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JSB-DP007

GC×GC-QTOF determination of age markers in diesel oil

Author application note: Daniela Peroni, JSB © 2016

Introduction

The composition of diesel oil changes with time as a result of degradation. The major components in a fresh oil are the linear alkanes where branched alkanes become predominant in highly degraded oil. The ratio between heptadecane (n-C_{17}) and 2,6,10,14-tetramethyl-pentadecane (or pristane) has the highest correlation with this process and is used, for instance, for age determination of diesel oil spills in soil by GC[1]. However, this approach is affected by large uncertainty because in mono-dimensional GC the markers are not separated from the matrix.
GC×GC, with its unmatched peak capacity, is a very powerful tool for the detailed separation of highly complex petrochemical samples and therefore for the determination of age markers in diesel.

Instrumentation and software

Agilent 7890B GC equipped with a Zoex ZX2 cryogen-free thermal modulator and an Agilent 7200B QTOF detector. All 2D data were displayed and analyzed using the GC Image High Resolution software.

Samples

The samples are diesel fuels purchased at a local petrol station.These were injected directly.

Results

In 1D-GC both linear and branched alkanes co-elute with the signal “hump” typical of diesel (Fig. 1). Additionally, with this particular column and method, n-C_{17} and pristane are fully co-eluting.

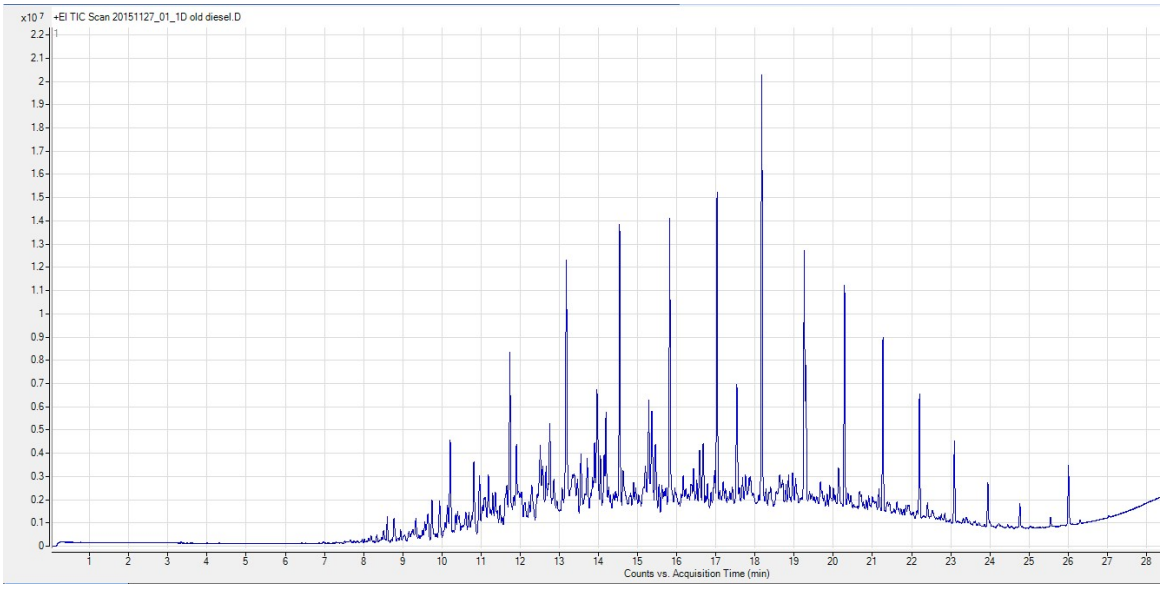

Fig. 1D –GC chromatograms of a diesel oil

Thanks to excellent mass accuracy granted by the QTOF, we can successfully extract selectively peaks specific for the two compounds (Fig.3). However, their strong similarity in structure and thus spectra makes this only partially efficient because the main *m/z* fragments are the same. Only fragments with very low intensity can be used to extract pristane. This is very valuable for identification but for quantification it would be preferable to select *m/z* fragments with higher abundance.

The 2D plot in Fig. 2 shows that GC×GC fully separates n-C_{17} and pristane from all the cyclic hydrocarbons, unsaturated hydrocarbons and aromatics. Moreover, the two analytes are almost fully resolved from each other. This leads to much cleaner spectra (Fig. 3) and consequently better library search. This better separation gives also the opportunity to do this calculation with a mass spec with lower resolution, like a nominal mass TOF or a single quadrupole MSD.

