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Fast Analysis of Paraffins, iso–Paraffins, Olefins, iso–Olefins, Naphthenes and Aromatics in Hydrocarbon Streams

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Introduction

The Varian PIONA+™ Analyzer was developed to characterize the complete hydrocarbon sample composition, including individual oxygenates, in a single analysis of spark ignition engine fuels by multi-dimensional gas chromatography. The sample is separated in the component groups per carbon number and in individual components through the use of multiple columns and traps. In the PIONA+ system, paraffins, iso–paraffins and iso–olefins, olefins, naphthenes and aromatics are identified. However, analysis time in the PIONA mode is about 180 minutes, which severely limits the number of samples that can be analyzed per day. A unique aspect of the design of the Varian PIONA+ Analyzer is the ability to independently heat the individual traps (concurrent heating). This application note describes work to determine if concurrent heating could be used to significantly reduce the analysis time and improve sample throughput.

Materials and Reagents

Varian Calibration Standard CP299107
Commercial Validation Standard CP912394

Instrumentation

Varian PIONA+ Analyzer
Varian 450-GC Gas Chromatograph
PIONA+ multi column module

Software
Galaxie™ Software from Varian with PIONA+ plug-in software

Results and Discussion

As shown in Figure 1, when the PIONA+ system is operated in the conventional mode, a total analysis time of 180 minutes is required to elute all of the component groups. However, as shown in Figure 2, through the use of concurrent heating of both Varian CP-Molsieve™ 5A and 13X traps, a reduction in total analysis time from 180 minutes to 95 minutes is obtained, i.e. ~50 % less.
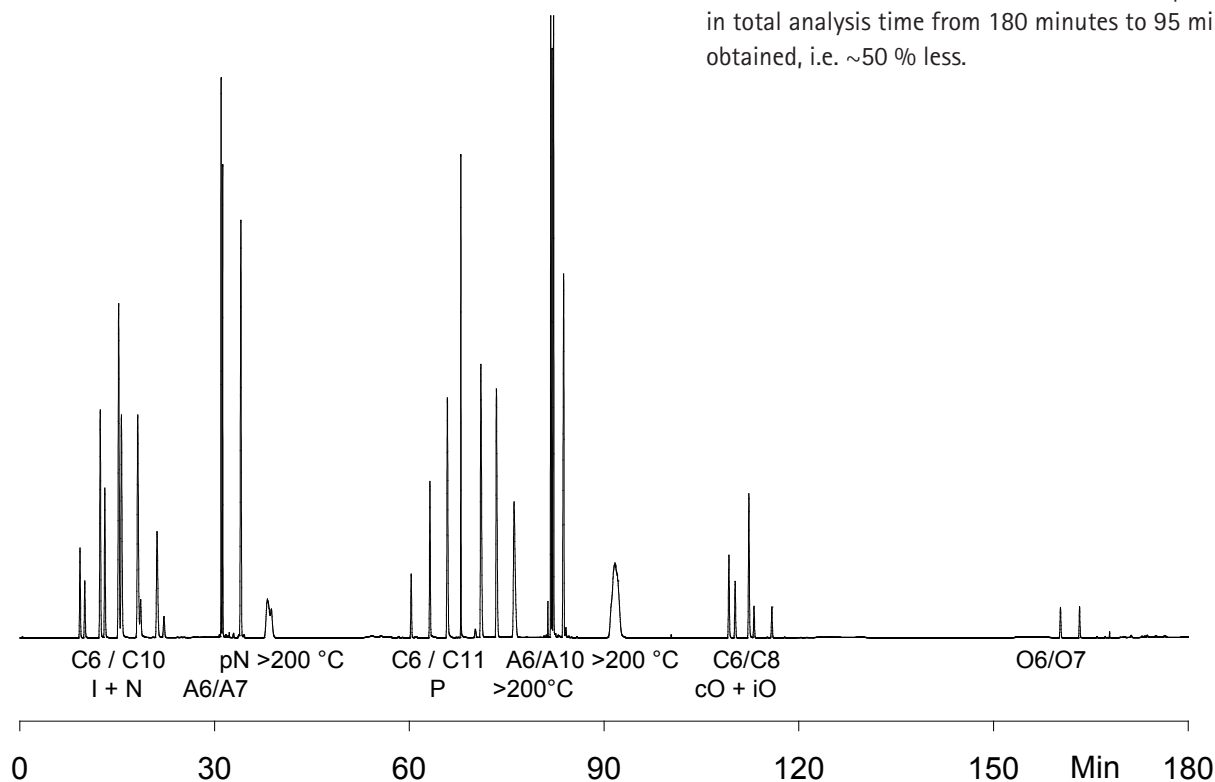

