HYPHENATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY AND TWO - DIMENSIONAL GAS CHROMATOGRPHY- MASS SPECTROMETRY FOR GROUP TYPE SEPARATIONS.

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ABSTRACT

The Fischer-Tropsch (FT) process produces a variety of compounds over a wide carbon number range and the fuels produced by this process are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. The characterization of these products is very challenging even when using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS). The separation between cyclic paraffins and olefins is especially difficult since they elute in similar positions on the GC×GC chromatogram and since they have identical molecular masses with indistinguishable fragmentation patterns. Previously, a High Performance Liquid Chromatography (HPLC) fractionation procedure was used prior to GC×GC-TOFMS analysis to distinguish between alkenes and alkanes, both cyclic and non-cyclic, however, there was severe co-elution of the solvents used in the HPLC fractionation procedure, and the volatile components in the sample and the dilution introduced by the off-line fractionation procedure made it very difficult to investigate components present at very low concentrations. The hyphenation of Supercritical Fluid Chromatography (SFC) to GC×GC is less complicated and the removal of the supercritical CO_2 can be easily achieved without any loss of the volatile sample components, eliminating the introduction of co-eluting solvents as well as the dilution effect. This paper describes the on-line hyphenation of SFC to a GC×GC system in order to comprehensively characterize the chemical groups (saturates, unsaturates, oxygenates and aromatics) in a FT sample.

Keywords:

Supercritical Fluid chromatography; Comprehensive two-dimensional gas chromatography; hyphenation; light oil.

1. INTRODUCTION

The Fischer-Tropsch (FT) process produces a variety of compounds over a wide carbon number range and involves a series of catalysed reactions of carbon monoxide and hydrogen. A large variety of synthetic fuels and chemicals are produced during product workup [1] that are practically free of sulphur- and nitrogen-containing compounds – alleviating environmental concerns when compared to crude- derived products. The high temperature FT (HTFT) products are rich in highly valuable olefins and oxygenates, which crude oil only contains at trace levels. For the HTFT processes, products are spread over gas, oil and water phases with only a small amount of wax that is formed. The analysis of any one of these phases is very challenging and typical oil phase samples may contain thousands of compounds. The characterization of these phases is very important for the study of FT selectivity models and their deviations [2]. Previously one dimensional separation techniques were used for the study of the selectivity models [2-9], however these techniques cannot separate all compounds, even when using high efficiency capillary columns providing peak capacities in the order of ~ 500-600 [10]. The introduction of comprehensive two-dimensional gas chromatography (GC×GC) provides several advantages for the analysis of these complex oil phase samples. The peak capacities are in the order of tens of thousands and peaks are often arranged in highly structured plots where peaks belonging to a homologous series are positioned along straight lines on a retention plane. Another advantage of GC×GC is the increase in sensitivity (up to 10 fold) compared to 1D GC because of the re-concentration of peaks in the modulator and the very fast separation achieved in the second dimension column that minimizes peak broadening and effectively increases the signal-to-noise ratio [11,12]. The application of GC×GC to the analysis of highly complex petrochemical mixtures has been described by a number of authors [12-17]. Even with the huge increase in separation power obtained by comprehensive GC, peak co-elution still occurs when very complex mixtures are analyzed. The separation between cyclic paraffins and olefins is especially difficult since they elute in similar positions on the GC×GC chromatogram. Time-of-flight mass spectrometry (TOFMS) is very powerful in group-type identification but is also not able to distinguish between the cyclic alkane and alkene component classes because of their identical molecular masses and similar fragmentation patterns. One way of improving the GC×GC

separation is to apply a fractionation step prior to GC×GC analysis [18-20]. Previously, an HPLC fractionation procedure using a silver-modified column was used prior to GC×GC-TOFMS analysis to distinguish between alkenes and alkanes, both cyclic and non cyclic [21, 22]. This robust fractionation step before GC×GC was used to separate saturated from unsaturated hydrocarbons since it is known that the silver ions interact with the alkene double bond by formation of a complex. It was shown by Mao *et al.* [21] that the complexation of silver ions with alkene double bonds occurs with both aliphatic and aromatic compounds. It was observed that the saturated hydrocarbons were not retained on the silver-modified column and eluted with the non-polar mobile phase, n-hexane, whilst the unsaturated hydrocarbons were retained on the column. The unsaturated hydrocarbons were subsequently released from the column by changing the mobile phase to the more polar acetone. The TOFMS was then utilised to distinguish between the non cyclic and cyclic alkanes eluted by the hexane solvent and the non-cyclic and cyclic alkenes eluted by the acetone solvent. Although this approach worked well, there was severe co-elution of the solvents used in the HPLC fractionation procedure and the volatile components of the sample [22]. Another drawback of this procedure is that the solvents used in the HPLC method diluted the sample and large amounts of the collected fractions had to be injected in order to detect the smaller peaks by GC×GC. Direct transfer of large volumes of collected fractions requires instrument modifications [24]. Low level components can go undetected without re-concentration of the collected fraction, a process that can lead to severe discrimination against the volatile compounds in the sample. The susceptibility of off-line hyphenated techniques to sample loss and contamination during collection and reconcentration has been described by other groups [23], emphasizing the need for an on-line pre-fractionation step. Supercritical Fluid Chromatography (SFC) utilizes supercritical CO_2 as mobile phase. The use of SFC for group type separation has been published before and the separation achieved with SFC has proved to be very similar to that obtained by HPLC [25-27]. The hyphenation of SFC to GC×GC is less complicated and has been achieved by other groups merely by decompression of the supercritical fluid through a restrictor into the GC injection port [28-30]. This allows the transfer of an eluting fraction from the supercritical phase to the gas phase with simultaneous loss of only the highly volatile CO_2. Utilizing SFC as pre-fractionation method would eliminate the introduction of co-eluting solvents as well as the dilution stemming from the HPLC fractionation procedure [22]. In order to comprehensively characterize the chemical groups (saturates, unsaturates, oxygenates and aromatics) in a sample, the on-line hyphenation of SFC to a GC×GC system is described. The first part of

this paper addresses the development and optimization of the SFC chromatographic conditions to achieve the group type separation whilst the second part deals with the GC×GC method. Subsequently the on-line hyphenation of SFC to the GC×GC and the results obtained from the analysis of an oil sample are also discussed. Some applications are also mentioned at the end of this paper.

2. EXPERIMENTAL

2.1 Chemicals

Analytical gases for both the SFC and the GC×GC were obtained from Afrox (South Africa). The HTFT Light oil, kerosene and narrow distillation cut samples were obtained from Sasol Synfuels, Secunda, South Africa. Standards of the various chemical groups were obtained from Sigma Aldrich (St Louis, MO, USA).

2.2 SFC group type separation.

A Selerity Series 4000 SFC system equipped with SFC pump, autosampler, SFC oven, a pneumatically actuated rotary injection valve and a flame ionization detector operated at a temperature of 400 °C was used for the group type separation on the SFC (Selerity Technologies, Utah, USA). The optimization of the group-type separation (saturates, unsaturates, aromatics and oxygenates) on the SFC was performed using a variety of standards typically found in a HTFT light oil sample. In order to achieve the group type separation, three analytical columns were used namely a PVA-Silica column (50 mm L x 1.0 mm ID, 5 µm d_p from Selerity Technologies, Utah, USA) that was used to retain the oxygenates whilst the Petrosil column (50 cm L x 1.0 mm ID, 5 µm d_p from Selerity Technologies, Utah, USA) was used to separate the aromatics from the unsaturates. A PetroAG silver-loaded cation exchange column (50 mm L x 1.0 mm ID, 5 µm d_p from Selerity Technologies, Utah, USA) was used to retain all the unsaturates. The SFC oven is also equipped with two six-port two-position switching valves to allow forward and backflushing of the analytical columns. The silver loaded column was operated in a secondary column oven at a temperature of 140 °C throughout to allow faster clearance of the olefins and other unsaturates through the column. The SFC mobile phase (carbon dioxide) was delivered at a constant pressure of 200 atm. The injection volume was 0.1 µl and the analysis temperature of 40 °C was used throughout. An external six-port, two-

position switching valve was used to direct the SFC effluent to either the FID on the SFC instrument or the GC×GC instrument. A split connector (Restek, Bellefonte, USA) was installed on the capillary going to the GC×GC in order to control the amount of effluent that is sent to the GC×GC. The SFC eluent was introduced into the PTV injector by an integral restrictor [31] inserted through the septum. The SFC columns were set up similar to the method described for the determination of olefin content in denatured ethanol by SFC [32] and once the retention times for each group was determined using the FID, the external valve could be switched on at these respective times to transfer the appropriate SFC fractions to the GC×GC.

2.3 GC×GC method.

The GC×GC instrument used was a Pegasus 4D from Leco Corporation (St. Joseph, USA) equipped with a time-of-flight mass spectrometer and a 7683B auto injector system (Agilent Technologies, Little Falls, USA). A programmed temperature vaporization (PTV) injector (Gerstel, Mulheim an der Ruhr, Germany) was used on this system. In previous studies the advantages of a polar × non-polar column set (in contrast to the more common non-polar × polar column set) for the analysis of Fischer-Tropsch oil products were described [16, 17]. Hence, in the first dimension a 60 m × 0.25 mm ID, 0.25 µm df StabilWax (Restek, Bellefonte, USA) and in the second dimension a 2 m × 0.1 mm ID, 0.1 µm df RTXi-5 column (Restek, Bellefonte, USA) was used in this study. Helium was the carrier gas at a constant flow rate of 1.2 mL/min. A split ratio of 400:1 and injection volume of 0.5 µL was used for the analysis of the light oil sample whilst for the hyphenation experiments the injector was operated in splitless mode. The first oven was programmed from 40 °C (2.0 min) to 255 °C at 2 °C/min. The secondary oven and modulator followed the first temperature program but started at 60 °C and 70 °C, respectively. TOFMS spectra were collected at 100 spectra/s. A GC×GC chromatogram of a typical light oil samples indicating the different chemical groups is shown in Figure 1.

Figure 1

2.4 Hyphenation of SFC and GC×GC.

The experimental set-up involved the insertion of the end restrictor from the ‘on’ position of the external six-port switching valve into the septum of a PTV injector. Previous studies

[30] indicated that the length of restrictor that is introduced into the injector does not affect yields of recoveries and therefore 5 cm of the restrictor was introduced into the injector. In order to transfer the peak of interest to the GC×GC, the external six-port valve was switched to the ‘on’ position at the start of the peak of interest. The analytes were cryogenically focussed at the head of a thick phase (0.05 m × 0.25 mm ID, 1.0 µm df) HP-1MS column (Agilent Technologies, Little Falls, USA) inside the injector by dispensing liquid nitrogen to the injector via a nitrogen cryogenic valve (Agilent Technologies, Little Falls, USA). The first dimension column (section 2.3) was connected to this HP-1MS column inside the column oven. The injector temperature was maintained at -50 °C during the transfer of the SFC effluent. The normal oven starting temperature of 40 °C was maintained throughout the effluent transfer. Once the whole peak of interest was transferred to the GC×GC, the external six-port valve was once again switched to the ‘off’ position sending the SFC effluent to the FID detector, allowing the SFC chromatographic run to finish normally. Once all the CO_2 passed through the GC×GC columns, the normal GC×GC analysis (section 2.3) was started by heating the PTV injector to 260 °C at a rate of 720°C/min.

3 RESULTS AND DISCUSSION

3.1 Optimization of SFC Fractionation

A variety of standards typically found in a HTFT light oil sample was used in order to optimize the valve switching times. These standards included alkanes, cyclic alkanes, olefins, cyclic olefins, dienes, cyclic dienes, alkylbenzenes, alcohols, carbonyls, and acids in the C5 – C25 carbon range.

Figure 2.

