“Taste and Odor Compounds in Potable Water by GC/MS/MS”

Nick Davies

Dŵr Cymru
Welsh Water

18th March 2014

University of Arizona

Dwr Cymru Welsh Water

- Welsh Water is a ‘not-for-profit company’
- **Serving 1.4 million** homes and businesses
- **3 million** customers
- **900 million litres** of water supplied every day
- **6th** Largest regulated water & sewerage company
- **4th** largest company in Wales
- **2,000+** employees work for Welsh Water
- **$400million** investment programme 2010-15 for drinking water quality

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Glaslyn (‘Blue Lake’)

- Located in Newport (S.E Wales)
- Project Commenced Feb 2012
- State of the Art Laboratory
- ~ £11 Million Investment
- Previously used as a call centre for a bank
- Environmentally Conscious

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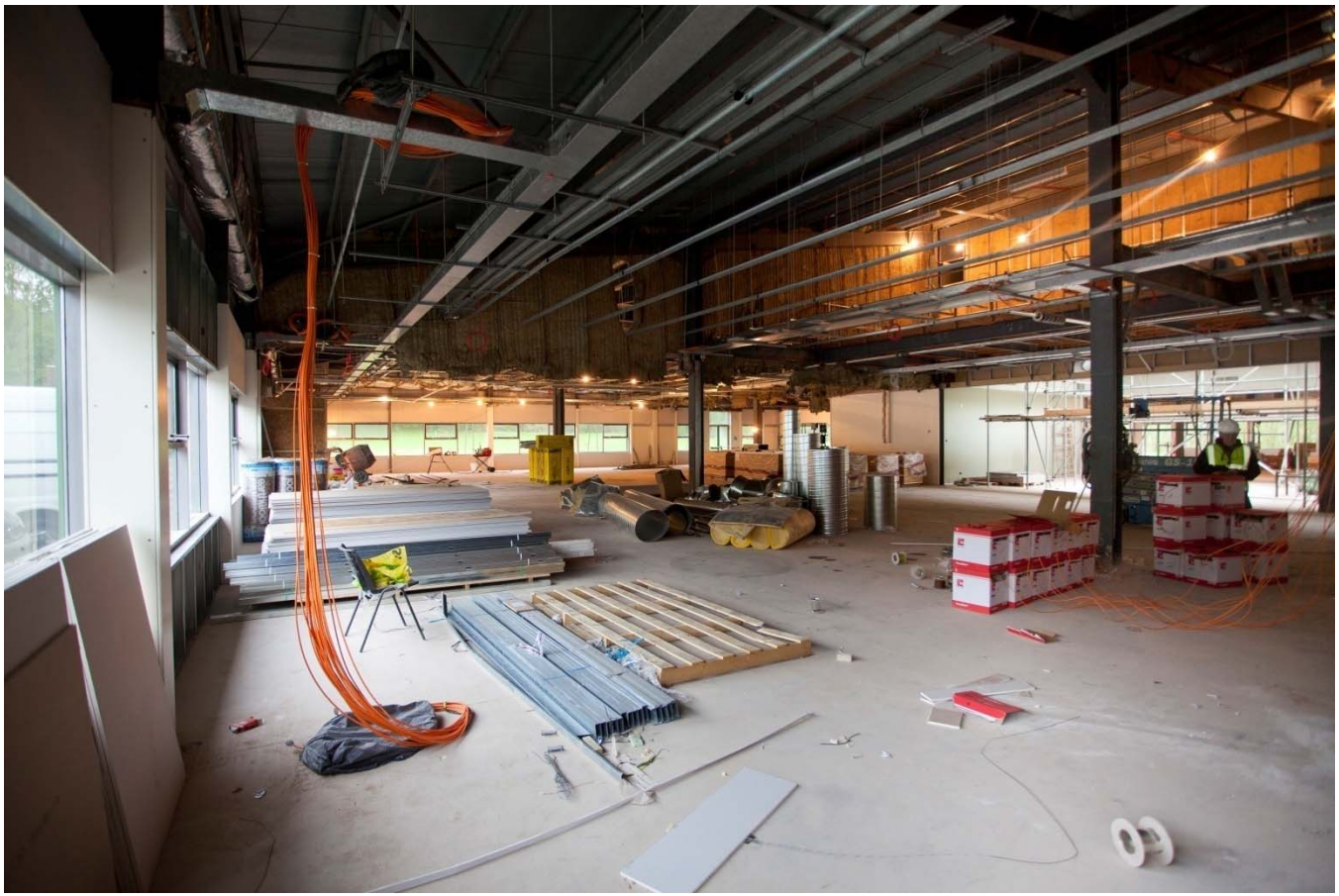
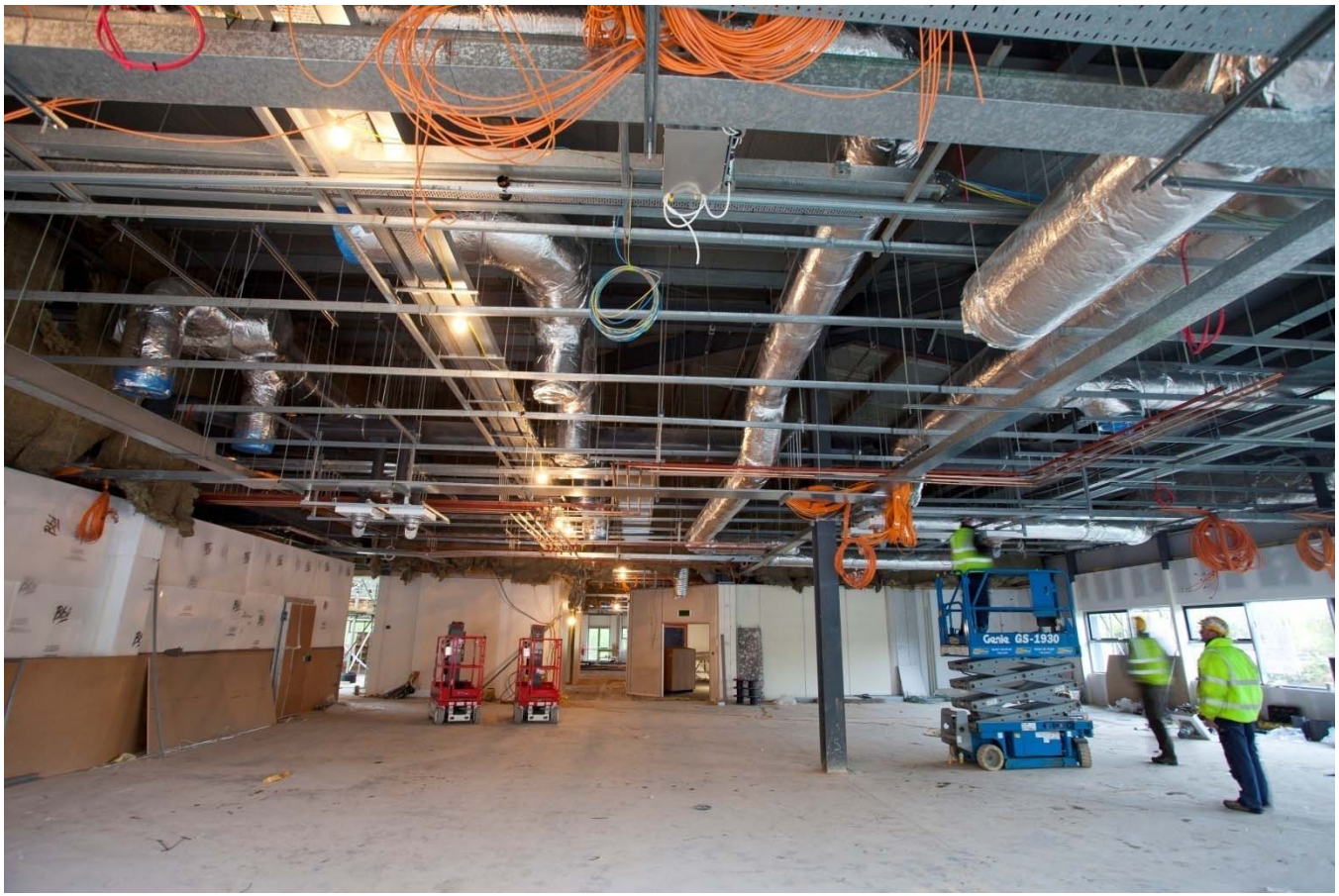


Dwr Cymru Welsh Water



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Taste and Odour and Its Potential Impacts

- **Regulatory Requirement –** Water must be fit for human consumption

  (1991 Water Industry Act &2003 Water Act)

- **Customer Confidence –** Tastes Good, Smells Good = Good?

- **Financial Implications –** Cost of Remedial Action, **Fines!!!**

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Case Study 2013 – MIB in Pontsticill Reservoir

- Serves population of ~ 300,000 (North of Cardiff)
- Nearly 300 complaints between August & October 2013
- Adverse Publicity – TV/Media Coverage
- Regulatory Notice Served – potential for prosecution with repeat event
- Impact on Customer Confidence

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pressdata

'Odd-tasting' water is fine, says supplier

Kathryn Williams
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WELSH Water has moved to reassure residents that its drinking water is safe to drink.

It follows complaints from homeowners about the taste of water from their taps in recent weeks, with reports of an odd "musty" aftertaste.

The water supplier has confirmed that the aftertaste is caused by a naturally developing algae at the source reservoirs, but stated that the substance was not harmful to those who drank the water.

Pam Morgan, who lives in Creigiau, Cardiff, told the Echo she noticed that her tap water tasted odd a couple of weeks ago.

"I phoned Welsh Water and the lady on the phone said a few people from the village had called up," said Ms Morgan, who lives at Maes Cadwgan.

"They said there was a bit of an algae problem and if I wanted someone to come out and test the water, I could."

A sampler from Welsh Water visited the property and tested the water, which is sourced from the Pontsticill and Llwyn-on reservoirs near Merthyr Tydfil.

Ms Morgan added: "The chap said that I could try boiling and then cooling the water in the fridge. And it's alright to make a cup of tea with, but cooling it in the fridge was no good for me, I still had an aftertaste. So I'm drinking bottled water now. I'm hoping it will change before long."

Ms Morgan's partner, Delme Bowen, said that they were satisfied that the substance was not harmful following their contact with Welsh Water.

A Welsh Water spokesman confirmed that some of the 300,000 households served by the two reservoirs would be experiencing an earthy taste in their water, but assured customers that it would be temporary.

The company has received 120 complaints about the taste of the water and are continuing to monitor the supply.

"The naturally occurring algae developed due to an increase in hot weather over the summer and is known as is known as methyl isoborneol (MIB).

It is detectable at low levels and is often picked up by those with a sensitive palate.

The spokesman added: "This is a temporary problem and has been caused by a naturally occurring substance that has been detected in Pontsticill and Llwyn-on reservoirs. This is not harmful to health and the water is being given additional treatment to help resolve this issue.

"We apologise for any inconvenience. If anyone has any queries regarding their water supply, they should visit www.dwrcymru.com or contact us on 0800 052 0130."

