ENVIRONMENTAL ANALYSIS

MONITORING FOR 'TASTE AND ODOUR COMPOUNDS' INCLUDING GEOSMIN AND MIB IN POTABLE WATER USING THE AGILENT 7000 TRIPLE QUADRUPOLE GC/MS

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Solution Note

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Abstract

A target based screening method for a variety of 'taste and odour' compounds has been developed on an Agilent 7000 Triple Quadrupole GC/MS. There are 20 target compounds in this analytical suite, which includes Geosmin, 2-Methyl Isoborneol, Phenols, Anisoles, Pyrazines as well as 2-EMD and 2-EDD. This method is capable of achieving detection limits of 1 ng/L for all compounds and the range of application is up to 50 ng/L.

Introduction

Taste and odours in drinking water can originate from a variety of potential sources [1]. These include natural products in the abstraction water, chemicals formed during water treatment, storage or distribution and the entry of materials into the distribution system that either react with compounds in the water or cause taste and odours themselves. The detection of 'off-taste' and 'odour' in drinking water is one of the principle causes of complaints from consumers to water companies. Some of these chemical contaminants have very low taste and odour thresholds and can be detected by consumers at very low concentrations, although this does not necessarily indicate that there is an associated health concern. Identifying some of these chemical residues is made all the more difficult by these low taste and odour thresholds, for example the odour threshold for Geosmin is approximately 15 ng/L, MIB 20 ng/L, whilst 2-EDD and 2-EMD are both 10 ng/L [2]. Combining the use of trained taste and odour panellists with rapid analytical screening methods provides an effective means of taste and odour identification. This method has been developed for the analysis of samples that have been identified as having objectionable taste and odour properties.

The samples are prepared using a Dichloromethane liquid/liquid extraction and then analysed on an Agilent 7000 Triple Quadrupole GC/MS (gas chromatograph with mass spectrometer triple quadrupole detector). This method can determine 20 'Taste and Odour' compounds, with a detection limit of 1 ng/L for all compounds.

Summary of Target Compounds, Odour Descriptions and Possible Sources

Compound	Odour Description	Possible Sources
2-Ethyl-4-methyl-1,3-dioxolane (2-EMD)	Sweet (Medicinal)	Industrial Waste
Phenol	Carbolic	Industrial Waste
2-Chlorophenol	Phenolic	Phenol Chlorination / Chloramination
2-Ethyl-5,5-dimethyl-1,3-dioxane (2-EDD)	Sweet (Tutti-fruity)	Industrial Waste
2-Bromophenol	Medicinal	Chlorination / Presence of Phenol and Bromide Ions
2-Isopropyl-3-methoxypyrazine (2-IPMP)	Mouldy / Musty/ Potato Bin	Actinobacteria
3-Chloroanisole	Musty	Biomethylation of Chlorinated Phenolic Compounds
4-Chloroanisole	Musty	Biomethylation of Chlorinated Phenolic Compounds
2-Chloroanisole	Musty	Biomethylation of Chlorinated Phenolic Compounds
2,4-Dichlorophenol	Medicinal	Phenol Chlorination / Chloramination
2,3-Dichlorophenol	Medicinal	Phenol Chlorination / Chloramination
2-Isobutyl-3-methoxypyrazine (2-IBMP)	Earthy / Green Pepper	Actinobacteria
2-Methyl Isoborneol (2-MIB)	Musty	Cyanobacteria, Actinobacteria
2,3,4-Trichloroanisole	Musty	Biomethylation of Chlorinated Phenolic Compounds
2,4,6-Trichlorophenol	Medicinal	Phenol Chlorination / Chloramination
2,6-Dibromophenol	Medicinal	Chlorination / Presence of Phenol and Bromide Ions
Geosmin	Earthy / Musty	Cyanobacteria, Actinobacteria
2,4,6-Trichloroanisole	Musty	Biomethylation of Chlorinated Phenolic Compounds
2,4,6-Tribromoanisole	Musty	Biomethylation of Brominated Phenolic Compounds
2,4,6-Tribromophenol	Medicinal	Chlorination / Presence of Phenol and Bromide Ions

Geosmin & 2-Methyl Isoborneol (MIB)

In water sources these compounds are both produced by some species of cyanobacteria and actinobacteria. MIB is produced during the life cycle of these bacteria whilst Geosmin is trapped in the cell bodies and released in high concentrations when these bacteria die. They can be directly related to summer algae blooms. Other sources can be attributed to the decay of timber, leaves and other naturally occurring organic matter commonly found in surface waters. Both of these compounds have extremely low odour thresholds. For Geosmin this is approximately 15 ng/L and for MIB 20 ng/L. They are responsible for many 'taste and odour' issues in drinking waters.

