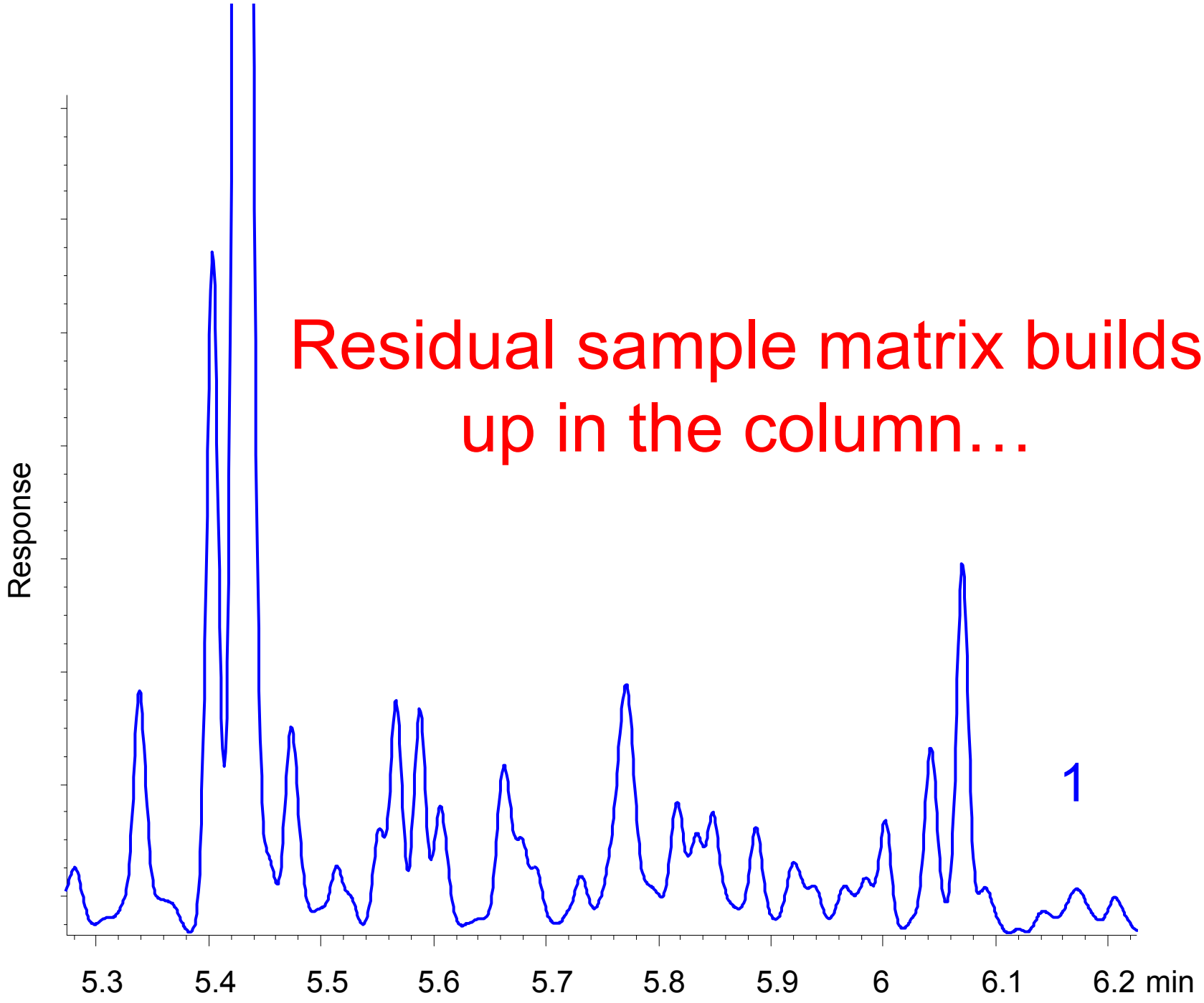
Considerations for Implementation and Optimization of Capillary Column Backflush

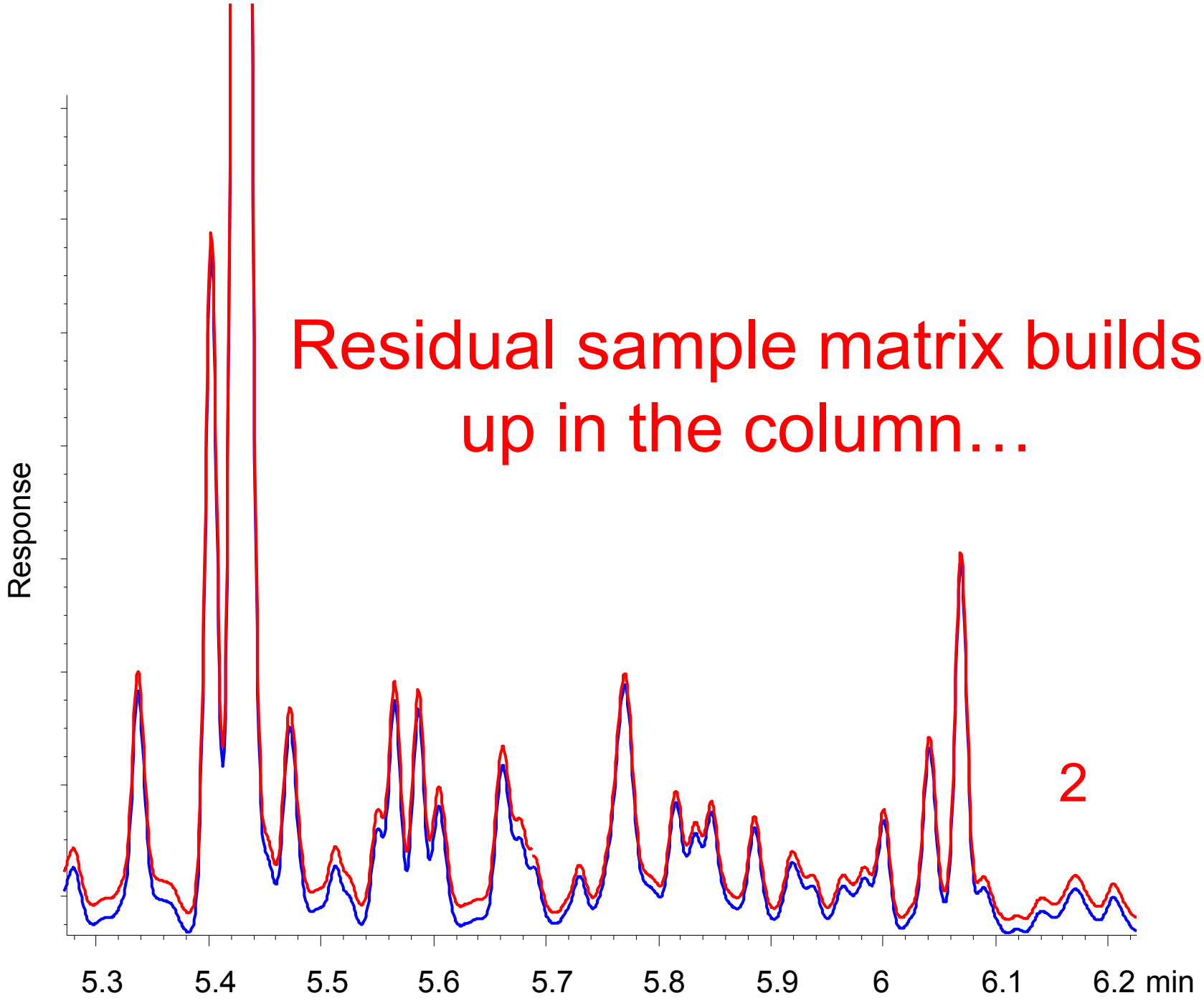
Matthew S. Klee
Agilent Technologies, Inc., Wilmington, DE 19808, USA

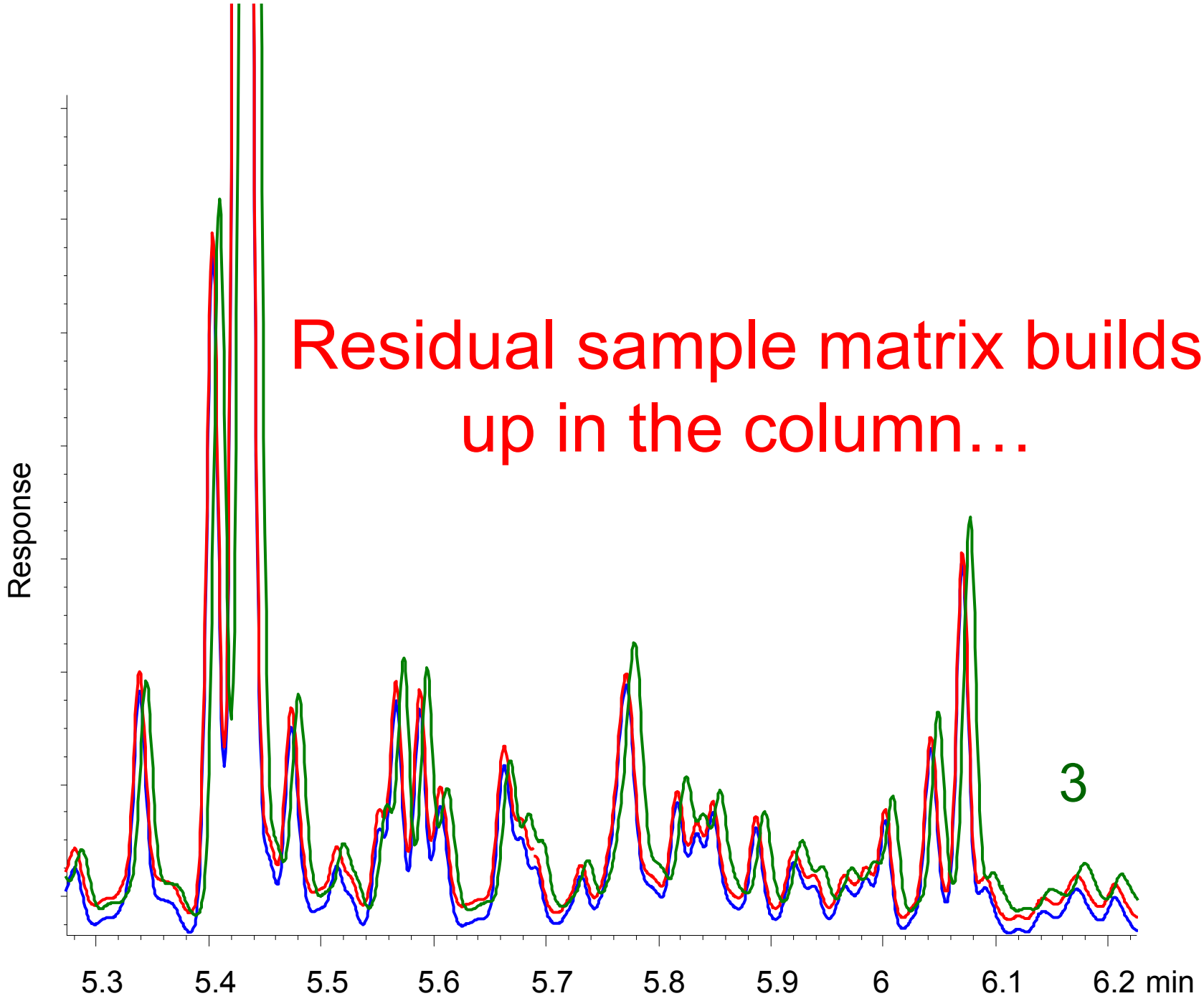
Why Should You Implement Capillary Column Backflushing?

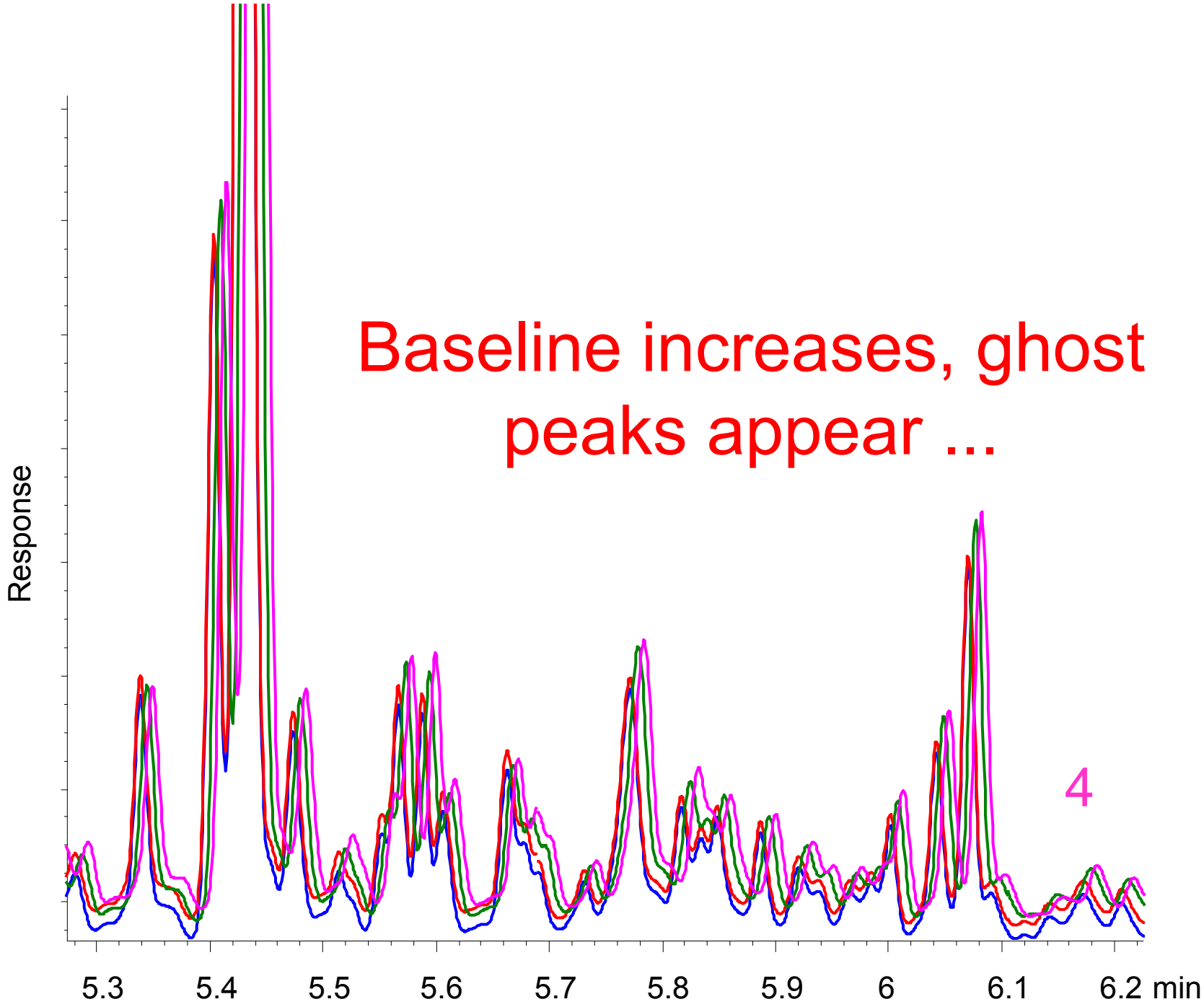
- More samples/day/instrument
- It is “green”; less gases + less power per sample
- Lower costs per sample
- Less frequent and faster GC & MSD maintenance
- Longer column life
- Better data quality
  - less chemical background (better detection limits)
  - cleaner mass spectra (better ion ratios)
  - better peak integration (less intervention)
- More rugged multidimensional methods
  - more stable peak retention times
  - less background

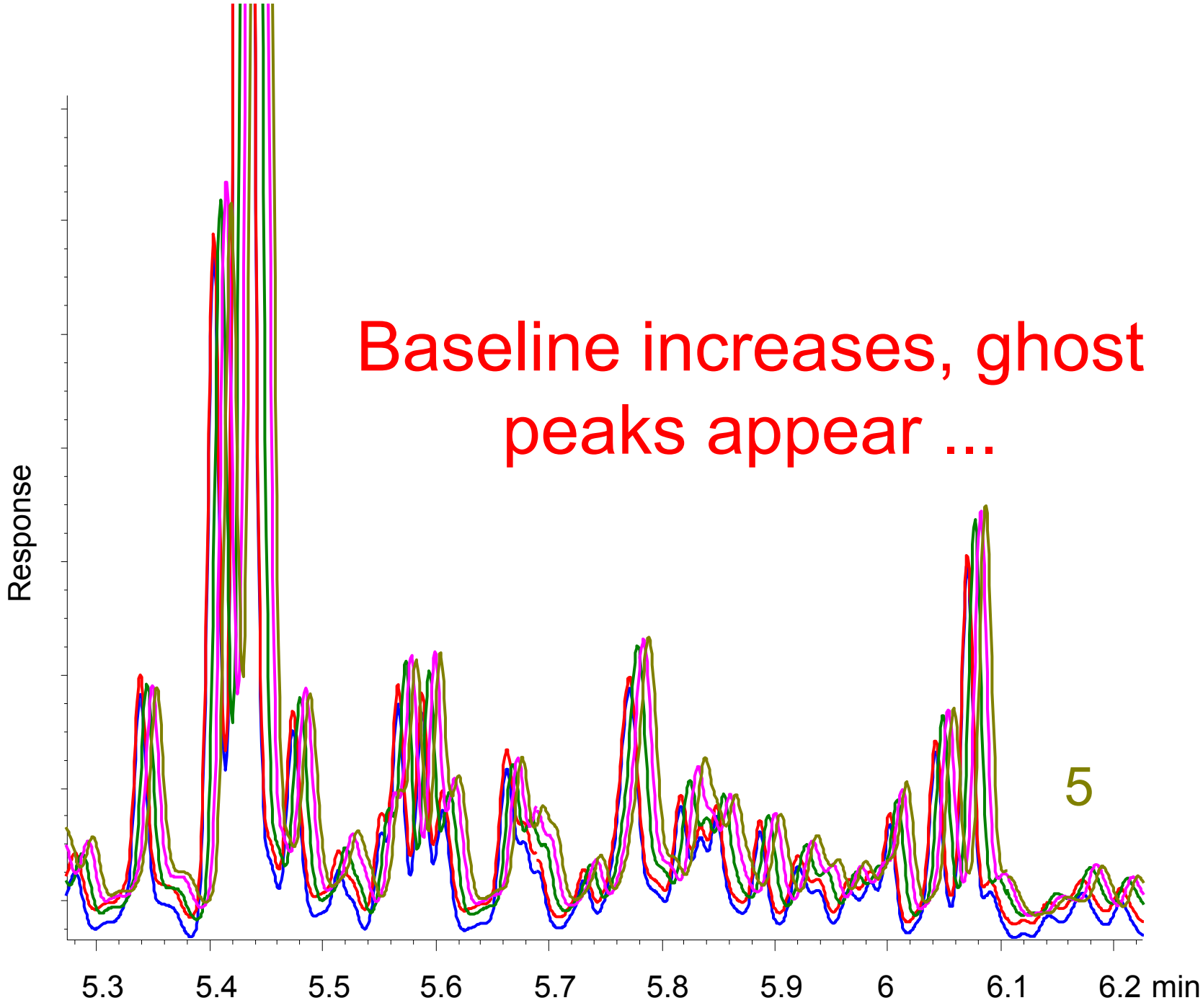
10 Runs With Backflush

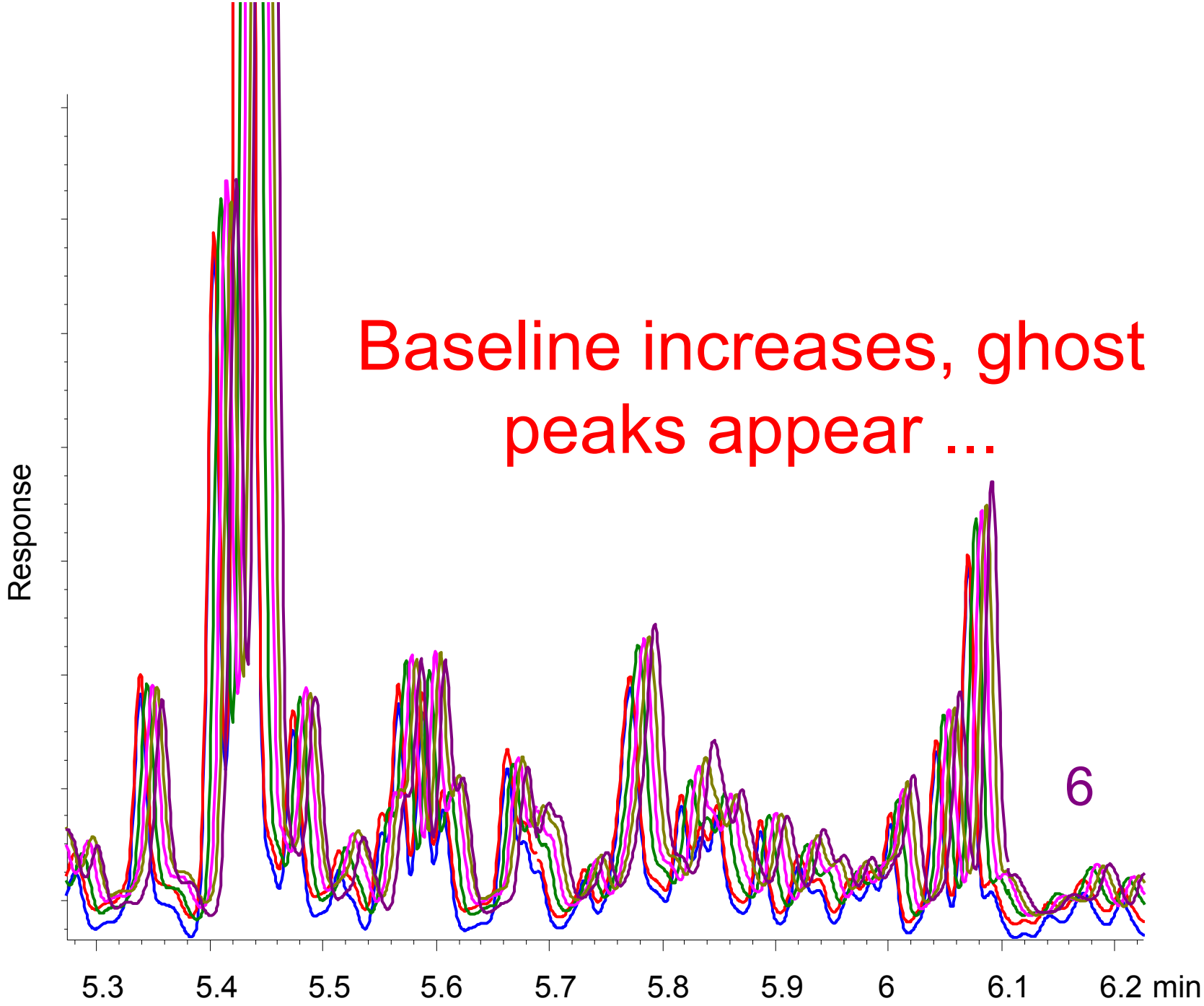

Residual sample matrix builds up in the column…
Response
1
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min