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Case Study 2013 – MIB in Pontsticill Reservoir

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Case Study 2013 - MIB in Pontsticill Reservoir

Findings:

- Caused by presence of Actinomycetes – No Anabaena detected
- Water Level Fluctuations a contributory factor
- Issue resolved by blending of water, adjustment of flows and PAC treatment

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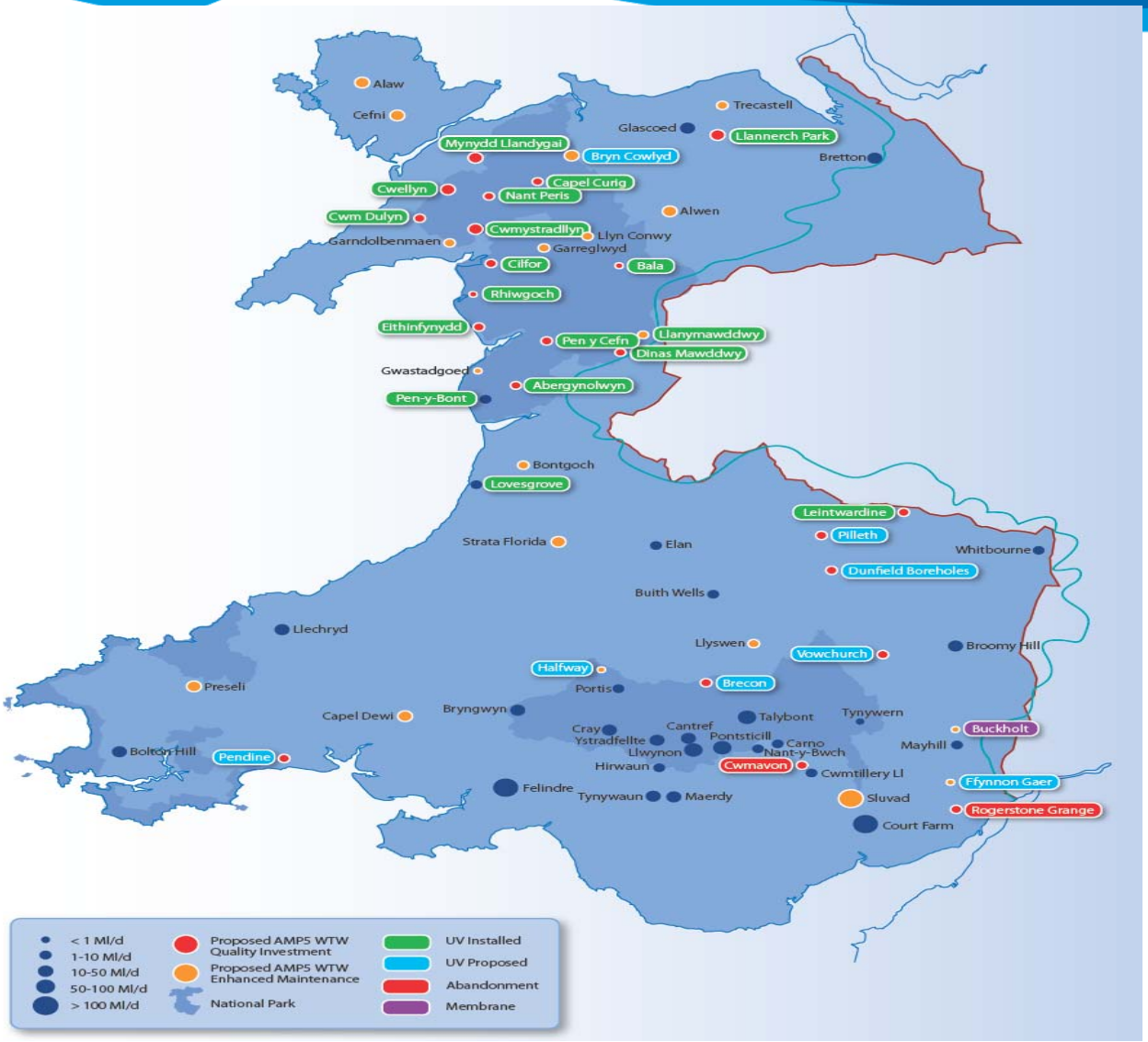
How a Screening Method for Taste & Odour Helps

- Allows for appropriate operational decisions to be made to reduce the risk
- Allows monitoring of effectiveness of remedial actions
- Allow the company to comply with stringent (UK) water quality standards
- Provide a better service to customers

Location of WTW Improvements



Taste and Odour Method

- Screening Method for compounds with objectionable Taste and Odour properties
- 20 Compounds within suite of analysis
- Calibration range 0 - 50ng/l (ppt)
- Limit of detection 1ng/l
- 1 litre of sample extracted with Dichloromethane (100mls)
- Dichloromethane concentrated to final volume of 0.5mls
- Originally analysed on 7890/5975C GC/MS (triple axis detector)

Compounds in Method

- Geosmin & 2-Methyl Isoborneol (MIB)
- Phenols – Chlorinated and Brominated
- Chlorinated and Brominated Anisoles
- Pyrazines (2-Isopropyl-3-methoxy)
  (2-Isobutyl-3-methoxy)
- 2-EMD and 2-EDD

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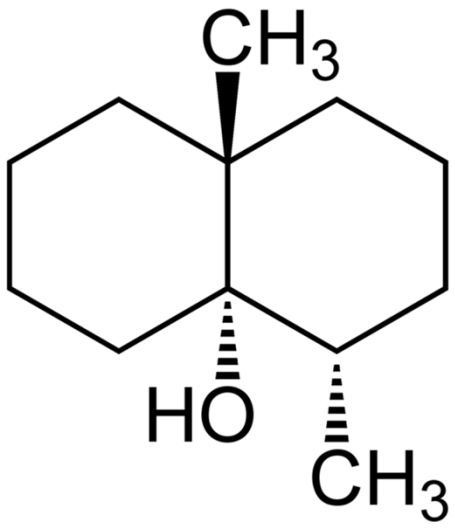
Geosmin

(4*S*,4a*S*,8a*R*)-4,8a-Dimethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-4a-ol

Its name is derived from the Greek γεω- "earth" and ὀσμή "smell".



Produced by several classes of microbes inc.

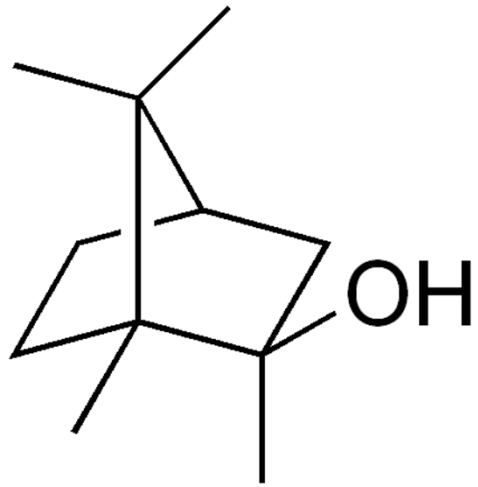
Cyanobacteria and Actinobacteria.

Released into water when microbes die

Responsible for earthy taste of Beetroot

2-Methyl Isoborneol (MIB)

1,6,7,7-Tetramethylbicyclo[2.2.1]heptan-6-ol



Produced by Blue-Green Algae (Cyanobacteria) such as Anabaena and also Actinomycetes.

MIB released on death of cells.

Very Low Taste & Odour Threshold (Low Parts per Trillion – ng/l)

Phenols: (Sources)

Phenol – precursor to pharmaceutical products e.g aspirin. Used in herbicide Manufacture.

Chlorophenols – Chlorination of Phenols. Breakdown of phenoxy herbicides

Bromophenols – Bromination of Phenolic compounds also used as fungicides, wood preservatives. Production of Flame Retardants

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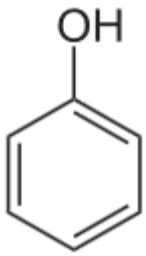
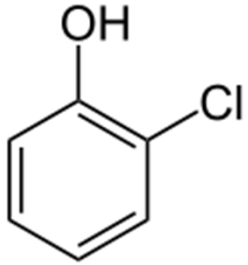
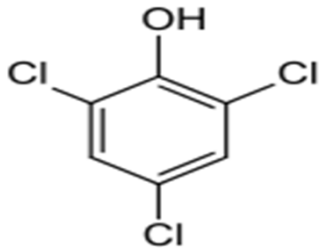
Phenol



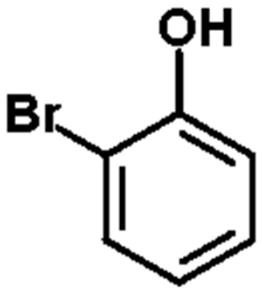
2-Chlorophenol



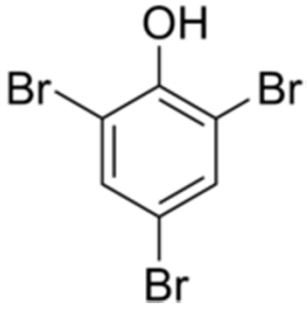
2,4,6 Trichlorophenol



2-Bromophenol



2,4,6 Tribromophenol



Anisoles

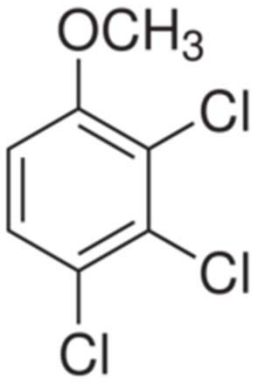
Formed when naturally occurring airborne fungi and/or bacteria(usually *Aspergillus* sp., *Penicillium* sp., *Actinomycetes*, Botrytis *cinerea*, *Rhizobium* sp., or *Streptomyces* are presented with phenolic compounds either chlorinated or brominated. A defensive mechanism of the fungi called 'Biomethylation' converts the phenolic compounds to the anisoles.

Very low thresholds for Taste and Odour (low ppt for chloroanisoles and sub-ppt for Bromoanisoles)

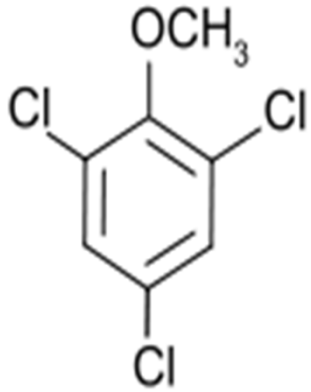
Compounds produce a musty, fungal aroma ***(2,4,6 TCA responsible for producing 'Cork Taint' in wine and also 'Rio Defect' in South American Coffee).***

Anisoles

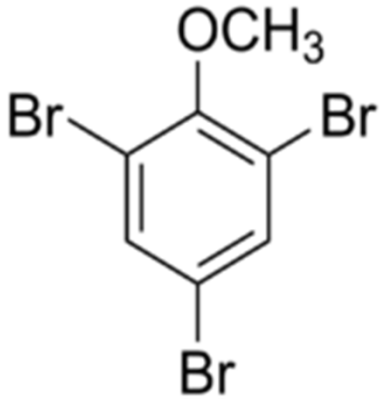
2,3,4 Trichloroanisole



2,4,6 Trichloroanisole



2,4,6 Tribromoanisole



Pyrazines

2-Isopropyl-3-methoxy pyrazine (IPMP)

2-Isobutyl-3-methoxy pyrazine (IBMP)

- Formed from actinobacteria in reservoirs.
- IBMP imparts an earthy odour reminiscent of green peppers
- IPMP imparts mouldy musty odour like potato skins/dug soil
- Both compounds considered to be importants determinants of green flavours in sauvignon blanc wines
- Very low thresholds for taste and odour (low ppt)

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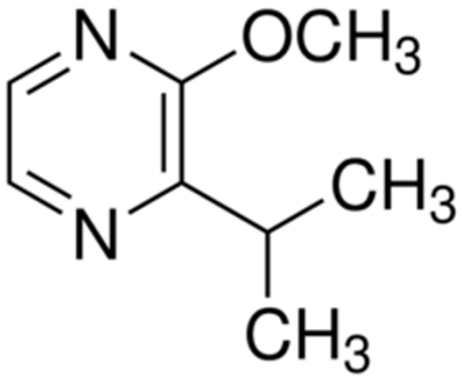
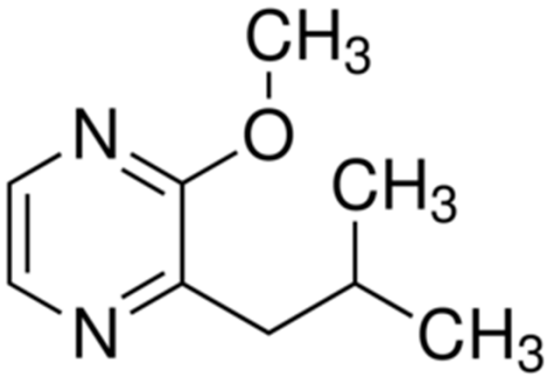
2-Isopropyl-3-methoxy pyrazine



2-Isobutyl-3-methoxy pyrazine



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2-Ethyl-5,5-dimethyl-1,3-dioxane (2-EDD)

2-Ethyl-4-methyl-1,3-dioxolane (2-EMD)

- Compounds by-products of Fibreglass and Resin Manufacture
- 2-EDD Odour threshold ~ 5-10ppt(Plastic/Stale/Acetate)
- 2-EMD Odour threshold ~ 5-10ppt (Sweet)
- Odour varied depending on concentration, more odorous at lower concentrations.

