# Operating Parameters for the Thermal Conductivity Detector in Scion 436 and 456 Gas Chromatographs

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The thermal conductivity detector was the only detector available on the first commercial gas chromatographs in the 1950's. This early detector had several important features:

- very simple hardware and associated electronics
- non-destructive, so sample components could be collected after separation for identification by off-line spectroscopic techniques, including nuclear magnetic resonance, infrared and mass spectrometers, and
- response to all analytes of sufficient concentration, except for the carrier gas.

These were hallmarks of the early detectors and are still true today. The thermal conductivity detector remains as a very viable and important tool in quantifying a variety of gases, such as hydrogen, helium, neon, oxygen, nitrogen, carbon monoxide, methane and carbon dioxide, and other major constituents in chemical mixtures.

Thermal conductivity is a physical property of all matter. It is a measure of the material's ability to transfer heat from one surface to another. In its gas chromatographic application, the transfer is the difference in the ability of the gaseous analyte to conduct heat compared with the column carrier gas. Small molecules - hydrogen and helium - are able to very effectively transmit heat, whereas larger molecules are less able in varying degrees.

| Analyte | Relative Conductivity to Hydrogen | Relative Conductivity to Helium | Relative Conductivity to Nitrogen | Relative Conductivity to Argon |
|---|---|---|---|---|
| **Hydrogen** | **1.00** | 1.25 | 7.17 | 10.36 |
| **Helium** | 0.80 | **1.00** | 5.72 | 8.27 |
| **Neon** | 0.26 | 0.32 | 1.84 | 2.66 |
| **Methane** | 0.19 | 0.24 | 1.36 | 1.96 |
| **Oxygen** | 0.14 | 0.18 | 1.04 | 1.50 |
| **Nitrogen** | 0.14 | 0.17 | **1.00** | 1.45 |
| **Carbon Monoxide** | 0.14 | 0.17 | 0.97 | 1.41 |
| **Argon** | 0.10 | 0.12 | 0.69 | **1.00** |
| **Carbon Dioxide** | 0.09 | 0.12 | 0.67 | 0.96 |

**Table 1. Relative thermal conductivities of various fixed gases at 49 °C.**
Ratios derived from data in CRC Handbook of Chemistry and Physics, 64th Edition,
(CRC Press, Inc, Boca Raton, Fl), 1983.

If we construct a detector cell with a hot surface in the center and cooler surroundings, and direct the column effluent through it, we can perceive a steady cooling of the hot surface from the carrier flow only. When an analyte arrives in the cell with a dissimilar thermal conductivity, the rate of cooling will be different. If we can sense that difference in cooling, then we can detect the analyte elution.
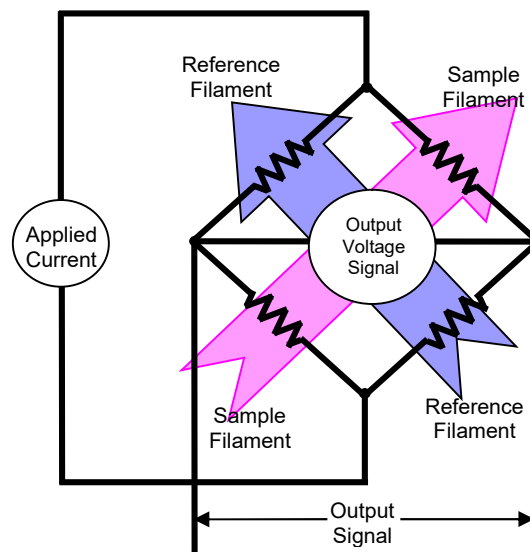
Construction of a typical cell involves insertion of special filaments inside a massive thermal block. Since the heat transfer from the filaments is measured as a change in temperature as the analytes pass through, usually two filaments are employed, with one acting as a reference to facilitate the sensing of the difference in response. The filaments are heated to a temperature separate and above the block temperature, to effect the measurement.

Early on, with the introduction of the Model 90P3 in 1964, Scion Aerograph installed a total of four filaments in the detector - two for the sample side and two for the reference - to provide better signal stability with decreased noise and enhance response. This configuration remains on all current Scion detectors.

We can sense a change in the temperature as the analyte comes through by applying a current to the filaments and monitoring the change of resistance for the sample filament relative to the reference, as the filaments heat or cool. The easiest method for generating a signal is to insert the four filaments into the classic Wheatstone bridge circuit. With the same carrier flow rates by sample and reference filaments, the signal can be nulled to zero electronically. Then, when an analyte starts passing by the sample filament, the circuit becomes out of balance and a voltage is generated proportional to the skew. This signal is then outputted to a data collection device and processed into a concentration value.

**Circuit representation of a Wheatstone bridge. When an analyte passes by both sample filaments, the circuit becomes imbalanced and an output signal is generated proportional to the amount of analyte.**

Since an analyte passing through this detector can more effectively cool the filaments if it passes slowly through the detector, sensitivity of thermal conductivity detectors is very dependent on the carrier gas flow rate. This process labels this detector as a "concentration"-style detector - the more concentrated the sample inside the detector or the more time it spends there (by a slower flow rate), the better the response. Similarly, if the cell volume is tiny, then the heat transfer from the filaments to the block is more rapid with the shorter transit distance and could yield bigger peaks. However, the tradeoff with small cells is that the surface area for the filaments is also reduced, lessening the opportunity for the analyte to strike the filament, and shrinking the filament resistance to make the "imbalance" of the Wheatstone less responsive. A compromise between cell volume and filament size must be taken to optimize the final performance of the detector.

Originally, these filaments were made of tungsten, a fairly rugged material that can readily withstand temperatures involved here. In 1965, with the introduction of the Aerograph 202-1B Moduline B GC Series, Varian converted over to an alloy of tungsten and rhenium that can tolerate a bit higher temperature than tungsten alone, with less deformation (especially when hot), and that is easier to form into wire for the filaments (more ductile). This alloy remains today in nearly all Scion thermal conductivity detectors. Special nickel filaments for this detector are available from Scion to handle corrosive gases, such as halogens ($F_2$, $Cl_2$, $Br_2$, $I_2$) and the halogen acids (HF, HCl, HBr, HI), better than tungsten-rhenium.[1]

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[1]    These nickel filaments impact the settings for the filament temperature and must be adjusted to effect an appropriate setting. Contact Varian or one of these authors for more details.

Most commercial instruments with thermal conductivity detectors set the current applied to filaments to generate heat needed to perform the measurement, and then they monitor the resistance change in the filaments due to the change in filament temperature to create a signal. When an analyte with less thermal conductivity than the carrier passes through, it will allow less cooling of the filaments. The filament temperature will rise and yield a change in the filament resistance, and thus a change on the signal. The major difficulty arises with this approach when the temperature exceeds the limit for the filaments, and the filaments burn out, disabling the detector.

Varian turned the tables with the introduction of the Varian 3700 Gas Chromatograph in 1975. Instead of maintaining constant current, the Model 3700 maintained a constant mean temperature for the filaments and then measured the current to maintain that temperature, using a modified Wheatstone bridge circuit to generate the signal. This process limits abuse of the filaments from overheating, since a lower temperature is always maintained, and any excessive current needed to maintain that temperature can be readily sensed and limited. Now on Scion gas chromatographs, the operator sets a filament temperature as an operating parameter to set the sensitivity of the detector. Any devastating current from excessive concentration of an analyte or a leak on the carrier gas generates an excessive current, shuts down the detector, and generates an error.