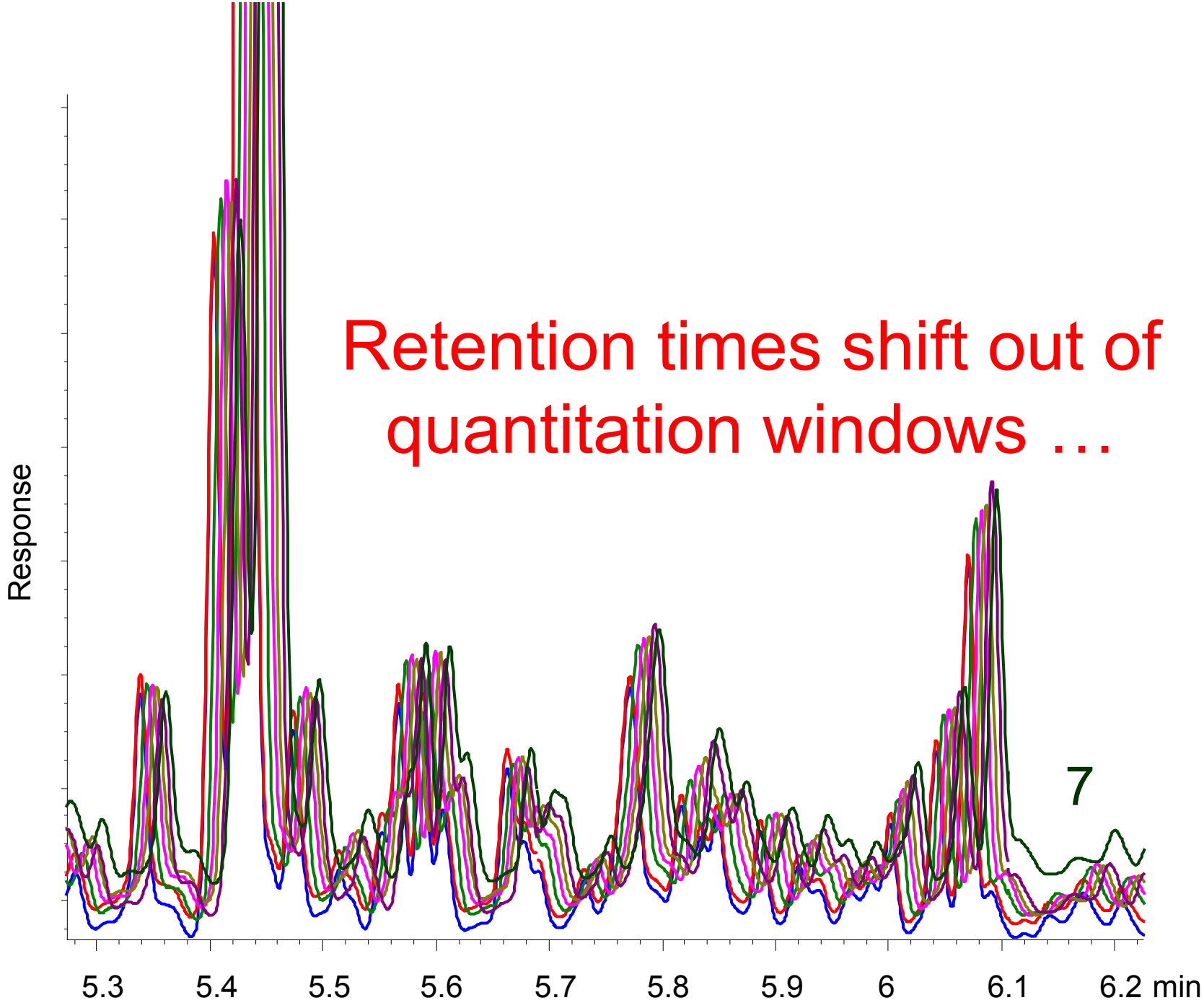

Residual sample matrix builds up in the column…
Response
2
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min

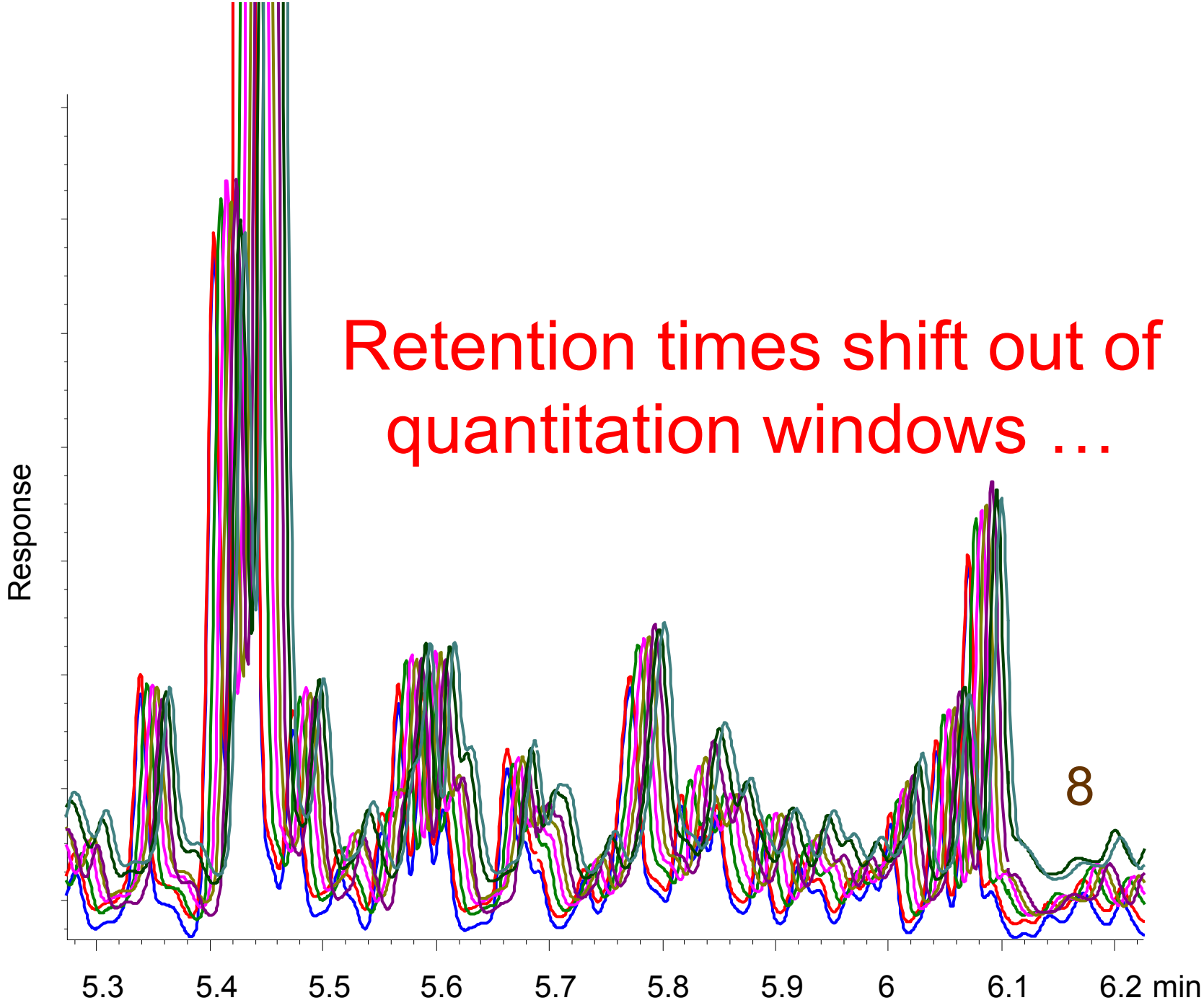

Residual sample matrix builds up in the column…
Response
3
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min

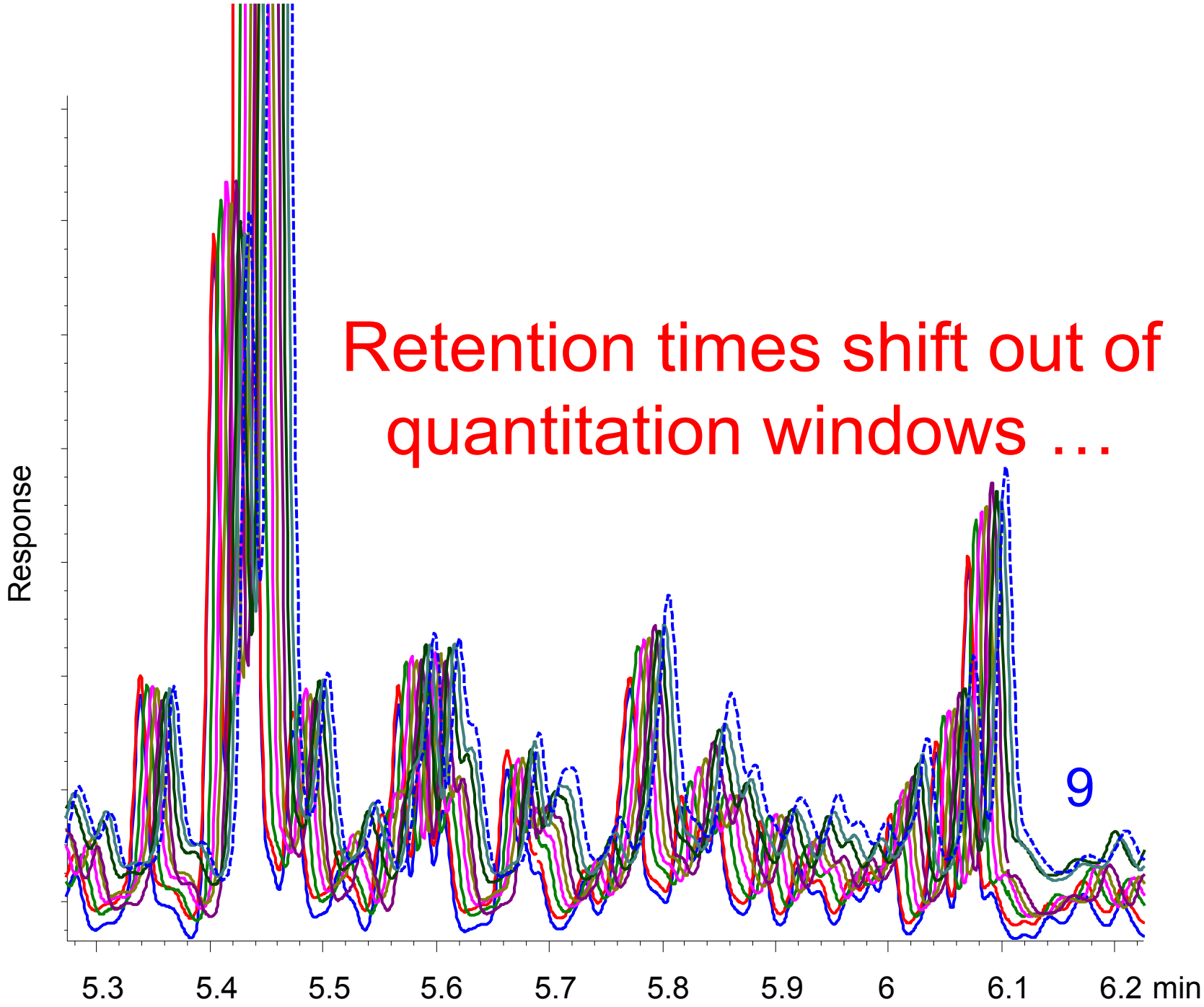

Baseline increases, ghost peaks appear ...
Response
4
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min