In order to separate oxygenates from the other compounds, the PVA column, Silica column and silver column were operated in forward flush mode connected in series (Figure 2A). In this position the oxygenates were retained on the PVA column whilst all the other groups eluted from the column within 3.0 min to be collected on the silica column. At this time valve A is switched to the negative position in order to operate the PVA column in backflush mode whilst the silica and silver columns are in stop-flow mode (Figure 2B). All the oxygenates retained on the PVA column were backflushed from the PVA column within

8.0 min and valve A was once again switched on (Fig 2 A) in order to elute the saturates, retain the aromatics on the silica column and to load all the olefins on the silver column. All the saturates eluted from the column at 10.0 min and at this time valve A was switched off whilst valve B was switched on removing the silica column from the flow path (Figure 2C), operating both the PVA column and silver columns in backflush mode in order to elute all the unsaturate species from the silver column. All the olefin species were eluted at 18.0 min and at this time both valves were switched on to include all the columns in forward flush mode (Figure 2D), with the silica column last in the series, to elute all the aromatics to the detector. At 25.0 min all the aromatics were eluted and the run was ended. The SFC-FID chromatogram obtained for the analysis of a light oil sample (Figure 3) shows the group type separation obtained.

Figure 3.

3.2 Hyphenation of SFC and GC×GC

As suggested by Adam *et al.* [30] cryofocussing of solutes was used in order to continuously trap analytes transferred from the SFC at the head of the GC×GC primary column. Initial attempts to trap solutes using this experimental set-up remained unsuccessful, resulting in the insufficient trapping of the volatile components in the light oil sample even at oven temperatures of -50 °C. This was mostly due to the fact that at this low trapping temperature the primary GC×GC column was operated out of its recommended operating conditions (minimum operating temperature of the stationary phase is 40 °C) and this resulted in a liquid-solid phase transition of the column stationary phase. Furthermore, upon subsequently heating the column, the solid-liquid phase transition is not immediate. This results in loss of efficiency, reduced sample capacity as well as poor retention time reproducibility. It was subsequently decided to cryofocussing the solutes on a thick phase column inside the PTV injector as described in section 2.4.

Figure 4.

It can be seen in Figure 4A that in the case of the saturated group of the light oil sample, the volatile compounds were trapped sufficiently and the resolution was similar to that obtained from the direct GC×GC analysis. It can be seen from this contour plot that the

saturates were isolated successfully and that none of the other groups of interest eluted in this fraction. The n-alkanes, branched alkanes and cyclic alkanes are easily distinguishable. The GC×GC results achieved without SFC fractionation can readily be imagined by superimposing A and B: Looking at the retention times of the cyclic alkanes on the contour plot, it can be seen that they would elute in the same area as the olefins and since the olefins are present in high concentrations in the original light oil sample, the cyclic paraffins would co-elute severely with the olefins, preventing classification and even detection. With SFC fractionation, however, no olefins were observed in the saturate fraction and the complexity of this area on the chromatogram was drastically reduced.

The GC×GC-TOFMS contour plot of the unsaturate fraction (Figure 4B) shows no traces of saturates, allowing clear separation of linear and branched olefins. Other unsaturates (cyclic olefins, dienes, cyclic dienes) also elute in this fraction whilst the aromatics were completely absent from this fraction. A distribution of light carbonyls (< C12) and esters is also observed in the olefin fraction. This is due to the fact that these light carbonyls and esters are not retained efficiently enough on the PVA-Silica column. The selectivity of the PVA-Silica column is towards alcohols and the less polar carbonyls and esters were not retained efficiently. This was not a major concern since these carbonyls elute in a different chromatographic region than the olefins and other unsaturates on the contour plot. The aromatics that usually co-elute with the carbonyls and esters in this region were completely removed from this fraction.

The aromatic fraction (Figure 4C) is also well separated from the other groups of interest and the branched carbonyls that elute in the same contour plot area were completely removed from this fraction. This enables the investigation of the aromatics in the light oil fraction without the added complexity of co-elution with other non aromatic compounds. It was also observed that not only monocyclic aromatic hydrocarbons elute in this aromatic group, but also bicyclic and polycyclic aromatic hydrocarbons.

The oxygenate fraction (Figure 4D) shows the full distribution of alcohols and carboxylic acids and phenols. Only a partial distribution (> C12) of the carbonyls were observed and as mentioned before, this is due to the lack of selectivity of the PVA-Silica method towards the lighter carbonyls. Remaining CO_2 can be observed in all the fractions indicating that small amounts of CO_2 were bleeding from dead-volumes of the multitude of connections, however, CO_2 is well separated from the rest of the compounds and does not interfere with analysis.

The GC×GC contour plots of the saturate, unsaturate, aromatics and oxygenate fractions confirm that the SFC fractionation procedure is highly successful in reducing the complexity of oil samples. The oil sample used for the development of the SFC separation method in this study has a wide carbon number range which shows that the SFC group separation is robust and could be applied to different distillation cuts within this carbon number range. The SFC-FID method in itself can also be used as a screening tool to monitor how different process conditions can influence the relative concentrations of these different groups, since these groups have now been well-characterized by GC×GCTOFMS.

3.2 Application of SFC-GC×GC-TOF

In order to compare the initial results obtained by the HPLC fractionation procedure with off-line GC×GC-TOF analysis [22] and the results obtained from the method developed in this study, the same kerosene sample analyzed in the previous study was analyzed by means of the SFC-GC×GC-TOFMS method, and the saturate and unsaturated fractions were compared [Fig 5]. It was observed that the areas where the HPLC mobile phases previously eluted on the contour plot (circle in fig 5) is now free of any interferences, whilst the peaks in this area were trapped sufficiently with SFC injection, resulting in a contour plot resolution similar to that of the direct GC×GC-TOF analysis. Similar contour plots to the HPLC fractionation for the saturated and unsaturated hydrocarbons are observed and this shows that the separation on the SFC was just as effective as the separation obtained using the HPLC.

Figure 5.

In order to evaluate the application of the SFC group type separation to a section within the broad carbon number range of the light oil sample, a narrow distillation cut was analyzed. From the conventional GC×GC contour plot of the unfractionated sample it can be seen that this sample is highly unsaturated whilst saturates, aromatics as well as oxygenates are also observed (Fig 6). The GC×GC-TOFMS contour plot of the saturate fraction (Fig 7A) once again shows linear, branched and cyclic paraffins without any interference from the unsaturated compounds in the sample. Most of the cyclic paraffins could not be identified without SFC pre-fractionation. The unsaturated fraction (Fig 7B) confirms a high degree of unsaturation (large amounts of dienes, cyclic olefins, cyclic dienes, bicyclic olefins etc) whilst the aromatics were also completely removed. A

distribution of light carbonyls (< C12) is once again observed in the olefin fraction. The aromatic fraction (Fig 7C) is well separated from the other groups and none of the highly unsaturated compounds eluted in this fraction. Only narrow distributions of alcohols and carboxylic acids at low concentrations were observed in the oxygenate fraction (Fig 7D). By applying the developed fractionation procedure to the narrow distillation cut sample, the complexity thereof could also be drastically reduced enabling its comprehensive characterization. This illustrates the applicability of the SFC separation to distillation cuts within the carbon number range of the light oil sample (< C25) without additional method modification.

Figure 6.

Figure 7.

4. CONCLUSIONS

A SFC method for the fractionation of (linear and cyclic) saturates, (linear and cyclic) unsaturates, aromatics and oxygenates of a light oil sample was developed. These fractions were transferred to the GC×GC-TOFMS in an on-line mode and the successful further separation of these groups of interest was obtained. Application of this procedure to the same sample previously analyzed by the HPLC fractionation procedure showed that the mobile phase interferences prevalent in the HPLC procedure was eliminated whilst volatile components were trapped sufficiently. The developed procedure can be applied without additional method modification to distillation cuts within the carbon number range of the light oil sample to reduce sample complexity. Further GC×GC method optimization for better utilization of the 2D separation space for the analysis for each group of interest will increase our capability to comprehensively characterize these groups.

REFERENCES

1. J. Collings, Mind over Matter – The Sasol Story. A Half-century of Technology Innovation, Johannesburg, South Africa, 2002, p4.
2. Steynberg, M.E Dry, Stud. Surf. Sci. Catal. 152 (2004) 406.
3. Y. Ji, H. Xiang, J. Yang, Y. Xu, Y, Li, B. Zhong, Appl. Catal. A 214 (2001) 77.

4. G.P. Van der Laan, Kinetics, Selectivity and Scale Up of the Fischer-Tropsch Synthesis, Ph.D. Thesis, Rijksuniversiteit Groningen, 1999.
5. H. Schulz, M. Claeys, Appli. Catal. 186 (1999) 71.
6. Puskas, R.S. Hurlburt, Catal. Today 84 (2003) 99.
7. E.W. Kuipers, C. Scheper, J.H. Wilson, M.S. Klee, J. Chromatogr. A 894 (1999) 25.
8. G.A. Huff, C.N. Satterfield, J. Catal. 85 (1984) 370.
9. H.G. Strenger, J. Catal. 92 (1985) 426
10. L.M. Blumberg, W.H. Wilson, M.S. Klee, J. Chromatogr. A 894 (1999) 15.
11. J. Dalluge, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, TrAC 25 (2006) 726.
12. P.J. Marriot, R. Shellie, TrAC 21 (2002) 573.
13. Z. Y. Lui, J. B. Philips, J. Chromatogr. Sci. 29 (1991) 227.
14. J. Beens, U. A.Th. Brinkman, Analyst 130 (2005) 123.
15. M. Abahcour, J. Beens, R.J.J. Vreuls, U. A. Th. Brinkman, Trends Anal. Chem. 25 (2006) 540.
16. R. Van der Westhuizen, R. Crous, A de Villiers, P. Sandra, J. Chromatogr A 1217 (2010) 8334.
17. R. Van der Westhuizen, M. Ajam, P. De Coning, J. Beens, A de Villiers, J. Chromatogr A 1218 (2011) 4478.
18. G. S Frysinger, R. B. Gaines, L. Xu, C. M. Reddy, Environ. Sci. Technol. 37 (2003) 1653.
19. R. Edam, J. Blomberg, H.-G Janssen, P. J. Schoenmakers, J. Chromatogr. A. 1086 (2005) 1200.
20. C. Vendeure, F. Bertoncini, D. Espinat, D. Thiebaut, M.-C. Hennion, J. Chromatogr. A 1090 (2005) 116.
21. D. Mao, H. v.d. Weghe, L. Diels, N. De Brucker, R. Lookman, G. Vanermen, J.Chromatogr. A, 1179 (2008) 33-40.
22. R. Van der Westhuizen, H. Potgieter, N. Prinsloo, A de Villiers, P. Sandra, J. Chromatogr A 1218 (2011) 3173.
23. I.L. Davies, K.D. Bartle, T. Williams, G.D. Andrews, Anal. Chem. 60, (1998) 204.
24. T. Hyotylainen, M.L.Riekkola, J. Chromatogr A 1000 (2003) 357.
25. P.E. Anderson, M Demirbruker, L.G. Blomberg, J. Chromatogr 595 (1992) 301.
26. J.M. Levy, J. High Resolut. Chromatogr. 17 (1994) 212.
27. Venter, E.R. Rohwer, A.E. Laubscher, J. Chromatogr A 847 (1999) 309.
28. Venter, E.R. Rohwer, Anal. Chem. 76 (2004) 3699.
29. J.M. Levy, J.P. Guzowski, W.E. Huhak, J. High Resolut. Chromatogr. 10 (1987) 337.

30. F. Adam, D. Thiebaut, F. Bertoncini, M Courtiade, M. Hennion, J. Chromatogr A 1217 (2010) 1386.
31. E.J. Guthrie, H.E. Schwartz, J. Chromatogr. Sci. 24, 236 (1986),.
32. Standard Test Method: ASTM D7347, Standard Test Method for Determination of Olefin Content in Denatured Ethanol by Supercritical Fluid Chromatography, ASTM International, West Conshohocken, USA, 2007.

FIGURE CAPTIONS

Figure 1. Contour plot obtained for the GC×GC-TOFMS analysis of a light oil sample with the polar x non-polar column configuration.

Figure 2. The SFC column configuration for the elution of oxygenates (A (0-3 min); B (3-8 min)), saturates (A; 8-10 min), unsaturates (C(10-18 min)) and aromatics (D (18-25 min)). (For detail see text.)

