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Advances in Crystallization Elution Fractionation

B. Monrabal,* L. Romero, N. Mayo, J. Sancho-Tello

Summary: Crystallization Elution Fractionation has been optimized to improve resolution power and reduce co-crystallization. Most important step to be optimized is the first separation cycle of Dynamic Crystallization which can be investigated with the help of Crystallization Analysis Fractionation experiments. A new approach to reduce co-crystallization and improve resolution is presented by applying successive cooling and heating cycles in a long column. The new process known as Multiple Crystallization Elution Fractionation adds extended separation at each cooling and heating cycles.

Keywords: CCD; CEF; CRYSTAF; crystallization; polyethylene; TREF

Introduction

Crystallization Elution Fractionation (CEF) is a new separation technique for the analysis of the Chemical Composition Distribution (CCD) in semicrystalline polymers. CEF was introduced in 2006 at the First International Conference on Polyolefin Characterization in Houston.[1] The CEF technique is based on a new separation principle referred to as Dynamic Crystallization[2] (patent pending) that separates fractions inside a column by crystallizability meanwhile a small flow of solvent is passing through the column; the separation in Dynamic Crystallization (DC) occurs during the cooling step and therefore results are comparable to Crystallization Analysis Fractionation[3] (CRYSTAF). CEF combines the separation power of DC in the crystallization step with the separation during dissolution of the Temperature Rising Elution Fractionation[4] (TREF) technique. CEF has been shown to be superior to TREF and capable to provide very fast analysis of the composition distribution of polyolefins for High Throughput applications.[2]

In this paper, the optimization of the Dynamic Crystallization process is investigated. Preliminary CRYSTAF results have proved to be very helpful to establish the most appropriate crystallization temperature range and crystallization flow to be used in following DC and CEF runs. The optimization obtained in DC will apply automatically to improve the CEF analysis.

A new process of running CEF with multiple crystallization-dissolution cycles in a long column is being presented. The new approach, which we will refer to as Multiple Crystallization Elution Fractionation, m-CEF, resembles the Zone Melting process for purification of crystalline solids.

Techniques Description

Temperature Rising Elution Fractionation

Temperature Rising Elution Fractionation (TREF) has been the most popular approach for the analysis of the CCD in polyolefins.[4] TREF analysis resembles a liquid chromatography separation where the sample is first dissolved in a proper solvent at high temperature and the solution is then introduced into a column containing an inert support; this is followed by a crystallization step at a slow cooling rate with no flow, during which polymer fractionation occurs by formation of crystal

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Polymer Characterization, c/ Gustave Eiffel 8, Valencia Technology Park, E-46980 Paterna, Spain
E-mail: benjamin.monrabal@polymerchar.com

aggregates of decreasing crystallinity as temperature goes down; fractionation takes place within this cycle without physical separation of the components; all the crystal aggregates, from different crystallinity or branch content being formed in the crystallization are still mixed together and are being deposited *in situ* on the same spot of the column where the initial polymer solution has been loaded.

TREF technique requires of a following temperature cycle to dissolve and physically separate those fractions or crystal aggregates. This is achieved by pumping new solvent while the temperature is being increased. The eluant dissolves fractions of increasing crystallinity as temperature rises. These fractions are monitored with an infrared detector to generate the CCD curve. The name Temperature Rising Elution Fractionation derives from this second temperature cycle.

In Figure 1a the TREF analysis of a blend of three components with different crystallizability is represented schematically in three steps: 1. Sample loading into the column, 2. Crystallization cycle where the components are being crystallized within the same spot where sample was loaded, and 3. Elution cycle where a solvent flow, F_e, is passed through the column to elute the fractions being dissolved as temperature rises. The three components of the blend are physically separated from each other in the last cycle as shown in Figure 1a.

A general practice in TREF is to load the column with a significant volume of the sample solution and this finite volume may have implications in the final resolution. To rationalize the interaction of sample volume, elution flow and heating rate in the TREF experiments, it is appropriate to define a new parameter which we will refer as Geometric Dispersion, GD, given by equation (1):

$$GD = \frac{H_r}{F_e} \times V_s \qquad (1)$$

where H_r is the heating rate, F_e is the elution flow and V_s is the volume of the sample solution after loading into the column.

