

Fast GCMSMS Analysis of 76 VOC Compounds using Headspace-Trap Sampling

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1. Fast analysis with HS trap

The analysis of regulated volatile organic compounds in drinking and waste water was shown to be compatible with fast GCMS when a LN2 cold trap (GL Sciences) was mounted at the top of the column directly under the injector [1]. Figure 1 shows a Q3 scan of the GCMS-TQ8040 tandem mass spectrometer of 76 volatile organic compounds (VOC) in water at a concentration of 1 ppb. The column used was a RTX624 20m, 0.18 μ m, and 1 μ m film. The run time was about 10 minutes.

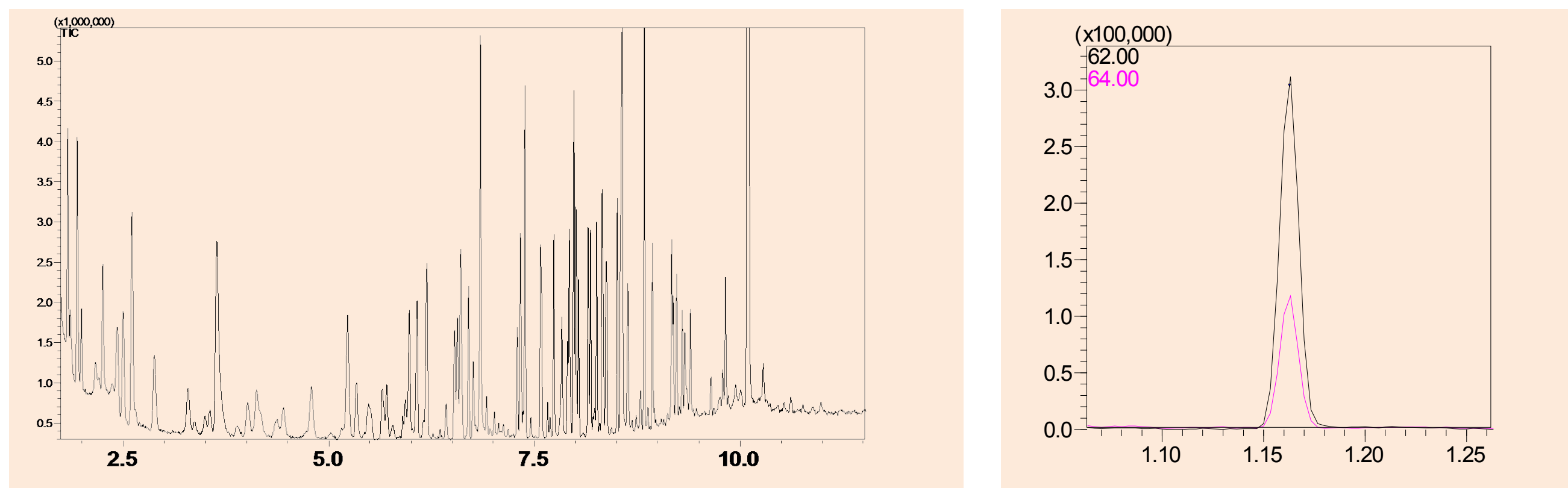


Fig. 1: left: TIC (Q3 scan) of 76 VOC in water after headspace sampling at 60 °C for 15 minutes. Concentration was 1 ppb. right: extracted traces m/z = 62 and 64 (Vinyl Chloride)

2. VOC and MRM

Most VOC molecules show molecular masses below m/z=200. Therefore, possible fragmentation in collision induced dissociation (CID) was checked in detail. Vinyl Chloride shows as largest electron impact fragments m/z=62 and m/z=64. Such a molecule hardly shows high intensity characteristic product ions, which are suitable for MRM mode. As an example the Q3 scan of Vinyl Chloride and Bromochloromethane is shown in figure 2. Product ion scans were performed using m/z=62 and m/z=130 as precursors. Figure 3 shows product ion scans for both compounds at 5V and 15V collision energy. For Vinyl Chloride fragments m/z=28 and m/z=29 are observed but the absolute intensity is rather small indicating that collision induced dissociation does not occur with high probability.

