Chapter 6

Analysis of diesel petroleum fractions

Table of Contents

Chapter 6

Analysis of diesel petroleum fractions

6.1   Introduction

The analysis of petroleum products is already well established and done routinely in many laboratories. The different techniques involved in the analysis of petroleum fractions are discussed in Chapter 4. In Chapter 4 it is also mentioned that GC x GC can be used as a valuable tool in the analysis of these samples. This section of the dissertation investigates the fingerprinting of different diesel samples. The eventual use of this fingerprinting technique would be to accurately identify diesel in pollution and arson studies.

A few interesting samples of specialist diesels were also examined for their differences in lubricating efficiencies. These samples were obtained from the Mechanical Engineering Department of the University of Pretoria and contained different diesel-paraffin mixtures used in the South African mining industry.

At the time of this study, no two-dimensional automated peak integration software for GC x GC was available, therefore, the fingerprinting and sample comparisons were done on a visual interpretation

of the three-dimensional data sets. These comparisons included overlaying the different chromatograms and trying to spot differences in composition and even some colour differences in the colour coded plots that would indicate a difference in intensity (amount). In short, the preliminary studies were done to see whether the technique could be applied to future studies in fingerprinting and quality control.

6.2   Experimental setup

Four different diesel samples were obtained from service stations in Pretoria. All the diesel samples in this section were analysed under the same gas chromatographic conditions. A temperature program of $1°C/min$ from $10°C$ to $270°C$ was used for the first-dimension, while the second-dimension was kept at a constant temperature difference of $20°C$ above that of the first. The optimum flow conditions determined in chapter 5 were used by selecting 110 kPa inlet pressure. A sample of $0.2\,\mu l$ was injected under a split of 1:65 at an inlet temperature of $250°C$. The FID was run at $300°C$ with air to hydrogen to nitrogen ratio of 400:50:50. A modulation period of six seconds was selected, based on the optimisation studies. The column set used was a HP-1 column for the first dimension and a RTX-1701 column for the second, the dimensions were the same as in the optimisation studies.

6.3   The analysis of four local diesels

Four local diesel samples were analysed to detect any compositional differences. Three of these diesels have their origin form crude oil and the fourth is a diesel synthesised by the Fischer-Tropsch process from coal. These four diesels show clear differences, even in their one-dimensional analysis (reconstructed from GC x GC data, see section 5.2.2.3 Data analysis and visualisation), as can be seen in the figure 22.
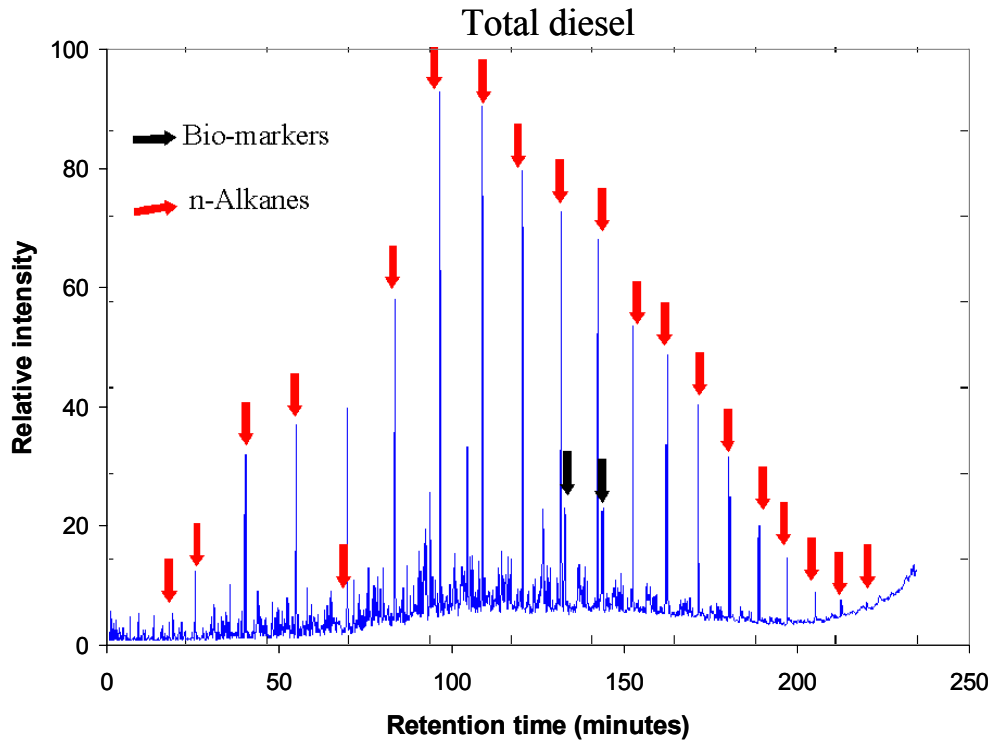
Fig. 22a A one-dimensional chromatogram of a Total diesel sample
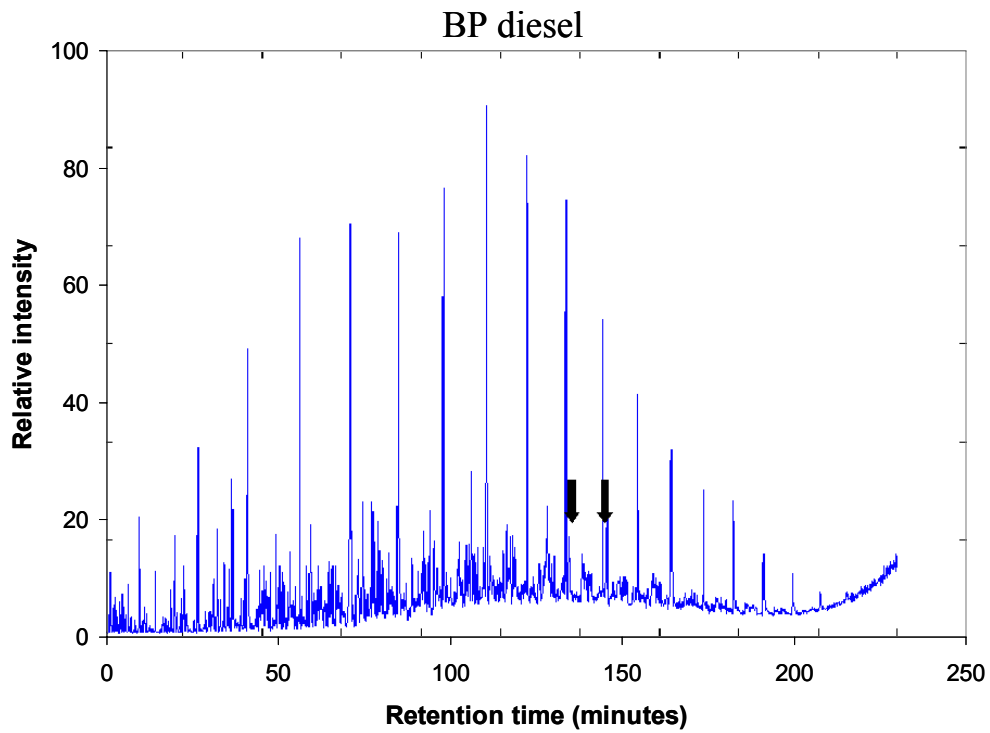
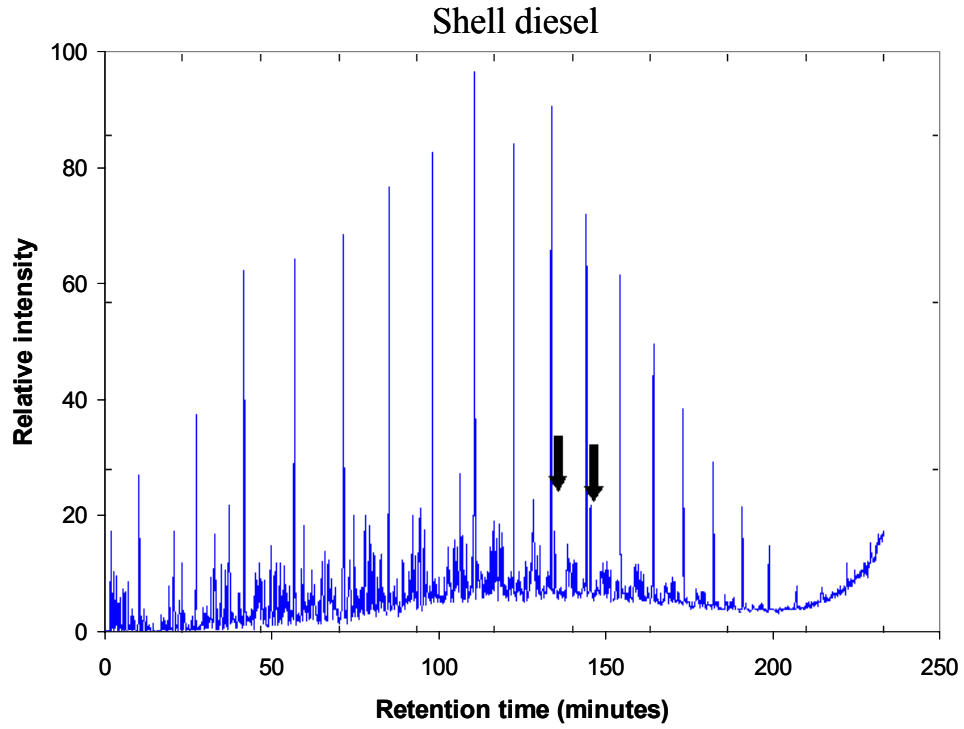*Fig. 22b A one-dimensional chromatogram of a BP diesel Sample*

