Determinazione del PFOS in biota tramite metodica QUECHERs e HPLC/HRMS:

Descrizione e validazione del metodo

Michele Mazzetti

ARPAT - Agenzia Regionale per la Protezione Ambientale della Toscana

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OUTLINE

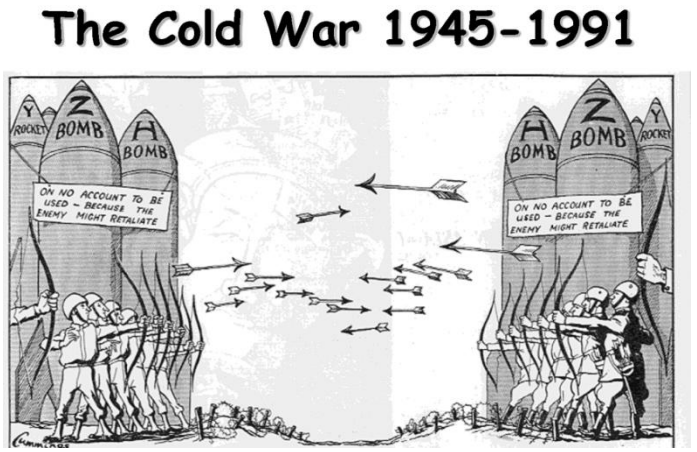
- Introduction
- PFAS Methods – solid matrices
- QuEChERS for PFAS
- Method Performance
- Conclusion

Fluorinated organic compound: Background history

Industrial application of fluorinated organic compounds started (Chlorofluorocarbons (CFC) as refrigerants).

The major turning point in the history of industrial fluoroorganic chemistry was the beginning of the Manhattan Project for development of nuclear weapons in 1941.
The Manhattan Project triggered the need for highly resistant materials, lubricants, coolants and the development of technology for handling extremely corrosive fluoroinorganic compounds

After 1945, with the beginning of the Cold War, various defense programs provided a constant driving force for further development of the chemistry and use of organofluorine compounds.
In the 1950s and 60s more civilian applications of fluorinated pharmaceuticals and materials moved into the forefront



"Modern Fluoroorganic Chemistry Synthesis, Reactivity, Applications", P Kirsch, 2004 WILEY-VCH

Fluorinated organic compound: Background history

Commercial Uses

Fluorinated surfactants can lower aqueous surface tension to less than 16 dynes/cm and function at very low concentrations (e.g., 100–500 mg/L or parts-per-million, ppm). They are effective in basic/acidic aqueous media and in organic solvents

- *superior wetting, spreading, and leveling properties for all types of surfaces. They give uniform film formation of coatings and eliminates pinholes and craters, even when applied to unclean surfaces*

- *extremely stable both chemically and thermally. Some of them are stable even in hot chromic acid, concentrated sulfuric acid or hydrofluoric acid*

- ***Aqueous Film-Forming Foams***
- ***Enhanced Oil Recovery***
- ***Coatings***
- ***Electroplating and Electrowinning***
- ***Electronics***

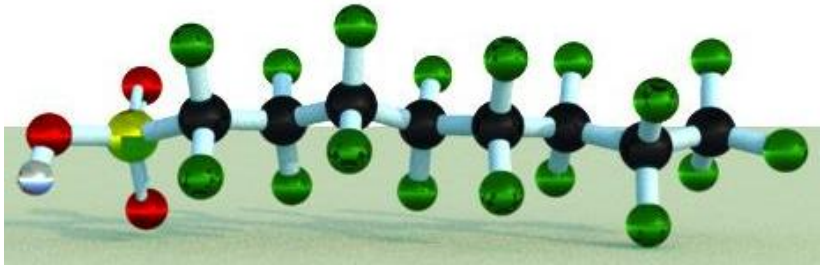
- ***Paper***
- ***Mining***
- ***Photographic Films***
- ***Fluoropolymer Polymerization Aid***
- ***Pesticide Application***

"Modern Fluoroorganic Chemistry Synthesis, Reactivity, Applications", P Kirsch, 2004 WILEY-VCH

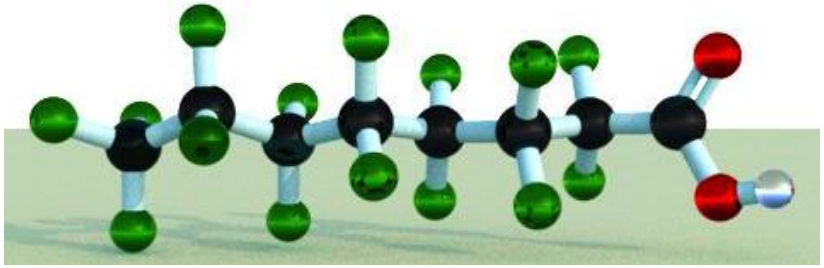
Fluorinated organic compound: Background history

Fluorinated surfactants have been commercially available since the 1950s.
The first available were perfluoroalkyl sulfonates (e.g., perfluorooctane sulfonate, $C_8F_{15}SO_3$, PFOS) and perfluoroalkyl carboxylic acids (e.g., perfluorooctanoic acid, $C_7F_{15}COOH$, PFOA) manufactured using the electrochemical fluorination (ECF) process.

PFOS



PFOA

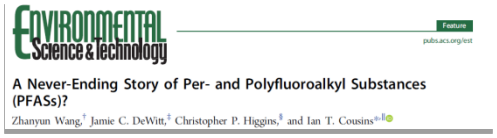


Perfluoroalkyl acids

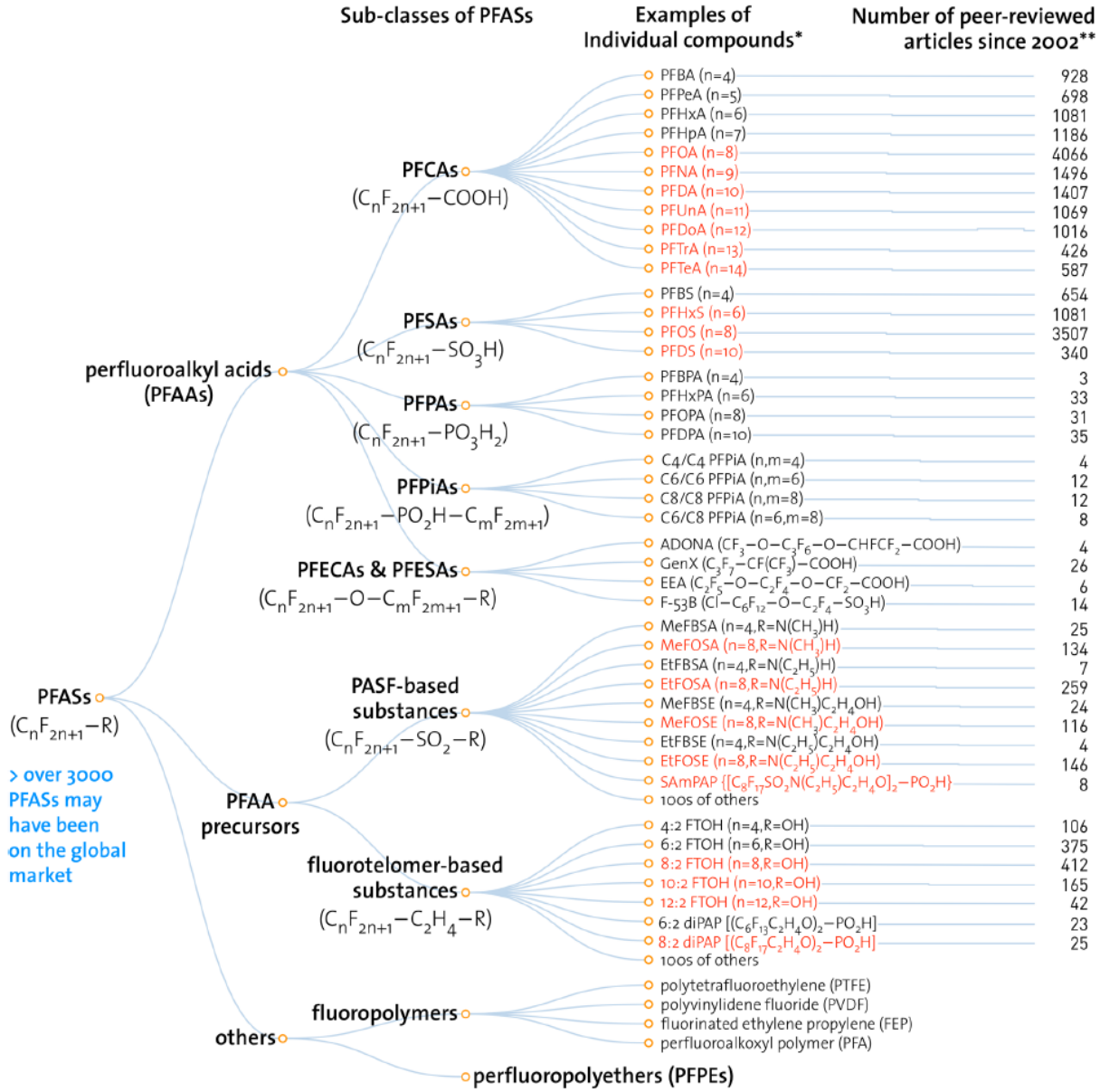
General name	Acronym	Structure
Perfluoroalkyl sulfonic acid	PFSA	$F(CF_2)_nSO_3H$
Perfluoroalkyl carboxylic acid	PFCA	$F(CF_2)_nCO_2H$
Perfluoroalkyl phosphonic acid	PFPA	$F(CF_2)_nP(=O)(OH)_2$
Perfluoroalkyl phosphinic acid	PFPIA	$F(CF_2)_nP(=O)(OH)$

