Detection and Quantification of Tert-Butyl Mercaptan (TBM) in a Natural Gas Matrix Using a Transportable Micro Gas Chromatography System with a Thermal Conductivity Detector

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3:35PM

Advances in Fuels and Petrochemical Analysis II

Presentation Outline

- Odorant Background
- Why Monitor Odorants?
- Odorant Regulations
- TBM and THT as Odorants
- The Need for Precise Analysis
- Instrumentation
  - 3000 Micro GC Highlights
  - Modular Design
  - Thermal Conductivity Detector (TCD)
- Data and Repeatability

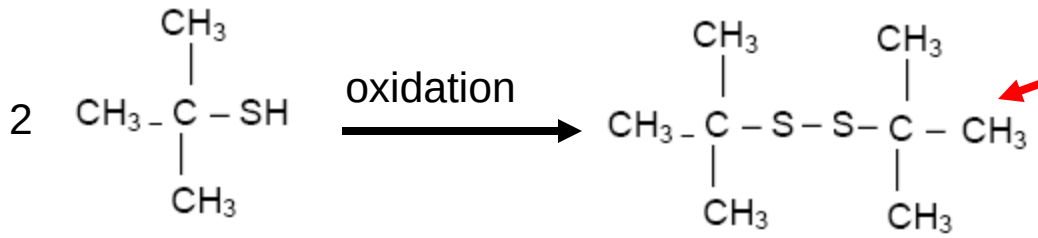
Odorant Background

- Natural gas is colorless and odorless
- Odorants are added to natural gas pipelines to serve as a leak indicator and warning agent
- Odorants are sold as blends of two or more mercaptans, alkyl sulfides, or cyclic sulfides
- Common odorants:
  - TBM – *Tert*-Butyl Mercaptan
  - IPM – Isopropyl Mercaptan
  - NPM – Normal Propyl Mercaptan
  - SBM – Secondary Butyl Mercaptan
  - THT – Tetrahydrothiophene/Thiophane
  - DMS – Dimethyl Sulfide
  - MES – Methyl Ethyl Sulfide

Why Monitor Odorants?

- **Many factors contribute to "Odor Fading" which will reduce the amount or intensity of the odorant over time**

- **Factors include:**
  - **Soil adsorption**
  - **Pipeline adsorption/absorption from plastic or steel pipes**
  - **Contaminants in "wet" natural gas (high amount of C4+ HCs) can mask odorants**
  - **Oxidation (air or rust are present) of mercaptans to disulfides**



Significantly less smell

  - **Presence of odorants such as ethyl and methyl mercaptan can convert added mercaptans (TBM, IPM, NPM) to disulfides**

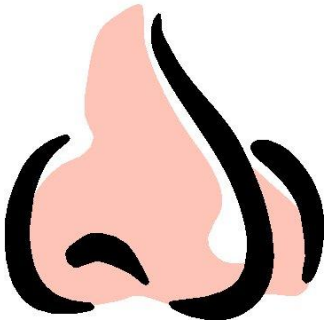
- **Thus, concentrations of odorant must be monitored frequently and consistently**

Odorant Regulations

- The Department of Transportation (DOT) requires odorants to be added in accordance with Federal Regulation 192.625

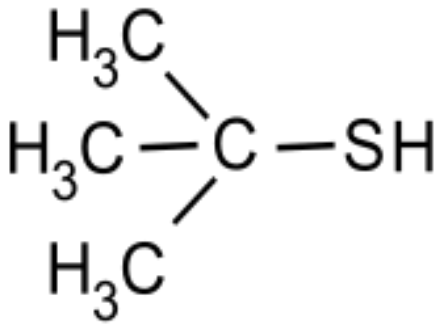
- There must be enough odorant so that a person with a "normal" sense of smell can detect it

- 192.625 does not specify which blend, how often to sample, or where to sample
  - It is left up to the operator to determine the blend, frequency, and location
  - Each natural gas operation is different
  - Factors that come into play:
    - Previous leak history
    - Age of pipelines
    - Presence of new lines in the system
    - Type of piping
    - "Wet" vs "Dry" natural gas
    - Naturally odorized vs. synthetically odorized