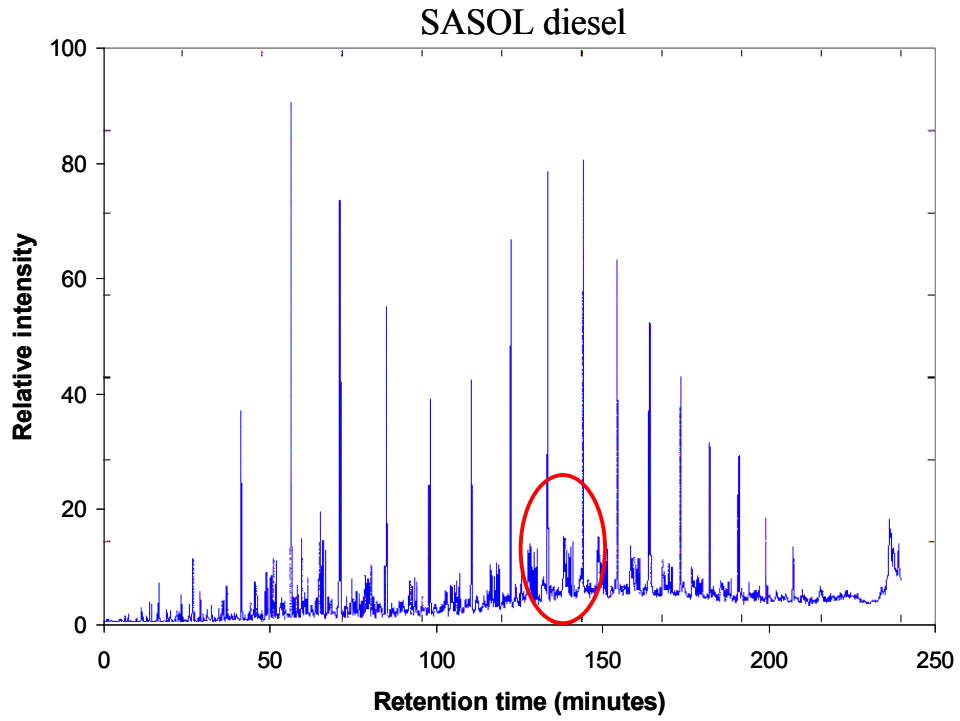*Fig. 22c A one-dimensional chromatogram of a Shell diesel sample*

Fig. 22d A one-dimensional chromatogram of a SASOL diesel sample

The differences in these chromatograms are quite obvious: The n-alkane pattern (the peaks standing out from the rest, marked in figure 22a with red arrows). The biomarkers (marked in black arrows, figure 22a-d) can only be observed in the oil refined diesels but not in the diesel from the Fischer Tropsch process (area circled with red).   There are also some differences in the smaller compounds seen between the n-alkanes, but no detailed information can be extracted due to peak overlap.

