Using Stir Bar Sorptive Extraction (SBSE) for Taste and Odour Measurements in Drinking Water

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Purpose of this presentation

- Brief introduction into Twister SBSE (focussed on Taste and Odour water contaminants)

Who are Anatune?

- **Where?** - Girton, Cambridge
- **Focus?** - Customer specific chromatography solutions
- **Technology?** - Novel automation, sample prep, introduction
- **Provide?** - complete sample preparation, automation & analytical packages

Partners, platforms and markets

- Agilent Technologies Value Added Reseller (VAR) since Oct 1999
- GERSTEL UK & Ireland Distributor since Apr 2003

Agilent Technologies
Premier Solution Partner

GERSTEL

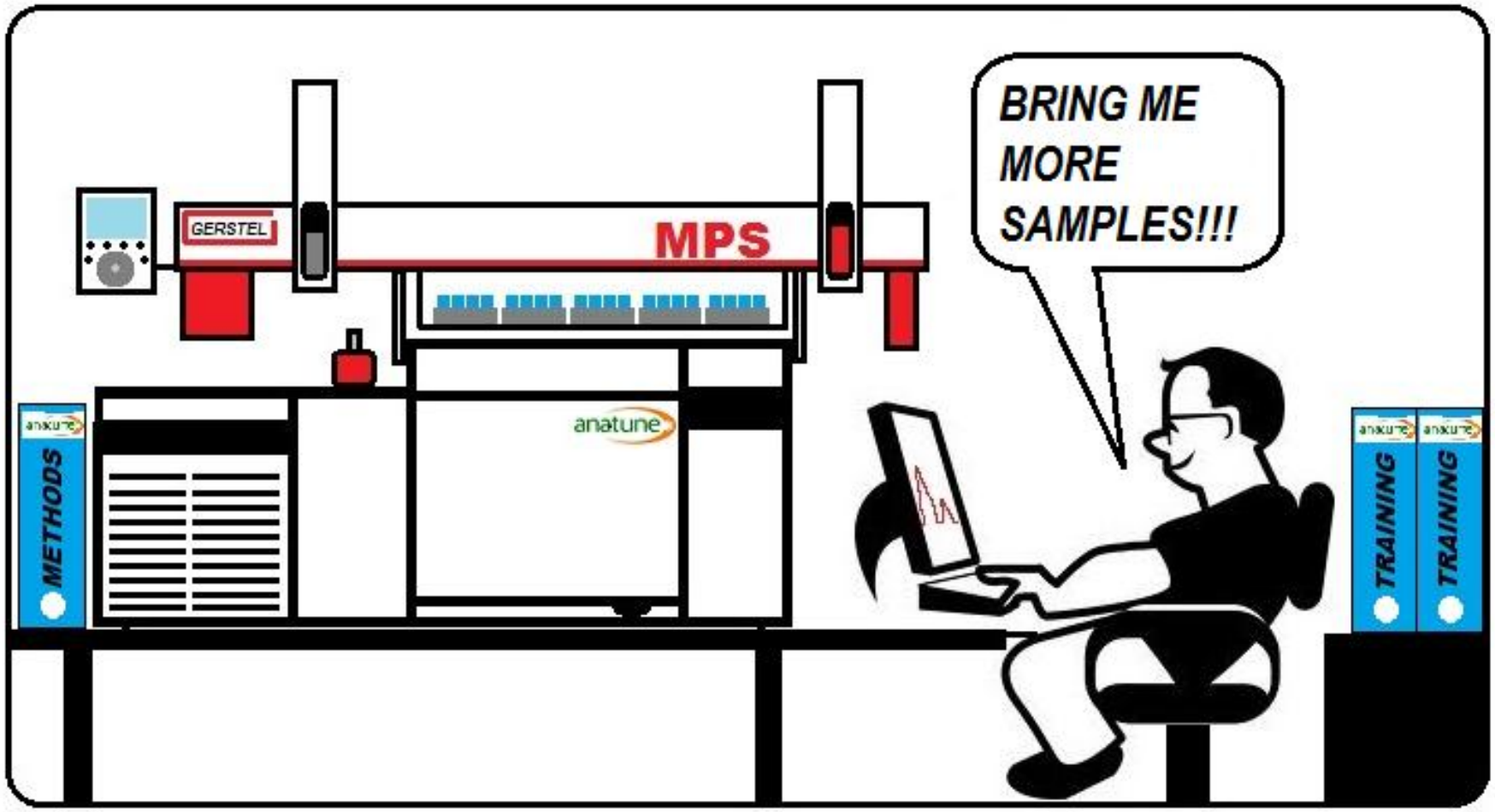
- GC and LC platforms - MSD, QqQ, qTOF
- Environmental, Flavour/Fragrance, Food/Beverage Markets

What do our customers need?

