

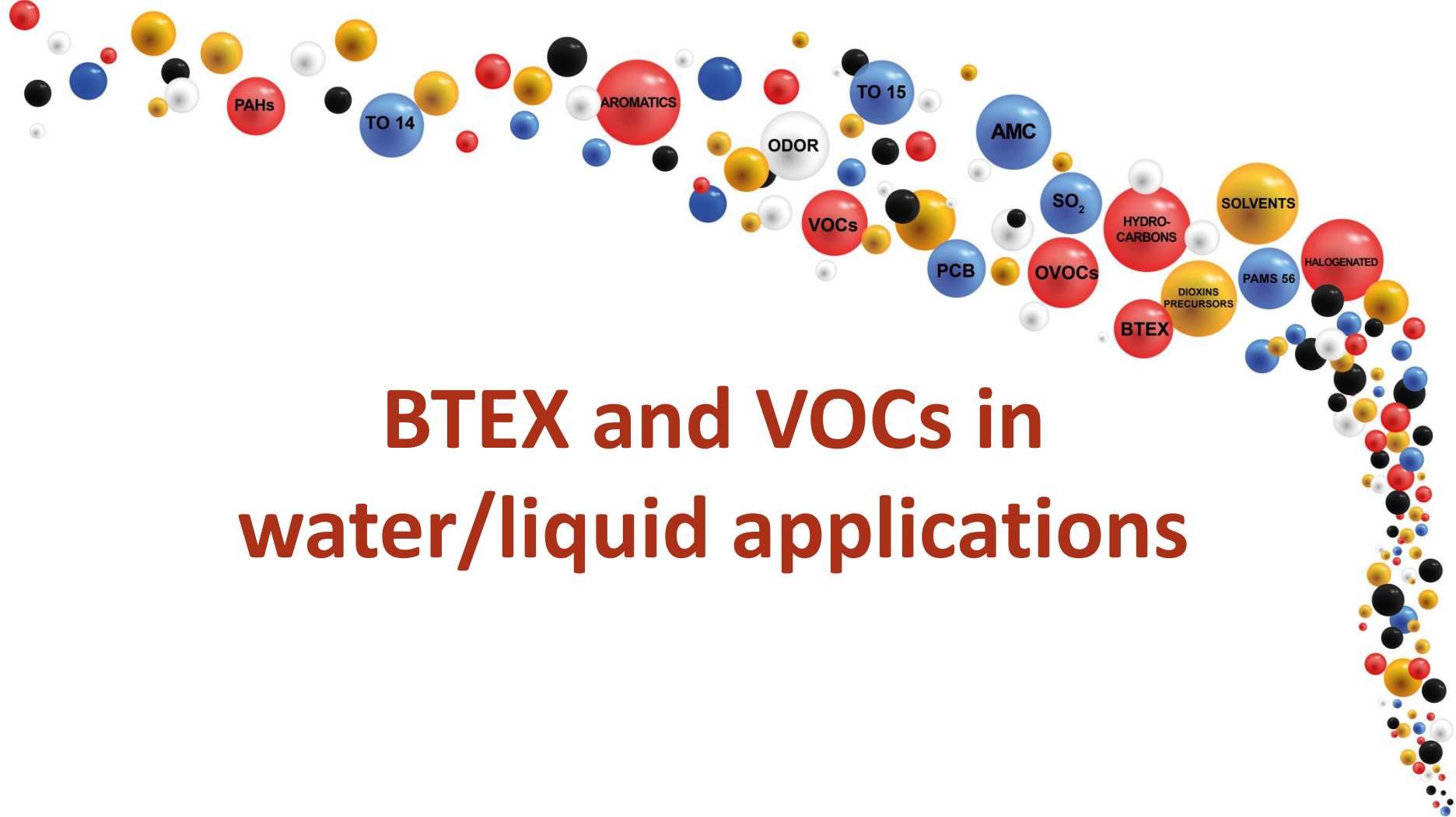


PAHs TO 14 AROMATICS TO 15 ODOR VOCs AMC SO₂ HYDRO-CARBONS SOLVENTS HALOGENATED
PCB OVOCs BTEX DIOXINS PRECURSORS PAMS 56

Liquid and water applications

Outline

- **BTEX and VOCs in water/liquid applications**
- Comparison with competitor
- Sulfurs in water/liquid applications
- Reference customers



BTEX and VOCs in water/liquid applications

Introduction

- Very small amount of VOCs can be dissolved in water
- Contamination in water (drinking water, rivers, waste water...) must be monitored
- Chromatotec[®] is well known worldwide for its leading-edge technology for online analysis of VOCs at ppt/ppb/ppm levels
- Purge and Trap system to extract VOCs from water and autoGC analysers to identify & quantify automatically contaminants



Introduction

- Water sample
 - Automatic sampling
- Gas extraction using the Chromatotec® Purge & Trap system.
- Gas analysis with our analyzers



Wall mounted version



Compact and transportable version

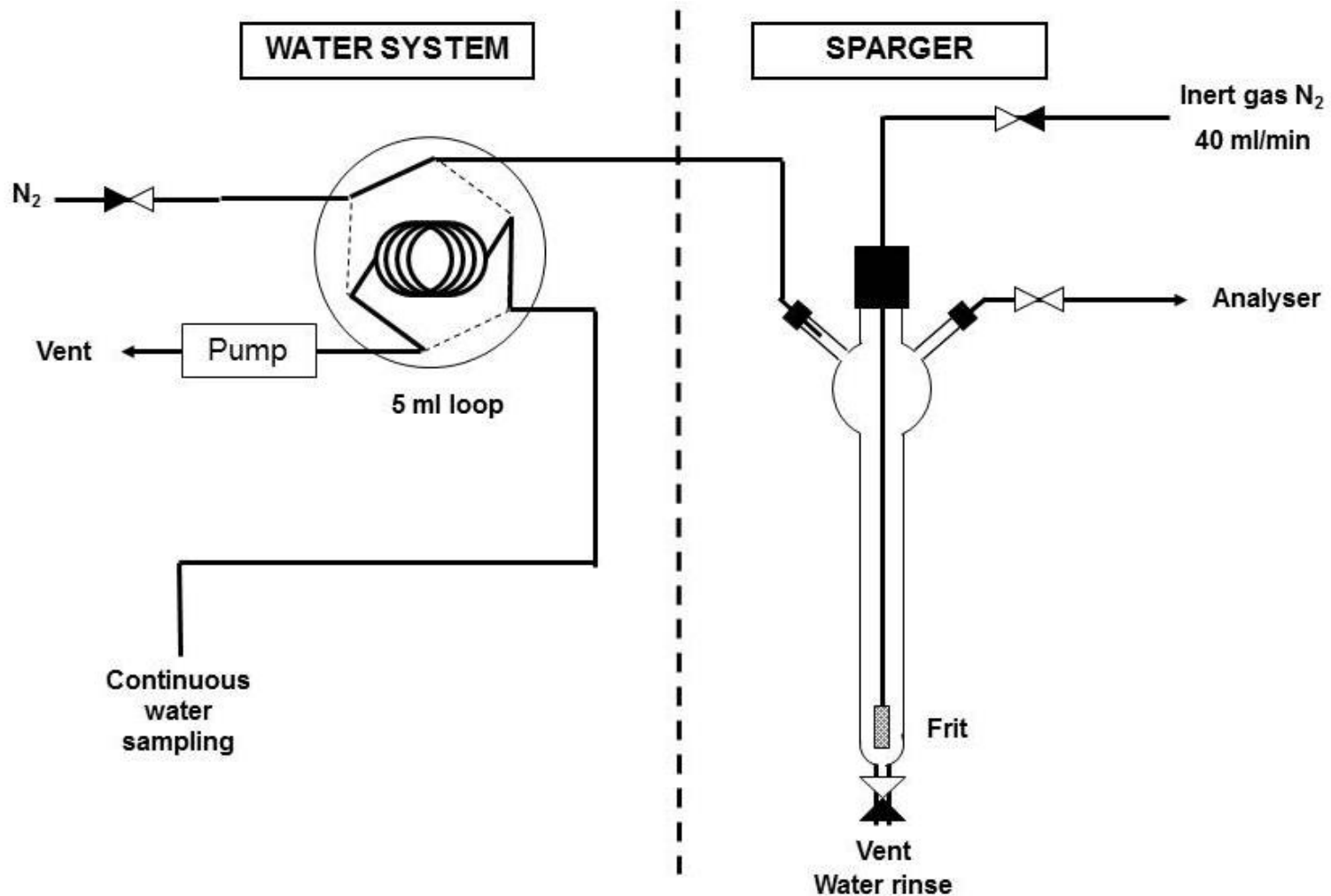
Water or liquid sampling

- Liquid sampling is quite important to avoid loss of compounds and have representative sample
 - Sampling system for Soil water (very polluted)
 - Filtering system like cyclonic filter can be used
 - Sampling system for Wastewater before treatment (polluted)
 - automatic dilution in option
 - Sampling system for Finished drinking water (clean)

