ANNEXURE A

INITIAL AUTOMATED METHOD DEVELOPMENT CONDITIONS

Table 5.3.2: Initial AMD conditions required for CID voltage determination (m/z = 78 for Benzene)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
78	3	25	48.0	20	20.00	Nonres
78	3	30	48.0	20	20.00	Nonres
78	3	35	48.0	20	20.00	Nonres
78	3	40	48.0	20	20.00	Nonres
78	3	45	48.0	20	20.00	Nonres
78	3	50	48.0	20	20.00	Nonres
78	3	55	48.0	20	20.00	Nonres
78	3	60	48.0	20	20.00	Nonres
78	3	65	48.0	20	20.00	Nonres
78	3	70	48.0	20	20.00	Nonres

Table 5.3.3: Initial AMD conditions required for CID voltage determination (m/z = 106 for Ethyl Benzene and Xylenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
106	3	25	48.0	20	20.00	Nonres
106	3	30	48.0	20	20.00	Nonres
106	3	35	48.0	20	20.00	Nonres
106	3	40	48.0	20	20.00	Nonres
106	3	45	48.0	20	20.00	Nonres
106	3	50	48.0	20	20.00	Nonres
106	3	55	48.0	20	20.00	Nonres
106	3	60	48.0	20	20.00	Nonres
106	3	65	48.0	20	20.00	Nonres
106	3	70	48.0	20	20.00	Nonres

Table 5.3.4: Initial AMD conditions required for CID voltage determination (m/z = 120 for Isopropyl Benzene and Propyl Benzene)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
120	3	25	53.1	20	20.00	Nonres
120	3	30	53.1	20	20.00	Nonres
120	3	35	53.1	20	20.00	Nonres
120	3	40	53.1	20	20.00	Nonres
120	3	45	53.1	20	20.00	Nonres
120	3	50	53.1	20	20.00	Nonres
120	3	55	53.1	20	20.00	Nonres
120	3	60	53.1	20	20.00	Nonres
120	3	65	53.1	20	20.00	Nonres
120	3	70	53.1	20	20.00	Nonres

Table 5.3.5: Initial AMD conditions required for CID voltage determination (m / z = 120 for C3-Alkylbenzenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
120	3	25	53.1	20	20.00	Nonres
120	3	30	53.1	20	20.00	Nonres
120	3	35	53.1	20	20.00	Nonres
120	3	40	53.1	20	20.00	Nonres
120	3	45	53.1	20	20.00	Nonres
120	3	50	53.1	20	20.00	Nonres
120	3	55	53.1	20	20.00	Nonres
120	3	60	53.1	20	20.00	Nonres
120	3	65	53.1	20	20.00	Nonres
120	3	70	53.1	20	20.00	Nonres

Table 5.3.6: Initial AMD conditions required for CID voltage determination (m / z = 117 for Indane)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
117	3	25	52.2	20	20.00	Nonres
117	3	30	52.2	20	20.00	Nonres
117	3	35	52.2	20	20.00	Nonres
117	3	40	52.2	20	20.00	Nonres
117	3	45	52.2	20	20.00	Nonres
117	3	50	52.2	20	20.00	Nonres
117	3	55	52.2	20	20.00	Nonres
117	3	60	52.2	20	20.00	Nonres
117	3	65	52.2	20	20.00	Nonres
117	3	70	52.2	20	20.00	Nonres

Table 5.3.7: Initial AMD conditions required for CID voltage determination (m/z = 134 for C4-Alkylbenzenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
134	3	25	59.3	20	20.00	Nonres
134	3	30	59.3	20	20.00	Nonres
134	3	35	59.3	20	20.00	Nonres
134	3	40	59.3	20	20.00	Nonres
134	3	45	59.3	20	20.00	Nonres
134	3	50	59.3	20	20.00	Nonres
134	3	55	59.3	20	20.00	Nonres
134	3	60	59.3	20	20.00	Nonres
134	3	65	59.3	20	20.00	Nonres
134	3	70	59.3	20	20.00	Nonres

Table 5.3.8: Initial AMD conditions required for CID voltage determination (m/z = 148 for C5-Alkylbenzenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
148	3	25	65.5	20	20.00	Nonres
148	3	30	65.5	20	20.00	Nonres
148	3	35	65.5	20	20.00	Nonres
148	3	40	65.5	20	20.00	Nonres
148	3	45	65.5	20	20.00	Nonres
148	3	50	65.5	20	20.00	Nonres
148	3	55	65.5	20	20.00	Nonres
148	3	60	65.5	20	20.00	Nonres
148	3	65	65.5	20	20.00	Nonres
148	3	70	65.5	20	20.00	Nonres

Table 5.3.9: Initial AMD conditions required for CID voltage determination (m/z = 162 for C6-Alkylbenzenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
162	3	25	71.7	20	20.00	Nonres
162	3	30	71.7	20	20.00	Nonres
162	3	35	71.7	20	20.00	Nonres
162	3	40	71.7	20	20.00	Nonres
162	3	45	71.7	20	20.00	Nonres
162	3	50	71.7	20	20.00	Nonres
162	3	55	71.7	20	20.00	Nonres
162	3	60	71.7	20	20.00	Nonres
162	3	65	71.7	20	20.00	Nonres
162	3	70	71.7	20	20.00	Nonres

Table 5.3.10: Initial AMD conditions required for CID voltage determination (m/z = 128 for Naphthalene)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
128	3	25	56.7	20	20.00	Nonres
128	3	30	56.7	20	20.00	Nonres
128	3	35	56.7	20	20.00	Nonres
128	3	40	56.7	20	20.00	Nonres
128	3	45	56.7	20	20.00	Nonres
128	3	50	56.7	20	20.00	Nonres
128	3	55	56.7	20	20.00	Nonres
128	3	60	56.7	20	20.00	Nonres
128	3	65	56.7	20	20.00	Nonres
128	3	70	56.7	20	20.00	Nonres

Table 5.3.11: Initial AMD conditions required for CID voltage determination (m/z = 142 for C1-Naphthalenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
142	3	25	62.9	20	20.00	Nonres
142	3	30	62.9	20	20.00	Nonres
142	3	35	62.9	20	20.00	Nonres
142	3	40	62.9	20	20.00	Nonres
142	3	45	62.9	20	20.00	Nonres
142	3	50	62.9	20	20.00	Nonres
142	3	55	62.9	20	20.00	Nonres
142	3	60	62.9	20	20.00	Nonres
142	3	65	62.9	20	20.00	Nonres
142	3	70	62.9	20	20.00	Nonres

Table 5.3.12: Initial AMD conditions required for CID voltage determination (m/z = 156 for C2-Naphthalenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
156	3	25	69.0	20	20.00	Nonres
156	3	30	69.0	20	20.00	Nonres
156	3	35	69.0	20	20.00	Nonres
156	3	40	69.0	20	20.00	Nonres
156	3	45	69.0	20	20.00	Nonres
156	3	50	69.0	20	20.00	Nonres
156	3	55	69.0	20	20.00	Nonres
156	3	60	69.0	20	20.00	Nonres
156	3	65	69.0	20	20.00	Nonres
156	3	70	69.0	20	20.00	Nonres

Table 5.3.13: Initial AMD conditions required for CID voltage determination (m/z = 170 for C3-Naphthalenes)

Parent Ion Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	CID Time (ms)	CID Amplitude (Volts)	Waveform Type
170	3	25	75.2	20	20.00	Nonres
170	3	30	75.2	20	20.00	Nonres
170	3	35	75.2	20	20.00	Nonres
170	3	40	75.2	20	20.00	Nonres
170	3	45	75.2	20	20.00	Nonres
170	3	50	75.2	20	20.00	Nonres
170	3	55	75.2	20	20.00	Nonres
170	3	60	75.2	20	20.00	Nonres
170	3	65	75.2	20	20.00	Nonres
170	3	70	75.2	20	20.00	Nonres

ANNEXURE B

ADDITIONAL FIGURES FOR AMD AND MS-MS DEVELOPMENT

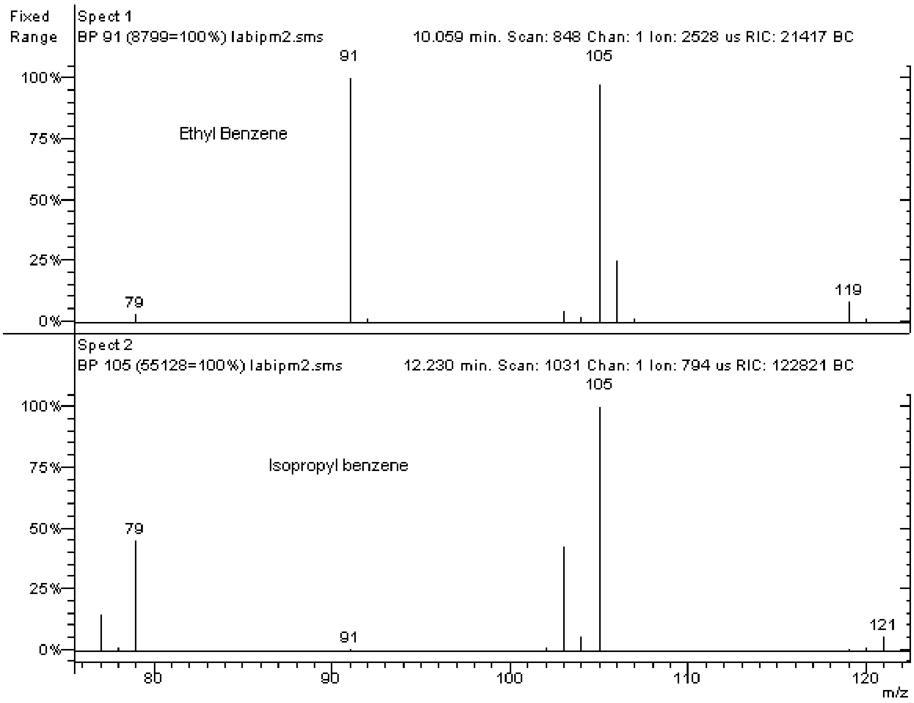

Figure 5.8.2: *AMD product ion mass spectrum for ethyl benzene (m/z=106) with the excitation storage level selected as 48 m/z and Isopropyl benzene (m/z=120) with the excitation storage level selected as 52.7m/z as calculated using the "q" calculator.*

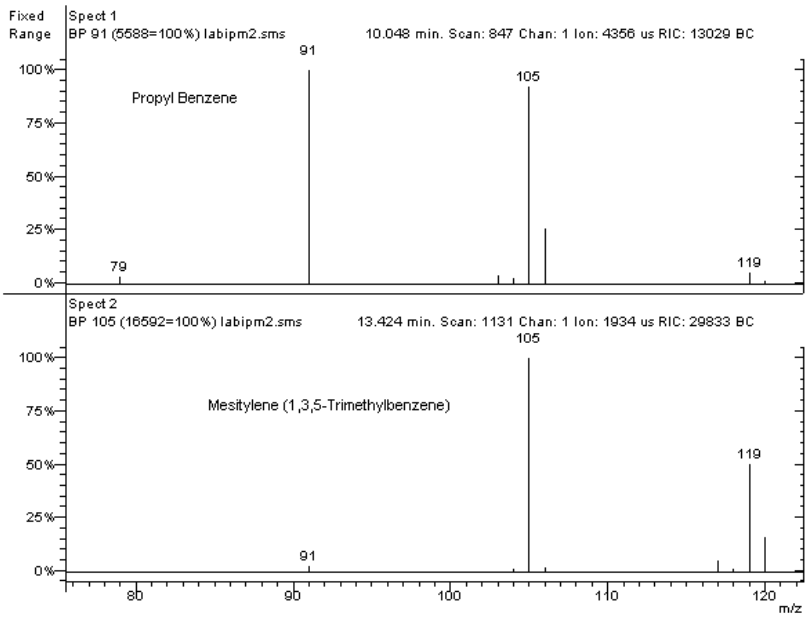

Figure 5.8.3: *AMD product ion mass spectrum for propyl benzene (m/z=120) and mesitylene (m/z=120) with the excitation storage level selected as 52.7m/z as calculated using the "q" calculator.*

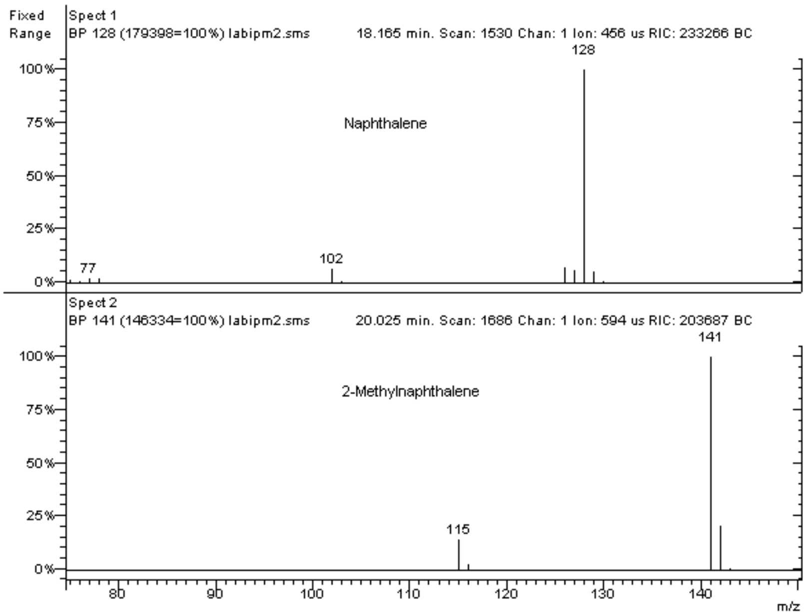

Figure 5.8.4: *AMD product ion mass spectrum for naphthalene (m/z = 128) and 2-methylnaphthalene (m/z = 142) with the excitation storage level selected as 56.2 m/z and 62.4 m/z as calculated using the "q" calculator.*

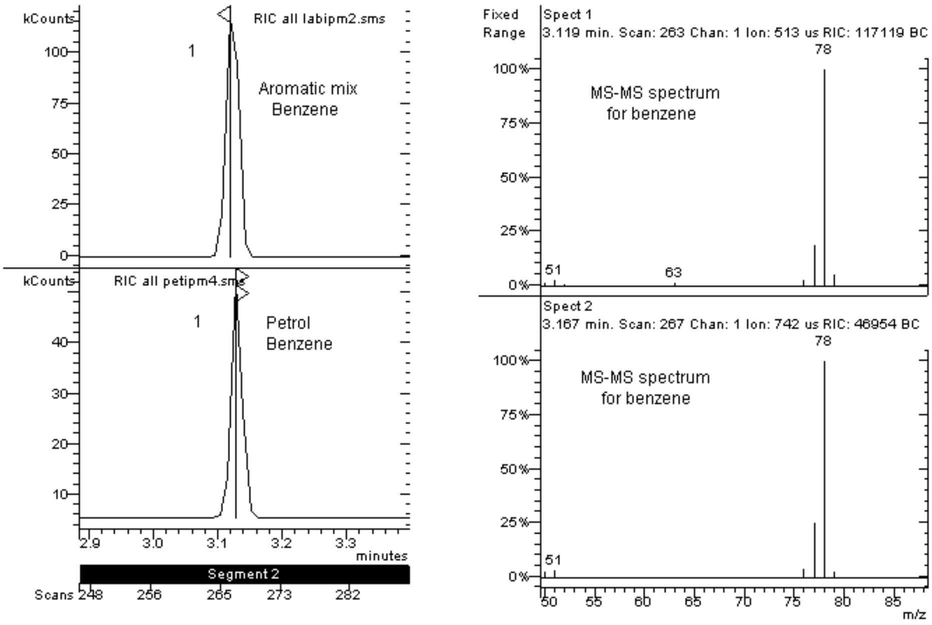

Figure 5.11.2: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for benzene (m/z=78), before finalizing the CID voltages.*

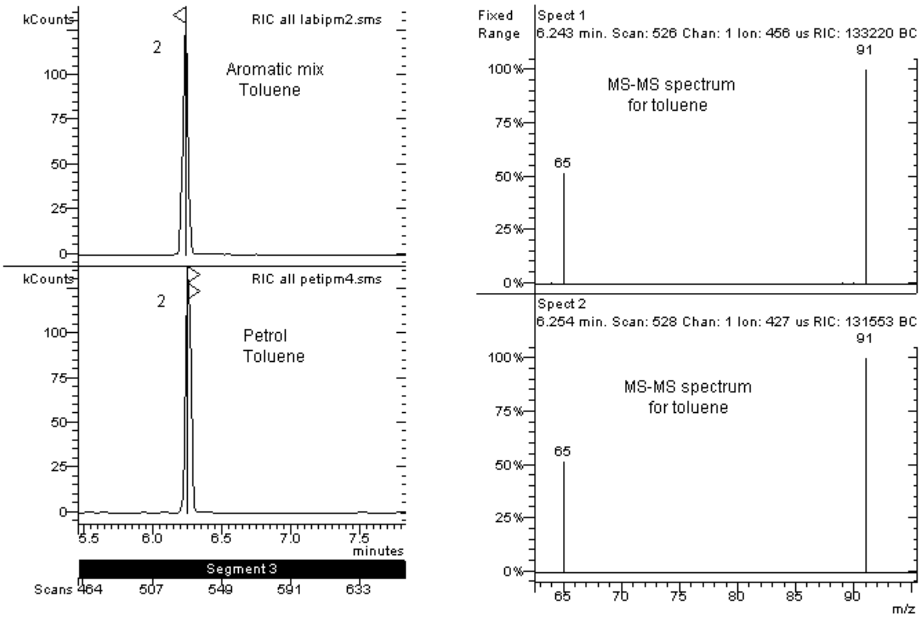

Figure 5.11.3: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for toluene (m/z=92), before finalizing the CID voltages.*

