Qualitative analysis of a commercial naphthenic acids mixture using comprehensive multidimensional gas chromatography-mass spectrometry ('2D-GCMS')

Report to the American Petroleum Institute

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Summary

Analysis of the methyl esters of a commercial naphthenic acids mixture using comprehensive multidimensional gas chromatography-mass spectrometry ('2D-GCMS') revealed the presence (as esters) of about 2000 compounds. These included over 20 tentatively identified (from the mass spectra and those of reference compounds), as n-acids, methyl and polymethyl (including isoprenoid) acids and cyclohexyl, perhydroindan, decalin and adamantane acids, similar to those reported previously in a commercial mixture.

A variety of monoaromatic acids and non-acids (e.g. polycyclic aromatic hydrocarbons) were also present, of which 10 were tentatively identified in the same manner to those above.

Use of an ionic liquid primary GC stationary phase provided an unprecedented resolution of the individual components of the mixture and the mass spectra were of excellent quality and fully library searchable (where such library spectra existed). Many other compounds could probably be identified if the spectra were interpreted and library-matched.

No quantitative analyses were conducted, but overall the major components of the mixture appeared to be n-acids, judging from the similarities in mass spectra of the unknowns and library spectra of n-acids (methyl esters). Many other individual acids were nearly as abundant as the n-acids, however.

1. Introduction

The American Petroleum Institute (API) require qualitative analysis of a commercial naphthenic acids mixture using comprehensive multidimensional gas chromatography-mass spectrometry ('2D-GCMS') to allow reliable identification of selected individual chemicals in the mixture (cf Rowland et al., 2011a).

Previous studies of the toxicological effects of the mixture have been made by the API and studies of the mixture composition have been made for the API by the University of Alberta, Edmonton, Canada following GCMS analysis of silylated derivatives (Swigert, personal communications). The latter method did not allow individual acids to be identified but did provide a semi-quantitative measure of the acid groups, based on the response of certain ions in the electron ionisation mass spectra of the derivatives. Effectively these assignments allowed a table to be constructed of the relative abundances of certain acid groups defined by carbon number (n) and undersaturation with hydrogen (assumed to be due to hydrogen loss due to ring formation) expressed as the term z in the formula $C_nH_{2n+z}O_2$ where z is zero (acyclic) or an even, negative, integer (e.g. -2,-4,-6 for monocyclic, bicyclic, tricyclic acids).

Contractually it was agreed that UoPEL would conduct a qualitative analysis of the acids mixture supplied by API and derivatised to form the methyl esters by 2D-GCMS and up to twenty mass spectra and/or selected ion chromatograms obtained. Where possible, spectra of reference compounds would also be provided.

Subsequently, following a multiway telephone discussion (11th June 2012), it was agreed that additional spectra of the five major components of the mixture, as revealed by 2D-GCMS of the methyl esters, would also be supplied and that information concerning the presence of some non-acids would also be obtained and reported to API.

2. Materials & Methods

2.1 Samples

A commercial preparation of naphthenic acids (Merichem, CAS No. 1338-24-5, ID No. CP006002) was supplied by API.

2.2 Methods

The commercial preparation of naphthenic acids was refluxed with boron trifluoride (12%) in methanol (Acros Organics, Geel, Belgium) and the products extracted into hexane. The extract was analysed by comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GCxGC/ToF-MS). Analyses were conducted using an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE, USA) fitted with a Zoex ZX2 GC×GC cryogenic modulator (Houston, TX, USA) interfaced with a Almsco BenchToF dx™ time-of-flight mass spectrometer (Almsco International, Lantrisant, UK) operated in positive ion electron ionisation mode

and calibrated with perfluorotributylamine. The scan speed was 50 Hz. The first-dimension column was an ionic liquid SLB-IL111 (Supelco, Bellefonte, PA, USA) 30 m × 0.25 mm × 0.20 µm and the second-dimension column was a 50% phenyl polysilphenylene siloxane BPX-50 (SGE, Milton Keynes, UK) 3.0 m × 0.25 mm × 0.15 µm. Helium was used as the carrier gas at a constant flow rate of 0.8 mL min^{-1}. Samples (1 µL) were injected at 280 °C splitless. The primary oven was programmed from 40 °C (hold for 1 min), then heated to 270 °C at 2 °C min^{-1} (held at 270 °C for 10 min). The temperature of the oven housing the secondary column was programmed to offset the primary oven by +40 °C. The modulation period was 8 s. The transfer line temperature was 290 °C and the ion source temperature was 280 °C. Data processing was conducted using GC Image™ v2.1 (Zoex, Houston, TX, USA).

3. Results & Discussion

Until recently, despite decades of attempts, very few individual acids had been identified in petroleum or in commercial petroleum-derived, so-called, 'naphthenic acids' mixtures. Early studies made as part of the famous API research project 6 were summarised in a textbook (Lochte & Littmann, 1955) and led to identification of mainly monocyclic acids. Later it became common practice to assume that such acids were representative-even though this was shown to be erroneous and the term 'naphthenic acids' considered inappropriate by Knoterus as early as 1957 (Knoterus, 1957).

Indeed, the assumption that naphthenic acids were only alicyclic acids continued to be commonplace until the highly chromatographically resolving technique known as comprehensive multidimensional gas chromatography-mass spectrometry, GCxGC-MS, 2D-GCMS and by a variety of other synonyms (Adachour et al., 2008) was used to study a commercial mixtures of acids treated by heating with boron trifluoride-methanol complex to convert acids to the methyl esters (Rowland et al., 2011a).

The results of the latter examination showed that a number of the acids in the mixture could be identified by comparison of the electron ionisation mass spectra and GCxGC retention times with those of reference acids. In the mixture examined in the studies by Rowland et al., (2011a,b), so-called straight chain acids dominated, but methyl and polymethyl branched acids, and monocyclic to tricyclic acids were also present (Rowland et al., 2011a, b). Also identified in the mixture examined in the studies by Rowland et al., (2011a,b) were a number of monoaromatic acids (Rowland et al., 2011b). Non-acids present in the mixture examined in the studies by Rowland et al., (2011a,b) included some polycyclic aromatic hydrocarbons and phenols.

Despite the above reports (Rowland et al., 2011a, b; West et al., 2011) very few, if any, subsequent attempts to use 2D-GCMS to characterise commercial naphthenic acids mixtures appear to have been made, even though the method was also shown to be applicable to supercomplex mixtures of acids from other sources, including oil sands processing (e.g. Rowland et al., 2011c, d, e).

Indeed, recent results from the same laboratory (West et al., 2012) have shown that the unprecedented chromatographic resolution reported by Rowland et al., (2011a) can be

improved upon still further by use of GCxGC columns with alternative stationary phases, notably with certain ionic liquids and effectively some mixtures can be more or less completely resolved (West et al., 2012).

In the present study, the latter conditions (viz: an ionic liquid GC primary stationary phase; West et al 2012 as described in 2.2 Methods above) were used to examine a mixture of acids supplied by the API and derivatised by heating with boron trifluoride-methanol complex to convert acids to the methyl esters.

The total ion current chromatogram is shown in Figure 1A and B (3 dimensional and 2 dimensional representations respectively). The five most abundant peaks are denoted peaks 1-5. The retention region of some minor monoaromatic acids (methyl esters) is also shown encircled (Figure 1).

Selected ion mass chromatograms of molecular ions of the five major compounds were used to illustrate the excellent chromatographic resolution of the individual compounds (Figure 2A and B). Figure 2A shows the whole extracted ion current mass chromatogram for *m/z* 242, typical of C_{14} z=0 acids (methyl esters). The major peak (peak 5) was tentatively assigned as due to the methyl ester of n-tetradecanoic acid from the mass spectrum and comparison with spectra from the National Institute of Standards & Technology (NIST) mass spectral library.Figure 2B shows partial extracted ion current mass chromatograms for *m/z* 186, 200, 214, 228 and 242, indicative of C_{10-14} z=0 acids (methyl esters). These illustrate the power of the 2D-GCMS method to resolve individual components of the mixture. The major peaks (peaks 1- 5) were tentatively assigned as due to the methyl esters of n-decanoic to n-tetradecanoic acids from interpretation of the mass spectra and comparison with spectra from the National Institute of Standards & Technology (NIST) mass spectral library.