"Polyfluorinated Chemicals and Transformation Products", T.P.Knepper, Springer-Verlag Berlin Heidelberg 2012

Fluorinated organic compound: Background history



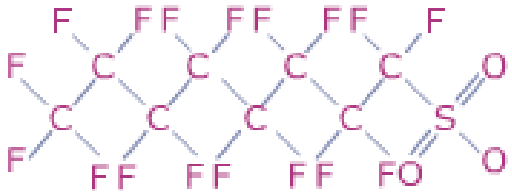
1. *PFAs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks with or without specific exemptions (for details, see OECD (UNEP 2015), Risk reductions approaches for PFASs.htpp>//oe.cd/1AN)*
2. *The numbers of articles (related to all aspects of research) were retrieved from SciFinder on Nov.1, 2016*



Environ.Sci.Technol. 2017 Mar 7;51(5):2508-2518

Perfluorinated organic compound: Environmental Regulatory Framework: Elements

IN EUROPEAN UNION



PFOS (Perfluorooctane sulfonate)

is classified as

- *as POP's (Reg. 757/2010) after PFOS was added to the Annex B of the Stockholm Convention in 2009*
- *Priority Substance for Water (Dir 2013/39/UE)*
- *Substance with Restriction limit as reported in Reg(EU) No 757/2010 amending Reg (CE) 850/2004*

PFOA (Perfluorooctanoic acid)

is classified as

- *Candidate in the SVHC List (Substances of Very High Concern) after MSC (Member States Commitee) identified in june 2013 PFOA as PBT.*
- *Substance with Restriction limits as reported in Reg. (UE) 2017/1000 (entry 68)*

Perfluorinated organic compound: Environmental Regulatory Framework: Elements

DIRECTIVE 2013/39 of August 2013

Environmental Quality
PAF

COMMISSION DIRECTIVE 2009/90/EC of 31 July 2009

Article 4

Minimum performance criteria for methods of analysis

Member States shall ensure that the minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50 % or below (k = 2) estimated at the level of relevant environmental quality standards and a **limit of quantification equal or below a value of 30 % of the relevant environmental quality standards.**

Requested LOQ = 2,1 x 10^{-4} µg/L **Requested LOQ = 3 µg/Kg**

(1)	(2)	(3					
No	Name of substance	CA numb					
			µg/L	*µg/L*	*µg/L*	*µg/L*	*µg/Kg wet weight*
(35)	Perfluorooctane sulfonic acid and its derivatives (PFOS)	1763-23-1	6,5 × 10^{-4}	1,3 × 10^{-4}	36	7.2	9.1

AA: annual average.
MAC: maximum allowable concentration.

Solid Matrix PFAS Methods

	ASTM D7968	EPA-821-R-11-007	537Ms / DoD
MATRIX	Soils	Sludge, Biosolids	Soils, Sediments, Biosolids, Tissues, etc
RL (ng/g)	0.025 - 0.75	0.25 - 10	***var***
PREPARATION	SLE (rotator) centrifuge, filter	digestion, incubation, SLE (shake), SPE	var
CLEAN-UP	Filtration	SPE WAX + filtration	var

SLE = Solid-Liquid Extraction
SPE = Solid Phase Extraction
WAX = Weak Anion Exchange

"Evaluation of QuEChERS Clean-up Sorbents for the Analysis of PFAS in Tissues and Biosolids
Syljohn Estil & Arnold Tesoro, LACSD Chemistry Research Group, August 2019

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Recent developments in Solid Matrix PFAS Methods

QuEChERS is considered accurate and highly productive at ultra trace levels10. Yet, for the analysis of PFAS in food, this method is not widely applied compared to the straighfoward SLE and IPE methods.
Recently, a one step QuEChERS extraction and purification was found to be successful.

U.S. FOOD & DRUG ADMINISTRATION

FDA Foods Program Compendium of Analytical Laboratory Methods: Chemical Analytical Manual (CAM)

METHOD NUMBER: C-010.01

POSTING DATE: 11/01/2019

POSTING EXPIRATION DATE: 10/31/2021

PROGRAM AREA: Chemical Contaminants

Determination of 16 Perluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Food using Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS)

Version 2019 (2019)

Author: Susan Genualdi and Lowri deJager

CFSAN/ORS reviewers: Tim Begley, Gregory Noonan

GLOSSARY

Analytical Methods

PAPER

View Article Online
View Journal | View Issue

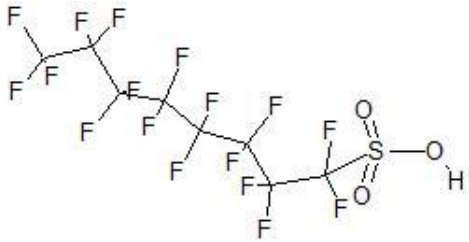
Check for updates

Cite this: *Anal. Methods*, 2018, 10, 5715

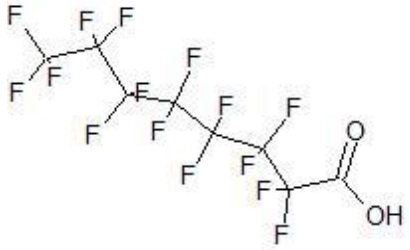
Simultaneous determination of legacy and emerging per- and polyfluoroalkyl substances in fish by QuEChERS coupled with ultrahigh performance liquid chromatography tandem ma spectrometry†

Yan Gao, Qinghe Zhang,* Xiaomin Li, Xiuqin Li and Hongmei Li

Perfluorinated organic compound: Challenges for the Analysis: Choice of Mass Detector



PFOS
ESI neg $[C_8F_{17}SO_3]^-$
mass=498.93022
nominal=498



PFOA
ESI neg $[C_8F_{15}O_2]^-$
mass=412.96643
nominal=413

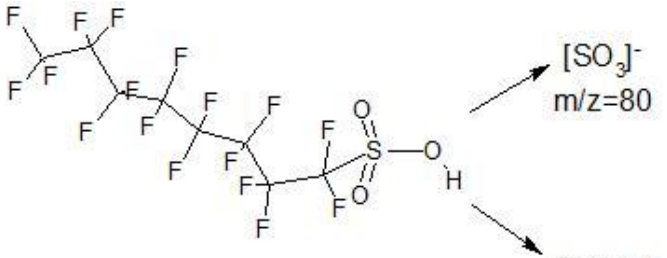
The main measurement technique for Perfluorinated compounds is liquid chromatography coupled to mass spectrometry after negative electrospray ionisation.