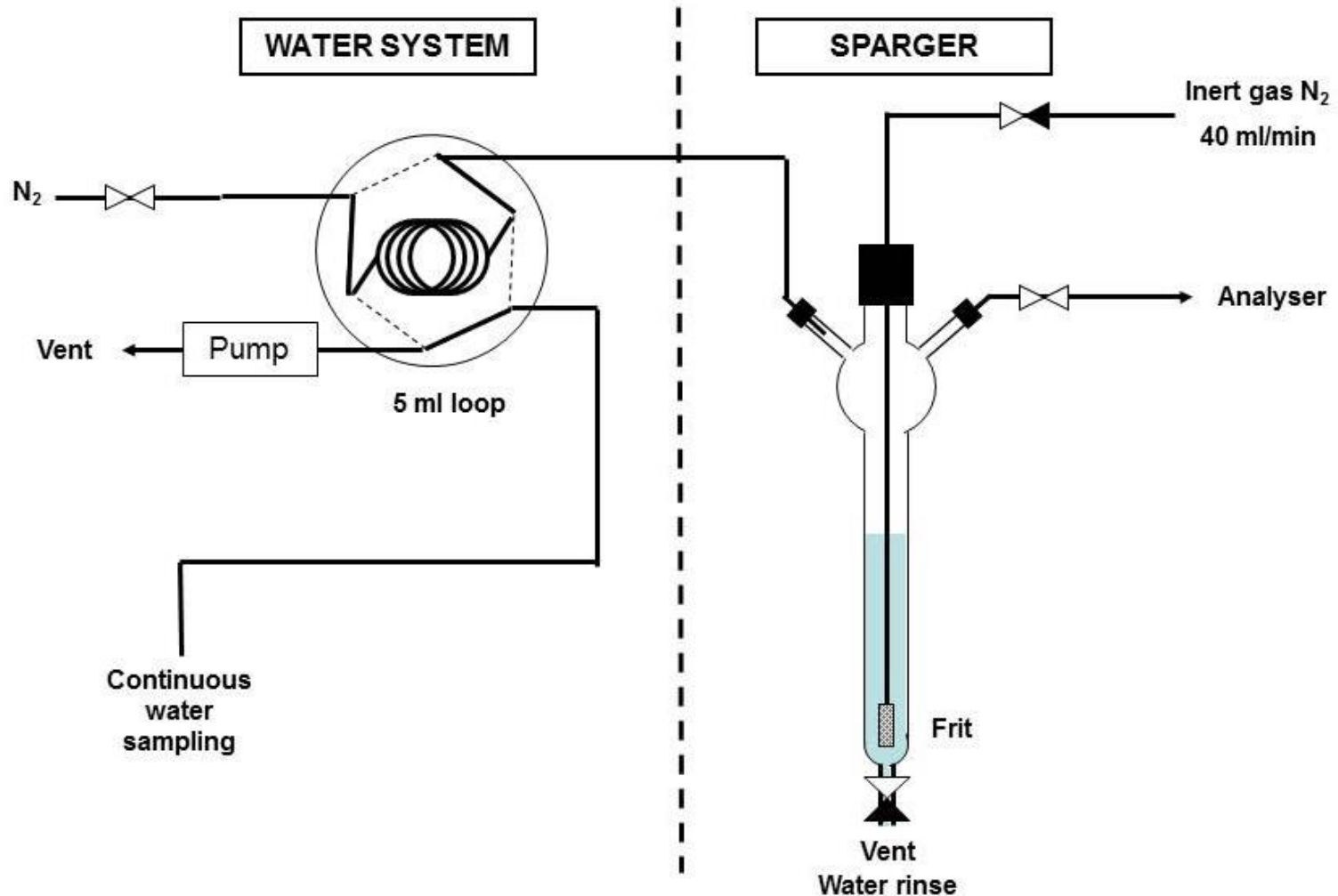
P & T US EPA 502-2 method

- Glass purging device is designed to sample **5 ml** of liquid with at least 5 cm deep sparger
- Dead volume must be less than 15 ml
- **Inert gas (N₂)** used to purge **5 ml of water** with less than **3 mm bubbles** created by the frit at the base of the sample.
 - N₂ generator is integrated with this automatic sparger.
- Automatic sampling loop rinsing process = representative sample without contamination between samples

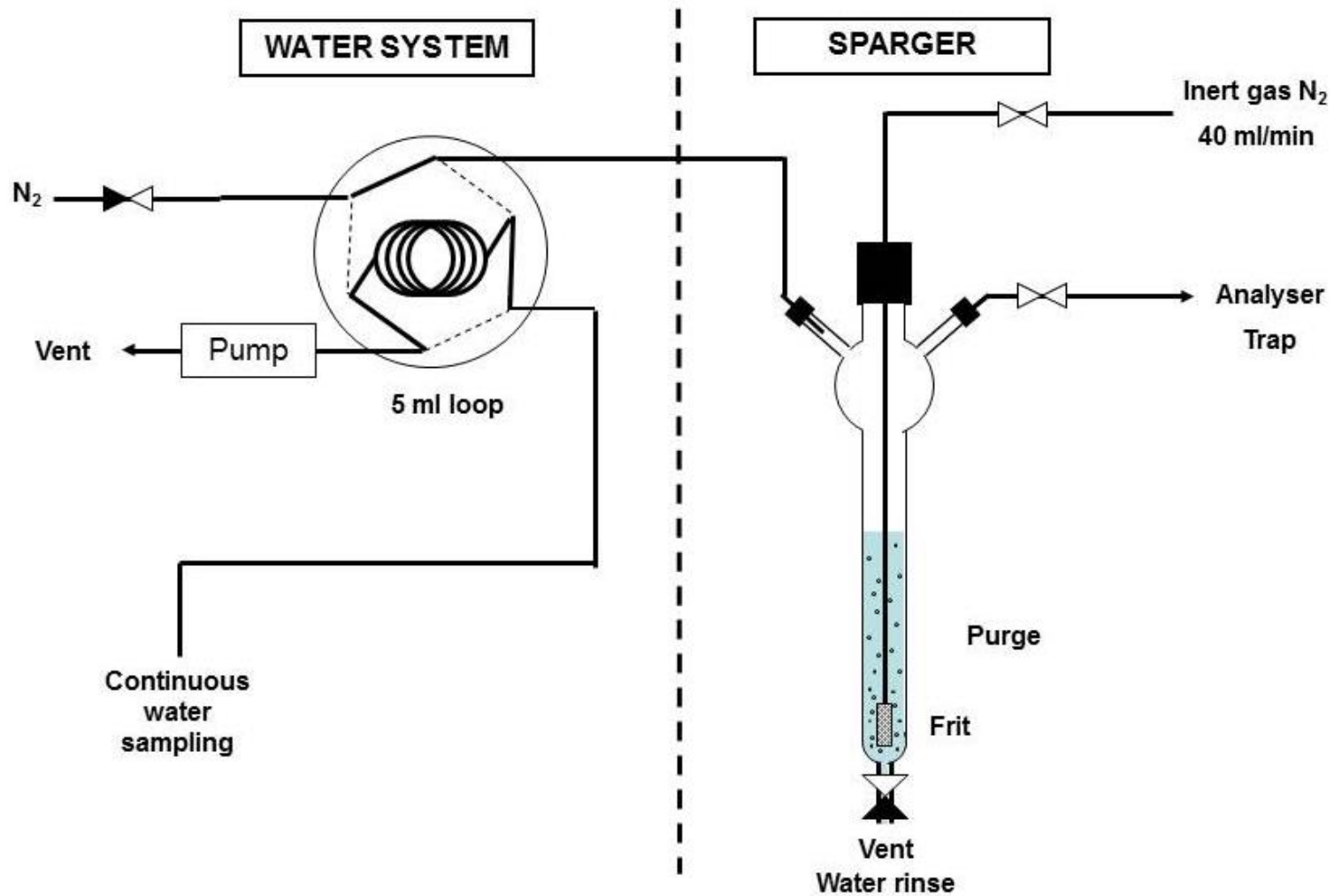
Water sampling



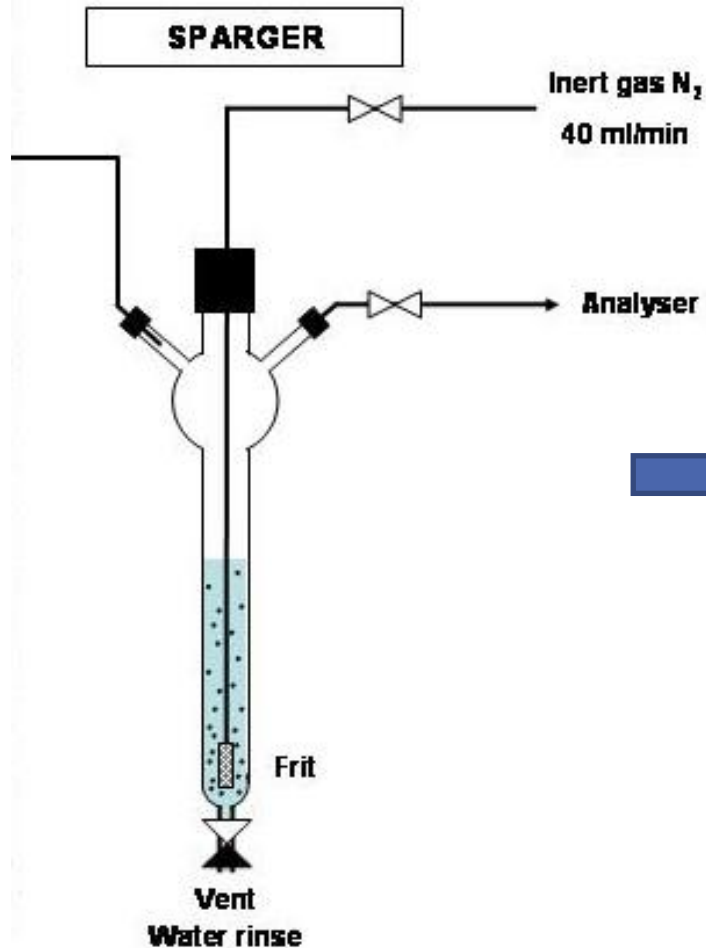
Water sampling



Water sampling



Water sampling



Chromatotec® Analyzer

- Continuous sampling
- Analysis and monitoring

Nitrogen

- N₂ generator: N₂ production contains less than
 - 2 ppm O₂
 - 100 ppt Total Hydrocarbon
 - Dew point < -30° C
- N₂ flow regulation for VOCs extraction: **40 ml/min**
 - Volume calculation is memorized in VISTACHROM
 - Unit display in mass (ng) or concentration (µg/L)

Purge & Trap

- **11 minutes purge & trap extraction for:**
 - Range = 0,01 to 200 μg per liter (water) or m^3 (air)
- airmoCAL is used for
 - VOCs linearity
 - Zero validation with blank
 - Calibration / Inter calibration by liquid and gas
- Multiple sample inlet in same sequence :
 - Air analysis above surface water or other
 - Water analysis with purge

Display software & Data transfer

- VISTACHROM display
 - Pressure, flow, temperatures on the supervisor
 - Purge sampling temperature
 - Communicate sampling / analytical / calcul parameters to final end user
- Automatic transfer of results using MODBUS to datalogger
- Possibility to display results on web interface
- Possibility to send data to local network using FTP

