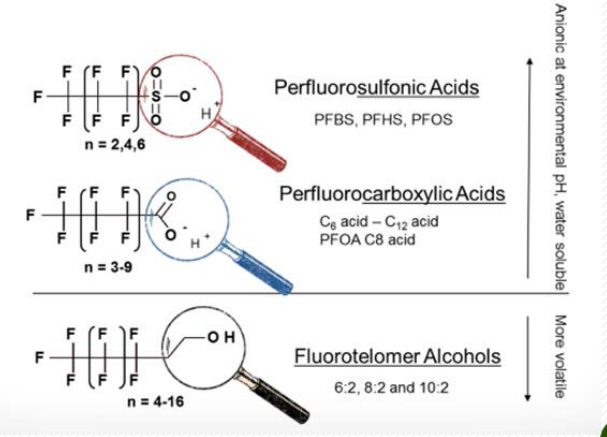
Sample Preparation of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Water analysis

PRESENTED BY

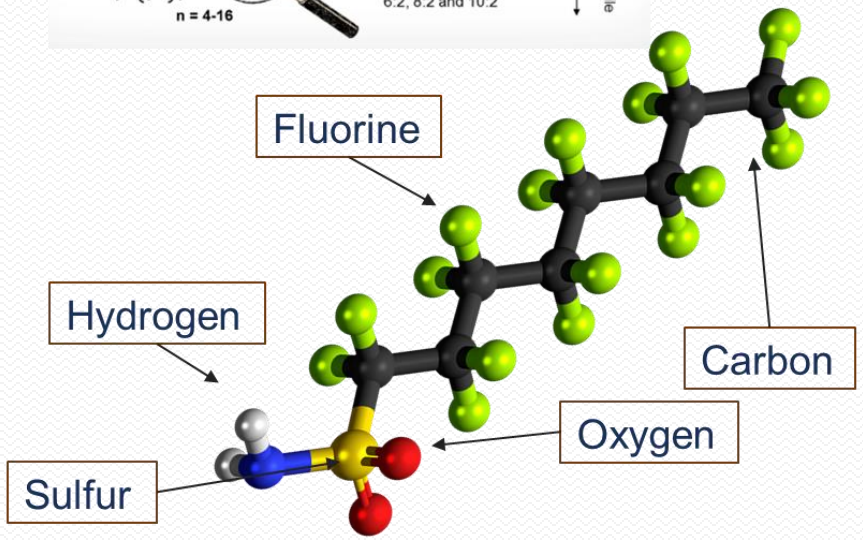
Mahitti Puanngam

Background – What are PFAS compounds?

aka - “Forever Chemicals”

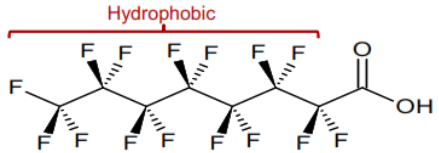


- PFASs are **P**er- and **P**oly**F**luorinated Alkyl **S**ubstances. Exclusively anthropogenic.
- Structures contain a hydrophobic perfluoroalkyl backbone and a hydrophilic end group
- Include a diverse range of compounds with a variety of chain lengths and end groups

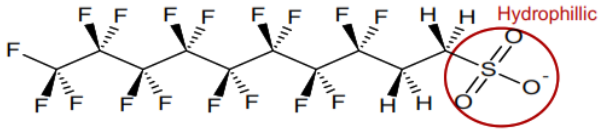


Persistent in the environment

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



Perfluorooctanoic acid
- PFOA
- Teflon®



8:2 Fluorotelomer sulfonate
- 8:2 FTS

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

https://pfas-1.itrcweb.org/

PFAS[1]	Development Time Period							
	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		