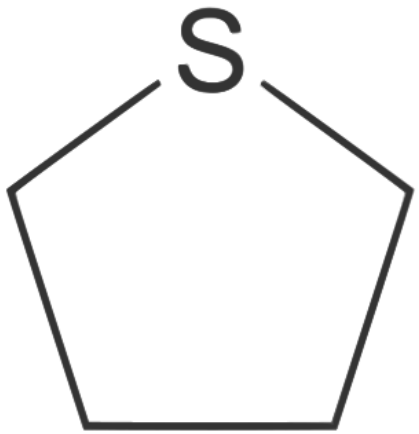
TBM as an Odorant

- **TBM is one of the most common odorants in the US**
  - **Highest resistance to oxidation (out of the mercaptans)**
  - **Low odor threshold (<0.1 ppb)**
  - **Excellent soil penetration**
  - **High freezing point (34°F, 1.1°C), so it must be blended with other odorants**
  - **A common blend is 80% TBM, 15% IPM, and 5% NPM**
  - **Industry expectation is ~1 ppm in the US**



THT as an Odorant

- **THT is a common odorant in Europe**
  - **Does not to oxidize**
  - **Low odor impact, not as pungent as TBM**
  - **Poor soil penetration**
  - **Common blends are 100% THT, or 50% THT with 50% TBM**
  - **Industry expectation is ~4 ppm in Europe**



The Need for Precise Analysis

- **Requirements:**
  - **Separation and quantification of TBM and/or THT at low ppm levels in a natural gas matrix**
  - **Simple and easy to use**
  - **Transportable or portable instrumentation**
  - **Precision**

Gas Chromatography as an Analysis Option

- Gas chromatography (GC) technology provides separation and analysis capabilities for TBM and/or THT in a natural gas matrix
- GC software provides users with component concentrations
- Thermal conductivity detectors (TCDs) are universal detectors that are simple to operate and meet the required sensitivity needs

Instrumentation

- INFICON 3000 Micro GC (MGC)
  - MEMS based TCDs and injectors
  - 0.5 to 4 mL/min flow rates

- 1-Channel Configuration (for TBM)
  - Channel A: 15 m 14% Phenyl, 86% Dimethylpolysiloxane (CPSil13CB)
    - 0.15 mm I.D.
    - Medium polarity
    - Large Variable Volume Injector (LVI) to provide the best sensitivity
    - Helium carrier gas

- Additionally, a second channel can be utilized to analyze THT:
    - 4 m 14% Cyanopropyl-phenyl, 86% Dimethylpolysiloxane (CPSil19CB, OV-1701)
    - LVI Injector

3000 Micro GC Highlights

- **User-friendly design**
  - **Simple**
  - **Out-of-the-box ready**
  - **Rugged for field use**

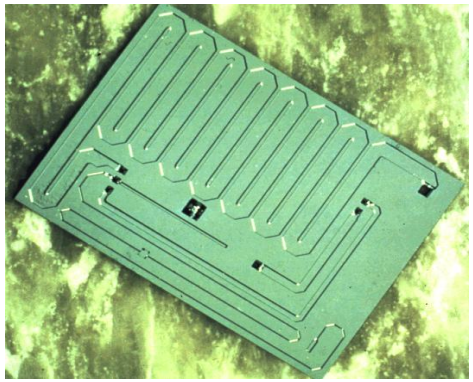
- **Size**
  - **Small footprint**
  - **Lightweight**
    - **2-Channel weighs 18 lbs**
  - **Low carrier gas consumption**
    - **< 5 cc/min per channel**

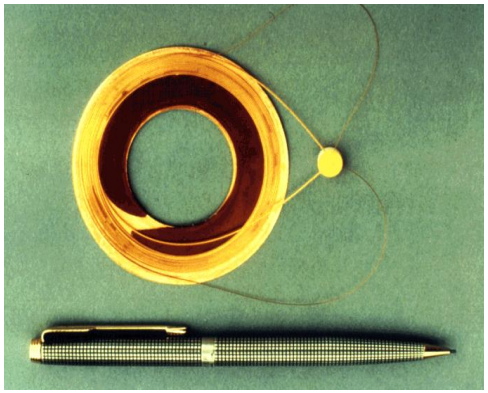
3000 Micro GC Highlight, cont.