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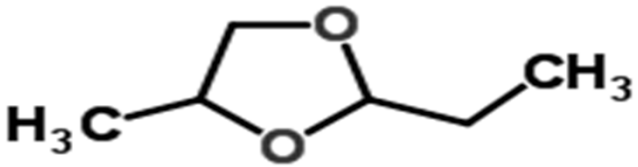
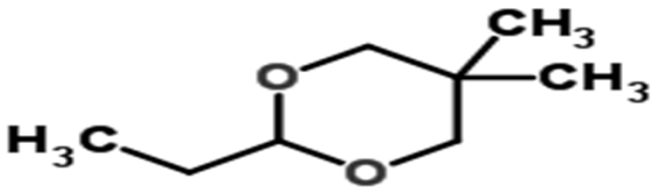
2-EMD



2-EDD



Extraction Summary

- 1 litre of sample extracted with 100mls of Dichloromethane
- Passed through a hydrophobic membrane (Horizon Dry Disk)
- Evaporated down to 0.5mls in a Turbovap
- D_8 Naphthalene (internal standard) added.
- Transferred to autosampler vial for analysis
- Direct Solvent Standards run at 0,10,20,30,40 and 50ng/l
- Quality Control Spike at 40ng/l
- Typical recovery approximately 85% for Geosmin and MIB

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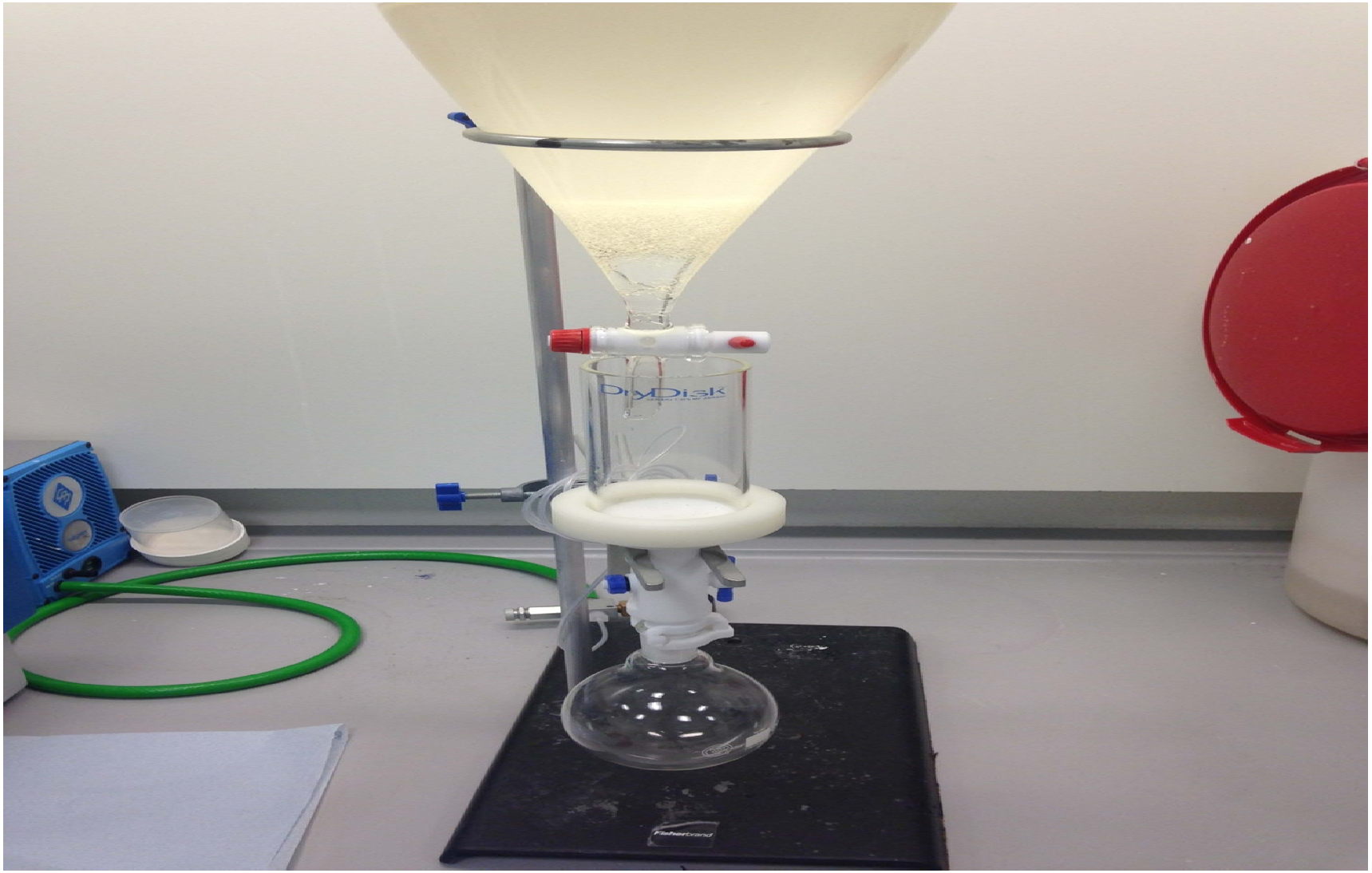

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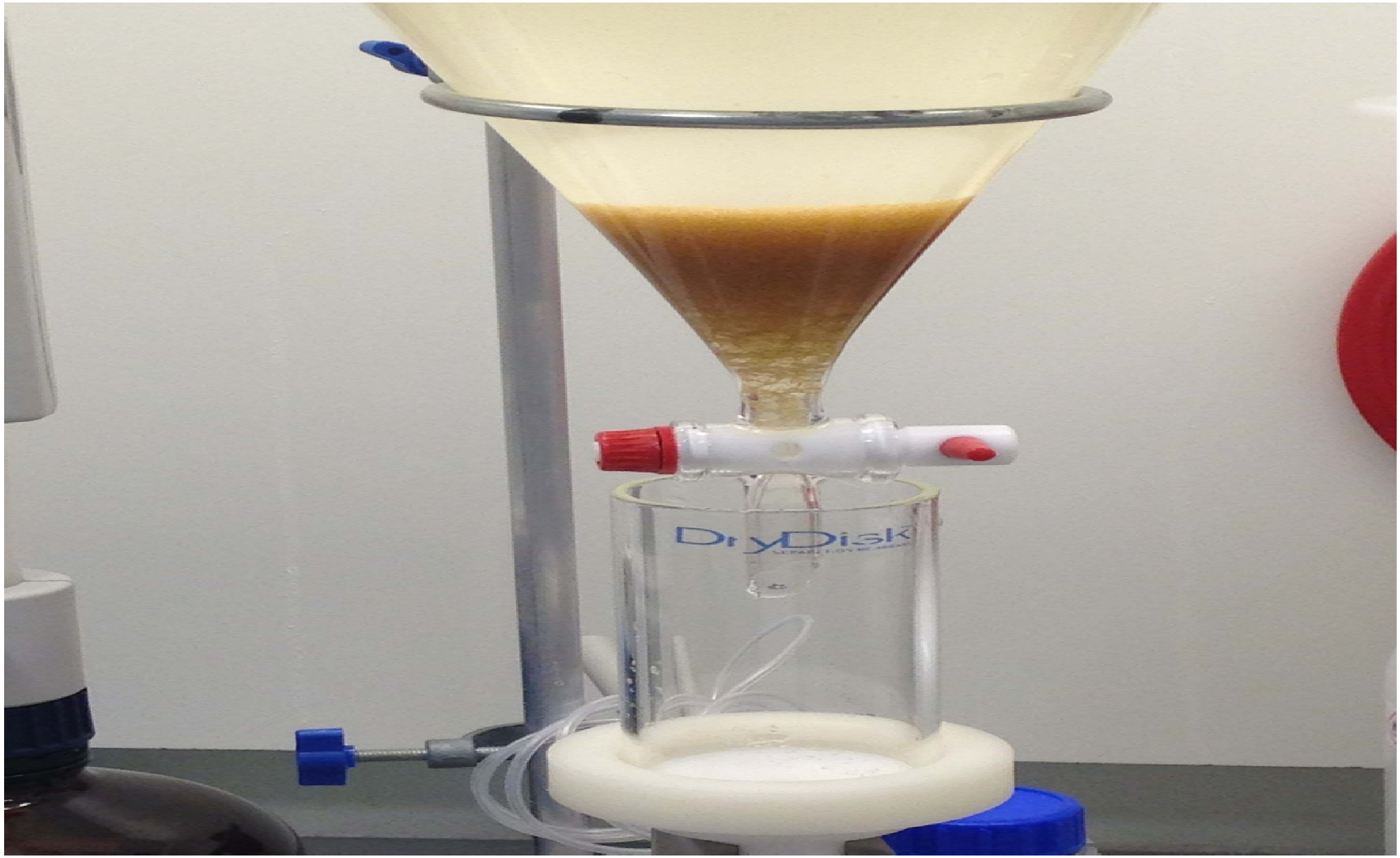

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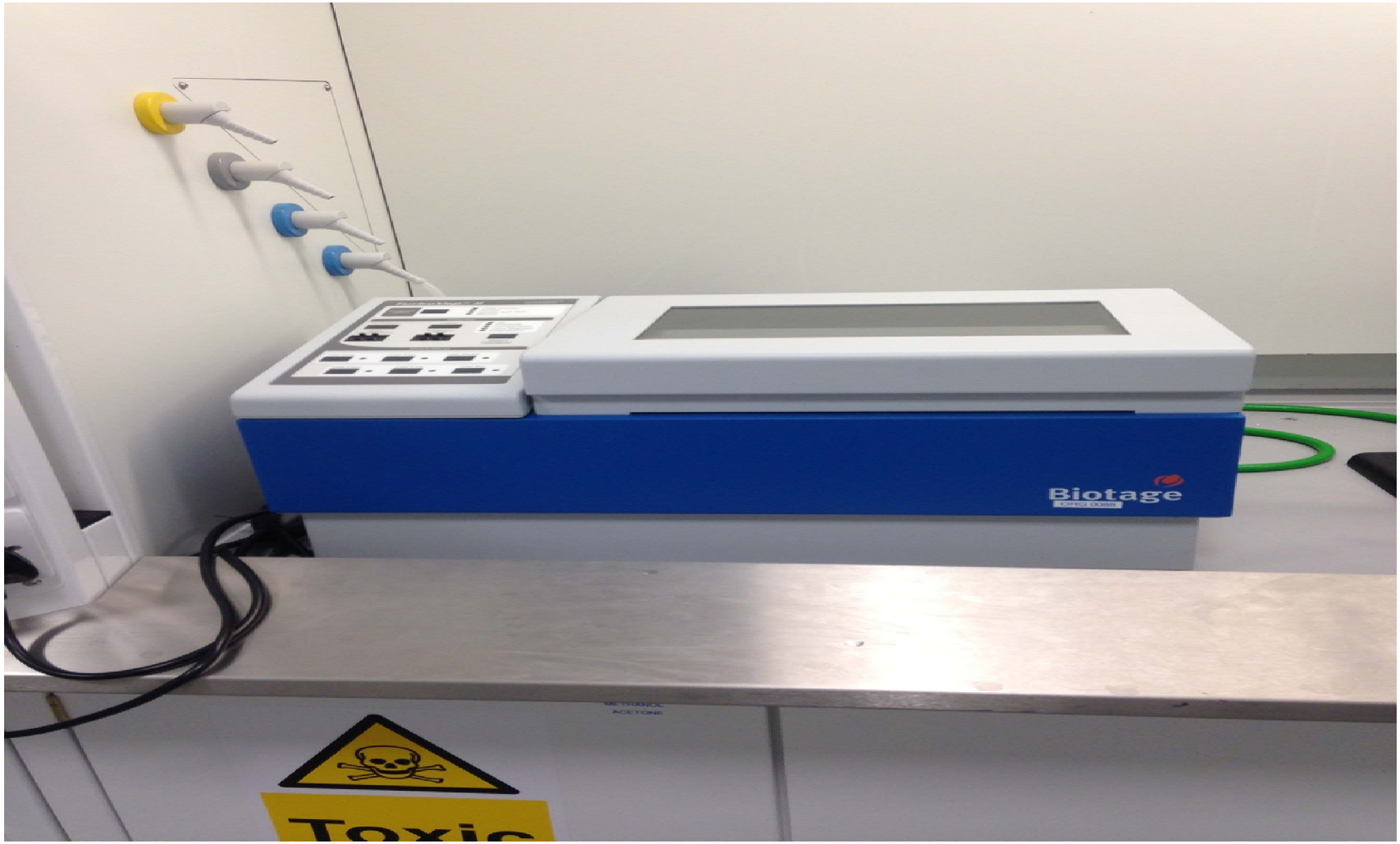

