

# Esempi analisi PFAS in campioni di Acque

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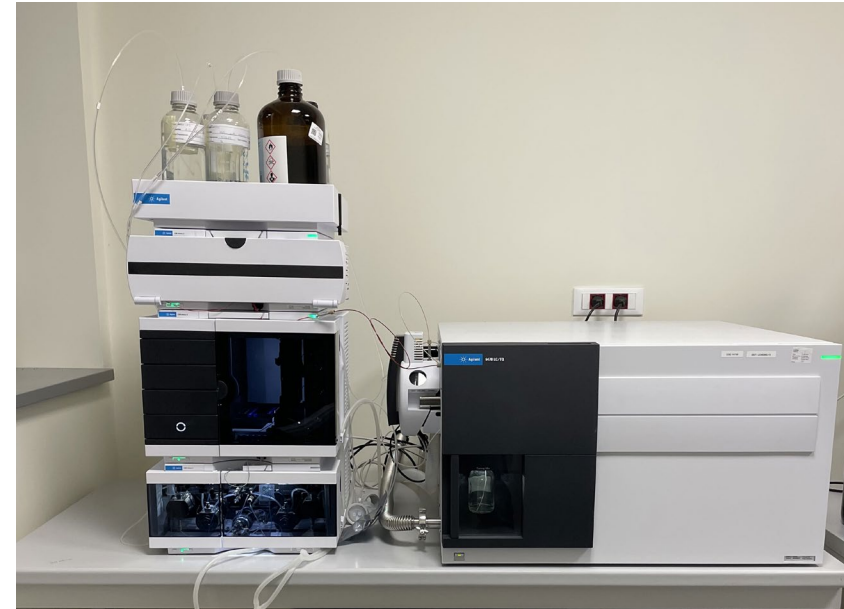
# Condizioni Strumentali

La fase di analisi strumentale viene condotta impostando le seguenti condizioni:

- Sistema HPLC-MS-MS: Agilent UPLC 1290 infinity II accoppiato con spettrometro di massa Agilent LC-MS 6495;
- Colonna: Phenomenex Luna Omega C18 RRHD Eclipse plus C18 100\*2.1 mm 3µm;
- Fase mobile: A:acqua ultrapura con 2 mM Ammonio acetato  
B: Metanolo assoluto;
- Flusso: 0.4 mL/min;
- Eluizione: gradiente;
- Stop time: 15 minuti;
- Temperatura colonna: 30°C;
- Volume di iniezione: 15 µl.

Di seguito sono riportati alcuni parametri impostati nella sorgente dello spettrometro di massa per eseguire l'analisi:

- Modalità acquisizione: ESI-;
- Gas temp.: 160 C;
- Capillary: 2500v;
- Nozzle: 500;
- Gas flow: 11 l/min.;
- Nebulizer: 30 V;
- Sheat gas temp.: 375°C;
- Sheat gas flow: 12 l/min..



# Maggiori criticità

- Effetti di sovrastima
  - - facilità di contaminazioni:
    - PFOA e PFBA
    - Necessità di una colonna di «ritardo» tra pompa e autocampionatore
    - Sistema di fluidica «PFC Free»
- Effetti di sottostima
  - - adsorbimenti: soprattutto su vetro
    - Analiti maggiormente interessati: PFAS a catena lunga  $\geq 10$
    - Attenzione al campionamento
- Difficoltà reperimento MR (ADV, cC604)
- Elenco sempre in evoluzione
- Incompatibilità metodi/normative (Reg. Piemonte, Reg. Veneto) per limiti e campo di applicazione (enti di accreditamento)



# Analisi PFAS in campioni di acque di scarico...ecc..

Metodi utilizzati:

-Iniezione diretta con ASTM D7979-20

-Preconcentrazione con ISO 21675-19

- Range calibrazione: 0.01-0.050-0.1-0.5-1-5-10 ug/L di ogni singolo PFAS in soluzione

## Il metodo ASTM-D7979-20

Il metodo ASTM-D7979-20 prevede un iniezione diretta del campione previa diluizione di questa con una pari quantità di metanolo e l'aggiunta di un'opportuna quantità di acido acetico e soluzione di PFAS marcati (surrogati).

Fattore di diluizione: 2

LOQ finale sul campione pari a **0.02 ug/L**

## Il metodo ISO 21675-19

Il metodo ISO 21675-19 prevede un'estrazione solido-liquido del campione con l'utilizzo di opportune cartucce adsorbenti (SPE WATERS OASIS Wax 500 mg 6cc) e una successiva concentrazione del campione sotto flusso di azoto.

Dopo aver montato accuratamente il sistema da vuoto si procede come segue:

### ***Condizionamento della colonna SPE, caricare nell'ordine:***

4 ml di una soluzione di metanolo + 0.1% NH<sub>3</sub>;

4 ml metanolo;

4 ml di acqua Q1 ultrapura (evitando di mandare a secco la parte adsorbente a fine condizionamento).

### ***Estrazione campione:***

**50 ml** di campione opportunamente addizionata con la soluzione di PFAS marcati in qualità di surrogati (il volume di campione può variare a seconda della natura dell'acqua campione), è consigliabile mantenere un flusso di 3-6 ml/min.

### ***Eluizione, nell'ordine:***

4 ml di tampone acetato 25mM a pH 4, scartare questa frazione di eluato, quindi centrifugare la cartuccia per rimuovere eventuali residui solidi dalla stessa (in caso di campioni limpidi evitare questo passaggio);

4 ml di metanolo;

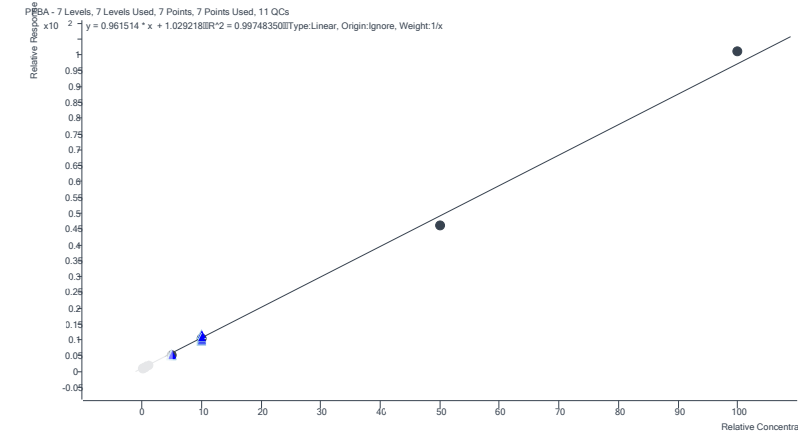
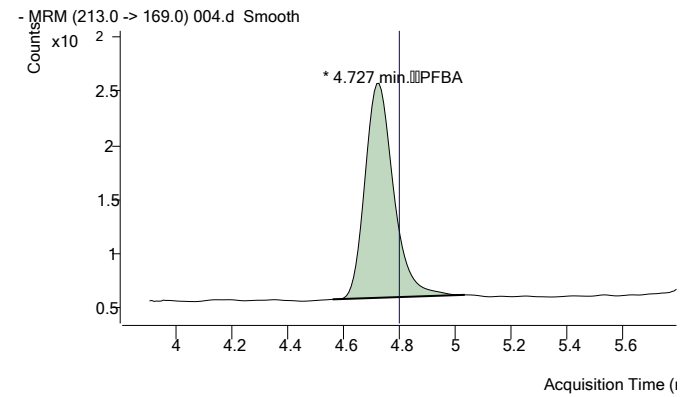
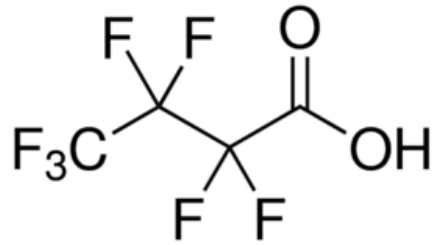
4 ml di metanolo + 0,1% di NH<sub>3</sub>.

Concentrare l'estratto sotto flusso di azoto fino a piccolo volume, quindi riportare ad un volume finale di 5 ml con una miscela acqua:Metanolo 50:50. L'estratto così ottenuto è pronto per la successiva determinazione in HPLC-MS-MS.

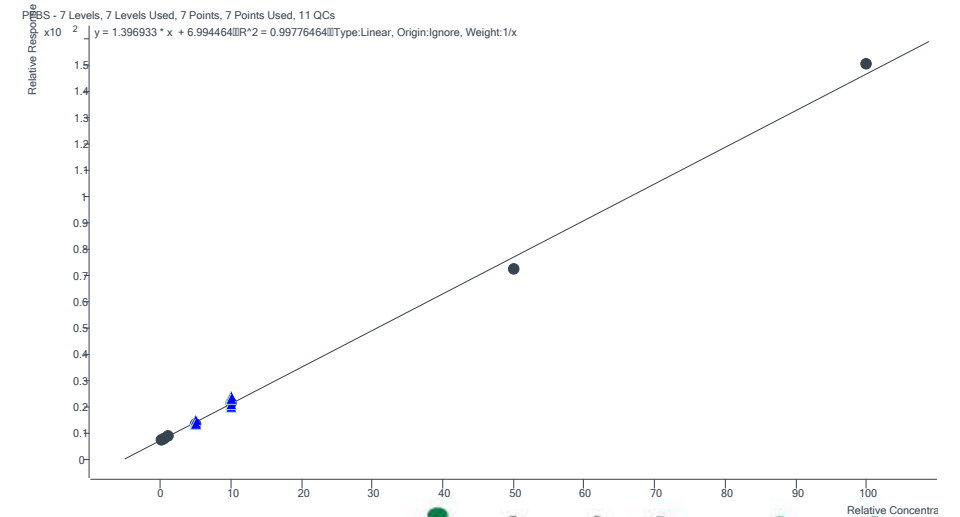
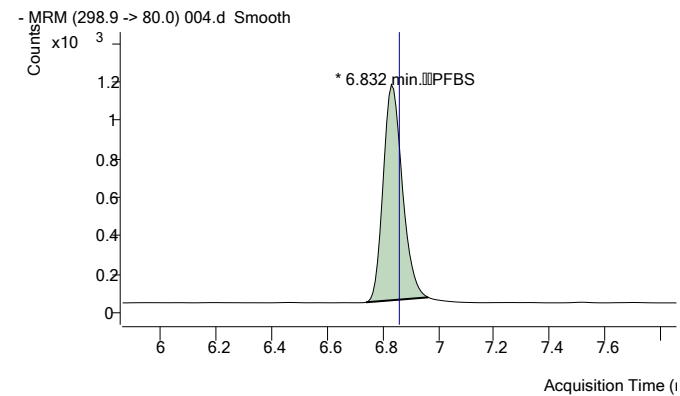
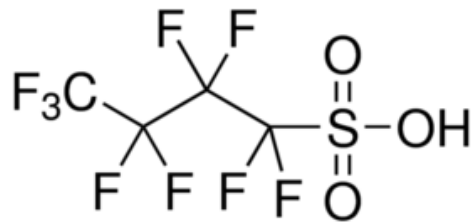
Fattore di preconcentrazione: 10

LOQ finale sul campione pari a 0.001 ug/L

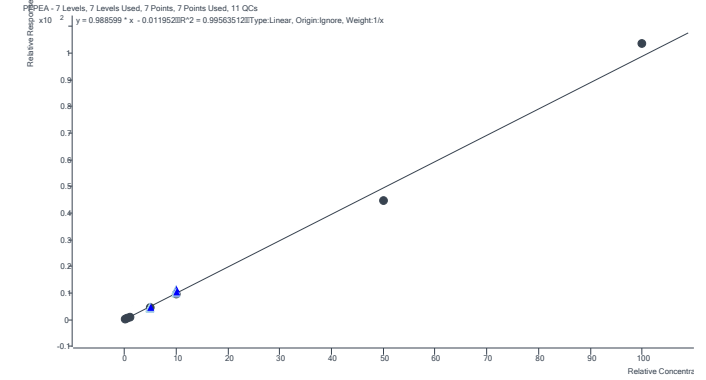
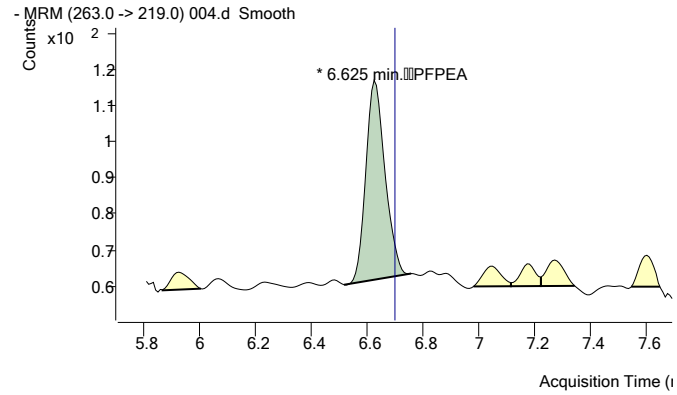
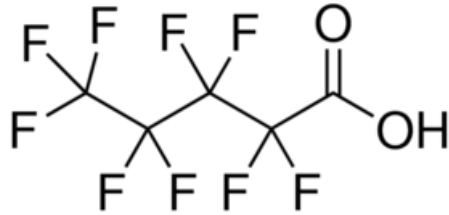
## Perfluorobutanoic acid (PFBA) CAS:375-22-4



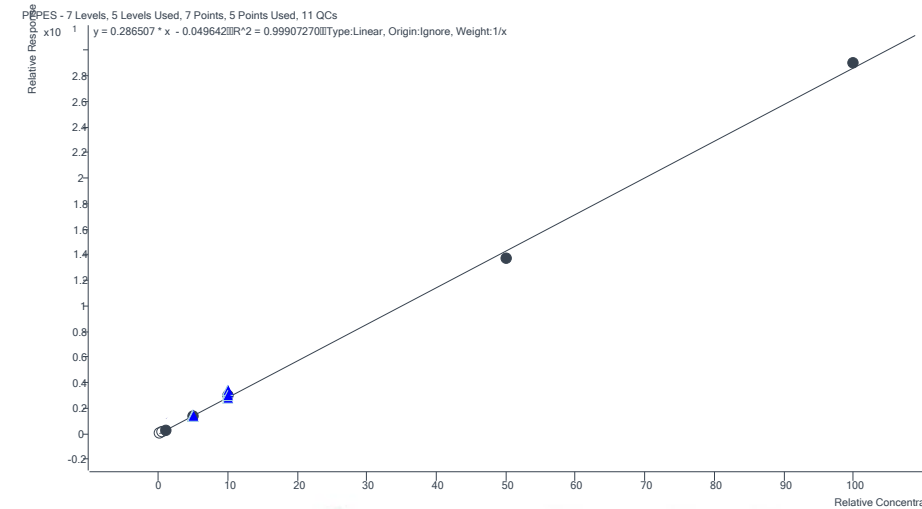
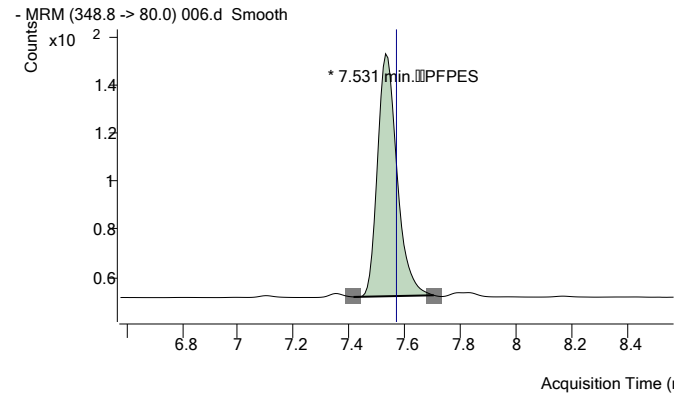
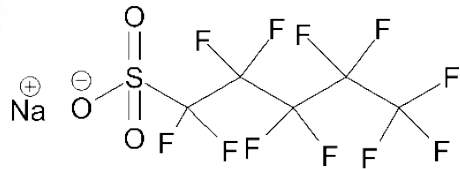
## Perfluorobutane sulfonic acid (PFBS) CAS:375-73-5



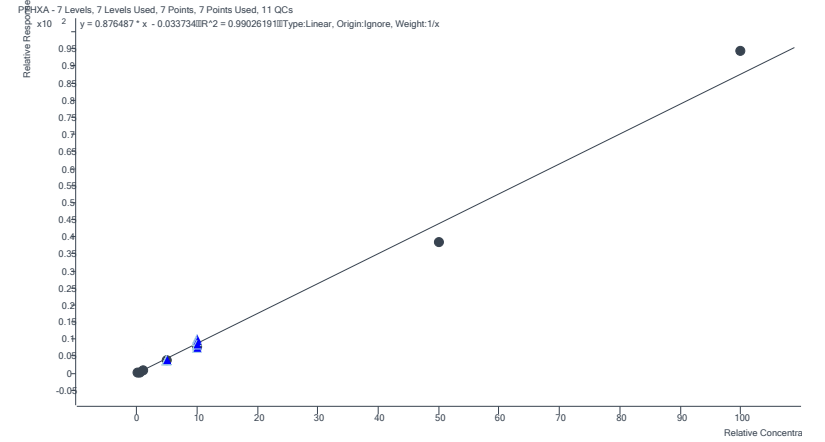
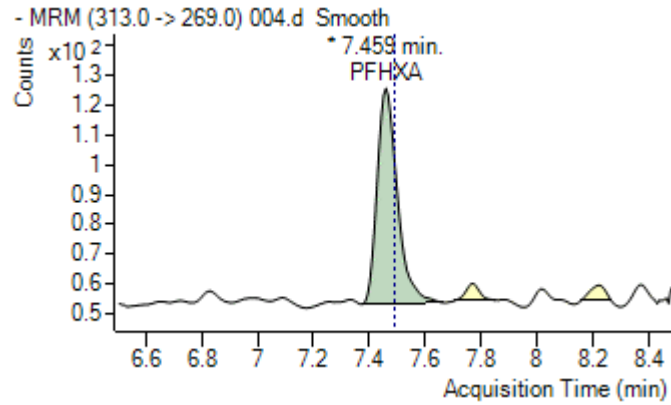
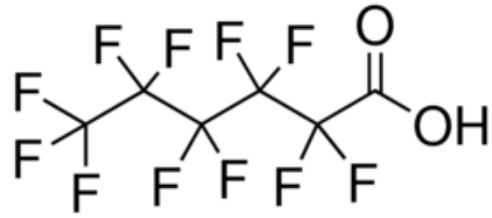
## Perfluoropentanoic acid (PFPeA) CAS:2706-90-3