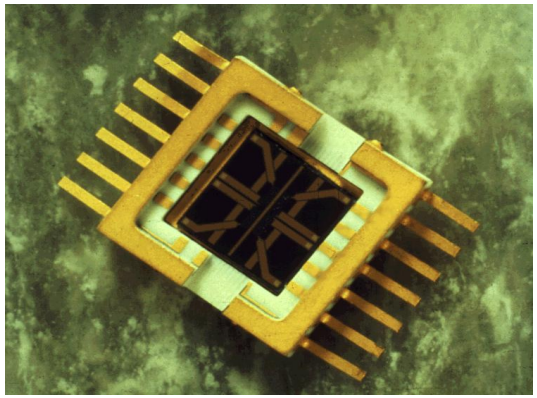
- **Fast**
  - Typical analysis times range from 1 to 3 minutes
  - TBM and THT can be analyzed in less than 90 seconds
- **Precise**
  - Precision equivalent to bench-top GCs
- **Transportable**
  - Easy to transport in the lab or in the field
  - On site sampling reduces the time and cost of sending samples to a lab

Modular Design Delivers Flexibility

- Each module is a self-contained GC comprising of a:
  - Micro-machined injector
  - High-resolution capillary column
  - Micro-machined TCD







- Modules can easily be replaced within minutes to adapt quickly to different application needs
- Minimal downtime

Chromatographic Module

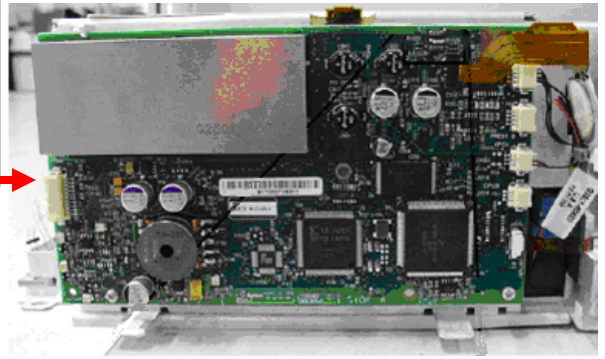
Injector

Capillary Column

TCD

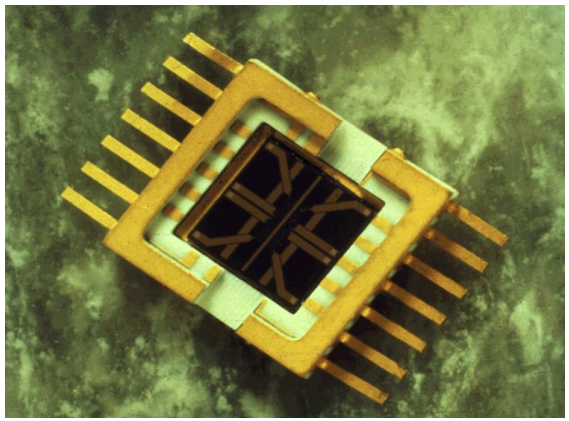
Digital Pneumatics (EPC)

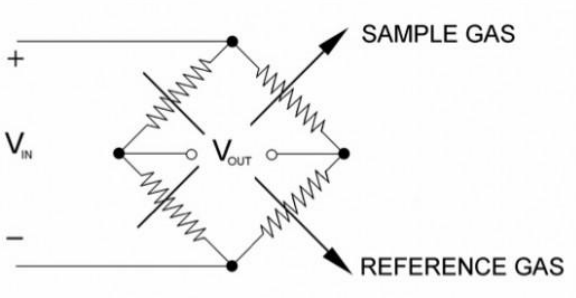
Electronic “D board” attached to back of module



Thermal Conductivity Detector (TCD)

