

A Transportable micro and Fast GC for Chemical Markers in Adulterated Fuels



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An abbreviated history - Dyes and Fuel Marking

- 1877 – Greville Williams in Hounslow – Early Inventor of Dyes for Leather / Textiles
- 1901 – Williams Hounslow purchase “LightHouse Chemical Co” Dewsbury UK.
- 1950’s – Morton International Salt Company Expands further into “speciality chemicals” through acquisition of MCC Dyes New Jersey – USA, NKI Dyes , Netherlands and Williams of Hounslow UK.
- 1950’s Williams Division of Morton introduces United Kingdom Tax Marking Programme
- 1960’s develop Automate Colours
- 1980’s Morton launches Mortrace™ Brand ID Fuel markers.
- 1999 – Morton International acquired by Rohm and Haas
- 2000’s – product rationalisation – sale of European “GOM” Business; launch of SpecTrace fuel markers.
- 2009- Rohm and Haas acquired by DOW – Fuel Markers group moved to sit with ANGUS division of DOW Chemicals.
- 2012 – Launch of ACCUTRACE™ brand marker technology offering.



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Branded Fuel Marketing

The Problem

Fuel Adulteration

- Unscrupulous dealers substituting all or part of branded fuel with adulterant(s)

– Examples

- generic fuel into branded fuel
- spent solvent into branded fuel
- octane cheating

Left unchecked, losses to adulteration are estimated to fall between 5 and 20% of a retailer's branded fuel volume

One bad experience with adulterated fuel can turn away the most brand loyal of consumers for a lifetime

Vehicle engines and emission systems are not designed to handle poor quality, adulterated fuel and cause substantial harm to the community



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GOVERNMENT FUEL TAXES

The Problem

Fuel Adulteration

- Unscrupulous criminals obtain Low Tax/Tax Free Fuel and add this into High Tax (Tax Paid) fuels

– Examples

- Home Heating Fuel into DIESEL
- Export fuel illegally never leaving.
- Kerosene into Gasoline

Left unchecked, losses to adulteration are estimated to fall between 3 and 12% of a countries Tax Paid Fuel Revenue

In countries that subsidize Road Fuels for the population, illegal exports can lead to fuel shortages.

e.g. UK Government losses 2011/2012 estimated at GBP 750 Million (USD \$1.2 Billion)
Poland \$1Billion Losses

Vehicle engines and emission systems are not designed to handle poor quality, adulterated fuel and cause substantial harm to the community



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The Challenge

- Multiple points in fuel supply chain
 - Multiple opportunities for diversion of fuels.
- Dealer Owned, Dealer operated networks



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Dow Fuel Marking *A history of technology*



Dow Fuel Marking Technology

ACCUTRACE™ Molecular Markers



- Secure
 - proprietary and unique
 - custom designed, novel chemistry
 - patent pending in many Countries
 - marker formula's are custom made and identities kept secret
 - robust
 - not prone to degradation or interference from other marker systems
 - admissible
 - in a court of law

ACCUTRACE provides you a secure solution – unique, robust, and admissible



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Dow Fuel Marking Technology

ACCUTRACE™ Molecular Markers

- Secure
 - The Gas Chromatography – Mass Spectroscopy (GC-MS) analytics used in the ACCUTRACE™ forensic test are commonly used today to detect and quantify drugs, explosives and other crime scene evidence
 - GC-MS has been cited in some sources as the “*preferred*” evidence for a court of law for drug determination

» http://www.bjc.org/bcc07_content.aspx?id=32348



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Falcon Analytical makers of the . . .