Phenols

Phenol is an industrial chemical used in the manufacture of resins, plastics, fibres, pharmaceuticals and herbicides. It can also be found in disinfectants and cleaners. Chlorophenols are produced during water treatment when phenol is present in the water. They are also a breakdown product of phenoxy herbicides. Bromophenols are produced during the chlorination of water when phenolic compounds and bromide ions are present in the water. They are also used as fungicides, wood preservatives and in the production of flame retardants.

Anisoles

These compounds are formed when naturally occuring 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. These compounds have very low taste and odour thresholds (low ng/L levels for chloroanisoles and sub ng/L levels for bromoanisoles).

Pyrazines

2-Isopropyl-3-methoxypyrazine (2-IPMP) and 2-Isobutyl-3-methoxypyrazine (2-IBMP) are formed from actinobacteria in reservoirs. They have very low taste and odour thresholds (low ng/L levels).

2-EDD and 2-EMD

These compounds are by-products of fibreglass and resin manufacture. Their odours are concentration dependent and they are in fact more odorous at lower concentrations. Their odour thresholds are both approximately 10 ng/L.

Analytical Technique

Sample Preparation

1 L of sample is extracted with 100 mL of Dichloromethane. The solvent is then passed through a Horizon Dry Disk (hydrophobic membrane) and evaporated down to 0.5 mL on a Turbovap. The extract is spiked with D8-Napthalene internal standard and transferred to an autosampler vial ready for analysis by GC/QQQ. A Quality Control Spike at 40 ng/L is also extracted. Direct solvent standards at 0, 10, 20, 30, 40 and 50 ng/L are analysed alongside the extracted samples and quality control spike.

Instrumentation

Agilent 7000 Triple Quadrupole GC/MS Operating Conditions

Gas Chromatograph	**Agilent 7890A GC with Multi-Mode Inlet**
Automatic Sampler	Agilent 7693 Injector and Autosampler
Inlet	Multi-Mode Inlet
Inlet Liner	Ultra Inert Splitless Single Taper Liner
Inlet Parameters	Pulsed Splitless, 60°C (0.5 min), 600°C/min to 300°C (30 min)
Injection Volume	2 µL
Column	30 m x 0.25 mm x 0.25 µm HP-5MS Ultra Inert Column
Carrier Gas	Helium, Constant Flow
Oven Temperature Program	35 °C (1.0 min), 10 °C/min to 150 °C, 20 °C/min to 270 °C
Run Time	18.5 min
Mass Selective Detector	**Agilent 7000 Triple Quadrupole**
Acquisition Mode	EI MRM
Source, Quad, Transfer Line Temperatures	230 °C, 150 °C, 300 °C respectively

MRM Transitions

Peak	Compound	Quantitation			Qualitation		
		Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)
1	2-Ethyl-4-methyl-1,3-dioxolane (2-EMD)	87.1	59.0	5	87.1	41.0	12
2	Phenol	94.0	66.0	10	94.0	65.0	20
3	2-Chlorophenol	128.0	92.0	5	128.0	64.0	20
4	2-Ethyl-5,5-dimethyl-1,3-dioxane (2-EDD)	115.0	69.0	5	115.0	45.0	15
5	2-Bromophenol	172.0	93.0	10	172.0	65.0	20
6	2-Isopropyl-3-methoxypyrazine (2-IPMP)	137.0	109.1	5	137.0	105.0	10
7	3-Chloroanisole	142.0	112.0	10	142.0	77.0	25
8	4-Chloroanisole	142.0	127.0	10	142.0	99.0	25
9	2-Chloroanisole	142.0	127.0	10	142.0	99.0	25
10	2,4-Dichlorophenol	162.0	63.0	30	98.0	63.0	5
11	2,3-Dichlorophenol	162.0	63.0	30	98.0	63.0	5
12	2-Isobutyl-3-methoxypyrazine (2-IBMP)	124.0	94.0	10	124.0	81.0	10
13	2-Methyl Isoborneol (2-MIB)	95.1	67.0	10	95.1	55.1	15
14	2,3,4-Trichloroanisole	210.0	194.9	10	210.0	166.9	25
15	2,4,6-Trichlorophenol	132.0	97.0	10	196.0	97.0	30
16	2,6-Dibromophenol	252.0	143.0	25	252.0	63.0	50
17	Geosmin	112.1	97.1	10	112.1	83.0	10
18	2,4,6-Trichloroanisole	210.0	194.9	10	210.0	166.9	25
19	2,4,6-Tribromoanisole	346.0	303.0	35	344.0	329.0	15
20	2,4,6-Tribromophenol	329.7	141.0	30	141.0	62.0	15
	Naphthalene D8 (Internal Standard)	136	108	30			

