Application Note

Instrument: Pegasus® BT

Analysis of Synthetic Greenhouse Gases and Ozone-Depleting Substances with Medusa Pegasus® BT GC-TOFMS

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Introduction

Synthetic greenhouse gases and ozone depleting substances in ambient air are important due to their global warming potential and the devastating effect on the ozone layer. The measurements are challenged by their low abundances and slow changes in the atmosphere. In order to properly represent/track their trend in the atmosphere (increasing/decreasing), the methods used must be sensitive down to their ppt to sub-ppt ambient air level and also precise (within 1% for most of the species). Linearity is especially important for species which vary greatly in the atmosphere due to pollution events, like in urban areas.

Currently the measurements within the Advanced Global Atmospheric Gases Experiment network (AGAGE, https://agage.mit.edu/) are performed by pre-concentration of 2 L ambient air using a Medusa system[1] and analysis on GC-qMS in selected ion monitoring (SIM) mode. The pre-concentration step is necessary in order to detect the low ambient levels. This method is sensitive, precise, robust, and linear, but it is unable to record the presence of species which are not already on the list. In contrast, time-of-flight mass spectrometers (TOFMS) are known for the ability to provide comprehensive compositions of the samples introduced, so in this work we have explored the capabilities of the LECO *Pegasus* BT TOFMS as a potential replacement for the quadrupole mass spectrometer (qMS) in the current Medusa GC-qMS system.

Experimental

Two sets of experiments were performed. In the first set, under the current AGAGE Medusa GC-qMS operation[1], two litres of compressed ambient air (S-025) were sampled in the Medusa system, analytes were trapped at -170 °C, unwanted components flushed away, and the target fraction (halogenated hydrocarbons) was thermally desorbed onto a Porabond Q (Agilent Technologies) plot column (25 m x 0.32 mm) housed in an Agilent 7890 GC. The detection was done on an Agilent 5975 qMS in SIM mode. More instrumental details are given in Table 1.

Table 1. Medusa GC-MS parameters for both tested configurations.

Parameter	Agilent 5975 MS system	LECO *Pegasus* BT TOFMS system
Sample/injection	2 L compressed ambient air (S-025), thermally desorbed	2 L compressed ambient air (S-025), thermally desorbed
Carrier Gas	He @ ~4 ml/min (pressure driven)	He @ ~4 ml/min (pressure driven)
Column	PoraBondQ 25 m x 0.32 mm x 5 µm	PoraBondQ 25 m x 0.32 mm x 5 µm
Temperature Program	Hold at 40 °C for 20 min, ramp to 200 °C @25 °C/min, and hold at 200 °C for 8 min	Hold at 40 °C for 20 min, ramp to 200 °C @25 °C/min, and hold at 200 °C for 8 min
Transfer Line	200 °C	200 °C
Ion Source	230 °C	200 °C
Electron Energy	70 eV	70 eV
Acquisition Rate	6 datapoints/s (SIM)	5 spectra/s
Mass Range	Up to 15 ions per segment (SIM)	33-250 amu

Another set of the same experiment was performed later with only one difference: the detection. Namely, the Agilent 5975 qMs was disconnected from the system and replaced with the LECO *Pegasus* BT TOFMS detector. The instrument was placed on a separate bench, 11 cm lower than the GC bench (Fig. 1). This was necessary because dismounting the existing GC-Medusa system and fitting it in the normal GC-TOFMS configuration was troublesome. With the TOFMS lowered, the transfer line aligned perfectly to the GC oven's side hole. TOFMS data were acquired and processed with ChromaTOF® ver. 5.20, but the acquisition start/stop was triggered by the Medusa acquisition software (GCWerks, www.GCWerks.com). Full mass spectra were recorded in the range 33 amu – 250 amu, at 5 Hz or 20 Hz. Peak deconvolution algorithm was applied to get peak true mass spectra, and components in the sample were identified against the NIST11 and a custom-built MS library. These results were compared to the ones previously obtained in the same experiment when the Agilent 5975 qMS was used for detection. The peaks retention times between the two systems differed for not more than 2 s, easing the identification of some low abundant species, especially the novel ones not present in the available MS library (NIST 11).

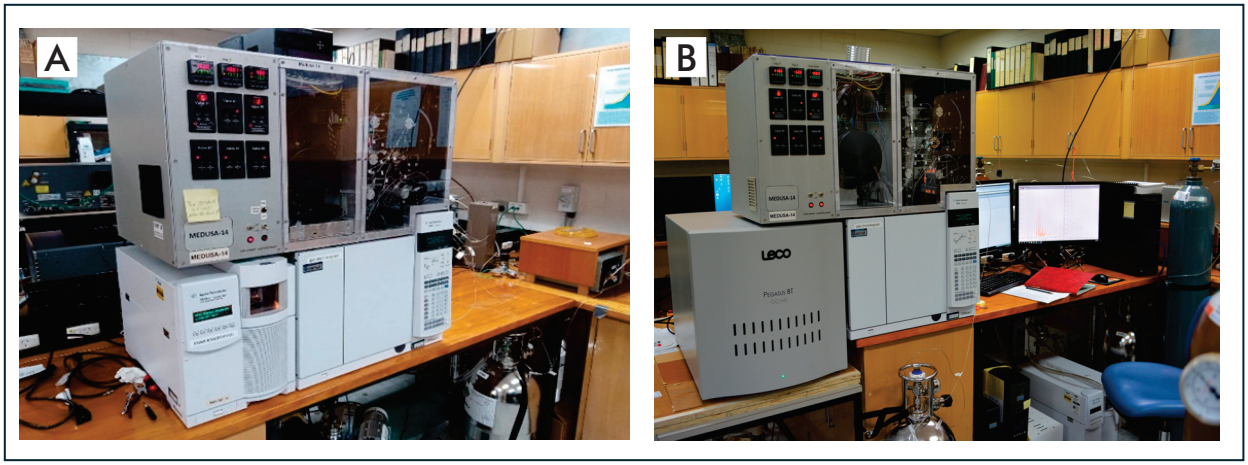

Figure 1. The experimental setup. (A) Medusa GCMS with quadrupole MS, and (B) Medusa GCMS with the LECO Pegasus BT TOFMS detector. The Medusa pre-concentration unit is sitting on the top of the GCMS.