Mass spectra of these five most abundant components of the total ion current chromatogram and the corresponding best match library spectra, are shown in Figure 3. The unknowns all appeared to be n-acids, judging from the similarities in mass spectra of the unknowns and library spectra of n-acids (methyl esters). No retention time comparisons were made with authentic compounds.

Mass spectra of a further nineteen unknowns (originally 20, but the acid denoted peak 2 (Figures 1-3) was also one of the initial 20 spectra supplied to API, so that spectrum was not duplicated), selected to include members of the z=0, -2, -4, -6 and -8 classes of acids, are shown in Figure 4A-S and of the corresponding best match library spectra in Figures 4ARef-SRef.

Also present in the sample were a number of non-acids, identified by comparison of the mass spectra with those of library spectra (Figure 5A-F) and of the corresponding best match library spectra in Figures 5ARef-5FRef. These were polycyclic aromatic hydrocarbons and polycyclic sulphur-containing aromatic hydrocarbons.

4. Conclusions

Analysis of the methyl esters of a commercial naphthenic acids mixture using comprehensive multidimensional gas chromatography-mass spectrometry (2D-GCMS) revealed the presence (as esters) of about 2000 components including: n-acids, methyl and polymethyl (including isoprenoid) acids and cyclohexyl, perhydroindan, decalin and adamantane acids, similar to those reported previously in a commercial mixture (Rowland et al., 2011a) and tentatively identified herein by comparison of the spectra with those of reference compounds. No retention time comparisons with reference compounds were made.

A variety of monoaromatic acids and non-acids (e.g. aromatic hydrocarbons) were also present.

Use of an ionic liquid primary GC stationary phase provided an unprecedented resolution of the individual components of the mixture and the mass spectra were of excellent quality and fully library searchable (where such library spectra existed).

No quantitative analyses were conducted, but the major components of the mixture appeared to be n-acids, as observed previously for a mixture of commercial acids (Rowland et al., 2011). Many other individual acids were nearly as abundant as the n-acids, however.

References:

Adachour, M., Beens, J., Brinkman, U. A. Th. (2008) Recent developments in the application of comprehensive two-dimensional gas chromatography. *J. Chromatogr. A*, 1186, 67-108.

Knoterus, J. (1957) The chemical constitution of the higher “naphthenic acids”. J. Inst. Petrol. 43,307-312.

Lochte, H. L., and Littmann, E. R. (1955) The Petroleum Acids and Bases. New York: Chemical Publishing Co. Inc. pp1-368.

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West, C.E., Jones, D., Scarlett, A.G. and Rowland, S.J. (2012) Separation, Identification and Characterisation of ‘Supercomplex’ Mixtures of Naphthenic Acids using GCxGC/ToF-MS. Poster presentation at 9th GCxGC symposium, Riva del Garda, Italy, May 27-June 1, 2012. Available at www.pegg.org.uk.

Table Legend

(note numerous synonyms are possible)

Table 1. Compound Names (all as methyl esters)

Peak	Compound Name	Z number
Figure 3 -Peak 1	*n*-Decanoic acid	0
Figure 3 -Peak 2	*n*-Undecanoic acid	0
Figure 3 -Peak 3	*n*-Dodecanoic acid	0
Figure 3 -Peak 4	*n*-Tridecanoic acid	0
Figure 3 -Peak 5	*n*-Tetradecanoic acid	0
Figure 4 - Peak A	13-methyltetradecanoic acid	0
Figure 4 - Peak B	2,6-dimethylheptanoic acid	0
Figure 4 - Peak C	2,6-dimethylundecanoic acid	0
Figure 4 - Peak D	2,6,10-trimethylundecanoic acid	0
Figure 4 - Peak E	3,7,11-trimethyldodecanoic acid	0
Figure 4 - Peak F	3-methylcyclohexane carboxylic acid	-2
Figure 4 - Peak G	Cyclohexyl-3-propanoic acid	-2
Figure 4 - Peak H	Adamantane-2-carboxylic acid	-6
Figure 4 - Peak I	Adamantane-1-ethanoic acid	-6
Figure 4 - Peak J	3,5-dimethyladamantane-1-carboxylic acid	-6
Figure 4 - Peak K	Perhydroindane carboxylic acid	-4
Figure 4 - Peak L	Perhydroindane ethanoic acid	-4
Figure 4 - Peak M	Decalin-2-carboxylic acid	-4
Figure 4 - Peak N	Decalin-1-ethanoic acid	-4
Figure 4 - Peak O	Decalin-1-ethanoic acid (isomer)	-4
Figure 4 - Peak P	Dimethylbenzoic acid	-8
Figure 4 - Peak Q	Ethylbenzoic acid	-8
Figure 4 - Peak R	Phenylpropanoic acid	-8
Figure 4 - Peak S	Trimethylbenzoic acid	-8

Figure Legends

Figure 1. A. Total ion current chromatogram (3 dimensional) and B. 2 dimensional representation resulting from 2D-GCMS of methyl esters of API supplied naphthenic acids. Peaks 1-5 are the 5 major components by peak height.

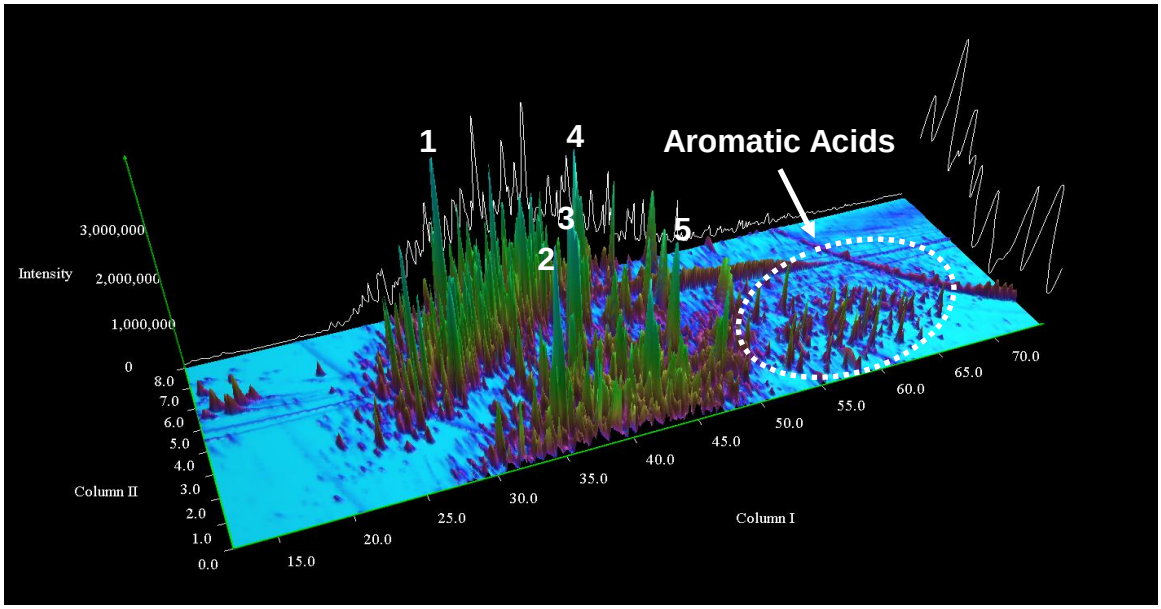
Figure 2. Extracted ion mass chromatograms resulting from 2D-GCMS of methyl esters of API supplied naphthenic acids. A. Whole chromatogram for *m/z* 242 illustrating distribution of $C_{14:0}$ acids (methyl esters). B. Partial chromatograms for *m/z* 186, 200, 214, 228 and 242 illustrating the distribution of $C_{10:0\text{-}14:0}$ acids (methyl esters).

Figure 3. Mass spectra resulting from 2D-GCMS of methyl esters of API supplied naphthenic acids, peaks 1-5 and related NIST library spectra (methyl esters).

Figure 4. Mass spectra resulting from 2D-GCMS of methyl esters of API supplied naphthenic acids, 19 selected unknowns representing acyclic, mono, bi , tricyclic and monoaromatic acids and related spectra (methyl esters) of reference compounds.

