

# PFAS – From hero to villain to criminal

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### The ultimate combiner

“Fervid Fluorine, Though just nine  
Knows her aim in life: combine!  
In fact, of things that like to mingle  
None’s less likely to stay single.”  
*(Adam’s Atoms: Making Light of the Elements; 1965)*

### Manmade forever chemicals

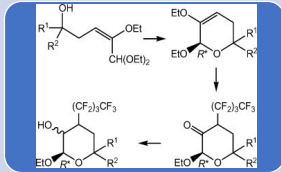
“You either die a hero, or you  
live long enough to see  
yourself become the villain”  
*Harvey Dent/Two-Face (The Dark Knight)*



2023

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## Stig Valdersnes



2002-  
2006



2006-



2019-

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## Outline



### History - Hero

- Fluorine
- Fluorocarbons and PFAS



### Current status - Villain

- Legislation
- Determination in food

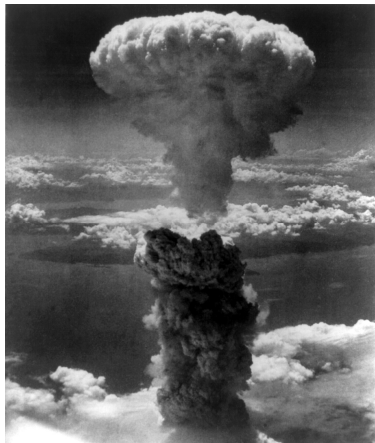


### Future – Criminal?

- Determination and screening in environment and food

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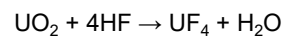
## Where did it all start?



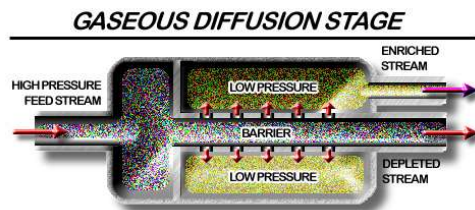
Hiroshima 1945

- Natural uranium is 99.28%  $^{238}\text{U}$  and 0.72%  $^{235}\text{U}$   
 $^1_0\text{n} + ^{235}_{92}\text{U} \rightarrow ^{140}_{54}\text{Ba} + ^{93}_{38}\text{Kr} + 3 ^1_0\text{n} + \text{energy}$

- Uranium ore (yellow cake) is converted to  $\text{UO}_2$



- Nearly all uranium enrichment plants utilize  $\text{UF}_6$  as feed



$\text{UF}_6$  is highly corrosive and perfluorinated materials were required for the process to work

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1886 Moissan isolates fluorine  
 1906 Nobel prize  
 Prize motivation: "in recognition of the great services rendered by him in his investigation and isolation of the element fluorine, and for the adoption in the service of science of the electric furnace called after him"



<https://www.nobelprize.org/prizes/chemistry/1906/moissan/facts/>

PERIODIC TABLE  
Atomic Properties of the Elements

NIST National Institute of Standards and Technology  
U.S. Department of Commerce  
Physical Measurement Laboratory www.nist.gov/pml  
Standard Reference Data www.nist.gov/srd

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS<sup>1</sup>

<sup>1</sup> second = 1/1024(177) periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of <sup>133</sup>Cs

speed of light in vacuum  $c = 299\,792\,458 \text{ m s}^{-1}$  (exact)

Planck constant  $h = 6.626\,070\,15 \times 10^{-34} \text{ J s}$  (exact)

elementary charge  $e = 1.602\,176\,634 \times 10^{-19} \text{ C}$  (exact)

Avogadro constant  $N_A = 6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$  (exact)

Boltzmann constant  $k_B = 1.380\,658 \times 10^{-23} \text{ J K}^{-1}$  (exact)

electron volt  $eV = 1.602\,176\,634 \times 10^{-19} \text{ J}$  (exact)

electron mass  $m_e = 9.109\,383\,704 \times 10^{-31} \text{ kg}$  (exact)

proton mass  $m_p = 1.672\,621\,923 \times 10^{-27} \text{ kg}$  (exact)

neutron mass  $m_n = 1.674\,927\,471 \times 10^{-27} \text{ kg}$  (exact)

fine-structure constant  $\alpha = 1/137.035\,999$

Rydberg energy  $R_\infty = 13.605\,693\,123 \text{ eV}$

Newtonian constant of gravitation  $G = 6.674 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$

For the most accurate values of these and other constants, visit [www.nist.gov/pml](http://www.nist.gov/pml).

