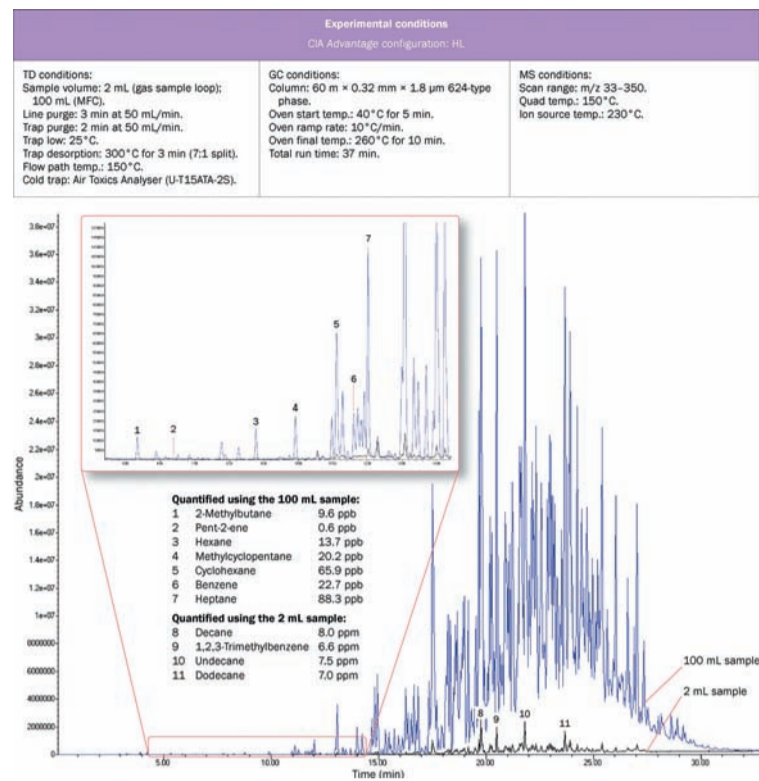


Figure 5. High-concentration diesel fraction vapours collected into a canister; selected peaks are indicated and their approximate concentrations given. Black trace: 2mL sample taken using a gas loop. Blue trace: 100mL sample taken using an MFC. Inset: Zoomed-in plot, demonstrating the greater sensitivity for the lighter VOCs that results from using MFC sampling

## Case Study 4 – Quantitative analysis of 'ozone precursors'

The trapping technology incorporated into the CIA Advantage gives excellent results for highly volatile compounds. Of current interest are the so-called 'ozone precursors', comprising hydrocarbons ranging in volatility from acetylene (ethyne) to trimethylbenzene, and deriving primarily from vehicle emissions. Recent regulations require round-the-clock sampling of these species in major urban centres, in order to monitor the link between periods of high traffic density and high pollution levels.

Of all the ozone precursors, the C<sub>2</sub> hydrocarbons present a particular challenge due to their extremely high volatility and small molecular size. Of these, acetylene (b.p. -89°C), is the most difficult to trap. The CIA Advantage is adept at handling compounds as volatile as this without liquid cryogen coolant, due to Markes' powerful combination of trap dimensions, sorbent capacity and electrical cooling. An example of the data that can be obtained is shown in Figure 6.

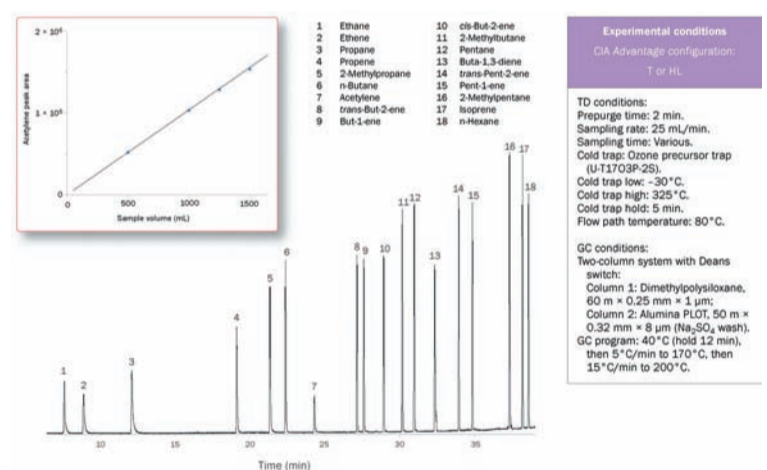


Figure 6. Splitless analysis of the C<sub>2</sub> to C<sub>6</sub> portion of an ozone precursor standard (2–10ng of components on-column) using an alumina PLOT column. Even though splitless injection was used for maximum sensitivity, the peak shape of the early-eluting compounds remains good. Inset: Quantitative cryogen-free retention of acetylene from air volumes up to 1.5 L

## Conclusions

The data presented in this article clearly demonstrates the ability of CIA Advantage systems to reliably accommodate the widest possible range of sample volumes and concentrations.

As well as analytical excellence over the full range of canister-compatible applications, the CIA Advantage offers the cost saving of cryogen-free operation. Moreover, the heated internal lines and efficient purge steps combine to avoid the problem of carryover, even with the least volatile compounds of interest.

This negligible carryover means that canister analysis can be confidently undertaken on samples of unknown concentration, facilitating automation and therefore increasing productivity. The flexibility of the CIA Advantage-HL model also allows 'High/Low' analysis (using both loop and MFC sampling) to be carried out on every sample if required.