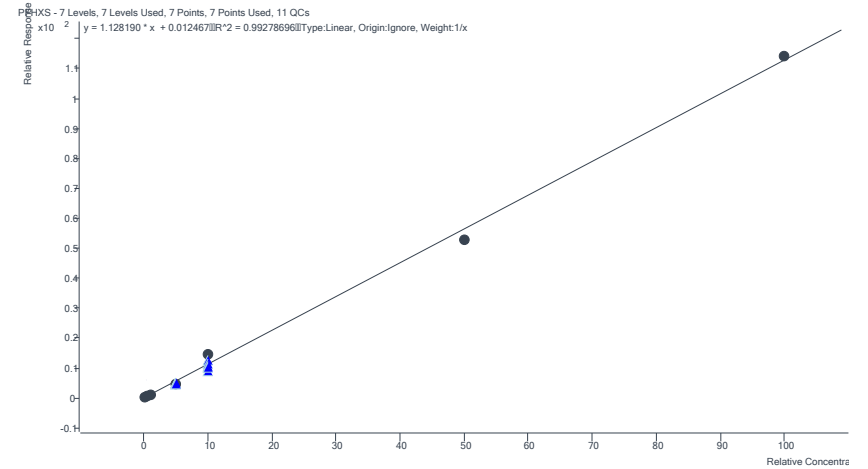
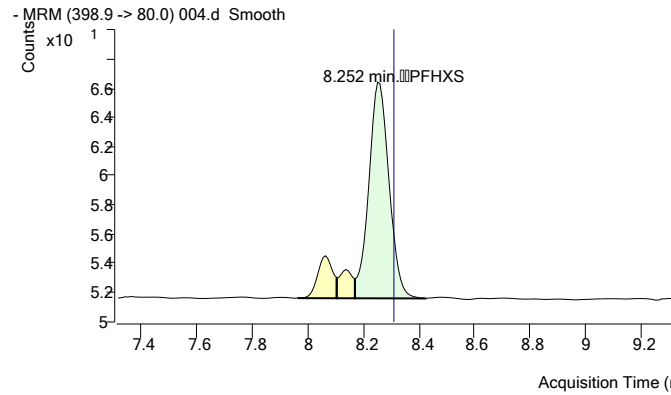
## Perfluoropentanesulfonic acid PFPeS 630402-22-1



# Perfluorohexanoic acid (PFHxA) CAS:307-24-4

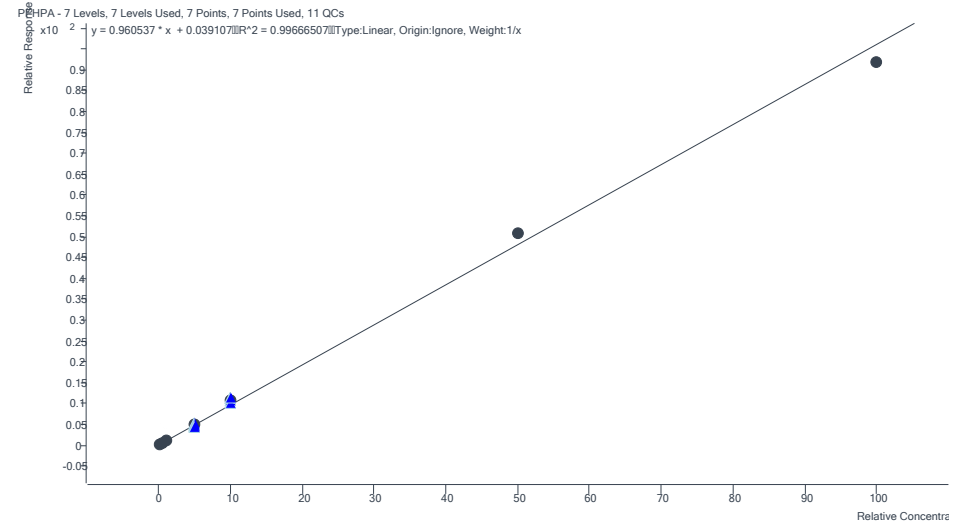
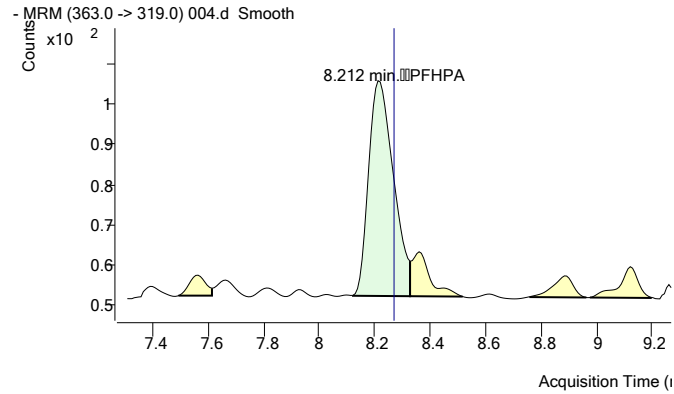
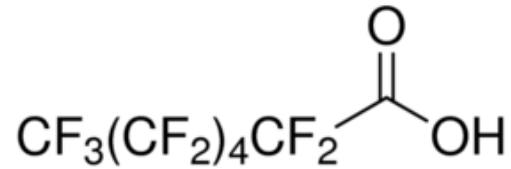


# PFHXS perfluorohexane sulfonic acid 3871-99-6

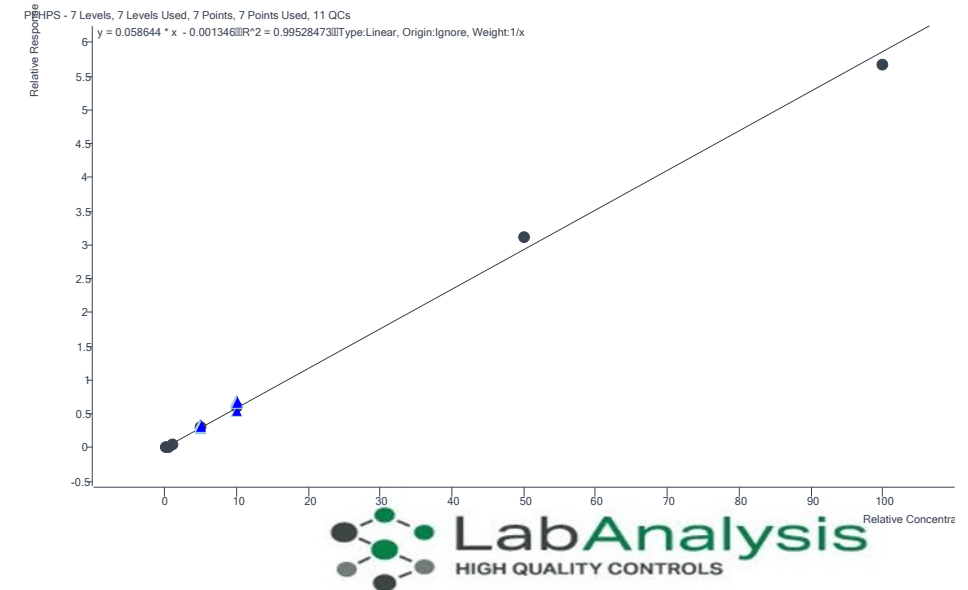
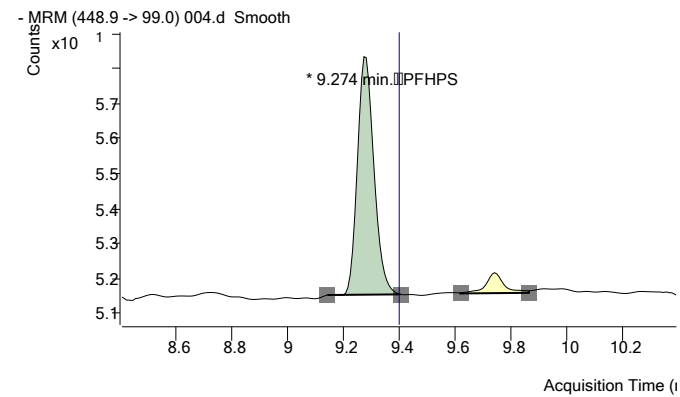
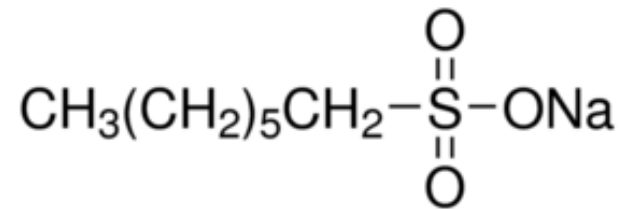




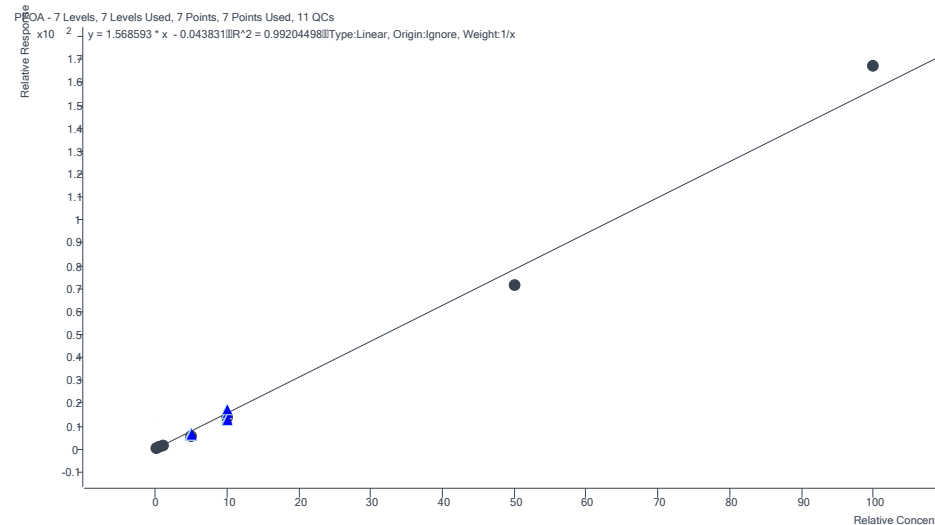
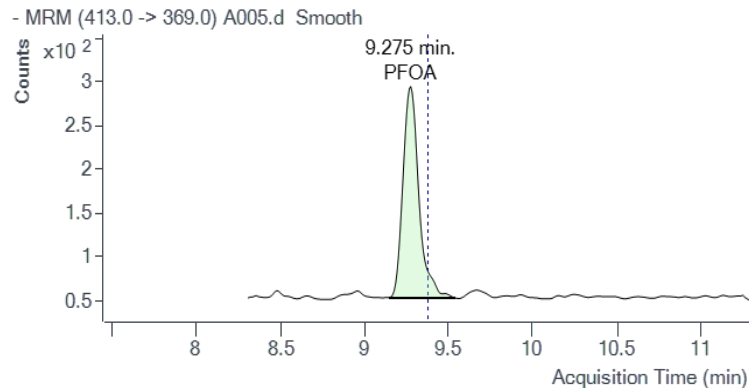
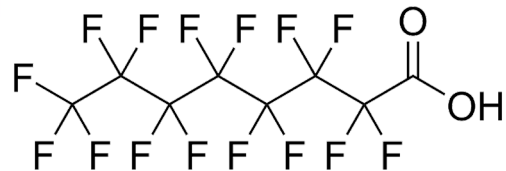
## PFHPA perfluoroheptanoic acid 375-85-9



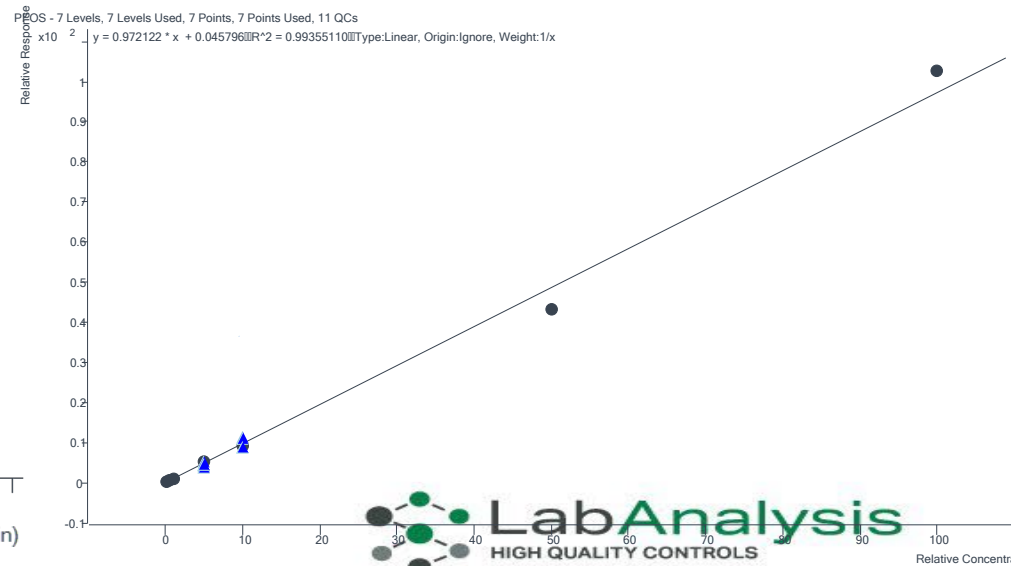
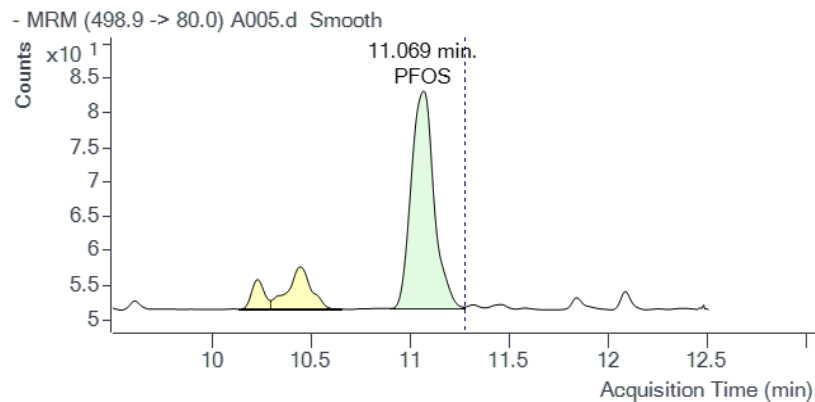
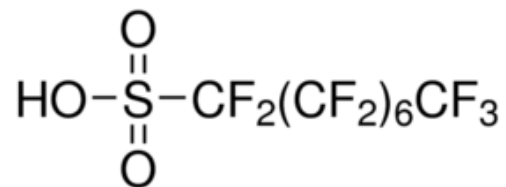
## PFHPS perfluoroheptanesulfonic acid 21934-50-9



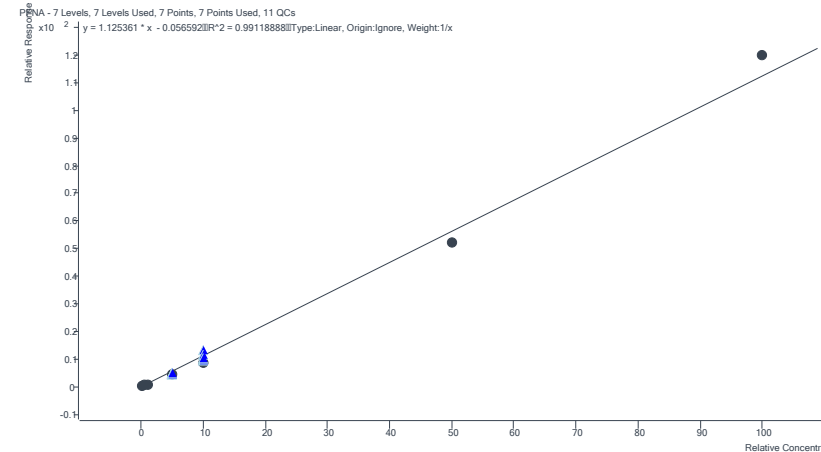
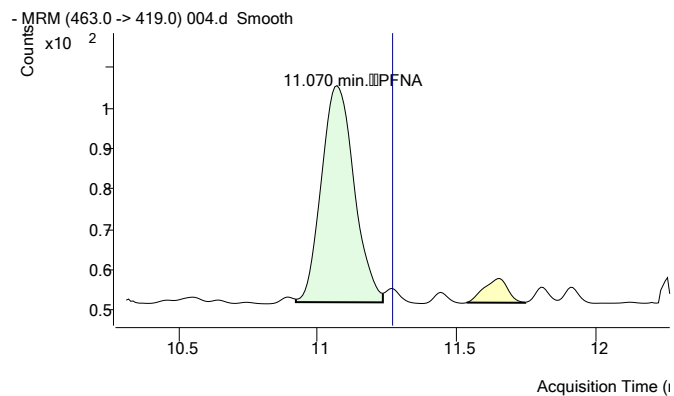
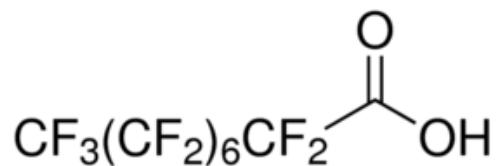
## Perfluorooctanoic acid (PFOA) 335-67-1



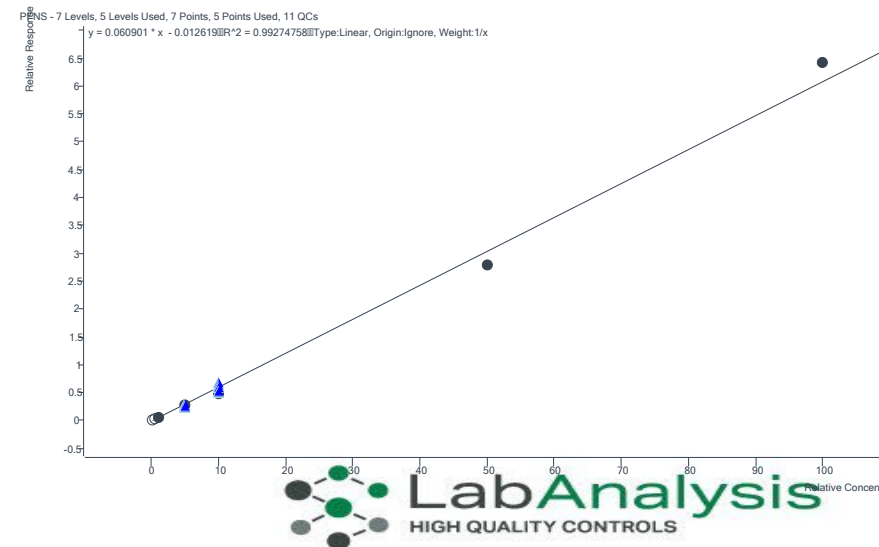
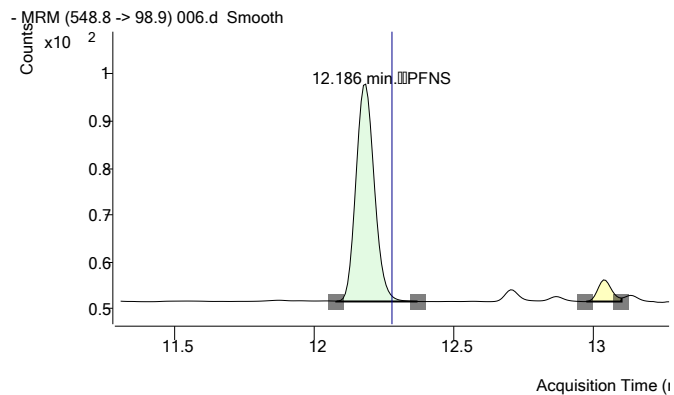
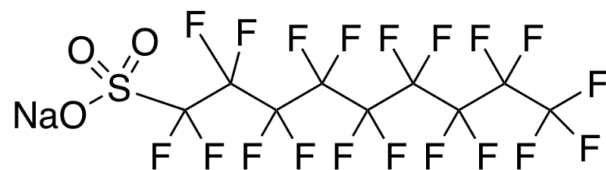
## PFOS perfluorooctane sulfonic acid 1763-23-1