Sensitivity
In this experiment, a series of 10 runs were recorded and the S/N was calculated by using *ChromaTOF* software (for TOFMS data), or graphically for qMS data. Please note that the current version of the Medusa GC-MS acquisition software GCWerks (for more details see www.GCWerks.com) does not allow automatic S/N ratio calculation. Based on the calculated S/N at the current concentrations of the species in the ambient air[2], and assuming a linear relationship between the concentration and the MS signal at the lower concentration end, the LOD was produced. The same quantitation ions were used in both experiments, with qMS and with TOFMS detection. Once the lowest abundant species were identified in the TOFMS data by using *ChromaTOF's* non-target deconvolution (NTD) algorithm, the routine quantification was facilitated by using the target analyte finding (TAF) option. While the NTD peak finding was time consuming process due to the file size, the TAF was a very quick step.

Precision
The measurement precision was derived from the results of a series of 24 repetition runs of an ambient air (S-025) sample. The standard deviation of each run was calculated against the mean value of the two bracketing standard runs and averaged across the whole series. Please note that the sample strategy within the AGAGE network is …air, std, air, std... The precision of qMS measurements was obtained in a similar way, as an average of the standard deviation across a long series of measurements of the same air sample (S-025).

Linearity
Linearity was assessed by measuring the response signal when introducing a varying volume of air sample for pre-concentration. The results from these runs were normalized to the usually performed runs at 2 L sample volume, and then normalized to the corresponding sample volume. Ideally, the linear detector should show a normalized response of 1 within the volume linearity range. The same corresponding ions were used for the response factor for both qMS and TOFMS experiments.

The sample volume was tightly controlled by the sampling time of a calibrated smart mass flow controller (Red-y Smart Controller GSC, Vogtlin, Switzerland) at a fixed flow rate of 100 ml/min used for the normal Medusa operation. The flow precision of the Red-y was better than 0.05 ml/min at the working 100 ml/min flow rate. For more details, please refer to Miller et al.[1]. Using this strategy, we were able to accurately sample any air volume within 0.1 to 5 L range. The same set of experiments was performed with qMS and TOFMS detection, and the results were compared.

Results

Sensitivity
The results obtained from the analysis of the selected low abundant species (see Table 2) routinely measured within the AGAGE group were used for comparison. In order to match the TOFMS data acquisition as much as possible to the qMS data acquisition, the TOFMS chromatograms were acquired at 5 Hz and processed at unit mass resolution (±0.5 amu), without data points smoothing. The LECO *Pegasus* BT TOFMS showed greater sensitivity than the Agilent 5975 MS for the same quantitation ions of the selected species in the ambient air (Table 2). Consequently, a better LOD was obtained for TOFMS data. The chromatograms of HCFC-133a in Figure 2 obtained by GC-qMS (a) and GC-TOFMS (b) show the difference in the sensitivity.

Table 2. Method sensitivity expressed in S/N and LOD for both qMS and TOFMS systems.

Specie	Quant. Ion	LECO TOFMS		Agilent qMS	
		S/N	LOD/ppq	S/N	LOD/ppq
CH3CCl3	99	264	23	54	110
HCFC-133a	118	210	6	35	37
HFC227ea	151	344	13	56	80
HFC245fa	64	445	17	-	-
HFC245fa	115	244	31	50	150