Calidus CS, for roadside analysis of ACCUTRACE™

–Highly Transportable

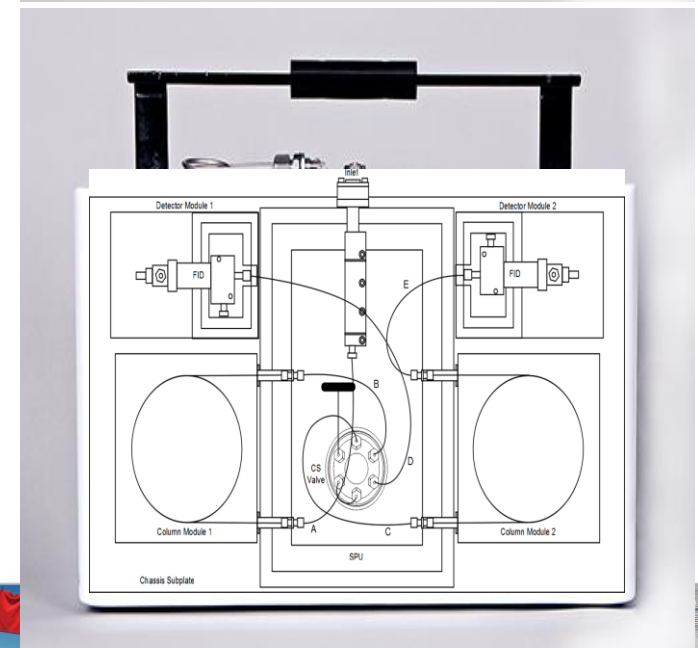
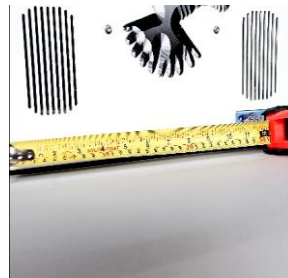
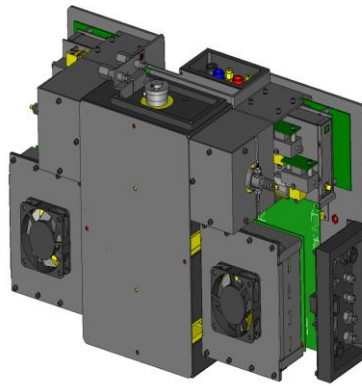
- ~ 11 kilograms
- < 300 Watts
- ~ 455 x 280 x 216 mm

–Economic

- Lowest Capital
- Lowest Consumables

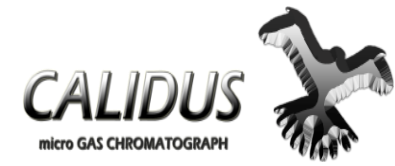
–Highest Durability

- Field proven
- Industry standard FIDs
- Temperatures well below spec limit on the CS valve



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Calidus CS for Roadside Analysis of Accutrace in Fuels at <125 ppb



- Standard Calidus CS
 - Relatively polar column on Channel 1
 - Relatively nonpolar column on Channel 2
 - Rugged, reliable, industry standard dual FIDs used
 - FID 1 used to determine heartcut timing and normalization of results
 - FID 2 used to measure ACCUTRACE
- CS Valve for Heartcut
 - High temperature rotary valve with pneumatic actuation
 - Special temperature control employed on valve body
 - Temperature well below the specification limit for the valve