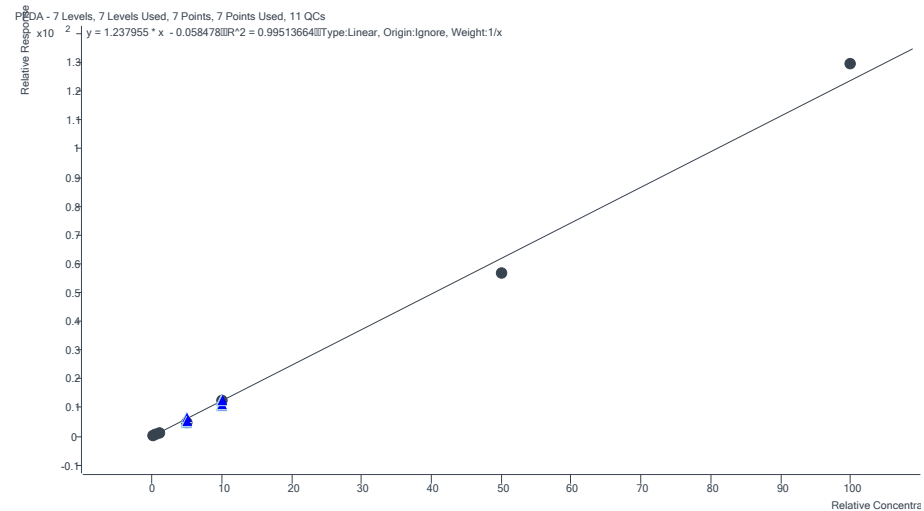
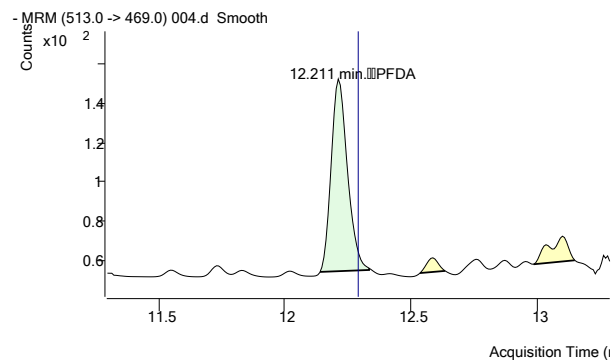
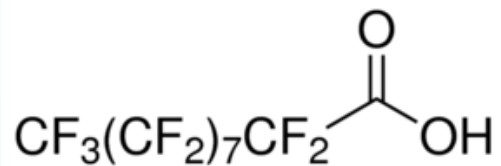
## PFNA perfluorononanoic acid 375-95-1



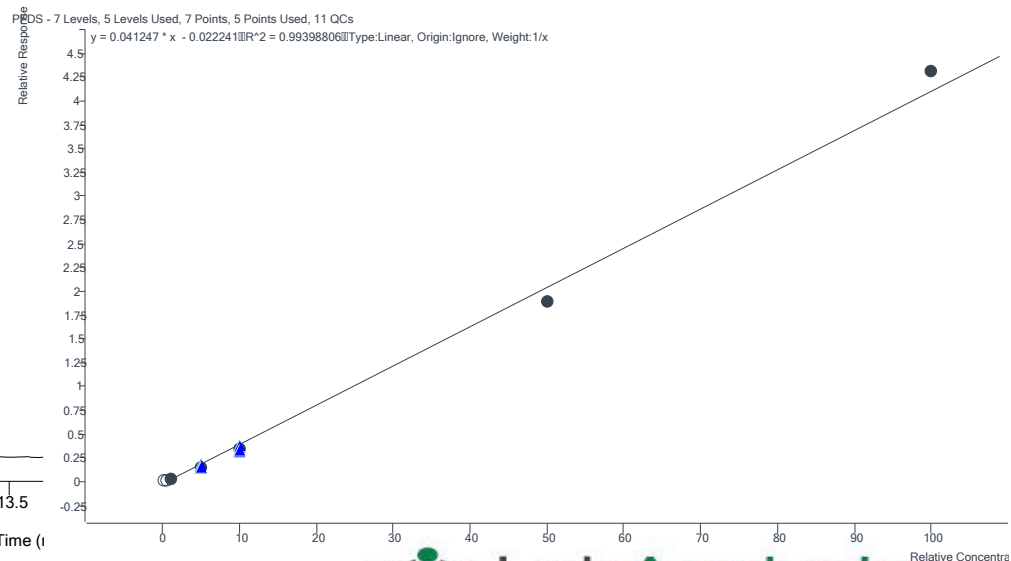
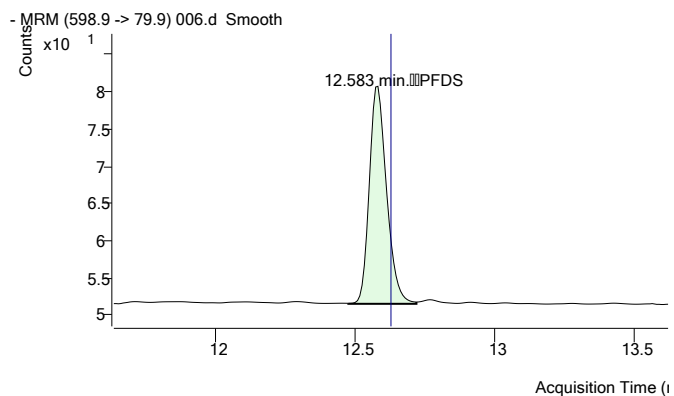
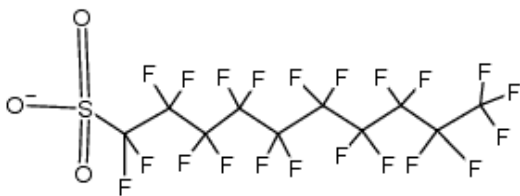
## PFNS perfluorononanesulfonic acid 98789-57-2



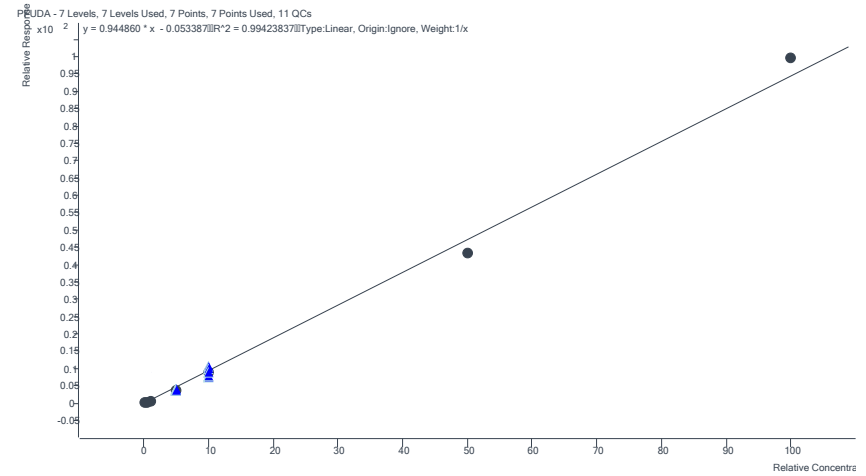
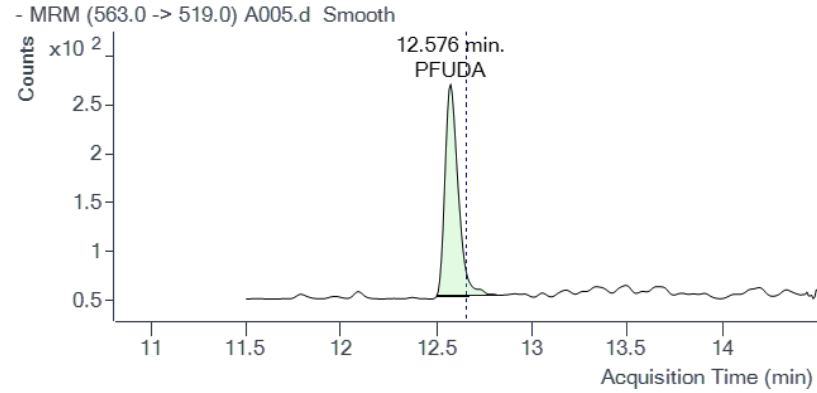
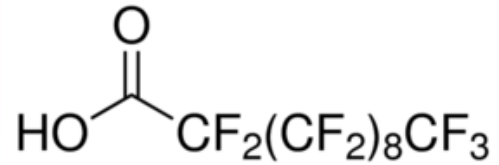
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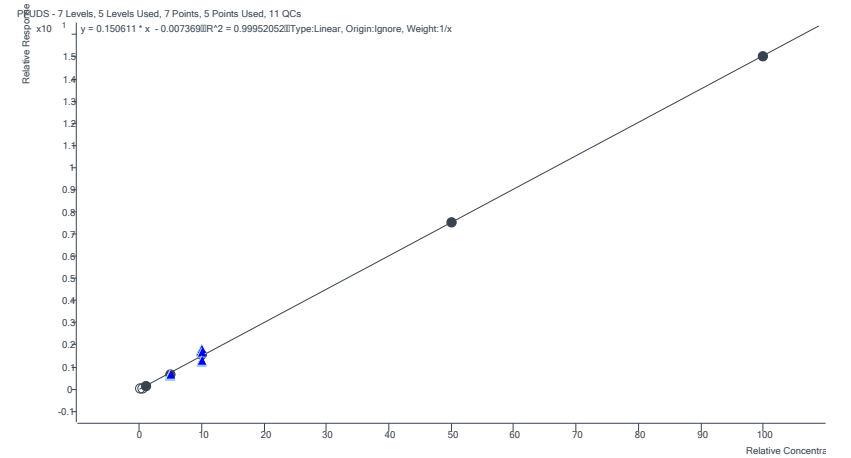
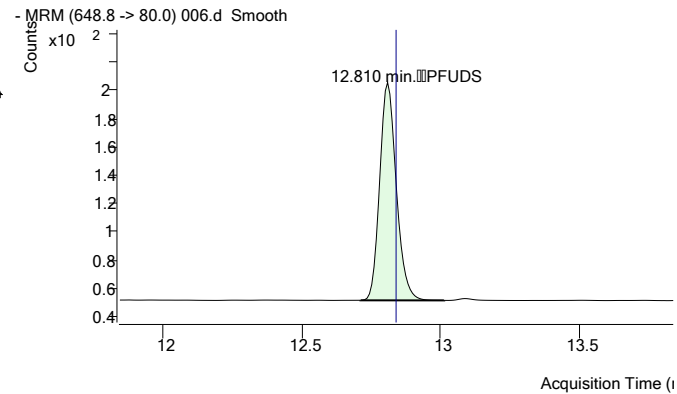
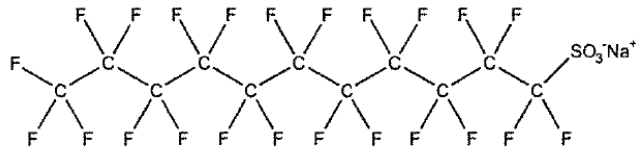
## PFDS perfluorodecanesulfonic acid 2806-15-7



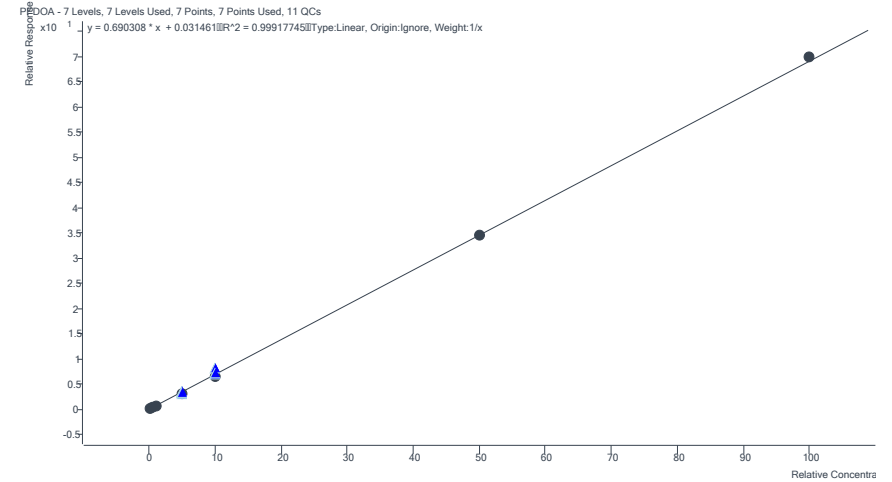
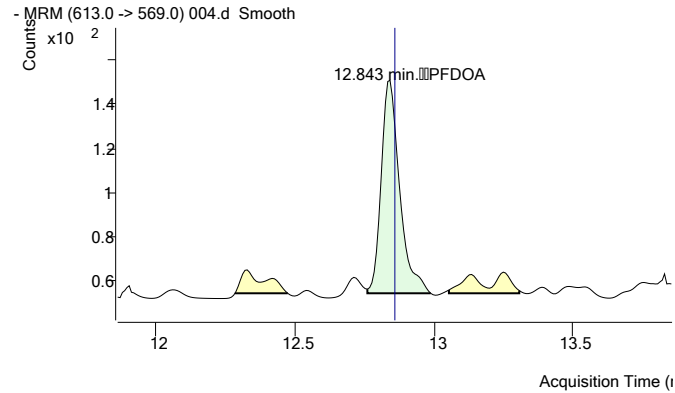
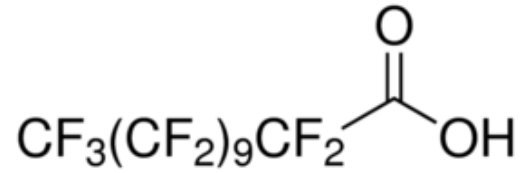
## PFUdA perfluoroundecanoic acid 2058-94-8



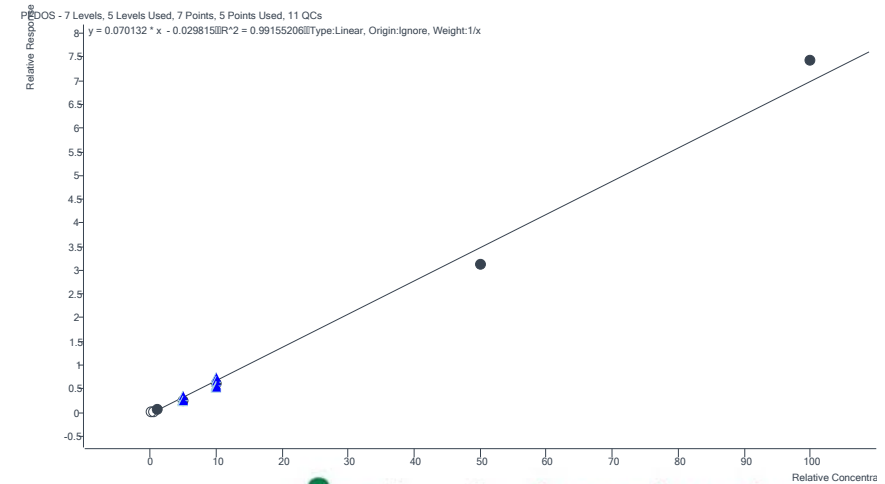
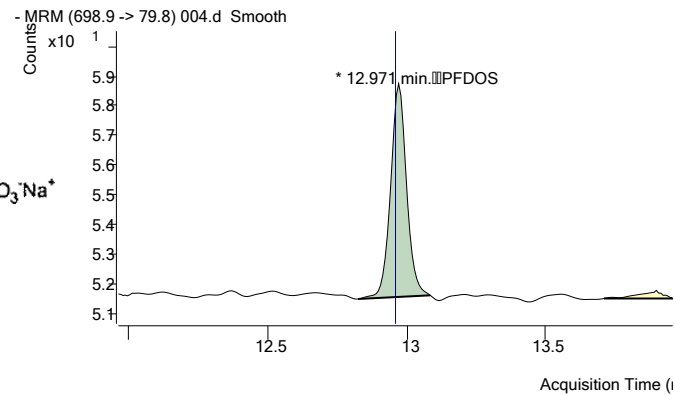
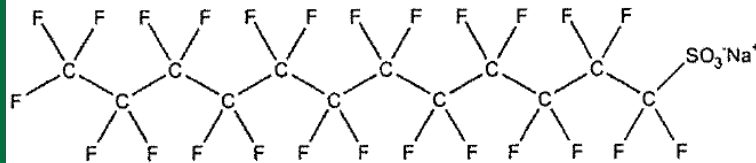
## PFUdS perfluoroundecanesulfonic acid 441296-91-9



## PFDODA perfluorododecanoic acid 307-55-1

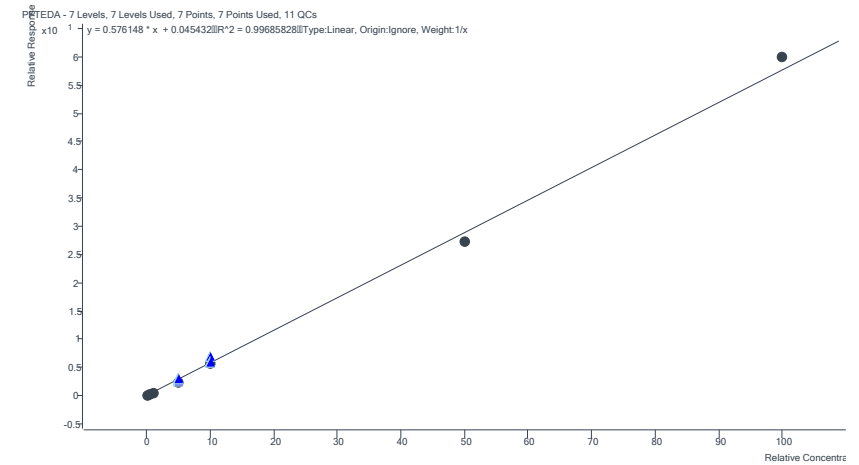
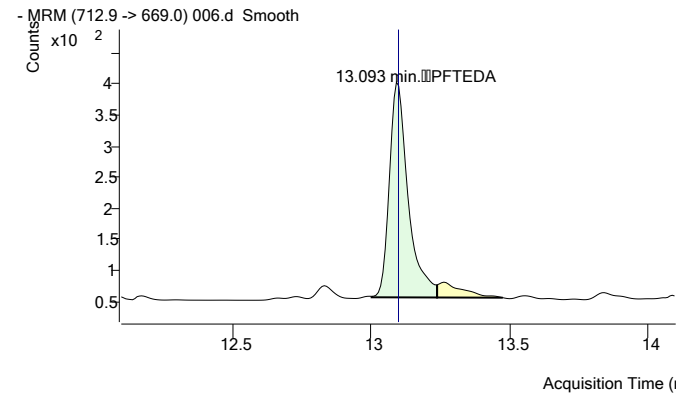
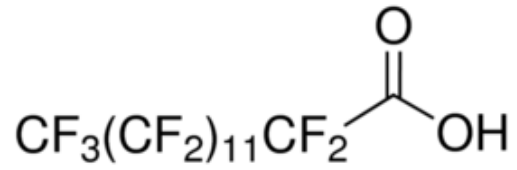