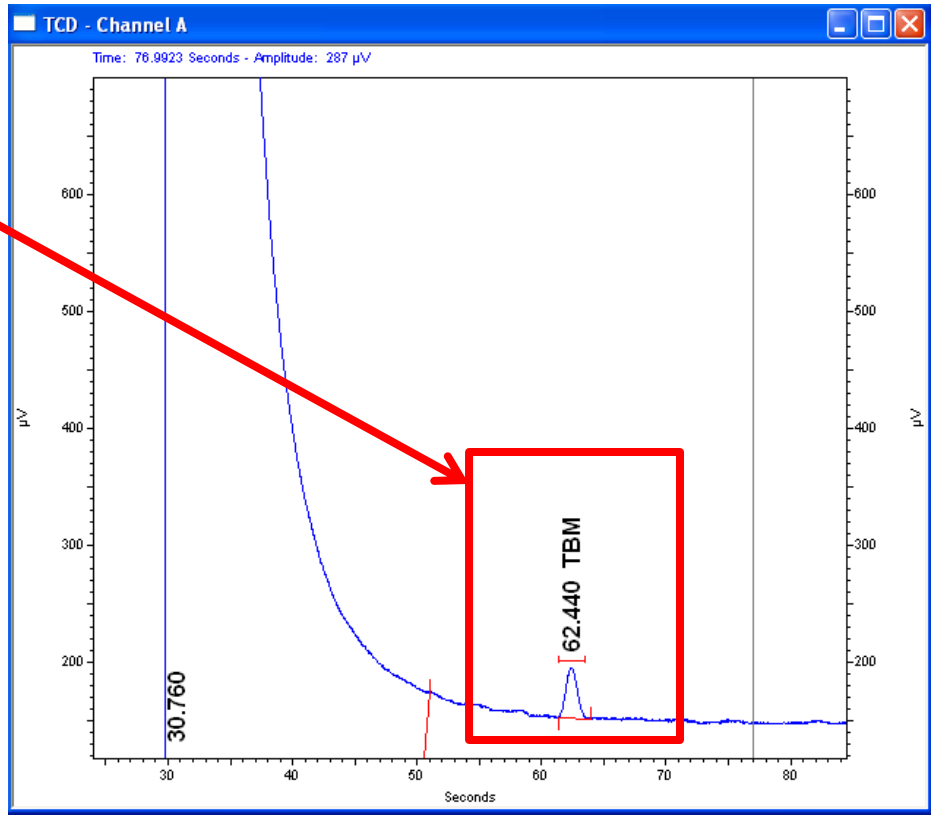
- Low internal volume
- Out-of-the-box ppm sensitivity
- Combined with LVI will give best sensitivity
- Dip switch for plug and play swapping option
- Linear from low ppm to 100%



