

Sample Preparation of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water analysis

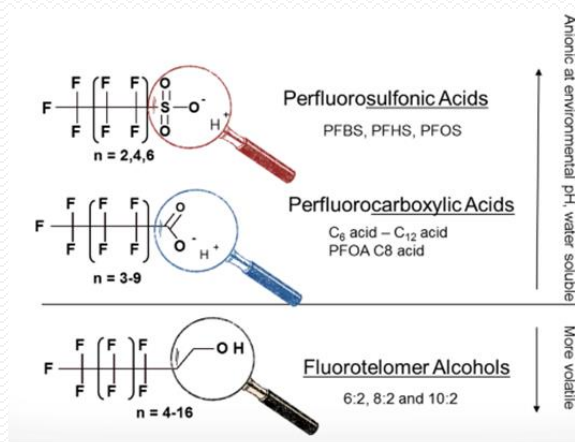
PRESENTED BY

Mahitti Puanggam

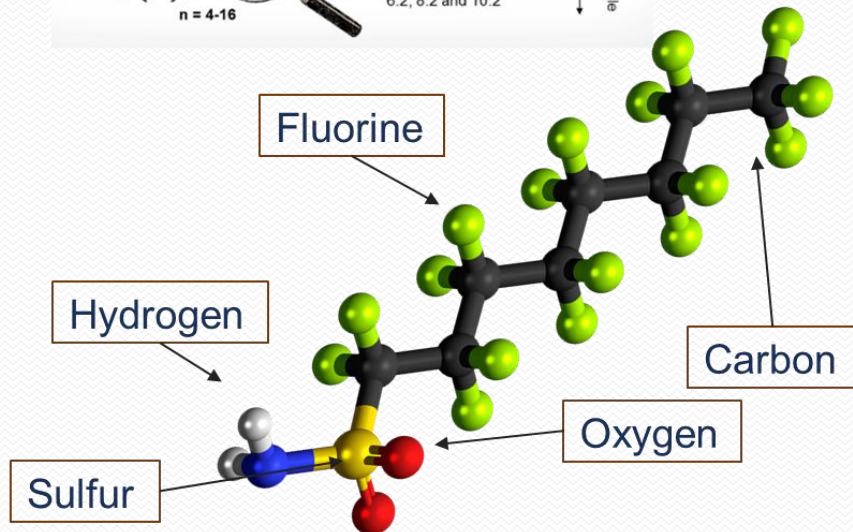
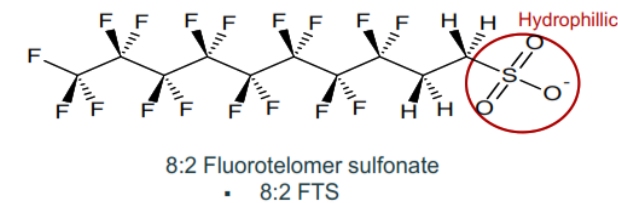
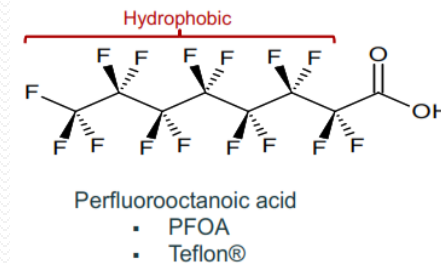


Background – What are PFAS compounds?

aka - “Forever Chemicals”



- PFASs are Per- and PolyFluorinated Alkyl Substances. Exclusively anthropogenic.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophilic end group
- Include a diverse range of compounds with a variety of chain lengths and end groups



Persistent in the environment

C-F bonds are very strong and do not break down

Health Concerns* <https://www.atsdr.cdc.gov/pfas/health-effects.html>

- Affect growth, learning, and behavior of infants and children
- Endocrine disruption
- Increase cholesterol levels
- Affect the immune system
- Increase risk of cancer
- Infertility

Background – What are PFAS compounds?