- Customers need more than just a standard system

How we help our customers

How we help our customers



GERSTEL Multi-Purpose Sampler

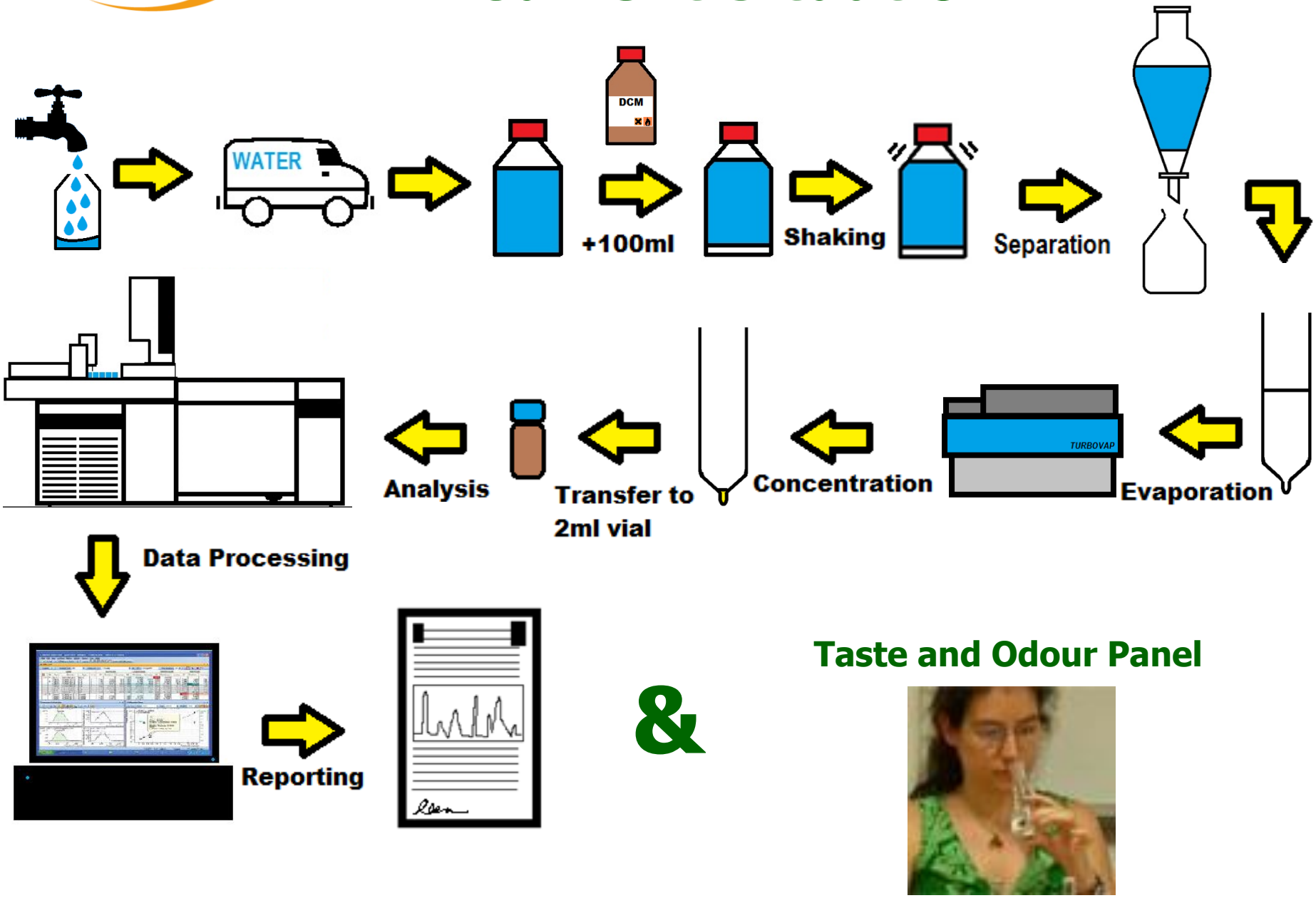
Turnkey solution example

- Anatune VOC Headspace solution
- 160/240 sample capacity
- Auto addition of internal standards & surrogates
- Minimal manual work, low cost per sample
- parallel processing of samples (PrepAhead)

Stir Bar Sorptive Extraction

- Current situation – Analysis of T&O Compounds
- Problems and Implications
- Introduction to Twister SBSE
- Twister Method
- Advantages of using Twister
- Results
- Developments and alternative ways of thinking?

Current Situation



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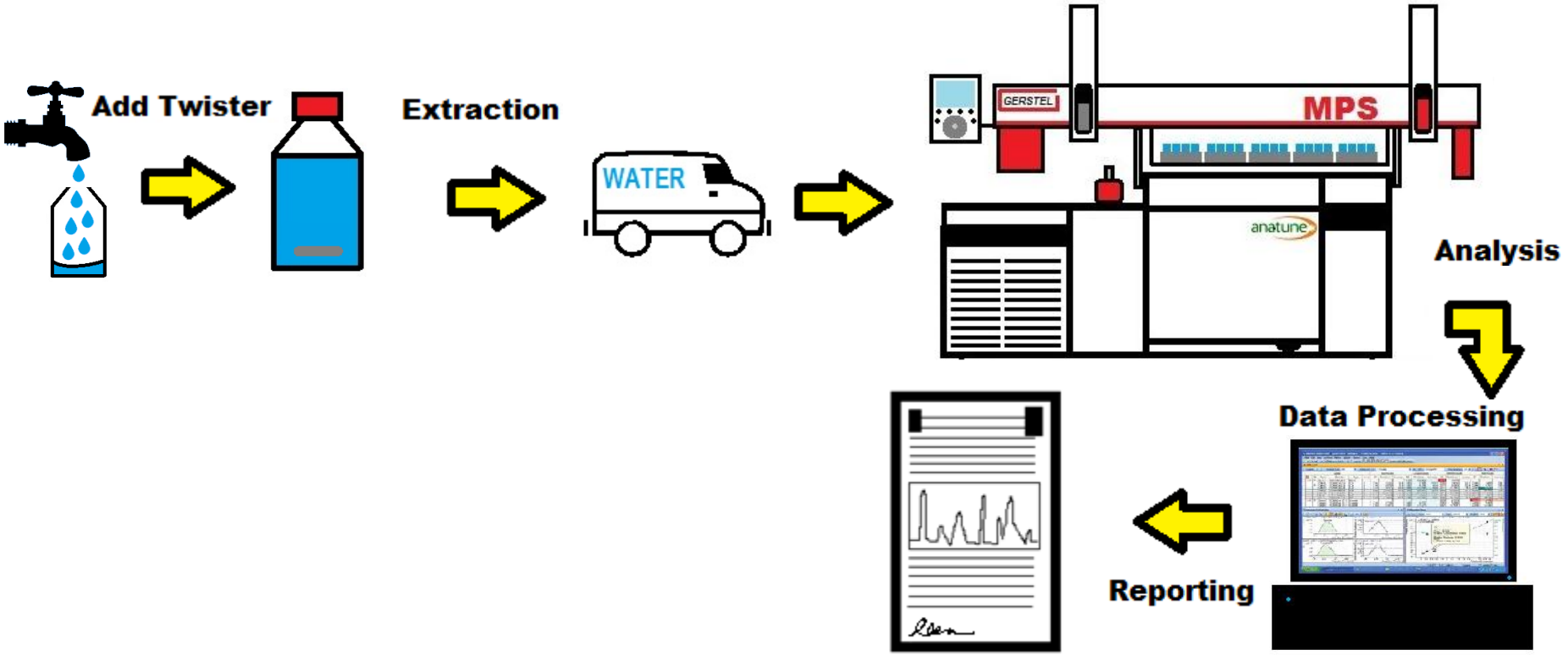
Taste and Odour Panel

Possible situation?



Taste and Odour Panel

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Problems/Implications

Problem	Implication
Slow extraction time	Takes longer to get results
Many long manual extraction steps	Large staff resource
Error prone sample prep	Result reproducibility issue?
Can't hit LOD's without pre-concentration	Time/staff needed for prep
High solvent usage/staff exposure	Cost for purchasing solvent, disposal & staff safety
Glassware contamination	Inaccurate results/repeat analysis, investigations etc.

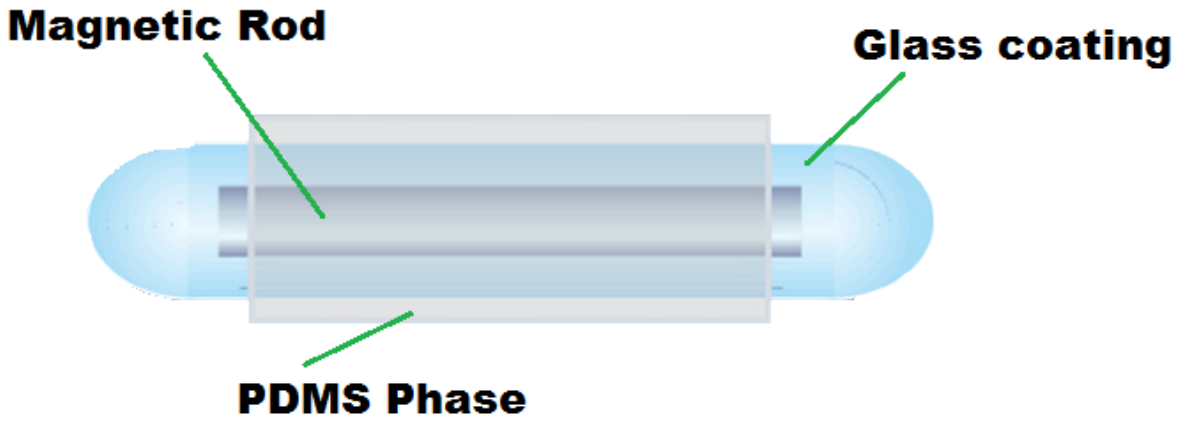
What else?

- Liquid-liquid extraction most used technique
- Solid Phase Extraction (SPE) as an alternative?
- Miniaturisation techniques (SPME) developed
  - Simple
  - Fast
  - Environmentally Friendly
  - More sensitivity?
- Stir Bar Sorptive Extraction……?