GD gives a measurement, in temperature units, of the contribution of the dispersed sample volume towards loss in final resolution; the lower the value of GD the less impact of the sample dissolution

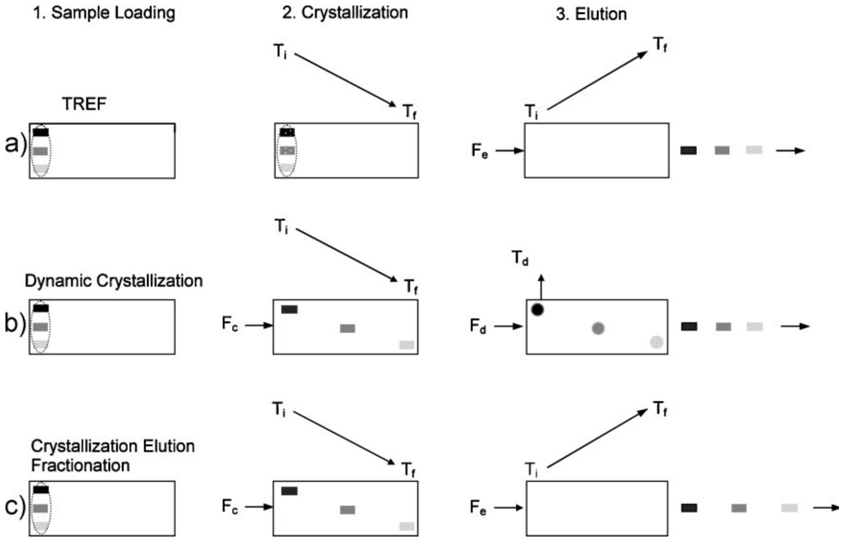


Figure 1.
Separation diagram by crystallizability. a) TREF separation process, b) Dynamic Crystallization, c) Crystallization Elution Fractionation.

volume. In the practice, for a constant V_s, one should increase elution flow rate (or reduce H_r) until eluted peaks do not narrow anymore; typically values of GD lower than 1°C will make contribution of the dispersed sample volume insignificant versus the intrinsic resolution of the technique.

Dynamic Crystallization

Dynamic Crystallization separates on similar principles and uses same hardware as TREF but the physical segregation of fractions occurs during the crystallization step. This new separation process is known as Dynamic Crystallization because a small flow of solvent is passed through the column during crystallization.[2] DC can be described, as well, through a three steps procedure as represented in Figure 1b but physical separation of the components takes place within the column itself in the Crystallization cycle. In Dynamic Crystallization a small flow of solvent, F_c, is passed through the column during cooling, in such a way that when a component reaches its crystallization temperature it is segregated from the moving solution and it is anchored on the support while the other components, remaining in solution, will move along the column until they will reach their own crystallization temperature. At the end of the crystallization cycle the three components are separated inside the column according to crystallizability as shown in Figure 1b.

Once completed the cooling cycle, the flow is interrupted and the column is heated for a few minutes at a temperature, T_d, where all components are dissolved, and after that, the elution cycle begins by adding a proper solvent flow, F_d, to dissolve and elute the components out of the column. The separation order of the components will be similar to CRYSTAF rather than TREF as separation occurs in the crystallization and not in the dissolution process and analytical conditions are far from thermodynamic equilibrium.

To maximize resolution power in DC it is very important: 1) to optimize the crystallization flow, F_c, and 2) select the right temperature cooling range. The Flow rate in the crystallization process, F_c, ensures that all components will crystallize within the column length and it is properly calculated by equation (2):

$$F_c = \frac{V_c}{\Delta T_c} \times C_r \qquad (2)$$

where V_c is the column volume, C_r is the crystallization rate and ΔT_c is the temperature cooling range.

Proper analysis by DC demands that the actual crystallization temperature range of the polymer components to be separated, ΔT_p, under a given set of conditions is within the experimental cooling temperature range ΔT_c used, and full power of the DC analysis will be obtained when ΔT_p is equivalent to the ΔT_c, resulting in the components crystallizing along the whole length of the column. For a given crystallization rate to be used in DC, the CRYSTAF analysis (performed under the same crystallization rate) should provide an excellent measurement of ΔT_p and therefore facilitating the selection of the right temperature cooling range ΔT_c in the DC analysis.