## PFDOS perfluorododecanesulfonic acid 1260224-54-1





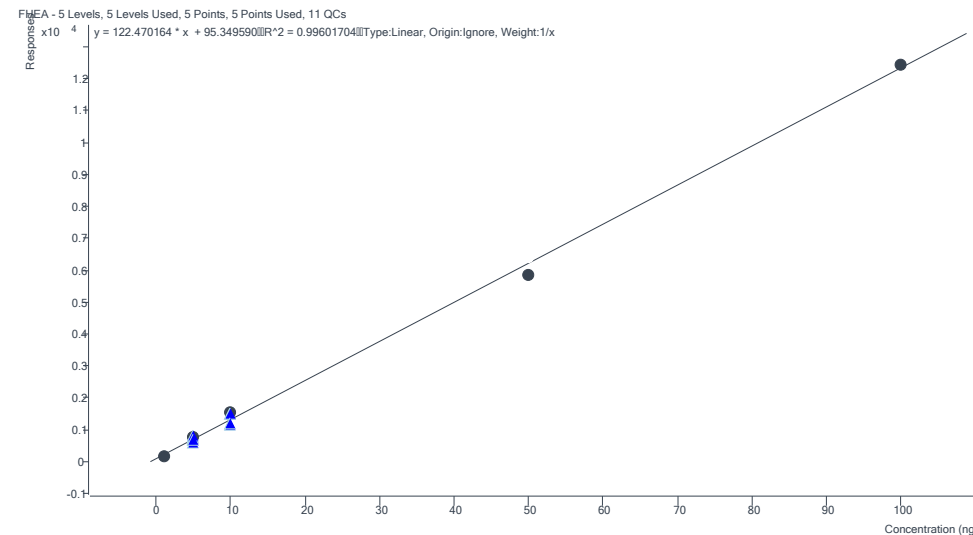
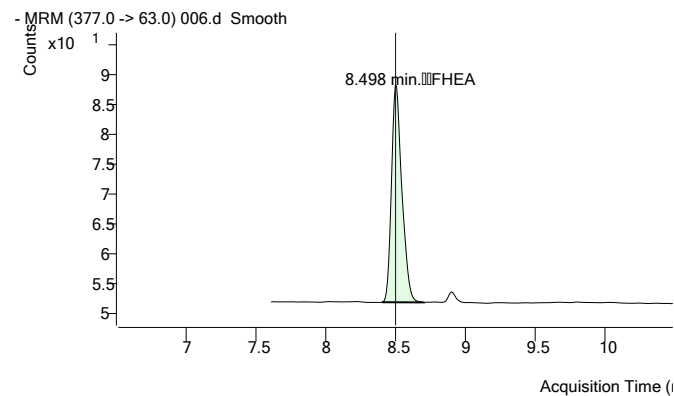
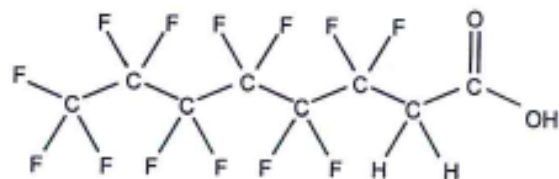
## PFTEDA perfluorotetradecanoic acid 376-06-7



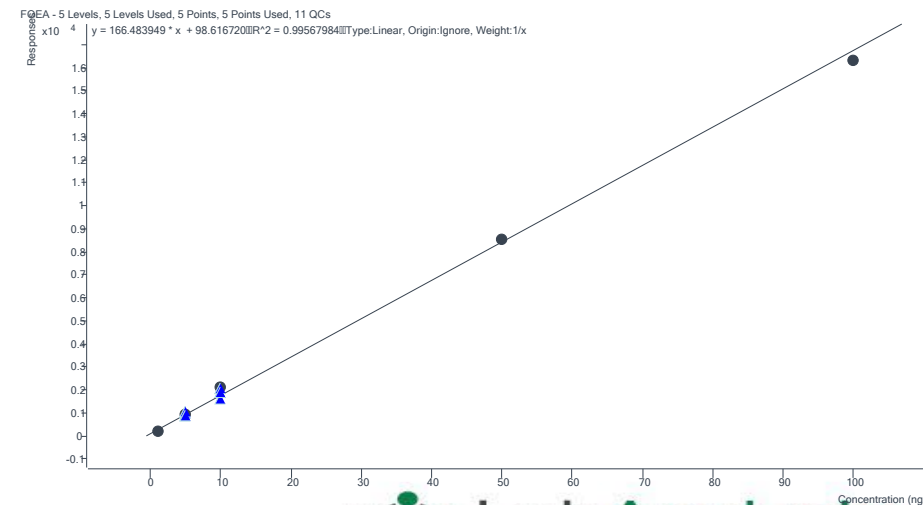
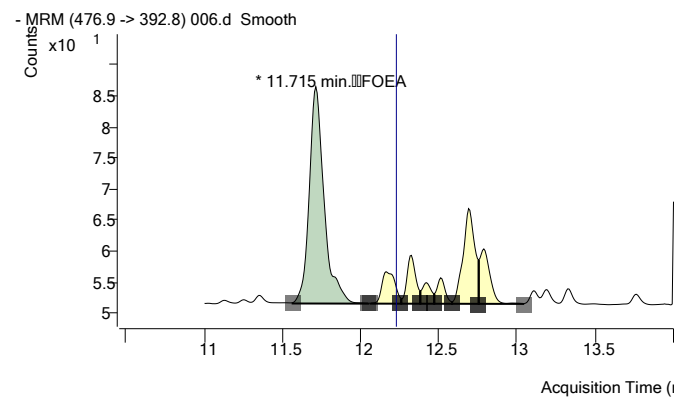
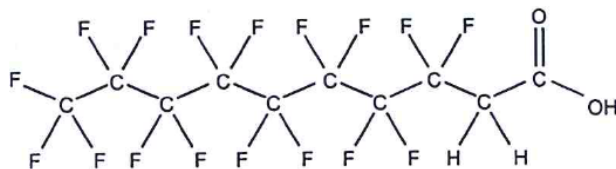
Seguono altri PFAS: i Telomeri



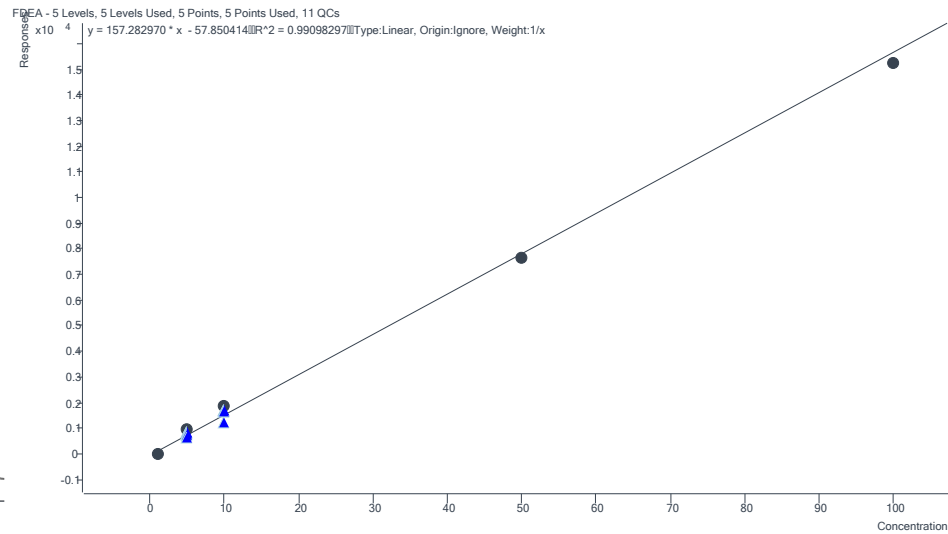
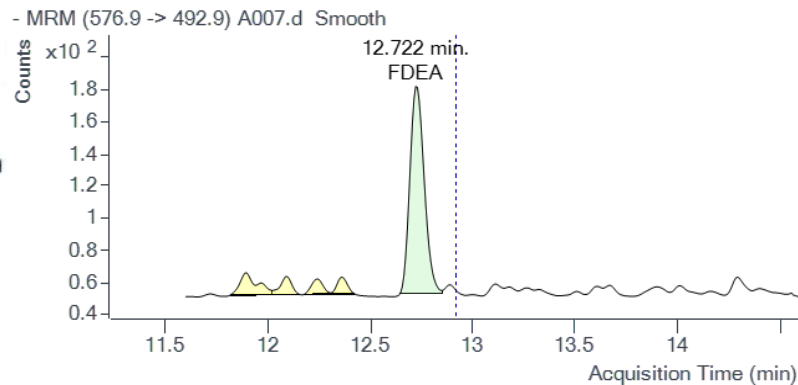
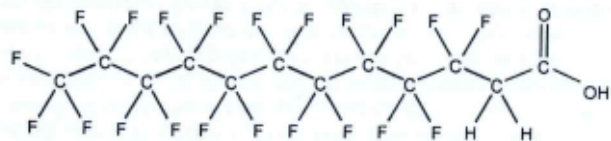
## FHEA 2-perfluorohexyl ethanoic acid 53826-12-3



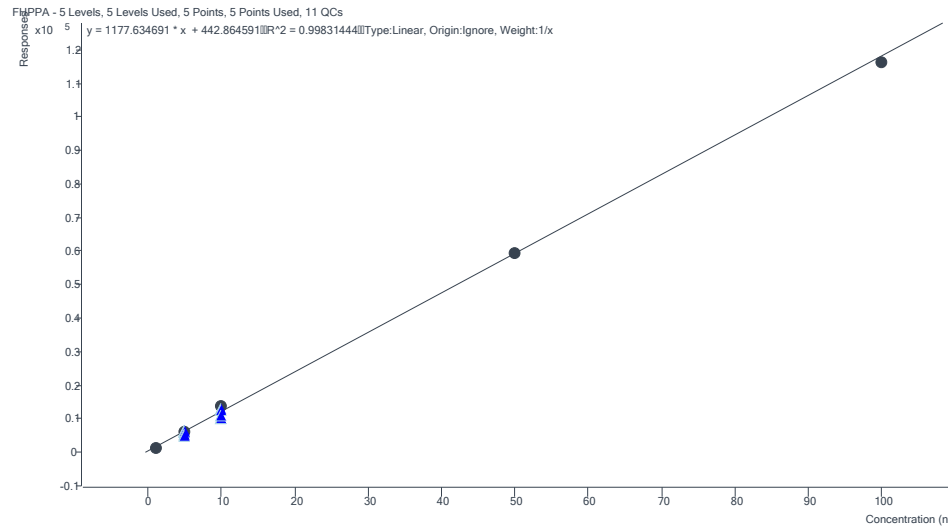
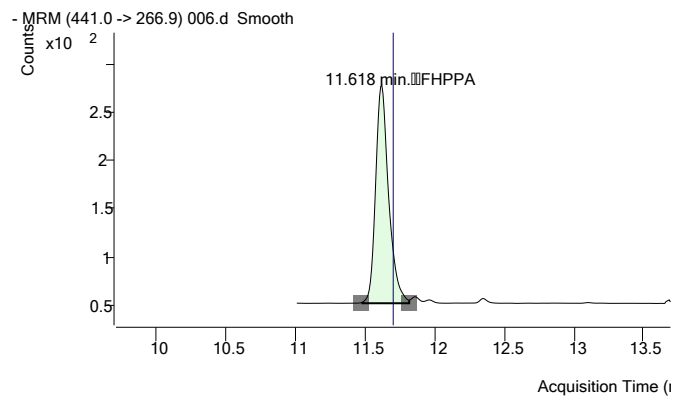
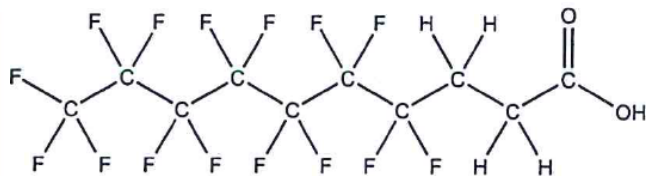
## FOEA 2-perfluorooctyl ethanoic acid 27854-31-5



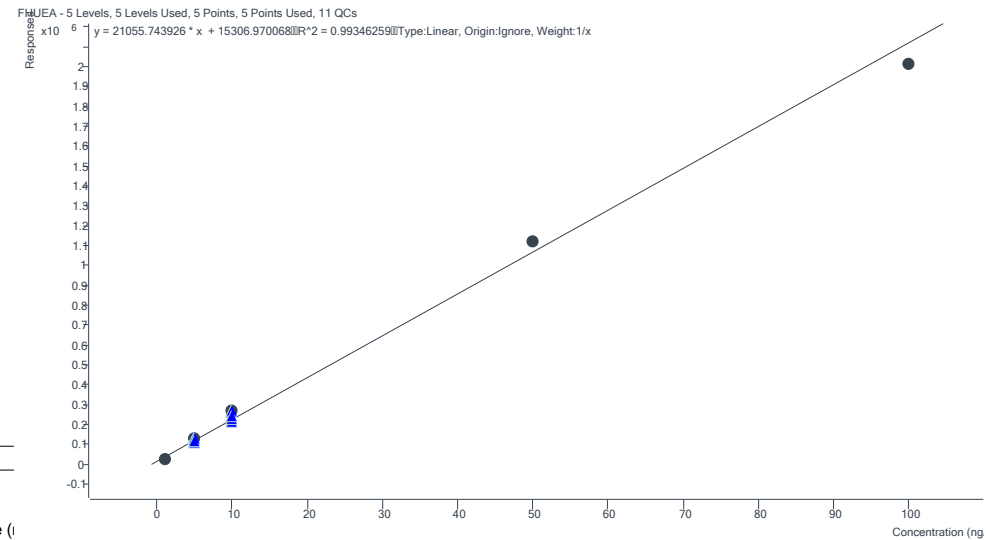
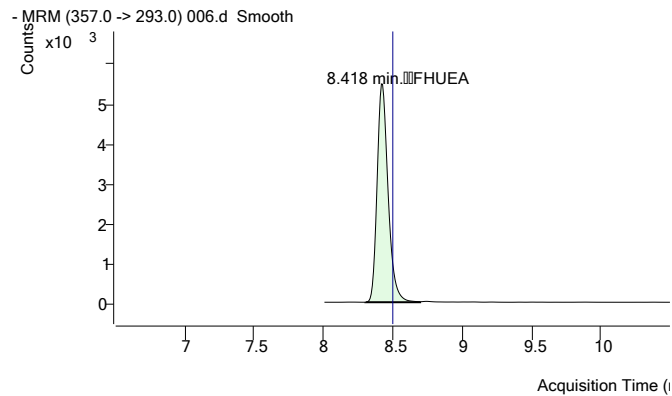
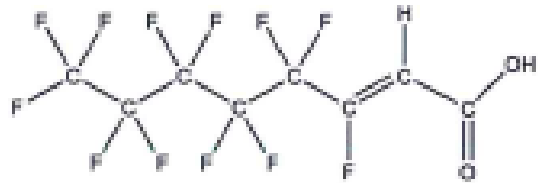
## FDEA 2-perfluorodecyl ethanoic acid 53826-13-4



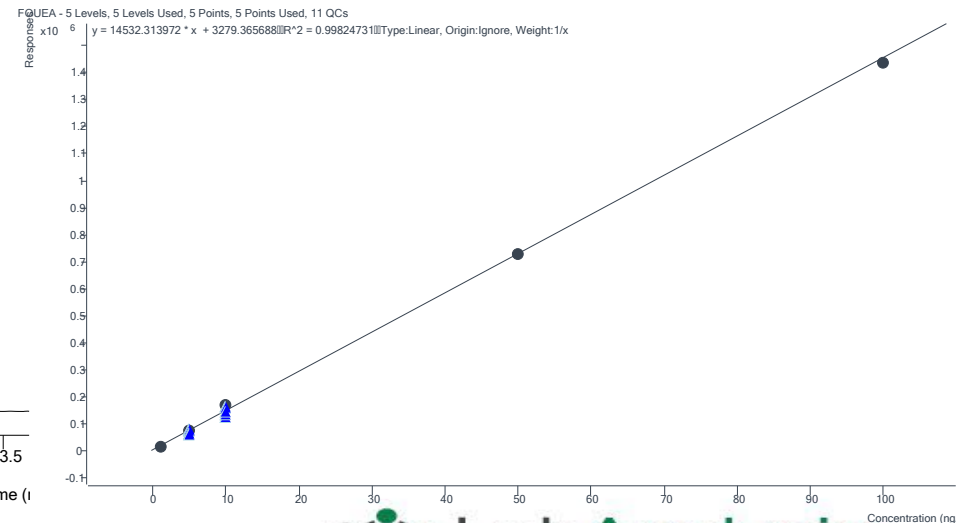
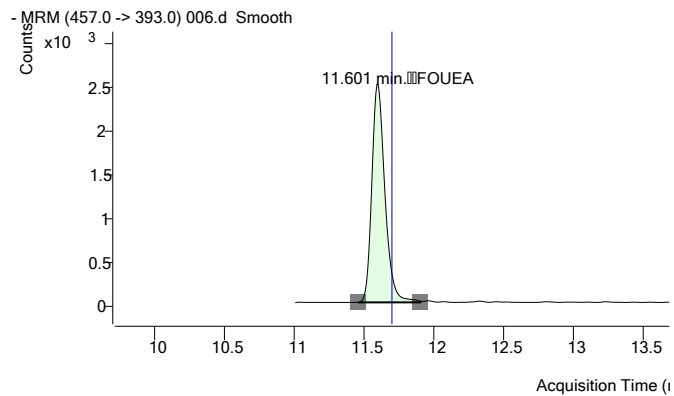
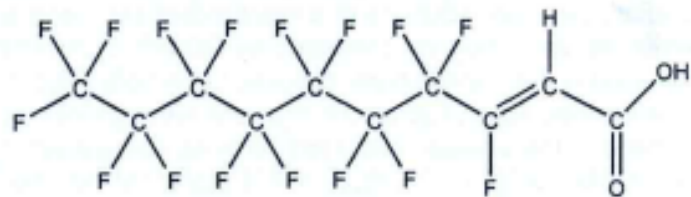
## FHPPA 3-perfluoroheptyl propanoic acid 812-70-4



## FHUEA 2H-perfluoro-2-octenoic acid 70887-88-6

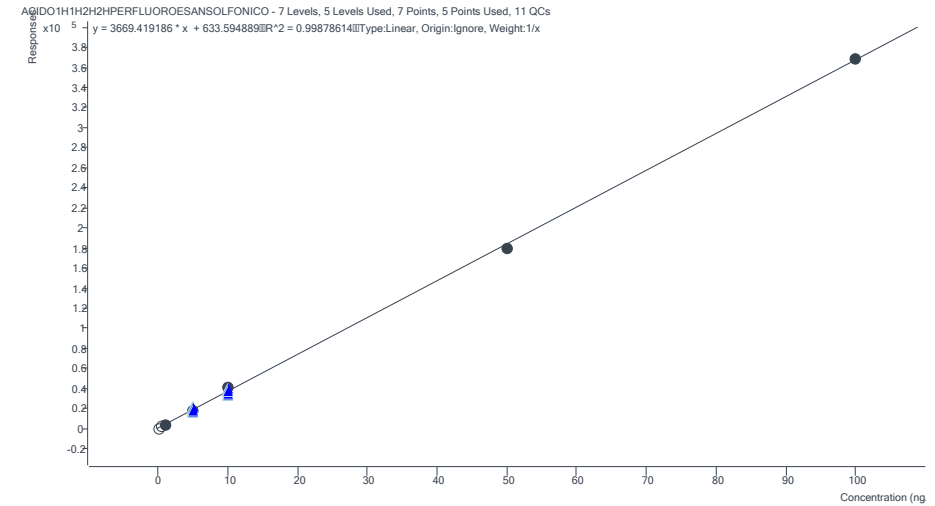
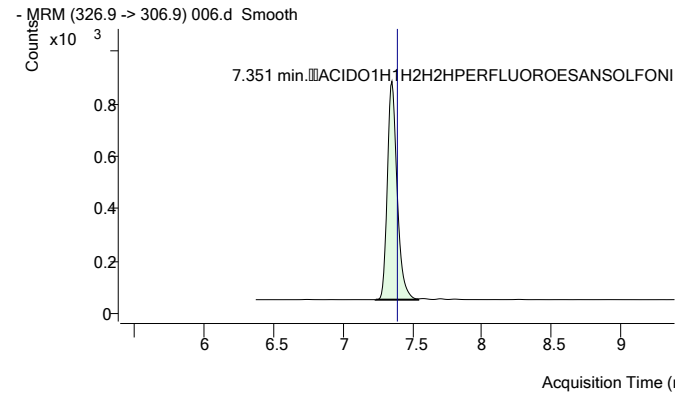
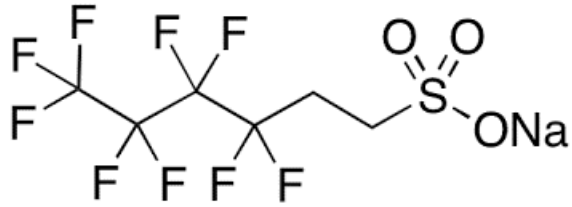