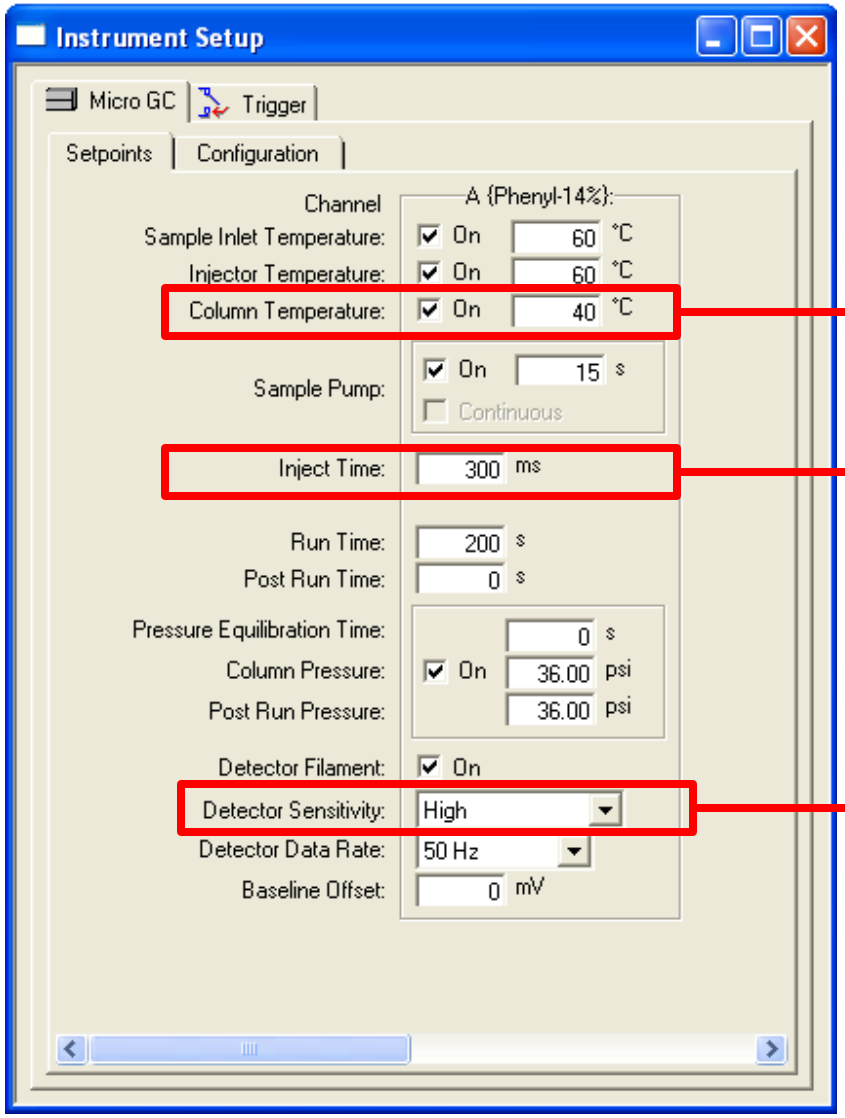


TBM in Natural Gas

- **Calibration gas:**
  - **2ppm TBM in nitrogen**
- **The 3000 Micro GC was connected to a water heater supplied with natural gas**
- **Expected TBM levels are ~1 to 3 ppm**