Figure 1. Chromatogram of a calibration sample CP299107 in conventional PIONA mode.
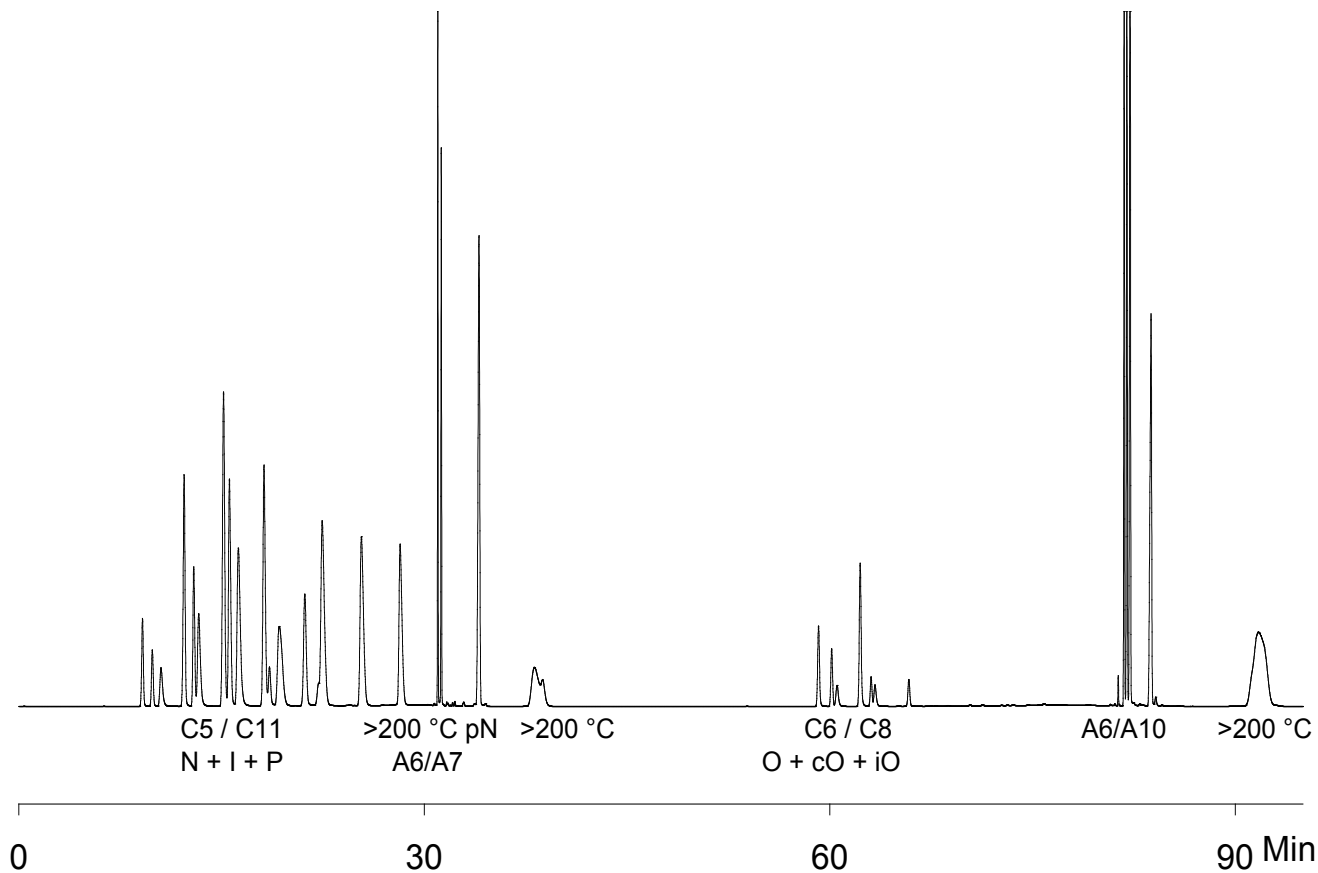
Figure 2. Chromatogram of calibration mix CP299107 in fast PIONA mode.