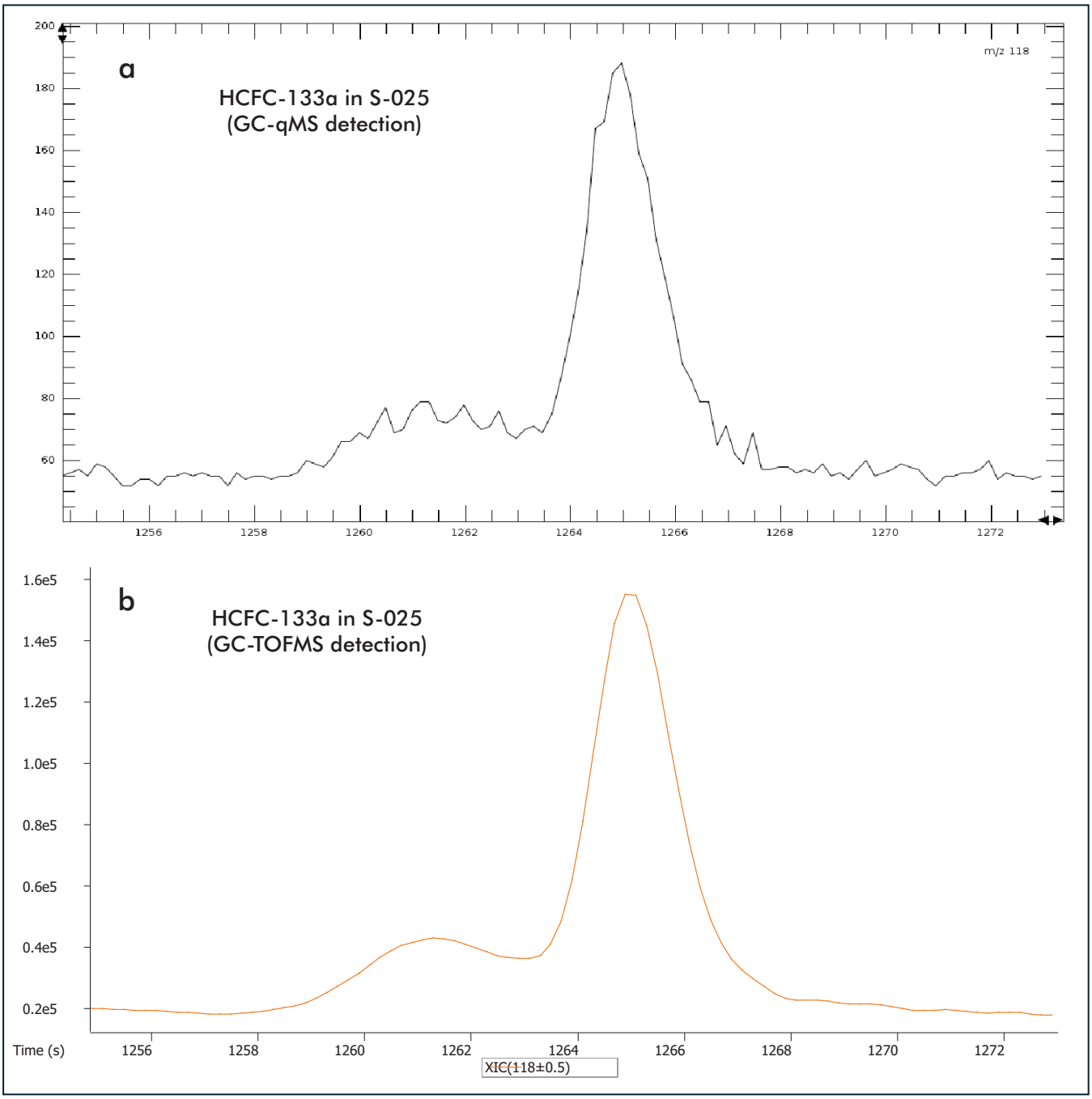

Figure 2. GC-qMS SIM chromatogram at 118 m/z (a) and GC-TOFMS extracted ion chromatogram at 118 m/z (b) for HCFC-133a in the air sample S-025. The concentration of HCFC-133a in the measured air, expressed as mol fraction in a dry air, was 0.4 ppt.

Table 3. Method precision for selected low or high abundant species, for both tested configurations.

Species (mol fraction in ppt)	*Precision (%)*	
	TOFMS	*AGAGE[2]*
CFC-12 (520)	0.14	0.1
COS (550)	0.18	0.5
CH_3CCl_3 (2.6)	0.85	0.7
HCFC-133a (0.4)	2.56	~2
HFC-227ea (1.2)	1.43	2.2
HFC-245fa (2.4)	1.53	~3

Linearity

While comparable linearity results between TOFMS and qMS detection were obtained for the lower abundant species in the air (i.e. those given in Table 1), some significant differences were observed for some of the most abundant species, for example carbonyl sulphide (COS) at 550 ppt (Fig. 3). The qMS showed significantly better linearity (±2%) compared to the results from the TOFMS detection (+5% to -13%) within the tested volume range of 0.1 L to 5 L. On the other hand, the linearity between TOFMS and qMS for another similarly abundant specie (CFC-12 at 520 ppt) was comparable at ±4% within the tested volume range (Fig. 4).

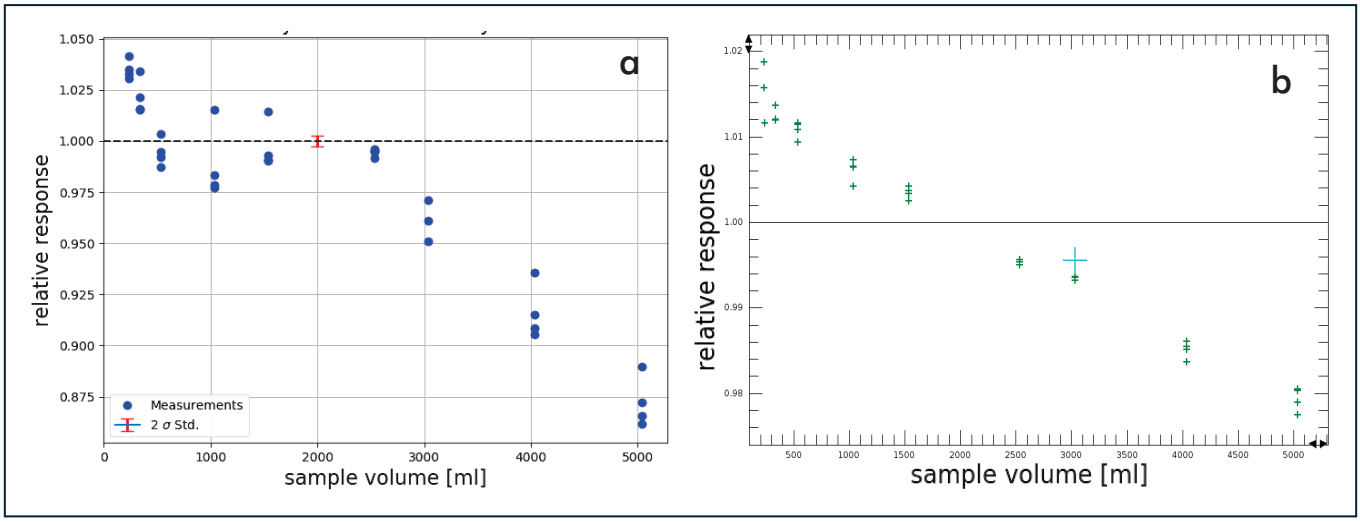

Figure 3. Linearity for COS on LECO TOFMS (a) and GC-qMS (b) for the same 60 m/z ion.

