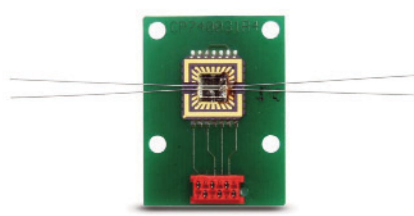
Hydrogen Detection with a TCD using Mixed Carrier Gas on the Agilent Micro GC

Application Note

Micro Gas Chromatography, Thermal Conductivity Detector



Author

Arnold Toonen
ECN
Petten, The Netherlands

Remko van Loon
Agilent Technologies, Inc.
Middelburg, The Netherlands

Abstract

This application note highlights percentage level analysis of hydrogen on an Agilent Micro GC using a mixed carrier gas. Hydrogen is typically analyzed with argon carrier gas on a thermal conductivity detector. Argon however, will result in a decreased sensitivity for the other permanent gases. Helium carrier gas is, in most cases, also not a suitable alternative. Mixtures of helium and hydrogen give nonlinear conductivity response and signal inversion with strange s-shape peaks when hydrogen concentration increases. The use of a mixture of 8.5% hydrogen in helium as the GC's carrier gas results in a hydrogen concentration in the detector above the point of inversion. The resulting negative peak for hydrogen can easily be integrated. This enables the detection of a broad range of hydrogen on the same channel as the other permanent gases, while maintaining the sensitivity for these compounds.

Introduction

The Dutch Energy Research Centre (ECN; Energieonderzoek Centrum Nederland) develops high-quality knowledge and technology for the transition to sustainable energy management with focus on energy conservation, sustainable energy, and efficient and clean use of fossil fuels. One of their research projects includes the development and optimization of biomass gasification installations and downstream gas cleaning technologies. ECN's biomass gasifier produces a clean, high-quality gas that can be used to generate power or heat, substitute natural gas, or other chemicals.

Besides other analysis equipment, an Agilent Micro GC is used for fast, accurate, onsite characterization of the gases formed by the gasification process. The Micro GC's portable field case, equipped with carrier gas supply and rechargeable batteries, provides measurements at ECN's customers site.

Thermal conductivity detector - principle of operation

A gas chromatograph with a nonselective thermal conductivity detector (TCD) typically analyzes small hydrocarbon gases. A thermal conductivity detector compares the thermal conductivity, which depends on the decomposition of a gas mixture, of two gas flows.

The GC column effluent, a mixture of sample compound and carrier gas, is connected to the measuring cell. At the same time, pure carrier gas flows through a reference cell. Both channels include electrically heated resistance wires (filaments), which are connected via a classical Wheatstone bridge circuit (Figure 1). A change in the temperature of the filament is affected by the thermal conductivity of the gas that flows around it. These temperature changes are measured as a change in electrical resistance. The signal is proportional to the concentration of the sample components.

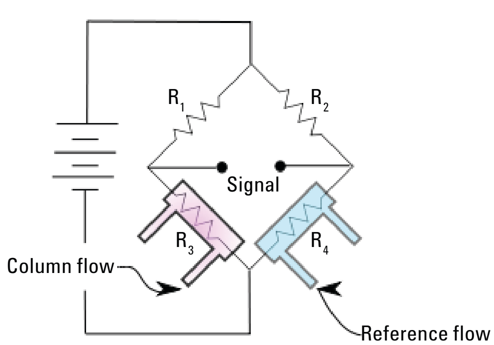


Figure 1. Schematic overview of a thermal conductivity detector.

The choice of carrier gas for GC-TCD analysis depends upon the sample compounds. Sensitivity for a compound increases when there is a larger difference in thermal conductivity between the carrier gas and that particular compound. Typically, helium is used because of its large difference in thermal conductivity compared to most compounds. However, nitrogen, hydrogen, and argon can be used as well.

The µTCD used in the Agilent Micro GC is based on the same principle. However, the µTCD is miniaturized to the dimensions of 1 × 1 cm and 20 nL internal volume for fast and more sensitive analysis (Figure on title page). Because the Micro GC is basically a gas analyzer the use of a general and sensitive µTCD for measuring the fixed gases is required.

Hydrogen analysis with a TCD using helium carrier gas

Normally, there are no strange occurrences in the thermal conductivities when mixing components, with the exception of helium-hydrogen mixtures [1]. As a result of their close thermal conductivity values, hydrogen gives a relatively low response on a TCD when using helium carrier gas. Moreover, at low concentrations, the signal for hydrogen is in the same direction as the other compounds. With increasing hydrogen concentrations, the carrier gas/component mix and, therefore, the thermal conductivity of this mix in the detector changes. This will result in a nonlinear response and inversion of the maximum of the peak. Increasing the hydrogen concentration more will eventually lead to a zero crossing and negative response on the detector [3].