Table 2-1. Discovery and manufacturing history of select PFAS

PFAS ¹	Development Time Period								https://pfas-1.itrcweb.org/
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	2000s	
PTFE	Invented	Non-Stick Coatings			Waterproof Fabrics				
PFOS		Initial Production	Stain & Water Resistant Products	Firefighting foam				U.S. Reduction of PFOS, PFOA, PFNA (and other select PFAS ²)	
PFOA		Initial Production	Protective Coatings						
PFNA					Initial Production	Architectural Resins			
Fluoro-telomers					Initial Production	Firefighting Foams		Predominant form of firefighting foam	
Dominant Process ³		Electrochemical Fluorination (ECF)						Fluoro-telomerization (shorter chain ECF)	
Pre-Invention of Chemistry /			Initial Chemical Synthesis / Production			Commercial Products Introduced and Used			

- Drinking water
 - Food chain – found in food, feed
 - Most people have been exposed => found in blood
- Bioaccumulation => PFAS compounds build up in biological systems over time



- Need related standards from supplier to quantify



PFAS Master List of PFAS Substances

Search for chemical by systematic name, synonym, CAS number, DTXSID or InChIKey

[CompTox Chemicals Dashboard \(epa.gov\)](#)

☐ Identifier substring search

List Details

Description: PFASMASTER is a consolidated list of PFAS substances spanning and bounded by the below lists of current interest to researchers and regulators worldwide. For all available lists on the dashboard view [these search results](#).

Per- and polyfluorinated alkyl substances (PFAS) represent a growing, increasingly diverse inventory of chemicals of interest to the general public, scientific researchers, and regulatory agencies world-wide. Accompanying data-gathering, testing, and environmental monitoring exercises, in turn, have led to the publication and sharing of various lists of PFAS chemicals, some exceeding several thousand substances. A major effort was undertaken by EPA researchers within the National Center for Computational Toxicology to curate and structure-annotate several public lists in DStox. The below list of registered PFAS lists, from within and outside EPA, encompass PFAS of potential interest based on environmental occurrence (through literature reports and analytical detection) and manufacturing process data, as well as lists of PFAS chemicals procured for testing within EPA research programs. The consolidated list contains a number of PFAS CAS-name substances, with a subset represented with defined chemical structures. There is no precisely clear definition of what constitutes a PFAS substance given the inclusion of various lists. PFASMASTER serves as a consolidated list of substances spanning and bounded by the below lists worldwide. This PFAS Master List will continue to expand as component lists grow.

Number of Chemicals: 12039

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASRL is an EPA research

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINV is a complete list of DMSO-solubilized PFAS in EPA's ToxCast inventory.

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFAS75S1 list is a prioritized subset of this larger chemical inventory.

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASINSOL is a list of chemicals procured, but found to be insoluble in DMSO above 5mM.

https://comptox.epa.gov/dashboard/chemical_lists/PFASOECD is a list of PFAS chemicals in the OECD New Comprehensive Global Database.

https://comptox.epa.gov/dashboard/chemical_lists/PFASKEMI is a list of PFAS chemicals from a KEMI Swedish Chemicals Agency Report (provided by Stellan Fischer).

https://comptox.epa.gov/dashboard/chemical_lists/PFASRIER is a list of PFAS compiled by a community effort in 2015.

https://comptox.epa.gov/dashboard/chemical_lists/EPAPFASCAT is a list of structure-based Markush PFAS categories (capabilities under development).

https://comptox.epa.gov/dashboard/chemical_lists/PFASSTRUCT is a list of all PFAS structures containing a specific defined substructures.

https://comptox.epa.gov/dashboard/chemical_lists/PFASDEV1 is a list of PFAS chemicals without explicit structures - polymers and other UVCB chemicals.

Number of Chemicals: 12039

EPA PFAS Drinking Water Laboratory Methods

Using EPA methods 533 and 537.1, both government and private laboratories can now effectively measure 29 PFAS in their drinking water.

- [Method 533: Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry](#)
- [Method 537.1: Determination of Selected Per- and Polyfluorinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry \(LC/MS/MS\)](#)
- [Method 537: Determination of Selected Perfluorinated Alkyl Acids in Drinking Water by Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry \(LC/MS/MS\)](#)

EPA methods 533 and 537.1

EPA's new validated Method 533 focuses on "short chain" per- and polyfluoroalkyl substances (PFAS) (i.e., those with carbon chain lengths of 4 to 12).

Method 533 complements EPA Method 537.1 (published November 2018) and can be used to test for 11 additional PFAS. Using both methods, a total of 29 unique PFAS can be effectively measured in drinking water.