Crystallization Elution Fractionation

Once developed the Dynamic Crystallization as a new separation process, it was easy to realize the possibility of combining this crystallization step with a final elution cycle, as in TREF, to obtain a new *extended* separation. This is represented in Figure 1c where the Dynamic Crystallization cycle, at a crystallization flow of F_c, is followed by the temperature rising elution cycle, with a flow F_e as in TREF. The new process is known as Crystallization Elution Fractionation (CEF) because it combines the separation obtained in the crystallization step with the one obtained in the elution cycle; this is schematically represented in Figure 1c by the extended separation of the three components at the exit of the column in CEF analysis as compared to the TREF approach.

It is quite interesting that the separation power of CRYSTAF (obtained by Dynamic

Crystallization) and TREF are combined in CEF when both systems are based on the same crystallizability principles, and when TREF requires both crystallization and dissolution cycles *per se*.

The superior resolution of CEF over TREF is due to the added DC separation within the column and therefore optimization of DC will maximize CEF separation as well.

Multiple Crystallization Elution Fractionation

Separation techniques based on crystallizability will have a limited resolution power related to the crystallization or dissolution temperature difference of the components to be separated; therefore, to improve resolution with crystallization techniques, most effort will have to be devoted to avoid or diminish co-crystallization.

A new approach to reduce co-crystallization has been considered by using multiple cooling/heating cycles (crystallization/dissolution cycles) in the CEF technique in such a way that every crystallization step begins with an extended separation which should reduce co-crystallization in the following cycle as shown schematically in Figure 2. The analysis by multiple Crystallization Elution Fractionation (m-CEF) will also resemble a distillation tower with multiple plates.

The whole separation will take place within the column length; only the last elution step, E_3 in Figure 2, will elute components out of the column towards the detector. m-CEF will require the use of long columns and will demand the assignment of a certain percentage of the column length/volume for each cycle; for simplicity purposes all the crystallization cycles (DC steps) should be performed at the same cooling rate, should have the same percentage of column length assigned and would be run at the same crystallization flow. The elution cycles could all have the same heating and flow rates; however, we cannot use the ‘‘focusing’’ effect of high elution flow rates to reduce the Geometric Dispersion, as discussed above with equation (1), because there is limited column length/volume to take advantage of it. The only alternative is to apply a high flow rate (lower GD) in the last elution cycle (E_3 in Figure 2) which takes the sample out of the column to focus the dispersed molecules of the same component into a narrow temperature range.

Experimental Part

Dynamic Crystallization, CEF, m-CEF and TREF experiments were performed in an automated CEF apparatus from Polymer ChAR, Spain. The operation of the CEF apparatus in the various modes has been described earlier[2] and the schematic diagram is shown in Figure 3. CRYSTAF experiments were performed in a CRYSTAF 300 equipment from Polymer ChAR. The solvent used was in all cases o-dichlorobenzene

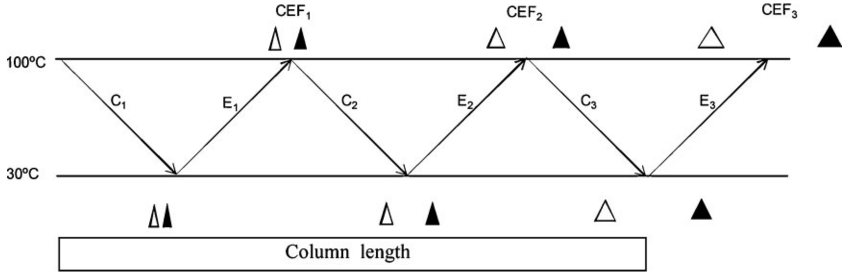


Figure 2.
Multiple Crystallization Elution Fractionation scheme. A x3-CEF experiment where every cooling and heating step provide an extra time separation between components.