When analysing the data in two dimensions these differences are much more visible. Peaks invisible in the one-dimensional GC due to overlap can now often be allocated to specific compound groups or, in some cases, uniquely identified. In figures 23a - 23d the differences in the composition can be seen more clearly. See also Table 8 for compound identification.
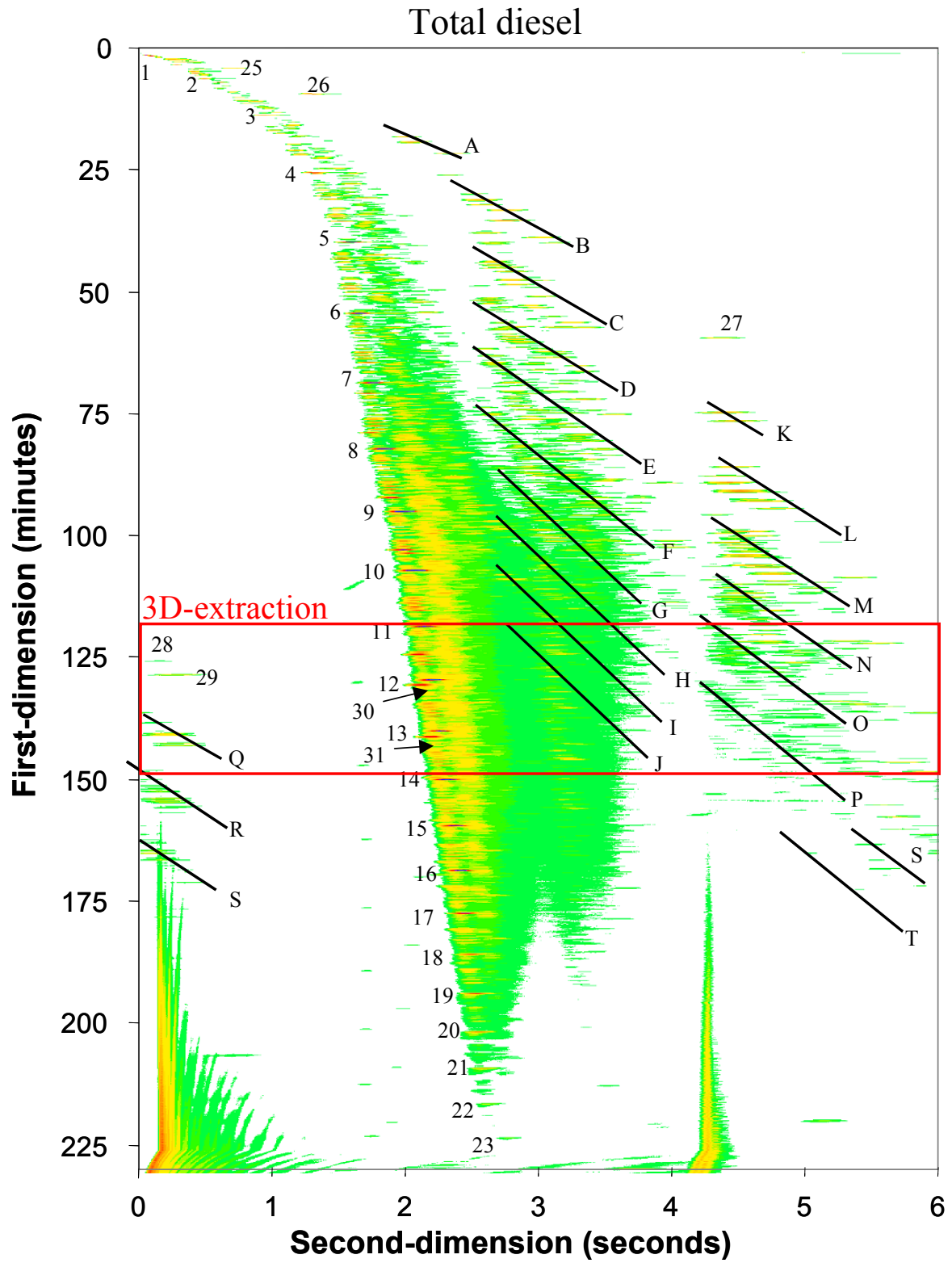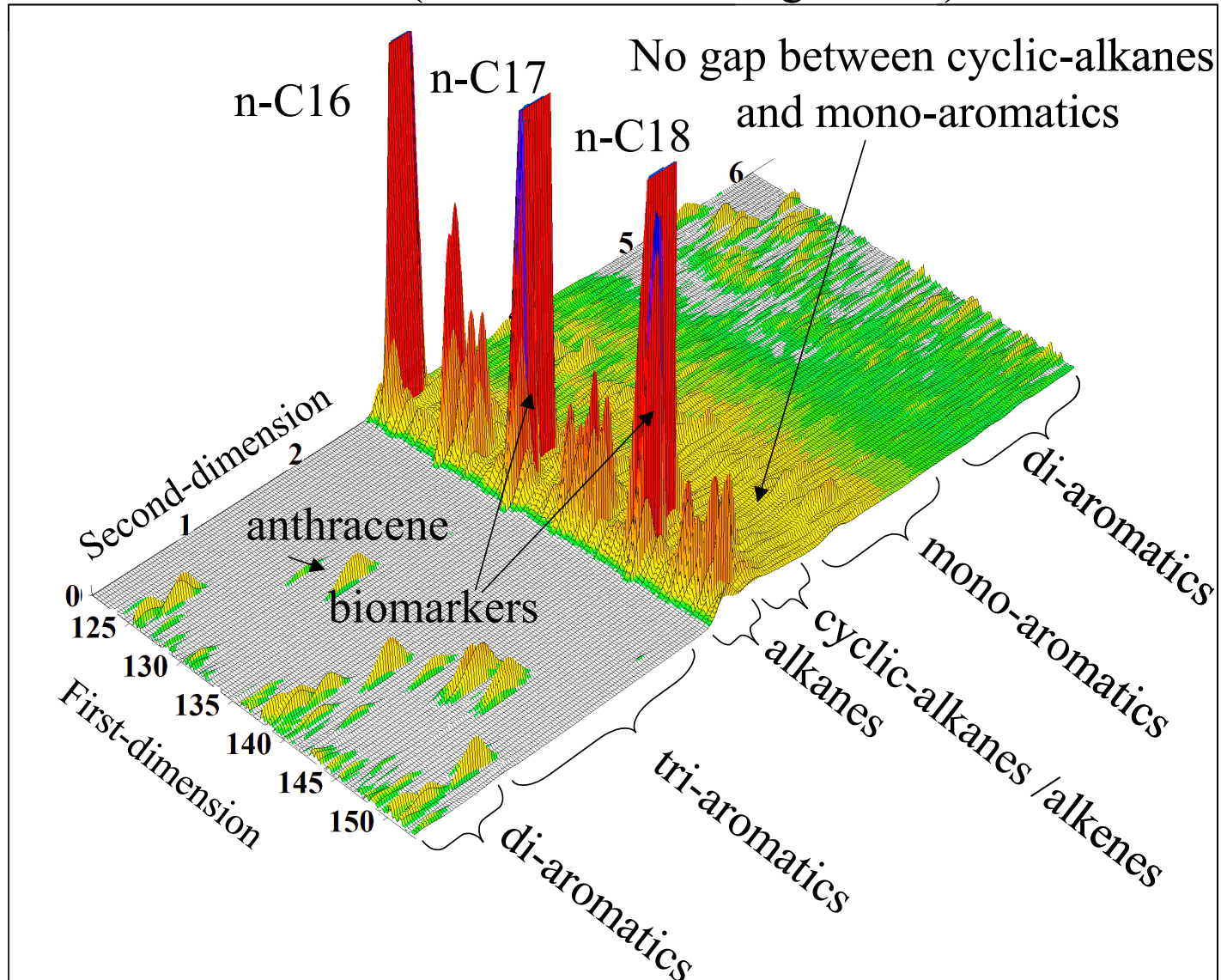
Fig. 23a A two-dimensional chromatogram of a Total diesel sample
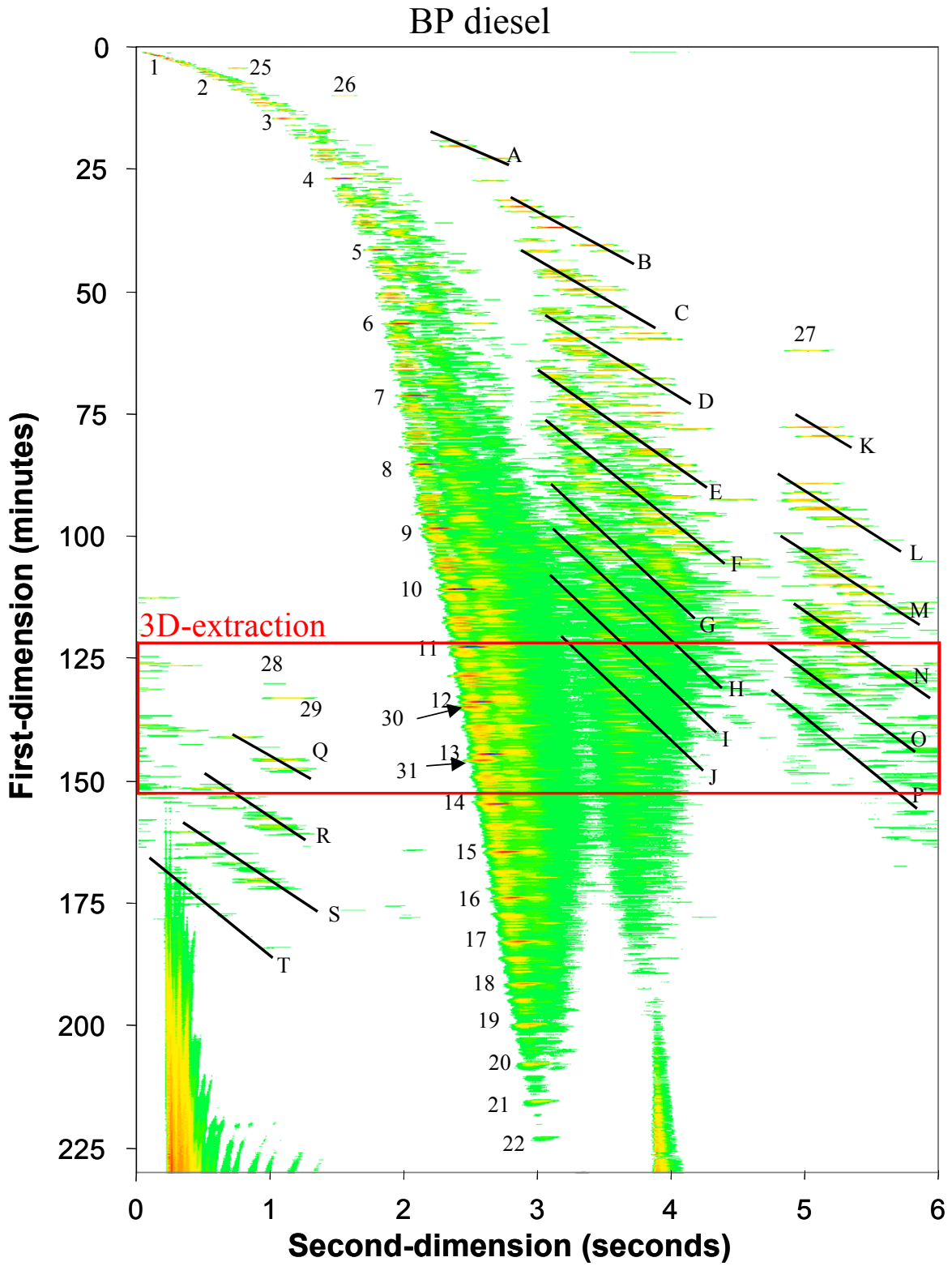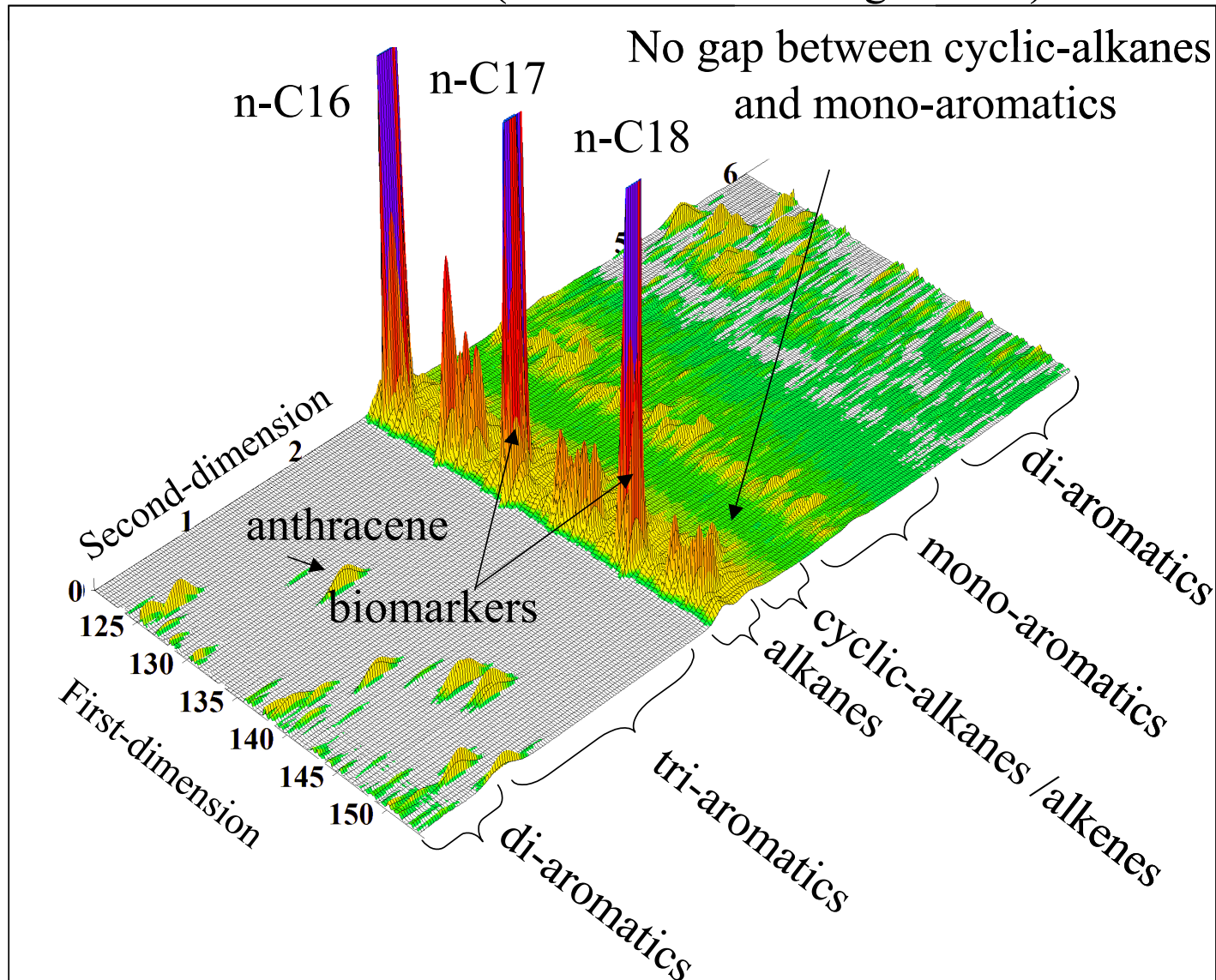
Total diesel (3D extraction of Figure 23a)