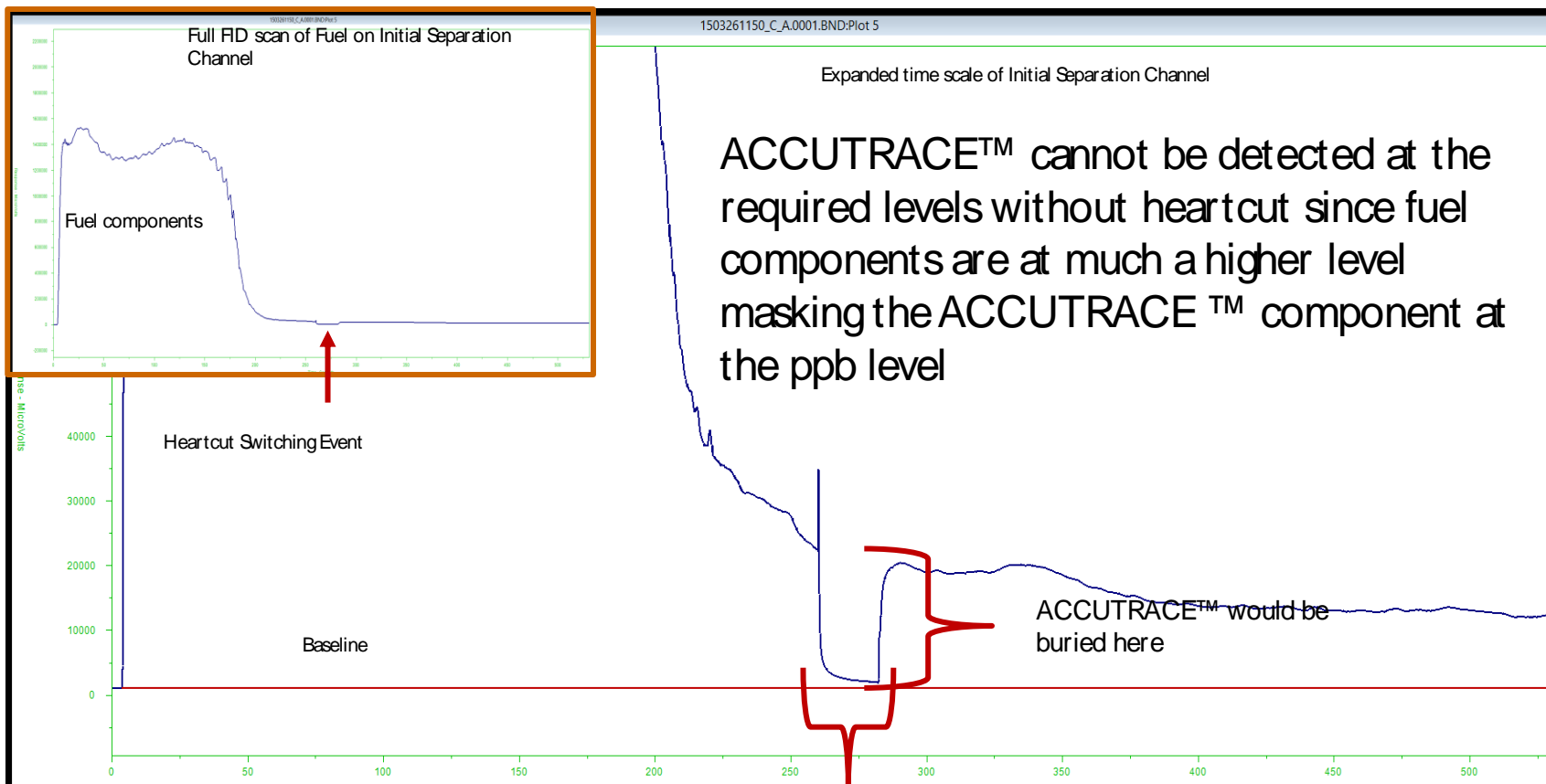


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Calibration Standard on Initial Separation Channel