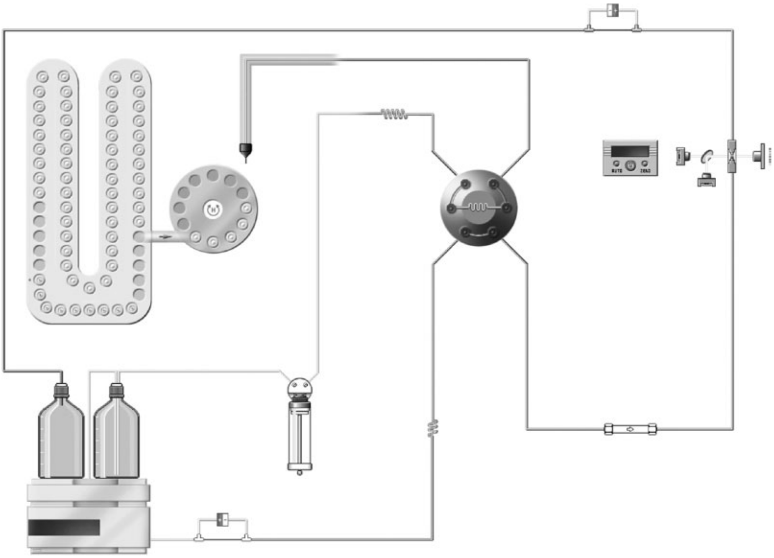


Figure 3.

Schematic diagram of the combined CEF, DC and TREF instrument. Samples taken from the Autosampler with a syringe through a loop are injected into the column head by the pump flow.

with 300 ppm of BHT and columns of 1/4″ o.d. and different length as will be discussed later were all packed with the same surface treated stainless steel shots.

For the optimization of the DC technique and testing of the m-CEF process the samples shown in Table 1 were selected. SSC-1, 2 and 3 are Ethylene-Octene copolymers produced with a single site catalyst and the NBS 1475 is an ethylene homopolymer. They were analyzed individually and in pairs as shown in Table 1. The selection of the pairs was based on the fact that analysis by TREF and CRYSTAF, at standard operating conditions, did show incomplete separation of the pairs and thus it would be easy to investigate the resolution improvement by the new techniques. In this publication only fast crystallization and dissolution cycles were investigated.

Table 1.

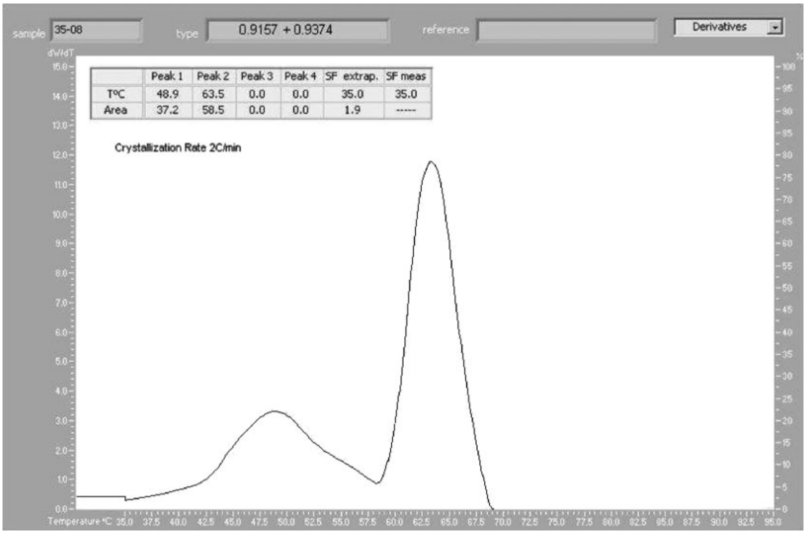
	Resin	Melt Index	Density
Pair 1	SSC – 1	1.03	0.9157
	SSC – 2	2.9	0.9374
Pair 2	SSC – 3	0.55	0.9231
	NBS 1475	2.07	0.9784

Results and Discussion

Dynamic Crystallization

A 50/50 blend of SSC-1 and SSC-2 was analyzed by CRYSTAF at 2 °C/min crystallization rate. The separation of the two components is nearly complete as shown in Figure 4. The temperature crystallization range at this cooling rate is between 70 and 40 °C which should be the basis for optimization of the DC experiment.