## FOUEA 2H-perfluoro-2-decenoic acid 70887-84-2



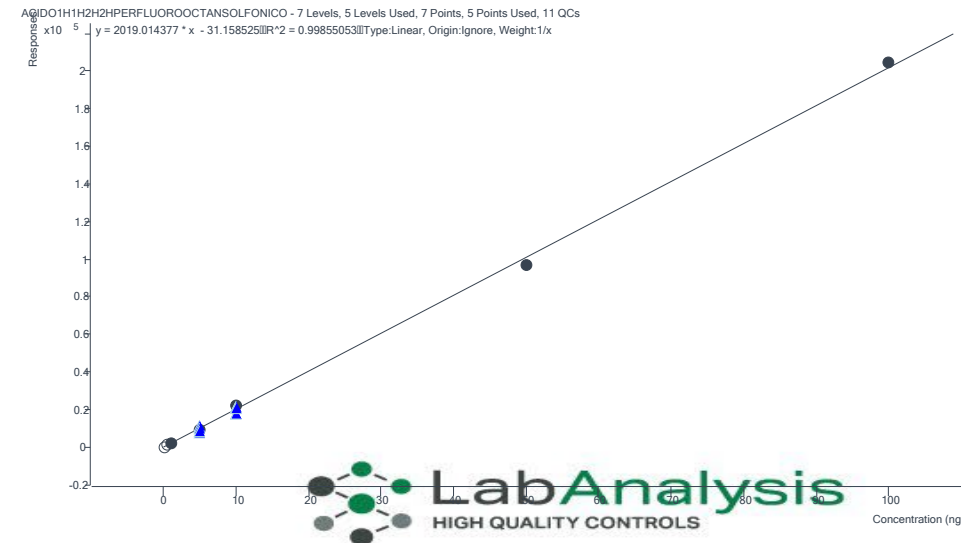
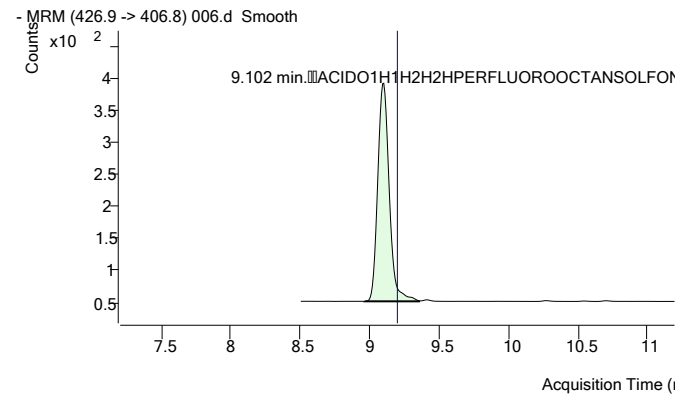
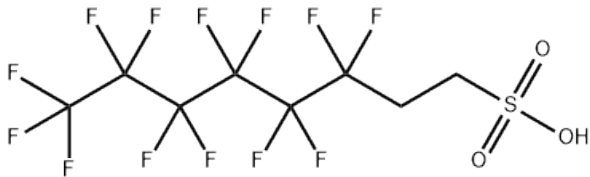
## 4:2 FTS

1H,1H,2H,2H-perfluorohexane sulfonic acid 757124-72-4

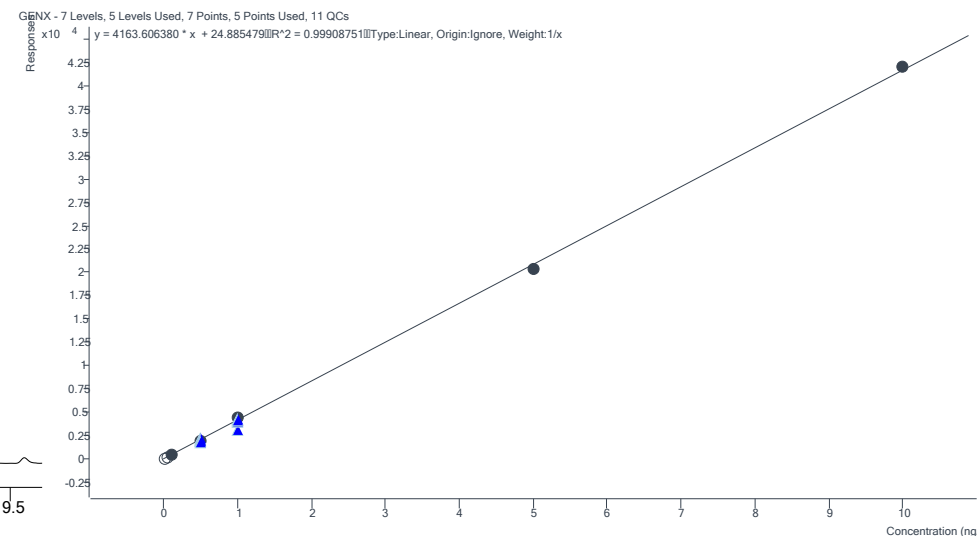
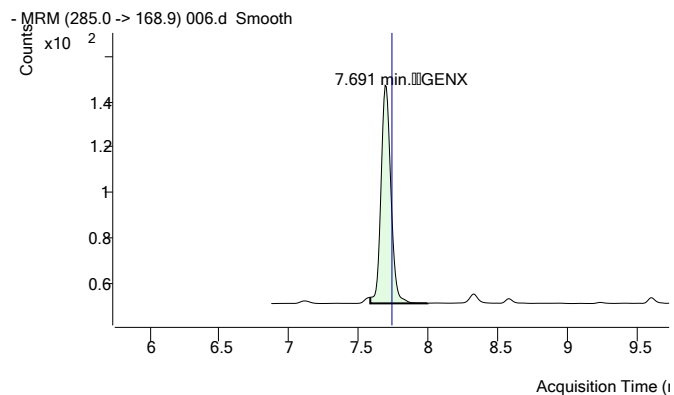
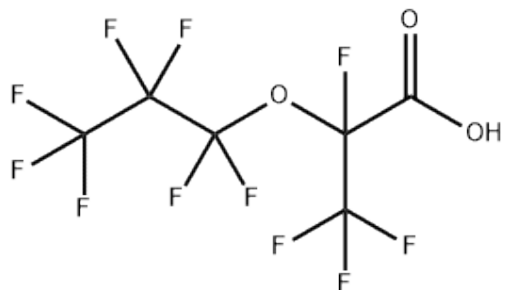


## 6:2 FTS

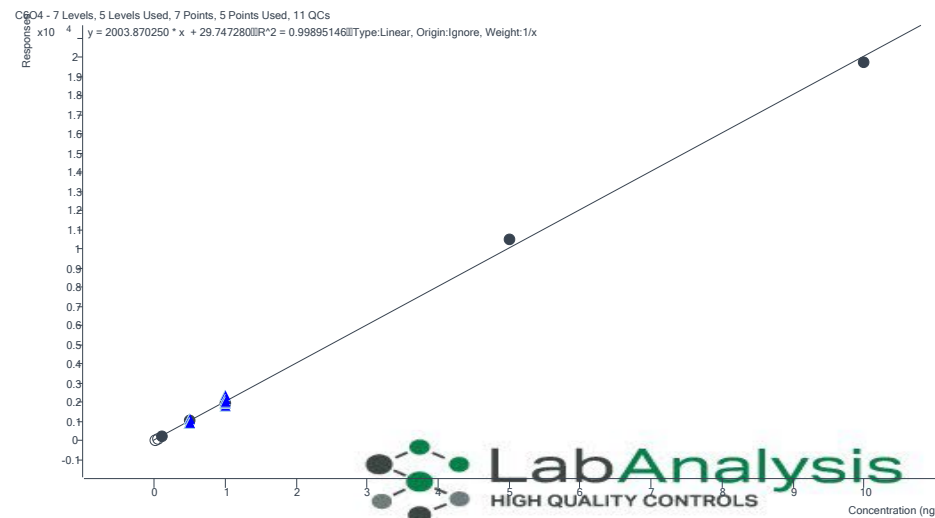
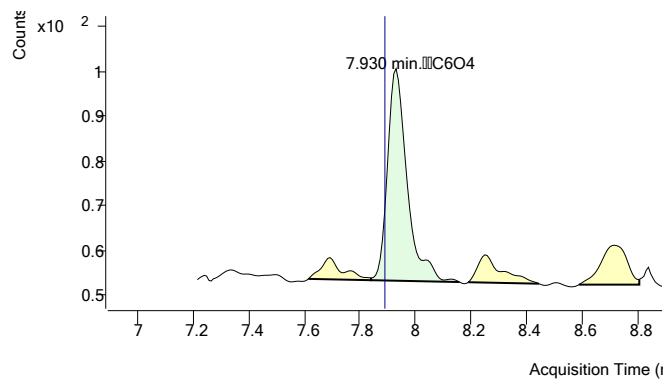
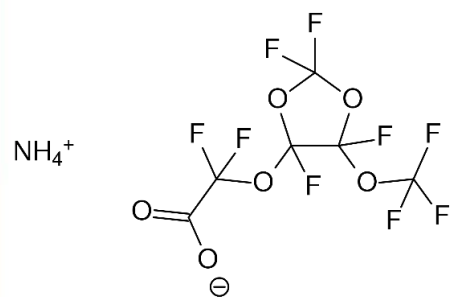
1H,1H,2H,2H-perfluorooctane sulfonic acid 27619-97-2



**HPFO-DA o FRD-903 o  
hexafluoropropylene oxide dimer acid  
2,3,3,3-Tetrafluoro-2-(heptafluoropropoxy)  
propanoic acid 13252-13-6**



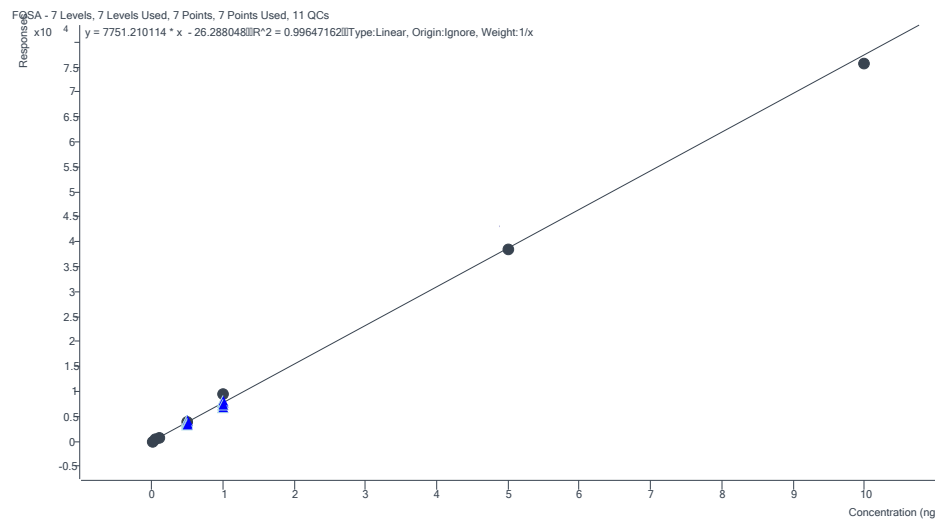
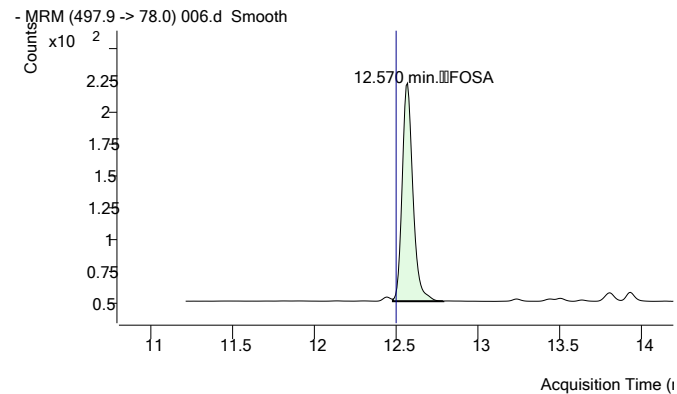
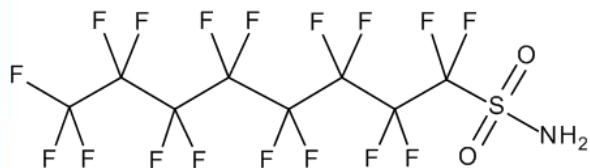
**C604  
Ammonium difluoro[[2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-  
1,3-dioxolan-4-yl]oxy]acetate 1190931-27-1**





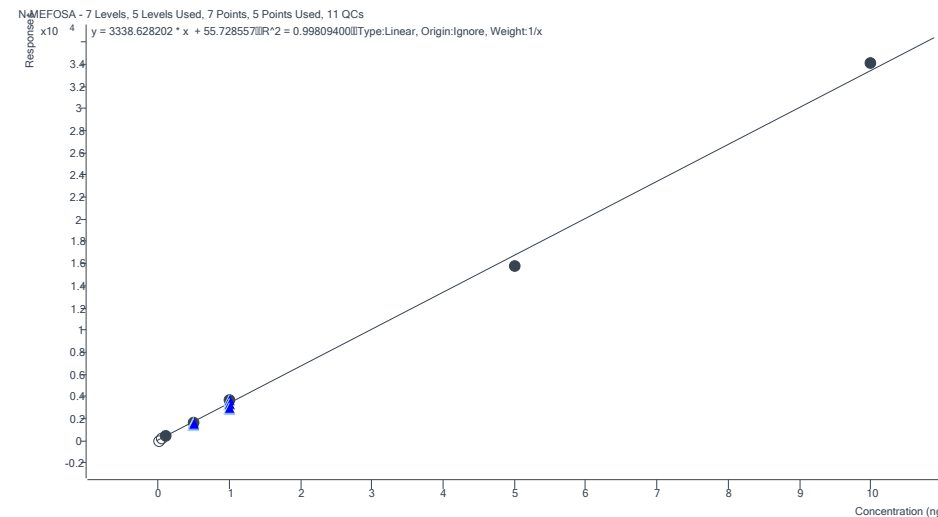
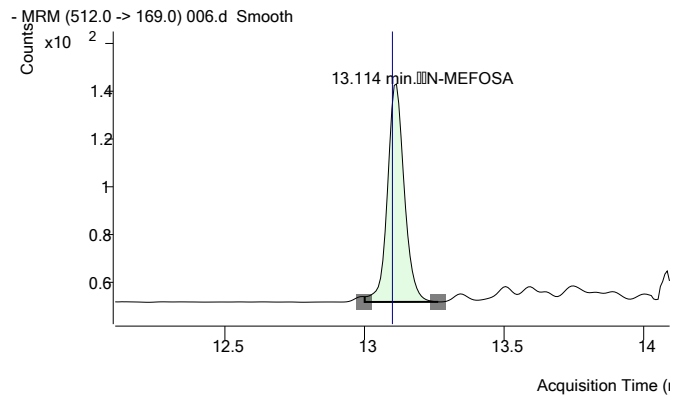
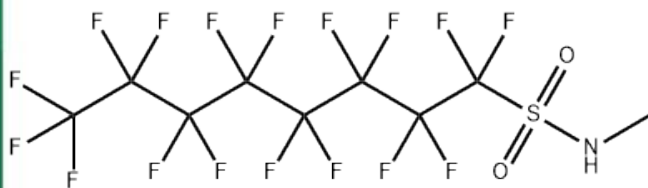
# FOSA