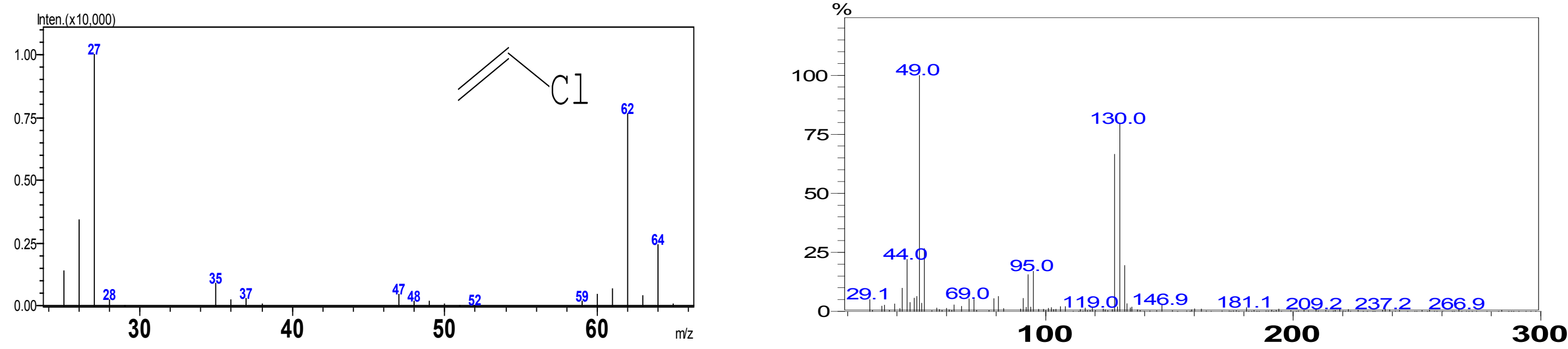


Fig 2: EI spectrum (Q3 scan) of Vinyl Chloride (left) and Bromochloromethane (right)