Solution

All in one including:

- airmoPURE (Zero Air generator)
- N2 generator
- Hydroxymchrom (H2 generator)
- airmoCAL (option: dilution)
- airmoVOC (624 model)
- Detectors: FID or PID or ELCD or Mass Detector
- Purge system for finishing drinking water (you need to complete with sampling system for non filtered water)



Wall mounted version



Compact and portable version

Transportable GC FID or GCMS system

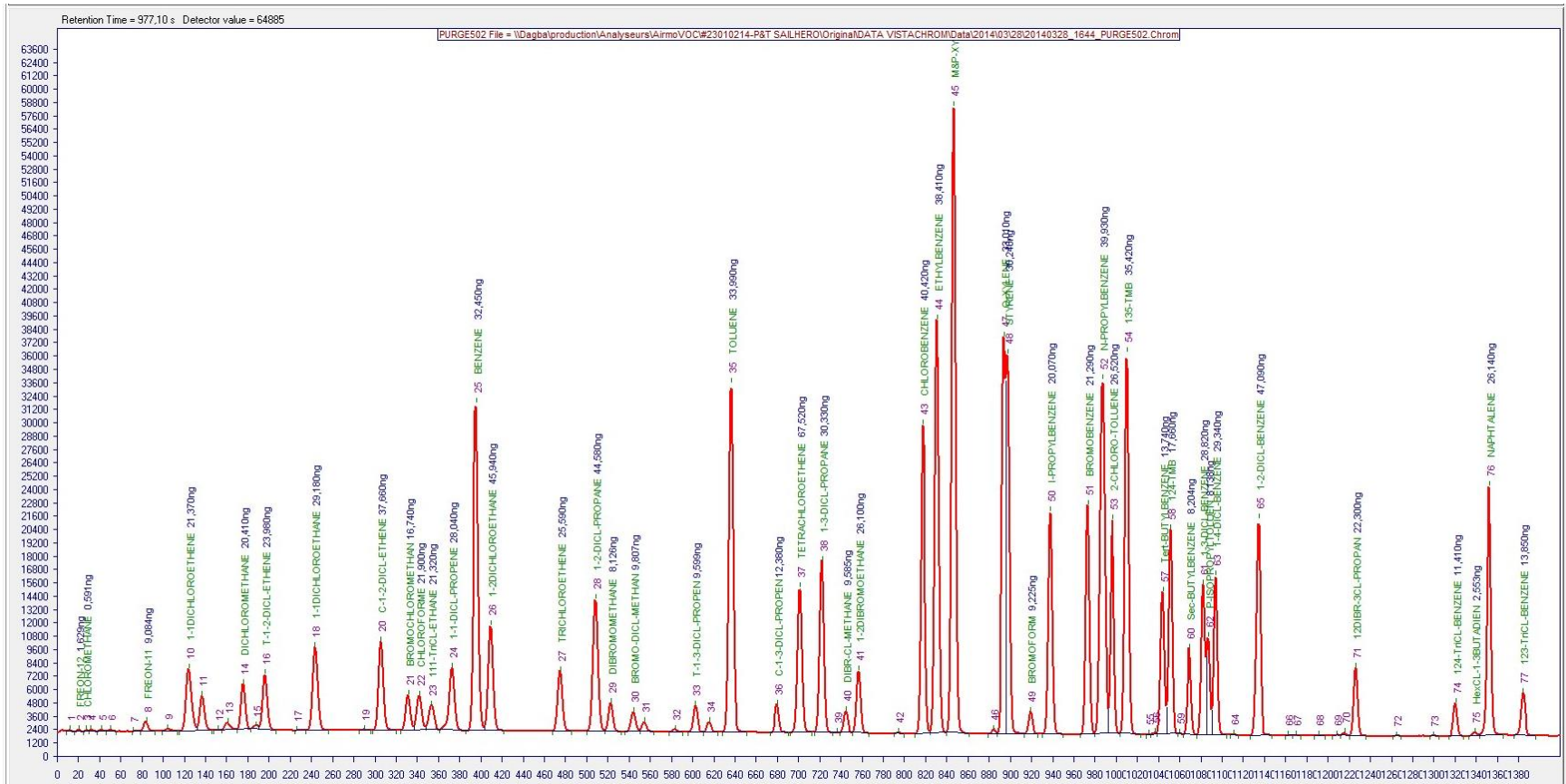
- 18U or 22U cabinet
- airmoVOC 624 with internal computer internal calibration
- DET QMS with internal vacuum pumps
- Water purge system mounted on the side of the cabinet
- Gas generators for H₂, N₂ and zero air 4U or 8 U



Outline

- VOC extraction using Purge & Trap system (US EPA 502.2 Method)
- Compounds tables
 - Method 502.2: 60 compounds
- Applications

airmoVOC 624 purge FID chromatogram: 502.2 standard containing 54 compounds



Analysis realized with a 40 minutes cycle.

It exists another standard which contains 6 compounds: dichlorodifluoromethane, Chloromethane, Vinyl chloride, Bromomethane, Chloroethane, Trichlorofluoromethane.

502.2 List: 60 compounds with airmoVOC 624 + DET QMS

	Analytes	CAS Registry Number		Analytes	CAS Registry Number
1	Benzene	71-43-2	31	1,3-Dichloropropane	142-28-9
2	Bromobenzene	108-86-1	32	2,2-Dichloropropane	590-20-7
3	Bromochloromethane	74-97-5	33	1,1-Dichloropropene	563-58-6
4	Bromodichloromethane	75-27-4	34	Cis-1,3-Dichloropropene	10061-01-5
5	Bromoform	75-25-2	35	Trans-1,3-Dichloropropene	10061-02-6
6	Bromomethane	74-83-9	36	Ethylbenzene	100-41-4
7	n-Butylbenzene	104-51-8	37	Hexachlorobutadiene	87-68-3
8	sec-Butylbenzene	135-98-8	38	Isopropylbenzene	98-82-8
9	tert-Butylbenzene	98-06-6	39	4-Isopropylbenzene	99-87-6
10	Carbon Tetrachloride	56-23-5	40	Methylene Chloride	75-09-2
11	Chlorobenzene	108-90-7	41	Naphtalene	91-20-3
12	Chloroethane	75-00-3	42	Propylbenzene	103-65-1
13	Chloroform	67-66-3	43	Styrene	100-42-5
14	Chloromethane	74-87-3	44	1,1,2,2-Tetrachloroethane	630-20-6
15	2-Chlorotoluene	95-49-8	45	1,1,1,2-Tetrachloroethane	79-34-5
16	4-Chlorotoluene	106-43-4	46	Tetrachloroethene	127-18-4
17	Dibromochloromethane	124-48-1	47	Toluene	108-88-3
18	1,2-Dibromo-3-Chloropropane	96-12-8	48	1,2,3-Trichlorobenzene	87-61-6
19	1,2-Dibromoethane	106-93-4	49	1,2,4-Trichlorobenzene	120-82-1
20	Dibromomethane	74-95-3	50	1,1,1-Trichloroethane	71-55-6
21	1,2-Dichlorobenzene	95-50-1	51	1,1,2-Trichloroethane	79-00-5
22	1,3-Dichlorobenzene	541-73-1	52	Trichloroethene	79-01-6
23	1,4-Dichlorobenzene	106-46-7	53	Trichlorofluoromethane	75-69-4
24	Dichlorodifluoromethane	75-71-8	54	1,2,3-Trichloropropane	96-18-4
25	1,1-Dichloroethane	75-34-3	55	1,2,4-Trimethylbenzene	95-63-6
26	1,2-Dichloroethane	107-06-2	56	1,3,5-Trimethylbenzene	108-67-8
27	1,1-Dichloroethene	75-35-4	57	Vinyl Chloride	75-01-4
28	cis-1,2-Dichloroethene	156-59-4	58	o-Xylene	95-47-6
29	trans-1,2-Dichloroethene	156-60-5	59	m-Xylene	108-38-3
30	1,2-Dichloropropane	78-87-5	60	p-Xylene	106-42-3

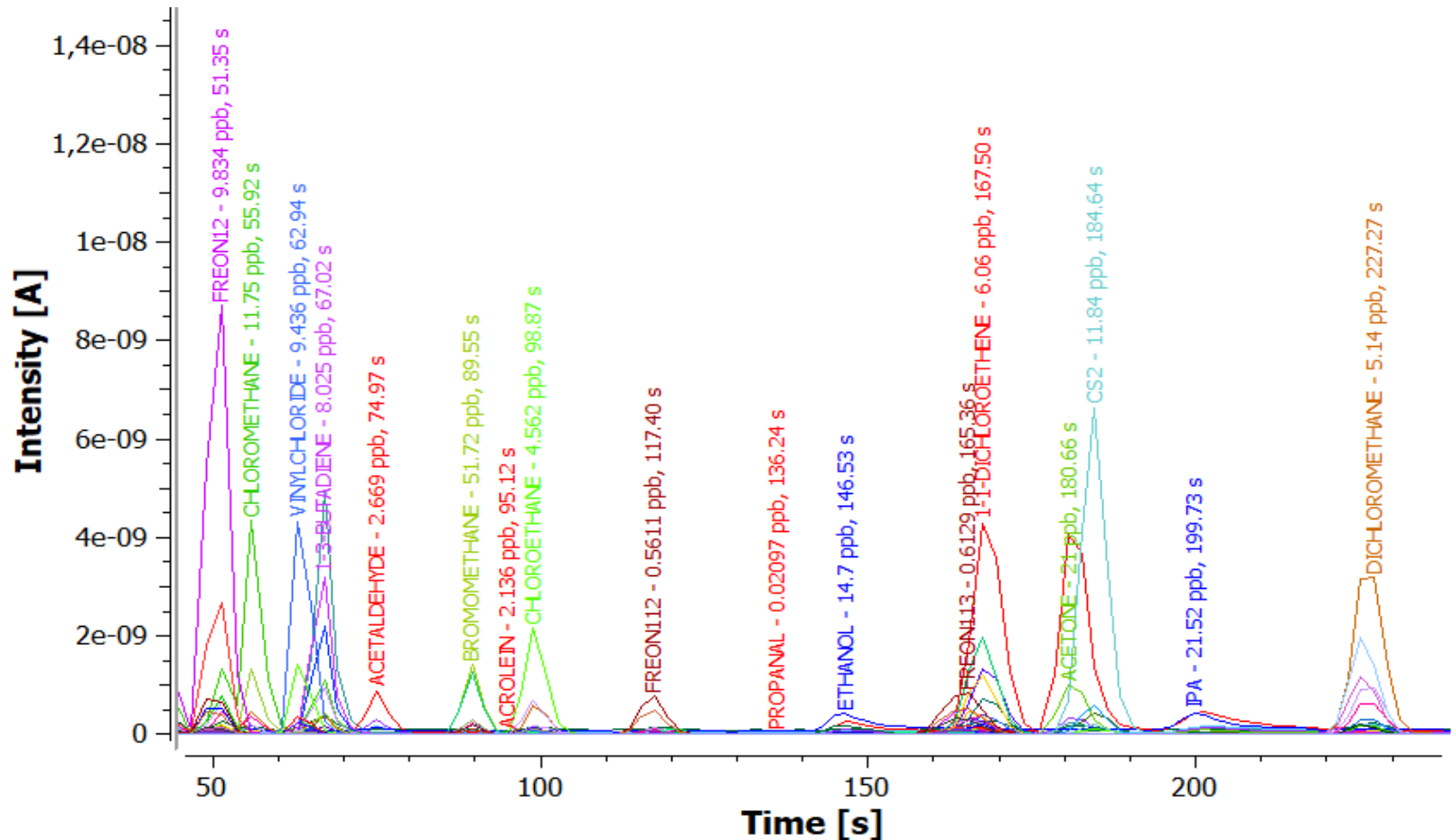
No risk of co elution or bad identification
More sensitivity on Halogenated compounds

