

Thermal Desorption Technical Support

Note 99: Using the CIA Advantage for automated cryogen-free analysis of canister air and gas

Key Words:

Canisters, US EPA Method TO-15, ozone precursors, air toxics, greenhouse gases

Summary

The *CIA Advantage* is an advanced system for the automated analysis of VOCs in air or gas sampled using canisters. This Application Note describes five *CIA Advantage* applications, demonstrating the system's ability to provide excellent analytical performance and versatility.



Foreword

Canisters are one of a suite of air sampling technologies for VOCs that are subsequently focused and analysed using thermal desorption with GC(MS). Canisters complement other air sampling approaches (pumped sorbent tubes, diffusive (passive) sampling, online air monitoring, *etc.*) – for their relative merits, and discussion of when each is best applied, see Markes' TDTs 79.

Introduction

With growing concern over the harmful effects of longterm 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 Application Note, we use five 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 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 (*i.e.* 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 this case, an Air Toxics Analyser trap was used, containing three sorbents tailored to the air toxics range.

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 an air toxics standard, and Figure 2 shows the response for each sample volume. Relative response factors, RSDs, R^2 values and absolute carryovers (over the whole concentration range) for all 62 compounds are given in Table A1 (see Appendix). The quality of the result is shown by the RSD (relative standard deviation)* for nearly all the compounds being <15% run-to-run, despite the wide range of sample volumes used. The flexibility of the CIA *Advantage* to analyse both high- and low-concentration samples in one sequence is shown by the fact that carryover cannot be detected for 82% of the compounds, and is below 0.07% in all cases. This feature of the CIA *Advantage* is explored in more detail in the next study.

* RSDs are calculated from the relative response factors across the entire calibration range (0.5–200 mL).

Experimental conditions CIA Advantage configuration: T or HL		
<p>TD conditions: Cold trap: Air Toxics Analyser (U-T15ATA-2S). Cold trap low: 25°C. Line purge: 1.0 min. Trap purge: 2.0 min. Cold trap high: 320°C for 3 min (splitless). Trap heating rate: 40°C/s.</p>	<p>GC conditions: Column: 60 m × 0.32 mm × 1.80 μm 624-type phase. Constant pressure: 10 psi. Oven: 40°C (5 min), 5°C/min to 230°C (0 min).</p>	<p>MS conditions: Source temperature: 230°C. Quadrupole temperature: 150°C. Transfer line temperature: 200°C. Scan range: m/z 35–300.</p>