Stir Bar Sorptive Extraction

- Marketed by GERSTEL as 'Twister'
- 1.5cm long magnetic stir bar sealed in glass
- High capacity PDMS phase on glass
- Adsorbs compounds from water onto PDMS phase whilst stirring in sample
- Different sizes and phase thicknesses

- thickness 0.5 mm, 10 mm length
- thickness 0.5 mm, 20 mm length
- thickness 1.0 mm, 10 mm length
- thickness 1.0 mm, 20 mm length



Recovery of Analytes onto Twister

- Same principle as liquid/liquid extraction

- with a small amount of immobilized "solvent" in the form of polydimethyl siloxane (PDMS)

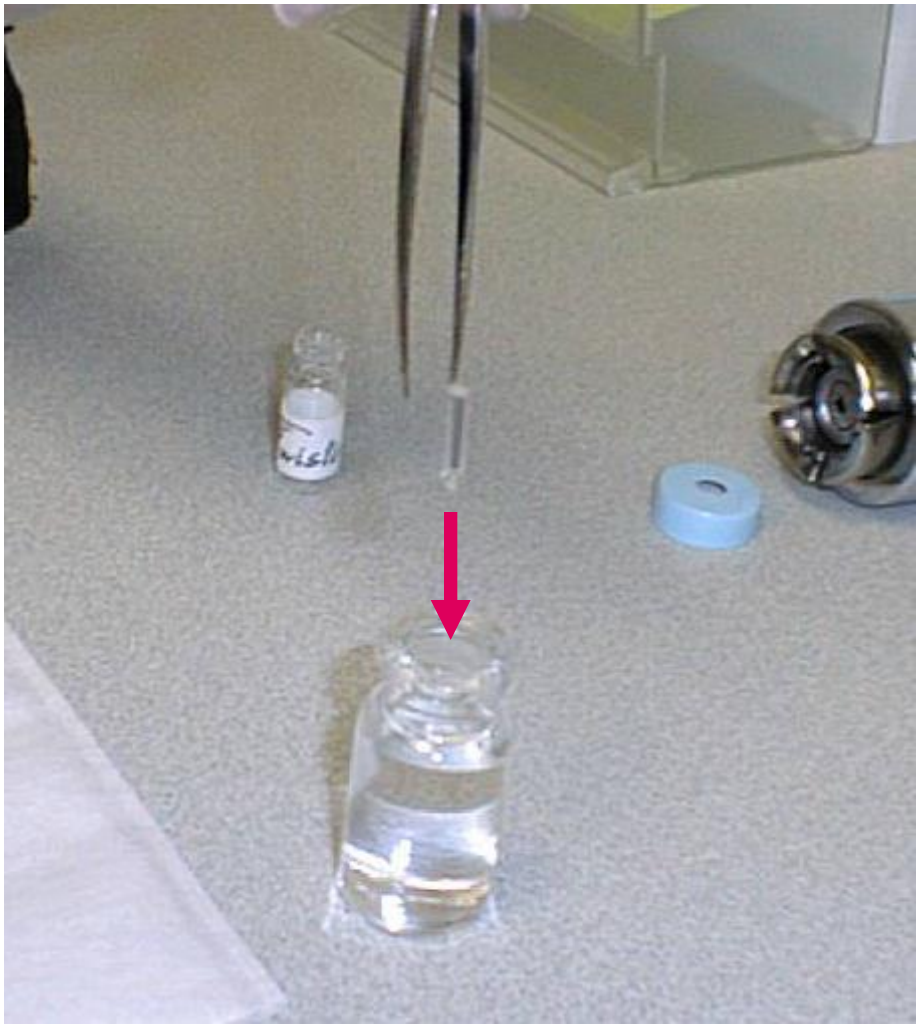
- Recovery of analytes onto stir bar

- How well the analyte can adsorb onto PDMS phase?
- Depend on hydrophobic and lipophilic characteristics of analyte
- Use calculated and theoretical octanol/water ratios (Log K o/w)
- PDMS behaves similarly to octanol

Conditioning of Twisters

- Conditioned before/after analysis
  - Thermally cycle PDMS up to 280 deg C
  - Flow of clean N2 at 80-100ml/min
  - 40 bars per conditioning cycle
  - Twisters are reusable – >50x