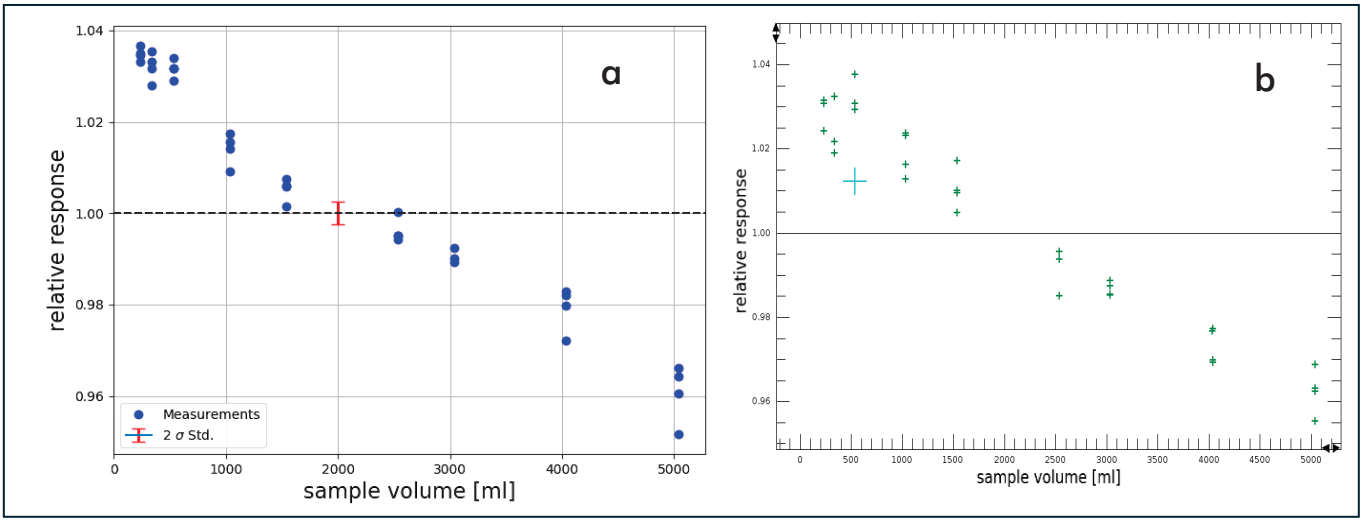

Figure 4. Linearity for CFC-12 on LECO TOFMS (a) and GC-qMS (b) for the same 85 m/z ion.

Sample information not available with Medusa GC-qMS
Unlike the Medusa GC-qMS system, where the signals from only pre-selected species at pre-selected time windows are recorded, the Medusa GC-TOFMS configuration continuously scans for all masses within the selected mass range which gives far more information about the sample composition. For example, around 350 peaks were detected at S/N of ≥3 in a clean background air (S-025), and more than 1200 peaks were detected in a polluted ambient air. Usually, 1/3 of these peaks are identified with a match quality of ≥700 against NIST11, where small number of them are either double entries or wrongly identified compounds due to lack of molecular fragmentation (poor mass spectra).

Full mass spectra availability for the entire chromatogram/sample can be very beneficial in this field.

- Matrix interference: Potential matrix interferences due to pollution events can be solved by selecting another quantifier ion from the TOFMS spectra which is not present in the matrix;
- Retain record of all the species present in the air at that time (in-situ measurements);
- Post-analysis data processing for species not originally targeted; We have found that the most abundant species in one old air archive sample from 1986 were aldehydes (see Supplement information). While we still cannot explain their occurrence in the air sample, the identification is unambiguous thanks to the full mass spectra of the whole sample.
- One-campaign analysis of air archives for all species; The analysis of an air from the Cape Grim Air Archive (CGAA) is usually performed in campaigns, each campaign targeting a particular class of species (CFCs, HFCs, PFCs etc.). Running the same samples on TOFMS will generate data for all the species in the samples, providing there is a calibration strategy in place.

Conclusions

Although the Medusa GC-TOFMS looks far from being a standard configuration for the analysis of synthetic GHG and ODS in the ambient air, the system has shown some promising features. While the GC-TOFMS precision was comparable to the current GC-qMS method, TOFMS has demonstrated better LOD for some of the lowest abundant atmospheric species. While the linearity of both detectors was comparable for lower abundant species, the qMs showed a wider linear range for some of the most abundant atmospheric species (COS). Apart from the better sensitivity, retaining the full mass spectra of the whole sample is the biggest benefit of the TOFMS configuration, which may ease the overall analysis of synthetic GHG and ODS in this field.

As a final conclusion, the experiment was performed truly unbiased: we used the same air sample, the same sample introduction, same air volume measurement, same matrix handling, and same components separation (column). The only difference was the different detection once the species were out of the GC column.

