One system for trace- and high-level air monitoring – the future of ambient air and soil gas analysis

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Abstract

As the harmful effects of low-level exposure to hazardous air pollutants become more evident, larger sample volumes combined with lower detection limits are needed. The trade-off can be the loss of ability to analyze the upper concentration range of a sample (necessary for most source-level and remediation-site testing). Historically, dilution of these samples was necessary prior to analysis. Dilution of air samples has traditionally been performed in several ways; however, this can limit applicability and has the potential to bias results.

CIA *Advantage*™ systems have been designed to allow samples comprising a wide range of concentrations to be analyzed without the need for dilution.

Using a combination of loop sampling, large-volume sampling and the ability to split flows, analyte levels from ppt to percent can be analyzed on one instrument, thereby dramatically increasing the dynamic range.

System setup

Typically, samples are collected into canisters of varying sizes. US EPA method TO-15 provides the method for ambient air analysis, but other areas of analysis, such as vapor intrusion and soil gas studies, effectively extend the scope of canister analysis.

Modern analytical systems for air monitoring applications are now expected to manage a wider range of sample concentrations. To do this effectively on a single analytical system, a new approach is required.

The CIA *Advantage,* an automated canister system incorporating the industry-leading UNITY 2™ thermal desorber, addresses this challenge.

For low concentrations, a large-volume mass-flow-controlled (MFC) sample is collected onto the UNITY 2 focusing trap. The trap is then desorbed, transferring the sample direct to the GC/MS.
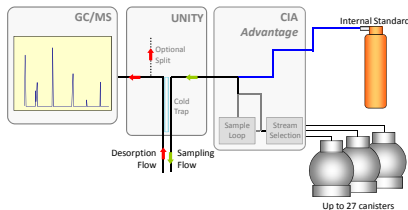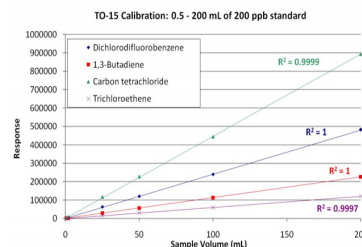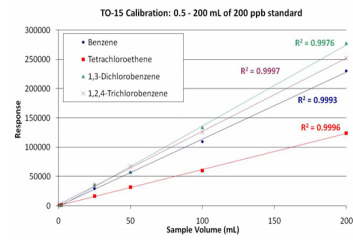
For high-concentration samples, or those with unknown concentration, a low-volume sample loop is employed. The loop is filled with sample and then transferred to the same cold trap used for MFC sampling. As well as the low volume, additional effective dilution can be achieved by using a split during transfer to the GC/MS.

Combining these approaches, sample volumes can easily range from 0.1–1000 mL, with split ratios increasing from splitless to 100:1, providing analysis over at least seven orders of magnitude.

System linearity

The first test of whether such a system is suitable to be used across a wide concentration range, is to prove that a single calibration curve can be used for both loop and MFC samples.

The calibration curves below were generated using a US EPA TO-15 gas standard with a combination of two loop and four MFC samples, for eight representative compounds from the complete set. An internal standard was added *via* a second loop that is common to both sample paths.

TO-15 Calibration: 0.5 - 200 mL of 200 ppb standard

- Benzene — $R^2 = 0.9976$
- Tetrachloroethene — $R^2 = 0.9997$
- 1,3-Dichlorobenzene — $R^2 = 0.9993$
- 1,2,4-Trichlorobenzene — $R^2 = 0.9996$

TO-15 Calibration: 0.5 - 200 mL of 200 ppb standard

- Dichlorodifluorobenzene — $R^2 = 0.9999$
- 1,3-Butadiene — $R^2 = 1$
- Carbon tetrachloride — $R^2 = 1$
- Trichloroethene — $R^2 = 0.9997$

The R^2 values demonstrate excellent linearity, clearly demonstrating that a calibration curve incorporating small-volume loop samples and high-volume MFC samples can be achieved.

System reproducibility

Equally important is reproducibility from run to run. A simple way to demonstrate this is to show the reproducibility of internal standard response over a number of runs. The table below presents the data obtained, and demonstrates impressive relative standard deviation (RSD) values.

Compound	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average	%RSD
1,2-Dichloroethane-d4	117961	114135	118691	121384	120701	119748	118770	1.99
Toluene-d8	59260	60010	60039	59622	61173	60801	60151	1.09
Bromofluorobenzene	29976	30491	30664	30293	30495	29984	30317	0.86

Trace- and high-level samples

If a system is to be suitable for both high-level and trace-level analysis, it is absolutely essential that sample carryover is minimal. Otherwise, it becomes impossible to run low-level samples immediately after a high-concentration sample.

This either leads to significant time cleaning the system with blanks until all target compounds are below reporting levels, or in the worst case to over-estimation of the concentration of target compounds in low-concentration samples.

Below is a demonstration of the CIA *Advantage* system immediately recovering from being subjected to an extremely overloaded sample.

Blue chromatogram – 40 mL of 1ppm std
Black chromatogram – 500 mL N₂ blank

Close-up view
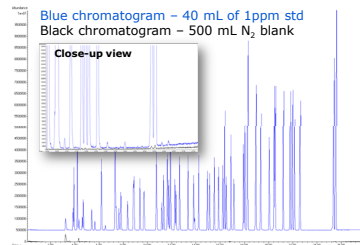
Taking trichlorobenzene as an example, the peak area in the blank run following overloading of the system is only 0.08%. This is effectively only 0.02 ppb.

It is also important for a system to be able to analyse samples without a split, to guarantee maximum sensitivity for low-concentration samples.

The following example of a low-level rural air sample highlights the excellent peak shape achieved from a splitless analysis using CIA *Advantage* systems.

1 L Rural air sample

IPA: 0.2 ppb
Toluene: 0.1 ppb
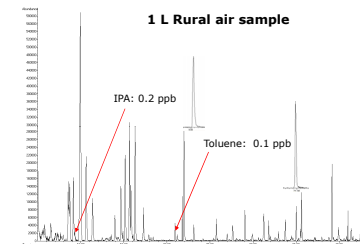
Conclusions

The data presented clearly highlight the capabilities of CIA *Advantage* systems to reliably analyse the widest possible range of sample concentrations.

Automated canister analysis can be carried out on a variety of sample types, with confidence that high-concentration samples will not affect the analysis of subsequent low-level samples. This allows the user to use a low-volume screening method on a number of canisters, with (if necessary), a second larger-volume sample being run to accurately assess samples with lower concentrations.

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Sample Loop | Stream Selection
Internal Standard
Desorption Flow | Sampling Flow
Up to 27 canisters

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