## Application Note

### *Instrument: Pegasus® BT 4D*

# Battling Fuel Washing: Accurate Quantitation of ACCUTRACE™ Plus in Commercial Diesel and Full Characterization of Petroleum Samples

Key Words: GCxGC-TOFMS, Fuel Washing, Fuel Marker, Petroleum, BPE, ACCUTRACE™ Plus

## *Introduction*

Government-subsidized farm fuels are often dyed to distinguish them from consumer diesels. "Fuel-washing," where dye is removed from fuel that is subsequently resold at a higher price, has been a major concern for many tax, regulatory, and law enforcement agencies. Moreover, the Customs Cooperation Working Party (CCWP) of the Council of the EU found that fuel laundering also results in serious environmental pollution due to the use of chemicals, which are often dumped as waste in nature and agricultural lands. In 2017, the EU Decision 2017/74 approved the "Solvent Yellow 124" (i.e., ACCUTRACE™ S10) as the common fiscal marker for the marking of gas oils and kerosene.[1] However, in 2019, a review of the usefulness of this marker revealed its lack of resilience to common removal methods. Thus, a need to replace the ACCUTRACE™ S10 with a more robust marker was desirable.

In this respect, a new marker, whose commercial name is the ACCUTRACE™ Plus (Butoxybenzene (BPE), CAS: 1126-79-0), has been evaluated and confirmed to comply with the safety and robustness requirements. Compared to the ACCUTRACE™ S10 dying marker agent, ACCUTRACE™ Plus is colorless and its marking level has been set at a harmonized range to simplify the implementation and control requirements across the entire European Union.[2]

In this application note, the workflow for the detection and quantification of BPE using the LECO's *Pegasus* BT4D GCxGC-TOFMS is demonstrated. Additionally, the complementary advantages of this advanced separation setup for the characterization of light to medium boiling point petroleum fractions is described.

