SGS GROUP
BENELUX

Environment, Health & Safety Services

PFAS risk – analysis - Do’s and Don'ts looked from an analytical perspective

WHEN YOU NEED TO BE SURE

SGS

Environmental, Health and Safety Services: portfolio

SGS ENVIRONMENTAL, HEALTH AND SAFETY SERVICES (BENELUX)

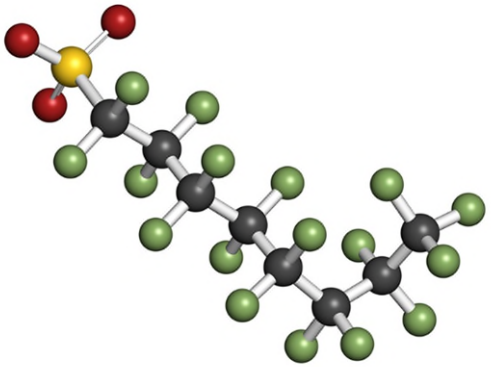
(SGS BELGIUM – SGS NEDERLAND – SGS EWACS – GRONDWIJZER – SGS SEARCH)

LABORATORY TESTING SERVICES	AIR MONITORING & FIELD SERVICES	STUDIES AND ASSESSMENTS' SERVICES	SOIL AND SUBSOIL SERVICES	WASTE & CHEMICALS' SERVICES
ON-SITE SAMPLING	AIR	ENVIRONMENTAL IMPACT	GEOTECHNICAL ASSESSMENT	WASTE COLLECTION & STORAGE
SAMPLE COLLECTION	ASBESTOS	PROCESS SAFETY	POLLUTION INVESTIGATION	WASTE HANDLING
ROUTINE TESTING (ENVILAB)	ODOR	PRODUCT COMPLIANCE & REACH	DRILLING & SAMPLING	EMERGENCY RESPONSE
HIGH END TESTING (IAC-IMA)	OCCUPATIONAL HEALTH	NOISE & VIBRATIONS	GEO-HYDROLOGY	CALAMITY INTERVENTIONS
RESEARCH, METHOD DEVELOPMENT & TROUBLESHOOTING	CALIBRATION & VALIDATION	COMPLIANCE, VERIFICATION & SUSTAINABILITY	TRACEABILITY VERIFICATION	REPACK & CONDITIONING

- Overview:

  - PFAS compounds - What
  - Sampling
  - Analysis
    - Technique
    - Reporting limits
    - Measurement Uncertainty
    - General uncertainty
    - Analysis
  - General approach
  - Treatment/Remediation

  - Conclusions

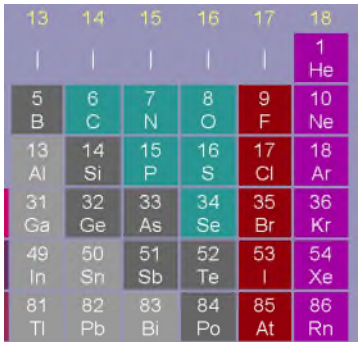


Take in mind!

- **Analytical results are to be interpreted under the conditions of the test/method**
- **Pragmatism to be applied within every step of the process**

What are PFAS compounds?

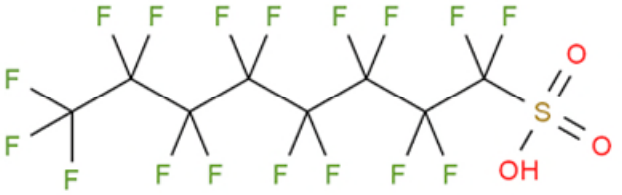
- PFAS = Poly & Per Fluorinated Alkyl Substance



- PFAS are a class of synthetic compounds containing thousands of chemicals formed from carbon chains with fluorine attached to these chains.
- The C-F bond is the shortest and the strongest bond in nature and is responsible for most of the unique and useful characteristics of these compounds.
- PFAS are surfactants that repel oil and water, reduce wear or surface adhesion.
- Introduced as early as 1948 (Teflon, or PTFE polymer) with a great increase in use in the late 1960s and 1970s.
- At low concentrations, many have significant water solubility.
- Problematic compounds due to:
  - Persistent
  - Bioaccumaltive
  - Toxic – Carcinogenic?