https://en.wikipedia.org/wiki/Firefighting_


https://en.wikipedia.org/wiki/Landfill

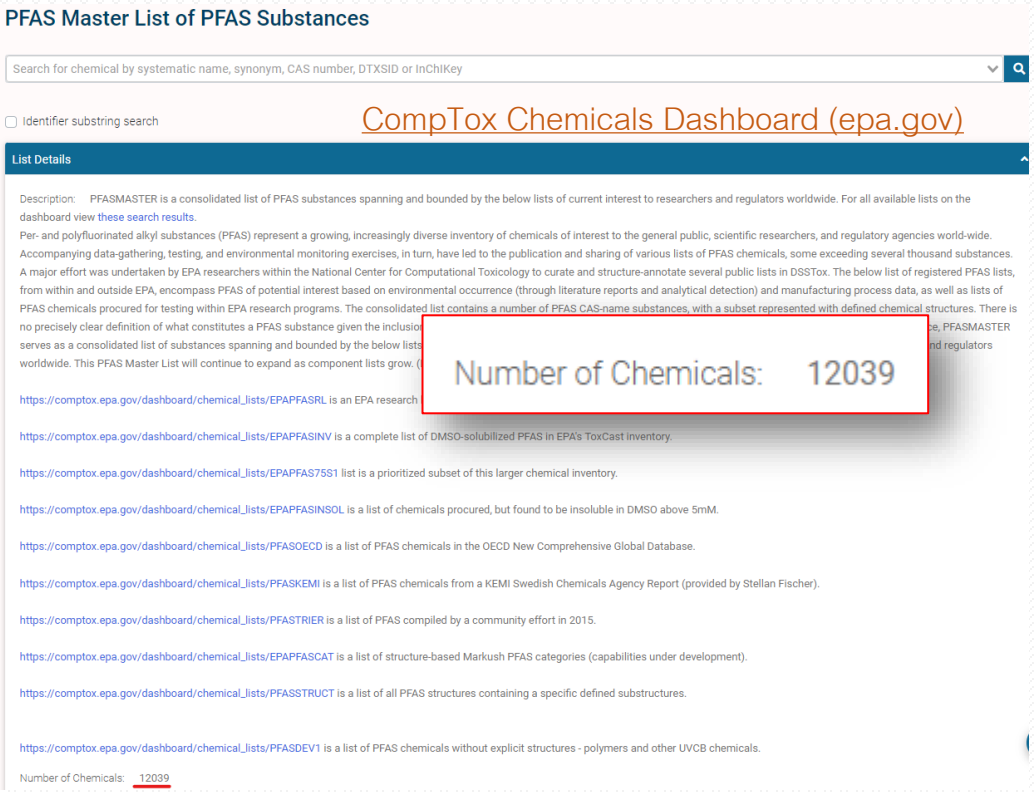
- Drinking water

Bioaccumulation => PFAS compounds build up in biological systems over time

- Food chain – found in food, feed
- Most people have been exposed => found in blood

Challenge to laboratory work

- Need related standards from supplier to quantify



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 acd	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	PFTrDA	72629-94-8		x

Office of Water (MS-140) EPA 815-B-19-021 December 2019

https://www.epa.gov/dwanalyticalmethods/comparing-epa-analytical-methods-pfas-drinking-water

Summary of the methods EPA 537.1

- 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 1mL volume with 96:4 % (vol/vol) methanol:water
- Addition of internal standards
- 10 µL injection into an LC-MS/MS equipped with a C18 column

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

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.

Automated SPE system for PFAS analysis

SOLUTIONS BY LCTech

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

FREESTYLE BASIC

Double walled needle with two independent lines

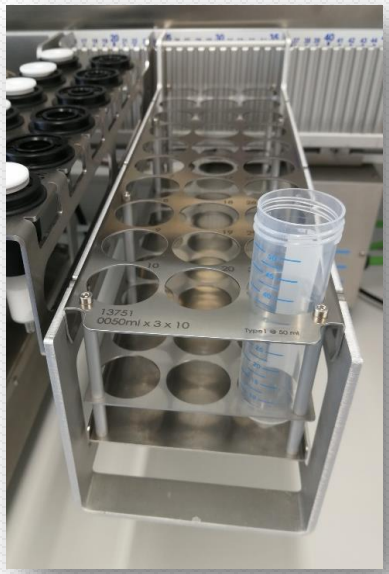
- In the needle
- Around the needle with spraying holes (360°)
- Hot sealed – no gap open

