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)

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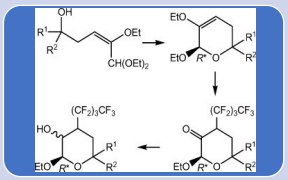
Stig Valdersnes



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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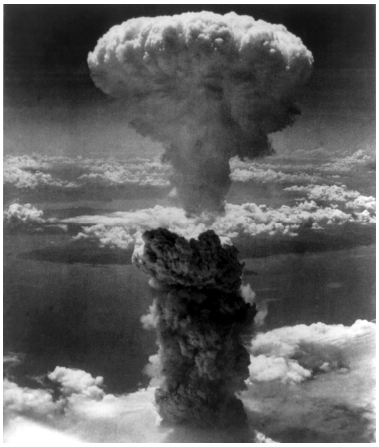
Where did it all start?



Hiroshima 1945

- Natural uranium is 99.28% ^{238}U and 0.72% ^{235}U

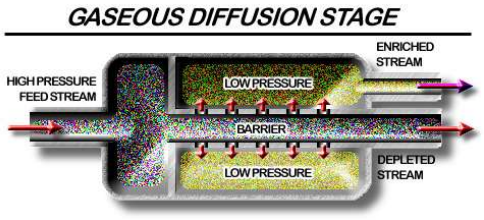
  $^{1}n + {}^{235}U \rightarrow {}^{140}Ba + {}^{93}Kr + 3\ {}^{1}n + \text{energy}$

- Uranium ore (yellow cake) is converted to UO_2

  $UO_2 + 4HF \rightarrow UF_4 + H_2O$

  Then $UF_4 + F_2 \rightarrow UF_6$

- Nearly all uranium enrichment plants utilize UF_6 as feed



UF_6 is highly corrosive and perfluorinated materials were required for the process to work

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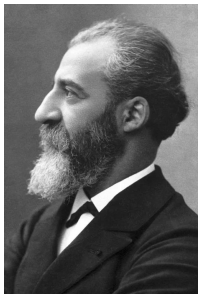
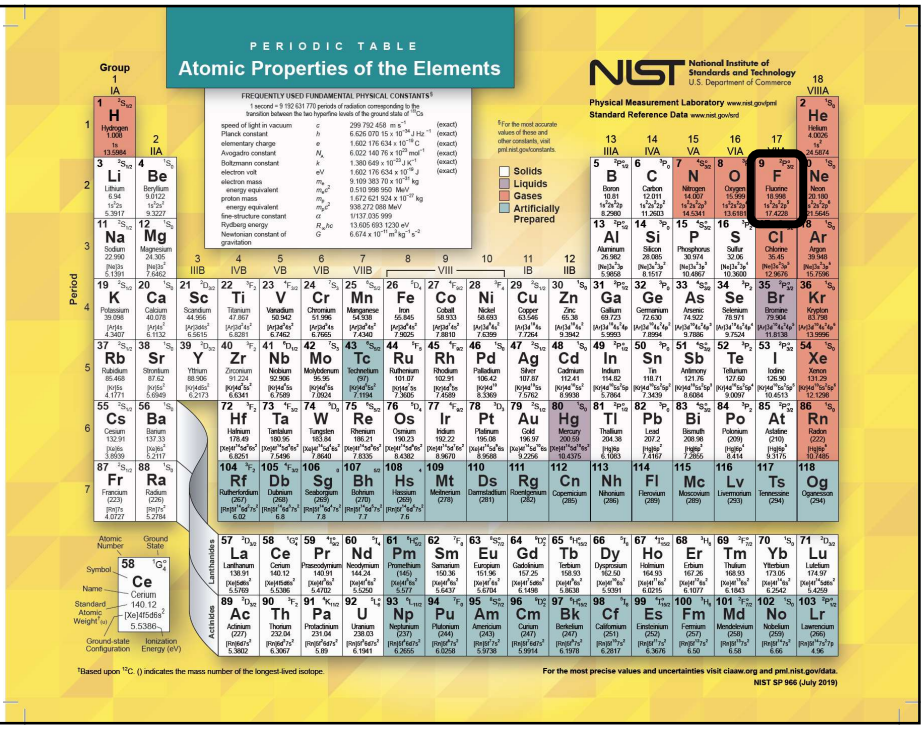


1886 Moissan isolates fluorine
1906 Nobel prize
Prize motivation: “in recognition of the great services rendered by him in his investigation and isolation of the element fluorine, and for the adoption in the service of science of the electric furnace called after him”