Material Heartcut into MXT-1 including Accutrace

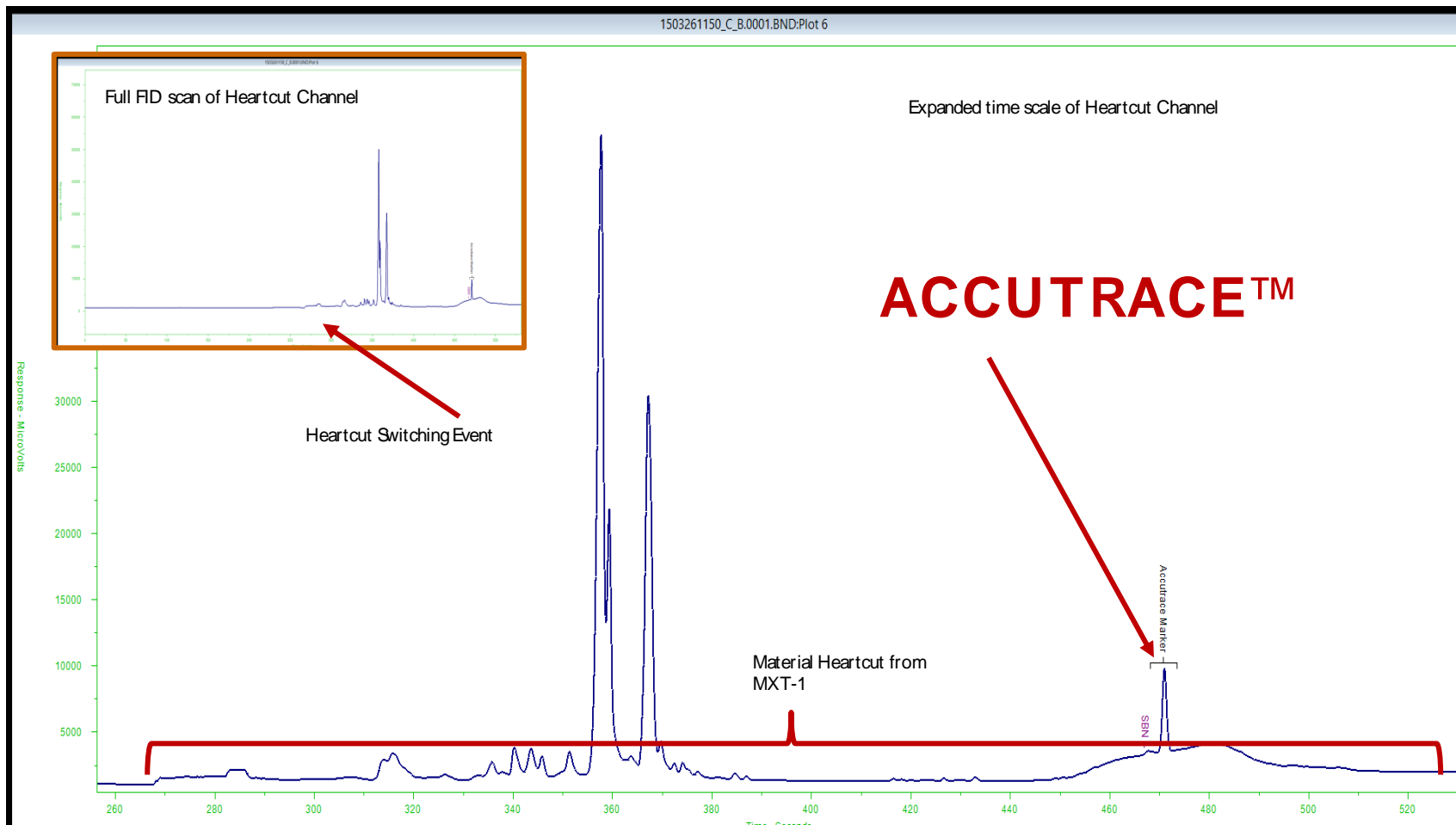


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Calibration Standard on Heartcut Channel

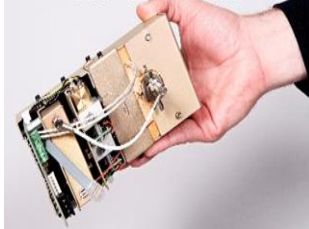


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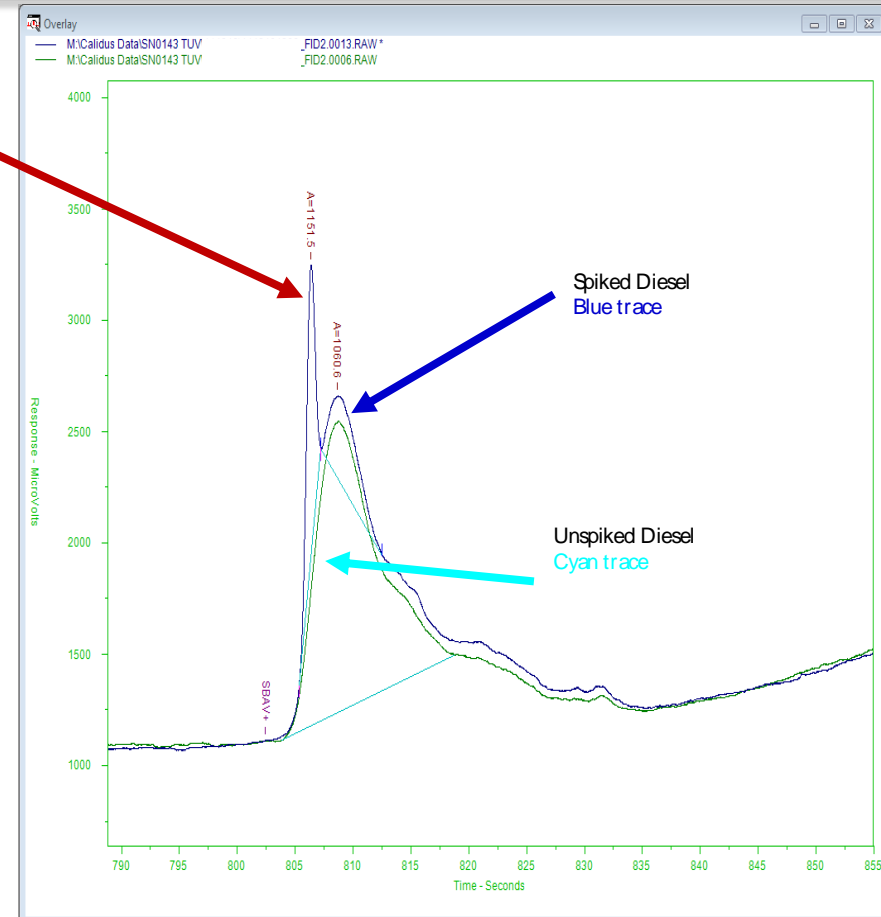