Fig. 23b A two-dimensional chromatogram of a BP diesel sample

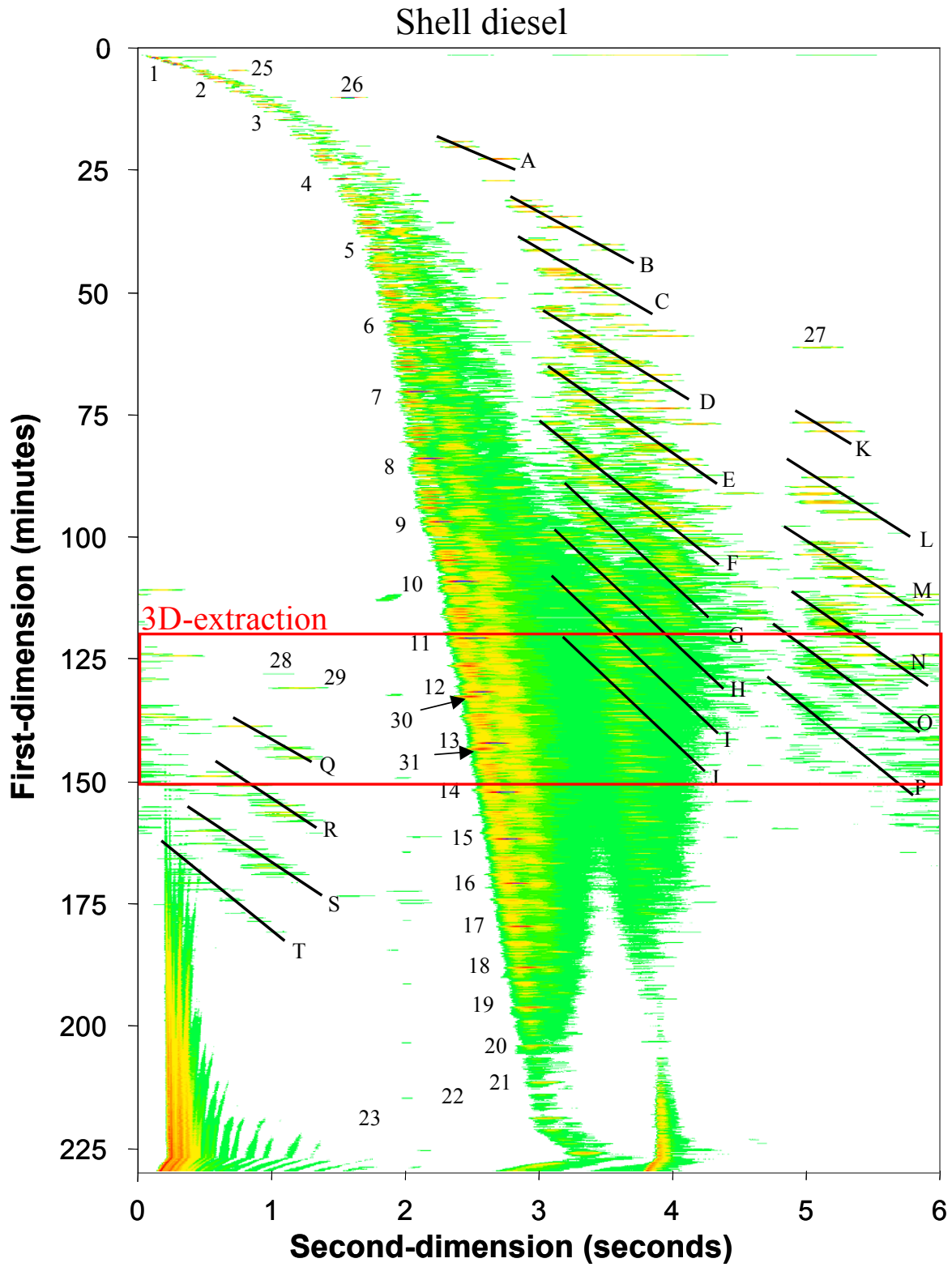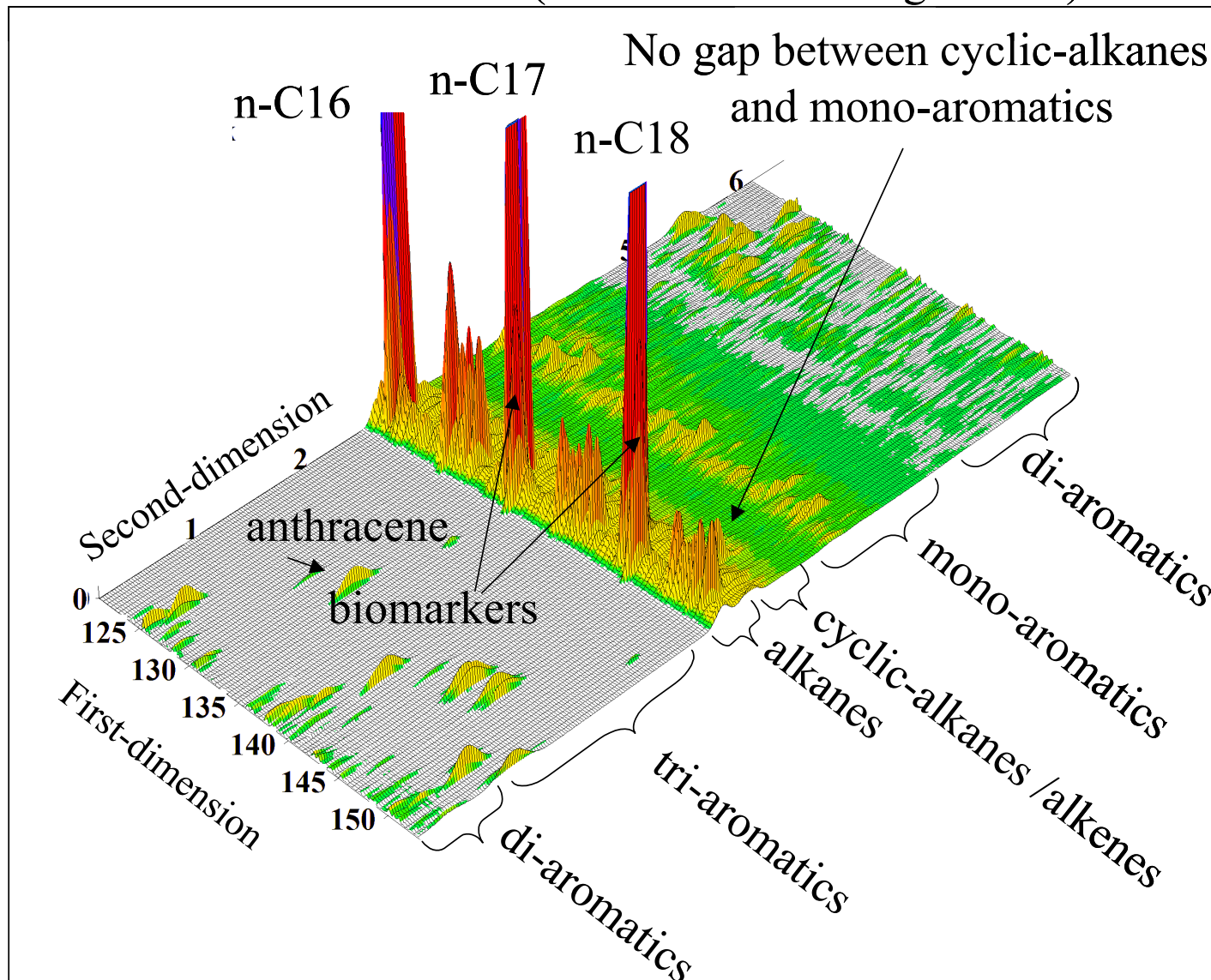# BP diesel (3D extraction of Figure 23b)