In ESI (negative mode)

The pseudomolecular ions $[M–H]^-$ is observed as the main generated ionic species. Perfluorocarboxylic acid, such as PFOA, exhibit in source fragmentation with loss of CO_2

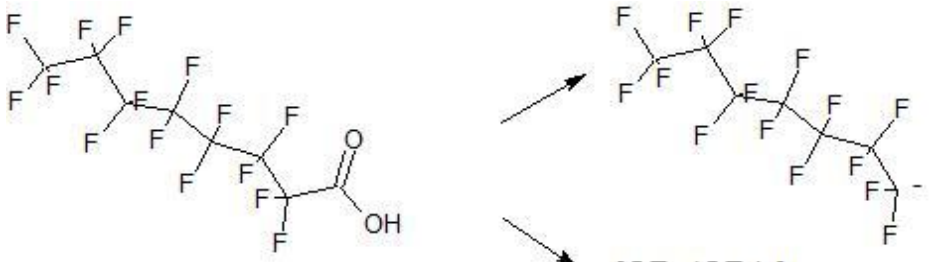
"Comparative study of low- versus high-resolution liquid chromatography-mass spectrometric strategies for measuring perfluorinated contaminants in fish", H. Kadar et al, . Food Additives and Contaminants Vol. 28, No. 9, September 2011, 1261–1273

Perfluorinated organic compound: Challenges for the Analysis: Choice of Mass Detector: behaviour in MSMS mode



PFOS
ESI neg $[C_8F_{17}SO_3]^-$
mass=498.93022
nominal=498

Loss of the hydrophilic sulfonate group was observed, leading to [SO_3] (m/z 80) and/or [FSO_3] (m/z 99) ions. However, these fragment ions remained of poor intensity and limited specificity.
Example of interferent in biological samples: taurodeoxycholic acid (TDCA)



PFOA
ESI neg $[C_8F_{15}O_2]^-$
mass=412.96643
nominal=413

For PFOA (Figure 2b), the observed fragmentation appeared slightly more effective, with the loss of CO_2 and subsequent fragmentation on the alkyl chain leading to [CF_3-(CF_2)n] ions where n equals 2, 3 or 5.

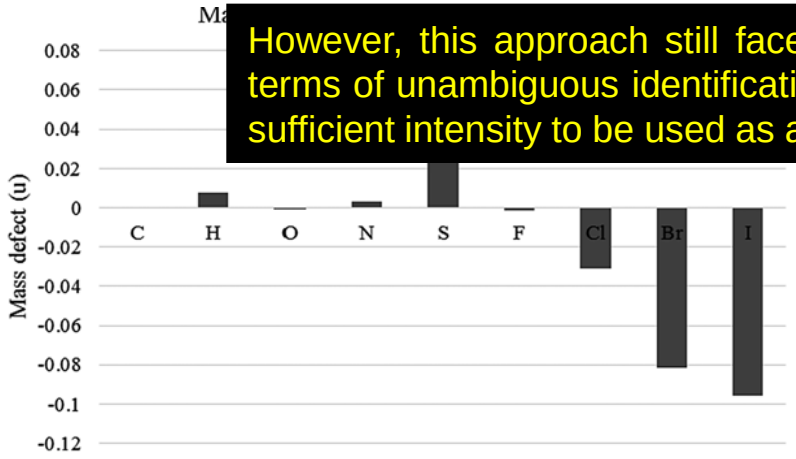
"Comparative study of low- versus high-resolution liquid chromatography-mass spectrometric strategies for measuring perfluorinated contaminants in fish", H. Kadar et al, . Food Additives and Contaminants Vol. 28, No. 9, September 2011, 1261–1273

Perfluorinated organic compound: Challenges for the Analysis: Choice of Mass Detector : behaviour in HRMS mode

The relative atomic mass of fluorine is 18.9984 and this value is less than the nominal mass (19).

In the case of hydrogen, the mass is larger than the nominal mass (1.008 vs 1)

Highly fluorinated compounds will therefore have lower monoisotopic masses than their respective nominal mass, in respect to compounds with only C–H bonds



However, this approach still faces some difficulties in fulfilling strict regulatory criteria in terms of unambiguous identification of the target analytes as only one ion is available with sufficient intensity to be used as a diagnostic signal.

The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment

Karl J. Jobst · Li Shen · Eric J. Reiner · Vince Y. Taguchi · Paul A. Helm · Robert McCrindle · Sean Backus

These properties can be very useful for the identification of PFASs with high resolution instruments capable of measuring monoisotopic mass.

"Toxicological Effects of Perfl uoroalkyl and Polyfluoroalkyl Substance", J.C DeWitt, Springer International Publishing Switzerland 2015

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Instrumental Choice

Orbitrap Exactive HCD

PFOS:
Biota: Pool of species

According to ISPRA guidelines, the species selected for the monitoring of PFAS, were:

Chelon labrosus

Liza aurata

Liza ramada

Liza saliens

Mugil cephalus

Sea and transiction waters:

All trophic levels betwee 2,3 and 3,5

Barbus plebejus

Leuciscus cephalus

Salmo truta

River and lakes

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Fluorinated organic compound: Sample Treatment: Fish

+

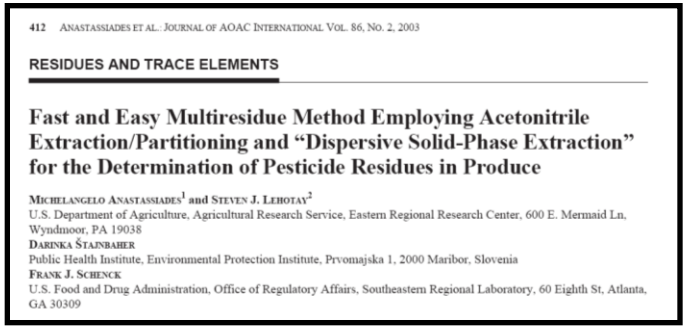
Analysis of PFOS in Fish: QUECHERs Extraction

Addition of 30 µl of 200 ng/ml methanolic solution of Extraction ILS ($^{13}C_8$-PFOS) to 2 g of fish omogeneate.