## perfluorooctanesulfonamide, 754-91-6



# N-ME-FOSA

## N-methyl-perfluorooctane-1-sulphonamide 31506-32-8

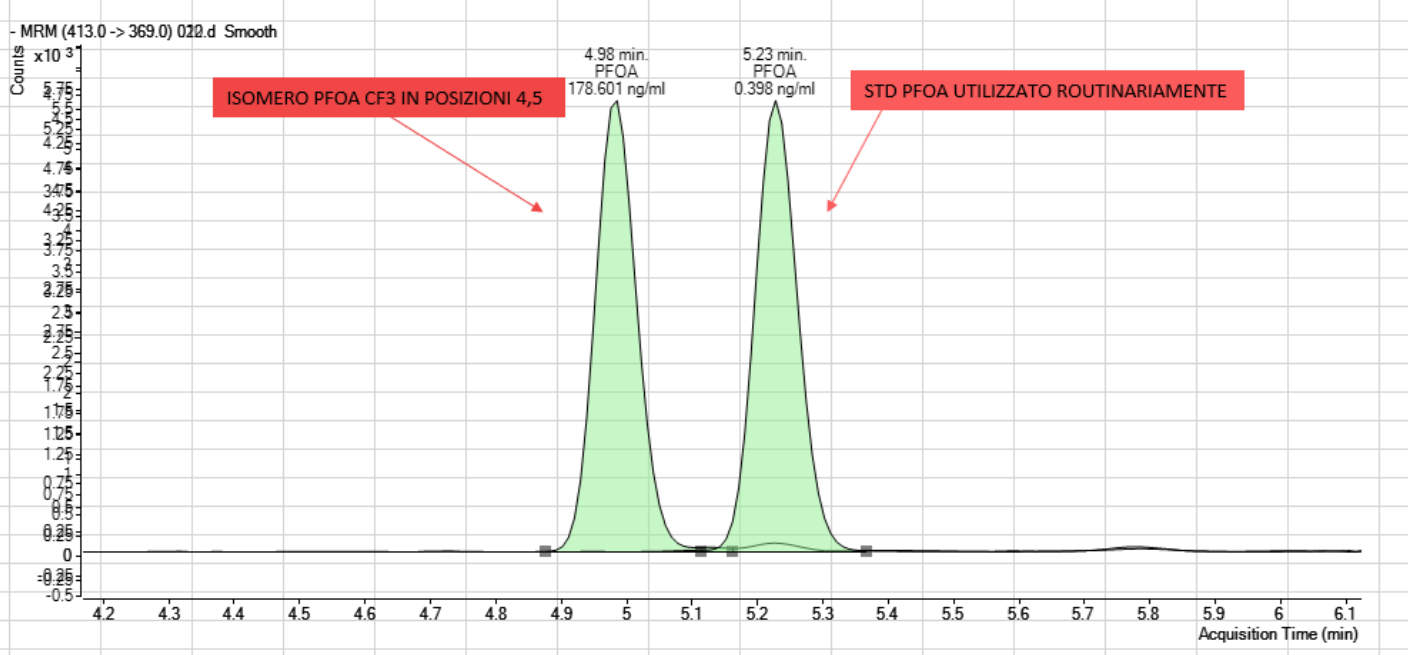
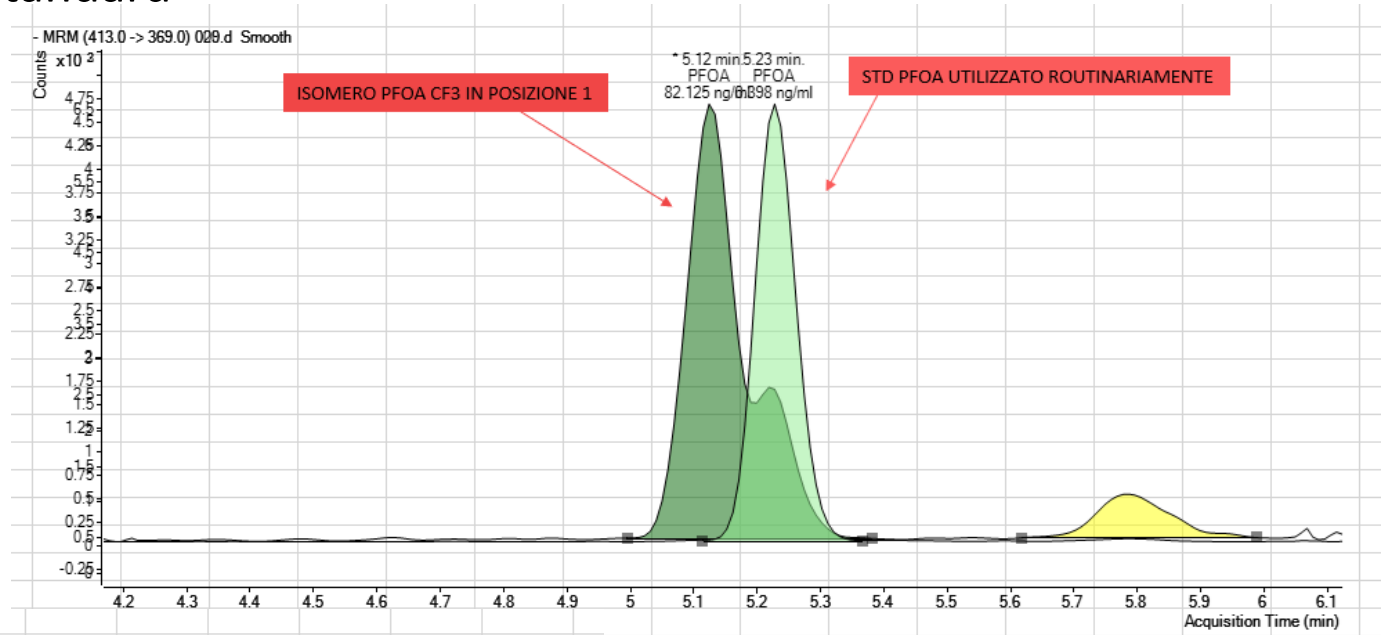






# Ramificazione PFAS: confronto tra Standard

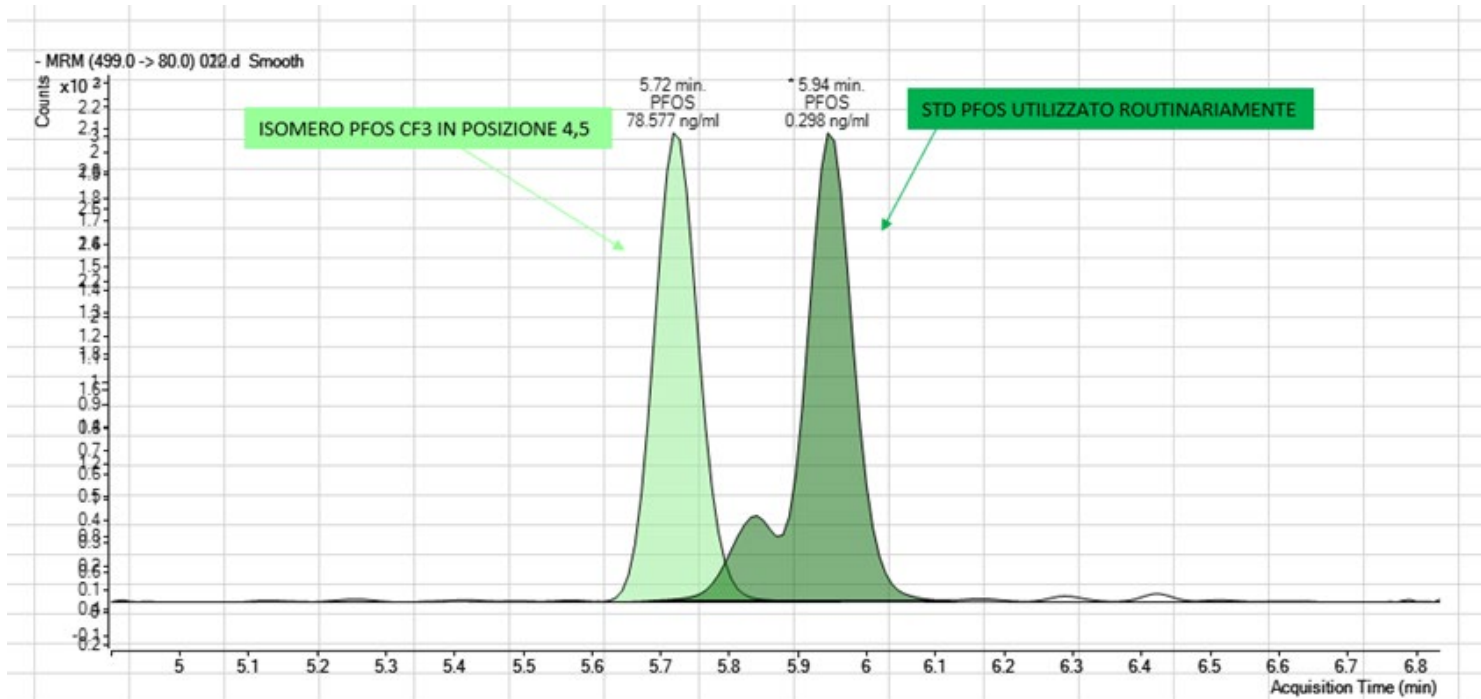
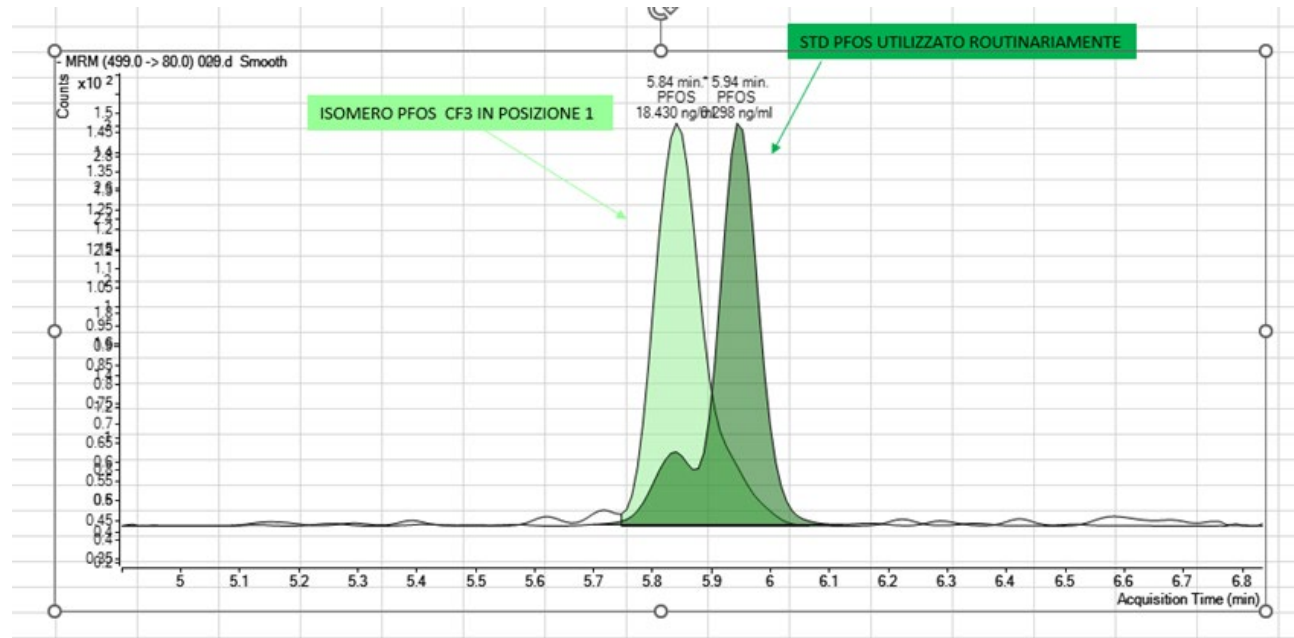
PFOA monoramificato



PFOA biramificato

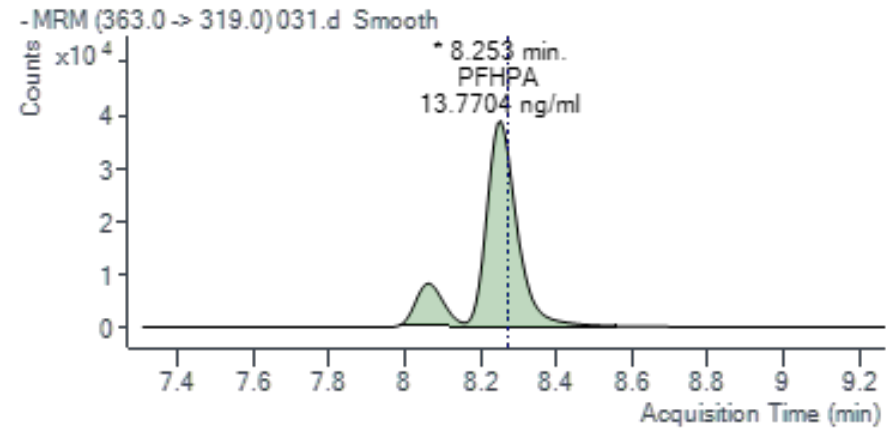
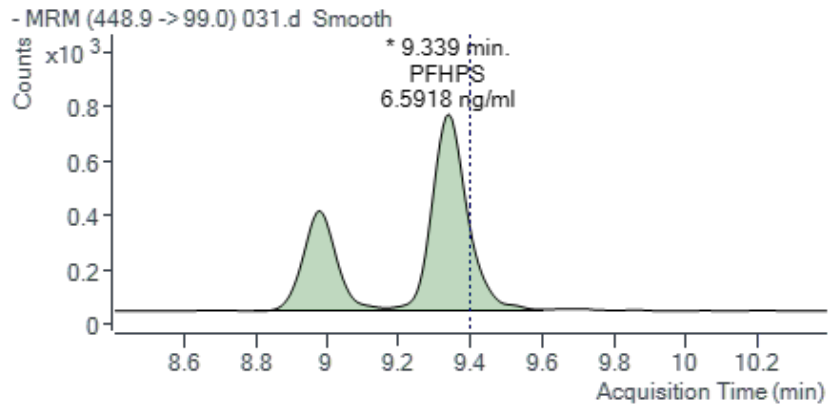
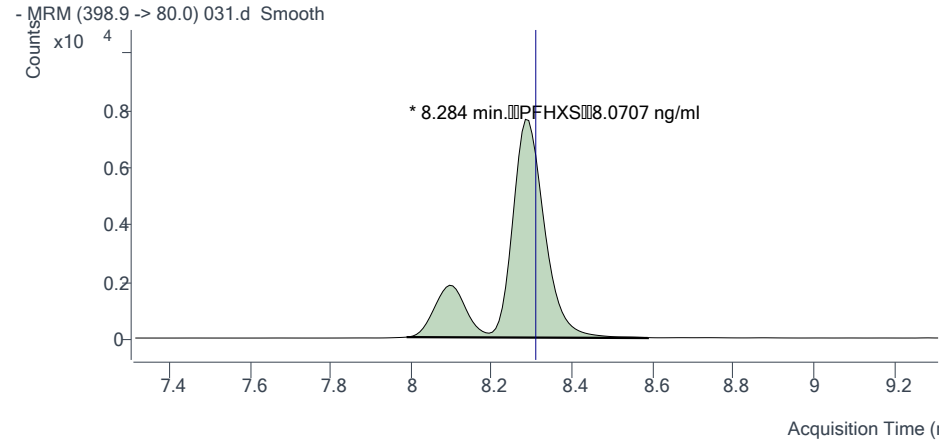
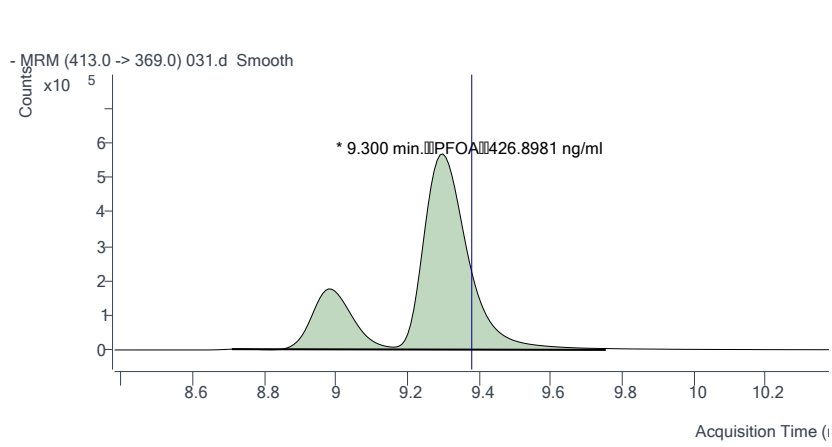
# Ramificazione PFAS: confronto tra Standard

PFOS monramificato



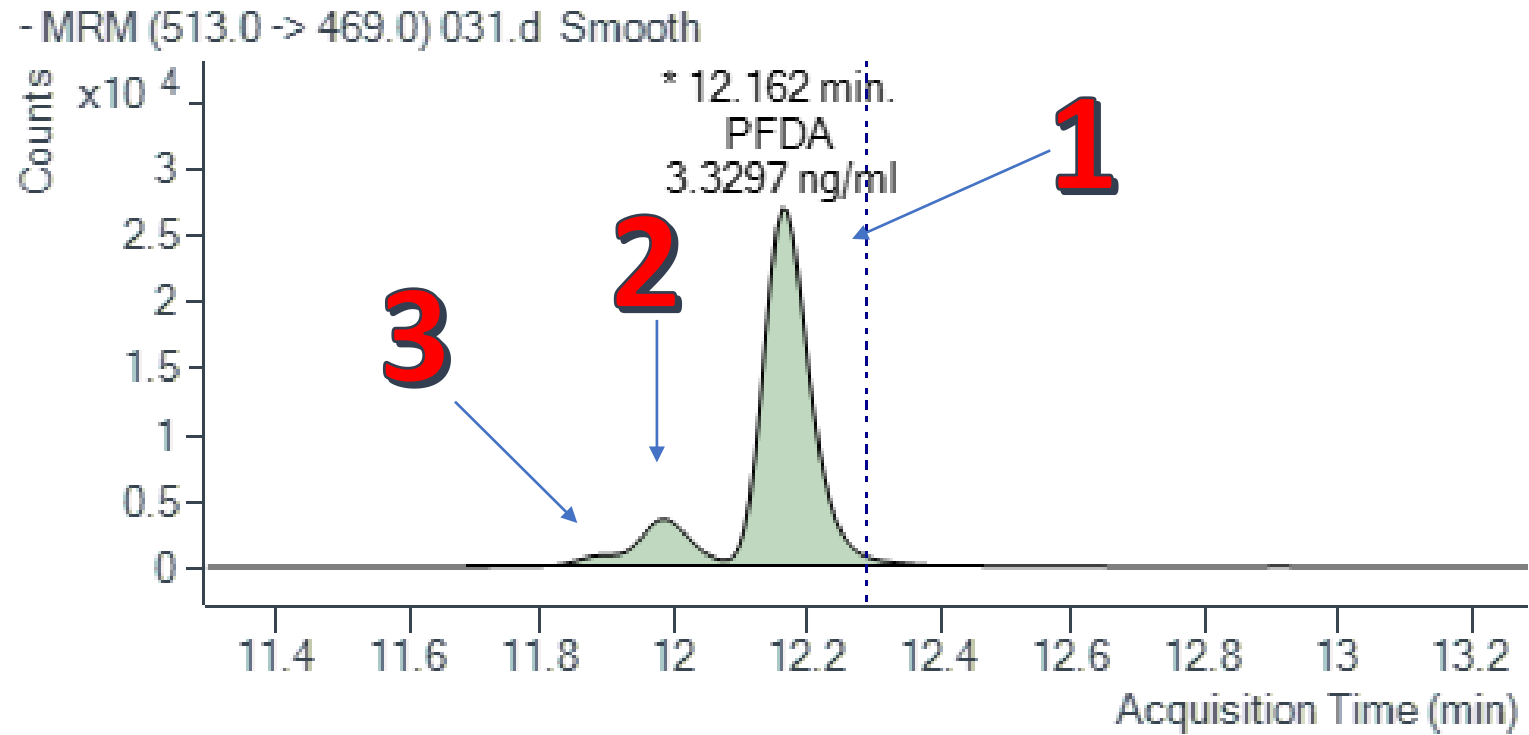
PFOS biramificato

# Campioni reali "DIVERTENTI" .....o quasi.....dipende dai punti di vista



# Campioni reali "DIVERTENTI" ....o quasi....dipende dai punti di vista

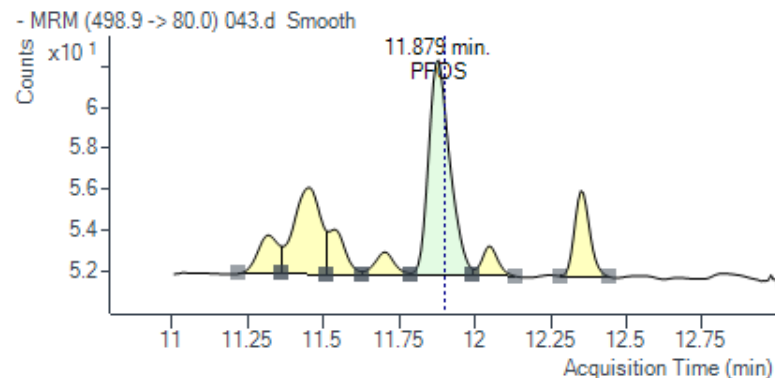
*"Trimodale"*



# Normative: Acque di scarico - REGIONE PIEMONTE 19 ottobre 2021, n. 25.

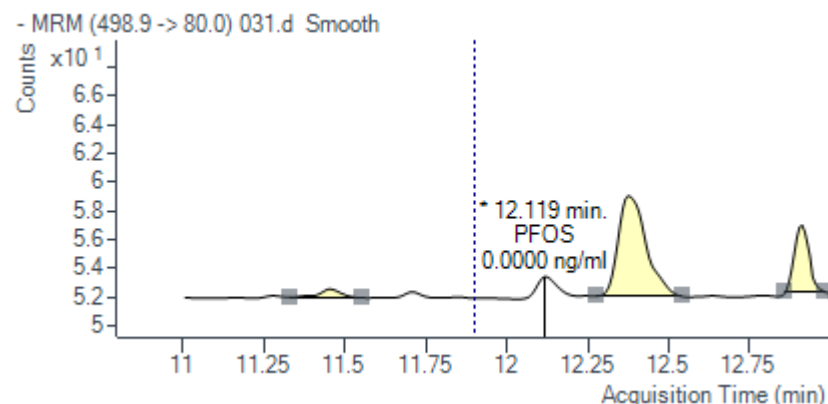
Valori-limite di emissione (VLE) per sostanze perfluoroalchiliche (PFAS) negli scarichi in acque superficiali (µg/L)