References

[1] Miller et al. Anal. Chem. **2008,** 80, 1536-1545

[2] Prinn et al. Earth Syst. Sci. Data, **2018,** 10, 985–1018,

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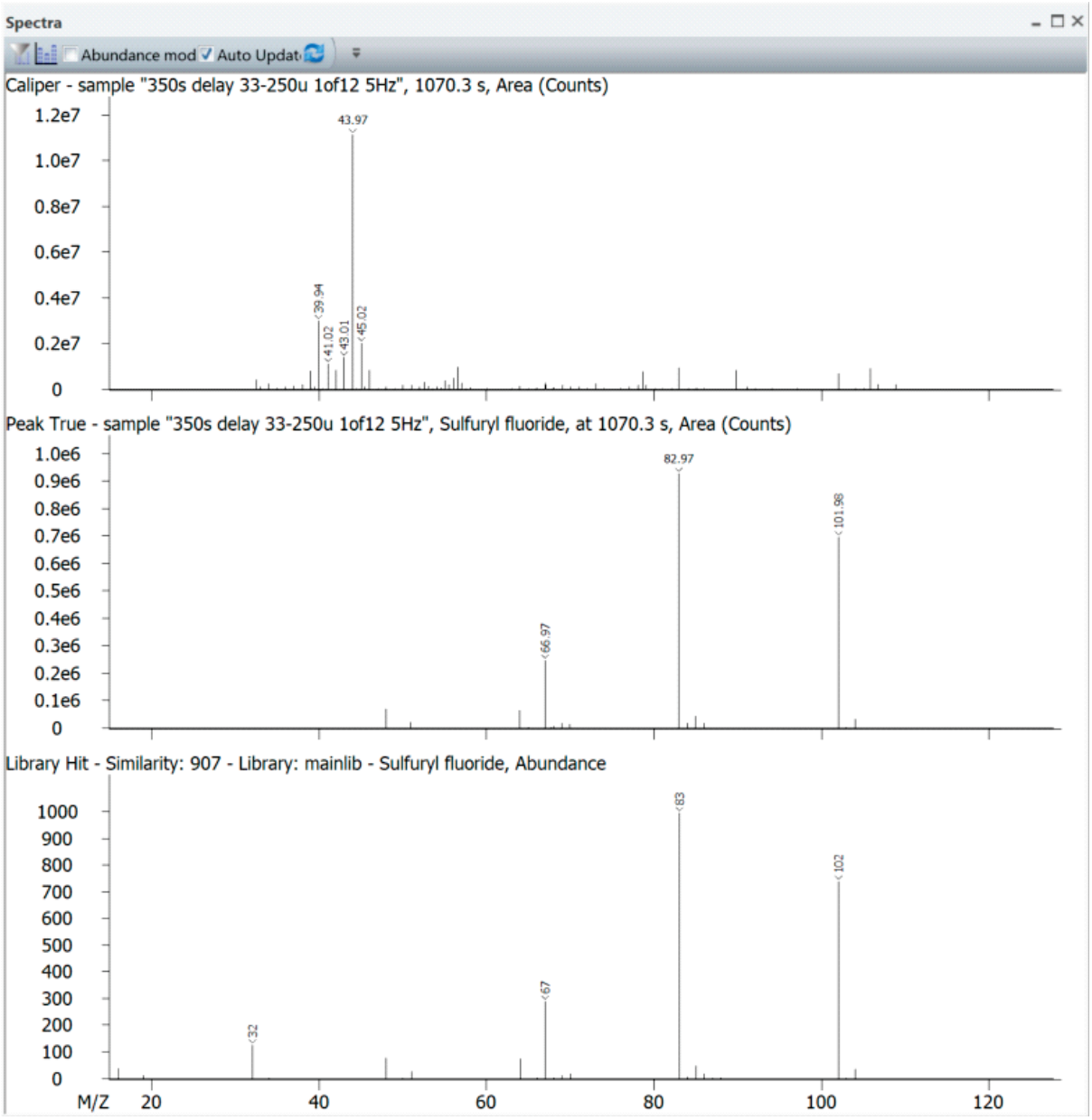