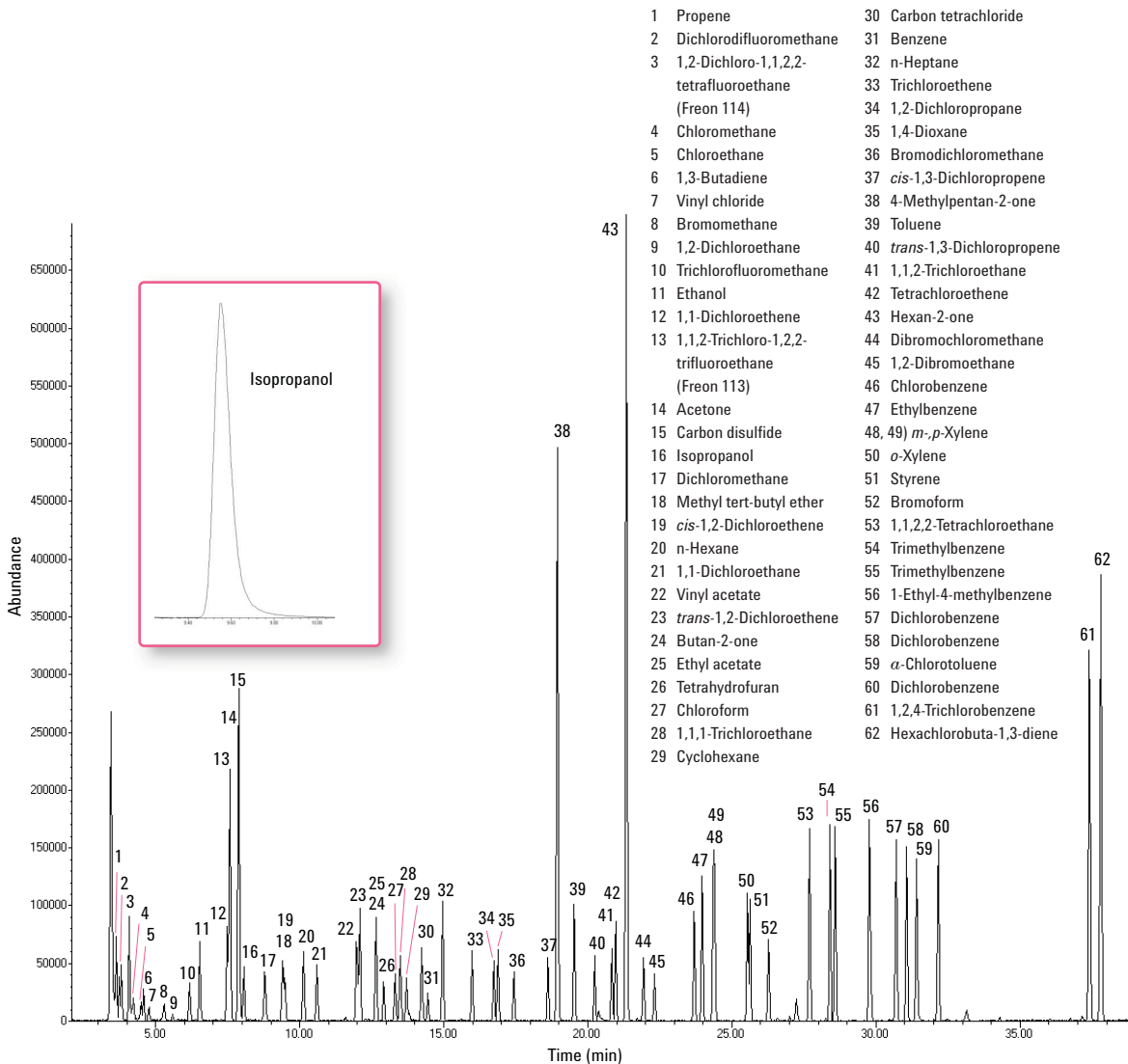


Figure 1. Total ion chromatogram for a 1 L standard containing 1 ppb air toxics, analysed splitless, cryogen-free and in full-scan mode using CIA Advantage with GC/MS (quad), according to US EPA Method TO-15. The inset shows the excellent Gaussian peak shape in an extracted-ion chromatogram of isopropanol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

Experimental conditions
CIA Advantage configuration: HL

TD conditions:

Cold trap: Air Toxics Analyser (U-T15ATA-2S).

Flow path temperature: 150°C.

Sampling: 0.5 and 2 mL samples collected using 0.5 mL loop; 25, 50, 100 and 200 mL sampled with MFC at 25 mL/min, with sampling time varied to produce required volume.

Trapping temperature: 25°C.

Trap purge: 2.0 min.

Cold trap desorption: 320°C for 3 min (5:1 split).

Trap heating rate: 40°C/s.