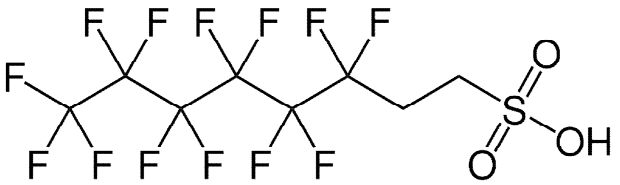
What are PFAS compounds?

- PFAS = Poly & Per Fluorinated Alkyl Substance
  - PFOS : **P**er **F**luoro **O**ctane **S**ulfonic acid



  - PFOA : **P**er **F**luoro **O**ctanoic **A**cid

  - PFAS: **P**oly **F**luorinated **A**lkyl **S**ubstances



What are PFAS compounds?

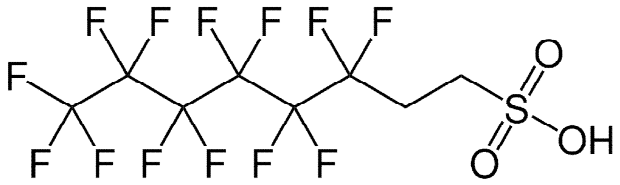
- PFAS = Denominiation
  - Carboxylic Acids

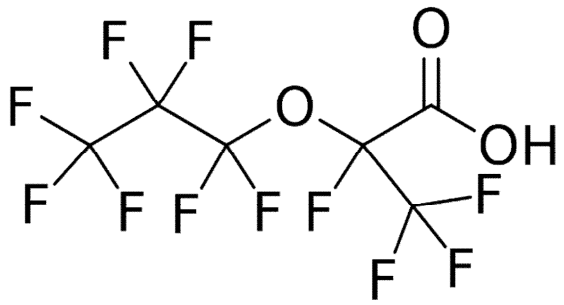
  - Butane → PFBA
  - Pentane → PFPeA
  - Hexane → PFHxA
  - Heptane → PFHpA
  - Octane → PFOA
  - Nonane…. → PFNA

  - Same goes for Sulfonic acids
    → PFBS
    → ….

What are PFAS compounds?

- PFAS = Alternative compounds





What are PFAS compounds?

- PFAS = Poly & Per Fluorinated Alkyl Substance
  - Group of compounds ?

Perfluoroalkylcarboxylic acids (PFCAs)
Perfluorbutanoic acid (PFBA)
Perfluorpentanoic acid (PFPeA)
Perfluorhexanoic acid (PFHxA)
Perfluorheptanoic acid (PFHpA)
Perfluoroctanoic acid (PFOA)
Perfluornonanoic acid (PFNA)
Perfluordecanoic acid (PFDA)
Perfluorundecanoic acid (PFUnDA)
Perfluordodecanoic acid (PFDoDA)
Perfluortridecanoic acid (PFTrDA)
Perfluortetradecanoic acid (PFTeDA)
Perfluorhexadecanoic acid (PFHxDA)
Perfluoroctadecanoic acid (PFODA)

Perfluoroalkanesulfonates (PFASs)
Perfluorbutanoic sulphonate (PFBS)
Perfluorhexanoic sulphonate (PFHxS)
Perfluoroctanoic sulphonate (PFOS)
Perfluordecane sulphonate (PFDS)
Perfluoroheptane sulfonic acid (PFHpS)

Perfluorooctanesulfonamides (FOSAs)
Perfluoroctanoic sulfonamide (PFOSA)
N-Methyl perfluorooctane sulfonamide (N-MeFOSA)
N-Ethyl perfluorooctane sulfonamide (N-EtFOSA)

Perfluorooctanesulfonamidoacetic acids (FOSAAs)
Perfluoro-1-octanesulfonamidoacetic acid (FOSAA)
N-Methyl perfluorooctane sulfonamidoacetic acid (N-MeFOSAA)
N-Ethyl perfluorooctane sulfonamidoacetic acid (N-EtFOSAA)

Perfluorooctanesulfonamidoethanols (FOSEs)
N-Methyl perfluorooctane sulfonamidoethanol (N-MeFOSE)
N-Ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE)

Telomer sulfonates (FTSs)
6:2 Fluorotelomere sulfonate (6:2 FTS)
8:2 Fluorotelomere sulfonate (8:2 FTS)
10:2 Fluorotelomere sulfonate (10:2 FTS)