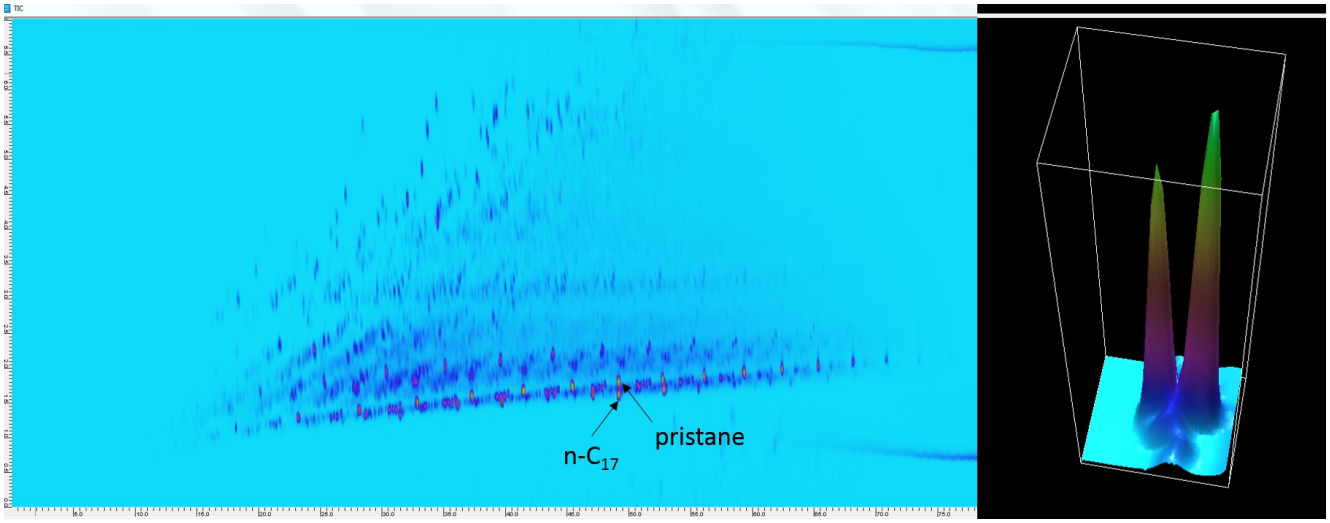

Fig. 2 - GC×GC chromatogram of a diesel oil (left) and 3D visualization of the separation between n-C_{17} and pristane (right)

It is now possible to use for both peaks the total TIC volume calculated by the GC Image software to calculate much more precisely the n-C_{17}/pristane ratio calculated for the 1–year-old and the new diesel oil is 1.14 and 1.35.

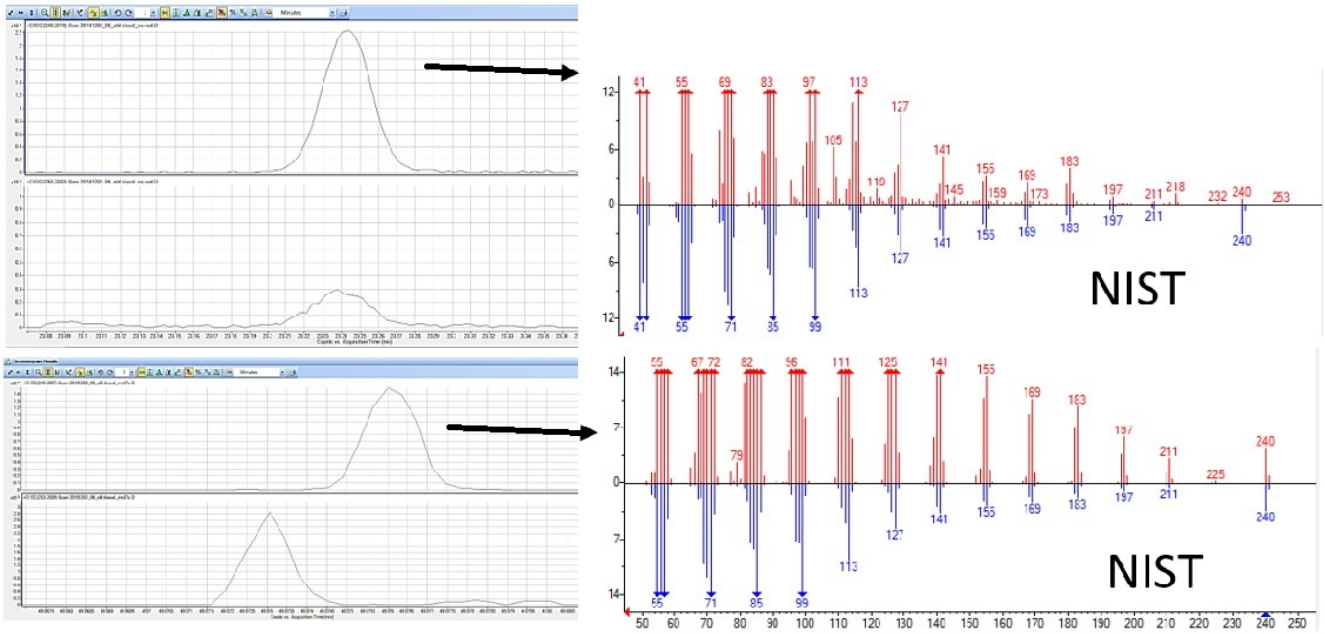

Fig. 3- EIC for 240.2817 m/z (n-C17) and 253.2883 m/z (pristane) in 1D-GC (top) and GC×GC (bottom). On the right side a zoom in of the spectra for the C_{17} peak are shown and compared to the NIST reference.