Figure 3. SFC-FID analysis of the HTFT light oil with valve switching times as well as the valve positions between switching times are indicated.

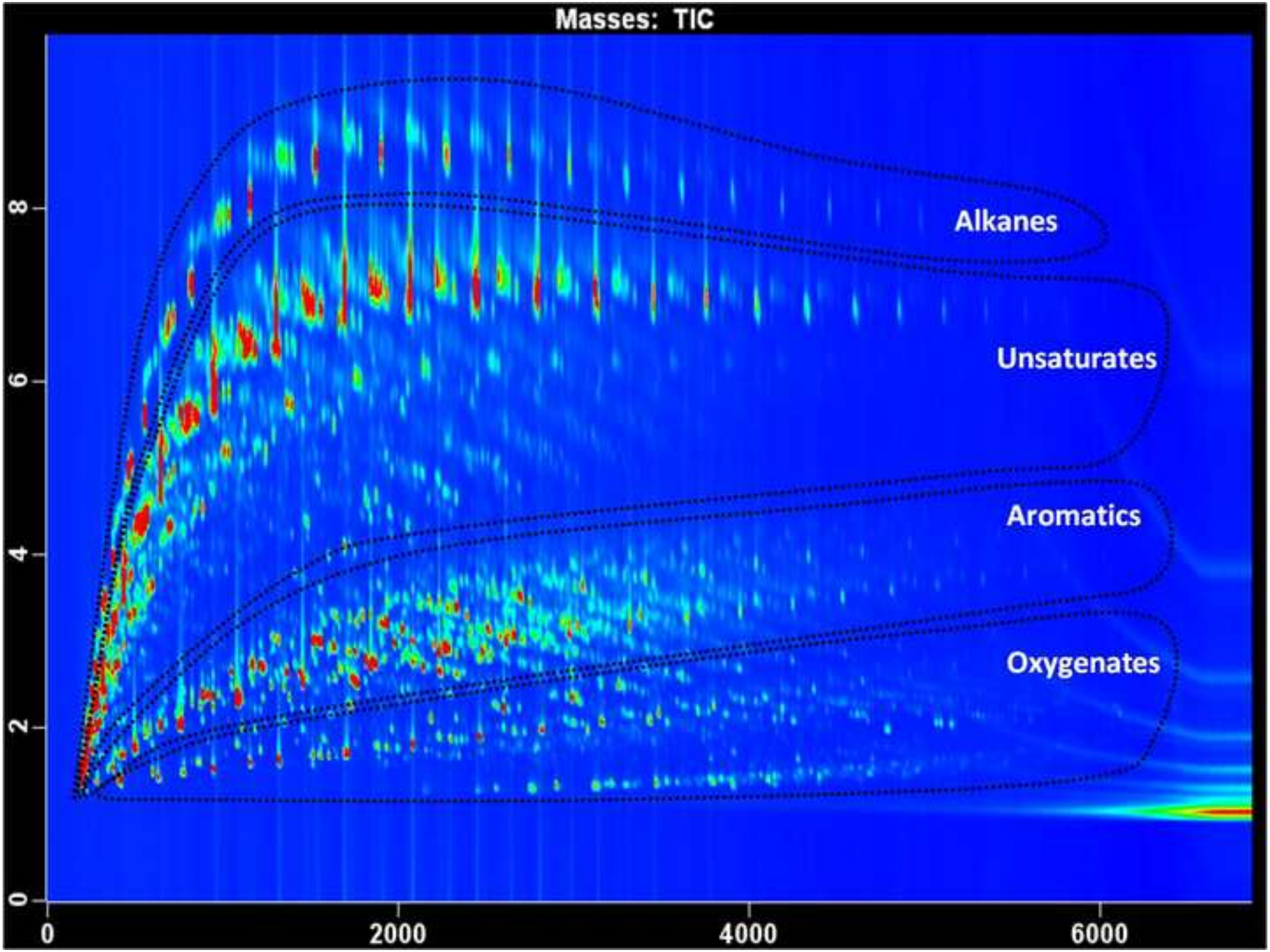
Figure 4. Contour plots obtained for the SFC-GC×GC-TOF analysis of the (A) saturate, (B) unsaturate, (C) aromatic and (D) oxygenate fractions of HTFT light oil.

Figure 5. Comparison between the contour plots obtained for HPLC GC×GC-TOF analysis of the (A1) saturate and (A2) unsaturate fractions [22] and the SFC-GC×GC-TOF analysis of the (B1) saturate and (B2) unsaturate fractions. (the circle indicates the area of concern where HPLC mobile phase elutes)

Figure 6. Contour plot obtained for the GC×GC separation of the highly unsaturate narrow cut sample with the polar x non-polar column configuration.

Figure 7. Contour plots obtained for the SFC-GC×GC-TOF analysis of the (A) saturate, (B) unsaturate, (C) aromatic and (D) oxygenate fractions of the highly unsaturated narrow cut sample.

Figure 1


Masses: TIC
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Unsaturates
Aromatics
Oxygenates
0
2
4
6
8
0
2000
4000
6000