Results and Discussion

Instrument

The Agilent 7000 Triple Quadrupole GC/MS was chosen for this method as it provides excellent selectivity and sensitivity. It utilises Mass Hunter Software which provides enhanced confidence in reporting.

MRM Optimisation

Each compound was run individually in Scan mode (MS1 Scan) to determine the precursor ion. Product ion scans were then produced at a variety of collision energies. For each compound, 2 MRM transitions were chosen, one for quantitation, the other for qualitation. The resolution for each transition was set to MS1 Wide and MS2 Unit. The analytical run was then divided into 6 time segments and the dwell times were adjusted to give a minimum of 3 cycles per second. Figure 1 shows a typical chromatogram of a 10 ng/L standard.

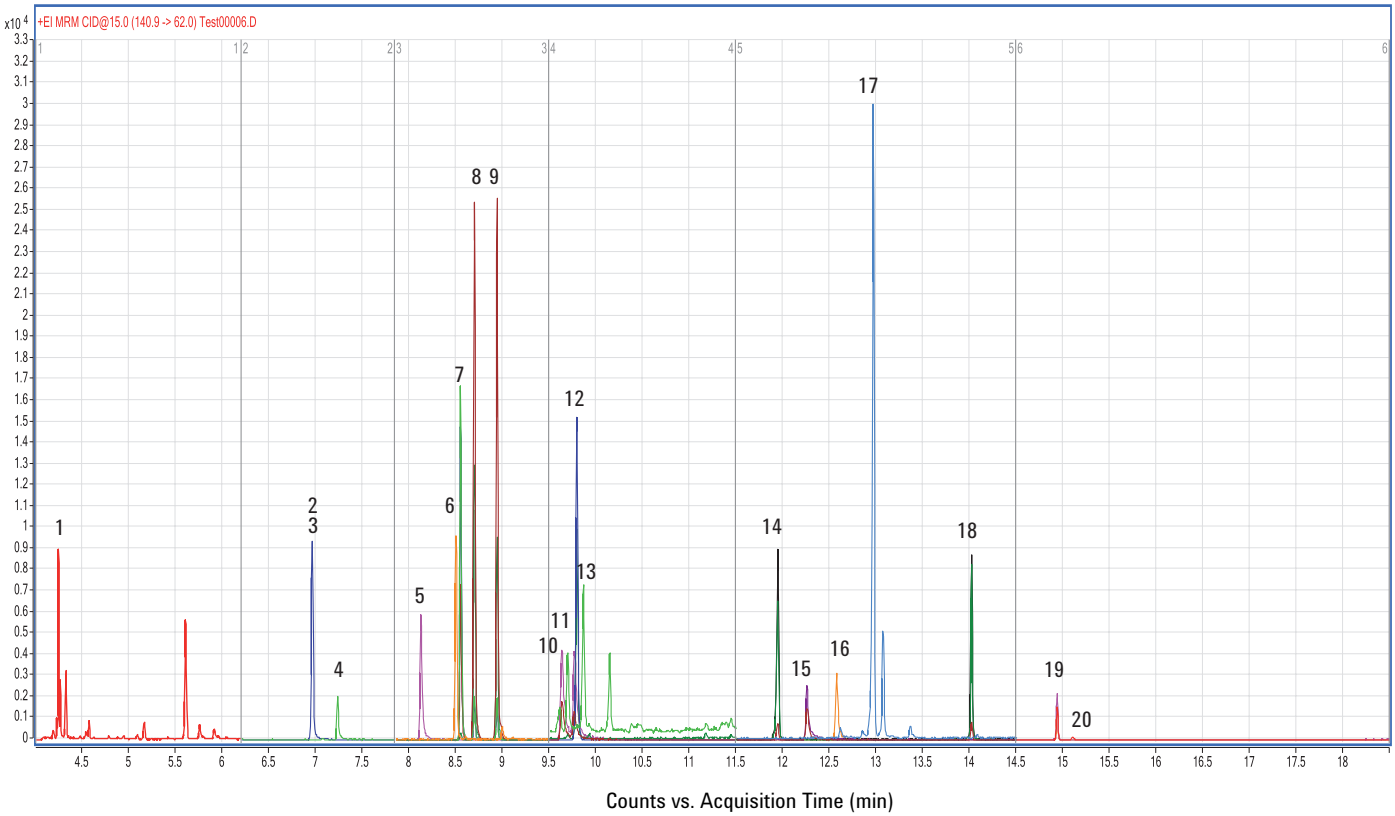

Figure 1: 10 ng/L Standard Chromatogram, no Internal Standard (Refer to MRM Transitions Table for Compound Names).

Analytical Method

The use of extracted samples and analysis on the Agilent 7000 Triple Quadrupole GC/MS ensured that low detection limits were achieved. In this method, the detection limits for all of the compounds are 1 ng/L. The calibration range for all compounds was 0 to 50 ng/L with standards at 0, 10, 20, 30, 40 and 50 ng/L. Figures 2 to 5 show screenshots from the Mass Hunter software, with typical calibration plots for Geosmin, MIB, 4-Chloroanisole and 2,3,4-Trichloroanisole. In each figure, a real sample result along with the signal/noise (S/N) measurement has been highlighted. All compounds demonstrate good S/N measurements. The Geosmin result at 1.1 ng/L, which is close to the reporting limit of 1 ng/L, has a S/N of 128:1 and 4-Chloroanisole at 2.1 ng/L has a S/N of 1653:1. This demonstrates that the detection limits for some compounds, should the method be fully validated to NS30 standards, may be even lower than 1 ng/L. 2,3,4-Trichloroanisole in the sample at 0.1 ng/L, well below the reporting limit of 1 ng/L, demonstrates this with a S/N of 138:1.

