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Method Development for PFAS Compounds by GC-MS Using Virtual Method Development

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Introduction and Background

PFAS (per- and poly-fluoro alkyl substances) are a class of chemical compounds with many industrial and commercial applications, including non-stick surfaces, rain-repellent fabrics, electronics, and numerous others.

While many PFAS compounds, such as the carboxylates (PFCA) and sulfonates (PFSA) are ionisable and non-volatile, and therefore amenable to LC analysis, neutral PFAS compounds such as fluorotelomer alcohols (FTOH), acrylates (PFAcr), perfluorinated sulfonamides (FOSA) and sulfonamide ethanols (FOSE) are volatile and can be better analysed by GC (gas chromatography) and GC-MS (gas chromatography – mass spectrometry).

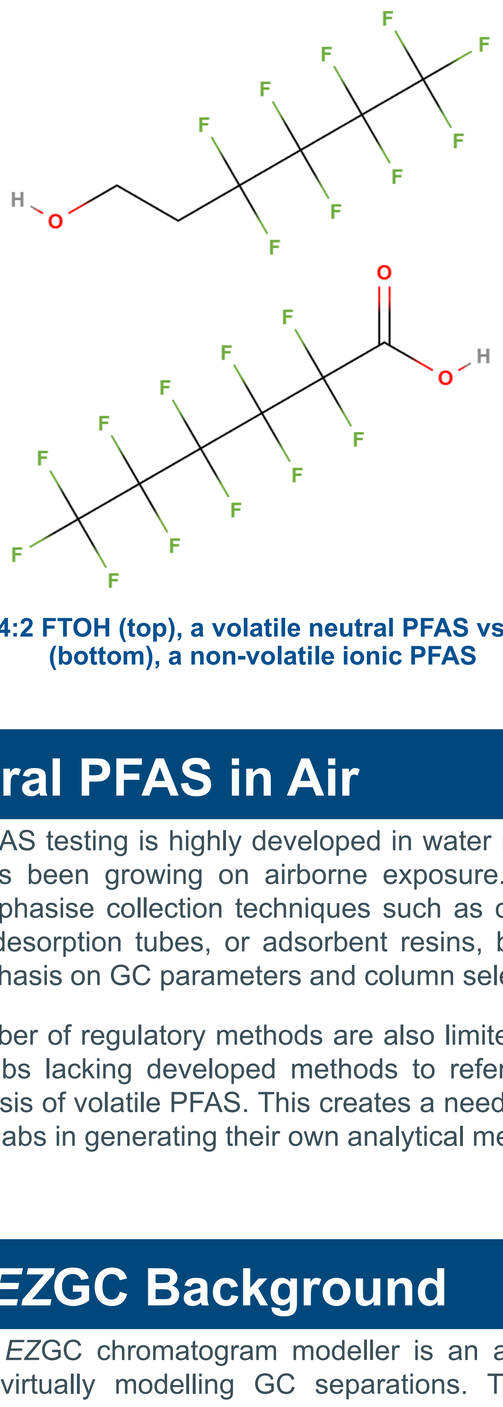

Fig 1. 4:2 FTOH (top), a volatile neutral PFAS vs. PFHxA (bottom), a non-volatile ionic PFAS

Neutral PFAS in Air

While PFAS testing is highly developed in water matrices, focus has been growing on airborne exposure. Studies often emphasise collection techniques such as canisters, thermal desorption tubes, or adsorbent resins, but place little emphasis on GC parameters and column selection.

The number of regulatory methods are also limited, which leaves labs lacking developed methods to reference for the analysis of volatile PFAS. This creates a need for tools to assist labs in generating their own analytical methods.

Pro *EZ*GC Background

The Pro *EZ*GC chromatogram modeller is an advanced tool for virtually modelling GC separations. This free, online simulator allows users to simply input a compound list and instantly receive separation conditions that can be implemented directly in the lab. Results can also be further refined to meet specific analytical needs. No experimental input is needed because Pro *EZ*GC models are based on robust algorithms and experimental data already generated by Restek's chemists.

The latest version of Pro *EZ*GC brings detector selection that allows you to model for both GC and GC-MS detection. With GC detection, Pro *EZ*GC behaves as it has in the past, separating targeted compounds by retention time. With GC-MS detection, compound targeting is focused only on those compounds in isobaric groups. This new version also has a refined Conditions tab interface, to enhance usability.

Try it out for yourself!

Current Models

Currently, Pro *EZ*GC libraries of PFAS have been made for the Rtx-200 and Rtx-VMS phases.