Figure 2a

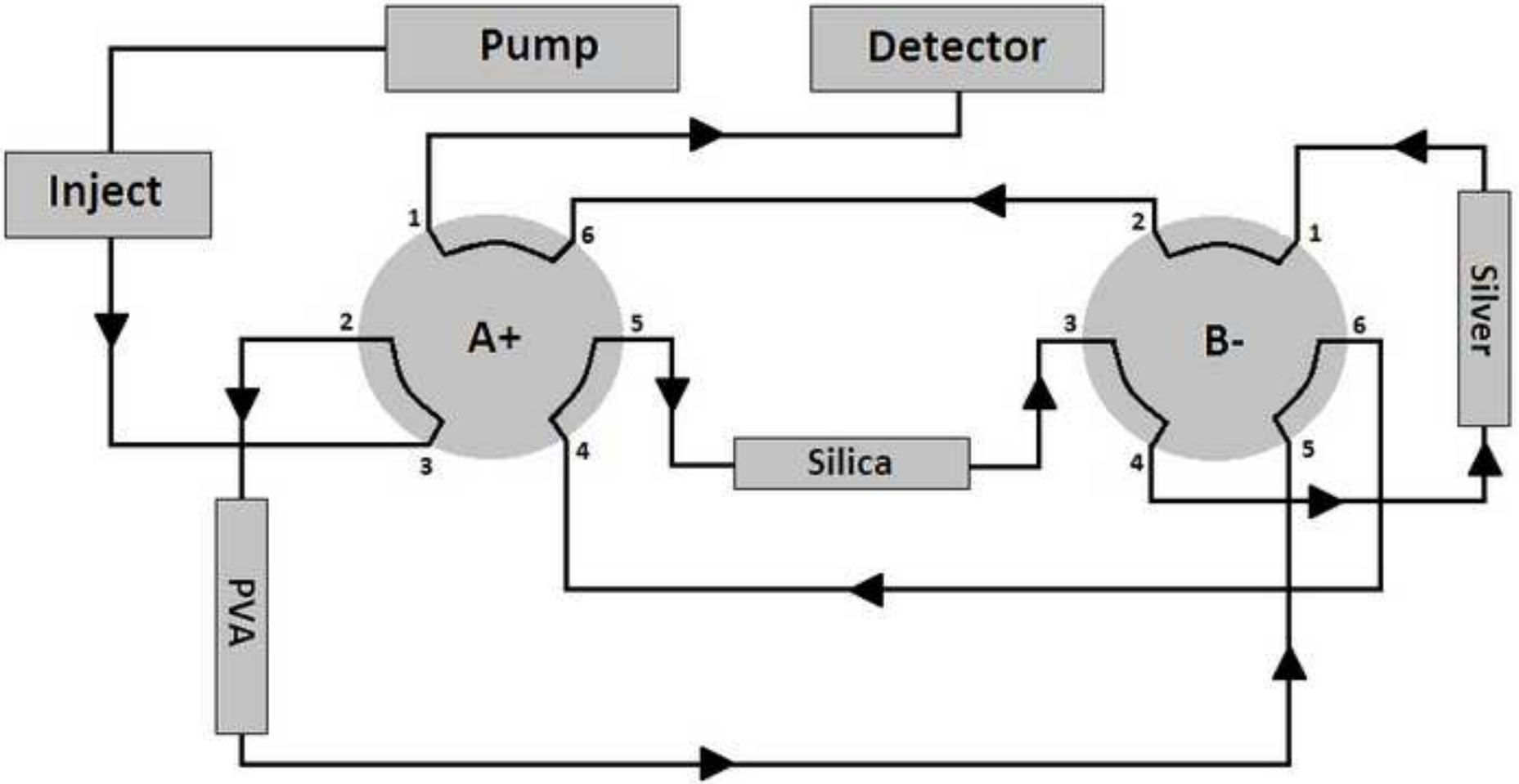

Figure 2b

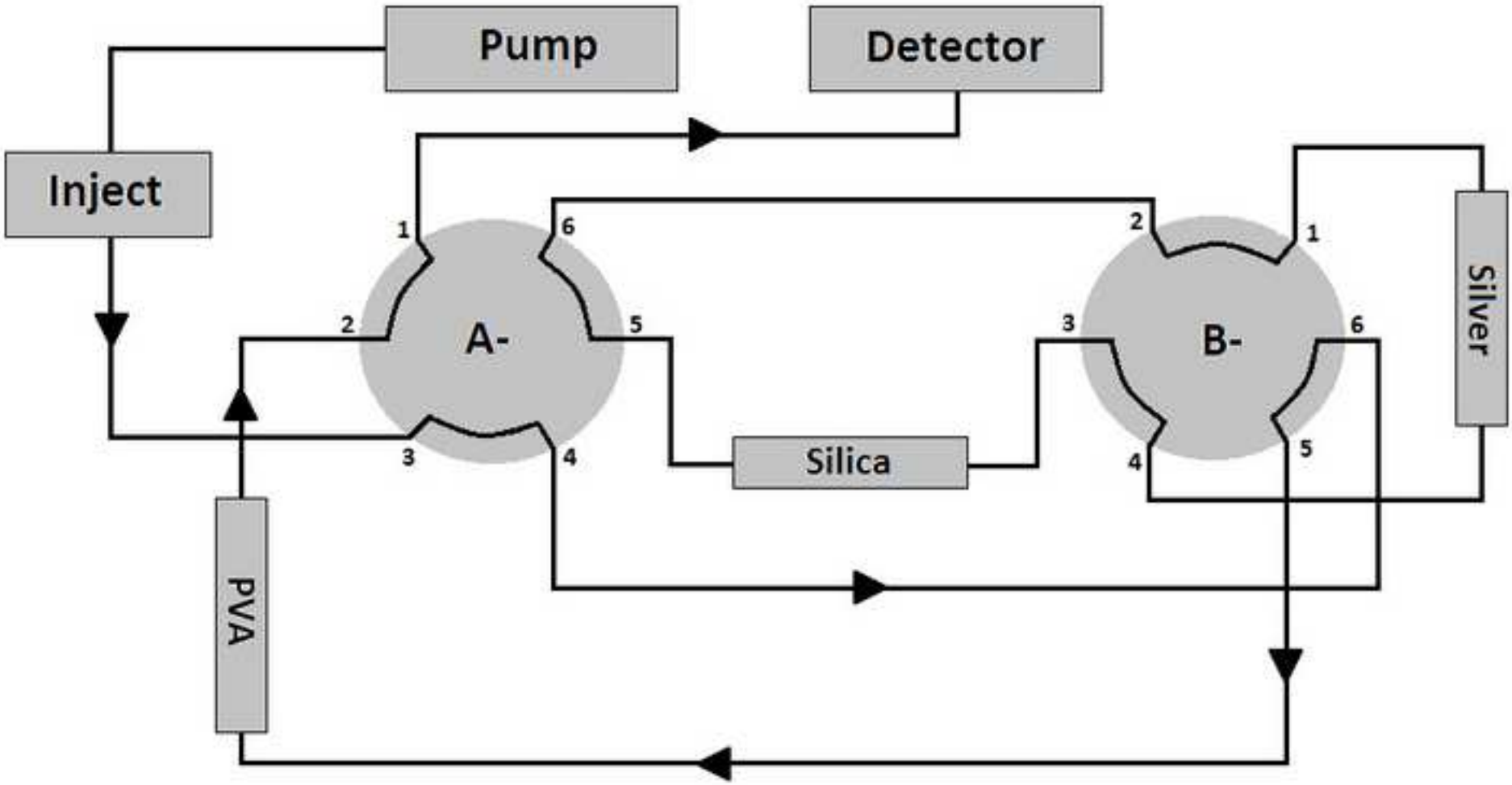

Figure 2c

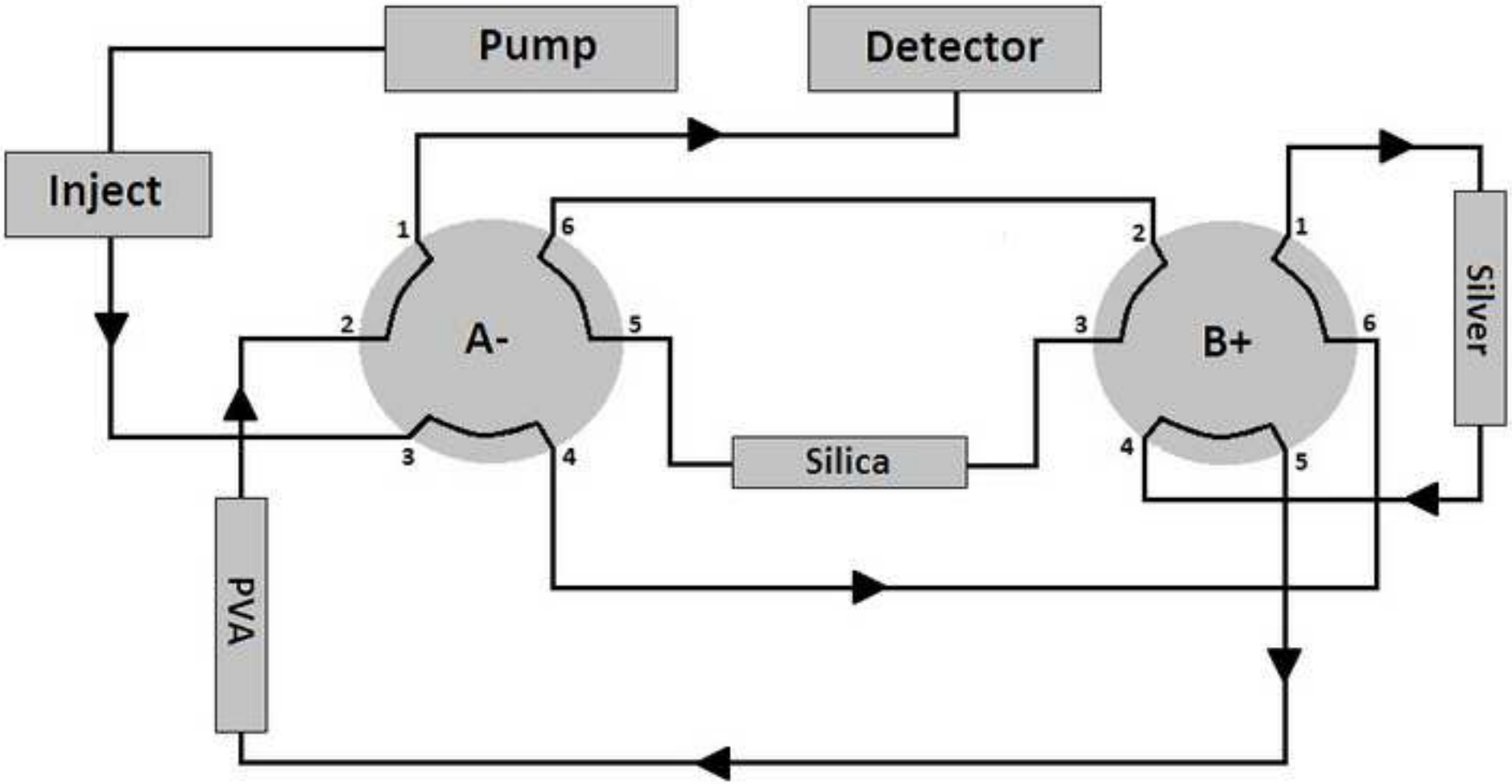

Figure 2d

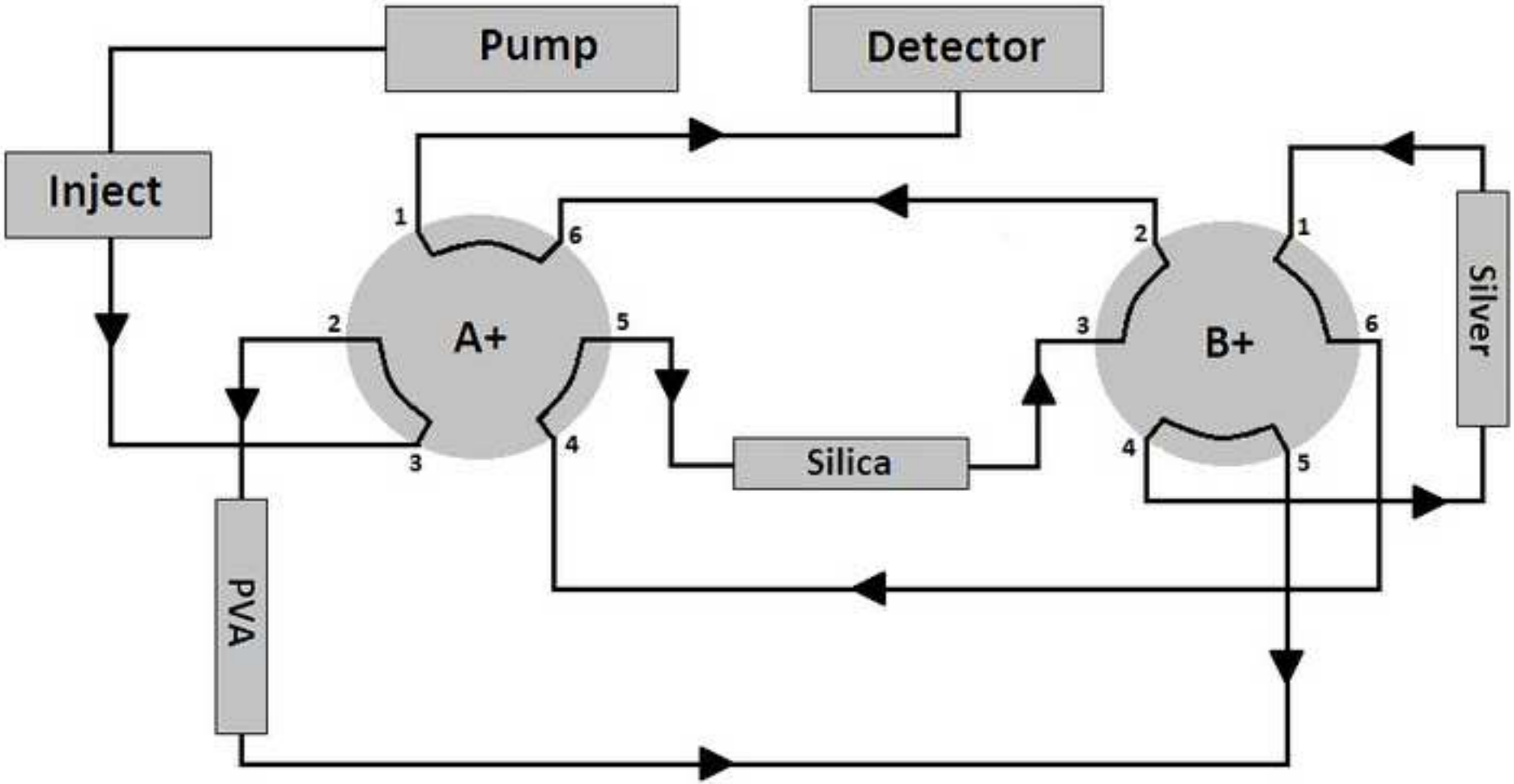

Figure 3

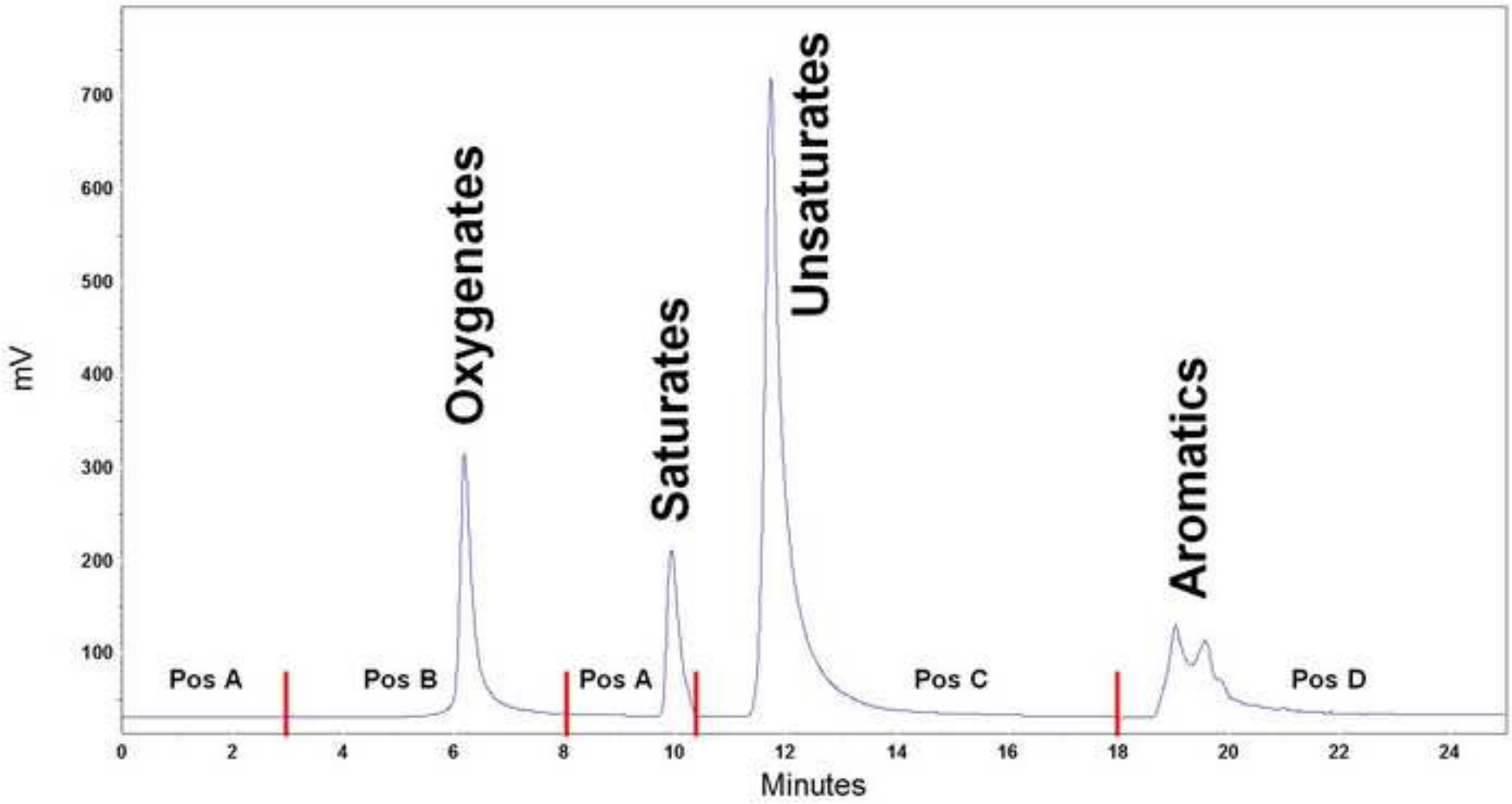
mV
700
600
500
400
300
200
100
Oxygenates
Saturates
Unsaturates
Aromatics
Pos A
Pos B
Pos A
Pos C
Pos D
0
2
4
6
8
10
12
14
16
18
20
22
24
Minutes