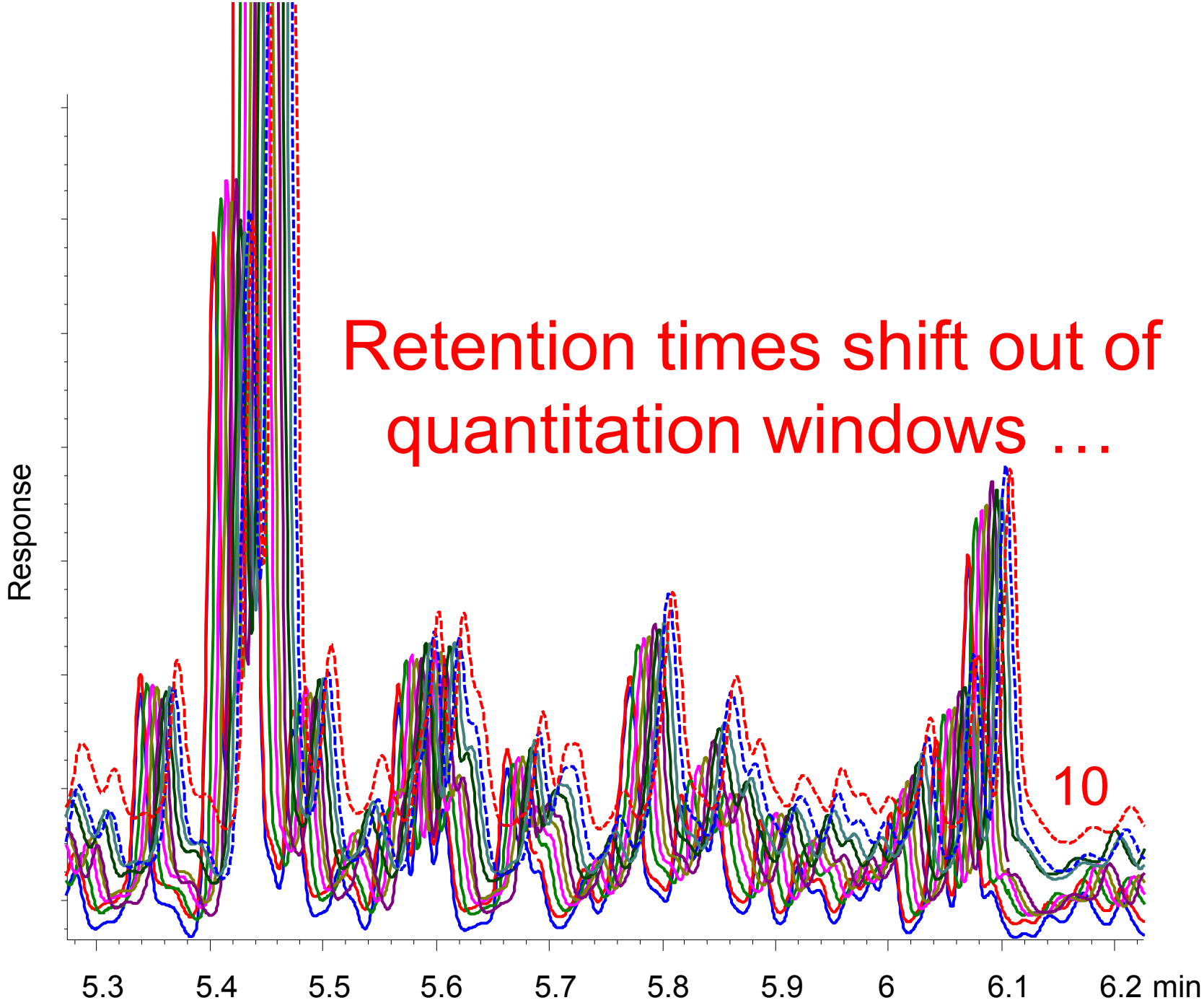

Baseline increases, ghost peaks appear ...
Response
5
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Baseline increases, ghost peaks appear ...
Response
6
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Retention times shift out of quantitation windows …
Response
7
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Retention times shift out of quantitation windows …
Response
8
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Retention times shift out of quantitation windows …
Response
9
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Retention times shift out of quantitation windows …
Response
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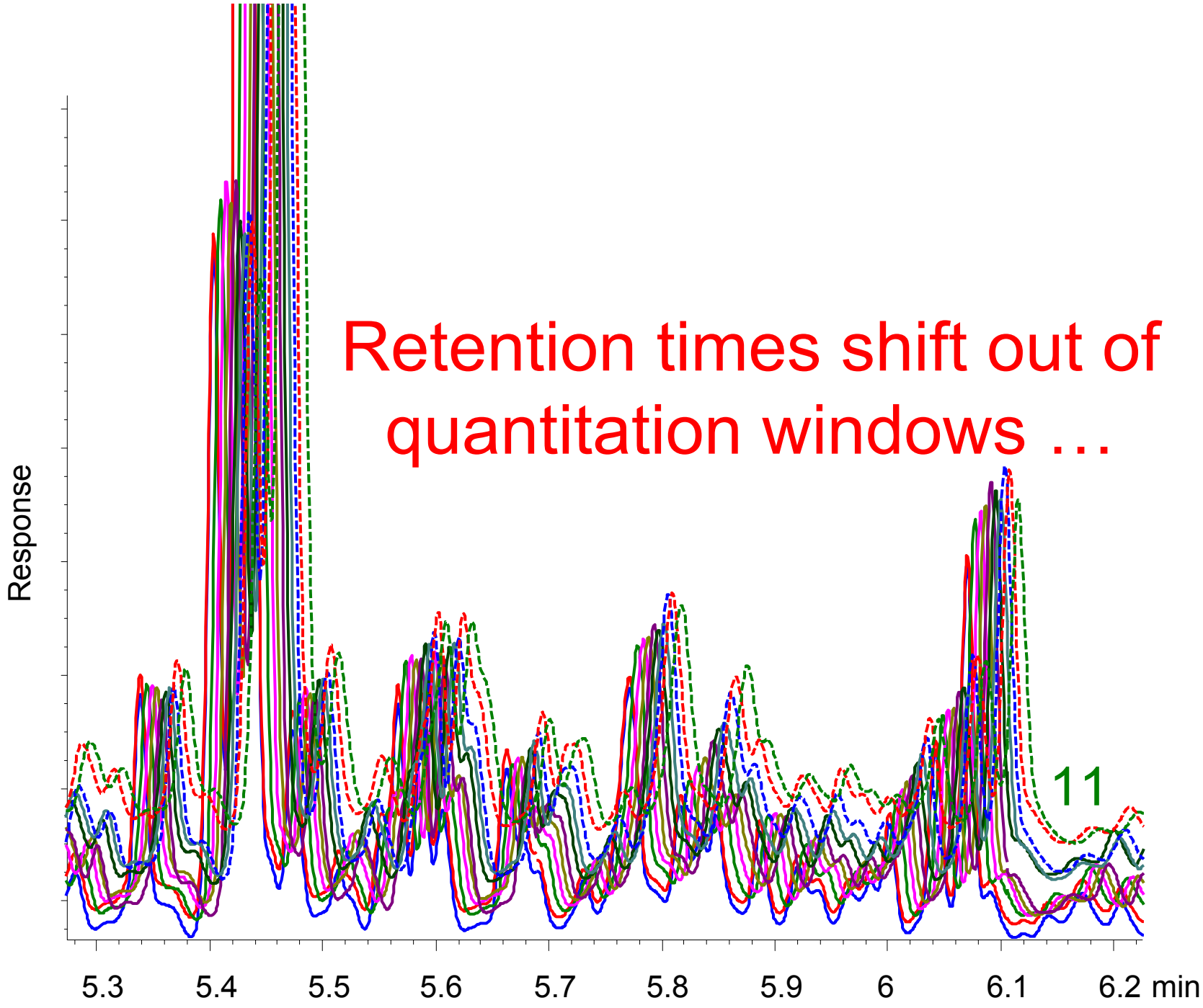
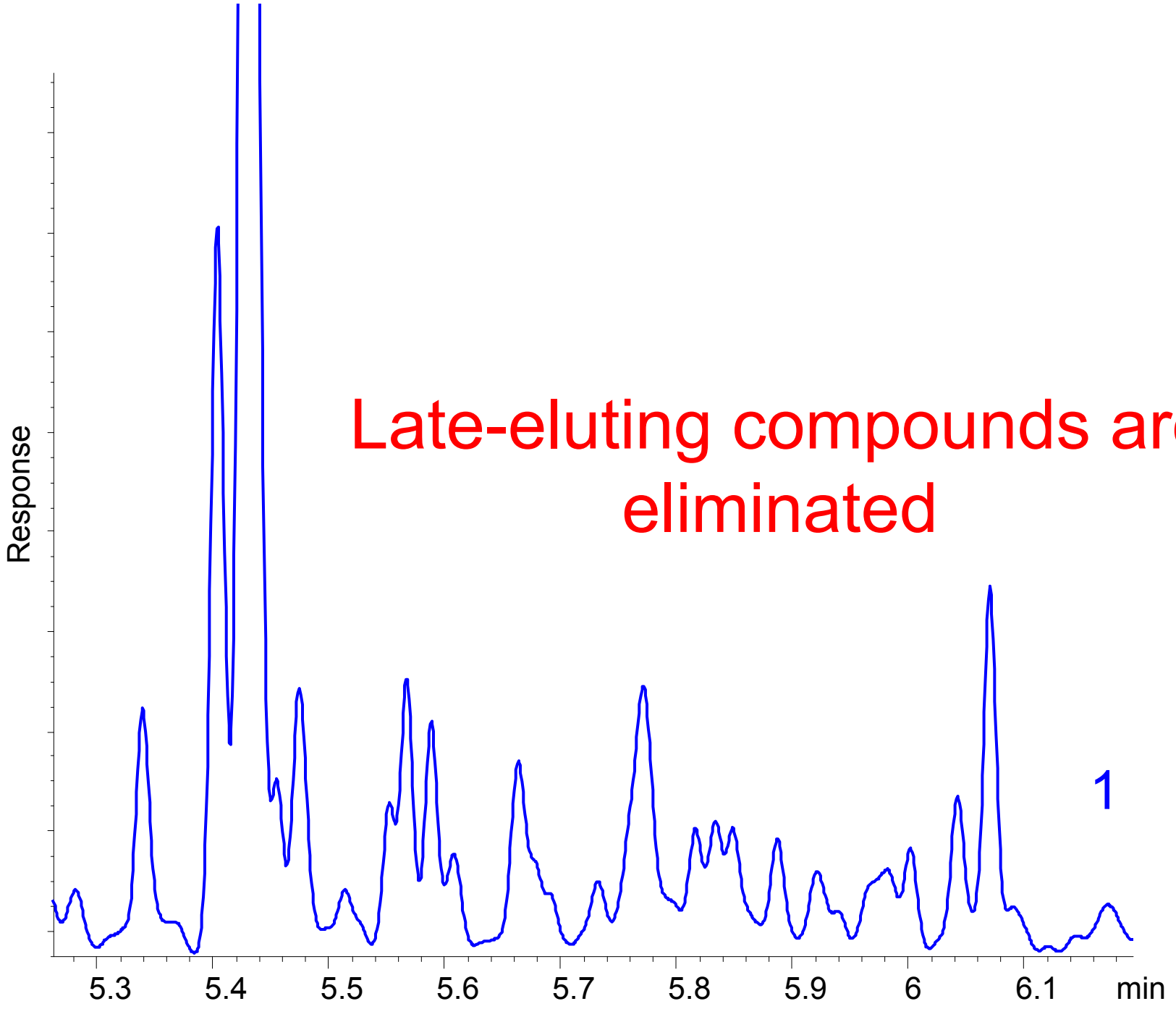
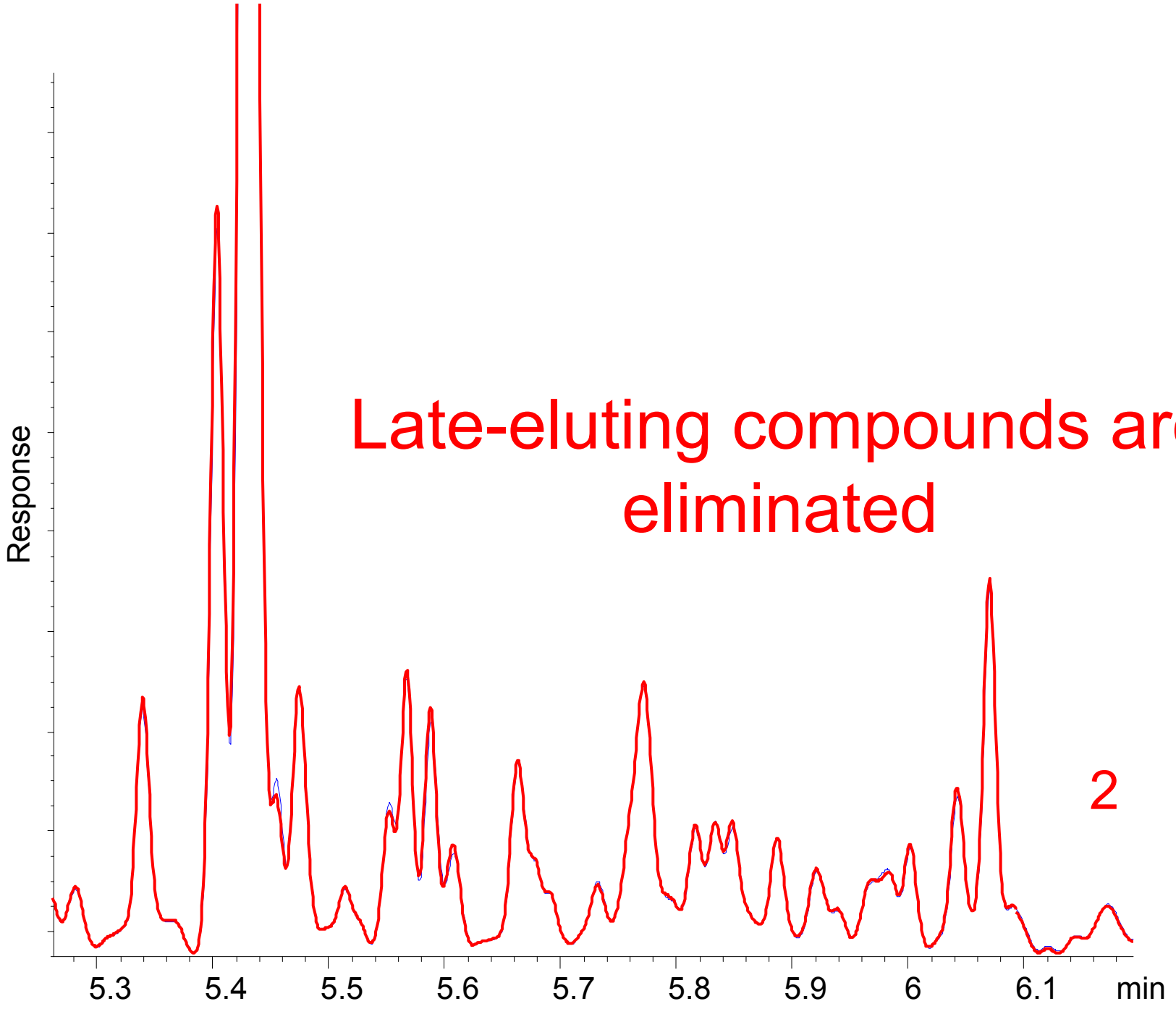
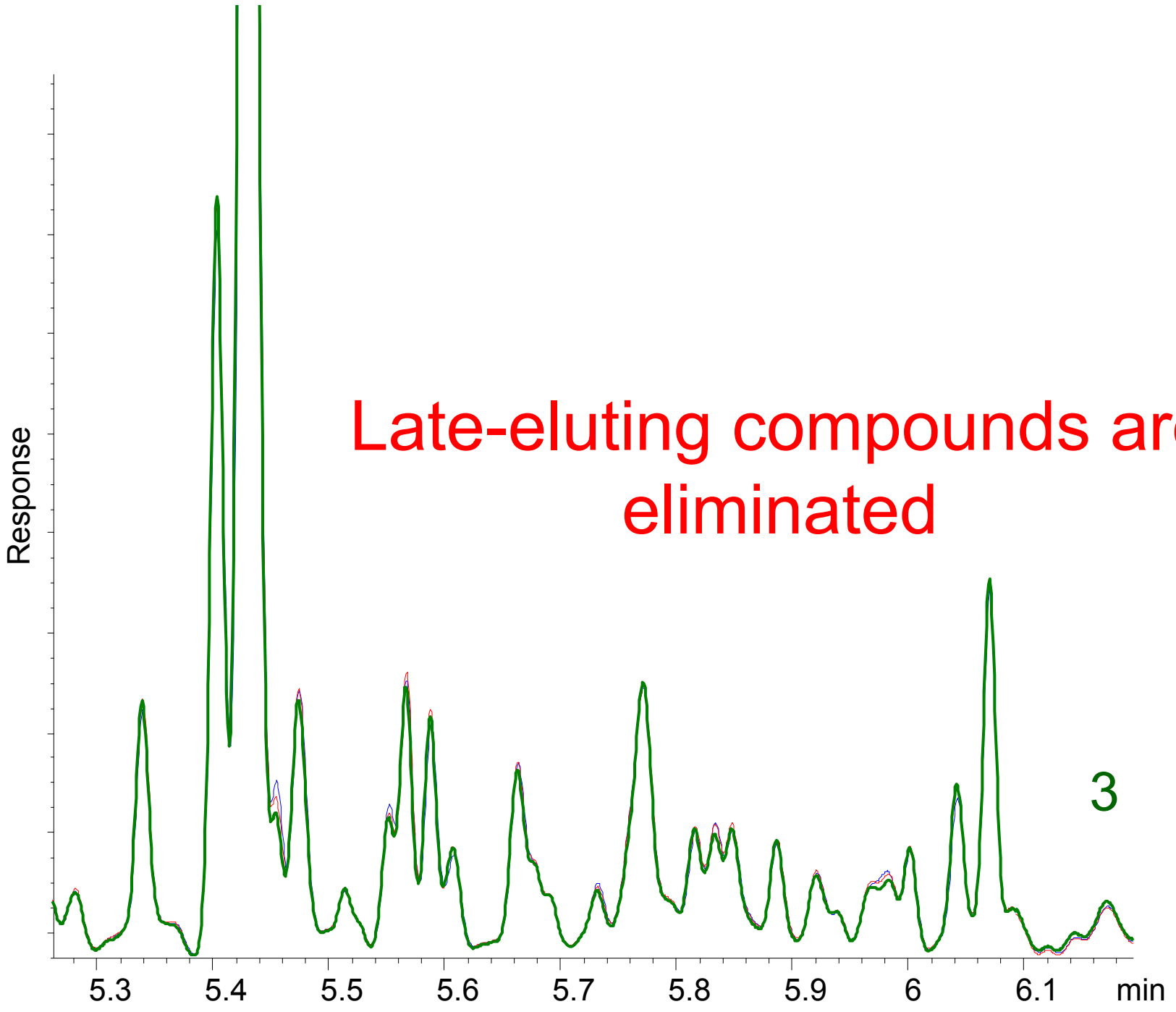
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min


Retention times shift out of quantitation windows …
Response
11
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2 min

10 Runs With Backflush


Late-eluting compounds are eliminated
Response
1
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


Late-eluting compounds are eliminated
Response
2
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


Late-eluting compounds are eliminated
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3
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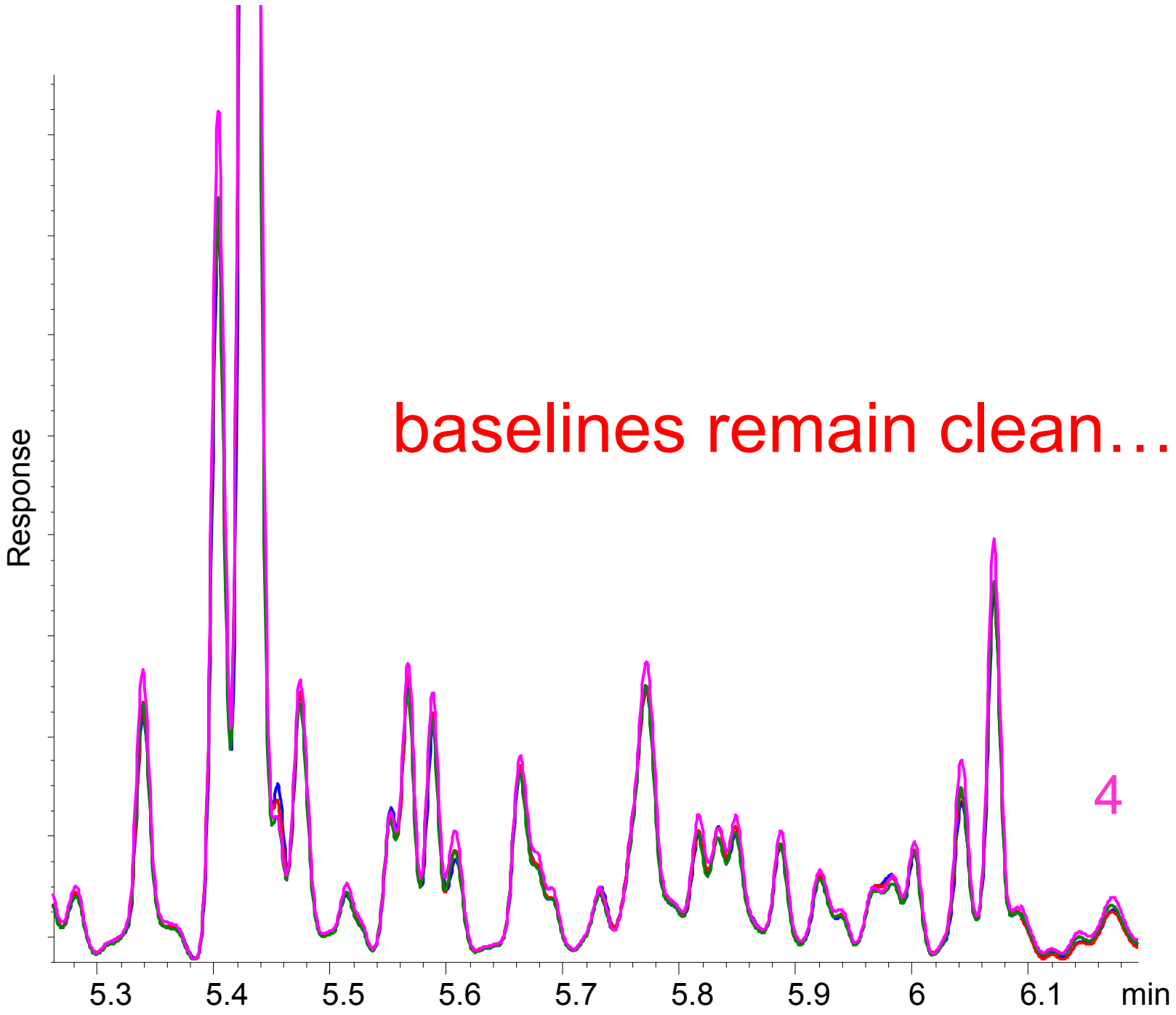
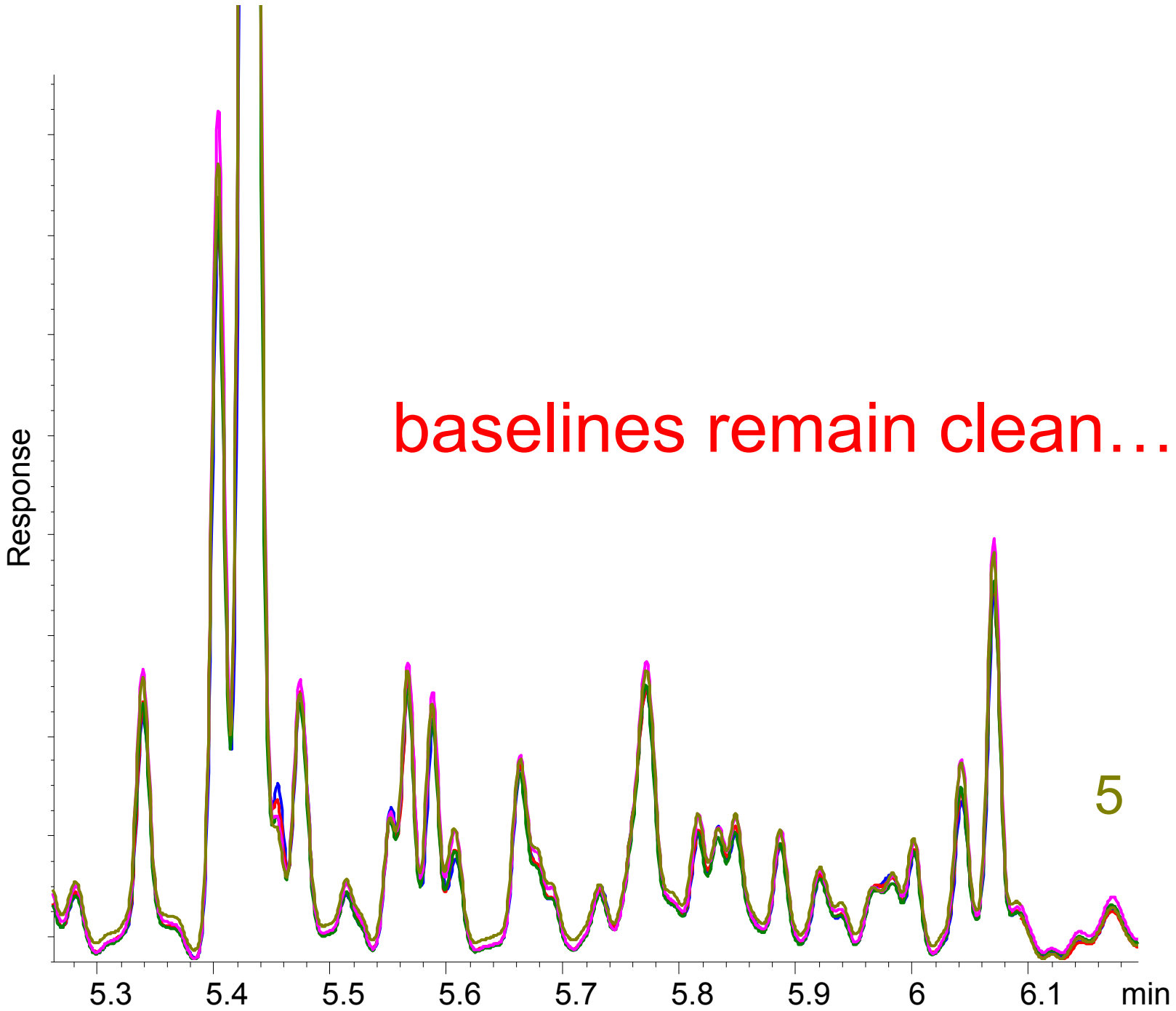
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