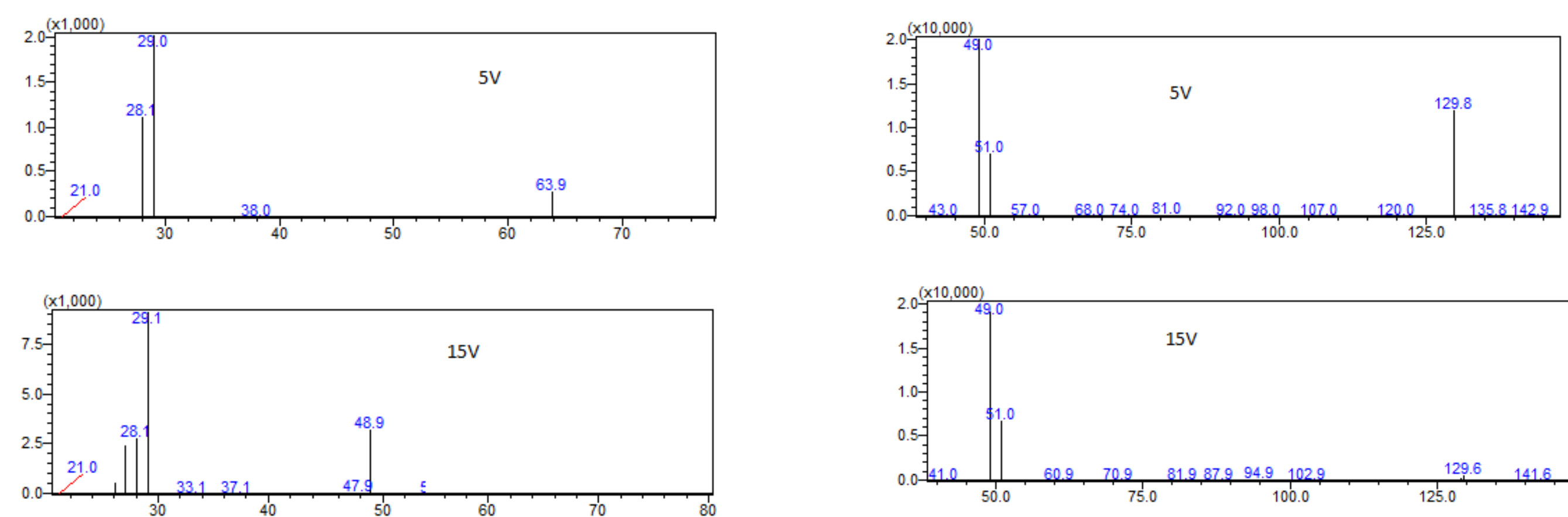


Fig. 3: Product ion scans for Vinyl Chloride (left) and Bromochloromethane (right)

Bromochloromethane shows a high intensity fragment at m/z=49. All 76 VOC related peaks were checked for most abundant CID fragments. Peak signal to noise values were compared when using „real“ mrm transitions and so called pseudo mrm where m/z (precursor) = m/z (product) and the resulting MSMS method is shown in table 1.