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



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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® 12 (CF_2Cl_2)*
- 1938 Plunkett discovers PTFE - *Teflon® - poly(C_2F_4) from Freon® 22 (CF_2HCl)*
- 1941 Bigelow discovers direct perfluorination
- 1947 Fowler publishes CoF_3 method of perfluorination & Miller publishes MFP polymer – *poly(C_2F_3Cl)*
- 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 nobel 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 McHarness, and Roy Plunkett digs out PTFE from gas cylinders in 1938

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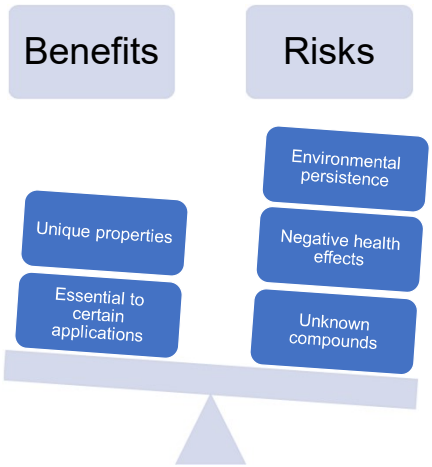
Novel regulatory approach needed



PFAS:

- Should be managed as a group

- Uses should be limited to essential uses only

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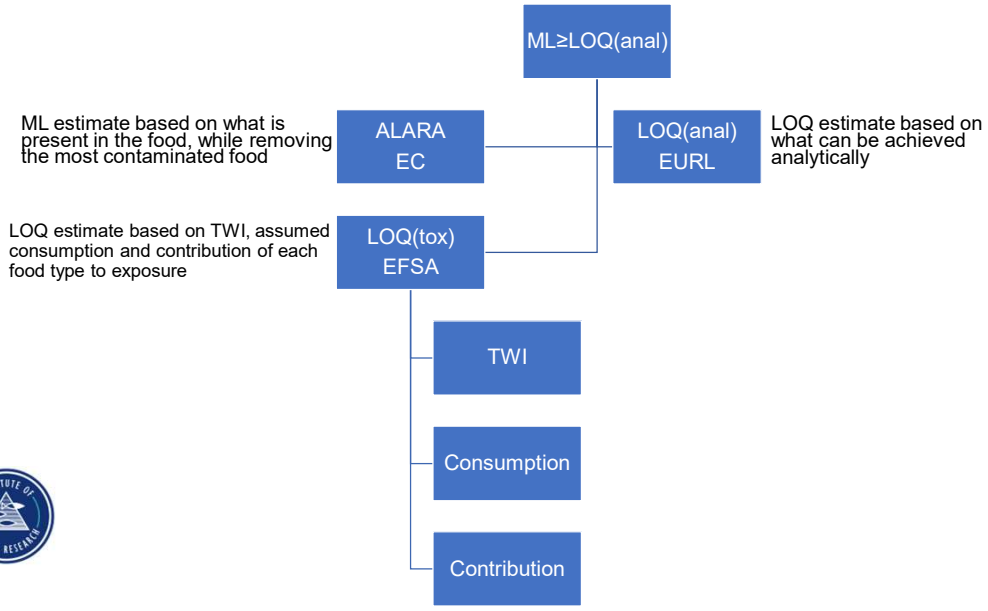
Integrated assessment to set ML in EC 915/2023



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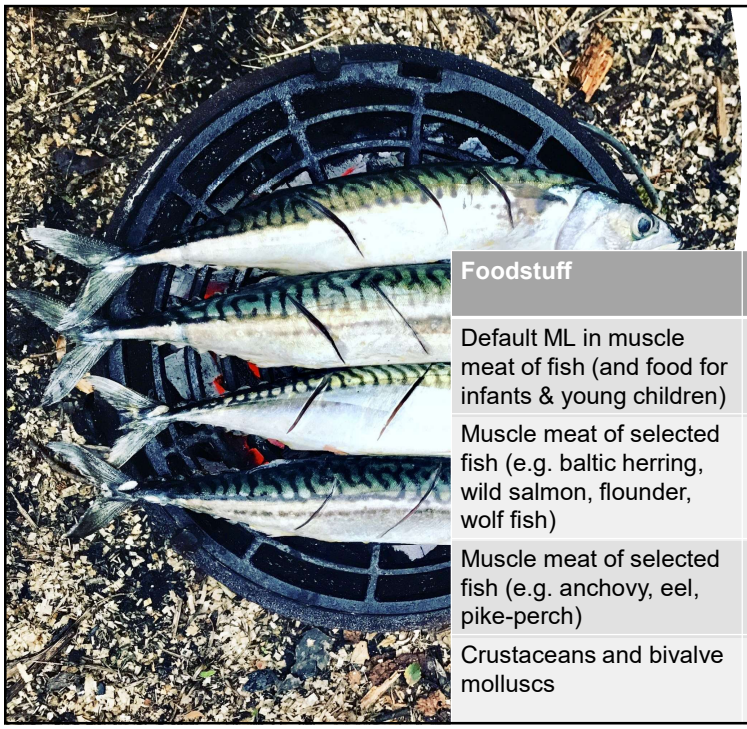