Result for 0.5 ppm in Diesel

FID Module



- The ACCUTRACE™ peak is well formed
 - There is still some residual diesel material from the heartcut
 - There is no indication of cold spots inhibiting the ACCUTRACE™ limit of detection
- The separation is very good
 - Quantification can be done with excellent repeatability and reproducibility
 - Analysis time is about 10 minutes

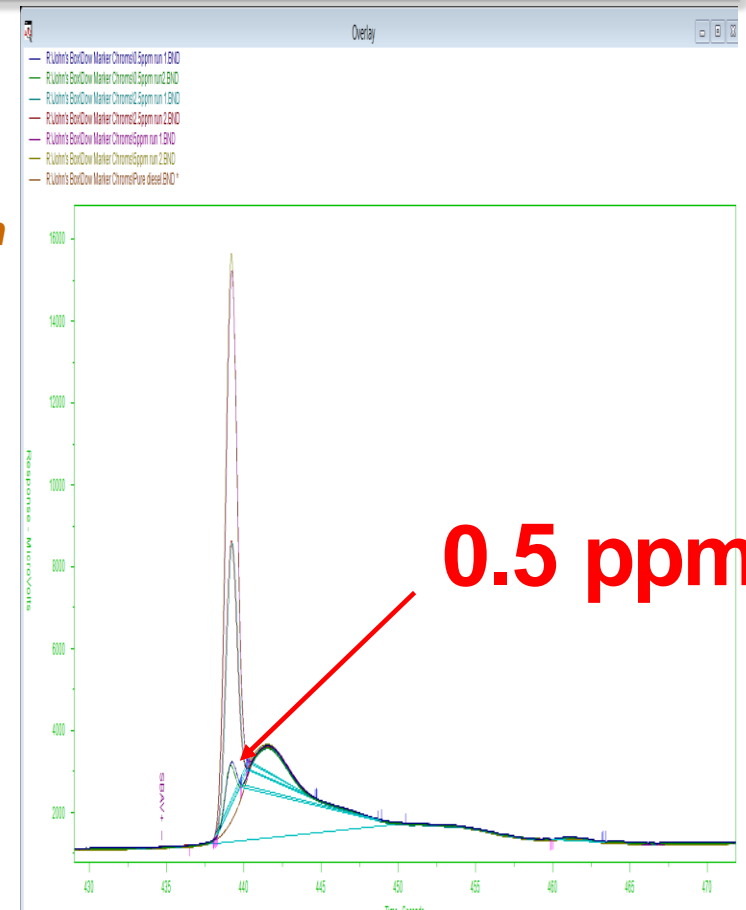


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5, 2.5 and 0.5 ppm Duplicate ACCUTRACE™ Overlays

- The ACCUTRACE™ component is clearly quantifiable down to 0.5 ppm
 - No special data treatment is necessary
 - Standard integration tools can be used even in the face of some residual diesel component presence
 - Duplicate analysis demonstrates great repeatability even at 0.5 ppm
 - A pass/fail limit of detection has been demonstrated at the 0.250 ppm level with confidence
- Setting the trigger at 0.125 ppm and a tolerance value insures
 - No false negatives
 - No false positives