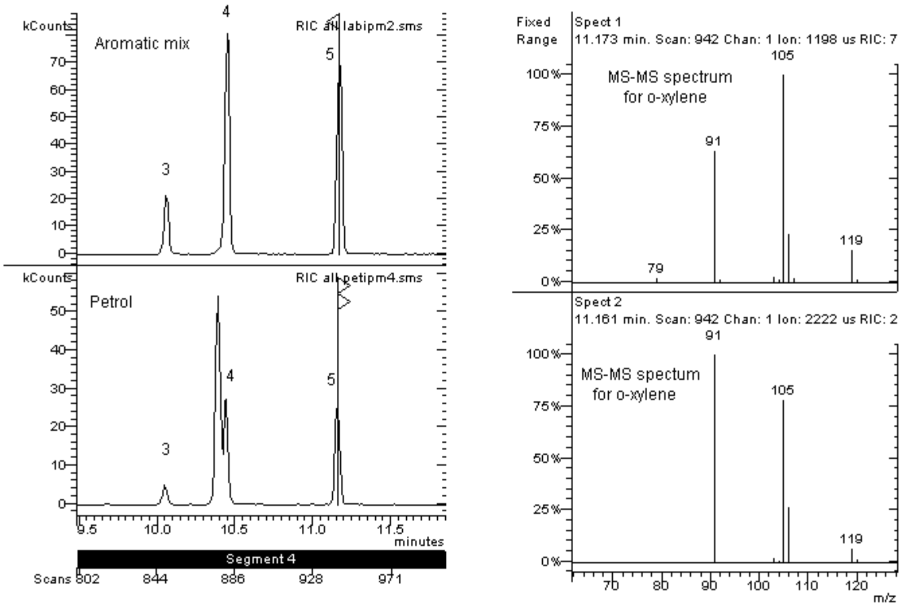

Figure 5.11.4: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for ethylbenzene and the xylenes using o-xylene (m/z=106), before finalizing the CID voltages.*

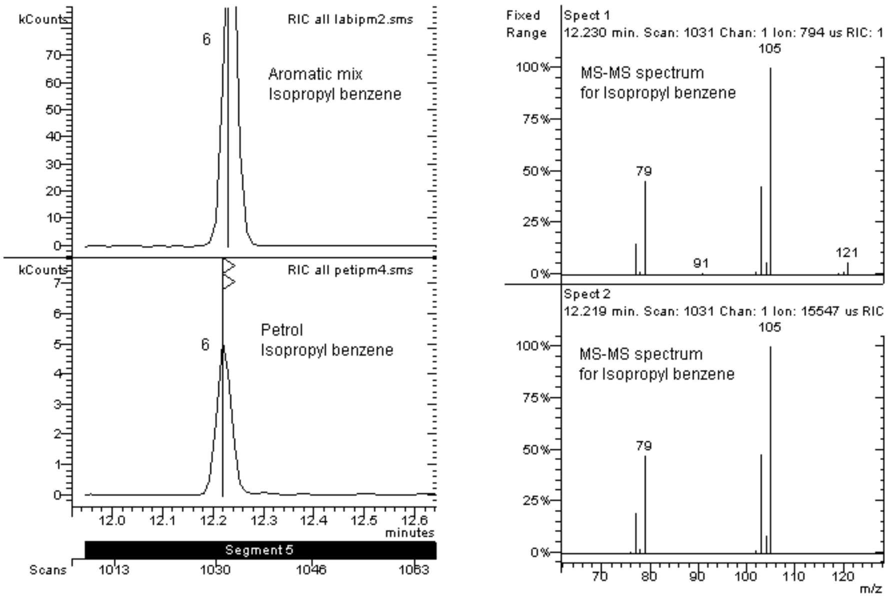

Figure 5.11.5: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for isopropylbenzene (m/z=120), before finalizing the CID voltages.*

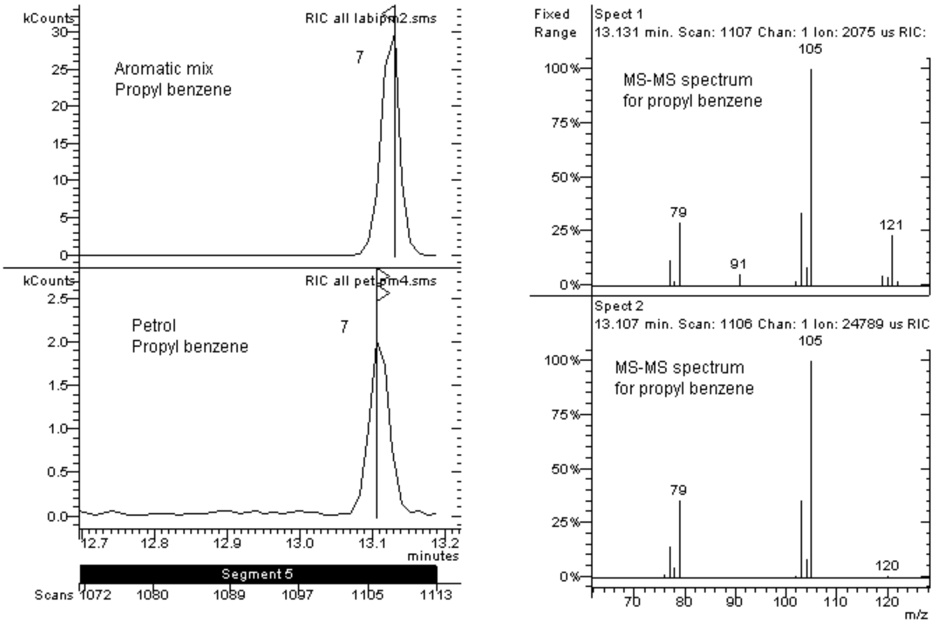

Figure 5.11.6: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for propylbenzene (m/z=120), before finalizing the CID voltages.*

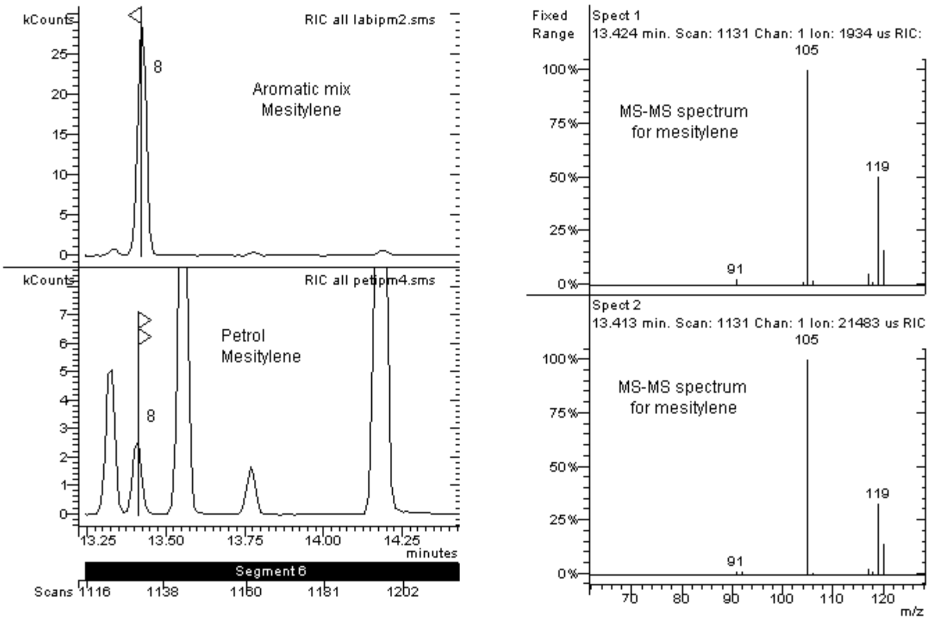

Figure 5.11.7: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for mesitylene (m/z=120), before finalizing the CID voltages.*

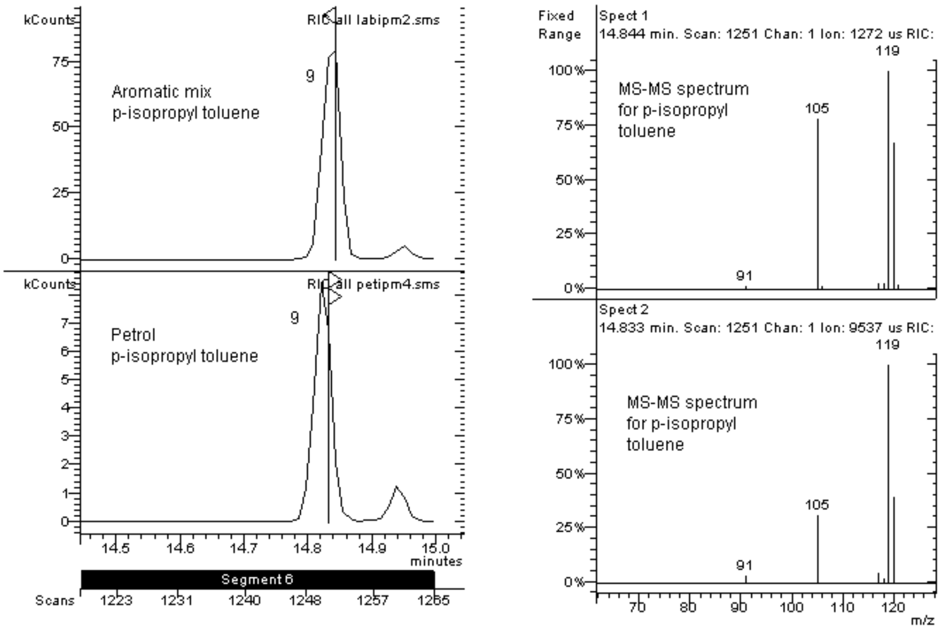

Figure 5.11.8: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for p-isopropyltoluene (m/z=120), before finalizing the CID voltages.*

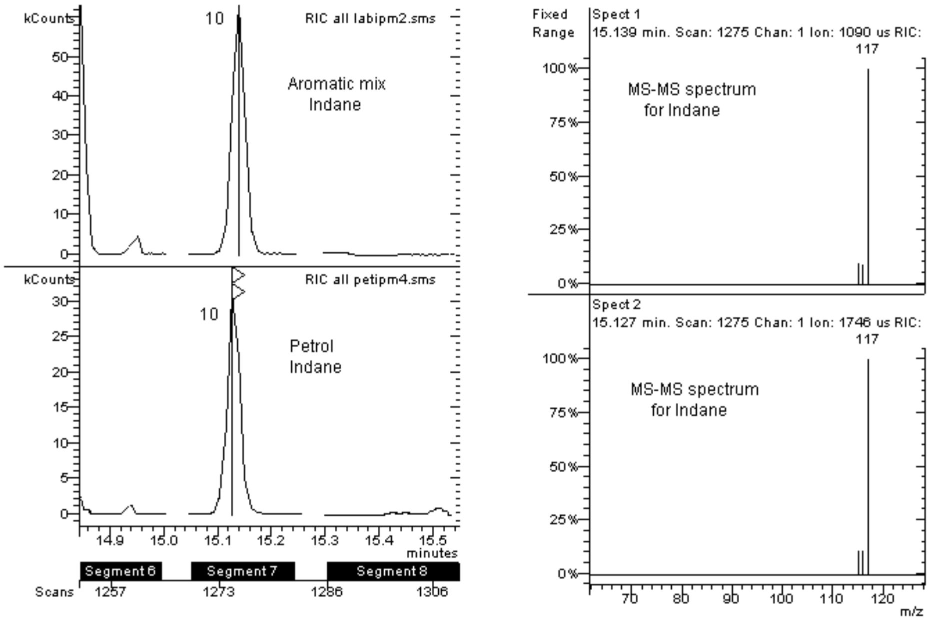

Figure 5.11.9: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the AMD product ion mass spectra for indane (m/z=117), before finalizing the CID voltages.*

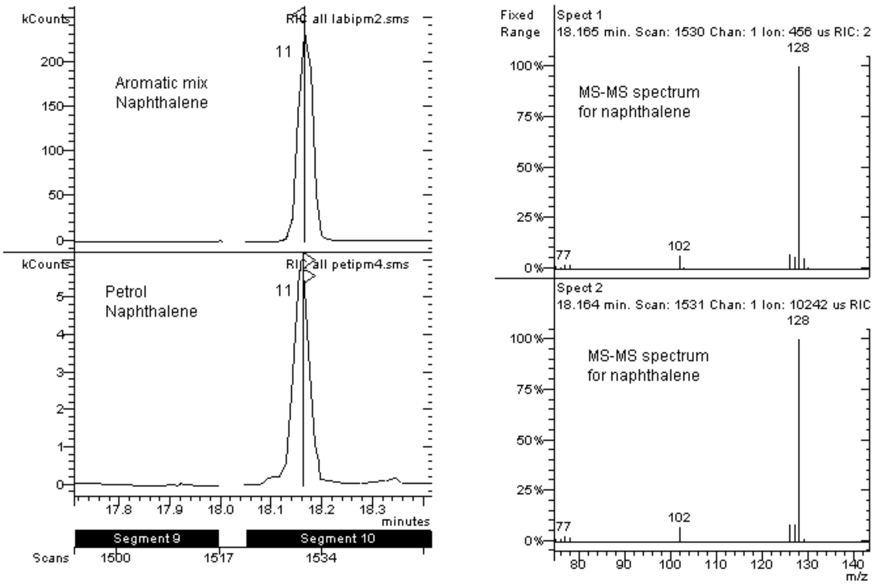

Figure 5.11.10: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for naphthalene (m/z=128), before finalizing the CID voltages.*

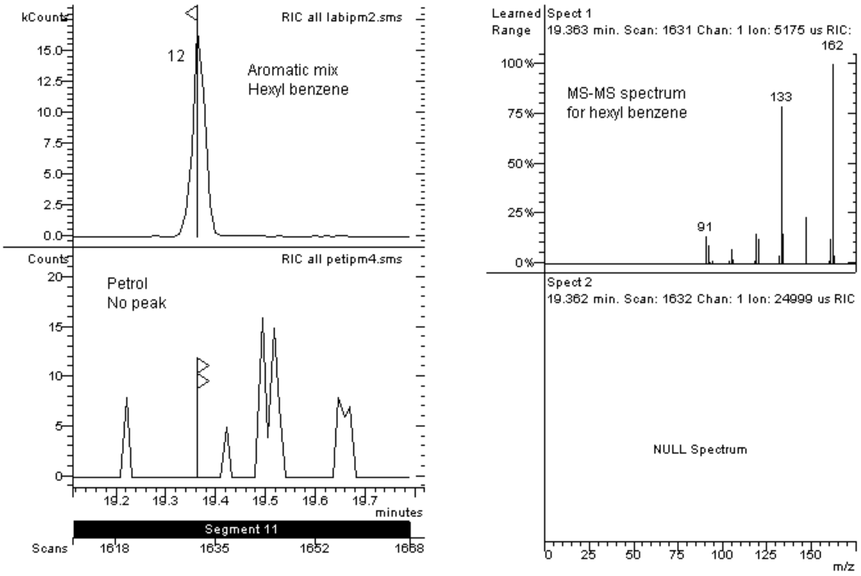

Figure 5.11.11: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for hexylbenzene (m/z=162), before finalizing the CID voltages. This indicates the need for correcting the voltages, since the hexylbenzene peak is minute in petrol.*