Figure 2 depicts the chromatograms for increasing hydrogen concentrations using helium carrier gas on an Agilent Micro GC, showing s-shaped peaks. This example clearly shows that, as a result of the peak shape, quantification and calibration are impossible in high percentage ranges. For other instrument parameters, nonlinear responses and points of inversion are found at different hydrogen concentrations. The phenomena depend on the concentration of hydrogen and helium in the detector cell. The detector concentration is a result of the column flow, which influences elution time and peak width, concentration of hydrogen in the sample, and injected volume.

Hydrogen analysis using 8.5% hydrogen in helium carrier gas

Normally, argon is the carrier gas of choice for hydrogen analysis. However, the use of argon significantly reduces sensitivity for the other permanent gases by a factor of approximately 5 to 10. Analyzing these compounds at low concentrations requires an additional column channel that runs on helium carrier gas.

Instrument settings

Column	10 m MS5A, backflush at 11 seconds
Column temperature	80 °C
Column pressure	150 kpa, He

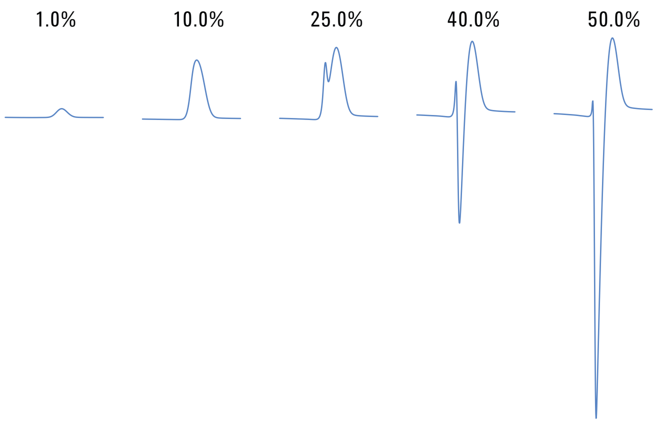


Figure 2. Peak shape of increasing hydrogen concentrations with helium carrier gas.

As an alternative, hydrogen can be mixed with the carrier gas to ensure that the concentration of hydrogen in the detector is greater than that of the point of inversion. In a study done by Cowper and DeRose, a commercially available mixture of 8.5% hydrogen and 91.5% helium was used. The mixed carrier gas resulted in sensitivities for the other compounds that were similar to that found with pure helium and a negative peak for hydrogen with no inversion [3].

A chromatogram for the analysis of permanent gases on an Agilent Micro GC equipped with a Molecular Sieve 5A column using 8.5% hydrogen in helium carrier gas mixture is shown in Figure 3. As described above, hydrogen elutes as a negative peak and all other compounds as positive peaks. The Agilent chromatography data system, OpenLAB CDS, provides tools (Figure 4) to integrate the negative hydrogen peak. Although a gas mixture is more expensive than a pure gas, the use of 8.5% hydrogen in helium carrier gas has an important advantage. It results in the analysis of up to high percentage levels hydrogen on the same analytical channel as the other permanent gases, while maintaining the sensitivity for these compounds.

Figure 5 shows a chromatogram for increasing hydrogen concentration, illustrating the extended analysis range that is possible using mixed carrier gas. R^2 value, for a calibration curve with a quadratic fit (Figure 6), was noted at 0.9992.

Instrument settings

Column	10 m MS5A, backflush at 7 seconds
Column temperature	80 °C
Column pressure	100 kpa, 8.5 % H_2 in He
Injection time	50 ms

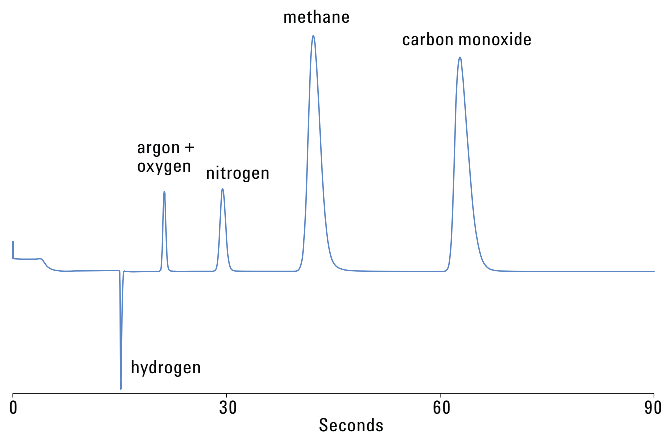


Figure 3. Chromatogram for permanent gas analysis on MolSieve 5A column, including negative hydrogen peak, using mixed carrier gas.