Figure 5. Mass spectra resulting from 2D-GCMS of methyl esters of API supplied naphthenic acids, non-acids and related NIST library spectra.

(A)


1
4
3
2
5
Aromatic Acids
Intensity
3,000,000
2,000,000
1,000,000
0
Column II
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
Column I

(B)

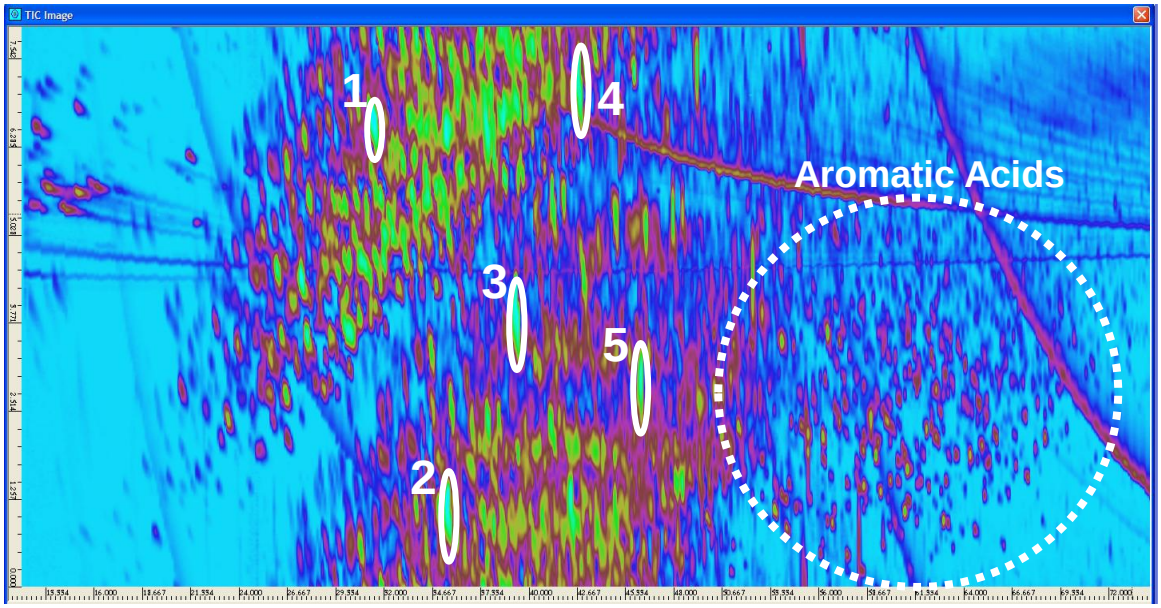
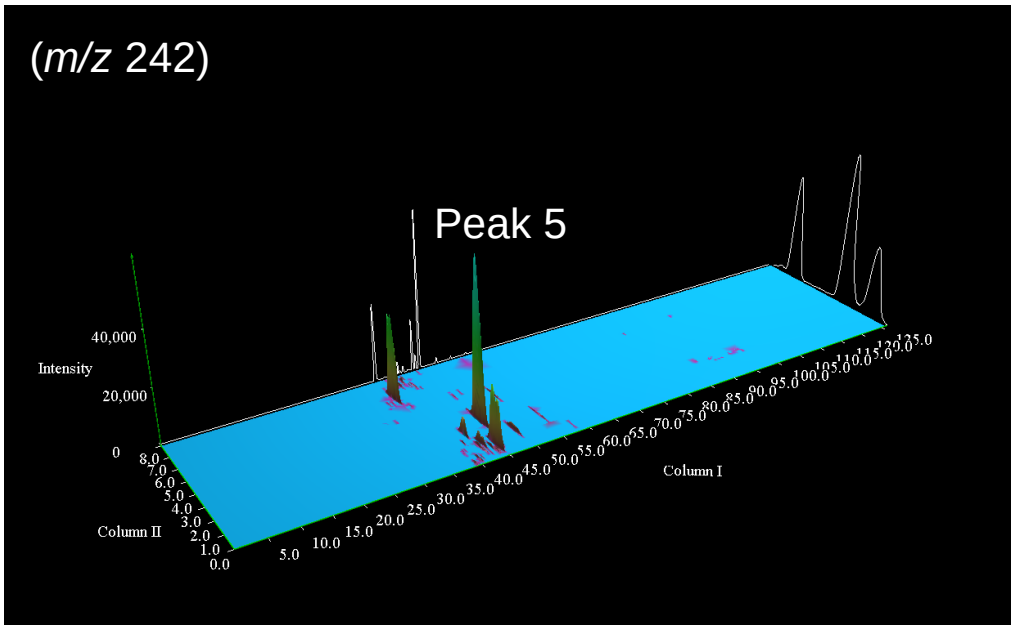

TIC Image
1
4
Aromatic Acids
3
5
2

Figure 1.

(A)


(m/z 242)
Peak 5
Intensity
40,000
20,000
0
Column II
Column I

(B)

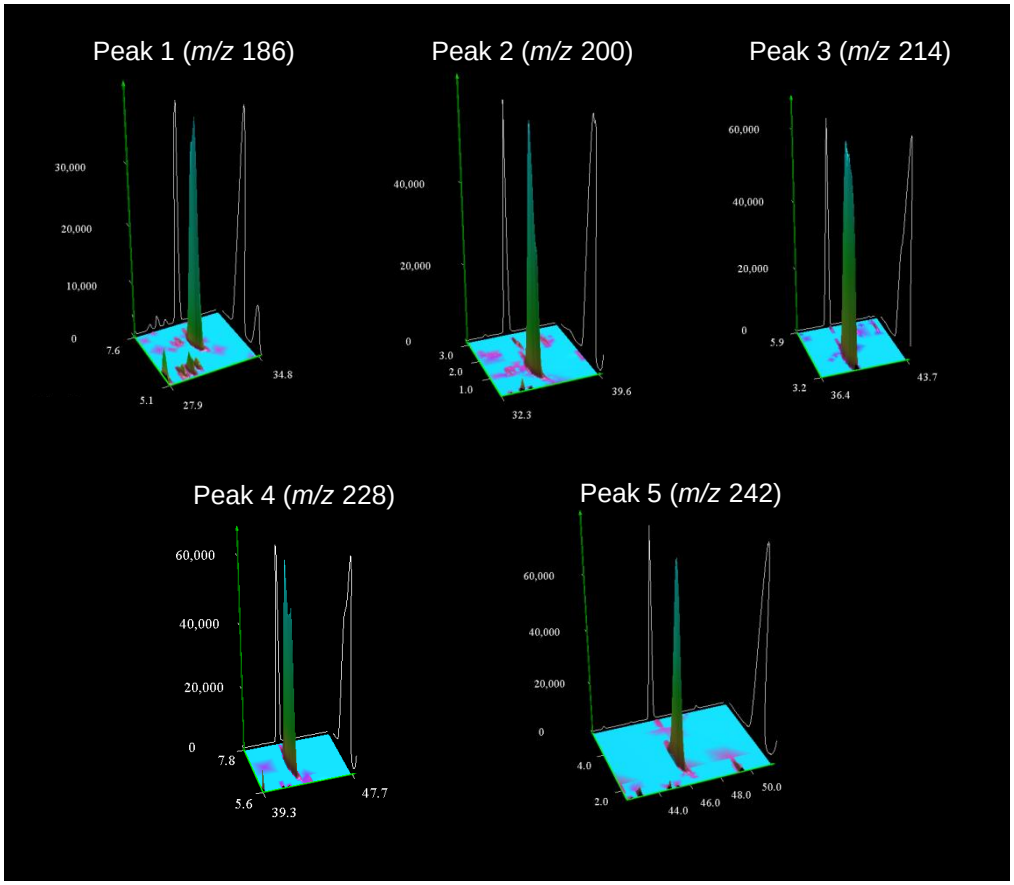

Peak 1 (m/z 186)
Peak 2 (m/z 200)
Peak 3 (m/z 214)
Peak 4 (m/z 228)
Peak 5 (m/z 242)

Figure 2.