Compound	T start	T end		Dwell T	mrm 1	CE 1	mrm 2	CE 2	Compound	T start	T end		Dwell T	mrm 1	CE 1	mrm 2	CE 2
Dichlorodifluoromethane	0.84	1.69	MRM	0.03	85.00>85.00	0	87.00>87.00	0	1,3-Dichloropropane	6.65	7.17	MRM	0.03	76.00>41.00	6	76.00>76.00	0
Chloromethane	0.84	1.69	MRM	0.03	50.00>50.00	0	52.00>52.00	0	Dibromochloromethane	6.65	7.17	MRM	0.03	128.95>128.95	0	130.95>130.95	0
Vinyl chloride	0.84	1.69	MRM	0.03	62.00>62.00	0	64.00>64.00	0	1,2-Dibromoethane	6.65	7.17	MRM	0.03	107.00>107.00	0	109.00>109.00	0
Vinyl chloride D	0.84	1.69	MRM	0.03	65.00>65.00	0	67.00>67.00	0	Chlorobenzene	7.17	7.48	MRM	0.04	112.05>77.00	13	112.05>112.05	0
Bromomethane	0.84	1.69	MRM	0.03	94.00>94.00	0	96.00>96.00	0	Ethylbenzene	7.17	7.48	MRM	0.04	91.10>91.10	0	106.10>106.10	0
Chloroethane	0.84	1.69	MRM	0.03	64.05>64.05	0	66.00>66.00	0	1,1,1,2-Tetrachloroethane	7.17	7.48	MRM	0.04	130.95>95.00	12	91.00>91.00	0
Trichlorofluoromethane	0.84	1.69	MRM	0.03	101.00>101.00	0	103.00>103.00	0	p-Xylene	7.17	7.48	MRM	0.04	106.00>91.00	13	91.00>91.00	0
CS2	1.69	2.06	MRM	0.1	76.00>76.00	0	78.00>78.00	0	m-Xylene	7.17	7.48	MRM	0.04	106.00>91.00	13	91.00>91.00	0
1,1-Dichloroethene	1.69	2.06	MRM	0.1	96.00>61.00	10	98.00>63.00	10	o-Xylene	7.48	7.86	MRM	0.05	106.00>91.00	13	91.00>91.00	0
Methylene chloride	2.06	2.66	MRM	0.1	84.00>49.00	5	86.00>49.00	5	Styrene	7.48	7.86	MRM	0.05	104.10>78.00	12	104.10>104.10	0
MTBE	2.06	2.66	MRM	0.1	73.00>73.00	0	73.00>43.00	23	Bromofluorbenzen	7.48	7.86	MRM	0.05	176.00>95.00	20	174.00>95.00	20
Hexan	2.06	2.66	MRM	0.1	57.00>57.00	0	57.00>41.00	15	Tribromomethane	7.48	7.86	MRM	0.05	172.90>172.90	0	170.90>170.90	0
trans-1,2-Dichloroethene	2.06	2.66	MRM	0.1	96.00>61.00	20	98.00>63.00	20	Isopropylbenzene	7.48	7.86	MRM	0.05	105.10>77.00	12	120.15>105.10	0
1,1-Dichloroethane	2.66	3.19	MRM	0.1	63.05>27.00	22	65.05>27.00	22	Bromobenzene	7.86	8.12	MRM	0.03	156.00>77.00	12	156.00>156.00	0
Diisopropylether	2.66	3.19	MRM	0.1	45.00>45.00	0	63.00>63.00	0	1,1,2,2-Tetrachloroethane	7.86	8.12	MRM	0.03	167.90>84.80	6	91.00>91.00	0
2,2-Dichloropropane	3.19	3.72	MRM	0.07	77.05>77.05	0	79.05>79.05	0	1,2,3-Trichloropropane	7.86	8.12	MRM	0.03	75.00>75.00	0	110.00>110.00	0
ETB	3.19	3.72	MRM	0.07	87.10>59.10	12	87.00>87.00	0	n-Propylbenzene	7.86	8.12	MRM	0.03	120.10>91.00	13	91.00>91.00	0
cis-1,2-Dichloroethene	3.19	3.72	MRM	0.07	96.00>61.00	20	98.00>63.00	20	2-Chlorotoluene	7.86	8.12	MRM	0.03	126.10>91.00	13	91.00>91.00	0
Bromochloromethane	3.72	4.61	MRM	0.04	129.95>49.00	21	128.00>49.00	21	1,3,5-Trimethylbenzene	7.86	8.12	MRM	0.02	120.10>105.00	13	105.00>105.00	0