In order to provide selectivity for the highly fluorinated PFAS compounds, many applications and methods use a 200-type column, which has a trifluoropropylmethyl stationary phase. This phase provides excellent retention and separation of a broad range of polar compounds, such as solvents and chlorofluorocarbons, allowing for the analysis of neutral PFAS and other volatile compounds simultaneously.

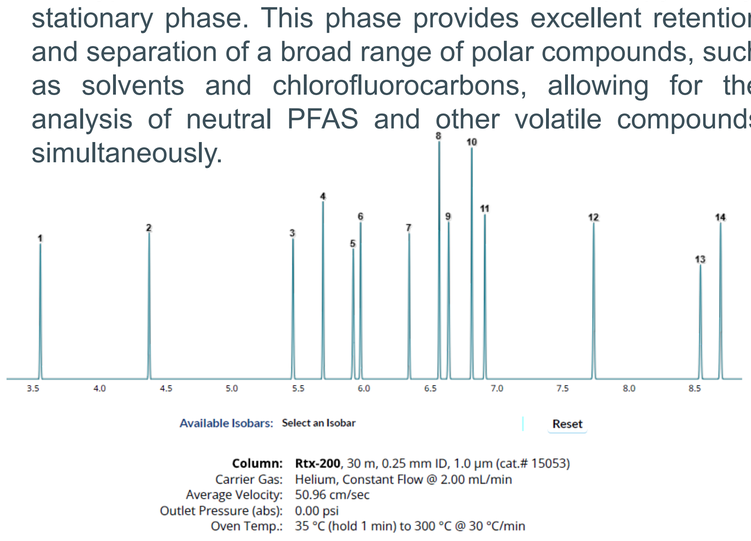

Fig 2. Modelled chromatogram of volatile PFAS

#	Compound	RT (min)	Temp (°C)
1	4:2 FTOH	3.55	111.5
2	6:2 FTOH	4.37	136.2
3	8:2 FTOH	5.46	168.8
4	10:2 FTOH	5.69	175.6
5	1*H*,1*H*-Perfluorooctyl methacrylate	5.92	182.5
6	6:2 FTMAC	5.97	184.2
7	8:2 FTMAC	6.34	195.2
8	10:2 Perfluoro dodecyl acrylate	6.57	202.0
9	8:2 Perfluorodecyl acrylate	6.64	204.1
10	10:2 FTMAC	6.81	209.3
11	NMeFOSA	6.91	212.3
12	NEtFOSA	7.73	237.0
13	NMeFOSE	8.54	261.2
14	NEtFOSE	8.69	265.8

Table 1. List of volatile PFAS compounds, retention times, and elution temperatures (bottom)

Column Selection and Flow

After initial model creation, the conditions tab allows for the selection of column dimensions and flow rates. In the example below the column length was changed to 60 meters and gas flow was optimised for efficiency over speed. In this case, this caused a co-elution between 8:2 and 10:2 Fluorotelomer alcohols.

Custom parameters allow for the selection of any column dimensions or flow rates, giving a high degree of flexibility in method parameters.

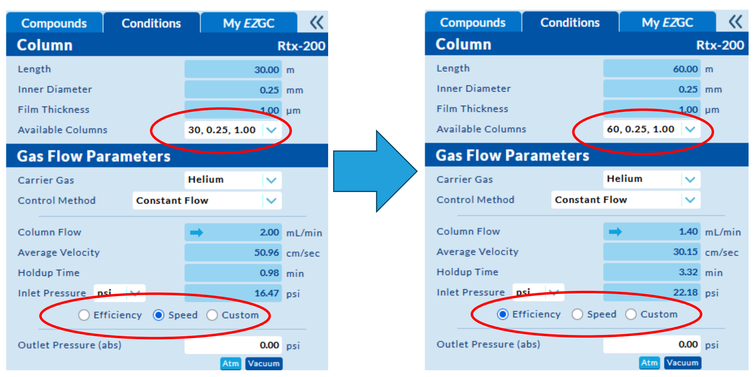

Fig 3. Adjustment of column length and flow (top), showing new modelled chromatogram with coelutions of compounds 3 and 4 (bottom)

Oven Conditions

Oven programs, including number of ramps and ramp rates, can also be adjusted. In this case, slowing the oven ramp allowed for separation of the co-eluting alcohols.