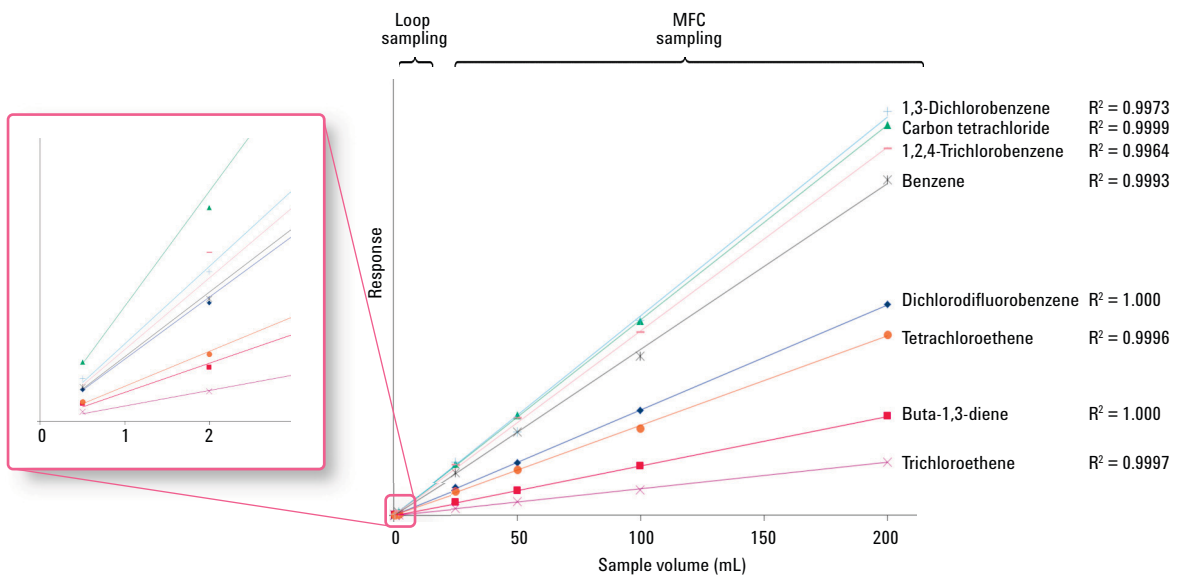


Figure 2. Responses for loop sampling (at 0.5 and 2 mL), and mass-flow-controlled sampling (at 25, 50, 100 and 200 mL) for selected compounds from an air toxics standard, showing that a single curve can be fitted to both sets of points. Vertical scaling has been applied to some of the plots to allow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

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 303 ng in the original.

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.

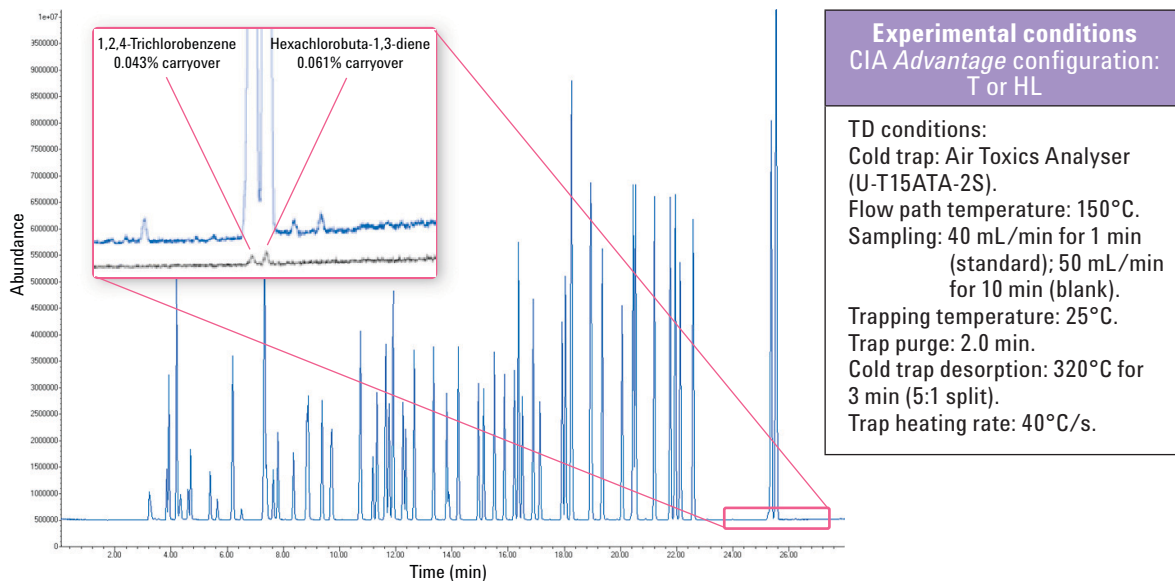


Figure 3. Main image: Low-split analysis of a 40 mL sample of a 1 ppm 62-component air toxics standard (i.e. a heavily overloaded sample). Inset: Expansion of the peaks for 1,2,4-trichlorobenzene and hexachlorobuta-1,3-diene, with the subsequent low-split analysis of a 500 mL nitrogen blank added in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