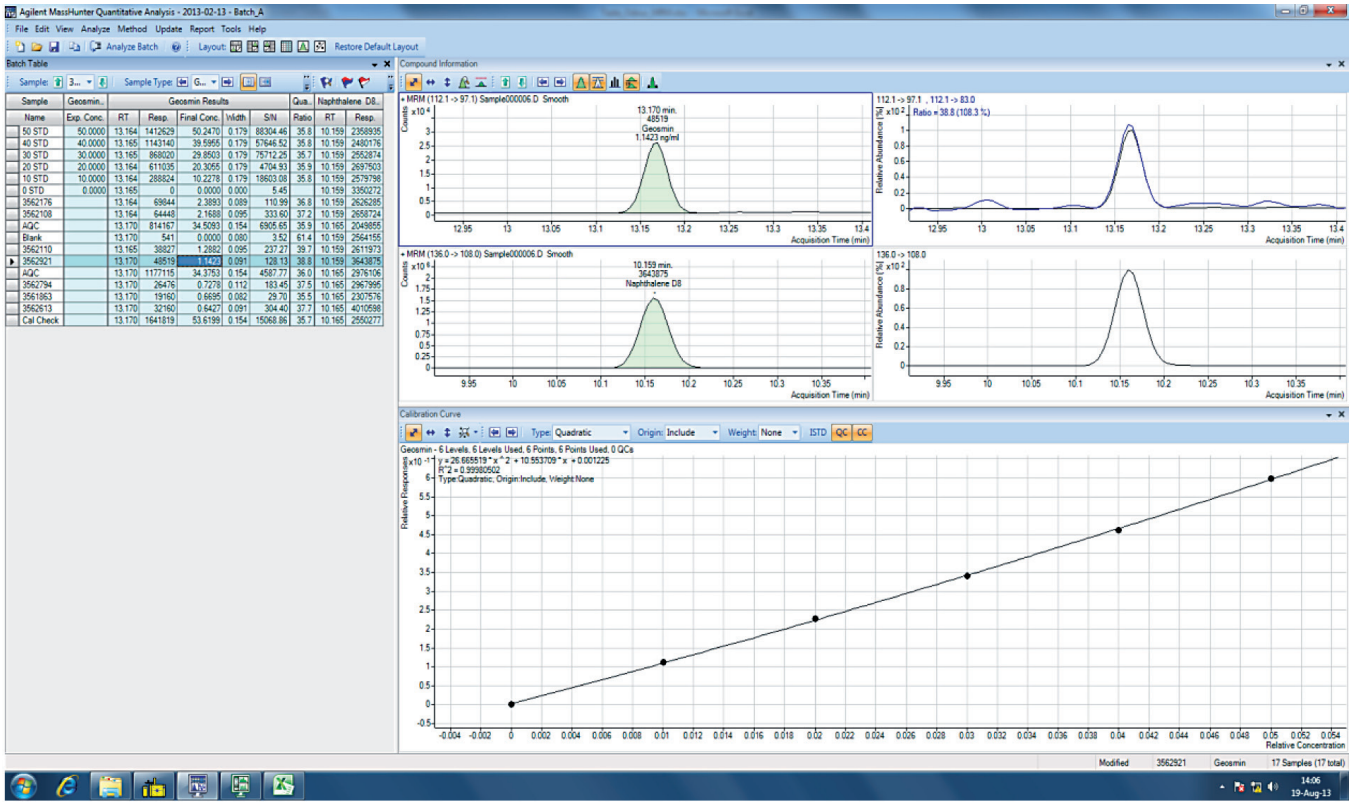

Figure 2: Geosmin in a water sample at a concentration of 1.1 ng/L (S/N: 128/1).