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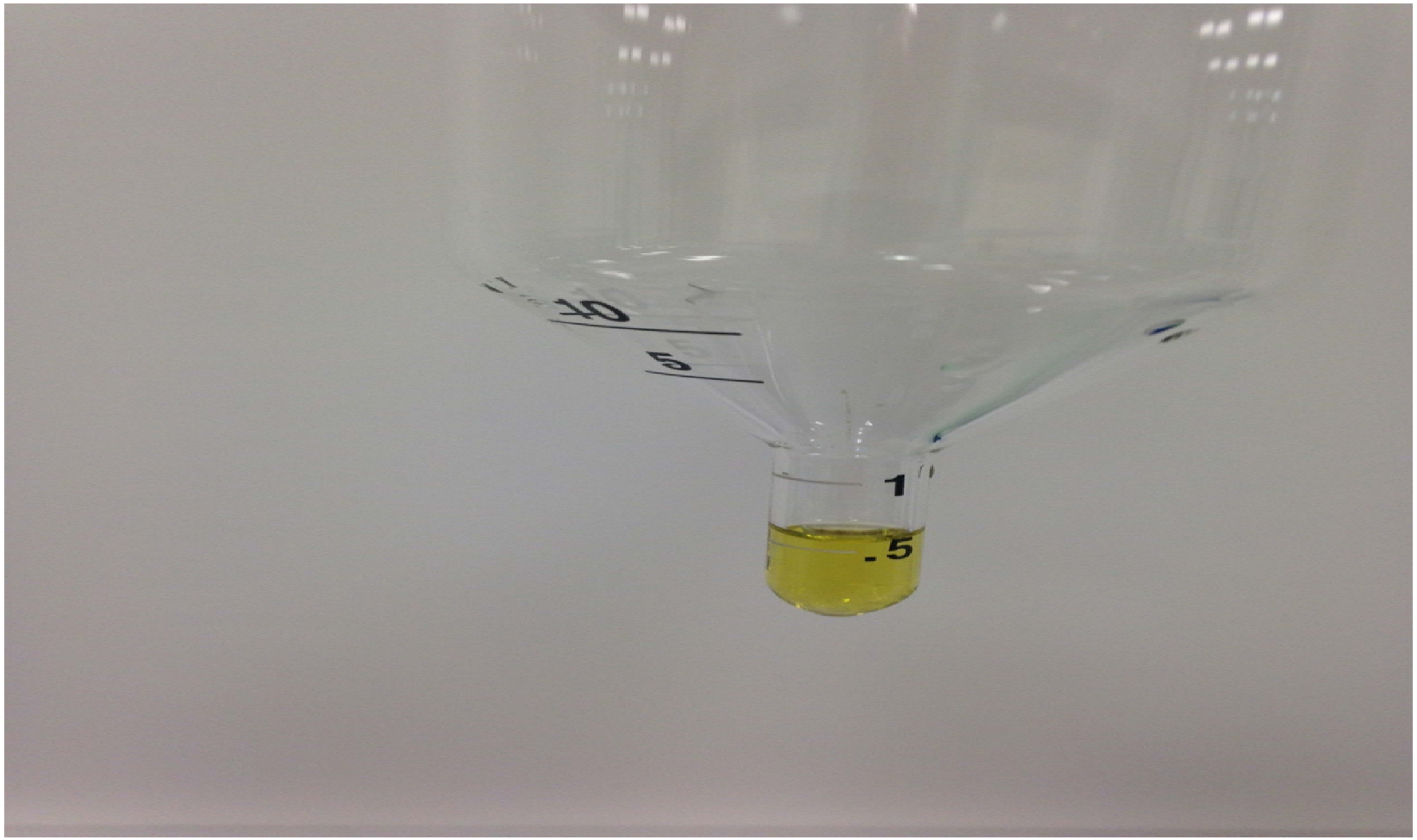

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Instrument/Method Conditions

7890GC/5975C GC-MS with Triple Axis Detector

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HP-5MS Ultra Inert Column 30 x 0.25 x 0.25 (P/N 19091-433UI)

Ultra Inert Splitless Single Taper Liner (P/N 5190-3162)

2µl Injection (Pulsed Splitless)

Constant Flow 1.2ml/min

Oven Program

35°C (Hold 1min)

Ramp 1: 10°C/min (150°C)

Ramp 2: 20°C/min (270°C)

Run Time: 18.5 minutes

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MS Parameters

MS Mode: SIM (5 SIM Groups) – Minimum Quant & 1 Qual per compound (see table)

Transfer Line: 300°C

Ion Source: 230°C

Quad: 150°C

EMV: Gain Factor 10

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Phenol	**94**,66,65
2-Chlorophenol	**128**,130,64
2 Bromophenol	**172**,174,65
2-Isopropyl-3-methoxypyrazine	**137**,152,124
3 Chloroanisole	**142**,112,99
4 Chloroanisole	**142**,127,99
2 Chloroanisole	**142**,99,127
2,4 Dichlorophenol	**162**,164,98
2,3 Dichlorophenol	**162**,164,126
2-Isobutyl-3-methoxypyrazine	**124**,151
2-Methyl Isoborneol (MIB)	**95**,107
2,3,4 Trichloroanisole	**195**,210,212
2,4,6 Trichlorophenol	**196**,198,200
2,6 Dibromophenol	**252**,250,254
Geosmin	**112**,97,125
2,4,6 Trichloroanisole	**210**,212,195
2,4,6 Tribromoanisole	**346**,344,329
2,4,6 Tribromophenol	**332**,330,328
2-EMD	**87**,59
2-EDD	**56**,115,69
Naphthalene D_8 (Int Std)	**136**,108

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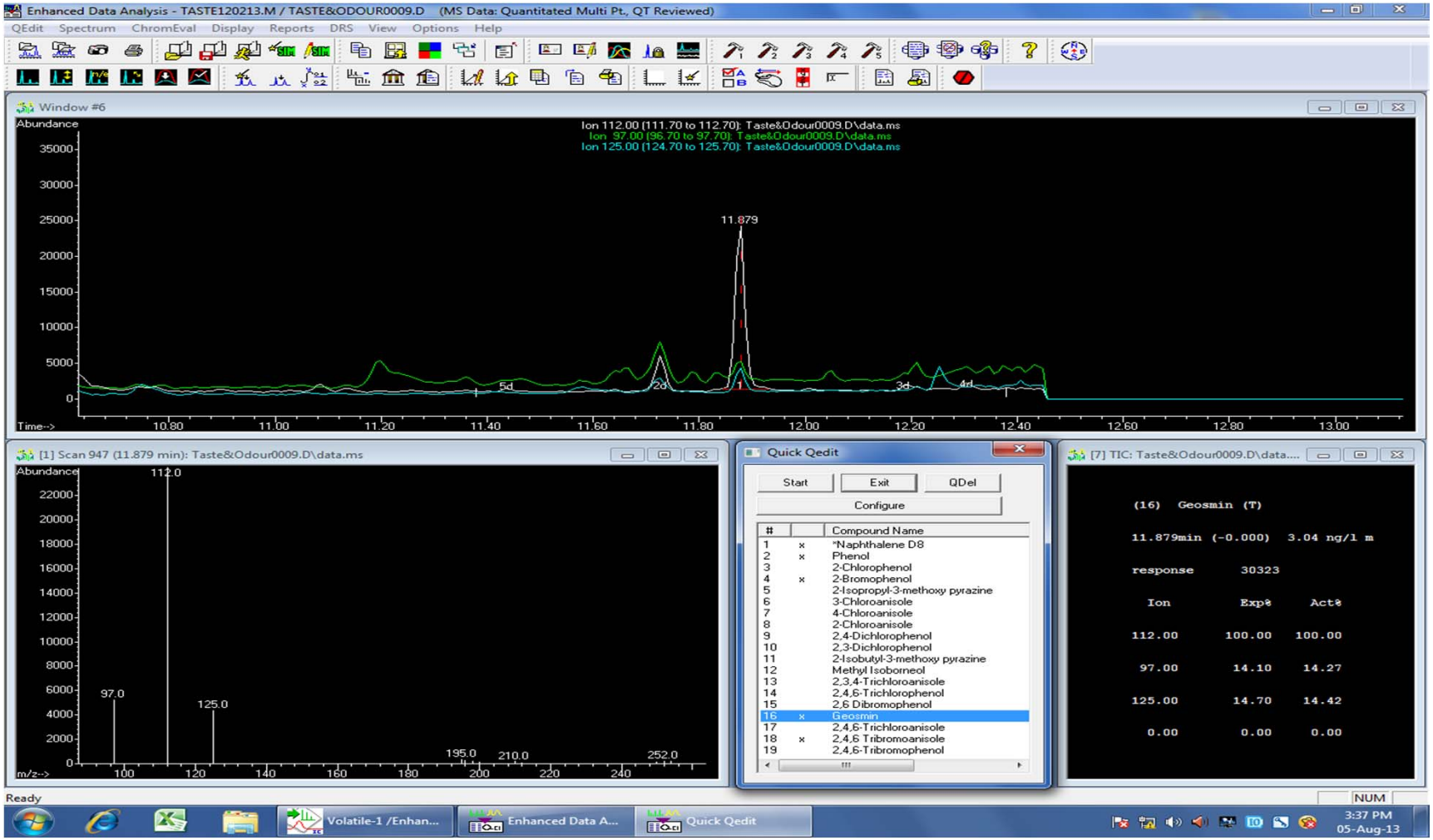

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Agilent 7000 GC-QQQ

Dwr Cymru Welsh Water

Agilent 7000 GC-QQQ

- **Greater Selectivity –** MRM against SIM
- **Greater Sensitivity –** Improved S/N
- **Mass Hunter Software –** Analyst Training
- **Enhanced Confidence in Reporting**
- **Instrument Capacity**

MRM Optimisation

- Each compound run separately in MS1 Scan (Precursor Ion)
- Product Ion Scans run at variety of Collision Energies
- 2 MRM transitions per compound
- 6 Time Segments (Dwell Times adjusted to give min 2 cycles/sec)

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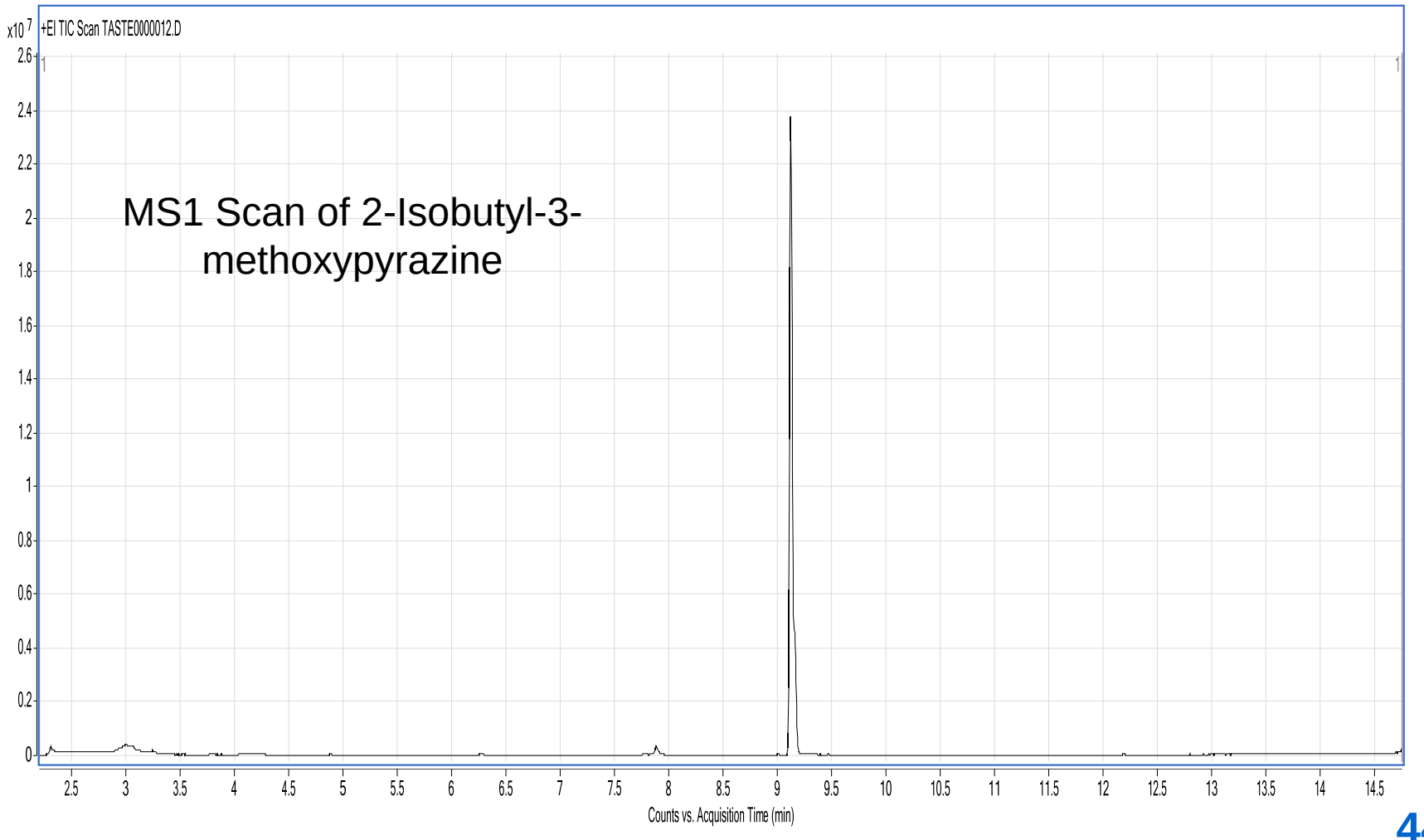