Varian has found that their detector design generates such low noise that they could implement an amplification of the signal without a concomitant increase in noise. By enabling a simple electronic enhancement of the signal by a factor of twenty, higher filament temperatures needed for low concentrations could be reduced and still provide adequate sensitivity for the small peaks. Scion's detectors now have three ranges – 0.05 - the most sensitive, 0.5 - medium sensitivity, and 5 - the least sensitive.[2] Their differences in response are exactly a factor of ten. And they can be time programmed to keep huge peaks on scale and still sense little peaks in the same chromatogram. This feature was carried on through all subsequent Varian gas chromatographs, including the Vista 6000, 3400, 3600, 3800 and 3900, Bruker 450 and Scion 436 and 456.

## <u>Concentration Units in Gas Analysis</u>

Quite often, concentrations involving detector performance are bantered about without much attention to units. "PPM" can imply one part per million in weight per unit volume (W/V), or one part per million in volume per unit volume (V/V). Typically, "PPM" in W/V is nanogram/milliliter, whereas "PPM" in V/V is microliter/liter. They differ by the molecular weight of the analyte involved and the molar gas volume corrected for temperature. The conversion is:

$$\text{ppm (V/V)} = \frac{\text{ppm (W/V) * room temperature (}^\circ\text{K) * 22.4 L/mole}}{\text{molecular weight (g/mole) * 273 }^\circ\text{K}}$$

As a result, 1 ppm W/V Methane (µg/ml) becomes:

$$\frac{1 \text{ ppm (W/V) * 298 * 22.4}}{16 * 273} = 1.53 \text{ ppm (V/V)}$$

Or, 1 ppm W/V Tridecane (µg/ml) becomes:

$$\frac{1 \text{ ppm (W/V) * 298 * 22.4}}{184 * 273} = 0.13 \text{ ppm (V/V)}$$

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[2] The significance of the numbers 5, 0.5 and 0.05 relate to the attenuation or magnification of the signal relative to a 1 mv recorder scale. Thus, range 0.05 is a 20X expansion of the normal signal, and range 5 is a five fold compression of the signal.

# Operating Parameters for Scion 436/456

The Scion thermal conductivity detector has more operating parameters that directly impact detector performance than most other GC detectors. A full understanding of the influences of these parameters allows operation to be optimized for the measurement at hand.

**Filament Temperature** – This setting has the most impact on peak size. The higher the filament temperature, the more cooling of the filaments when an analyte passes through, and thus generating more sensitivity for the measurement. Lower settings extend life of filaments.
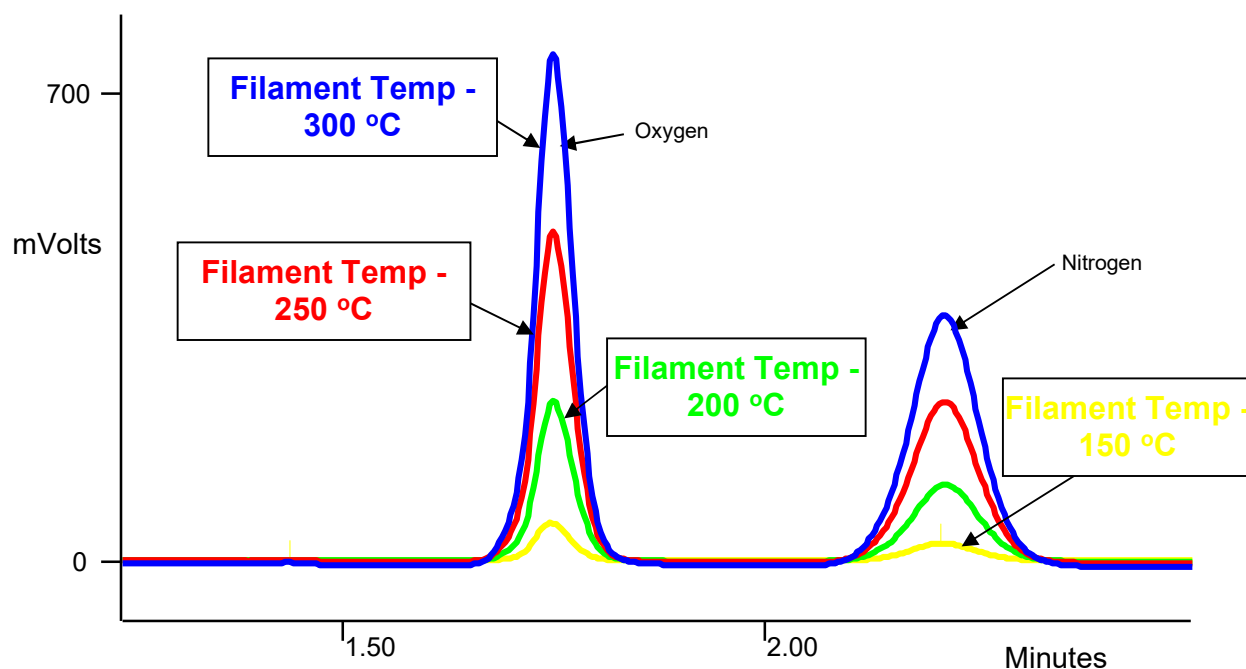


**Figure 1. Filament temperature has a major impact on peak size.** By choosing an appropriate setting allows sufficient sensitivity for the analysis at hand while still maintaining filament lifetime. Column temperature: 80 $^o$C; helium carrier, filament current (150 $^o$C) - 134 ma, (200 $^o$C) - 226 ma, (250 $^o$C) - 286 ma, (300 $^o$C) - 336 ma.

**Filament Temperature Limit** – With Scion detectors, the filament temperature maximum is limited by a user selected choice of 390 $^o$C or 490 $^o$C, with the 390 $^o$C limit designed to protect filaments for most routine applications. If performance must be pushed, then the limit should be changed to allow a higher filament temperature setting, resulting in bigger peaks, with a compromise in shorter filament lifetimes.

**Block Temperature –** The difference in temperature between filaments and the detector block provides much of the control over sensitivity with this detector. With a lower block setting, filaments can be cooler and still achieve the needed performance. However, the block temperature should be high enough to prevent any potential condensation of major sample constituents and column bleed, especially water from the sample. By design, the block has a huge thermal mass to maintain very consistent temperature base and a more stable baseline, and it does take awhile to achieve a stable temperature after any abrupt change.
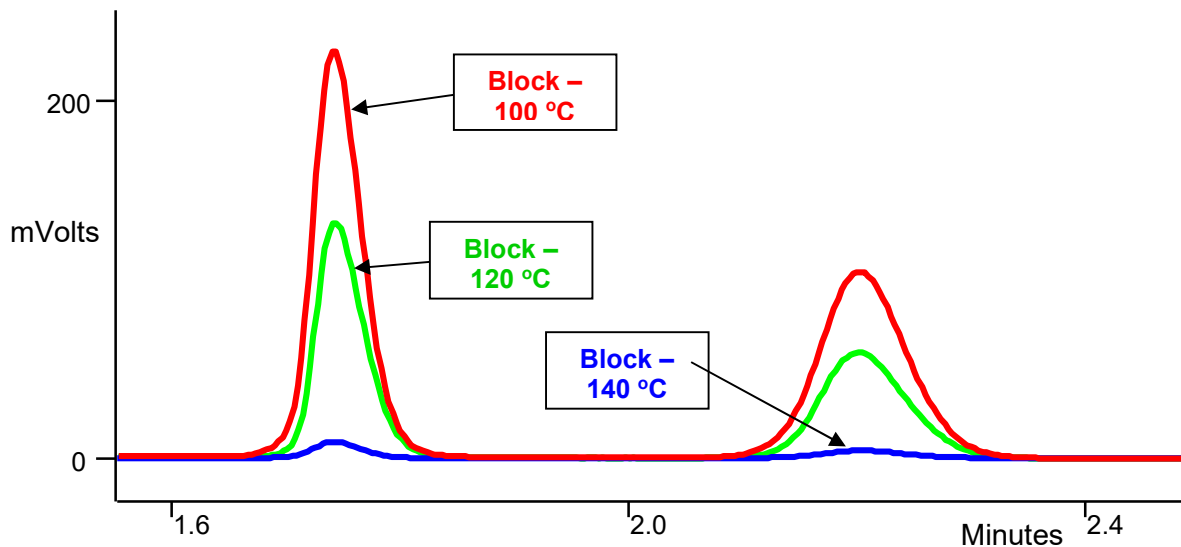
**Figure 2. Peak size is very sensitive to the difference in temperatures between the filaments and the detector block.** The smaller the difference, the smaller the peaks. 1000 ppm V/V oxygen and nitrogen with helium carrier, filament temperature: 150 °C, range - 0.05.