Shell diesel

Fig. 23c A two-dimensional chromatogram of a Shell diesel sample
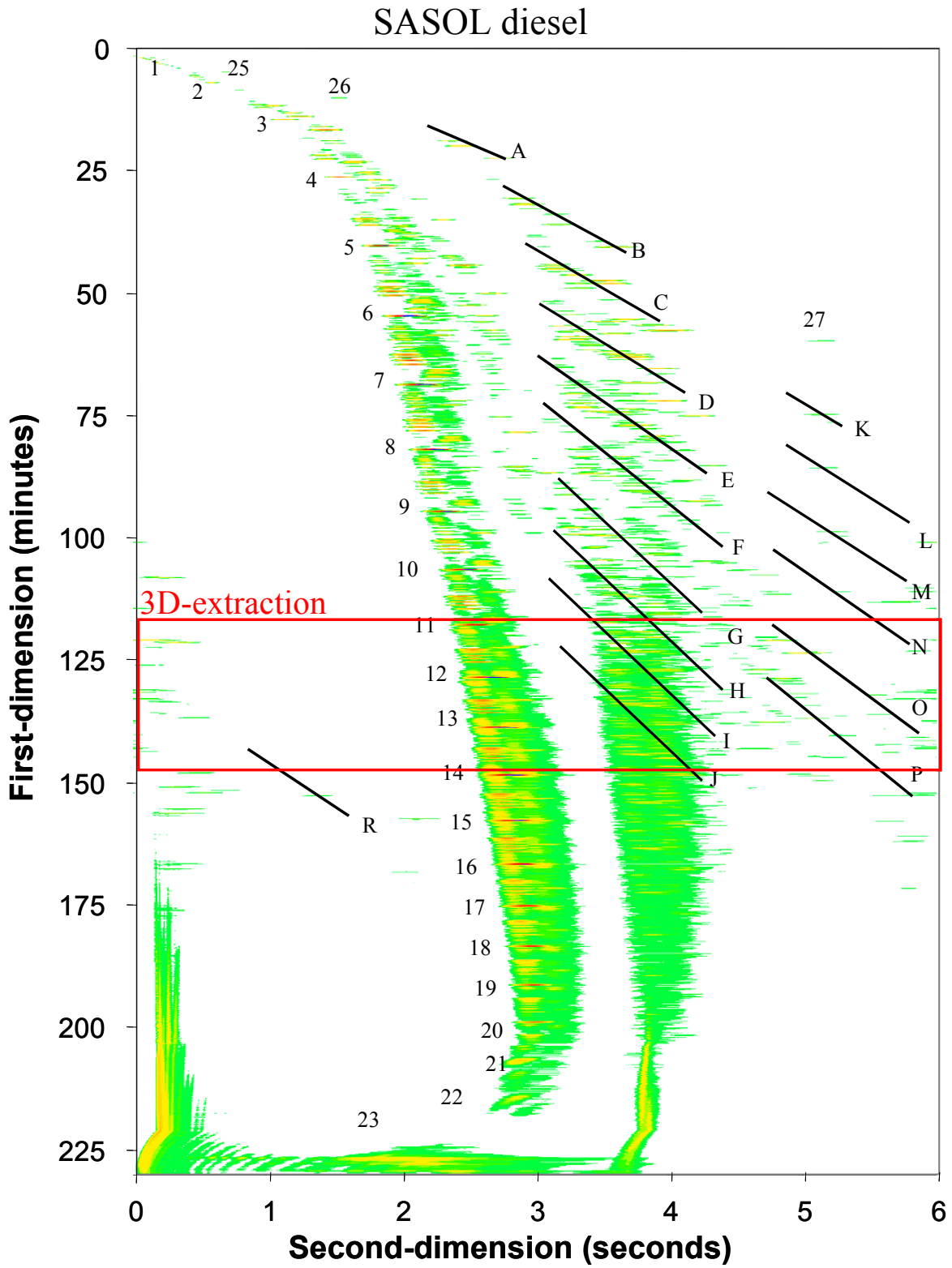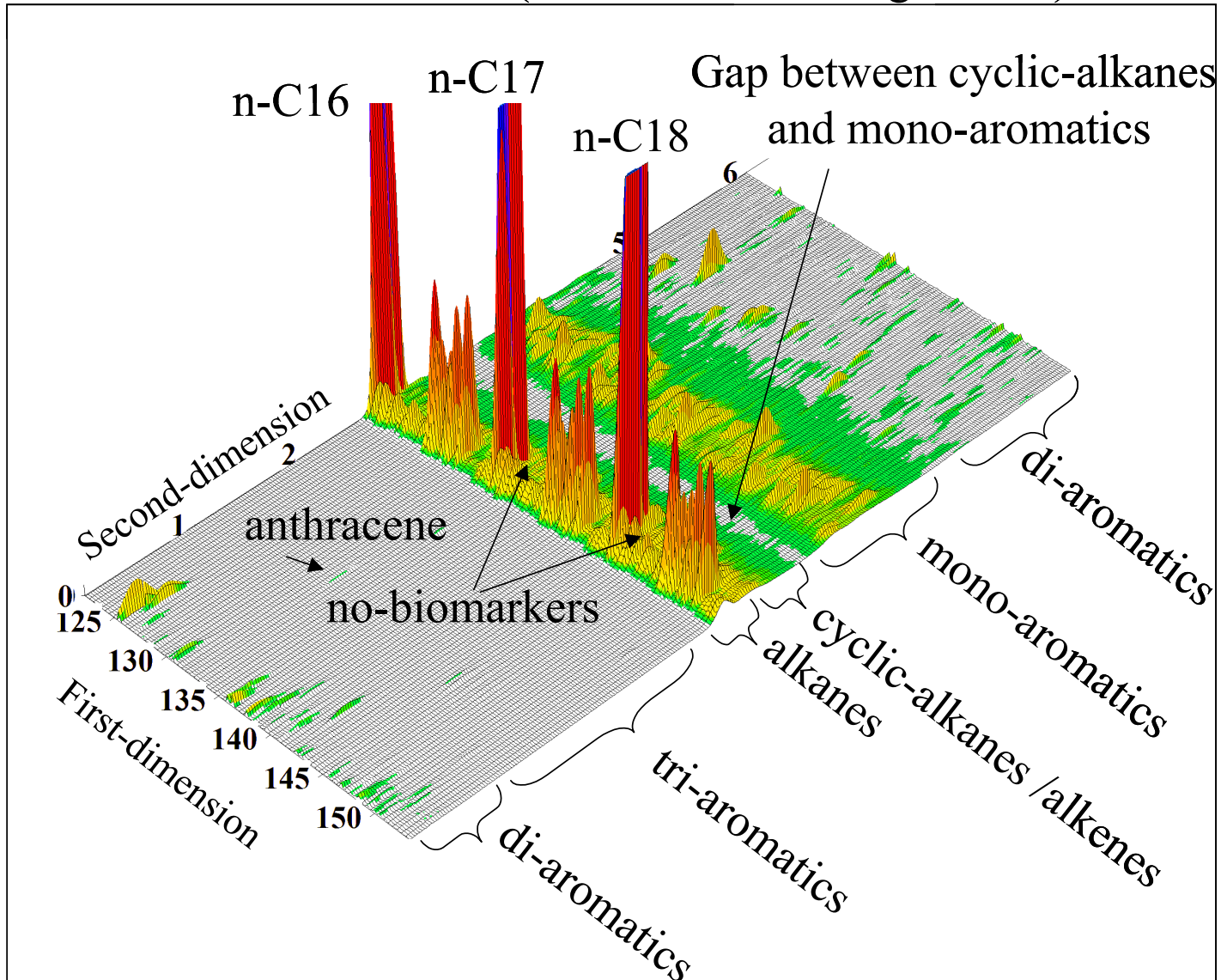
Shell diesel (3D extraction of Figure 23c)