- **GenX** (FRD902/903)

PFAS compounds

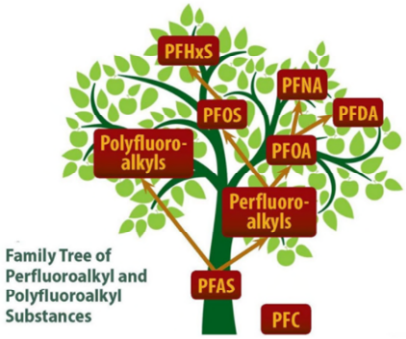


*Image courtesy of https://**www.atsdr.cdc.gov**

- PFAS have been used since the late 1940s.
  - 70 years of use
  - Dupont Teflon® : non-stick surfaces
  - 3M Scotchguard® : water and stain resistance coatings
  - Dupont Zonyl® : food packaging
- PFAS have been used in various industries:
  - Textile and Leather – Oil and Water repellant.
  - Paper Products
    - Non-food contact: cardboard, masking papers
    - Food contact: fast food wrappers, microwave popcorn bags, pizza boxes
  - Metal Plating – Mist suppression, electroplating, cleaner
  - Semiconductor and Photo imaging – etching, anti-reflective coatings
  - Wire Manufacturing – Insulation, wear reduction
  - Plastics Manufacturing – Composite resins, increase strength and flexibility

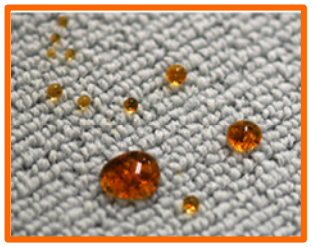
PFAS compounds – What?

- Group of compounds
  - In use since 40/50-ties
  - SGS started analysis early 2000 with a known group of +/- 12 PFAS compounds
  - Both PFOS as well as PFOA are the best known and studied examples
  - Nowadays several thousands
- Wonder product?
  - Stable (heat, chemical)
  - Soluble in water
  - Binds easily with other material
- Down side
  - Bioaccumulation
  - C-F very strong bonding
  - Potential threats to ecological & human health

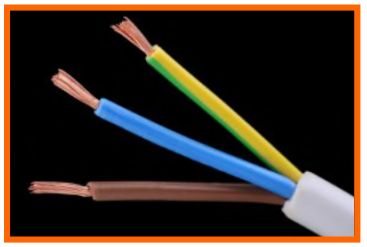
PFAS compounds

- AFFF – Aqueous Film Forming Foams
  - Developed by US Navy in the 1960s
  - Complex mixtures of known and unidentified PFAS
  - Designed for hydrocarbon fuel fires
  - AFFFs were produced to meet a fire fighting specification not a chemical composition, so various formulations exist
- Sites that used or stored AFFF
  - Military installations
  - Commercial airports
  - Fire training areas and local fire departments
  - Petroleum refineries and storage areas
  - Chemical manufacturing plants
- Other Sources
  - Landfills
  - Biosolids

Problem?!



Waterproof and stain resistant carpets & textile



Electric wire insulators

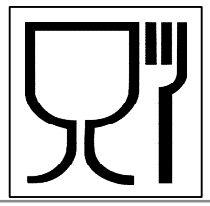
Nonstick cookware

Perfluorinated compounds PFCs

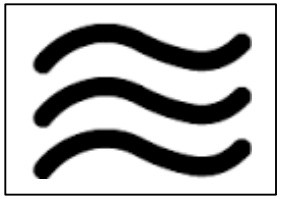
Personal care products

Fire-fighting foam

Fast food wrappers & pizza boxes (grease-proof)

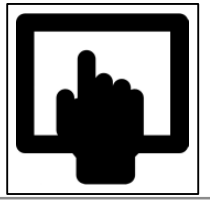


Food



Water (surface/drinking)

Soil



Direct contact

Inhalation

PFAS impacted sites

- Industrial facilities that manufactured PFAS or used PFAS in their production chain
- Industrial facilities that have older wastewater impoundments or landfills
- Airports, Ports and other locations that use/used foam for fire fighting
- Former Department of Defense sites
- Municipal or industrial landfills
- Sites in areas with PFAS “regional issues”

Processes and product uses/sources of PFAS include the following:

Processes	Product Uses/Sources
Fluoropolymer coatings	Some grease-resistant paper
Plastics/polymers	Fast food containers/wrappers
Oil and water repellent (Teflon™, Stainmaster® carpets, Scotchgard™ and Gore-Tex®)	Microwave popcorn bags, pizza boxes, candy wrappers
Surfactants used in fire fighting foams	Non-stick cookware such as Teflon™ coated pots/pans
Mist suppressants for metal plating operations	Stain-resistant coatings such as Scotchgard™ used on carpets, upholstery and other fabrics
Photomicrolithography process to produce semiconductors	Water-resistant clothing such as Gore-Tex®
Photography and film products	Adhesives, Aviation hydraulic fluids, cleaning products
	Personal care products such as shampoo, dental floss, and cosmetics (nail polish, eye makeup)
	Paints, varnishes and sealants

SITES WITH RISK OF PFAS RELEASES

PFAS Source	Risk Score	
Military Facilities	100	
Chemical manufacturing	100	
Landfills	100	
Fire training areas	75	
Airports	75	
Petroleum refineries	75	
Textiles	50	
Furniture	50	
Paper	50	
Rubber/plastics	50	
Fire Stations	25	
Metal Fabrication	25	

Sampling Do’ and Don’ts

- Banned materials or points of interest during sampling

- Is theory in relation to practice?
  - The expected contamination from different materials is far less than described in theory
  - Biggest issue is silicon (small) sampling tube

How to Sample for PFAS

- Because of the potential presence of PFAS in common consumer products and in equipment typically used to collect soil, groundwater, surface water, sediment, and drinking water samples as well as the need for very low reporting limits, special handling and care must be taken when collecting samples for PFAS analysis to avoid sample contamination.

Sampling equipment:

- Don’t use: Pumps and Tubing: Teflon™ and other fluoropolymer-containing materials *(**Do use**: high density polyethylene [HDPE])*
- Don’t use: Passive diffusion bags
- Don’t use: Low density polyethylene (LDPE) Hydrasleeves (Do use *HDPE Hydrasleeves)*
- Don’t use: Decontamination: Decon 90 *(**Do use** Alconox® or Liquinox®, potable water. followed by deionized PFAS-free water rinse)*
- Don’t use: Sample storage and preservation: LDPE or glass bottles, Teflon™-lined caps, chemical ice packs (i.e., Blue ice®) *(*Do use *HDPE or polypropylene containers with HDPE or polypropylene caps, regular ice in Zip-loc bags)*

Sampling equipment:

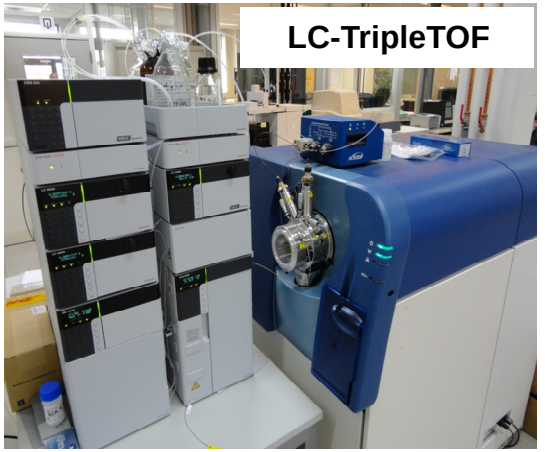
- Clothing: Don’t use, clothing or boots with Gore-Tex® or other synthetic water-resistant and/or stain-resistant materials, Tyvek material, fabric softener *(*Do use *clothing made of cotton preferred)*
- Field documentation: Don’t use waterproof/treated paper or field books, plastic clipboards, water proof markers, Post-its and other adhesive paper products *(*Do use *loose plain paper, metal clipboard, ballpoint pens)*
- Don’t use Personal care products on day of sample collection: cosmetics, moisturizers, hand cream, sunscreen, and other related products, insect repellent
- Don’t use Aluminum foil, Food and beverage: pre-packaged food, fast food wrappers or containers

Field/Equipment Blanks

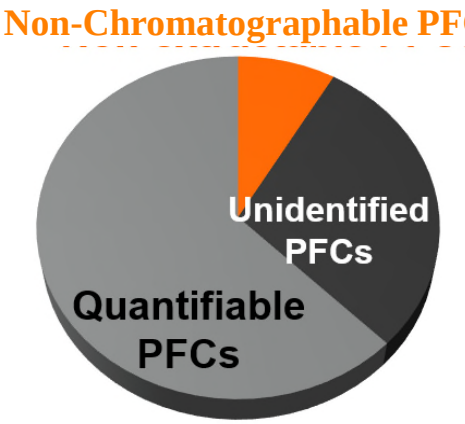
- When sampling for PFAS, it is recommended that additional and/or more frequent field/equipment blanks be collected prior to and during sampling to check for residual PFAS on sampling equipment due to the potential for cross-contamination issues and the need for very low reporting limits.
- Use Trip Blank for PFAS as required by EPA.