Easy to use - method

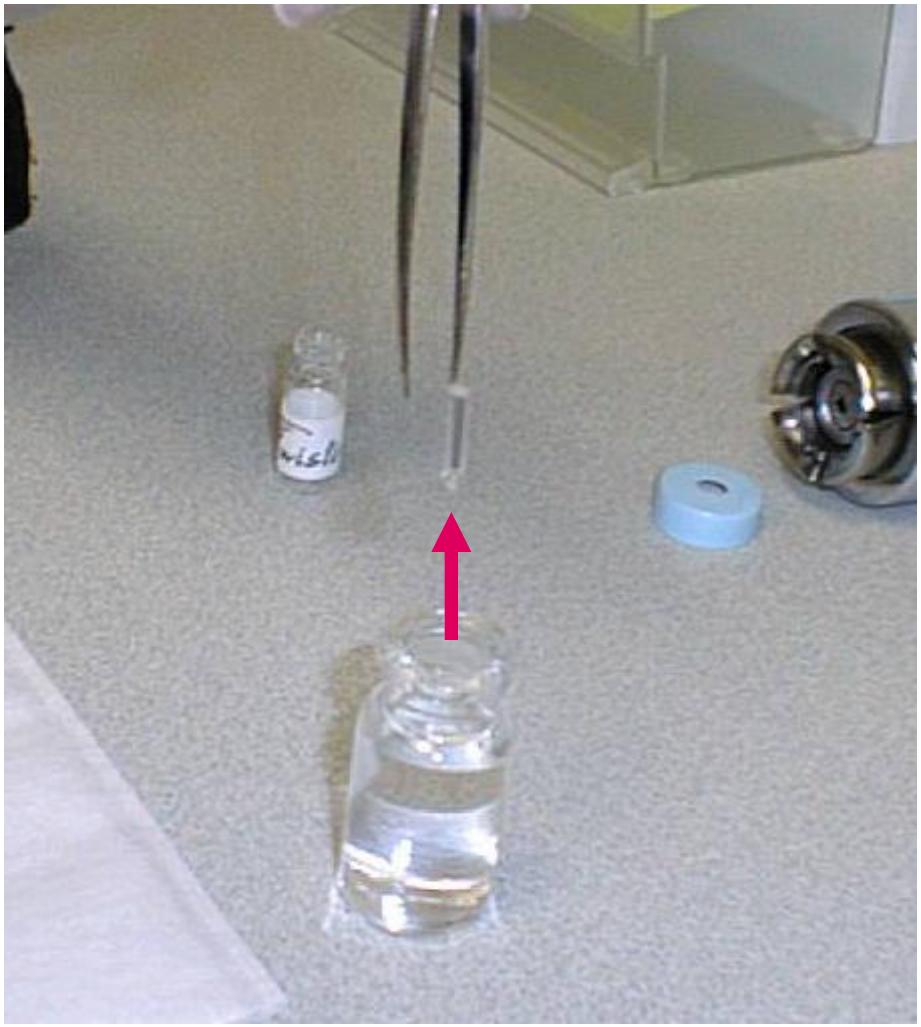


- Add Twister to sample

Easy to use - method

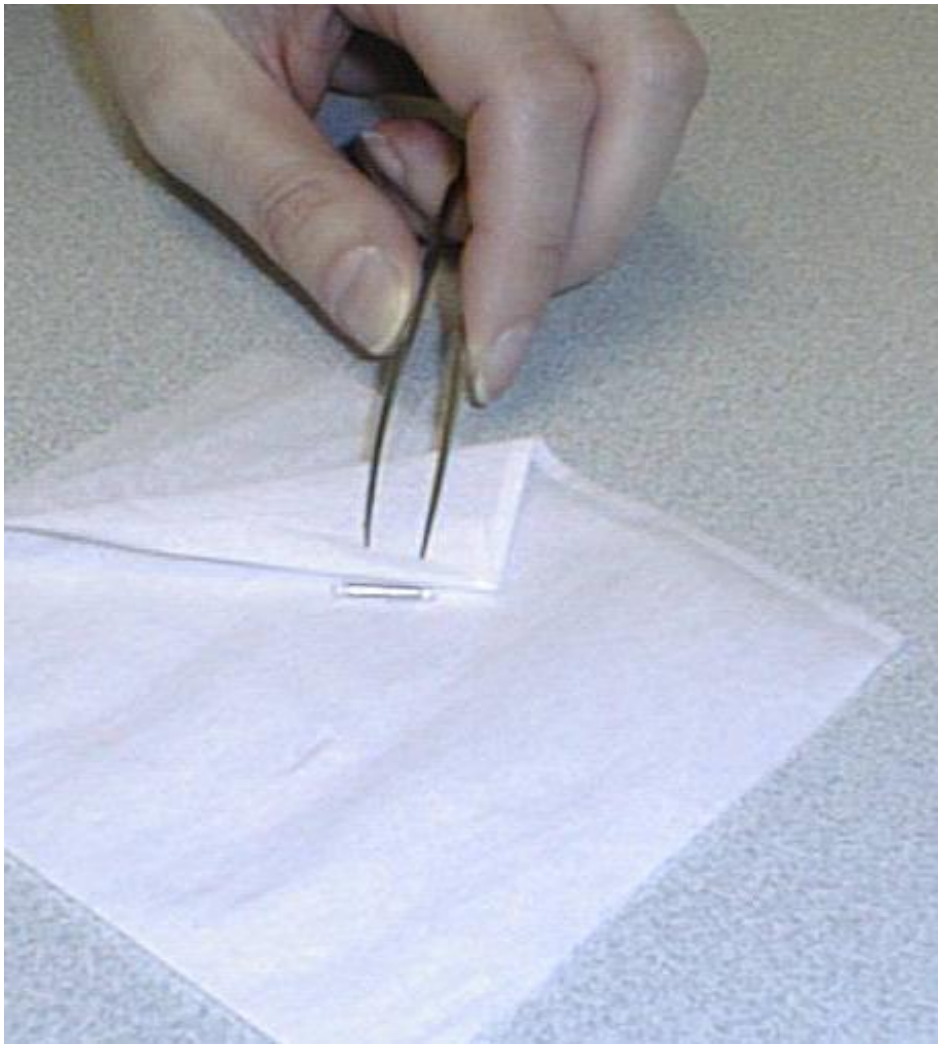
- Add Twister to sample
- Stir for 1 hour

Easy to use - method



- Add Twister to sample
- Stir for 1 hour
- Remove Twister and rinse with DI water

Easy to use - method



- Add Twister to sample
- Stir for 1 hour
- Remove Twister and rinse with DI water
- Dry with lint-free tissue

Easy to use - method

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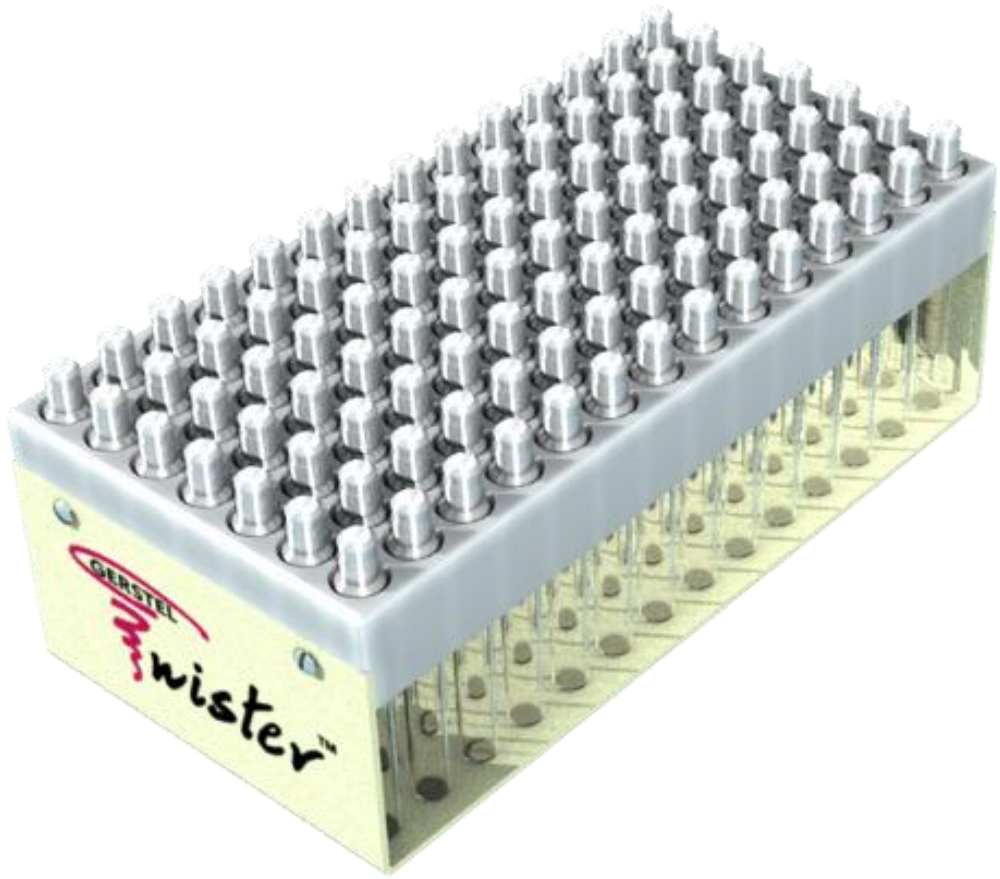
- Insert into TDU Tube