Fig. 4 shows an example of the great mass accuracy provided by the QTOF. The error for the molecular mass of n-C_{17} is <1.5 ppm. This feature allows to identify the target compounds with much greater confidence.

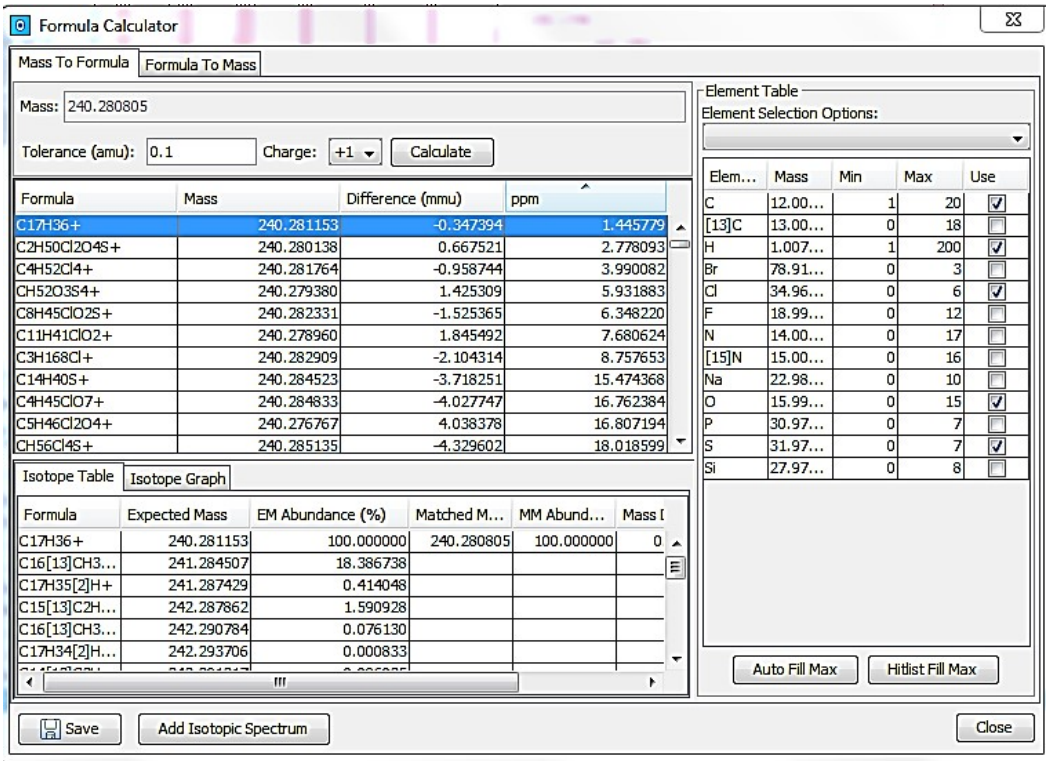

Fig. 4- Example of mass accuracy achievable with the GC×GC-QTOF for the molecular ion of n-C_{17}

Conclusions

- With GC×GC it is possible to separaten-C_{17} and pristane from the complex matrix of the diesel oil in a single, simple analysis.
- The ZX2 cryogen-free thermal modulator provides excellent resolution in the second dimension.
- The identification benefit from the higher resolution: the MS spectra are cleaner and give better Match Factors.
- The unmatched mass accuracy of the QTOF at a scan speed of 50 Hz makes it an excellent tool for identification not only with GC but also with GC×GC.
- The n-C_{17}/pristane ratio is calculated with much better accuracy and sensitivity. This can be used for a more precise estimation of the age of diesel oil.

References:

[1] L.B. Christensen, T. H. Larsen, Groundwater Monitoring & Remediation, 13 (1993) 142-149.

HEAD OFFICE

JSB International
Tramstraat 15
5611 CM Eindhoven
T +31 (0) 40 251 47 53
F +31 (0) 40 251 47 58

INFO@GO-JSB.COM
WWW.GO-JSB.COM

SALES AND SERVICE

NETHERLANDS
Apolloweg 2B
8239 DA Lelystad
T +31 (0) 32 087 00 18
F +31 (0) 32 087 00 19

GERMANY, AUSTRIA, SWITZERLAND
Max-Planck-Strasse 4
D-47475 Kamp-Lintfort
T +49 (0) 28 42 9280 799
F +49 (0) 28 42 9732 638

BELGIUM
Grensstraat 7, Box 3
1831 Diegem
T +32 (0) 27219211
F +32 (0) 27207622

UK & IRELAND
Cedar Court, Grove Park Business Est. White
Waltham, Maidenhead, Berks, SL6 3LW T +44
(0) 16 288 220 48
F +44 (0) 70 394 006 78