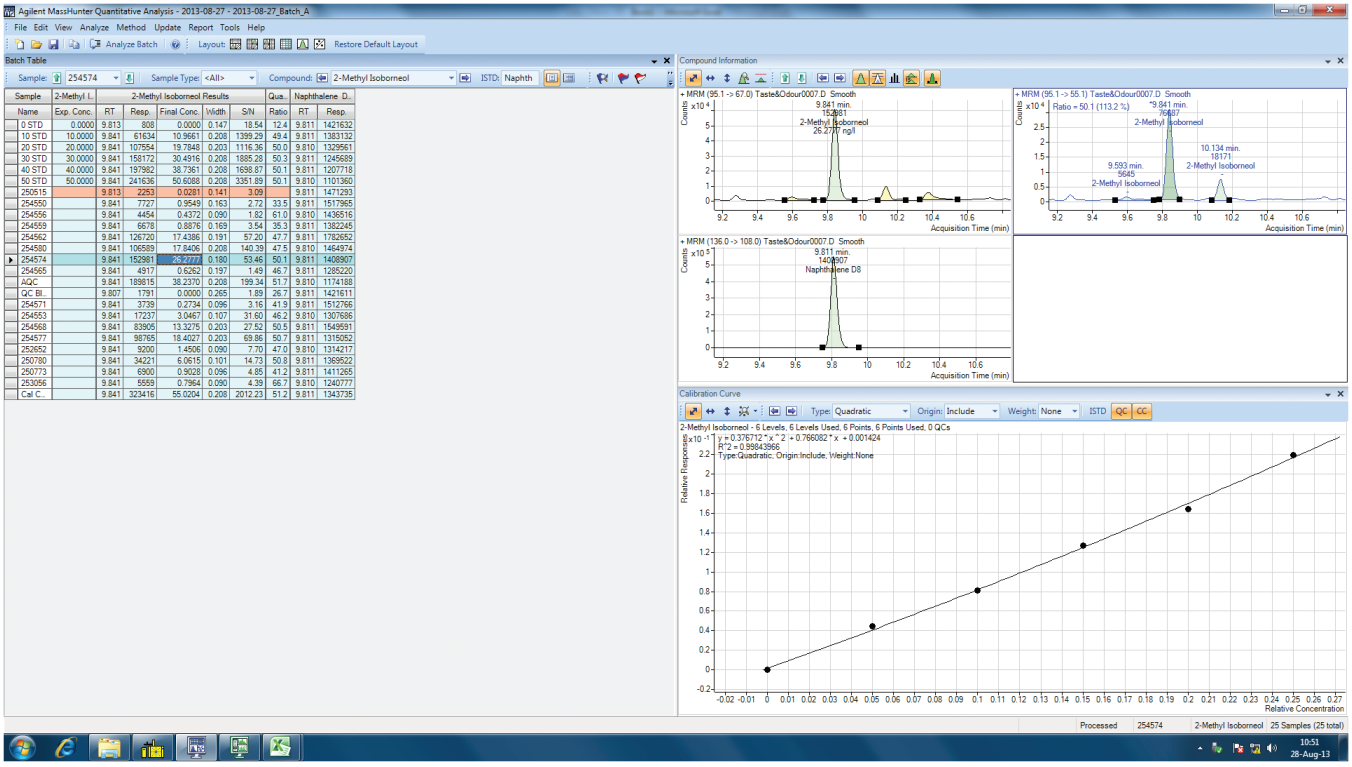

Figure 3: MIB in a water sample at a concentration of 26.3 ng/L (S/N: 53/1).