3000 Micro GC Method Parameters



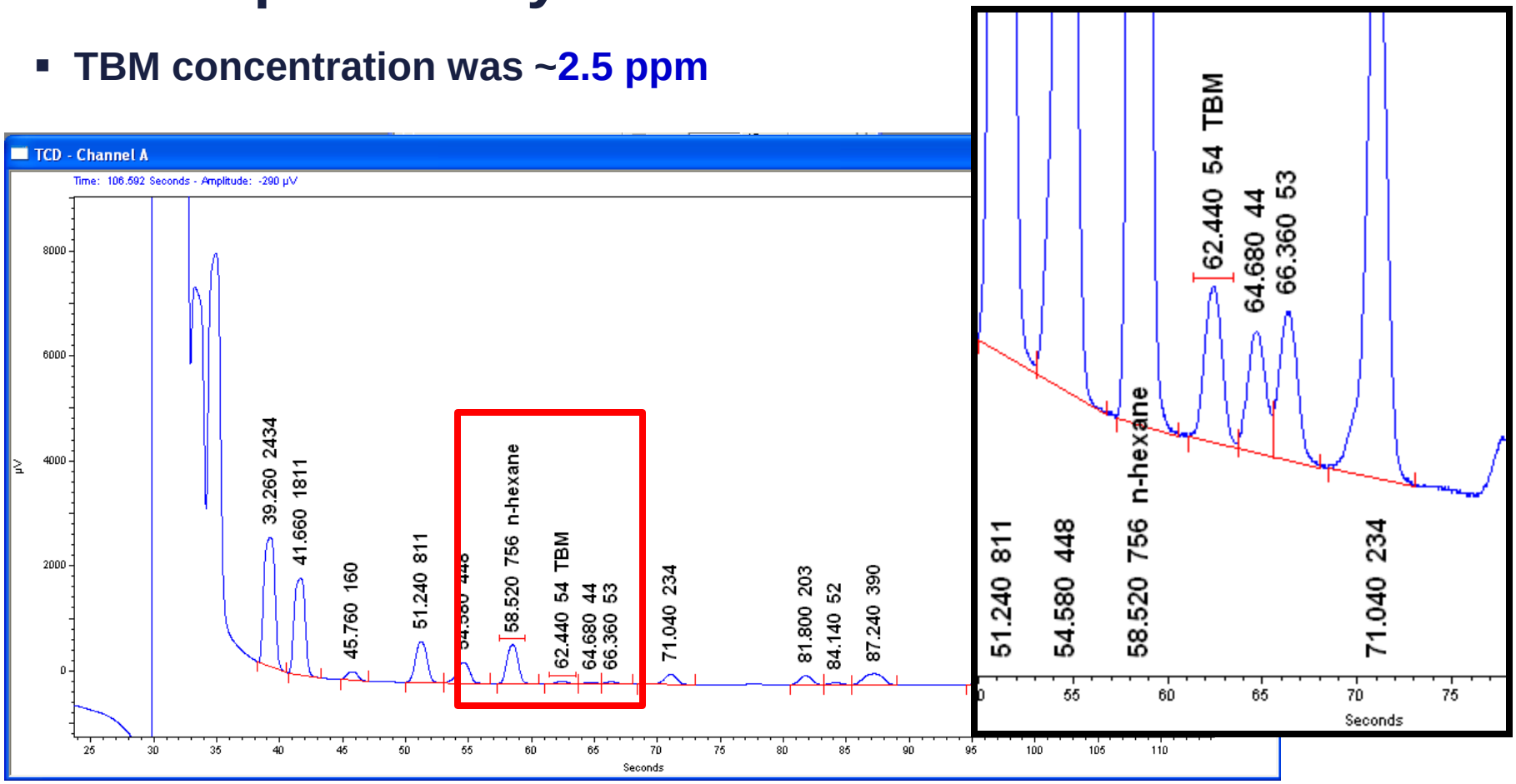
Low temperature

High inject time

High detector sensitivity

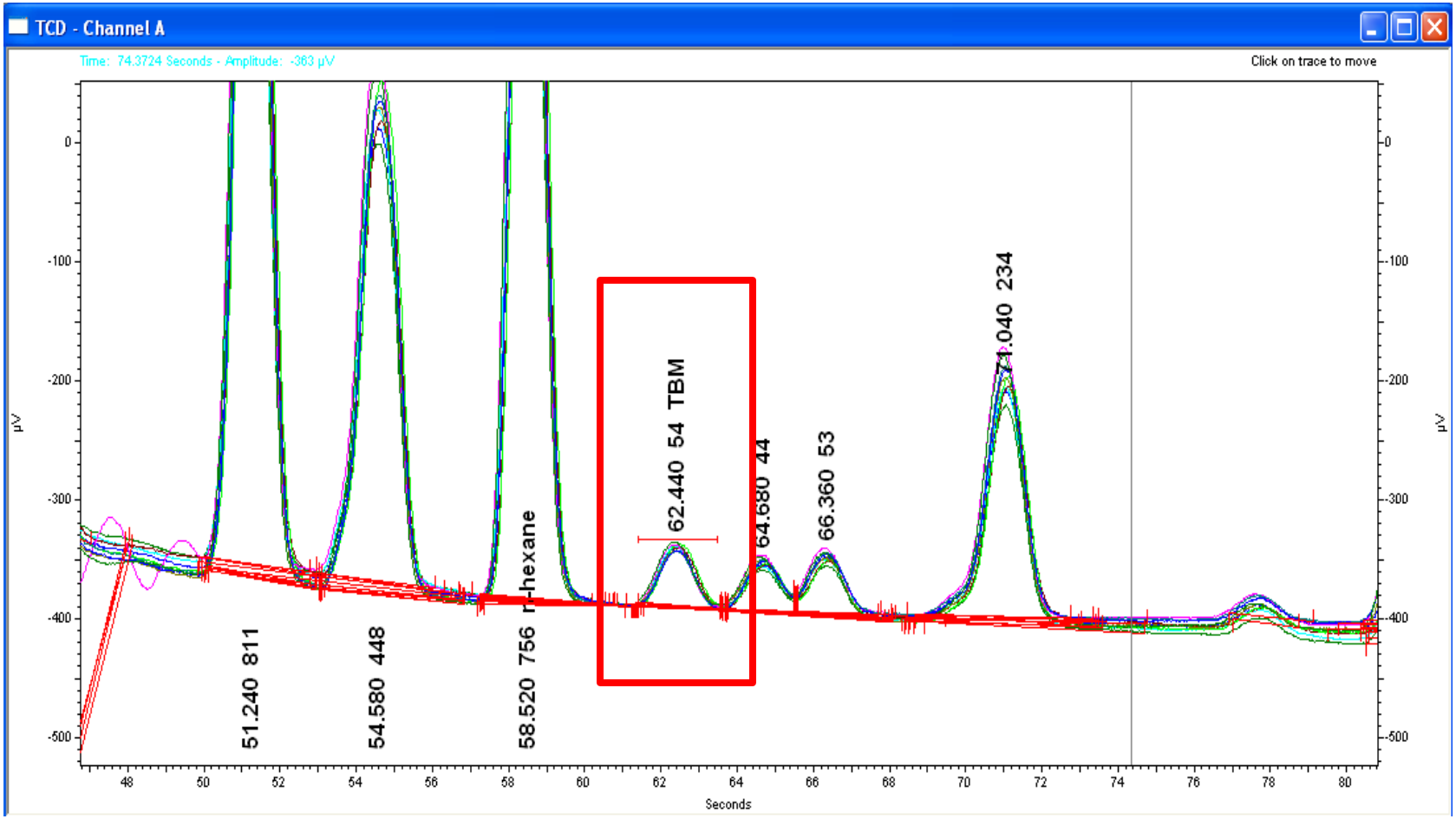
TBM Repeatability in Natural Gas– 10 Runs

