Improving Confidence in the Identification of Pesticide Residues by GC/MS using Target Deconvolution

Chris Sandy[1] , Marc Tischler[2]
[1]Agilent Technologies UK Ltd., 610 Wharfedale Road, Winnersh, Berkshire, RG41 5TP, UK
[2]Agilent Technologies Inc., 5301 Stevens Creek Blvd, Santa Clara, CA 95051-7201,USA

Introduction

The bench top gas chromatograph / single quadrupole mass spectrometer (GC/MS) instrument has been in use a routine analytical tool for the identification and quantitation of target analytes for the last 25 years. Over this time period, GC/MS systems have become more sensitive, providing ever lower limits of detection for target analytes in a wide range of sample types ranging from Food, Environmental, Forensic / Clinical and Flavour / Fragrance.

However, what hasn't changed is the method of identifying analytes based on retention time and the ratio of qualifier ions to a single quantification ion. Whilst this method works well for the identification of target analytes in relatively 'clean' chromatograms, complex extracted samples such as those obtained from Food and / or Environmental samples often have interfering compounds from the sample matrix which can cause false positive and false negative results and make data review both more labour intensive and less objective.

One way to achieve better selectivity from a unit mass resolution GC/MS system is to employ mass spectral deconvolution and comparison of full, deconvoluted component mass spectra to a reference database. Thus the use of deconvoluted component spectra can provide additional confidence in the identification of target analytes over-and-above that provided by retention time and ion ratio measurements.

The Agilent Technologies 7890B / 5977A Bench top GC/MS System

Mass Spectral Deconvolution

In simple terms, mass spectral deconvolution provides additional selectivity by the grouping of ions that co-maximize in time to produce deconvoluted 'component' mass spectra. Part of the deconvolution process includes the correction of spectral skewing that is a feature of scanning mass spectrometers. One example of a popular deconvolution program is the Automated Mass Spectral Deconvolution Identification System (AMDIS) that may be freely downloaded from the NIST website http://chemdata.nist.gov/mass-spc/amdis/. Agilent has been using AMDIS for the deconvolution of unit mass GC/MS data since the introduction of Deconvolution and Reporting Software (DRS) for the MS ChemStation in April 2004.

A diagram summarizing the process of mass spectral deconvolution to resolve the spectra of co-eluting analytes is shown in Figure 1.

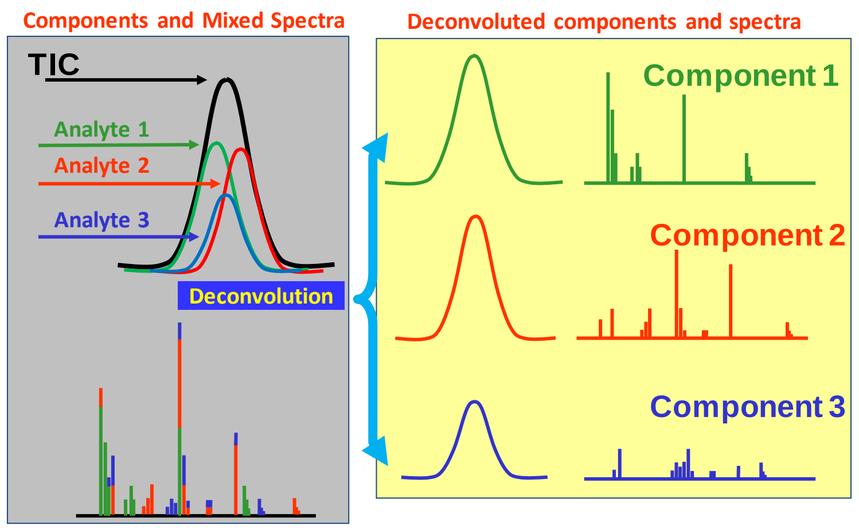

Figure 2. Overview of the process of mass spectral deconvolution

MH Target Deconvolution

The latest revision of Mass Hunter (MH) Quantitative analysis software (Version B.06.00), released in March 2013, includes a fully integrated feature called 'Target Deconvolution' (TD). TD provides additional confidence in target analyte identification through the seamless implementation of automated mass spectral deconvolution and the matching of full, deconvoluted component spectra to a reference mass spectral database. Figure 3 shows a flow diagram of how TD is incorporated in to Mass Hunter Quant software.