Legend:  
 Solids (white)  
 Liquids (light blue)  
 Gases (light green)  
 Artificially Prepared (yellow)

|   |    |    |      |  |  |  |  |  |  |  |  |  |    |    |    |    |    |    |    |    |    |    |    |    |    |    |     |     |     |     |     |
|---|----|----|------|--|--|--|--|--|--|--|--|--|----|----|----|----|----|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|
| 1 | 2  |    |      |  |  |  |  |  |  |  |  |  |    |    |    |    |    | 18 |    |    |    |    |    |    |    |    |     |     |     |     |     |
| 1 | IA | 2  | IIIA |  |  |  |  |  |  |  |  |  | 13 | 14 | 15 | 16 | 17 | 18 |    |    |    |    |    |    |    |    |     |     |     |     |     |
| 1 | H  | He |      |  |  |  |  |  |  |  |  |  |    |    |    |    |    |    | He |    |    |    |    |    |    |    |     |     |     |     |     |
| 2 | Li | Be | B    |  |  |  |  |  |  |  |  |  | 6  | C  | N  | O  | F  | Ne |    |    |    |    |    |    |    |    |     |     |     |     |     |
| 2 | Li | Be | B    |  |  |  |  |  |  |  |  |  | 6  | C  | N  | O  | F  | Ne |    |    |    |    |    |    |    |    |     |     |     |     |     |
| 3 | Na | Mg | Al   |  |  |  |  |  |  |  |  |  | 13 | Si | 14 | 15 | 16 | 17 | 18 |    |    |    |    |    |    |    |     |     |     |     |     |
| 3 | Na | Mg | Al   |  |  |  |  |  |  |  |  |  | 13 | Si | 14 | 15 | 16 | 17 | 18 |    |    |    |    |    |    |    |     |     |     |     |     |
| 4 | K  | Ca | Sc   |  |  |  |  |  |  |  |  |  | 21 | Ti | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34  | 35  | 36  |     |     |
| 4 | K  | Ca | Sc   |  |  |  |  |  |  |  |  |  | 21 | Ti | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34  | 35  | 36  |     |     |
| 5 | Rb | Sr | Y    |  |  |  |  |  |  |  |  |  | 39 | Zr | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52  | 53  | 54  |     |     |
| 5 | Rb | Sr | Y    |  |  |  |  |  |  |  |  |  | 39 | Zr | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52  | 53  | 54  |     |     |
| 6 | Cs | Ba | La   |  |  |  |  |  |  |  |  |  | 57 | Ce | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70  | 71  | 72  |     |     |
| 6 | Cs | Ba | La   |  |  |  |  |  |  |  |  |  | 57 | Ce | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70  | 71  | 72  |     |     |
| 7 | Fr | Ra | Ac   |  |  |  |  |  |  |  |  |  | 87 | Th | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 | 104 |
| 7 | Fr | Ra | Ac   |  |  |  |  |  |  |  |  |  | 87 | Th | 88 | 89 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 | 104 |

Atomic Number, Ground State, Name, Standard Atomic Weight, Ground-state Configuration, Ionization Energy (eV)

<sup>1</sup>Based upon <sup>12</sup>C. ( ) indicates the mass number of the longest-lived isotope.