**Range** – Unless performance must be pushed hard, a more sensitive range setting permits a lower filament temperature to preserve filament life. However, if big peaks and small peaks occur on the same chromatographic run, a range change appropriately timed can allow both peaks to be measured properly.[3]
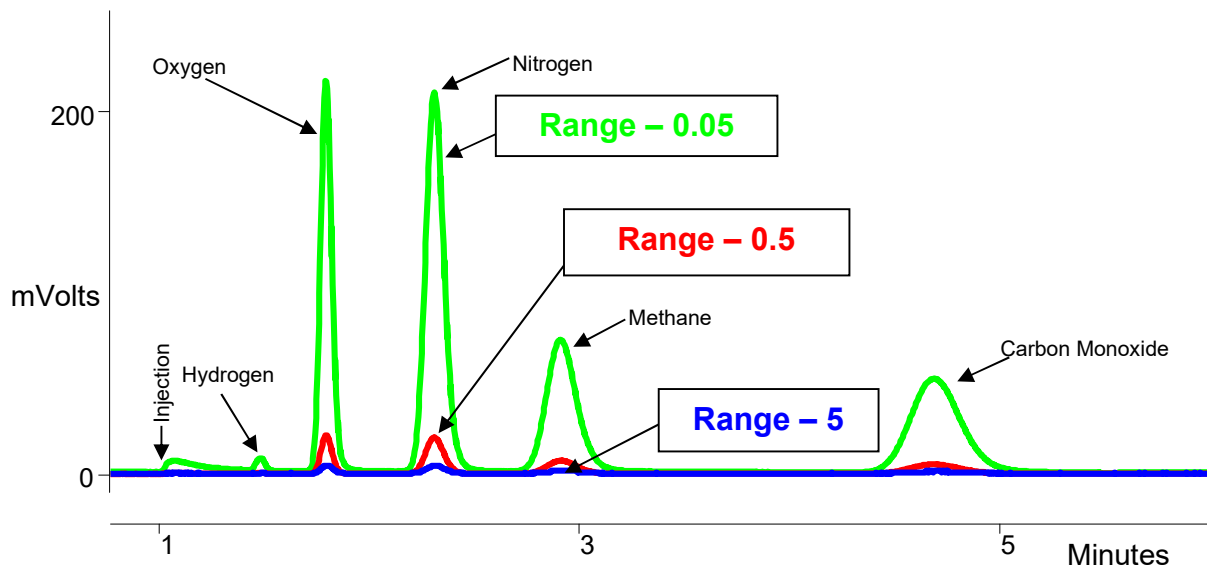


**Figure 3. Choice of detector range can directly impact the size of a peak.** By selecting the most sensitive range of 0.05, the filament temperature can be lowered to preserve the lifetime of the filaments, or to enlarge small peaks not readily detected with a less sensitive scale.

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[3] A companion parameter to Range is Attenuation; this is employed only with an attached strip chart recorder and is completely inactive with any employed data system.

**Auto-Zero** – The detector can exhibit baseline shifts after range changes or valve actuations.  To assist peak integrations with a data workstation, rezeroing can be time-programmed to occur after these perturbations.  Also, an auto-zero activation at the start of the run allows the electronics to balance the Wheatstone bridge automatically.  An auto-zero in the middle of a run must be accompanied by an appropriate "integration inhibit" action to ensure that the baseline upset during this action does not improperly alter the peak area assignment of nearby peaks.

**Polarity** – Response of this detector to an analyte is relative to the thermal conductivity of the carrier gas.  Sometimes the response is less than the carrier, and sometimes more.  Normally the detector is set up to generate positive peaks with helium as the carrier.  With a switch to nitrogen or argon, the peaks may be positive, or they can be negative, depending on the analyte's relative thermal conductivity to the carrier and which channel becomes the active pathway.  Peaks can also invert if two columns are installed and the column attached to the reference cell becomes the active column.   Data workstations normally handle only positive peaks, so the signal polarity must be inverted when these negative peaks elute.  Polarity can be time-programmed to handle both positive and negative peaks in the same chromatogram.
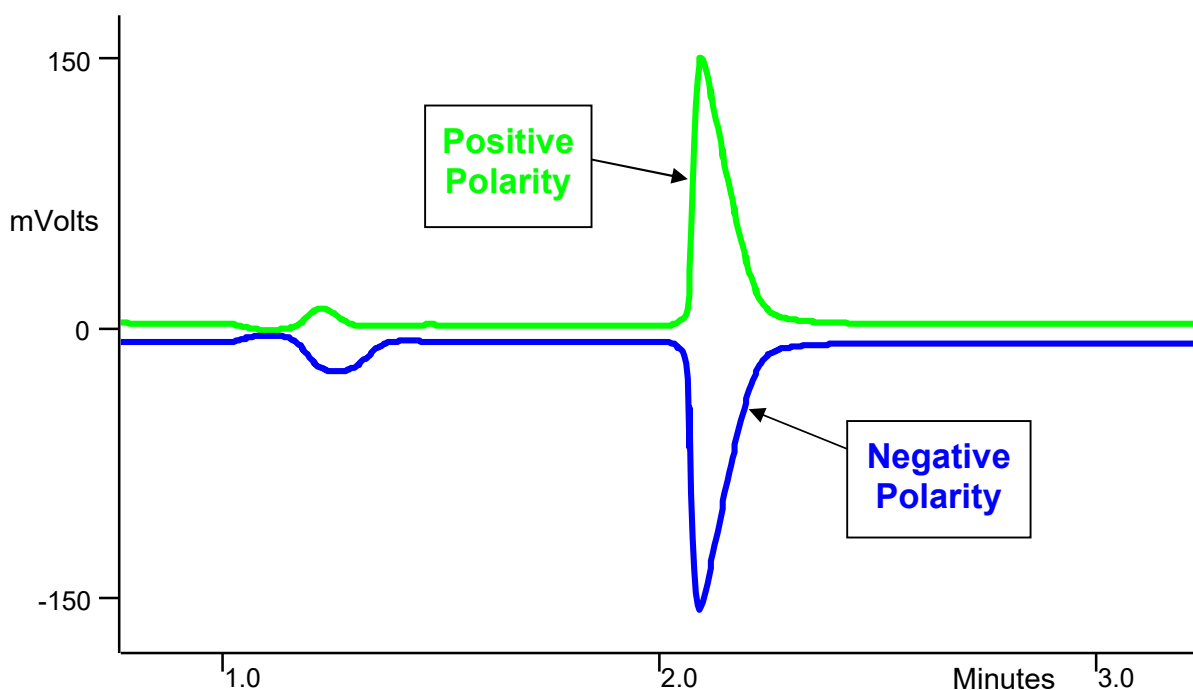


**Figure 4.  Peaks detected with a thermal conductivity detector can be positive going or negative going, depending on the thermal conductivity of the analyte relative to the carrier, and also which detector cell becomes the active path.**  The choice for the polarity of the signal is usually determined empirically and altered as appropriate.  $CO_2$ with Ar carrier, injection volume 0.1 ml, column temp: 80 °C, range - 0.5, TCD block temperature: 120 °C, filament temperature: 200 °C, current - 100 ma.

