Fast and Reliable Trace Gas Analysis – Improved Detection Limits for the Agilent 490 Micro GC

Technical Overview

Trace gas analysis is a challenge in today's world. The ability to analyze lower component levels enables you to do better quality control, and gain more reliable results. To meet your requirement for fast and accurate gas analysis outcomes, we have made continuous product quality improvements resulting in lower limits of detection (LOD) for our gas analysis platform – the Agilent 490 Micro GC.

To match your gas application requirements, you can equip the 490 Micro GC with one to four independently controlled column channels. Each column channel is a complete miniturized gas chromatograph with:

- Electronic carrier gas control,
- Micro-machined injector,
- Narrow-bore analytical column, and
- Micro thermal conductivity detector (µTCD).

This setup provides fast gas analysis, with typical run times of 30 to 90 seconds.

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Up to Five Times Improved Detection Limit

The limit of detection (LOD) for chromatography systems depends on the analyte peak signal compared to the baseline noise. Column type influences chromatographic separation and peak shape. For gas analysis, a wall-coated open tubular (WCOT) column gives the sharpest peaks, and provides the best signal-to-noise ratios (S/N). Porous layer open tubular (PLOT) columns and micro-packed columns have solid stationary phases with less efficiency. They give broader peaks and, therefore, slightly higher detection limits.

Until recently, LOD specifications were set to 1 ppm for WCOT columns and 10 ppm for PLOT and micro-packed columns. The latest enhancements for the Agilent 490 Micro GC show up to five times improved LODs, down to 0.5 ppm for WCOT columns, 2 ppm for PLOT columns, and 10 ppm for micro-packed columns. Table 1 gives an overview of the detection limits per column type. You can find more details about instrument specifications in the 490 Micro GC Data Sheet [1].

Table 1.   Agilent 490 Micro GC Specifications for LOD

Column type	LOD (ppm)*
Wall coated open tubular column Agilent CP-Sil 5 CB, CP-Sil 13 CB, CP-Sil 19 CB, and CP-WAX 52 CB	0.5
Porous layer open tubular and micro-packed column Molsieve 5A, PoraPLOT Q, PoraPLOT U, Aluminum oxide, SilicaPLOT, MES, and HayeSep A	2
Micro-packed column CP-COx	10

* Detection limits are typical for selected components provided that the proper column length and chromatographic conditions are used.

Example for WCOT Columns — 0.5 ppm Hydrocarbons on the CP-Sil 5 CB Column

Analysis of hydrocarbons is a typical application for the Agilent CP-Sil 5 CB column. This WCOT column is also used to analyze the high end of this sample in the natural gas analyzers that are based on the 490 Micro GC. Agilent Application Note 5991-0275EN [2] highlights this capability. The chromatogram in Figure 1 exhibits baseline separation and substantial peak area for *n*-hexane, *n*-heptane, and *n*-octane at the detection limit (approximately 0.5 ppm per compound).

Repeatability, calculated for 10 replicate analyses at twice the detection limit for *n*-heptane, is 1.3 % relative standard deviation (RSD) for concentration and 0.05 % for retention time. Figure 2 depicts an overlay of five of these replicate runs.
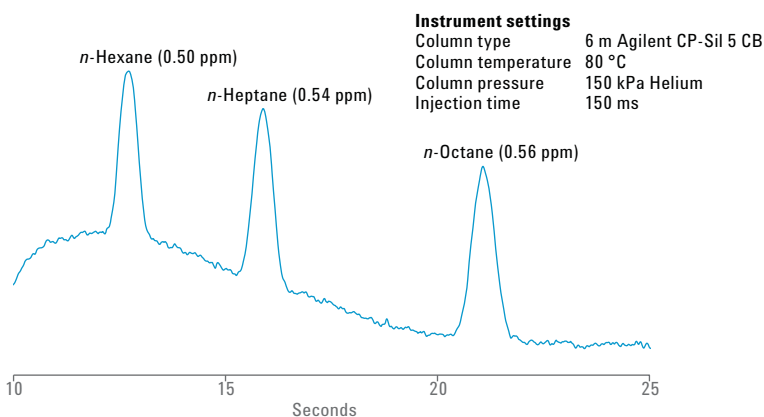

Figure 1.   *The Agilent CP-Sil 5 CB column channel shows excellent peak area and baseline separation at the detection limit for three alkanes.*
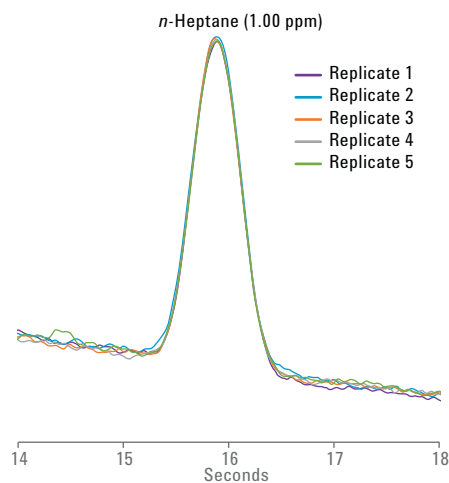