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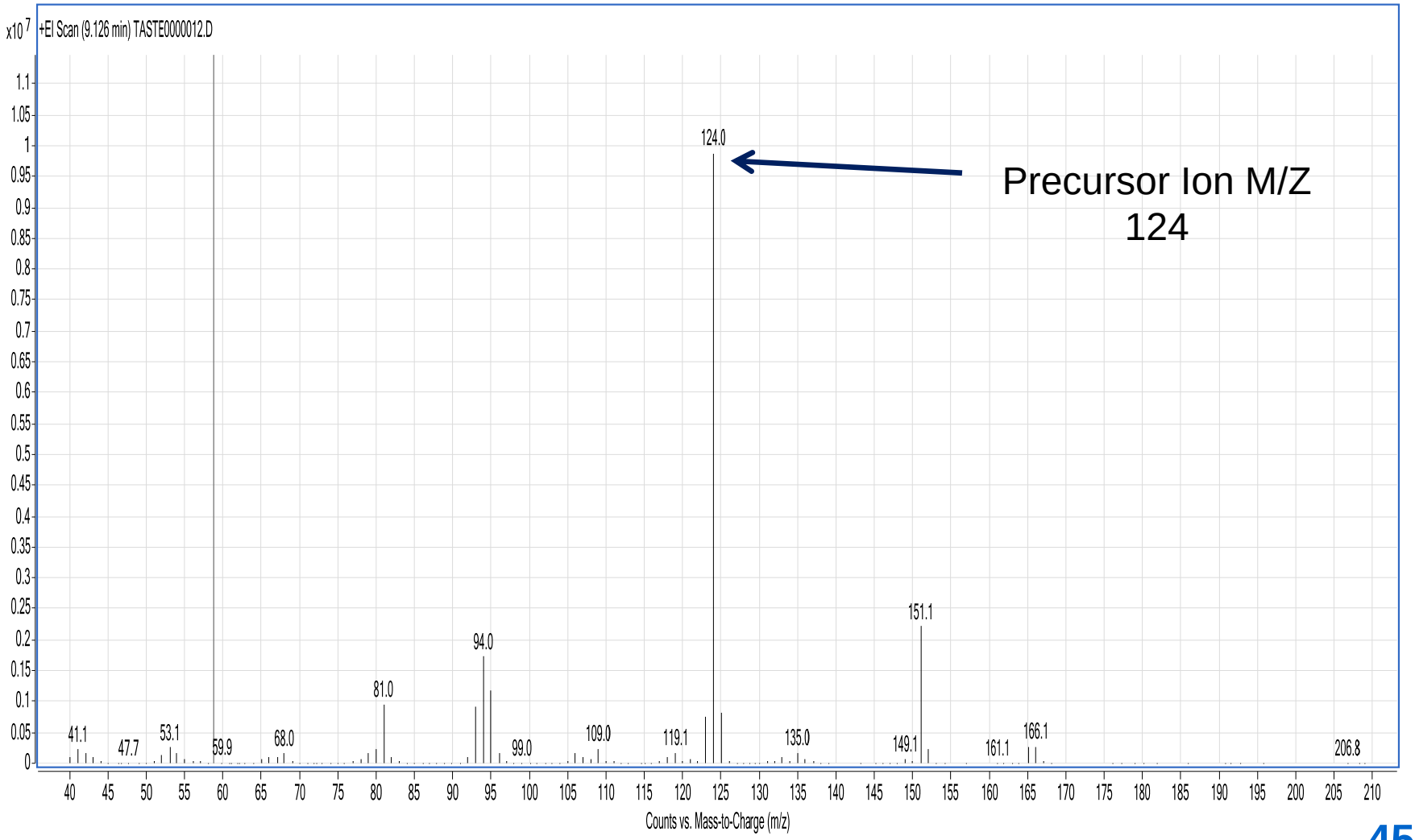

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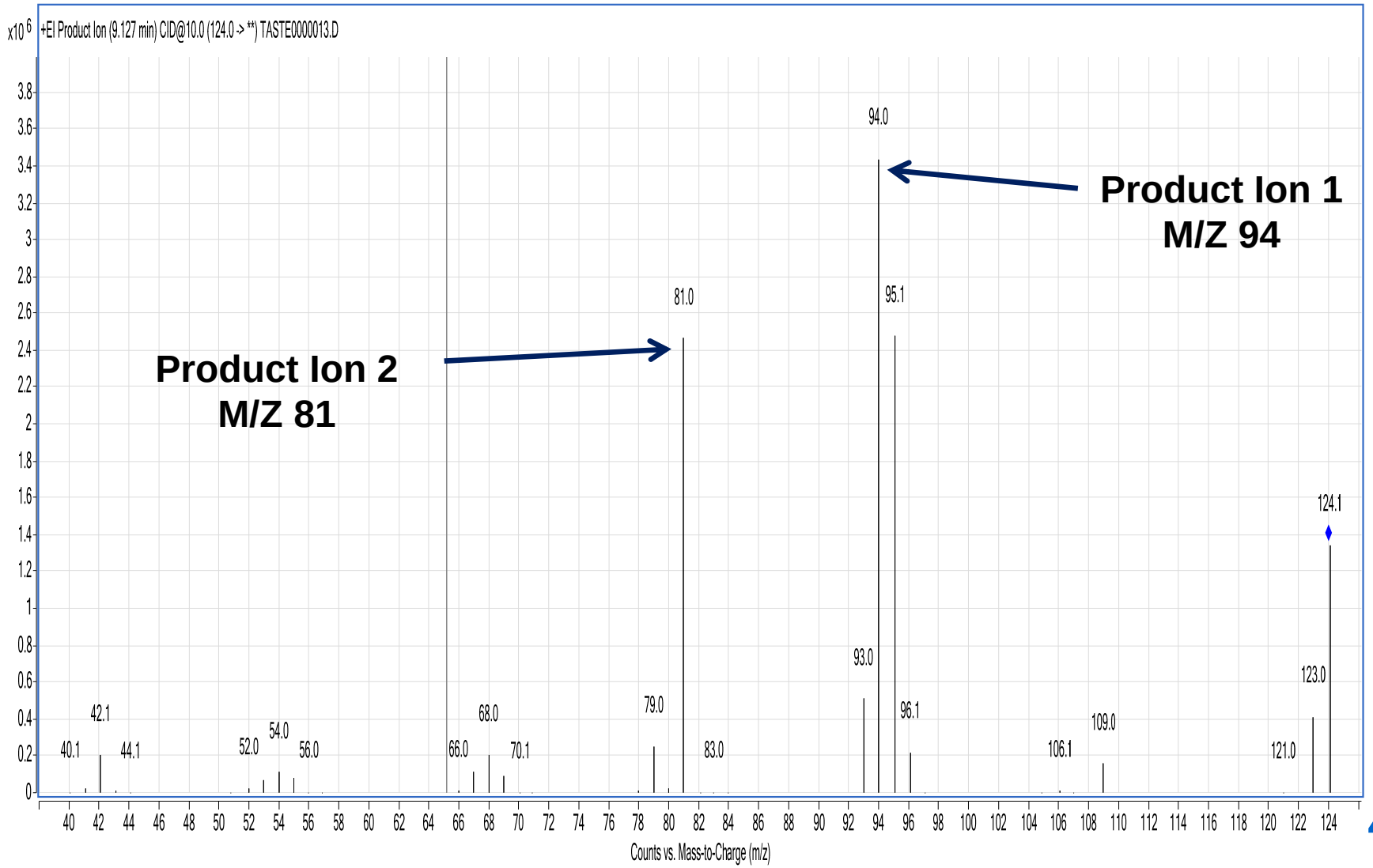

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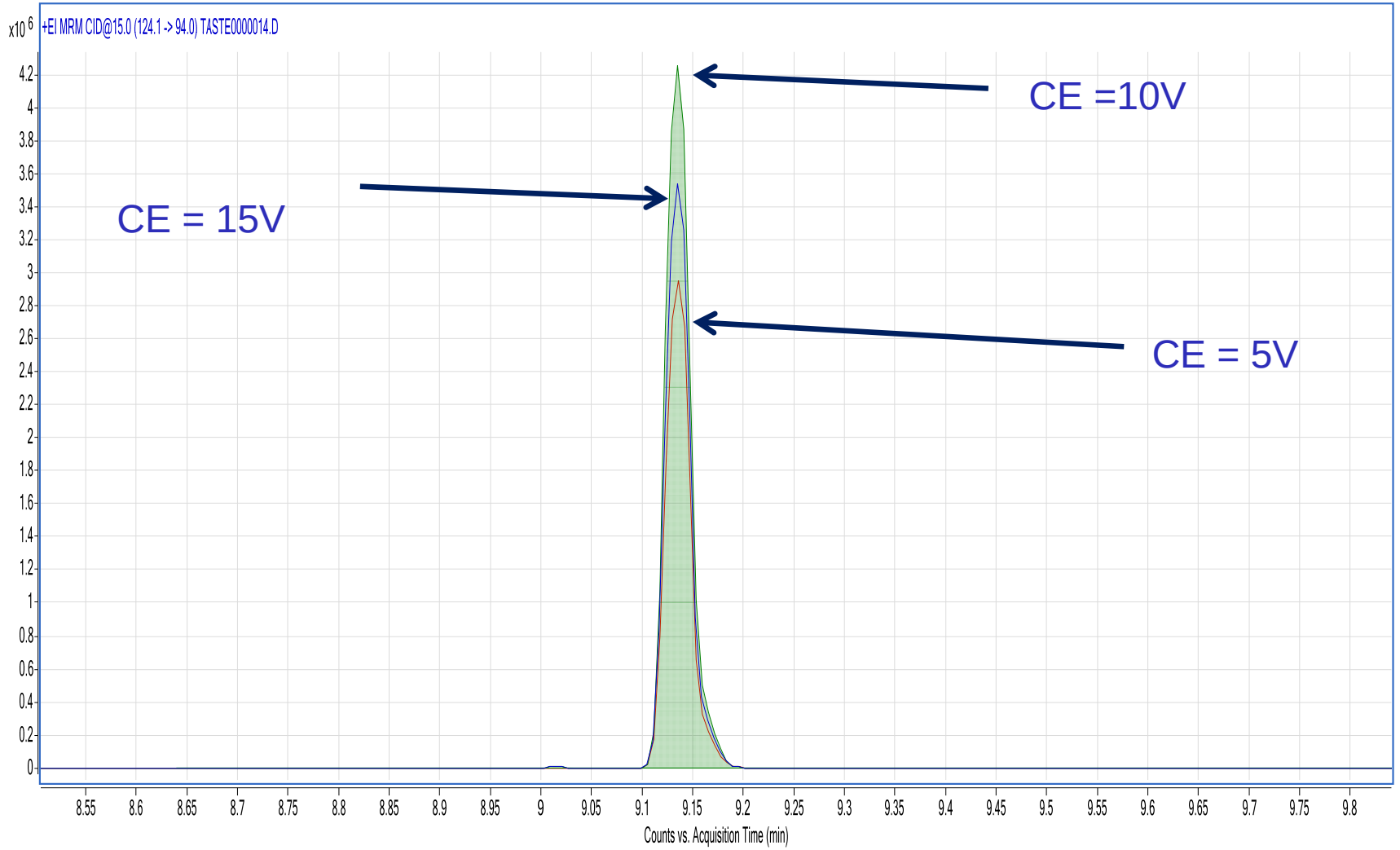

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Compound	Precursor	MS1 Res	Product Ion	MS2 Res	Collision Energy
Phenol	**94**	**Wide**	**66**	**Unit**	**10**
Phenol	94	Wide	65	Unit	20
2-Chlorophenol	**128**	**Wide**	**92**	**Unit**	**5**
2-Chlorophenol	128	Wide	64	Unit	20
2-Bromophenol	**172**	**Wide**	**93**	**Unit**	**10**
2-Bromophenol	172	Wide	65	Unit	20
2-IPMP	**137**	**Wide**	**109.1**	**Unit**	**5**
2-IPMP	137	Wide	105	Unit	10
3-Chloroanisole	**142**	**Wide**	**112**	**Unit**	**10**
3-Chloroanisole	142	Wide	77	Unit	25
4-Chloroanisole	**142**	**Wide**	**127**	**Unit**	**10**
4-Chloroanisole	142	Wide	99	Unit	25

Dwr Cymru Welsh Water

Compound	Precursor	MS1 Res	Product Ion	MS2 Res	Collision Energy
2-Chloroanisole	**142**	**Wide**	**127**	**Unit**	**10**
2-Chloroanisole	142	Wide	99	Unit	25
2,4 DC Phenol	**162**	**Wide**	**63**	**Unit**	**30**
2,4 DC Phenol	98	Wide	63	Unit	5
2,3 DC Phenol	**162**	**Wide**	**63**	**Unit**	**30**
2,3 DC Phenol	98	Wide	63	Unit	5
2-IBMP	**124**	**Wide**	**94**	**Unit**	**10**
2-IBMP	124	Wide	81	Unit	10
2-MIB	**95.1**	**Wide**	**67**	**Unit**	**10**
2-MIB	95.1	Wide	55.1	Unit	15
2,3,4 TCA	**210**	**Wide**	**194.9**	**Unit**	**10**
2,3,4 TCA	210	Wide	166.9	Unit	25