For the most precise values and uncertainties visit [www.nist.gov/pml](http://www.nist.gov/pml) and [www.nist.gov/srd](http://www.nist.gov/srd).  
 NIST SP 966 (July 2019)

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# Some landmark events in fluorine chemistry

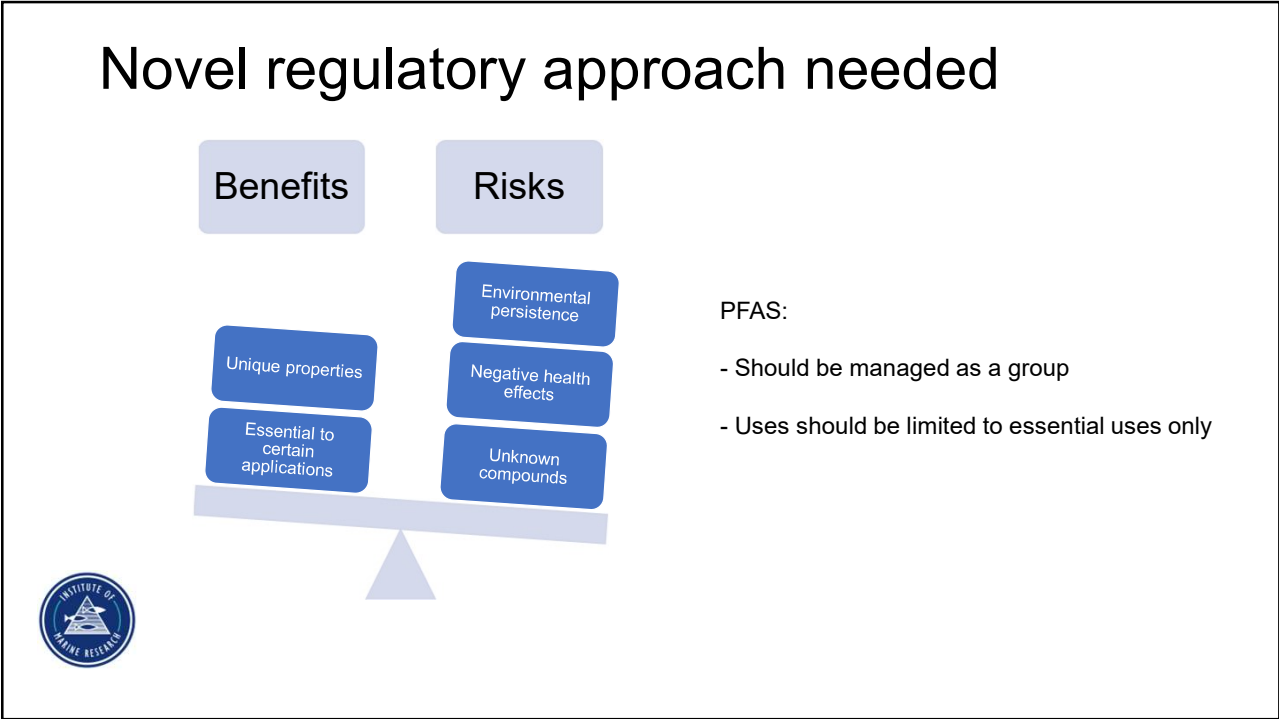
- 1886 Moissan isolates fluorine
- 1892 Swarts discover Cl/Br to F exchange using  $SbF_3$  - *difluoroethanol*
- 1928 Midgley invents CFCs - *Freon*<sup>®</sup> 12 ( $CF_2Cl_2$ )
- 1938 Plunkett discovers PTFE - *Teflon*<sup>®</sup> - *poly(C<sub>2</sub>F<sub>4</sub>)* from *Freon*<sup>®</sup> 22 ( $CF_2HCl$ )
- 1941 Bigelow discovers direct perfluorination
- 1947 Fowler publishes  $CoF_3$  method of perfluorination & Miller publishes MFP polymer - *poly(C<sub>2</sub>F<sub>3</sub>Cl)*
- 1949 Simons publishes electrochemical fluorination
- **1950s PFAS used in consumer applications such as non stick and protective coating**
- 1954 Fried pioneers work in medicinal fluorine chemistry & fluorinated anesthetics are invented
- **1960s PFAS based firefighting foams**
- 1962 Bartlett discovers noble gas chemistry of fluorine - ( $XePtF_6$ )
- 1966 Clark and Gollan demonstrates that a mouse can survive by breathing an oxygenated PFAS
- **1970s Occupational studies detect PFAS in blood of exposed workers**
- 1974 Molina and Rowland develops model of ozone depletion
- 1979 Margraves "direct" perfluorination discoveries
- **1987 Montreal protocol ban CFCs**
- **1990s PFAS detected in the general population**
- **2000s Stockholm convention and PFAS started to be listed for restriction and elimination**
- 2003 O'Hagan isolates the first fluorinating enzyme
- **2020s Ban of all fluorocarbons/PFAS?**



