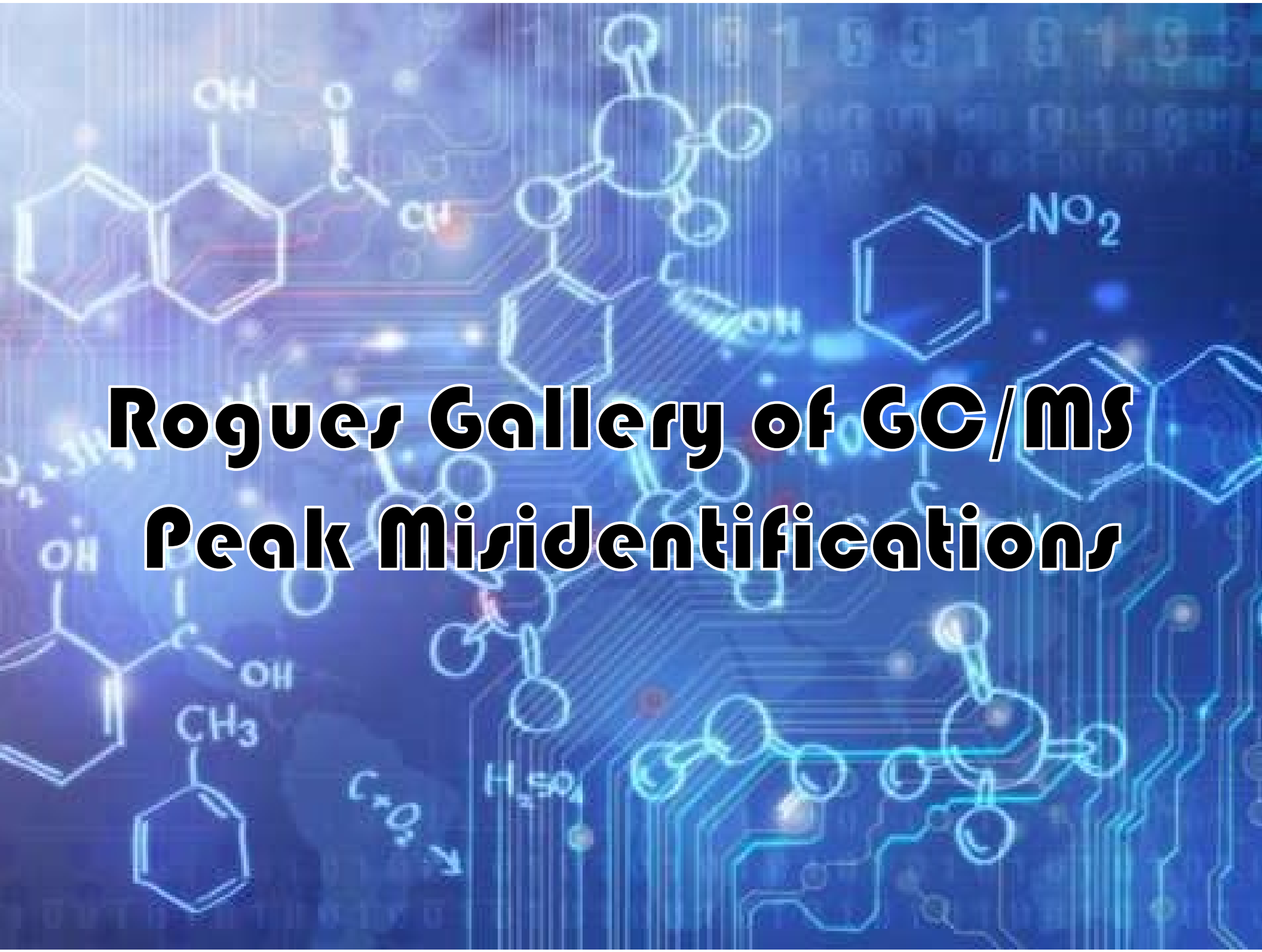

Rogues Gallery of GC/MS
Peak Misidentifications

Ensuring Accurate Compound Identification:

1) During Review of Initial Calibration Peaks
2) During Analyst Review of Sample Spectra

● GC/MS initial calibration involves updating reference mass spectra and retention times for all target compounds using data acquired from one of the calibration runs. Updated spectra can exhibit coelutions.

● **All mass spectra and retention times must be reviewed and verified during QEdit and before updating**. Saving an incorrect spectrum can perpetuate the tendency to make the same calibration error again.

● **If unsure of what any target compound's spectrum should look like, use the desktop shortcut to open a PDF file of 107 VOC NIST spectra**.

● **Characteristic ions for each compound are stored in the calibration table and should be checked to ensure appropriate ions are included**.

Critical Elements to Consider When Checking Compound Identification in an Initial Calibration:

● A few coelutions during calibration are almost inevitable due to simultaneous analysis of 107 VOC target compounds, surrogates, and internal standards. In some cases, primary, secondary, and/or tertiary ions can be affected by partial or complete peak overlap, which may increase the chances of compound misidentification.

● **All spectra must be checked in the 50 ppb initial calibration standard** that should be processed and updated first. **Manually check any unfamiliar spectra against the NIST library to explain all missing or extraneous ions**.

● **If co-elution of target compounds is suspected, check the NIST spectra of both components** in order to account for all ions seen in the spectrum before updating. Ensure it is really a coelution, not a misidentification.

● **If a quantitation ion does not fully separate from a nearby peak, consider editing the calibration table to designate an alternate ion free of interferences** as the quantitation ion. Examples are shown in later slides.

● **If a required target compound cannot be found** by looking at QEdit for primary, secondary, and tertiary ions matching the expected NIST ion ratios, **manually plot characteristic ion chromatograms over +/- 2 to 3 minutes**.

● If the compound of interest is still absent, **see if other instruments can detect it** or not. The problem might be an instrument-specific detection sensitivity problem, a column-specific co-elution, or a degraded standard mix.

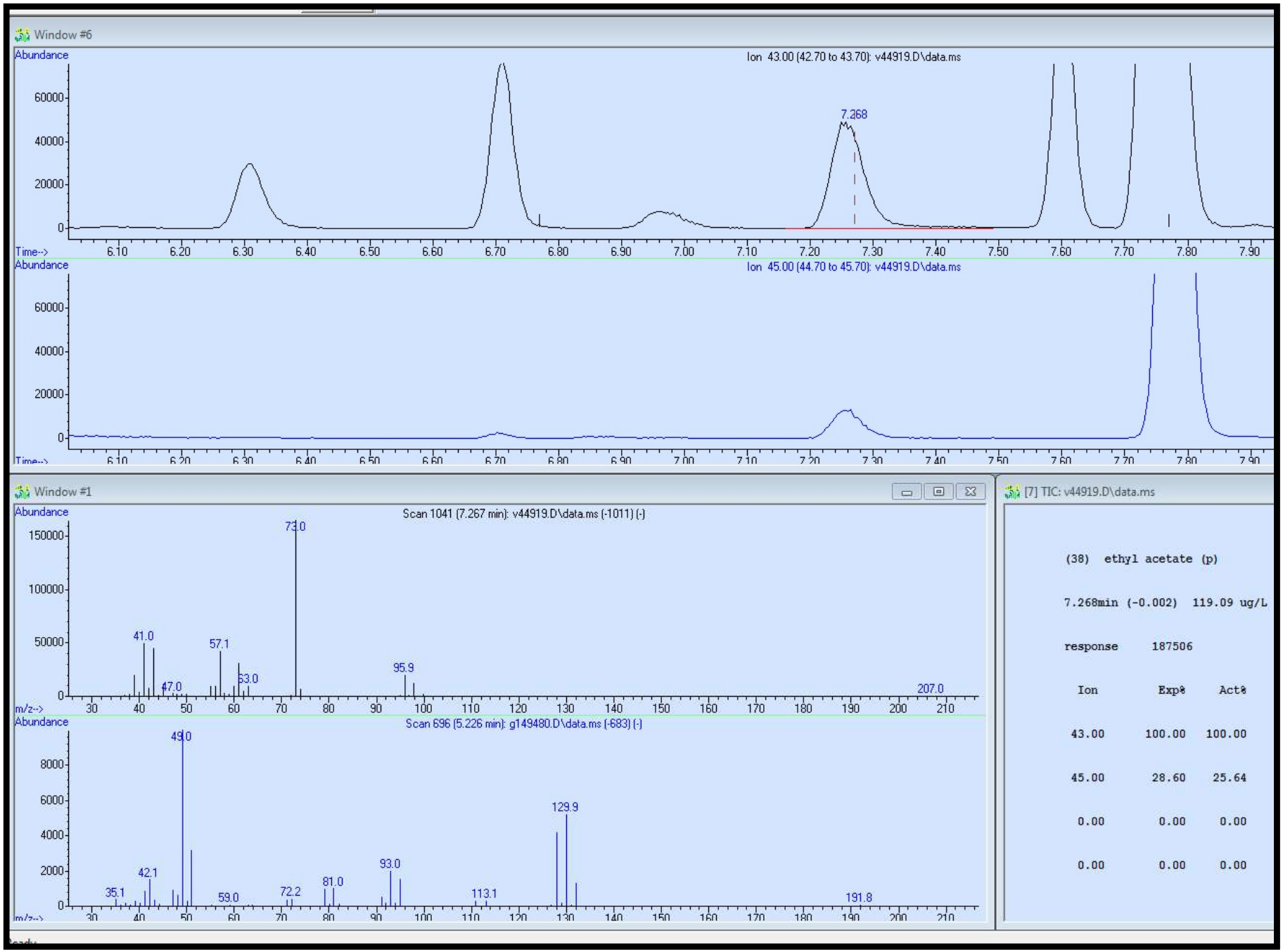
● **If a target compound isn't visible at any level in the ICAL, then false positive hits in the ICAL quant reports must be deleted or zeroed-out in the calibration table**. Never use an incorrect peak to update spectra.

Some Recent Examples of Target Compound Misidentification in GC/MS Volatiles Analysis

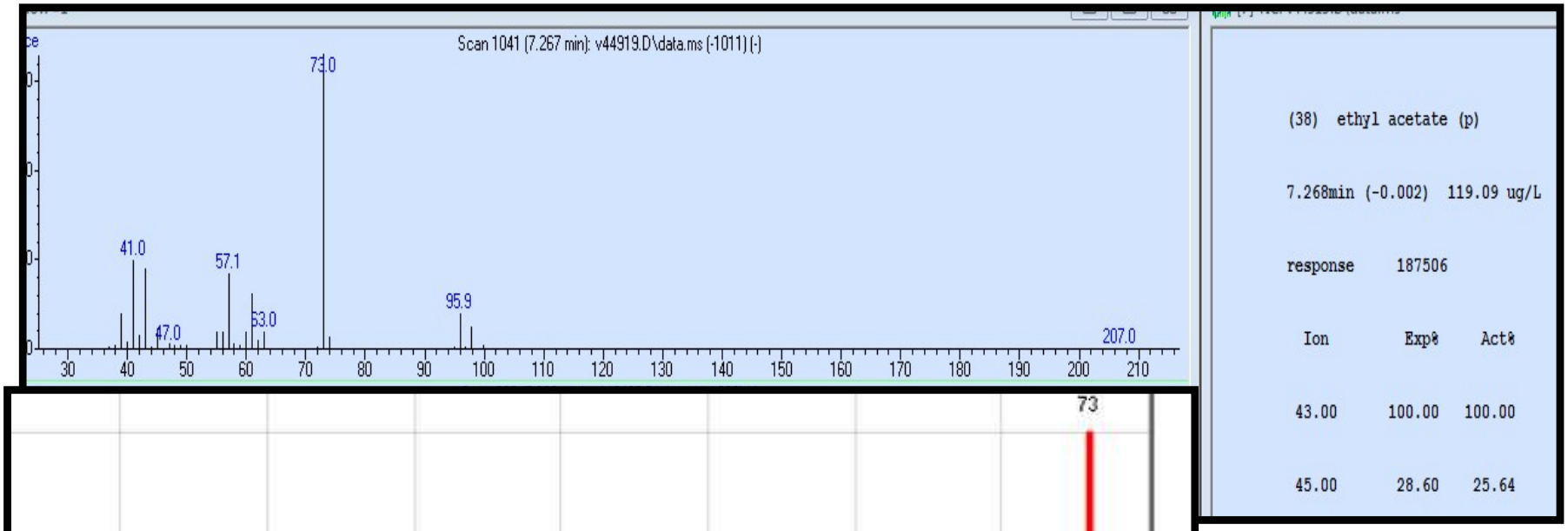
- **<u>Part 1: Finding and resolving misidentifications in Calibration Standards:</u>**

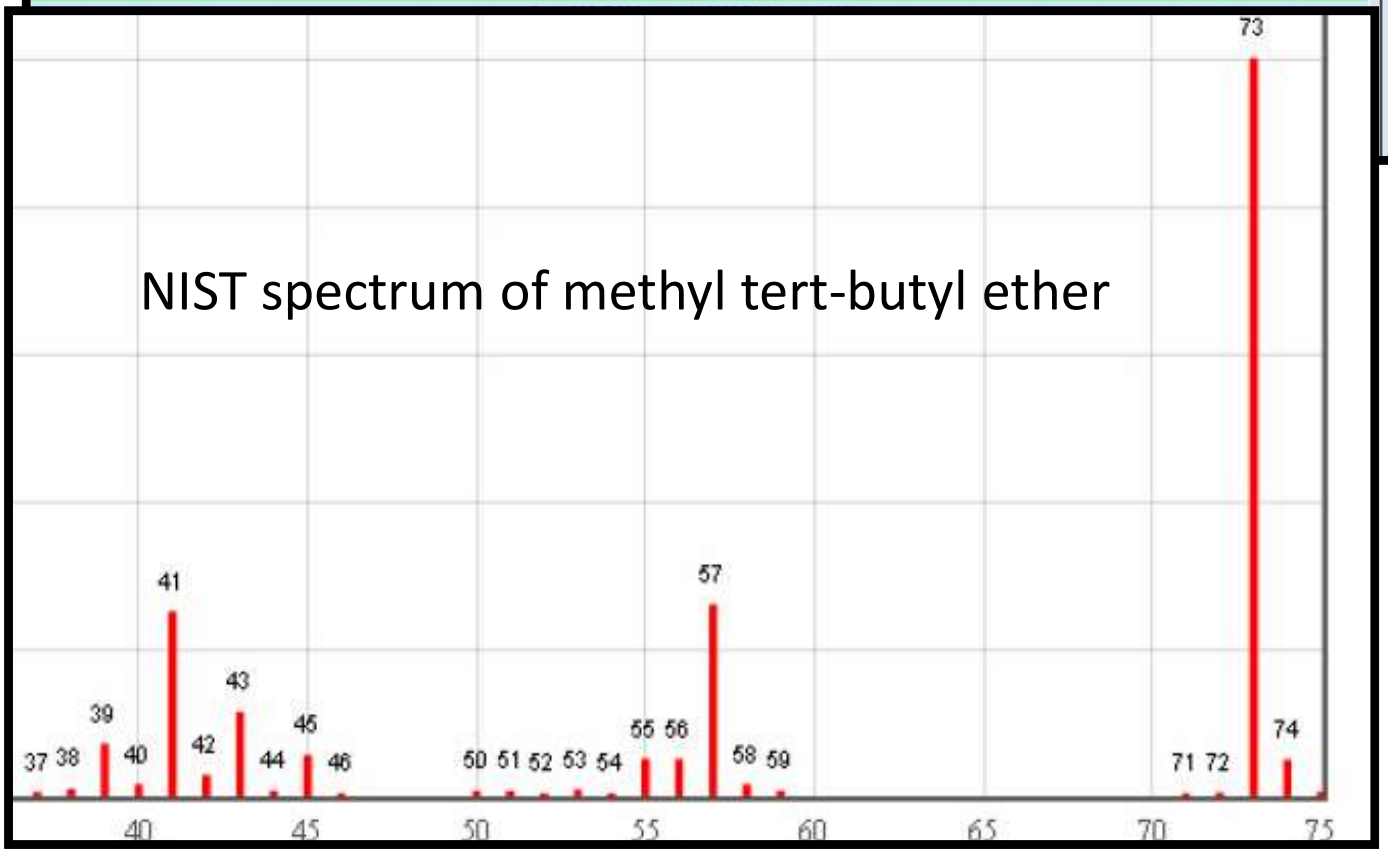
- Compare mass spectra of calibration peaks to the NIST library
- Also compare to other NIST spectra if a coelution is suspected
- Plot ion chromatograms to search for missing compounds
- Check if absent in second source (BS) or on other instruments
- Implement the best solution to prevent future misidentification
- Change quantitation ions to avoid coelution/integration errors

Ethyl acetate misidentified in 100ppb ICAL at 7.27 min. on instrument V:

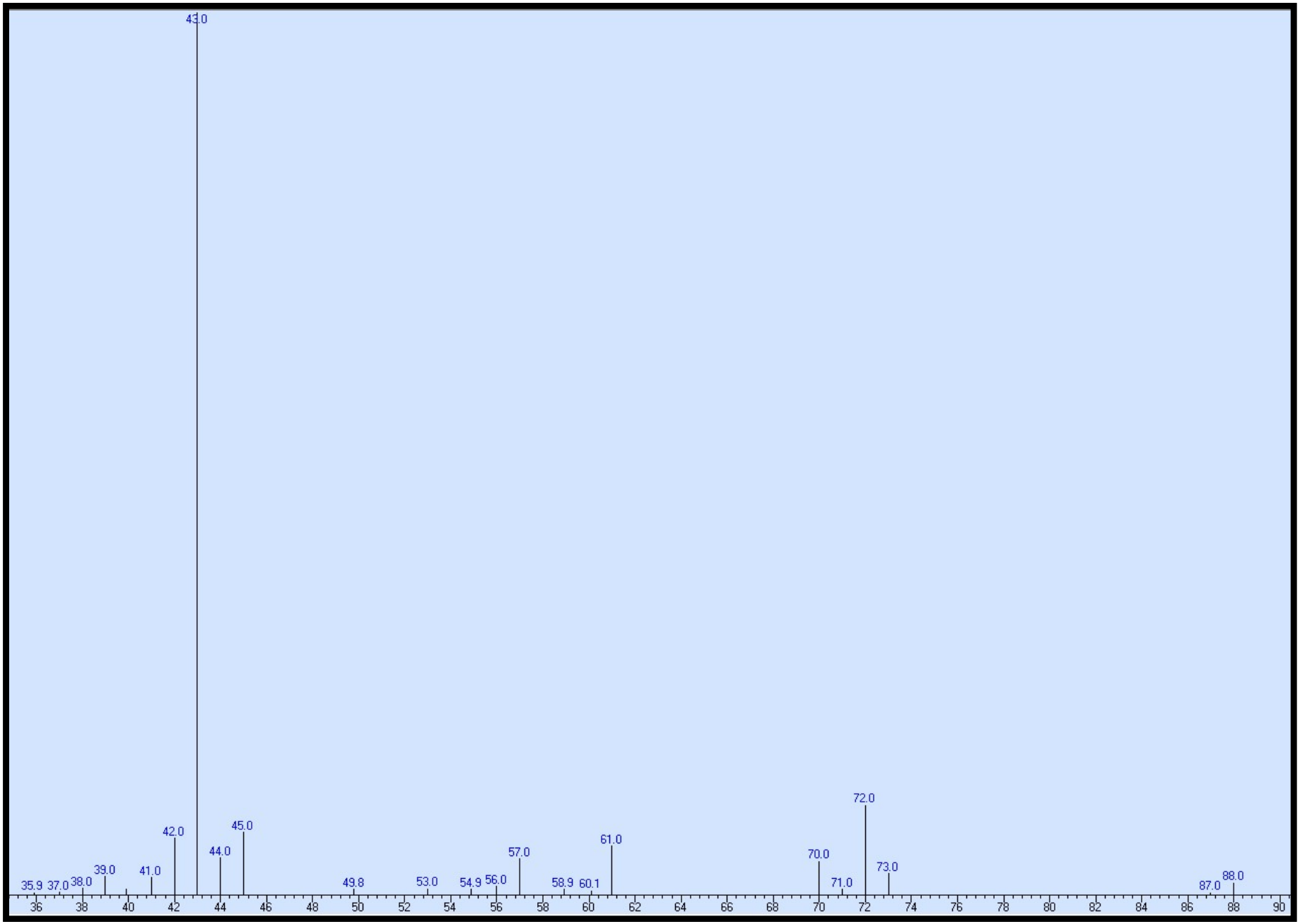


Misidentified ethyl acetate peak in 100 ppb ICAL matches MTBE:

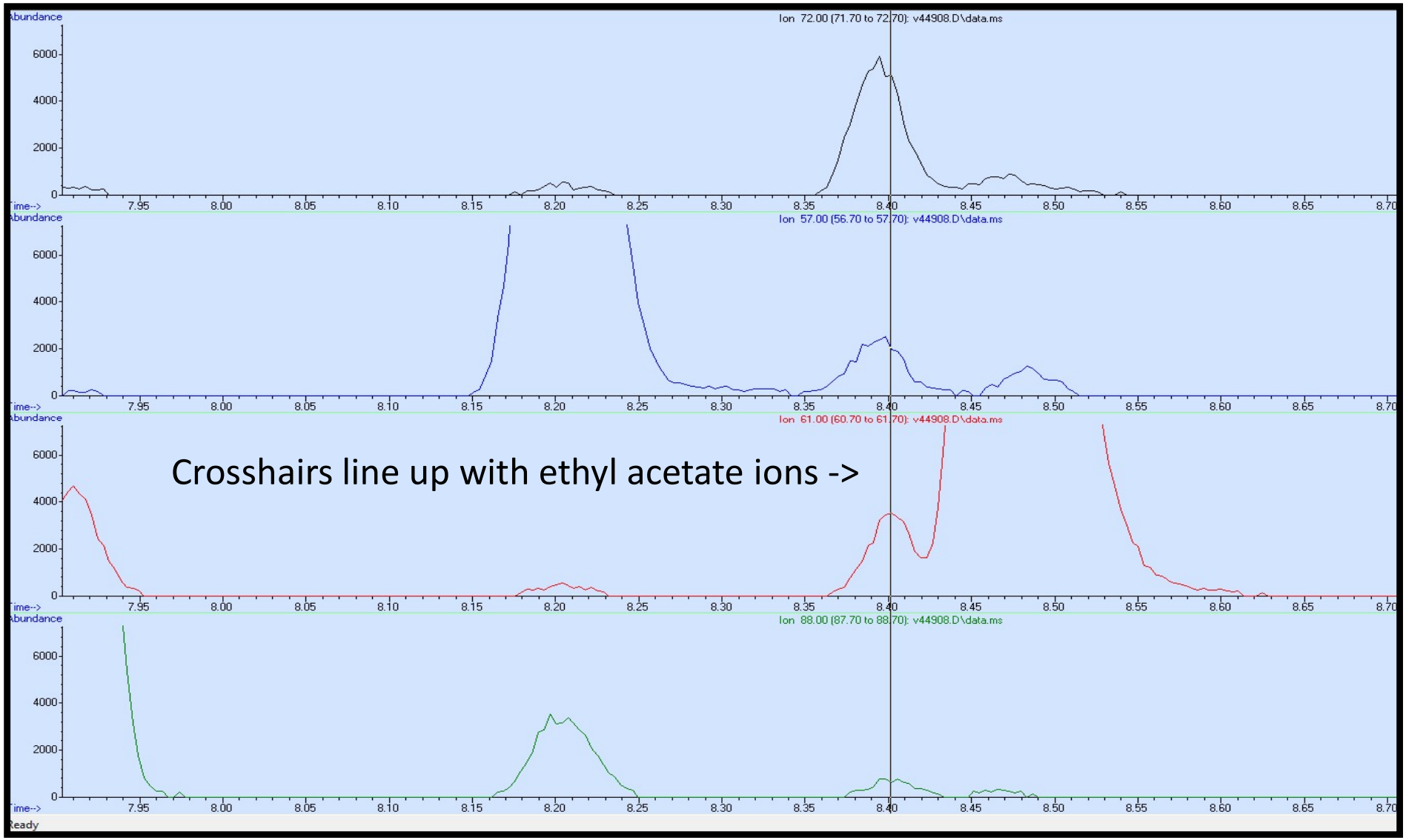




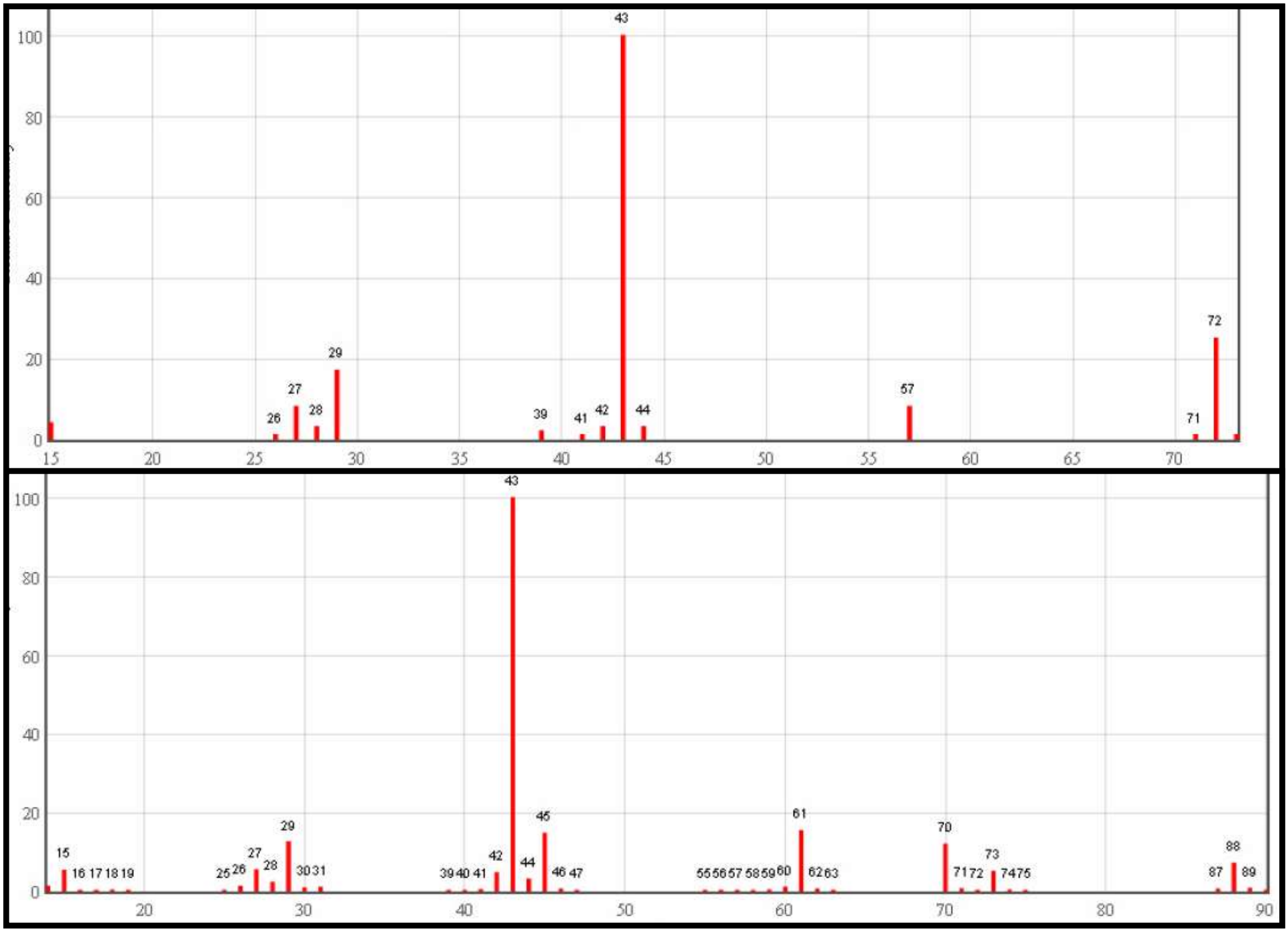
Ethyl acetate actually present at 8.40 min in BS solution run on same day