Figure S1a. Identification of sulfuryl fluoride at 2 ppt in the ambient air

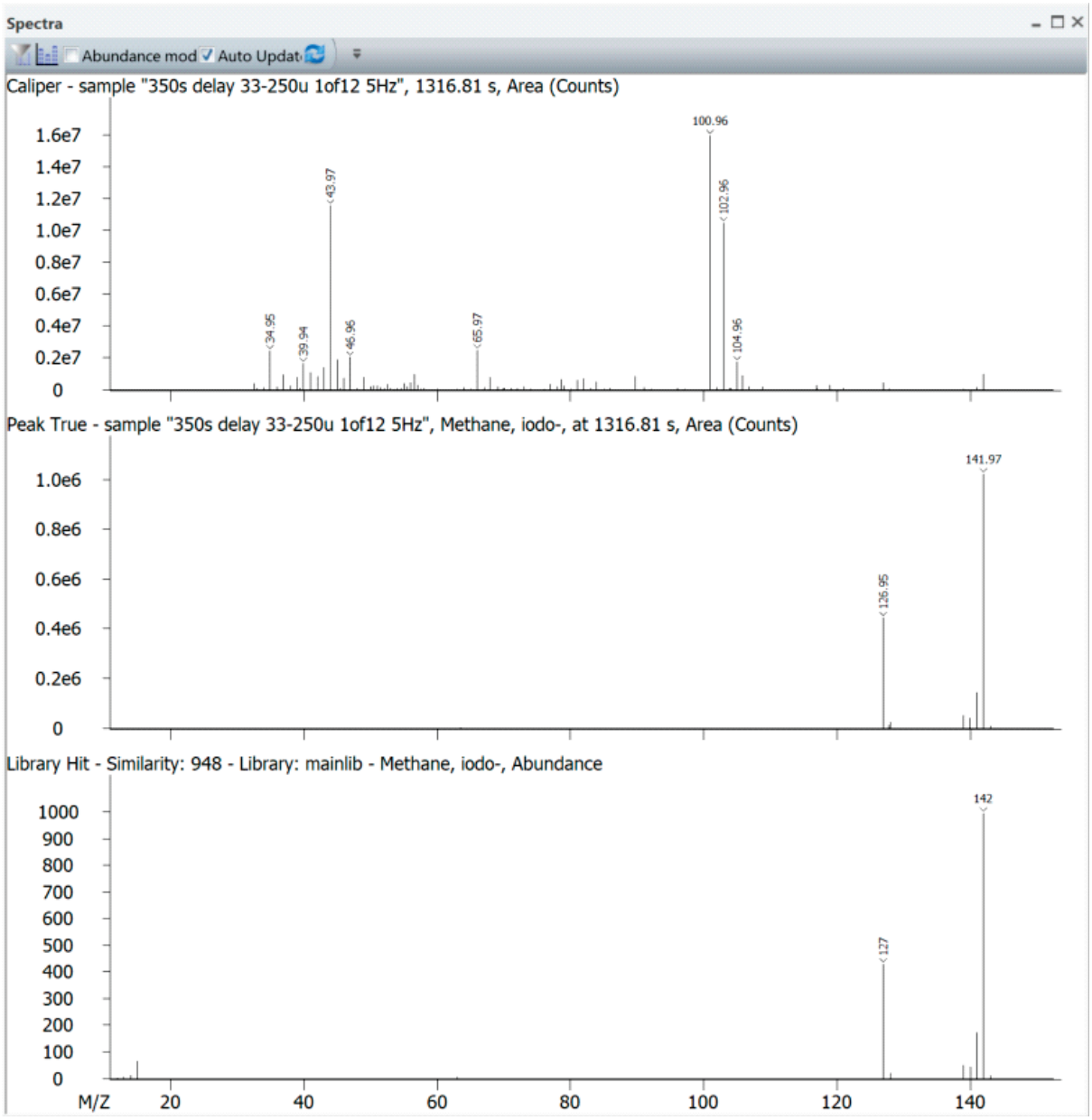

Figure S1b. Identification of methyl iodide at 0.6 ppt in the ambient air

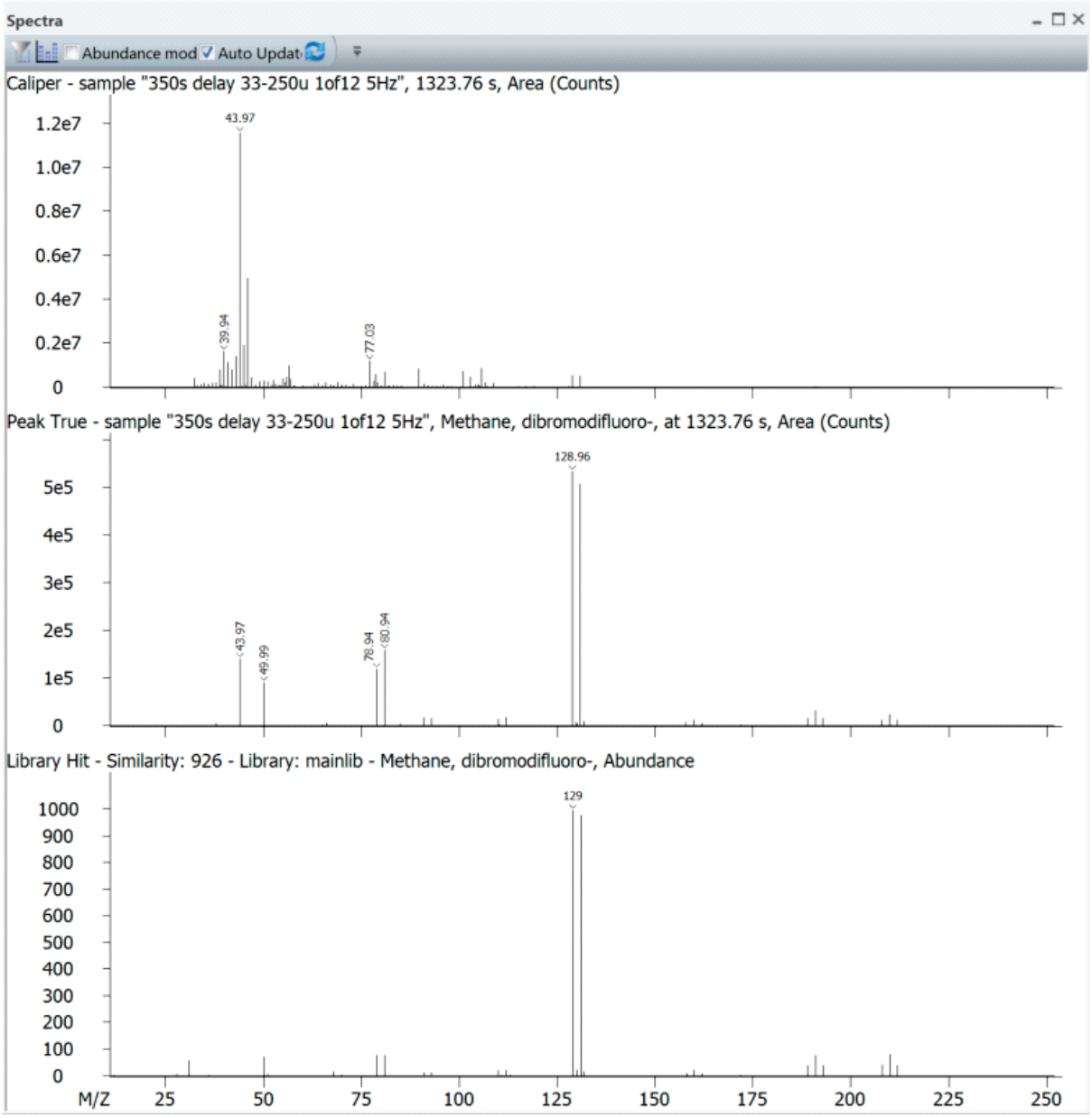

Figure S1c. Identification of halon 1202 at low ppt in the ambient air

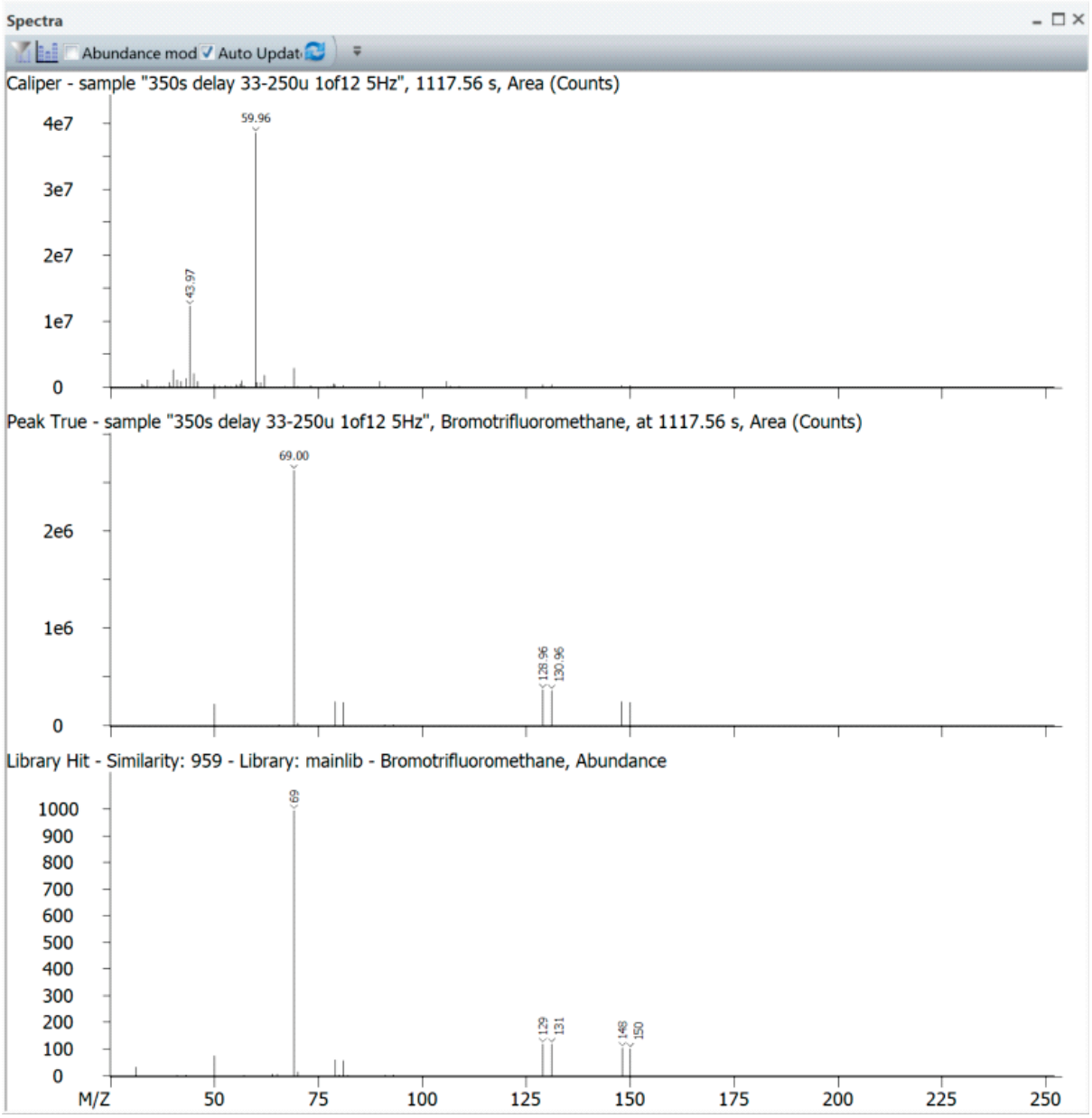

Figure S1d. Identification of halon 1301 at 3 ppt in the ambient air

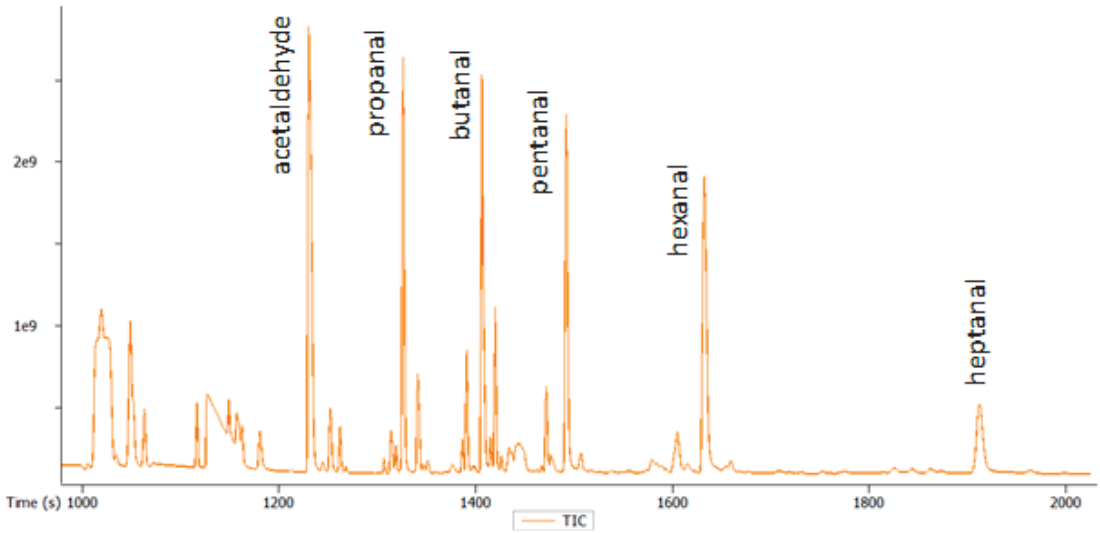

Figure S2. Chromatogram of an old (1986) Cape Grim air archive sample where the most abundant peaks were identified as aldehydes. Normally, they wouldn't be identified with the standard Medusa GC-qMS system.

Table S1. Unfiltered peak list of the compounds identified at 700+ similarity against the NIST11 MS library. Please note that some of the false-positive identified species are result of coincidental match of their ions in their poor spectra (just one or a few ions in the spectra).