Fig. 23d A two-dimensional chromatogram of a SASOL diesel sample

SASOL diesel (3D extraction of Figure 23d)

The two-dimensional chromatograms of the four diesel samples can readily be differentiated. The most obvious of these differences is in the group separations (aliphatic, mono-aromatic, di-aromatic and tri-aromatic), the Total and Shell diesel shows almost no separation between the aliphatic and mono-aromatic components while in the BP diesel there is a slight separation and in the SASOL diesel baseline separation is observed. This is due to the relative concentrations of the cyclic-alkanes (or alkenes) and the mono-aromatic compounds.   Differences in case of individual compounds are also found, this can be seen as peaks differing in colour in the respective chromatograms. Another obvious difference is that the tri-aromatics (groups Q,R,S and T) and biomarkers (peaks 30 and 31) in the SASOL diesel are almost absent. To be more specific on the concentration variances software for quantitative analysis (peak integration) is required.

6.4   Analysis of diesel-paraffin mixtures

The use of these mixtures in the mining industry arises from their much cleaner exhaust emissions. This is essential in a closed environment where the air needs to be circulated and remain safe for human activity. These specially blended fuels for the mining vehicles perform exactly the same as the diesels used on the surface but because of their lower aromatic content, their lubricating properties are greatly reduced. In diesel engines the lubrication of the fuel is a very important factor and can have a big influence on the lifespan and functionality of the engine.

As was seen in the previous section, a huge portion of the diesel constitutes aromatic compounds.

In the Fischer-Tropsch diesel it was mentioned that there is a clear gap between the cyclic-alkanes and the mono-aromatic part of the chromatogram, due to a lower concentration of the latter group. The Fischer Tropsch process is known to produce diesel fractions of lower aromatic content. Low aromatic content diesels provide less lubrication and are known to produce cleaner exhaust emissions.

The same applies to the paraffin in that it has a high cetane number but almost no aromatics to improve the lubrication. A further advantage of the paraffin is improved combustion of its shorter alkane chain lengths, hence the cleaner exhaust gasses. To improve the lubricating properties of the paraffin, aromatic compounds or a well lubricating diesel can be added. The study undertaken by the Department of Mechanical Engineering at the University of Pretoria was focussed at determining the fraction of diesel to give the optimal lubricating properties [56].

As the project of determining the best diesel-paraffin mixture was still in progress at the end of this study, we can only speculate on the significance of our analytical results. Figure 24 shows the different diesel-paraffin combinations evaluated. In the respective chromatograms, changes can be seen in the alkane boiling point range (with the addition of diesel to the paraffin there are more alkanes of higher mass). Also, as expected, the polar fraction of the paraffin increases with the addition of diesel, to such an extend that, in the 66% diesel sample, even some tri-aromatics (group Q the $(CH_x)_1$-anthracene and peak 29 anthracene) are observed. The mono-aromatics and di-aromatics also increase with diesel concentration. In the pure paraffin sample, only the mono-aromatics up to group G and di-aromatics up to group L can be observed. In the 66% paraffin