↓ equilbrate for 24 hours at -18ºC

Addition of 2 ml of water and 1 ceramic homogeneizer,

↓ vortex agitation for 1 minute



412 ANASTASSIADES ET AL.: JOURNAL OF AOAC INTERNATIONAL VOL. 86, NO. 2, 2003

RESIDUES AND TRACE ELEMENTS

Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce

MICHELANGELO ANASTASSIADES[1] and STEVEN J. LEHOTAY[2]
U.S. Department of Agriculture, Agricultural Research Service, Eastern Regional Research Center, 600 E. Mermaid Ln, Wyndmoor, PA 19038
DARINKA ŠTAJNBAHER
Public Health Institute, Environmental Protection Institute, Prvomajska 1, 2000 Maribor, Slovenia
FRANK J. SCHENCK
U.S. Food and Drug Administration, Office of Regulatory Affairs, Southeastern Regional Laboratory, 60 Eighth St, Atlanta, GA 30309

Addition of 10 ml of acetonitrile

↓ vortex agitation for 1 minute

Addition of 1 pouche of reagent mix for QUECHERs extraction compliance to EN15662

↓ vortex agitation for 1 minute

Centrifugation and collection of liquid phase

↓

Withdrawal of 1,2 ml of solution and addition of 0,3ml of water

pH Adjustment in QUECHERs Extraction Step

Various Buffers tested → **Compromise: Citrate Buffer**

4g Magnesium sulphate anhydrous,

- 1 g Sodium chloride (not essential but kept for **better selectivity**),
- **1 g Trisodium citrate dihydrate and**
- **0.5 g Disodium hydrogencitrate sesquihydrate**

Merits:

- ✓ ***Good recoveries even for very acidic pesticides*** *(dicamba ....)*
- ✓ ***Good recoveries for base- and acid-sensitive pesticides***
- ✓ ***Improved Selectivity*** *(less co-extractives from* ***acidic samples****)*
- ✓ ***No negative effect on PSA cleanup*** *(unlike Acetate Buffer)*

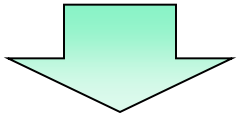
Impact of Lipids on Workflow

- **Inability to meet detection criteria**
  - Longer method development time
  - Method troubleshooting
  - Variability depending on matrix
  - QC/LOQ issues/reruns
  - **Indeterminate time**
- **Data variability**
  - High RSDs
  - Data accuracy
  - Variability depending on matrix
  - **Reruns, data analysis time**

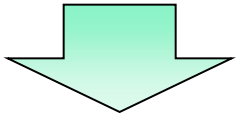
- **Mass Spec Cleanliness**
  - Cleaning the source
  - Cleaning/replacing capillary
  - Liner Lifetime/Inlet issues
  - Establishing vacuum levels
  - Retuning
  - Any additional troubleshooting
  - **4 hours - > 1day**
- **Lipid Build Up on Column**
  - Column longevity / GC column cutting
  - Back pressure
  - Column flushing / equilibration
  - **Approximately 2 hours**

Analysis of PFOS in Fish: Clean-up

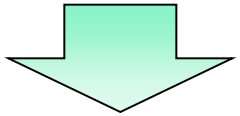
Load 1,5 ml of diluite extraction solution on the top of an Agilent EMR Captiva 3 mL, 300 mg



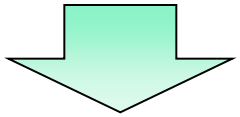
Allow extract flow under gravity and collect into a polypropylene tube



Load 300 µL of Acetonitrile/Water = 80/20, flow under gravity and collect with the previous fraction



Drain with positive pressure (Syringe) and vortex the combined eluates



Take 300 µl of combined eluates, put into a polypropylene vial and add 4,5µl of ILS injection solution (1,2,3,4- $^{13}C_4C4_4$ –PFOS , 200 ng/ml: 0,9 ng, approximately 3 ng/ml)

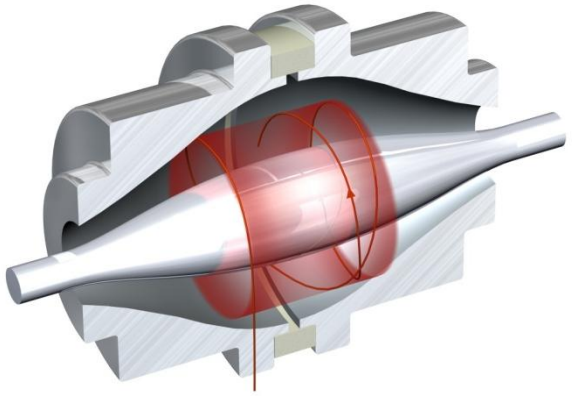
PFOS in Fish: Analytical condition

UHPLC: Thermo Accela 1250 pump

- *TRAP column: 50x2.1 mm (1.9 µm) Waters Fusion (between pump and injection valve)*
- Analytical column : Phenomenex Kinetex F5, 100 mm, 3 mm, 2,6 µm
- Mobile Phase: [A] 5mM NH_4OOCH+2%MeOH + 0.025% HCOOH; [B] MeOH 85%+iPrOH 15%
- Gradient from 90/10 to 10/90 in 20 min., Flow: 400 µL/min
- Column Temperature: 40 ºC

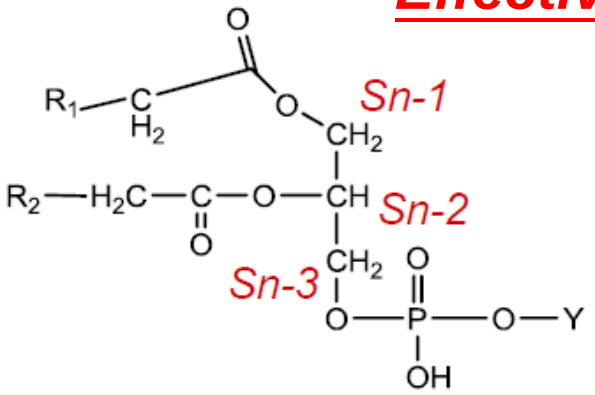
Thermo Orbitrap Exactive

- ESI negative
- Full scan, Resolution 50000, accuracy 5 ppm



Analyte	Deprotonated ion	Target ion
Perfluorooctanesulfonic acid	$C_8F_{17}O_3S$	498.93022
$^{13}C_8$ Perfluorooctanesulfonic acid (ILS)	$^{13}C_8F_{17}O_3S$	506.95706
1,2,3,4 $^{13}C_8$ Perfluorooctanesulfonic acid (ILS)	1,2,3,4 -$^{13}C_4C_4F_{17}O_3S$	502.94364

Effectiveness of Clean Up Step



Phospholipid: general structure

Phosphatidylethanolamine (PE)

Y= NH_2

Phosphatidylcholine (PC)

Y= $N(CH_3)_3$

Phosphatidylglycerol (PG)

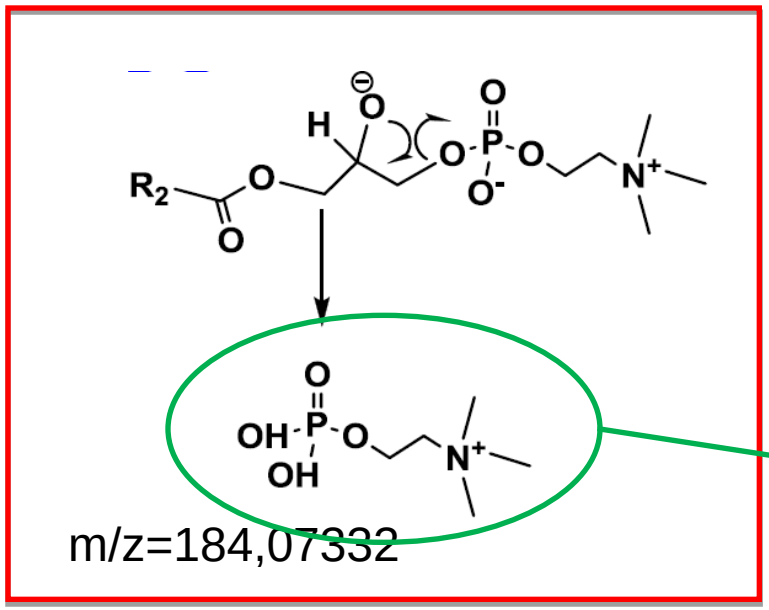
Y= OH, OH

Phosphatidylserine (PS)

Y= O, OH, NH_2

Phosphatidylinositol (PI)