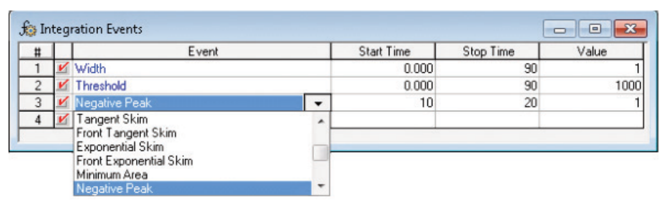


Figure 4. Integration setting for negative peaks.

Instrument settings

Column	10 m MS5A, backflush at 7 seconds
Column temperature	80 °C
Column pressure	150 kpa, 8.5% H_2 in He
Injection time	50 ms

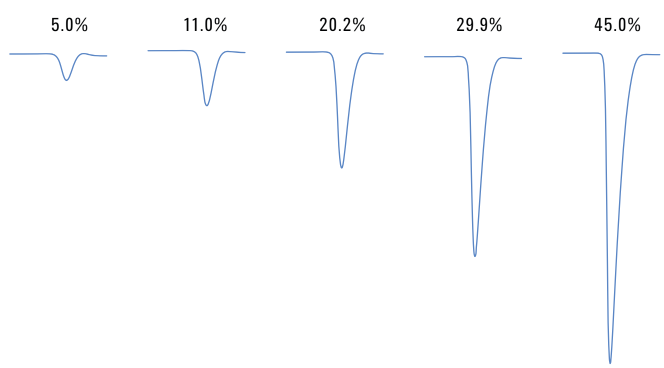


Figure 5. Increasing hydrogen concentrations with mixed carrier gas (8.5% H_2 in He).

Conclusion

The Agilent Micro GC with µTCD provides fast results for accurate, rich trend analysis and better informed decision making. Out-of-lab measurements are accomplished by the self-contained portable field case, featuring carrier gas supply and rechargeable batteries.

For hydrogen analysis with a thermal conductivity detector, argon is advised as the GC's carrier gas. Argon however, results in decreased sensitivity for the other compounds analyzed on the same analytical channel. This requires an additional channel running on helium carrier gas for low level detection for the other permanent gases. Helium carrier gas results in strange s-shaped peaks and nonlinear responses due to signal inversion at high concentrations.

To overcome this, hydrogen can be mixed with the carrier gas to ensure the concentration of hydrogen in the detector is higher than that of the point of inversion. A mixture of 8.5% hydrogen in helium will result in negative hydrogen peaks without inversion over a large percentage range. Moreover, sensitivity for the other compounds on the same analytical channel remains similar to when 100% helium carrier gas is applied. Although a gas mix is more expensive than pure helium, all compounds of interest analyzed on a single column channel is an important advantage.

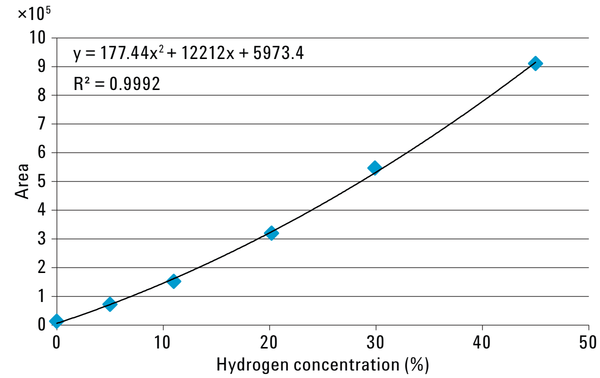


Figure 6. Calibration curve (quadratic fit) for hydrogen using 8.5% H_2 in He carrier gas.

References

1. N. Reuter "CSD Global Technical Support Technical Tip #23 The Thermal Conductivity Detector, TCD - Detector Information" Agilent Technologies.

2. K. Snavely and B. Subramaniam "Thermal Conductivity Detector Analysis of Hydrogen Using Helium Carrier Gas and HayeSep D Column" Department of Chemical and Petroleum Engineering, University of Kansas *Journal of Chromatographic Science* Vol. 36 April 1998.

3. C.J. Cowper and A.J. DeRose "The Analysis of Gases by Chromatography" British Gas Corporation, London Research Station, Section 4.7 Mixed Carrier Gas, pages 56–60, 1983.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem/microgc

Printed in the USA
October 24, 2013
5991-3199EN

Agilent Technologies