baselines remain clean…
Response
4
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min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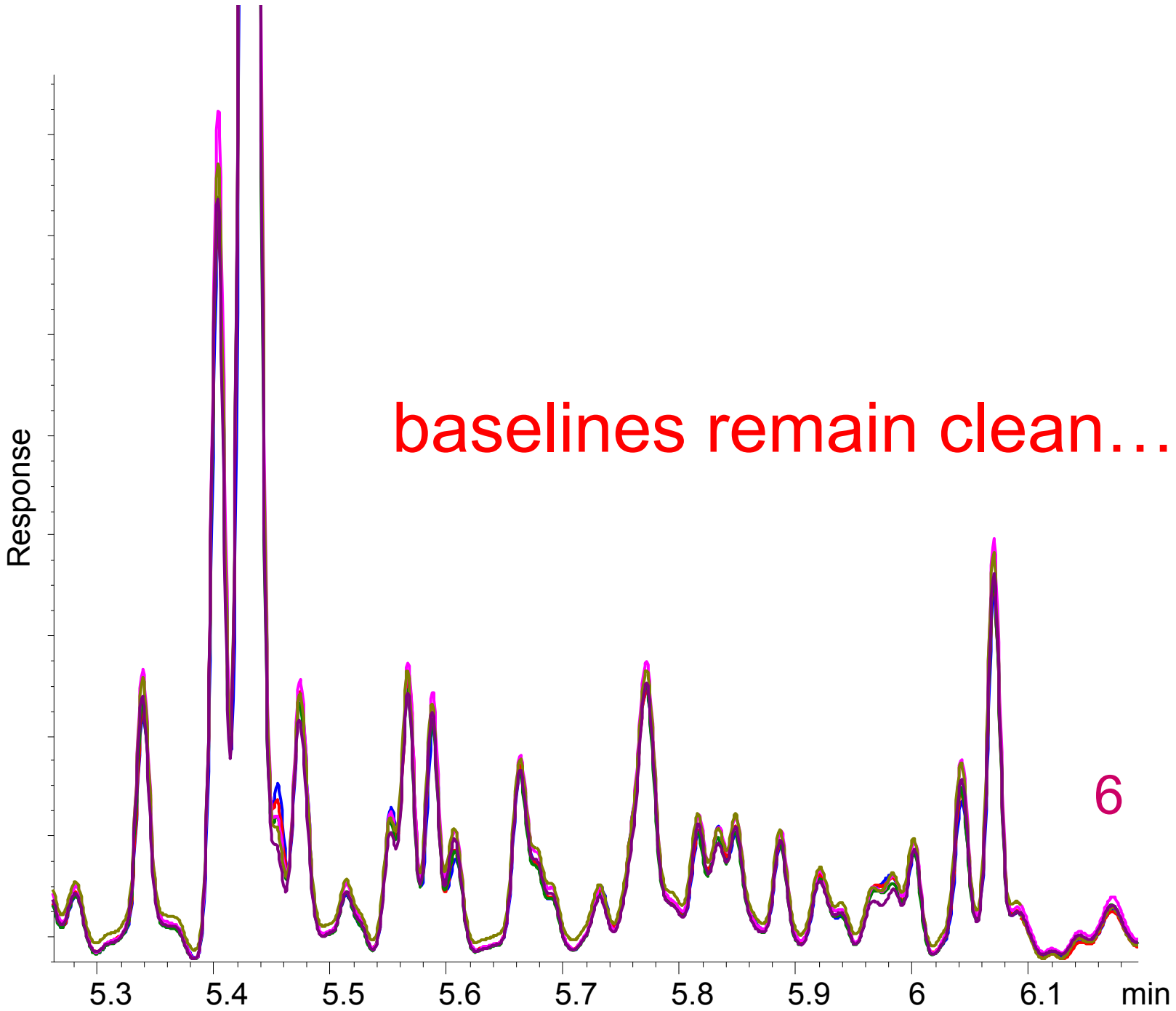
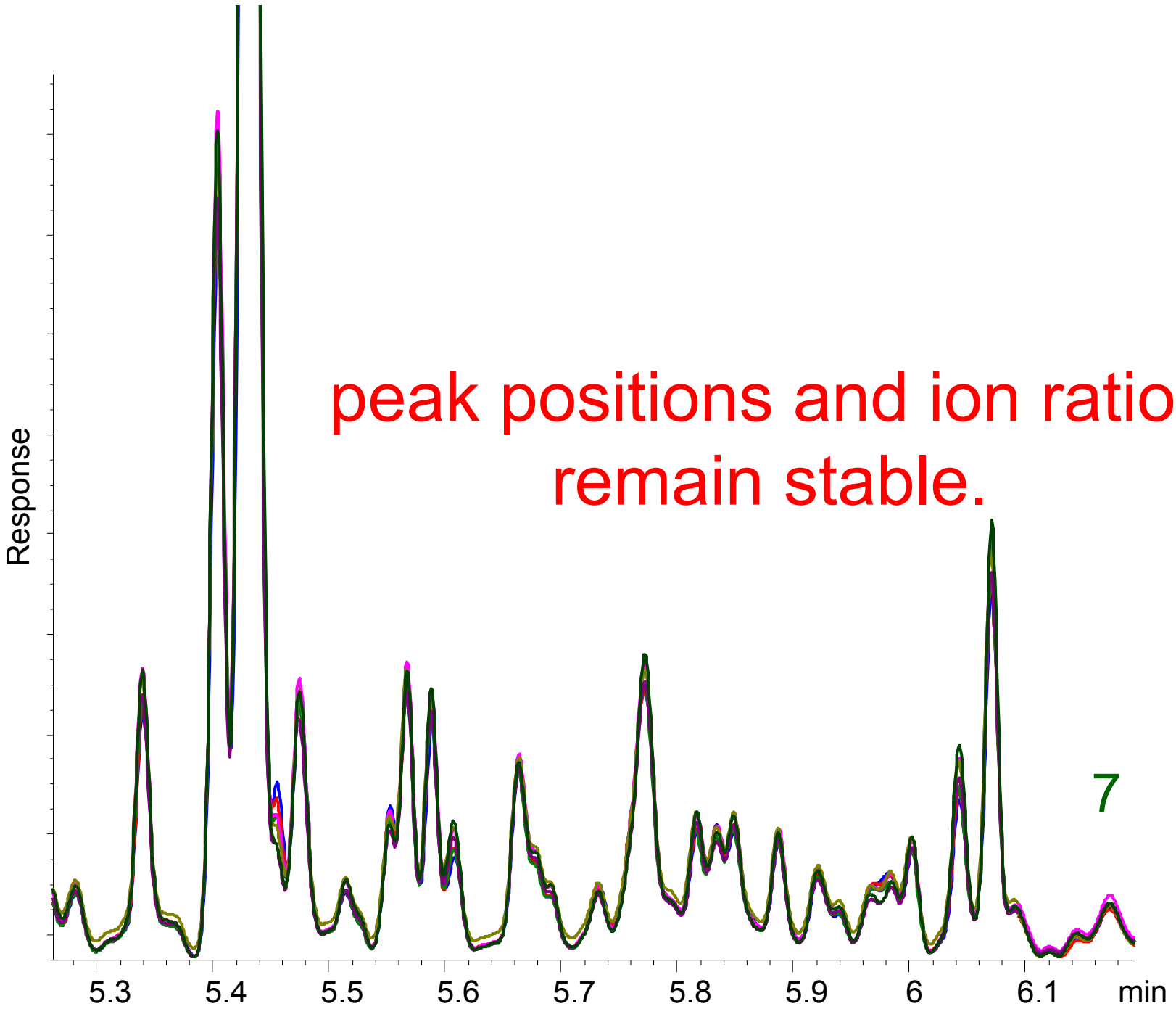
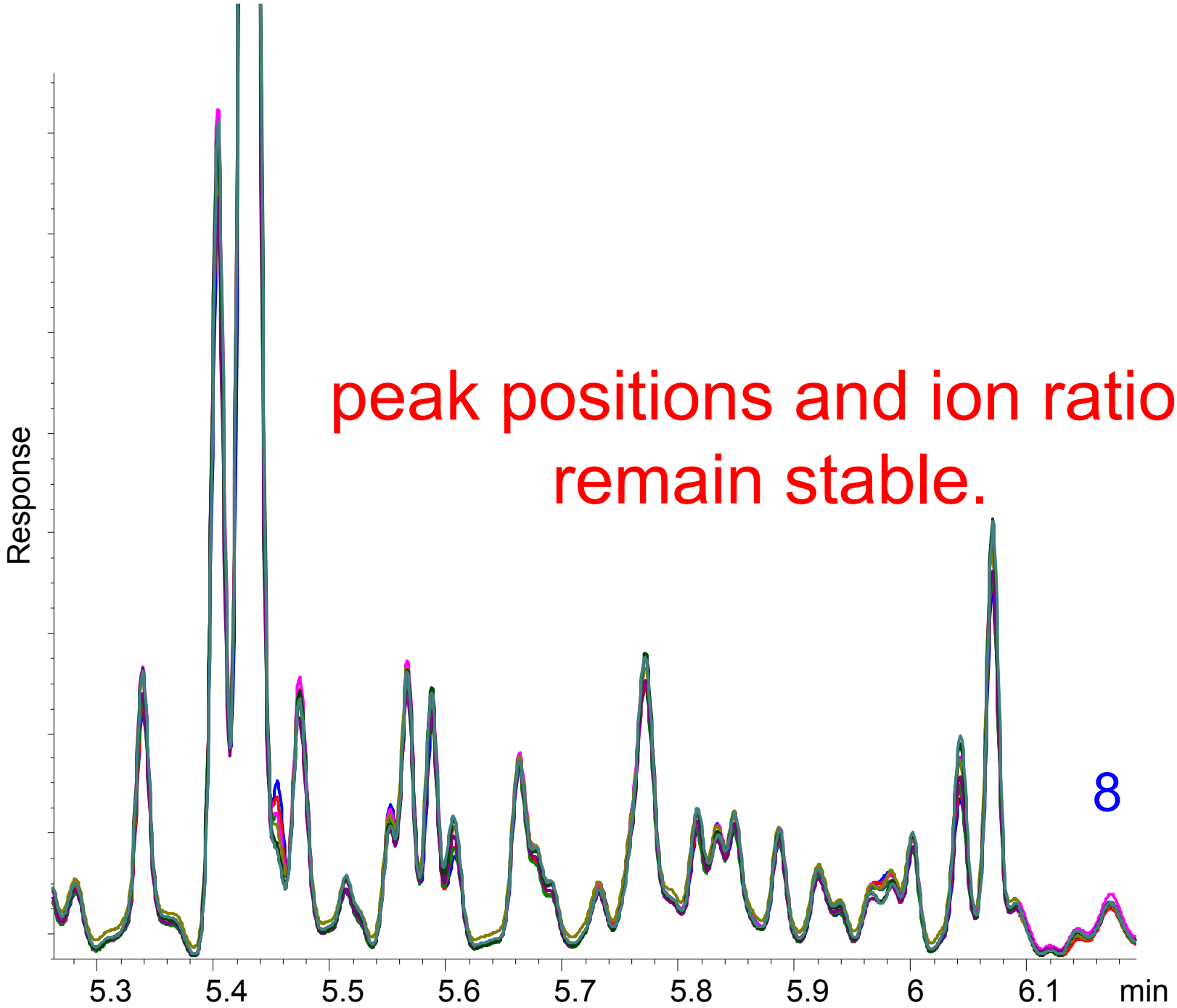
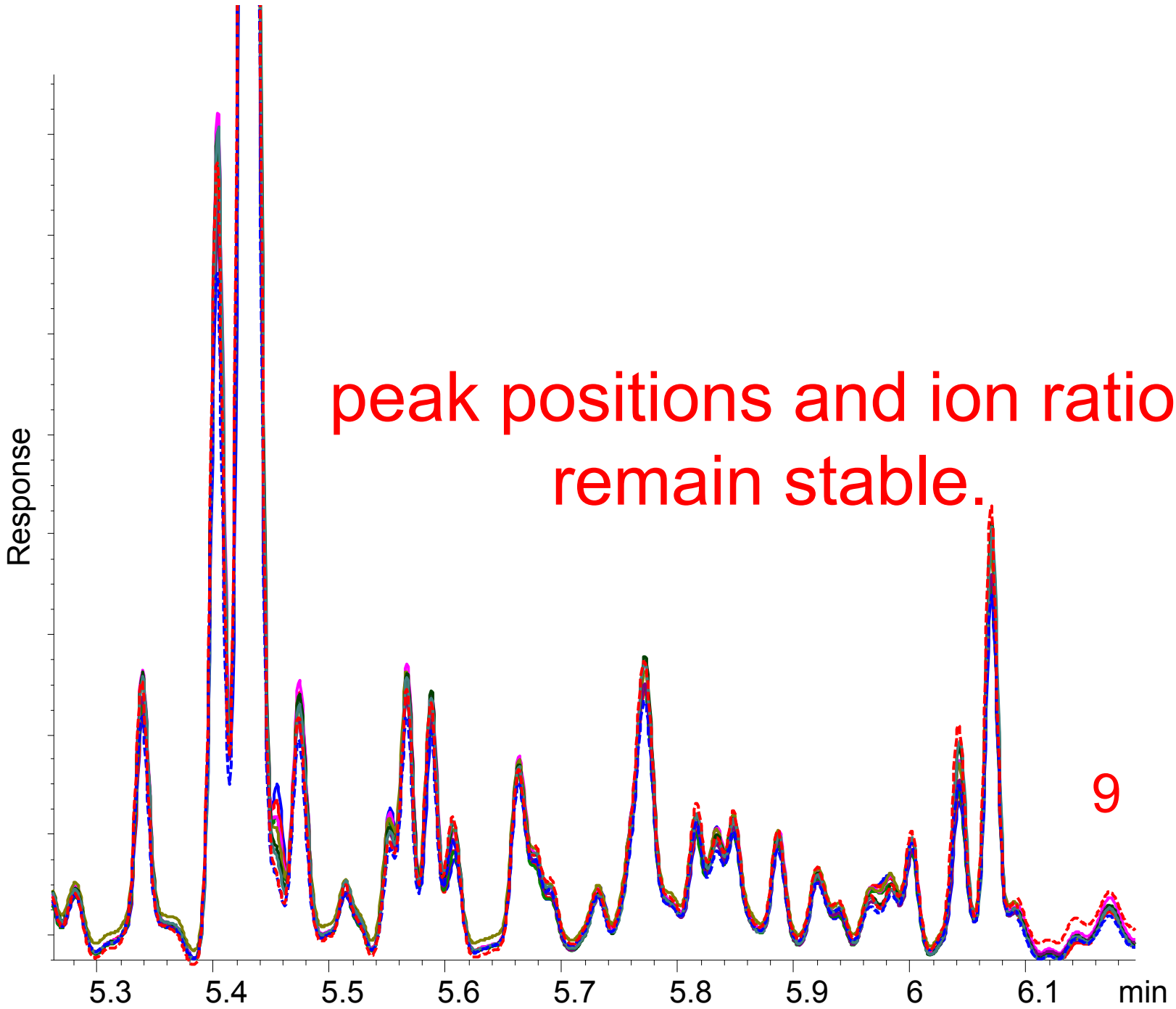
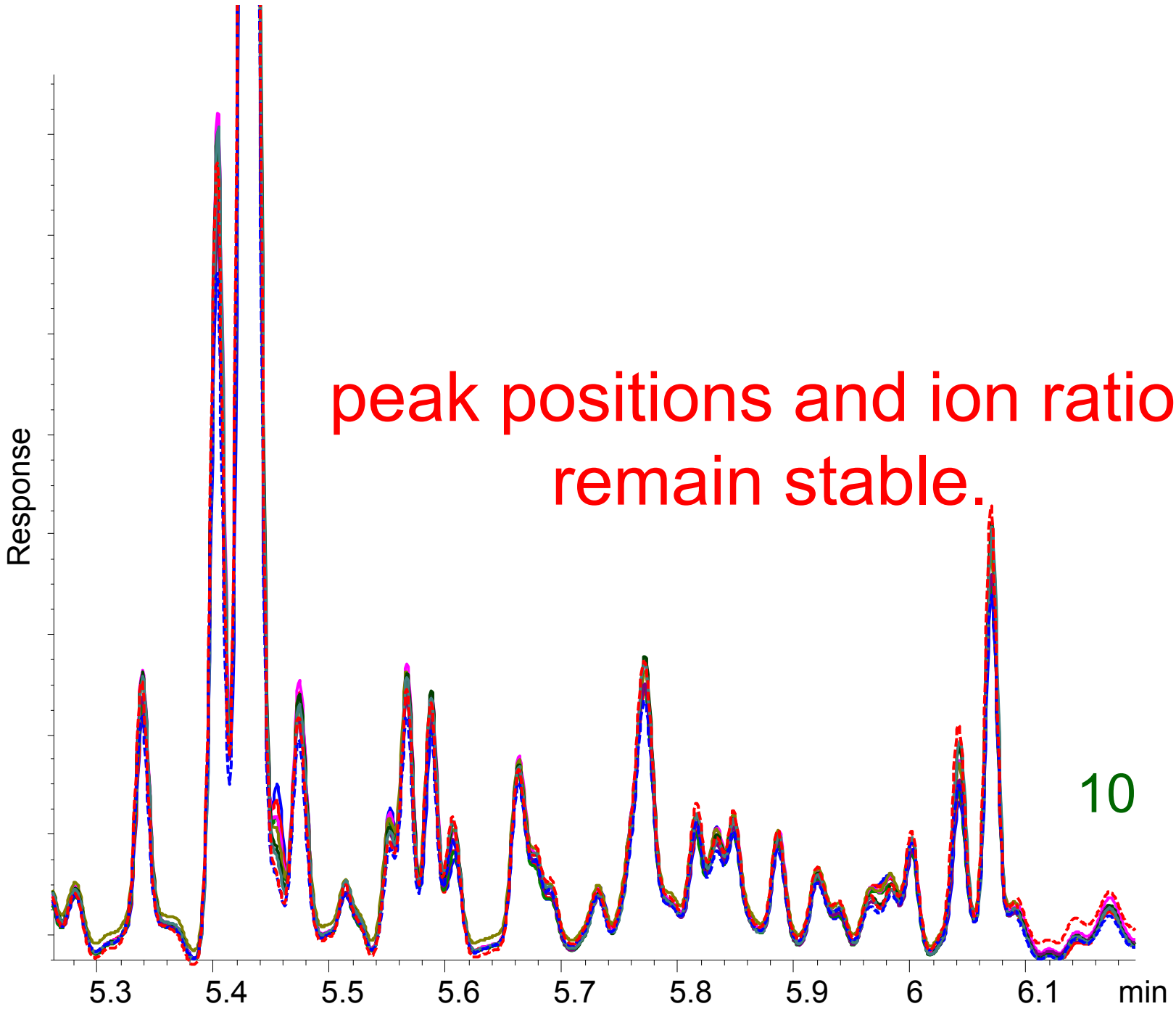

baselines remain clean…
Response
6
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


peak positions and ion ratios
remain stable.
Response
7
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


peak positions and ion ratios
remain stable.
Response
8
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


peak positions and ion ratios
remain stable.
Response
9
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min


peak positions and ion ratios
remain stable.
Response
10
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
min

Applications meriting consideration

Any analysis with

- Extended temperature programs and/or bakeout times after the last peak of interest elutes
- Frequent maintenance due to dirty samples
- Significant carry-over, ghost peaks, increasing baseline
- Late eluting compounds of no analytical interest
- Long overall analysis times

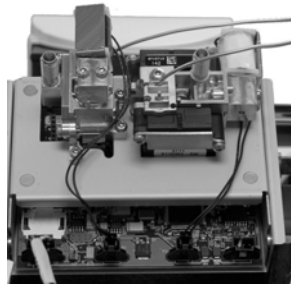
Purged devices that enable backflush

Deans switch

QuickSwap

Purged Splitters
2-Way

PCM



Flow modulator

Purged
Ultimate Union

3-Way

EPC

Setting up Backflush

1. Start with working method
2. Extract pertinent method information from method files
3. Select BF configuration
4. Set up and verify hardware
5. Install columns and test configuration
6. Screen standard on new configuration
7. Lock with migrated RTL calibration if RTL method
8. Pick last peak of interest using graphical tool, from which BF timing and conditions are recommended
9. Verify BF works
10. Fine tune BF conditions if necessary

Three Configurations and Two Modes of BF

Post-Column

- Post-run backflush

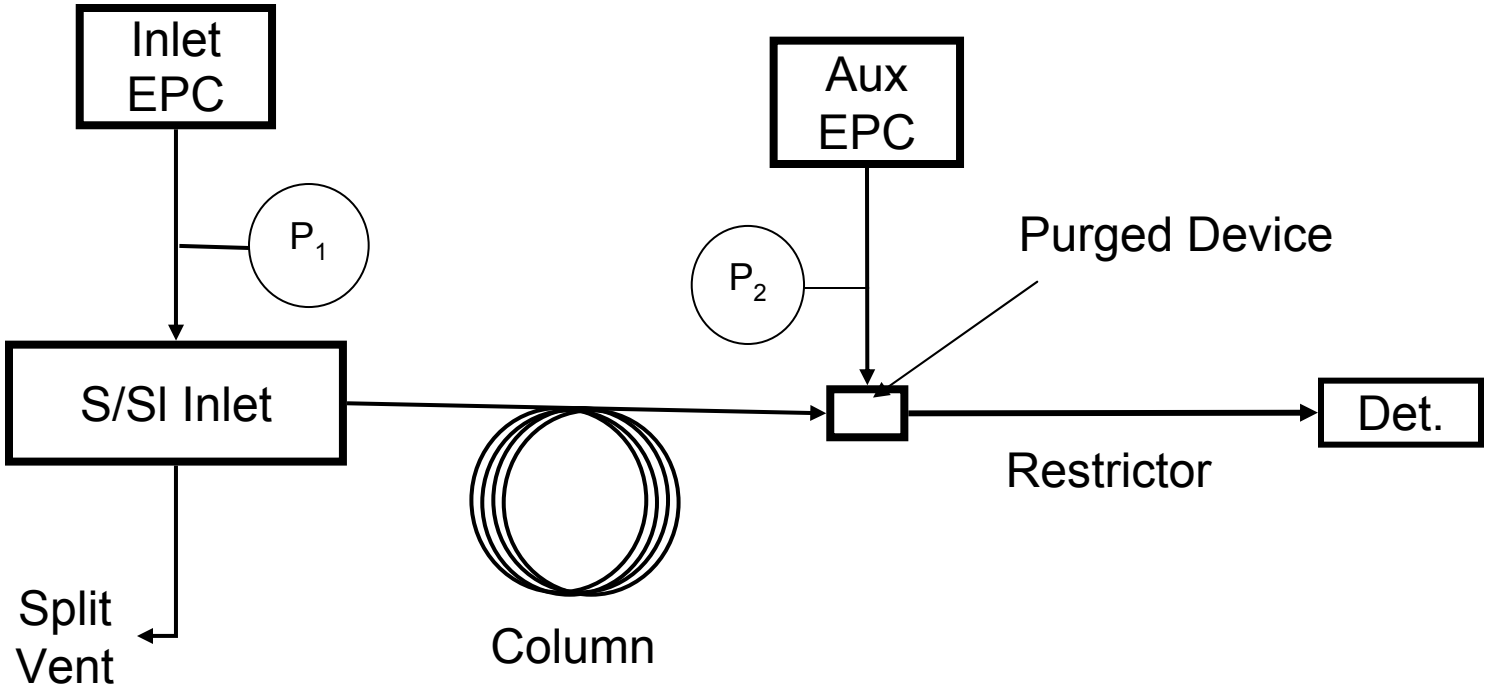
Uncoated Pre-Column

- Concurrent backflush

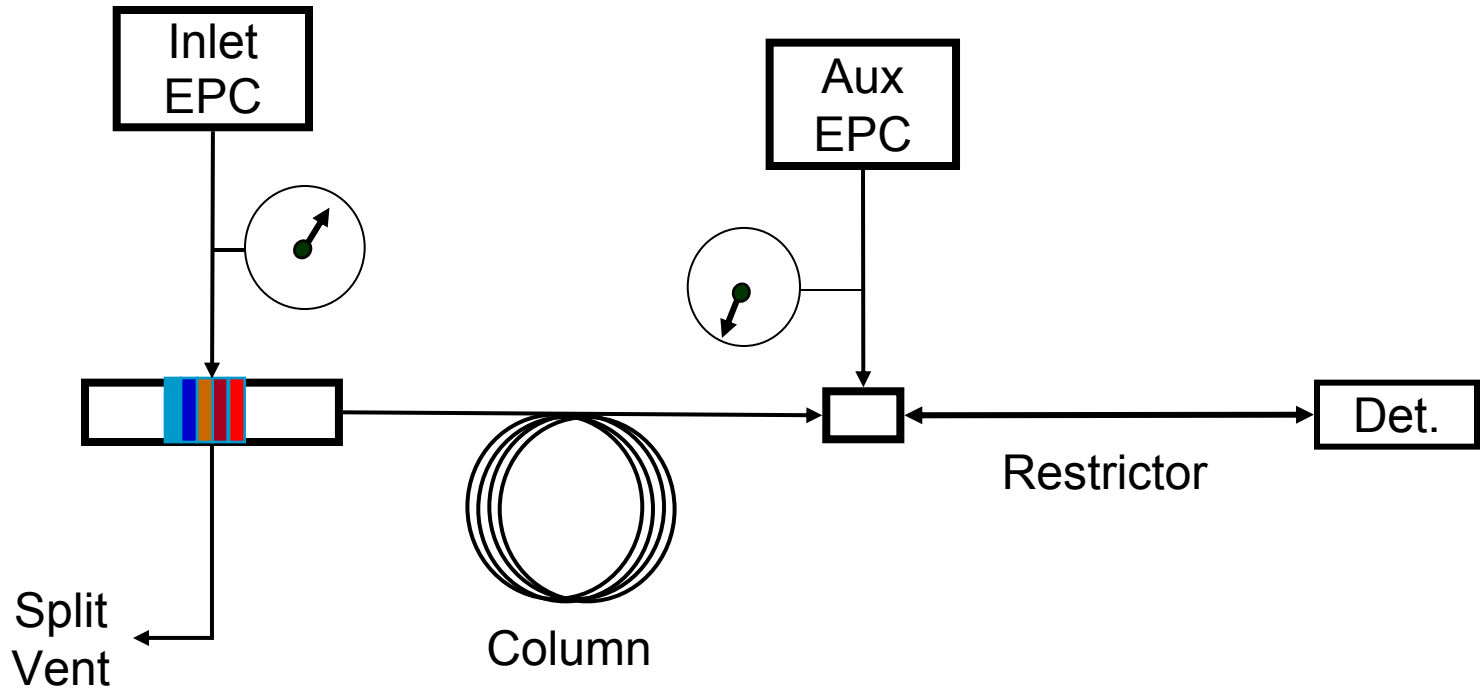
Coated Pre-Column (split column)