Y= HO, HO, OH, OH, OH



Phosphocoline-H^+

Phosphatidylcholine: Typical fragmentation

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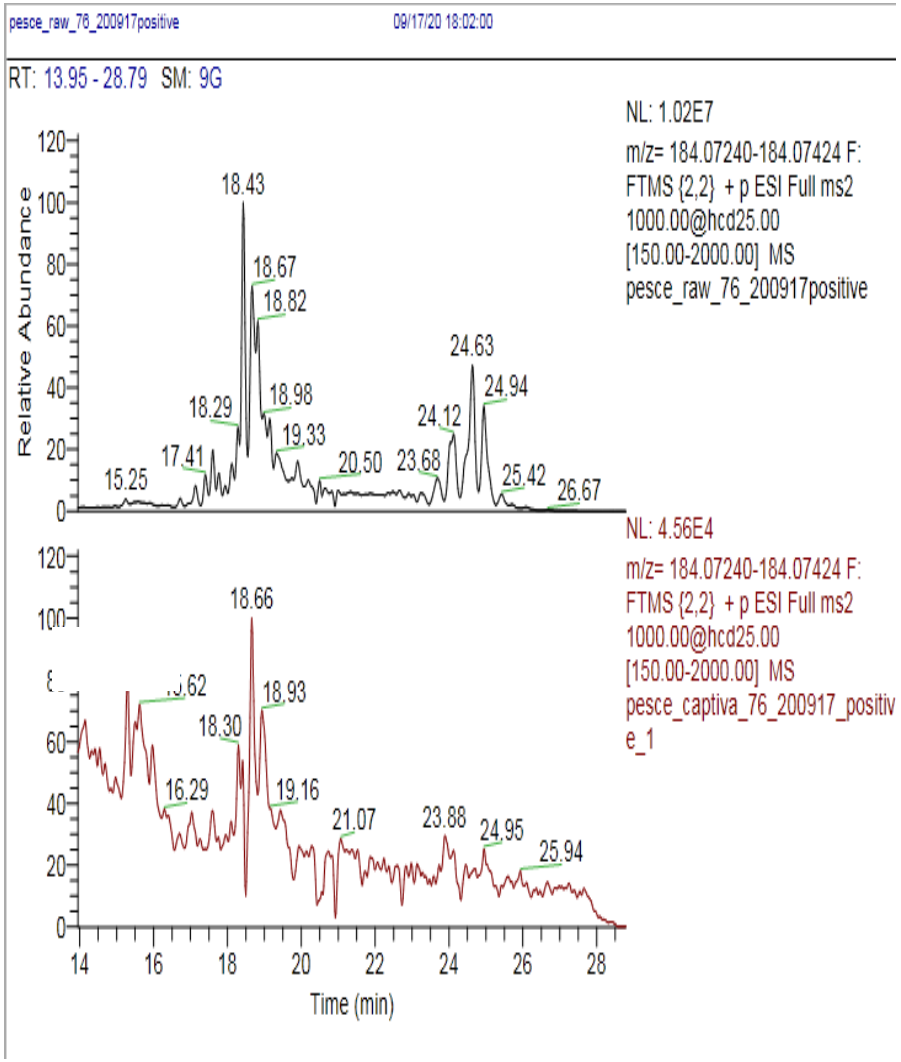
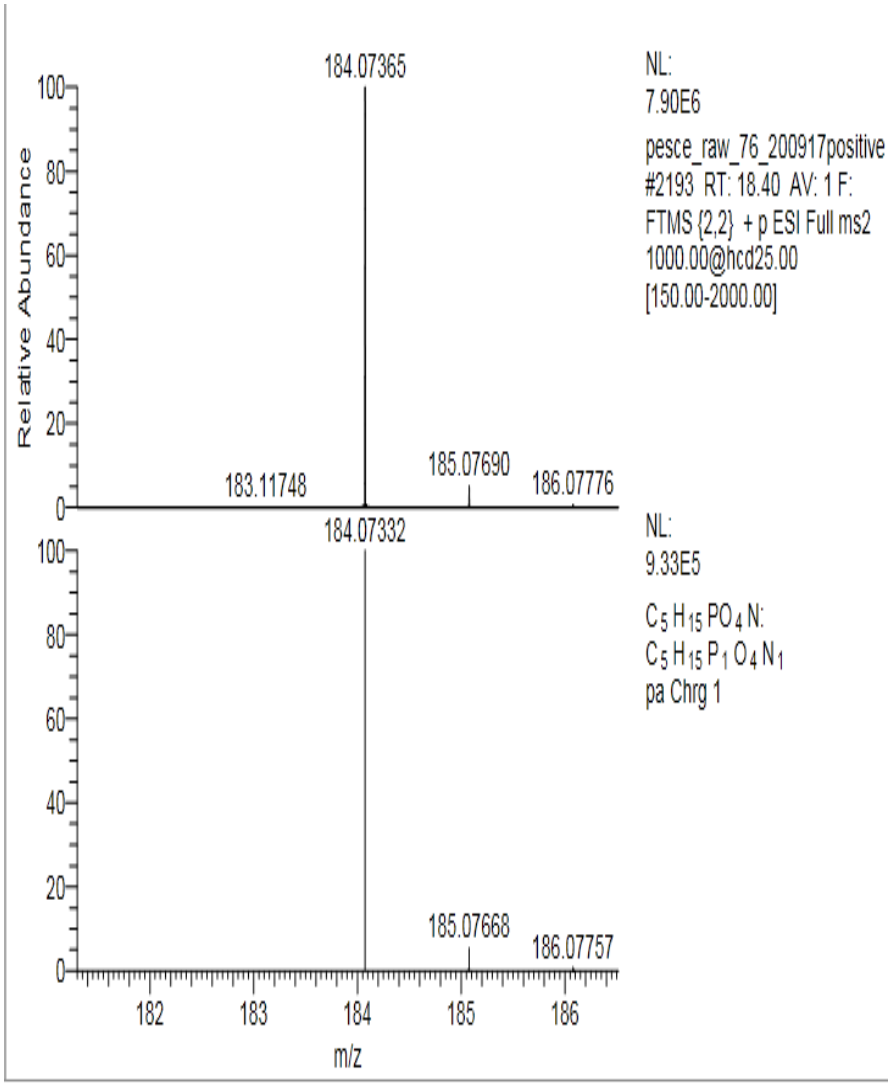
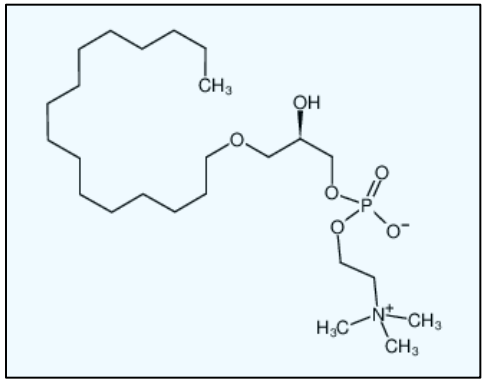
Effectiveness of Clean Up Step





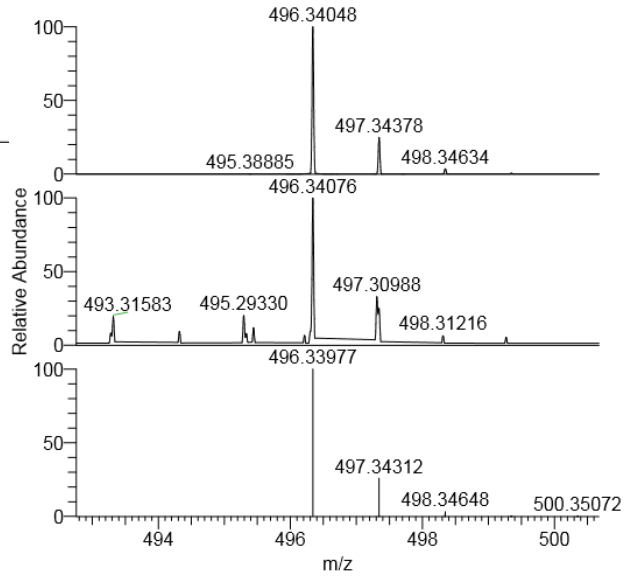
Effectiveness of Clean Up Step



Lysolecithin

Lysophosphatidylcholine (LPC)

