Enhanced Sensitivity Miniaturized Thermal Conductivity Detector for the Determination of Water, Ammonia, and Trace Impurities in Industrial Solvents

R. Facchetti[1], P. Magni[1] , M. Santoro[1] , F. Pigozzo[1], A. Caruso[1], W. Liu[1], E. Phillips[2] Thermo Fisher Scientific, Milan, Italy[1]; Thermo Fisher Scientific, Austin, Texas, US[2]

Overview

Purpose: Demonstrate the benefits of using a newly designed miniaturized-cell dual-filament Thermal Conductivity Detector (TCD) to increase sensitivity and linearity. This allows for a high sensitivity determination of trace components in industrial solvents by gas chromatography without the use of flame detectors or more expensive mass spectrometry detectors.

Methods: Organic solvents and industrial samples have been analyzed by gas chromatography using a Split/Splitless (SSL) injector and a Thermal Conductivity Detector.

Results: High sensitivity and reproducible results are demonstrated for the determination of various target analytes by TCD, showing sensitivity of single digit part-per-millions. Compared to traditional water detection methods, the GC-TCD method is simpler, more sensitive and accurate.

Introduction

Thermal Conductivity Detector (TCD) is useful in a wide variety of capillary and packed column applications. Most TCDs consist of four tungsten-rhenium filaments in a Wheatstone bridge configuration. Electric current flows through the four filaments causing them to heat up. Carrier gas (typically helium which has very high thermal conductivity) flows across the filaments eliminating heat at a constant rate. When a sample component with lower thermal conductivity exits the column and flows across the sample filaments, the temperature of the filaments increases, unbalancing the Wheatstone bridge and generating a peak as the sample molecules transit through the detector. This makes TCD respond universally without relying upon specific elements or structures. The TCD detector detects all molecules and is most commonly used for fixed gas (O_2, N_2, CO, CO_2, H_2S, NO, NO_2, etc.), water and solvents analysis where the target analytes do not respond well on other detectors. TCD is also employed when the auxiliary or combustion gases required by flame ionization or other detectors are unsafe or impractical. Most TCDs available are bulky and have limited sensitivity not being able to detect concentrations below 100 parts-per-million, at best. A new innovative dual-filament TCD , which is part of the newly introduced Thermo Scientific TRACE 1300 Series GC is adopted in this study. Its design, the miniaturized cell, and a strict temperature control allow for high-sensitivity, fast acquisition speed determinations providing, in some cases, a valid alternative to the more common Flame Ionization Detectors (FID).

Some companies constantly deal with aggressive samples like acids and amines. They require robust GC instrumentation that can withstand these matrices and provide accurate quantitative determinations. For those involved in the large-scale buying of almost any industrial solvent, an accurate determination of water becomes imperative as companies do not want to pay for a constituent which is available from a faucet.

FIGURE 1. Thermo Scientific TRACE 1310 GC

This is particularly true if the product is high priced, if the water content in organic solvents affects the reactions, or if it makes a decisive influence on the production's yield and the selectivity of the reactions. Also in medicines, chemical products, foods and synthetic fibers, water content is one of the important characteristic data. In all these cases, and whenever using a flame detector is not possible, a TCD is the ideal solution thanks to its ease of use, sensitivity and relatively low price.

Methods

FIGURE 2. GC parameters for water content determination in industrial solvents

TRACE 1310 GC Method:
Initial temperature: 50 C
Initial time: 1 minute
Ramp 1: 15 C/min
Final temperature: 150 C for 5 min
SSL injector temperature: 250 C
Injection mode: split
Injection volume: 1 µL
Split ratio: 10:1
Carrier: Helium at constant flow
Flow rate: 1.0 mL/min
Acquisition rate: 100 Hz
TCD detector temperature: 200 C
Filament temperature: 250 C
Column: Thermo Scientific TRACE TR-5 (30 m X 0.32 mm X 3 µm, Fused silica)

FIGURE 3. GC parameters for ammonia determination in Ammonium Hydroxide

TRACE 1310 GC Method:
Initial temperature: 60 C
Initial time: 4 minutes
Ramp 1: 5 C/min
Temperature: 80 C for 5min
Ramp 2: 10 C/min
Final temperature: 160 C for 3 min
SSL injector temperature: 250 C
Injection mode: split
Injection volume: 1 µL
Split ratio: 10:1
Carrier: Helium at constant flow
Flow rate: 1.0 mL/min
Acquisition rate: 100 Hz
TCD detector temperature: 200 C
Filament temperature: 250 C
Column: Thermo Scientific TRACE TR-Wax (260W236P, 60 m X 0.32 mm X 0.5 µm, Fused Silica)