- TBM concentration was ~**2.5 ppm**



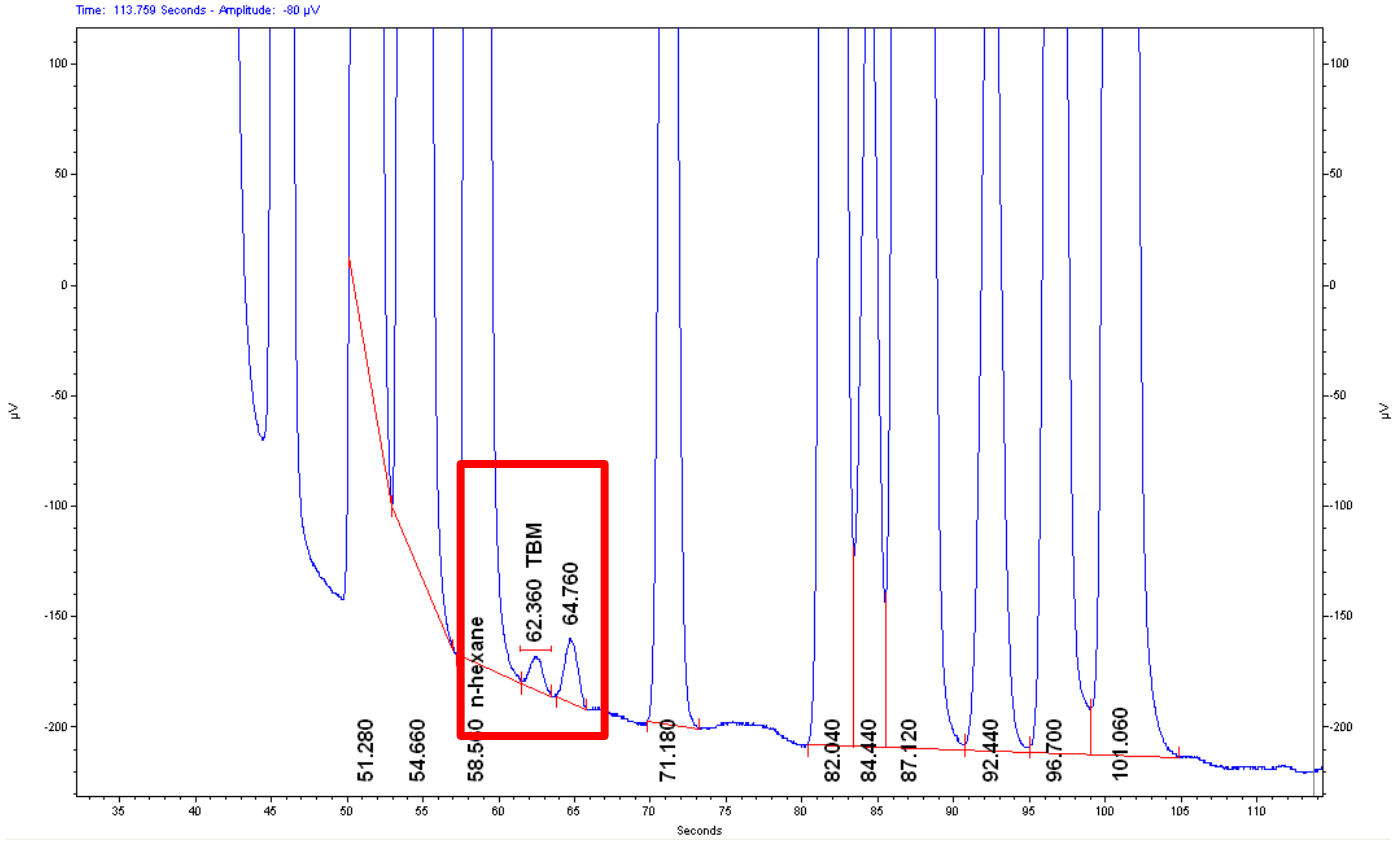
Channel	Number of Analyte	Compound	Retention Time	Area %RSD
A	1	TBM	62.44	2.581