Analysis - Technique

- LC-MS/MS



- LC-MSMS technique → Target analysis
- Specific technique
- (Very) Low reporting limits
  - Normative values?



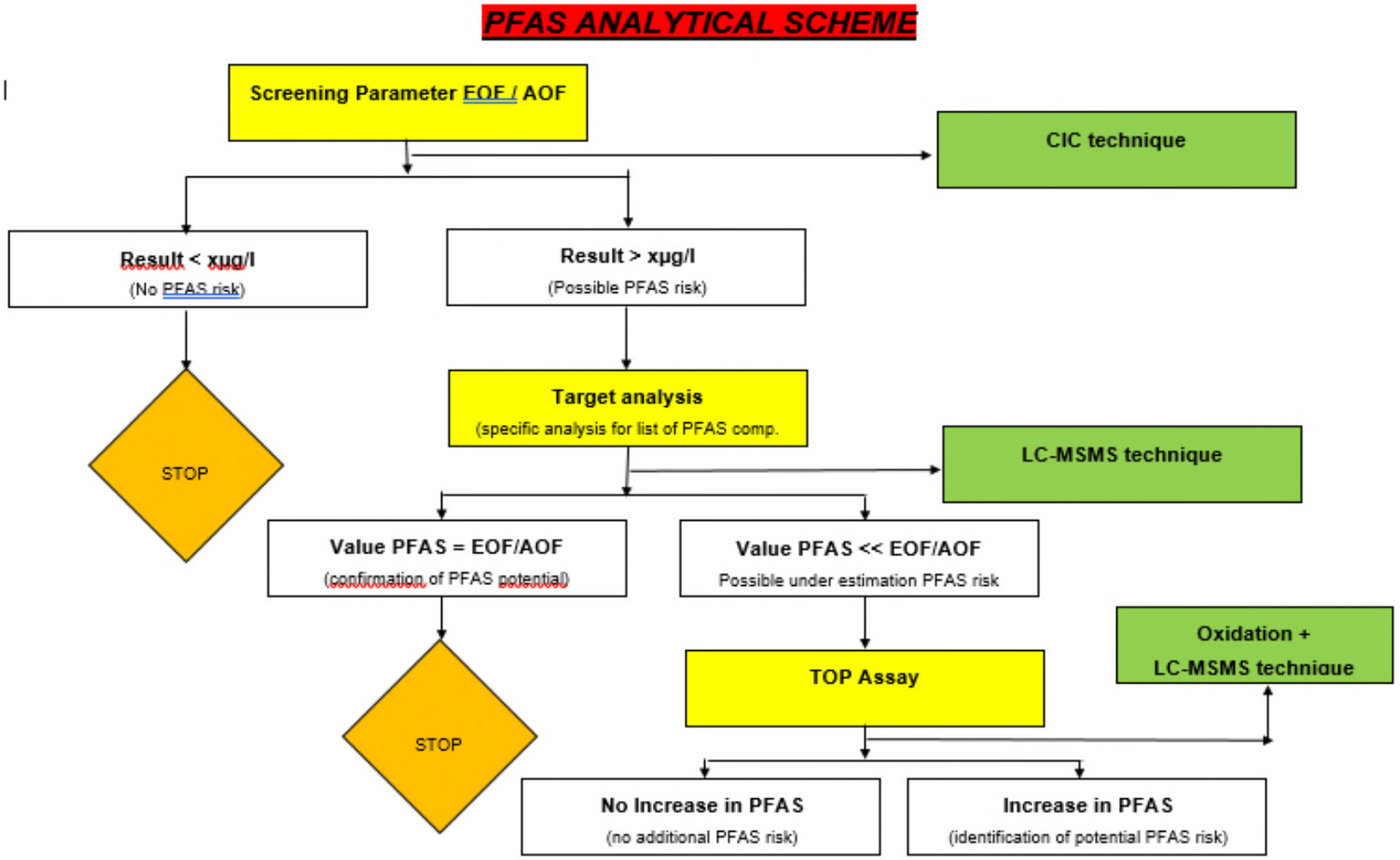
IAC methods (LC-MS/MS)