FIGURE 4. GC parameters for polar solvents determination

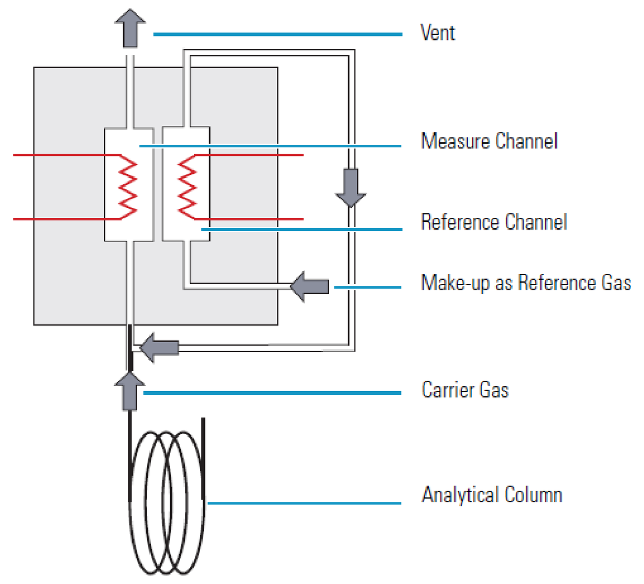
TRACE 1310 GC Method:
Oven temperature: 150 C, isothermal
SSL injector temperature: 250 C
Injection mode: split
Injection volume: 1 µL
Split ratio: 80:1
Carrier: Helium at constant flow
Flow rate: 1.0 mL/min
Acquisition rate: 100 Hz
TCD detector temperature: 250 C
Filament temperature: 350 C
Column: Plot (10 m X 0.25 mm X 3 µm)

The Instant Connect TCD module

The instant connect Thermal Conductivity Detector (TCD), shown in Figure 5, is a micro TCD detector for the TRACE™ 1300 Series Gas Chromatographs. The TRACE 1300 GC modules can be easily swapped by the user to ensure extreme versatility. Their plug-in concept allows the user to mount modules and replace them in a few minutes and be readily operative after installation. The instant connect TCD module features a miniaturized cell ideal for high-sensitivity trace-level quantitative determinations. It includes the detector body, two micro-volume Ni/Fe filaments, the electronics for temperature and reference gas control in a compact and self sufficient build. The whole pneumatics are integrated into the manifold minimizing the risk of leaks and contaminations. The detector guarantees a linear range of 10^5 and an acquisition rate of up to 300 Hz, which is ideal for fast GC applications. Its miniaturized cell volume allows a considerable reduction of gases flowing through the cell, down to 0.5 mL/min of reference gas, which makes this detector ideal for narrow-bore columns applications and enhances the detector sensitivity. The reference gas flow is also used as make-up for the column effluent so to ensure sharp analytical peaks. Anyway, its design has been optimized to be compatible also with 1/8" and 1/16" packed columns for laboratories still adopting those.

FIGURE 5. Instant connect TCD detector module

FIGURE 6. Instant Connect TCD Schematics



Results

Water determination by TCD

Water quantitative determination has been run on the following industrial solvents : methanol, ethanol, acetone and 1-methoxyl, 2-propanol (MPO) . Method linearity has been measured injecting a range from 20 part-per-million to 10 % water content in solvent, running 5 replicates of each calibration point to measure system's reproducibility. R^2 is 0.9998, and RSD% is well below 2% even at the lowest concentration injected. A minimum detection limit of 3.3 ppm (as 3x S/N) has been calculated for water.