Trichloromethane	3.72	4.61	MRM	0.04	83.00>83.00	0	85.00>85.00	0	4-Chlorotoluene	7.86	8.12	MRM	0.02	126.10>91.00	13	91.00>91.00	0
1,1,1-Trichloroethane	3.72	4.61	MRM	0.04	97.00>61.00	22	99.00>63.00	22	tert-Butylbenzene	8.12	8.71	MRM	0.02	119.10>91.00	14	91.00>91.00	0
Tetrachloromethane	3.72	4.61	MRM	0.04	116.95>116.95	0	118.95>118.95	0	1,4-dichlorobenzene D4	8.12	8.71	MRM	0.02	146.00>111.00	16	146.00>146.00	0
1,1-Dichloropropane	3.72	4.61	MRM	0.04	110.00>75.00	20	112.00>77.00	20	1,2-dichlorobenzene D4	8.12	8.71	MRM	0.02	146.00>111.00	16	146.00>146.00	0
Benzene	4.61	4.9	MRM	0.2	78.10>78.10	0	52.00>52.00	0	Hexachloroethane	8.12	8.71	MRM	0.02	201.00>166.00	20	203.00>168.00	20
1,2-Dichloroethane	4.9	5.4	MRM	0.07	98.00>62.00	10	99.90>64.00	10	1,2,4-Trimethylbenzene	8.12	8.71	MRM	0.02	120.10>105.00	13	105.00>105.00	0
Heptane	4.9	5.4	MRM	0.07	71.10>43.10	12	71.10>71.10	0	sec-Butylbenzen	8.12	8.71	MRM	0.02	134.10>105.00	13	105.00>105.00	0
Fluorobenzene	4.9	5.4	MRM	0.07	96.10>96.10	0	70.00>70.00	0	4-Isopropyltoluene	8.12	8.71	MRM	0.02	134.20>119.00	13	119.00>119.00	0
Trichloroethene	5.4	5.81	MRM	0.2	130.00>95.00	13	132.00>97.00	20	1,3-Dichlorobenzene	8.12	8.71	MRM	0.02	146.05>111.00	12	111.00>111.00	0
1,2-Dichloropropane	5.81	6.27	MRM	0.06	63.00>63.00	0	62.00>62.00	0	1,4-Dichlorobenzene	8.12	8.71	MRM	0.02	146.05>111.00	12	111.00>111.00	0
Dibromomethane	5.81	6.27	MRM	0.06	173.90>92.90	20	94.90>94.90	15	n-Butylbenzene	8.12	8.71	MRM	0.02	134.00>91.00	12	91.00>91.00	0
Bromodichloromethane	5.81	6.27	MRM	0.06	83.00>83.00	0	85.00>85.00	0	Bis(2-chloro-1-methyl)ether	8.12	8.71	MRM	0.02	69.00>41.00	12	69.00>69.00	0
cis-1,3-Dichloropropene	6.27	6.65	MRM	0.06	75.05>75.05	0	77.05>77.05	0	1,2-Dichlorobenzene	8.12	8.71	MRM	0.02	146.05>111.00	12	111.00>111.00	0
Octane	6.27	6.65	MRM	0.06	85.20>43.10	13	43.10>43.10	0	1,2-Dibromo-3-chloropropane	8.71	9.03	MRM	0.1	156.90>75.00	14	43.00>43.00	0
Toluene	6.27	6.65	MRM	0.06	91.10>65.00	15	91.10>91.10	0	1,3,5-trichlorobenzene	8.71	9.03	MRM	0.1	180.00>145.00	20	182.00>147.00	20
Toluene D8	6.27	6.65	MRM	0.06	98.20>98.20	0	100.20>100.20	0	1,2,4-Trichlorobenzene	9.03	10	MRM	0.05	179.95>145.00	13	179.95>179.95	0
trans-1,3-Dichloropropene	6.65	7.17	MRM	0.03	110.00>75.00	15	75.00>75.00	0	1,1,2,3,4,4-Hexachloro-1,3-butadiene	9.03	10	MRM	0.05	224.85>189.80	14	224.85>224.85	0
Tetrachloroethene	6.65	7.17	MRM	0.03	165.95>130.90	22	128.90>94.00	15	Naphthalene	9.03	10	MRM	0.05	128.10>128.10	0	128.10>128.10	0
1,1,2-Trichloroethane	6.65	7.17	MRM	0.03	97.00>61.00	15	97.00>97.00	0	1,2,3-trichlorobenzene	9.03	10	MRM	0.05	179.95>144.90	13	179.95>179.95	0