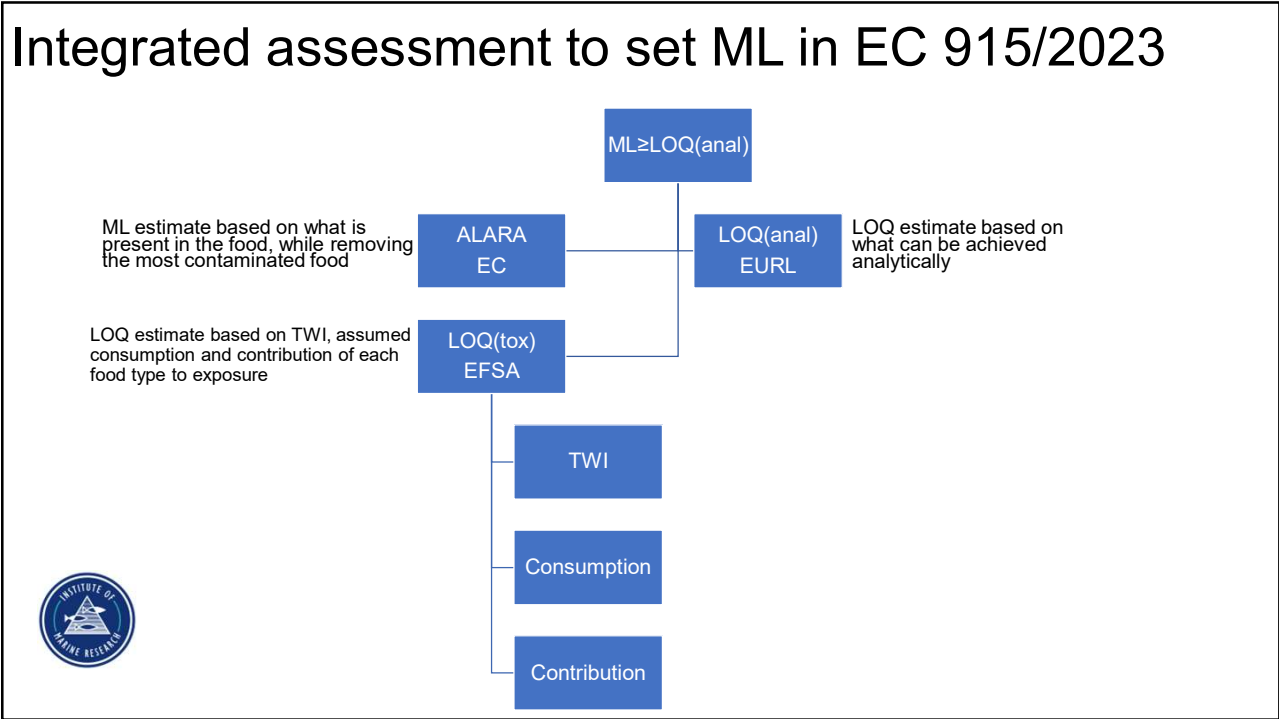
Jack Rebok, Robert McHarnes, and Roy Plunkett dig out PTFE from gas cylinders in 1938