DC analysis was performed at the same crystallization rate of 2 °C/min in a column of 1 meter length and 3.7 mm i.d. The empty volume of this packed column was 6.7 mL. The crystallization flow F_c was calculated as per equation (2), and to prevent plugging the column frit or crystallizing outside the column, the crystallization range provided by CRYSTAF was extended from 70–40 °C to 80–40 °C and the column volume used was 6 instead of 6.7 mL, resulting in $F_c = 0.3$ mL/min. Once completed the crystallization, the flow was stopped and the temperature increased up to 120 °C to dissolve the polymer spots inside the column, and after 5 minutes an elution flow $F_e = 0.5$ mL/min was used to elute the two components.



sample 35-08

type 0.9157 + 0.9374

reference

Derivatives

	Peak 1	Peak 2	Peak 3	Peak 4	SF extrap.	SF meas
T°C	48.9	63.5	0.0	0.0	35.0	35.0
Area	37.2	58.5	0.0	0.0	1.9	-----

Crystallization Rate 2C/min

Figure 4.
CRYSTAF analysis of a 50/50 blend of SSC-1 and SSC-2 at 2 °C/min.

The temperature-flow profile of the DC experiment and the results obtained are shown in Figure 5. The separation of the two components in DC is quite comparable to the separation by CRYSTAF when both are run at the same crystallization rate. The small peak eluted as soon as the elution flow started corresponds to the soluble fraction (non crystallizing) which also is present in the CRYSTAF analysis.

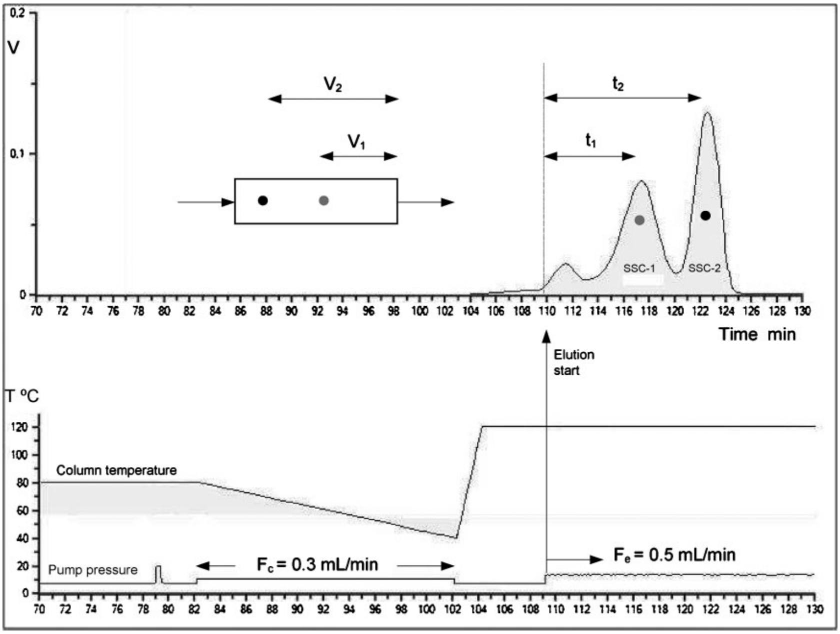


Figure 5.
DC analysis of a 50/50 blend of SSC-1 and SSC-2 at 2 °C/min.

The position (colored spots) where the two components (SSC-1 and SSC-2) crystallized in the column during the Dynamic Crystallization can be easily calculated from the elution times as shown in Figure 5.

CEF versus TREF

The DC experiment in previous section is the basis for optimization of the CEF technique; from the position of the two components in the column during crystallization as shown in Figure 5 we can realize that crystallization temperature range could be reduced down to 80–50 °C to extend the separation of the two components along the column (SSC-1 represented by a gray spot will then be deposited further to the end of the column) and this will demand an F_c of 0.4mL/min when applying equation (2).

The CEF analysis of the same blend was analyzed at the same cooling rate of 2 °C/min and with a heating rate of 2 °C/min. The results are shown in Figure 6 and are compared to TREF results obtained at the same cooling and heating rates (2 °C/min).

The extended separation between peaks in CEF over TREF (8 °C) corresponds to the extra DC separation (present in CEF only), that at a heating rate of 2 °C/min results in 4 min separation time, which at an elution flow of 1 mL/min corresponds to an extended volume separation of 4 mL indicating that DC deposited the fractions (colored spots in Figure 6) well along the column length and 4 mL apart out of the accessible 6.7 mL of the column empty volume.

Resolution in CEF was quite superior to TREF as shown by the baseline between peaks being closer to zero in CEF.