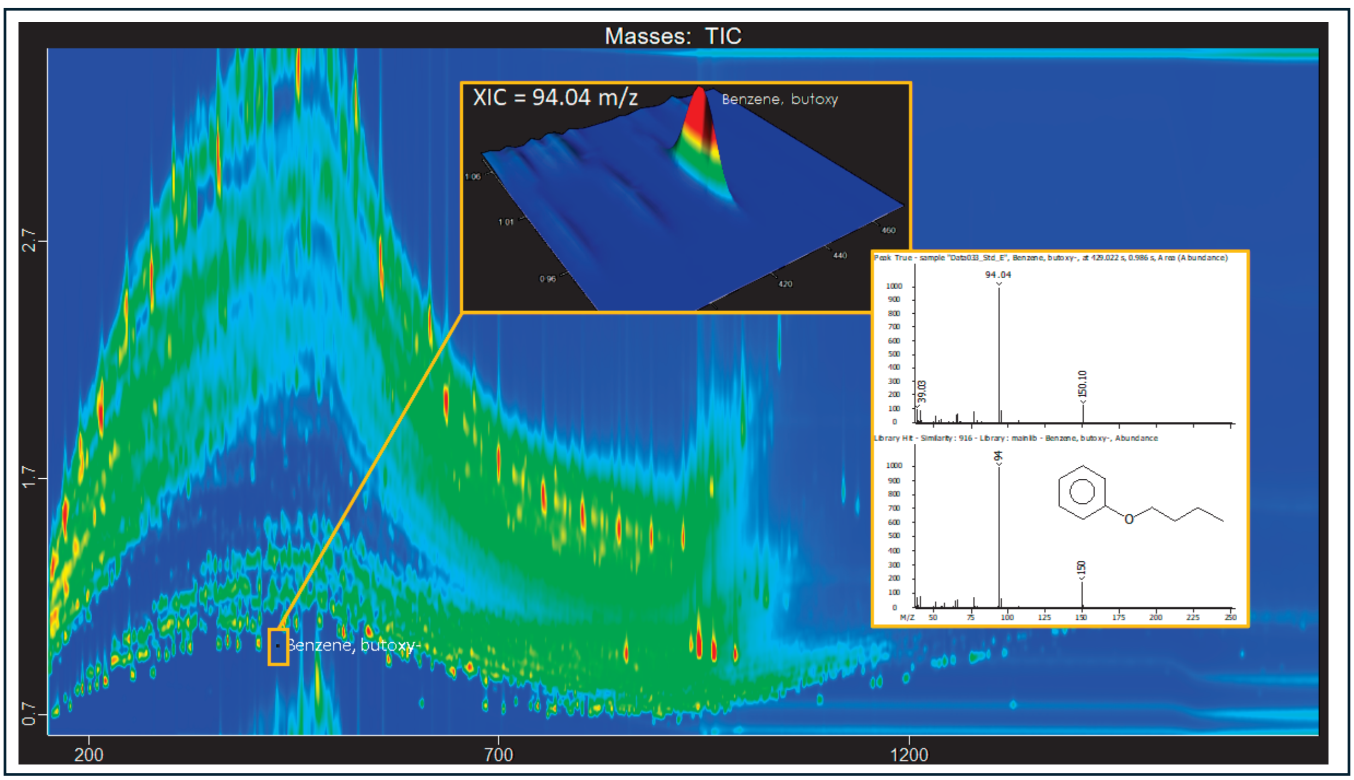


***Figure 1. Total ion chromatogram (TIC) for BPE detection and mass spectral confirmation in a spiked commercial diesel B7.***

## Experimental

Commercially available B7 diesel (containing 7% biodiesel) and kerosene samples were spiked with BPE (LGC Standards, CAS: 1126-79-0) at different levels corresponding to marker dosages between 1 % and 125 %, (i.e., concentration levels ranging between 0.095 mg/L and 11.875 mg/L). A total of six matrix-matched calibration solutions were prepared according to the following concentrations: 0.095, 0.190, 0.475, 0.950, 9.500, and 11.875 mg/L. Spiked and non-spiked B7 diesel and kerosene samples were analyzed on a *Pegasus* BT4D GCxGC-TOFMS system with full mass range acquisition. In addition, two spiked samples at 1 % and 100 % dosage (0.095 and 9.5 mg/L, respectively) were analyzed for recovery purposes. ChromaTOF® brand software was used to identify the fuel marker at low ppb levels, utilizing peak finding with both deconvolution and Target Analyte Find features. Table 1 displays the analytical parameters applied for the GCxGC and TOFMS parameters. A total run time of 30 minutes was attained for the BPE targeted method. The same instrumental setup was also used for petroleum characterization.

**Table 1: Analytical Parameters**

| **Gas Chromatograph** | **Agilent 7890B with LECO Dual Stage QuadJet™ Modulator** |
|---|---|
| **Injection** | 0.4 µL injection, Split 200:1 @ 250 °C |
| **Carrier Gas** | He @ 1.4 mL/min, Constant Flow |
| **Primary Column** | Stabilwax-MS 30 m x 0.25 mm ID x 0.25 µm coating (Restek) |
| **Secondary Column** | Rxi-5SilMS 0.6 m x 0.15 mm ID x 0.15 µm coating (Restek) |
| **Oven Temperature Program** | 100 °C (0.2 min), ramp 5 °C/min to 140 °C, ramp 15 °C/min to 250 °C (10 min), ramp 15 °C/min to 260 °C (3.8 min) |
| **Secondary Oven** | +5 °C (relative to the main oven temperature) |
| **Modulator** | +15 °C (relative to the secondary oven temperature) |
| **Modulation Time** | 3 s |
| **Transfer Line** | 250 °C |
| **Mass Spectrometer** | **LECO *Pegasus* BT 4D** |
| **Ion Source Temp** | 250 °C |
| **Mass Range** | 40-600 m/z |
| **Acquisition Rate** | 250 spectra/s |

## Results

BPE separation and quantification poses many challenges as it typically elutes in a congested chromatographic region, for example in an area where many other substances (such as n-i paraffins, olefins, cyclic paraffins, and aromatics) elute (Figure 1). Moreover, the BPE mass spectrum does not show specificity, as its most abundant m/z fragments (m/z 94 and m/z 150) are common to many of the classes reported above. Thus, the identification of BPE by GC-MS is even more challenging from an analytical point of view. In this respect, the application of GCxGC-TOFMS is crucial for accurate detection and quantitation of BPE in petroleum samples due to enhanced separation capacity and the subsequently cleaner mass spectra which are obtained.