**Time Constant** – Scion has provided a dampening of noise through a user choice of time constants[4] – "fast" for a response of 50 millisecond, and "slow" for a 220 millisecond dampening. To assist in quieting the signal as much as possible for low level studies, especially when filament temperature is elevated to maximize sensitivity, the time constant can be set to "slow", with a reduction in the noise level of about a factor of 2. However, under normal operating conditions, noise with the thermal conductivity detector on the Scion 436 is so quiet, that changing the time constant from "fast" to "slow" shows no noticeable change in the perceived noise. Only under severe operating conditions with elevated filament temperatures and expanded ranges will noise be impacted by the choice of time constant. Therefore, to enable the trace to follow more faithfully the actual signal the time constant should be left in the "fast" position for most measurements.

Another approach to dampening out random noise is to alter the frequency of conversion and/or the bunching rate of the analog-to-digital converter. By choosing a rate that provides typically 20 bunch points across the top of the peak, the true shape of the peak will be defined and allow random noise to be averaged together to enhance the detection of low level concentrations. For example, a bunch rate of 4 points at 40 hertz analog-to-digital data collection is quite appropriate for peaks with 2 second width$_{½height}$. If measured peaks had peak widths about 10 seconds at half height, a change of bunch rate to 16 points would suppress noise by a factor of 2 and still maintain fidelity of the true peak shape. Any change in bunch rate will alter the measured noise by the square root of the ratio of the bunch rates. For example, adjusting the bunch rate from 4 to 16 will effect a noise reduction of a factor of 2. However, the date conversion rate will be changed to 2.5 hertz and would undoubtedly impact the shape of sharper chromatographic peaks due to the fewer number of data points to define them.
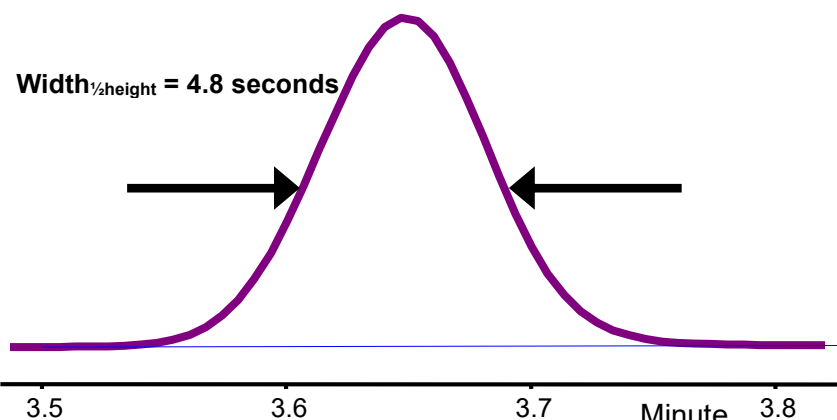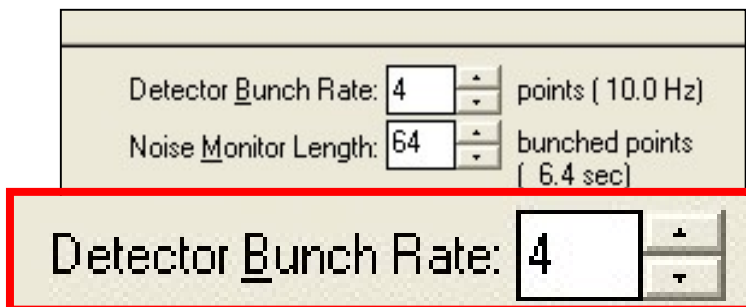


**Width$_{½height}$ = 4.8 seconds**

**Figure 5. Peak widths at half heights are measured by taking one half of the height and determining the peak width at that height.** Many workstations automatically list this width in the report to assist in setting bunch rates.

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[4]    Time constant is defined as the response delay to a step change in the signal. A change in value will effect a change on the noise level of an analog detector signal. A value of "50 millisecond" corresponds to a 67% achievement of the step change in the signal after 50 milliseconds. A longer time constant will suppress random noise, but also affect the faithfulness of the trace to follow sharp chromatographic signals. The choice can be selected empirically, or by selecting a value that represents about one third of the peak width of the analyte. For example, if the chromatographic peak width$_{½height}$ were 4 seconds (typical for normal packed columns), a time constant of 220 milliseconds would most likely still provide a true representation of the peak and yet maximize the suppression of random noise.
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**Carrier Flow Rate** – This parameter becomes a compromise between reasonable analysis times and detector sensitivity.  A very low flow will maximize detector sensitivity, but significantly lengthen the overall measurement timing.   High flows to achieve ultra-fast separations will deteriorate performance as the analytes do not reside long enough in the cell to effectively cool the filaments as much as a lower flow would.  If all other parameters have been fully optimized, then a decrease in flows can enhance sensitivity.
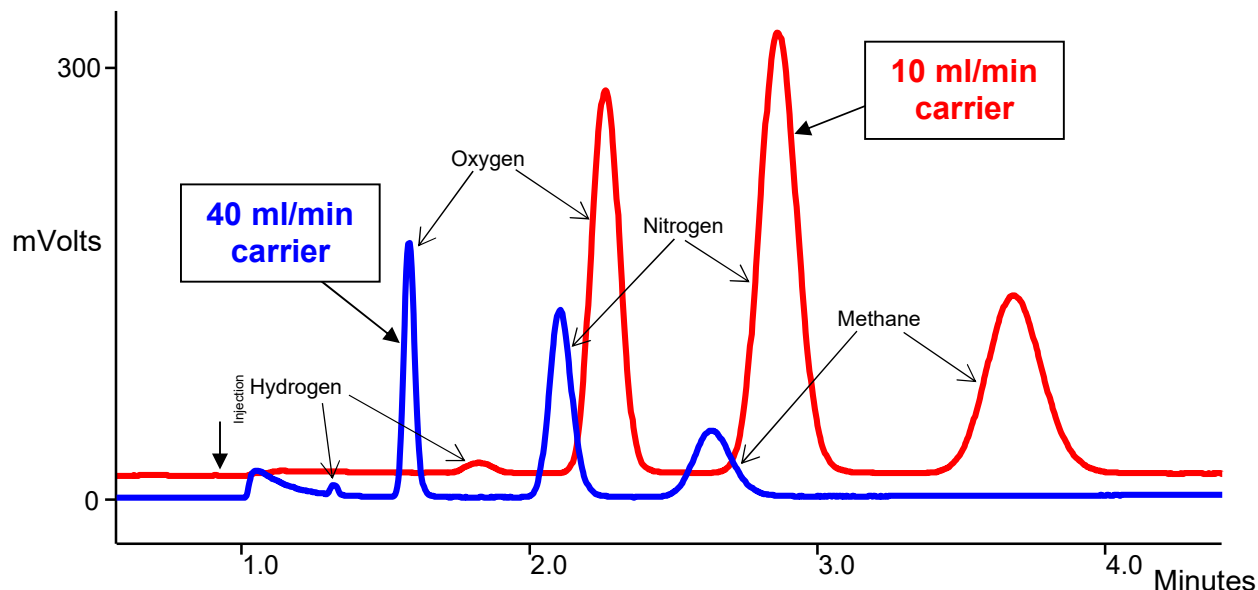


**Figure 6.   Carrier flow rate has a direct impact on performance of the thermal conductivity detector**, as this detector is a concentration-dependent detector and its response is critically dependent on how long an analyte spends inside the detector. Changing the flows from 40 ml/min to 10 ml/min, lengthens the analysis, but the peak sizes increase by nearly a factor of four.  Sample - 1000 ppm V/V of each listed analyte, column - Molecular Sieve 5A, 45/60 mesh, 1/8" X 6' stainless steel at 80 °C

Due to the critical impact of flows through the thermal conductivity detectors, flow rates are best maintained with true flow controllers, such as Scion's Electronic Flow Controller Type 23 or digital flow controller (P/N 03-917146-00)[5], and detector reference flows with Detector Electronic Flow Controller Type 13 (single reference flow), 14 (reference plus make-up flows) or 16 (reference plus make-up for $H_2$ carrier) or reference digital flow controller (P/N 03-917146-00)[5].   These devices maintain a constant set flow even with changes in column temperatures or column configurations.