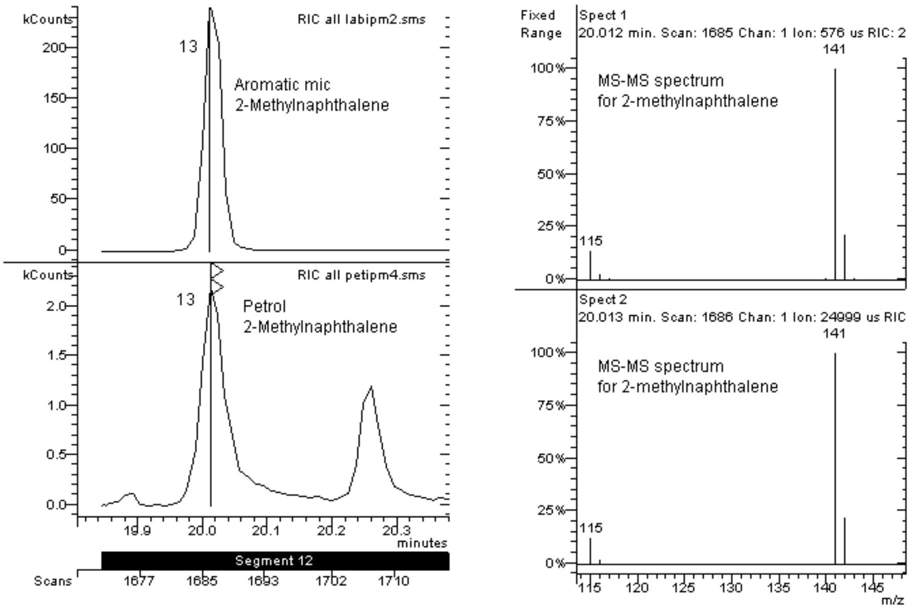

Figure 5.11.12: *Comparison between a simulated aromatic mix (upper trace) and a petrol standard (lower trace) of the product ion mass spectra for 2-methylnaphthalene (m/z=142), before finalizing the CID voltages.*

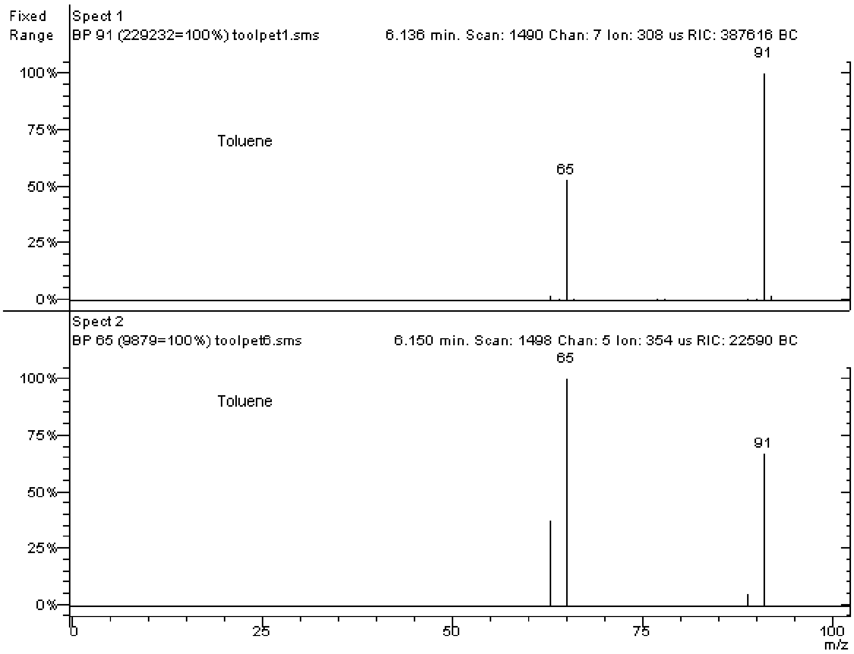

Figure 5.12.2: *Comparison between the initial and final AMD product ion mass spectra for toluene.*

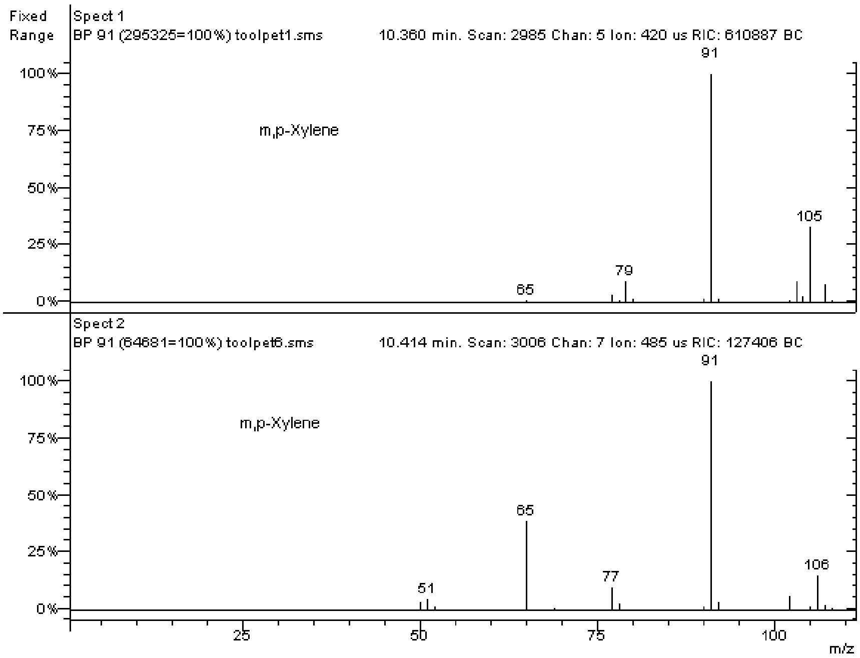

Figure 5.12.3: *Comparison between the initial and final AMD product ion mass spectra for ethyl benzene, m,p-xylene and o-xylene using m,p-xylene as an example.*

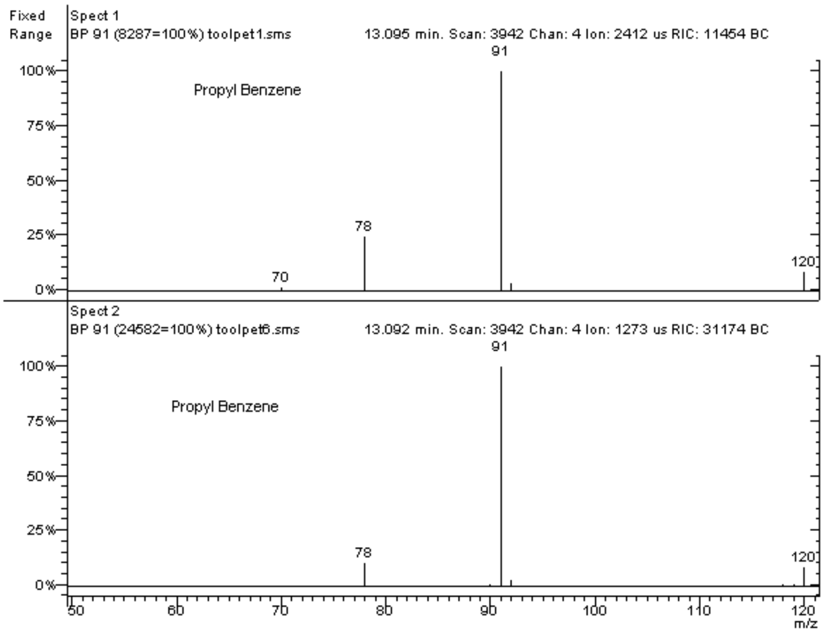

Figure 5.12.4: *Comparison between the initial and final AMD product ion mass spectra for isopropyl benzene and propyl benzene, using propyl benzene as an example.*

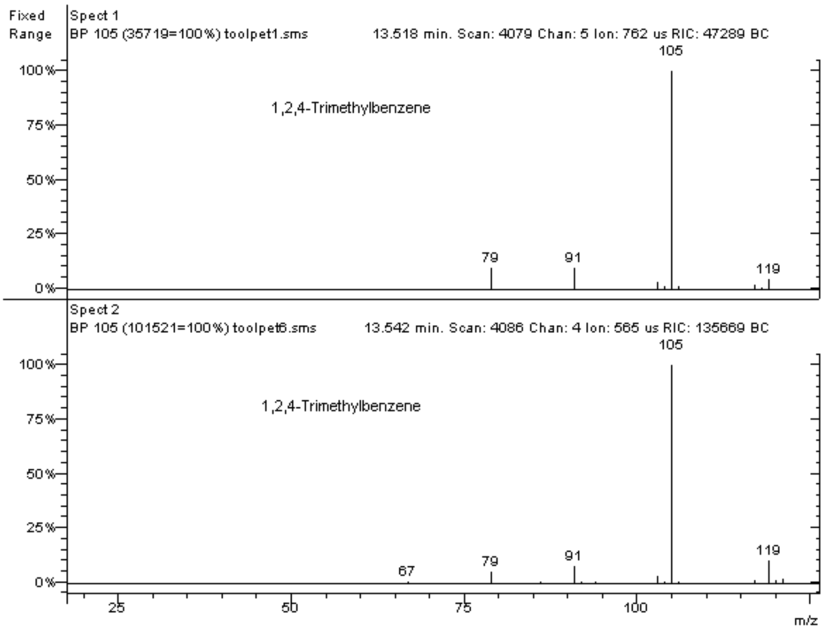

Figure 5.12.5: *Comparison between the initial and final AMD product ion mass spectra for the C3-alkylbenzenes, using 1,2,4-trimethyl benzene as an example.*

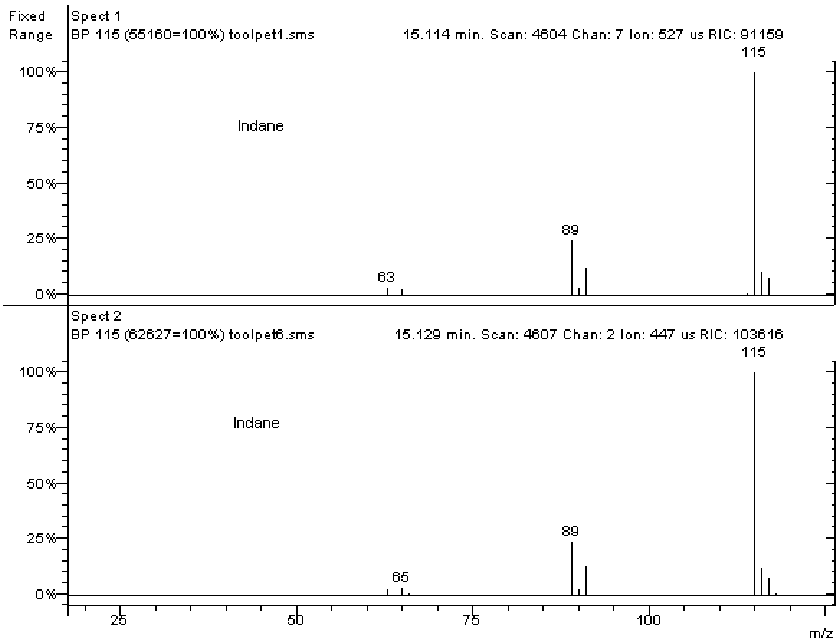

Figure 5.12.6: *Comparison between the initial and final AMD product ion mass spectra for Indane.*

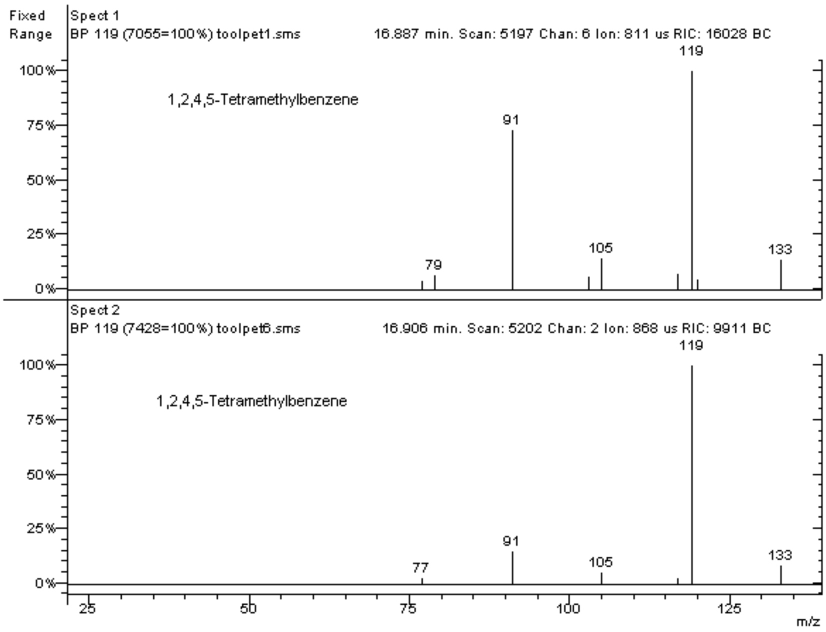

Figure 5.12.7: *Comparison between the initial and final AMD product ion mass spectra for the C4-alkylbenzenes, using 1,2,4,5-tetramethyl benzene as an example.*

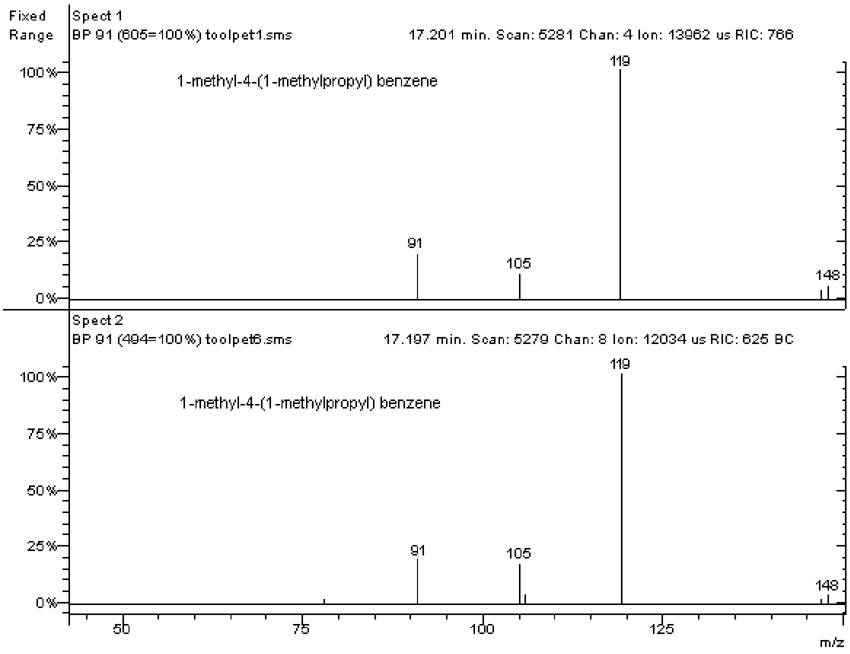

Figure 5.12.8: *Comparison between the initial and final AMD product ion mass spectra for the C5-alkylbenzenes, using 1-methyl-4-(1-methylpropyl) benzene as an example.*

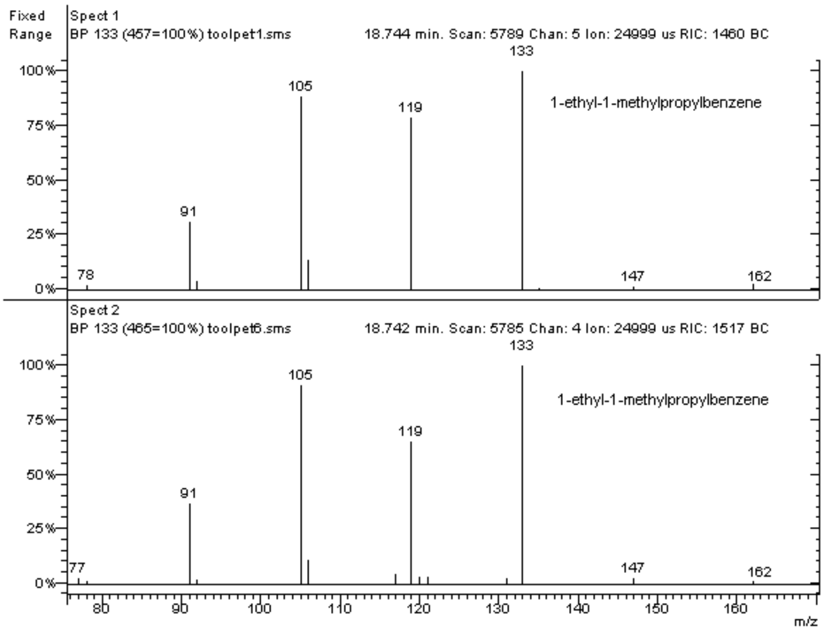

Figure 5.12.9: *Comparison between the initial and final AMD product ion mass spectra for the C6-alkylbenzenes, using 1-ethyl-1-methylpropyl benzene as an example.*