BPE shows very little retention in the secondary column (2D), resulting in an extremely narrow chromatographic band (FWHH = ~0.03 s). This poses an extra challenge, namely the acquisition of sufficient data points allowing for reliable quantitation. LECO's Pegasus BT4D allows fast acquisition rates (up to 500 spectra/s). In this case, a rate of 250 spectra/s enabled efficient peak reconstruction and quantification of the fuel marker (Figure 2).

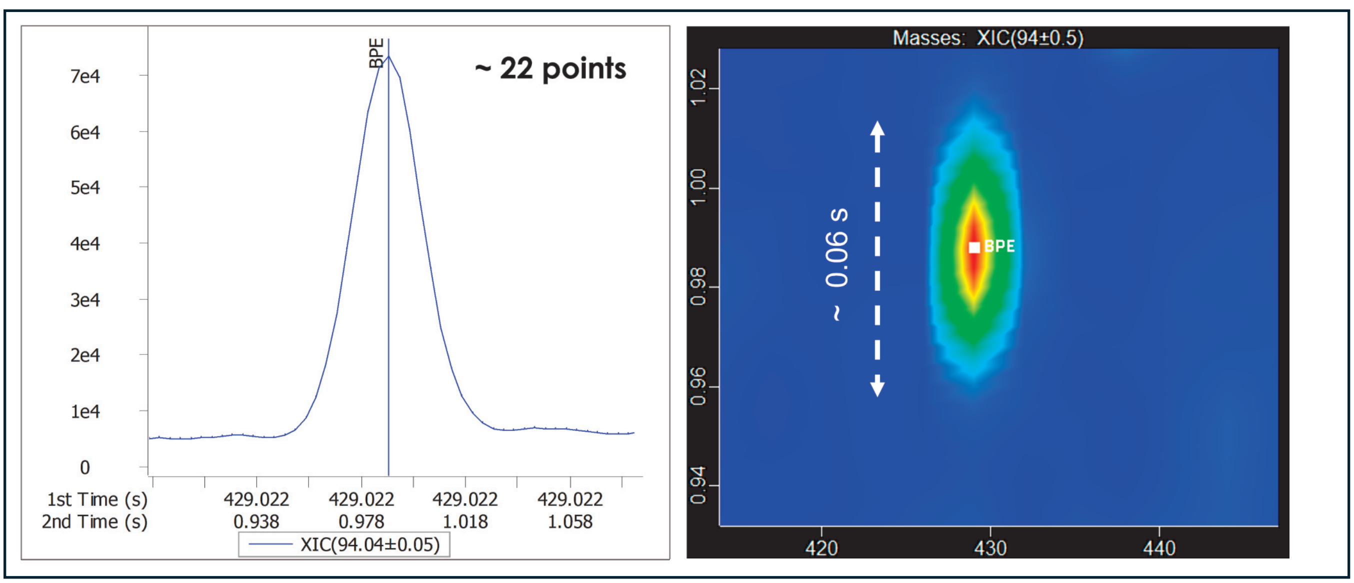


***Figure 2. Extracted ion chromatogram (XIC) at m/z = 94.04 ±0.05 of BPE at target dosage level of 1%, corresponding to 0.095 mg/L. BPE has peak width at base (wb) of ~0.06 s.***

Figure 3 shows the matrix-matched calibration curve constructed for BPE. A correlation coefficient ($R^2$) of 0.99956 was obtained, confirming the reliability of the curve for quantification purposes. Accuracy was measured for all calibration points and ranged from 0.1 to 10 % (Table 2).