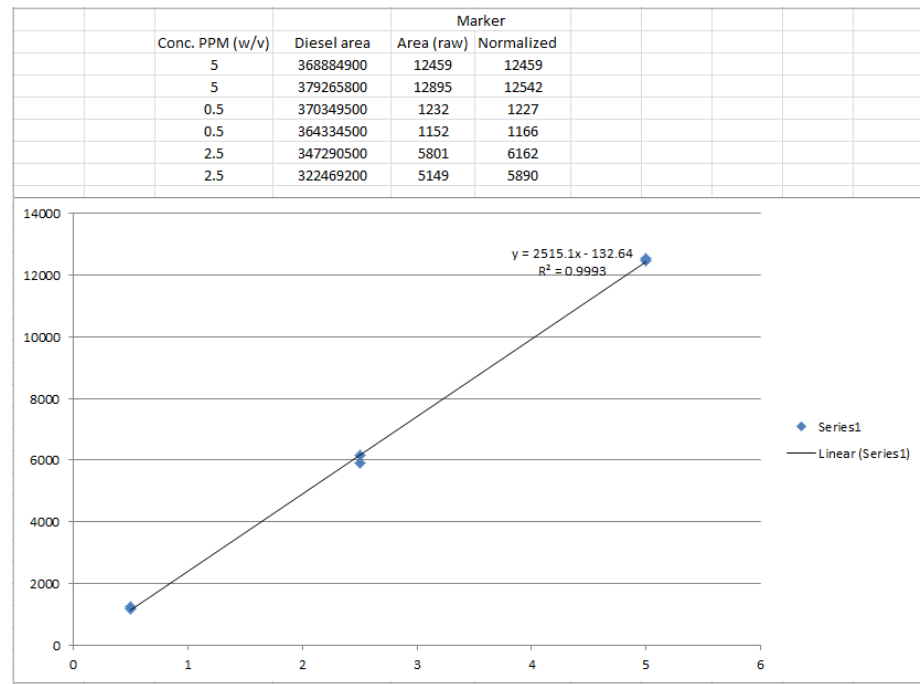
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Linearity with and without Normalization