Figure 4a

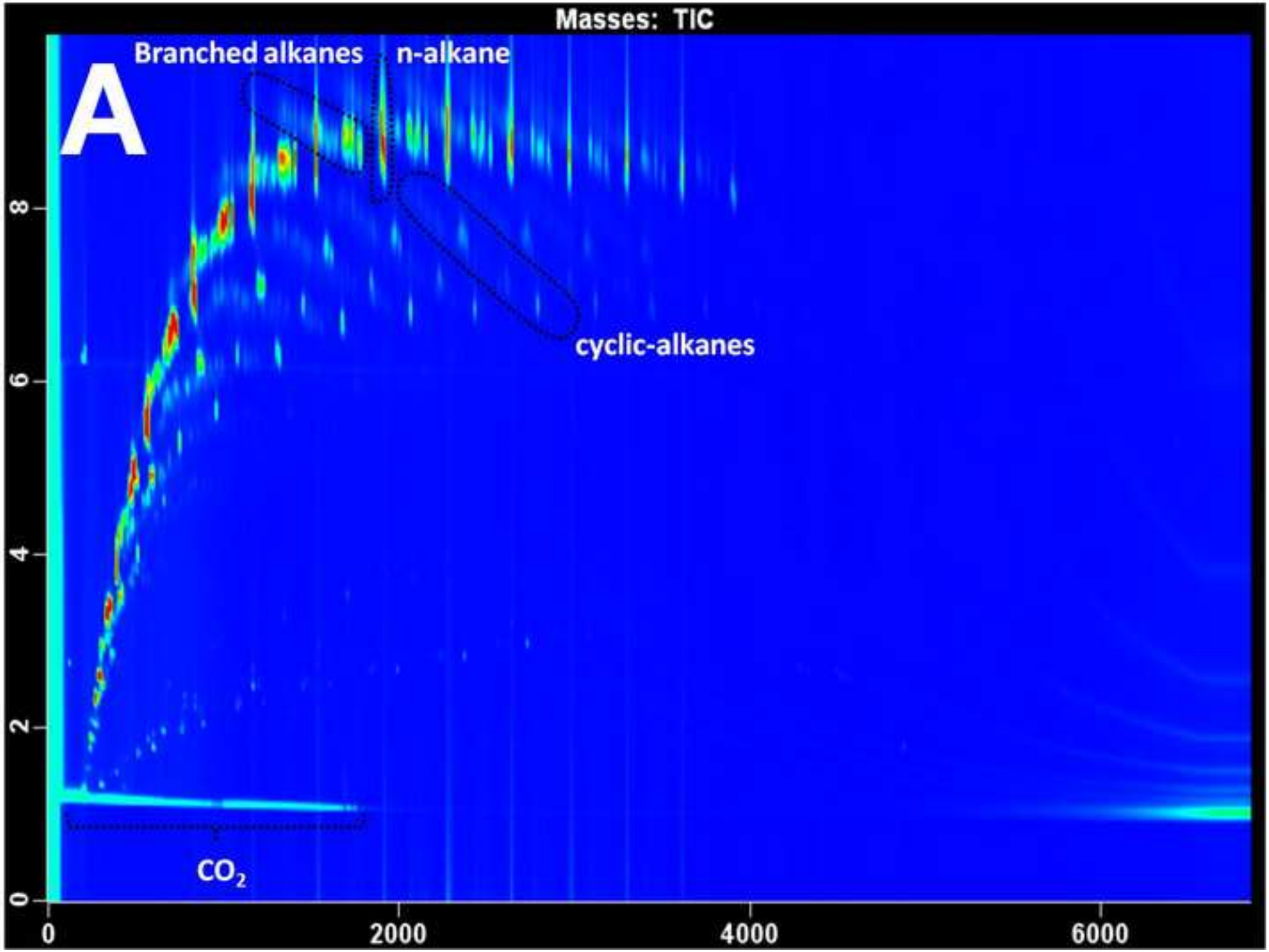
Masses: TIC
A
Branched alkanes
n-alkane
cyclic-alkanes
CO_2
0
2
4
6
8
0
2000
4000
6000

Figure 4b

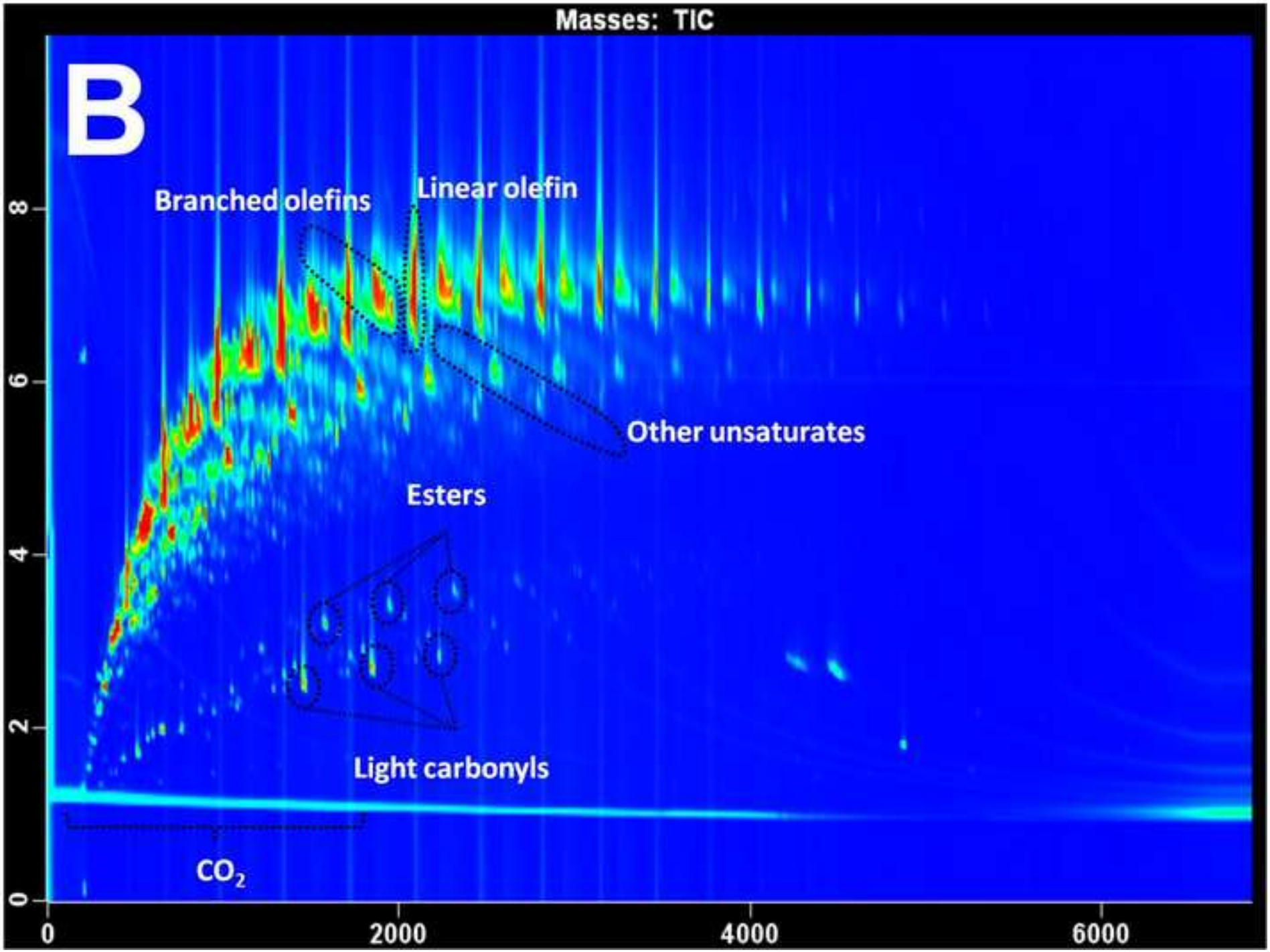
Masses: TIC
B
Branched olefins
Linear olefin
Other unsaturates
Esters
Light carbonyls
CO_2
0
2
4
6
8
0
2000
4000
6000

Figure 4c

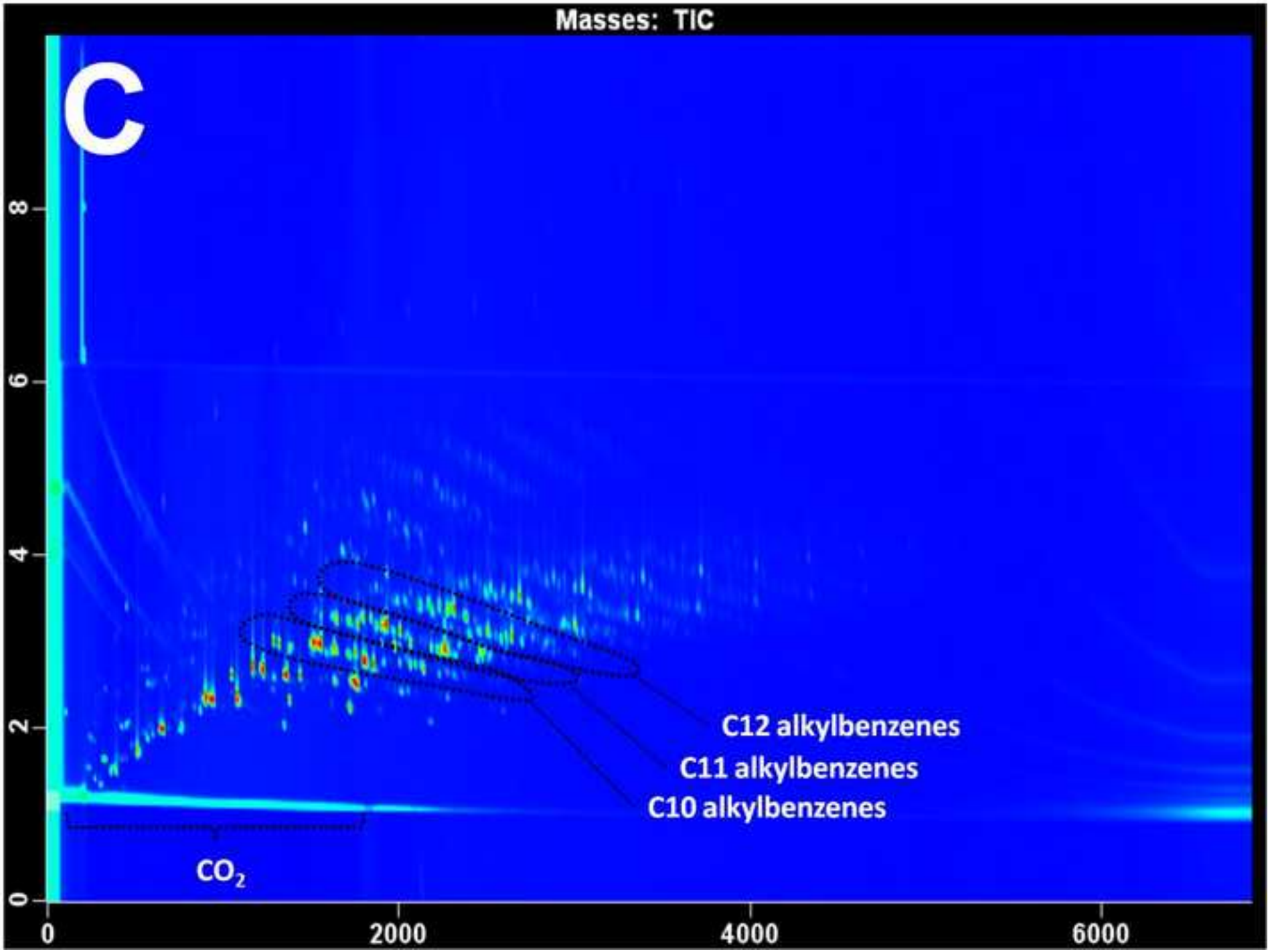
Masses: TIC
C
8
6
4
2
0
0
2000
4000
6000
C12 alkylbenzenes
C11 alkylbenzenes
C10 alkylbenzenes
CO_2