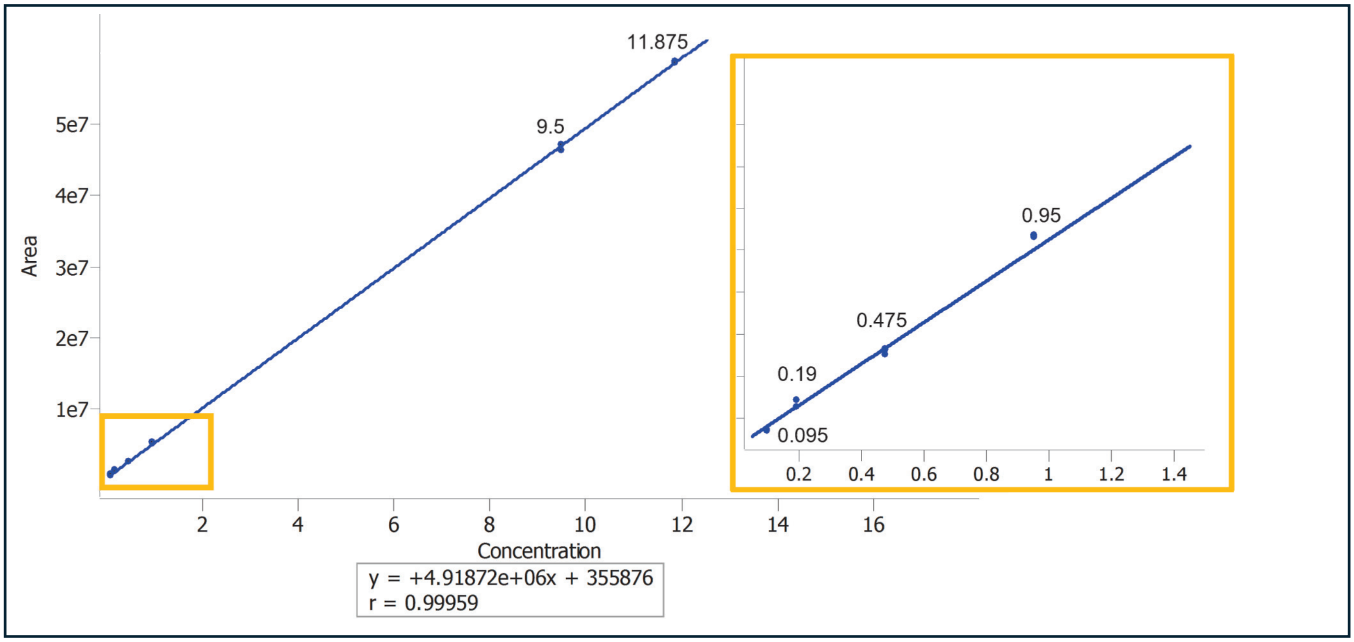


***Figure 3. Linearity of BPE for 1-125% dosage level corresponding to 0.095 to 11.875 mg/L of BPE.***

**Table 2. Calibration accuracy for BPE.**

| Name | RT (s) | Area | Amount (mg/L) | Calculated concentration (mg/L) | Difference (abs.) | S/N |
|---|---|---|---|---|---|---|
| **BPE** | 430.01 | 727860 | 0.095 | 0.084 | 0.011 | 102.12 |
| **BPE** | 430.01 | 1289900 | 0.19 | 0.198 | 0.008 | 197.27 |
| **BPE** | 430 | 2672900 | 0.475 | 0.479 | 0.004 | 332.03 |
| **BPE** | 430 | 5299100 | 0.95 | 1.012 | 0.062 | 542.9 |
| **BPE** | 430 | 47032000 | 9.5 | 9.476 | 0.024 | 3448.6 |
| **BPE** | 430 | 58919000 | 11.875 | 11.888 | 0.013 | 4004.6 |

Significantly, the lowest calibration level (0.095 mg/L) shows a peak signal-to-noise (S/N) of ~100, (reported in Table 2 and shown in Figure 4), enabling the required limit of quantitation (LOQ) to be easily exceeded.