Easy to use - method



- Add Twister to sample
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- Remove Twister and rinse with DI water
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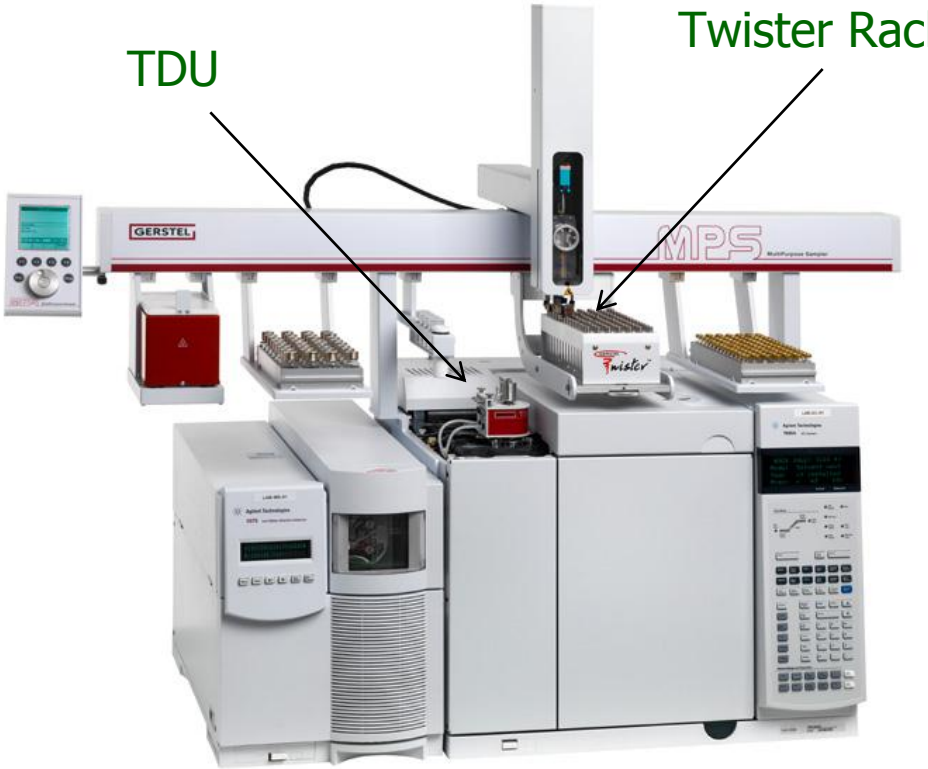
- Insert into TDU Tube
- Place tube in Twister rack

Easy to use - method



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- Place tube in Twister rack
- Place rack on MPS Autosampler

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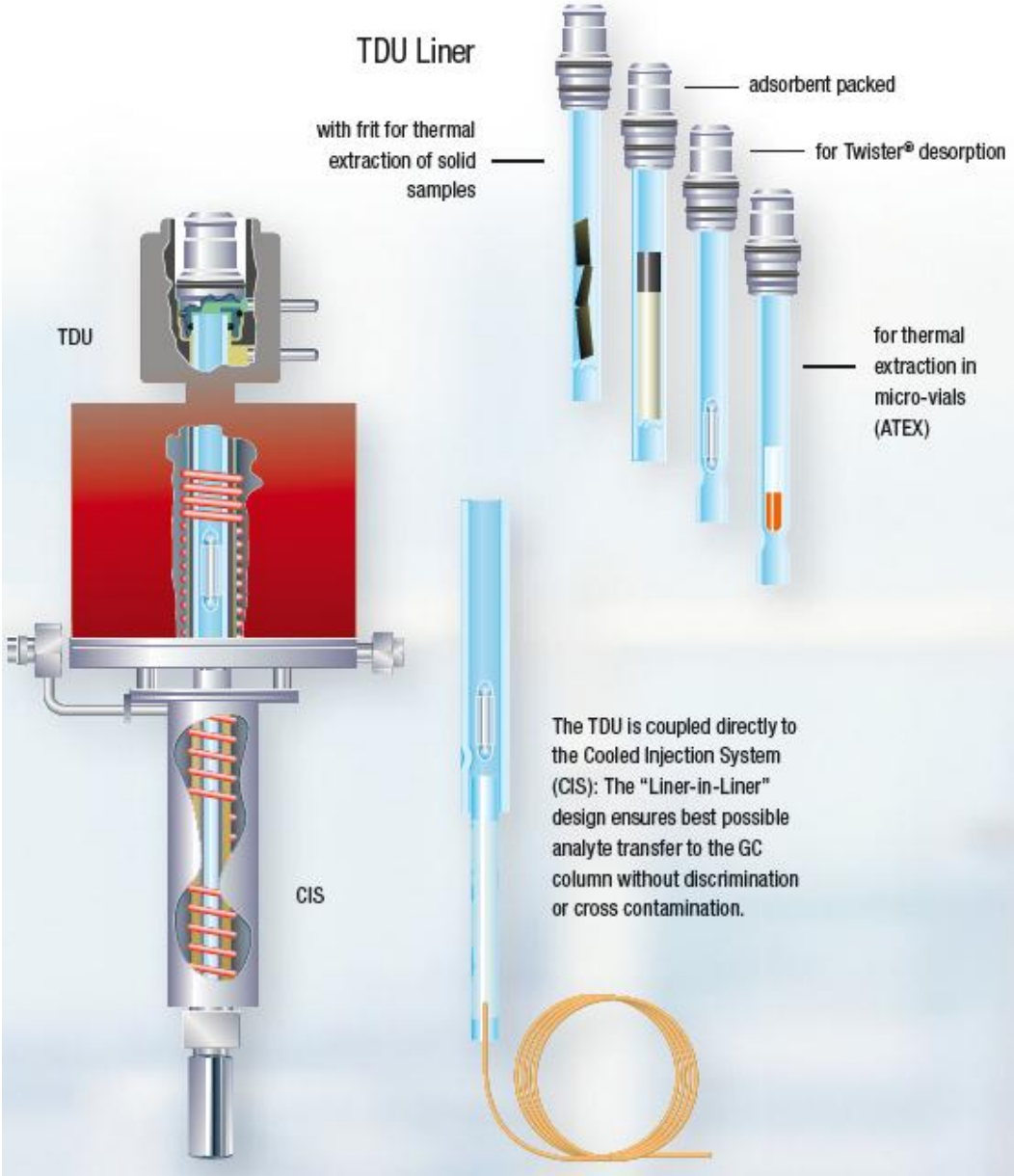
- Stir for 1 hour
- Remove Twister and rinse with DI water
- Dry with lint-free tissue
- Insert into TDU Tube
- Place tube in Twister rack
- Place rack on MPS Autosampler
- Automated Thermal Desorption and analysis

GERSTEL CIS/TDU Setup

- CIS – Cooled Injection System
- PTV Inlet or
- Cryotrap (-150C)
- TDU – Thermal Desorption System
- Automated TD of

1. Stir Bars
2. Adsorbent tubes
3. Solid samples
4. High matrix liquid samples



Benefits of using Twister

- High productivity
  - parallel extraction – multiple using stir plate
  - automated analysis using MPS Auto sampler
- Time and cost savings through minimal sample preparation
- Very sensitive – ng/l in SIM mode
- Good reproducibility – 4-15%
- Reliable results - simple sample handling, reduced risk of error
- Green technology - Low solvent usage/disposal
- Safer
- Multiple reuse of each twister after easy reconditioning

- 1 Twister = £35.00. 50 extractions = £0.70 each

- Can be applied to other analysis – pesticides, PAH's etc

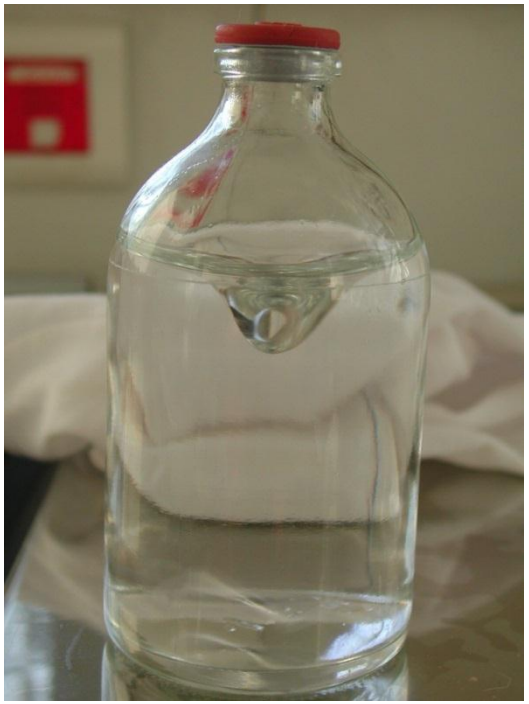
Extraction location?