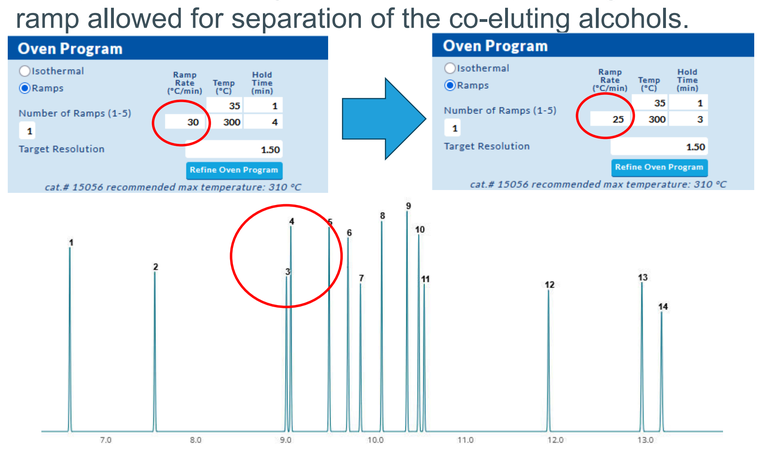

Fig 4. Adjustment of oven ramp (top), and separation of previously co-eluting compounds (bottom)

Pro *EZ*GC Model Vs. True Values

The accuracy of Pro *EZ*GC is shown below, where a modelled chromatogram is shown to be within 4% of the true value. Higher accuracy can be obtained with exact dead time and column length calculations, but this shows a high degree of accuracy even with nominal column lengths.

These models can be made within seconds, saving precious lab time, making Pro *EZ*GC a powerful tool that can simplify your PFAS method development needs.

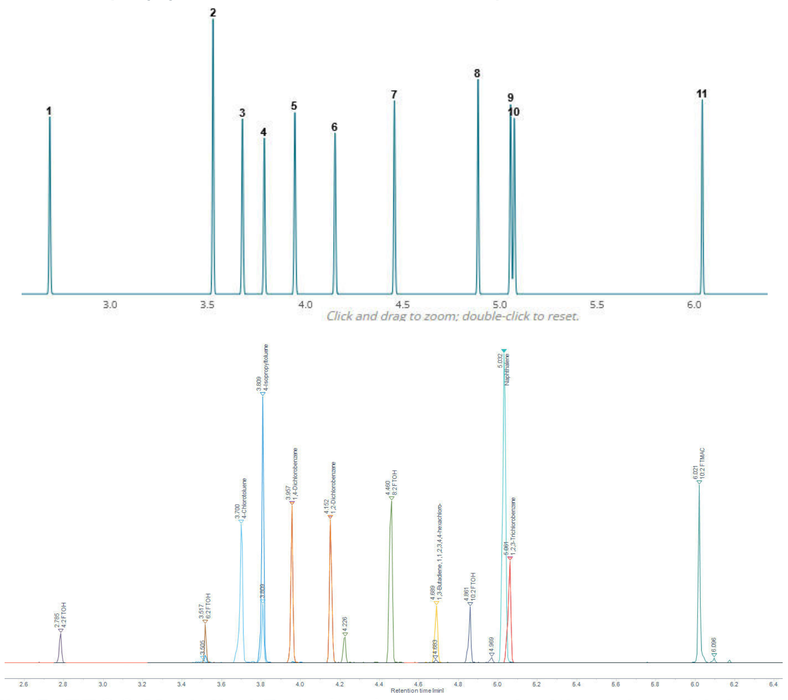

Fig 5. EZGC Modelled Data (top), compared with real world data (bottom) highlighting retention time accuracy

#	Compound	*EZ*GC (min)	Actual (min)	Accuracy
1	4:2 FTOH	2.69	2.78	96.8%
2	6:2 FTOH	3.52	3.52	100.0%
3	4-Chlorotoluene	3.68	3.70	99.5%
4	4-Isopropyltoluene	3.79	3.81	99.5%
5	1,4-Dichlorobenzene	3.94	3.96	99.5%
6	1,2-Dichlorobenzene	4.15	4.15	100.0%
7	8:2 FTOH	4.46	4.46	100.0%
8	10:2 FTOH	4.88	4.86	100.4%
9	Naphthalene	5.05	5.03	100.4%
10	1,2,3-Trichlorobenzne	5.07	5.06	100.2%
11	10:2 FTMAC	6.04	6.02	100.3%

Table 2. Pro *EZ*GC model vs actual chromatogram (top), and accuracy of modelled vs actual chromatogram (bottom)

Future Work

With the ever-growing list of potential PFAS contaminants, the Pro *EZ*GC modeller will be updated with new compounds periodically to address customer and regulatory needs.

In addition, additional column phases will be added to allow for simultaneous analysis of PFAS and other volatile and semi-volatile contaminants.

For more information about this poster presentation, please contact john.gallant@restek.com

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