Pressure controlled devices, such as Electronic Flow Controller Type 24, or Dean's pressure column switching, should be employed with extreme caution, as downstream changes to flow restrictions, such as column temperature or column configurations, can impact flow to the detector. Constant _**pressure**_ is maintained with these devices – **NOT FLOW**, and adjustments must be made to ensure that the flow through the sample side matches that through the reference cell for the complete run duration.

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[5]    Varian has long labeled their analog flow controller with a "counting" dial as a digital flow controller.

**Carrier Gas –** The thermal conductivity detector measures the difference in cooling effects between the carrier gas and the analyte - the bigger the difference, the better the sensitivity achieved. Helium is a common carrier gas and has a significant difference with most other analytes and is often the carrier of choice. Hydrogen has a higher thermal conductivity that could result in enhanced performance, but this carrier carries some risk if a leak occurs, especially in the column oven. Certain applications, as discussed below can dictate a different carrier. Since thermal conductivities of nitrogen and argon are not significantly different than that of air, filament protection offered with helium and hydrogen will be disabled automatically when employing nitrogen or argon carrier gases.
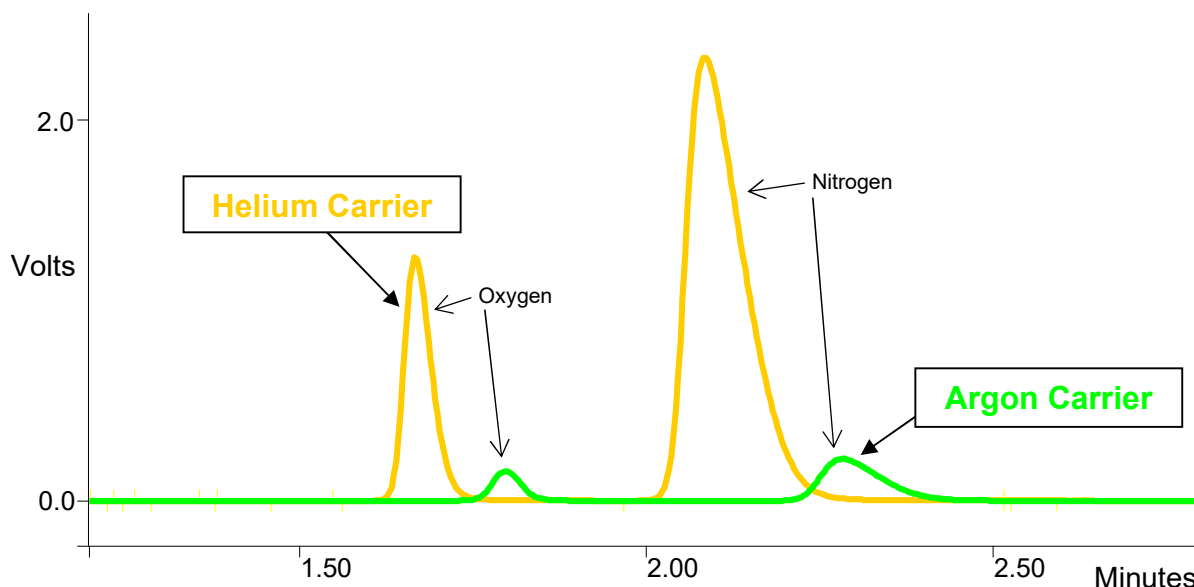


**Figure 7. Response differences with Helium versus Argon carrier gas for ambient air.** Injection volume - 0.1 ml, column temperature: 80 °C, range - 0.05; TCD block temperature: 120 °C, filament temperature: 150 °C, filament current (He carrier) - 136 ma, filament current (Ar carrier) - 68 ma. Note the retention time shift due to a change in calibration of the flow controller with the different carrier.

**Balance (%)** – After the Wheatstone bridge is balanced with an auto-zero action, the status of the balance control is displayed, from -99% to +99% on the status screen of the Scion GC. When the signal is zeroed automatically at the start of a run, the "Balance (%)" display will indicate how much the bridge is askew, as a percentage. This reading gives a continuous status of the condition of the filaments. As it approaches + or - 90%, a replacement of the detector is eminent, and when it reaches + or - 99%, the instrument will fault out and the detector will become non-functional, necessitating a detectot replacement. A continuous drift in this value over time may indicate a leak that is causing one set of filaments to oxidize, or sample and reference filaments have seriously degraded.

**Reference Flow –** This detector operates on comparison of the response of the sample pathway compared with the reference. To keep the detector bridge circuitry as balanced as possible, the reference flow should match total flow for the sample channel - column flow plus any "make-up" flow. And of course the reference gas must match that employed with the sample side.

**Make-up Flow –** When carrier flow is well lower than the reference flow, and the reference flow cannot be brought low enough to properly balance the detector, additional flow can be added through the make-up flow parameter of the Detector Electronic Flow Controller. This supplement is quite useful when micro-packed columns or Megabore capillary columns (0.53 mm ID) are employed.

**Baseline Subtraction** – Measurements with a thermal conductivity detector often involve gases, along with valving, to inject samples and to perform special actions, such as column bypass or backflushing to vent, or column switching. These actions frequently generate severe pressure surges and radically impact baseline stability with the flow-sensitive thermal conductivity detector. These perturbations can be minimized somewhat with balancing restrictors and pressure regulators plumbed in series with requisite flow controllers, but baseline shifts and disturbances still can affect peak area assignments, and can be diminished by performing measurements with a system blank and then subtracting point-by-point those baseline variations to yield a better chromatogram that can be processed more accurately into areas by the data processor.
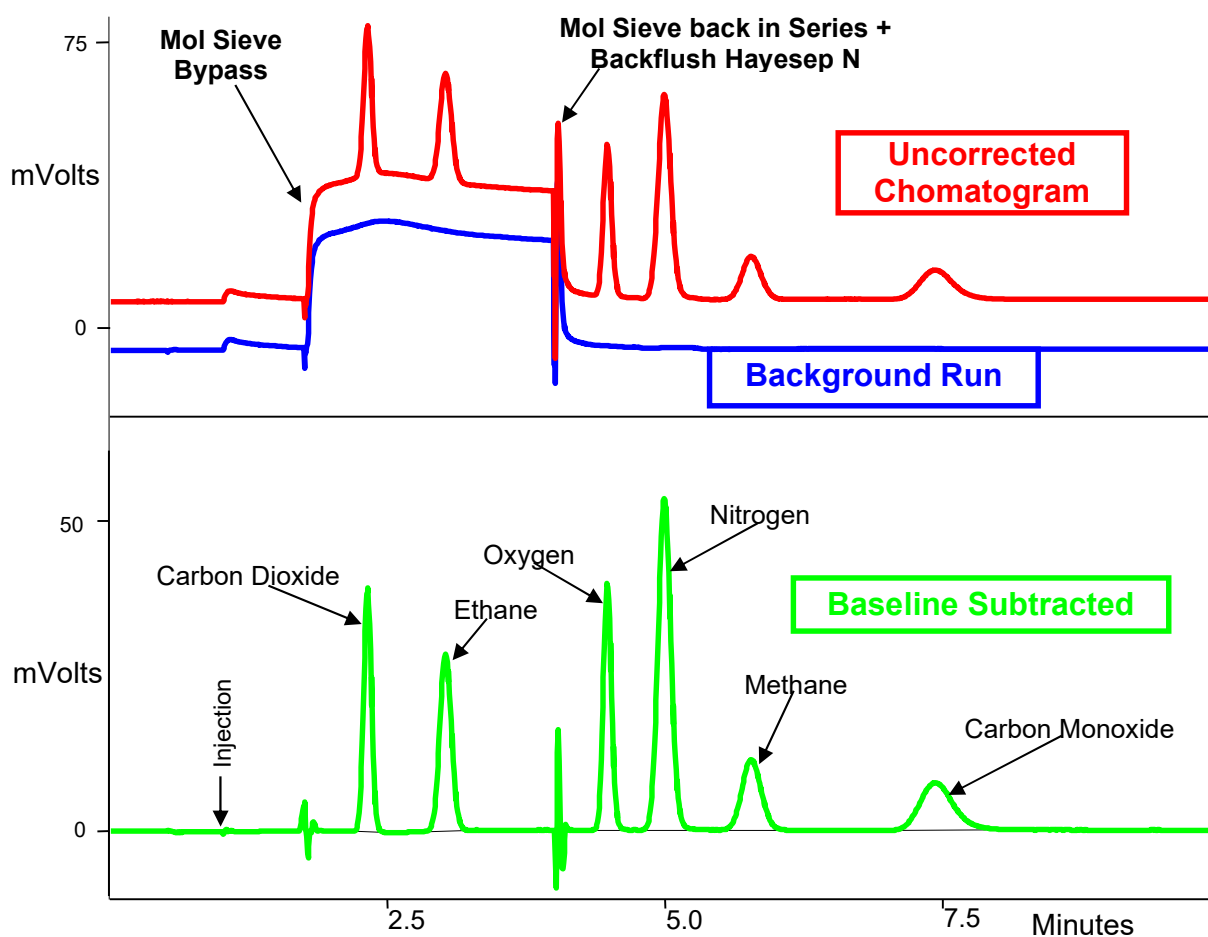