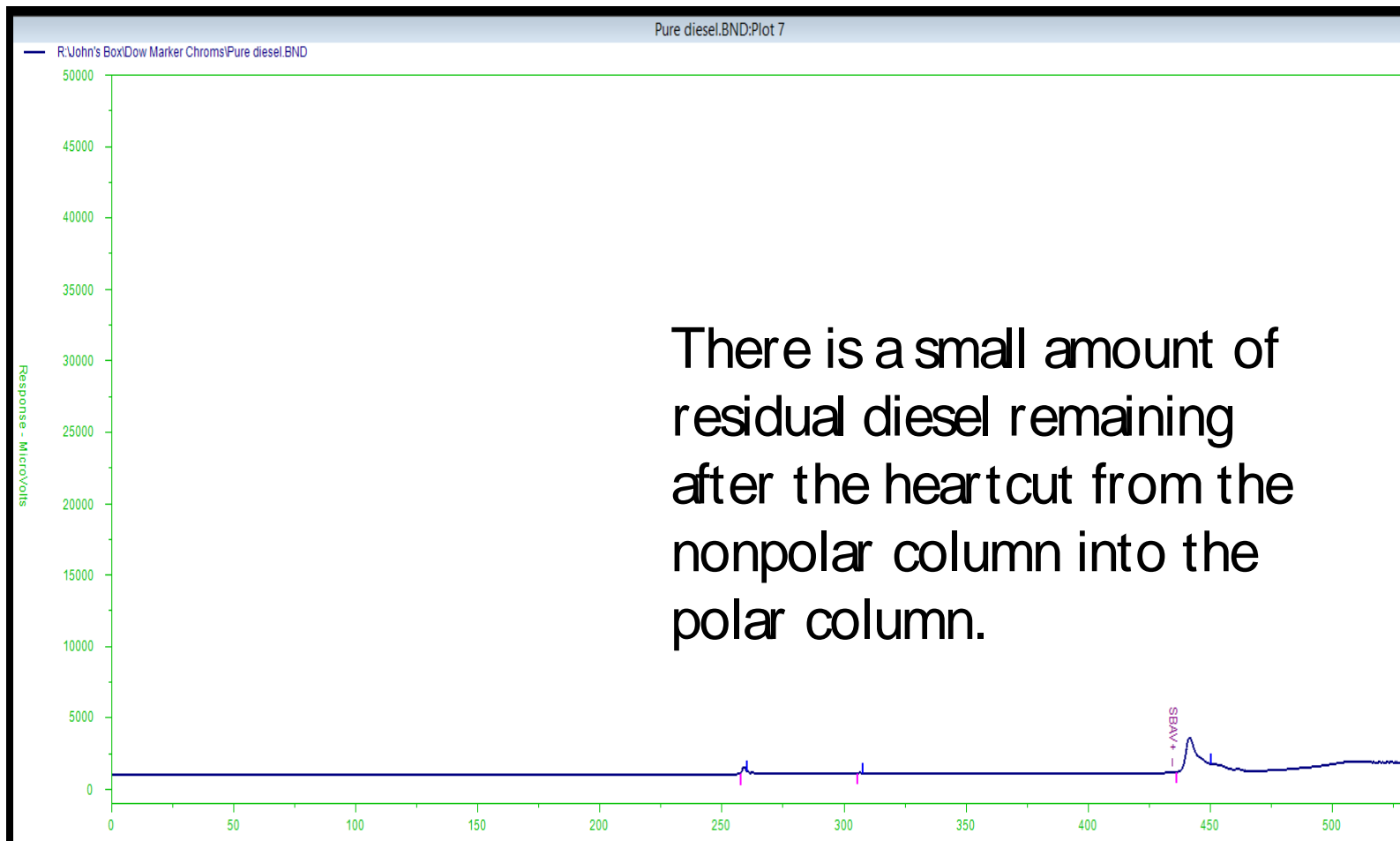


- Duplicate runs from previous slide
 - For a present/not present analysis, this result is far more than adequate
 - Linearity for quantification is quite good at $R^2 = 0.9993$
- The second FID is used for normalization
 - Removes the variance in sample quantity injected
 - Improves linearity and confidence in the measurement





Pure Diesel



There is a small amount of residual diesel remaining after the heartcut from the nonpolar column into the polar column.