2-Hydroxy-3-(palmitoyloxy)propyl 2-(trimethylammonio)ethyl phosphate



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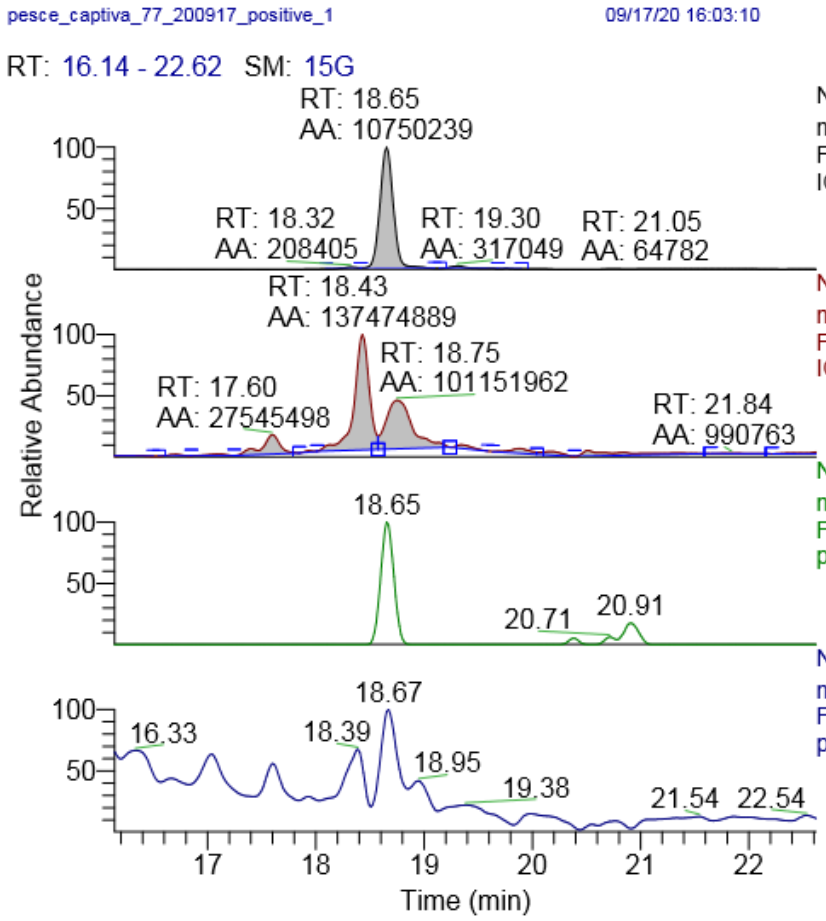
Effectiveness of Clean Up Step



NL: 1.26E6
m/z= 496.33729-496.34225 F: FTMS {2,2} + p ESI
Full ms2 1000.00@hcd25.00 [150.00-2000.00] MS
ICIS Pesce_RAW_77_200917_positive

NL: 1.51E7
m/z= 184.07228-184.07412 F: FTMS {2,2} + p ESI
Full ms2 1000.00@hcd25.00 [150.00-2000.00] MS
ICIS Pesce_RAW_77_200917_positive

NL: 1.29E4
m/z= 496.3372[illegible]4225 F: FTMS {2,2} + p ESI
Full ms2 1000.[illegible]5.00 [150.00-2000.00] MS
pesce_captiva_[illegible]7_positive_1

NL: 3.36E4
m/z= 184.07228-184.07[illegible]
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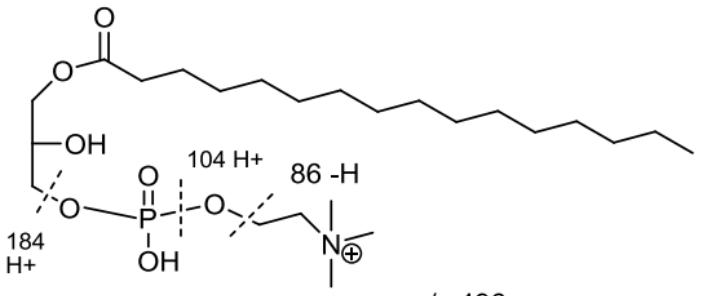
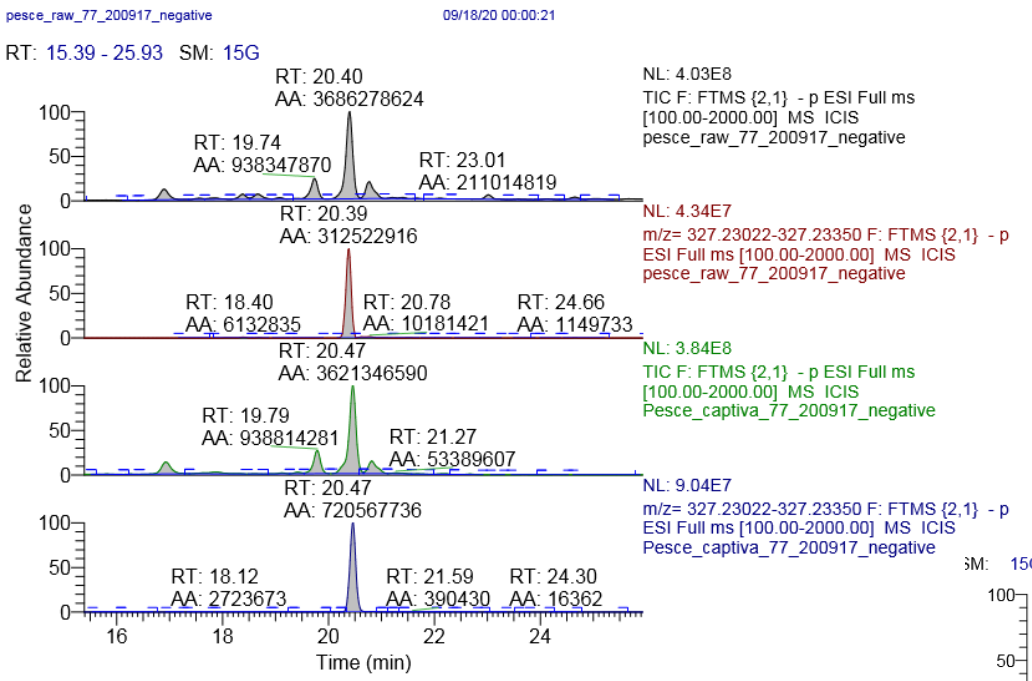
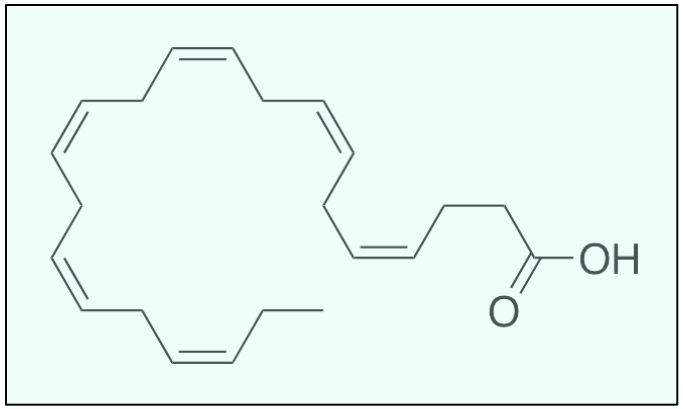
pesce_captiva_77_200917_[illegible]