Multiple Crystallization Elution Fractionation

To investigate the separation by multiple Crystallization Elution Fractionation (m-CEF) we had to find out a pair of components that under normal TREF analysis will show a poorer separation than that of Figure 6 and thus, resolution improvement by m-CEF could be easily investigated. The analysis of pair 2 in Table 1 appears to be a good candidate as shown by the TREF results at 0.5 °C/min in Figure 7. In spite of a lower crystallization rate being used, the resolution of the two components is worst than TREF result of pair 1 in Figure 6. The peak eluting at the tail of NBS 1475 should be disregarded in this investigation as it corresponds to a Melt and Recrystallization phenomena appearing in crystalline components when fast crystallization rates are being used.

The m-CEF experiments were done in a longer column 3.1 m ¼″ o.d., 3.7 mm i.d. and a column empty volume of 22.4 mL that was rounded to 20 mL for the purpose of F_c

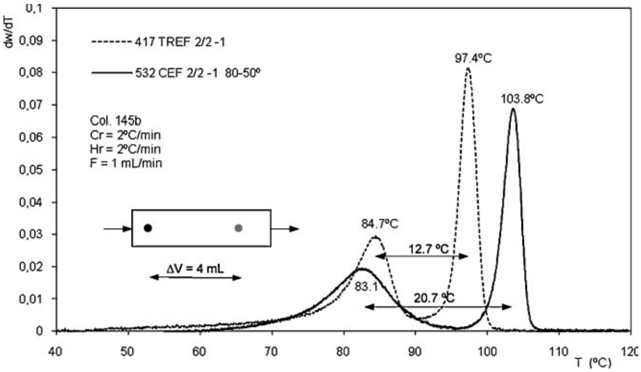


Figure 6.

CEF and TREF analysis of a 50/50 blend of SSC-1 and SSC-2 at 2 °C/min cooling rate. Crystallization flow in CEF was 0.4 mL/min. Elution flow in both CEF and TREF was 1 mL/min.

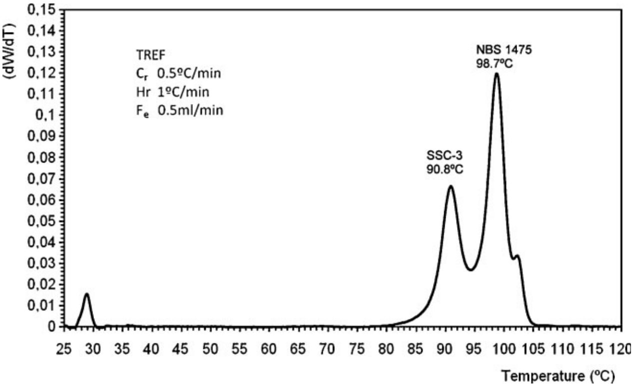


Figure 7.
TREF analysis of a 50/50 blend of SSC-3 and NBS 1475 at 0.5 °C/min crystallization rate.

calculation and to prevent crystallization outside the column.

There is quite a range of possible operating conditions in terms of cooling, heating and flow rates and the way that column volume is assigned per cycle as discussed in the Techniques Description section. All the experiments in this publication were done at a fast cooling rate of 2 °C/min and 5 °C/min heating rate in every cycle with exception of last elution cycle that was heated at 2 °C/min.

The column accessible volume assigned to each cooling or heating cycle was calculated by dividing total volume by the number of cooling and heating steps minus one which corresponds to the last elution step outside of the column. As an example, if we perform a 5 cycles CEF, that we will refer as x5-CEF, there will be nine heating