Other compounds analyzed with airmoVOC 624 + DET QMS

	Analytes	CAS Registry Number
1	1-3 Butadiene	106-99-0
2	Acetaldehyde	75-07-0
3	Freon 112	76-13-1
4	Propanal	123-38-6
5	Ethanol	64-17-5
6	Freon113	76-13-1
7	Acetone	67-64-1
8	CS ₂	75-15-0
9	IPA	67-63-0
10	MTBE	1634-04-4
11	MPK	107-87-9
12	MVK	78-94-4
13	MEK	78-93-3
14	Ethyl Acetate	141-78-6
15	THF	109-99-9
16	Chloroforme	67-66-3
17	CCL ₄	56-23-5
18	1-4 Dioxane	123-91-1
19	MethylMetacrylate	80-62-6
20	MIBK	108-10-1
21	MBK	591-78-6
22	Benzylchloride	100-44-7

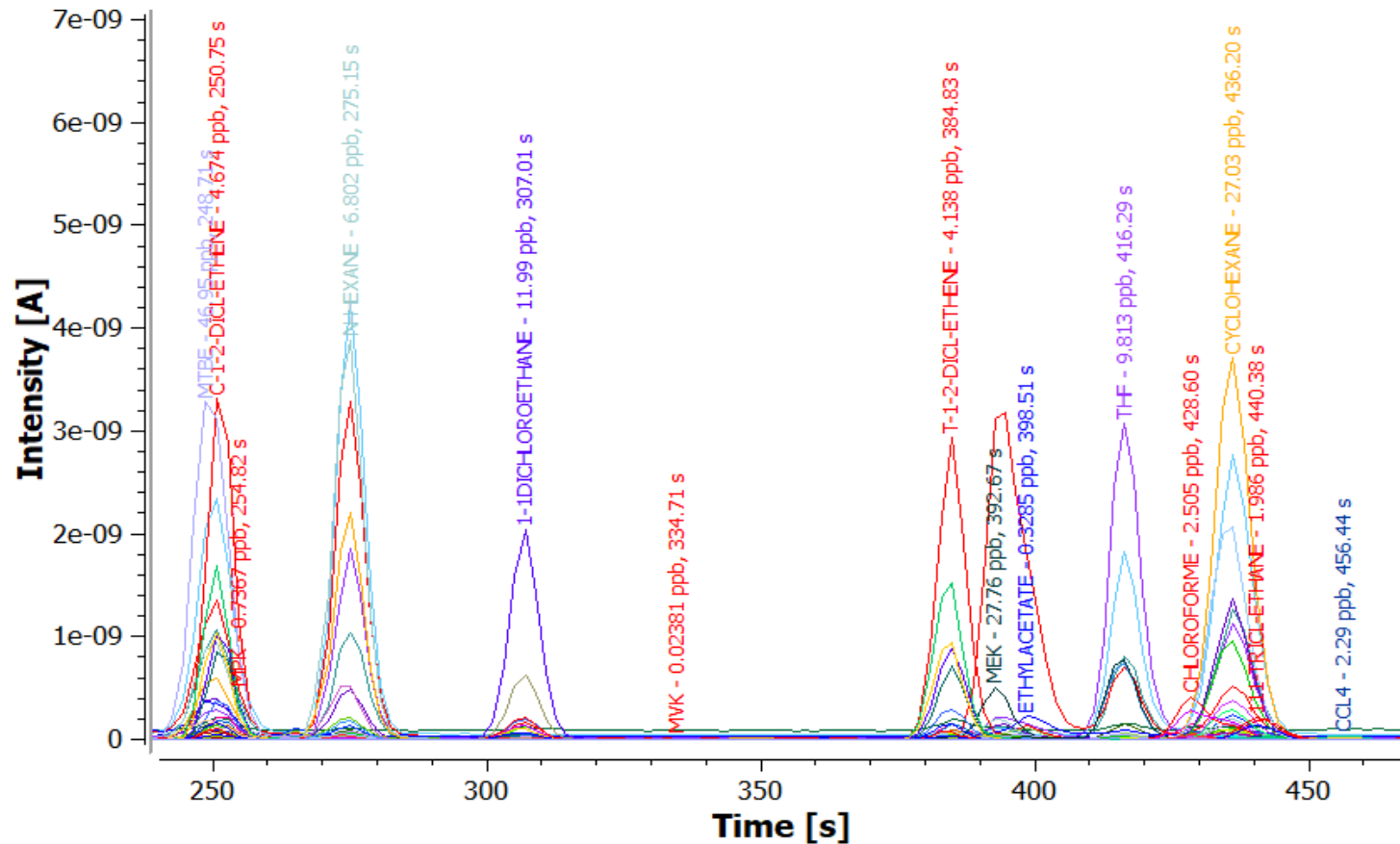
This VOCs compounds list is based on international standard TO15 and US EPA method 502-2 and other VOCs can be analyzed under request

airmoVOC 624 + DET QMS purge chromatogram: first part



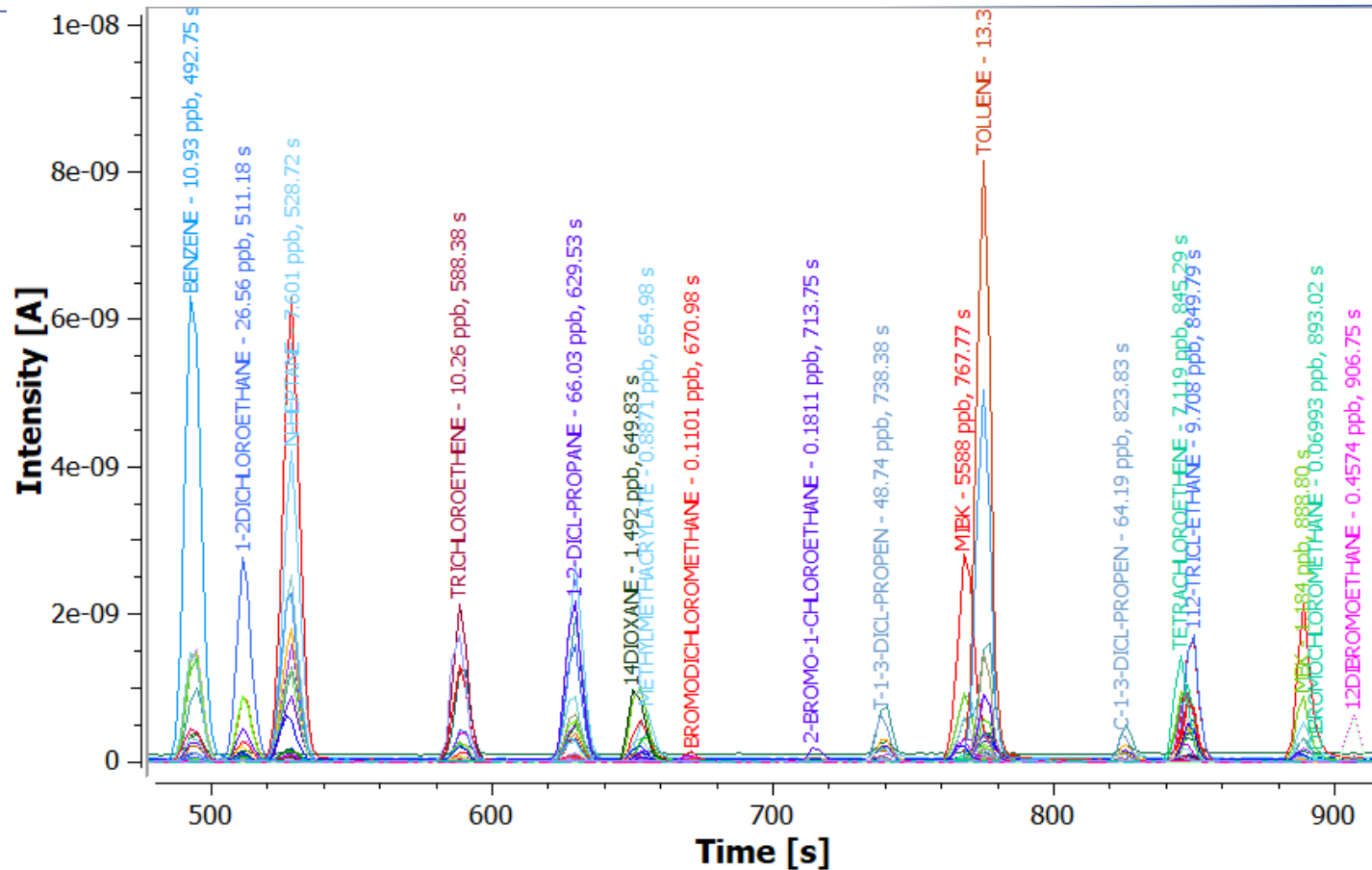
Analysis realized with a 40 minutes cycle on TO15 in SCAN mode