BS solution shows 2-butanone coelutes with ethyl acetate at 8.40 min.: Plot of ions 72, 57, 61, 88 display m/z 57, 72 from 2-butanone, vs. m/z 61, 88 from ethyl acetate



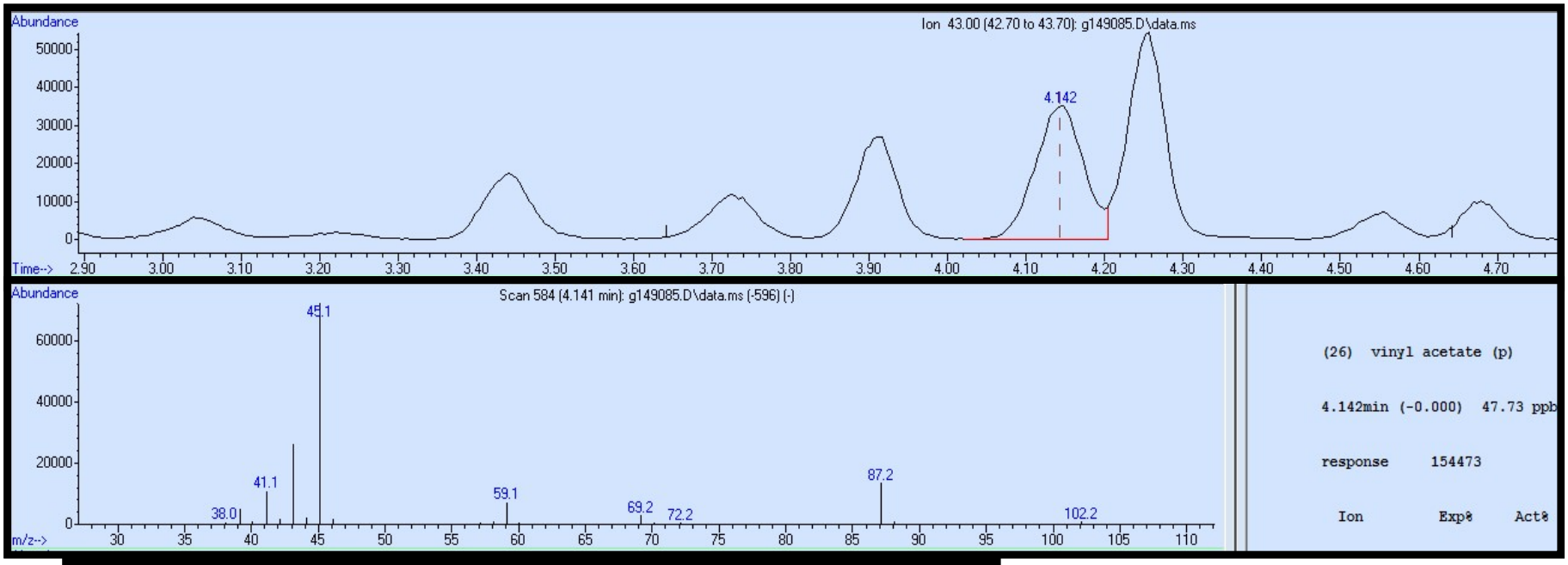
Comparison of NIST spectra for 2-butanone (top) vs. ethyl acetate (bottom)

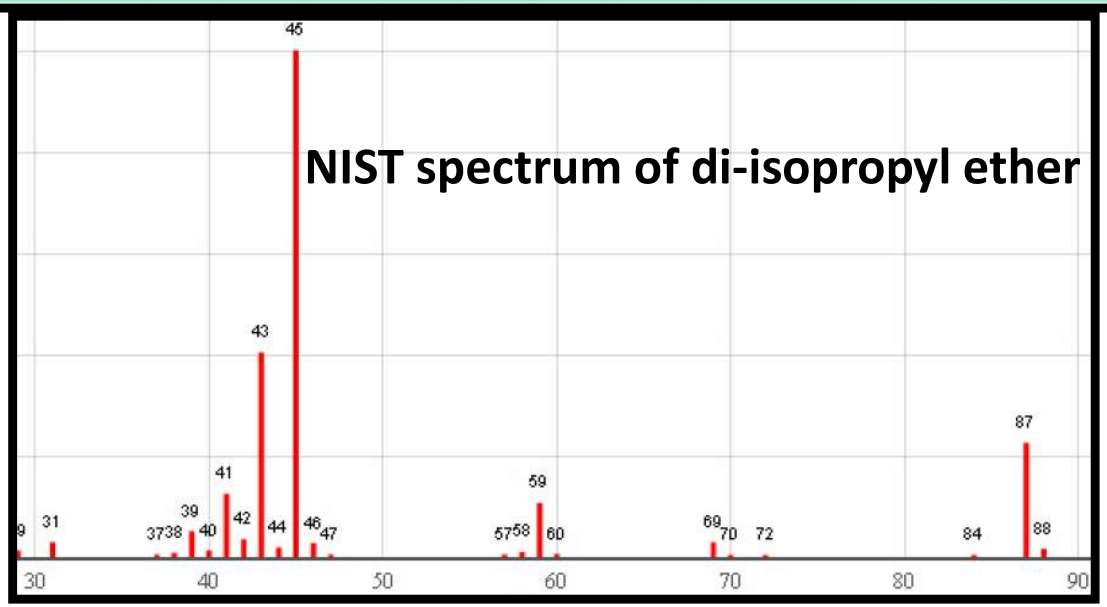


Ethyl Acetate: Problem Solution

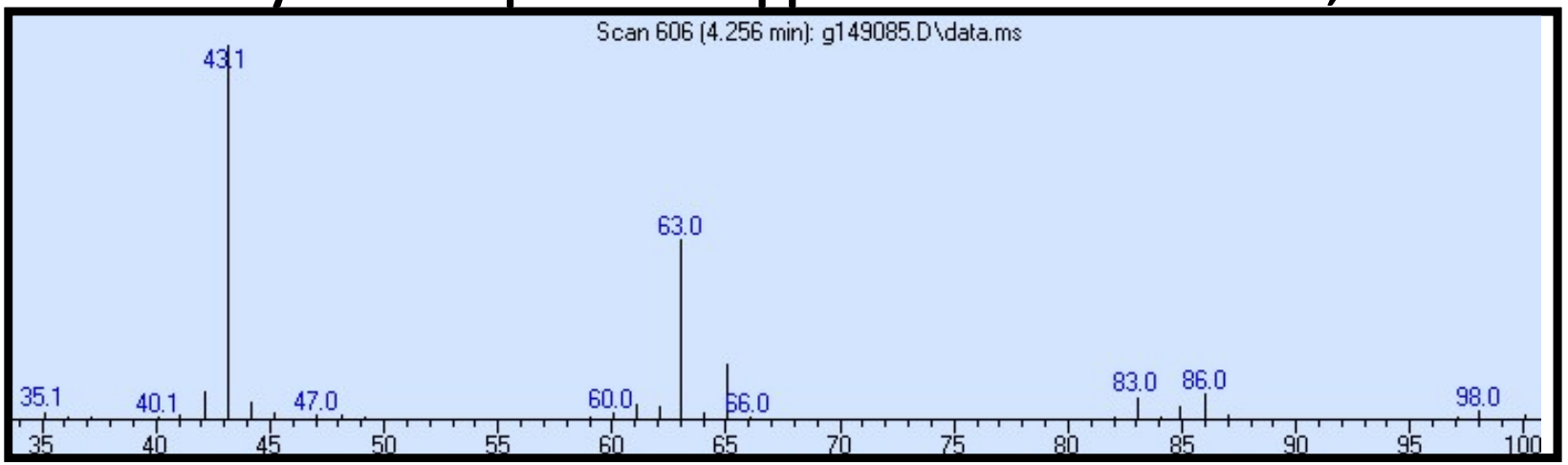
- **Extent of Problem**: Evaluation of QC data from several instruments involved searching for the correct characteristic ions in standard chromatograms and proved that this compound is missing from the primary standard used for initial calibration, but is present in the second source solution used for Blank Spikes (BS).
- **Problem Solution**: Ethyl acetate will not be reported as a target compound until a new primary stock standard is obtained. Any false calibration hits must be deleted from the ICAL quant reports and the ICAL calibration table. When a new standard is received, initial calibration for ethyl acetate will search for the target peak in the neighborhood of the retention time for 2-butanone. It may also be more cost effective to purchase separate stock mixtures for components that degrade more quickly than most chemicals.
- **Changes to Identification Criteria**: Since 2-butanone and ethyl acetate coelute on several instruments and share the common primary ion m/z 43, the quantitation ion for ethyl acetate should be changed on affected instruments to a unique ion (45, 61, 70, or 88).

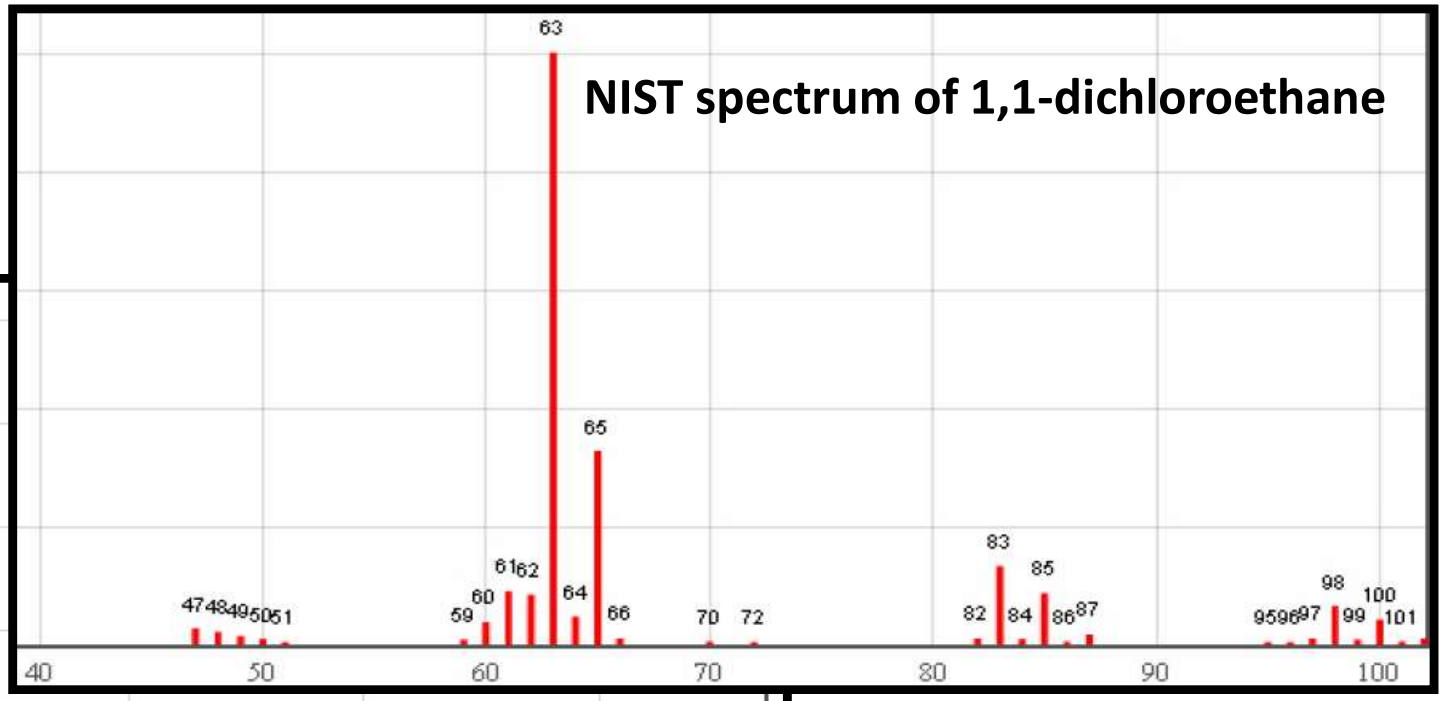
Vinyl acetate: wrong peak was used in the 50ppb ICAL on instrument MSG. This spectrum is actually di-isopropyl ether at a retention time of 4.14 min.

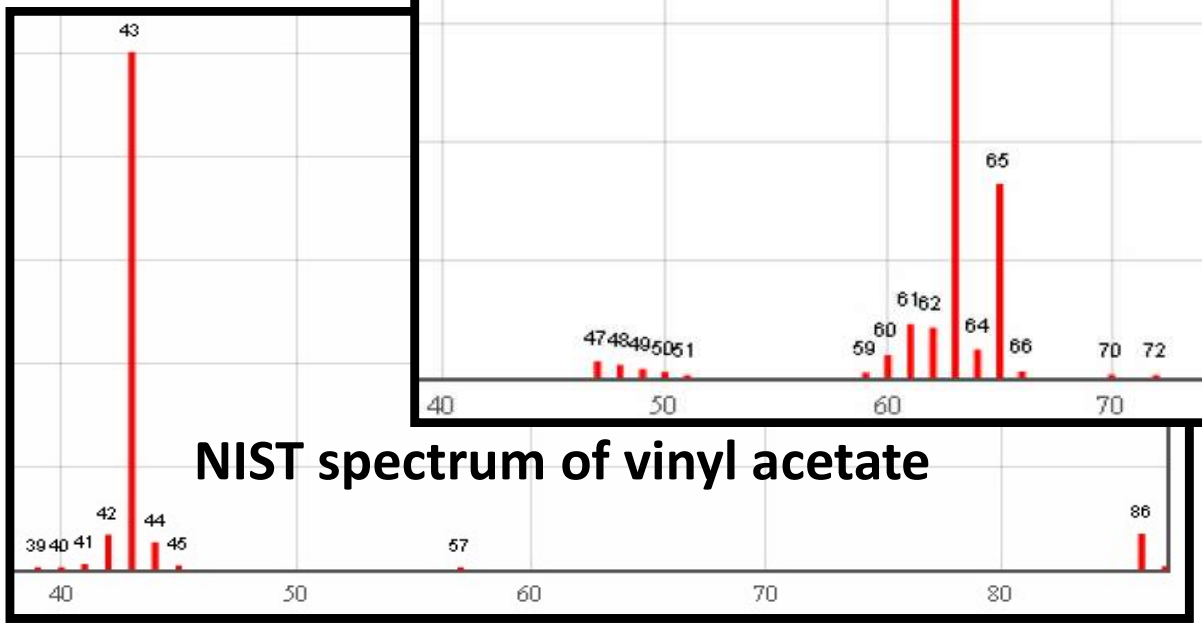




Correct vinyl acetate peak in 50 ppb ICAL coelutes with 1,1-dichloroethane



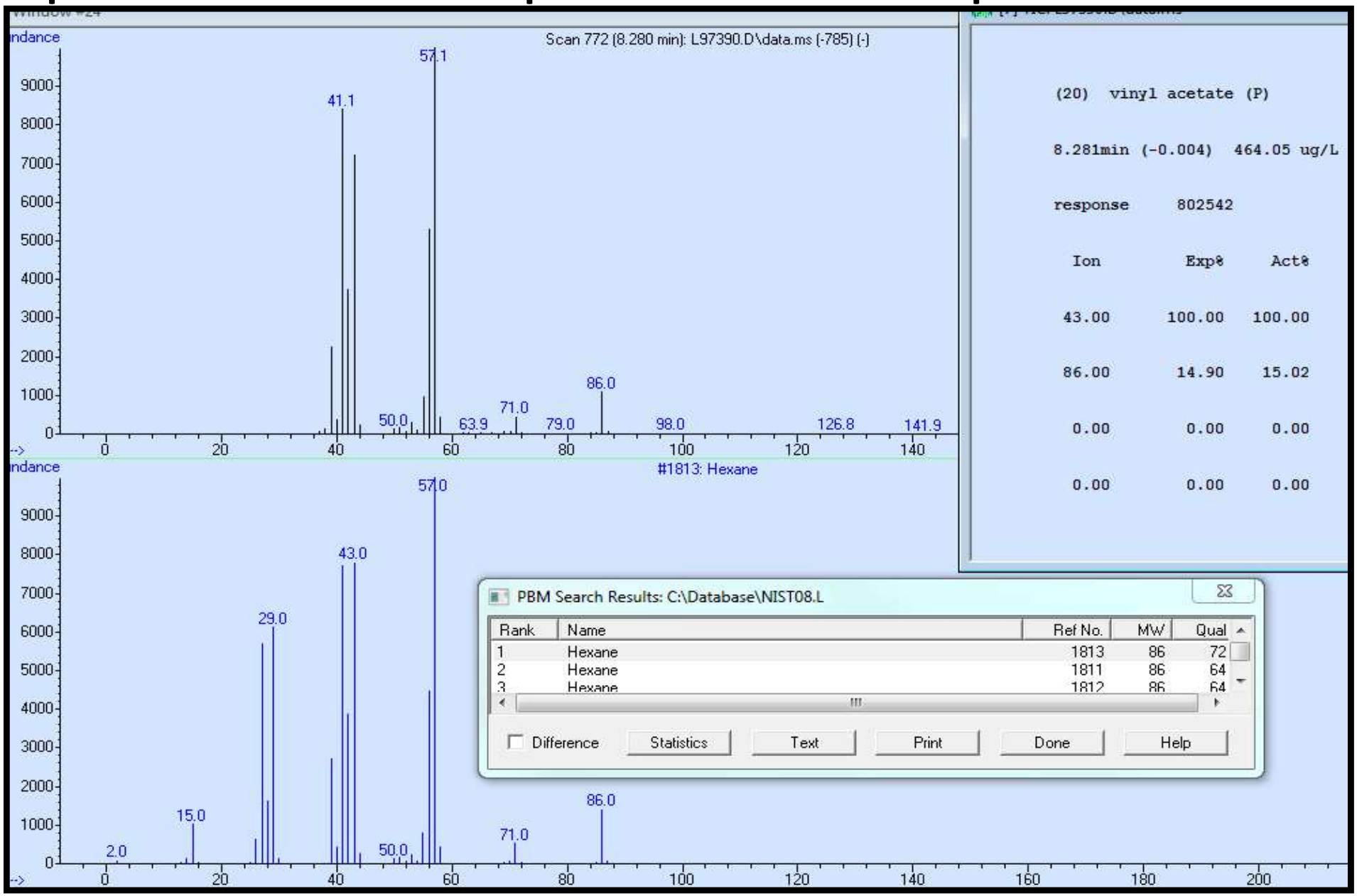




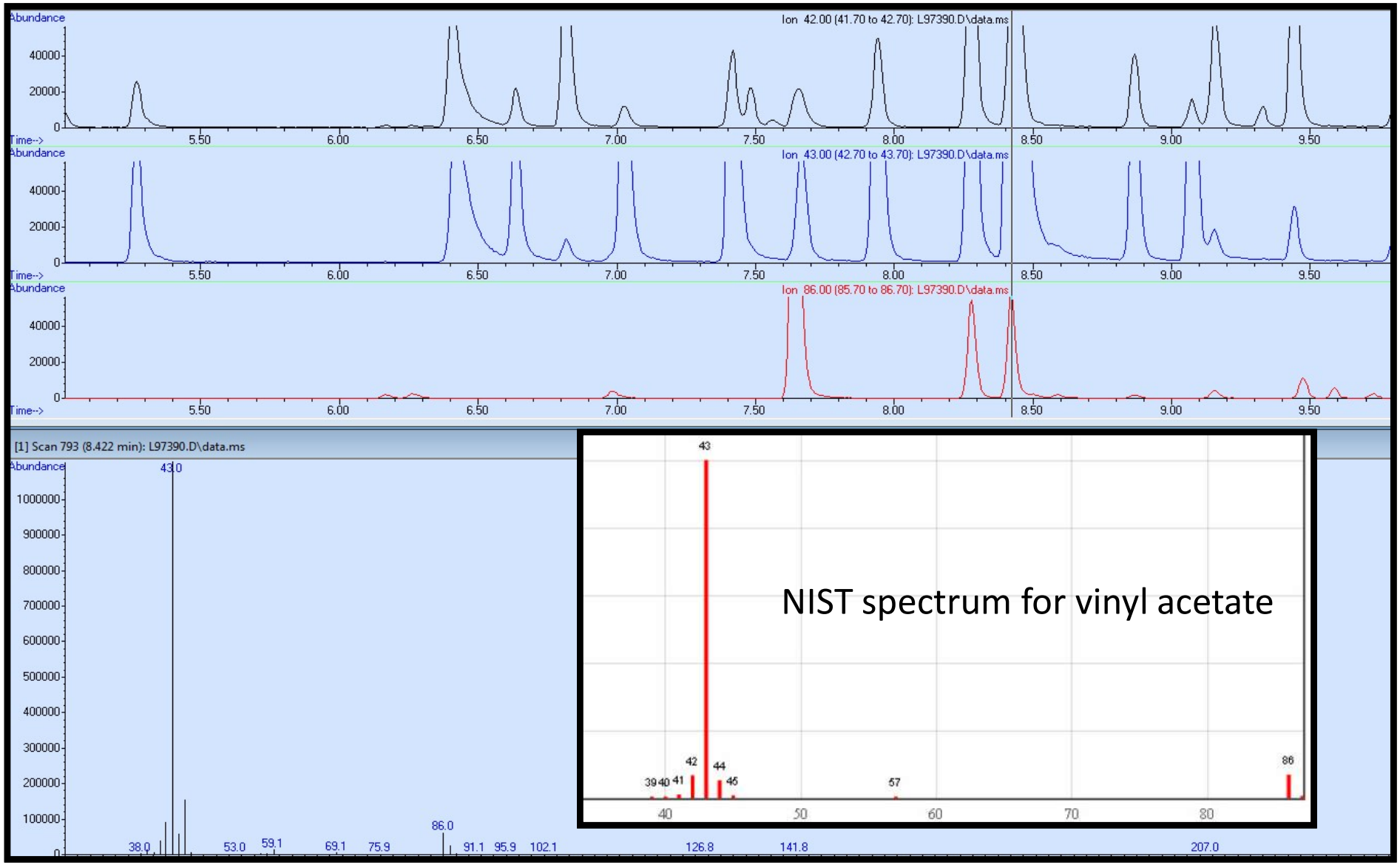
Vinyl Acetate: Problem Solution (Instrument G)

- **Extent of Problem**: This compound was noted as misidentified on instrument G. It is present in both primary calibration standards and second source solutions.
- **Problem Solution**: Vinyl acetate elutes very close to the retention time for 1,1-dichloroethane. QEdit may be used to reintegrate the correct peak and update the right spectrum.
- **Changes to Identification Criteria**: Since vinyl acetate and 1,1-dichloroethane elute within 0.1 minutes and share a primary ion m/z 43, this problem may re-occur. Vinyl acetate does not have any other significant intensity secondary ions to enable selecting an alternate quantitation ion. A cooler initial temperature and slower ramp could improve separation.