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Compound	Precursor	MS1 Res	Product Ion	MS2 Res	Collision Energy
2,4,6 TCPhenol	**132**	**Wide**	**97**	**Unit**	**10**
2,4,6 TCPhenol	196	Wide	97	Unit	30
2,6 DBPhenol	**252**	**Wide**	**143**	**Unit**	**25**
2,6 DBPhenol	252	Wide	63	Unit	50
Geosmin	**112.1**	**Wide**	**97.1**	**Unit**	**10**
Geosmin	112.1	Wide	83	Unit	10
2,4,6 TCAnisole	**210**	**Wide**	**194.9**	**Unit**	**10**
2,4,6 TCAnisole	210	Wide	166.9	Unit	25
2,4,6 TBAnisole	**346**	**Wide**	**303**	**Unit**	**35**
2,4,6 TBAnisole	344	Wide	329	Unit	15
2,4,6 TBPhenol	**329.7**	**Wide**	**141**	**Unit**	**30**
2,4,6 TBPhenol	141	Wide	62	Unit	15
Naphthalene D_8	**136**	**Wide**	**108**	**Unit**	**30**

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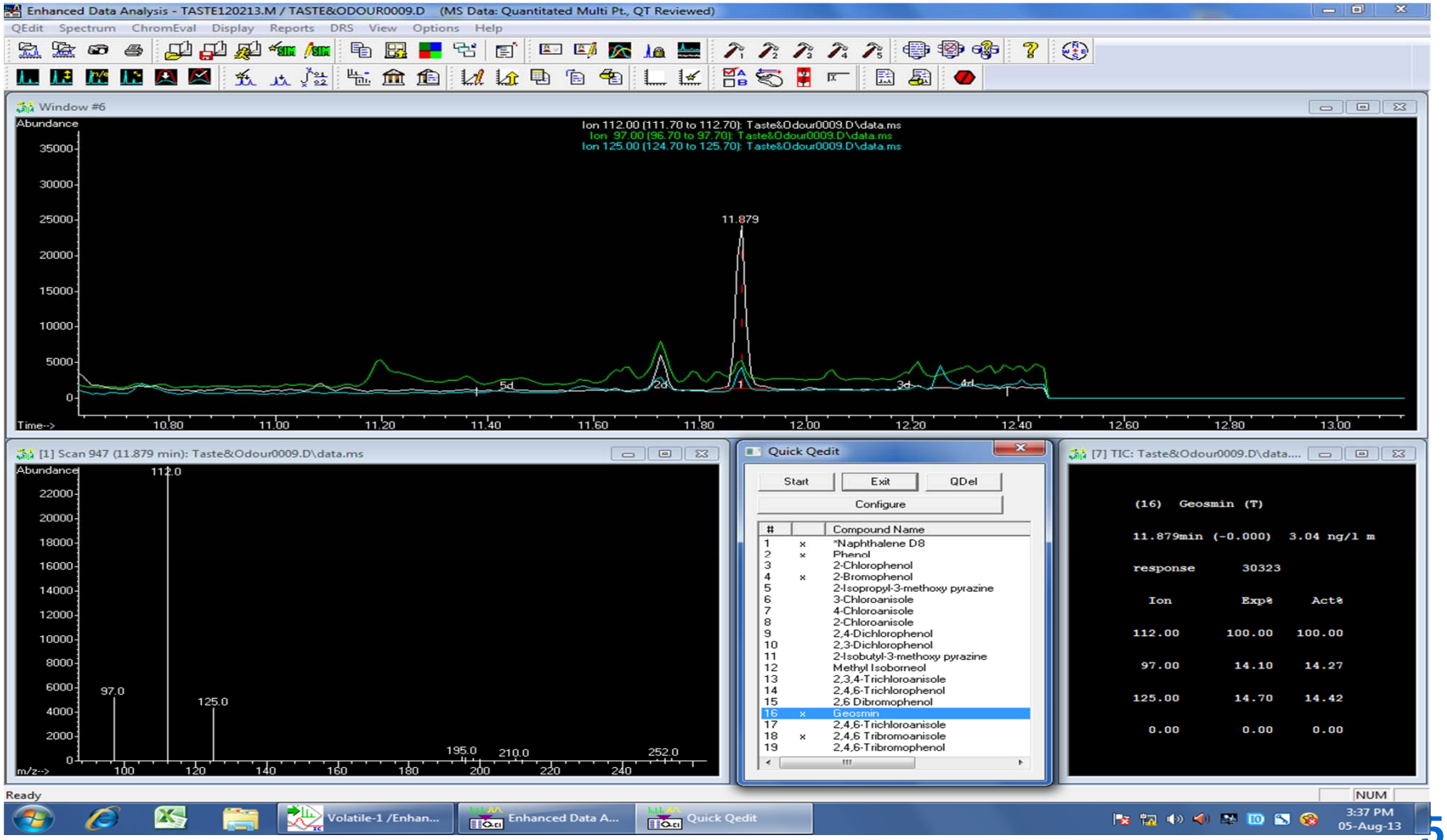

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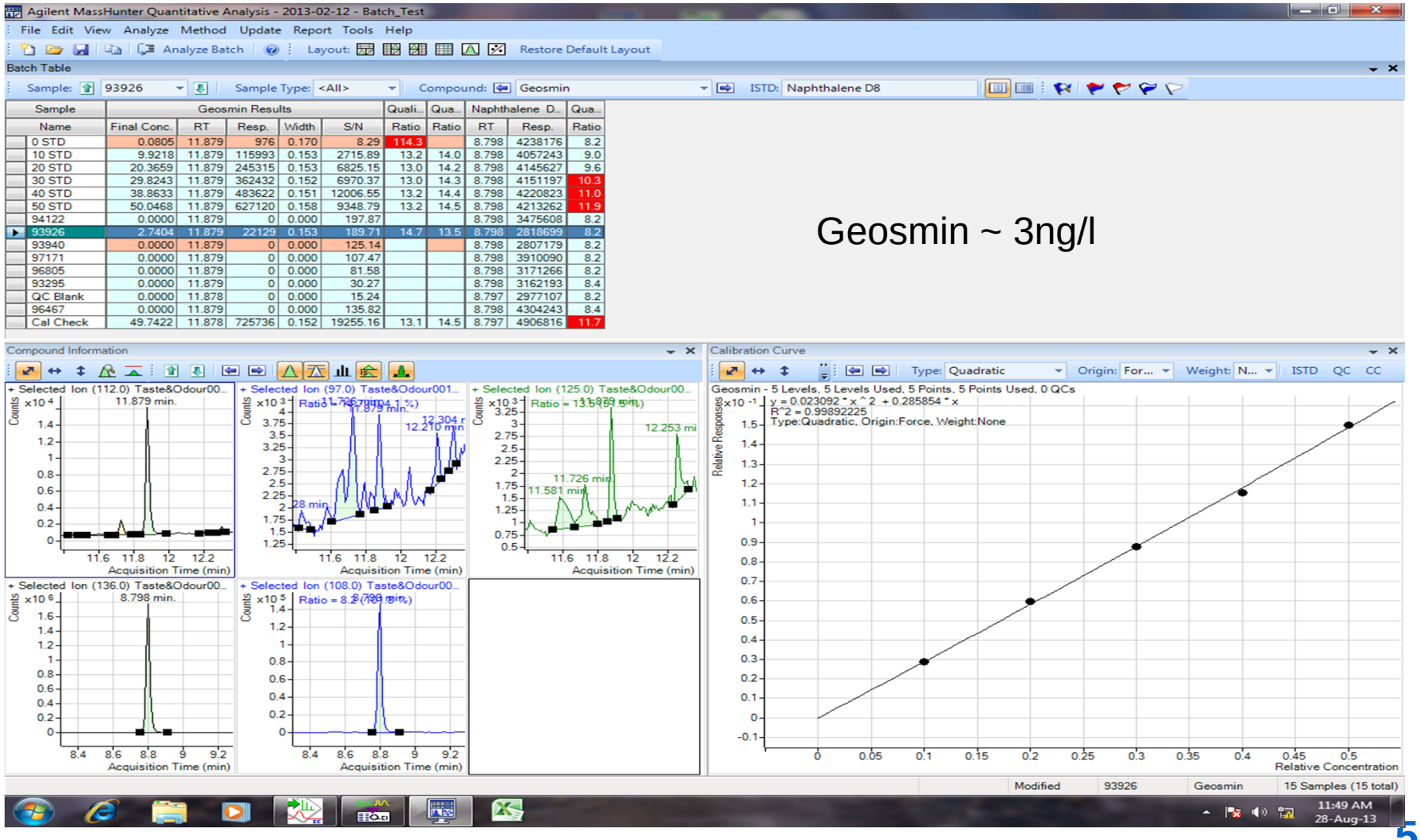
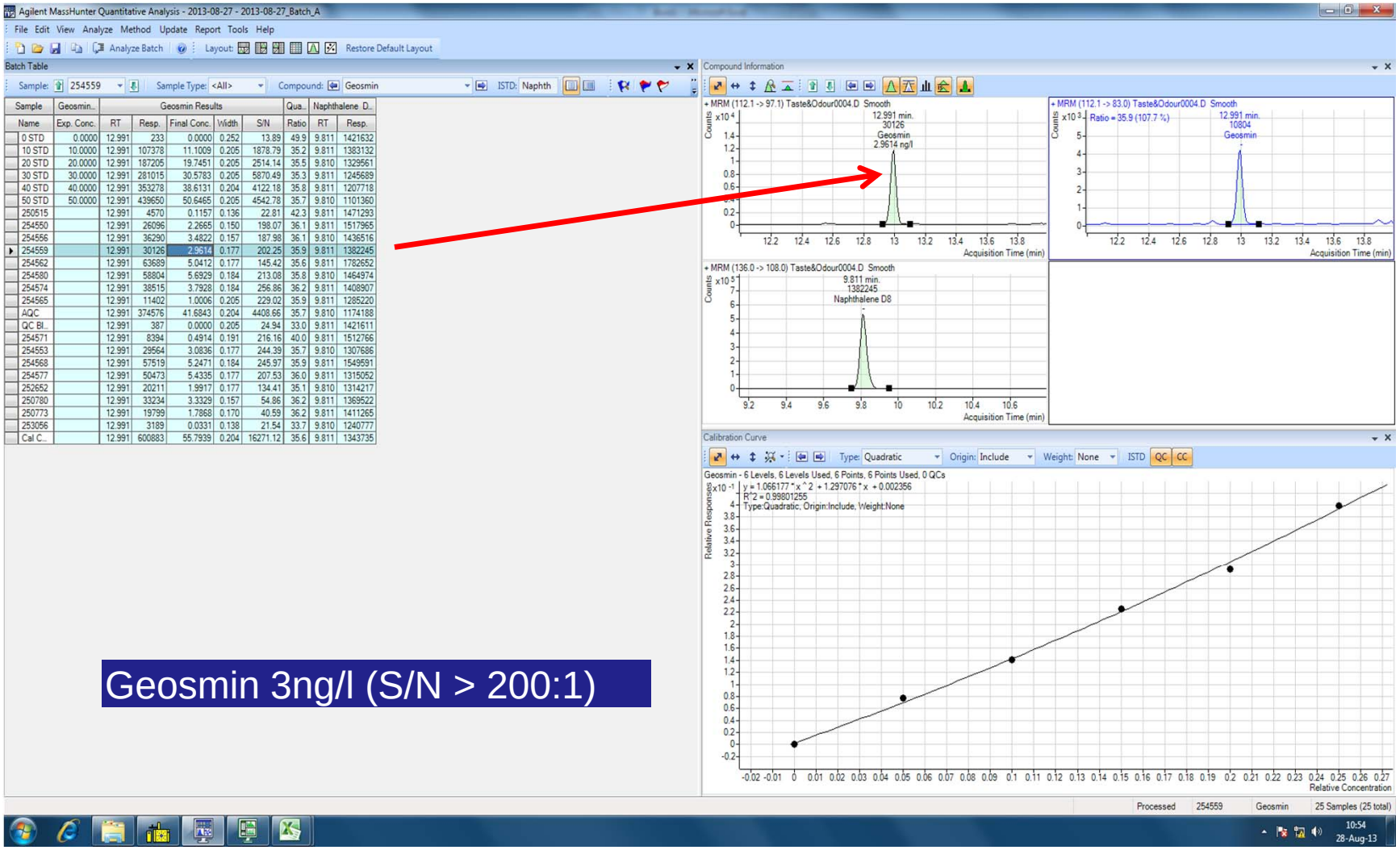