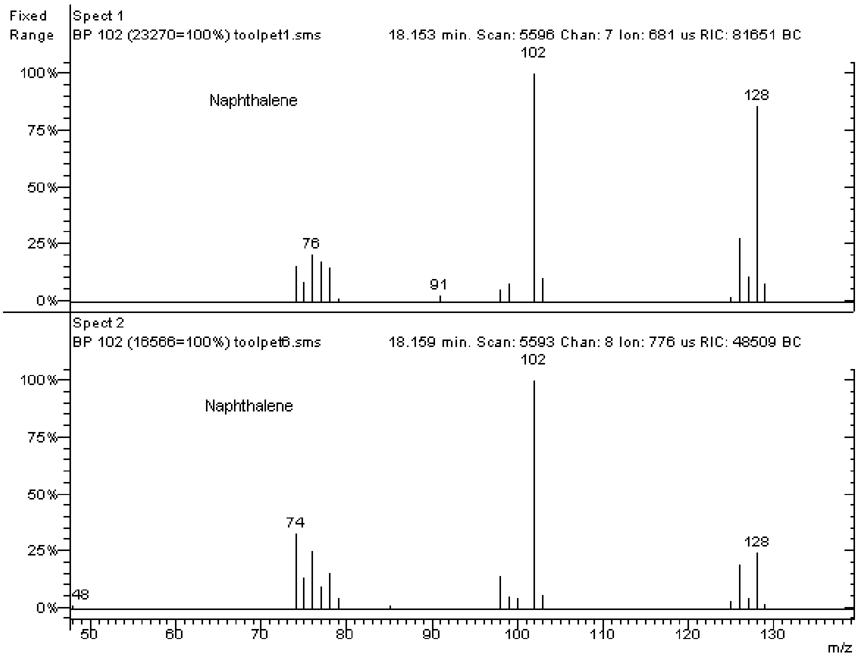

Figure 5.12.10: *Comparison between the initial and final AMD product ion mass spectra for naphthalene.*

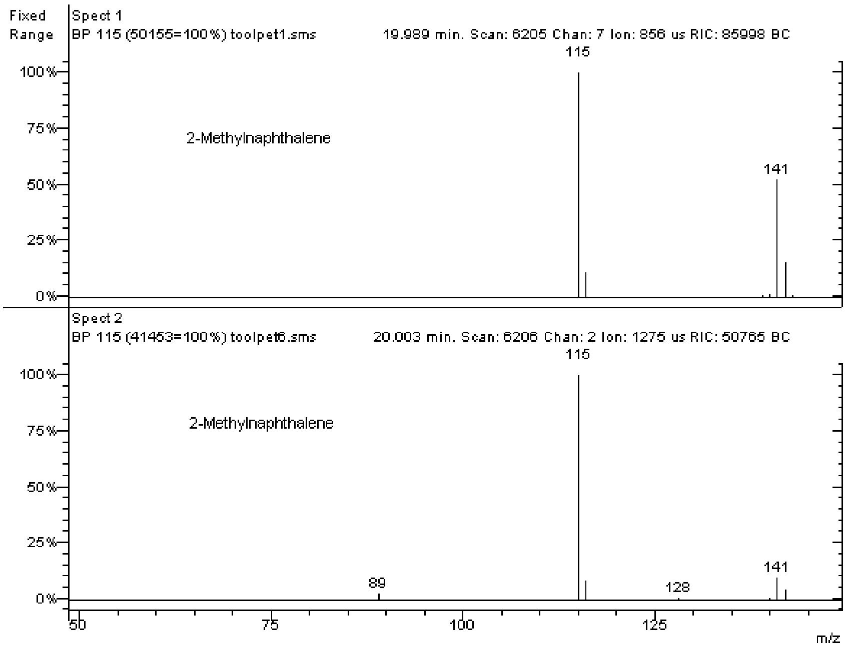

Figure 5.12.11: *Comparison between the initial and final AMD product ion mass spectra for the C1-alkylnaphthalenes, using 2-methylnaphthalene as an example.*

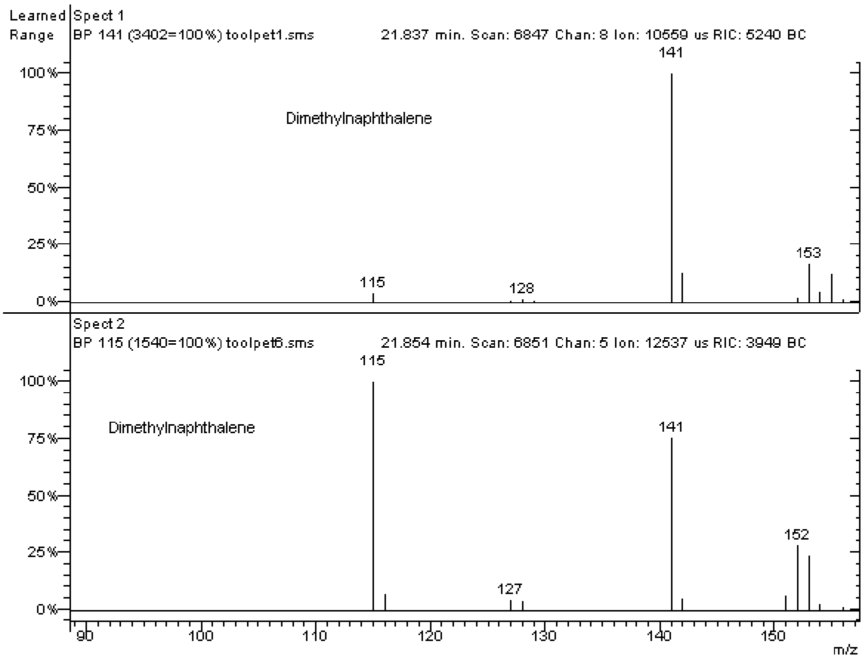

Figure 5.12.12: *Comparison between the initial and final AMD product ion mass spectra for the C2-alkylnaphthalenes, using Dimethylnaphthalene as an example.*

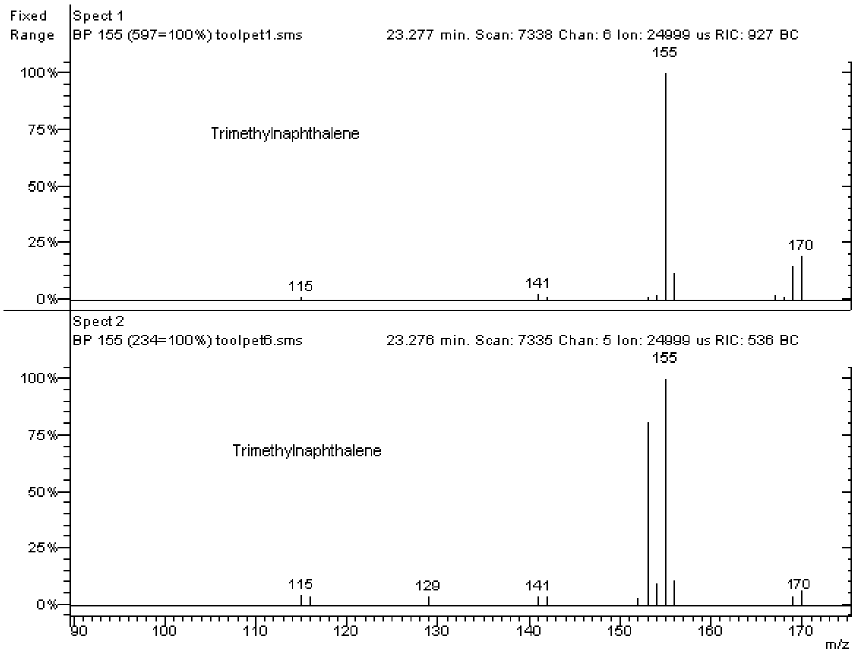

Figure 5.12.13: *Comparison between the initial and final AMD product ion mass spectra for the C3-alkylnaphthalenes, using trimethylnaphthalene as an example.*