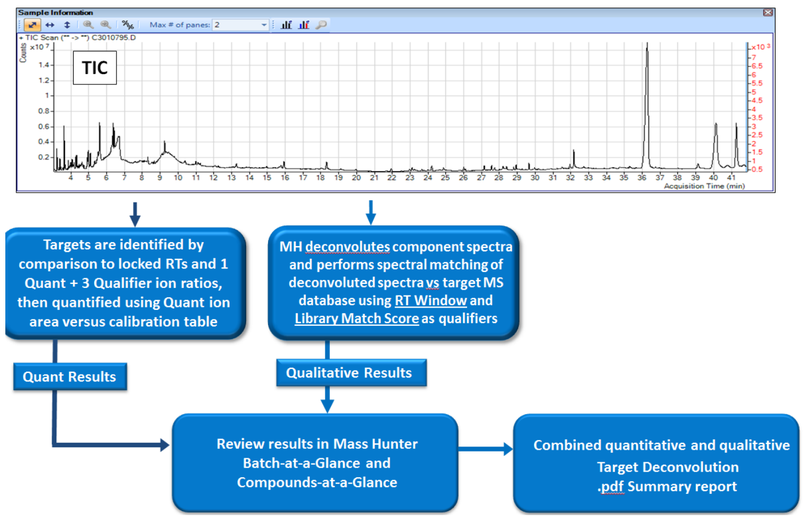

Figure 3. Target Deconvolution workflow in Mass Hunter Quant SW

Data Review

After data processing, data may be reviewed interactively, quickly and efficiently using the Batch-at-a-Glance (BAG) and Compounds-at-a-Glance (CAG) features of the MH Quant software. An annotated screen shot of the target deconvolution results from an analyte identified in a grape extract is shown in Figure 4.

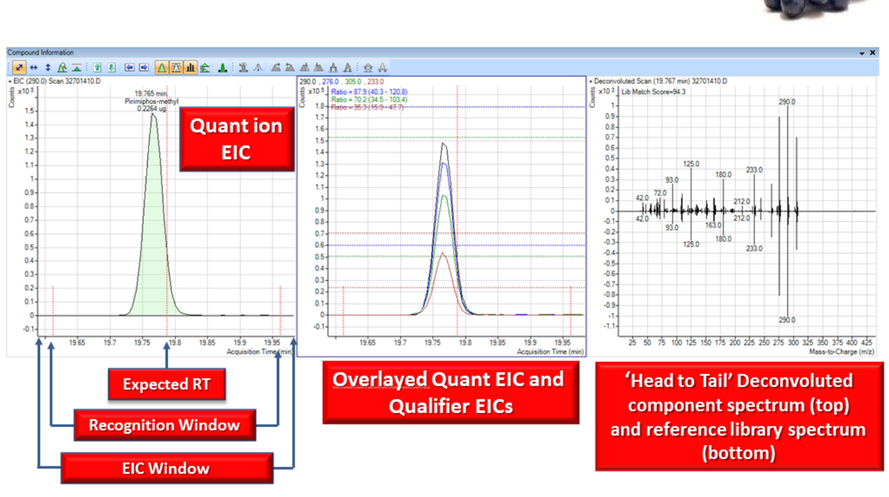

Figure 4. Target Deconvolution analyte data review in Mass Hunter Quant SW

The right hand graphic shows the library match score (LMS) and head-to-tail display of the deconvoluted component spectrum and the spectrum from the reference library.

Additional, powerful data review is provided by the fully customizable CAG feature of MH Quant software. The compounds from an individual sample or set of samples can be reviewed and compared interactively and MH outliers used to highlight non-compliant target analytes. MH has 48 standard outliers and the analyst may create additional custom outliers. Non-compliant target analytes are shaded in the CAG display grid allowing the operator to quickly review results and perform additional actions such as manual integration, if required. A screen-shot showing 25 of the 926 target analytes screened in a grape extract sample with the shading of analyte chromatograms which fail outlier conditions is shown in Figure 5. The reference target MS database used was created by converting the retention time locked (RTL) Agilent Pesticide and Endocrine Disruptor MS Library to MH format.

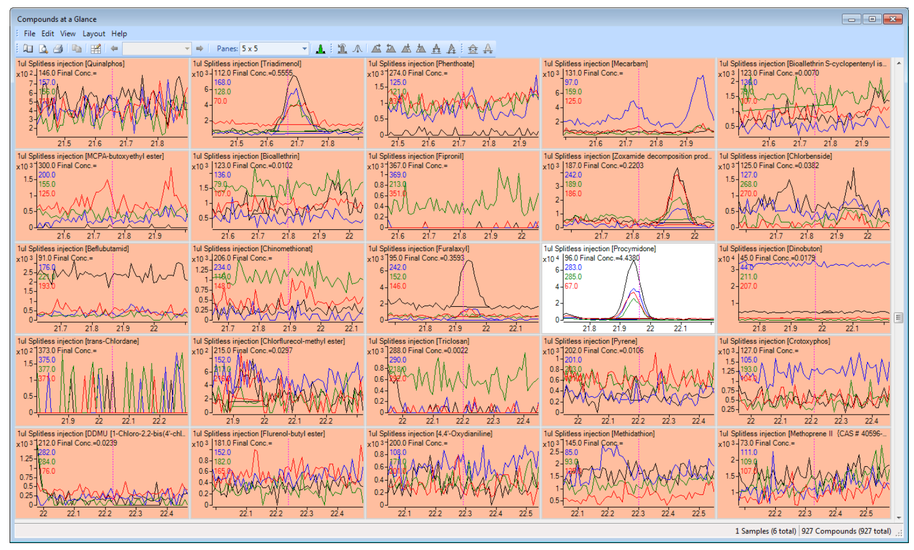

Figure 5. Compounds-at-a-Glance review of target analytes in a grape extract. Analytes failing outlier tests are shaded red.