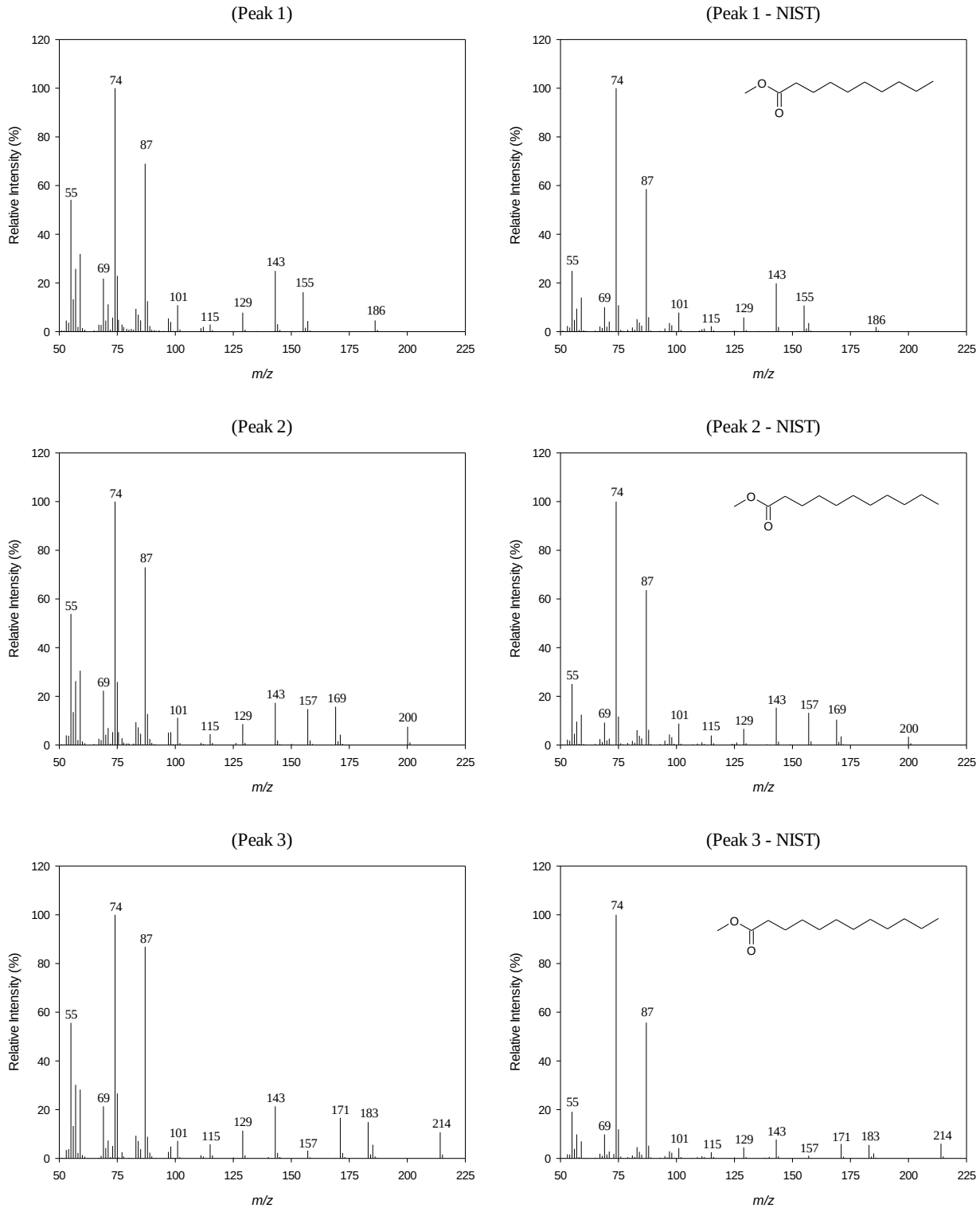

(Peak 1)
(Peak 1 - NIST)
(Peak 2)
(Peak 2 - NIST)
(Peak 3)
(Peak 3 - NIST)
Relative Intensity (%)
m/z

Figure 3.

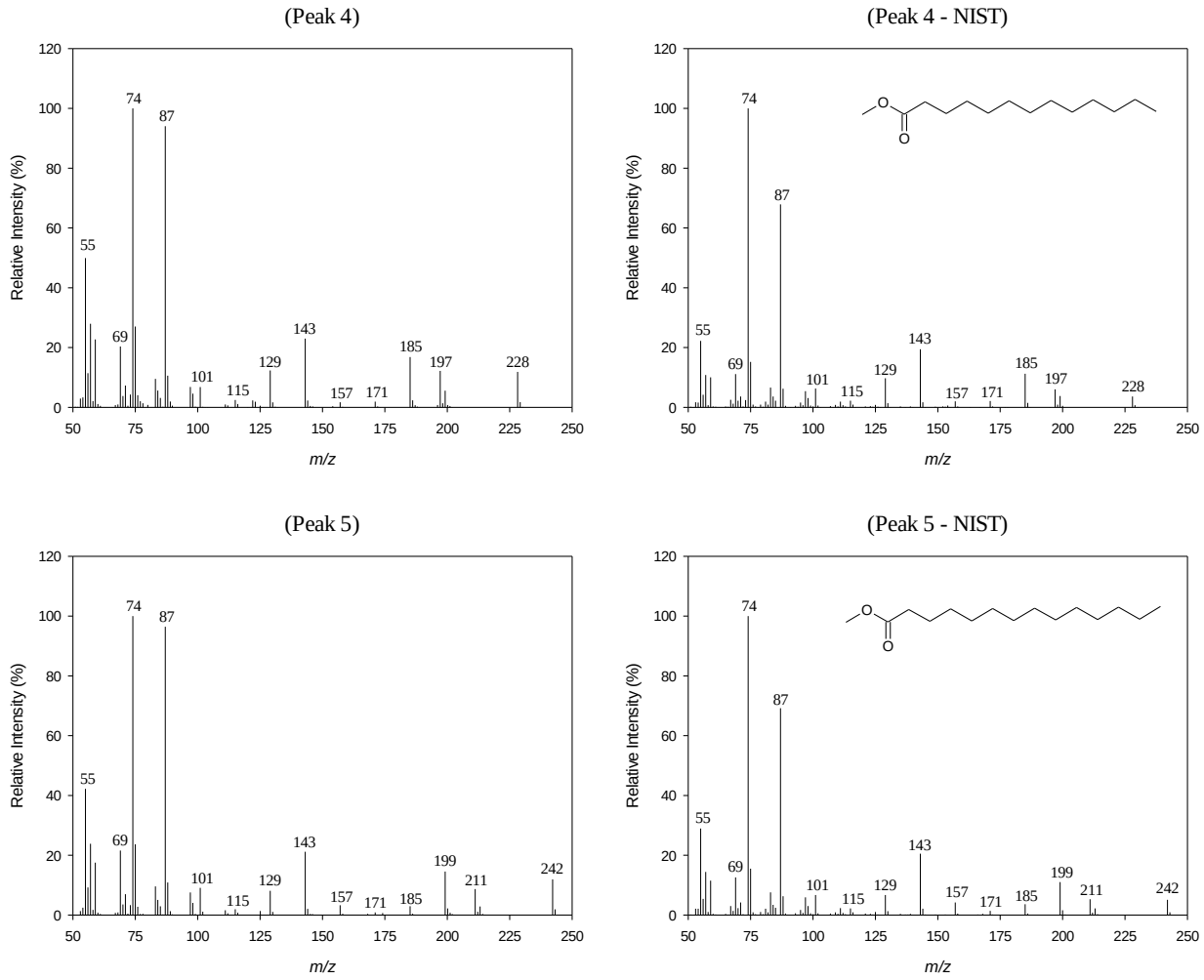


Figure 3 (Cont.)