**Figure 8. Gas analysis often involves valve actuations to perform specific tasks to accomplish the separation, such as placing columns in series/bypass, and backflushing columns of unwanted contaminants to vent.** These actions can produce baseline upsets, which can be properly corrected by baseline subtraction, to yield a flatter baseline for better peak area assignments. Sample - 1000 ppm mixture in helium, Hayesep N (6', 60/80 mesh) and Molecular Sieve 5A (6', 45/60 mesh) plumbed in series/bypass with backflush to vent; carrier He; column: 80 °C TCD block: 120 °C; filament temperature: 180 °C; range - 0.05.

# Sensitivity

Peak size with a thermal conductivity detector is very dependent on a number of user selectable parameters.  This makes it very difficult to compare competitive detectors on how well a detector performs against its rivals.  By computing a component response under the ultimate conditions for that detector, some semblance of a judgment can take place.  One approach to generate a sensitivity factor (S) is to compute the ratio:

$$S = \frac{\text{detector peak height (mv)}}{\text{analyte concentration (mg/ml)}}$$

Unfortunately, as might be expected, this evaluation is strictly dependent on the analyte chosen and conditions employed with the chromatography and detector.  Unfortunately, an industry standard has not yet been set for this specification, and extreme care must be exercised when comparing numbers with dissimilar analytes.

# Maximizing Sensitivity

The thermal conductivity is naturally the least sensitive detector in gas chromatography, as well as the least selective.  To maximize sensitivity, the range setting should be placed at 0.05, with the coolest possible block temperature, with helium or hydrogen carrier, a high filament temperatures, "slow" time constant to help suppress noise, and reduced carrier flow rate.  These conditions should be maintained only during the experiment and be reverted back to less hazardous settings thereafter, to preserve filaments.

To achieve stable baselines under these conditions, the system should be set to the required settings and allowed to stabilize at least an hour before measurements.

# Maximizing Filament Lifetime

All actions to lower filament temperatures will length filament lifetimes.[6]  Instead of upping the filament temperature to gain sensitivity, using a more sensitive range setting will enhance peak sizes and allow the filaments to be lower in temperature.  A lower block temperature also permits a lower filament temperature with sustained peak sensitivities.

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[6]    Filament lifetime is a function of many operating conditions and cannot be predicted.  Under extreme conditions, the life can be as short as a few seconds; and with proper care, they can last years.  Particularly important is to turn off the filament temperature when the detector is not in use to prevent accidental exposure to harmful conditions when in standby settings.

# Detectivity or Minimum Detectable Quantity (MDQ)

Peak size is critically dependent on a number of operating parameters, as discussed above. How low a concentration for an analyte can be measured is determined on the settings for the filament and block temperatures, carrier gas employed and the analyte involved. Again, the industry has not agreed upon a standard for this measure. One proposed assessment for detectivity (D) is:

$$D = 2 * \frac{\text{Peak-to-peak noise (mv)}}{\text{Sensitivity (mv*ml/mg)}}$$

Unfortunately, this determination remains very subjective as noise can be readily altered by digital averaging. Also, sensitivity is very dependent on a variety of variables, as discussed above.

A better measure is to determine area count reproducibility at or near the expected limit and then compute three times the standard deviation of a replicate series of at least 7 runs at that level or near that level.[7] This approach takes into account all of the variables involved with this detector, including the impact on the final measure and how low a level can be realistically quantified.

$$\text{Detection Limit} = 3.14 * \frac{\text{standard deviation of (or more) runs}}{\text{area of std / concentration of std}}$$

| Consecutive Run Number | Area Counts for 4 ppm V/V $CO_2$ |
|---|---|
| 1 | 14967 |
| 2 | 13947 |
| 3 | 13896 |
| 4 | 13776 |
| 5 | 12804 |
| 6 | 13036 |
| 7 | 13416 |
| 8 | 14109 |
| Average Area Counts | 13744 |
| 3.14 * Std Dev Area Counts | 2119 |
| Response Factor | 13744 / 4 = 3436 Cts/ppm V/V |
| **Detection Limit (ppm V/V)** | **0.6 ppm V/V** |

**Table 2. Determination of $CO_2$ detection limit based on 390 ppm V/V carbon dioxide in 0.01 ml ambient air, equivalent to 4 ppm V/V at 1 ml injection volume.** Instrument conditions: Column - Hayesep N, 60/80 mesh, 6', 1/8" stainless steel, oven temperature: 80 °C, TCD block temperature: 120 °C, filament temperature: 240 °C, filament current - 274 ma, TCD range - 0.05.

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[7] This computation provides a 99% confidence level that the resulting level can be detected. The multiplier factor changes with the number of measurements involved, per the Student's t-distribution.

# Practical Performance Levels

GC manufacturers have set their published detector specifications at very low levels for competitive comparisons and arguments, often rivaling performance of the more sensitive flame ionization detector, but they often can only achieve these results under very demanding conditions and with carefully-selected analytes. Some even equivocate a bit by stating that the listed performance "may be affected by laboratory environment". Under reasonable detector settings, concentration levels down to near 100 ppm V/V can be achieved readily for most gas analytes without severely impacting the filament lifetimes by pushing operating parameters. Lower levels are achievable, but needed parameters to reach these levels can impact life spans for the filaments in the detector.

Thermal conductivity detectors are designed to measure higher concentrations, such as bulk materials in mixtures, and gas components not handled suitably with other more sensitive detectors, due to severe detector overloading on these other detectors. Thermal conductivity detectors are not intended to work well with capillary columns for several reasons. Sample capacity is not normally high enough with capillaries to put concentrations into the range of this detector, as these narrow columns suffer from severe peak distortion and retention shift from column overloading when enough sample is injected into them to be detectable by this detector. And use of a split injector, such as the Scion 1177, normally employed with capillaries to diminish the amount of sample inserted into the capillary to reduce the overload, just exasperates the problem by venting off much of the sample before the column and prior to reaching the detector. This detector works well with packed columns, and with Megabore capillaries, together with direct injection, such as the Scion 1041 Injector, or with valving.