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

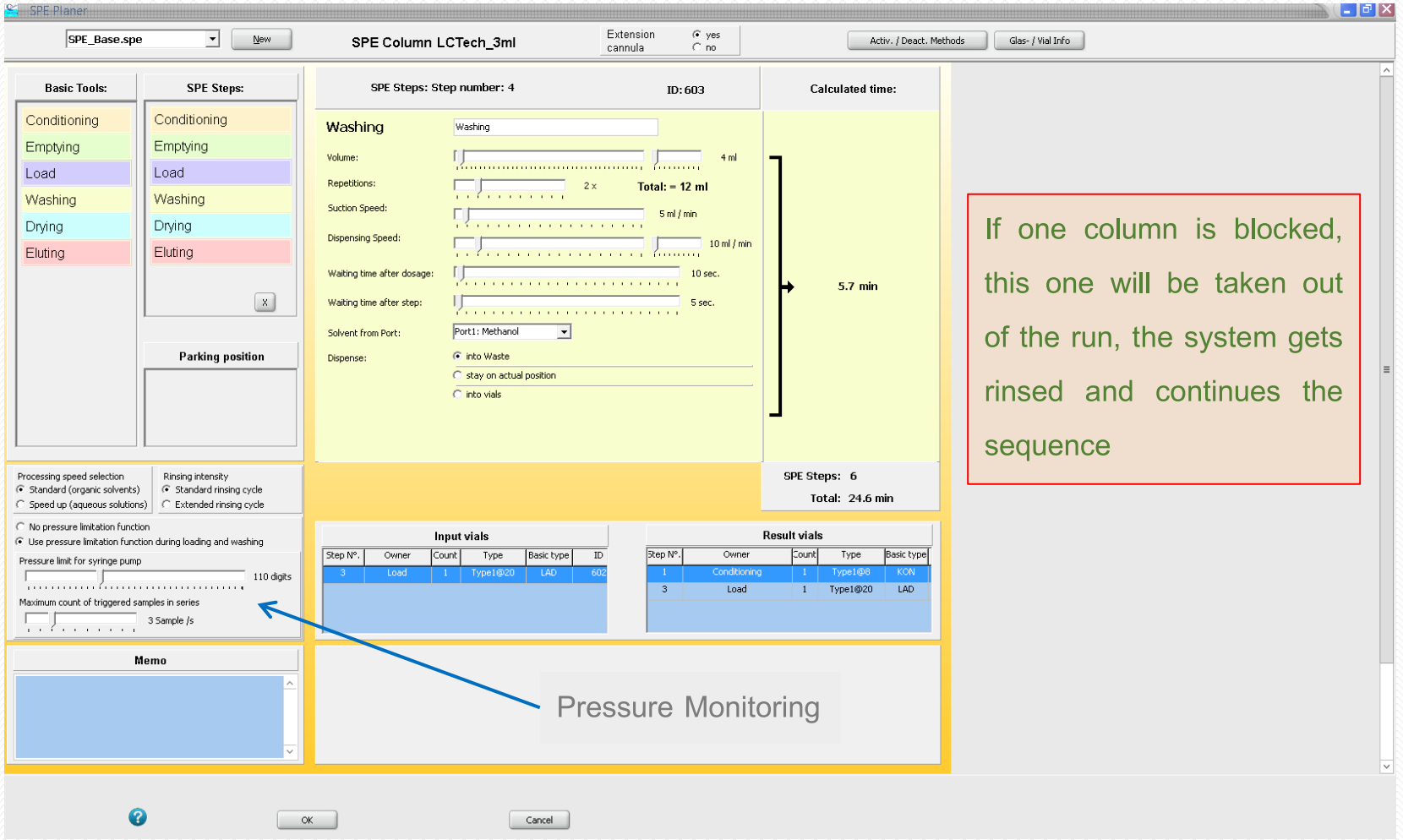
Flexibility just by adapters.

Application of US EPA 537.1 - labware



FREESTYLE SPE Module

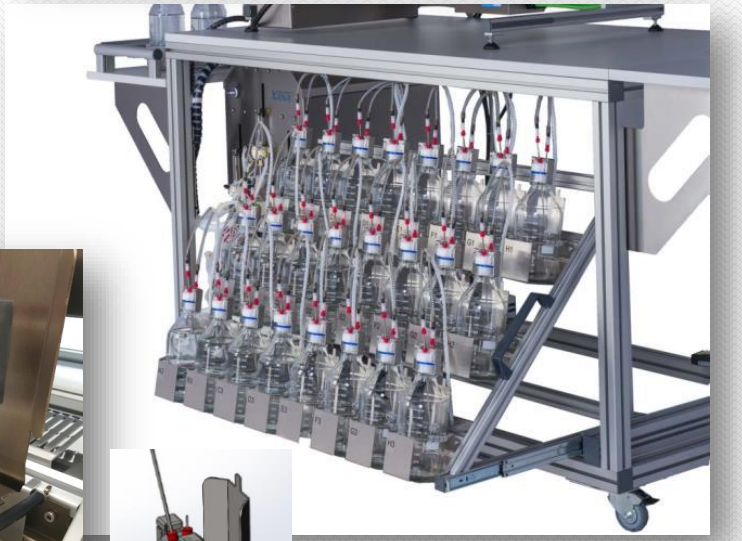
SPE Method: Non-stop policy – this is an unique feature