FIGURE 7. Water determination in industrial solvents

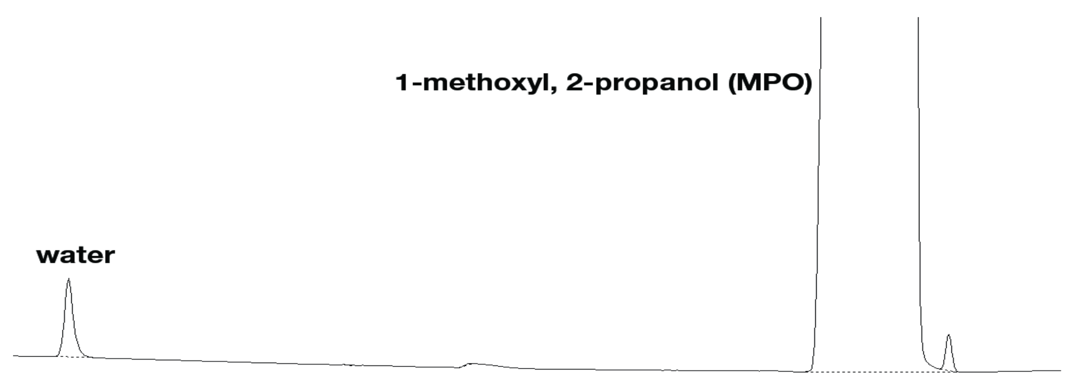
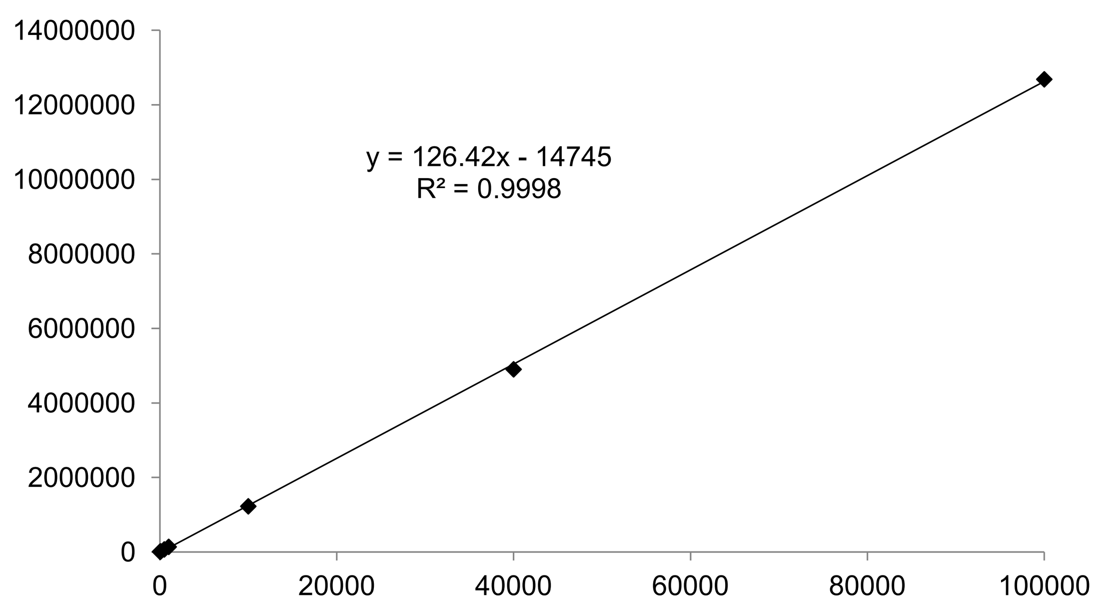


TABLE 1. Water std. concentration and % RSD (5 replicates each)

Std. concentration (mg/L)	RSD % (n=5)
20	1.68
50	1.23
100	1.72
500	1.33
1000	0.85
10000	0.22
40000	1.11
100000	1.01

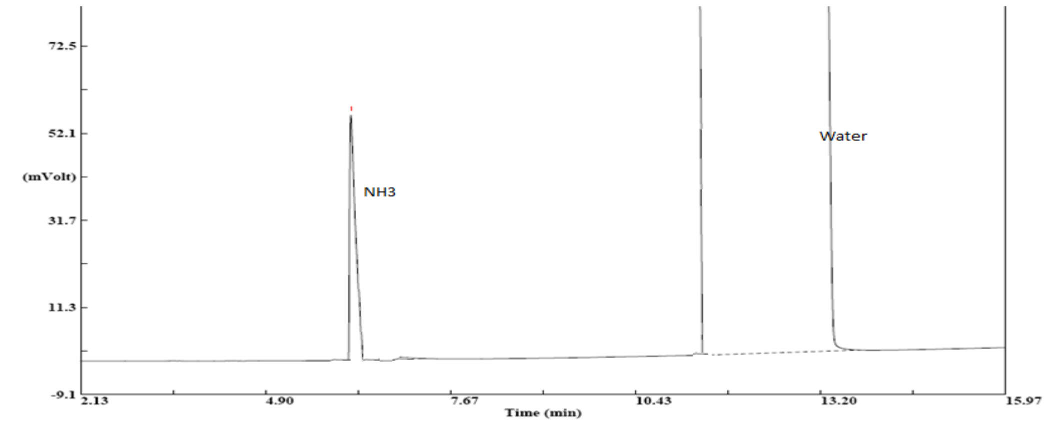
FIGURE 8. Water calibration curve from 20 ppm to 10%