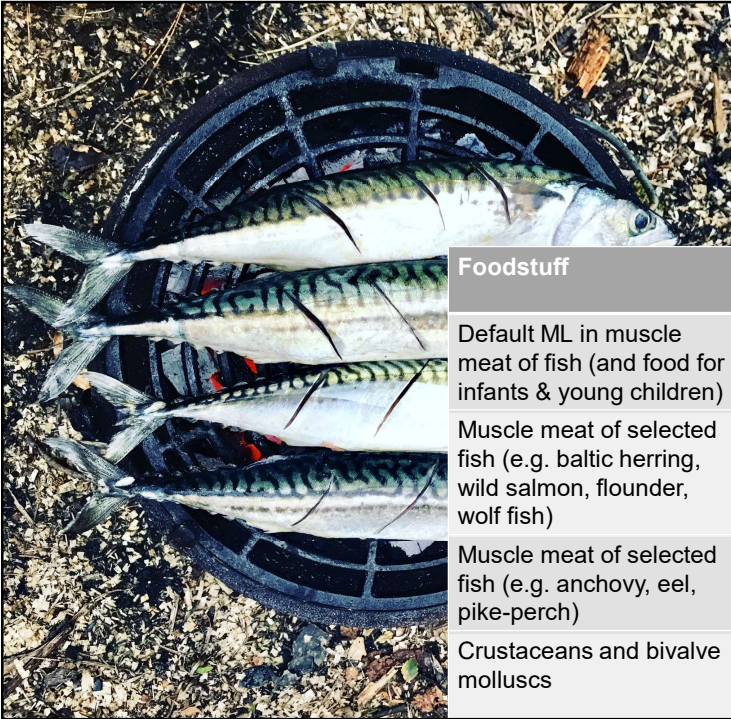
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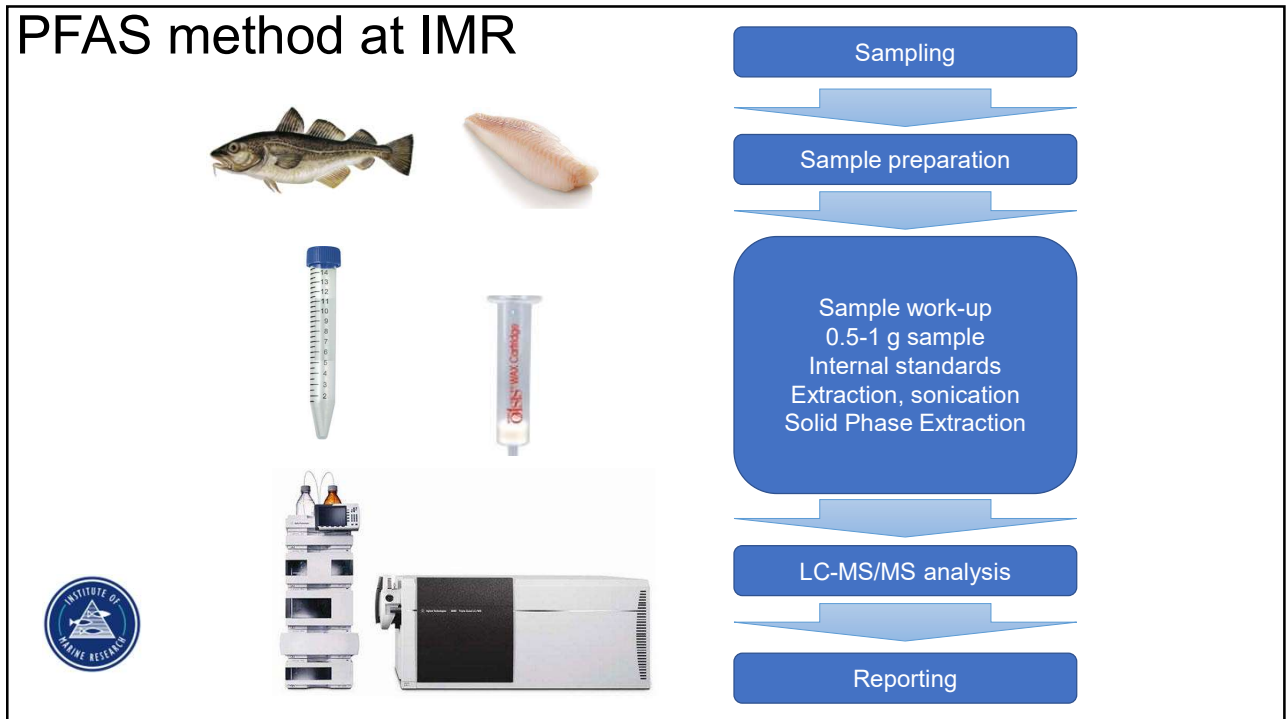
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## PFAS regulatory maximum limits (MLs) seafood ( $\mu\text{g}/\text{kg}$ )