Regulated Method	EPA 537	EPA 537.1	EPA 533
Application	Drinking water		
Publish year	2009	2020 (Rev.2)	2019
# analytes	14	18	25
Quantitation method	External standard	External standard	Isotope dilution
Sample preparation	Solid Phase Extraction (SPE)		
Analytical Technique	Liquid Chromatography tandem Mass spectrometer (LC-MS/MS)		

Analyte	Abbreviation	CASRN	Method 533	Method 537.1
11-Chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	11Cl-PF3OUdS	763051-92-9	x	x
9-Chlorohexadecafluoro-3-oxanonane-1-sulfonic acid	9Cl-PF3ONS	756426-58-1	x	x
4,8-Dioxa-3H-perfluorononanoic acid	ADONA	919005-14-4	x	x
Hexafluoropropylene oxide dimer acid	HFPO-DA	13252-13-6	x	x
Perfluorobutanesulfonic acid	PFBS	375-73-5	x	x
Perfluorodecanoic acid	PFDA	335-76-2	x	x
Perfluorododecanoic acid	PFDoA	307-55-1	x	x
Perfluoroheptanoic acid	PFHpA	375-85-9	x	x
Perfluorohexanoic acid	PFHxA	307-24-4	x	x
Perfluorohexanesulfonic acid	PFHxS	355-46-4	x	x
Perfluorononanoic acid	PFNA	375-95-1	x	x
Perfluorooctanoic acid	PFOA	335-67-1	x	x
Perfluorooctanesulfonic acid	PFOS	1763-23-1	x	x
Perfluoroundecanoic acid	PFUnA	2058-94-8	x	x
1H,1H, 2H, 2H-Perfluorohexane sulfonic acid	4:2FTS	757124-72-4	x	
1H,1H, 2H, 2H-Perfluorooctane sulfonic acid	6:2FTS	27619-97-2	x	
1H,1H, 2H, 2H-Perfluorodecane sulfonic acid	8:2FTS	39108-34-4	x	
Nonafluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	x	
Perfluorobutanoic acid	PFBA	375-22-4	x	
Perfluoro(2-ethoxyethane)sulfonic acid	PFEESA	113507-82-7	x	
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	x	
Perfluoro-4-methoxybutanoic acid	PFMBA	863090-89-5	x	
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	x	
Perfluoropentanoic acid	PFPeA	2706-90-3	x	
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	x	
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA	2991-50-6		x
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA	2355-31-9		x
Perfluorotetradecanoic acid	PFTA	376-06-7		x
Perfluorotridecanoic acid	PFTTrDA	72629-94-8		x

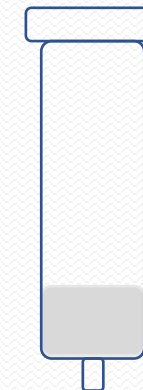
Summary of the methods EPA 537.1

Due to potential adsorption of analytes onto glass, polypropylene containers were used for all standard, sample and extraction preparations

- 250 mL water sample with added surrogates is loaded onto an offline SPE cartridge
- Rinsing of bottle with MeOH, this rinsate applied for elution
- Concentration to dryness
- Adjusted to 1 mL volume with 96:4 % (vol/vol) methanol:water
- Addition of internal standards
- 10 μ L injection into an LC-MS/MS equipped with a C18 column



POLYPROPYLENE BOTTLES
POLYPROPYLENE CENTRIFUGE TUBES
POLYPROPYLENE AUTOSAMPLER VIAL & CAP



SPE CARTRIDGES –
0.5 g, 6-mL SPE cartridges
containing styrene-divinylbenzene
(SDVB) sorbent