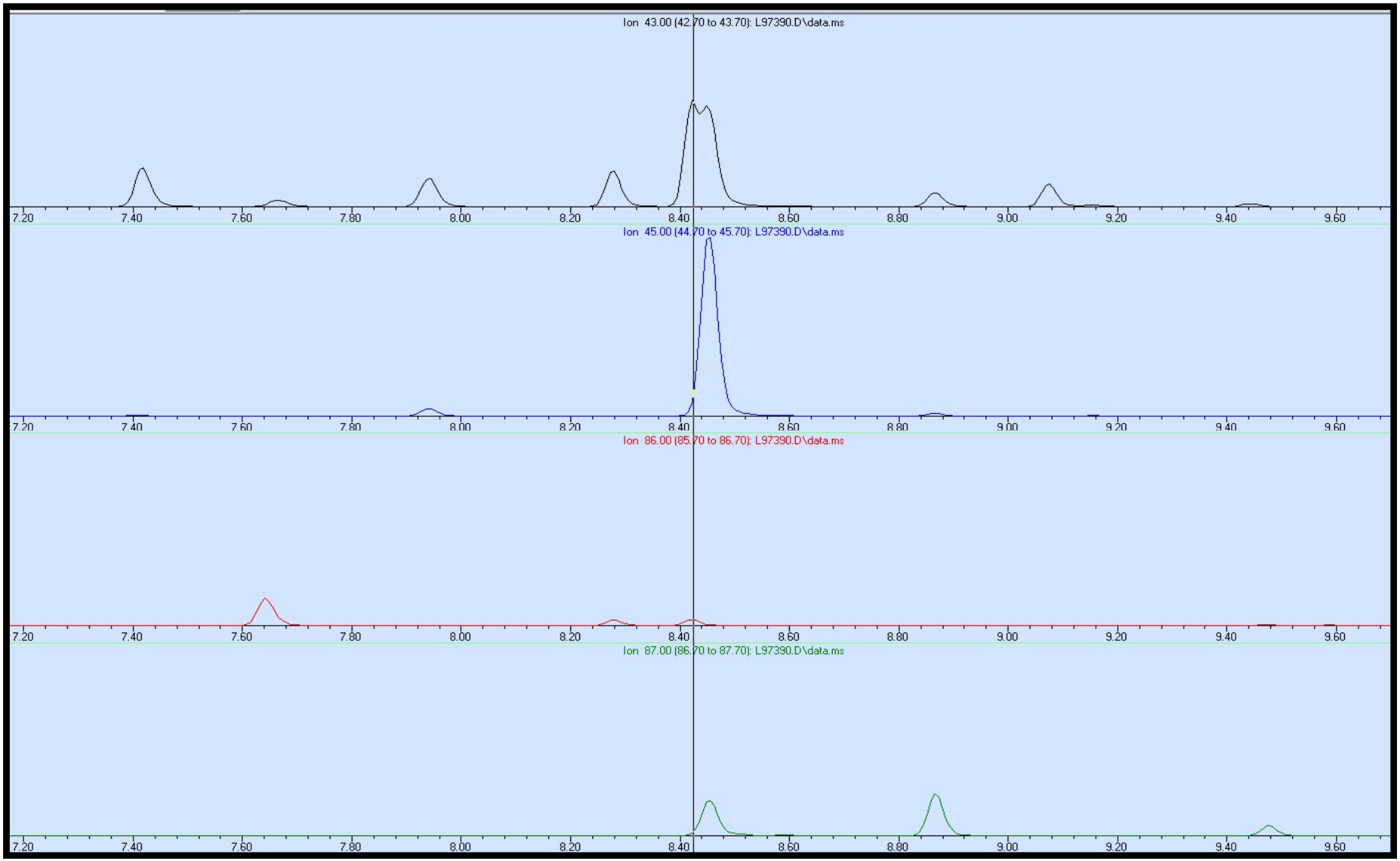
Vinyl acetate misidentified in 400ppb ICAL standard on instrument L. Spectrum associated with peak at 8.28 minutes represents hexane.



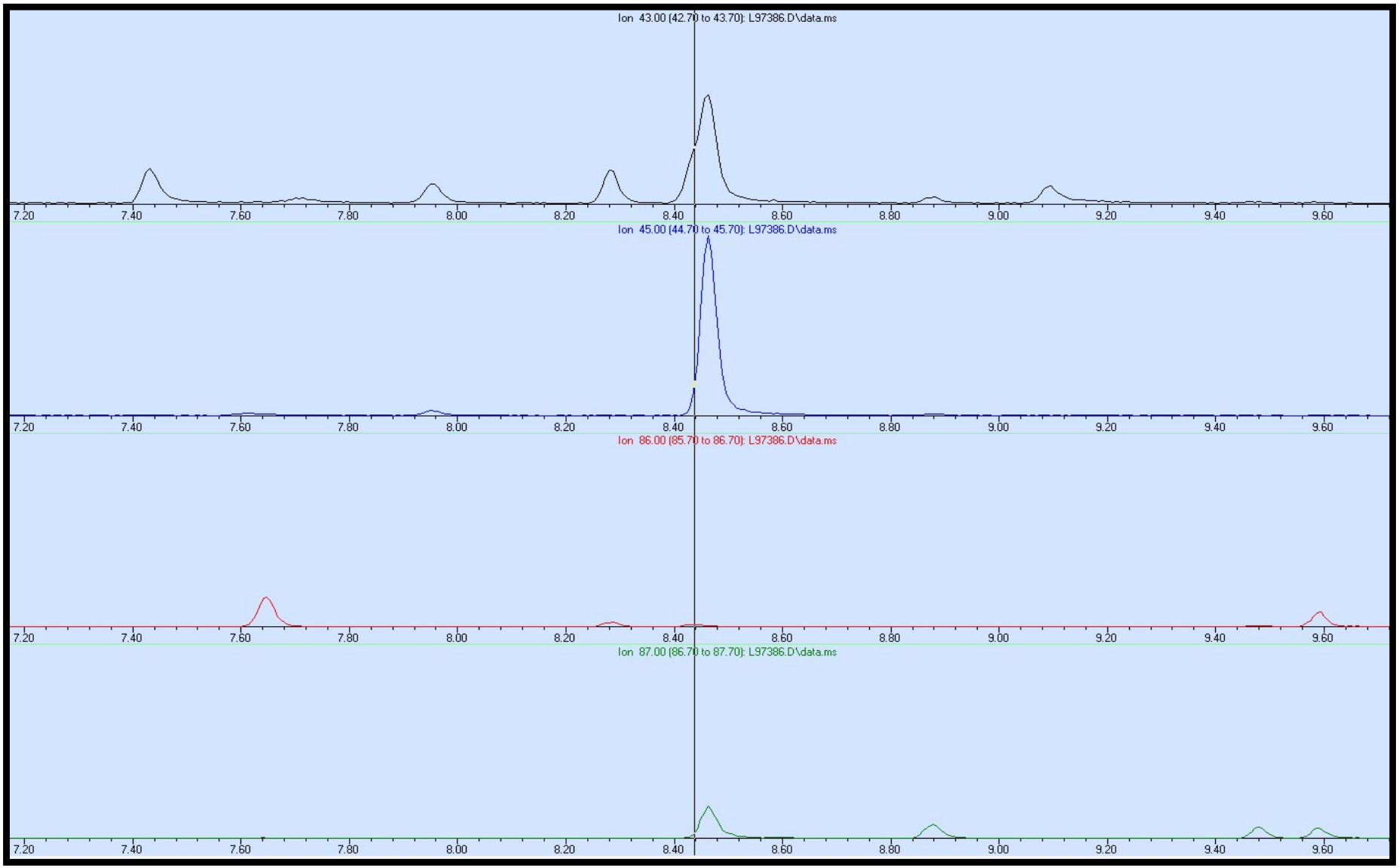
Vinyl acetate correctly identified at 8.422 minutes on instrument L. Ion chromatograms show crosshairs at the peak for the m/z 86. A coelution is noted for m/z 43. The spectrum at RT 8.422 matches NIST library.



Vinyl acetate base peak m/z 43 partially coelutes with di-isopropyl ether on instrument L. Crosshairs on ion chromatograms locate vinyl acetate ions 43 and 86, with ions 45 and 87 from di-isopropyl ether.



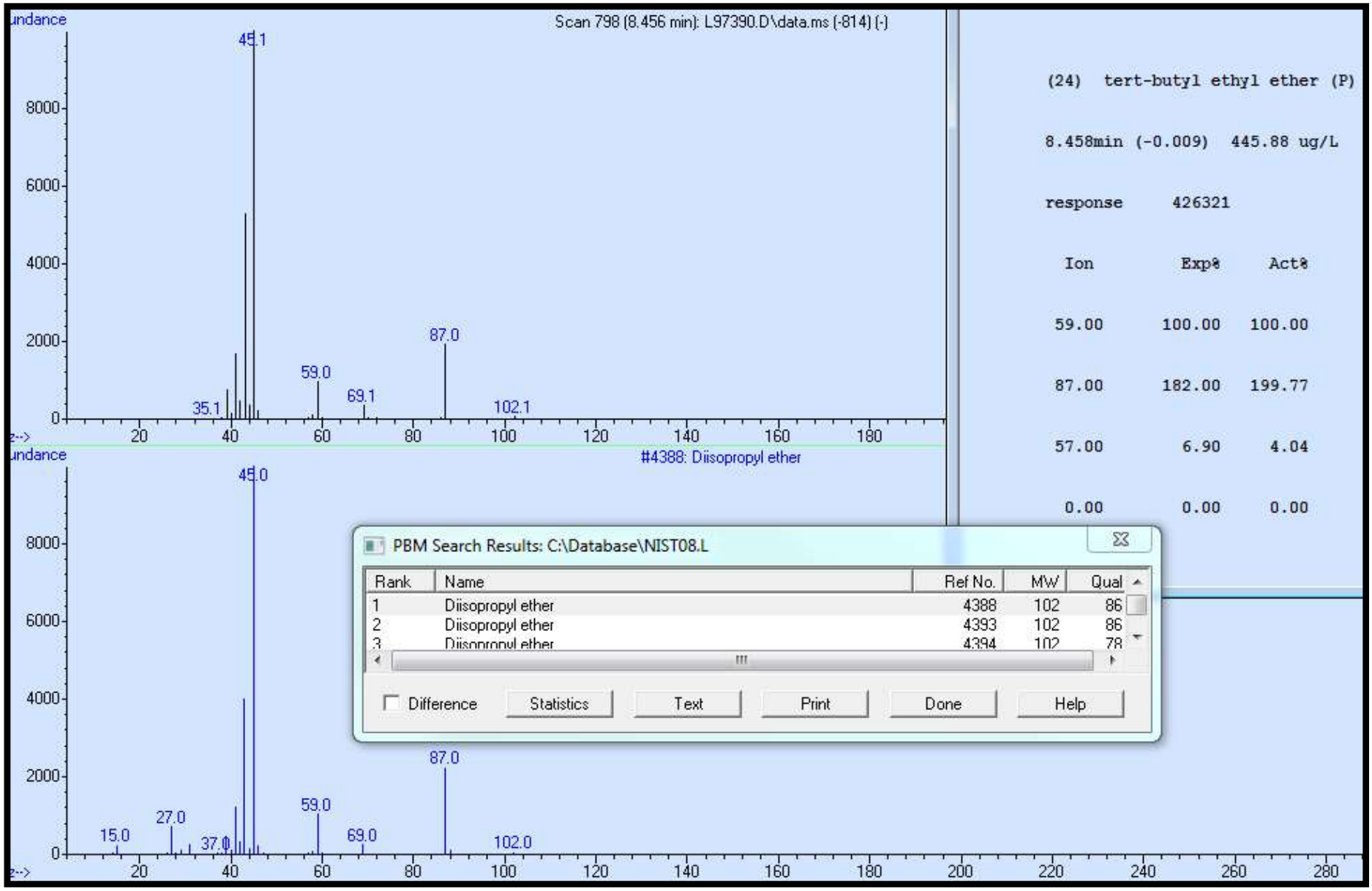
Vinyl acetate base peak ion 43 is not resolved from a coelution with di-isopropyl ether in the lower concentration ICAL standards, as shown in the ion chromatograms for the 20 ppb ICAL standard.



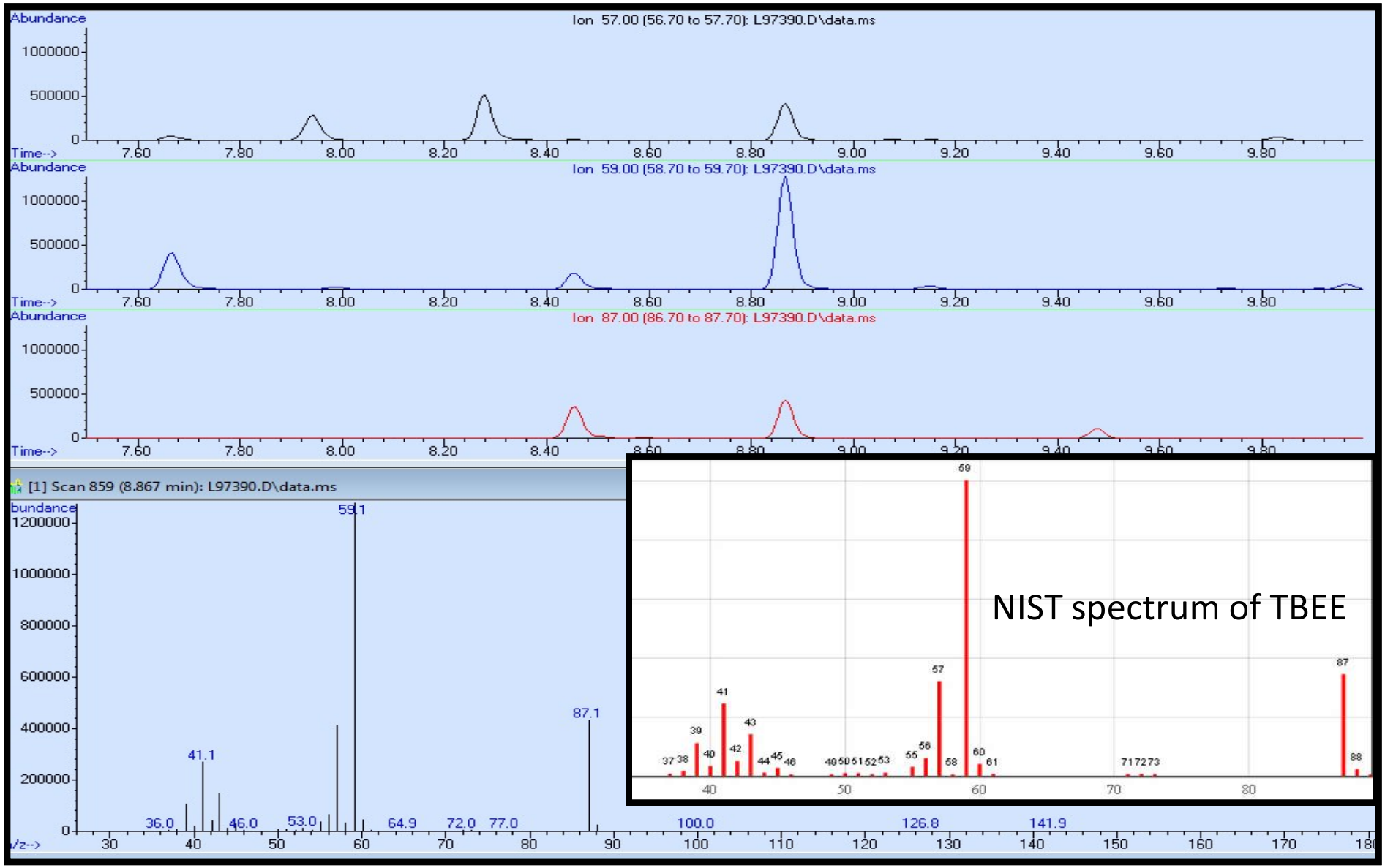
Vinyl Acetate: Problem Solution (Instrument L)

- **Extent of Problem**: This compound was noted as misidentified on instrument L. It is present in both primary calibration standards and second source solutions.
- **Problem Solution**: Vinyl acetate elutes 0.14 minutes after the retention time for hexane and exhibits common ions 43 and 86. The correct peak for vinyl acetate has a partial coelution of ion 43, which is also part of di-isopropyl ether.
- **Changes to Identification Criteria**: A cooler initial column temperature and slower ramp could improve separation. Ion 86 could be selected as an alternate quantitation ion, but due to its lower intensity, this would increase the MDL.

Tert-butyl ethyl ether (TBEE) misidentified in the 400ppb ICAL standard run on instrument L. The mass spectrum at 8.46 minutes is di-isopropyl ether.

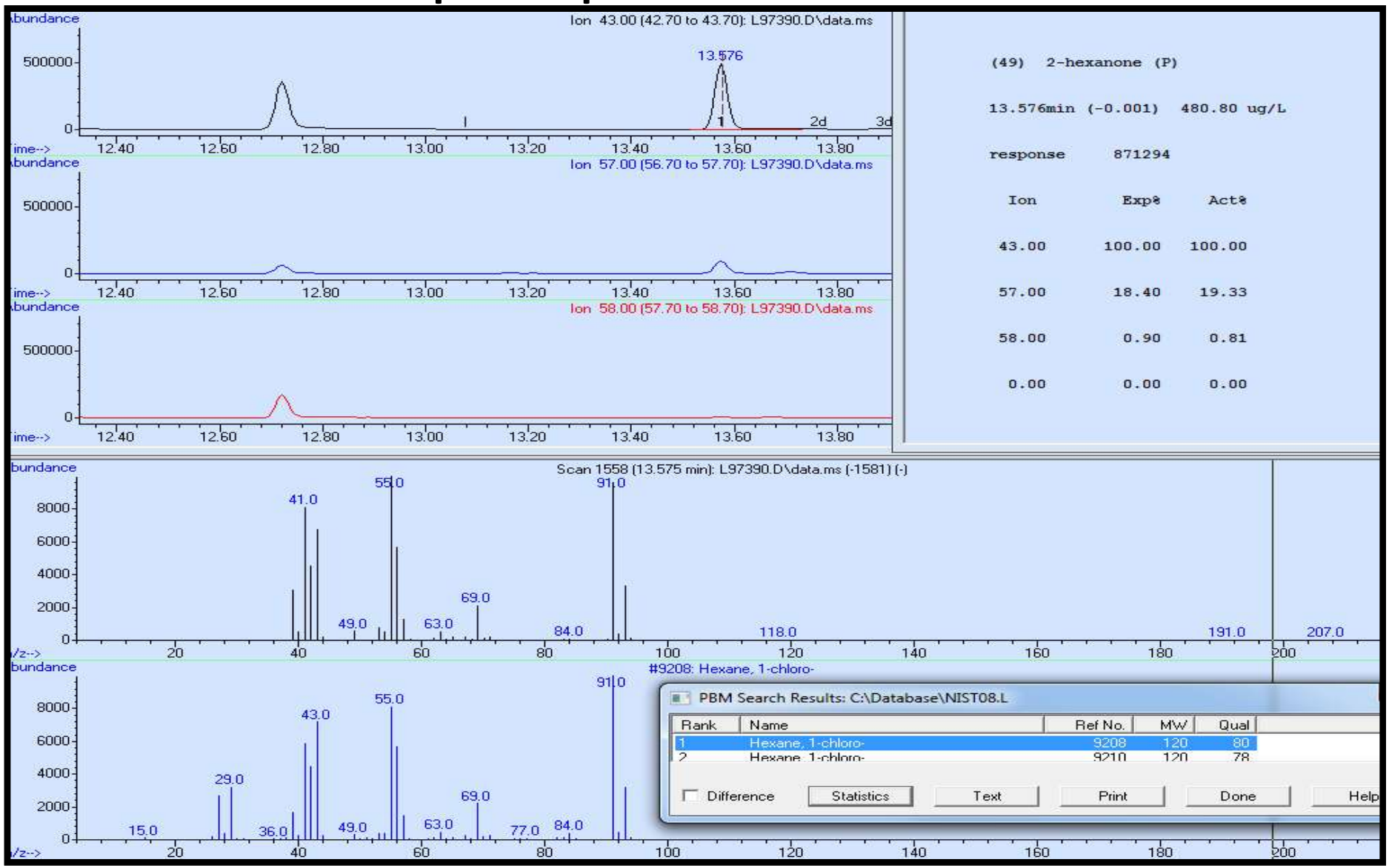


Tert-butyl ethyl ether correctly identified at 8.87 minutes on instrument L. Ion chromatograms display the characteristic ions m/z 59 and 87. The mass spectrum at the retention time of 8.87 minutes matches the NIST library.

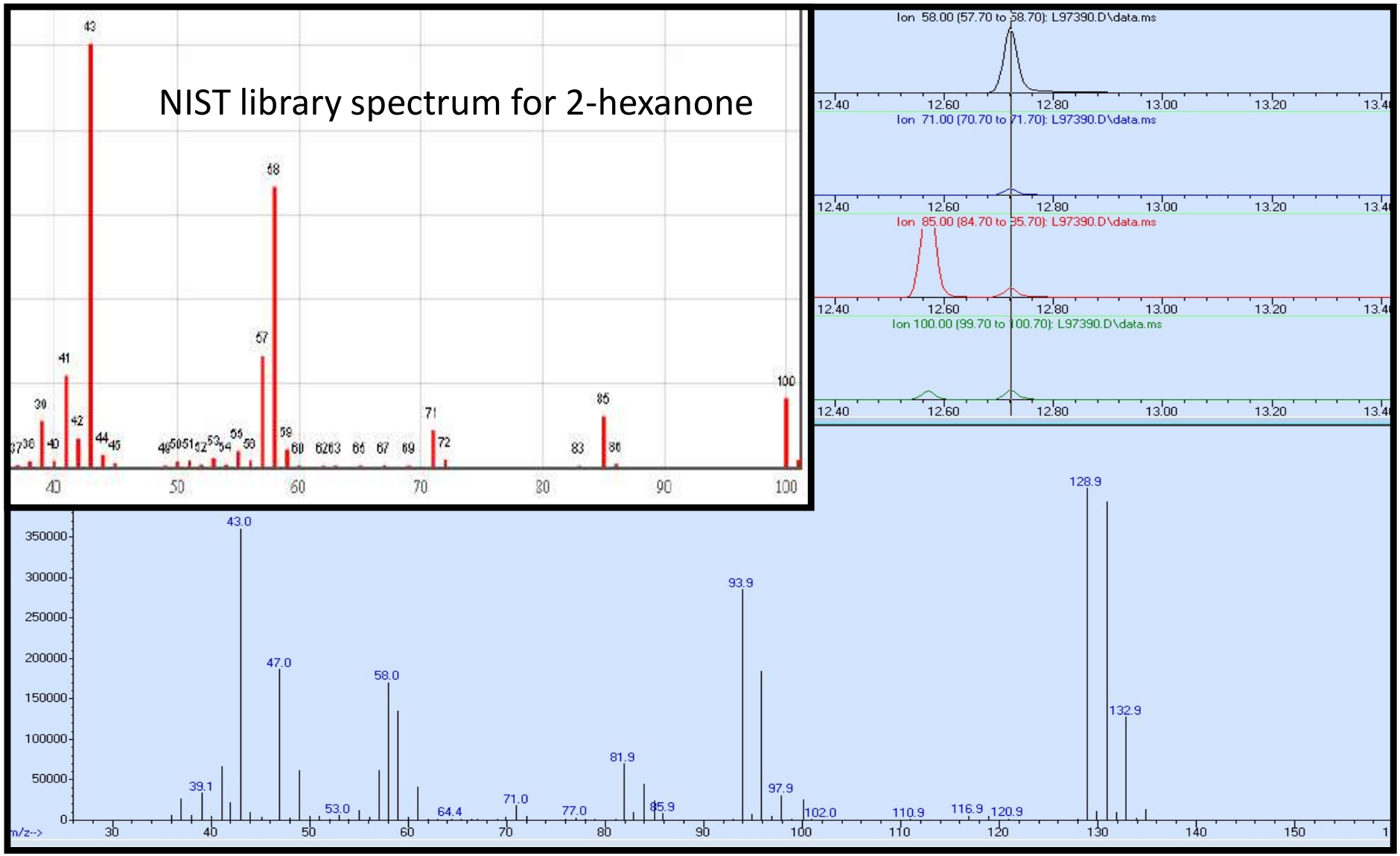


Tert-butyl ethyl ether problem solution: Instrument L recently had a new GC column installed and retention times of all target compounds had to be re-established. When assigning retention times for the first time on a new GC column, check that all characteristic ions from the NIST library spectrum are present in the correct ratio and that any extraneous ions are accounted for via a library search. The target compound TBEE elutes 0.51 minutes apart from the misidentified peak, so the problem is not likely to reoccur using the same method and column configuration on this instrument.

2-Hexanone was misidentified in the 400ppb ICAL standard at a retention time of 13.58 minutes on instrument L. A library search determined that this peak represents an isomer of 1-chlorohexane.