PFAS regulatory maximum limits (MLs) seafood (µg/kg)

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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PFAS method at IMR

Sampling

Sample preparation

Sample work-up
0.5-1 g sample
Internal standards
Extraction, sonication
Solid Phase Extraction

LC-MS/MS analysis

Reporting

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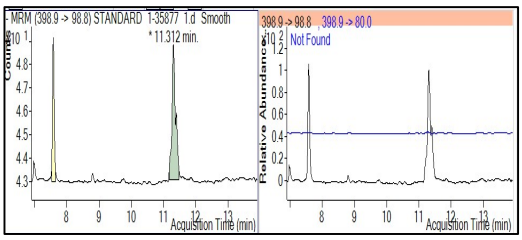
Exploris 120 Orbitrap HRMS vs 6410B MS/MS

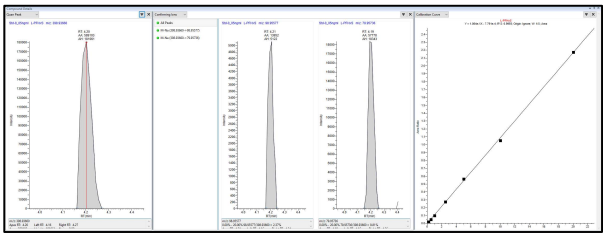
PFHxS

6410



0,2 ng/ml

Orbitrap



0,05 ng/ml

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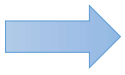
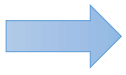
Ongoing Validation of quantiative confirmation method

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

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





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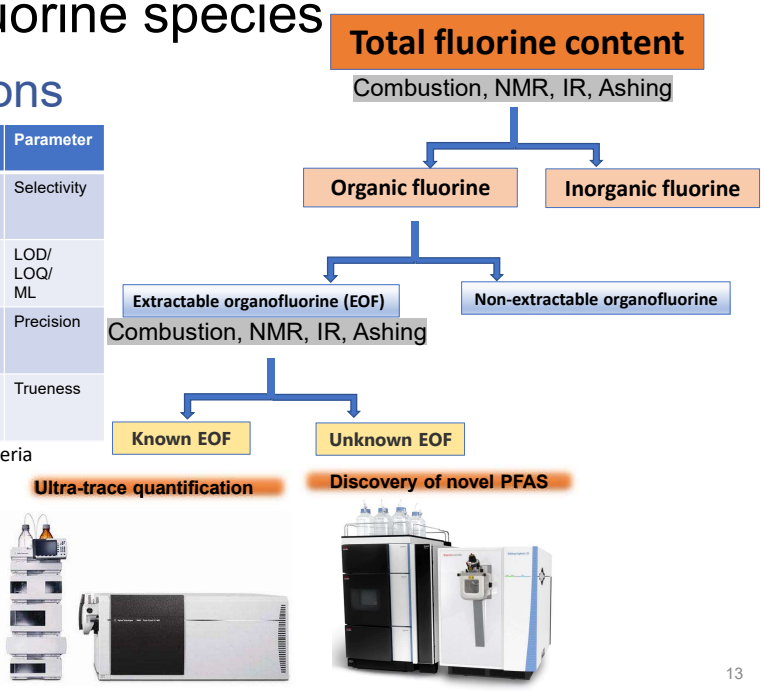
Determination of fluorine species