Figure 4d

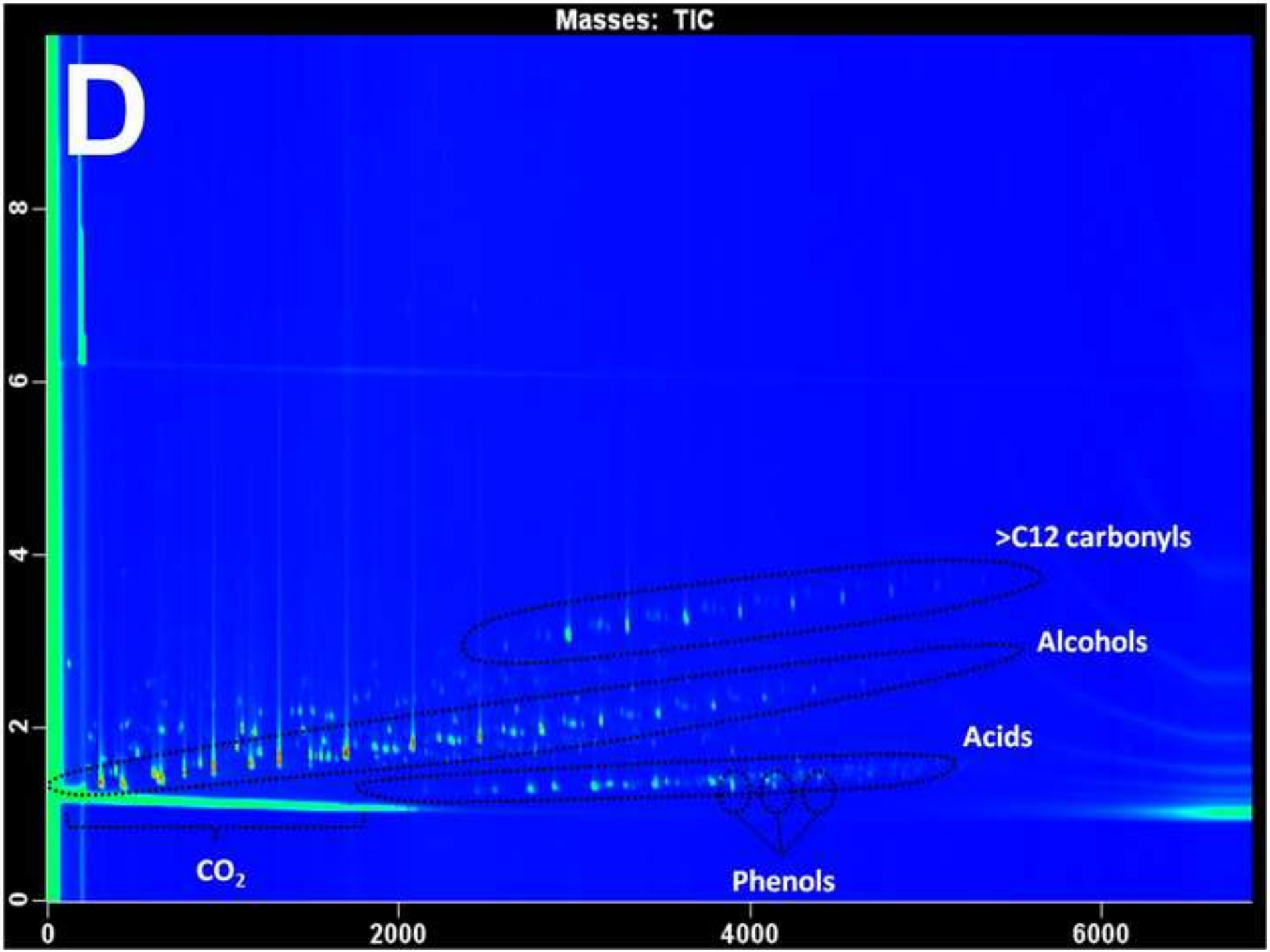
Masses: TIC
D
8
6
4
2
0
0
2000
4000
6000
>C12 carbonyls
Alcohols
Acids
CO_2
Phenols

Figure 5A1

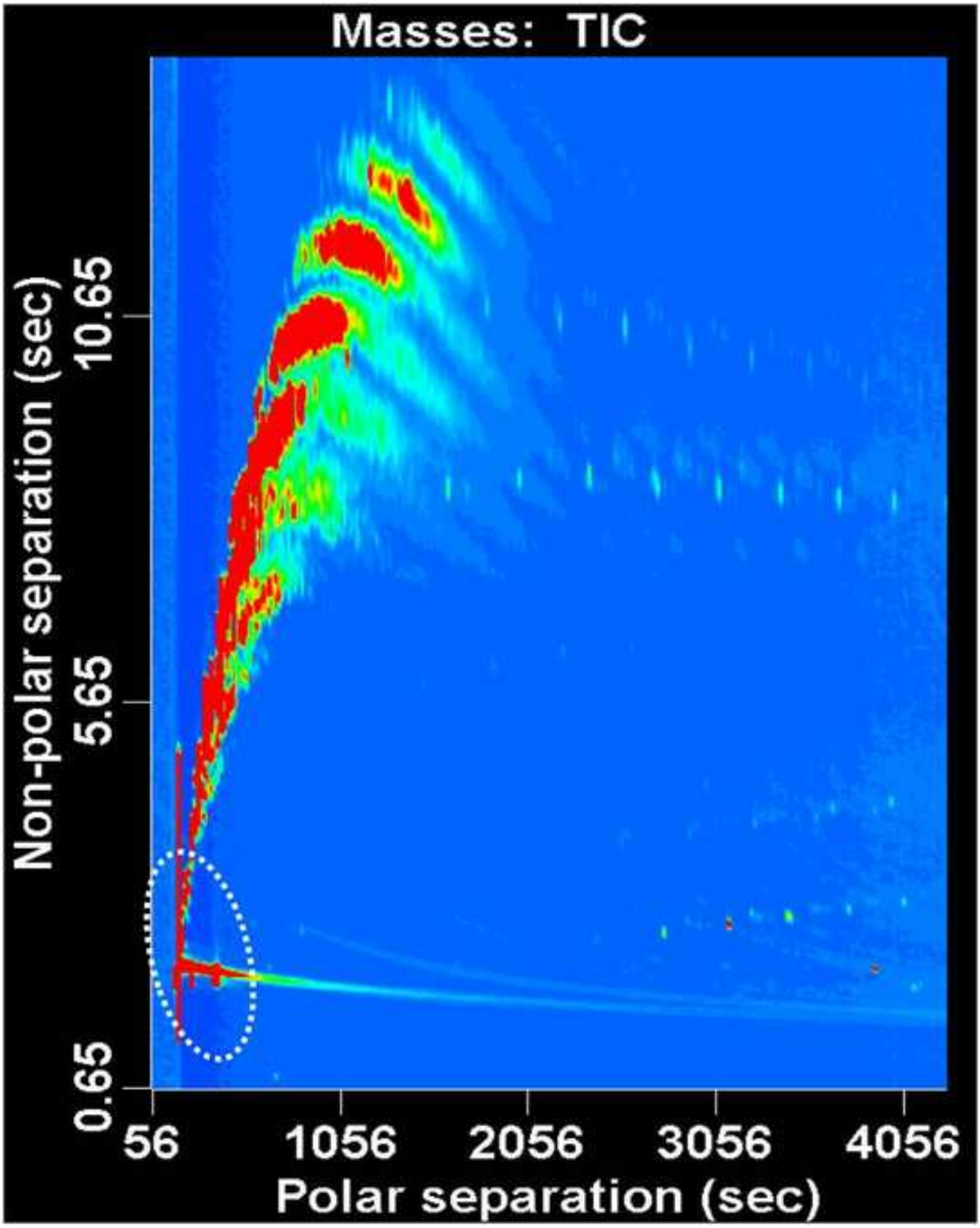
Masses: TIC
Non-polar separation (sec)
10.65
5.65
0.65
56
1056
2056
3056
4056
Polar separation (sec)

Figure 5A2

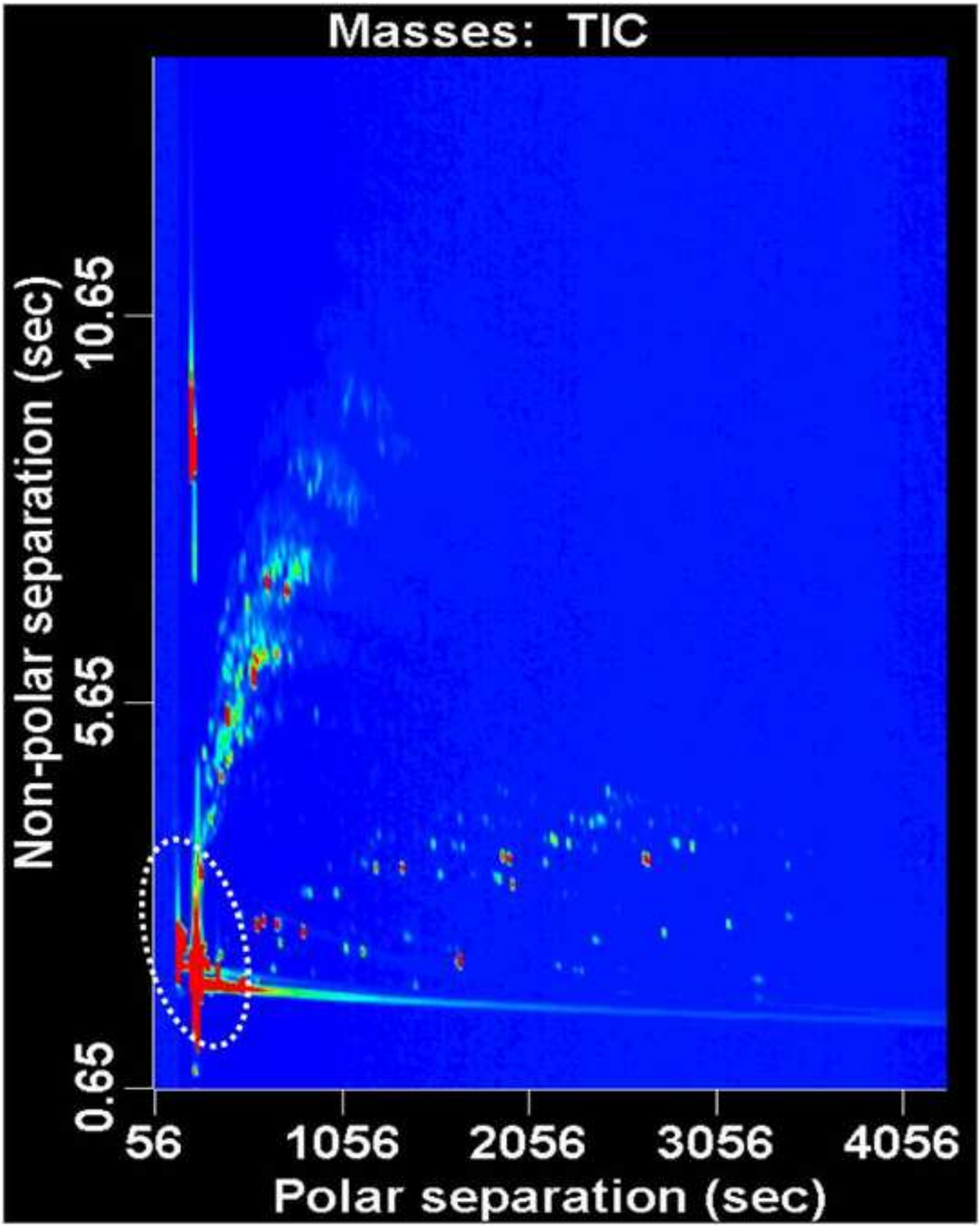
Masses: TIC
Non-polar separation (sec)
10.65
5.65
0.65
56
1056
2056
3056
4056
Polar separation (sec)