- Post-run
- Concurrent

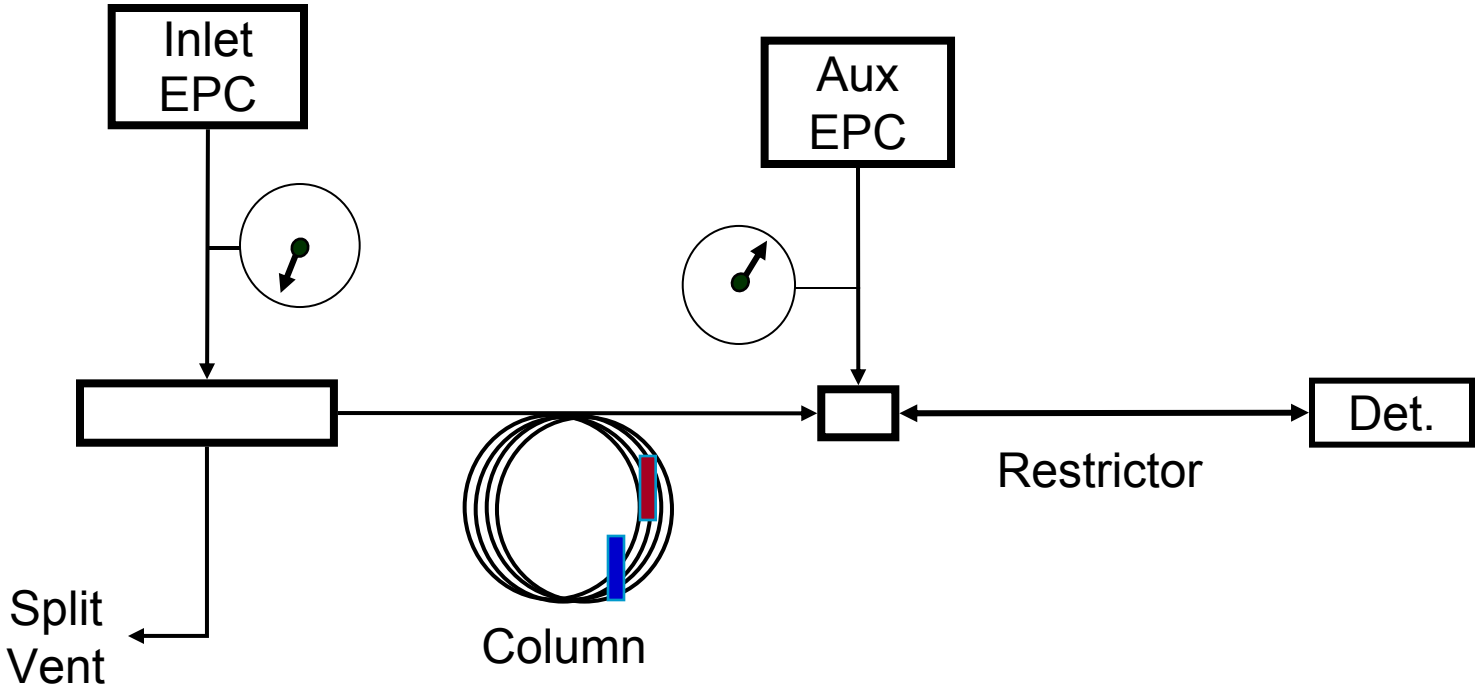
Post-Column Configuration



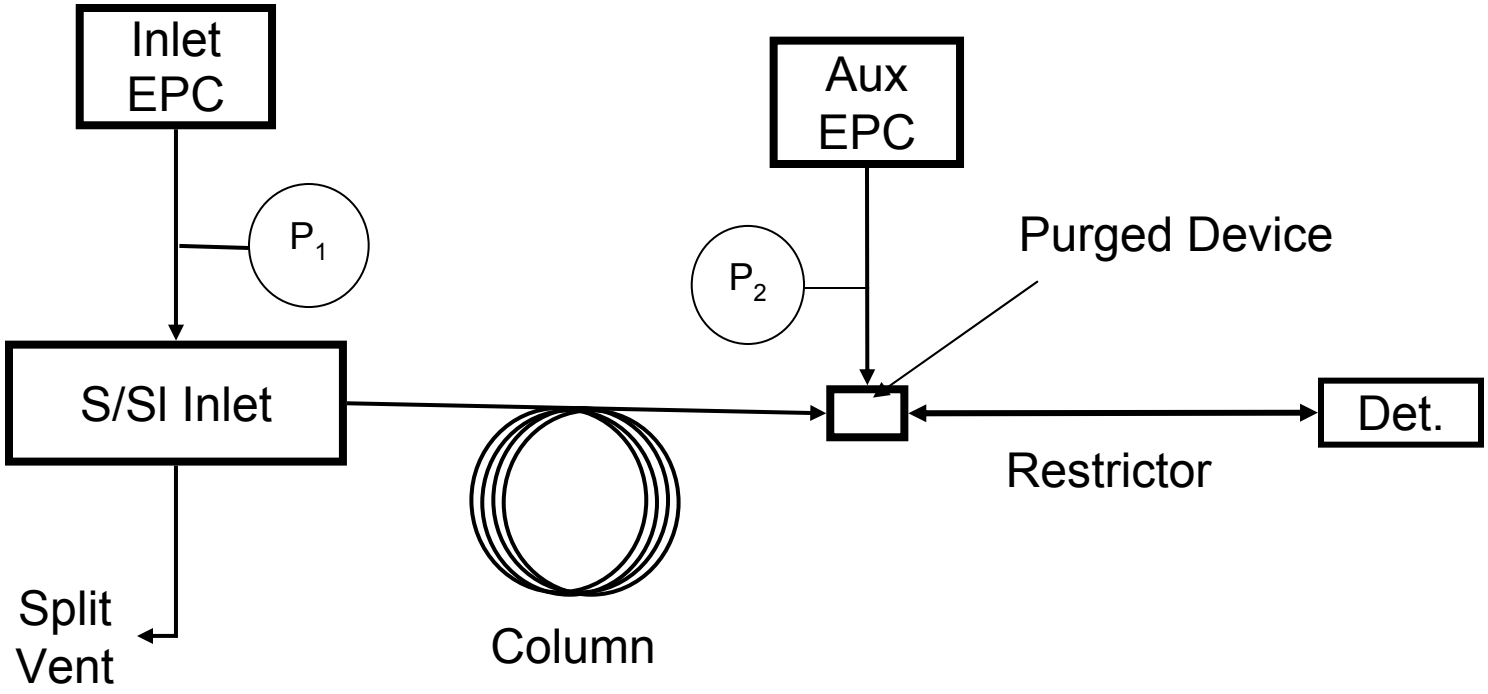
Post-Column Analysis



Post-Column Backflush



Post-Column Configuration



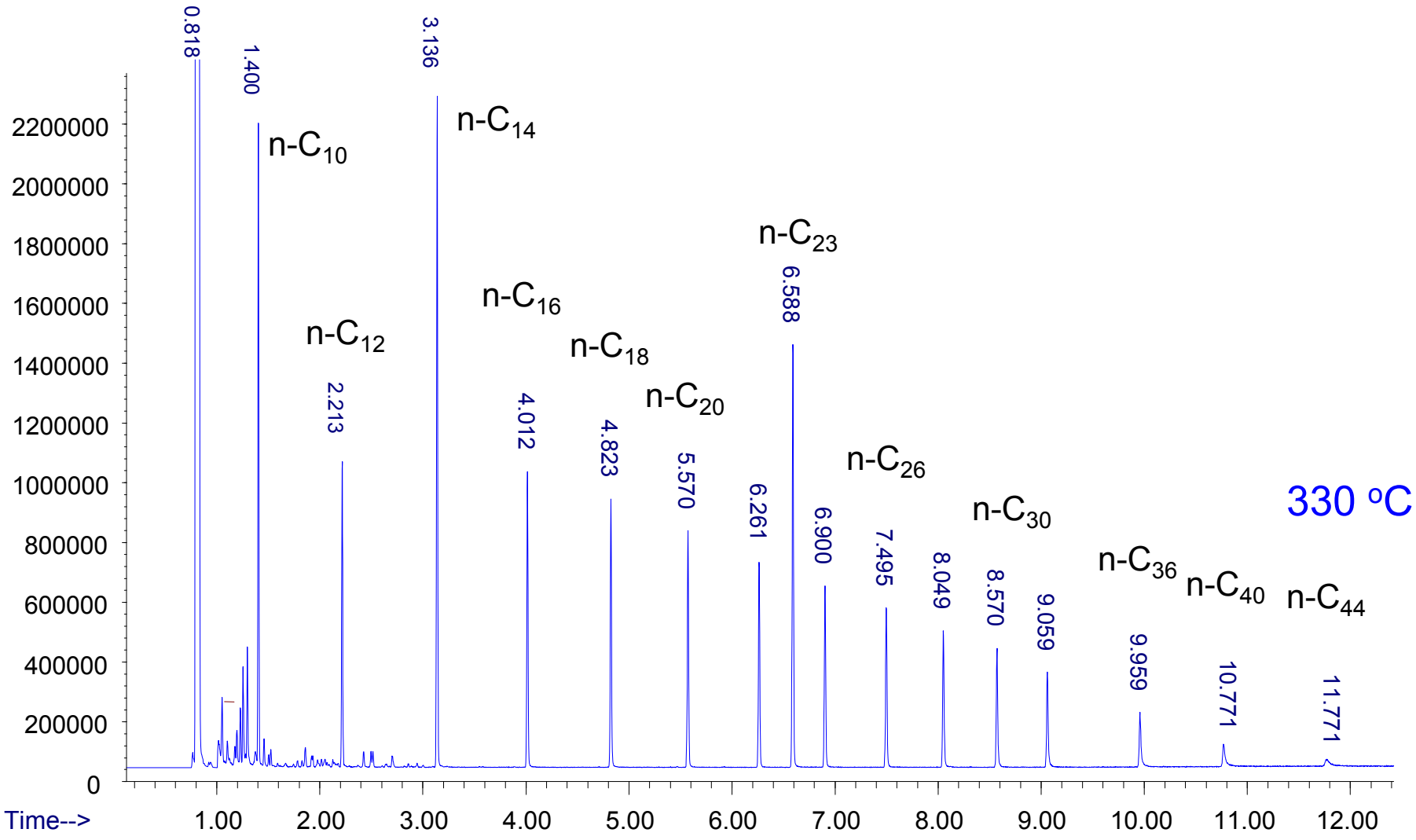
What are the benefits of post-column backflush?

- Easiest mode to understand, and implement; Backflushing is very simple
  - Immediately after the last component of analytical interest elutes (obvious), data acquisition ends and backflush is initiated at that temperature.
  - The determination and verification of backflush timing is the fastest of the three approaches
  - Run has ended and data acquisition is stopped (MSD filaments, quad and detector are OFF) during backflush
- RTL implementation is very straightforward and rugged to apply
- The analytical column is one single unit with constant mass flow through its full length (no degradation in original separation efficiency)
- Compatible with pressure pulsed injections

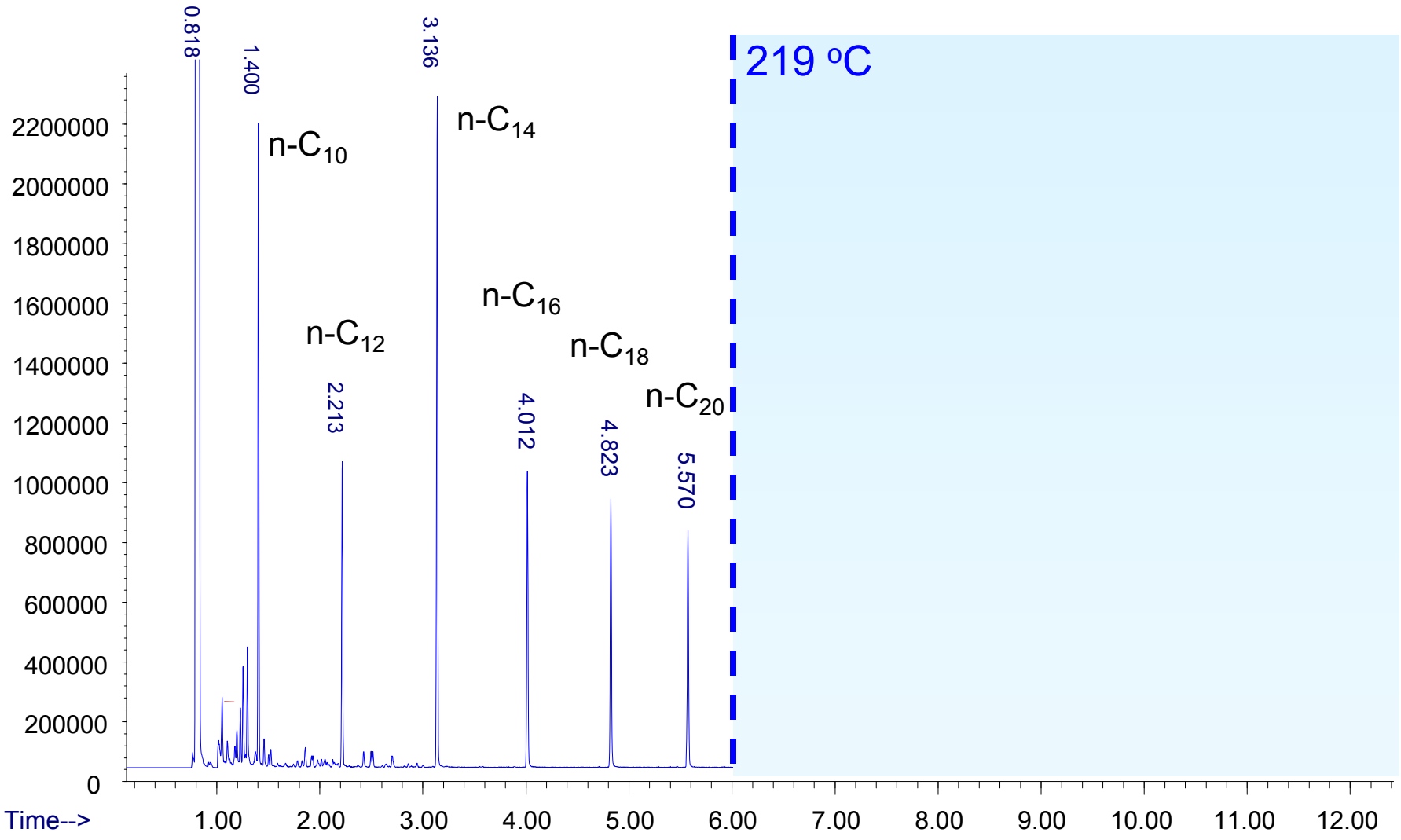
What are the downsides of post-column backflush mode and use of QuickSwap?

- Flow is added to the column effluent
  - The choice of restrictor dictates the flow that to the MSD
  - Even a prudent choice in restrictor can reduce sensitivity 15-20%
  - Larger than necessary i.d. (bad choice in restrictor) can decrease sensitivity and S/N much more dramatically
- The restrictor is uncoated, so there is a possibility of increased loss of labile compounds.