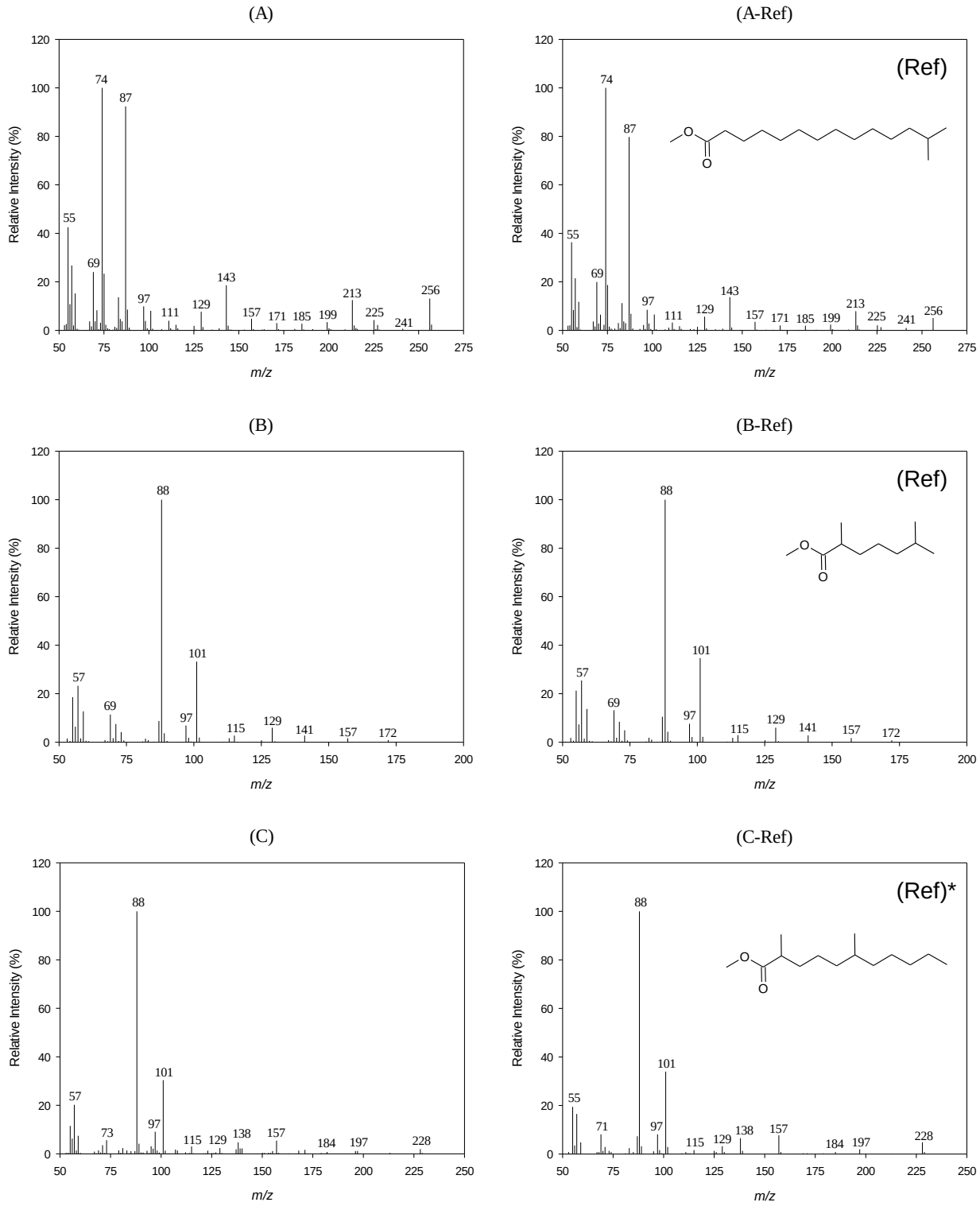


Figure 4.

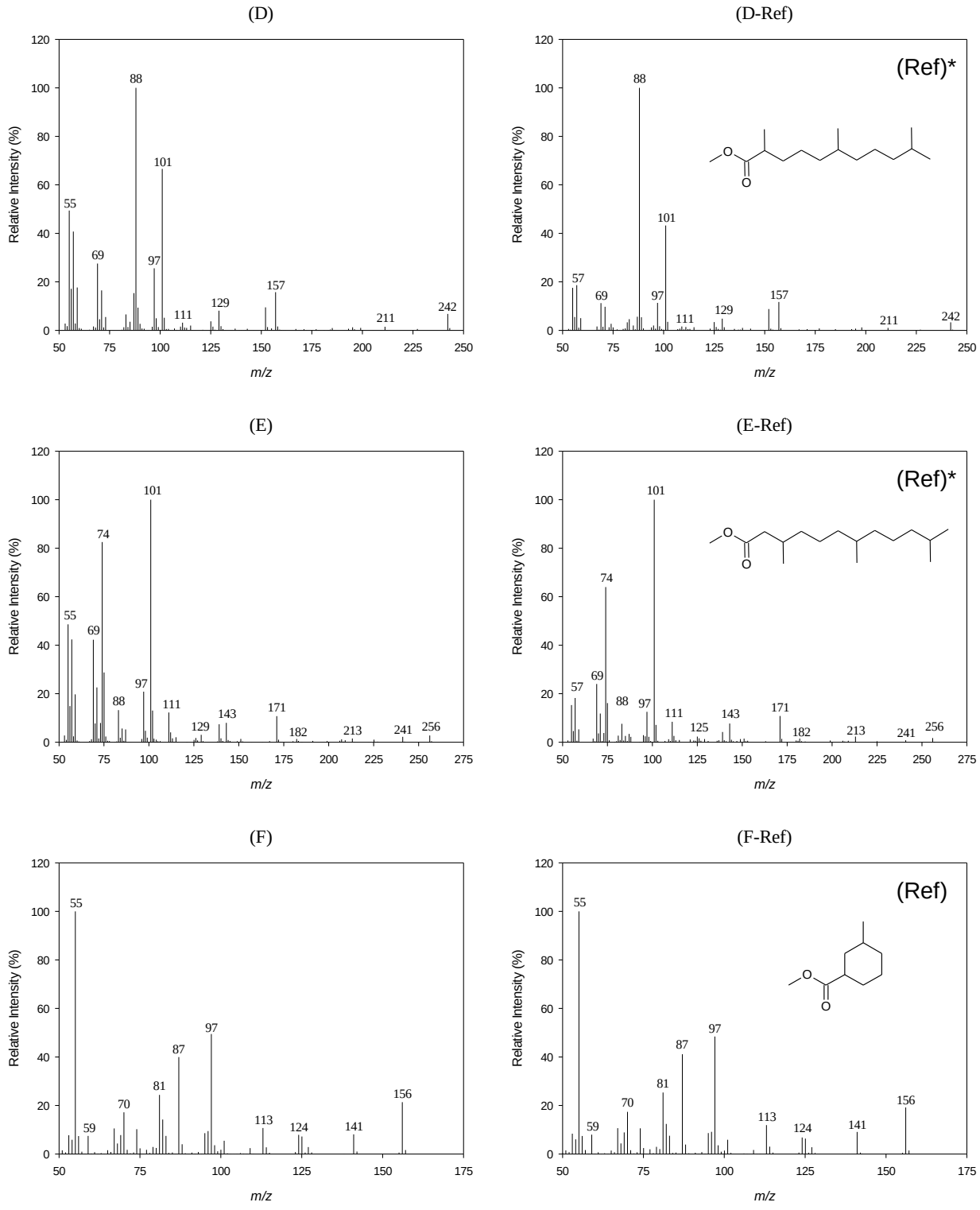
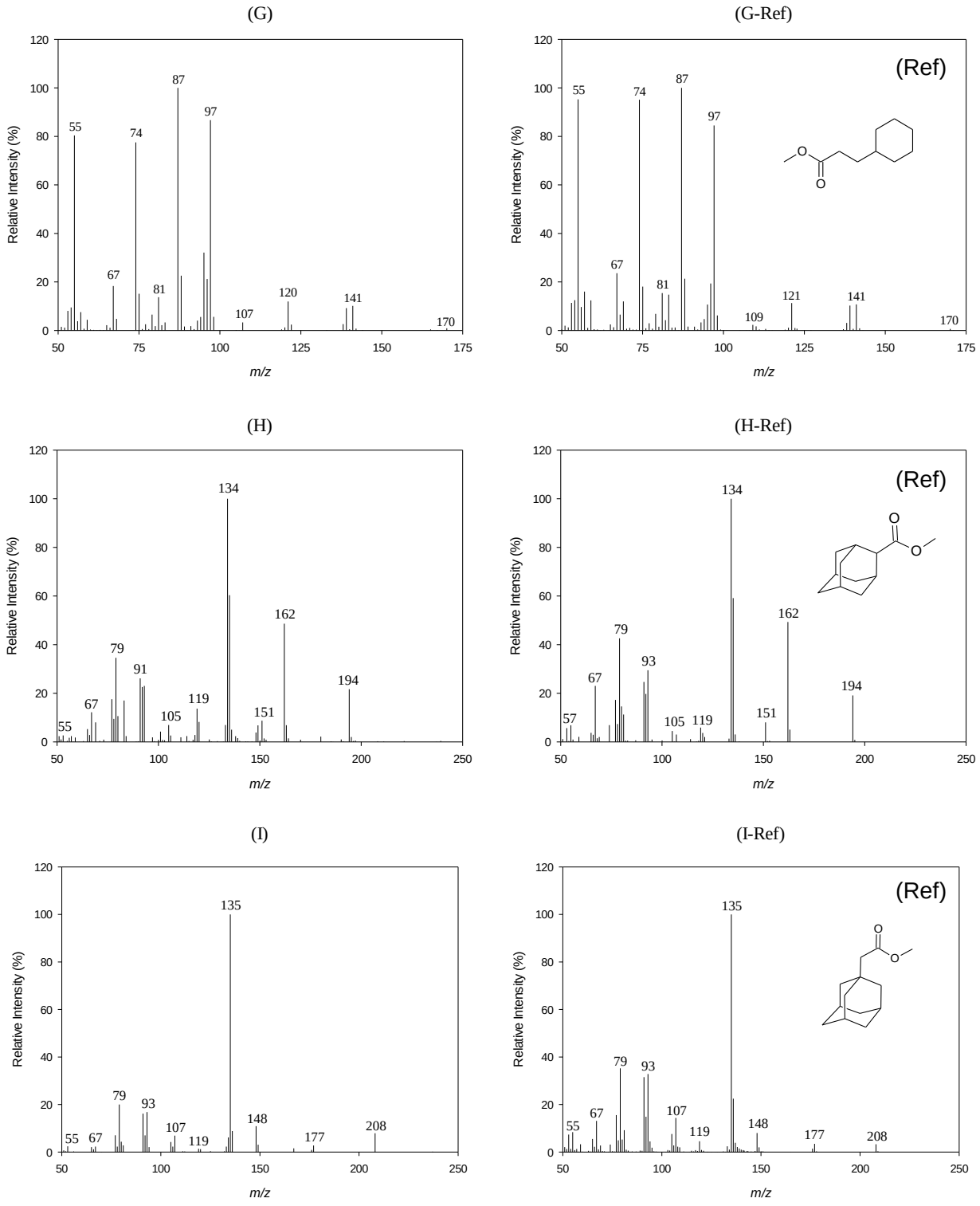