- Can be carried out at customer tap/WTW instead of lab
- 'Captures' problem compounds immediately
- No time for compounds to degrade (sample point to lab extraction)
- Twisters stable for 7 days before analysis (4°C)
- Veolia Water – Twister analysis in Paris, extraction worldwide

Example

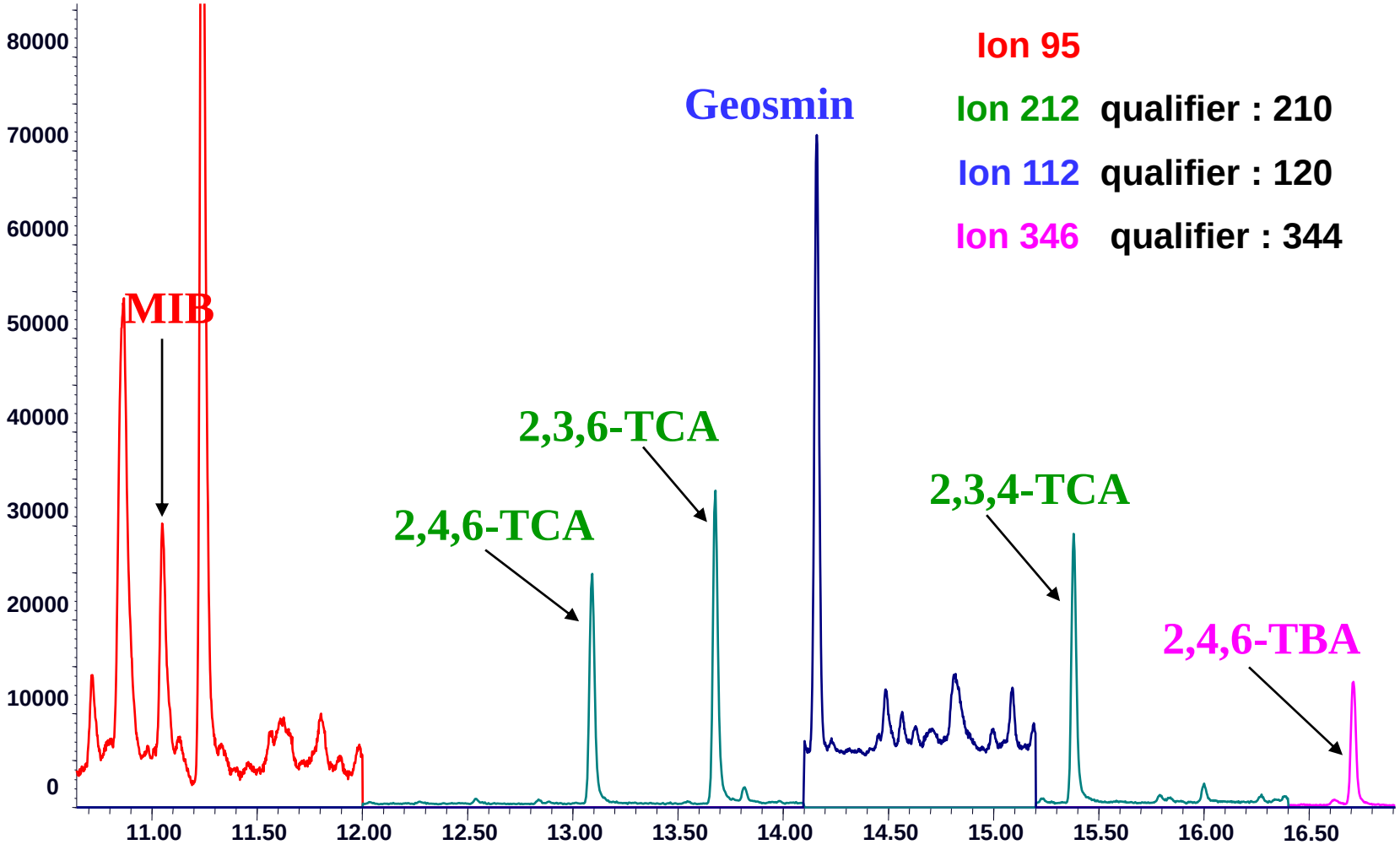
Name	Abbreviation	Taste	Odor threshold, ng/L	CAS number
2-methylisoborneol	MIB	Earthy	5–10	N/A
2,4,6-trichloroanisole	2,4,6-TCA	Musty	0.1–2	6130-75-2
2,3,6-trichloroanisole	2,3,6-TCA	Musty	0.1–2	50375-10-5
Geosmin	Geosmin	Camphor	1–10	19700-21-1
2,3,4-trichloroanisole	2,3,4-TCA	Musty	0.2–2	54135-80-7
2,4,6-tribromoanisole	2,4,6-TBA	Musty	0.15–10	607-99-8

- 100ml Water
- 40ul Internal Standard
- 2hr extraction
- Thermal Desorption
- GC-MS Analysis



Tap water spiked with 2ng/l

- GC-MS Analysis – Agilent 5973/6890

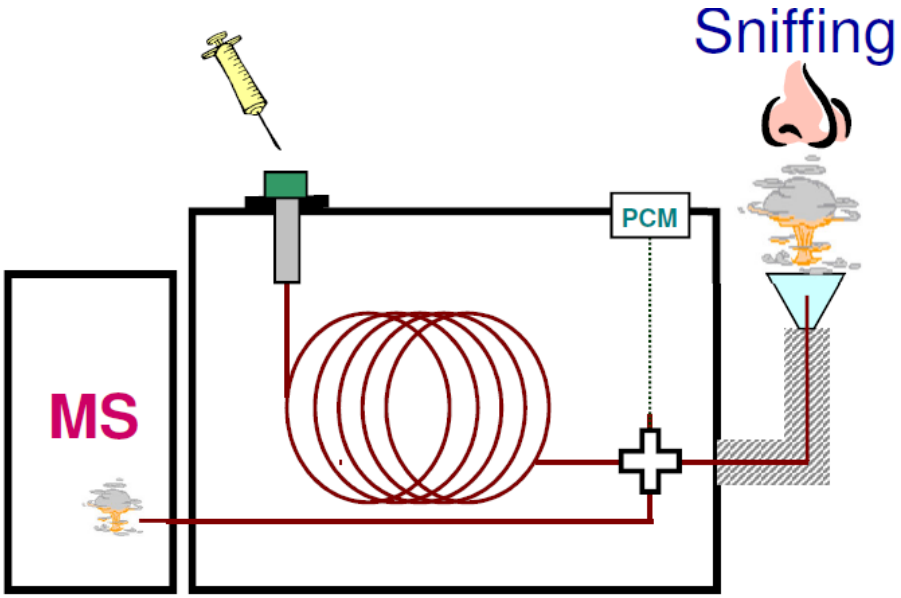


Results

	R	LOQ, ng/L	Repeatability %	Trueness %	Reproducibility %
MIB	0.9987	1	4–10	89–110	13
2,4,6-TCA	0.9998	0.1	1–5	97–110	4
2,3,6-TCA	0.9998	0.1	4–11	97–117	5
Geosmin	0.9991	0.5	2–10	83–101	9
2,3,4-TCA	0.9998	0.2	7–15	87–110	13
2,4,6-TBA	1.0000	0.2	2–9	91–104	15