Sostanza o gruppi di sostanze	N° CAS	Valore-limite di emissione (VLE) allo scarico (µg/L) <sup>1</sup> e termini temporali per il loro conseguimento dalla data di entrata in vigore del presente provvedimento
Acido perfluorooctansolfonico e suoi sali (PFOS)	1763-23-1	<b>0,02</b> nei primi 36 mesi dalla data di entrata in vigore <b>0,00065</b> dopo 36 mesi dalla data di entrata in vigore
Acido perfluorooctanoico (PFOA)	335-67-1	<b>0,30</b> nei primi 36 mesi dalla data di entrata in vigore <b>0,10</b> dopo 36 mesi dalla data di entrata in vigore
Acido perfluorobutanoico (PFBA)	375-22-4	<b>7,0</b> alla data di entrata in vigore
Acido perfluoropentanoico (PFPeA)	2706-90-3	<b>3,0</b> alla data di entrata in vigore
Acido perfluoroesanoico (PFHxA)	307-24-4	<b>1,0</b> alla data di entrata in vigore
Acido perfluorobutansolfonico (PFBS)	375-73-5	<b>3,0</b> alla data di entrata in vigore
Acido perfluoro-n-eptanoico (PFHpA)	375-85-9	<b>1,0</b> alla data di entrata in vigore
Acido perfluoroesansolfonico (PFHxS)	355-46-4	<b>1,0</b> alla data di entrata in vigore
Acido perfluoro-n-nonanoico (PFNA)	375-95-1	<b>1,0</b> alla data di entrata in vigore
Acido perfluorodecanoico (PFDeA)	335-76-2	<b>1,0</b> alla data di entrata in vigore
Acido perfluoroundecanoico (PFUnA)	2058-94-8	<b>1,0</b> alla data di entrata in vigore
Acido perfluoro-n-dodecanoico (PFDoA)	307-55-1	<b>1,0</b> alla data di entrata in vigore
Perfluoro {acetic acid, 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt (cC6O4)	1190931-27-1	<b>7,0</b> a partire dal 13° mese e fino al 24° mese dalla data di entrata in vigore <b>3,5</b> dal 25° mese al 36° mese dalla data di entrata in vigore <b>0,5</b> dal 37° mese dalla data di entrata in vigore in poi
1-Propene, 1,1,2,3,3,3-hexafluoro-, telomer with chlorotrifluoroethene, oxidized, reduced, hydrolyzed (ADV)	329238-24-6	<b>2,0</b> a partire dal 13° mese e fino al 24° mese dalla data di entrata in vigore <b>0,5</b> dal 25° mese dalla data di entrata in vigore in poi
altri PFAS (molecole con catena a 3-6 atomi di Carbonio, anche di nuova generazione)	-	<b>3,0</b> (per ogni singolo composto) alla data di entrata in vigore
altri PFAS (molecole con catena a 7 atomi di Carbonio o più, anche di nuova generazione)	-	<b>1,0</b> (per ogni singolo composto) alla data di entrata in vigore



PFOS: 1 ng/L in soluzione

Concentrazione a **0.1 ng/L** finale sul campione con SPE offline (metodo ISO 21675)



MB PFOS: 1 ng/L in soluzione

Normative:

DIRETTIVA (UE) 2020/2184 DEL PARLAMENTO EUROPEO E DEL CONSIGLIO  
del 16 dicembre 2020  
concernente la qualità delle acque destinate al consumo umano

PFAS Totale	0,50	µg/l	Per «PFAS — totale» si intende la totalità delle sostanze per- e polifluoro alchiliche. Tale valore di parametro si applica esclusivamente dopo l'elaborazione di orientamenti tecnici per il monitoraggio di tale parametro in conformità dell'articolo 13, paragrafo 7. Gli Stati membri possono quindi decidere di utilizzare uno o entrambi i parametri «PFAS — totale» o «Somma di PFAS».
Somma di PFAS	0,10	µg/l	Per «somma di PFAS» si intende la somma di tutte le sostanze per- e polifluoro alchiliche ritenute preoccupanti per quanto riguarda le acque destinate al consumo umano di cui all'allegato III, parte B, punto 3. Si tratta di un sottoinsieme di sostanze «PFAS — totale» contenenti un gruppo perfluoroalchilico con tre o più atomi di carbonio (vale a dire $-C_nF_{2n-}$ , $n \geq 3$ ) o un gruppo perfluoroalchilietere con due o più atomi di carbonio (vale a dire $-C_nF_{2n}OC_mF_{2m-}$ , $n$ e $m \geq 1$ ).



Allegato III, B

3. Somma di PFAS

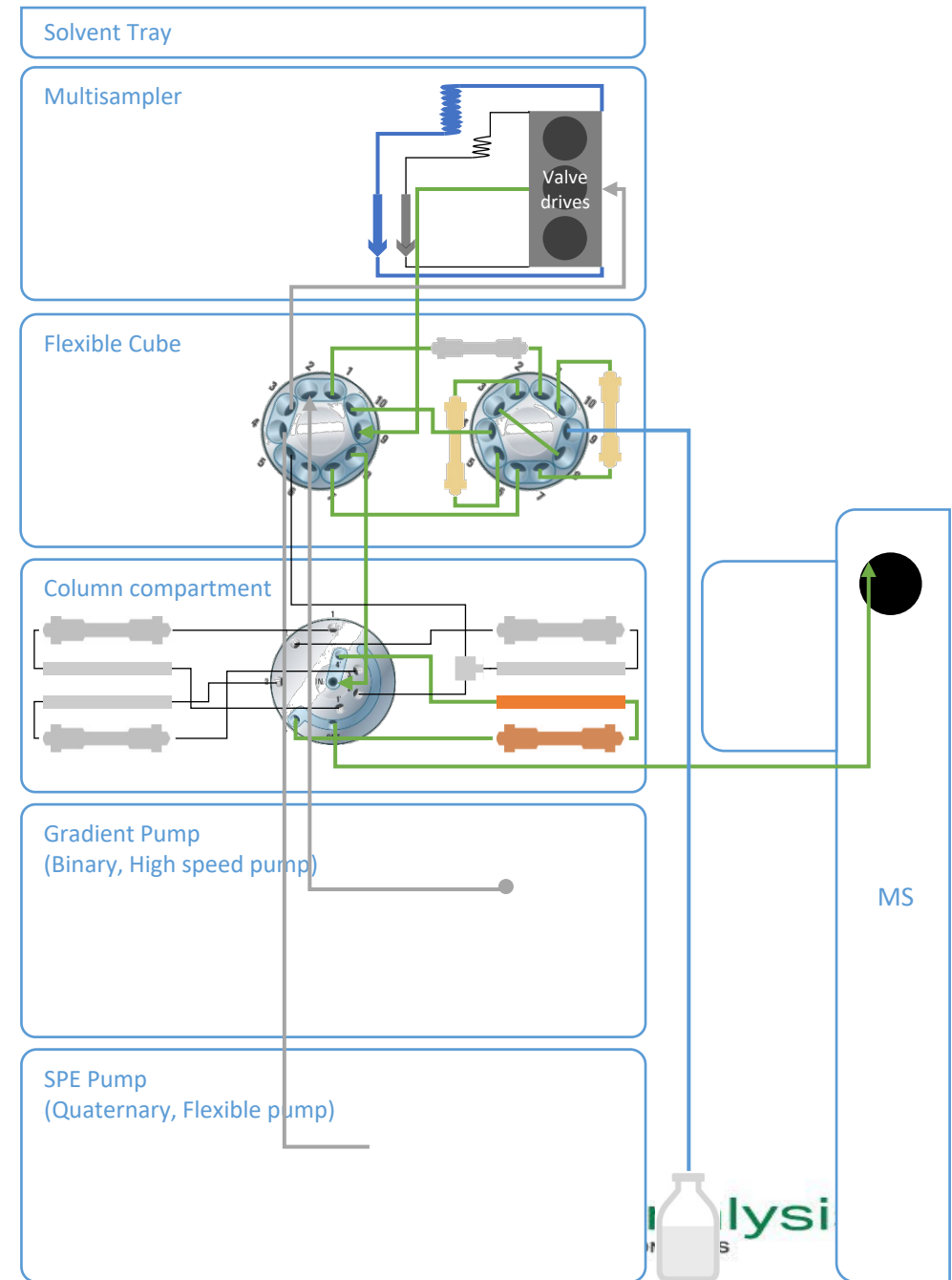
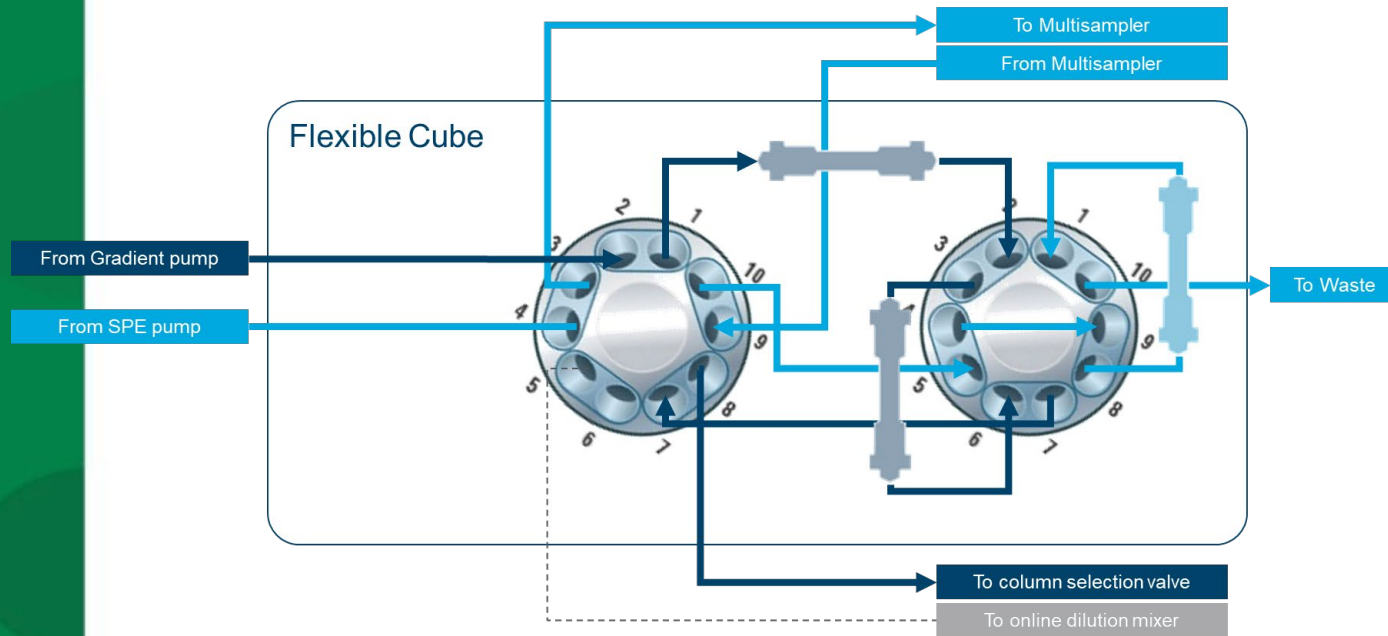
Le seguenti sostanze sono analizzate sulla base delle linee guida tecniche sviluppate conformemente all'articolo 13, paragrafo 7: — acido perfluorobutanoico (PFBA) — acido perfluoropentanoico (PFPeA) — acido perfluoroesanoico (PFHxA) — acido perfluoroeptanoico (PFHpA) — acido perfluorooctanoico (PFOA) — acido perfluorononanoico (PFNA) — acido perfluorodecanoico (PFDA) — acido perfluorundecanoico (PFUnDA) — acido perfluorododecanoico (PFDoDA) — acido perfluorotridecanoico (PFTrDA) — acido perfluorobutanosolfonico (PFBS) — acido perfluoropentansolfonico (PFPeS) — acido perfluoroesansolfonico (PFHxS) — acido perfluoroeptansolfonico (PFHpS) — acido perfluorooctansolfonico (PFOS) — acido perfluorononansolfonico (PFNS) — acido perfluorodecansolfonico (PFDS) — acido perfluoroundecansolfonico — acido perfluorododecansolfonico — acido perfluorotridecansolfonico .

7. Entro il 12 gennaio 2024, la Commissione stabilisce linee guida tecniche sui metodi analitici per quanto riguarda il monitoraggio delle sostanze per- e polifluoro alchiliche comprese nei parametri «PFAS — totale» e «somma di PFAS», compresi i limiti di rilevazione, i valori di parametro e la frequenza di campionamento.

Tali sostanze sono controllate quando la valutazione e gestione del rischio dei bacini idrografici per punti di estrazione effettuata in conformità dell'articolo 8 conclude che vi è la probabilità che tali sostanze siano presenti in una determinata fornitura d'acqua.

# Sviluppi «futuri»

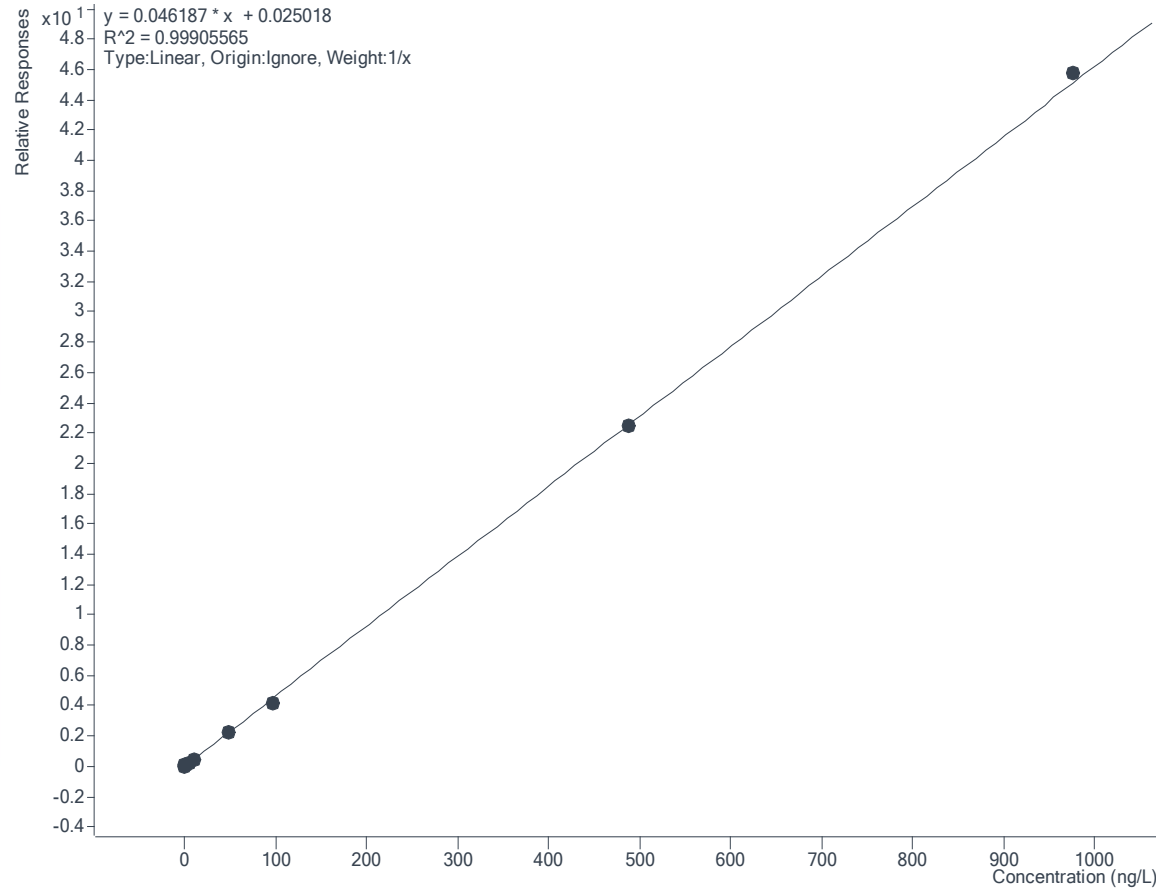
- On-line SPE



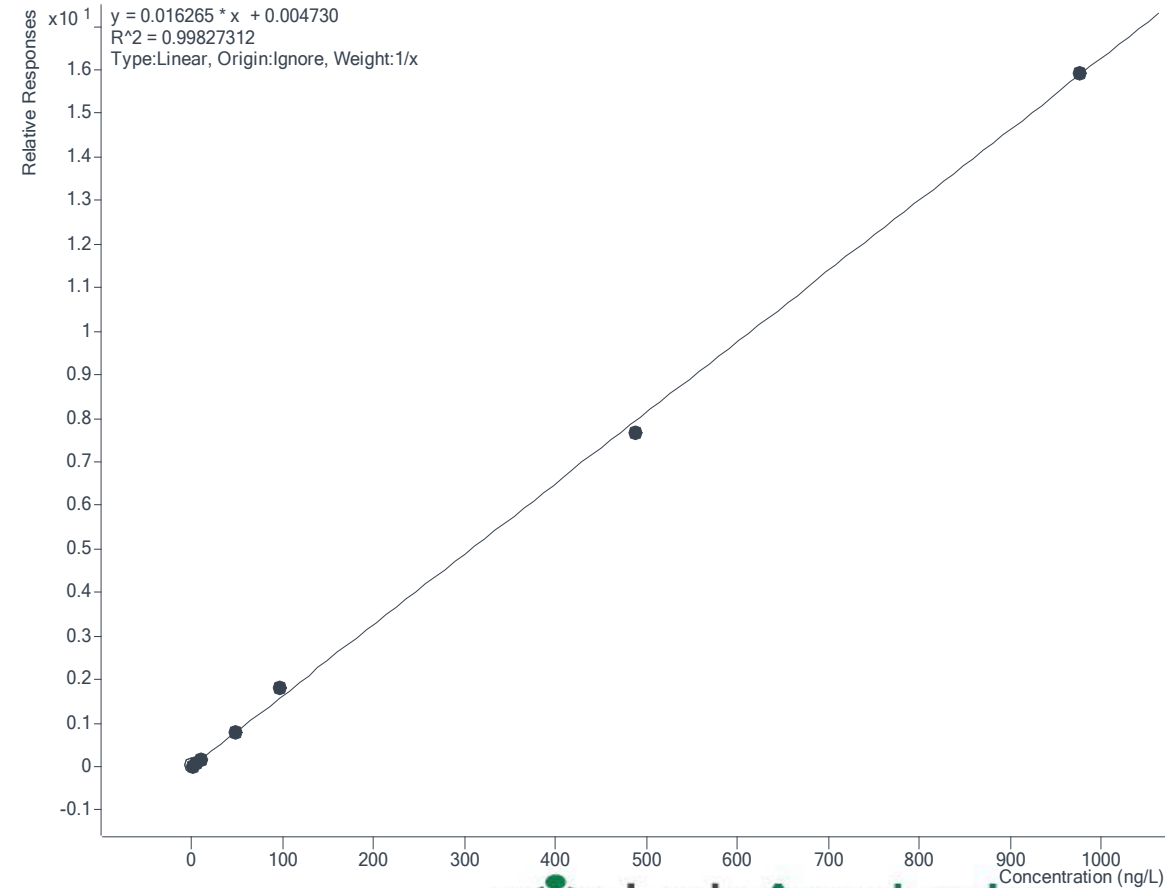
# Sviluppi «futuri»