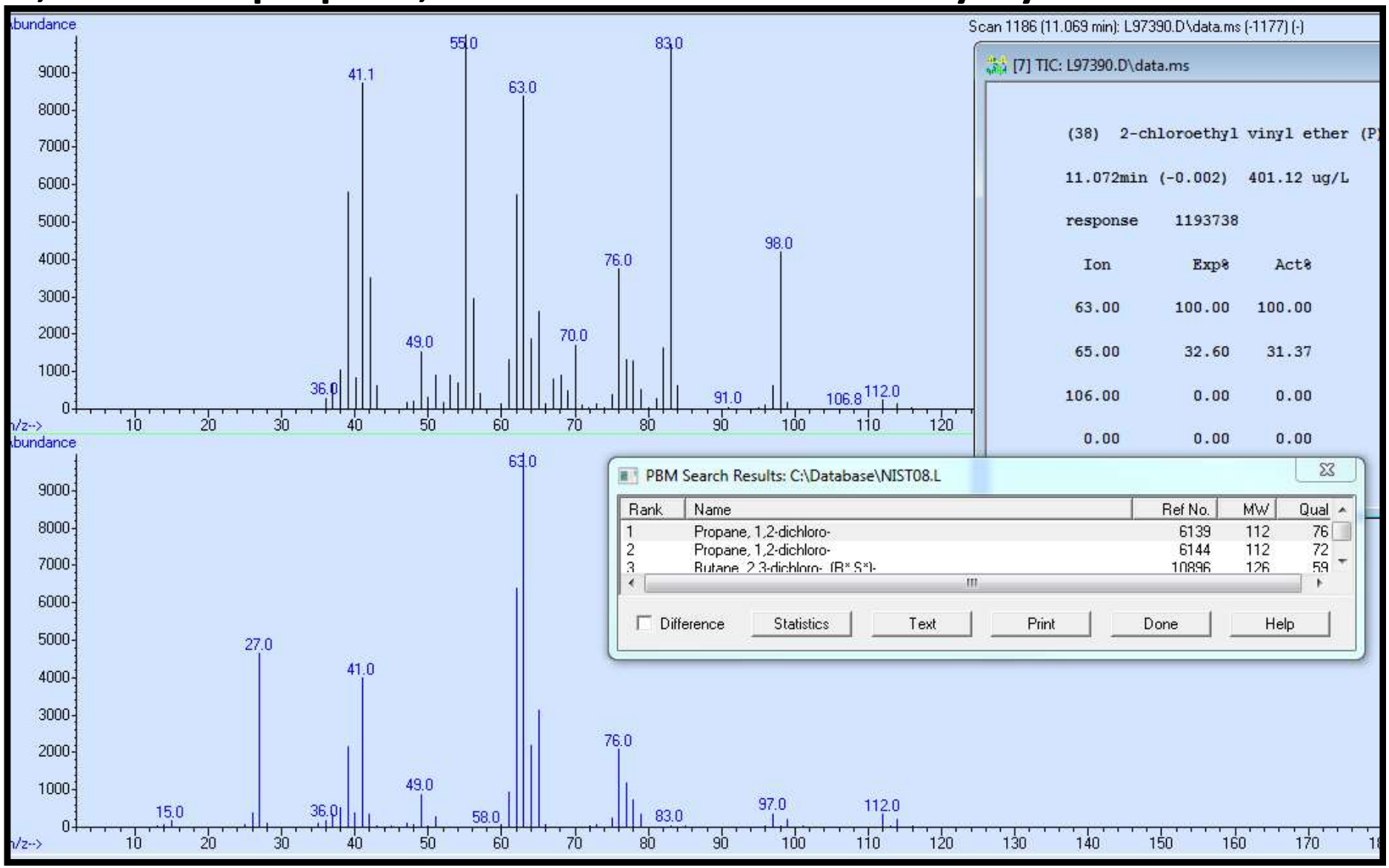


Crosshairs show 2-hexanone peak at 12.73 min. on instrument L. Ions 43, 58, 71, 85, 100 are present. Peak coelutes with tetrachloroethene (ions 47, 59, 82, 94, 129, 164, and m+2 and m+4 chlorine isotopes).

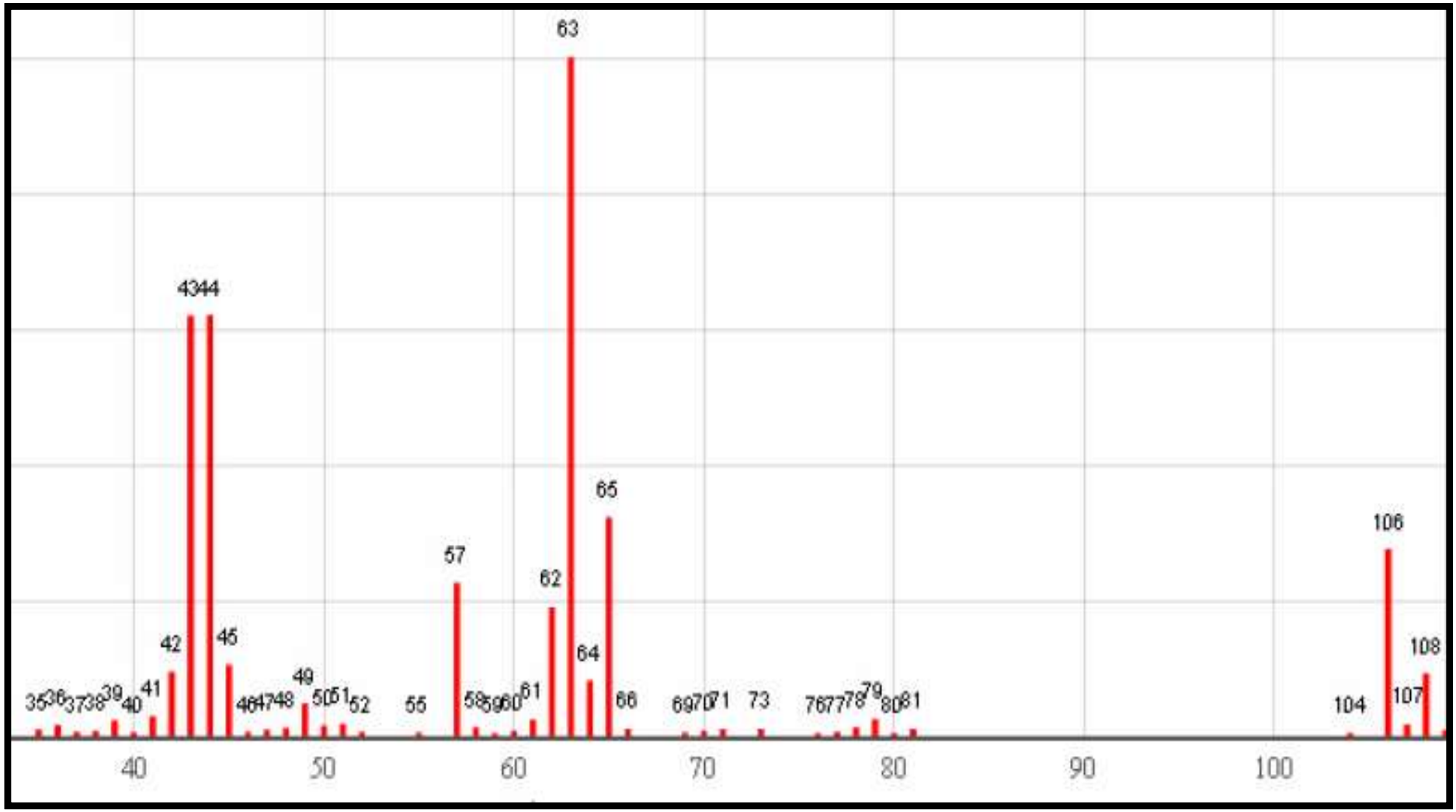


2-Hexanone problem solution: Instrument L recently had a new GC column installed and retention times of all target compounds had to be re-established. When assigning retention times for the first time on a new GC column, check that all characteristic ions from the NIST library spectrum are present in the correct ratio and that any extraneous ions are accounted for via a library search. The target compound 2-hexanone elutes 0.85 minutes apart from the misidentified peak, so the problem is not likely to reoccur using the same method and column configuration on this instrument.

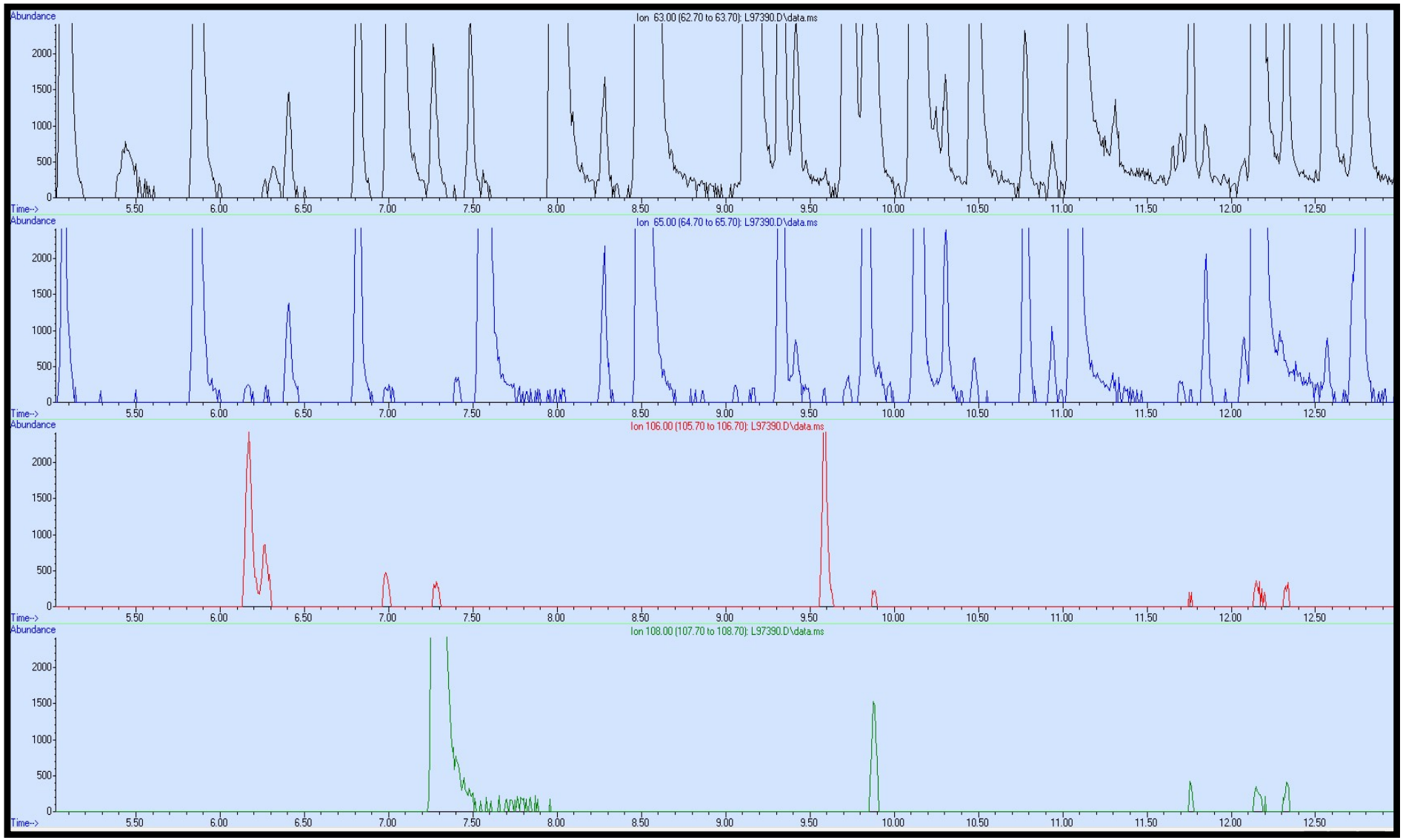
2-Chloroethyl vinyl ether was misidentified at 11.07 minutes in the 400ppb ICAL standard on instrument L. The mass spectrum matches 1,2-dichloropropane, which coelutes with methyl cyclohexane.



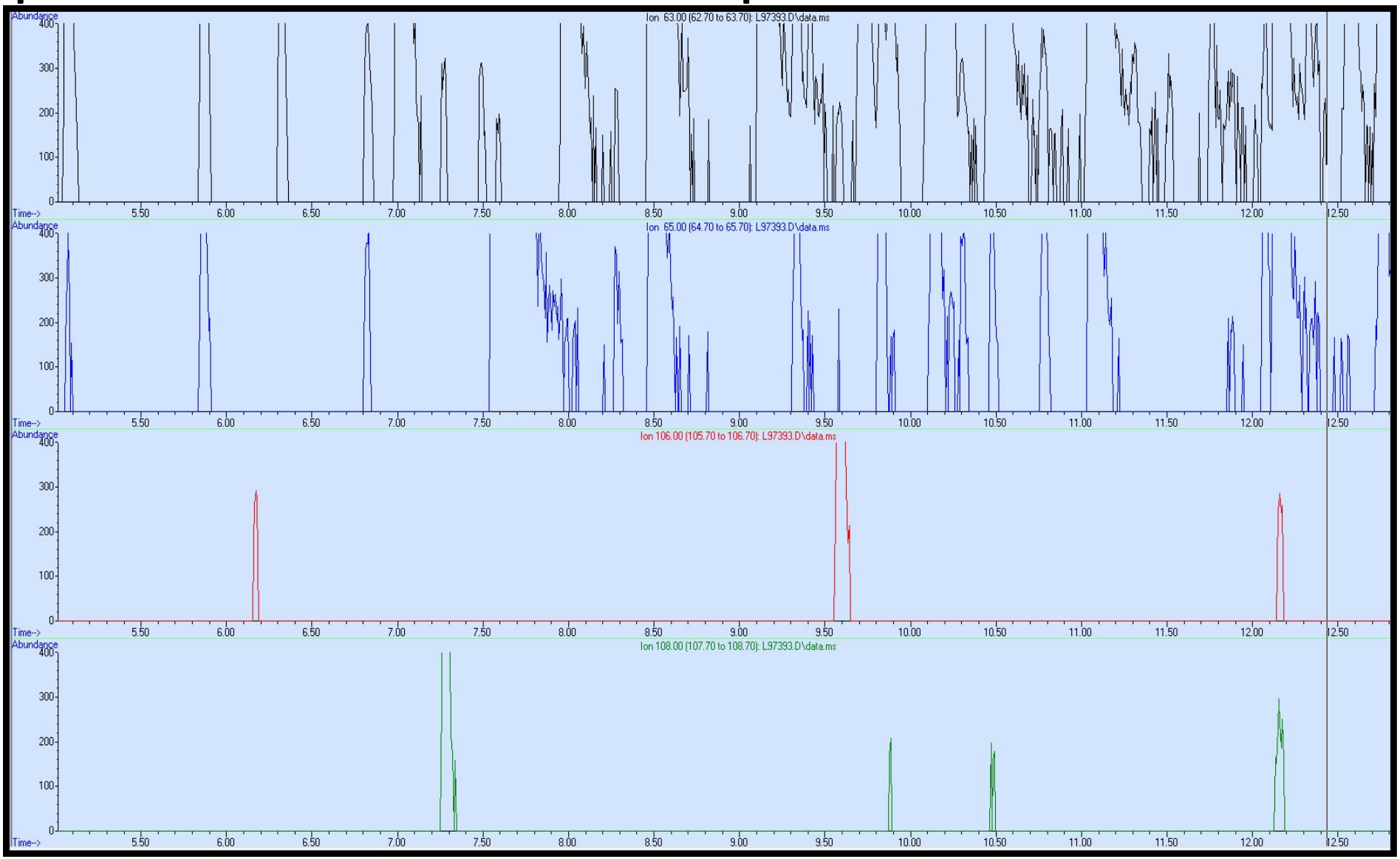
NIST library spectrum for 2-chloroethyl vinyl ether. Key ions include m/(m+2) chlorine isotope ions in a 3:1 ratio (m/z 63:65 and 106:108).



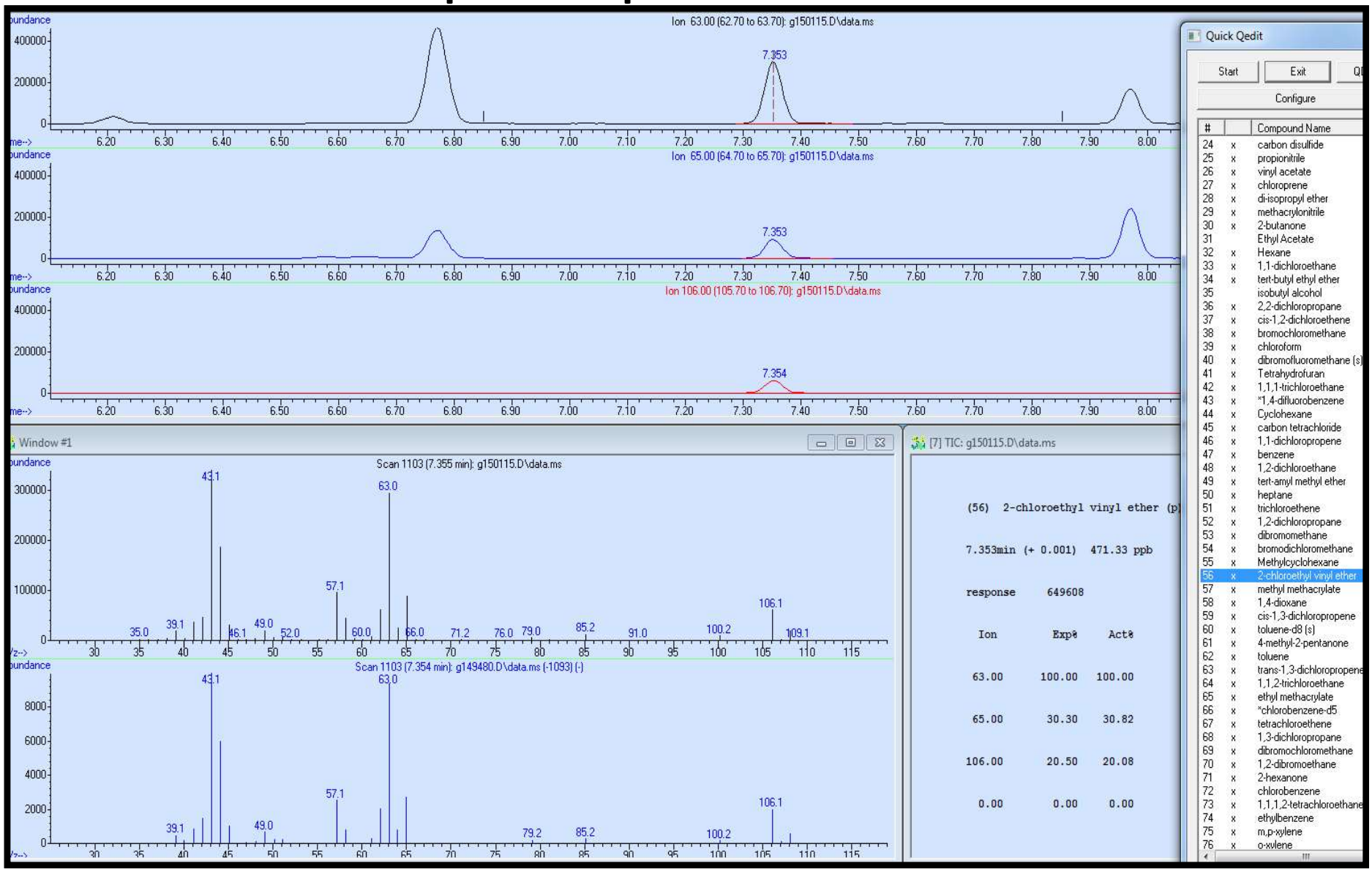
On instrument L, ion chromatograms from the 400 ppb ICAL standard show 2-chloroethyl vinyl ether is not present. Peaks for characteristic ions 106 and 108 do not coelute with any peaks for ions 63 and 65.



Plot of ion chromatograms on instrument L for BS solution also does not display evidence of 2-chloroethyl vinyl ether. All peaks for ion pairs 63 and 65 do not coincide with peaks for ions 106 and 108.



2-Chloroethyl vinyl ether was identified at 7.36 min. in 400ppb ICAL on instrument G. All major ions present (43, 44, 57, 63, 65, 106, 108). This confirms the compound is present in calibration solutions.

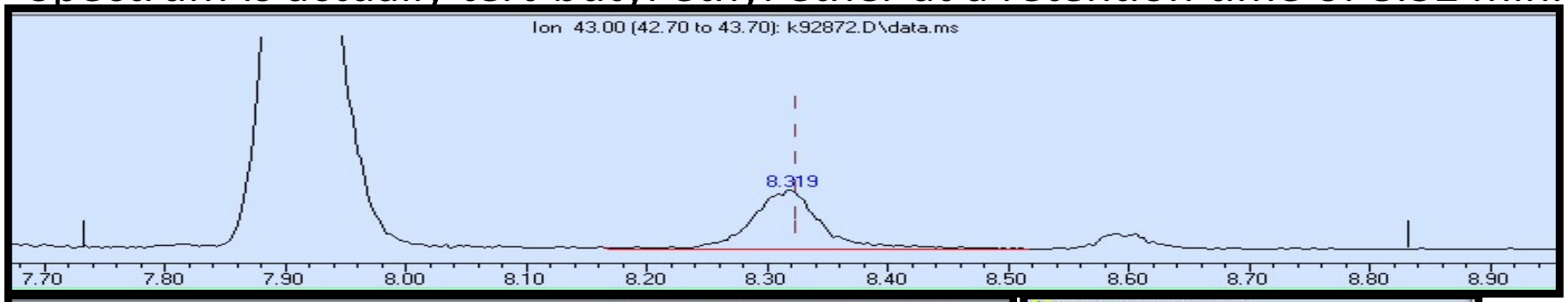


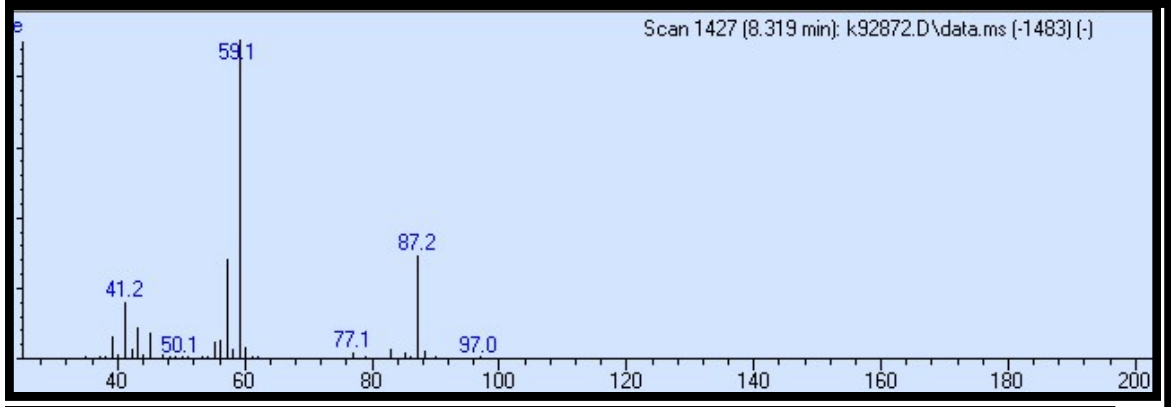
2-Chloroethyl vinyl ether: Problem Solution

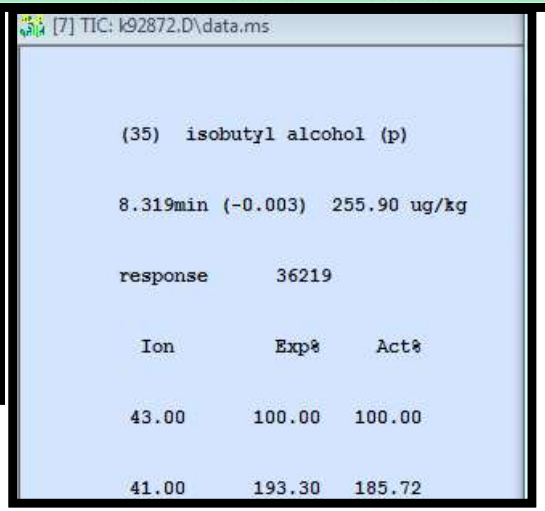
- **Extent of Problem**: This compound was detected in primary and second source calibration standards run on instrument G, but was not able to be detected on instrument L.

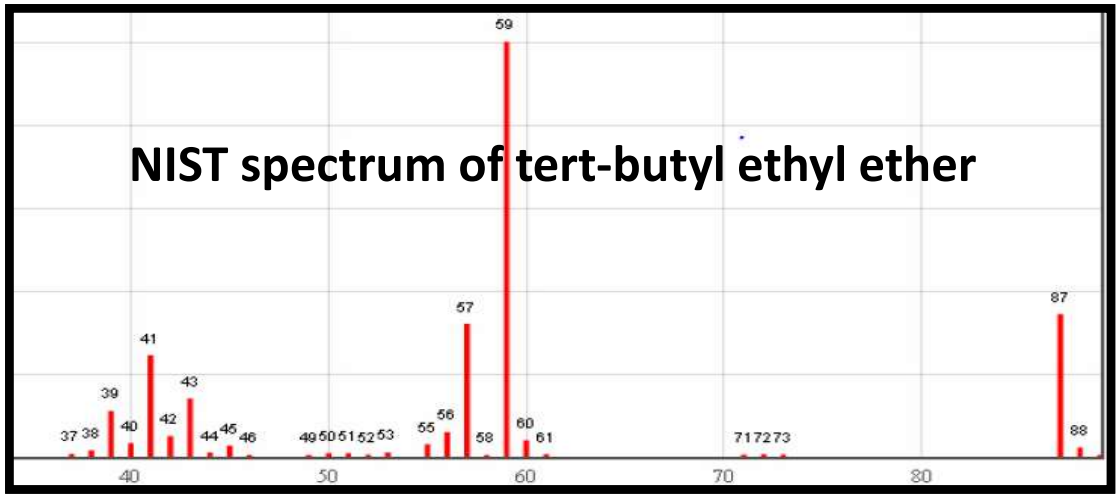
- **Problem Solution**: Instrument L cannot be used at this time for the analysis of 2-chloroethyl vinyl ether. Note that 2-Chloroethyl vinyl ether is considered a difficult-to-analyze target compound. Instrument L is configured with a Tekmar brand purge and trap concentrator, while instrument G utilizes an OI Corporation sample concentrator. These two brands utilize brand-specific sorbent traps, different materials for the sample loading loop, and different water management systems, which may affect performance.

Isobutyl alcohol: wrong peak was used in the 50ppb ICAL on instrument MSK. Spectrum is actually tert-butyl ethyl ether at a retention time of 8.32 min.