Figure 4 (Cont.)



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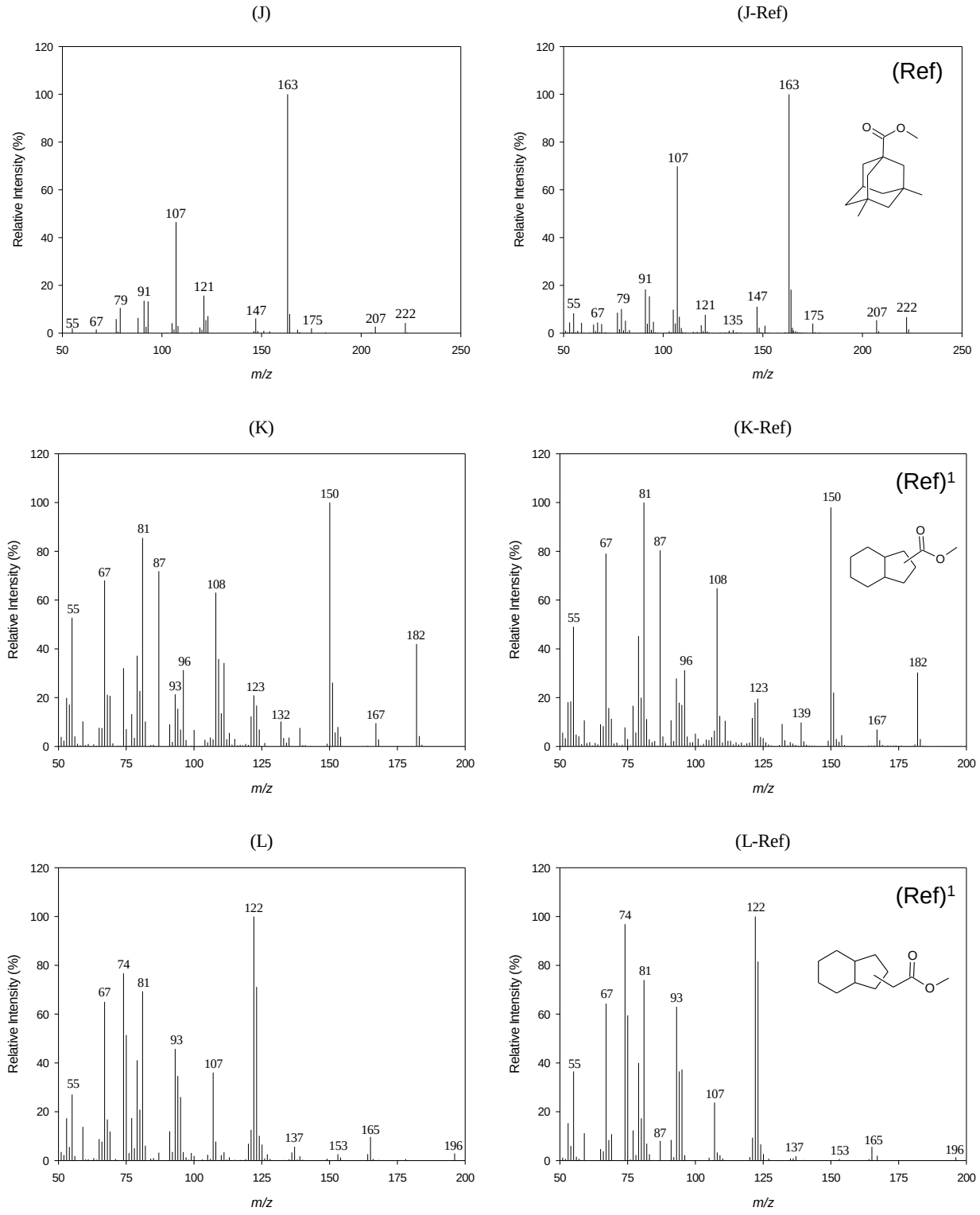