airmoVOC 624 + DET QMS purge chromatogram: second part



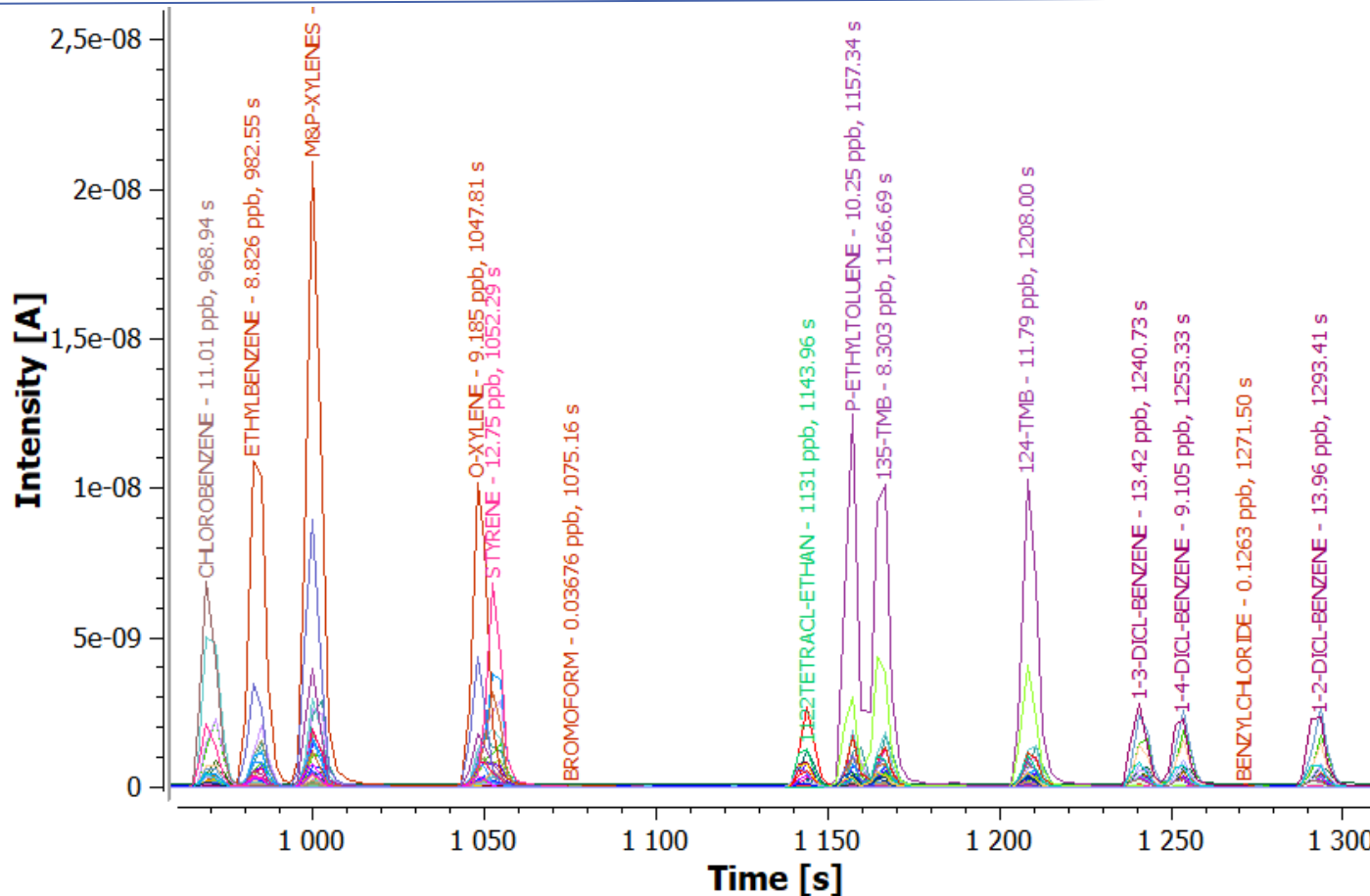
Analysis realized with a 40 minutes cycle on TO15 in SCAN mode

airmoVOC 624 + DET QMS purge chromatogram: third part



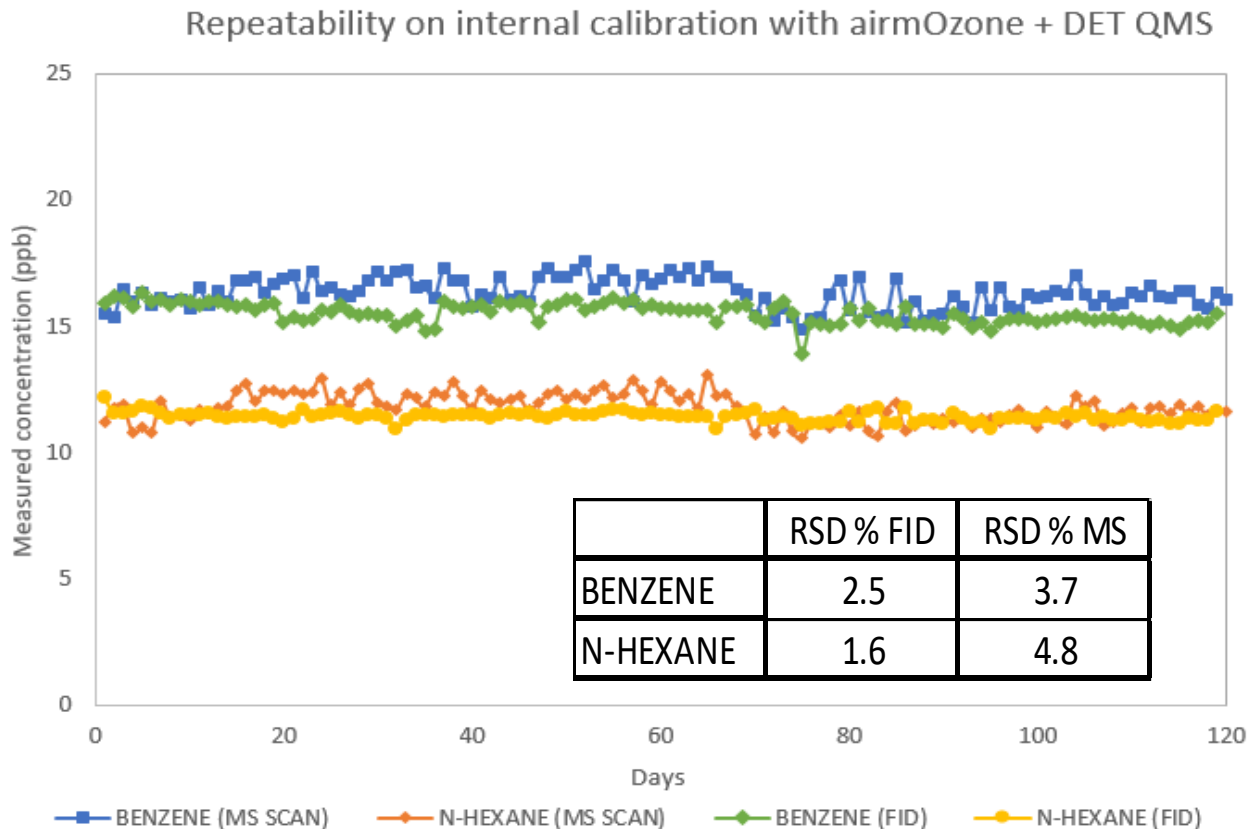
Analysis realized with a 40 minutes cycle on TO15 in SCAN mode

airmoVOC 624 + DET QMS purge chromatogram: fourth part



Analysis realized with a 40 minutes cycle on TO15 in SCAN mode

Long time concentration drift



More than 3 months without any tune or calibration !



Applications

- Environment for trace level
 - Raw source water
 - River water / Seawater / Rain water
- Drinking water for trace level
 - Finished drinking water
- Industrial application
 - Waste water treatment plant
 - Refinery / Petrochemical site for water monitoring
Before throwing the water back into the river
 - Process monitoring

Main Benefits vs existing solution

- Stand alone solution with inbuilt gas generators and calibration !
 - Cylinder free system
- Same system can analyse VOCs from water and from air with multiple stream inlet
- Up to 32 sample streams with same system
- Integrated automatic 'blank' method to be sure that no contaminants are presents on second analysis of same sample
 - => no memory effect

Main Benefits vs existing solution

- Certified and recognized VOCs auto GC
- Auto calibration with auto data validation
- Liquid calibration possible thanks to very low volume of liquid sample necessary
 - 5 ml per sample
 - Cyclic sampling
- Full remote control for remote diagnostic, validation of data, calibration and chromatogram post process !