	Compound	*Similarity*
1	Methyl nitrate	999
2	Carbon dioxide	987
3	Ethane, 1-chloro-1,1-difluoro-	975
4	Methyl formate	975
5	Propanal	975
6	Propene	973
7	Methane, bromo-	970
8	Acetaldehyde	968
9	Chloromethane	967
10	Isobutane	965
11	Trichloromonofluoromethane	964
12	Ethane, 1,1,1-trifluoro-	963
13	Pentafluoroethyl chloride	963
14	Chlorotrifluoromethane	962
15	Dichlorodifluoromethane	962
16	Bromotrifluoromethane	959
17	Ethane, 1,1,2-trichloro-1,2,2-trifluoro-	957
18	Carbon disulfide	956
19	Krypton	955
20	Ethane, 1,2-dichloro-1,1,2,2-tetrafluoro-	955
21	Xenon	954
22	Enflurane	954
23	Tetrafluoromethane	953
24	Styrene	953
25	Ethane, pentafluoro-	950
26	Benzene, 1,3-dichloro-	950
27	Propane	949
28	Acetic acid, methyl ester	949
29	Methane, iodo-	948
30	Butane, 2-methyl-	948
31	Trichloromethane	948
32	Methyl formate	947
33	Dimethyl ether	947
34	Methylene chloride	945
35	Octane, 4-methyl-	945
36	Ethene, trifluoro-	944
37	Cyclopropane	943
38	Dimethyl sulfide	942
39	Acetone	942
40	Methacrolein	941
41	Difluorochloromethane	940
42	Cyclopropane, ethylidene-	940
43	2-Butanone	935
44	Benzene	932
45	3,3,3-Trifluoropropene	930
46	Difluoromethane	927
47	1,3-Butadiyne	927
48	Methane, dibromodifluoro-	926
49	Acetic acid ethenyl ester	925
50	1-Octene	925
51	Heptanal	925
52	Pentane, 1-chloro-	924
53	Carbon Tetrachloride	923
54	Isoflurane	917
55	Argon	916
56	Methane, dibromochloro-	915
57	(Z)-Difluorodiazene	914
58	Toluene	909
59	Methyl Isobutyl Ketone	909
60	Argon	908
61	Argon	908
62	Sulfuryl fluoride	907
63	Perfluoropropane	907
64	Pentane	907
65	Cyclopropane, ethyl-	906
66	Butane, 1-chloro-	903
67	Hexane, 1-chloro-	902
68	Heptane, 2,4-dimethyl-	900
69	Ethane, hexafluoro-	898
70	Butanal	898
71	2-Butanone, 3-methyl-	897
72	Ethane, 2-chloro-1,1,1,2-tetrafluoro-	895
73	Octane	895
74	Mesitylene	895
75	Argon	894
76	2-Hexene, 5,5-dimethyl-, (Z)-	892
77	Methane, bromodichloro-	891
78	Benzene, chloro-	890
79	Ethene, chlorotrifluoro-	889
80	Mesitylene	889
81	Norflurane	888
82	Benzene, (1-methylethyl)-	888
83	Butane	884
84	Methane, dibromo-	883
85	2-Propanone, 1-chloro-	882
86	Ethane, 1,1,2,2-tetrachloro-1,2-difluoro-	881
87	Benzene, 1,3-dimethyl-	880
88	1,1-Dichloro-1-fluoroethane	873
89	2-Butanone, 3,3-dimethyl-	872
90	Isopropylcyclobutane	871
91	Dibromonitromethane	871
92	Trimethylsilyl fluoride	869
93	Cyclobutane, octafluoro-	860
94	Benzene, 1-ethyl-2-methyl-	860
95	2-Propynenitrile, 3-fluoro-	857
96	Ethyl formate	854
97	n-Propyl chloride	854
98	p-Xylene	848
99	sec-Butylamine	847
100	Ethylene glycol, dinitrate	845
101	2-Propanone, 1,1,1-trifluoro-	842
102	Formic acid, butyl ester	842
103	Furan	830
104	(3H)Indazole, 3,3-dimethyl-	828
105	Benzene, 1-ethyl-2-methyl-	827
106	(Trifluoromethyl)acetylene	821
107	2-Hexene, 4,4,5-trimethyl-	820
108	Nitrous oxide	817
109	Fluorodichloromethane	816
110	Urea, N,N'-dimethyl-	816
111	n-Hexane	814
112	Hexane, 1-chloro-	814
113	Ethyl Acetate	812
114	Ethanol	811
115	2-Ethylacrolein	811
116	Ethane, 1,1,2,2-tetrafluoro-	810
117	Ethane, 1,2-dichloro-1,1-difluoro-	810
118	2,3-Hexanedione	804
119	2-Octanamine	803
120	Furan, 2-methyl-	797
121	2-Aminocyanoacetamide	794
122	Furan, 2,5-dimethyl-	792
123	Cyclobutanol, 2-ethyl-	790

Table S1. Continued from previous page.

	Compound	*Similarity*
124	Benzene, 1-ethyl-2,4-dimethyl-	787
125	Methylphosphonic acid, fluoroanhydride, tert-butyldimethylsilyl ester	786
126	Propanoic acid, anhydride	785
127	Thiophene	783
128	Propanoyl chloride, 2,2-dichloro-	783
129	2-Heptene, (E)-	783
130	Ethene, chloro-	782
131	Cyanic acid, 2-methylpropyl ester	781
132	Benzene, 1-methyl-3-(1-methylethyl)-	781
133	Octane	779
134	Butanal, 4-hydroxy-3-methyl-	776
135	Heptane	775
136	2,4,5-Trihydroxypyrimidine	774
137	2-Pentene, 2,4-dimethyl-	771
138	1-Pentanone, 1-(4-methylphenyl)-	769
139	Cyclopentene	764
140	1-Propene, 1,1,3,3,3-pentafluoro-	763
141	d-Proline, N-methoxycarbonyl-, pentyl ester	763
142	Silane, difluorodimethyl-	759
143	1H-Tetrazole-1,5-diamine	759
144	Desflurane	757
145	2-Hexene, (E)-	756
146	dl-Alanyl-l-alanine	755
147	Ethane, pentafluoro-	755
148	Butane, decafluoro-	755
149	Ethyl Chloride	753
150	Cyclopropanemethanol, 2,2,3,3-tetramethyl-	752
151	1-Methyldodecylamine	749
152	2-Pentene, (E)-	749
153	Glutaraldehyde	746
154	Ethyne, chloro-	741
155	Trifluoromethyldifluorophosphine	735
156	2-Butene, 2-methyl-	734
157	2-Butanone, 1,1,1-trifluoro-	733
158	Propanamide, 2-hydroxy-	732
159	3-Hexanone	728
160	Dimethyl-(allyl)-silyloxybenzene	726
161	Butanoic acid, 3-amino-2-methyl-	725
162	trans-4,4-Dimethyl-2-hexene	722
163	Ethane, 1-chloro-1,1,2,2-tetrafluoro-	718
164	Benzeneethanamine, 2-fluoro-?,3-dihydroxy-N-methyl-	716
165	N,N,O-Triacetylhydroxylamine	713
166	Sulfur hexafluoride	711
167	Propane, 1,1,1,3,3,3-hexafluoro-	710
168	Furan, 2-ethyl-	710
169	2-Butanone	710
170	2,2,3,3,4,4,5,5-Octafluoropentanal	709
171	1H-Pyrazole, 4,5-dihydro-5-propyl-	709
172	2,2,3,3,4,4,5,5-Octafluoropentanal	703
173	Propanoic acid, 2-oxo-, ethyl ester	701