Sample	Geosmin Results					Quali...	Qua...	Naphthalene D...		Qua...
Name	Final Conc.	RT	Resp.	Width	S/N	Ratio	Ratio	RT	Resp.	Ratio
0 STD	0.0805	11.879	976	0.170	8.29	114.3		8.798	4238176	8.2
10 STD	9.9218	11.879	115993	0.153	2715.89	13.2	14.0	8.798	4057243	9.0
20 STD	20.3659	11.879	245315	0.153	6825.15	13.0	14.2	8.798	4145627	9.6
30 STD	29.8243	11.879	362432	0.152	6970.37	13.0	14.3	8.798	4151197	10.3
40 STD	38.8633	11.879	483622	0.151	12006.55	13.2	14.4	8.798	4220823	11.0
50 STD	50.0468	11.879	627120	0.158	9348.79	13.2	14.5	8.798	4213262	11.9
94122	0.0000	11.879	0	0.000	197.87			8.798	3475608	8.2
93926	2.7404	11.879	22129	0.153	189.71	14.7	13.5	8.798	2818699	8.2
93940	0.0000	11.879	0	0.000	125.14			8.798	2807179	8.2
97171	0.0000	11.879	0	0.000	107.47			8.798	3910090	8.2
96805	0.0000	11.879	0	0.000	81.58			8.798	3171266	8.2
93295	0.0000	11.879	0	0.000	30.27			8.798	3162193	8.4
QC Blank	0.0000	11.878	0	0.000	15.24			8.797	2977107	8.2
96467	0.0000	11.879	0	0.000	135.82			8.798	4304243	8.4
Cal Check	49.7422	11.878	725736	0.152	19255.16	13.1	14.5	8.797	4906816	11.7

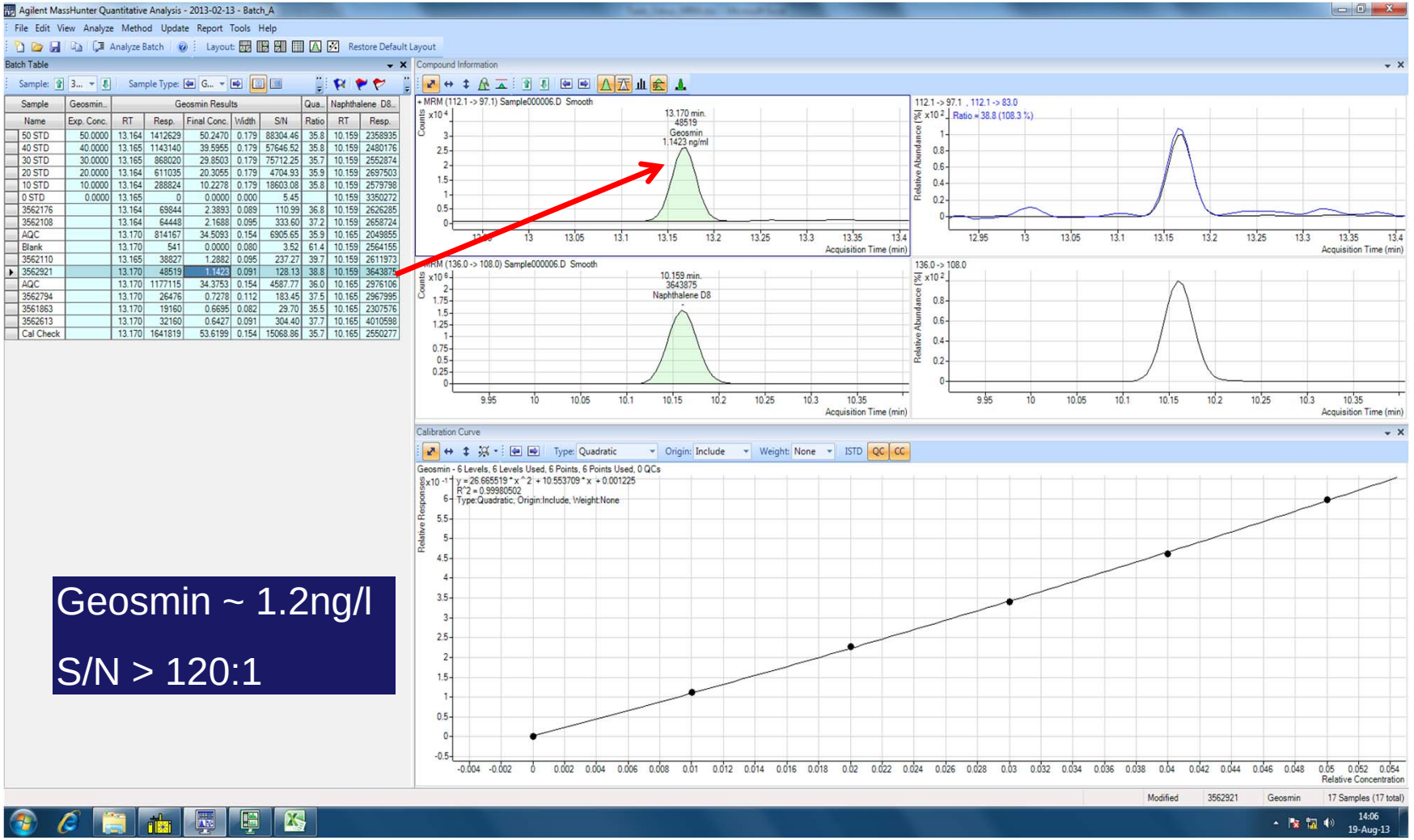
Geosmin ~ 3ng/l

Dwr Cymru Welsh Water



Geosmin 3ng/l (S/N > 200:1)