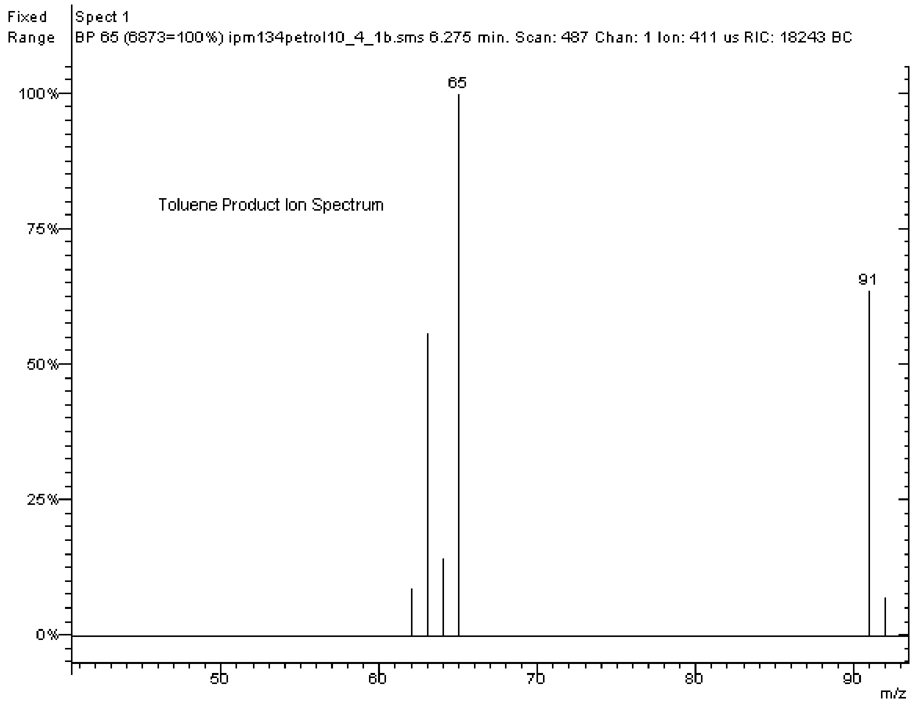

Figure 5.13.2: *MS-MS product ion mass spectrum for toluene.*

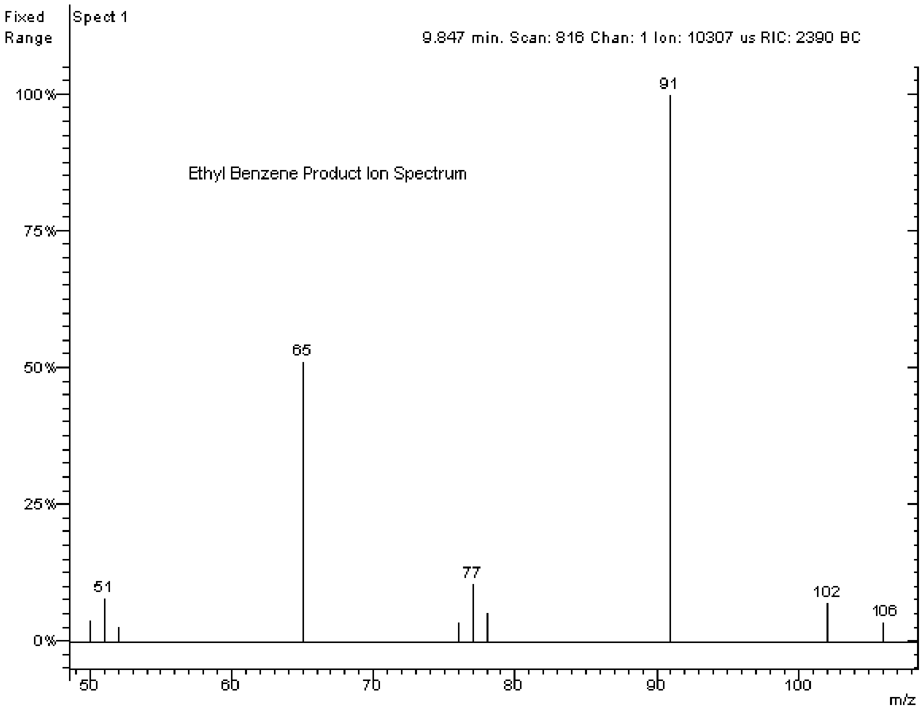

Figure 5.13.3: *MS-MS product ion mass spectrum for ethyl-benzene.*

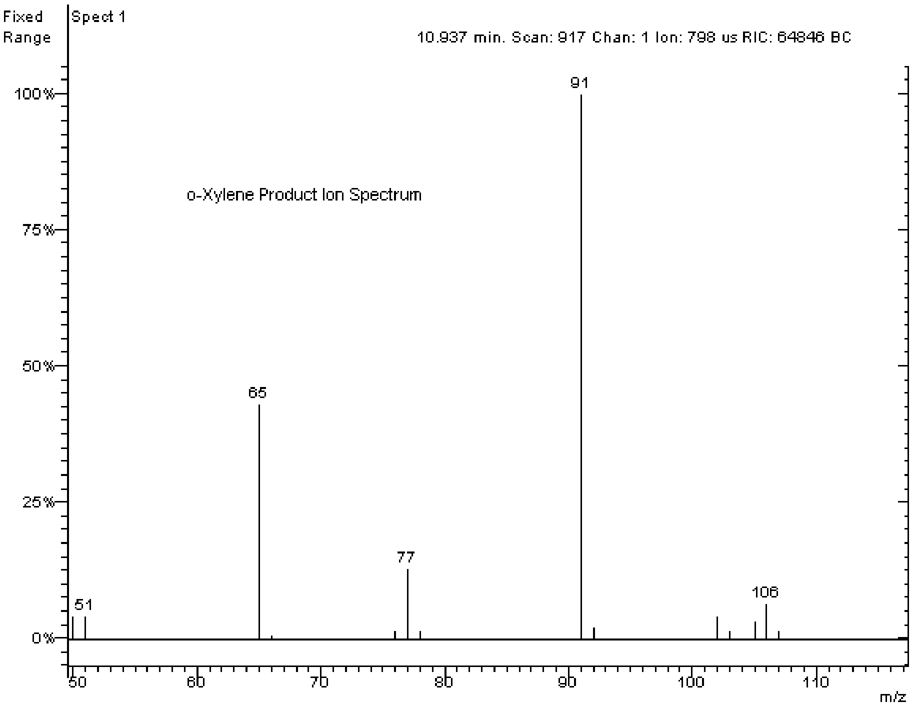

Figure 5.13.4: *MS-MS product ion mass spectrum for o-xylene.*

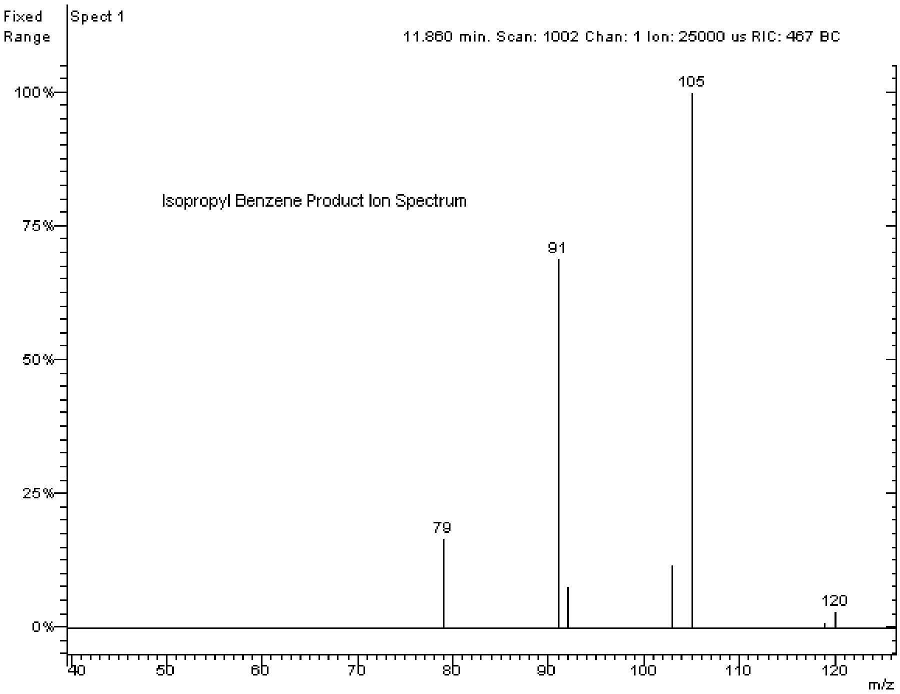

Figure 5.13.5: *MS-MS product ion mass spectrum for isopropylbenzene.*

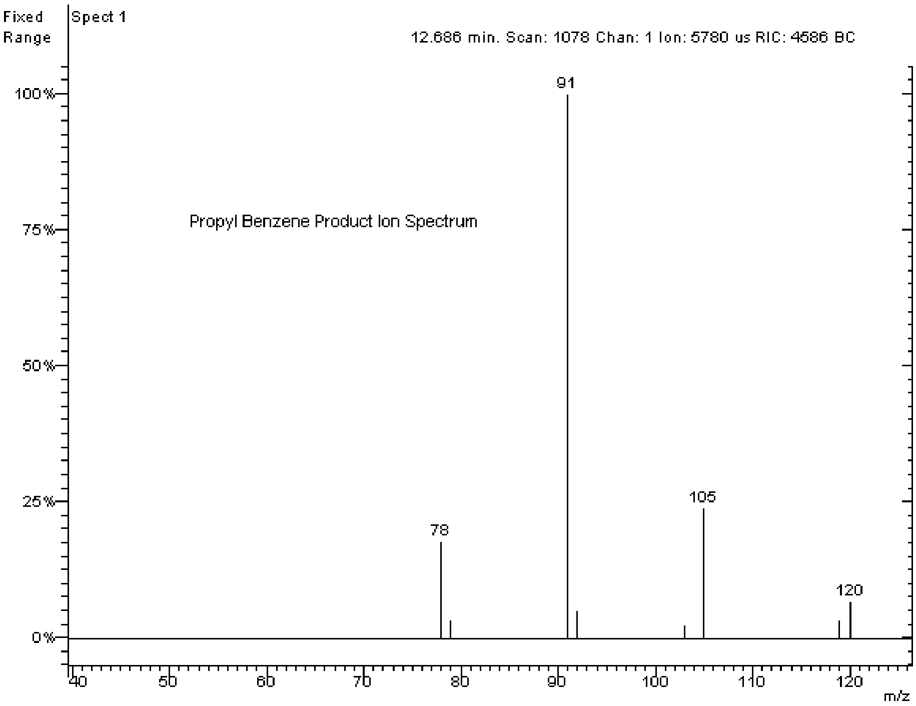

Figure 5.13.6: *MS-MS product ion mass spectrum for propyl-benzene.*

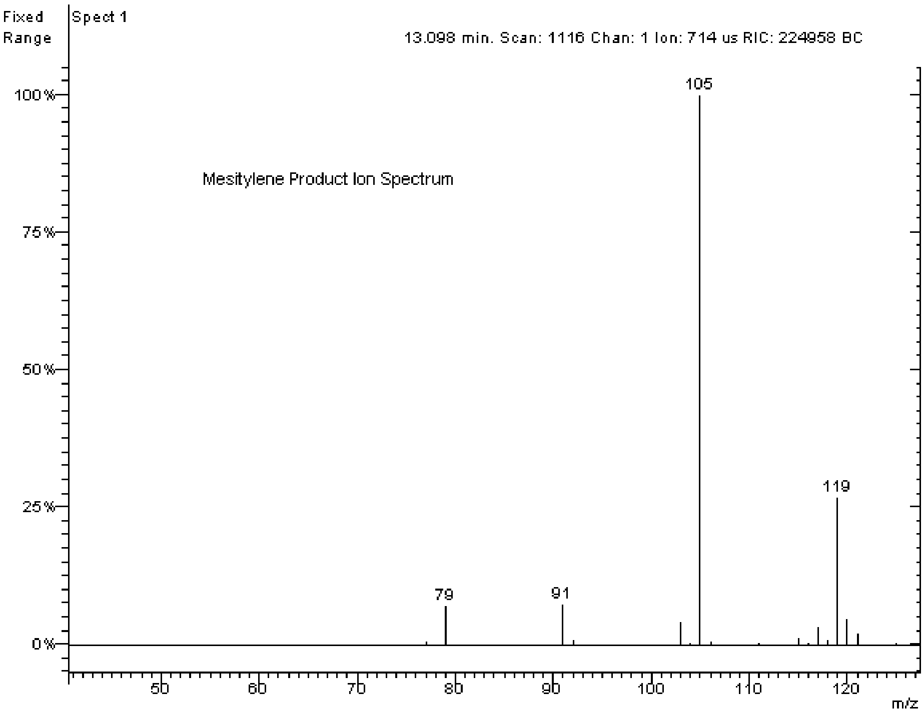

Figure 5.13.7: *MS-MS product ion mass spectrum for mesitylene.*

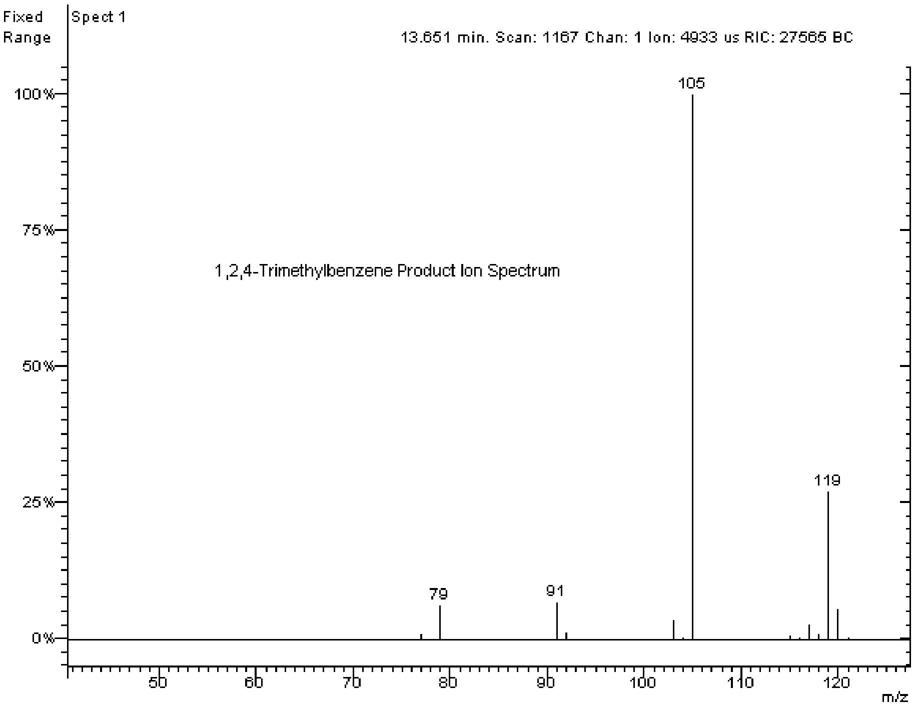

Figure 5.13.8: *MS-MS product ion mass spectrum for 1,2,4-trimethylbenzene.*

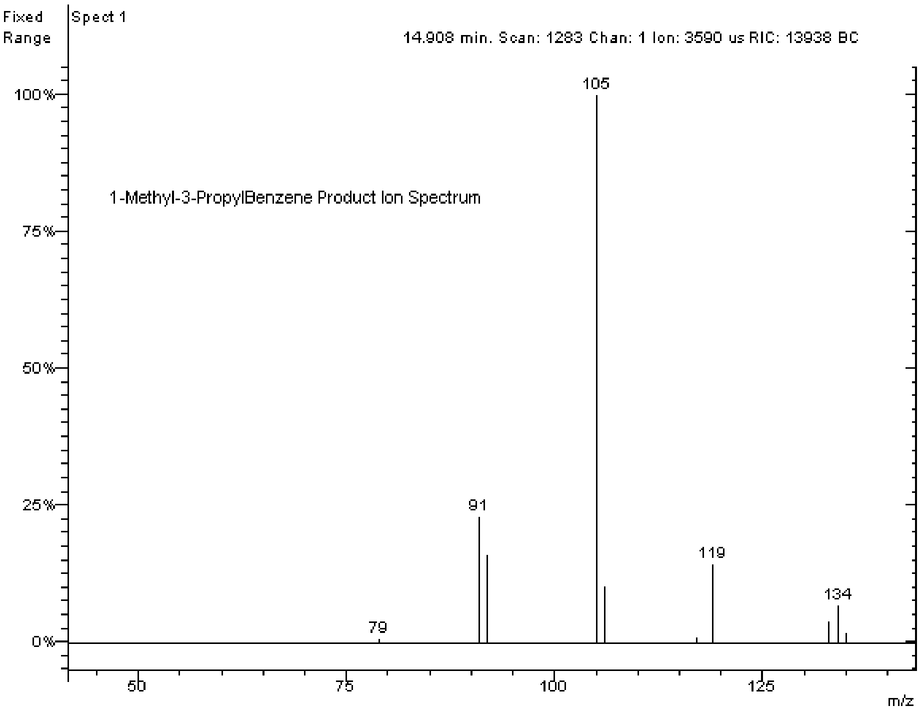

Figure 5.13.9: *MS-MS product ion mass spectrum for 1-methyl-3-propylbenzene (C4-alkylbenzene).*

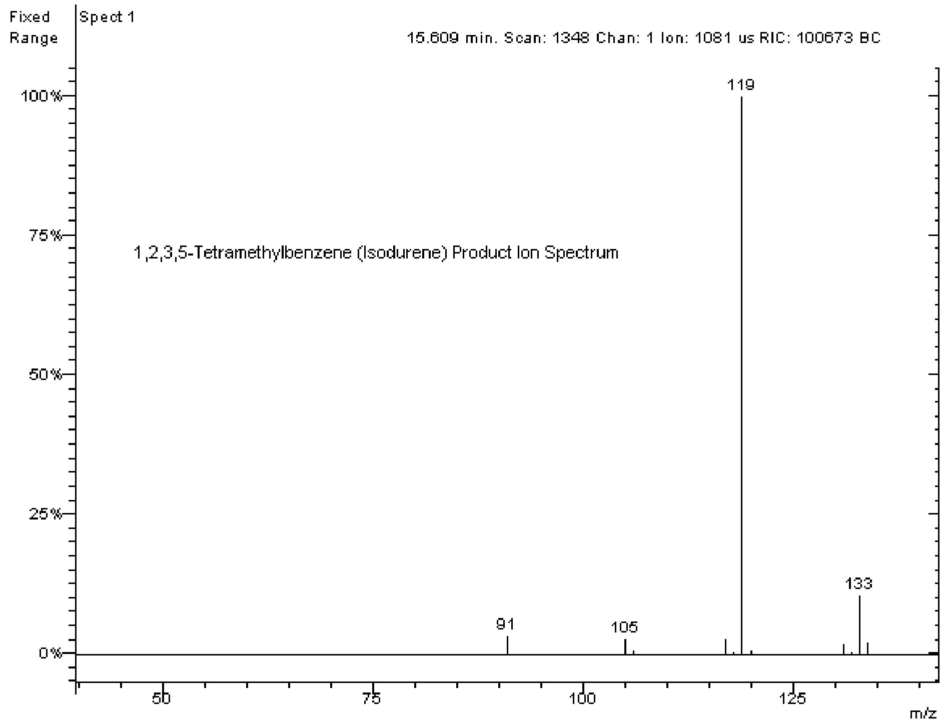

Figure 5.13.10: *MS-MS product ion mass spectrum for 1,2,3,5-tetramethylbenzene (C4-alkylbenzene).*

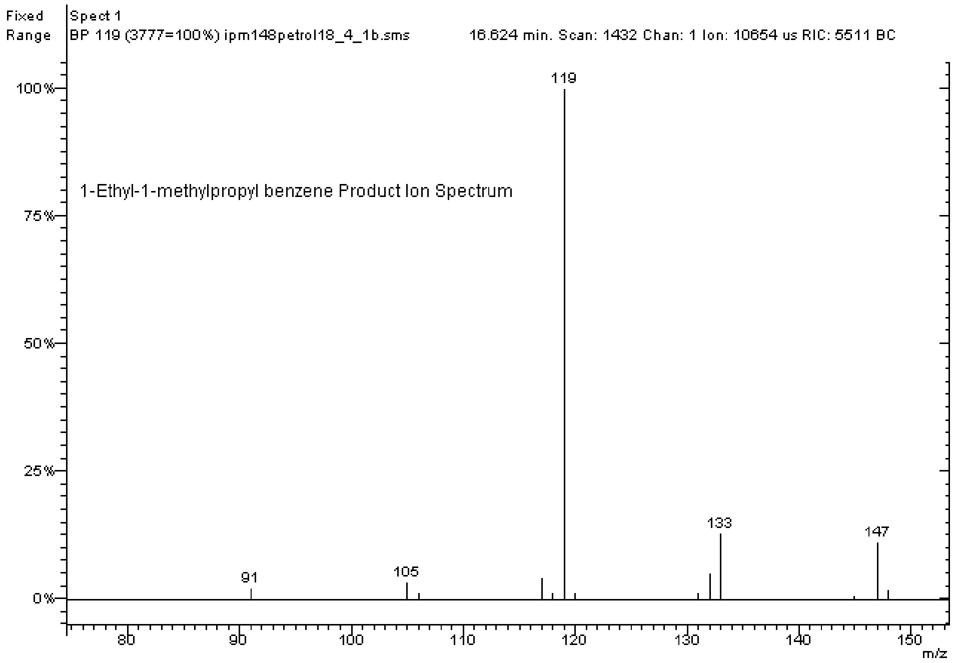

Figure 5.13.11: *MS-MS product ion mass spectrum for 1-ethyl-1-methylpropylbenzene (C5-alkylbenzene).*

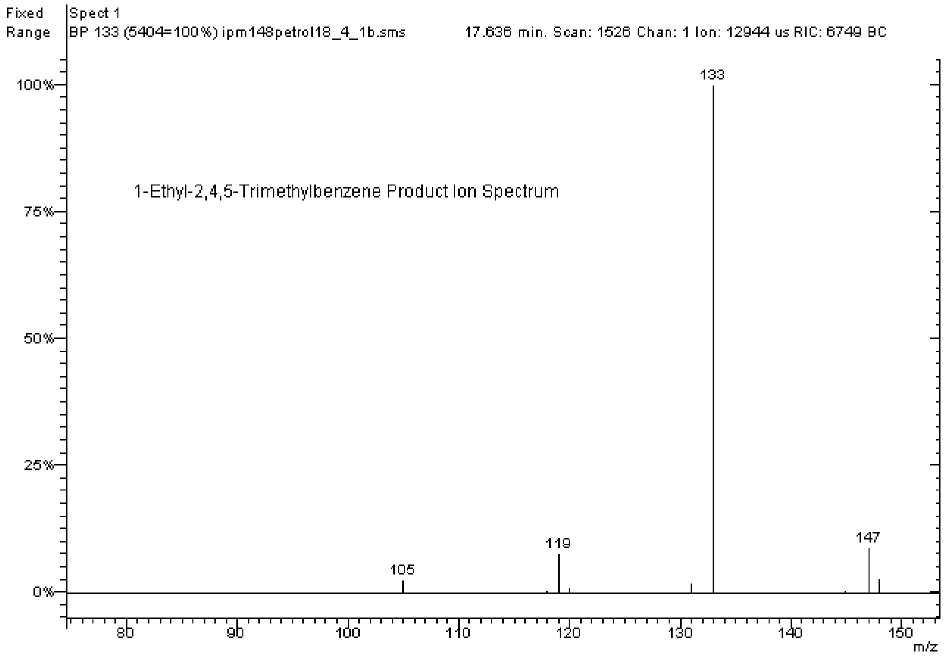

Figure 5.13.12: *MS-MS product ion mass spectrum for 1-ethyl-2,4,5-trimethylbenzene (C5-alkylbenzene).*

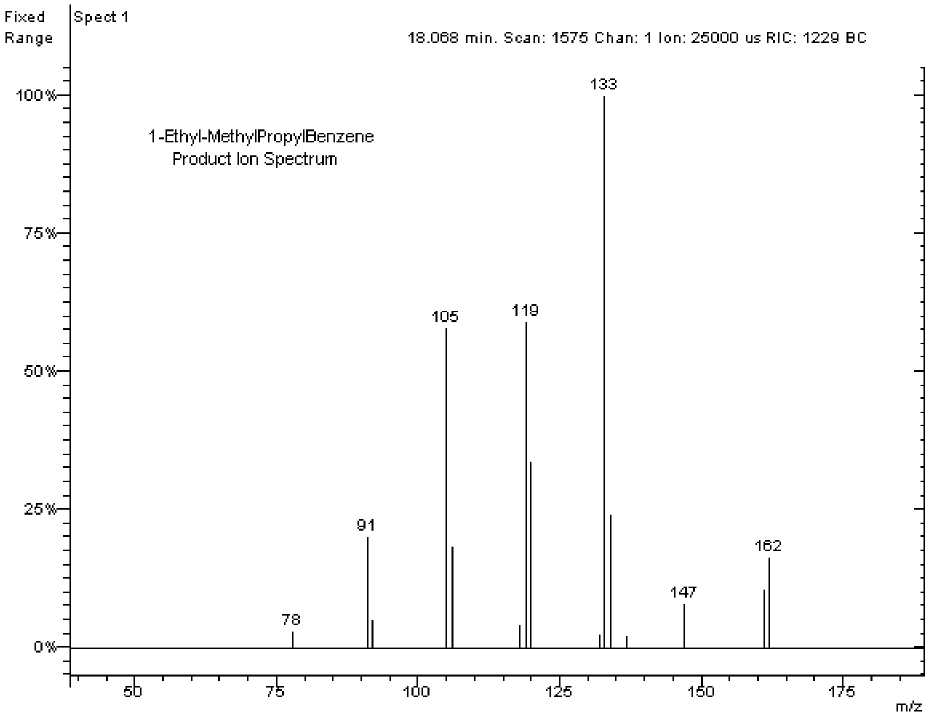

Figure 5.13.13: *MS-MS product ion mass spectrum for 1-ethyl-methylpropylbenzene (C6-alkylbenzene).*