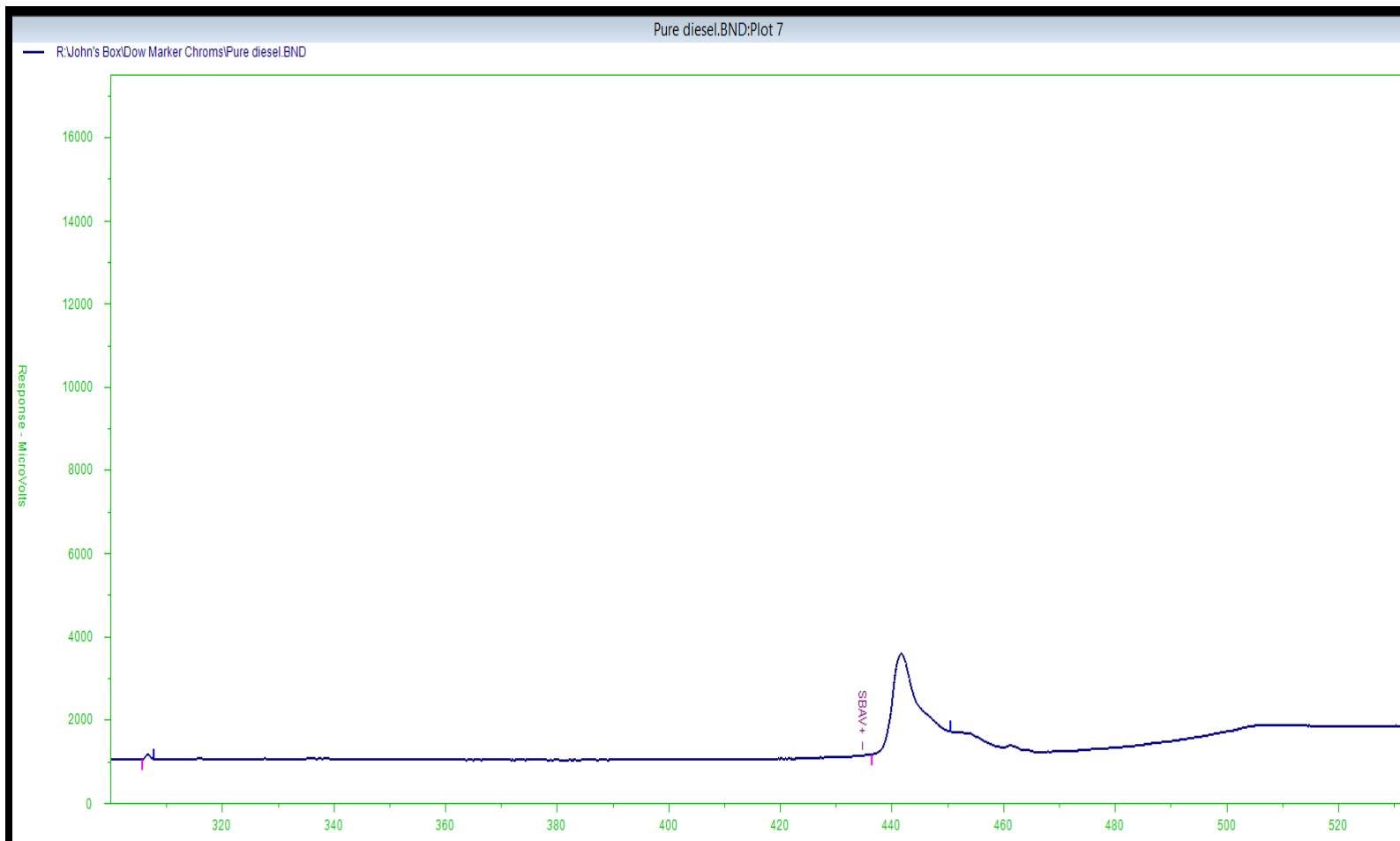


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Pure Diesel Expanded Scale

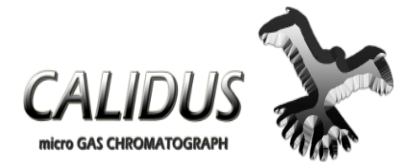
CALIDUS
micro GAS CHROMATOGRAPH



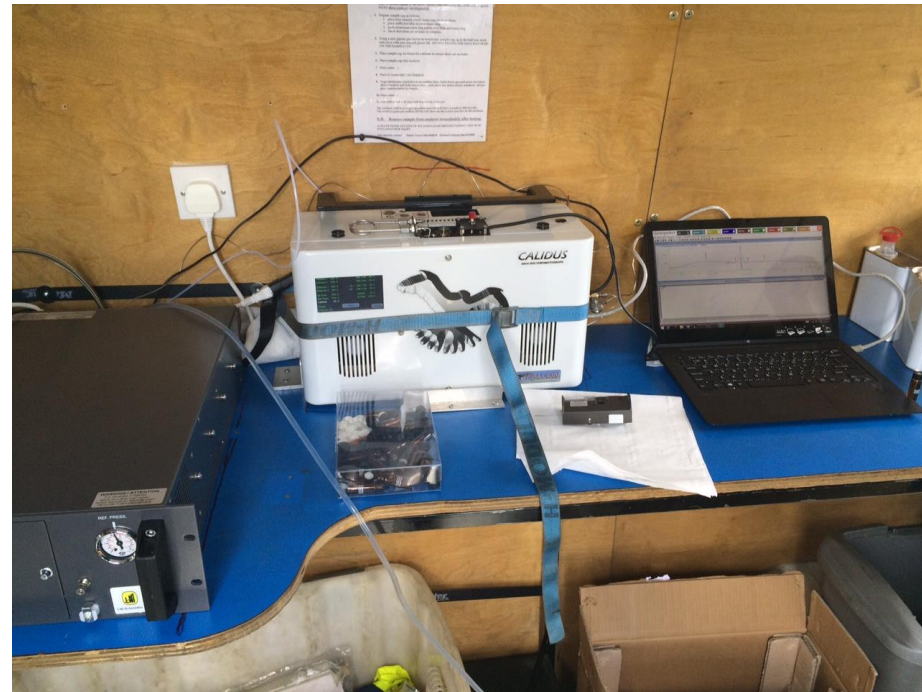
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First Deployment in Irish Enforcement Vehicle



- **Temporary Installation including**
 - *Calidus Fast Gas Chromatograph*
 - *Laptop including CPMT automation*
 - *FID Grade hydrogen/air generator*
 - *Air compressor*
 - *Clearly, all in temporary mounting for demonstration purposes*
- **Picture from 5/26/2015**
 - *Calidus/CPMT maiden voyage*
- **FIRST DETECTION of ACCUTRACE™**
 - *FAIL Alarm indicating ACCUTRACE™ >250 ppb*
 - *1st quantification was 1.38 ppm*
 - *2nd analysis validation run was 1.37 ppm*



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Summary

Calidus GC Deployed for Fuel Fraud Roadside Testing

- 125 ppb detection limit for ACCUTRACE™ fuel marker
- Based on two dimensional GC heartcut method to distinguish marker from fuel matrix
- Robust method to changes in fuel source and fuel adulterants
- Hydrogen generator and air compressor eliminate need for compressed gas cylinder placarding
- Roadside results confirmed by lab GC/MS with selected ion monitoring.



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Next Steps

- Questions?
- Actions?



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