Ammonia determination by TCD

Ammonia determination by gas chromatography has always been considered rather difficult and different detectors could be used. Especially for trace analysis of ammonia in gaseous samples PID and GC/MS are preferred while TCD robustness makes it amenable for higher-concentrations and liquid samples. The instant connect TCD of the TRACE 1300 Series GC robustness has been proven by running extensive sequences of ammonia, amines and acetic acid samples without showing any performance decrease or quality issue.

FIGURE 9. Ammonia determination in water. Chromatogram of diluted NH3, H2O, NH3 concentration: 3%(V/V)



TCD analysis using narrow bore columns

TCD performance using narrow-bore columns and its capacity of eluting polar components without sacrificing peak shapes has been investigated evaluating retention time and peak areas reproducibility over a sequence of 12 consecutive runs of a solvents standard mix (500 ppm each in methanol). RT and Area RSD% are below 0.6 and 2% respectively.

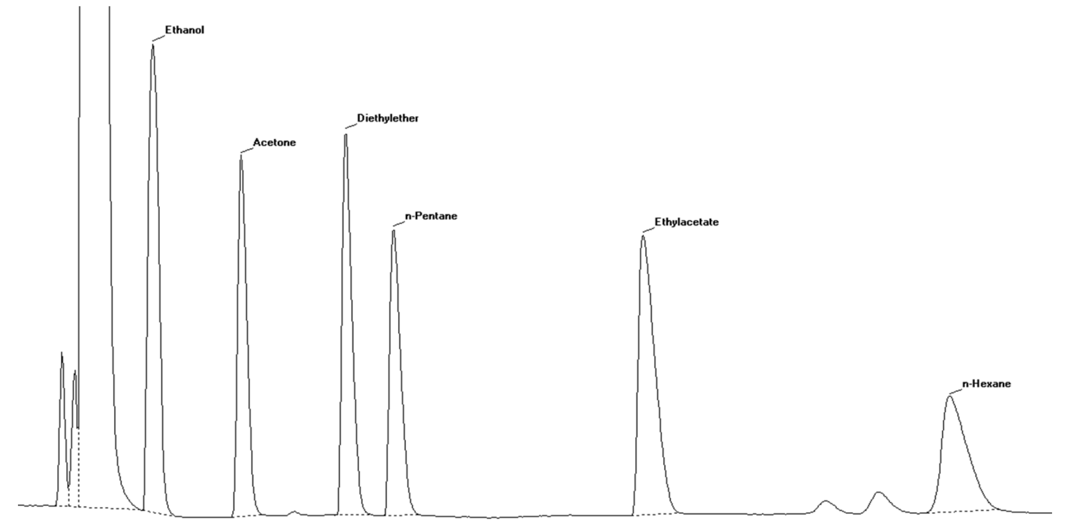


TABLE 2. Solvents analysis on narrow bore column. RT and Area statistic (n=12)

	Ethanol	Acetone	Diethylether	n-Pentane	Ethylacetate	n-Hexane
RT mean	0.6742	0.9008	1.1696	1.2935	1.9362	2.7270
RT Std Dev	0.0037	0.0013	0.0013	0.0010	0.0035	0.0025
RT Std Dev %	0.5549	0.1405	0.1142	0.0793	0.1800	0.0934
Mean Area	727042	481937	545134	458182	669358	424808
Area Std Dev	12711	6314	7674	6797	9452	6538
Area Std Dev%	1.75	1.31	1.41	1.48	1.41	1.54

Conclusion

The instant connect TCD detector of the TRACE 1300 Series GC is a robust and sensitive detector, which shows excellent linearity, repeatability and sensitivity. Whenever the use of flame detectors is not possible for safety reasons, the instant connect TCD becomes a valid and reliable alternative thanks to its performance and reliability. Compared to traditional water detection methods, GC-TCD method is simpler, more sensitive and accurate, The detection limit of water in industrial solvents has been calculated down to single-digit part-per-millions.