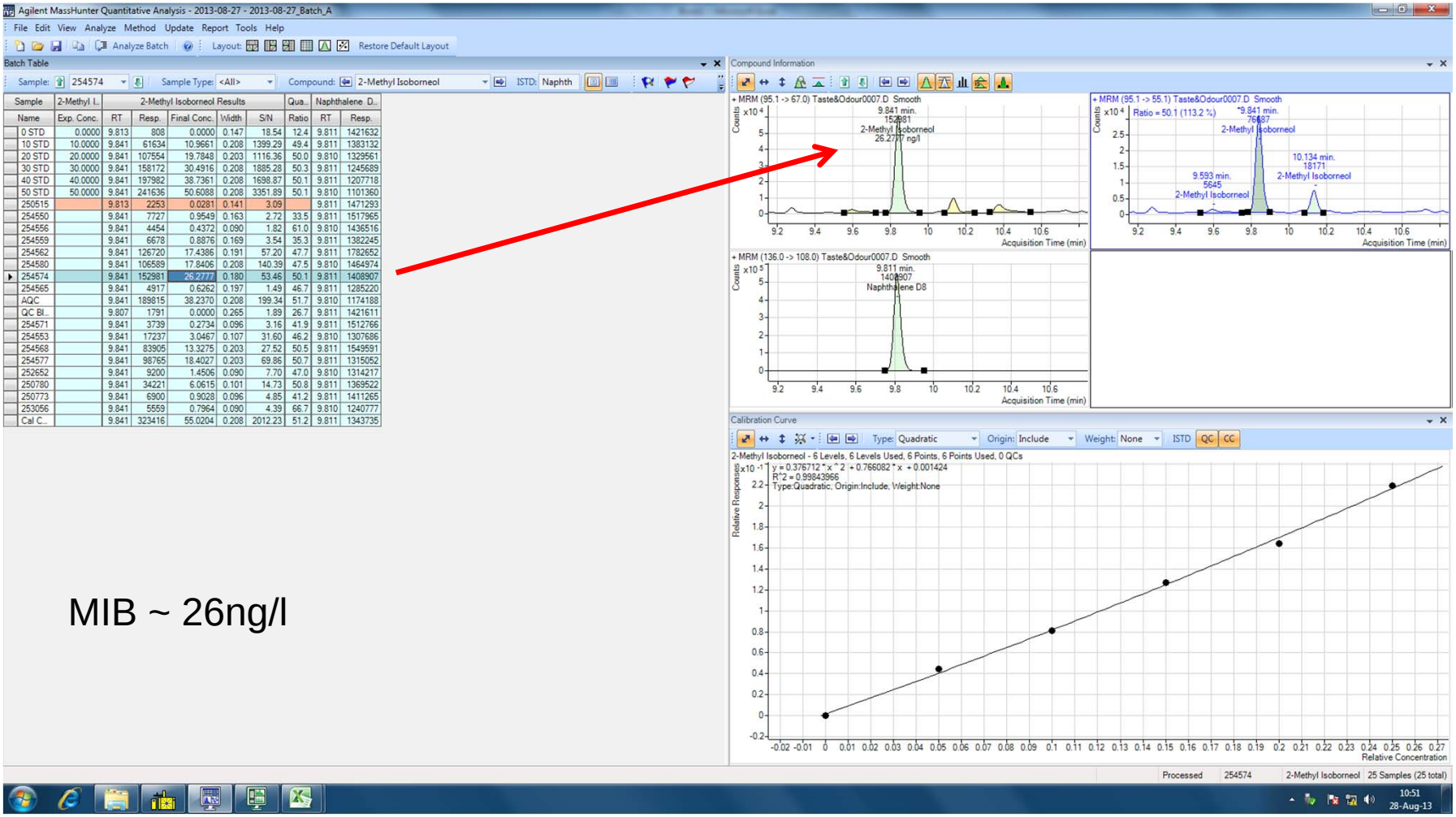
Dwr Cymru Welsh Water



Geosmin ~ 1.2ng/l

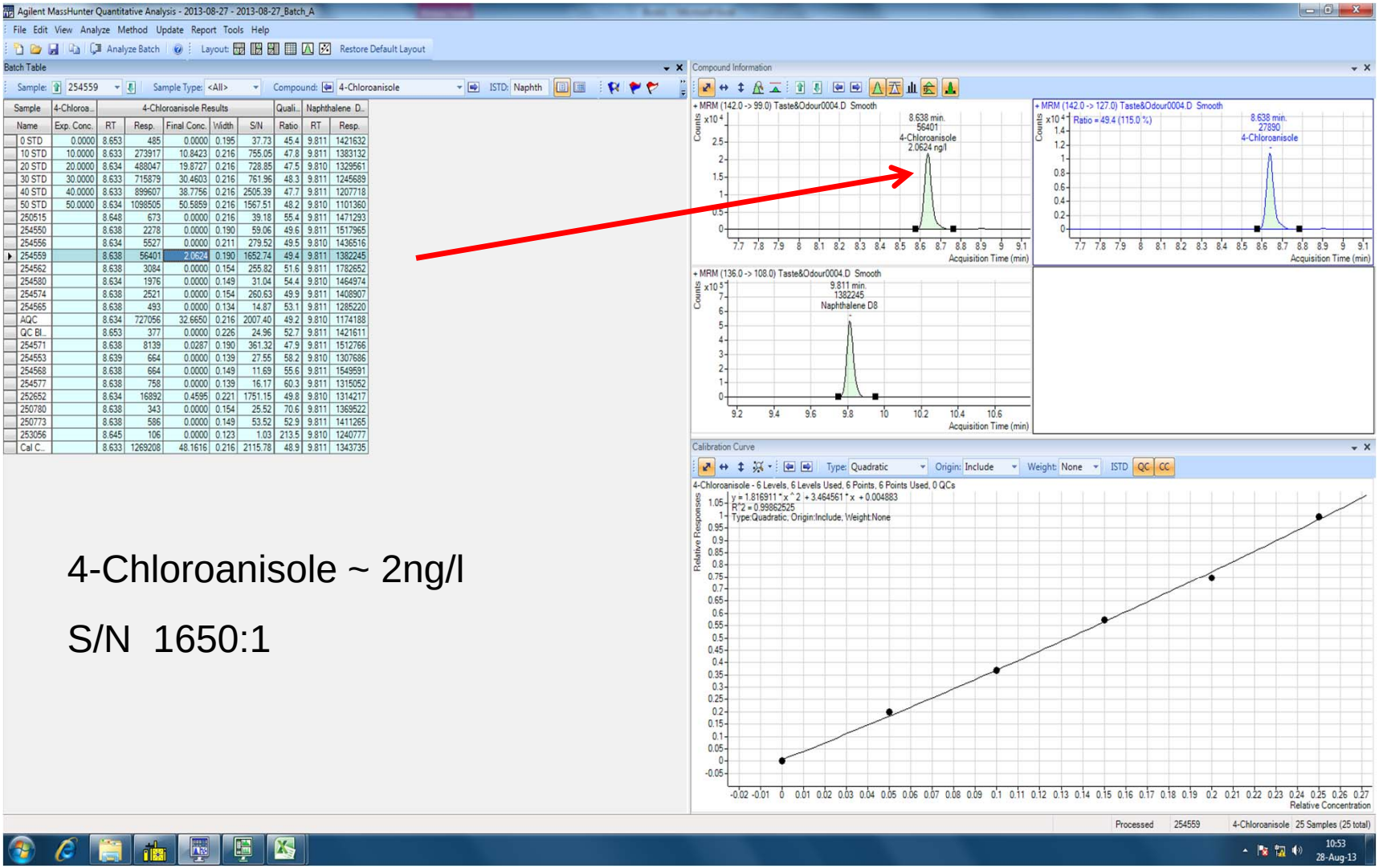
S/N > 120:1

Dwr Cymru Welsh Water



MIB ~ 26ng/l

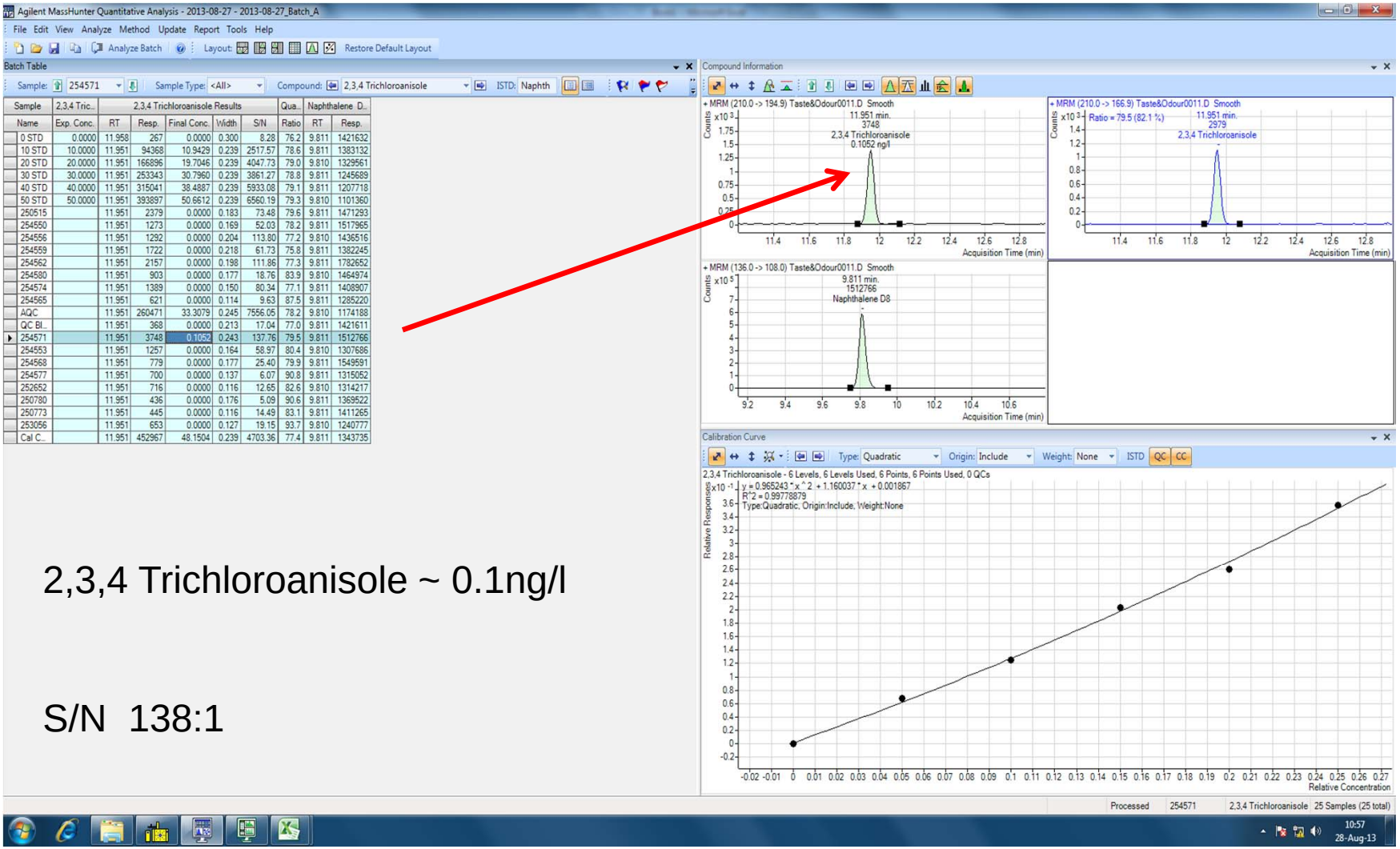
Dwr Cymru Welsh Water



4-Chloroanisole ~ 2ng/l

S/N 1650:1

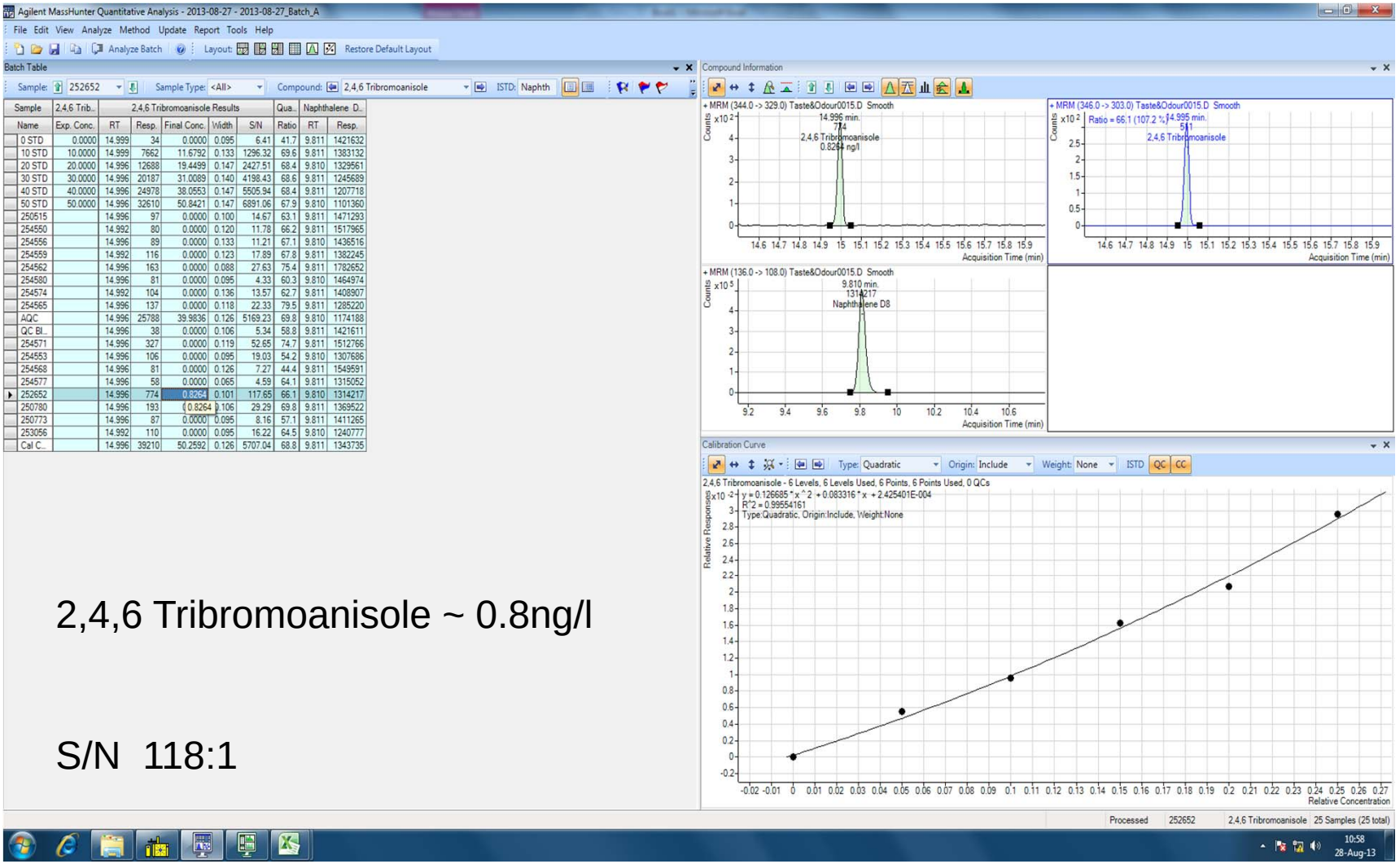
Dwr Cymru Welsh Water



2,3,4 Trichloroanisole ~ 0.1ng/l

S/N 138:1

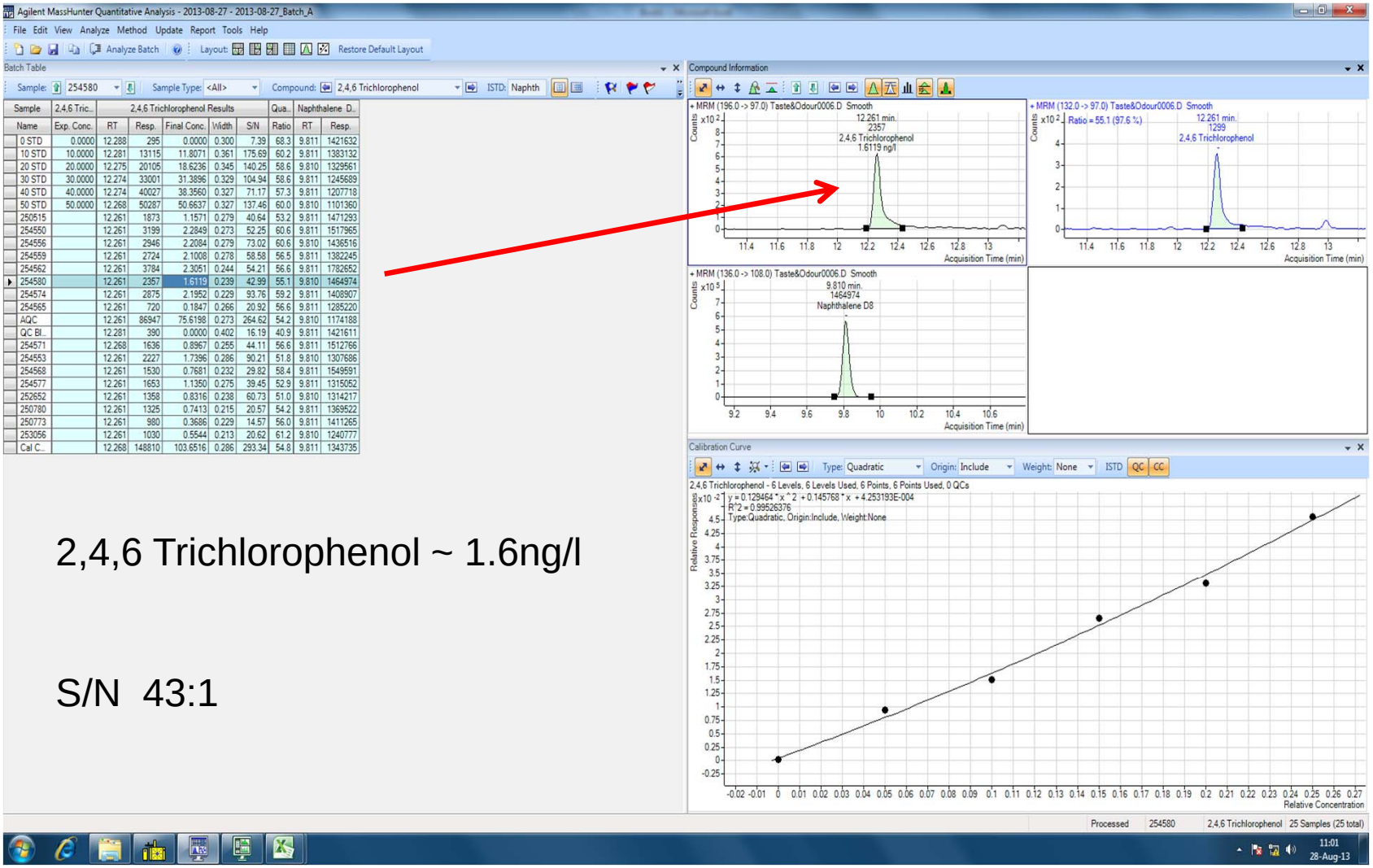
Dwr Cymru Welsh Water



2,4,6 Tribromoanisole ~ 0.8ng/l

S/N 118:1

Dwr Cymru Welsh Water



2,4,6 Trichlorophenol ~ 1.6ng/l

S/N 43:1

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The Future

- Solid Phase Extraction
- Smaller Sample Volumes
- Validate Method (NS30)
- UKAS Accreditation
- Microcystin Monitoring

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Acknowledgments

Sharon Evans (Head of Water Quality)

Paul Woodbridge (Laboratory Manager)

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Application Note: (5991-3721EN)

Monitoring for 'Taste and Odour' Compounds including Geosmin and MIB in Potable Water using the Agilent 7000 Triple Quad.

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Questions