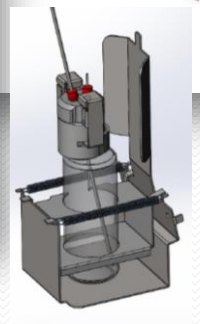


If one column is blocked, this one will be taken out of the run, the system gets rinsed and continues the sequence

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

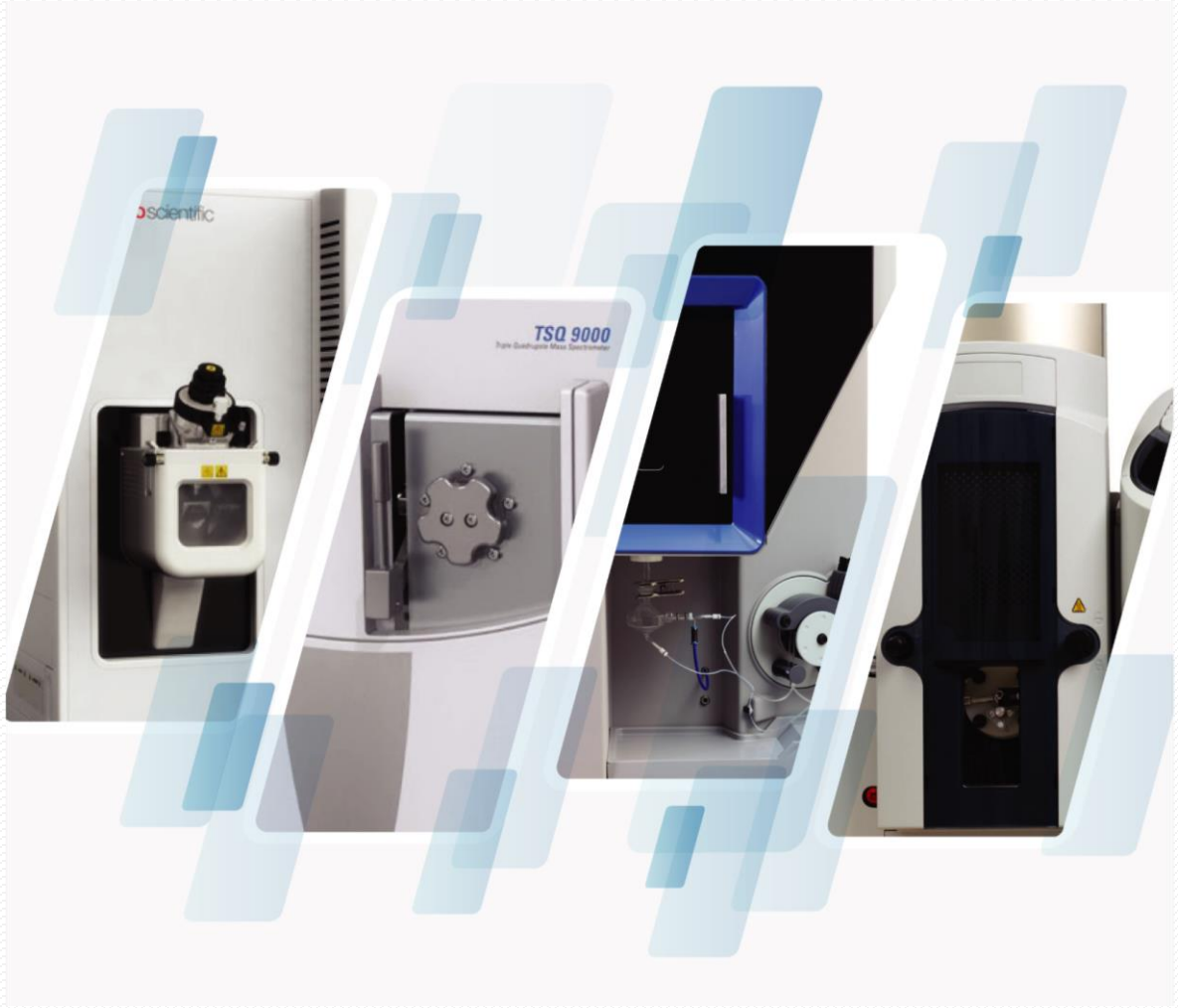
ติดตามกิจกรรมของทางบริษัทได้ที่

www.scispec.co.th

/scispec

@scispec

crm@scispec.co.th



ThermoFisher SCIENTIFIC

MARKES international

FRONTIER LAB

GAS

CTC Analytics

LC Tech
SAMPLE PREPARATION & ANALYSIS

908devices

YOUR SCIENTIFIC SPECIALIST