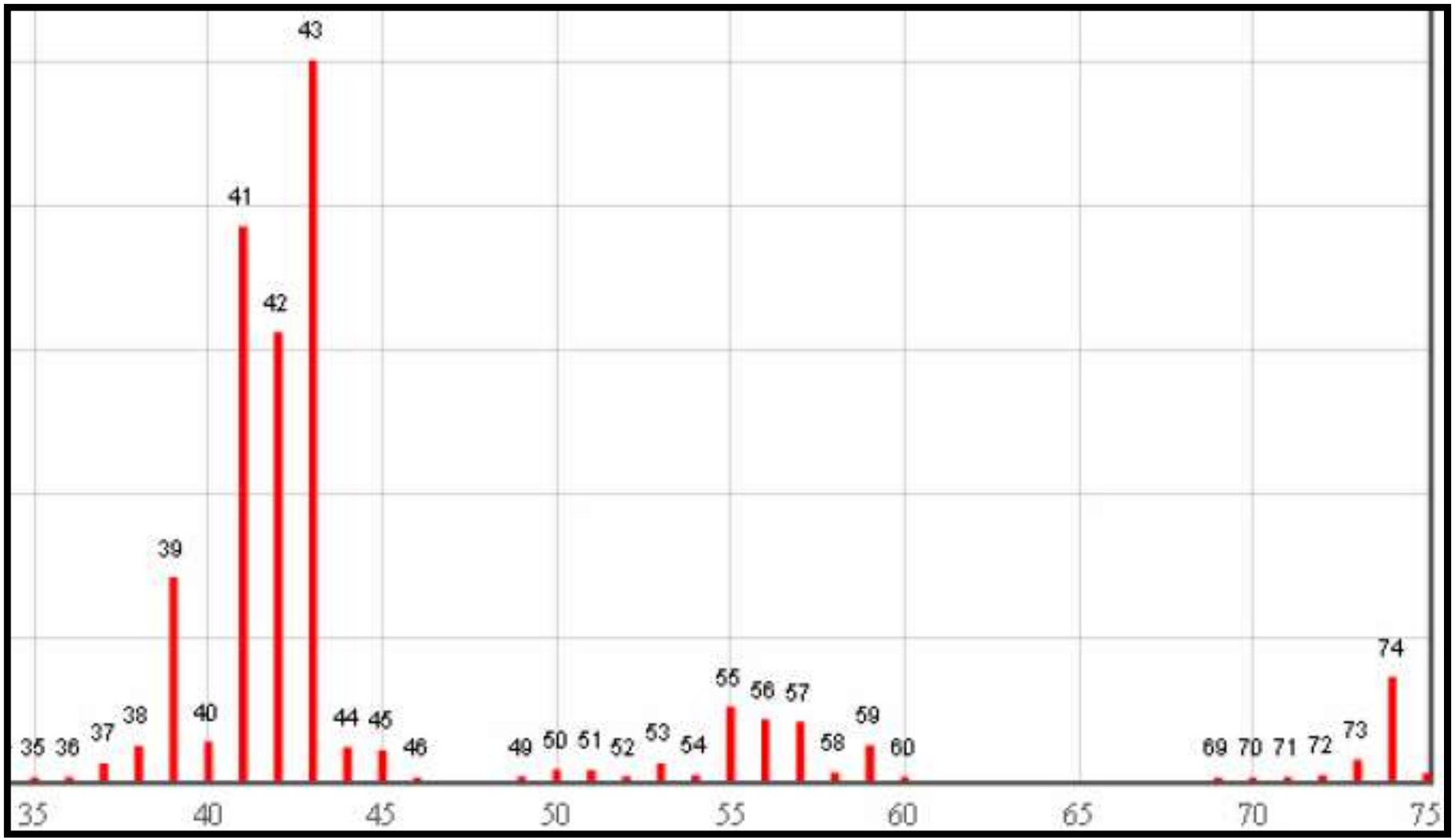




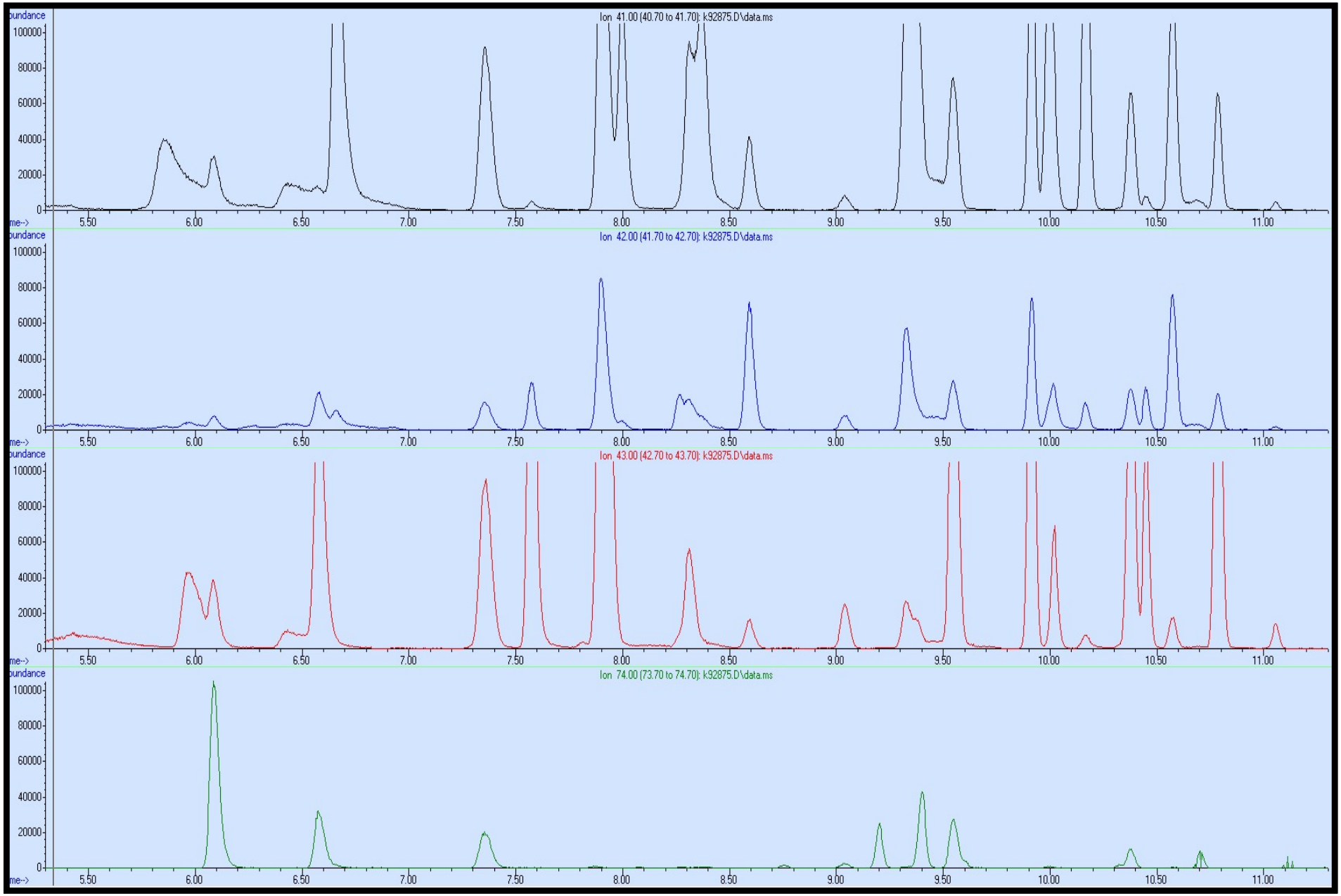




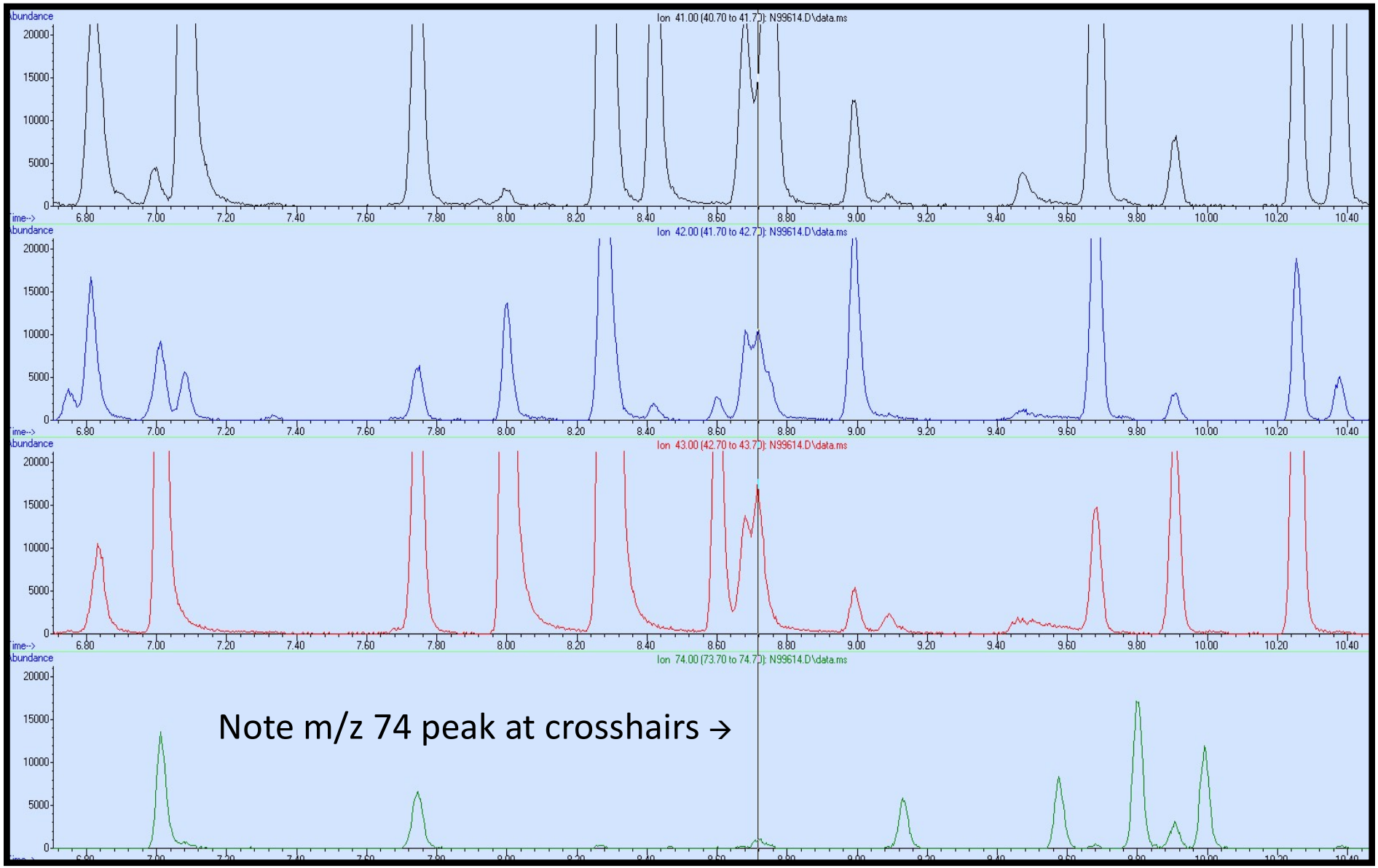
Isobutyl alcohol NIST mass spectrum: m/z 74 most unique ion vs. 41, 42, 43



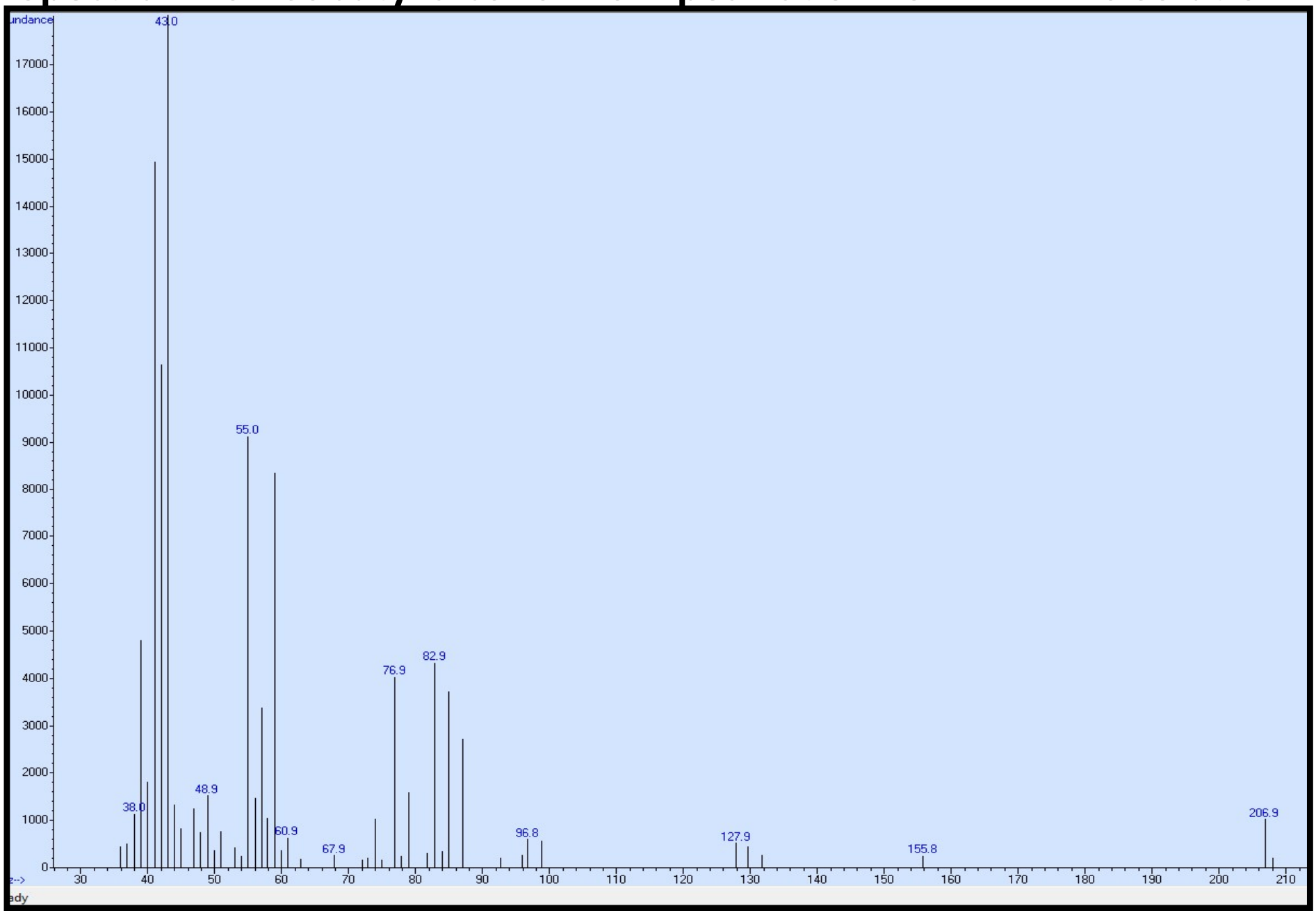
Isobutyl alcohol ions in 400 ppb ICAL: no m/z 74 peaks match NIST spectrum.



On instrument N, isobutyl alcohol is potentially in the BS solution, but not found in CCV. Coelution interference with shoulder peaks for m/z 41, 42, 43.



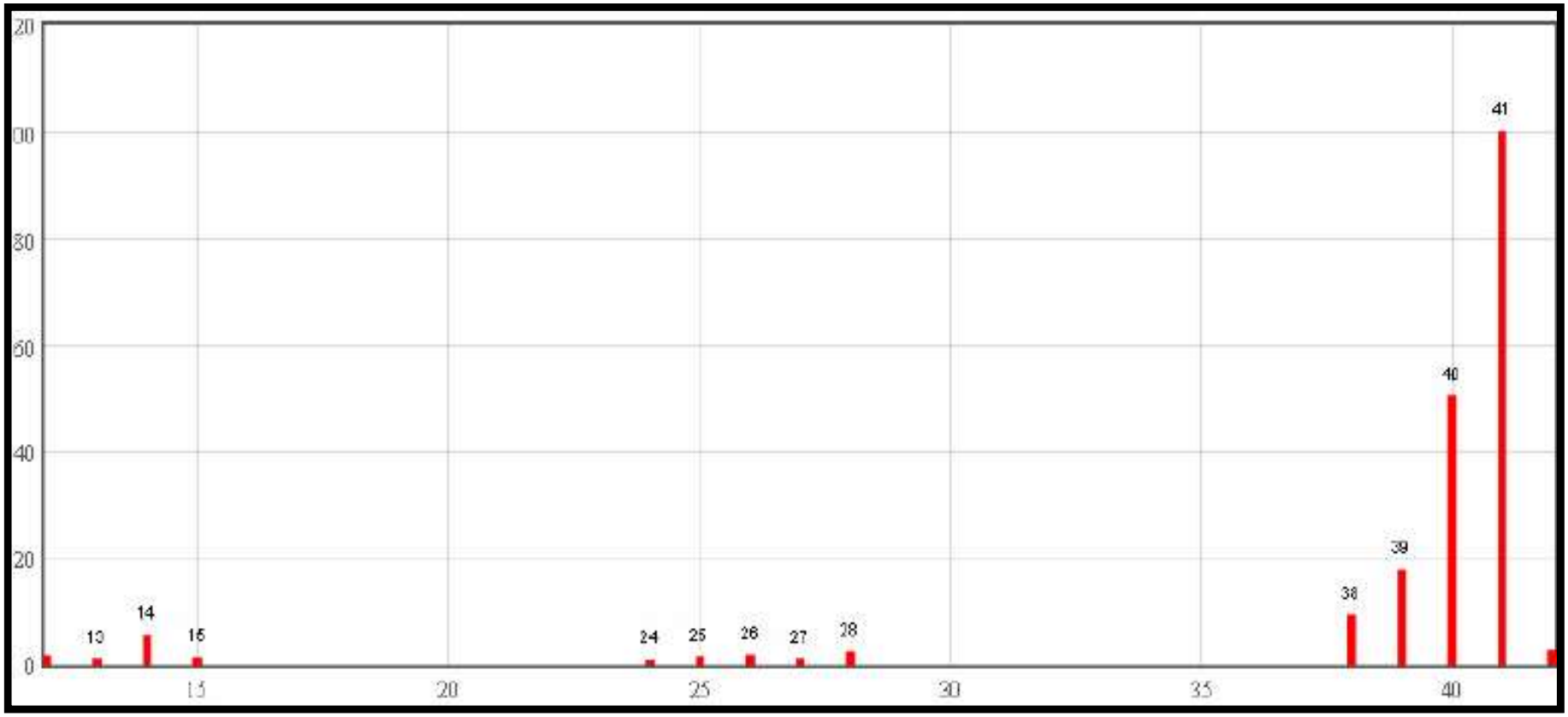
Spectrum for isobutyl alcohol from peak at 8.715 min. in BS solution:



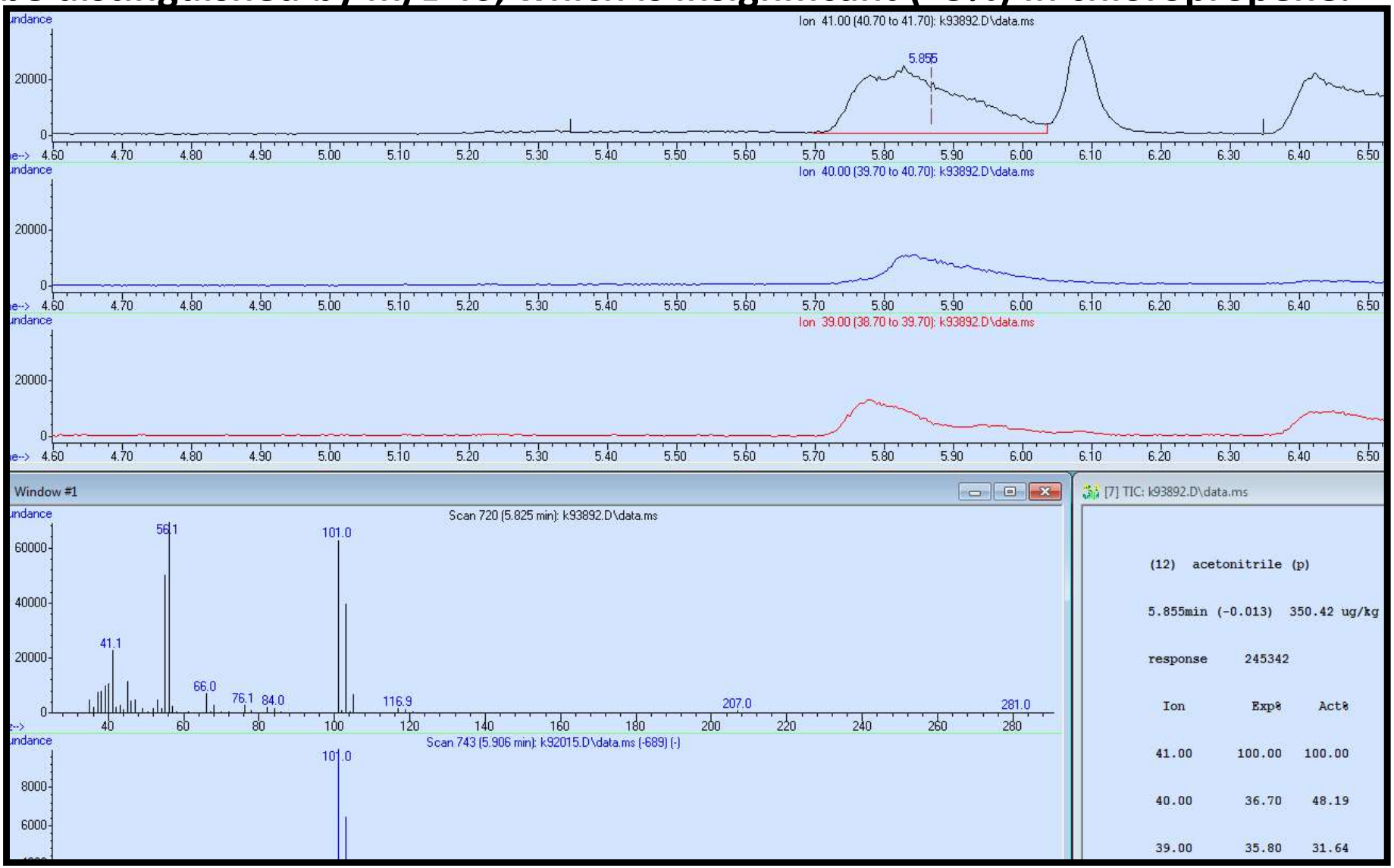
Isobutyl alcohol: Problem Solution

- **Extent of Problem**: Evaluation of QC data involved searching for the correct characteristic ions in standard chromatograms from several instruments. This compound is known to have low purge efficiency and appears to be at too low of a concentration for detection in the presence of common ion interferences. It has not been detected in the current ICAL standard solution and is difficult to resolve in the second source solution.
- **Possible Solutions**: Using current standard mixes, isobutyl alcohol cannot be analyzed as a target compound. False positive calibration hits should be deleted from the ICAL quant reports and the ICAL calibration table. Steps to remedy the problem include: (1) Test a direct injection to demonstrate elution time and presence in current standards; (2) Prepare a single component solution of isobutyl alcohol and purge at a higher concentration; (3) If detection sensitivity is too low, future standard mixtures may require a 100x higher concentration vs. other components; (4) Use a heated purge to increase sensitivity.
- **Changes to Identification Criteria**: Many target compounds share isobutyl alcohol's characteristic ions m/z 41, 42, and 43, so the quantitation ion should be changed to a more selective and unique ion (m/z 74) to avoid future misidentification.

Acetonitrile: NIST mass spectrum displays only 3 readily detectable ions – m/z 39, 40, and 41. Many compounds exhibit 1 or more of these ions.



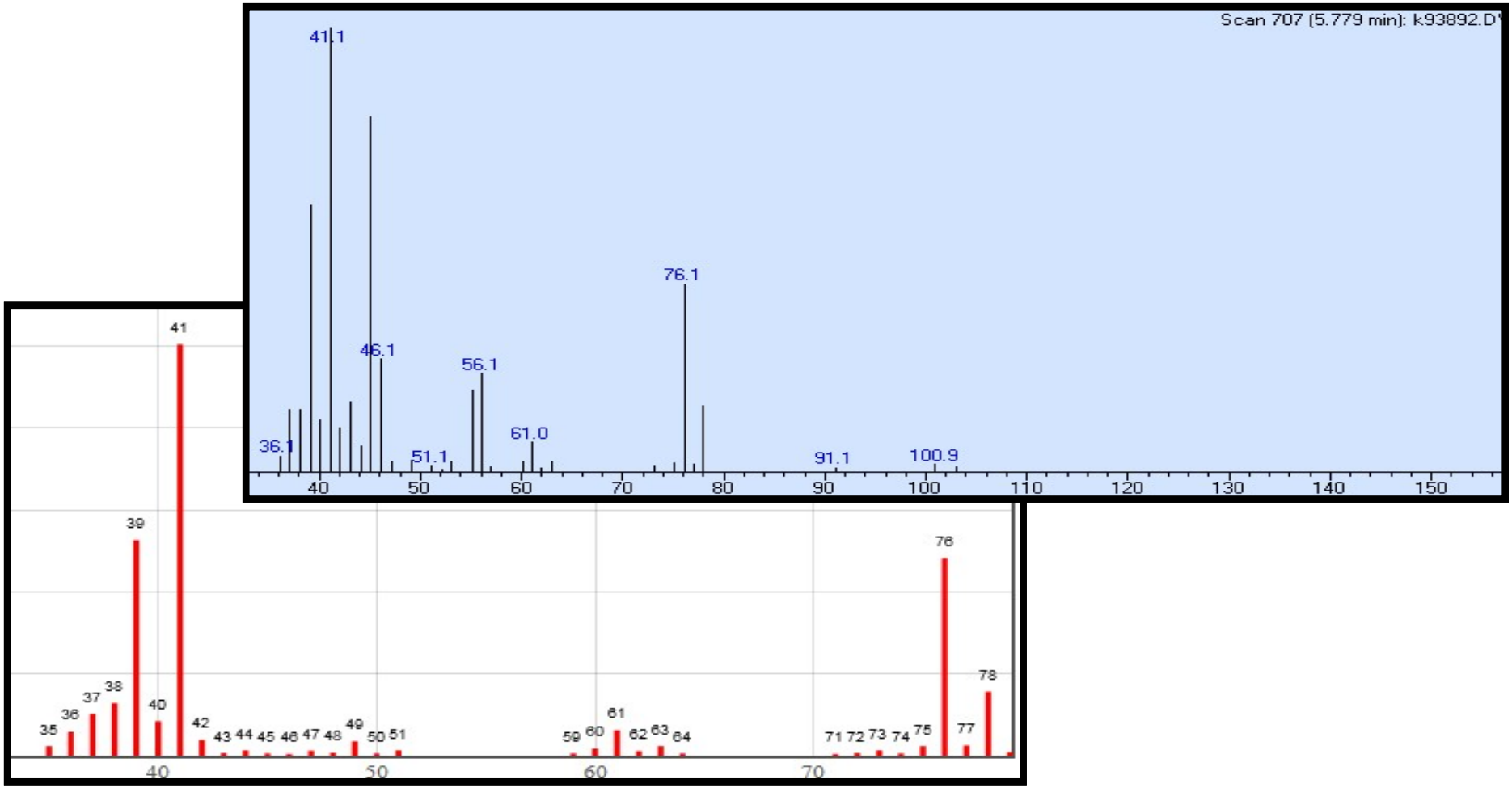
On instrument MSK, acetonitrile elutes at 5.825 min., 0.04 min. after a chloropropene isomer, which has common ions 39 and 41. Acetonitrile can be distinguished by m/z 40, which is insignificant (<5%) in chloropropene.