However, attempts to enhance detectivity by employing large sample injections or large sample loops can dramatically impact the chromatography due to sample capacity of the column system, even with packed columns, and difficulties become more pronounced with capillary columns. Too much sample analyte can result in significant shift in retention times and a resulting potential of unexpected coelutions of nearby compounds. This retention shift can yield gross misassignment of peaks, if not carefully monitored.
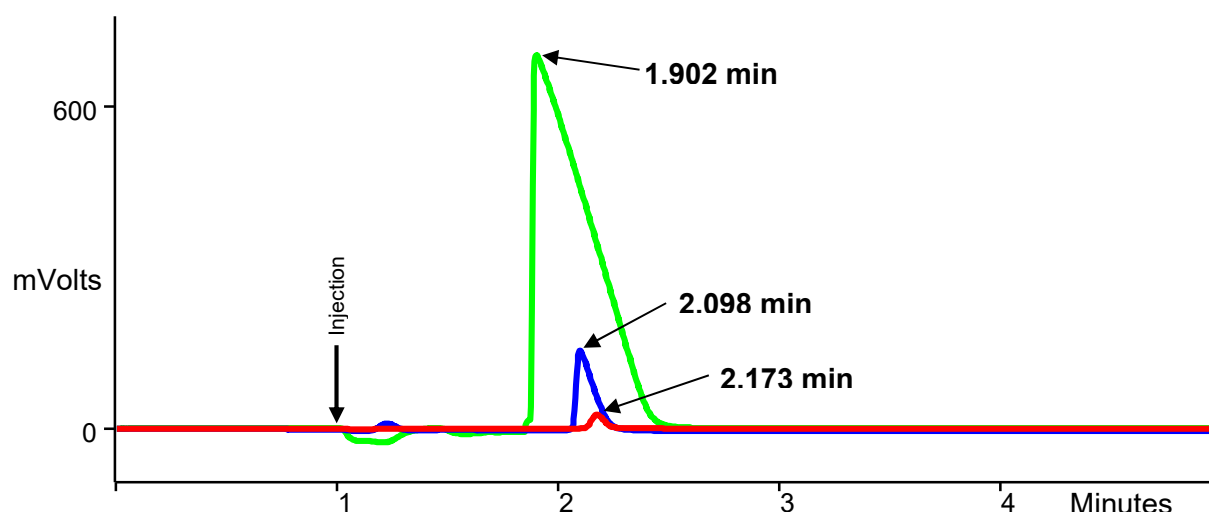


**Figure 9. Column overload can severely impact peak shape and dramatically shift retention times as much as 0.27 minutes or more**, as illustrated with measurement of pure Carbon Dioxide with argon carrier and various injection volumes. Red chromatogram is 0.01 ml injection, blue is 0.1 ml, and green is 2 ml loading. Column - Hayesep N, 60/80 mesh, 6' X 1/8", stainless steel, column temperature: 80 °C.

# Special Applications

**Dual Columns** – Detectors with separate sample and reference cells can be configured with two injector/column sets to allow both to be available for measurements by simply changing the polarity setting and then injecting the sample into the appropriate injector.  Thus, the operator readily can perform different analyses, including peak confirmations with a differing column phase, by simply injecting sequentially into two columns, one attached to one side and the other to the reference, and switching polarity to keep peaks positive, without changing hardware.

**Dual TCD** – The measurement of the full complement of fixed gases mandates use of two separate carrier gases - nitrogen or argon carrier for helium and hydrogen, and helium carrier for the rest - to maximize the differences in thermal conductivities.  By having two full and independent sets of filaments in one detector oven, the instrument can be set up to readily perform detection of the full set of gases with a single sample loading and without any hardware reconfigurations.  The system configuration will need to occupy two detector slots, with separate filament controls for each, even though only one thermal zone is utilized.

**TCD in series with another detector** – As the thermal conductivity detector is non-destructive of analytes, it can be plumbed in series with another detector, most commonly a flame ionization detector. The second detector can provide confirmation of the peak assignment and quantitation for compounds that are detected or not detected on both detectors.
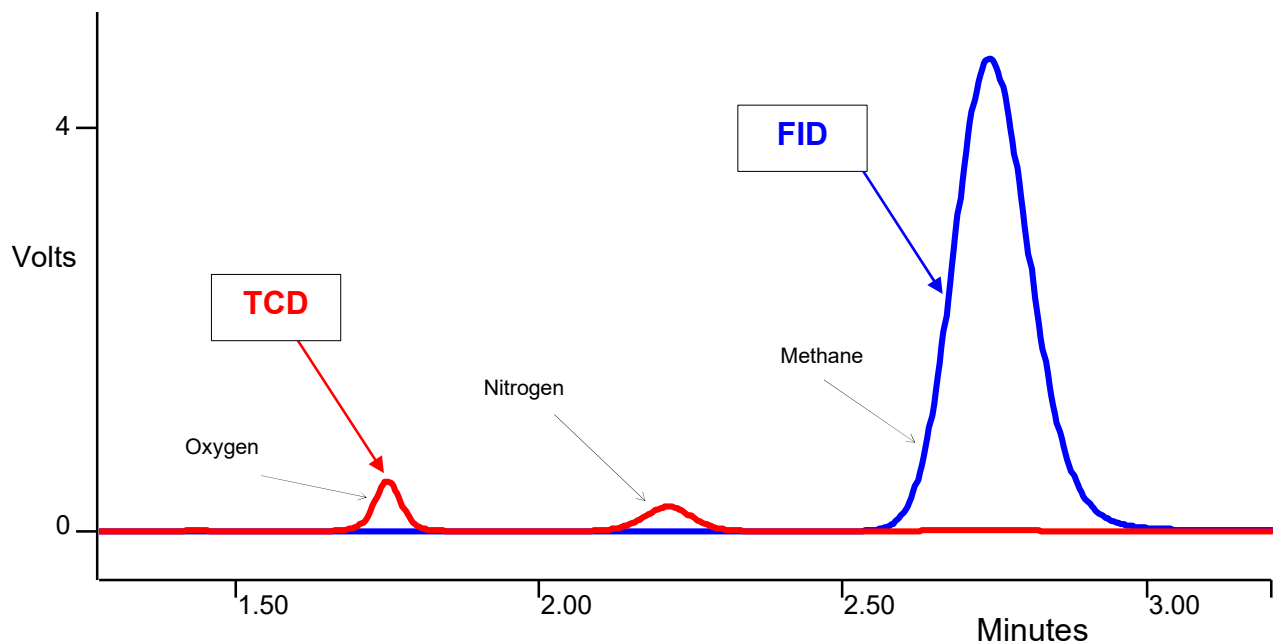


**Figure 10.  Since the thermal conductivity detector is nondestructive, it can be readily plumbed in series with other detectors to measure analytes with both.**  As an example, a flame ionization detector, with typical sensitivity often at least 1000 times that of the TCD, can readily pick out organic compounds, such as methane, from the inorganic gases - oxygen, nitrogen, carbon monoxide and carbon dioxide.