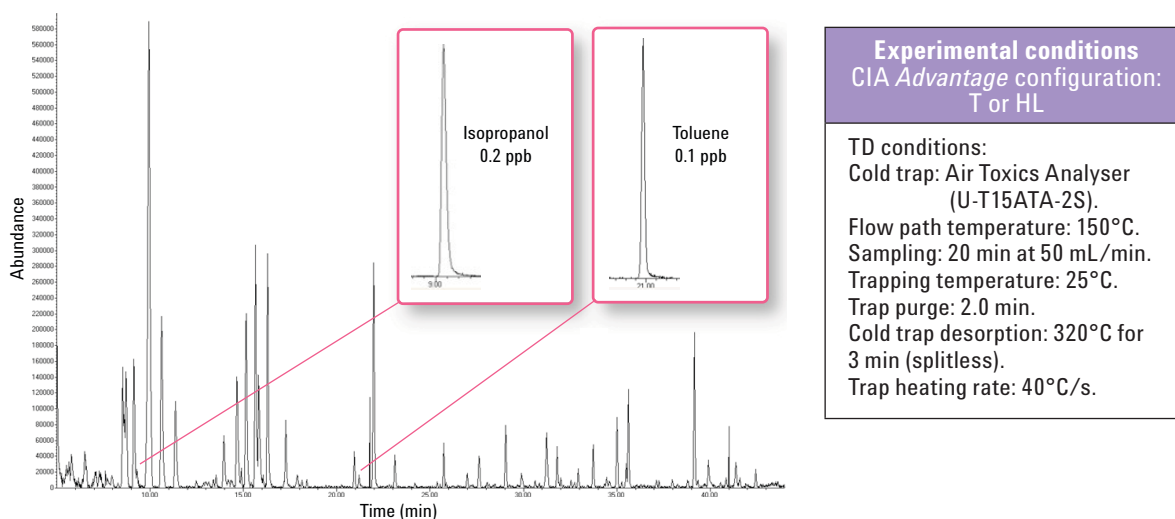


Figure 4. A low-level rural air sample, highlighting the excellent peak shape achieved in the extracted-ion chromatograms of isopropanol and toluene following splitless analysis using the CIA *Advantage*

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

Experimental conditions CIA <i>Advantage</i> configuration: HL		
<p>TD conditions: Sample volume: 2 mL (gas sample loop); 100 mL (MFC). Line purge: 3 min at 50 mL/min. Trap purge: 2 min at 50 mL/min. Trap low: 25°C. Trap desorption: 300°C for 3 min (7:1 split). Flow path temp.: 150°C. Cold trap: Air Toxics Analyser (U-T15ATA-2S).</p>	<p>GC conditions: Column: 60 m × 0.32 mm × 1.8 µm 624-type phase. Oven start temp.: 40°C for 5 min. Oven ramp rate: 10°C/min. Oven final temp.: 260°C for 10 min. Total run time: 37 min.</p>	<p>MS conditions: Scan range: m/z 33–350. Quad temp.: 150°C. Ion source temp.: 230°C.</p>