Acetonitrile spectrum (5.825min) in 400 ppb ICAL on MSK displays three coelutions:

- **Trichlorofluoromethane (m/z 66, 68, 101, 103) (ΔRT = +0.081 min) (m/z 40 is N.D.)**
- **Acrolein (m/z 52, 53, 55, 56) (ΔRT = +0.0 min) (m/z 40 is about 2% of m/z 56)**
- **2-Chloropropene (m/z 39, 41, 61, 76, 78) (ΔRT = -0.046 min) (m/z 40 is 4% of 41)**

First spectral comparison: 2-Chloropropene (5.78 min on MSH) versus NIST spectrum:



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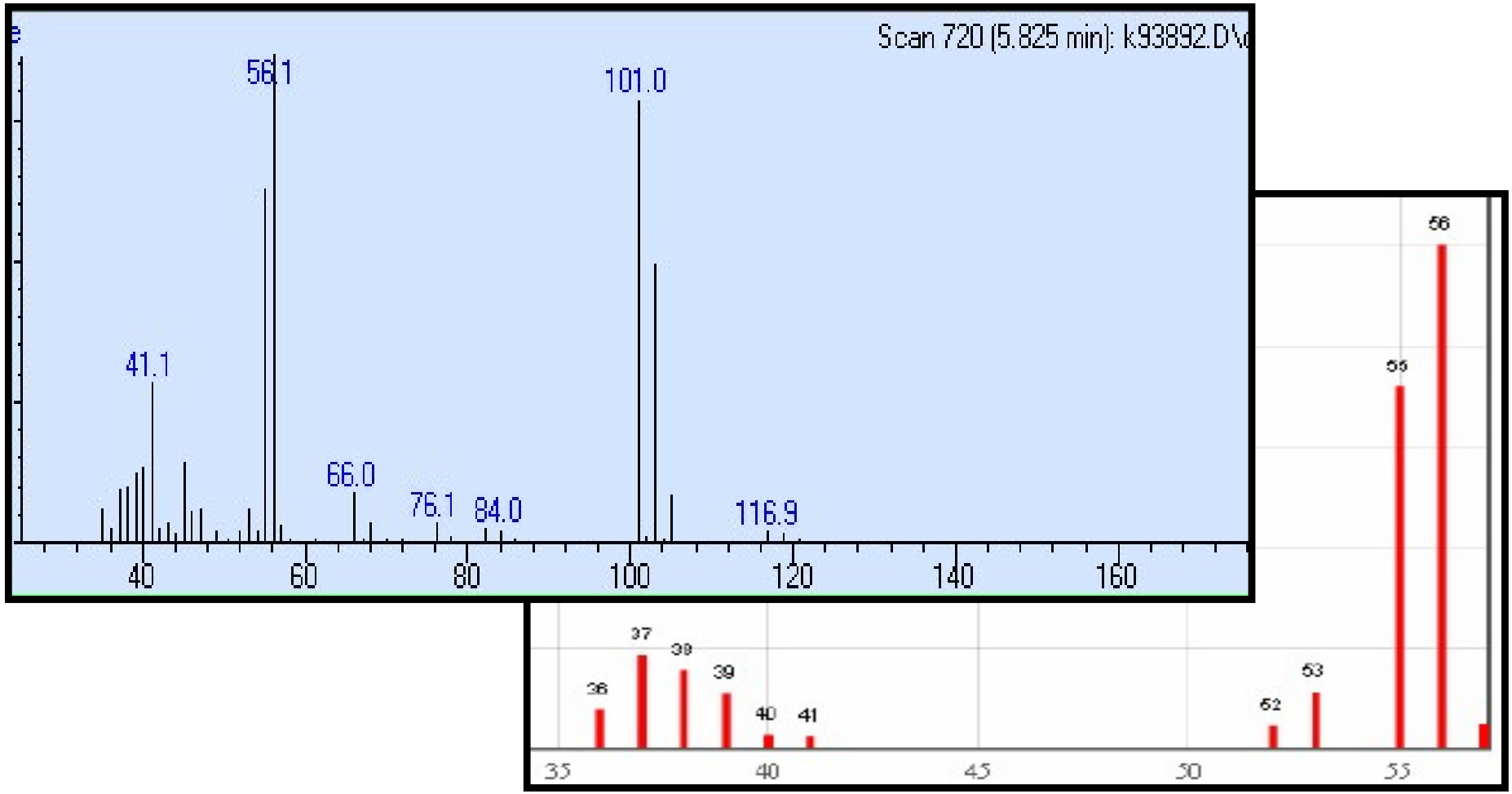
- **Acrolein (m/z 52, 53, 55, 56) (ΔRT = +0.0 min) (m/z 40 is about 2% of m/z 56)**
- **2-Chloropropene (m/z 39, 41, 61, 76, 78) (ΔRT = -0.046 min) (m/z 40 is 4% of 41)**

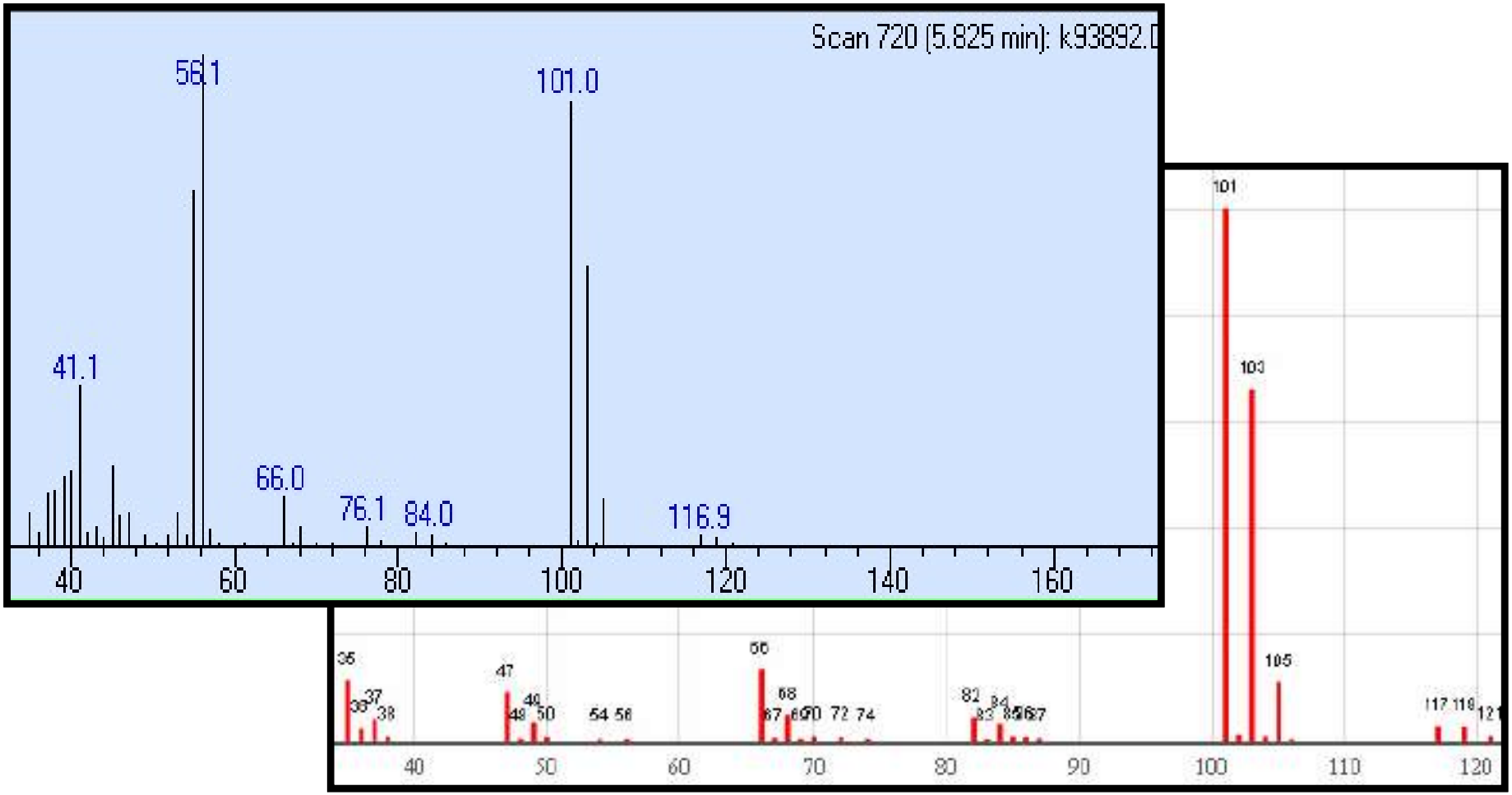
Second spectral comparison: Acrolein (5.825 min on MSK) versus NIST spectrum:



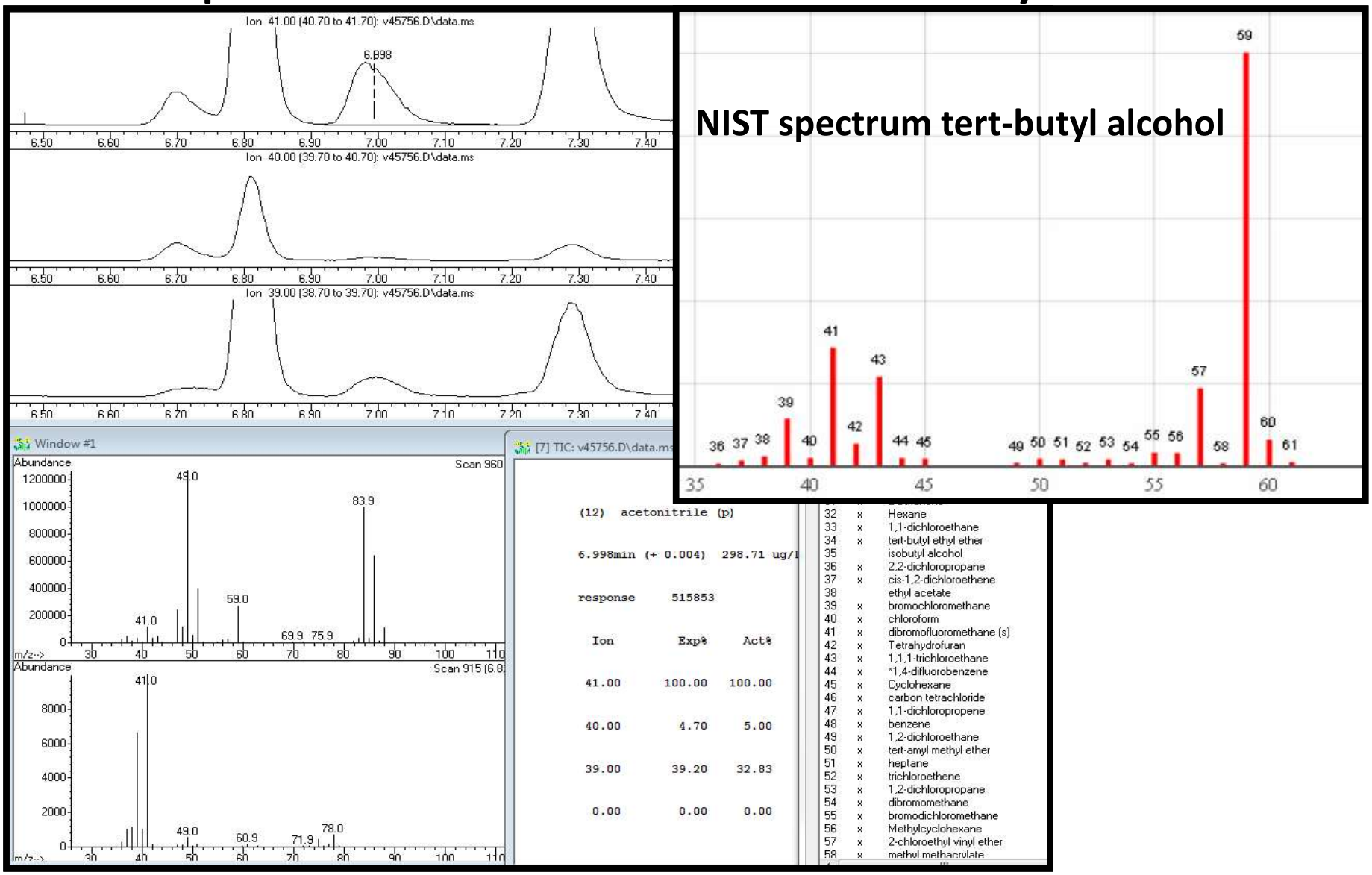
Acetonitrile spectrum (5.825min) in 400 ppb ICAL on MSK displays three coelutions:

- **Trichlorofluoromethane (m/z 66, 68, 101, 103) (ΔRT = +0.081 min) (m/z 40 is N.D.)**
- **Acrolein (m/z 52, 53, 55, 56) (ΔRT = +0.0 min) (m/z 40 is about 2% of m/z 56)**
- **2-Chloropropene (m/z 39, 41, 61, 76, 78) (ΔRT = -0.046 min) (m/z 40 is 4% of 41)**

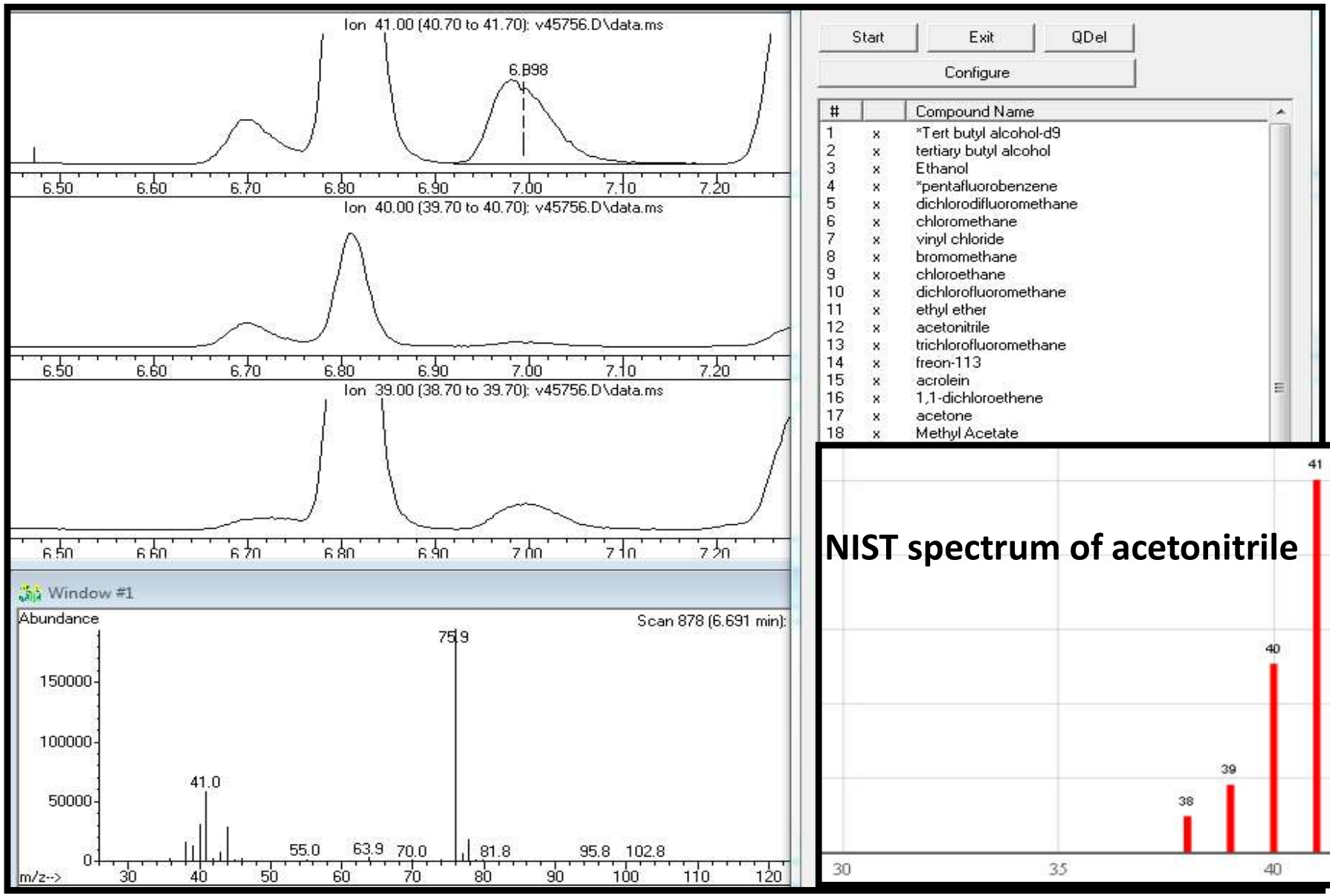
Third spectral comparison: Trichlorofluoromethane (5.906 min on MSK) versus NIST:



On instrument V, acetonitrile was misidentified in ICAL. The mass 41 quant. ion peak at retention time of 6.98 minutes is tertiary butyl alcohol. Spectrum also shows coelution with methylene chloride.



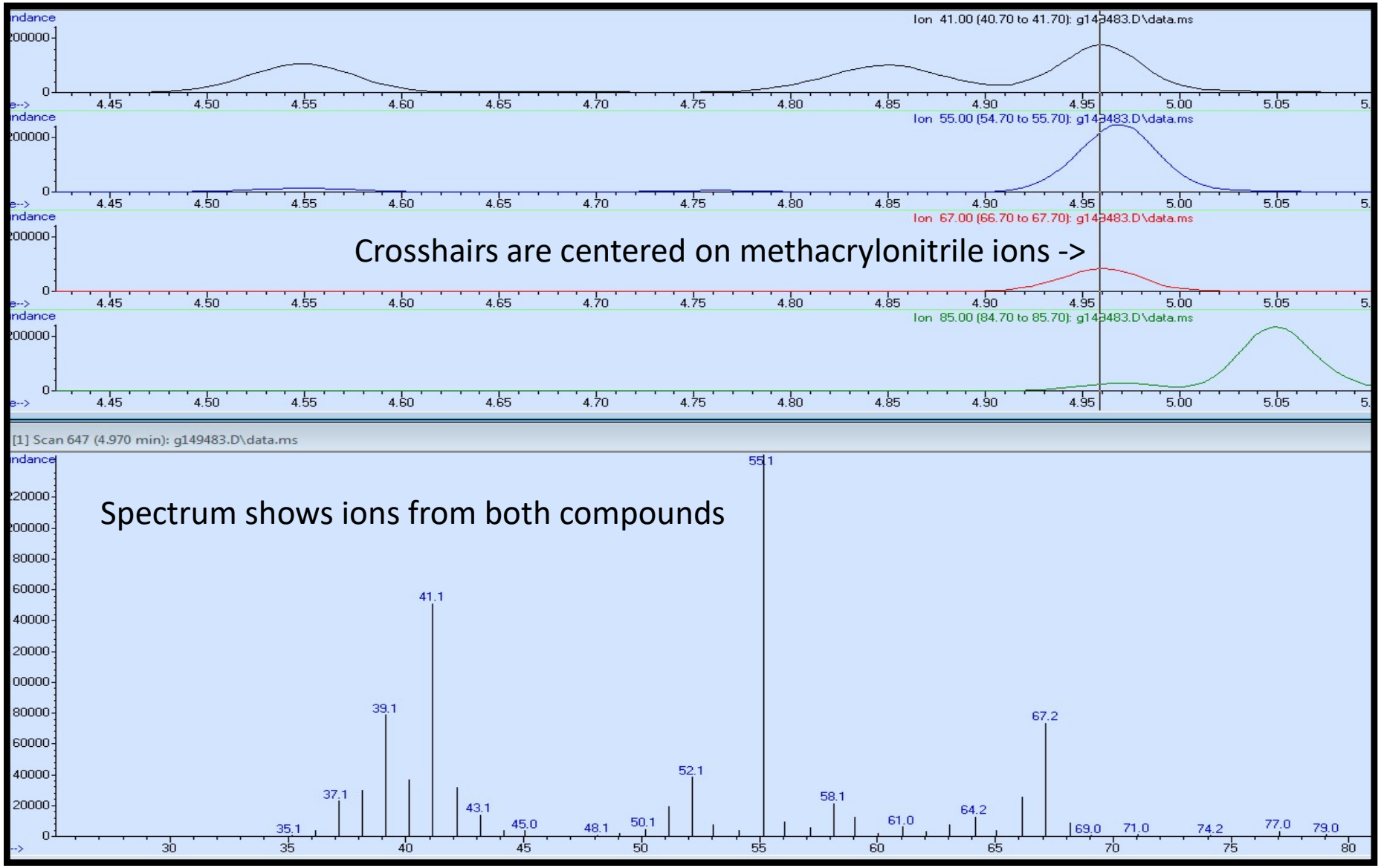
In 400 ppb ICAL on instrument V, acetonitrile elutes at retention time 6.691 minutes. Coelutes with carbon disulfide, but no shared ions.



Acetonitrile: Problem Solution

- **Extent of Problem**: This compound was noted as misidentified on multiple instruments. It is present in both primary calibration standards and second source solutions.
- **Problem Solution**: Acetonitrile elutes very close to the retention time for three compounds and has very few ions. M/z 40 is the only ion that can always be distinguished from coeluting compounds, so this ion must always be present and should have an appropriate ratio relative to ions 39 and 41.
- **Changes to Identification Criteria**: The quantitation ion for acetonitrile should be changed to m/z 40 to prevent bias from coeluting compounds. Since m/z 39 and m/z 41 are obscured by coelutions, using a cooler initial temperature and slower ramp may improve separation and mass spectrum quality.

Methyacrylonitrile (ions 39, 40, 41, 51, 52 66, 67): On MSG, the proper peak at 4.97 min. shows extraneous ions (55, 58, 85) from methyl acrylate, a coeluting nontarget present in the calibration mix and with ΔRT = +0.01 min. All key ions are different.

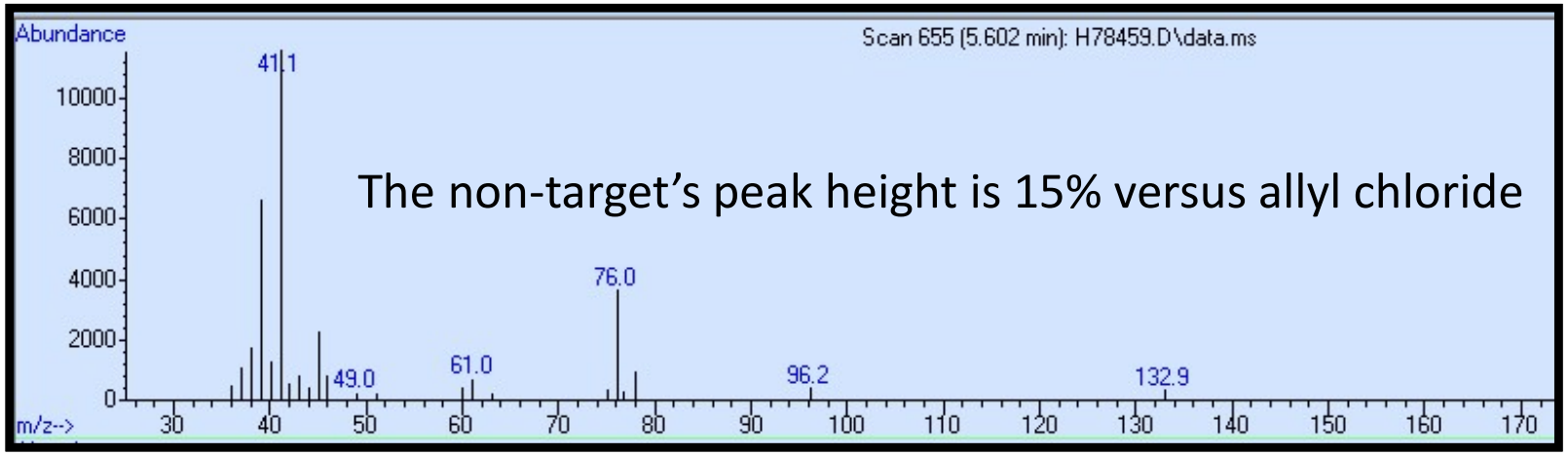


Methacrylonitrile: Problem Solution

- **Extent of Problem**: This compound was noted as coeluting with a nontarget compound found in calibration standards.
- **Problem Solution**: Analysts should be aware that the extraneous ions should not be included as characteristic ions in the calibration table. This compound could be requested to be omitted when ordering new calibration solutions.
- **Changes to Identification Criteria**: No changes are required.