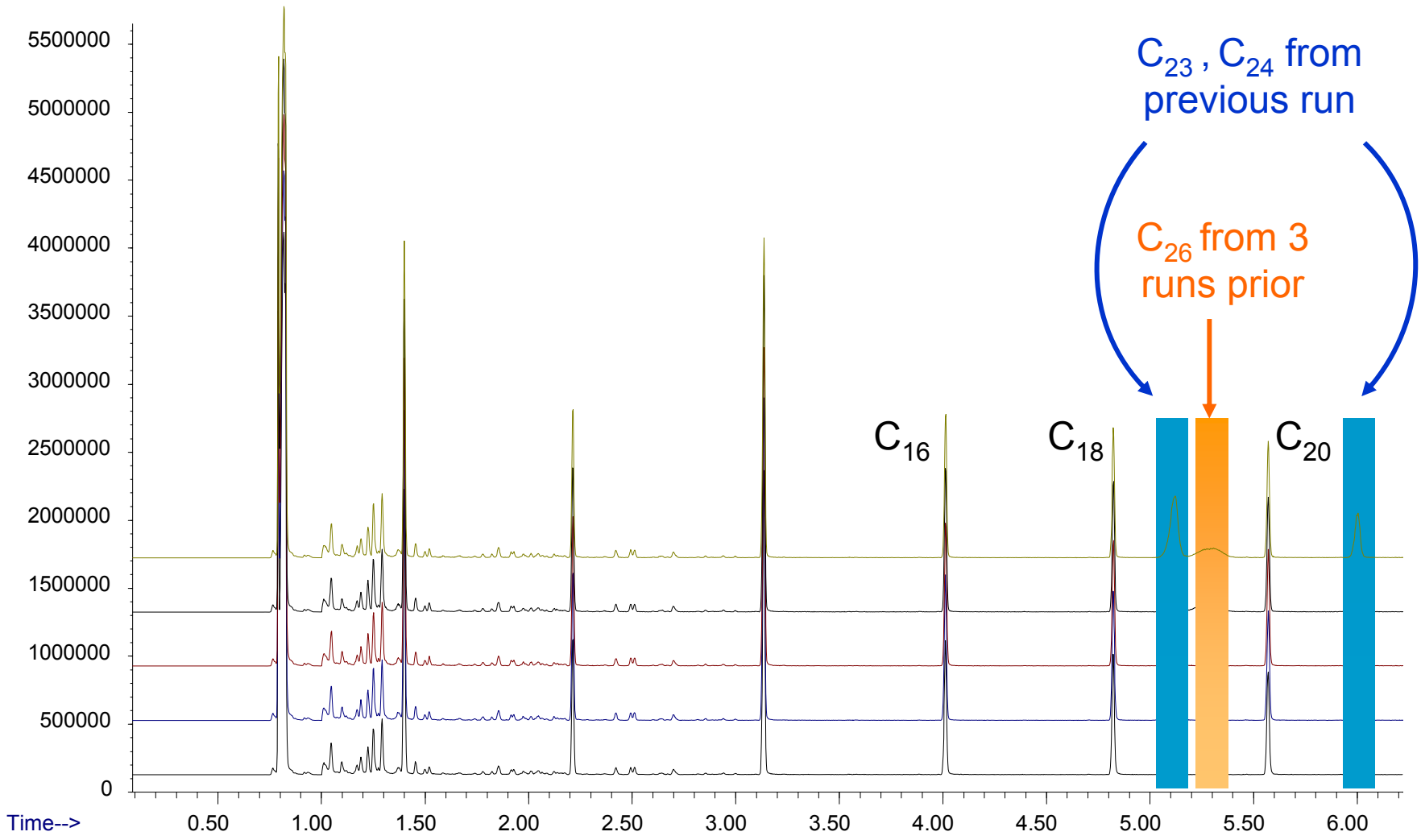
Reference TIC – CF Screening Conditions



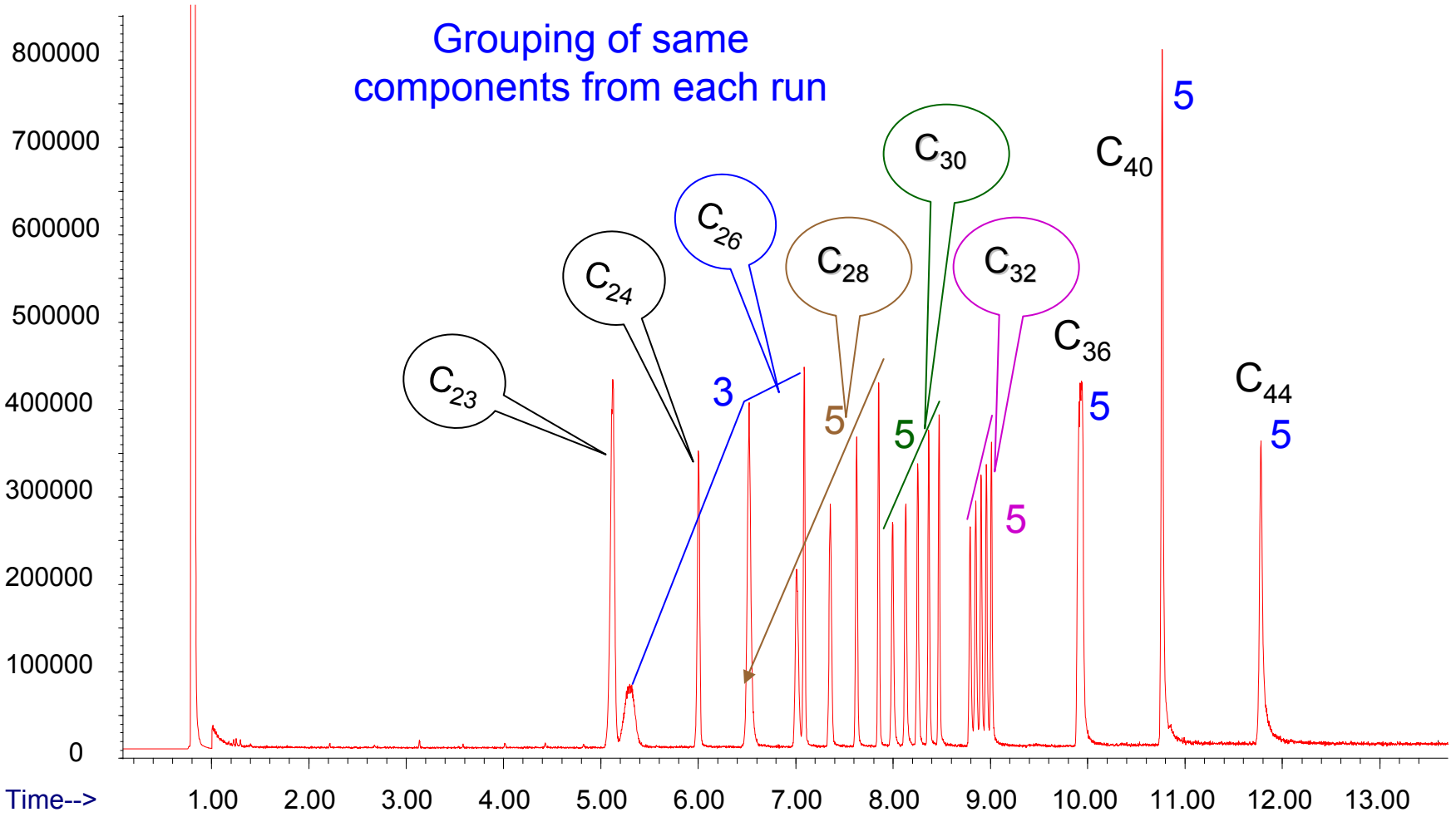
Reference Chromatogram



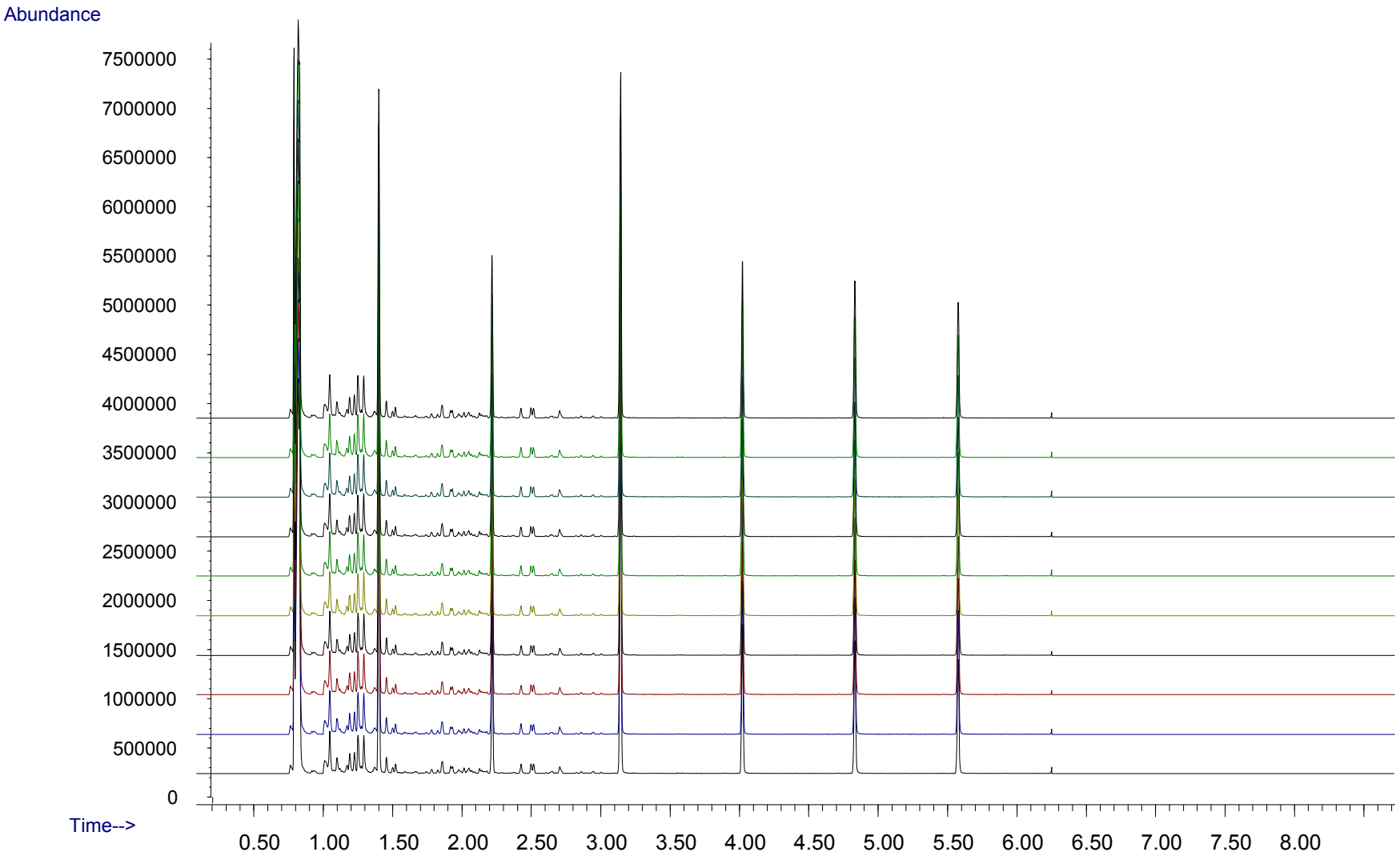
5 Runs Stopping @ 6.25 min, no BF, Showing Carryover Into Subsequent Runs



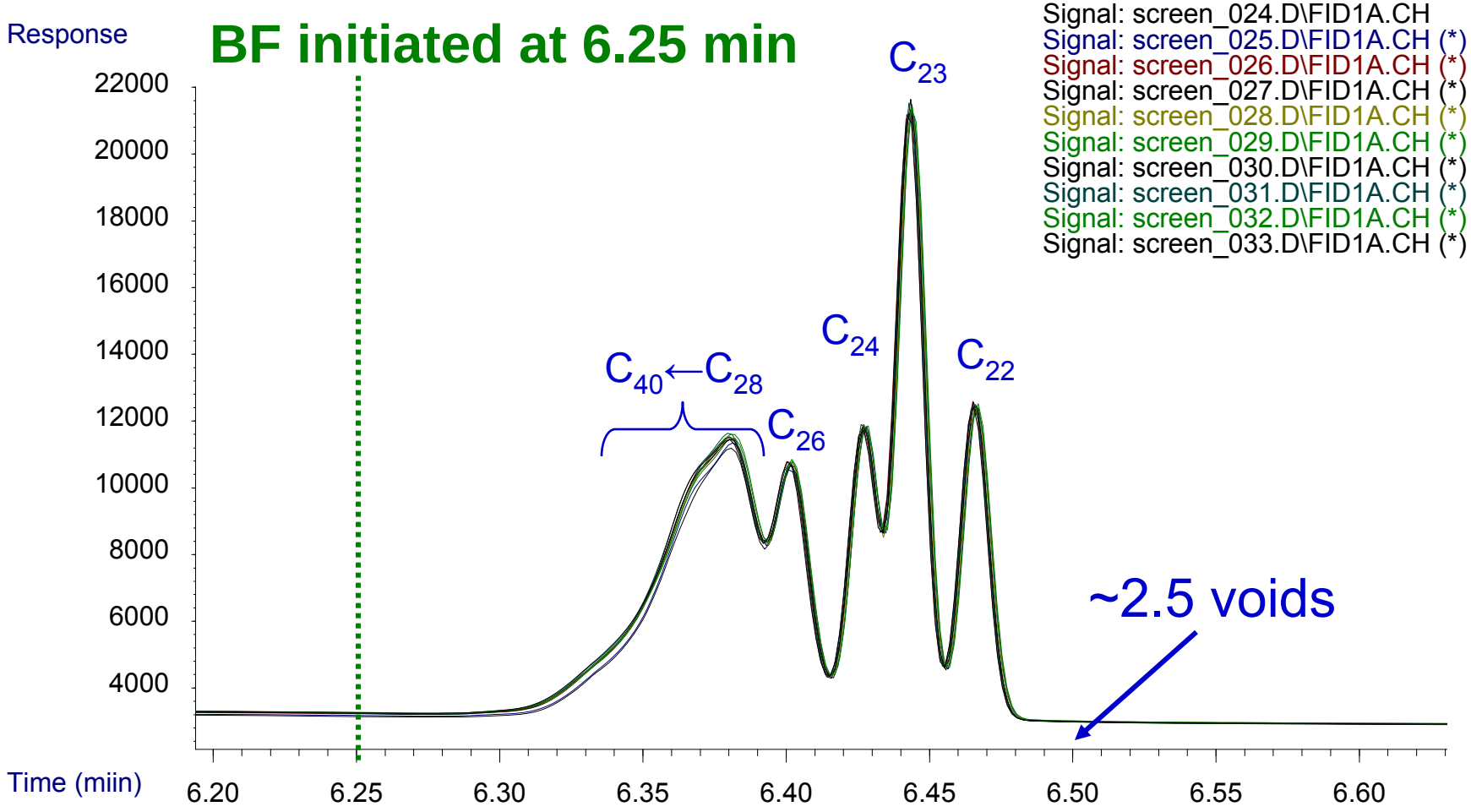
Solvent Blank Full Temperature-Programmed Analysis After Five 6.25 min Abbreviated Runs