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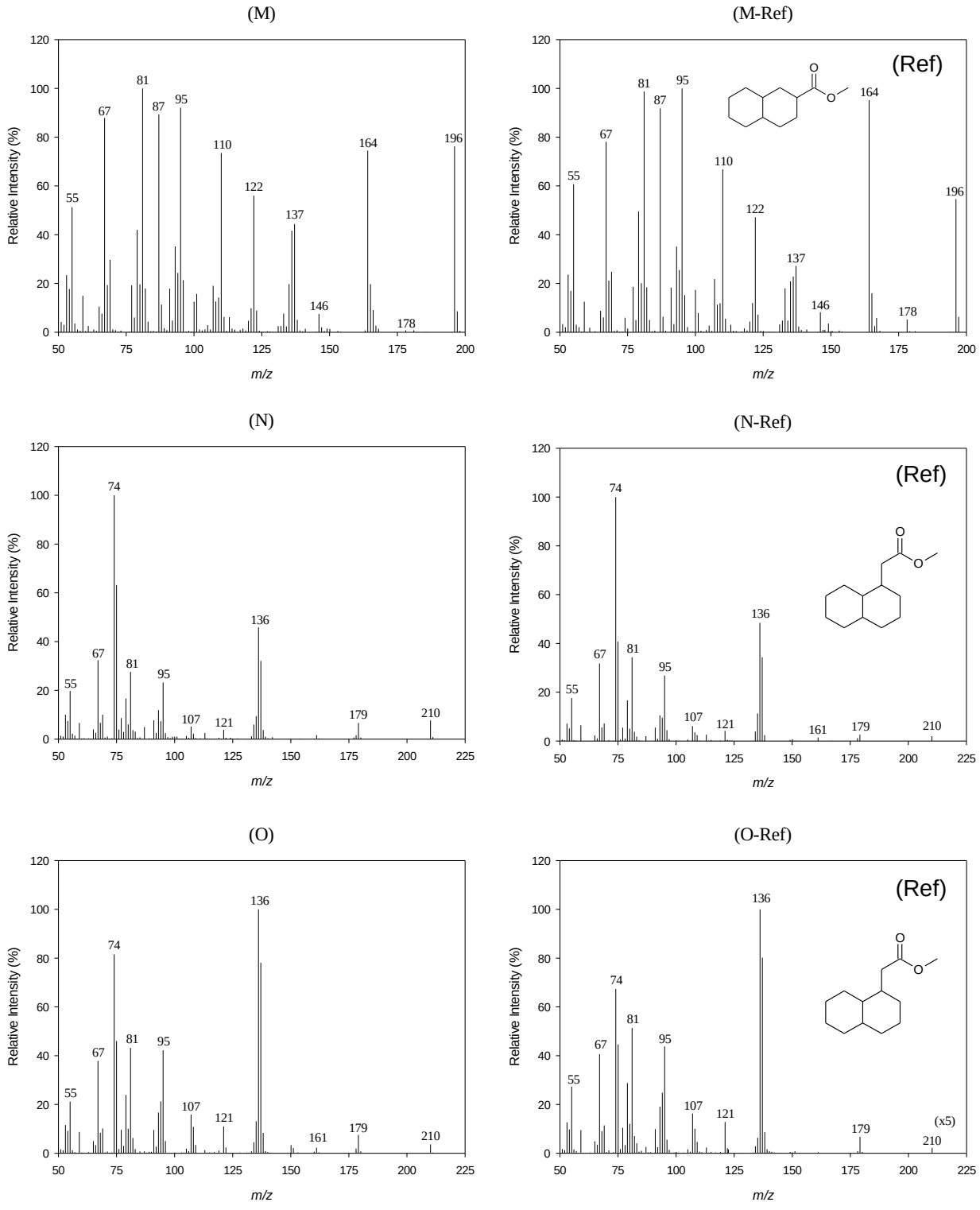


Figure 4 (Cont.)

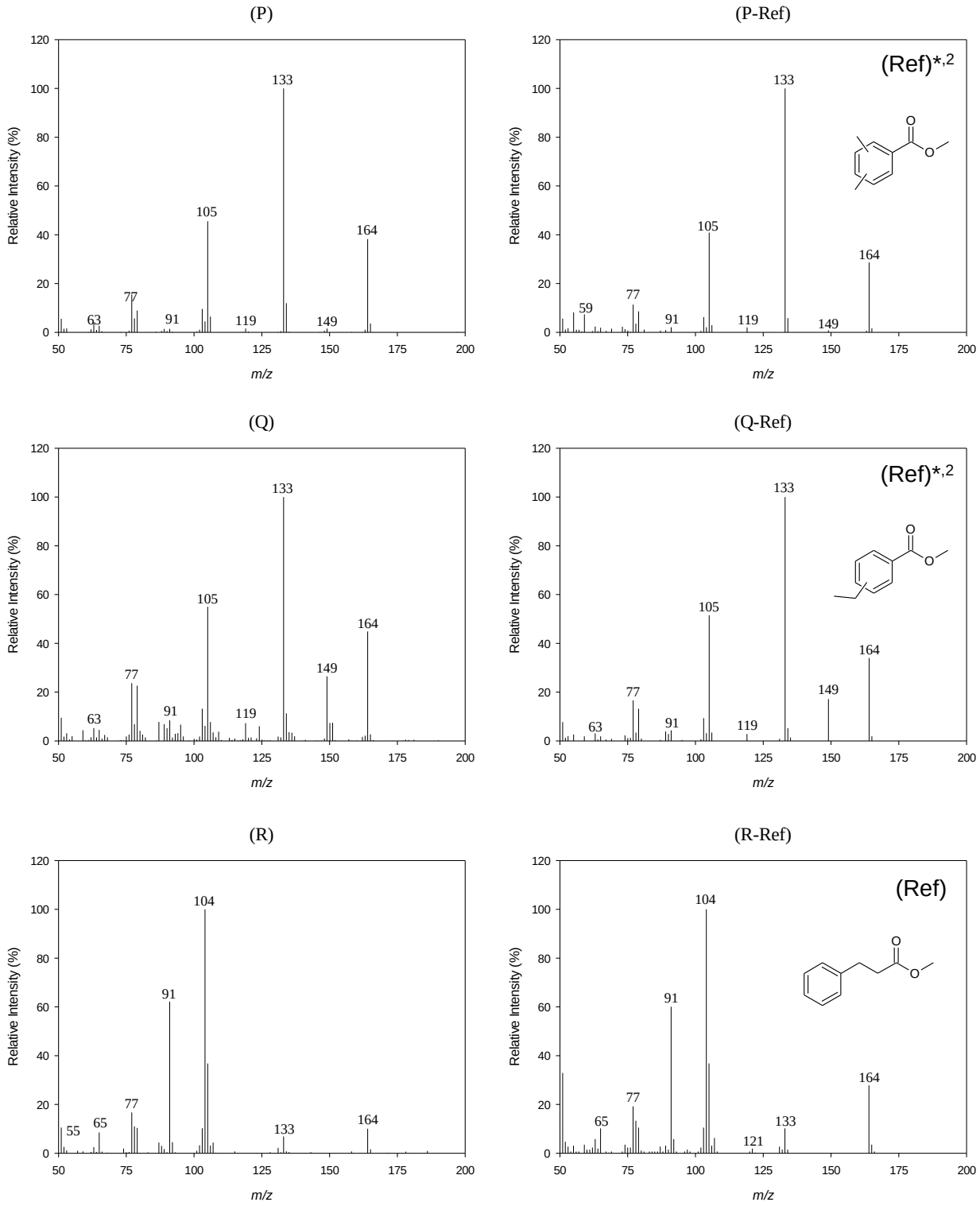
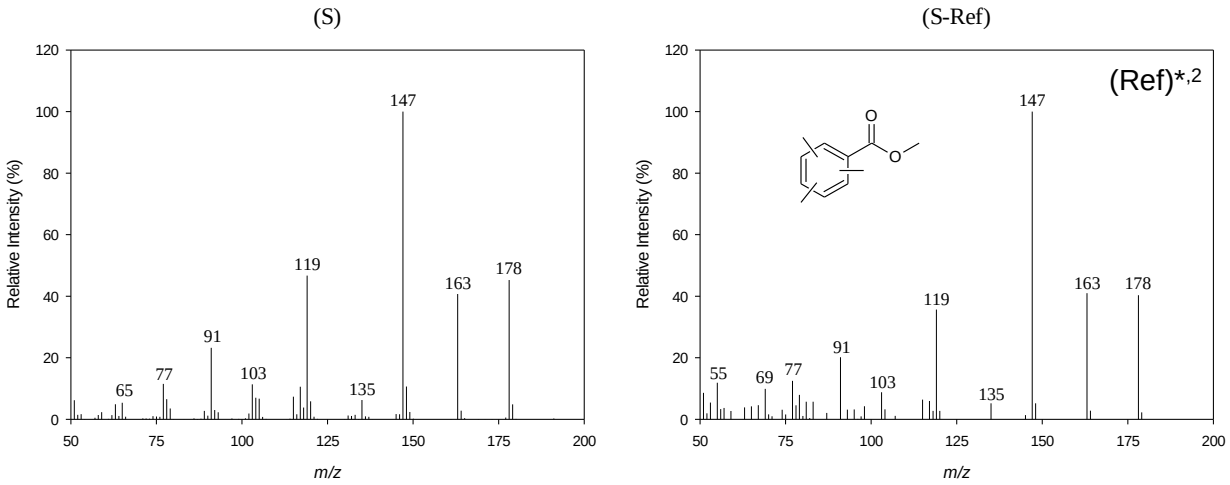


Figure 4 (Cont.)