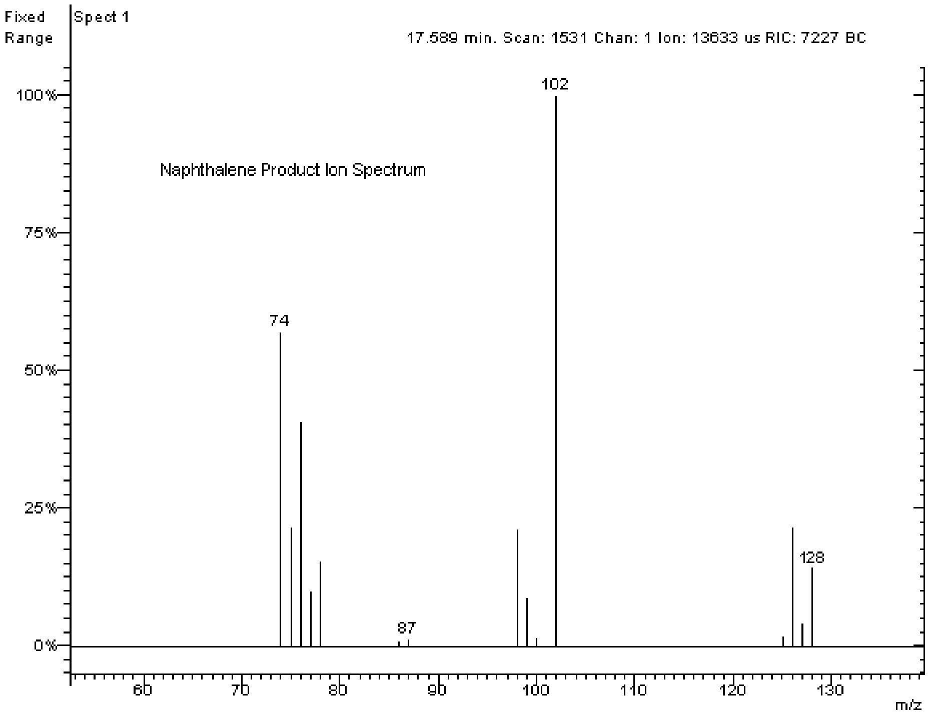

Figure 5.13.14: *MS-MS product ion mass spectrum for naphthalene.*

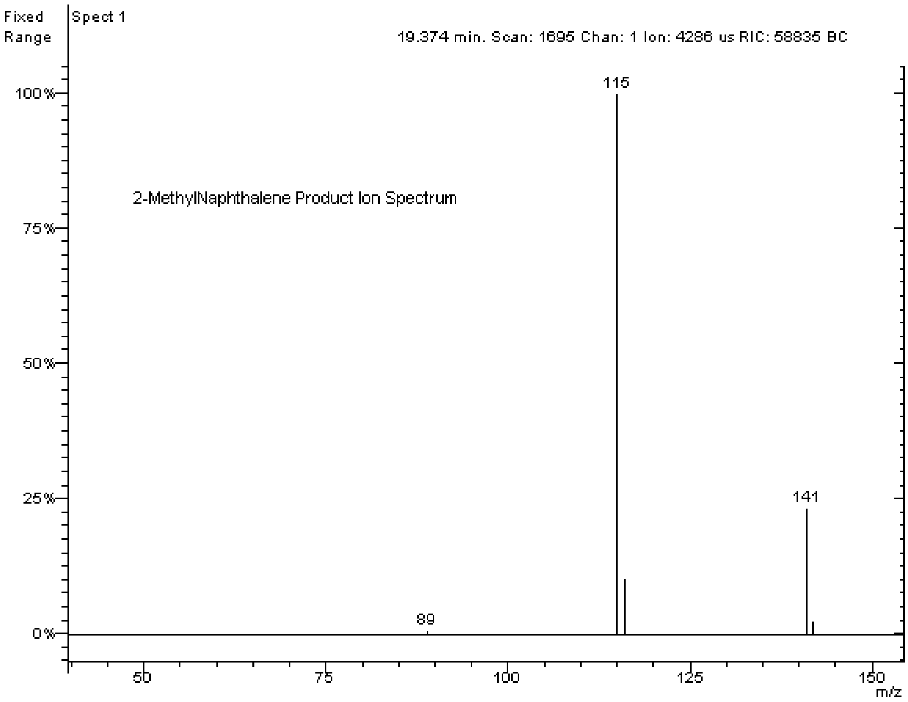

Figure 5.13.15: *MS-MS product ion mass spectrum for 2-methylnaphthalene.*

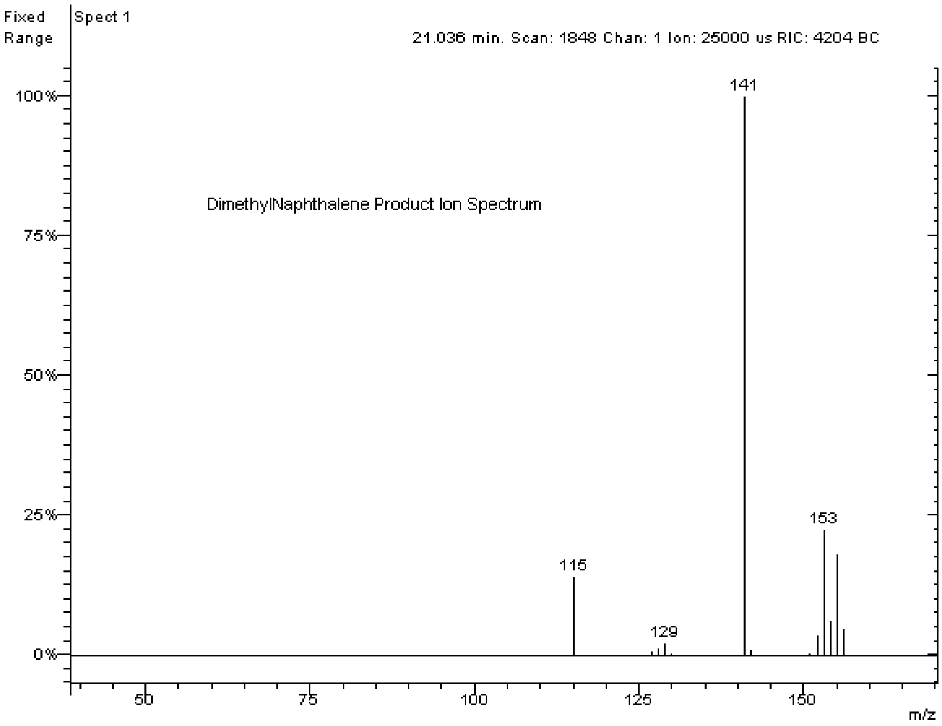

Figure 5.13.16: *MS-MS product ion mass spectrum for Dimethylnaphthalene.*

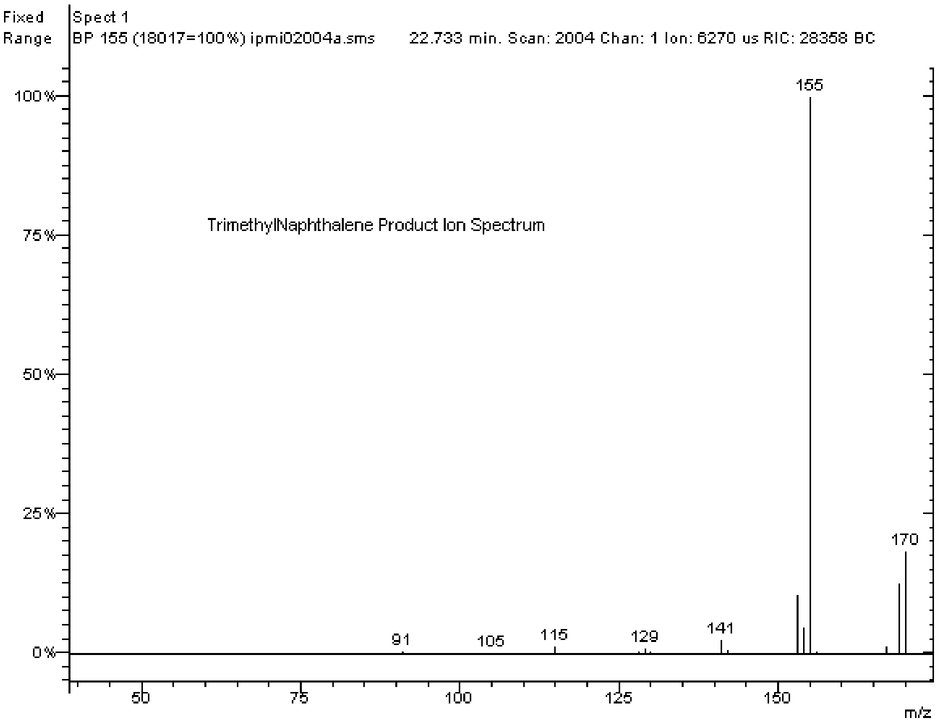

Figure 5.13.17: *MS-MS product ion mass spectrum for Trimethylnaphthalene.*

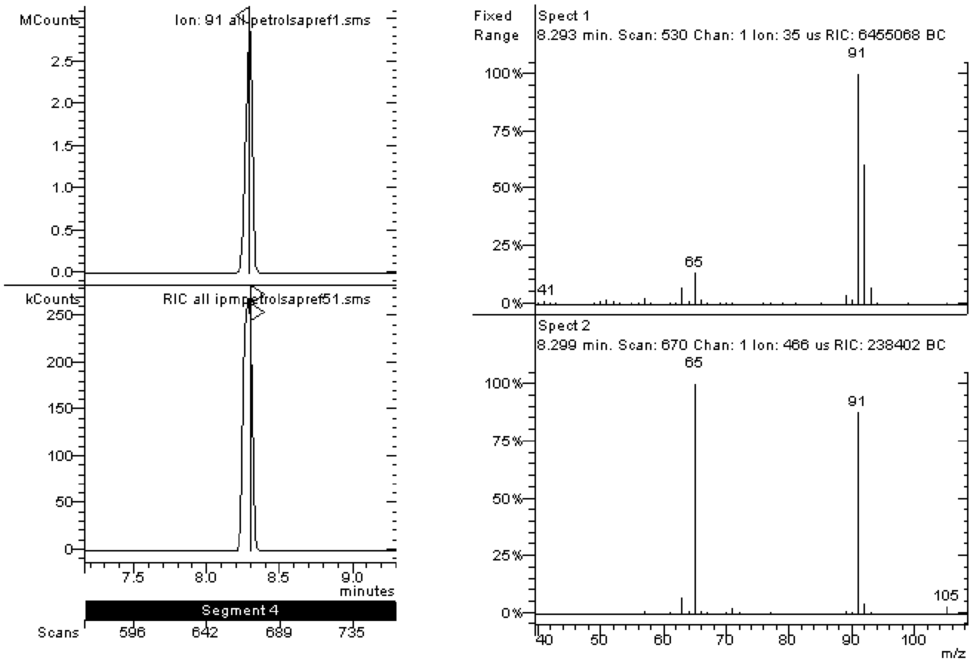

Figure 5.14.2: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for toluene.*

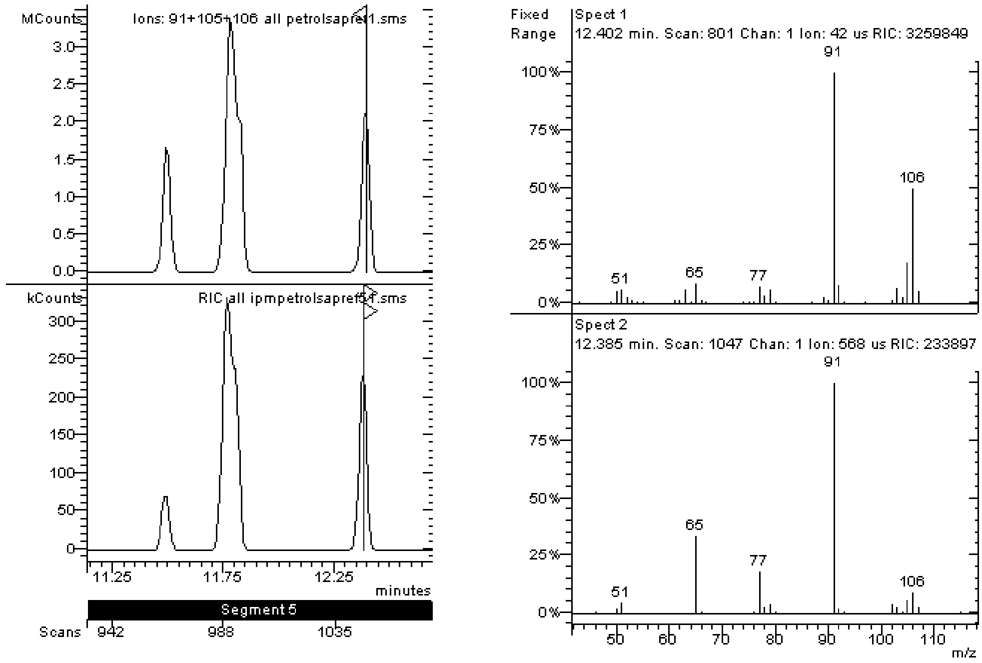

Figure 5.14.3: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for o-xylene.*

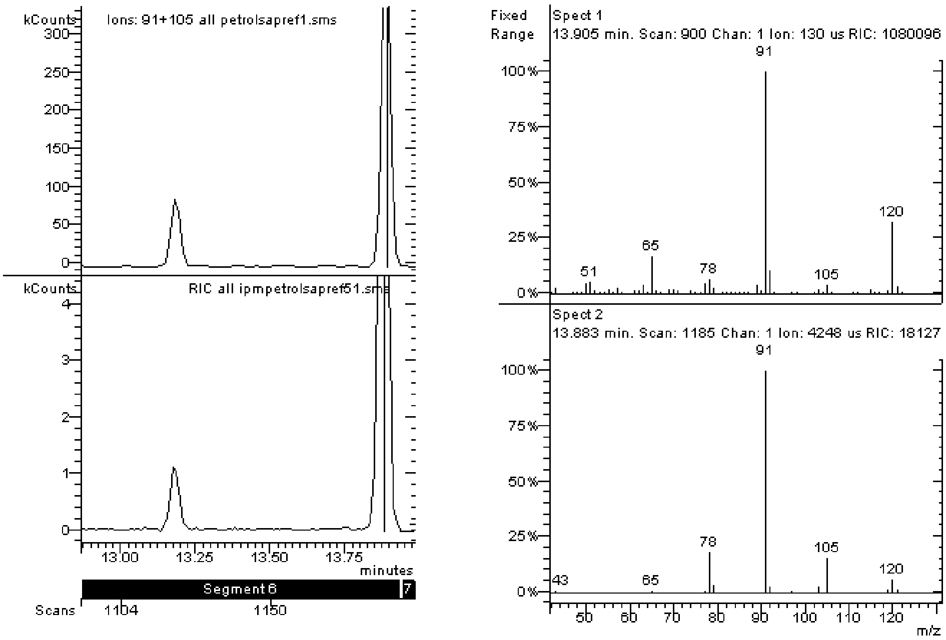

Figure 5.14.4: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for propylbenzene.*

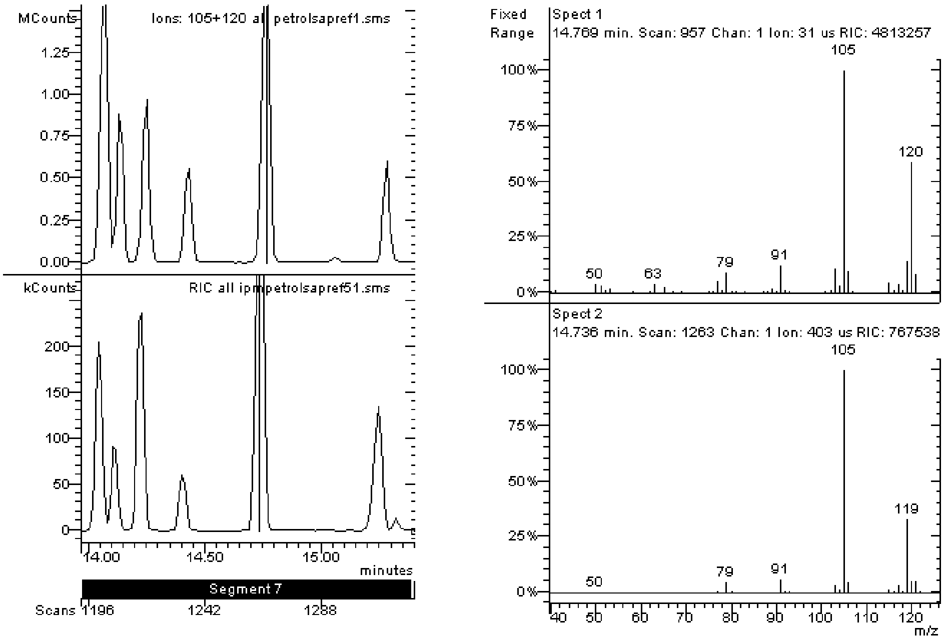

Figure 5.14.5: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for 1,2,4-trimethylbenzene.*