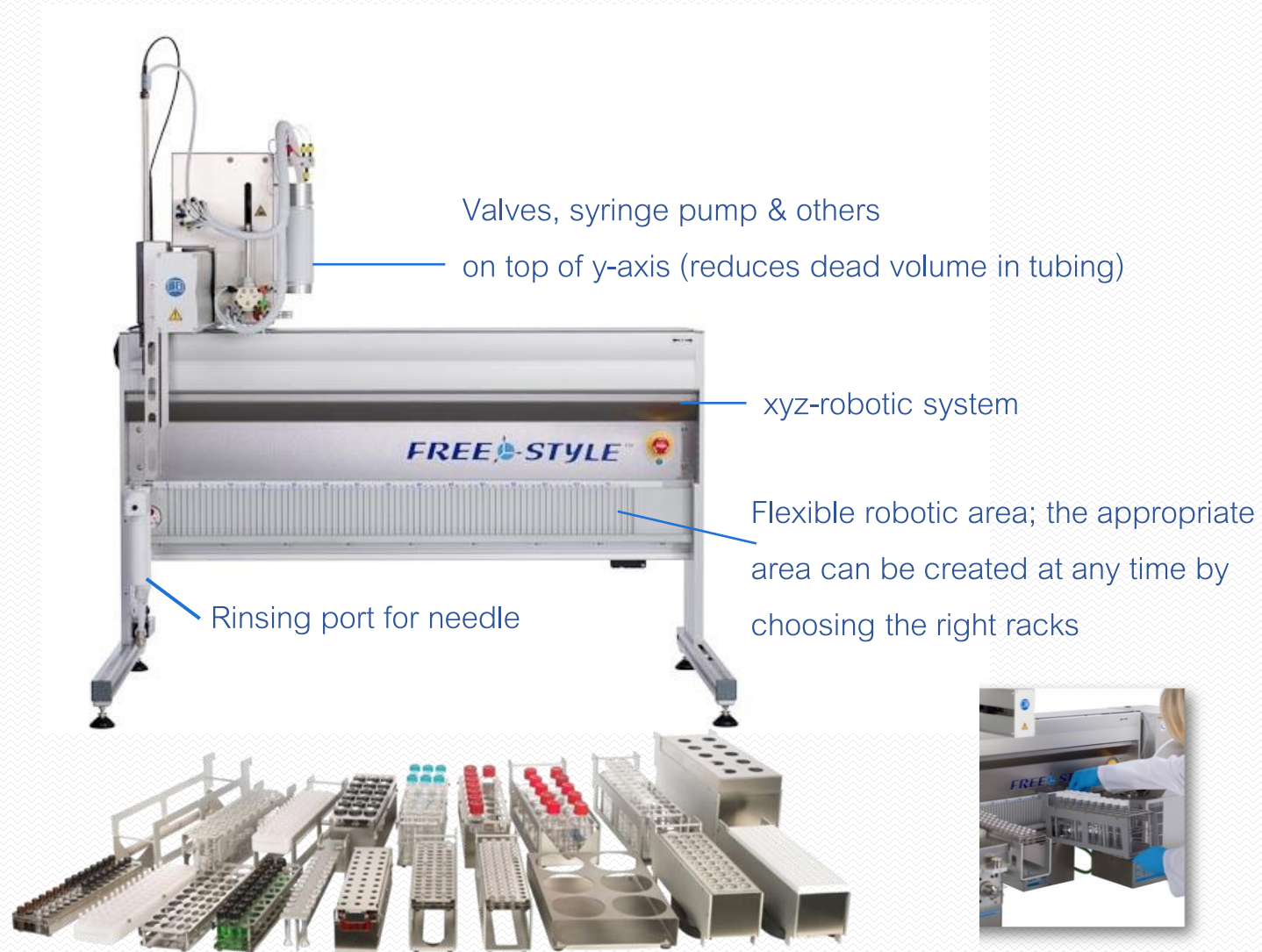
NOTE: During the course of method development, it was discovered that while idle for more than one day, PFAS built up in the PTFE solvent transfer lines. To prevent long delays in purging high levels of PFAS from the LC solvent lines, they were replaced with PEEK™ tubing and the PTFE solvent frits were replaced with stainless steel frits. It is not possible to remove all PFAS background contamination, but these measures help to minimize their background levels.



- ✓ Minimized fluoroplastic components
- ✓ Constantly low PFAS background
- ✓ robust automation for 24/7 operation



FREESTYLE BASIC



Double walled needle with two independent lines

- In the needle
- Around the needle with spraying holes (360°)
- Hot sealed – no gap open



FREESTYLE SPE Module

- For all standard SPE-cartridges from 1 mL up to 15 mL
- Positive pressure up to 4 bar for all steps in which liquids are used.
- One rack for all kind of columns
- Columns can be moved to any place in the robotic area – large variation for Elution profiles
- Standard six or even fifteen solvents