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



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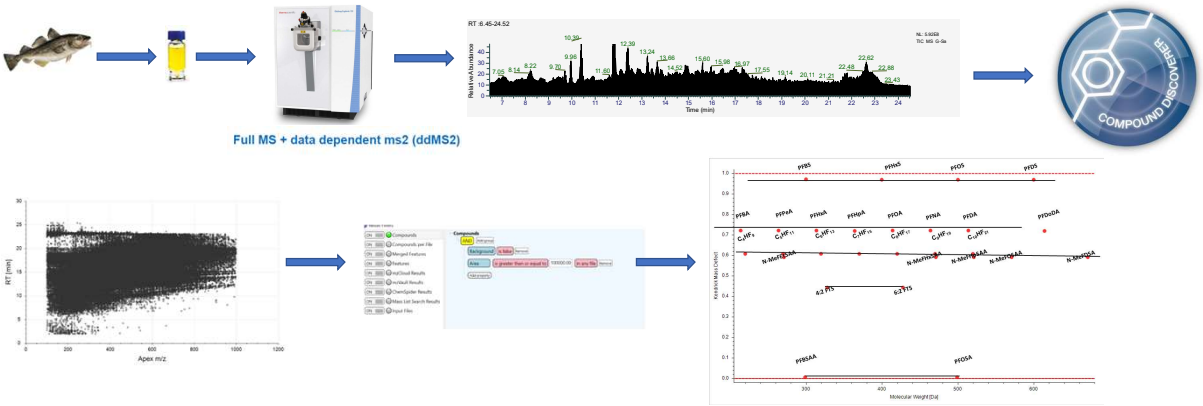
Workflow for nontarget qualitative screening method



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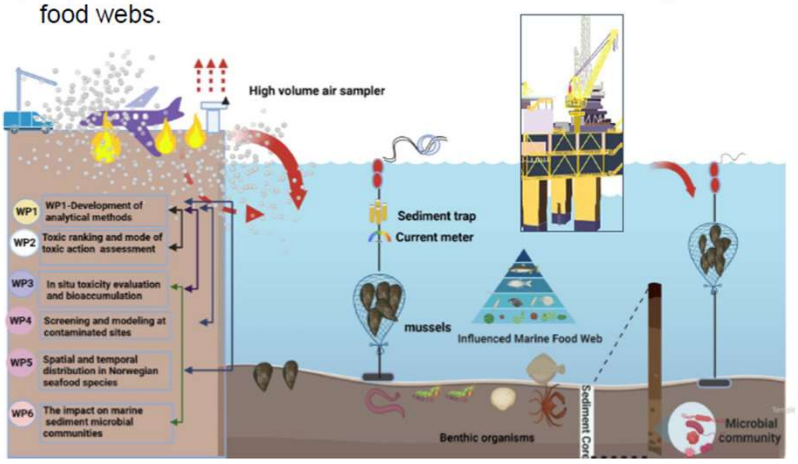
Fate and effects of perfluoroalkyl substances and their precursors and alternatives in Norwegian marine environments and seafood species (FEARLESS)

The Research Council of Norway

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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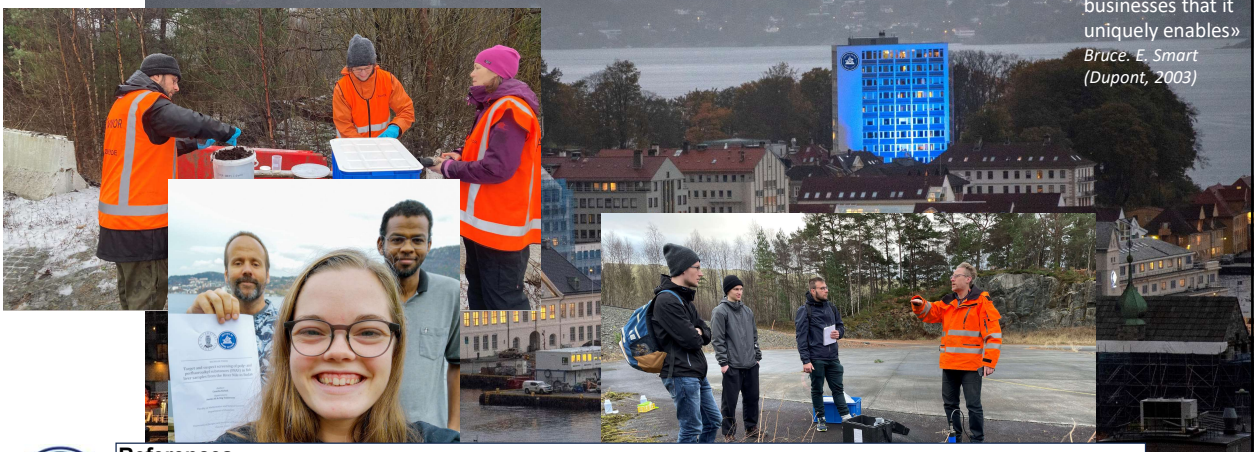
Thank you for your attention !

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



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