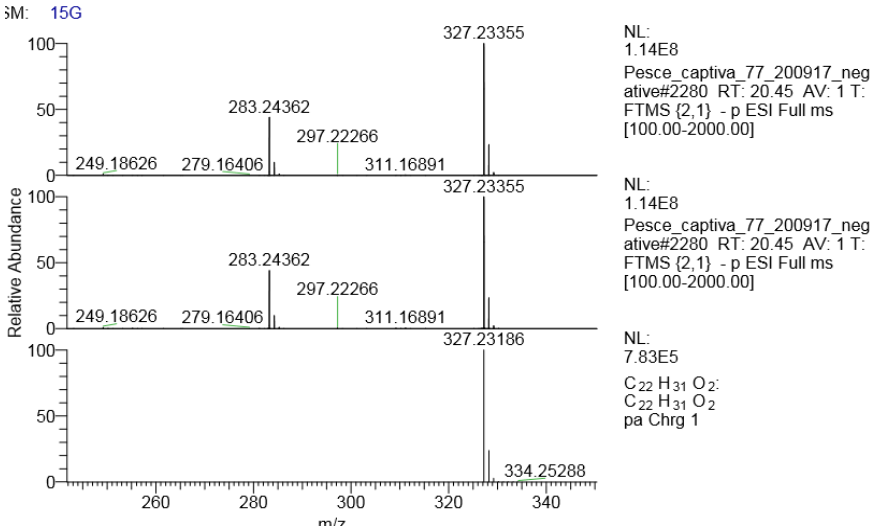
m/z 496

Effectiveness of Clean Up Step





Docosahexaenoic acid (DHA)



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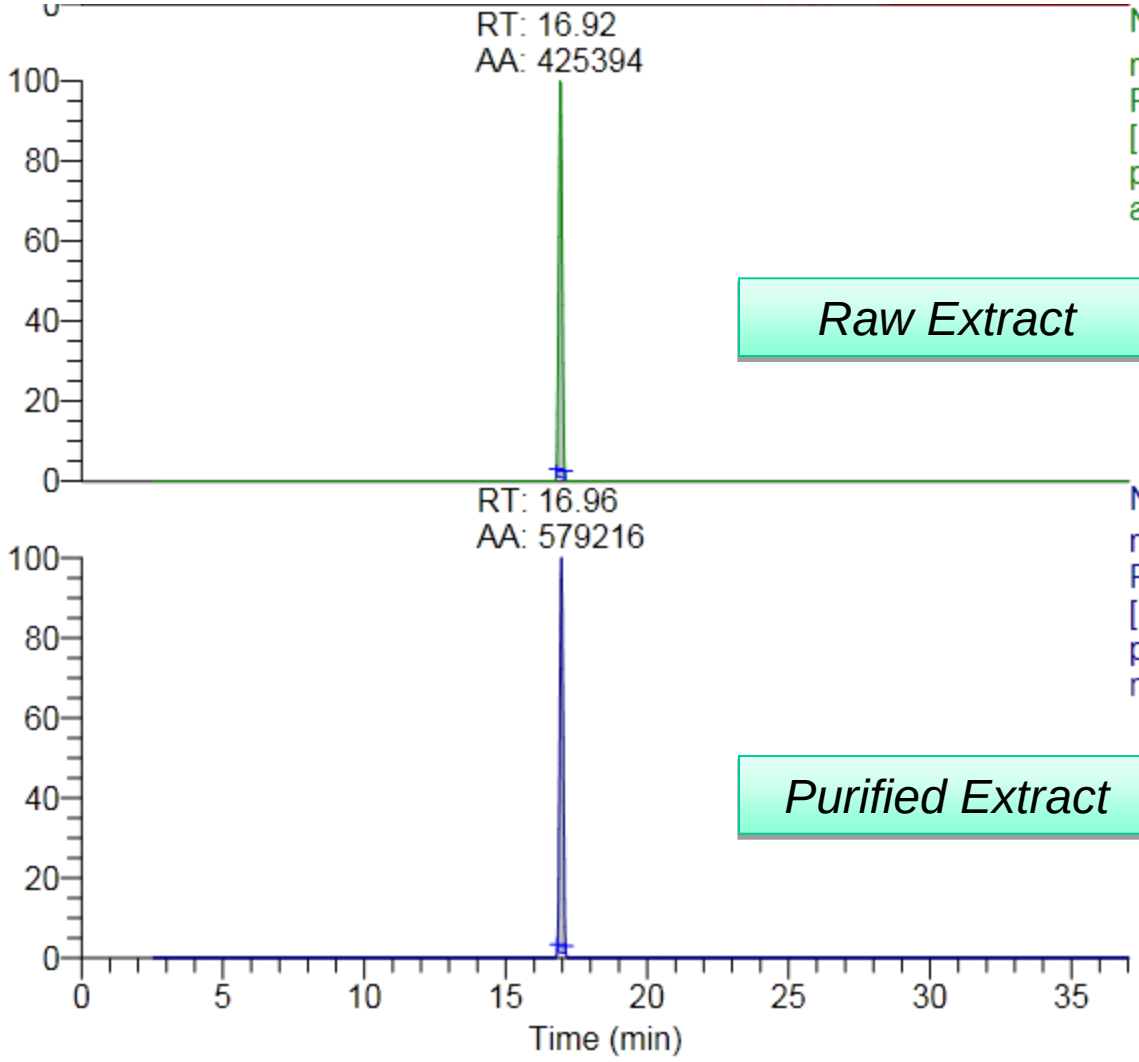
Effectiveness of Clean Up Step



Validation Study

JRC REFERENCE MATERIALS REPORT

CERTIFICATION OF THE MASS FRACTION OF PERFLUORALKYL SUBSTANCES (PFASs) IN FISH TISSUE (PIKE-PERCH): IRMM-427

Pikeperch, is a species of ray-finned fish from the family Percidae. It is found in freshwater and brackish habitats in western Eurasia.

	MASS FRACTION	
	Certified value (ng/g)	Uncertainty (ng/g)
Linear perfluorooctane sulfonate (L-PFOS) (1)	16(2)	1,7(2

1) As defined by using liquid chromatography mass spectrometry.
2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory with a method of determination including liquid chromatography mass spectrometry. Sulfonates are expressed on an anion basis. The certified/ values and their uncertainties are traceable to the International System of Units (SI).
3) The uncertainty of the certified / indicative value is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008

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Validation Study

The IRMM 427 (certified concentration around 16 ng/g) was analyzed compliance to ARPAT-MICAVL015 during the period between 7/01/2020 - 24/02/2020 for a total of 19 times with different analysts.

Application Note 1

ERM
European Reference Materials

Comparison of a measurement result with the certified value

January 2010

Author: Thomas Linsinger
European Commission - Joint Research Centre
Institute for Reference Materials and Measurements (IRMM)
Retieseweg 111, 2440 Geel, Belgium
Email: thomas.linsinger@ec.europa.eu
www.erm-crm.org

The comparison of a measurement result on a certified reference material with the certified value is explained. The method compares the difference between the certified and measured values with its uncertainty, i.e. the combined uncertainty of certified and measured value. Guidance on how to determine the standard uncertainties of certified values as well as standard uncertainties of measurement results is given.

A second level of concentration (about 2 ng/g) was investigated through the partecipation to the Inter-agency exercise during summer of 2019

Validation Study

After the measurement of a CRM the absolute difference between the mean meas ... *s*

To evaluate method performance,

Δ_m is compared with U_Δ:

If

$$\Delta_m \leq U_\Delta$$

Then

there is no significant difference between the measurement result and the certified value.