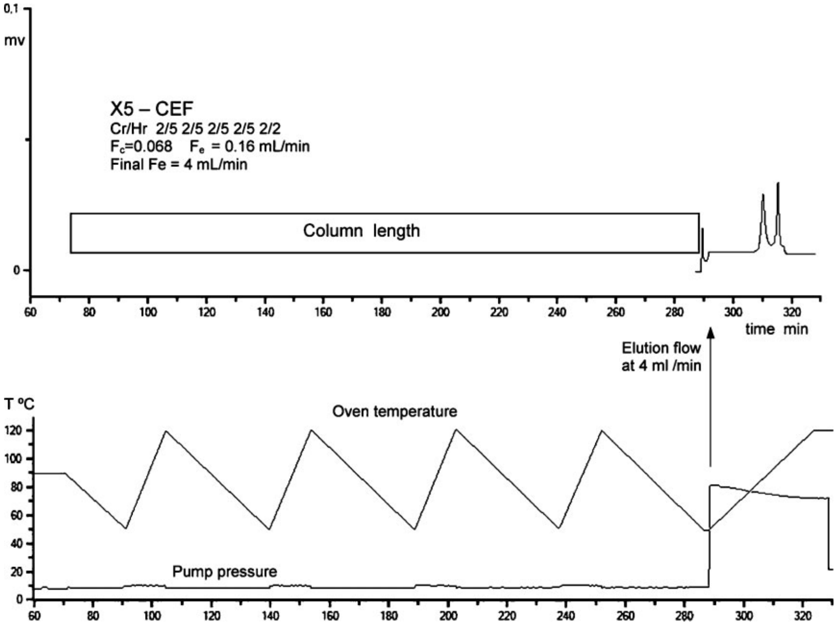


Figure 8.
x5-CEF analysis of a 50/50 blend of SSC-3 and NBS 1475 with following crystallization and heating rates Cr/Hr x4(2/5)/2/2 °C/min and following Crystallization and Elution Flow rates F_c/F_e x4(0.068/0.16)/0.068/4 mL/min.

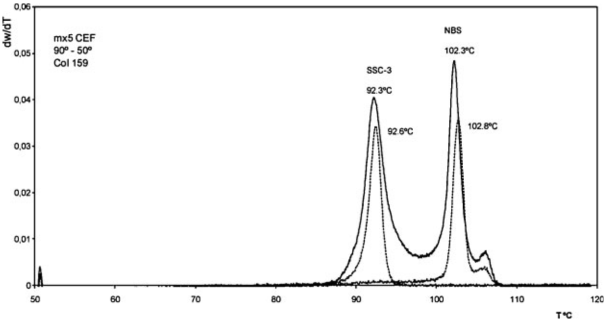


Figure 9.
x5-CEF analysis of a 50/50 blend of SSC-3 and NBS 1475 with following crystallization and heating rates Cr/Hr x4(2/5)/2/2 °C/min and following Crystallization and Elution Flow rates F_c/F_e x4(0.068/0.16)/0.068/4 mL/min.

or cooling steps inside the column with 2.2 mL of accessible column volume each. As we are going to use a temperature range of 120 to 50 °C we can calculate the crystallization flow for the cooling at 2 °C/m, which in this example will be $F_c = 0.068$ mL/min. The elution flow in the heating steps at 5°C/min will result in $F_e = 0.16$ mL/min.

With such small elution flows in the heating cycles we certainly will lose "focusing" in the temperature scale because of the large Geometric Dispersion as per equation (1) but increased flow rates would demand much longer columns and reduced heating rates would increase significantly analysis time. We are going to compensate the sample dispersion/diffusion in the internal cycles by increasing the flow significantly in the last elution step outside the column. Elution Flow rates of 1, 2 and 4 mL/min have been tested and it has been shown that for multiple cycles an elution flow of 4mL/min was the best option. In all the m-CEF experiments presented a $F_e = 4$ mL/min was used in the last elution cycle.

The flow and temperature profile of x5-CEF analysis of the 50/50 blend SSC-3 and NBS 1475 is shown in Figure 8. It is interesting to notice that the most crystalline component (NBS 1475) crystallizes below 90 °C but we need to heat over 100 °C to redissolve it, as we are far from equilibrium conditions. In other words, the crystallization cycles contribute in the DC separation only when reaching 90 °C and below.

The x5-CEF results of the blend and individual components are shown in

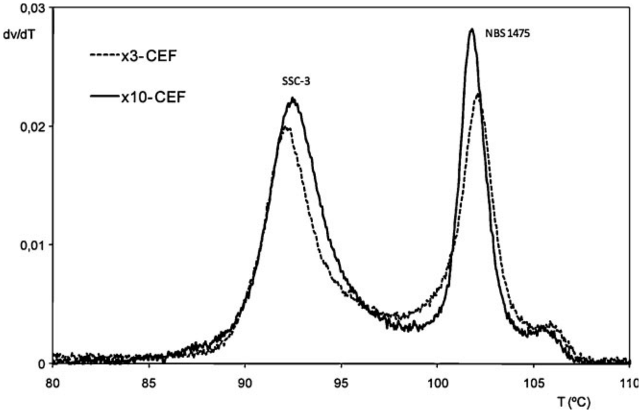


Figure 10.
m-CEF analysis of a 50/50 blend of SSC-3 and NBS 1475 at x3 and x10 cycles.