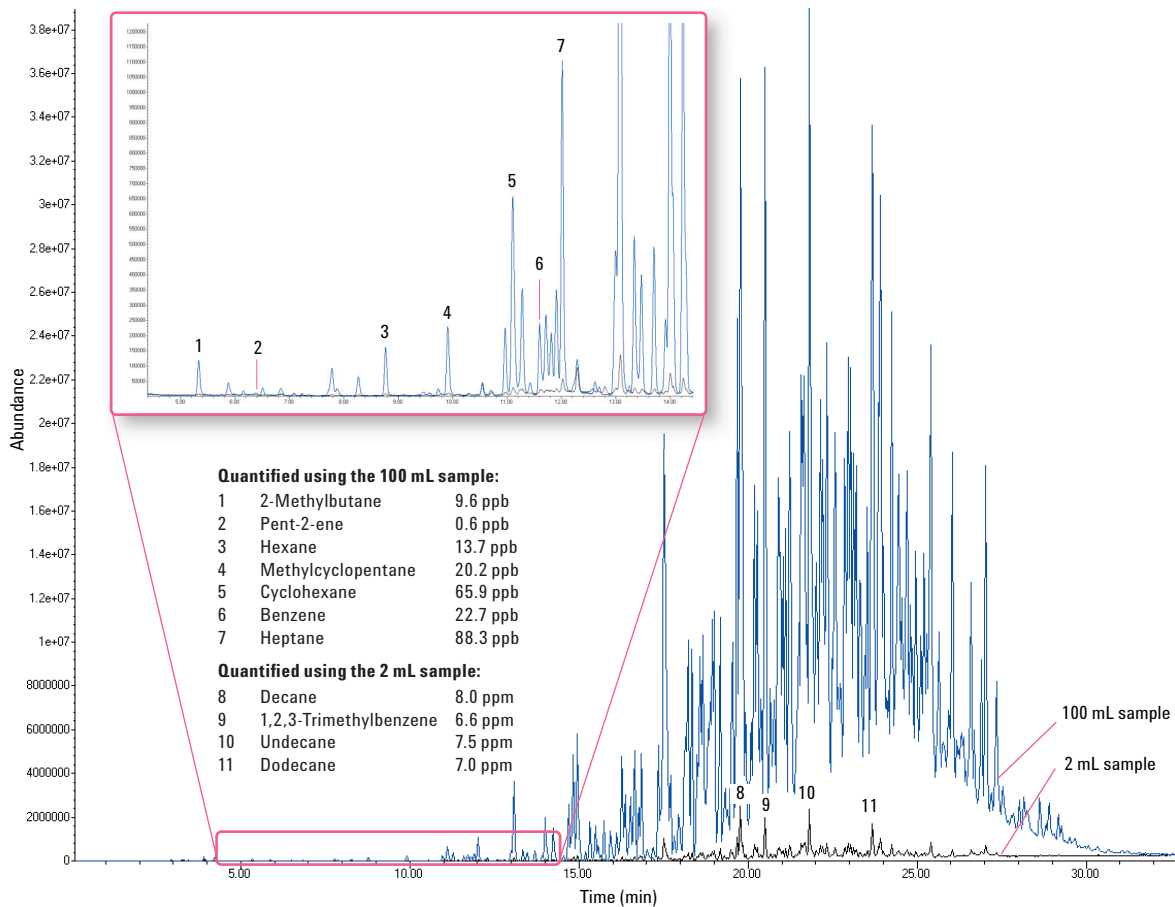


Figure 5. High-concentration diesel fraction vapours collected into a canister; selected peaks are indicated and their approximate concentrations given. Black trace: 2 mL sample taken using a gas loop. Blue trace: 100 mL sample taken using an MFC. Inset: Zoomed-in plot, demonstrating the greater sensitivity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

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.

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 monitoring 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 C₂ 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' uniquely powerful combination of trap dimensions, sorbent capacity and electrical cooling. An example of the data that can be obtained is shown in Figure 6.