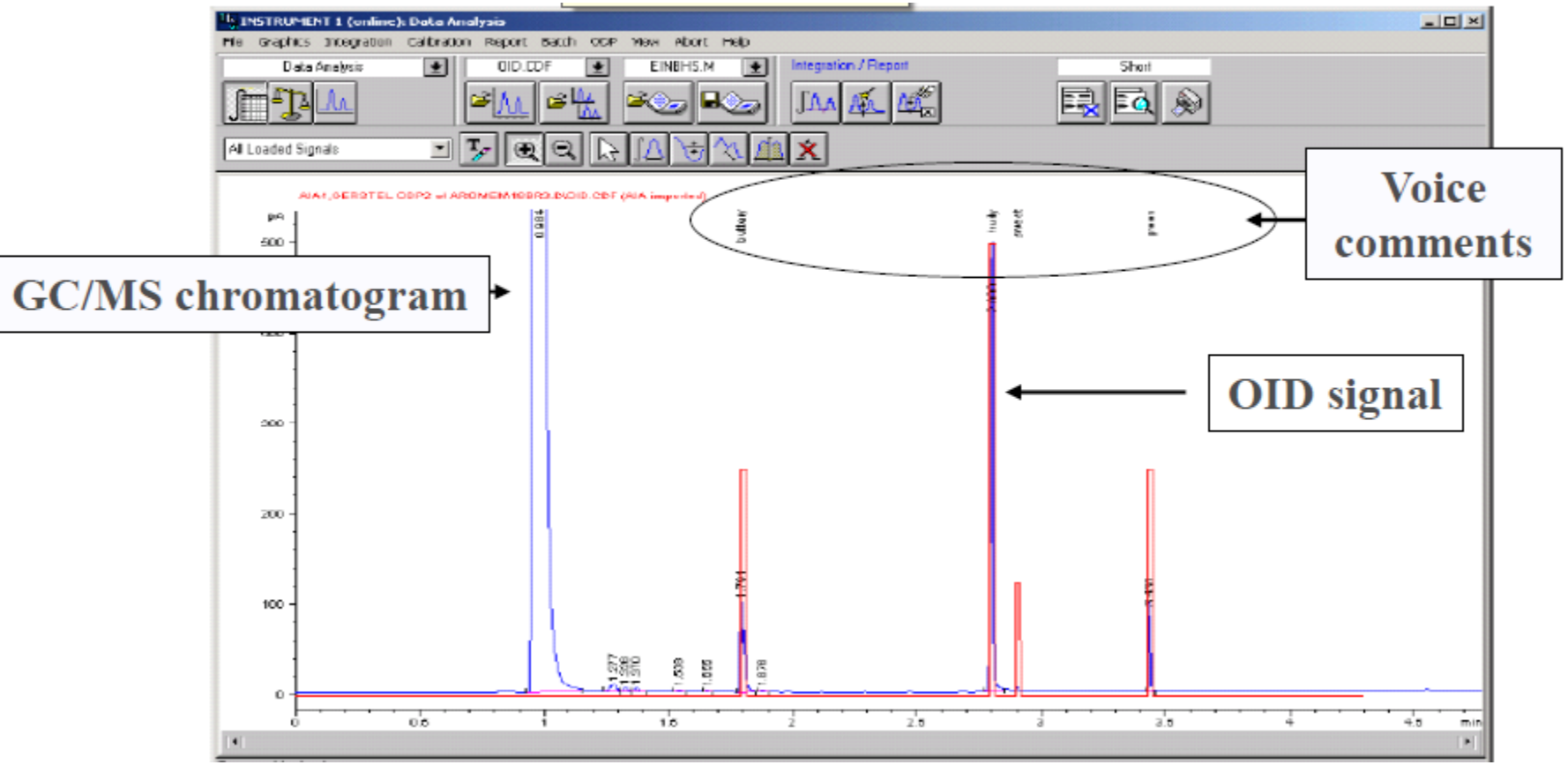
GC-SBSE-Olfactometry-MS

- Optional Olfactory Detection with voice recognition
- Olfactory detection in parallel with GC/MS analysis
- Voice descriptors added directly to Chromatogram
- Olfactogram (Intensity input) added to chromatogram
- Widely used for off odours, flavour and fragrance

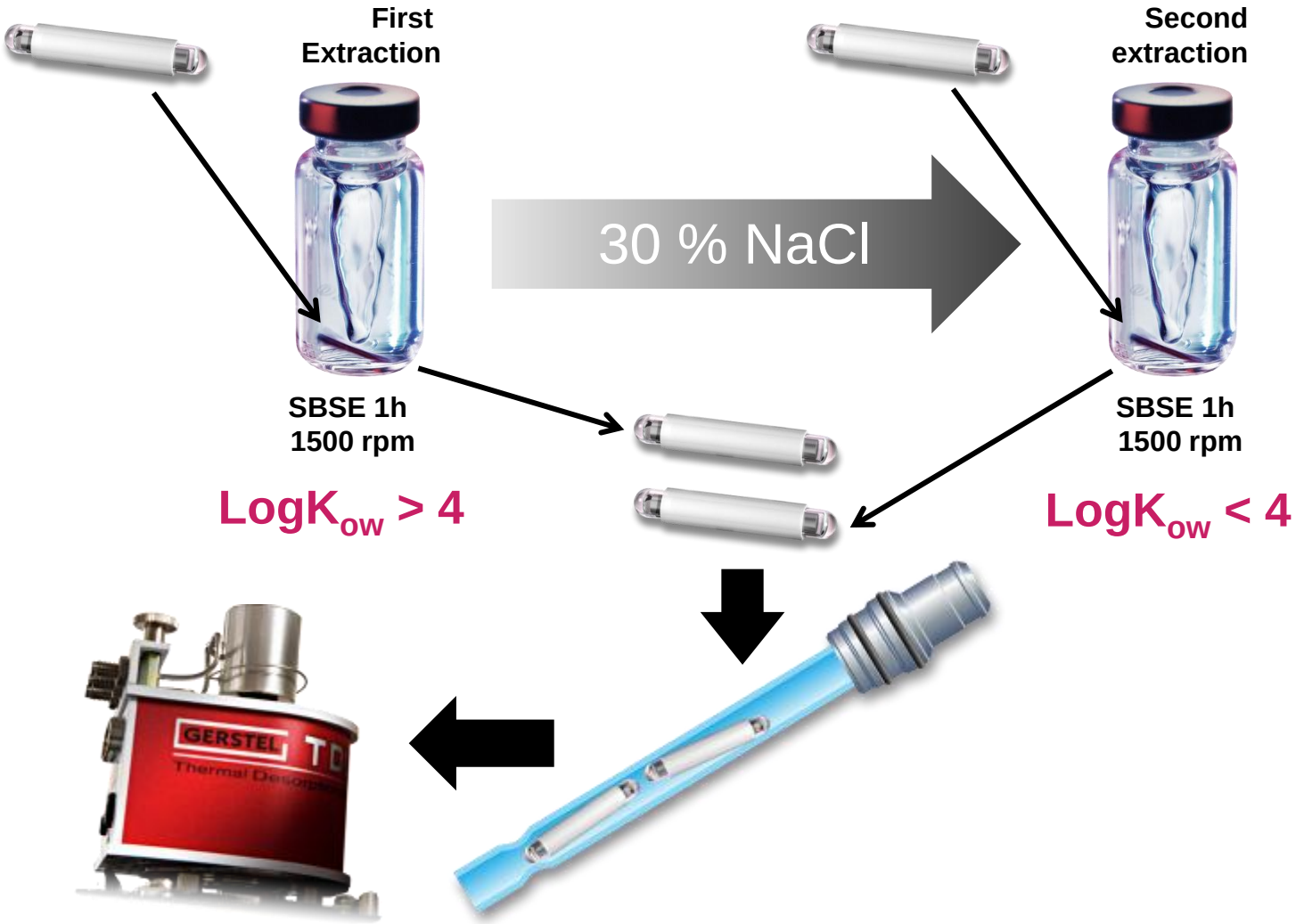


Using the ODP with SBSE

- Closes loop between complaint, analysis and T+O Panel
- Help to determine the complaint compound