	FOOD	SOIL	WATER		Fire-fighting foam (AFFF)
			Surface/drinking	Waste	
Sample volume	1 gram	5 gram	50 mL (250 ml)	25 mL	1 gram
Extraction method	Sonication	Sonication	Solid Phase Extraction (SPE)	Solid Phase Extraction (SPE)	Dilution
Typical LOQ per compound	5 – 10 µg/kg PFOS: 5 µg/kg PFOA: 5 µg/kg	1 – 10 µg/kg DM PFOS: 0,5 µg/kg DM PFOA: 0,5 µg/kg DM	20 ng/L (0.5 ng/L)	100 ng/L	100 µg/kg

IAC methods (LC-MS/MS)

FLEXIBLE SCOPE – EXPERTISE IS VERY IMPORTANT

Proposal for General Approach on PFAS subject



Treatment / Remediation

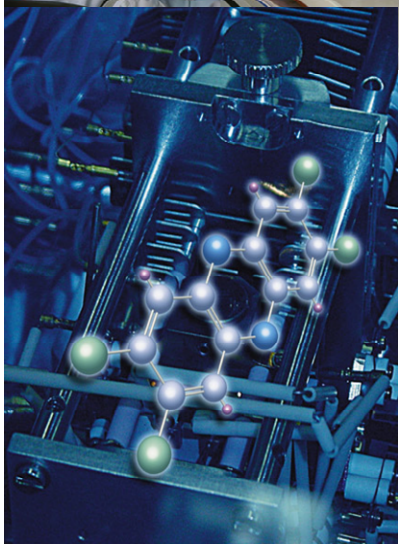
- Properties makes it complicated for removal
- Combustion only at (very) high temperatures (> 1100°C) and limit number of facilities able to do so
- Soil treatment via leachability processes?
- Groundwater treatment via Activated charcoal / Ion exchangers
- A lot of alternative techniques are studied around the world

Conclusions

- Sampling: Pragmatism – silicon tubing
- PFAS compounds is a fast growing group of compounds meaning that a group/indicative parameter based approach is required
- Reflections are to be made on the reporting limits in relation to evaluation / normative values (to be discussed)
- A lot of study / evaluation needs to be done
- Feed-back between different stake holders (Legislation, Consultants, laboratories) is mandatory

SGS Institute for applied Chromatography
Antwerp center of Excellence

Mission Statement: Client oriented interface between " academic and Routine approach"



- Some of the unique capabilities and techniques:
  - GC techn.: HRGC/HRMS, GC/MS/MS. GCxGC/MS-FID
  - LC techn.: LC/MS; LC/MSMS, UPLC-TOF(Time of flight), UPLC-Q-TOF
  - ICP/OES, ICP/MS, HR –ICP/MS (sector field),
  - Isotope Ratio Mass Spectroscopy (IRMS-Thermo),
- Applications:
  - Dioxin/Furans, Dioxin Like PCB, Marker PCBs, (various matrices)
  - Brominated Compounds, PBDE's PBDF/d, PBB's HBCD, TBBA, PAH's
  - PerFluorinitated Compounds –PFC-PFOS/PFOA)
  - Pesticides, residue analysis,
  - Drugs and Precursor in Various Matrices,
  - Brominated Dioxins (PBDD/F),
  - Polychlorinated Naphthalene's,
  - PFAS and Precursors,
  - Oil related analysis
    - Spill Analysis (Dual technique approach- biomarkers/ Carbon Isotope ratio}
    - Fingerprinting using GC x GC technique
  - Environmental Forensic,
  - Illegal drug dump site investigation
  - Metals Speciation
  - Water source identification based on H and O isotopes (δ18O,δ2H)

CONTACT

CONTACT TO US

MANY THANKS FOR YOUR ATTENTION!

SGS IS THE WORLD'S LEADING INSPECTION, VERIFICATION, TESTING AND CERTIFICATION COMPANY.

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