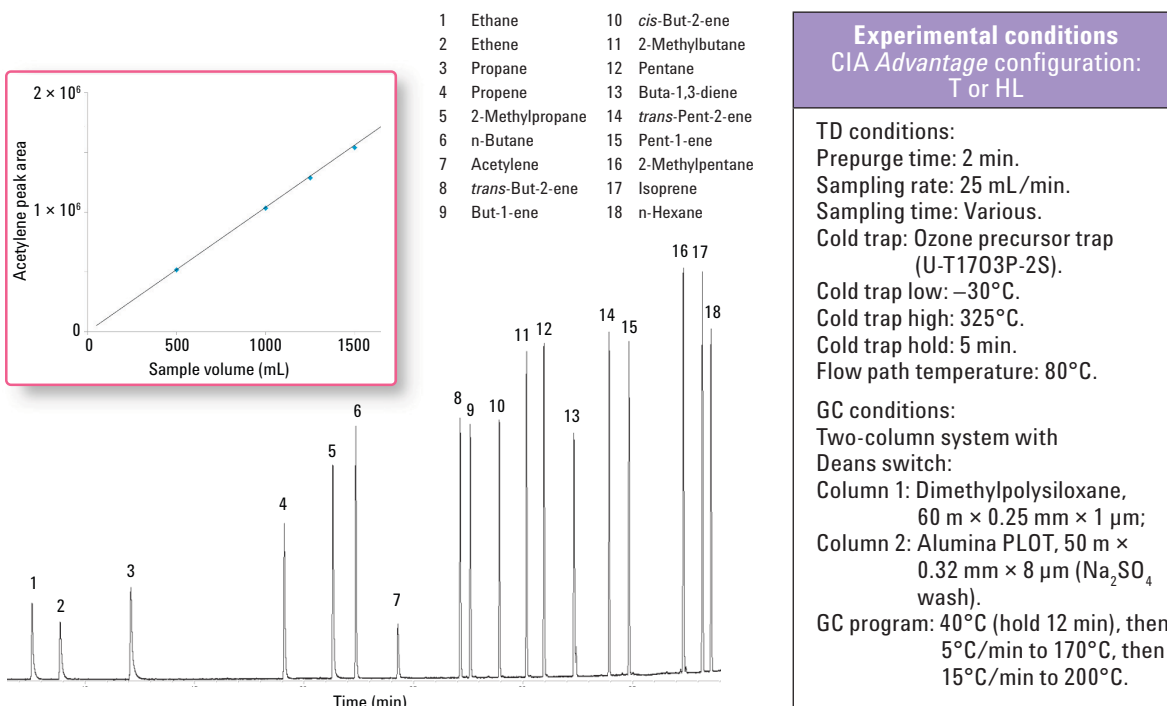


Figure 6. Splitless analysis of the C₂ to C₆ portion of an ozone precursor standard (2–10 ng of components on-column) using an alumina PLOT column. Even though splitless injection was used for maximum sensitivity, the peak shape of the early-eluting compounds remains good. Inset: Quantitative cryogen-free retention of acetylene from air volumes up to 1.5 L

Experimental conditions CIA Advantage configuration: T or HL
TD conditions: Cold trap: Greenhouse Gases Analyser (U-T16GHG-2S). Flow path temperature: 120°C. Sampling: from 2.5 min (at 10 mL/min) to 10 min (at 50 mL/min)(sample passed through a Nafion dryer to remove moisture). Trapping temperature: -30°C. Trap purge: 1.0 min. Cold trap desorption: 300°C for 3 min (splitless).
GC conditions: Column: J&W GS-AL/KCl 50 m × 0.53 mm with 5 m × 0.18 mm fused silica on MS end acting as a restrictor. Constant pressure: 18 psi. Oven: 60°C (4 min) then 8°C/min to 150°C (0 min).
MS conditions: Quad temperature: 150°C. Source temperature: 230°C. Full scan range: m/z 10–300. SIM ions (dwell time): 30 (100), 69 (100), 119 (20), 127 (100).

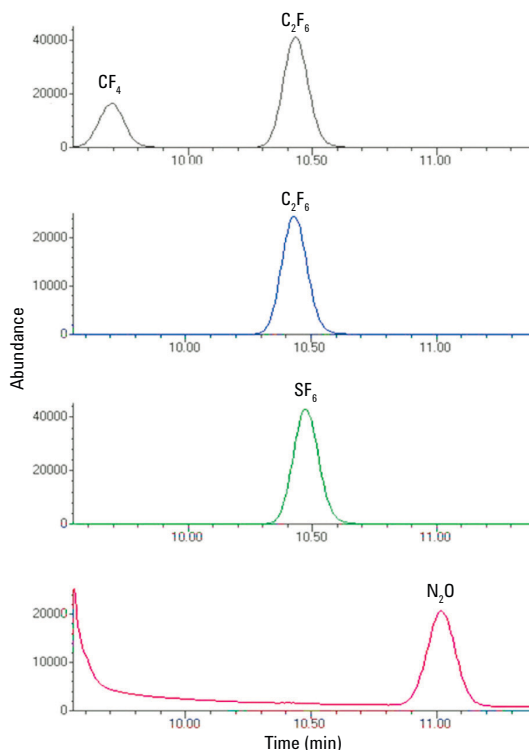


Figure 7. Extracted-ion spectra for: (a) CF₄ (m/z 69, CF₃); (b) C₂F₆ (m/z 119, C₂F₅); (c) SF₆ (m/z 127, SF₅); (d) N₂O (m/z 30, NO) from a full-scan analysis of 25 mL of a 100 ppb gas standard

Case study 5 – Detecting perfluorocarbons

Ultra-volatile perfluorocarbons are of concern as long-lived greenhouse gases, despite being present in the atmosphere at very low concentrations. The most volatile of these, carbon tetrafluoride (b.p. -128°C) has a half-life in the atmosphere of many thousands of years, and has more than 5000 times the global warming potential of CO₂. Similarly, hexafluoroethane (b.p. -78°C) has over 10,000 times the global warming potential of CO₂. The extreme volatility of such compounds makes them very difficult to trap and measure at trace levels.