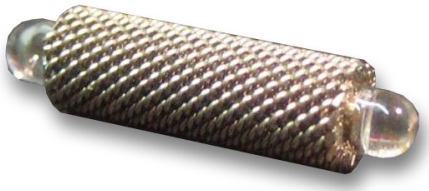


Dual SBSE

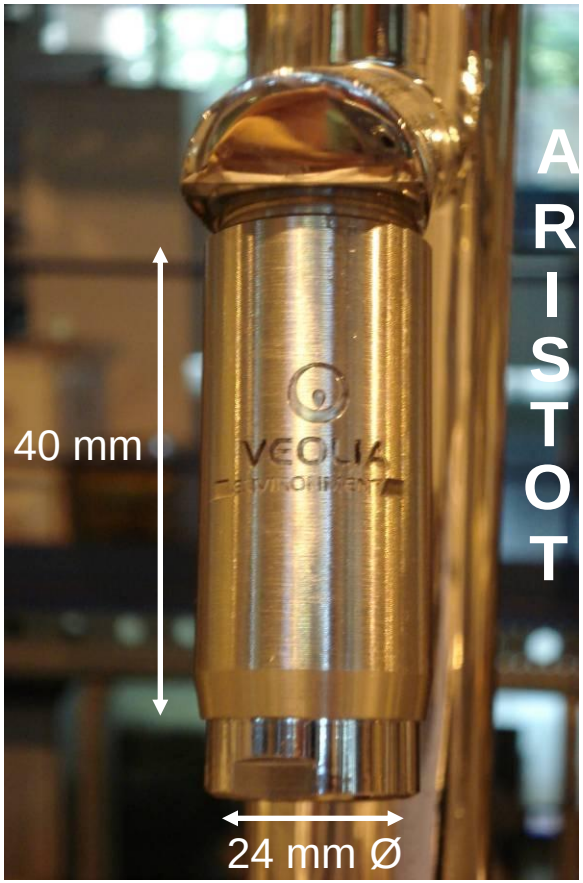

First
Extraction
Second
extraction
30 % NaCl
SBSE 1h
1500 rpm
SBSE 1h
1500 rpm
LogK$_{ow}$ > 4
LogK$_{ow}$ < 4
GERSTEL
TD
Thermal Desorption

Ethylene Glycol Twister

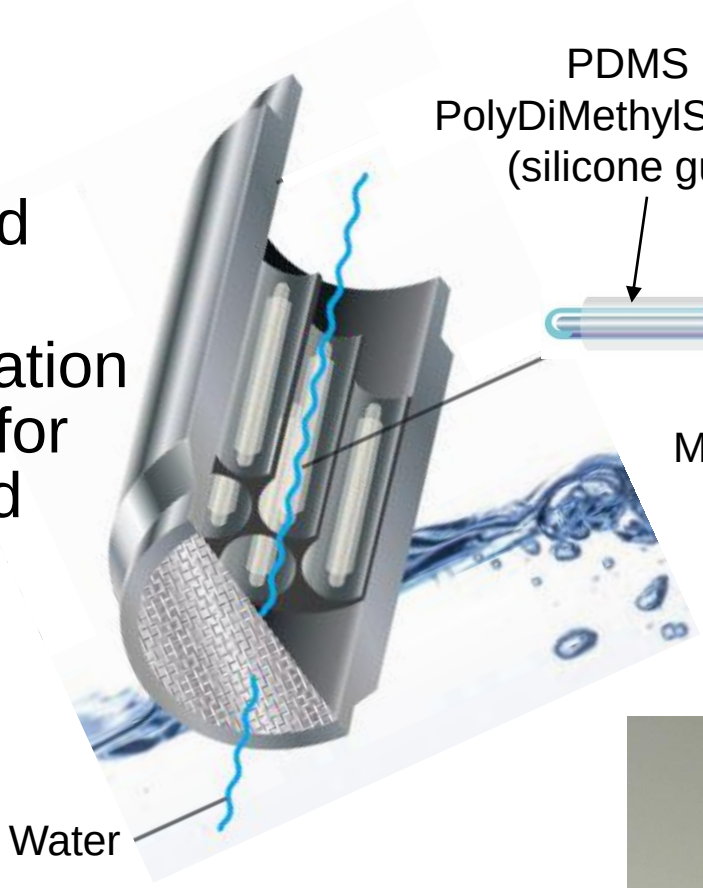
- Sorbent phase is a mixture of silicone and ethylene glycol
  - Efficient concentration of non-polar analytes similar to the PDMS Twister
  - Concentration of polar analytes that form hydrogen bonds acting as proton donors, for example phenols
  - Low limits of detection and good recovery due to large phase volume



Further Developments – Veolia France – David Benanou



Advanced
Relevant
Investigation
Sampler for
Taste and
Odor at
Tap



- Easy & quick installation (tap nozzle dismounting)
- Continuous bars enrichment at each tap opening

System flexibility – using same hardware as Twister - MultiFlex

Single System - multiple uses, easily reconfigurable

1. Remove TDU - Use CIS for Large Volume/Liquid Injection

2. Headspace Analysis with autospiking

3. Automated Thermal Extraction

4. Internal Std, Surrogate, Cal Prep, Dilution

5. Add more GERSTEL Hardware to MPS Rail

Anatune MPS Multi-Flex

The Ultimate R&D Tool

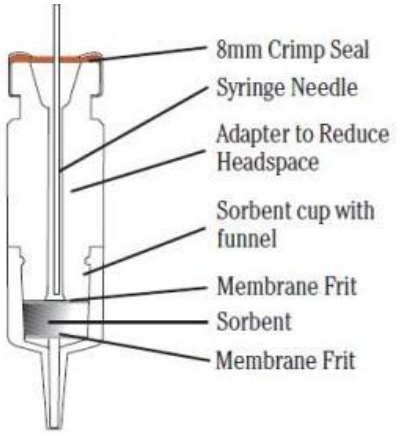
Agilent SQ, QQQ and
QTOF Platforms

Anatune developments with Multi-Flex

Automated extraction and analysis

- Dual Head MPS
- ITSP Micro SPE

1. NDMA & Metaldehyde
2. T+O Compounds & Phenol



GC-QTOF Multi-Flex Developments

- Highly sensitive and selective Mass Spectrometer
- Accurate mass on a familiar platform
- Known unknown analysis
- Sold 1st system to University of York in September
- GC-QTOF Workshops next week
- Applications work/demos planned

Conclusion - Payoff

- Cheaper – Labour/Consumables
- Fast, easy, reliable
- Less solvent consumption/exposure
- Low LOD's reached
- Capture of analytes close to source
- Olfactory detection enhances results/investigation
- Analysis of non-T&O compounds
- GERSTEL MPS flexible
- Anatune happy to collaborate with customers – any ideas?
- Think outside the box

Any questions

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Thank you for your attention