mixture, group M of the di-aromatics appears and group I of the mono-aromatics appears in the 50% paraffin sample. The 66% diesel mixture almost contains all the groups also observed in the pure diesel sample apart from groups J and N. Interesting phenomena, like why the 66% paraffin mixture has better lubricating properties than pure diesel, [56] cannot be explained at this stage.
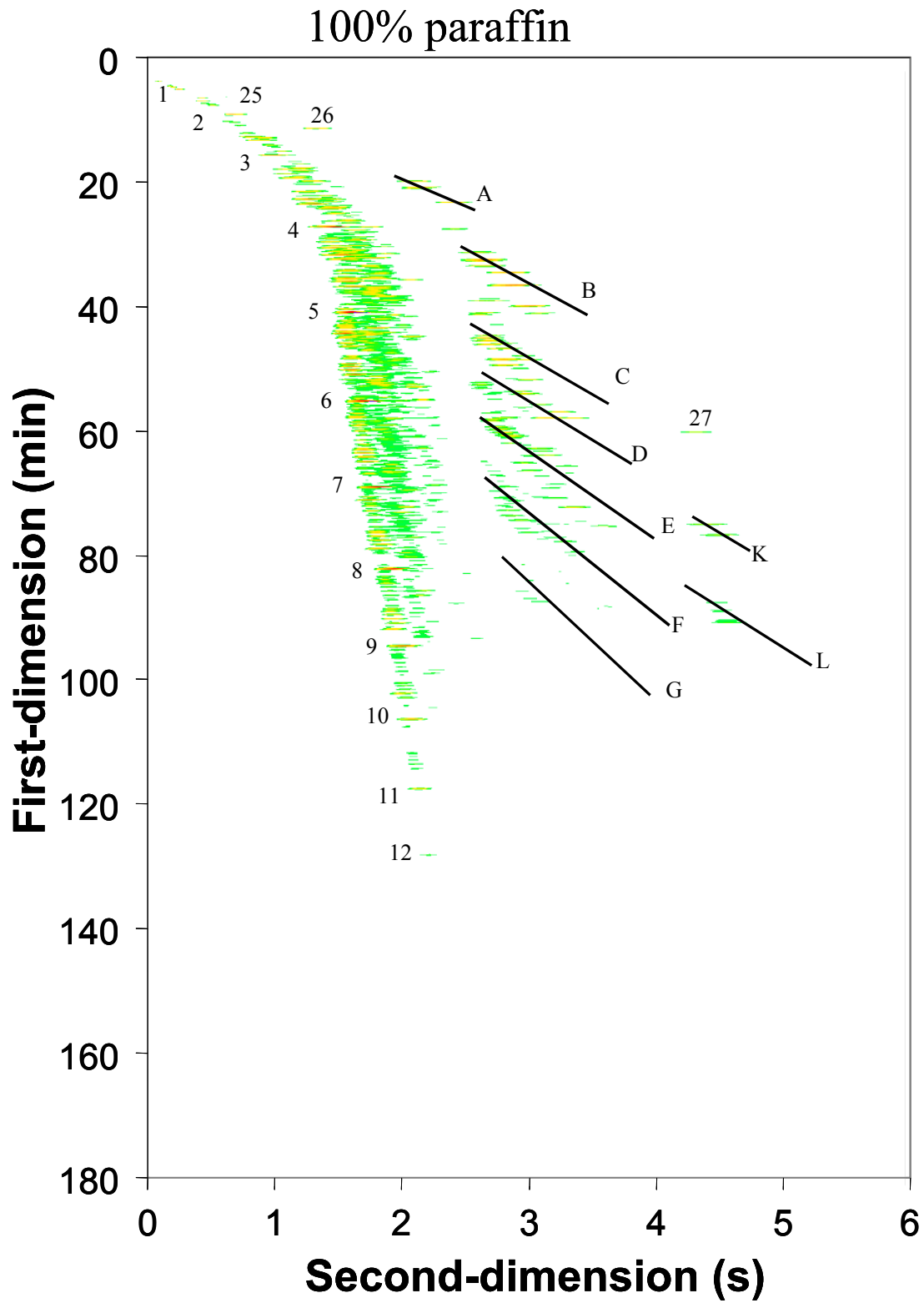
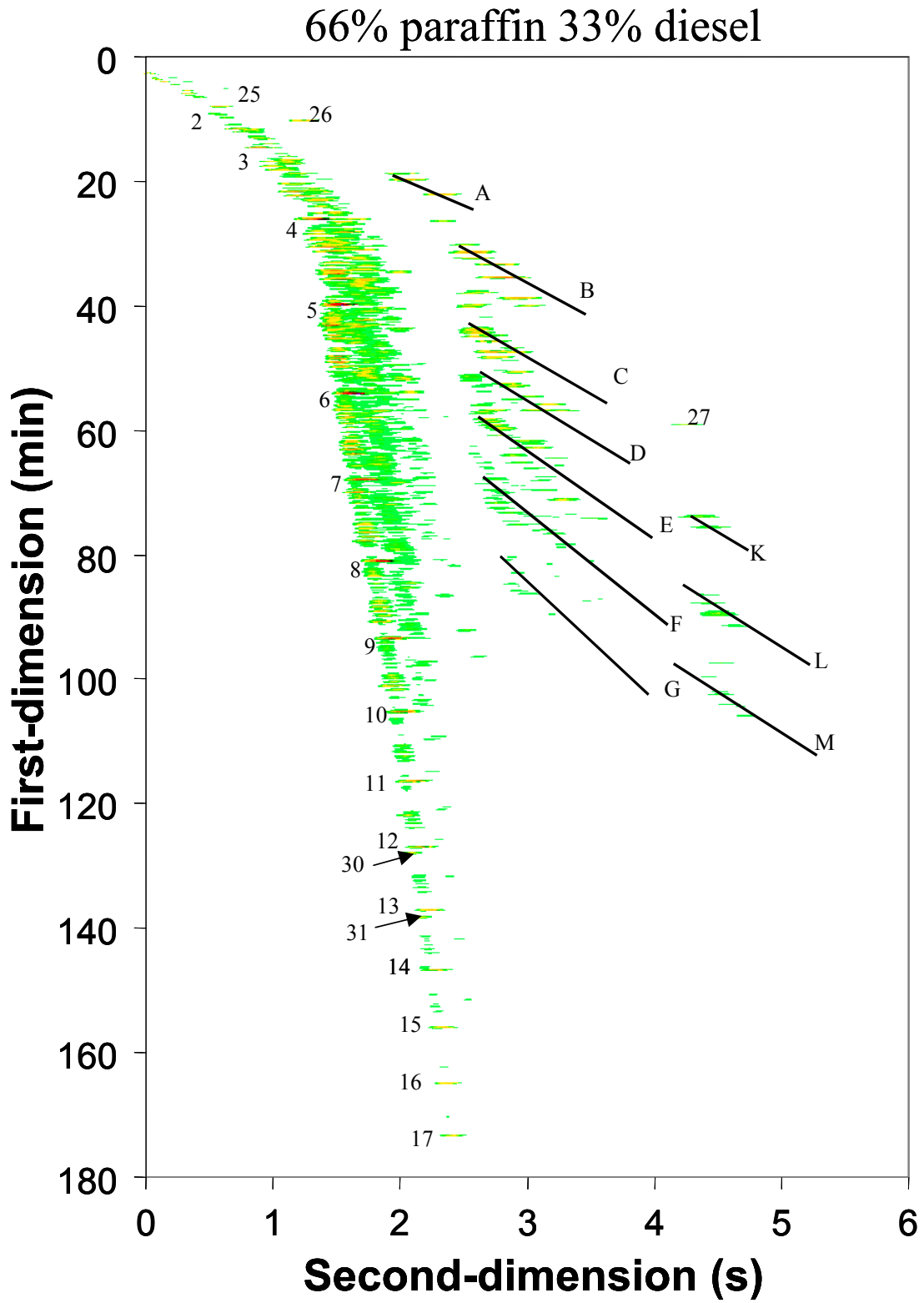*Fig. 24a A two-dimensional chromatogram of a 100% paraffin sample*