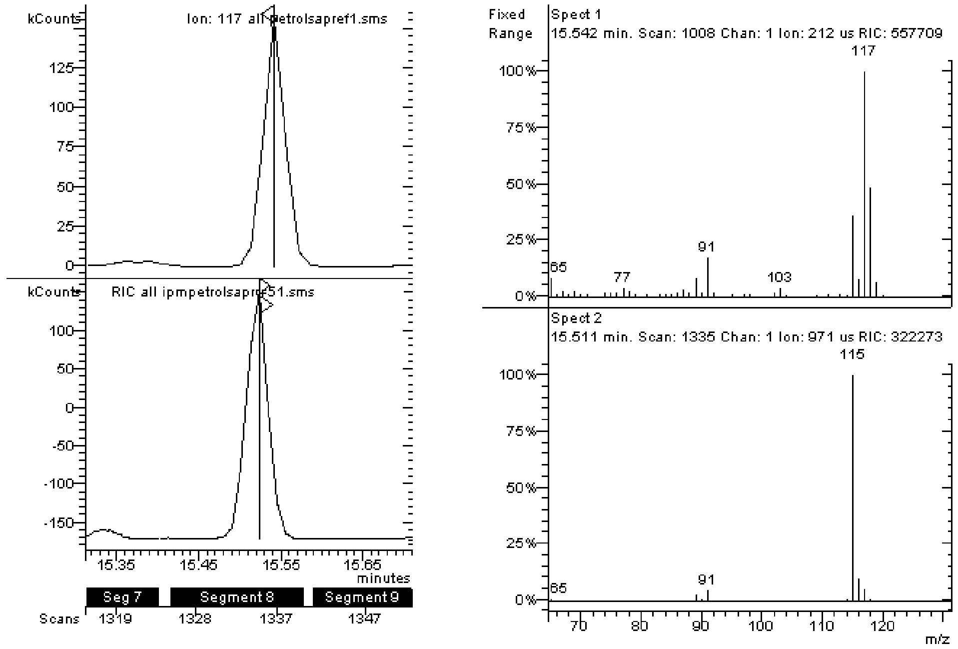

Figure 5.14.6: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for Indane.*

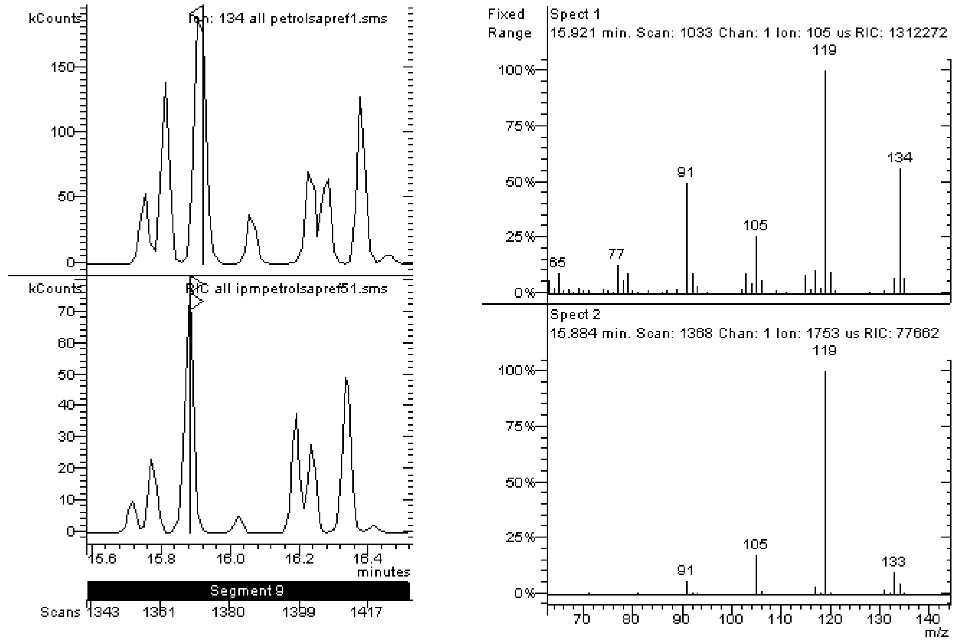

Figure 5.14.7: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for 1,2,3,5-tetramethylbenzene.*

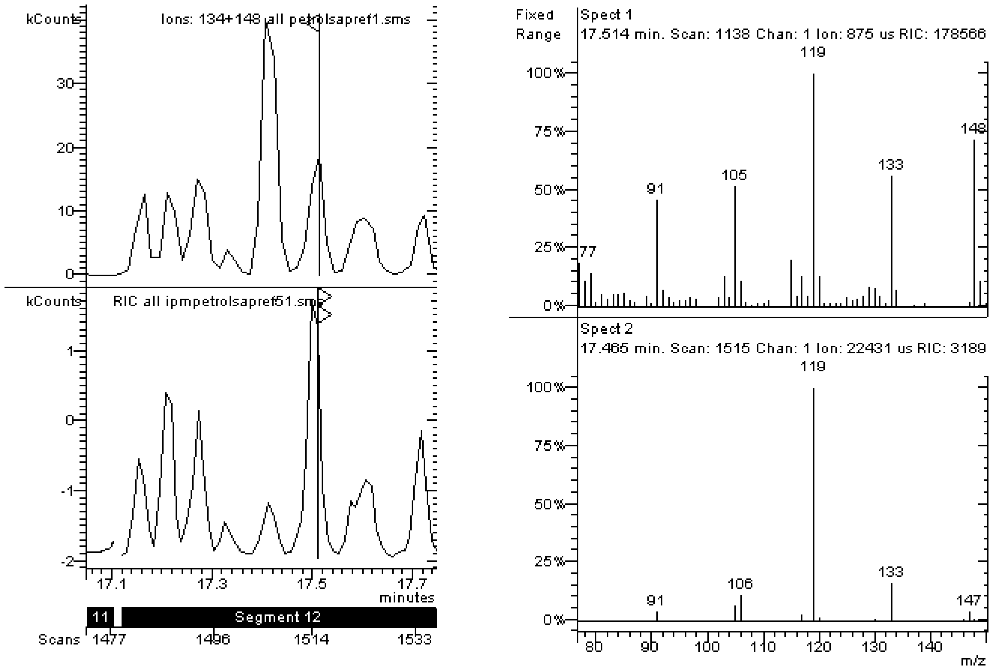

Figure 5.14.8: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for 1-ethyl-1-methylpropylbenzene.*

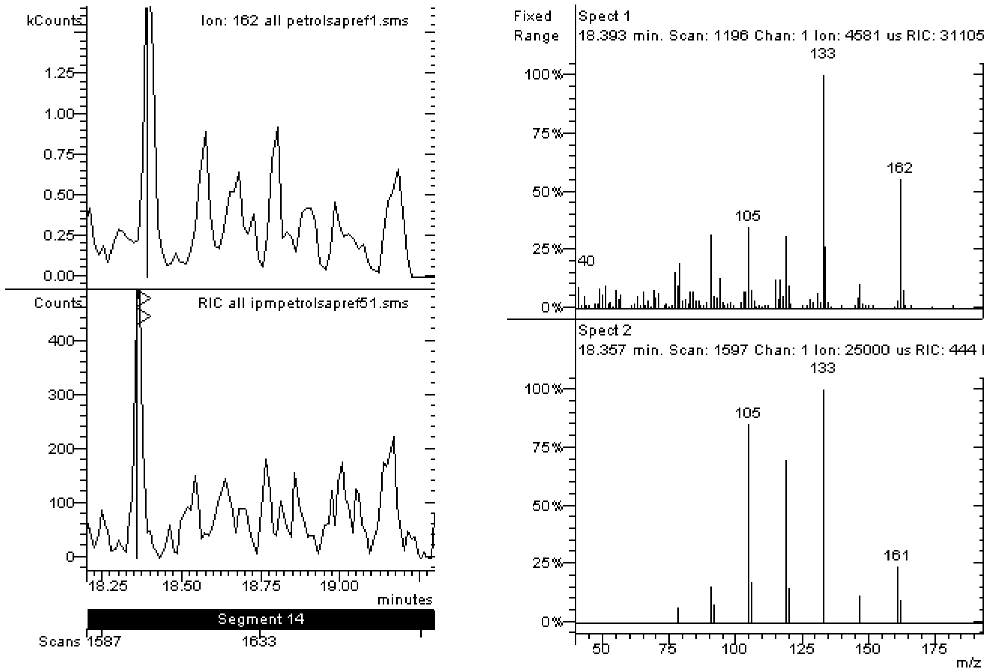

Figure 5.14.9: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for 1-ethyl-methylpropylbenzene.*

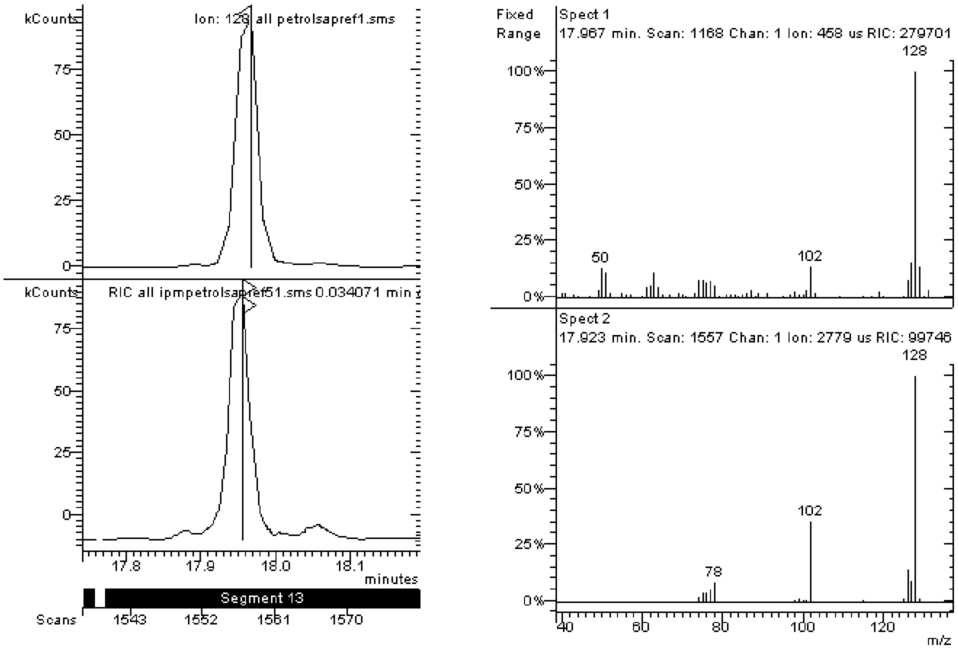

Figure 5.14.10: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for naphthalene.*

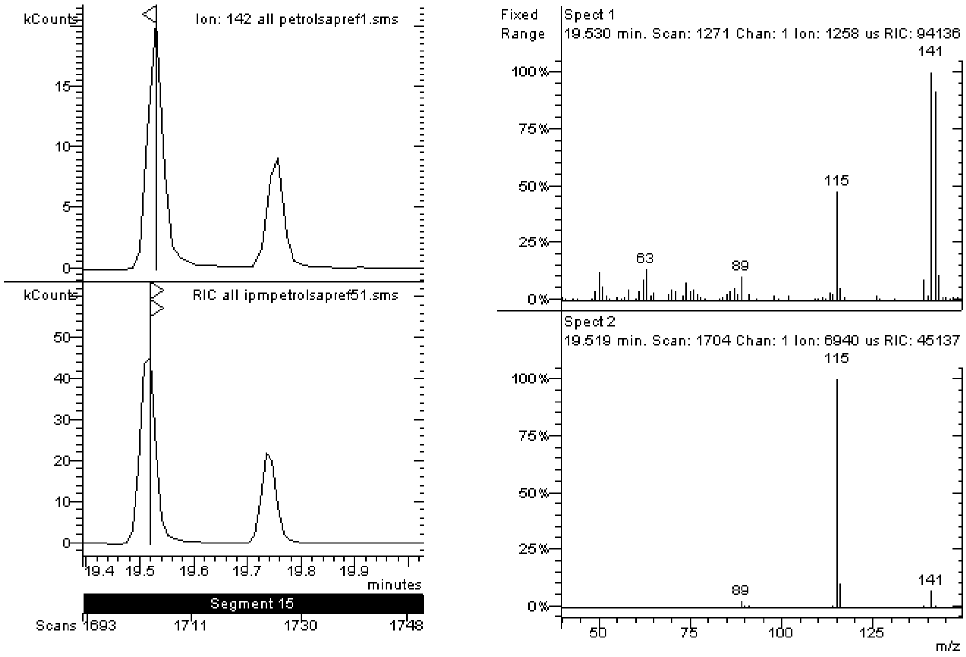

Figure 5.14.11: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for 2-methylnaphthalene.*

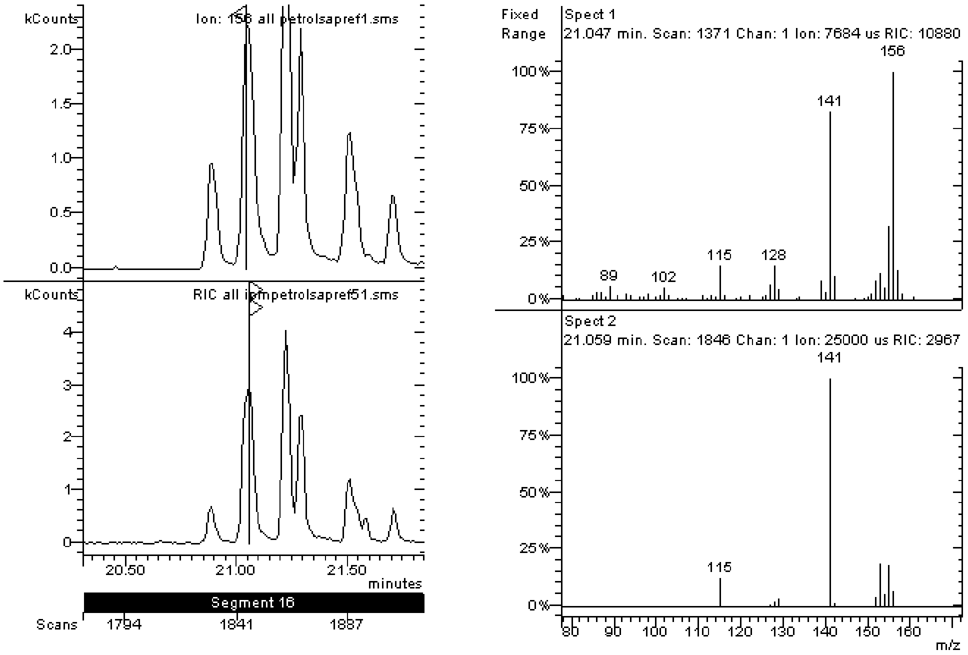

Figure 5.14.12: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for dimethylnaphthalene.*

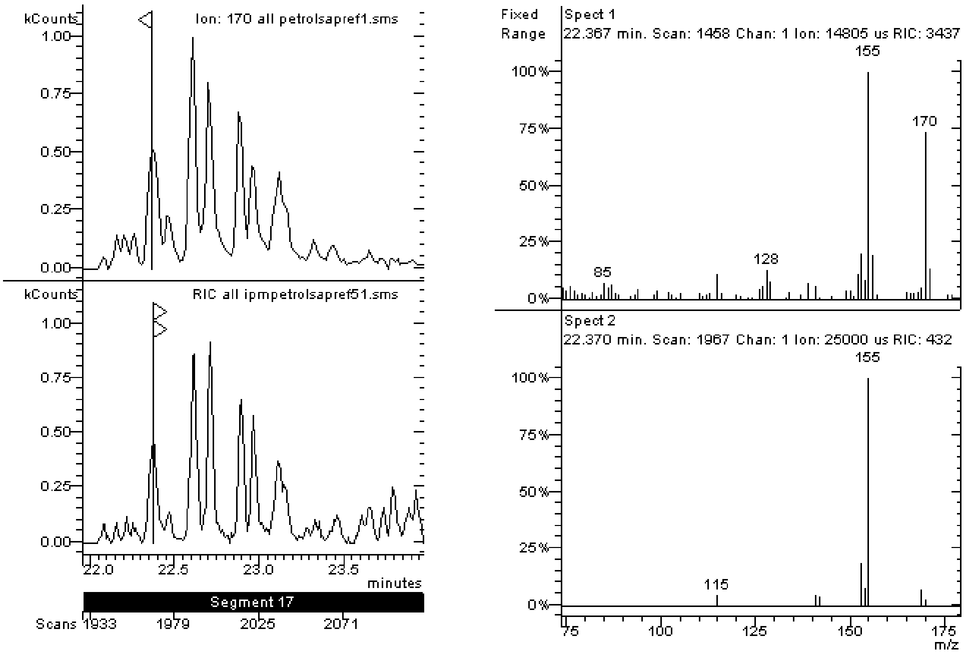

Figure 5.14.13: *Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for trimethylnaphthalene.*

ANNEXURE C

NOTES FOR THE FIRE INVESTIGATOR

C.1 AN IMPORTANT DEVELOPMENT IN FIRE DEBRIS ANALYSIS

Gas chromatography-tandem mass spectrometry (GC-MS-MS) is an extremely sensitive technique and has been used to detect petrol (gasoline) in samples that were months old [38, 96, 98]. In one case the technique was used on a sample from a vehicle fire in northern Ontario that took place in the winter. The burned automobile, a Mercedes, had been reported stolen by its owner. It had been covered in snow and reserved in a compound for three months while the insurance company was trying to decide how to proceed with the case. With the help of analysis by GC-MS-MS the insurance company was able to show that the fire was intentionally set by the owner due to the presence of petrol on the floor of the burned car interior. The claim was resolved without going to court.