The reduction in analysis time is achieved by carefully optimizing the temperature settings of the various traps and columns and invoking simultaneous heating of the CP-Molsieve traps.

This approach, referred to as the "FastPIONA" mode, results in the elution of the paraffins immediately after their naphthene and iso-paraffin counterparts. Yet the elution integrity of the component groups remains intact with no negative influence on either naphthene or iso-paraffin groups.
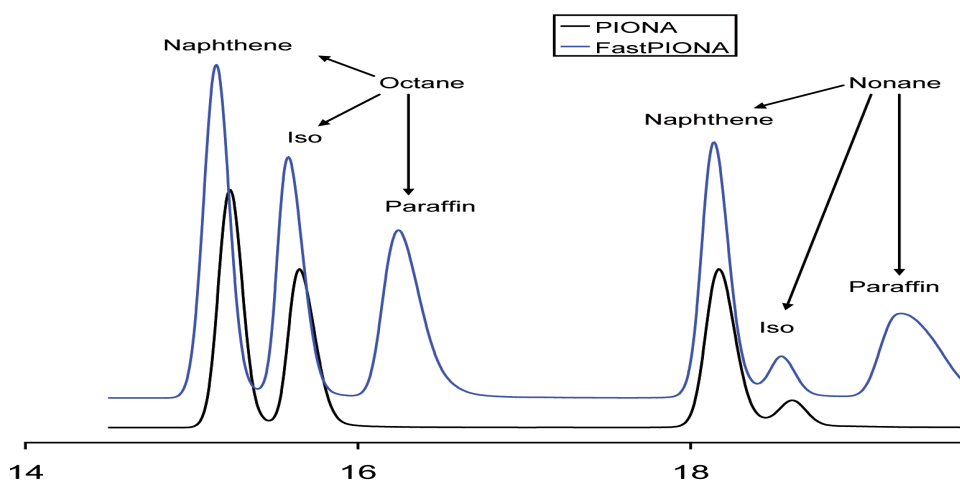

Figure 3. Close-up view of C8 and C9 components. Separation in both conventional and fast PIONA mode.

Figure 3 shows a close-up of the resulting elution sequence. The same results occur for the olefin group separations. The cyclic and iso-olefins normally elute from 100–130 minutes and the n-olefins, in conventional PIONA mode, from 150–180 minutes.

However, through the use of concurrent heating they completely elute between 55 and 70 minutes (Figure 4). In the example of Figure 5, a commercial standard was analyzed for O-PIONA (oxygenates, paraffins, iso-paraffins, olefins, iso-olefins, naphthenes and aromatics) utilizing the concurrent heating approach described above. Note that the oxygenates elute separately from the other component groups and are easily identified and calculated by the PIONA+ software.
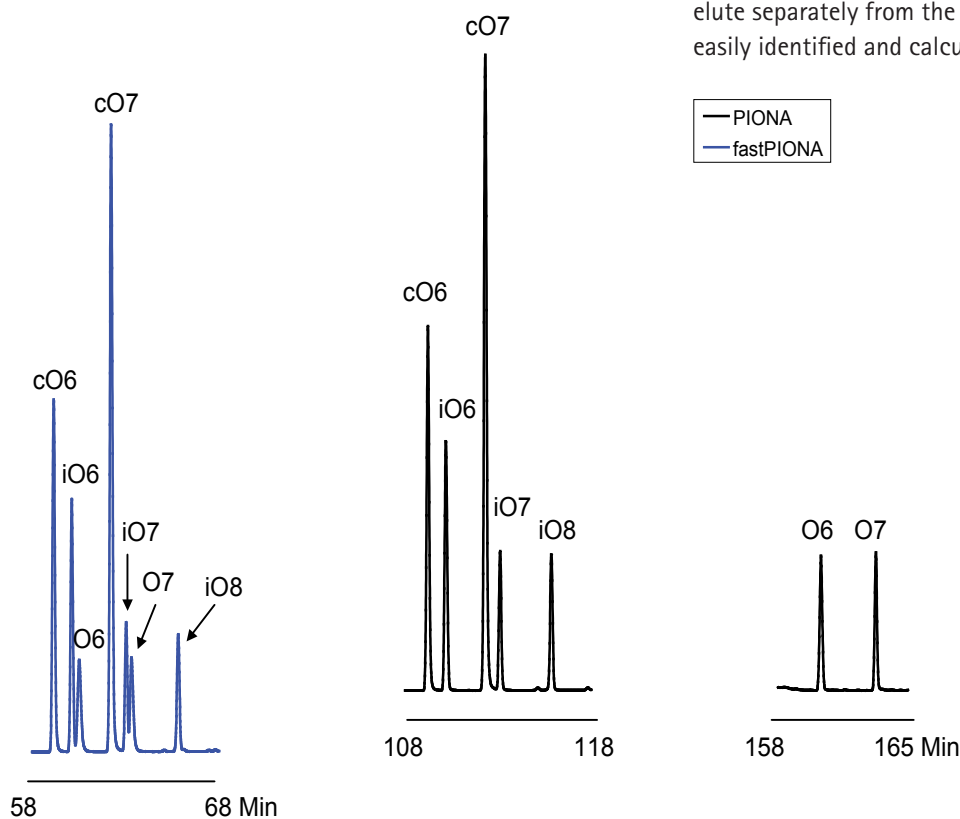