Figure 5B1

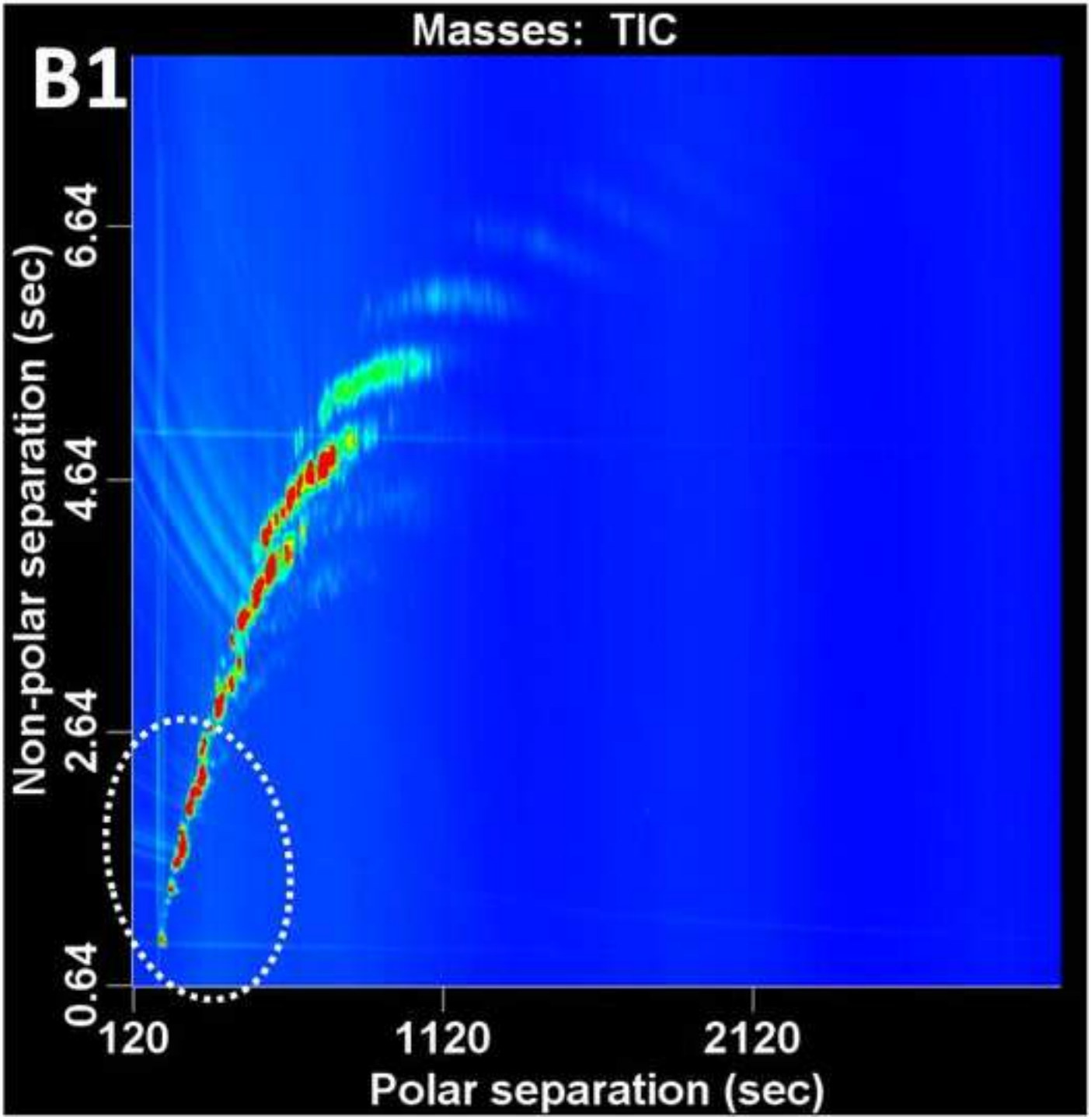
Masses: TIC
B1
Non-polar separation (sec)
6.64
4.64
2.64
0.64
120
1120
2120
Polar separation (sec)

Figure 5B2

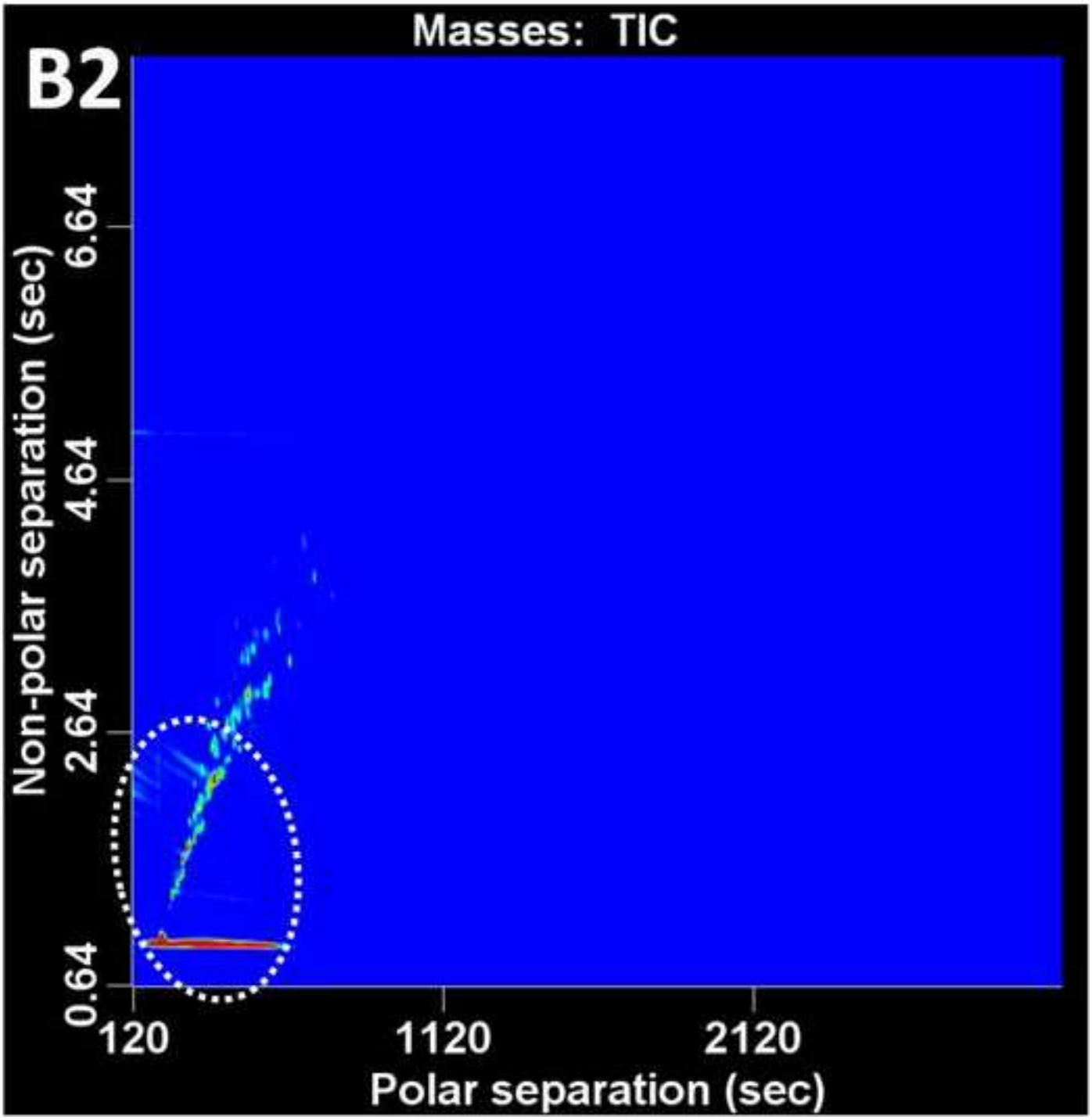
Masses: TIC
B2
Non-polar separation (sec)
6.64
4.64
2.64
0.64
120
1120
2120
Polar separation (sec)

Figure 6

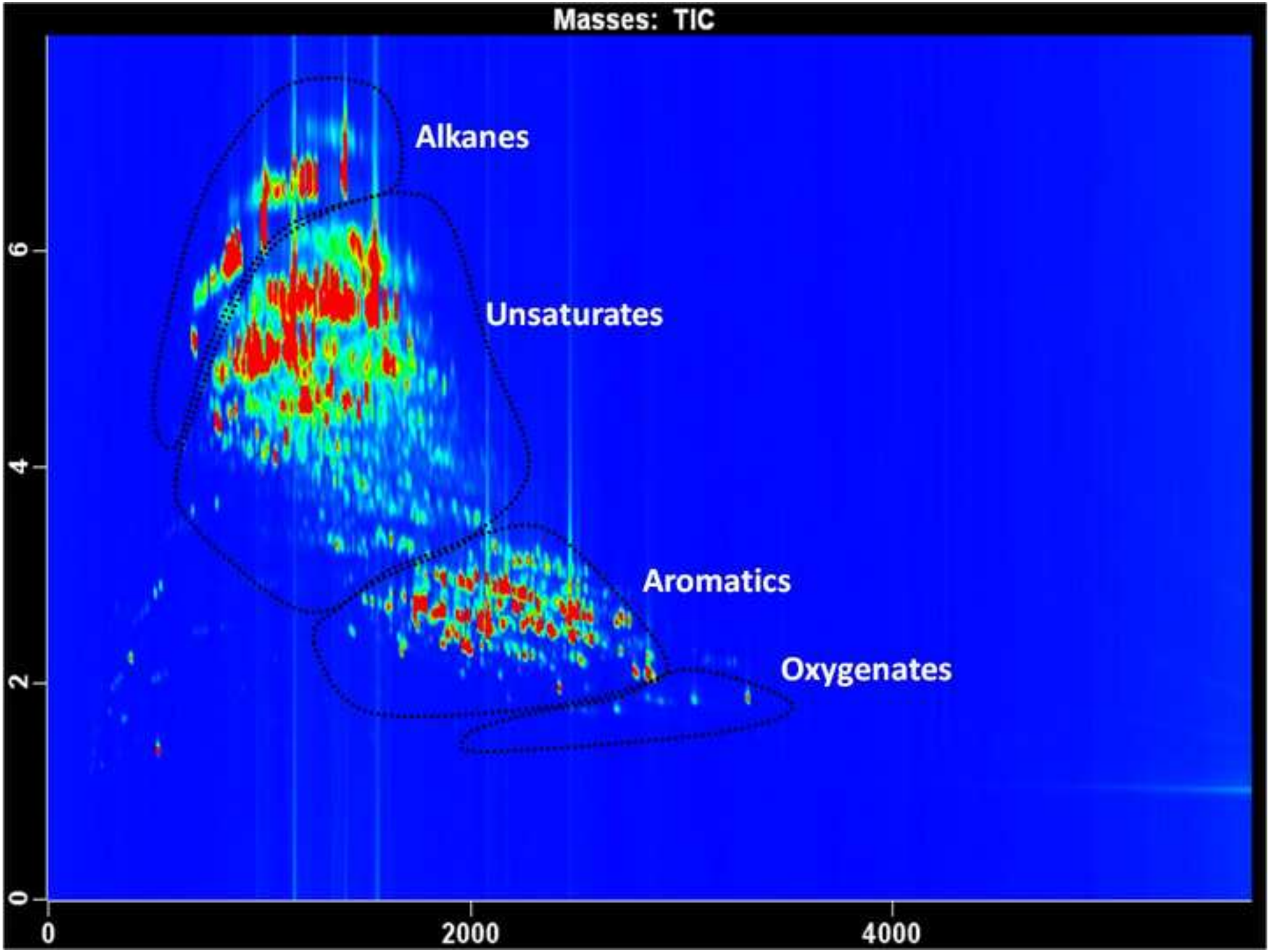
Masses: TIC
Alkanes
Unsaturates
Aromatics
Oxygenates
0
2
4
6
0
2000
4000