Ref = Standard compound
Ref* = NIST Library Match
Ref[1] = Rowland et al. (2011) Rap. Comm. Mass. Spec 25: 1741-1751
Ref[2] = Rowland et al. (2011) Env. Chem. Lett. 9: 525-533

Figure 4 (Cont.)

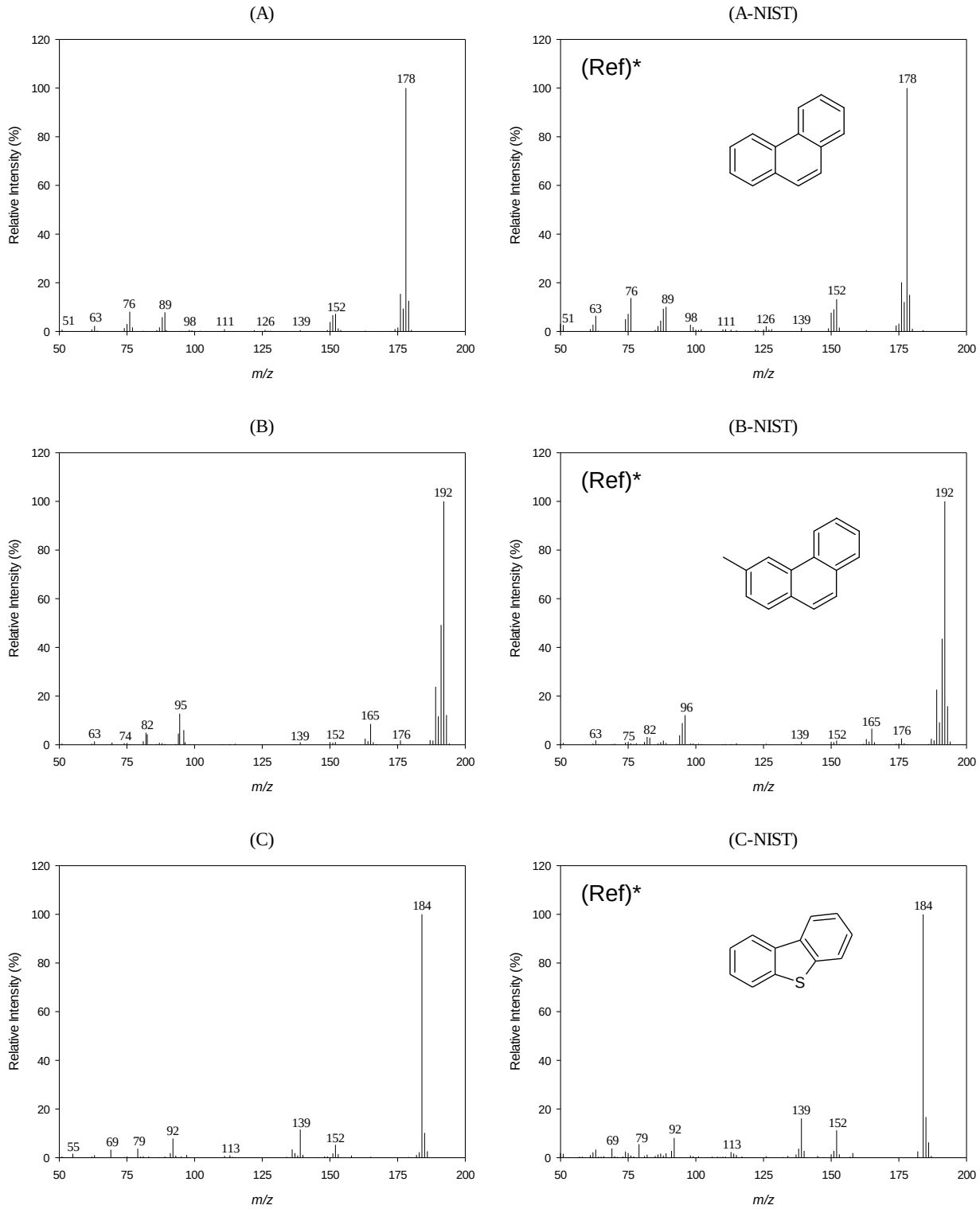

(A)
(A-NIST)
(Ref)*
(B)
(B-NIST)
(Ref)*
(C)
(C-NIST)
(Ref)*
Relative Intensity (%)
m/z
178
192
184
51
63
76
89
98
111
126
139
152
165
176
74
82
95
55
69
79
92
113
96
75
S

Figure 5.

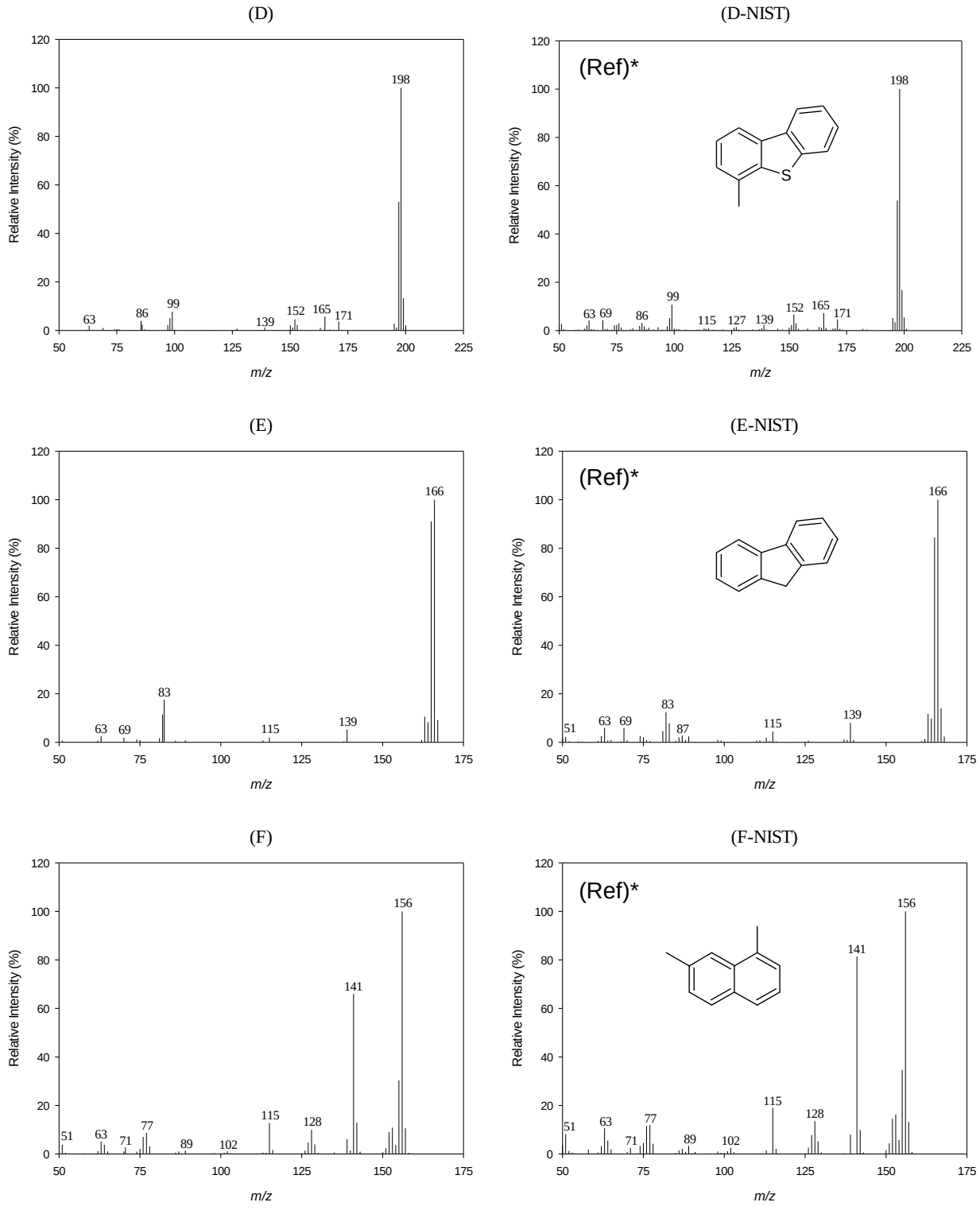


Figure 5 (Cont.)