- On-line SPE

PFOA - 9 Levels, 9 Levels Used, 9 Points, 9 Points Used, 7 QCs



PFOS - 9 Levels, 7 Levels Used, 9 Points, 7 Points Used, 7 QCs

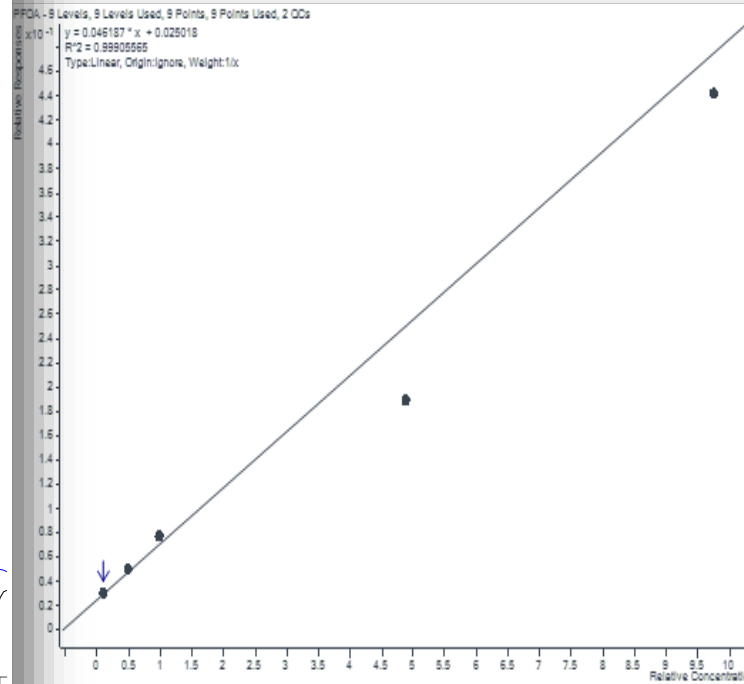
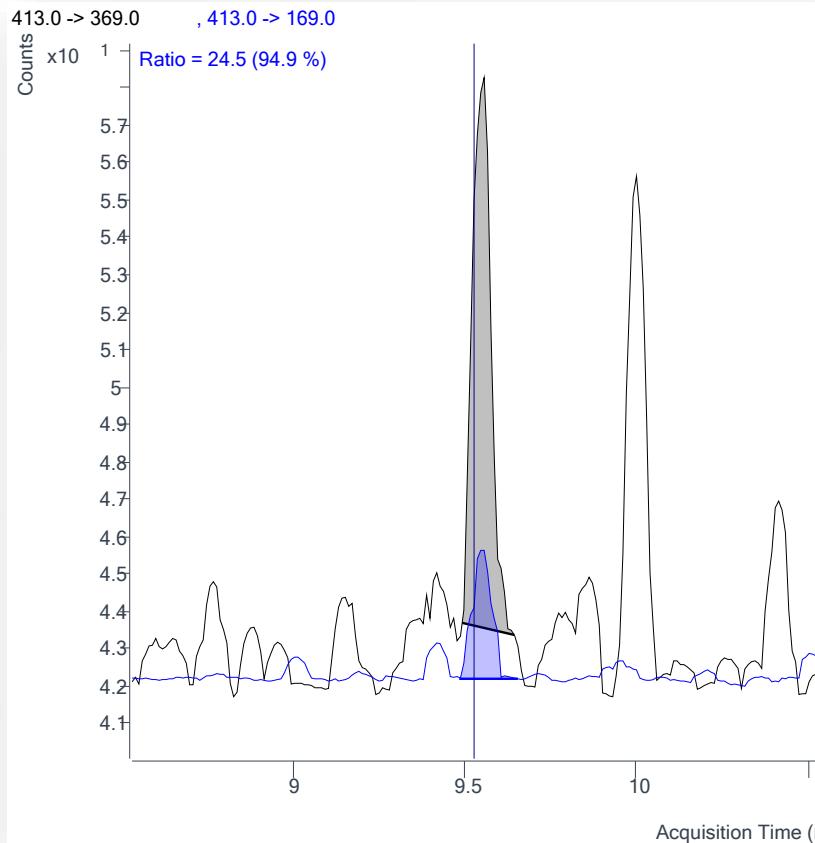




# Sviluppi «futuri»

- On-line SPE

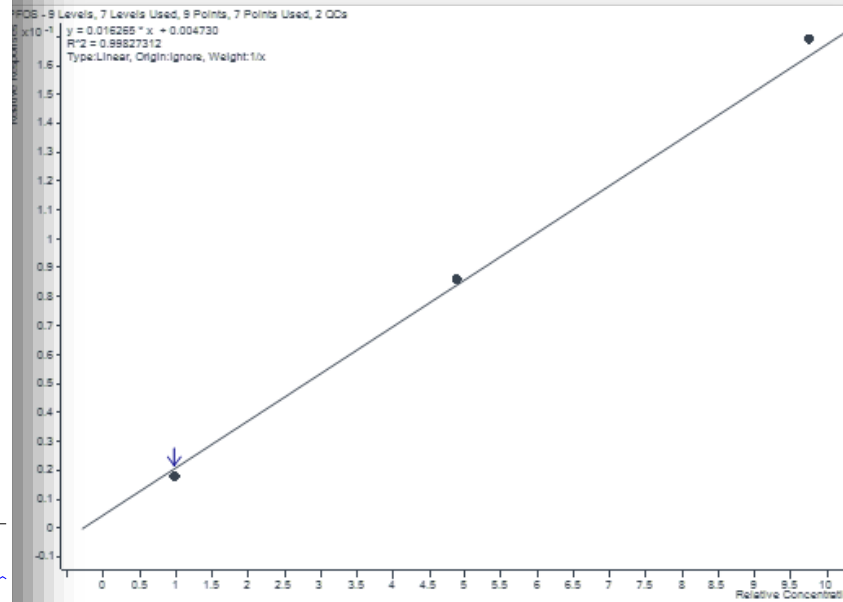
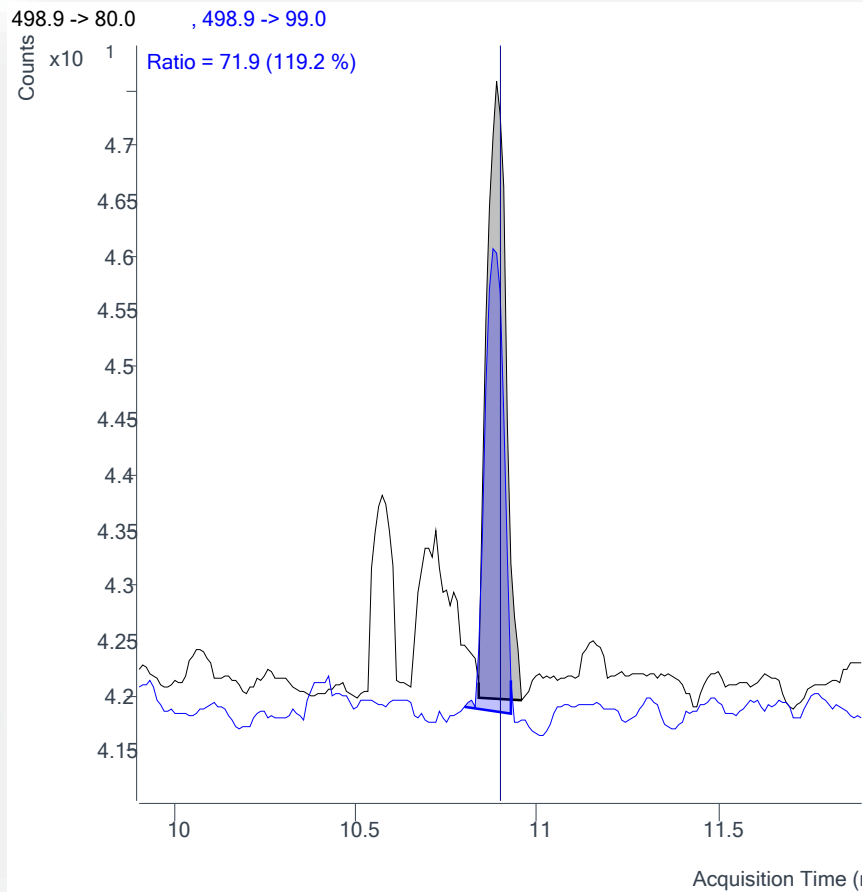
PFOA 0.1 ng/L or 0.1 ppt



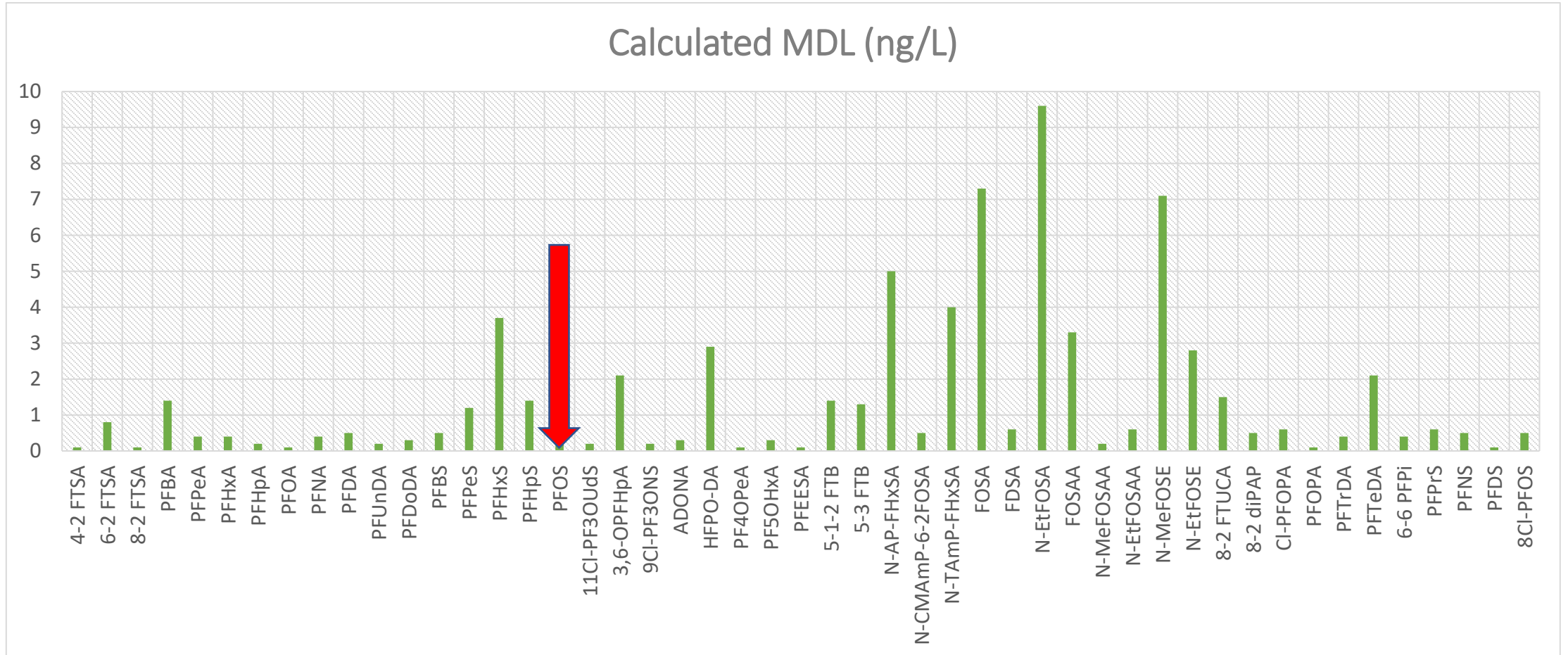
# Sviluppi «futuri»

- On-line SPE

PFOS 0.1 ng/L or 0.1 ppt



# Sviluppi «futuri»



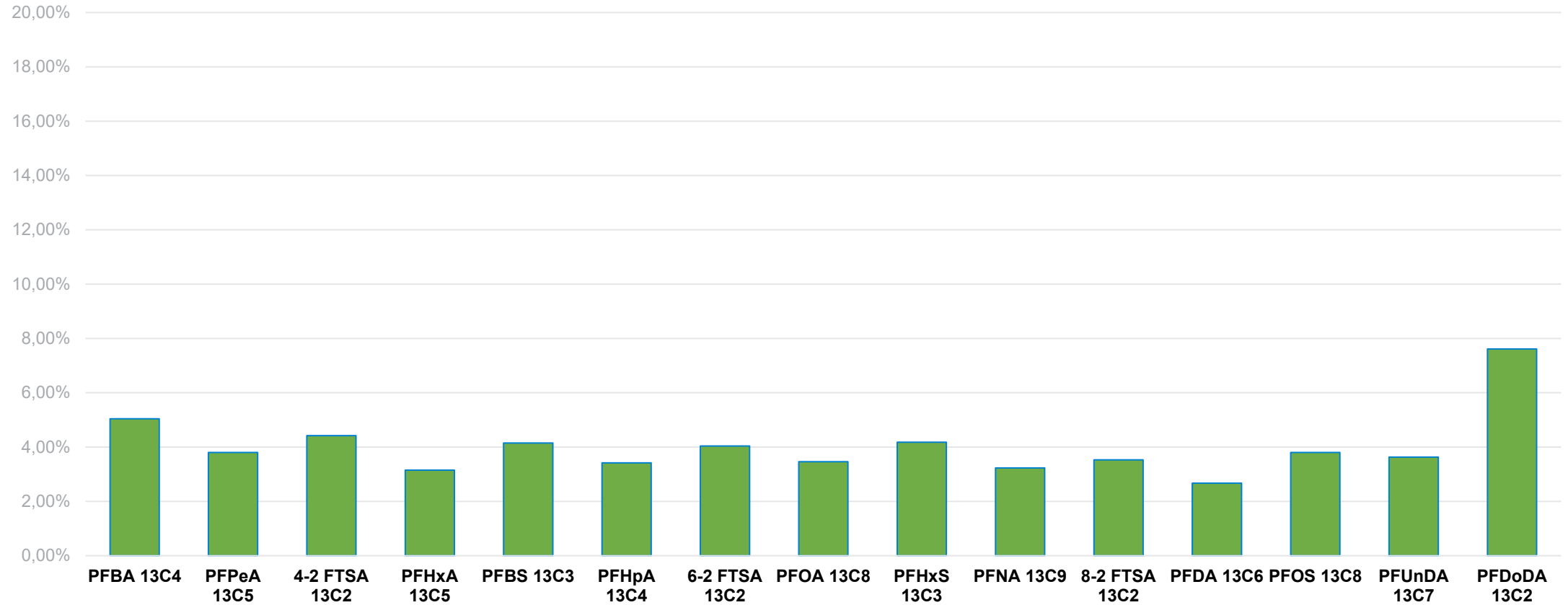
$$MDL = T_{(n-1, 1-\alpha=0.99)} (S)$$

MDLs for 47/60 PFAS are <4 ng/L

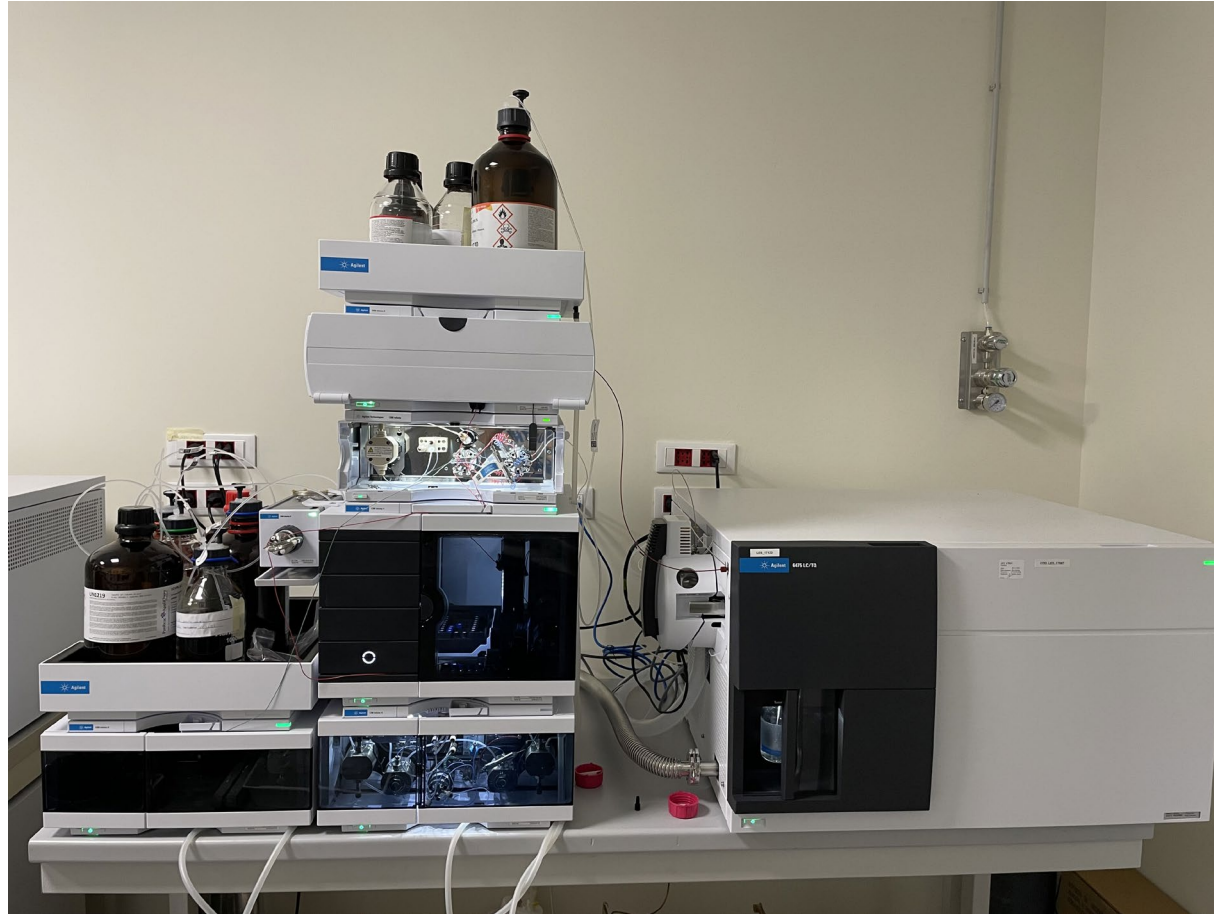
# Sviluppi «futuri»

- On-line SPE

Response RSD (%)



# Ns sistema SPE on-line



# Grazie per l'Attenzione

- [guido.premoli@labanalysis.it](mailto:guido.premoli@labanalysis.it)
- [andrea.serra@labanalysis.it](mailto:andrea.serra@labanalysis.it)