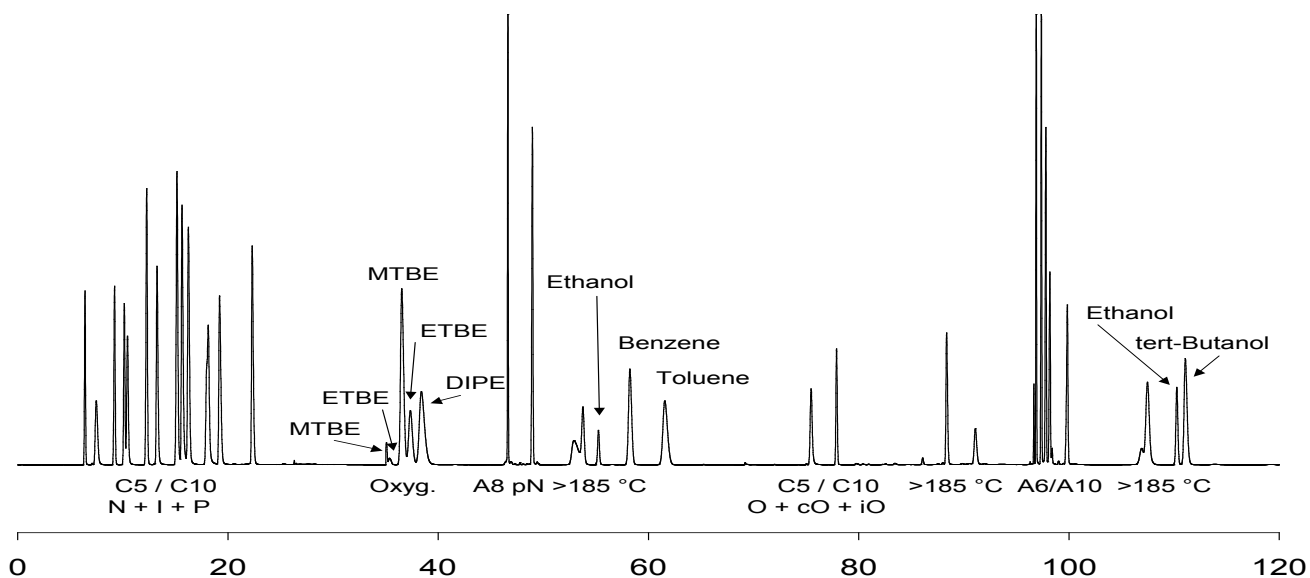**Figure 4.** Close-up view of olefins in conventional and fast PIONA mode.

Figure 5. Chromatogram of a commercial standard in fast O-PIONA mode.

Conclusion

Temperature programming a CP-Molsieve 5A trap (concurrent heating) together with a CP-Molsieve 13X trap greatly reduces the total analysis time of PIONA+ type analysis and, in some cases, can improve the performance. Total analysis time is reduced by one third in the case of O-PIONA and by as much as half for PIONA. The reduction in analysis time is possible without any hardware changes and can be achieved without any negative effect on the quality of the component class separation. In addition, the analyses remain compliant with the method BS.EN 14517.

Reference

BS.EN 14517:2004. Methods of test for petroleum and its products. BS 2000-526: Liquid petroleum products. Determination of hydrocarbon types and oxygenates in petrol. Multidimensional gas chromatography method. British Standards Institution, London, UK.