Figure 7 shows the exceptional performance of the cryogen-free trapping technology used in the CIA Advantage in focusing ultra-volatile greenhouse gases including perfluorocarbons.

Conclusions

The data presented in this Application Note 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.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

For More Information

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Appendix

Compound	Average relative response factor	RSD (%)	R ²	Carryover (%)
Acetone	870	11	0.9980	ND
Benzene	1285	7	0.9993	ND
Bromodichloromethane	1306	12	0.9995	ND
Bromoform	1017	14	0.9988	ND
Bromomethane	1364	11	0.9992	ND
Buta-1,3-diene	1279	9	1.0000	ND
Butan-2-one	846	10	0.9989	ND
Carbon disulfide	5346	12	0.9991	ND
Carbon tetrachloride	4748	13	0.9999	ND
Chlorobenzene	1362	8	0.9996	ND
Chloroethane	927	12	0.9990	ND
Chloroform	4614	11	0.9985	ND
Chloromethane	1823	9	0.9935	ND
<i>a</i> -Chlorotoluene	2472	22	0.9930	0.030
Cyclohexane	2447	9	0.9993	ND
Dibromochloromethane	1091	10	0.9994	ND
1,2-Dibromoethane	989	10	0.9993	ND
1,2-Dichlorobenzene	1494	8	0.9978	0.050
1,3-Dichlorobenzene	1578	9	0.9973	0.053
1,4-Dichlorobenzene	1614	8	0.9981	0.062
Dichlorodifluoromethane	4908	10	1.0000	ND
1,1-Dichloroethane	3677	10	0.9987	ND
1,2-Dichloroethane	893	10	0.9989	ND
1,1-Dichloroethene	1031	9	0.9986	ND
<i>cis</i> -1,2-Dichloroethene	1142	11	0.9990	ND
<i>trans</i> -1,2-Dichloroethene	1064	10	0.9995	ND
Dichloromethane	2128	11	0.9979	ND
1,2-Dichloropropane	538	9	0.9996	ND
<i>trans</i> -1,3-Dichloropropene	1011	10	0.9991	ND
<i>cis</i> -1,3-Dichloropropene	898	11	0.9998	ND
1,4-Dioxane	321	12	0.9999	ND

Compound	Average relative response factor	RSD (%)	R ²	Carryover (%)
Ethanol	1185	13	0.9928	ND
Ethyl acetate	451	9	0.9981	ND
Ethylbenzene	727	11	0.9996	ND
1-Ethyl-4-methylbenzene	850	8	0.9975	0.032
Freon 113	2414	10	0.9980	ND
Freon 114	2593	15	0.9981	ND
<i>n</i> -Heptane	471	12	0.9998	ND
Hexachlorobuta-1,3-diene	1119	17	0.9957	0.043
<i>n</i> -Hexane	2769	11	0.9990	ND
Hexan-2-one	673	7	0.9995	ND
Isopropanol	2961	8	0.9967	ND
4-Methylpentan-2-one	589	17	0.9995	ND
Methyl tert-butyl ether	ether	1575	15	0.9984
Propene	1406	4	0.9987	ND
Styrene	1456	11	0.9990	0.014
1,1,2,2-Tetrachloroethane	1461	10	0.9989	ND
Tetrachloroethene	686	8	0.9996	ND
Tetrahydrofuran	2153	8	0.9991	ND
Toluene	1896	6	0.9999	ND
1,2,4-Trichlorobenzene	1540	8	0.9994	0.061
1,1,1-Trichloroethane	5096	11	0.9982	ND
1,1,2-Trichloroethane	587	10	0.9986	ND
Trichloroethene	653	9	0.9997	ND
Trichlorofluoromethane	5410	12	0.9972	0.022
1,2,4-Trimethylbenzene	1146	9	0.9990	0.027
1,3,5-Trimethylbenzene	1171	10	0.9990	0.042
Vinyl acetate	401	11	0.9975	ND
Vinyl chloride	1545	11	0.9987	ND
<i>m</i> - and <i>p</i> -Xylene	943	7	0.9990	ND
<i>o</i> -Xylene	905	7	0.9993	ND

Table A1. Relative response factors, RSDs, R² values and absolute carryovers for the TO-15 compounds analysed in Case study 1. RSDs are calculated from the relative response factors across the entire calibration range (0.5–200 mL)

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