Table 1: MSMS transitions used in the method

3. MRM calibration with VOCs

Calibration runs with internal standards (selected deuterized) were performed. The concentrations used cover 0.05, 0.2, 0.5 and 1 ppb. Figure 4 shows peaks for the lowest concentration and calibration curves for a selection of compounds. Figure 5 shows the peaks measured when the MS was set to selected ion mode (Q3) for Vinyl Chloride and others. The GCMS-TQ8040 can be operated in mrm/sim (mrm/scan) modes so that the best setting in terms of sensitivity can be selected.

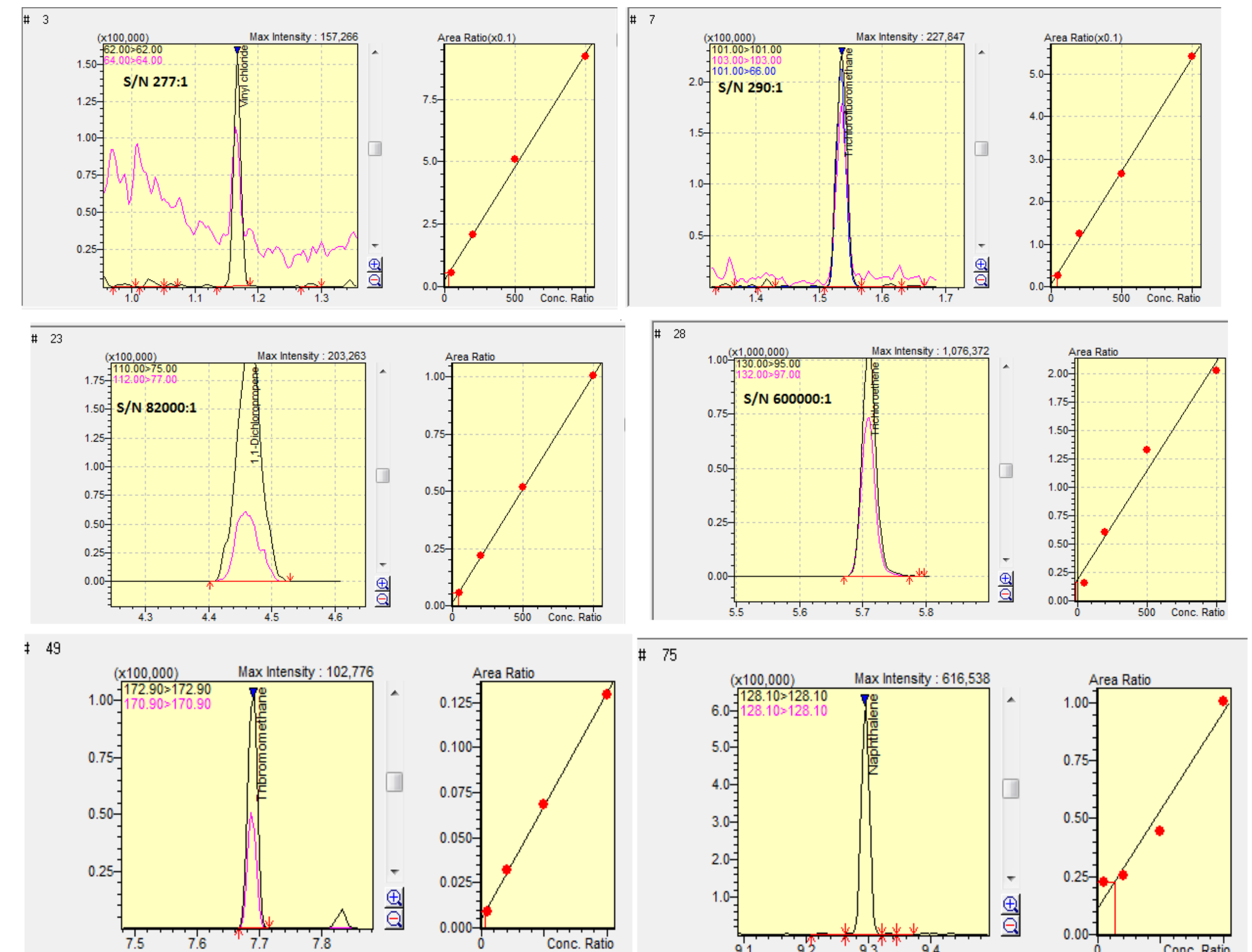


Fig. 4: selected compounds of the VOC mix which were acquired in (pseudo) mrm

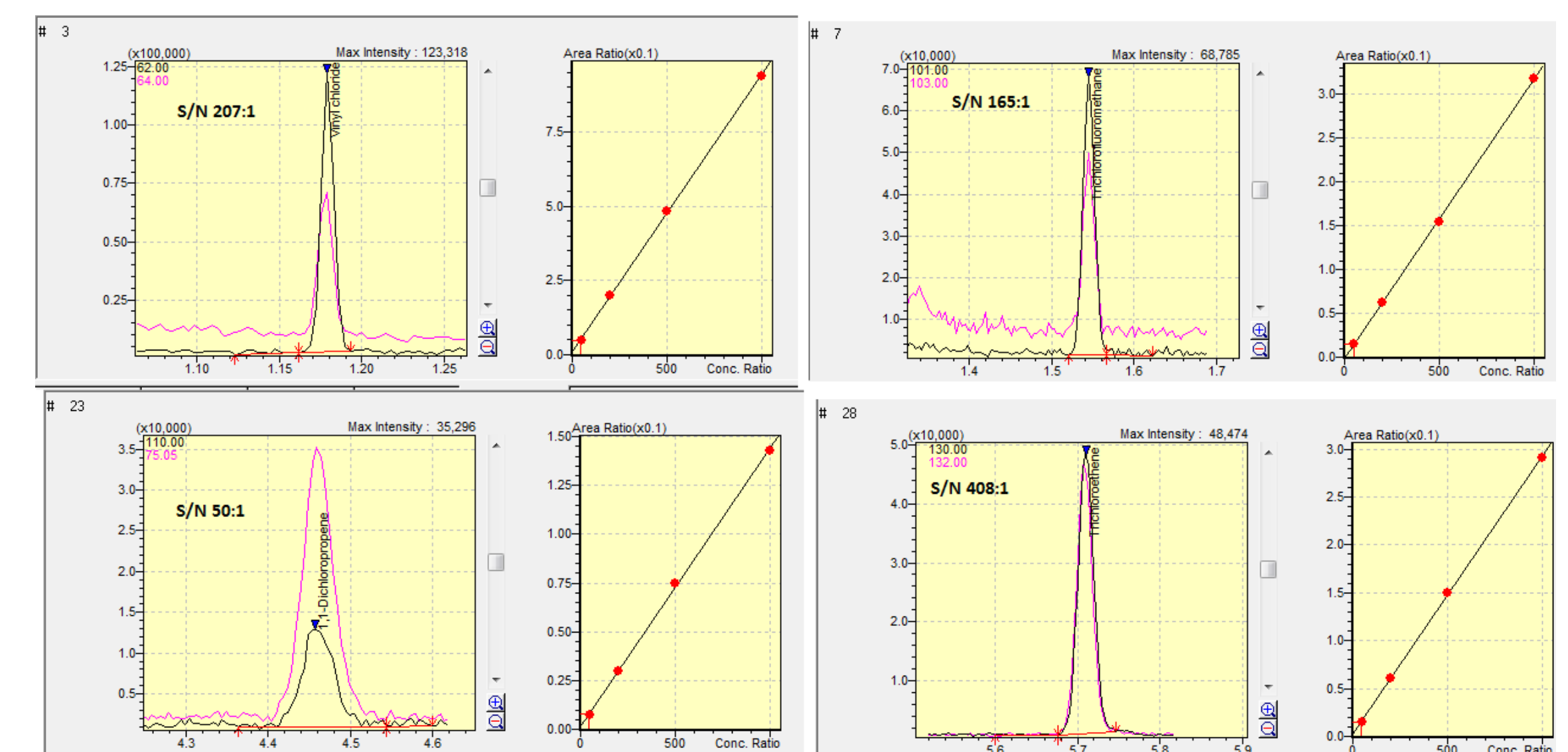


Fig. 5: compounds measured in SIM mode (Q3) for comparison

The signal to noise (RMS) calculation indicates that the method using mrm mode gives much higher values compared to SIM (Q3) for most of the compounds. For molecules which show EI base signals below m/z 100 the sensitivity is comparable in SIM and pseudo mrm mode.

4. Conclusion

Using triple quadrupole instrumentation the sensitivity can be drastically increased for many volatile organic compounds (VOC). For compounds with molecular ion mass below m/z = 100 the sensitivity in pseudo mrm and SIM is comparable. This is due to the fact that in SIM the signal intensity might be higher compared to pseudo mrm mode but the noise is also increased.

[1] H.-U. Baier, P. Meletis and S. Schröder, LCGC The Application Notebook March 2, 2012