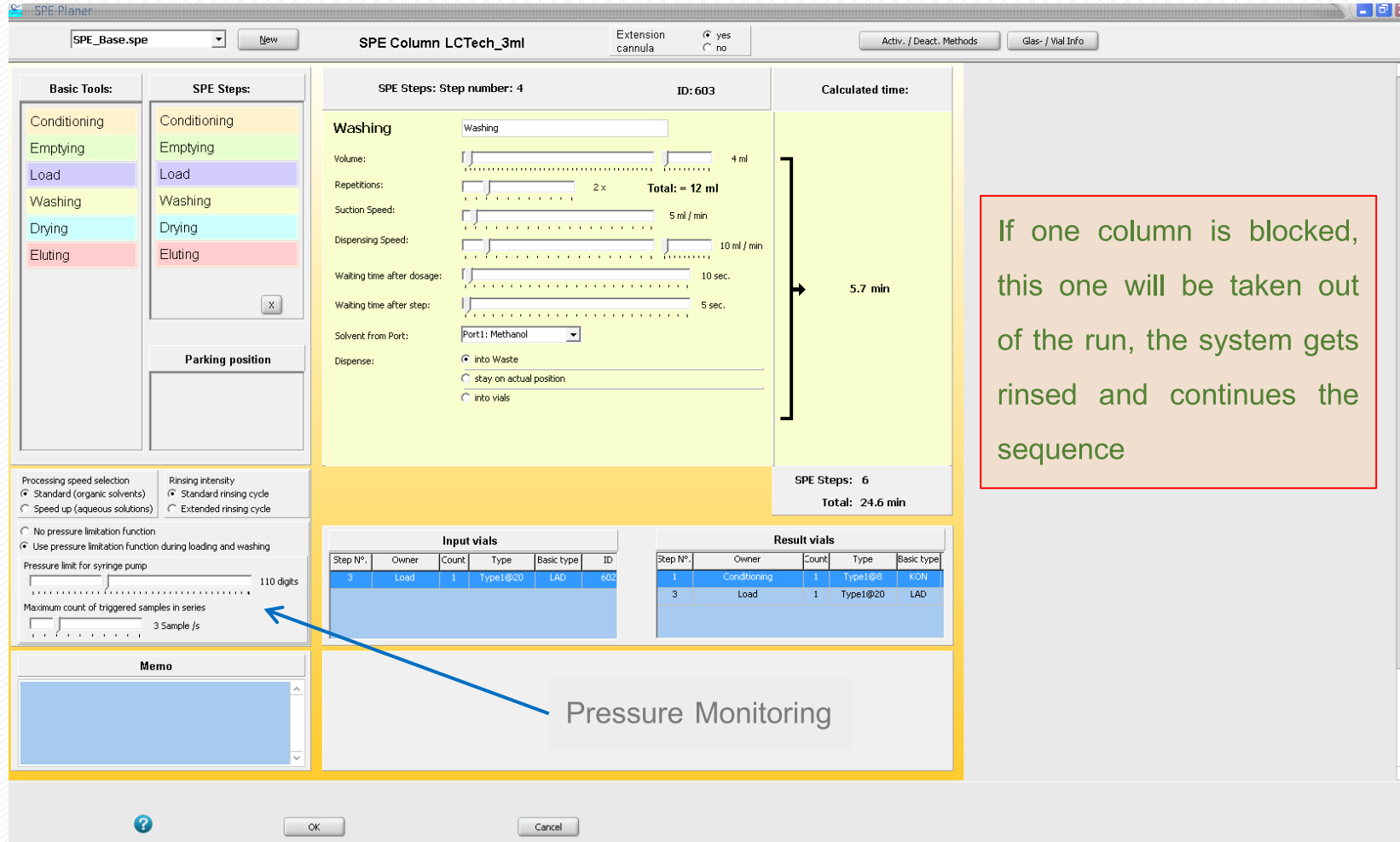


Flexibility just by adapters.

Application of US EPA 537.1 - labware



SPE Method: Non-stop policy – this is an unique feature



The screenshot displays the SPE Planner software interface. The main window is titled "SPE Column LCTech_3ml" and shows the configuration for a method with 6 steps. The "Washing" step is highlighted, showing a volume of 4 ml, 2 repetitions, and a total volume of 12 ml. The calculated time for this step is 5.7 min. The total time for all 6 steps is 24.6 min.

A red box highlights the text: "If one column is blocked, this one will be taken out of the run, the system gets rinsed and continues the sequence".

A blue arrow points to the "Pressure Monitoring" section, which includes a "Pressure limit for syringe pump" set to 110 digits and a "Maximum count of triggered samples in series" set to 3 Sample /s.