BTEX and VOCs in water competitors



INFICON CMS 5000

CHROMATOTEC
airmoVOC WMS



SYNSPEC

BTEX and VOCs in water competitors



Online Gas and Liquid Analyzer Experts

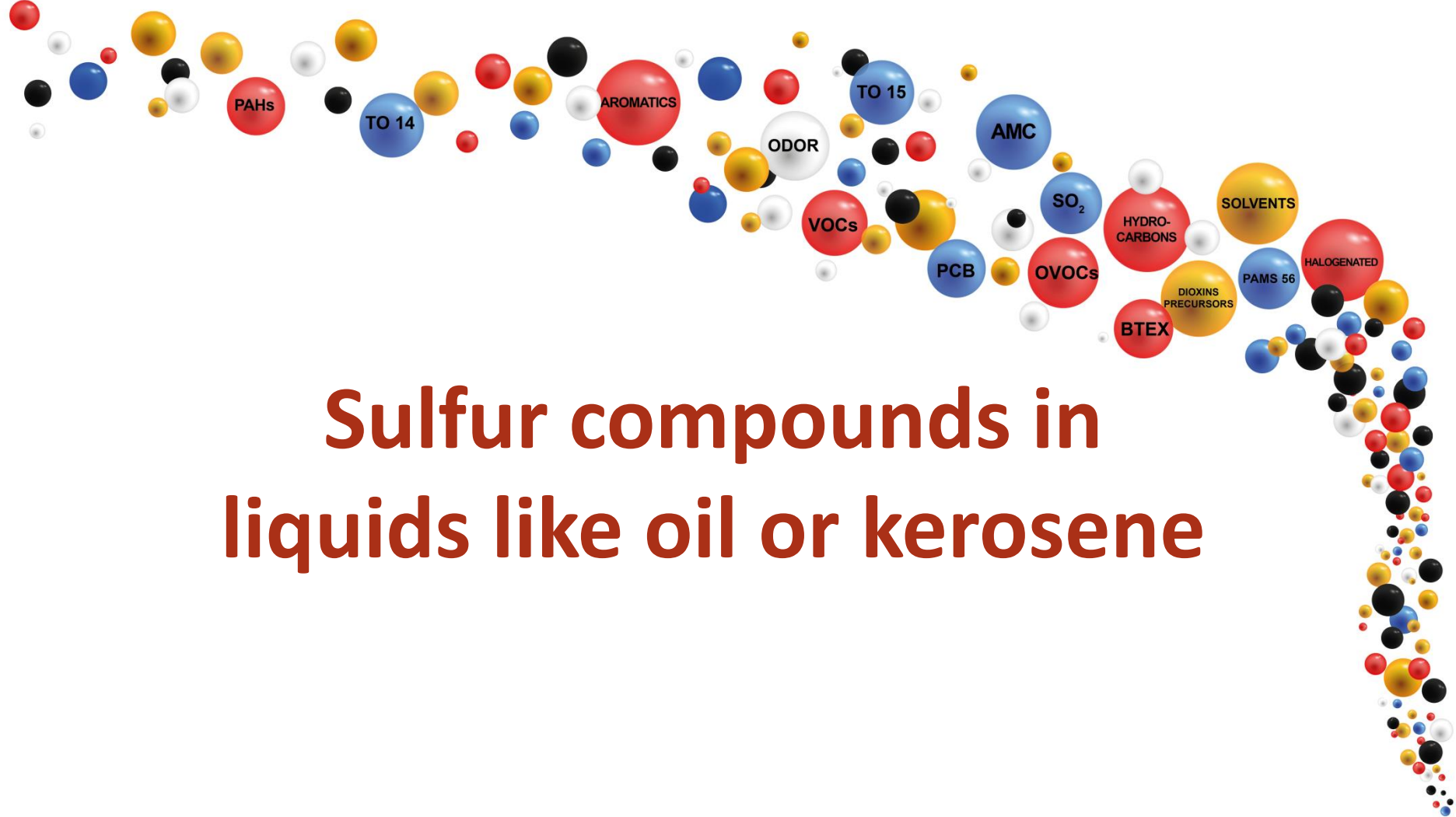
	ENFICON	SYNSPEC	CHROMATOTEC
Certification on benzene	No	Mcert using 30m column only on PID	Mcert on PID and FID and selected by US EPA
Certification test on other VOCs	NO	NO	N-Hexane; I-Octane; N-Heptane; Toluene; N-Octane; Ethyl-Benzene; M&P Xylenes; O-Xylene; 135-TMB; 124 TMB; 123 TMB
Columns	Fused silica : breakable and maintenance cost	Fused silica 15m : breakable and maintenance cost	Metallic capillary column 30m more than 5 years lifetime
Detector	MAID (Specific Detector from ENFICON only : no international standard)	PID or FID	PID or FID or FID + MS Linear detector !
Carrier gas	Argon from cylinder only	PID version: Nitrogen	PID version : Nitrogen from NITROXYCHROM FID version: Hydrogen from HYDROXYCHROM
LDL	Benzene 1 ppb in water		Benzene 0,010 ppb in water
Stability	5 running consecutive benzene 5ppb, RSD<15%		RSD on RT < 0,3% over 48h RSD on Concentration < 2% over 48h on 1 ppb Benzene

BTEX and VOCs in water competitors



Online Gas and Liquid Analyzer Experts

	ENFICON	SYNSPEC	CHROMATOTEC
Supervisor and communication		Internal comptuer with Windows®7	Internal industrial computer including WINDOWS® 10 MODBUS RTU/TCP IP / Gesytec 2
Compounds	From BTEX to 18 compounds	From BTEX to up to 40 compounds	From BTEX to 60 compounds from US EPA 502-2 method
Gas calibration	Cylinder	Cylinder	Cylinder and/or internal permeation tube with multipoint check in option. Linearity and stability allow to use response factor
Liquid calibration	Very difficult due to continuous purge system = need <u>1,5 Liter</u> of liquid standard = expensive	Very difficult due to continuous purge system = need several litters of liquid standard = expensive	Liquid calibration possible thanks to very low volume of liquid sample necessary <u>5 ml</u> per sample Cyclic sampling
Number of analysis per day	4 to decrease argon consumption		From 24 to 48 depending on compounds list and cycle time from 30 to 60 min



Sulfur compounds in liquids like oil or kerosene

Outline

- Analytical configuration
- Analytical results

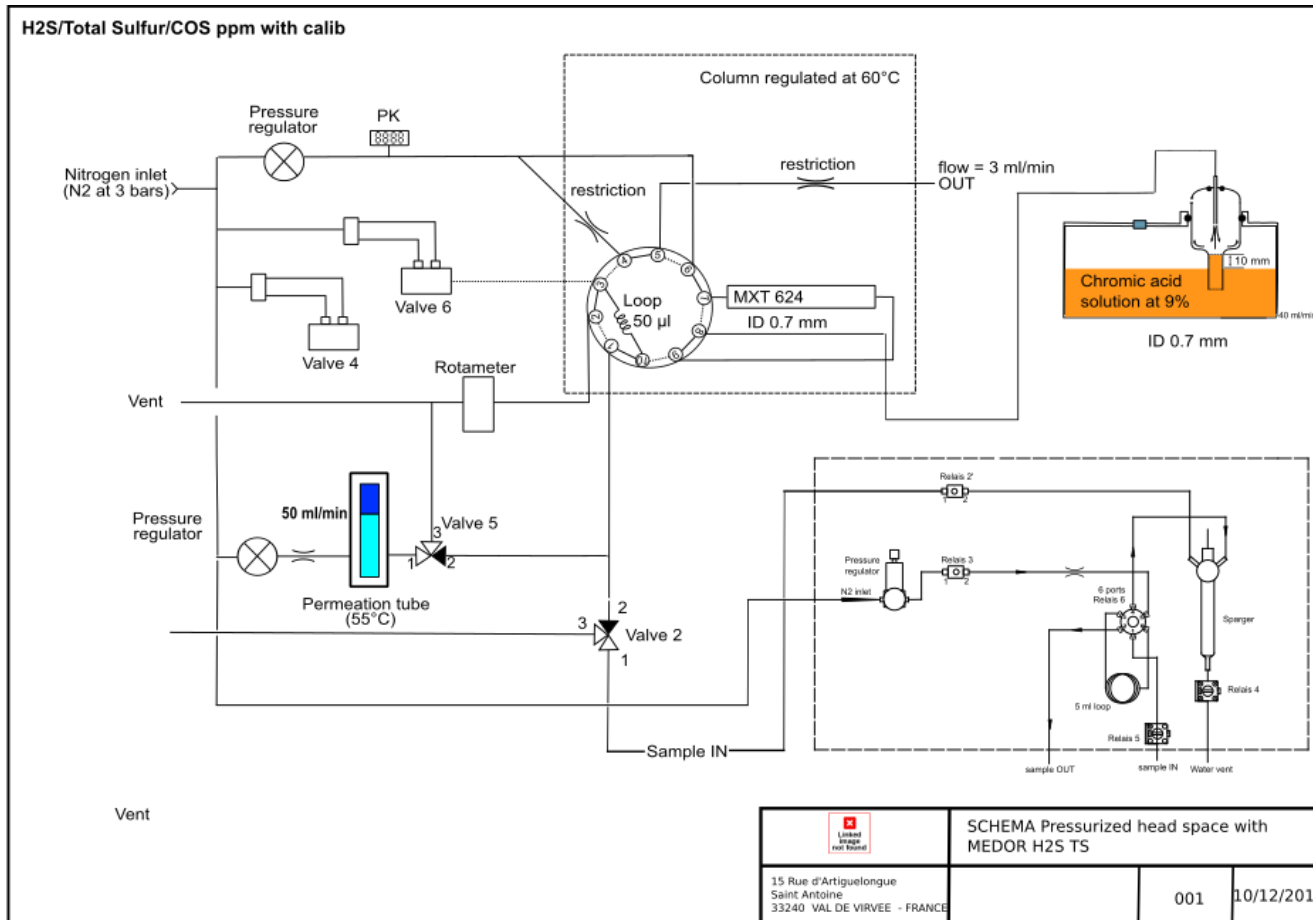


Analytical configuration

- MEDOR H2S/TS
 - Standard instrument
- Sampling system
 - To vaporize only light molecules to the gas phase using **pressurized head space**