The uncer ... *rtainty of the certified va* ... *t according to*

$$U_{CRM} = U_{Certified\,Value}/2$$

3) The uncertainty of the certified value is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of approximately 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

Validation Study

Choice of quantification Mode

$$C_x = (A_x / A_{xILS}) \times C_{xILS}$$

Barbara Maier and Michael Vogeser, Clin Chem Lab Med 2012; 51(4): 833–837

Significant difference between the measurement result and the certified value

SIDA (Stable Isotope Diluition Analysis	NO
Pure Solvent Standard	YES
Matrix Standard	YES
Processed Solvent Standard	NO

Validation Study

Partecipation of Laboratory in n Proficiency Test

Uncertainty

$$\bar{u}_{Cref} = \frac{\sum u_{Cref,j}}{n}$$

→ Average of Uncertainties of n PT

$$d_i = x_i - C_{ref}$$

→ Difference between the measurement results and assigned value of the ith sample of the interlaboratory comparison

(Laboratory Bias in ith PT)

$$D_{iRel} = d_i / C_{ref}$$

→ Relative Difference of the ith sample of the interlaboratory comparison

$$D_{ms,rel} = \sqrt{\frac{\sum D_{i,rel}^2}{N}}$$

→ Root mean square of the relative difference

(Standard Deviation of Relative Bias)

Unichim Manual 206/1, Rev 2015

Validation Study

	Pure Solvent Standard	Processed Standard	Matrix Standard	SIDA
Extended Uncertainty	41.1	44.4	42.2	38.4

Sist

e

Random error

Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing

Michael Thompson

School of Biological and Chemical Sciences, Birkbeck College (University of London), Gordon House, 29 Gordon Square, London, UK WC1H 0PP

Received 12th January 2000, Accepted 31st January 2000

The Analyst COMMUNICATION

$$U_{c,rel} = k$$

$$\sigma = \begin{cases} 0.22c & \text{if } c < 1.2\times10^{-7} \\ 0.02c^{0.8495} & \text{if } 1.2\times10^{-7} \le c \le 0.138 \\ 0.01c^{0.5} & \text{if } c > 0.138 \end{cases}$$

ainty

m Manual 206/1, Rev 2015

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Validation Study

Inter-Agency Exercise

Laboratory	A	B	C	D	E	G
	2,37	1,90	2,53	1,00	2,52	3,95
	2,18	1,80	2,42	1,30	2,98	3,46
	2,38	2,20	2,56	1,10	3,65	3,66
Mean	2,31	1,97	2,50	1,13	3,05	3,69
Dev. St.	0,11	0,21	0,07	0,15	0,57	0,25
CV%	4,88	10,58	2,94	13,48	18,63	6,68

1° G = 3 LAB	1,00	Mean	1,55	2,37
	1,10	Dev. St.	0,48	2,18
	1,30	CV%	31,00	2,38
	1,80			2,52
	1,90			2,98
	2,18			3,65
2G = 4 Lab	2,20	Mean	2,40	1,90
	2,37	Dev. St.	0,12	1,80
	2,38	CV%	5,03	2,20
	2,42			2,53
	2,52			2,42
	2,53			2,56
3° G = 3 Lab	2,56	Mean	3,38	
	2,98	Dev. St.	0,51	
	3,46	CV%	15,19	
	3,65			
	3,66			
	3,95			

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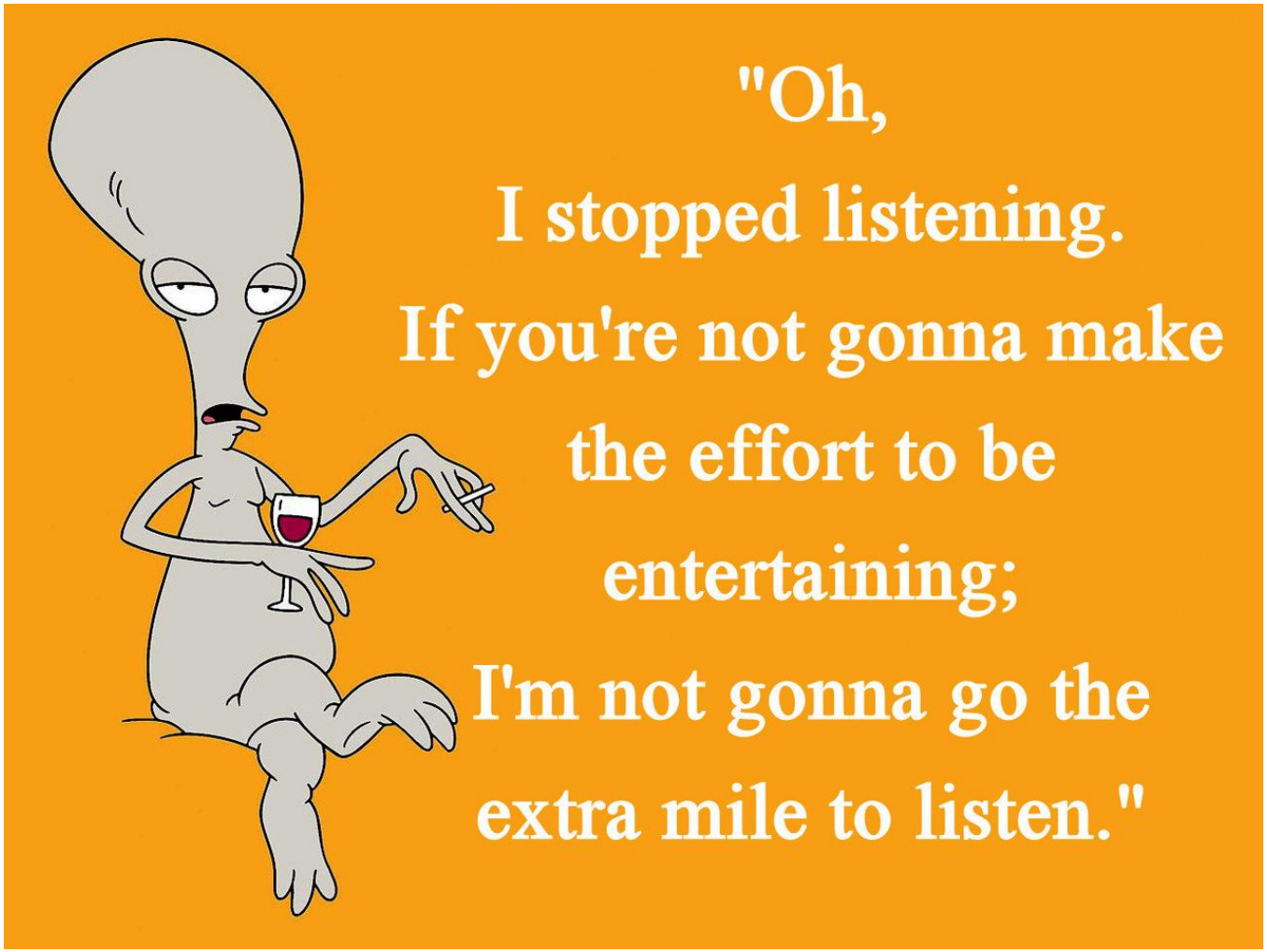
Validation Study

Summary

Quantification Mode:	***SIDA***
Range:	***2 - 16 µg/Kg***
Uncertainty (conc. equal or higher than 9.2 µg/kg):	***50%***
Uncertainty (conc. less than 9,2 µg/kg):	***57 %***
LOQ:	***2 ng/g***
Limit of repeatibiliy:	***20%***


"Oh,
I stopped listening.
If you're not gonna make
the effort to be
entertaining;
I'm not gonna go the
extra mile to listen."

Thanks