The "Input vials" and "Result vials" tables are also visible:

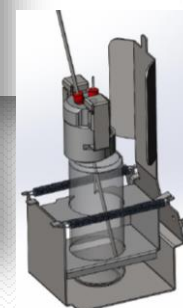
Step N°	Owner	Count	Type	Basic type	ID
3	Load	1	Type1@20	LAD	602

Step N°	Owner	Count	Type	Basic type
1	Conditioning	1	Type1@9	KON
3	Load	1	Type1@20	LAD

FREESTYLE XANA Module



- Polypropylene transfer tube system according to material chapter of the method
- Pumps 3 samples in parallel with flow rates: 1 – 30 mL/min.
- Conditioning, Washing, Rinsing and Drying of 3 columns in parallel with Up to 8 solvents for conditioning, rinsing and washing
- Detection of empty bottles, positions that are not taken aren't processed!
- Loading with positive pressure (tolerates back pressure up to 4 bar)
- 6 positions for loading, drying or eluting of columns (parallel loading of 3 samples and drying of 3 samples)



FREESTYLE in action





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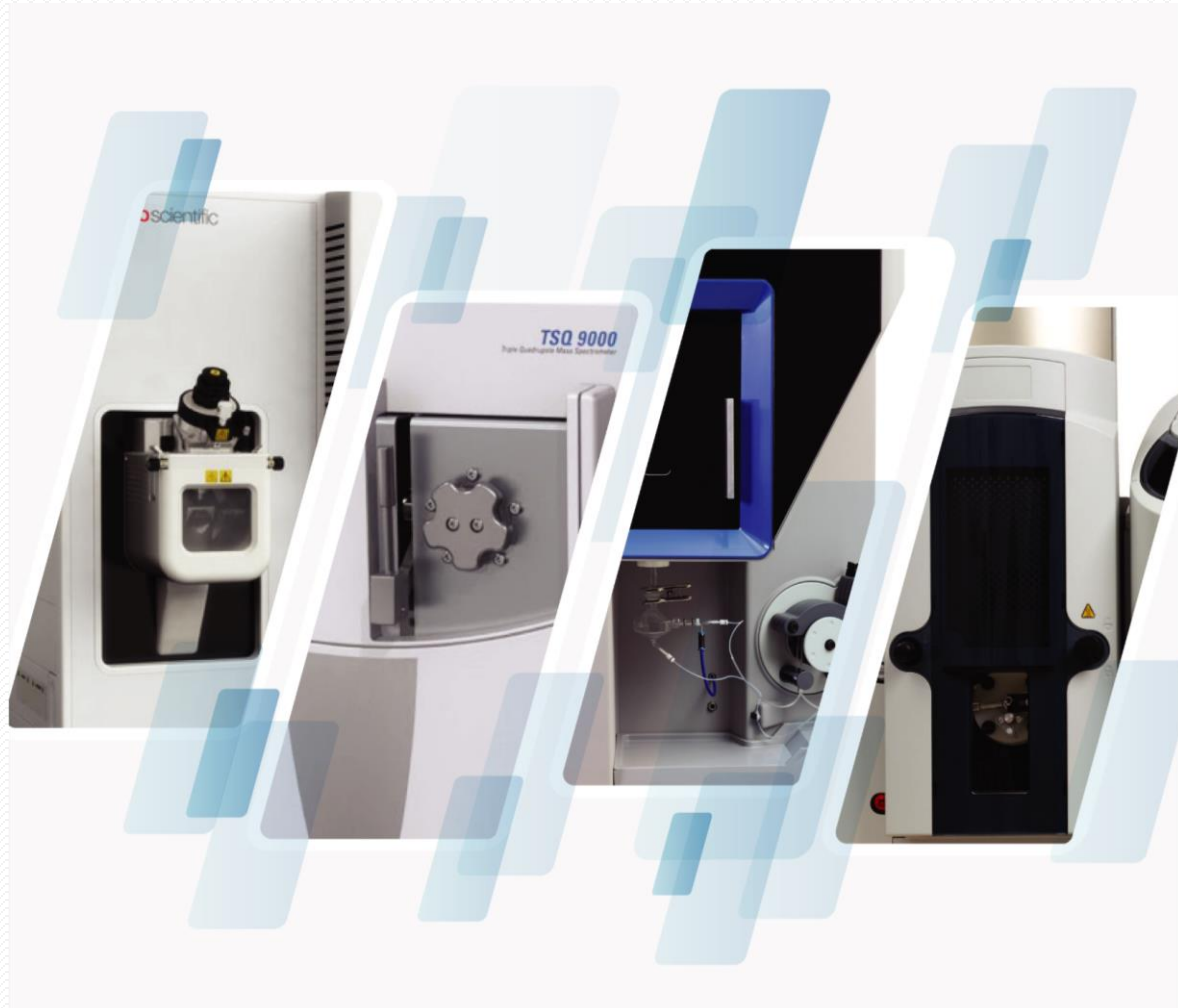
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