**Oxygen and Argon** – Measurement of oxygen in argon in very problematic as these two gases are extremely difficult to chromatographically separate without severe column conditions. If they are processed with helium as the carrier, the resulting peak usually represents both oxygen and argon combined. However, if argon is employed as the carrier, its contribution from the sample to the signal is cancelled and only the oxygen response is detected, albeit with reduced sensitivity due to the closeness in their thermal conductivities. Measuring argon in air by using oxygen as a carrier is not recommended due to the detrimental effects a continuous flow of oxygen will have on hot filaments in the detector.
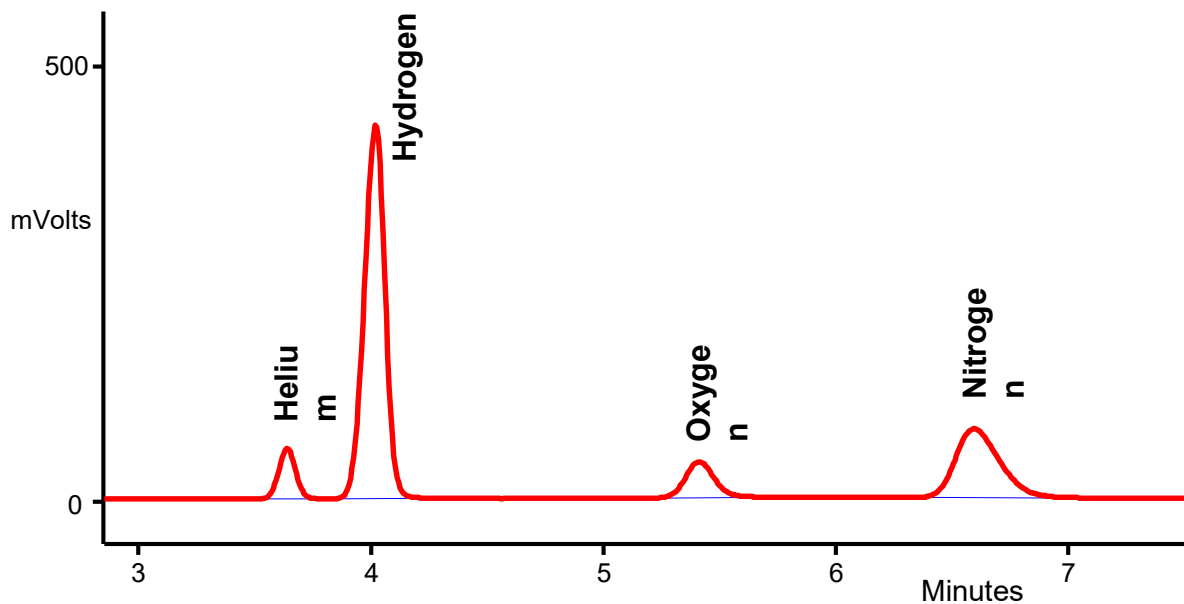


**Figure 11. Measurement of Oxygen without contribution of coeluting argon is accomplished by employing Argon as the carrier gas**. Since argon in the sample is matched with the carrier, only Oxygen is measured at 5.4 minutes. Concentrations – Helium - 1.3 %V/V, Hydrogen - 7.3 %V/V, Oxygen - 10.0 %V/V, Nitrogen - 33.6 %V/V, balance - Argon.

**Hydrogen, with Helium as Carrier** – Pure hydrogen has a higher thermal conductivity than helium and normally we would expect a peak in the opposite direction to that of the other fixed gases, with helium as the carrier. However, hydrogen exhibits the very odd behavior of exhibiting a thermal conductivity less than helium for lower concentrations and thus a peak similar to other analytes. Peculiarly, as the peak concentration grows as hydrogen elutes off the column, the signal starts in one direction and then suddenly inverts at a higher concentration as its thermal conductivity starts behaving as expected. Then as the peak tails off to lower concentrations, the peak inverts back to the same direction as the start, generating the classic "W" peak for hydrogen with helium as carrier.[8] Obviously this peak cannot be integrated to yield a meaningful concentration. If instead nitrogen or argon were used as carrier, hydrogen would behave as expected and would be integrated and computed accurately into a concentration value.

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[8] Some reports have discussed a similar behavior with carbon dioxide with argon carrier, but this effect could not be duplicated by the authors.
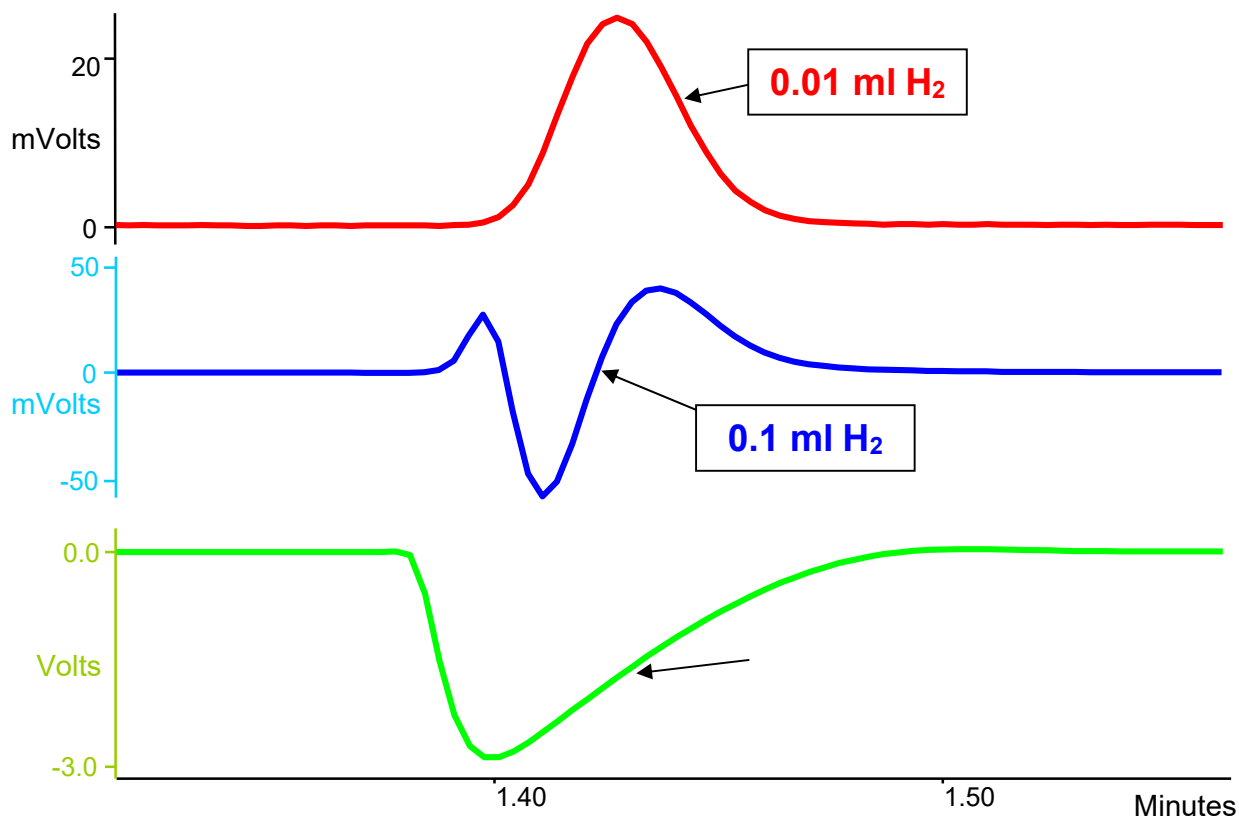
**Figure 12.** **High concentrations of hydrogen with helium carrier can produce severe disruptions in the chromatographic peak for hydrogen due to the reversal of thermal conductivity as the detection concentration of hydrogen changes during elution.** At low effective concentrations (0.01 ml injection of pure Hydrogen), the $H_2$ peak is positive and nicely Gaussian shaped, as expected. As hydrogen concentrations at the detector increase with larger injection volumes, the thermal conductivity of hydrogen relative to helium reverses at the higher detector concentrations, giving a "W" shaped peak that becomes impossible to accurately quantify. At extraordinarily large concentrations, the hydrogen peak is fully reversed and mandates a polarity reversal in detector settings to yield a positive peak, albeit severely distorted by column overloading.

(Please note changes in ordinate scales for the different chromatograms shown.)

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