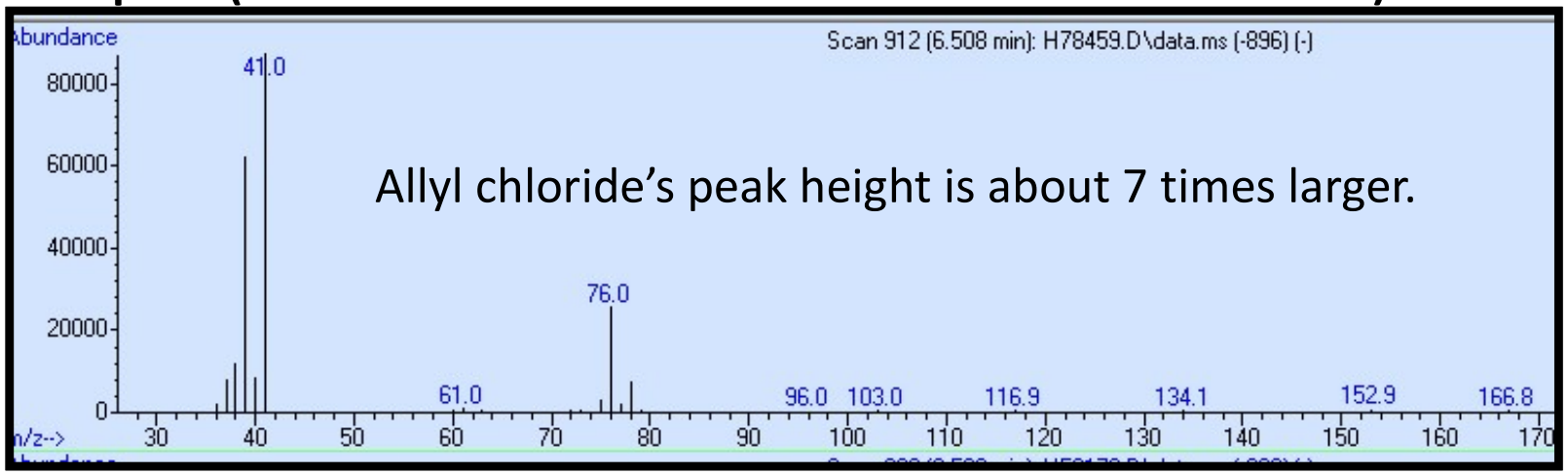
2-chloropropene, a non-target isomer of allyl chloride, has a similar mass spectrum and is present in calibration solutions. Elution time is 0.9 min earlier. Instruments are calibrated to the correct peak for allyl chloride.

First peak (5.602 minutes on instrument H – elutes near acetonitrile and acrolein):



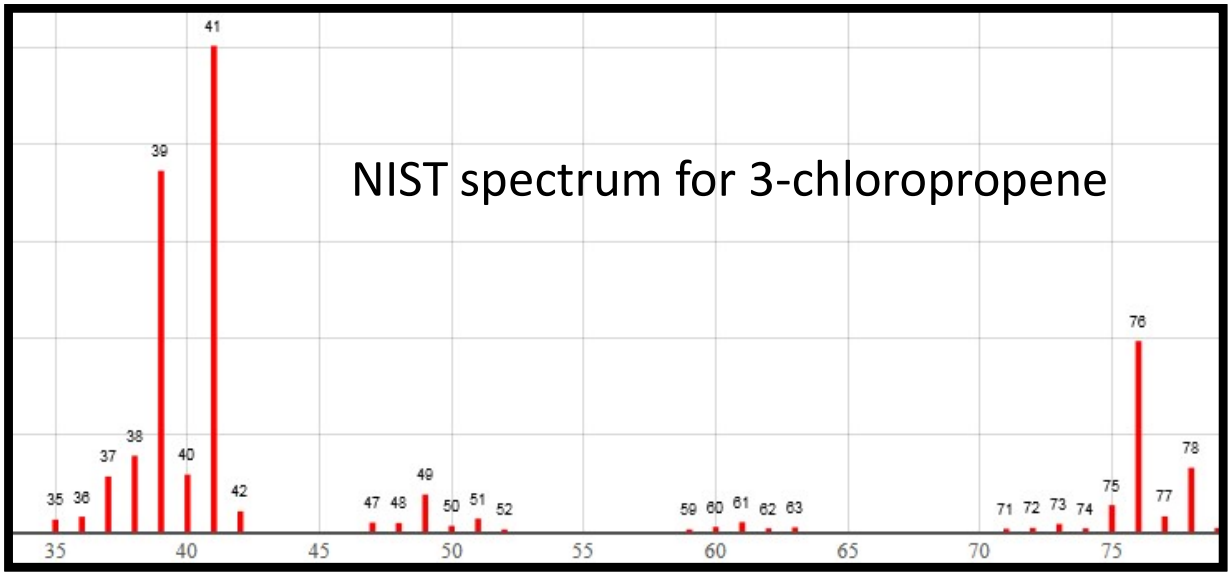
The non-target's peak height is 15% versus allyl chloride

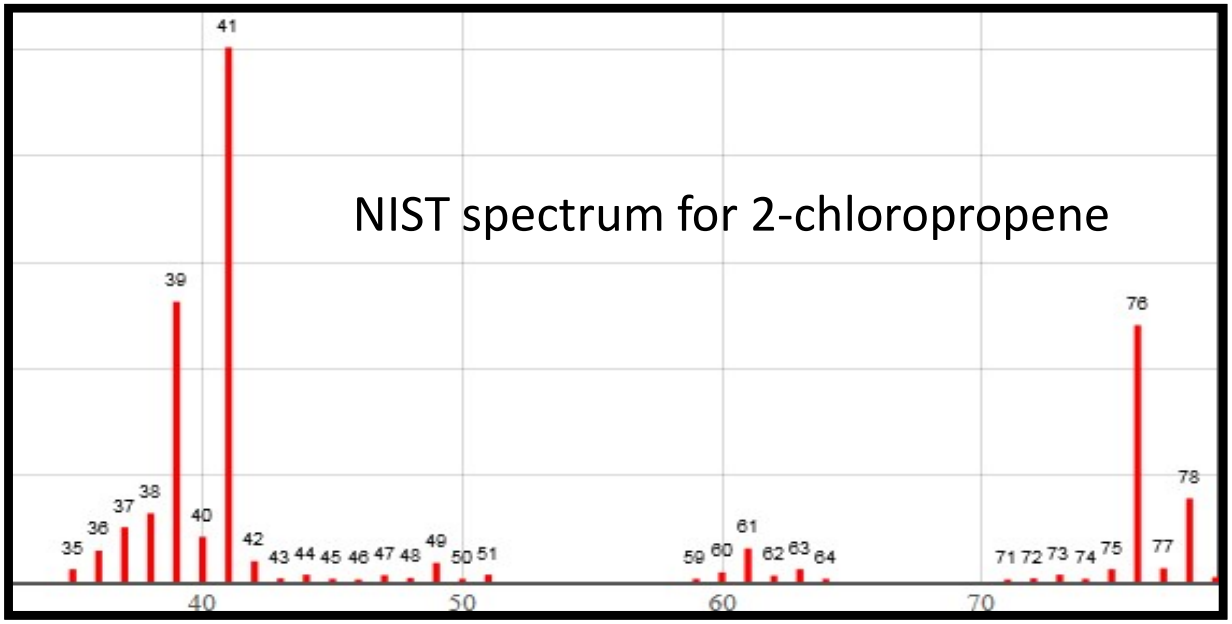
Second peak (6.508 minutes on instrument - elutes near Freon 113):

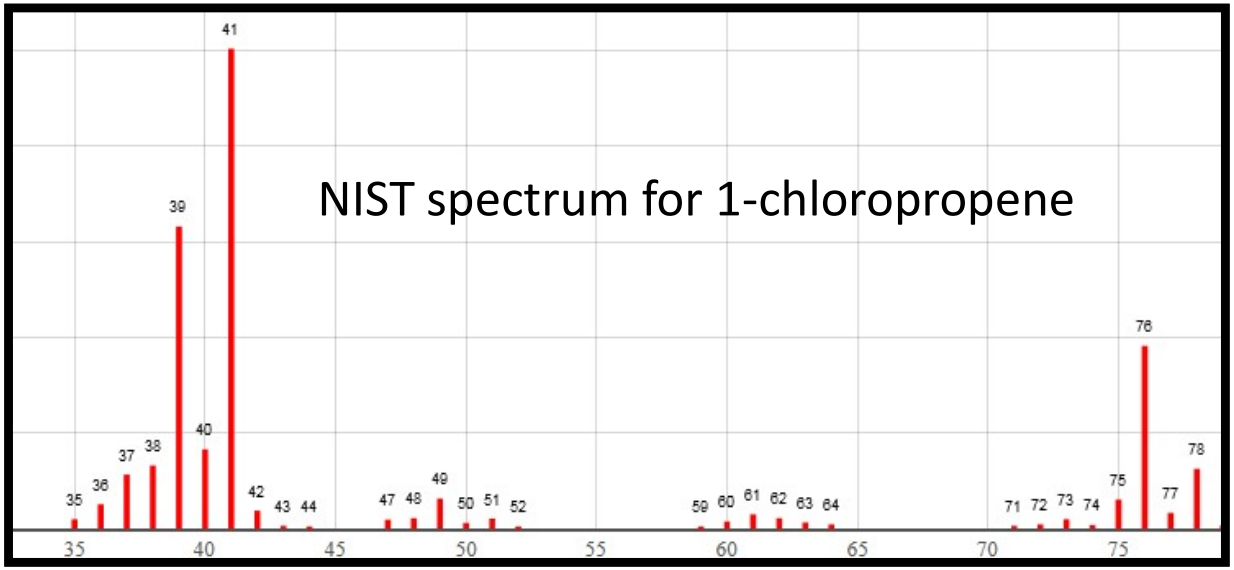


Allyl chloride's peak height is about 7 times larger.

Allyl chloride is a synonym for 3-chloropropene. Chloropropene isomer spectra:







Allyl chloride and 1-chloropropene have nearly indistinguishable spectra, while 2-chloropropene has different relative ion ratios for m/z 39:41, and for m/z 61:41.

Relative to the base peak m/z 41, 2-chloropropene has a larger m/z 61 (6% versus 2% or 3% in allyl chloride), and also a smaller m/z 39 (53% vs. 73% in allyl chloride).

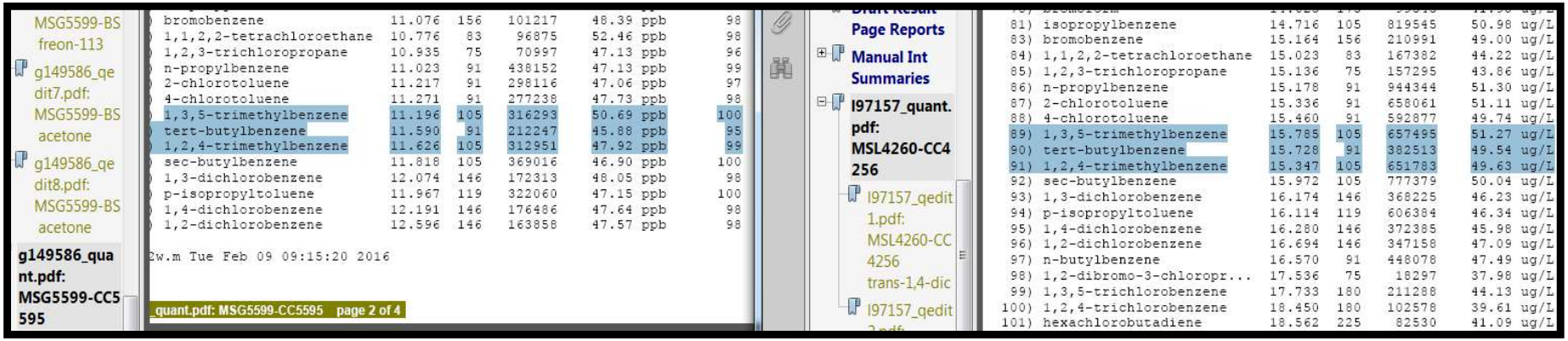
On instrument H, the calibration peak at retention time 6.508 minutes has a spectrum consistent with the NIST spectrum for allyl chloride.

The earlier-eluting peak at 5.602 minutes more closely matches the NIST spectrum for 2-chloropropene.

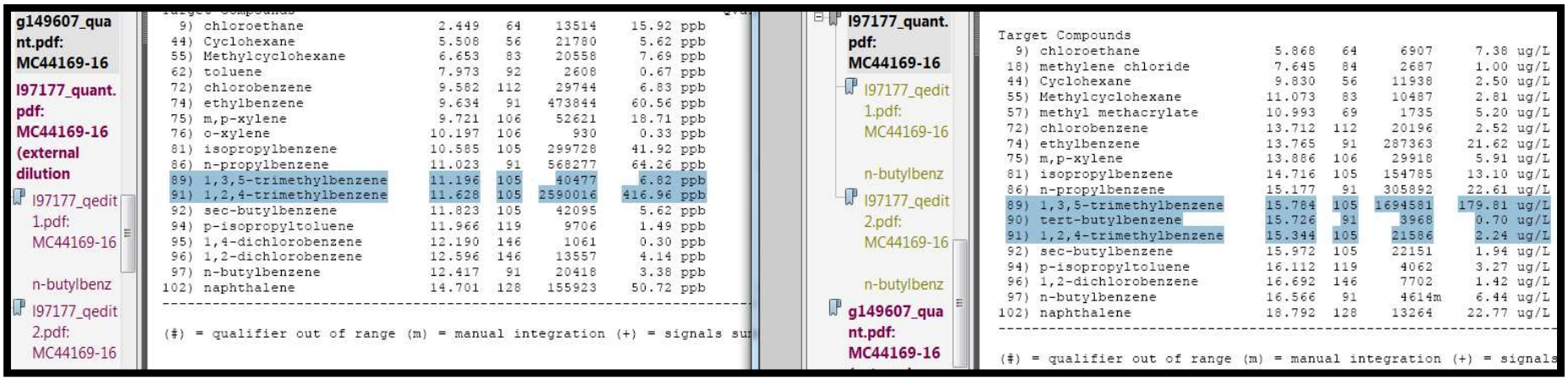
The later-eluting peak also has a much larger base peak intensity (85,000 counts). This is consistent with the first peak representing an impurity, which displayed only 11,000 counts.

1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene retention times were switched in instrument L's calibration table. This was noted when a sample was rerun on another instrument, yielding reversed isomer concentrations.

Opposite elution order reported in continuing calibration runs on instruments G and L:

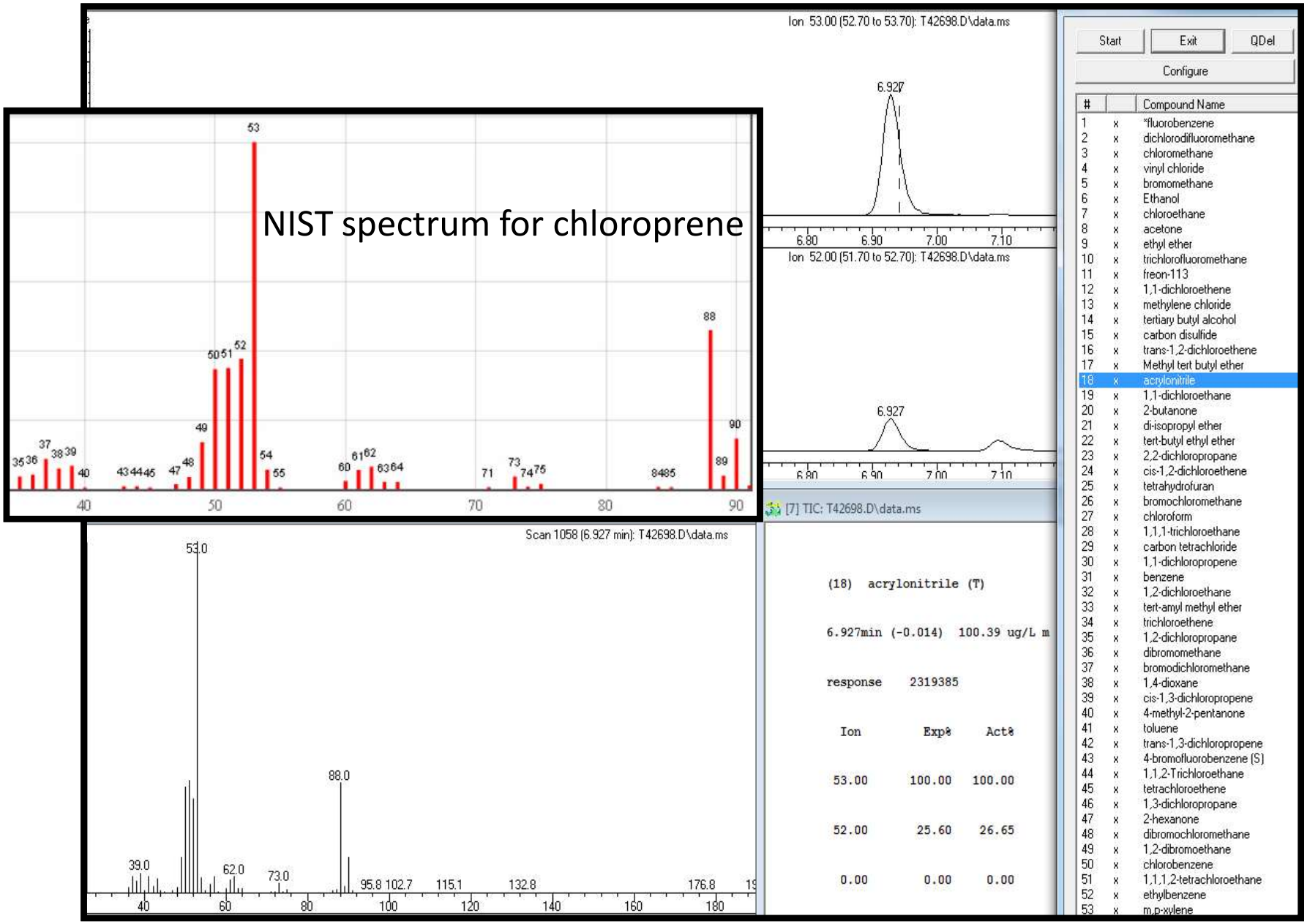


Reversed isomer concentrations reported in MC44169-16 with instruments G and L:

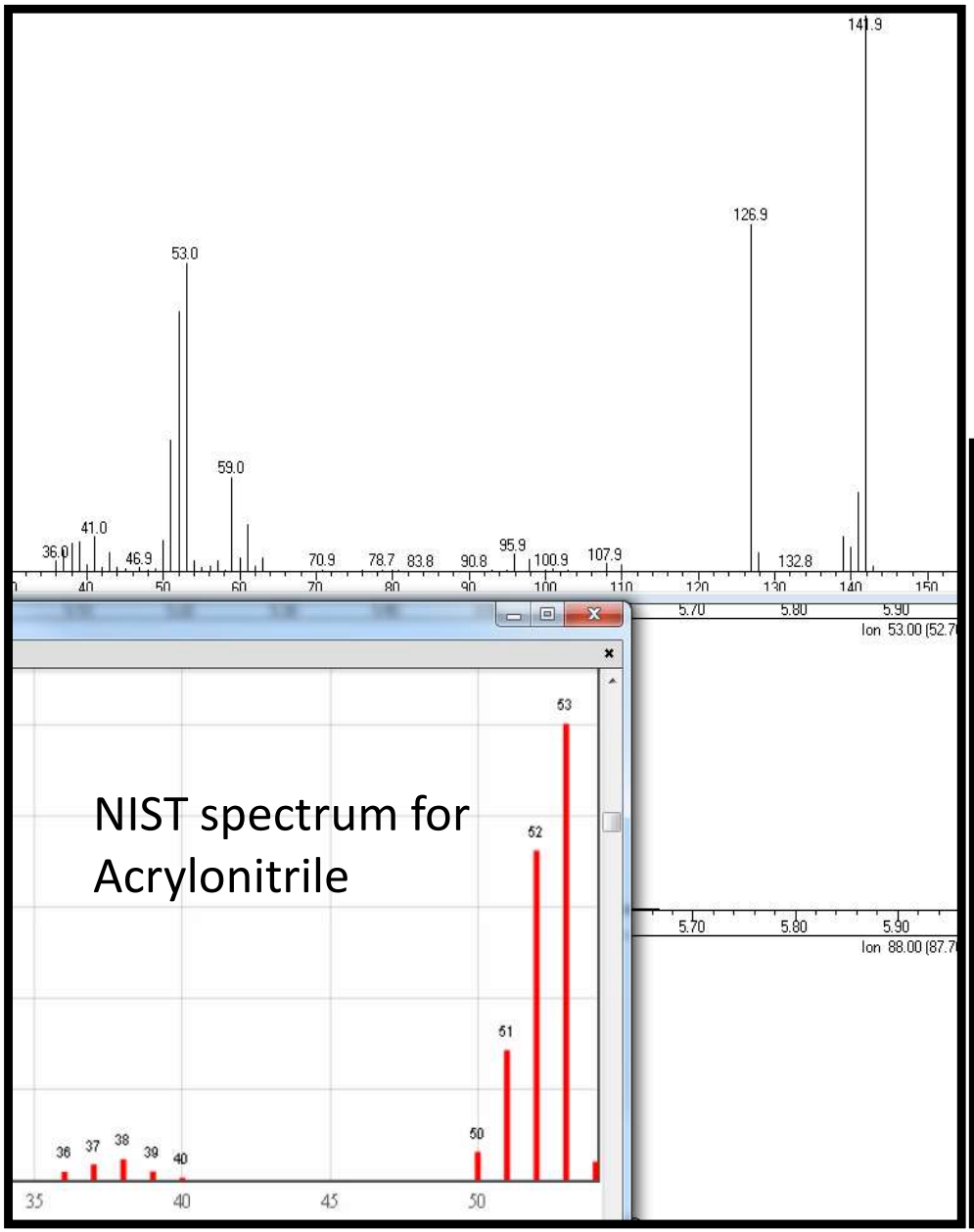


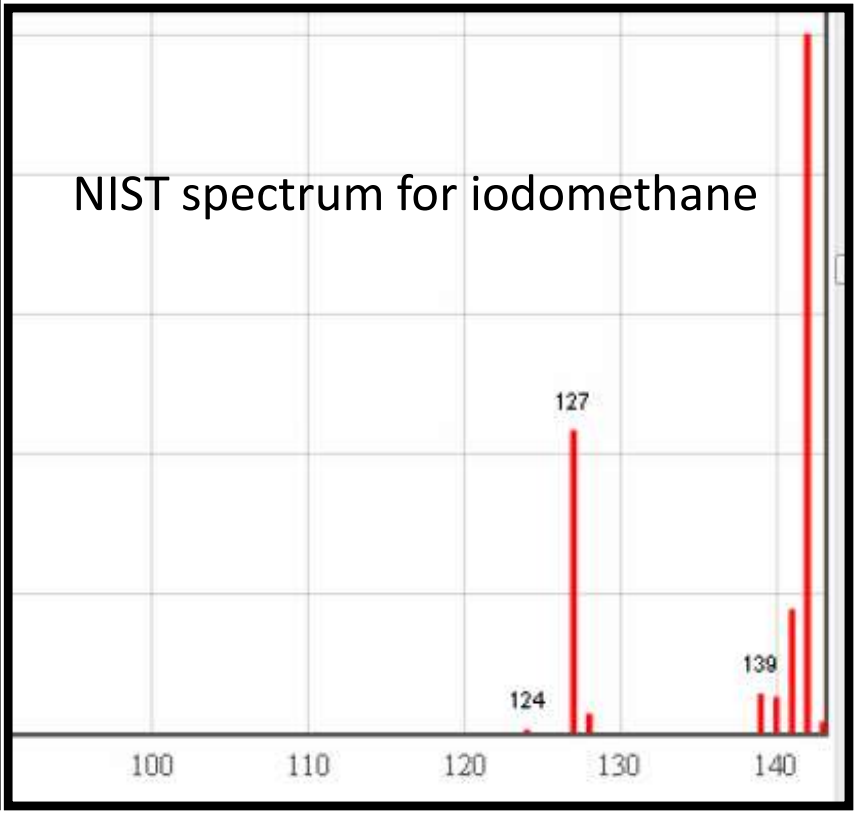
<u>1,2,4-Trimethylbenzene and 1,3,5-trimethylbenzene problem solution</u>:
Instrument L recently had a new GC column installed and retention times of all target compounds had to be re-established. When assigning retention times for the first time on a new GC column, check that the relative elution order of target compound isomers are consistent with calibration data for other instruments that employ the same or a very similar GC column.

Acrylonitrile misidentified in ICAL 80 ppb standard on instrument MST. Peak at 6.93 min. is chloroprene.



On instrument T, acrylonitrile elutes at 5.55 minutes and coelutes with iodomethane.