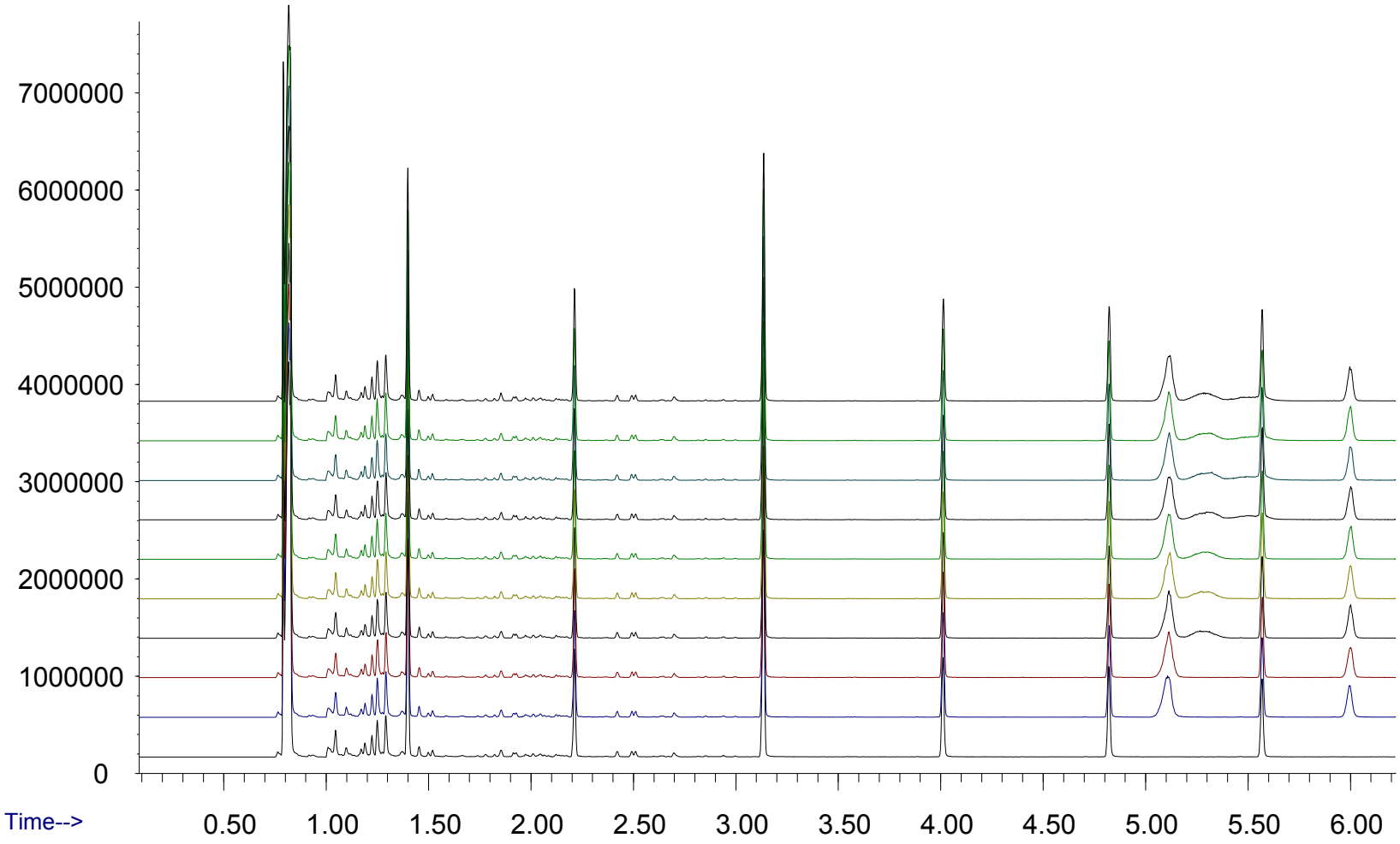
Ten Sequential Runs with BF @ 6.25 min



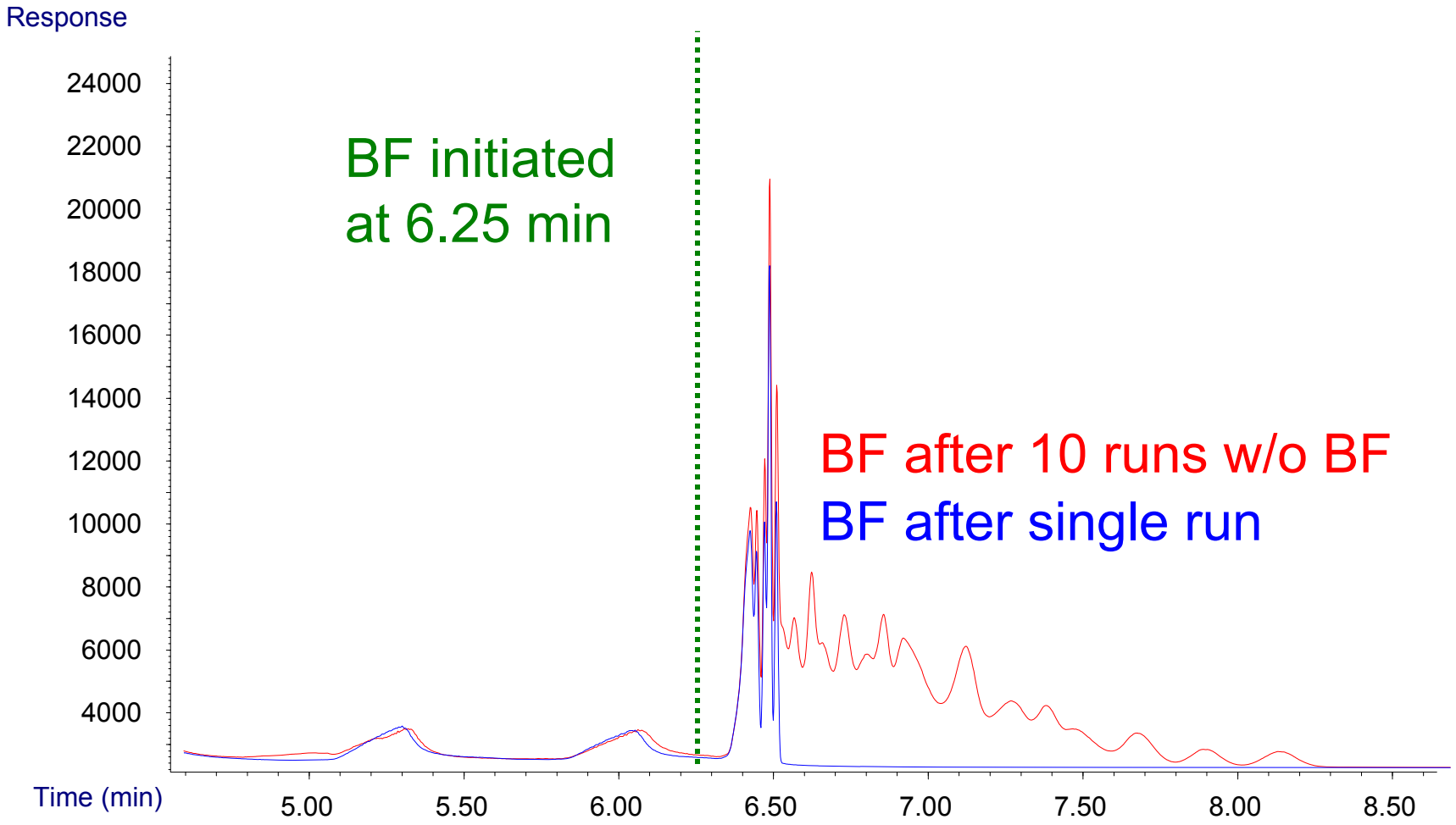
BF Signals from 10 sequential BF Runs



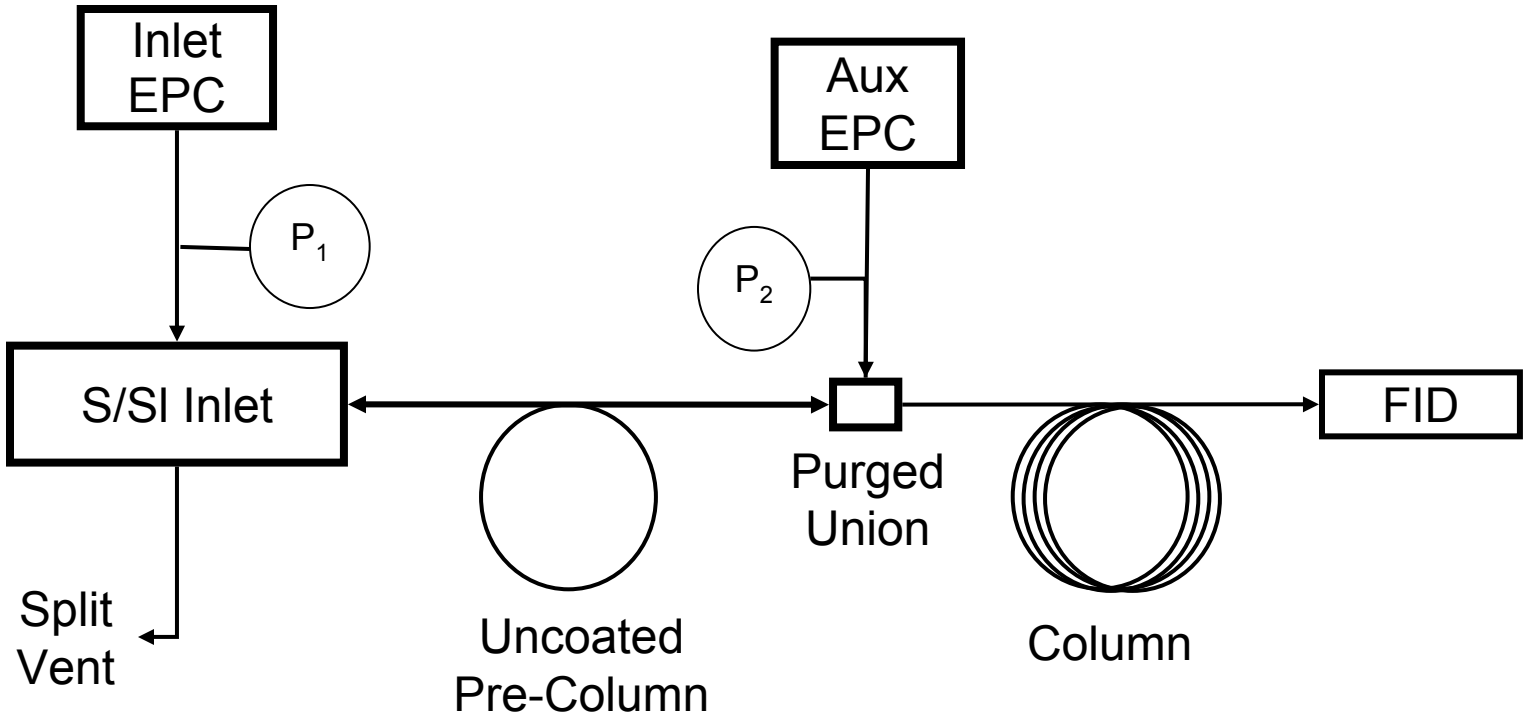
Ten 6.25 min Runs without BF



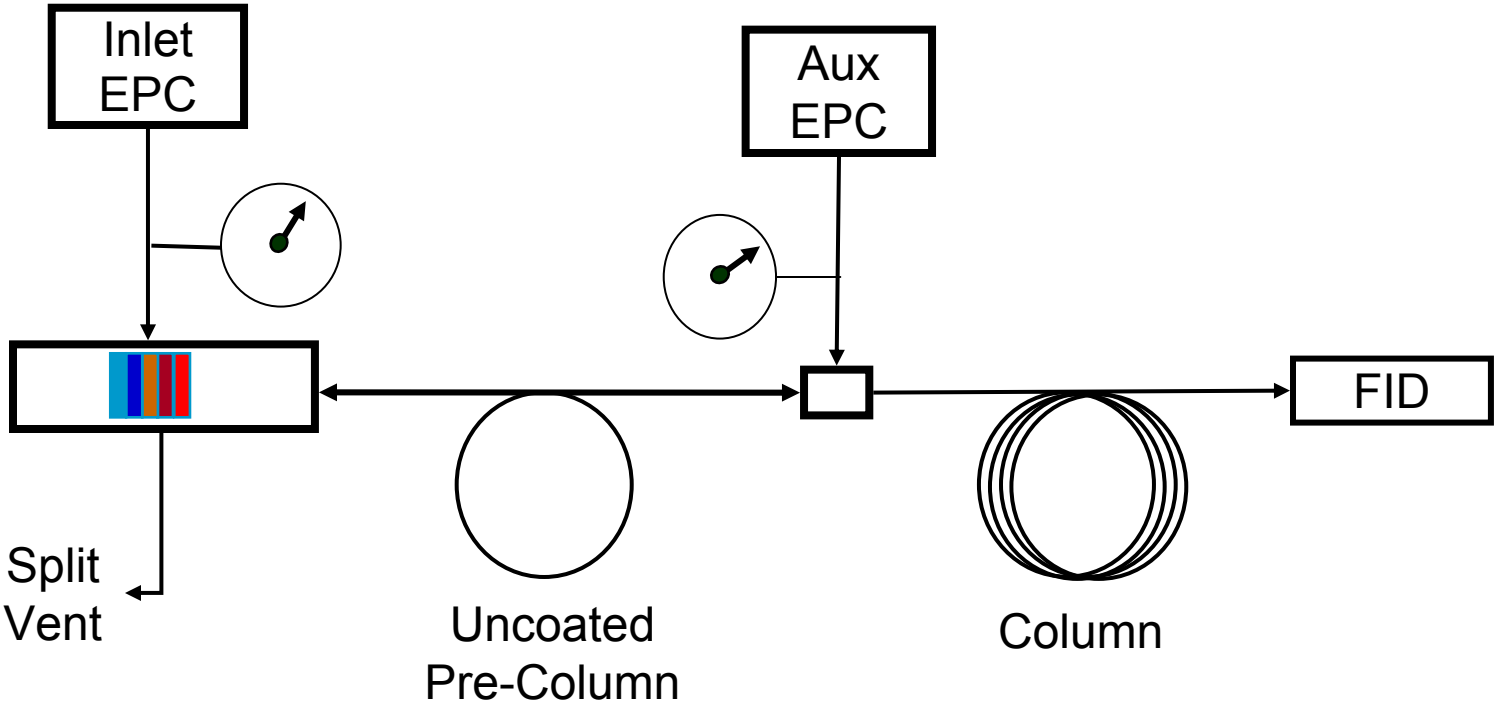
Backflush after 10 runs vs. each run



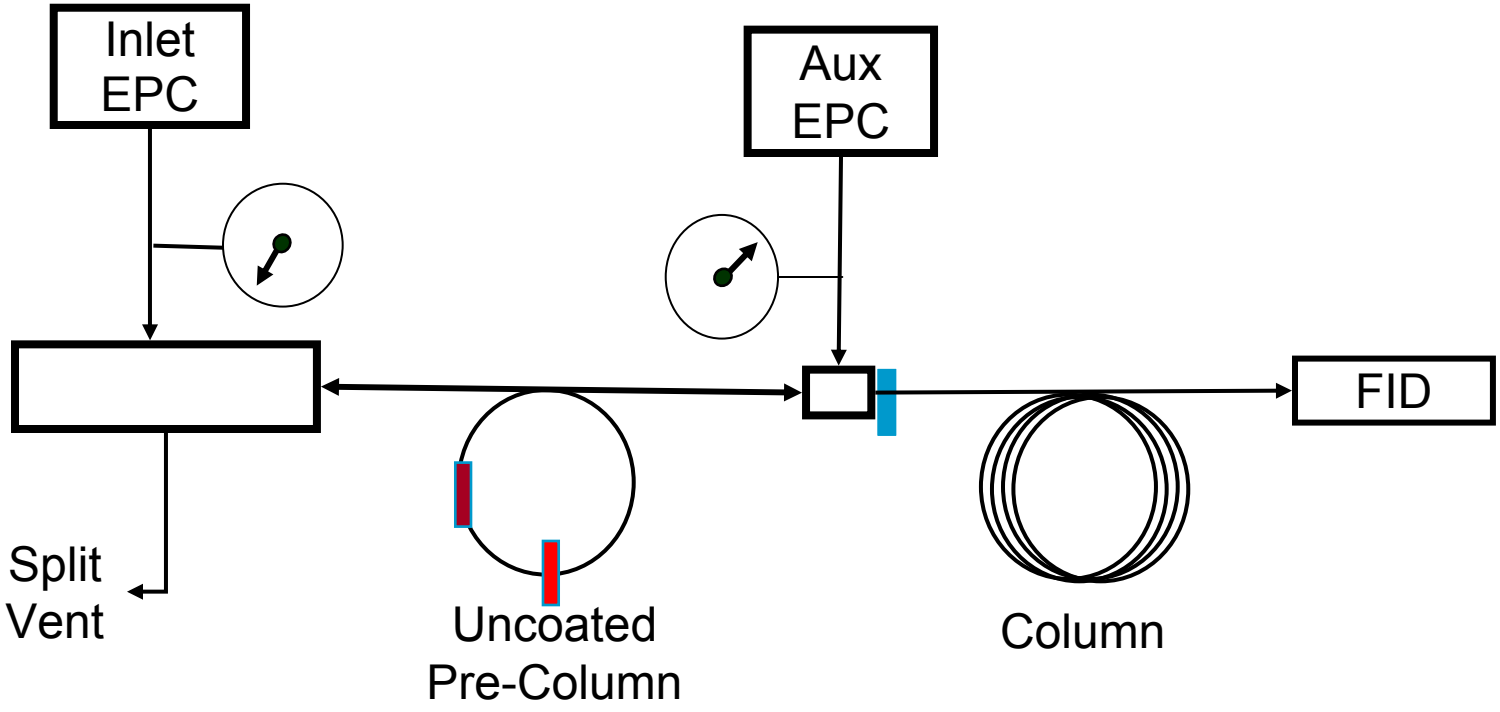
Uncoated Pre-Column Configuration



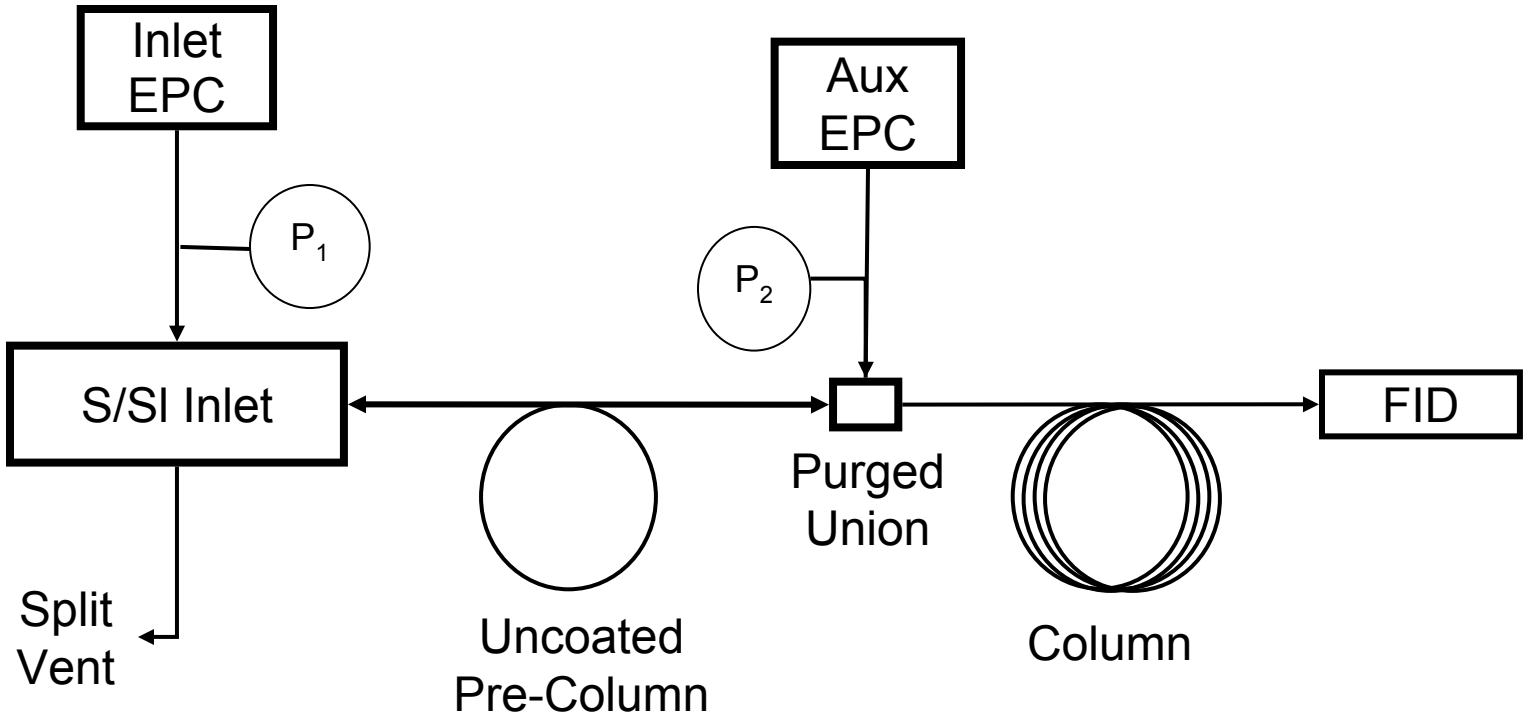
Uncoated Pre-Column Analysis



Uncoated Pre-Column Backflush



Uncoated Pre-Column Configuration



What are the benefits of using uncoated (but deactivated) pre-columns for backflush?

- Decoupling of retention of pre-column from analytical column, therefore more suitable for replication on multiple systems/locations, more rugged.
  - Sample components are transferred to the analytical column at low temperatures and are focused by the stationary phase of the analytical column, decoupling retention of the two sections (resulting in more rugged conditions)
- The heavy components are backflushed more quickly (at lower temperatures and/or with fewer column void volumes), making this the fastest backflush technique (often components are completely backflushed within seconds).
- Fastest backflush of all modes and concurrent with the analysis so when the last compound of interest has eluted, the run can stop and get ready for the next analysis (maximizing lab throughput)
- Analytical column mass flow is constant through total analytical column length (maximum efficiency)

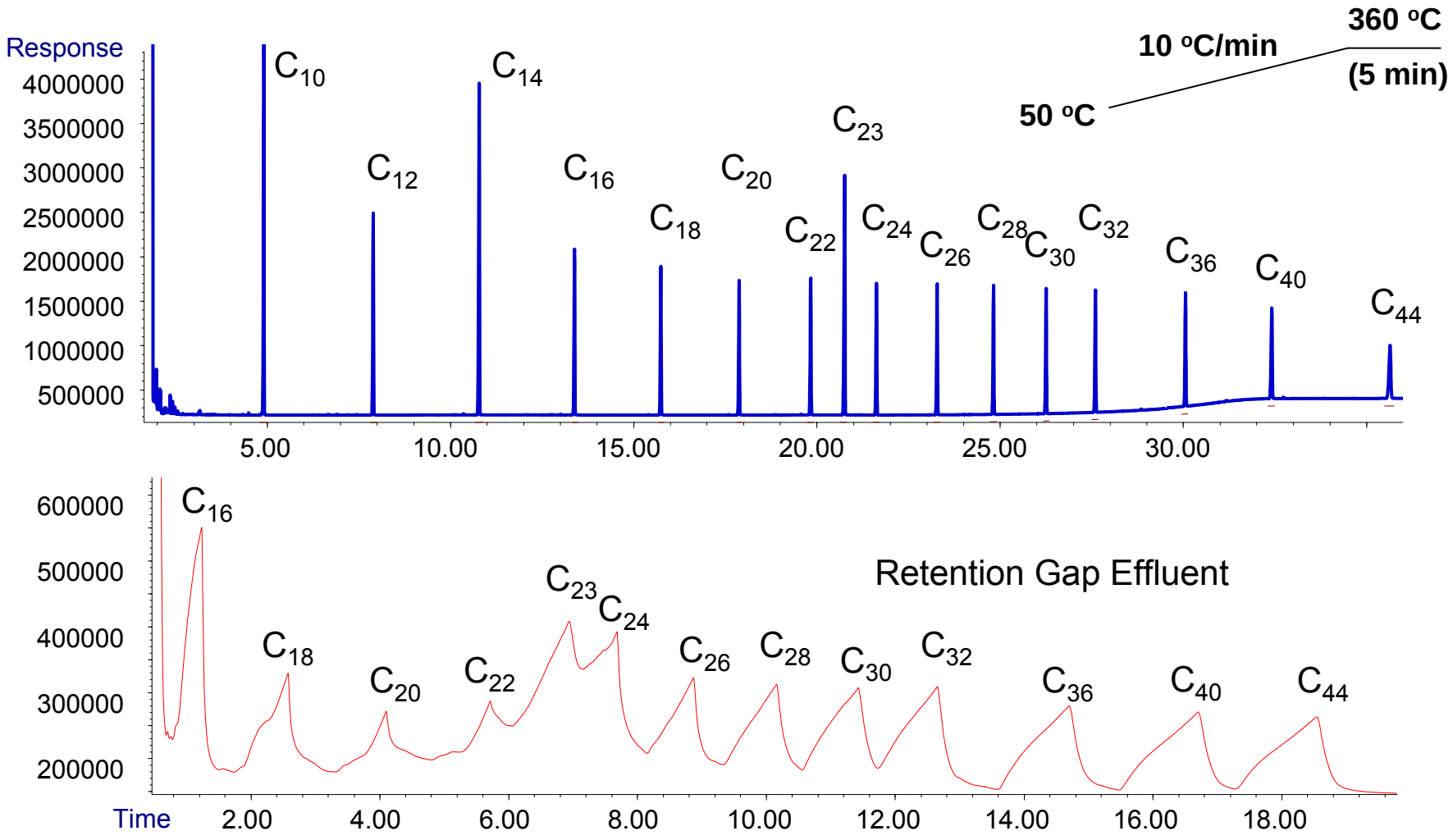
What are the benefits of using uncoated (but deactivated) pre-columns for backflush?

- Flow to detectors during backflush is the least of all BF configurations – exactly the same as original method
- Most flexibility in choice of pre-column dimensions (especially i.d.) and flow rates
- Retained matrix has least influence on initial peak shapes and retention times
- Cheapest to replace when necessary.
- Highest accuracy in transfer of retention time locking methods

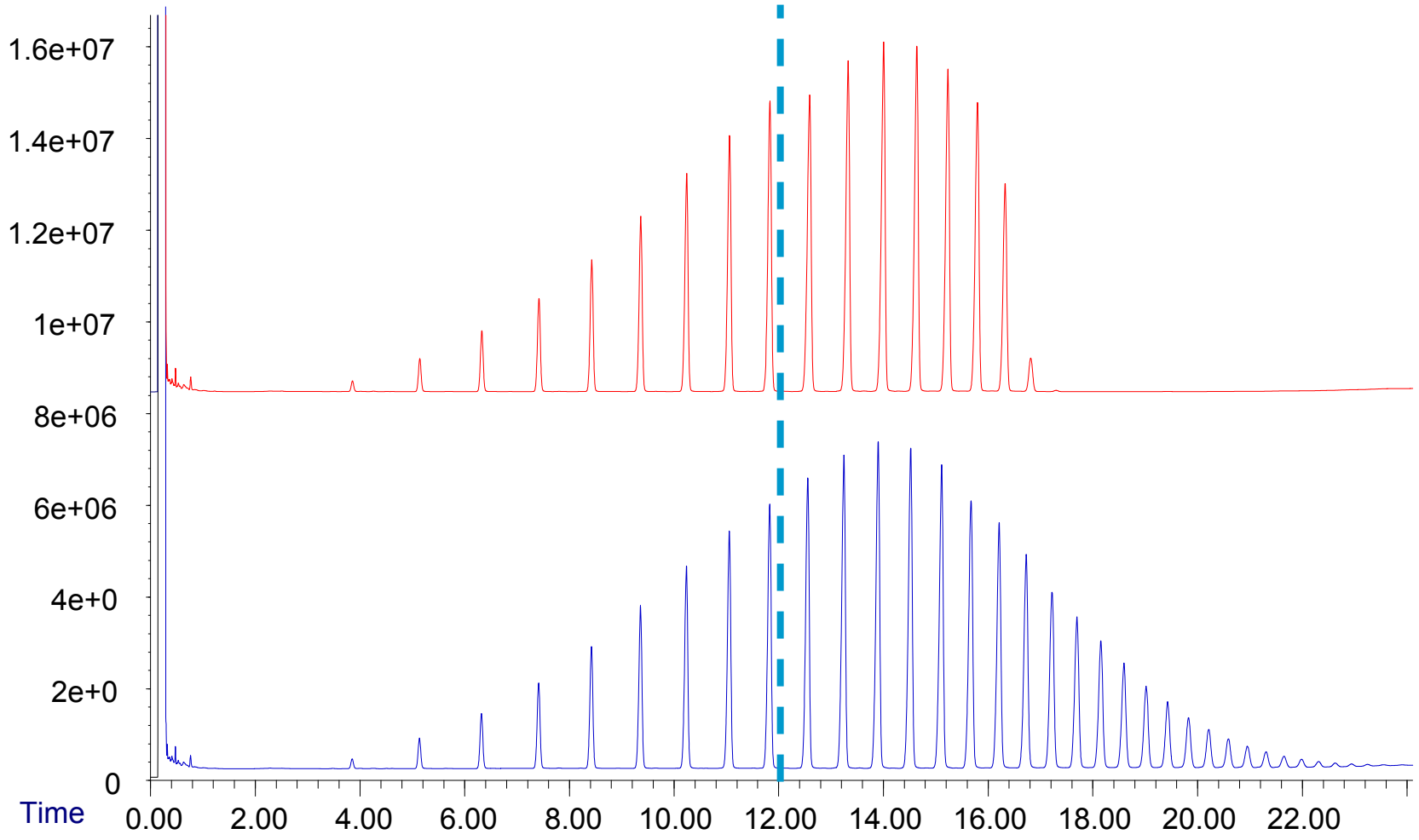
What are the limitations of using uncoated pre-columns for backflush?