| Foodstuff  | PFOS | PFOA | PFNA | PFHxS | Sum PFAS4 |
|--|------|------|------|-------|-----------|
| Default ML in muscle meat of fish (and food for infants & young children)            | 2.0  | 0.2  | 0.5  | 0.2   | 2.0       |
| Muscle meat of selected fish (e.g. baltic herring, wild salmon, flounder, wolf fish) | 7.0  | 1.0  | 2.5  | 0.2   | 8.0       |
| Muscle meat of selected fish (e.g. anchovy, eel, pike-perch)                         | 35   | 8.0  | 8.0  | 1.5   | 45        |
| Crustaceans and bivalve molluscs   | 3.0  | 0.7  | 1.0  | 1.5   | 5.0       |

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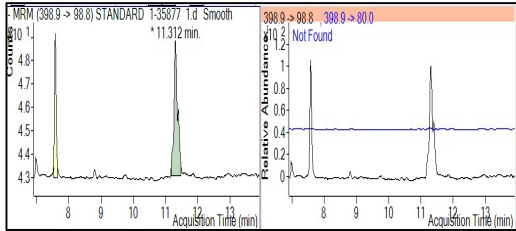
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# Exploris 120 Orbitrap HRMS vs 6410B MS/MS

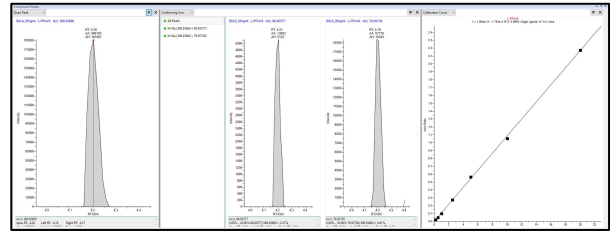
PFHxS

6410

Orbitrap



0,2 ng/ml



0,05 ng/ml



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## Ongoing Validation of quantitative confirmation method

**Spike recoveries** (@/below ML in salmon) – Criteria (80-120 ± 20)%

| PFAS           | L-PFHxS<br>(0.2 ng/g) | L-PFOS<br>(0.2 ng/g) | PFOA<br>(0.2 ng/g) | PFNA<br>(0.5 ng/g) |
|----------------|-----------------------|----------------------|--------------------|--------------------|
| Recovery ± RSD | 86 ± 4                | 92 ± 14              | 96 ± 14            | 101 ± 7            |



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# Determination of fluorine species

## Applications


| Question  | Purpose  | Qualitative/Quantitative | Screening/Confirmation | Parameter    |
|---|----------|--------------------------|------------------------|--------------|
| Which analytes are present in the sample?         | Research | Qualitative              | Screening              | Selectivity  |
| Is the analyte present above a certain level?     | Control  | Qualitative              | Confirmation           | LOD/ LOQ/ ML |
| How much of the analyte is present in the sample? | Research | Quantitative             | Screening              | Precision    |
| Is the level in the sample above a certain level? | Control  | Quantitative             | Confirmation           | Trueness     |

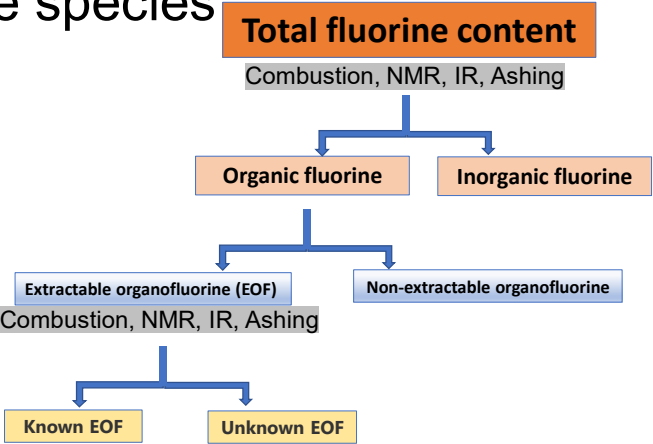
Preference for methods based on set performance criteria rather than design or descriptive characteristics