Fig. 24b A two-dimensional chromatogram of a 33% diesel 66% paraffin mixture
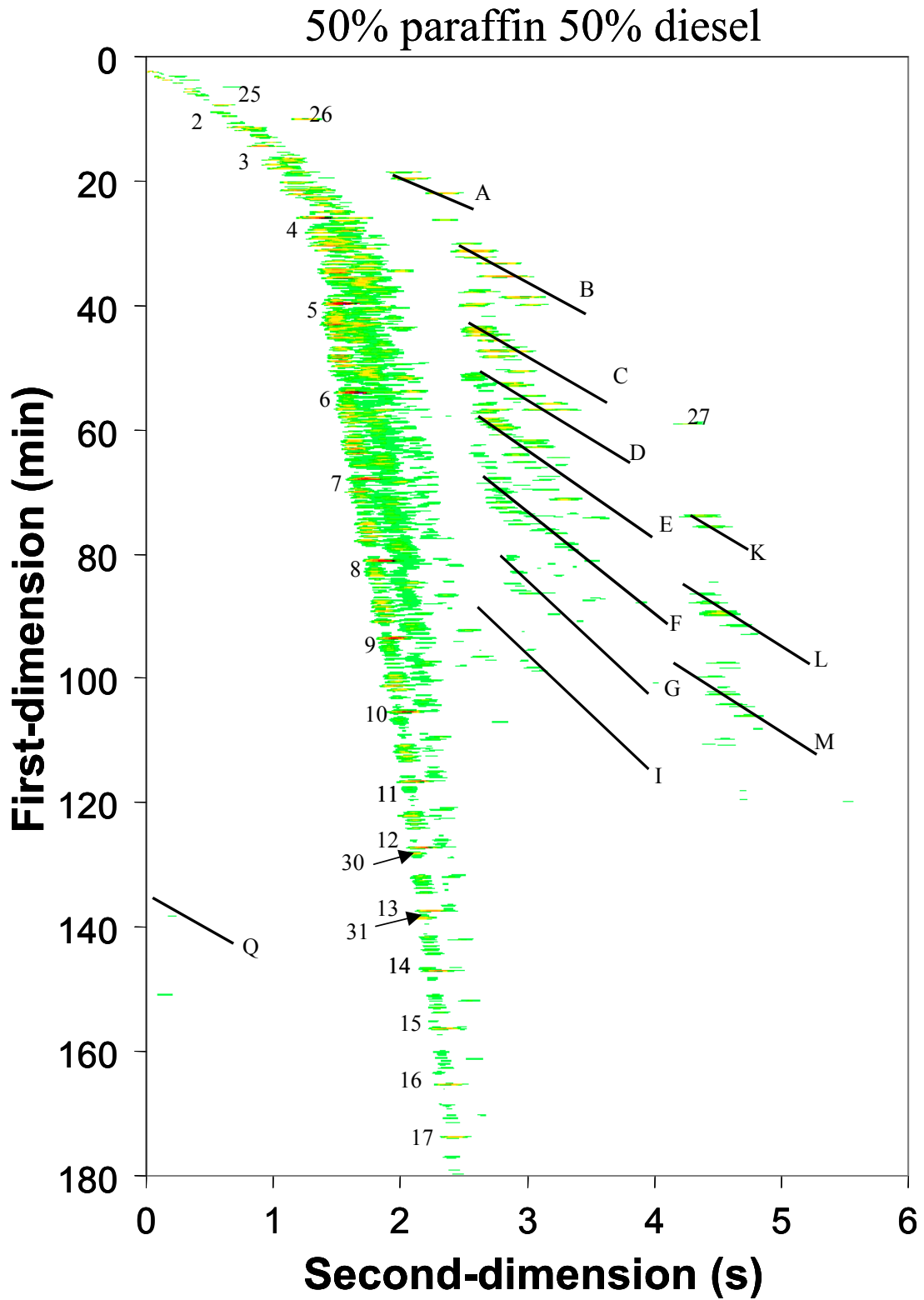
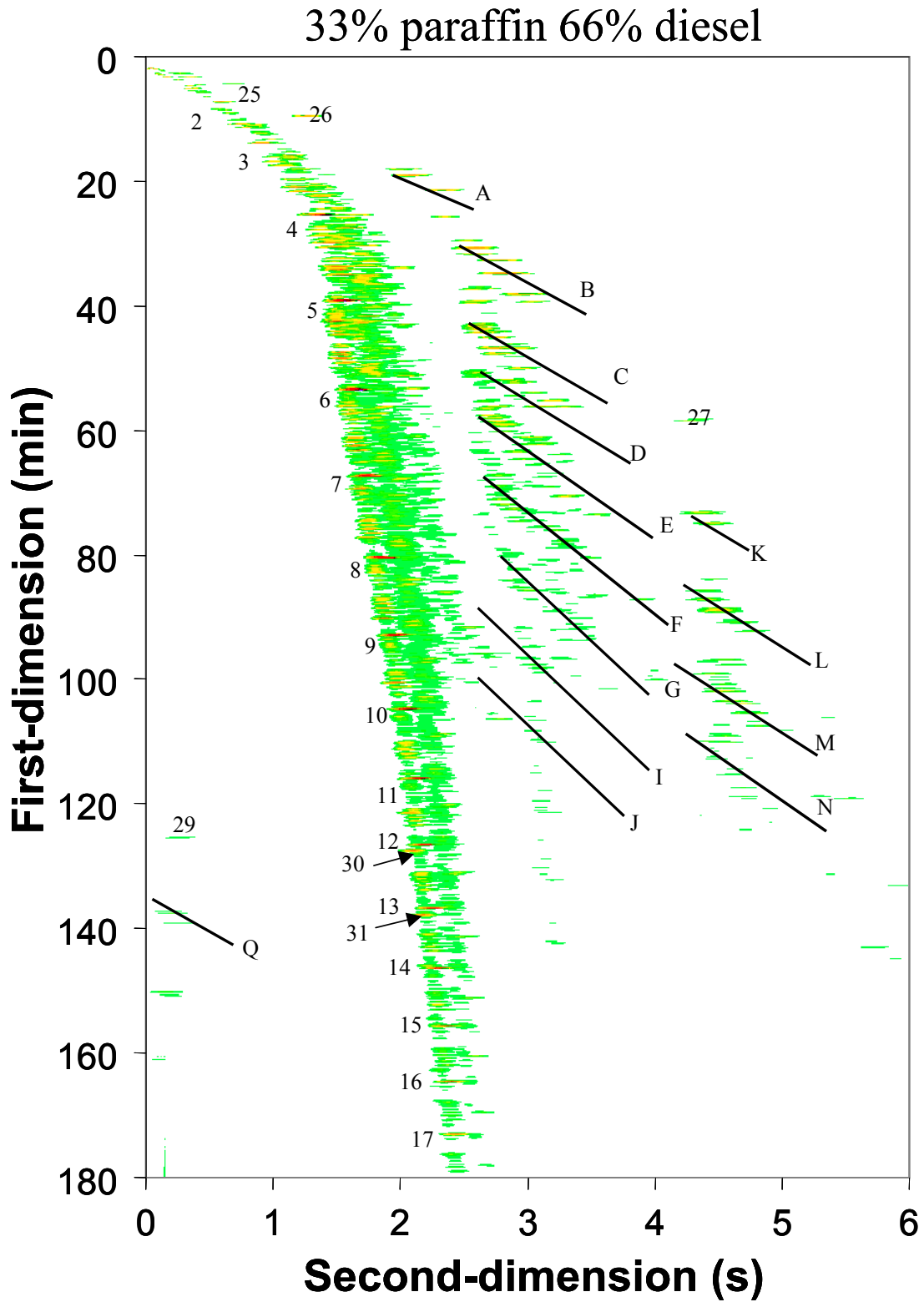Fig. 24c A two-dimensional chromatogram of a 1:1 diesel : paraffin mixture

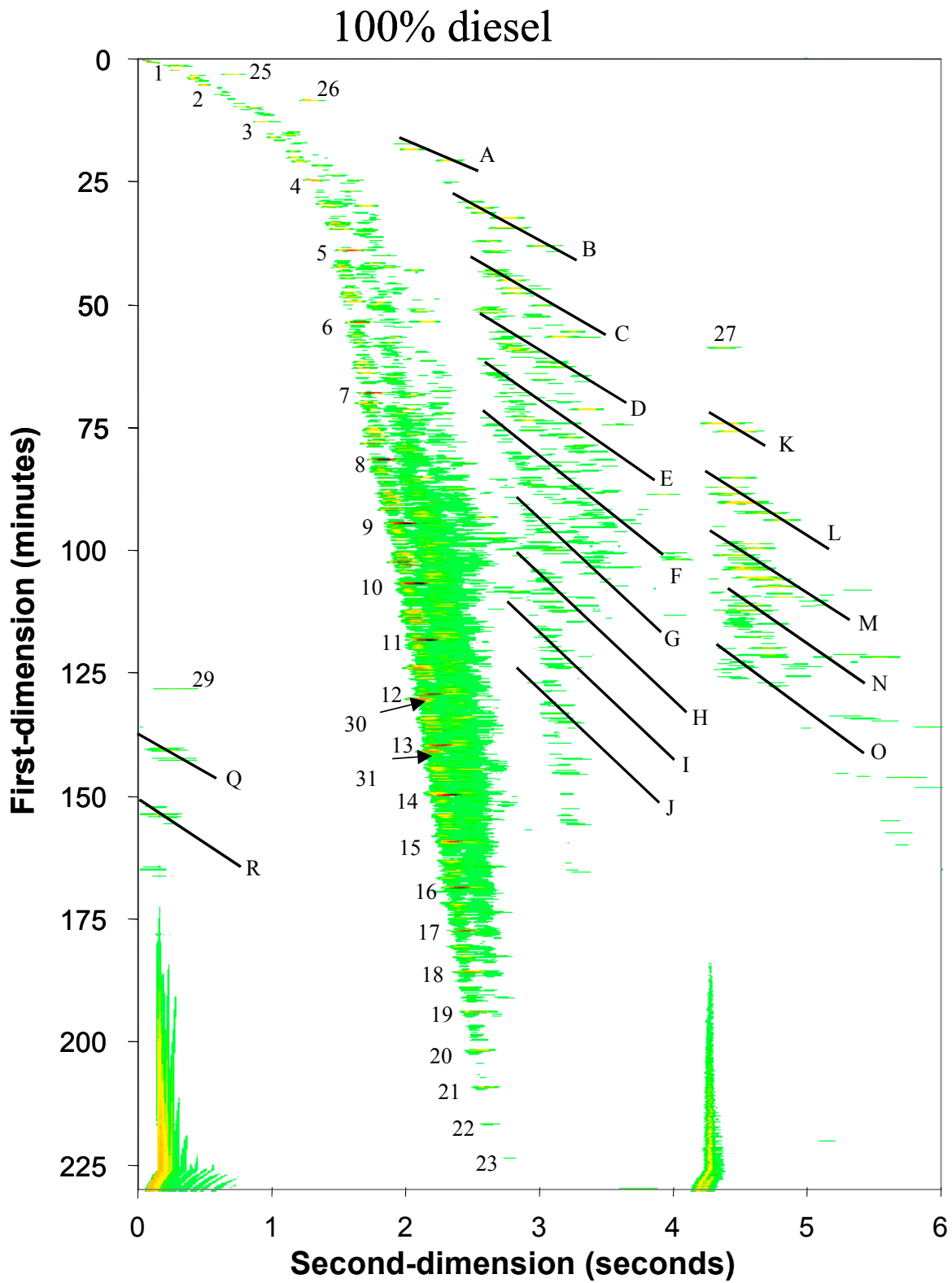*Fig. 24d A two-dimensional chromatogram of a 66% diesel 33% paraffin mixture*

100% diesel

Fig. 24e A two-dimensional chromatogram of a 100% diesel sample