TD Reporting

Turning vast amounts of analytical data into usable reports is a key requirement of modern analytical software. Accompanying the new TD feature of MH Quant software is very fast reporting of TD results using a pre-defined .pdf template. The TD report shows those analytes identified by mass spectral deconvolution and the Purity metric is used to correct quantitative results for interference from any closely eluting component that co-elutes with a target analyte. An example .TD .pdf report is shown in Table 1.

Targeted Deconvolution Report

Sample Name: 1ul Splitless injection
Data File: C3010795.D
Quant Batch Name: C:\Users\csandy\Desktop\LGC Grapes RTL 1x ESTD\GRAPES\QuantResults\TD_Grapes_II.batch.bin
Last Calib Update: 5/17/2013 2:52:27 PM

R.T.	Cas #	Compound Name	Amount/Conc	LMS	R.T. Diff(sec)	Purity
3.5347	62-53-3	Aniline	0.0209	46	-0.7	100.0
3.5255	108-95-2	Phenol	0.1349	82	-1.4	100.0
3.8376	541-73-1	1,3-Dichlorbenzene	0.0039	70	4.8	100.0
4.1955	95-48-7	2-Methylphenol	0.0369	82	-3.0	40.5
4.3698	106-44-5	4-Methylphenol	0.0333	78	-2.7	95.8
4.3698	108-39-4	m-Cresol	0.0274	76	-3.2	95.4
7.0678	92-52-4	Biphenyl	0.0041	68	-2.2	100.0
7.6001	30560-19-1	Acephate	0.1159	49	-5.4	100.0
7.9672	85-41-6	Phthalimide	0.0193	76	-0.8	68.0
8.5637	33704-61-9	Cashmeran	0.0623	57	-3.4	100.0
8.7472	90-43-7	o-Phenylphenol	0.0387	84	-2.1	100.0
8.8757	100-02-7	4-Nitrophenol	0.0294	59	1.4	100.0
9.9586	84-66-2	Diethyl phthalate	0.0355	86	0.0	93.4
11.0047	126-73-8	Tributyl phosphate	0.6418	95	5.2	99.7
15.9327	84-69-5	Diisobutyl phthalate	1.6577	96	2.3	100.0
16.6761	61676-87-7	Cymiazole	0.0102	46	-8.1	97.7
18.4105	84-74-2	Di-n-butylphthalate	0.2626	89	-0.3	100.0
19.1722	90-98-2	4,4'-Dichlorobenzophenone	0.0348	78	-1.7	96.8
19.9614	10544-50-0	Sulfur (S8)	0.1515	49	-3.3	100.0
20.1541	81-84-5	Naphthalic anhydride	0.0046	80	-1.8	100.0
21.6867	55219-65-3	Triadimenol	0.0358	69	1.1	100.0
21.9436	32809-16-8	Procymidone	0.2848	95	-1.1	99.7
24.6416	85509-19-9	Flusilazole	0.0486	76	2.9	100.0
25.9998	563-12-2	Ethion	0.2273	90	-0.1	100.0
28.4042	36734-19-7	Iprodione	0.1179	82	0.8	100.0
28.6244	18181-80-1	Bromopropylate	0.0038	63	0.5	100.0
28.7988	115-32-2	p,p'-Dicofol	0.1366	87	0.1	100.0
29.3310	84-61-7	Dicyclohexyl phthalate	0.0209	57	2.5	100.0
29.6614	117-81-7	Bis(2-ethylhexyl)phthalate	0.6410	96	0.8	100.0
30.6892	13457-18-6	Pyrazophos	0.0319	72	-1.8	100.0
32.4145	999029-03-7	Cyfluthrin III {CAS # 68359-37-5}	0.0057	52	-3.8	100.0
32.5888	999030-03-4	Cyfluthrin IV {CAS # 68359-37-5}	0.0112	45	3.2	97.0

Table 1. Target Deconvolution .pdf report for a Grape extract

Conclusions

- **Target Deconvolution is a standard feature of MH Quant SW, version B.06.00**
- **TD provides increased confidence in the identification of target analytes by GC/MS**
- **Mass Hunter Quant software provides extremely fast data processing and powerful, fully customizable data review through Batch-at-a-Glance and Compounds-at-a-Glance**
- **Outlier flagging aids interactive data review**
- **TD .pdf reports convert analytical data into usable information**