**Ultra-trace quantification**






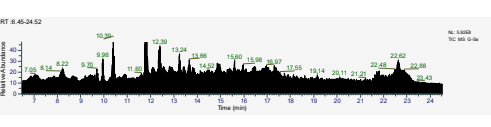

**Discovery of novel PFAS**



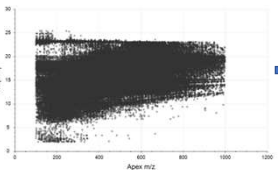

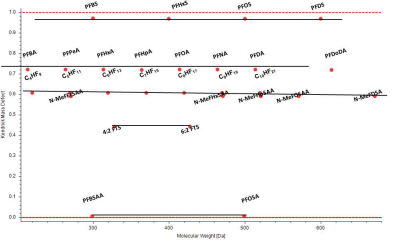







# Workflow for nontarget qualitative screening method








Full MS + data dependent ms2 (ddMS2)

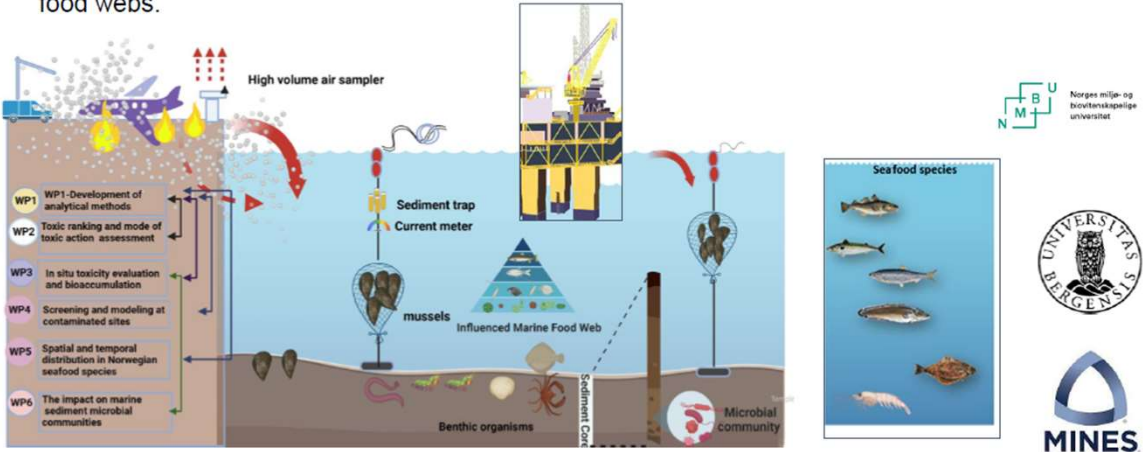



### Fate and effects of perfluoroalkyl substances and their precursors and alternatives in Norwegian marine environments and seafood species (FEARLESS)



**FEARLESS main objective:**

- 1) How marine organisms could be impacted by PFAS their precursors and alternatives
- 2) Explore the transfer and transformation of unknown organofluorine substances in marine food webs.



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# Thank you for your attention !



«the future of fluorine rests with the products, processes and businesses that it uniquely enables»  
*Bruce. E. Smart (Dupont, 2003)*

**References**

Commission Staff Working Document Poly- and perfluoroalkyl substances (PFAS), Brussels, (2020)  
 Letter to the EU Commission: Elements for an EU-strategy for PFASs, December 2019  
 Fluorine chemistry at the millennium, William R. Dolbier Jr., Journal of Fluorine Chemistry 126 (2005) 157-163  
 The Manhattan project, H. Goldwhite, Journal of Fluorine Chemistry 33 (1986) 190-132  
 Fredrich Swarts: Pioner in organic fluorine chemistry, G. B. Kauffman, Journal of chemical education 32 (1955) 301-303

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