A severe fire took place at a house leaving what investigators described as a total burn or black hole. Several soil samples were taken from the basement floor at locations indicated by a canine trained to detect ignitable liquids. Mason jars were used as the sample containers. The investigators noted that the fuel oil tank, located in the basement, had ruptured as a result of the fire, thus contamination of the samples by fuel oil may be expected. The analysis by GC-MS easily detected the weathered fuel oil but also indicated traces of a few compounds that were indicative of petrol. There was insufficient information in this analysis to determine a positive result for petrol. To guard against a false negative result, GC-MS-MS was used to isolate the weak petrol components. The method was effective at reducing the overall chemical interference. This improved the signal of the compounds that were isolated and was significantly more sensitive than the GC-MS analysis. The presence of highly weathered petrol was confirmed in this complex sample with a very high degree of certainty at ultra trace levels.

C.2 SHOES OF AN ARSONIST - CLUE OR CONFUSION?

Shoes worn by suspects of arson are often submitted to the forensic laboratory for analysis to determine if an ignitable liquid can be found on them. When analysed, interesting GC-MS patterns are obtained and, at times, ignitable liquids are identified on the shoes. With the use of GC-MS and selected ion profiling, even more information can be seen in these samples; however, caution must be exercised. Shoes themselves seem to inherently produce patterns that could be identified as petroleum distillates commonly used as accelerants [110].

Knowing that plastics, glues, dyes, protectants and other synthetic products are used in shoe construction, shoes were analysed to examine the GC-MS patterns obtained. A variety of shoes were subjected to the analysis, most being athletic shoes. Some of the shoes were brand new, some were old and well-worn, and others somewhere in-between. The shoe styles ranged from canvas sneakers (“tekkies”) to ladies synthetic pumps, leather walking shoes and both leather and synthetic athletic shoes. The shoes were analysed by GC-MS and a variety of results were obtained. Nearly every pair of shoes gave a complex total chromatographic ion profile. Some of the shoes had numerous peaks in the petrol region, some with apparent heavy petroleum distillate patterns and several with both. Selected ion profiles of several shoes showed aromatic patterns similar to those for petrol and alkane patterns similar to those for diesel. These patterns were observed most strongly in the newest shoes, but were also observed in shoes that were older and well-worn. What was interesting was that the type of shoe was not a factor in producing petrol and diesel patterns; leather athletic shoes along with vinyl dress pumps and canvas sneakers gave similar results [110, 111].

The patterns obtained could be attributed to one or more of the many components of the shoes. Shoes can be made of a variety of materials such as leather, plastic, cloth and rubber. They also have several components that may be glued together. Various types of glues and cements are used in shoes, including the soles, insoles and sock linings. Leather for shoes is subjected to tanning (which may include the application of vegetable oil or mineral oil), dying, wax and other coatings. Water-repellant chemicals may also be applied to some shoes. It is important for those analysing shoes for the presence of accelerants to be aware of their potential to provide similar patterns to those obtained from ignitable liquids. With the patterns that shoes can produce themselves, especially those seen when using GC-MS selected ion profiling, caution must certainly be used. Obtaining new shoe comparison samples when analysing suspect shoes, though difficult, may be a way to determine if the pattern obtained is from the shoe itself. If an outside source is confirmed, then the investigator must prove whether the source is incidental or actually connected with the crime scene [110, 111].

The question arises as to how long will ignitable liquids remain on shoes and articles of clothing? The answer lies in testing the evaporation and weathering rates of accelerants from materials typically encountered in the investigation of a suspicious fire, such as scene material, shoes and clothing from a suspect arsonist. One difficulty in studying this question is that evaporation rate depends on so many variables, namely, volatility, temperature, air movement, substrate absorption characteristics, to name but a few – that there is no set of standard conditions and no single study that can cover all situations [110, 111, 112].

C.3 LIMITATIONS ENCOUNTERED IN CASEWORK DUE TO MATRIX DEGRADATION

A fire was discovered in an abandoned house and was quickly extinguished. Fire investigators determined the origin of the fire and collected a carpet sample from that location. Investigation outside yielded a petrol can abandoned in the yard. The can itself, the soil under the can and the carpet were submitted to the laboratory for analysis. The petrol recovered from the can was relatively fresh. Evaporated petrol was found on the carpet taken from inside the house. A comparison was made and it was concluded that the fire was deliberately set using petrol. The petrol recovered from the soil was presumably the same petrol coming from the can. However, the petrol in the soil sample shows evaporative alteration as well as probable microbial degradation. The petrol recovered from the soil had been so severely altered that little could be concluded regarding the possible origin based solely on the volatile hydrocarbon composition. This finding alerts to the necessity of taking into account the matrix type of the sample and weathering and degradation of the matrix and not only the possibility of finding ignitable liquid traces on the sample [113].

Another incident involved a fire that started in the early hours of the morning in a garage and which quickly spread to the adjoining house where a family of five was asleep. There were no injuries, but costly damage was caused to the structure. The fire investigation unit pinpointed the origin of the blaze in a bundle of petrol-soaked newspapers. Samples from the interior of this bundle were taken as evidence. Petrol was also taken from the motor vehicle parked in the garage. A suspect was almost immediately identified. The trunk of the owner's motor vehicle was searched the next morning and two partially filled petrol cans and an "empty" jar with an attached lid was collected as evidence. The samples were submitted to the laboratory for analysis. Analysis of the various petrol samples revealed that they were evidently different from each other. It was concluded that the petrol soaked newspaper was not sourced from the petrol found in the petrol tank of the motor vehicle, but rather could have been from one of the two partially empty petrol cans recovered from the boot of the vehicle. The study involved compensating for evaporation of the different petrol samples and examining the lead content of the petrol. Additional knowledge of the history of the petrol in the cans, for instance, were the cans empty before filling, what was the source of the petrol in the cans, *etc*., could help to make the "could have" statement more specific [113, 114].

C.4 VEHICLE TEST BURNS

A study was conducted, for training purposes, how to properly extinguish vehicle fires. Concurrently, the performance of various materials that could be used as samples by fire investigators was evaluated. The investigation was specifically aimed at studying the expected background of different intrinsic materials prior to pyrolysis, to verify the sampling technique, to investigate the retention of accelerants on different materials, to study the preferred sampling sites and to study the effects of time or weathering on the samples.

Pre and post-fire samples were taken from preferred locations, based on the experience of the fire investigators, from two vehicles intentionally set ablaze. When available, seat cushion foam, foot-well carpet and under-pad, and under-seat carpet and under-pad have provided the best samples for the analysis and determination of the presence of an accelerant. Courtroom defense sometimes suggested that oil, grease or other repair shop fluids, including paraffin and petrol, could be present at the foot-well from use by service personnel or the vehicle owner tracking it in on the bottom of shoes. While only two vehicles were examined in this test, one objective was to determine if any background hydrocarbon material was present in these well-used vehicles, and if this background would interfere with the detection and confirmation of the accelerant used, as may be claimed by defence council in court.

The study showed that seat-cushion chip-foam is an excellent material to sample if it can be found after a fire. Any pieces of foam are preferred samples. Carpet taken from beneath the driver’s seat is not a good comparison sample, but may be a good sample after a fire, especially if it’s the only one available. Residues of soot found on glass are carbon, an excellent absorber of volatile compounds if it is of the soft porous type, can provide a positive result. The surface of standing water in the vehicle can be a useful sample. Different materials have different backgrounds and absorb differently. The use of certain hand cleaners used as a cleansing agent for tools is justified, but care should be taken to use it sparingly and to ensure that surfaces are wiped thoroughly to remove the cleaner prior to taking the next sample. Excess residue from the cleaner will not interfere in the identification of an ignitable liquid, but can complicate the analysis and would require clarification in court [24, 115].

Although the analysis of samples taken five days after the fire still resulted in positive identification of the ignitable liquids used as accelerants, a significant amount of the ignitable liquid had been lost due to weathering. Although this can be problematic, some ignitable liquids can still be detected even months after the event. This study convincingly demonstrated the value of laboratory analysis by GC-MS. The specificity of this technique combined with the highly sensitive full-scan operation of an ion trap mass spectrometer was found to be essential for confirming the presence of an accelerant in the samples taken five days after the test burn. The confirmation analysis by GC-MS-MS again demonstrated the ability to report a positive result for a sample having such small amounts of an ignitable liquid that it would have been reported as negative by GC-MS, even though the sample was more than a year and a half old [96, 98, 115].

C.5 COLLECTION OF SOOT SAMPLES AFTER A FIRE

Smoke can be regarded as the combination of hot gases, water vapour and a variety of microscopic and macroscopic particulates carried aloft by the convective motion of hot gases and vapours. Layers of these particulates can be carried for a long distance and deposit or condense on surfaces as visible and/or microscopic soot [1, 9]. Soot has been characterised and used as an investigative tool in determining the source material or accelerant used to fuel a fire [24, 116]. Soot is a form of carbon and is an excellent absorbent of chemicals, thus providing some history of the environment before and/or during a fire. Soot can easily retain the chemical traces of the source material used to start a fire and can be obtained from any surface such as glass, metal, wall surfaces, fabrics, etc. The success in obtaining information from a laboratory analysis is directly dependant on the ability to take an appropriate sample and in using a good sample container. The quantities of the chemicals that are analysed in soot are at trace levels and therefore the container used must be pre-cleaned to remove potential interferences that may make the results more difficult or impossible to interpret. Nylon evidence bags are the most suitable and do not have to be pre-cleaned. It is important to use an appropriate sampling material to obtain a large quantity of soot. Preferred material would include gauze pad, cotton ball, paper towel, white "Kleenex" tissue or white toilet paper. Any of these materials are acceptable. For the best analysis, the fire investigator should obtain the sampling material prior to going to the scene and not use previously stored material, *e.g.,* not stored in the boot of a car where at one time automotive fluids may have been carried. It is important to remember that blanks must be kept contaminant free for comparison purposes. At the scene consider using several cotton balls, combining the materials and avoiding cross contamination of samples after storage. Fabric is also a very good adsorbent and can easily retain traces of accelerants if they are used to start a fire. A large quantity of fabric does not necessarily make for a better sample. Damp samples are best since the water helps retain the traces of accelerants that are often found in protected areas, *i.e*., under debris where weathering is minimised. Samples submerged in water are probably not useful, however, soot samples that are floating on the surface may be useful as they may soak up accelerants that float on the water surface [117].

Soot can therefore be used as an adsorbent for trace accelerants, the main concern is obtaining enough sample for analysis. Smoke damage always leads to soot deposition and soot should always be considered as a potential sample if no other sample material is evident.

C.6 VOLATILE RESIDUES IN POST MORTEM SAMPLES FROM AN ARSONIST

To reveal that arson has been perpetrated is often difficult and sometimes impossible when examining evidence for traces of highly volatile ignitable liquids. The reason is that residues of such agents cannot be found in the ashes, unless they have been protected from evaporation during the fire. Organs and body fluids from a fire death may, then, provide the necessary evaporation shield, a circumstance that should favour the arson analysis of such a material. It has been shown that highly volatile additives or components of petrol were found in post mortem samples from victims of violent fires [109].

A motorist witnessed a bright flash in the side mirror of his car and a vehicle suddenly ran off the road. The vehicle came to a full stop in a field after about 20 meters. It was immediately engulfed in flames and soon totally destroyed in a violent fire. One of the few identifiable remains at the scene of the event was the severely burnt body of a male. No clothing was left, all soft tissues charred, the intestines exposed, both hands and partial bones burnt off and about half of the brain remained, but only as charred tissue. The deceased was later identified as a divorcee, who prior to the accident had stabbed his two children to death while he was baby-sitting in his ex-wife's home. Even though the circumstances of the car fire pointed to possible suicide, the possibility of an accidental fuel tank explosion had to be excluded. As a result of the destruction of the car, this question could not be answered by a conventional fire investigation of the ashes. The only site where possible accelerant residues might have survived the fire was the interior fluid or tissue of the body and, thus, blood and lung tissue were selected [109].

Among the organics detected in the lung tissue were a series of alkanes with three to thirteen carbon atoms and diethyl ether. To confirm whether or not lung tissue from victims of non-arsons could contain diethyl ether or low-boiling paraffins, control samples from deaths due to accidental fires (where chemicals were not involved) and from fatal intoxications of various types were randomly chosen from the laboratory's pool of routine investigations. Diethyl ether and 2-methylbutane boil at around 30°C and most of the other hydrocarbons at less than 100°C. Yet 18 such compounds could clearly be seen and also identified, even though the matrix they were residing in probably had been exposed to very high temperatures during the fire. None of the control samples of accidental fires or various intoxications contained diethyl ether or low-boiling paraffins. Post mortem samples should therefore not be overlooked as a test material in an arson analysis, particularly if an accelerant with low-boiling components is targeted. The variety of arson accelerants is abundant. Moreover, the body of a fire victim may contain a large number of unforeseen compounds, derived both from the fire gases inhaled and from substances formed after death due to the intense heat a body is often submitted to during the event. Arson analysis of the remains thus requires sophisticated mass spectrometry with a high sensitivity and broad selectivity to make it appropriate for both isolating and identifying trace amounts of unknown volatiles [109].

C.7 CANINE ACCELERANT DETECTION – HOW RELIABLE IS IT?

Canines trained to alert to traces of ignitable liquids at a fire scene are useful for identifying locations from which to collect samples for laboratory analysis. In some instances, no samples are collected or laboratory tests are negative for accelerants. Due to these analyses findings, an attempt may be made to introduce information regarding the canine alert to indicate the presence of an ignitable liquid at the scene by the handler at the trial. Canine handlers contend that the dog has greater sensitivity to typical accelerants than laboratory techniques but scientists counter that, while sensitive, the specificity of canine detection is unknown. Unverified canine indications have been used in a number of cases and challenges to several of these have reached the appellate level. Examination of court decisions on admissibility of canine alerts shows that they have been as varied as the arguments for and against [19 - 21].

It is generally accepted that a trained accelerant detection canine has an important role to play in searching a fire scene. With their sensitive noses, dogs quickly locate areas for collecting relevant samples. When these samples test positive in the laboratory, the results are very useful in expert testimony.

While dog handlers contend that the canine’s nose is more sensitive than the instruments used in the laboratory, they ignore the inherent conflict between sensitivity and selectivity. Scientists argue that the mechanism by which a dog recognises a particular scent is not understood and that it has been demonstrated that canines sometimes alert to pyrolysis products at the fire scene. Unless confirmed by laboratory analysis, canine alerts cannot be considered sufficiently reliable for introduction in court. If a trial is the search for the truth, there is no role for unreliable testimony in the courtroom. Several areas need attention to expand the role of canines in fire investigation. At the scene, when a clear alert occurs, samples should always be collected for laboratory examination. Careful records should be kept of these so that the laboratory results can be used to develop information on the types of materials responsible for unconfirmed alerts. Laboratory testing can also provide a “rate of confirmation” for a particular canine that can be used to guide future training, resulting in a decrease in false alerts and a significant increase in the confirmation rate. Additional research into the canine sensory mechanism is required to provide a basis for developing even more effective training programs. Until there is additional understanding of how a dog reacts to targeted odours and the effects on this reaction by the presence of closely related odours, there will be controversies over admissibility of canine testimony. These contentious issues will be resolved at the trial or appellate level as the courts struggle with the issue of unconfirmed accelerant canine alerts and reliability [21].