Figure 2.   *Overlay of five replicate runs at 1.08 ppm n-heptane demonstrates reliable repeatability.*

Example for PLOT Columns — C2 Hydrocarbons Down to 2 ppm on PoraPLOT U

The 490 Micro GC equipped with an Agilent PoraPLOT U column is used for the fast analysis of nitrogen, carbon dioxide, methane, ethane, and propane. Agilent Application Note 5990-9508EN clearly demonstrates this capability [3]. In addition, this PLOT column delivers baseline separation of the C2 hydrocarbons. Figure 3A shows a chromatogram for ethane, ethylene, and acetylene at the 2 ppm level – its specification for LOD. Compared with the old specification, this is a five-fold improvement. In addition to excellent separation and low-ppm detection limits, the µTCD on the 490 Micro GC shows outstanding linearity. The R^2 values are 0.999, as depicted in Figure 3B.

A good repeatability is calculated at detection limit level (2 ppm), approximately 5% RSD for ethane, ethylene, and acetylene. These values are significantly decreased at 5 times the detection limit (10 ppm) to 0.55–1.18% RSD. Retention time repetability over the full range was measured at lower than 0.02 to 0.08% RSD. Tables 2 and 3 give an overview.

Acetylene (2.04 ppm)
Ethylene (2.00 ppm) Ethane (2.00 ppm)

A

Instrument settings
Column type   10 m Agilent PoraPLOT U
Column temperature   60 °C
Column pressure   150 kPa Helium
Injection time   100 ms

Seconds

B

Ethane
R² = 0.9990
Ethylene
R² = 0.9991
Acetylene
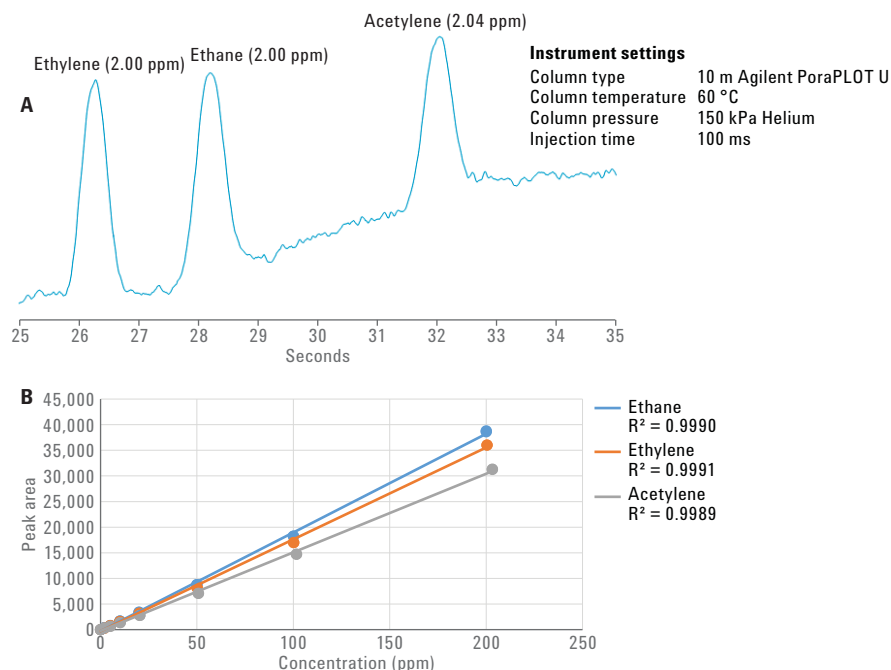R² = 0.9989

Peak area

Concentration (ppm)

Figure 3.   Chromatogram (A) shows excellent peak area and separation at the detection limit of 2 ppm. Calibration curve (B) for these compounds demonstrates good linearity.

Table 2.   Repeatability Data for Peak Area for the Ethylene, Ethane, and Acetylene Analysis

RSD % (n = 10) for concentration (ESTD) Concentration (ppm)	Ethylene	Ethane	Acetylene
2	5.08	5.37	4.37
10	0.55	1.18	1.14
200	0.12	0.21	0.15

Table 3.   Repeatability Data for Retention Time for Ethylene, Ethane, and Acetylene Analysis

RSD % (n = 10) for retention time (RT) Concentration (ppm)	Ethylene	Ethane	Acetylene
2	0.071	0.085	0.082
10	0.023	0.019	0.023
200	0.030	0.020	0.017

Example for Micro-packed Columns — 10 ppm Level Carbon Dioxide on CP-COx Column

The detection limit specification for micro-packed column type CP-COx is set to 10 ppm. This column type is typically used for the analysis of permanent gases, including carbon dioxide. Agilent application note 5990-7054EN shows an example [4]. Figure 4 shows a chromatogram of 10 ppm carbon dioxide using helium carrier gas.