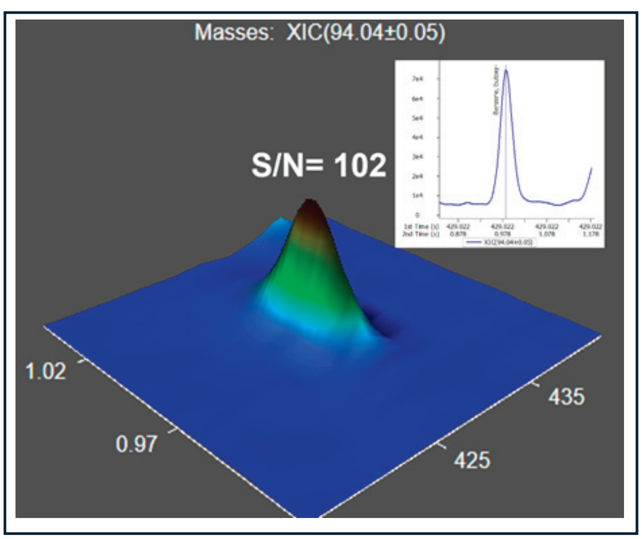


***Figure 4. BPE signal-to-noise (S/N) recorded at 0.095 mg/L.***

A recovery test was also performed by injecting a spiked diesel sample at two different concentration levels (0.095 and 9.5 mg/L), corresponding to 1 % and 100% dosage of BPE (n=3). The calculated recoveries were 97.9 % and, 99.6 %, respectively.

In addition, the same instrument configuration was also used for petroleum characterization experiments. Figure 5 shows a 3D-contour plot of the same diesel sample where the GCxGC-TOFMS method was fully optimized, resulting in a detailed and comprehensive separation.

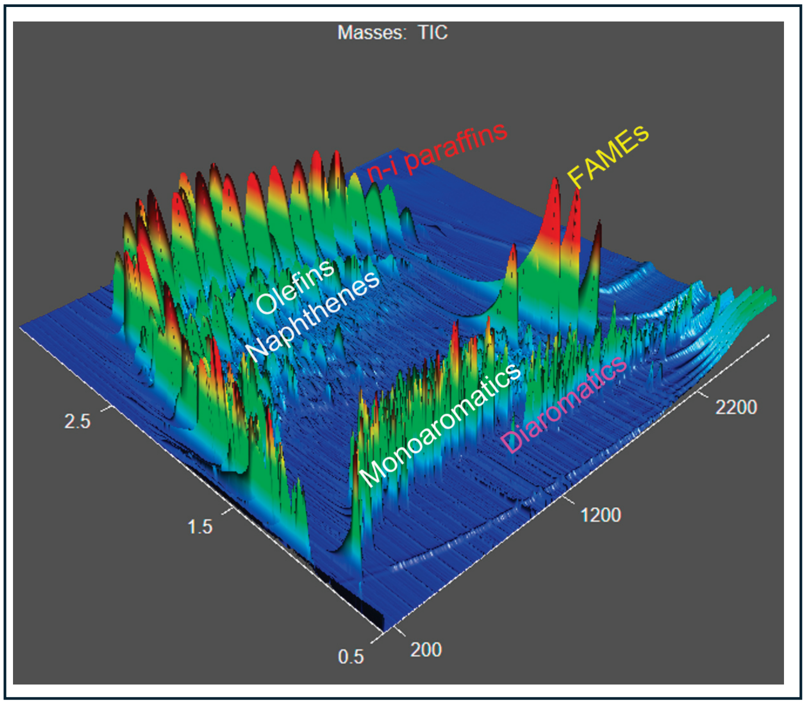


***Figure 5. Optimized GCxGC separation of the diesel sample.***

Beneficially, this enabled a bulk characterization of the sample, exploiting the Classification feature in *ChromaTOF* software, which utilizes the structured nature of GCxGC contour plots in conjunction with mass spectral filters (Figure 6).