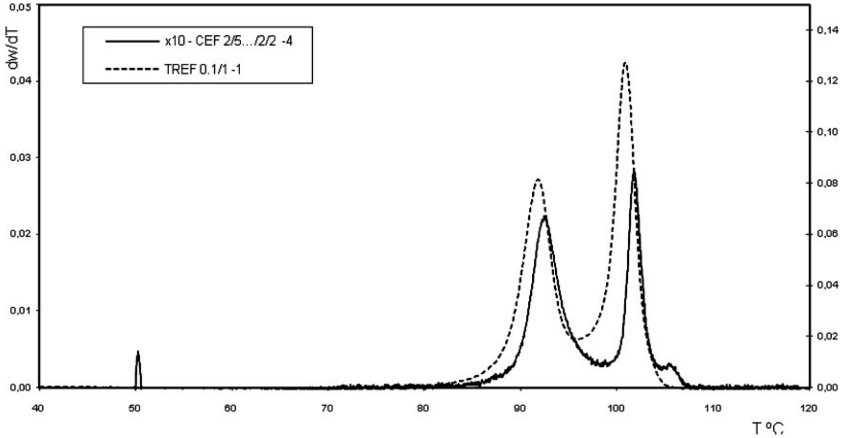


Figure 11.
x10-CEF analysis of a 50/50 blend of SSC-3 and NBS 1475 at Cr-Hr of 2 °C/min–5 °C/min compared to TREF analysis at 0.1 °C/min–1 °C/min.

Figure 9. The separate analysis of SSC-3 and NBS 1475 components shows two peaks not interfering each other. The analysis of the blend shows a resolution significantly better than TREF analysis at 0.5 °C/min of Figure 7, although co-crystallization is still present and no baseline resolution is obtained.

A comparison of the resolution achieved in the separation of SSC-3 and NBS 1475 by using different number of cycles in m-CEF is shown in Figure 10. Small improvement in resolution (baseline between peaks closer to zero) is shown when increasing the number of cycles.

In Figure 11 the x10-CEF analysis of the blend is compared with a high resolution TREF analysis obtained at a low crystallization rate of 0.1 °C/min. The obtained resolution by x10-CEF is superior to TREF in spite of having performed the analysis at fast crystallization (2 °C/min) and heating rates (5 °C/min) cycles.

Conclusion

Dynamic Crystallization analysis can be optimized by knowing the crystallization range of the samples to be analyzed at a given cooling rate and adapt the initial and final temperature of the experiment accordingly.

CRYSTAF results obtained at the same cooling rate provide a direct measurement of the optimum crystallization range to be used in DC. CRYSTAF and DC results are equivalent in resolution when using the same cooling rates.

The extended separation power of CEF over TREF comes from the extra separation in the DC step; therefore, optimizing DC separation has a significant impact on the CEF optimization.

A new approach to reduce co-crystallization by using multiple crystallization-elution cycles, m-CEF, has been presented. It has been shown that increasing the number of cycles improves the resolution of the technique and minimizes co-crystallization. There is a significant amount of work to be done to better understand these techniques, investigate the influence of the many parameters involved and to further optimizing them.

There is also a possibility to perform Multiple DC inside the column by stopping the flow in each heating cycle (separation being achieved only in the crystallization steps) or performing Multiple TREF inside a column by stopping the flow in each cooling cycle (separation being achieved only in the dissolution steps); only the last elution outside the column will bring out the separation in both cases. Although interesting to investigate, Multiple DC or Multiple TREF should be less efficient than m-CEF where we obtain further separation at both cooling and heating cycles.

Most of the work being done so far has been using fast cooling and heating rates as the CEF technique was initially designed for high throughput analysis[2]; future work will focus on achieving maximum resolution by using slower crystallization and heating rates.

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