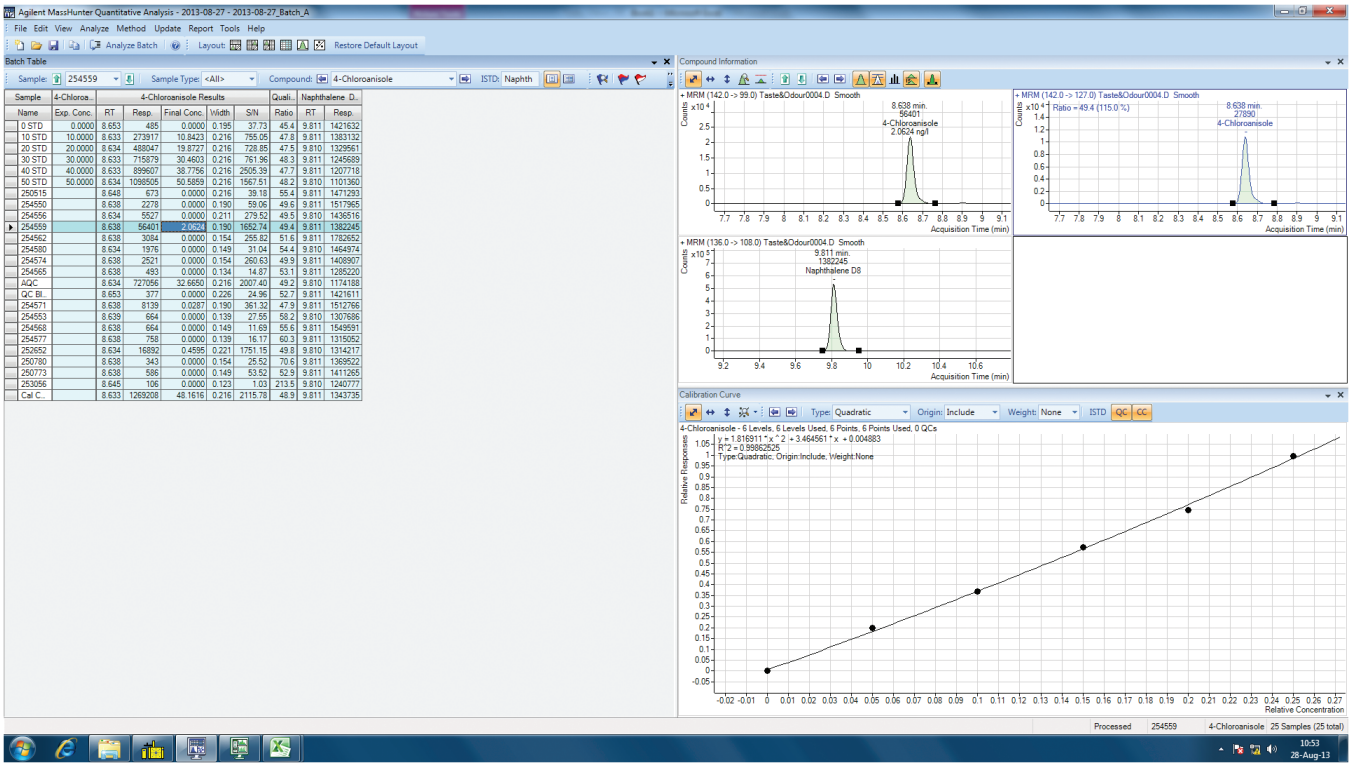

Figure 4: 4-Chloroanisole in a water sample at a concentration of 2.1 ng/L (S/N: 1653/1).