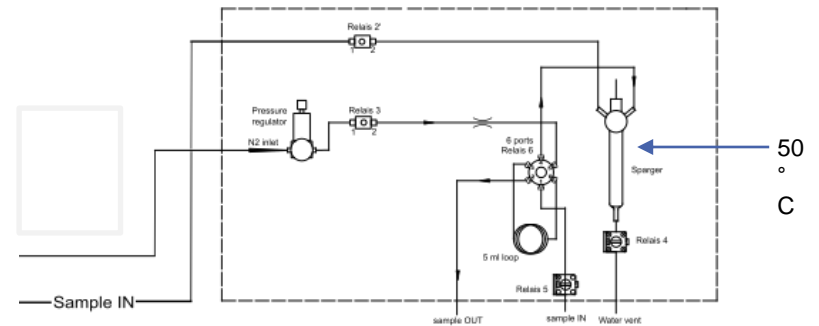


Pneumatic diagram



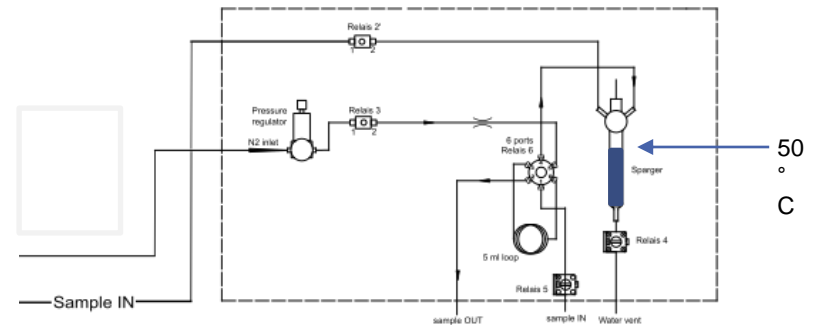
Pressurized sampling system

1. Sample goes through the sampling loop



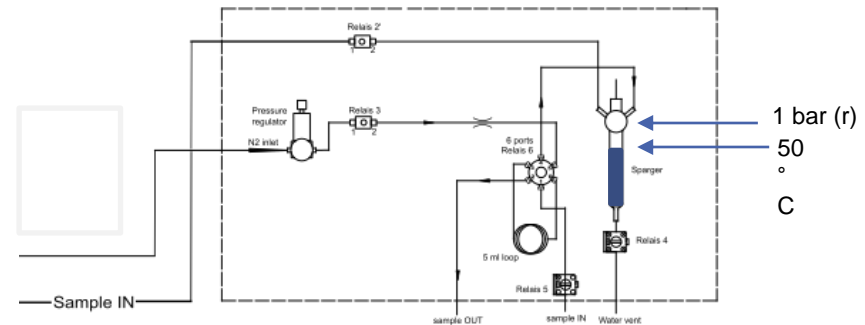
Pressurized sampling system

1. Sample goes through the sampling loop
2. Sample is injected to the purge system



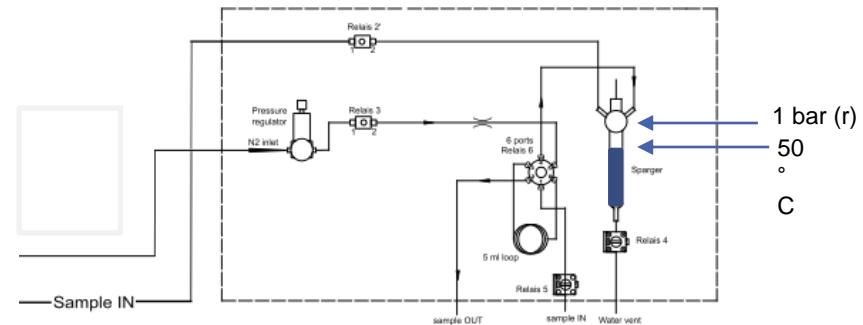
Pressurized sampling system

1. Sample goes through the sampling loop
2. Sample is injected to the purge system
3. N_2 gas pressurized the head space



Pressurized sampling system

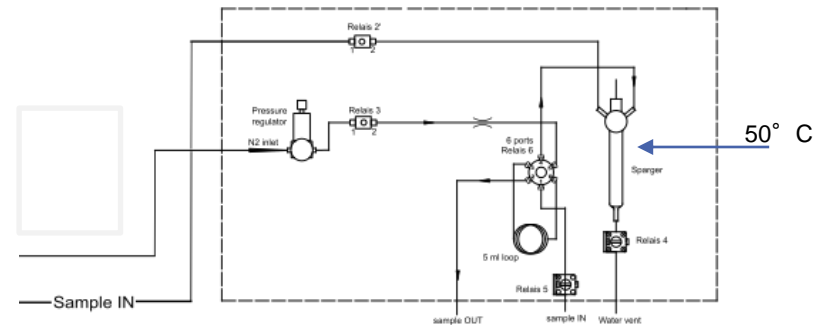
1. Sample goes through the sampling loop
2. Sample is injected to the purge system
3. N₂ gas pressurized the head space
4. 8 minutes equilibrium



-
- 0.3 bar
(50 °C)

Pressurized sampling system

1. Sample goes through the sampling loop
2. Sample is injected to the purge system
3. N₂ gas pressurized the head space
4. 8 minutes equilibrium
5. Injection of the gas sample containing N₂ and small fraction of liquid sample which migrated to the gas phase
6. Liquid is flushed from the pressurized head space system



Sampling systems

Pressurized head space

- Only gaseous molecules migrate to the gas phase
- No risk of condensation in the system

Analytical Lab tests

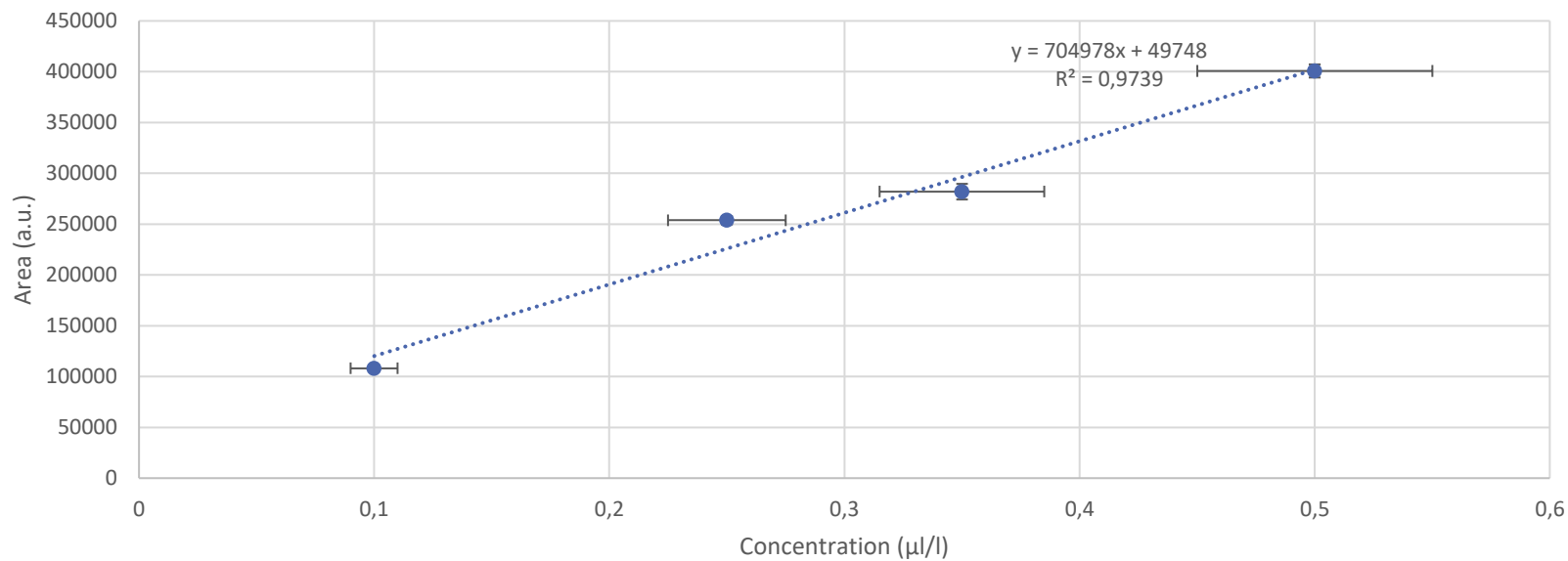
- Test in Water
 - Linearity
 - Stability
- Test in Kerosene (C11-C14)
 - Linearity
 - Stability
 - Carry over

Sample preparation

- Peristaltic pump is used to inject the Water or Kerosene into a bag
- Injection of DMS using septum
- C° for dilution in water ($\mu\text{l/l}$)
 - 0.1
 - 0.25
 - 0.35
 - 0.5

Test in Water

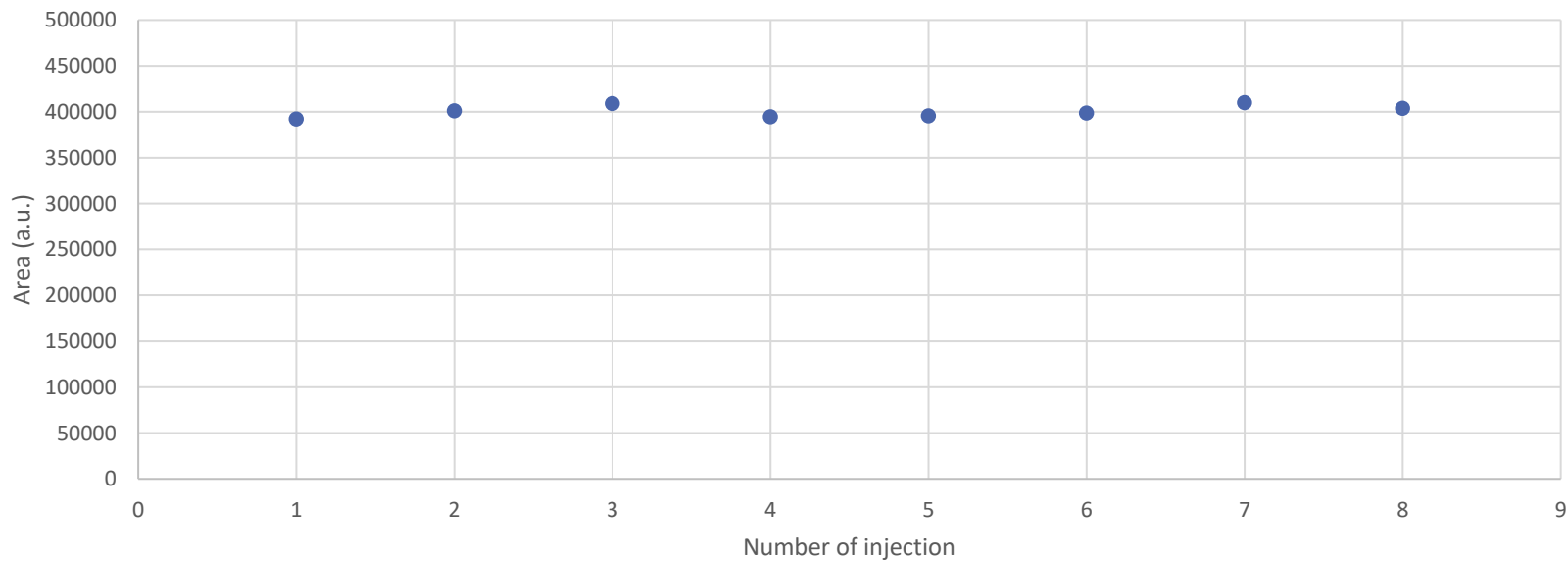
DMS in Water using pressurized Head space