Figure 7a

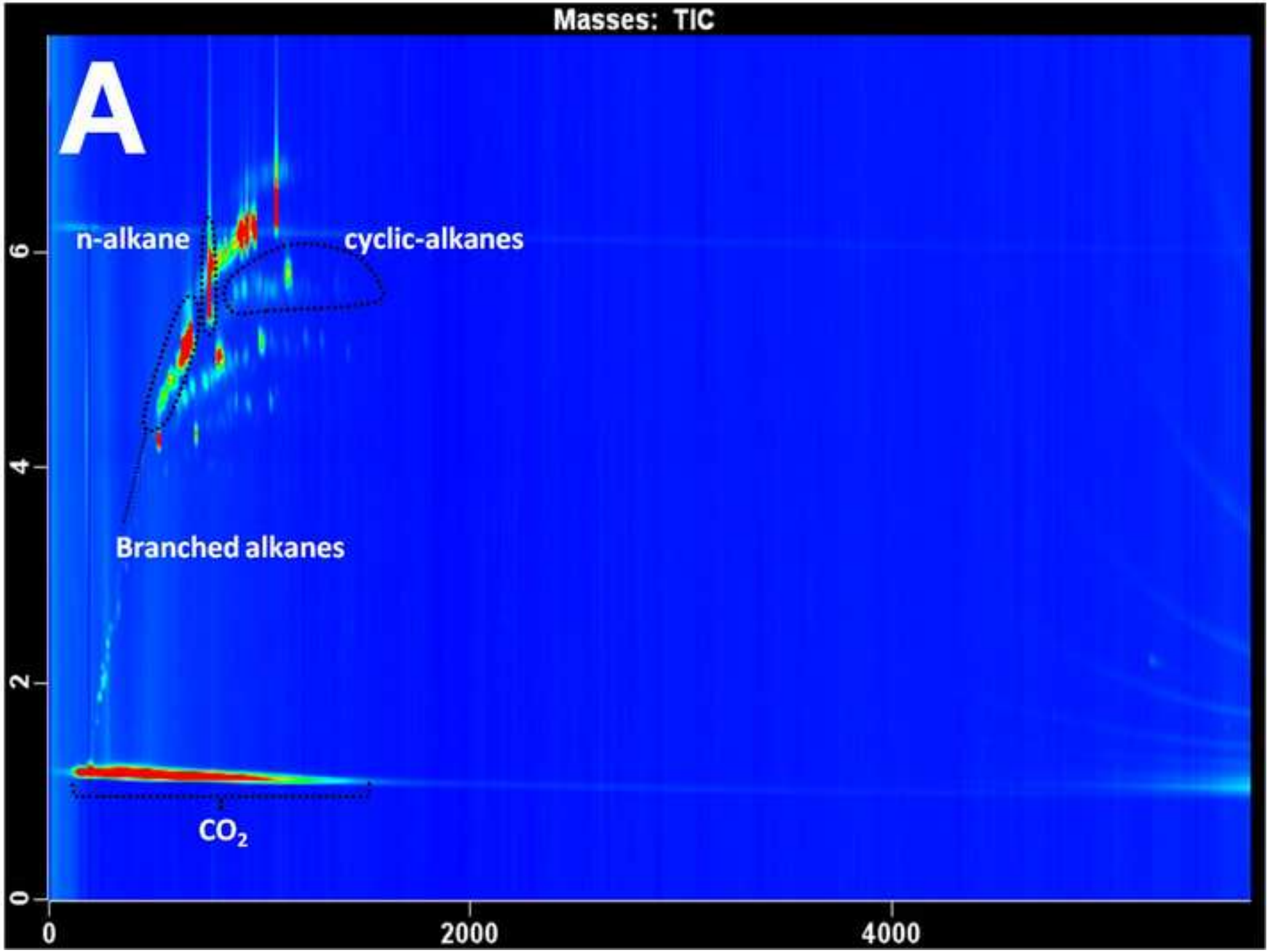
Masses: TIC
A
n-alkane
cyclic-alkanes
Branched alkanes
CO_2
0
2
4
6
0
2000
4000

Figure 7b

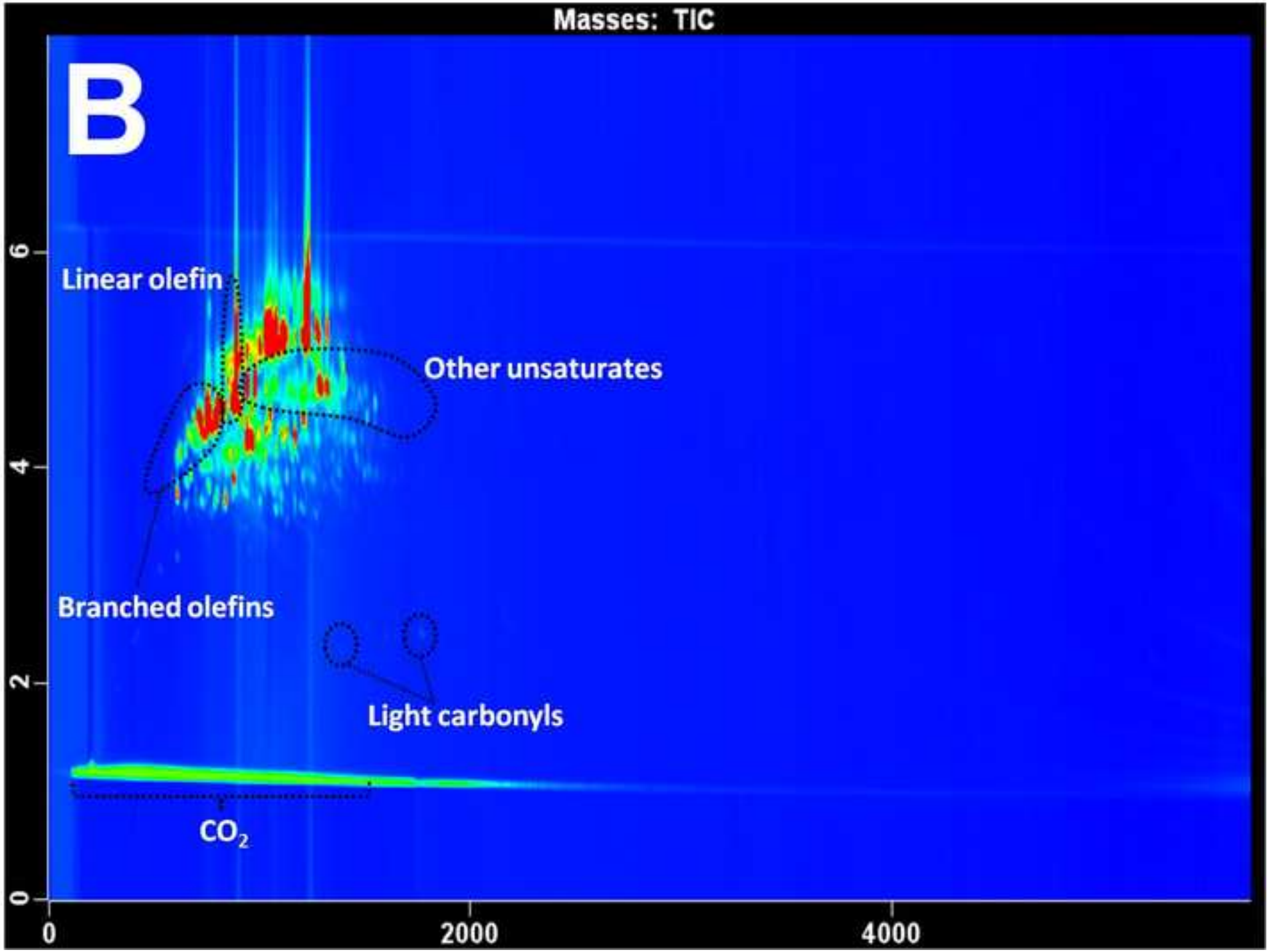
Masses: TIC
B
Linear olefin
Other unsaturates
Branched olefins
Light carbonyls
CO_2
6
4
2
0
0
2000
4000

Figure 7c

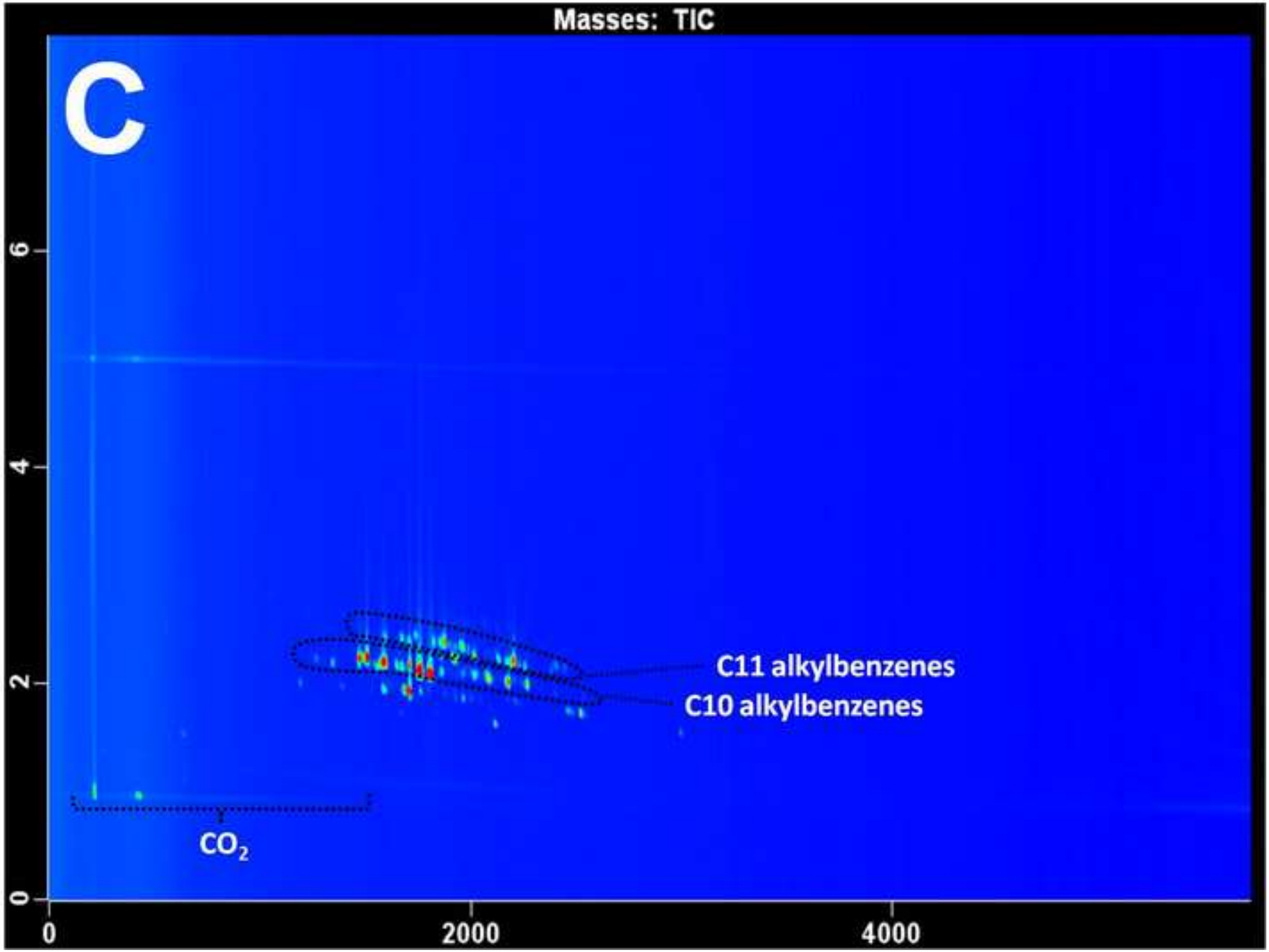
Masses: TIC
C
6
4
2
0
0
2000
4000
C11 alkylbenzenes
C10 alkylbenzenes
CO_2

Figure 7d