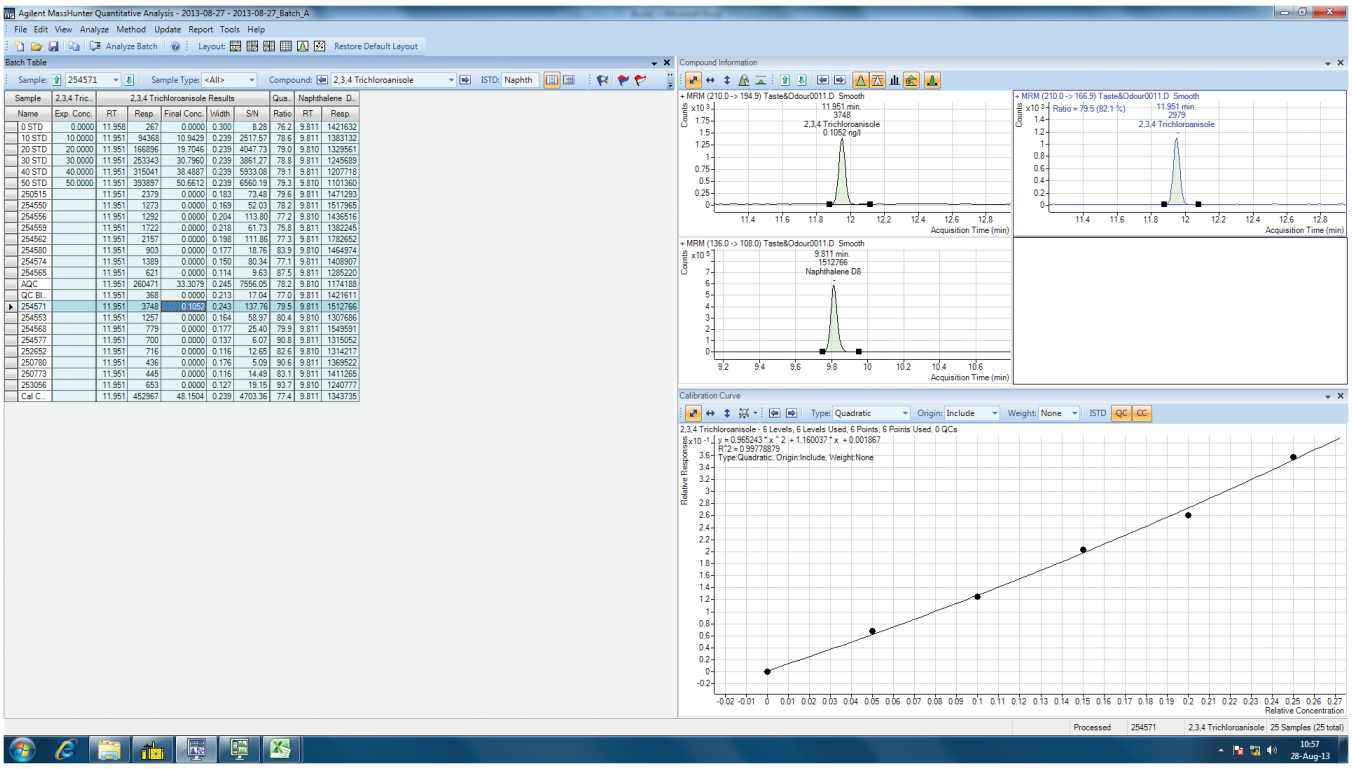

Figure 5: 2,3,4-Trichloroanisole in a water sample at a concentration of 0.1 ng/L (S/N: 138/1).

Conclusions

A method has been developed that for the determination of 'taste and odour' compounds in potable water using the Agilent 7000 Triple Quadrupole GC/MS. There are 20 target compounds in the analytical suite, including Geosmin, MIB, Phenols, Anisoles, Pyrazines as well as 2-EMD and 2-EDD. The method demonstrates excellent sensitivity with LODs of 1 ng/L for all compounds.

References

1. H.R. Rogers, "Factors causing off-taste in waters, and methods and practices for the removal of off-taste and its causes," DETR/DWI 5008/1, **2001**.

2. "The determination of taste and odour in drinking waters (2010)," Environment Agency (England and Wales, UK), Methods for the examination of waters and associated materials.

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Published in USA, December 18, 2013
5991-3721EN

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