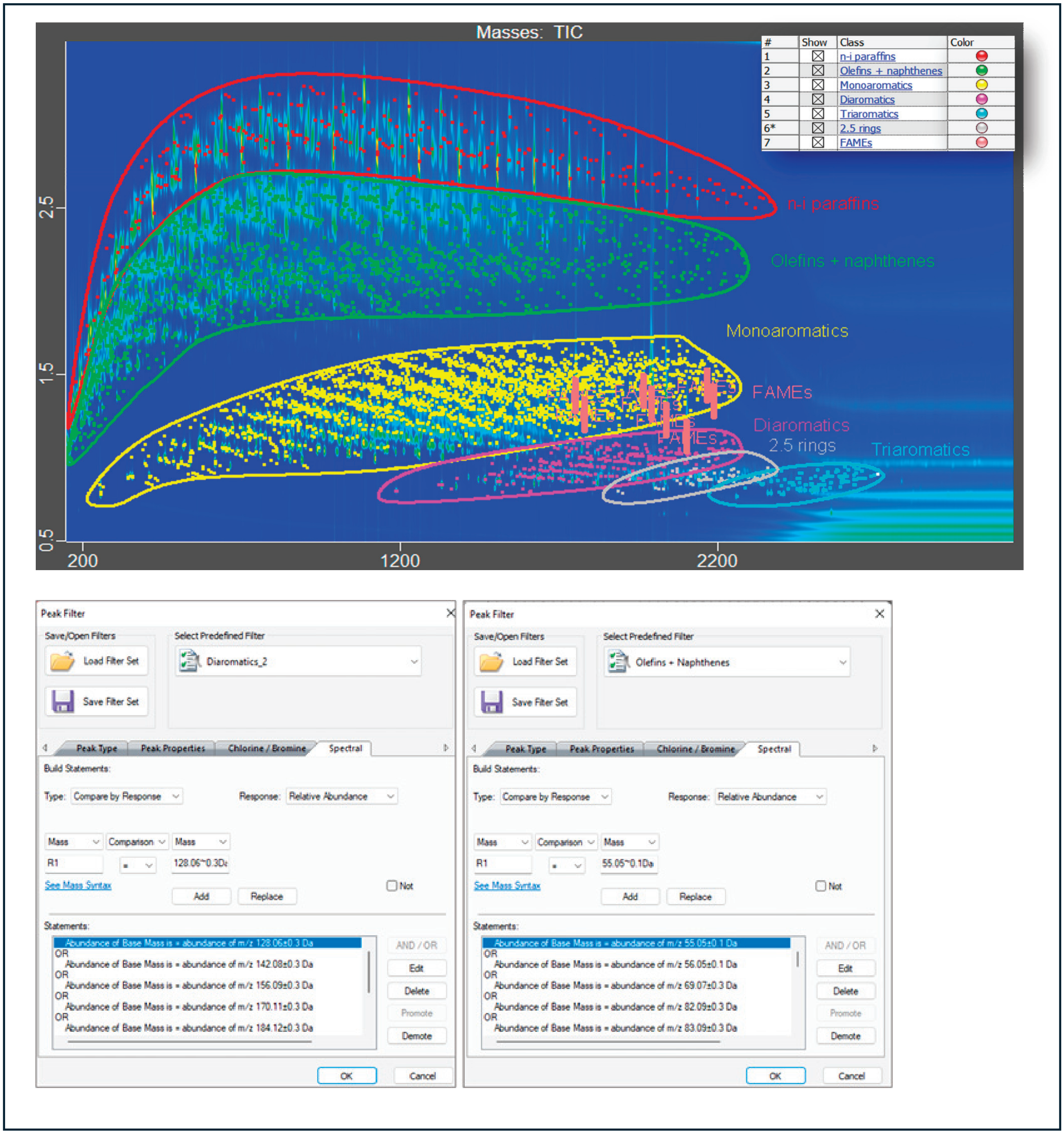


***Figure 6: Bulk characterization using the Classification feature in conjunction with Peak Filters.***

## *Conclusion*

The flexibility of LECO's *Pegasus* BT4D GCxGC-TOFMS technology was demonstrated via this value-adding workflow solution for the determination and quantification of the newly selected fiscal fuel marker BPE, as well as the full characterization of low to medium petroleum fractions. Both methodologies were developed using the same GCxGC column configuration, thus removing downtime associated with column or hardware changes. The ability to run both applications using the same setup can be a significant benefit, saving time and costs for laboratories required to deliver both characterization and regulatory testing for fuel and petroleum related products.

## *References*


[1]LECO Application Note, Fuel Washing Diesel 203-821-522
https://knowledge.leco.com/component/edocman/application-note-fuel-washing-diesel-pegasus-bt-522/viewdocument/1656?Itemid=1656

[2]COMMISSION IMPLEMENTING DECISION (EU) 2022/197 of 17 January 2022 establishing a common fiscal marker for gas oils and kerosene https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32022D0197