Repeatability for 20 consecutive analyses at 5 times LDL specification (50 ppm) is measured at 0.16% RSD for retention time and 2.6% for external standard concentration, as shown in Table 4. An overlay of five of these runs is given in Figure 5A. Excellent linearity is determined for 10 to 300 ppm carbon dioxide; the regression coefficient for linear curve fitting for this range is 0.9999 (Figure 5B).
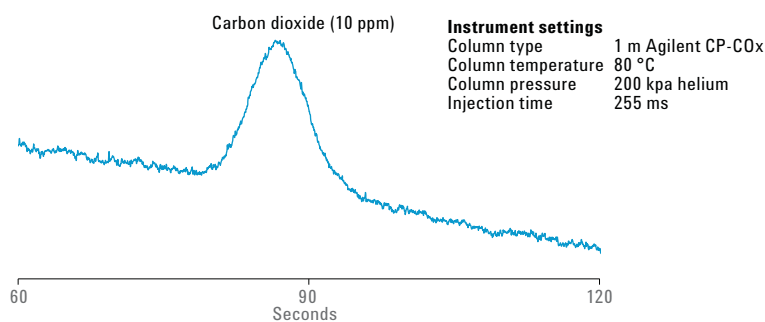

Carbon dioxide (10 ppm)

Instrument settings
Column type — 1 m Agilent CP-COx
Column temperature — 80 °C
Column pressure — 200 kpa helium
Injection time — 255 ms

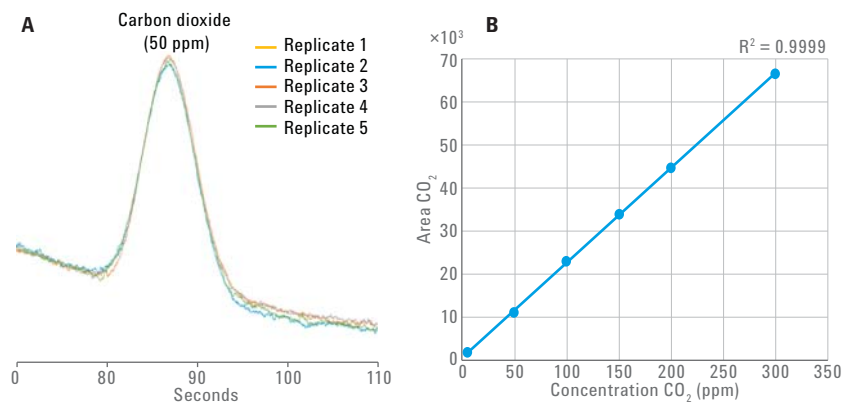*Figure 4.   LOD performance of the Agilent CP-COx column.*

Figure 5.   A) Overlay of five replicate runs of carbon dioxide at 50 ppm on an Agilent CP-COx column. B) Excellent linearity, with regression coefficient for linear curve (10–300 ppm CO_2) determined at 0.9999.

Table 4.   Repeatability Data for Carbon Dioxide on the CP-COx Column

Carbon dioxide (50 ppm)	RSD % (n = 20)
Retention time	0.16 %
Concentration; external standard method	2.6 %

Reliable Trace Analysis

The 490 Micro GC delivers sensitive gas analysis in seconds. With the recent detection limit improvements that resulted from product quality enhancements, the 490 Micro GC provides reliable trace gas analysis down to 0.5 ppm for WCOT columns, 2 ppm for PLOT columns, and 10 ppm for micro-packed columns. Contact an Agilent Representative today to find out more about Agilent Micro GC solutions for your application.

References

1. Agilent 490 Micro GC Natural Gas Analyzers, *Agilent Technologies Data Sheet*, publication number 5991-0301EN (**2012**).

2. R. van Loon, Fast Analysis of Natural Gas Using the Agilent 490 Micro GC Natural Gas Analyzer, *Agilent Technologies Application Note*, publication number 5991-0275EN (**2012**).

3. R. van Loon, Analysis of Biogas Using the Agilent 490 Micro GS Biogas Analyzer, *Agilent Technologies Application Note*, publication number 5990-9508EN (**2011**).

4. S. Darphorn-Hooijschuur, *et al*. Permanent Gases on a COX Module Using an Agilent 490 Micro GC, *Agilent Technologies Application Note*, publication number 5990-7054EN (**2012**).

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