- More difficult to determine backflush timing than post-column approach (but easier than coated column approach).
- Wider peaks than with coated column approach
- RT dependent on amount and sample matrix
- Highest possibility of sample degradation (least inert)
- Retention time most dependent on residual sample matrix

Retention in Retention Gaps



12 min BF vs. reference



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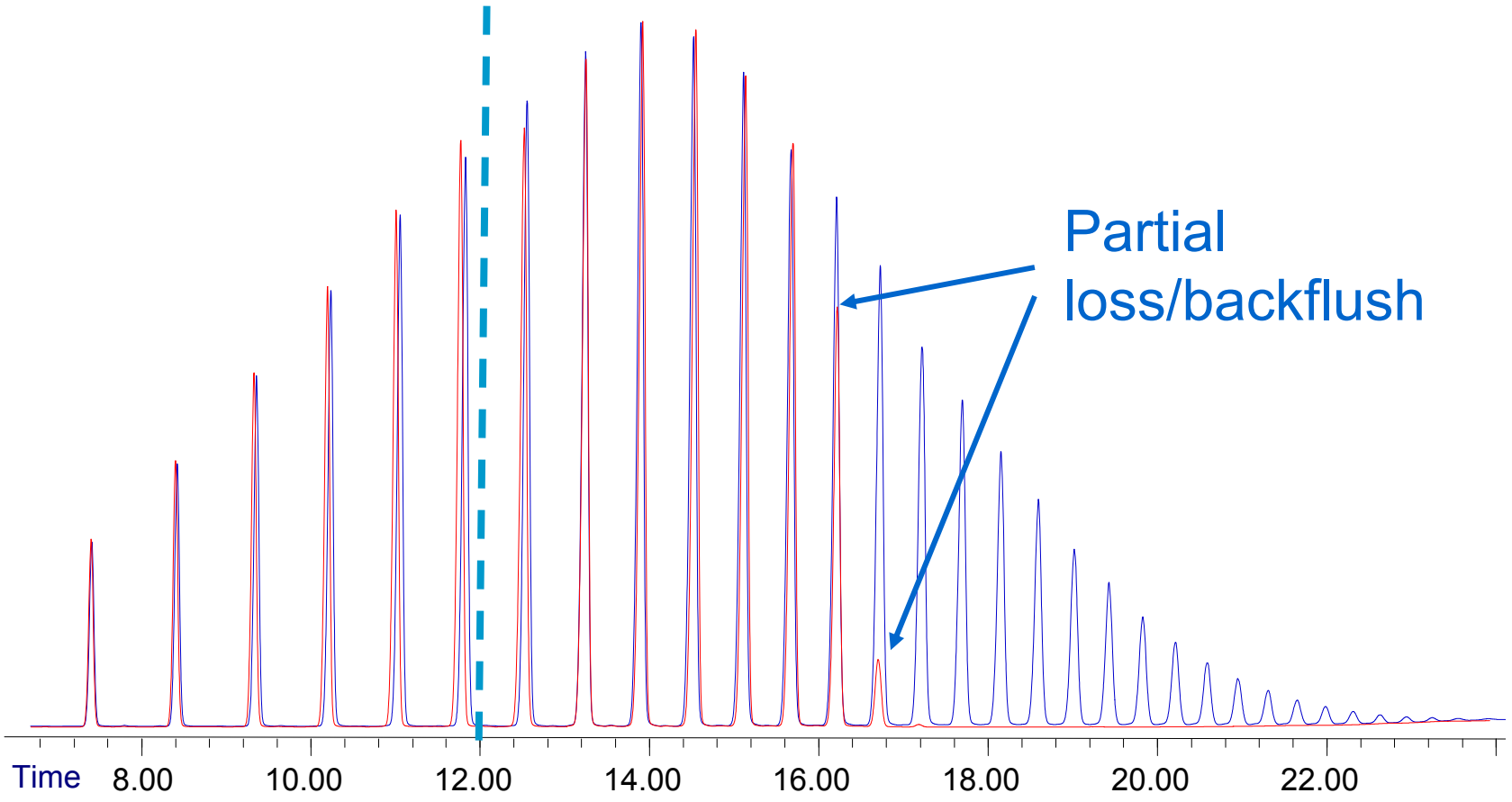
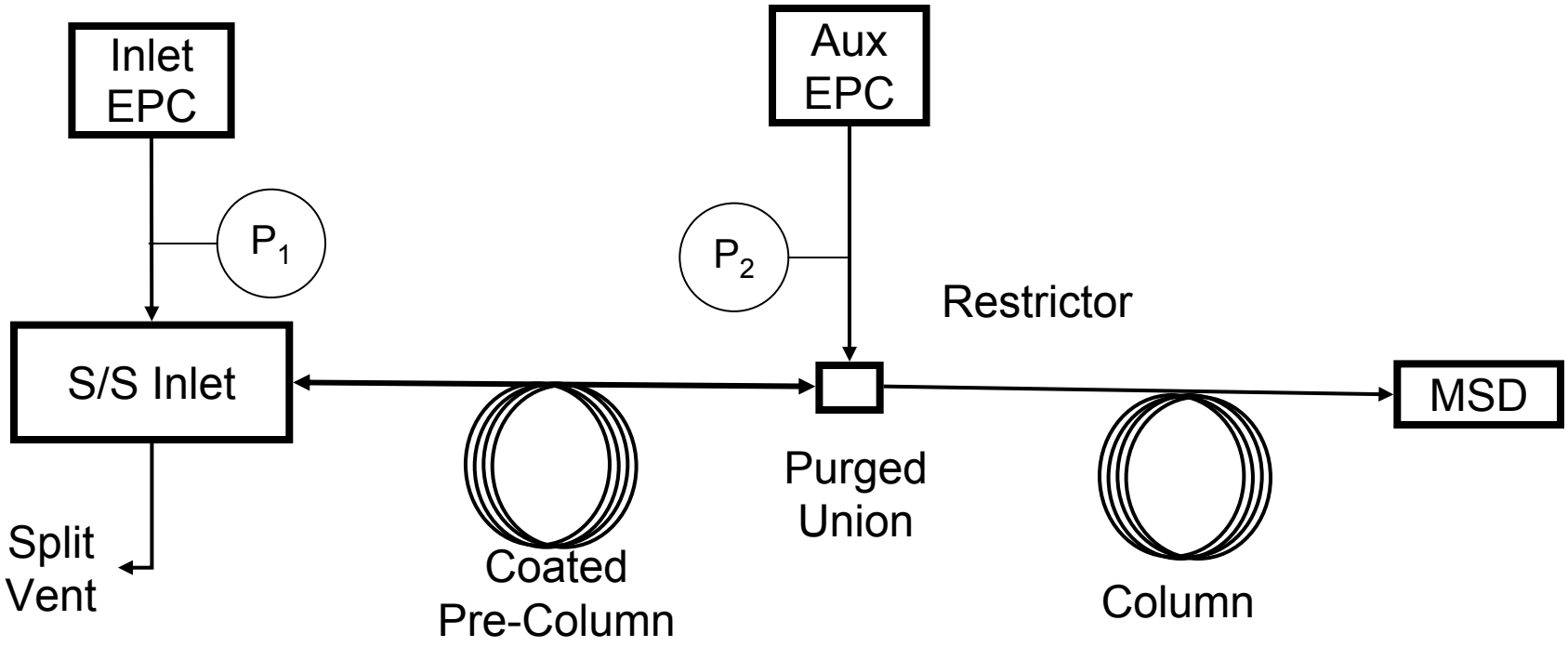
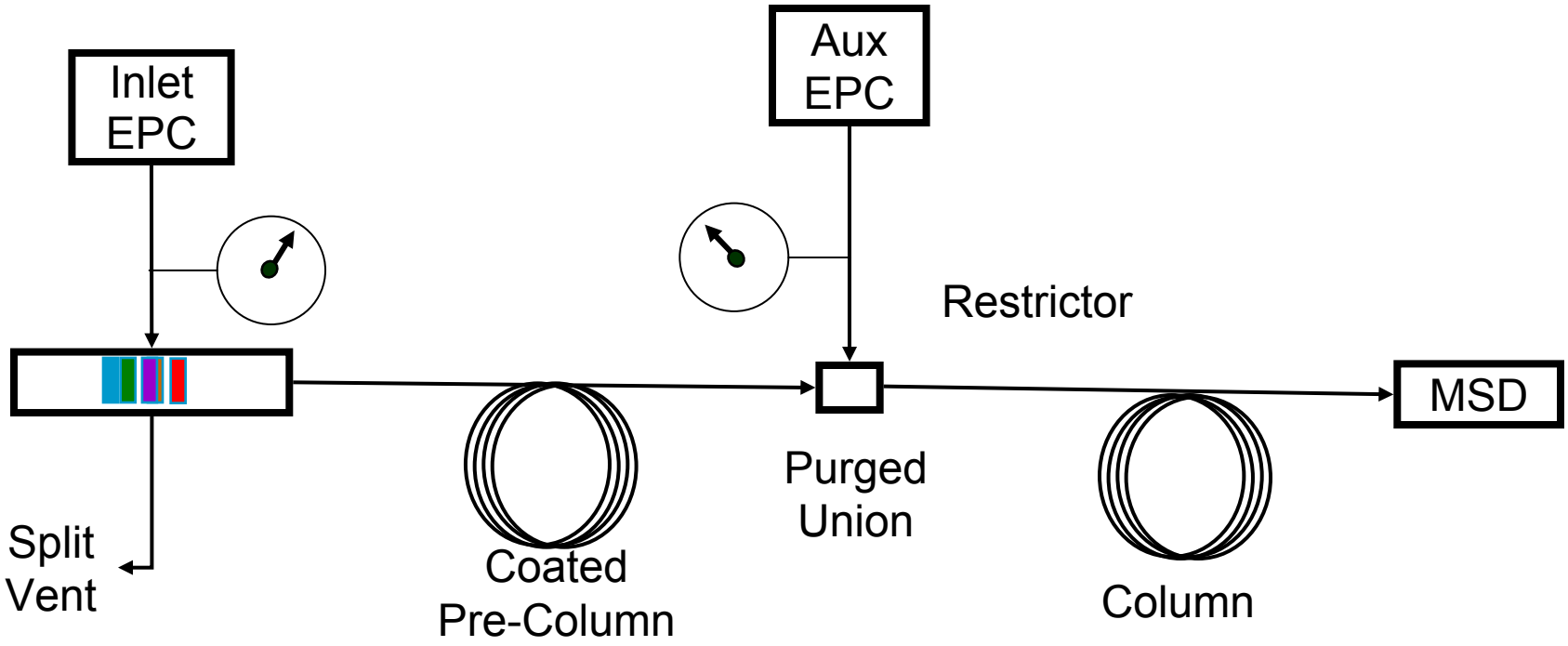


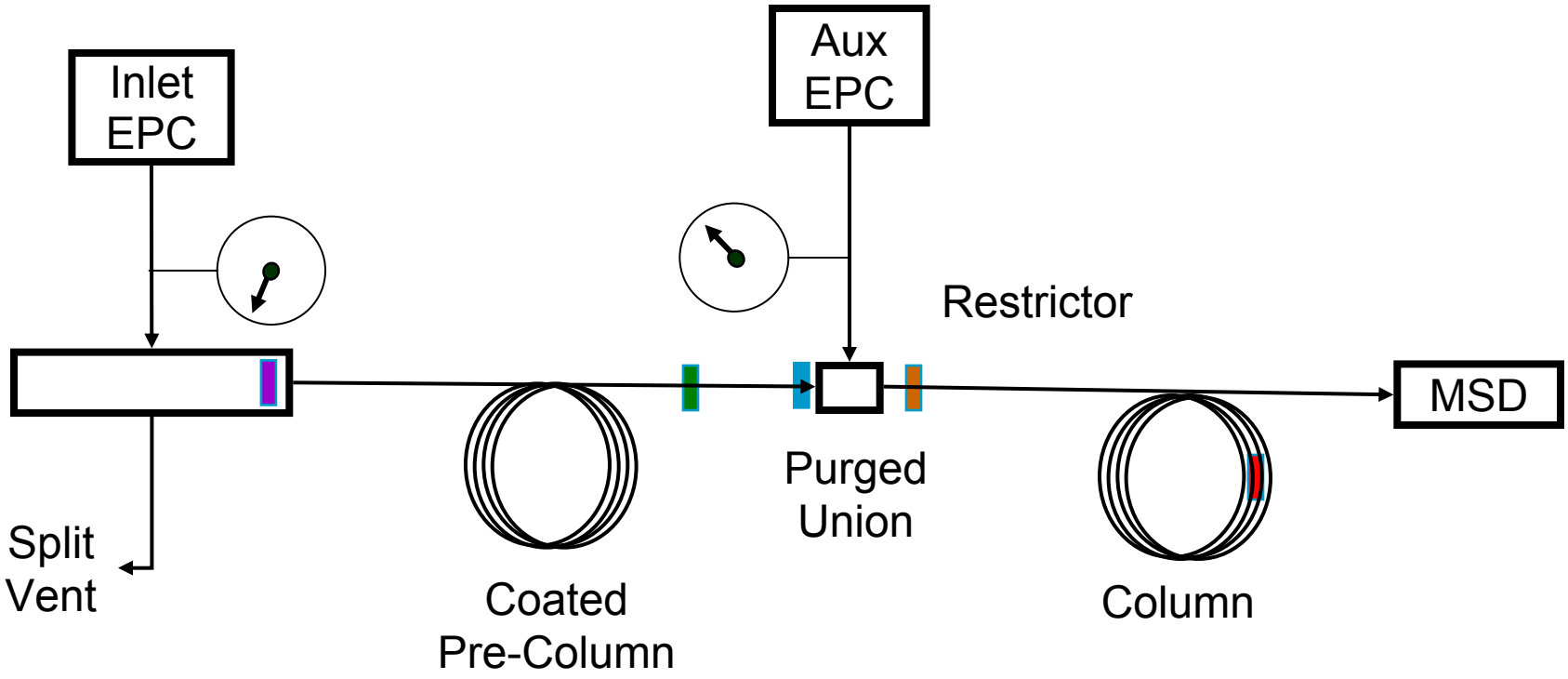
Coated Pre-Column Configuration



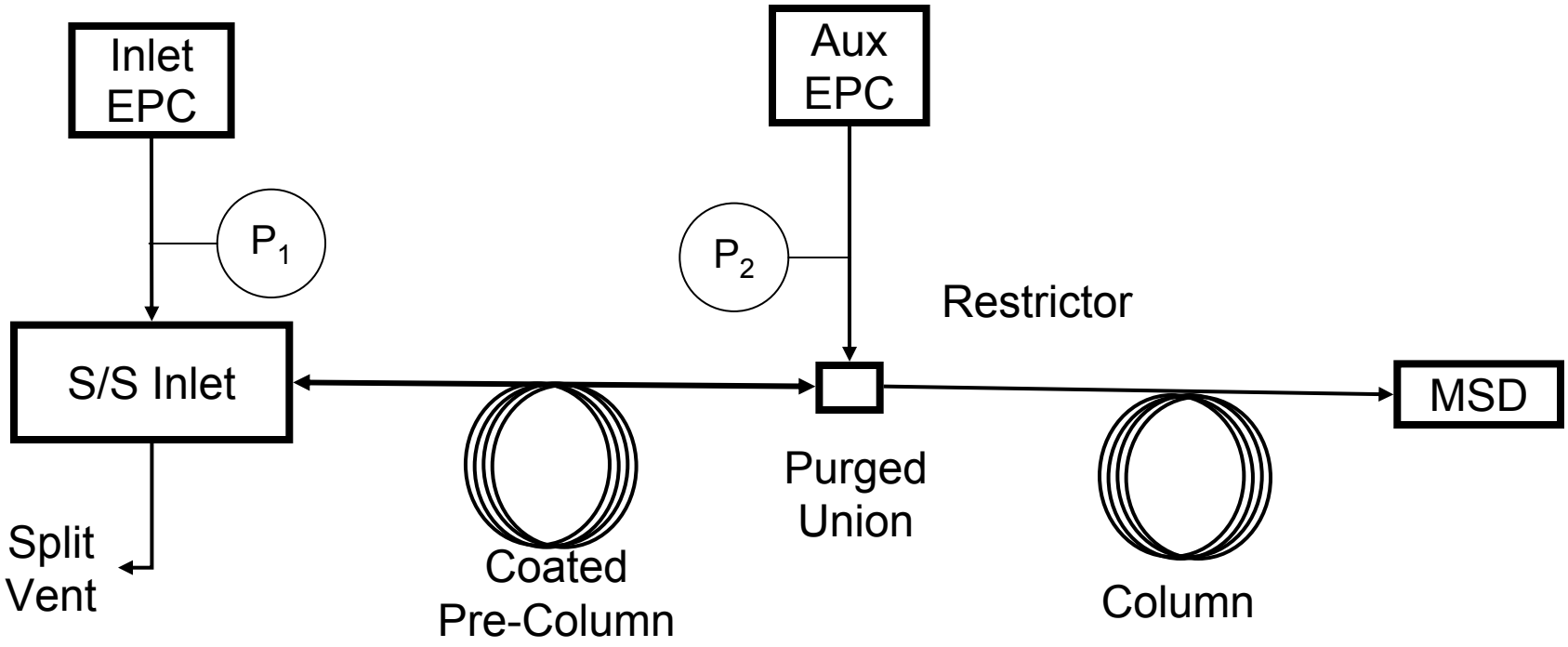
Coated Pre-Column Analysis



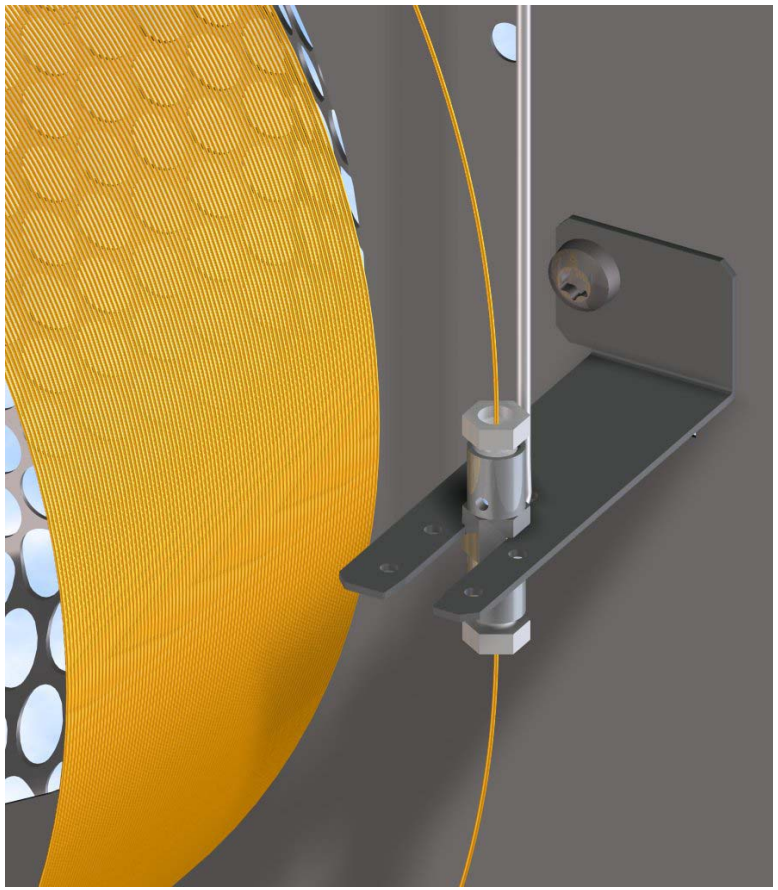
Coated Pre-Column Backflush



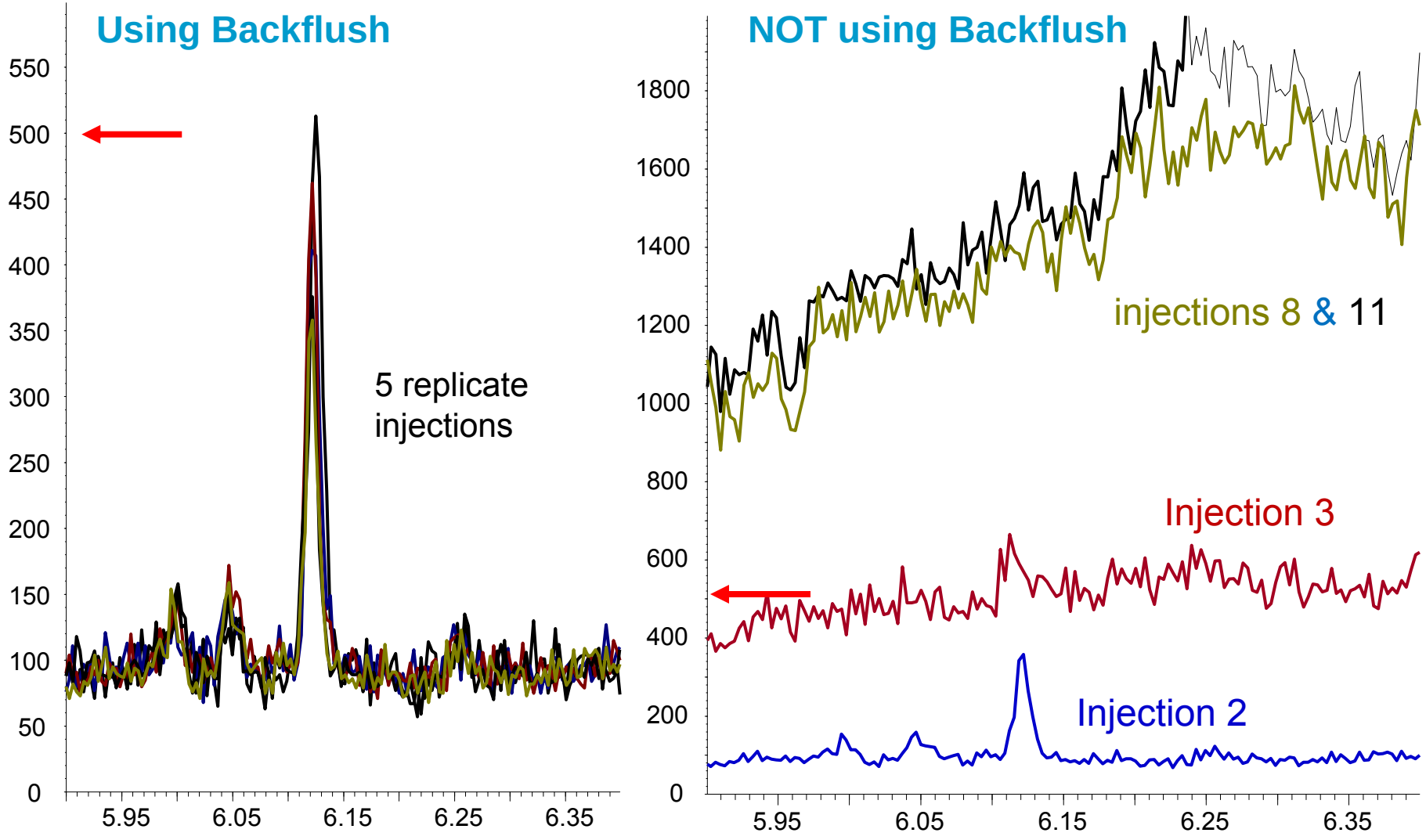
Coated Pre-Column Configuration



Purged Ultimate Union



100 OFN fg in 1% diesel



What are the benefits of using coated pre-columns for backflush?

- Most inert approach when analyzing “active” compounds
- Ability to tune onset of backflush between closely eluting components
- Backflushing can happen concurrent with the analysis (when short pre-columns are used)
- Compatible with diffusion pump MSDs
- Fairly simple to implement
  - Cut sections of existing columns to use as pre-columns
  - Use commercially available coated columns that total the length of original column (e.g., two 15 m columns instead of the original 30 m column)

What is the downside of using coated pre-columns for backflush?

- Most difficult approach to determine backflush temperature/time
- More expensive to replace than uncoated columns
- Backflushing occurs later into the run than with uncoated columns, so less time for concurrent backflush
- Longer backflushing times than with uncoated pre-columns
  - When using long pre-columns, lower reversed flow during backflush
  - Components are retained more because of stationary phase so need more column void volumes to backflush than with uncoated pre-columns
- Contaminants have more influence on retention times of subsequent runs than with uncoated pre-columns (same issue as post-column configuration).

Conclusions

Capillary column backflush provides many potential benefits for routine GC analyses

Three possible configurations offer some flexibility depending on sample and method constraints

Several available purged devices enable rugged and reliable implementation and automated control of capillary column backflushing