TBM Repeatability in Natural Gas – 10 Run Overlay



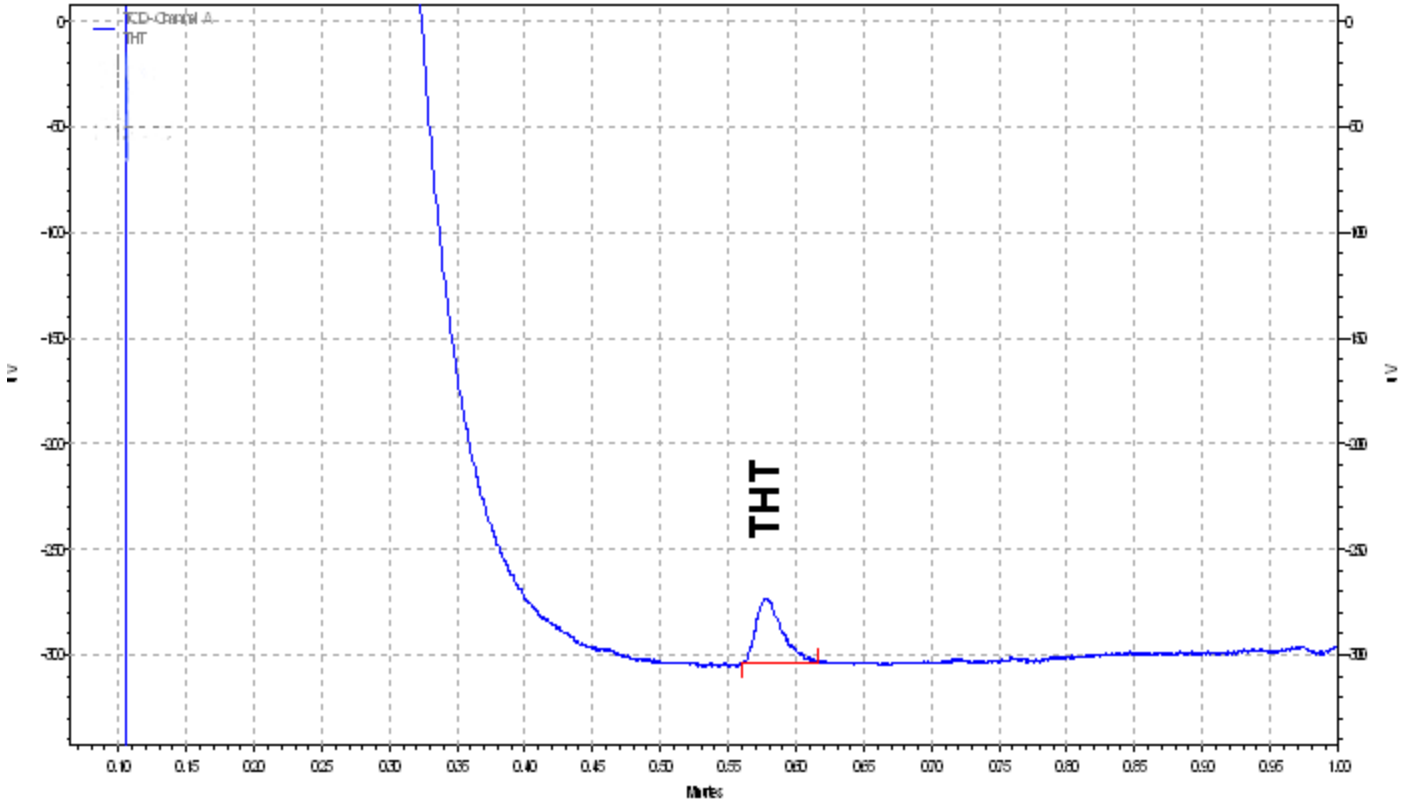
TBM Limit of Detection

- **2 ppm TBM standard was diluted with a gas-tight syringe into a natural gas standard containing C6+ components**
- **~0.75 ppm of TBM was analyzed**



THT in Natural Gas

- **Calibration gas:**
  - **5 ppm THT in methane**
  - **14% Cyanopropyl-phenyl, 86% Dimethylpolysiloxane column**



Conclusion

- Using 1 or 2 channels, the 3000 Micro GC is an excellent instrument to analyze low ppm levels of TBM and THT odorants
- Within 90 seconds, the complete separation TBM and THT was achieved
- 2.5 ppm TBM has a repeatability of less than 3 %RSD over the course of 10 sequential runs
- The 3000 Micro GC was able to detect down to **0.75 ppm** of TBM in a natural gas matrix

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Questions?