Test in Water

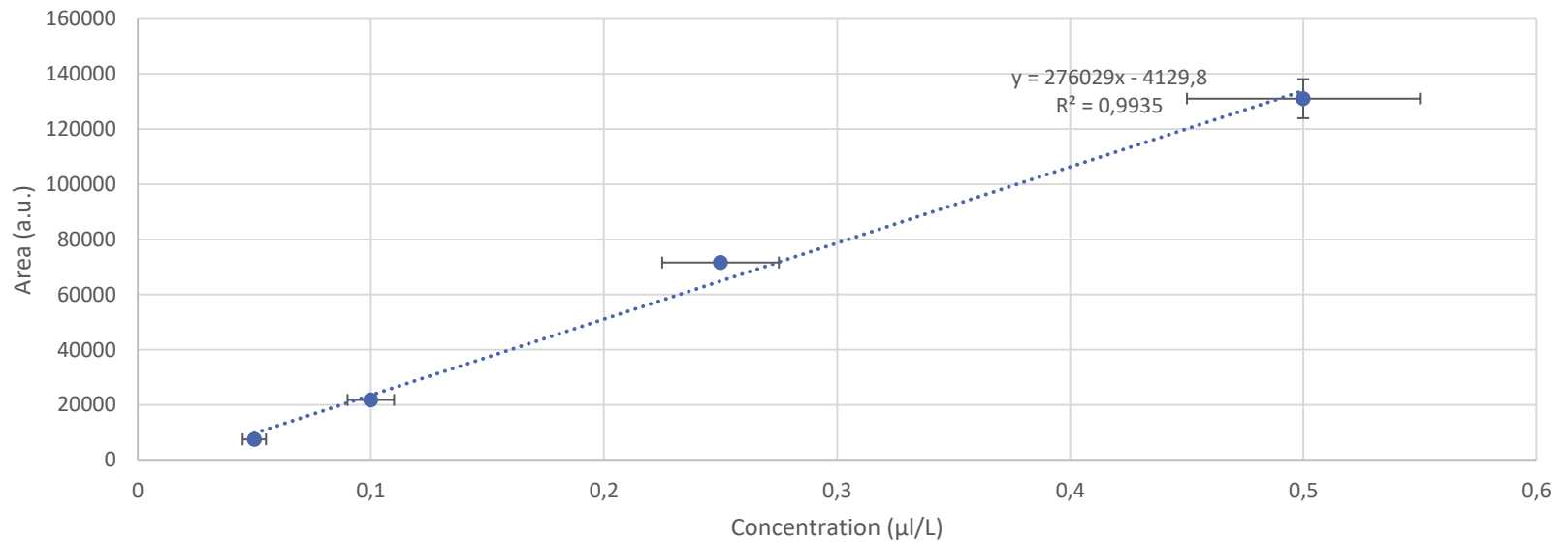
C° in liquid µl/l	mean	STDV	STDV (%)
0.5	400765	6577	1.6

Area for 0.5 µl/l



Test in Kerosene

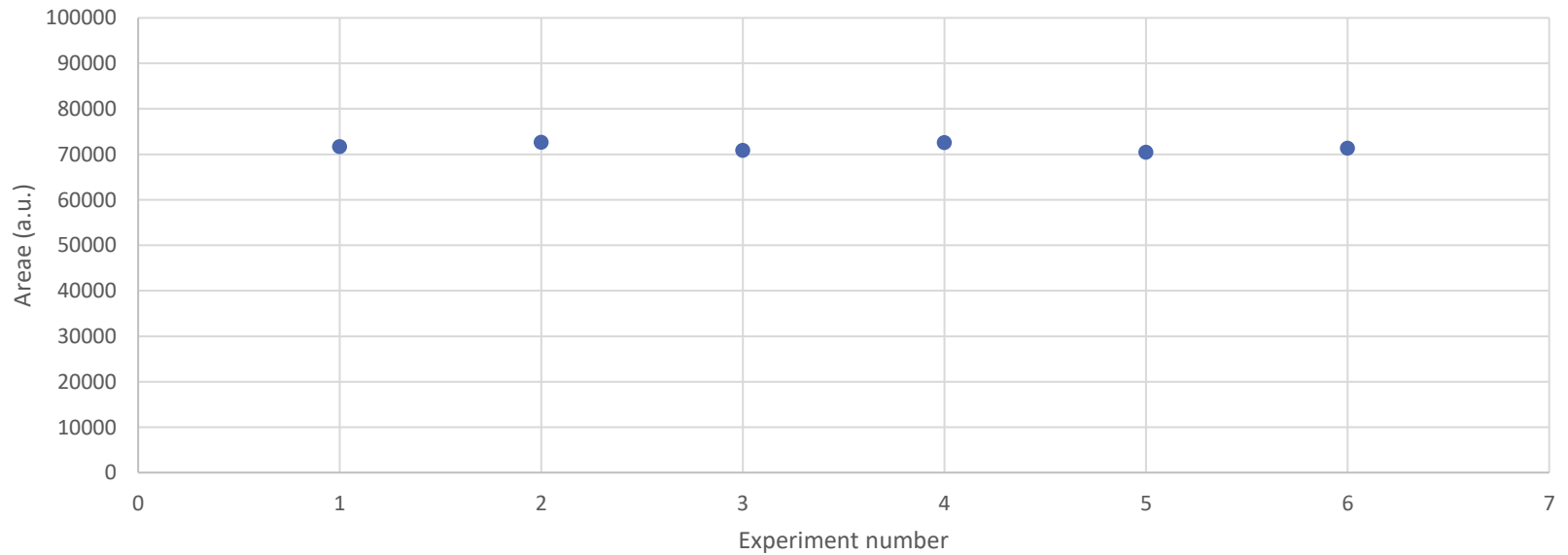
DMS in Kerosene using pressurized Head space



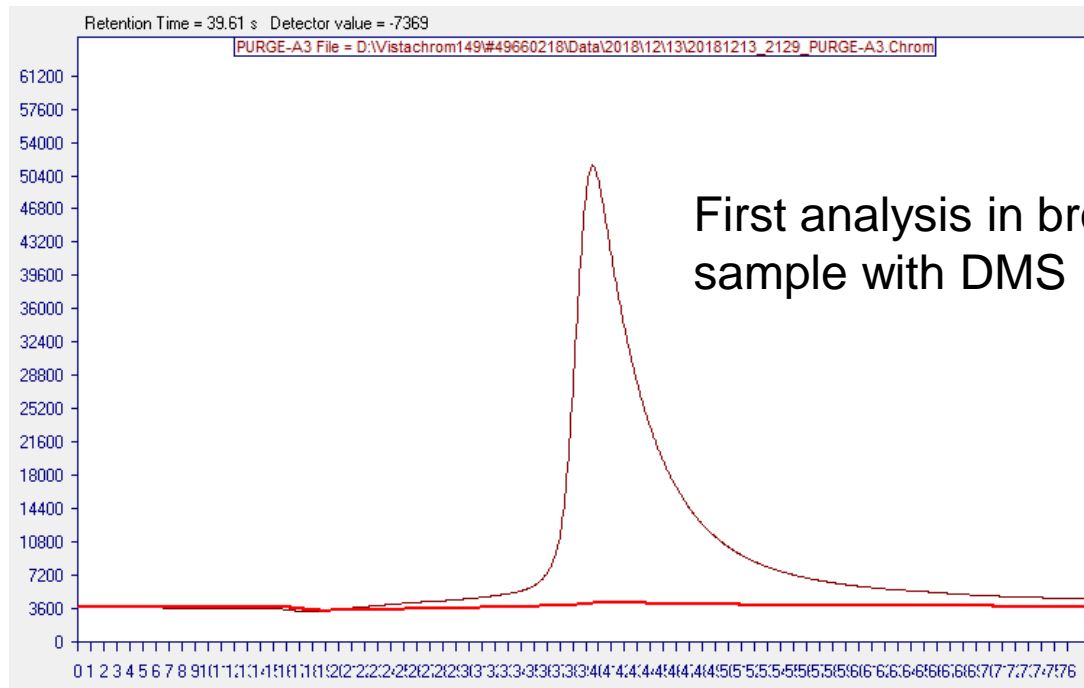
Test in Kerosene

C° (μl/L)	Mean	STDV	STDV (%)
0.25	71610	878	1.2

Measurement of DMS in Kerosene at 0.25μl/L



Carry over



Second analysis in red with same sample than first analysis

Requirement for presampling system

- Sampling must be handled with care for example but not exhaustive:
 - particle free ($<5\mu\text{m}$)
 - stable sample pressure required at 50 +/- 1 bar for example
 - MFC for liquid sample flow and pressure regulation highly recommended

Some reference customer

- Acrylonitrile and Benzene in acrylamine in production line: SNF France
- VOCs in ground water :
 - Guannan county in Lianyungang EPB Jiangsu China
 - Yancheng EMC Jiangsu China 2 units
 - Jiangyan district in Taizhou Jiangsu China
- BTEX in water from refinery recovery water :
 - France TOTAL Feyzin (under process)
- VOCs in drinking water:
 - South Korea research project
 - France sources ALMA (under process)



Conclusion

- All our competences and experiences on air quality monitoring (European Certifications, US EPA Test, Chinese National Certification...) allow us to develop water quality monitoring
- Specific and adequate sample conditioner systems are provided depending on customer and application needs
- Calibration is carried out with gas sample.
- Various & tunable detectors available :
 - FID (reference detector: linear and stable)
 - Other detectors: PID and ELCD (502.2 method),
 - Mass Detector (524 method).
- Totally standalone solution with full remote control



**THANK YOU FOR YOUR
ATTENTION!**

Questions?