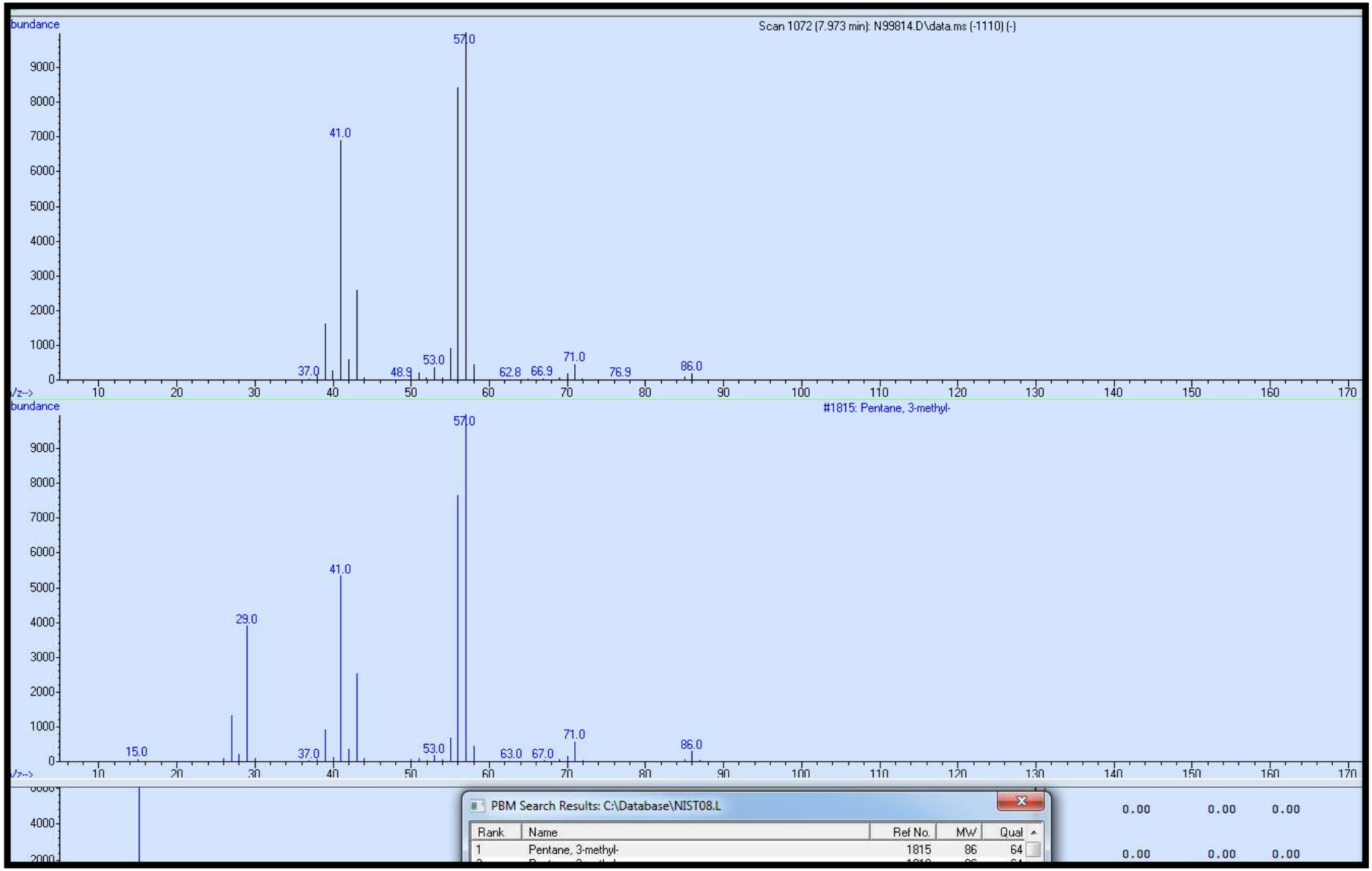


<u>Acrylonitrile problem solution</u>: This compound has a simple spectrum with only 3 major ions. All ions should be verified present and in the proper ratios, and any extraneous ions should be accounted for.

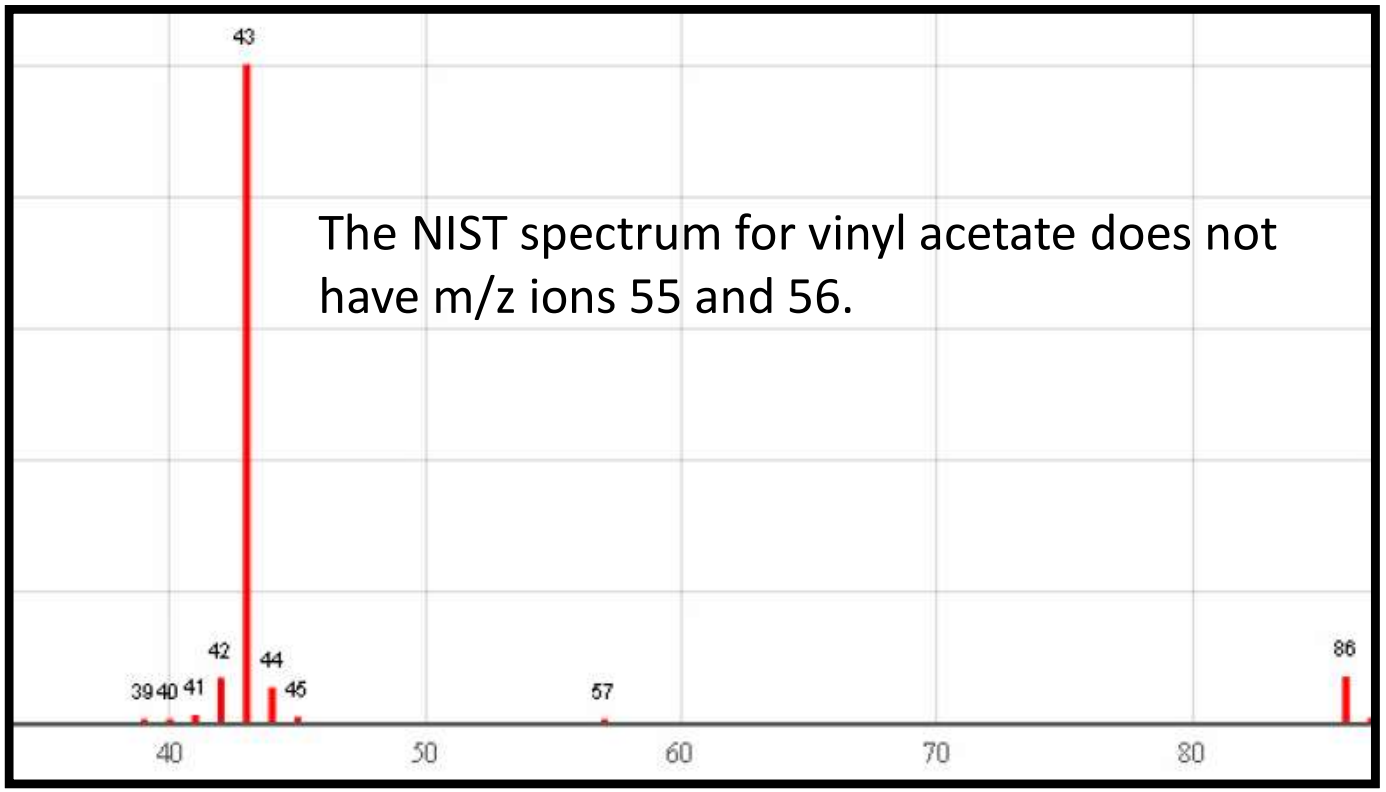
- **Part 2: Recent examples of target compound misidentification in sample analysis:**

- If peaks in reference spectrum are missing in the sample, examine the mass spectrum of the same target compound in the NIST library (use the shortcut link to the VOC NIST spectra PDF file)
- If extraneous peaks are in the sample, do a forward library search of the NIST library to see if spectrum represents a different compound
- Check that peak apexes line up for characteristic ion chromatograms due to the possibility of a partial coelution of two compounds
- Verify that sample retention times are correct (delta RT) since isomer identity could be mistaken
- For chlorinated and brominated target compounds, verify the sample contains the proper isotopic abundance patterns

<u>Vinyl acetate</u>: False positive sample hit closely matches an isomer of 3-methyl pentane, based on NIST library search results shown below.

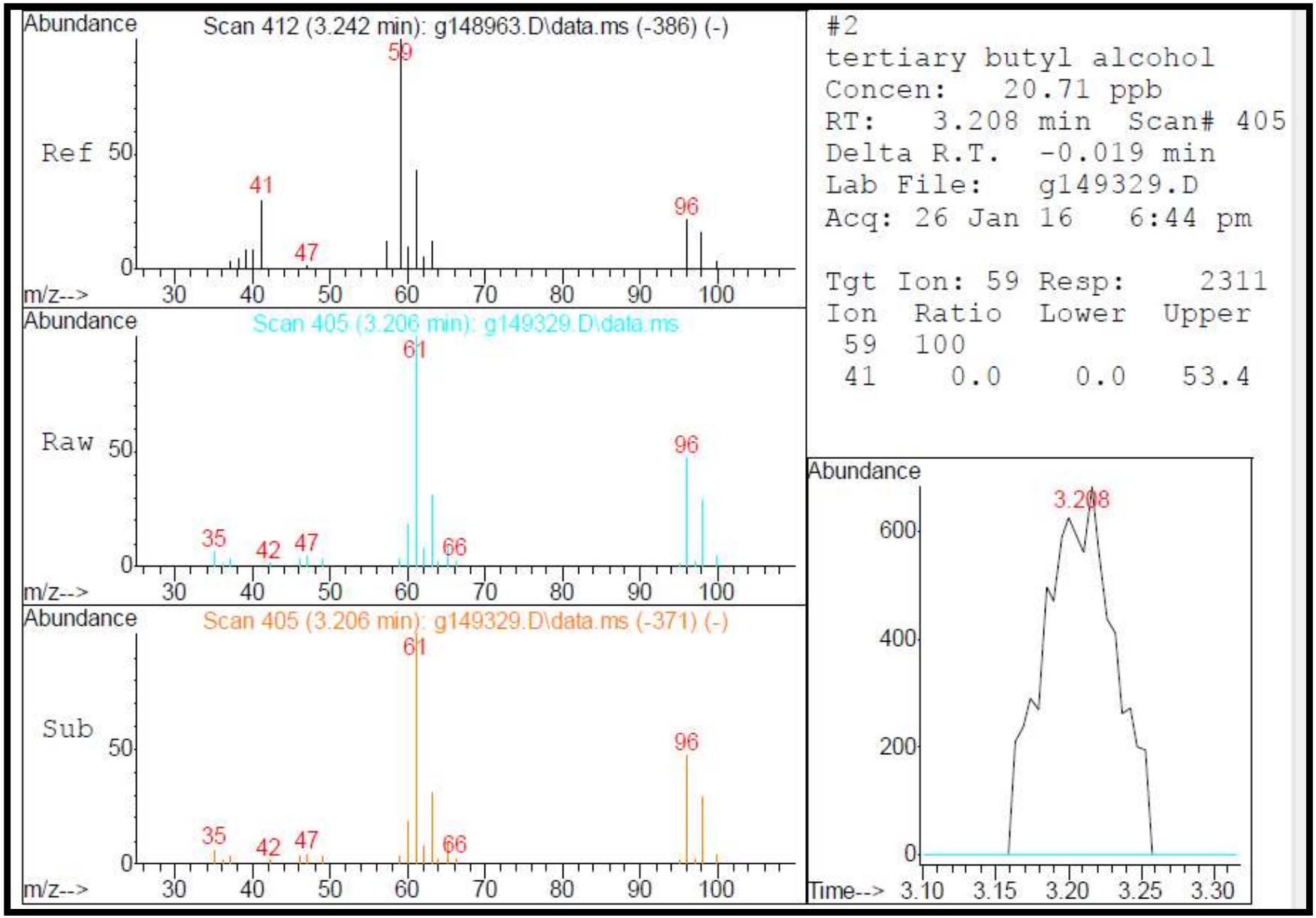


<u>Problem solution</u>: When checking vinyl acetate sample hits in QEdit, look for extraneous ions (m/z 55 and 56). This particular hydrocarbon has been misidentified as vinyl acetate in several samples run on various instruments. If unsure of an identification of a target compound, do a NIST library search.



The NIST spectrum for vinyl acetate does not have m/z ions 55 and 56.

Tertiary Butyl Alcohol: A false positive result was reported in a sample due to a coelution with 1,1-dichloroethene, which displays a minor ion m/z 59.

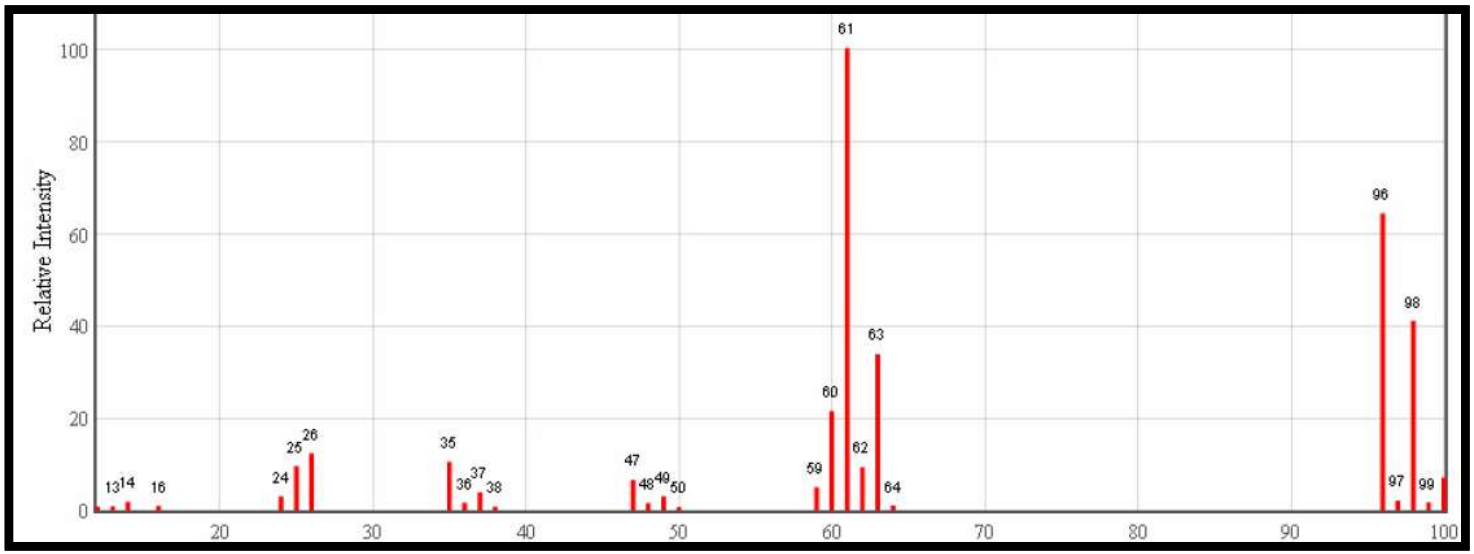


#2
tertiary butyl alcohol
Concen: 20.71 ppb
RT: 3.208 min Scan# 405
Delta R.T. -0.019 min
Lab File: g149329.D
Acq: 26 Jan 16 6:44 pm

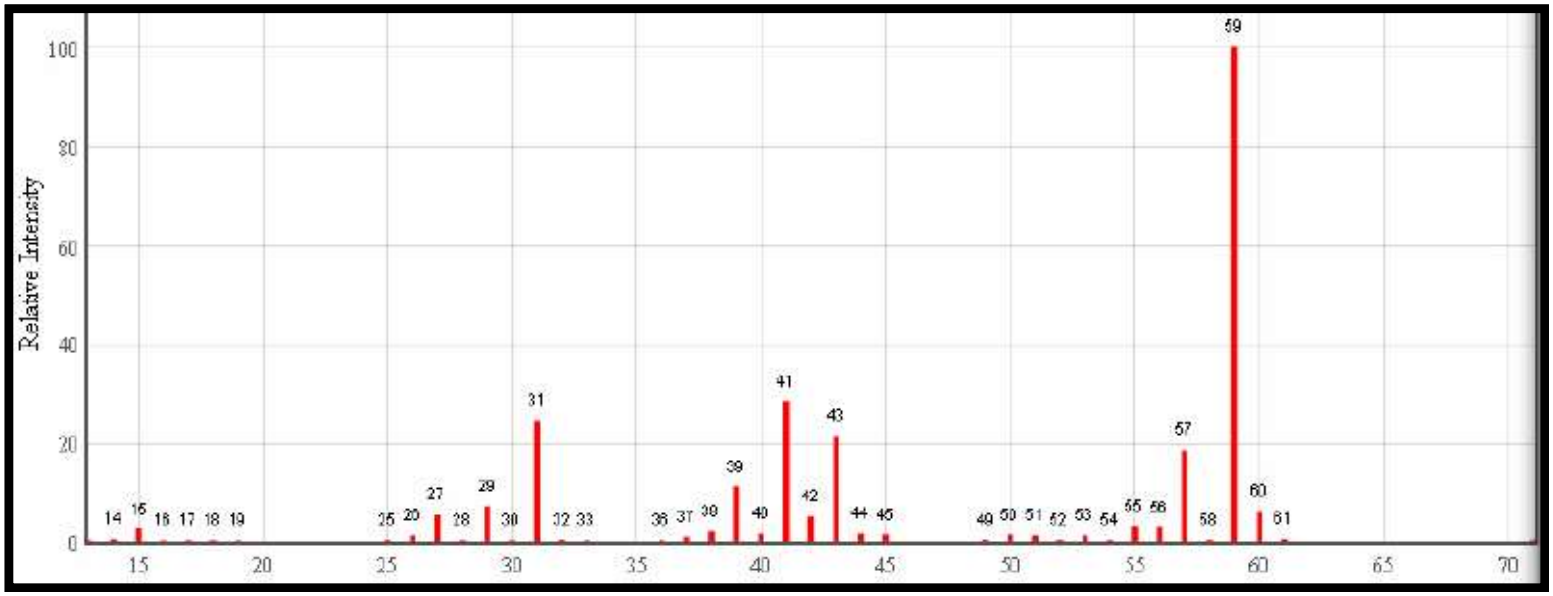
Tgt Ion: 59 Resp: 2311

Ion	Ratio	Lower	Upper
59	100		
41	0.0	0.0	53.4

NIST spectrum for 1,1-dichloroethene (note minor m/z ion 59):



NIST spectrum for tertiary butyl alcohol (note base peak m/z ion 59):

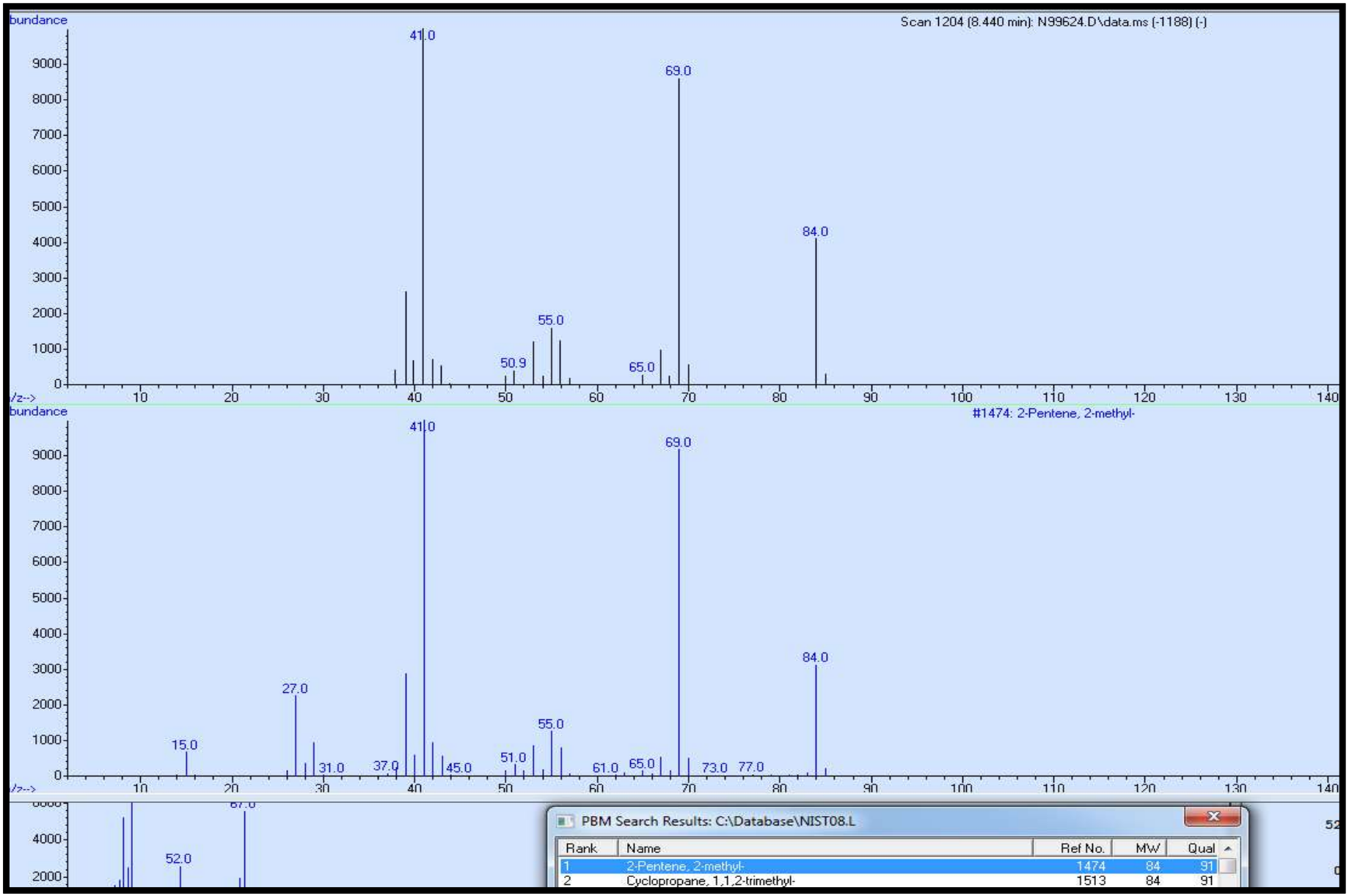


Problem solution: When checking sample spectra for candidate target compound hits using QEdit, be on the lookout for reference mass spectra that contain coelutions. A casual look at the reference spectrum might suggest that tertiary butyl alcohol was matched due to the presence of m/z ions 61, 63, 96, and 98. However, since 1,1-dichloroethene coelutes with tertiary butyl alcohol, the reference spectrum contains both components.

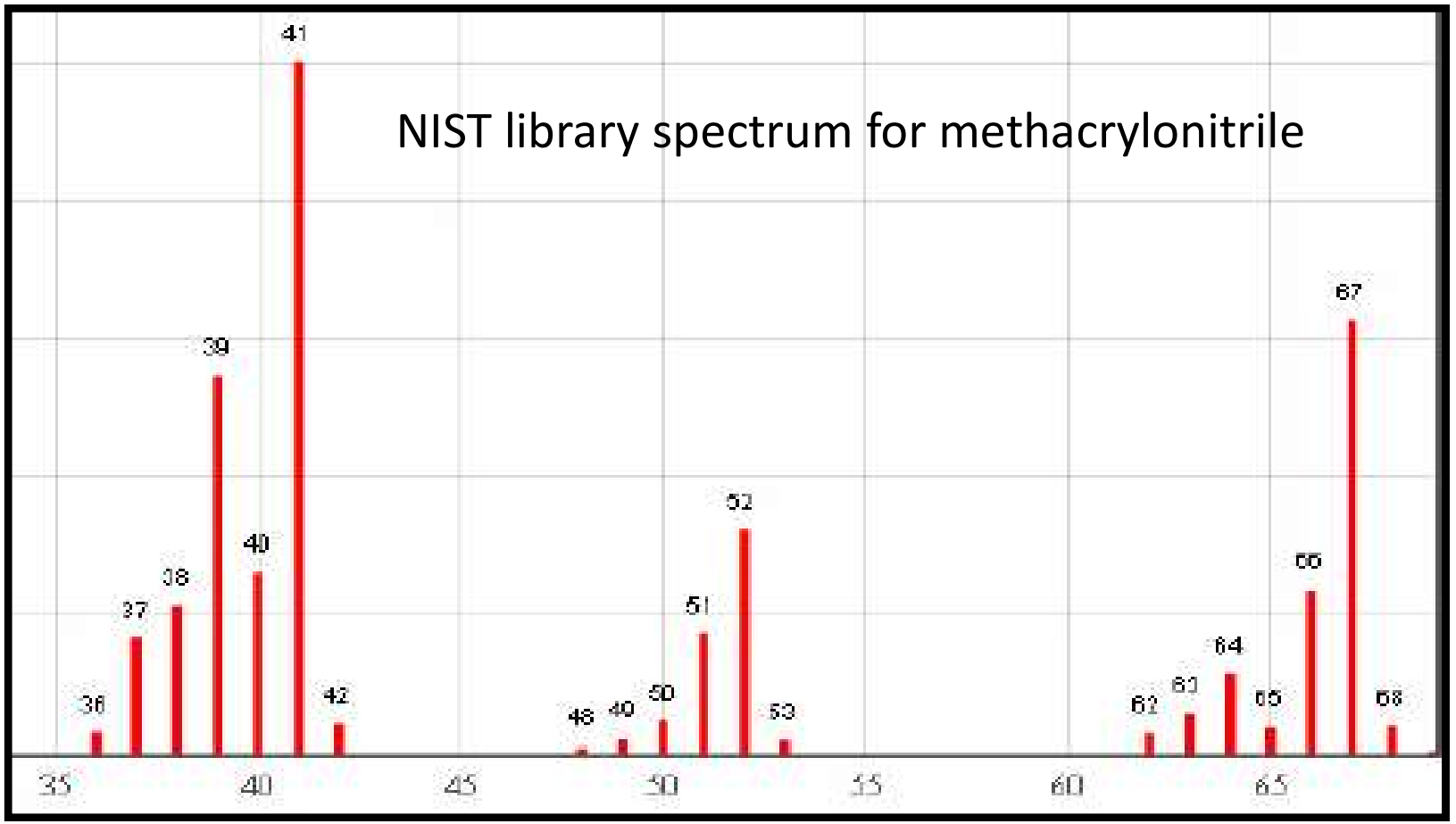
Identification of tertiary butyl alcohol should be based on only m/z ions 41 and 59. The key ions for a target compound should be displayed in the characteristic ion ratio summary shown in QEdit.

Whenever in doubt regarding the proper characteristic ions, a desktop shortcut link can be used to open a PDF file in the public directory that contains the NIST mass spectra for all volatile target compounds, listed and indexed in approximate elution order.

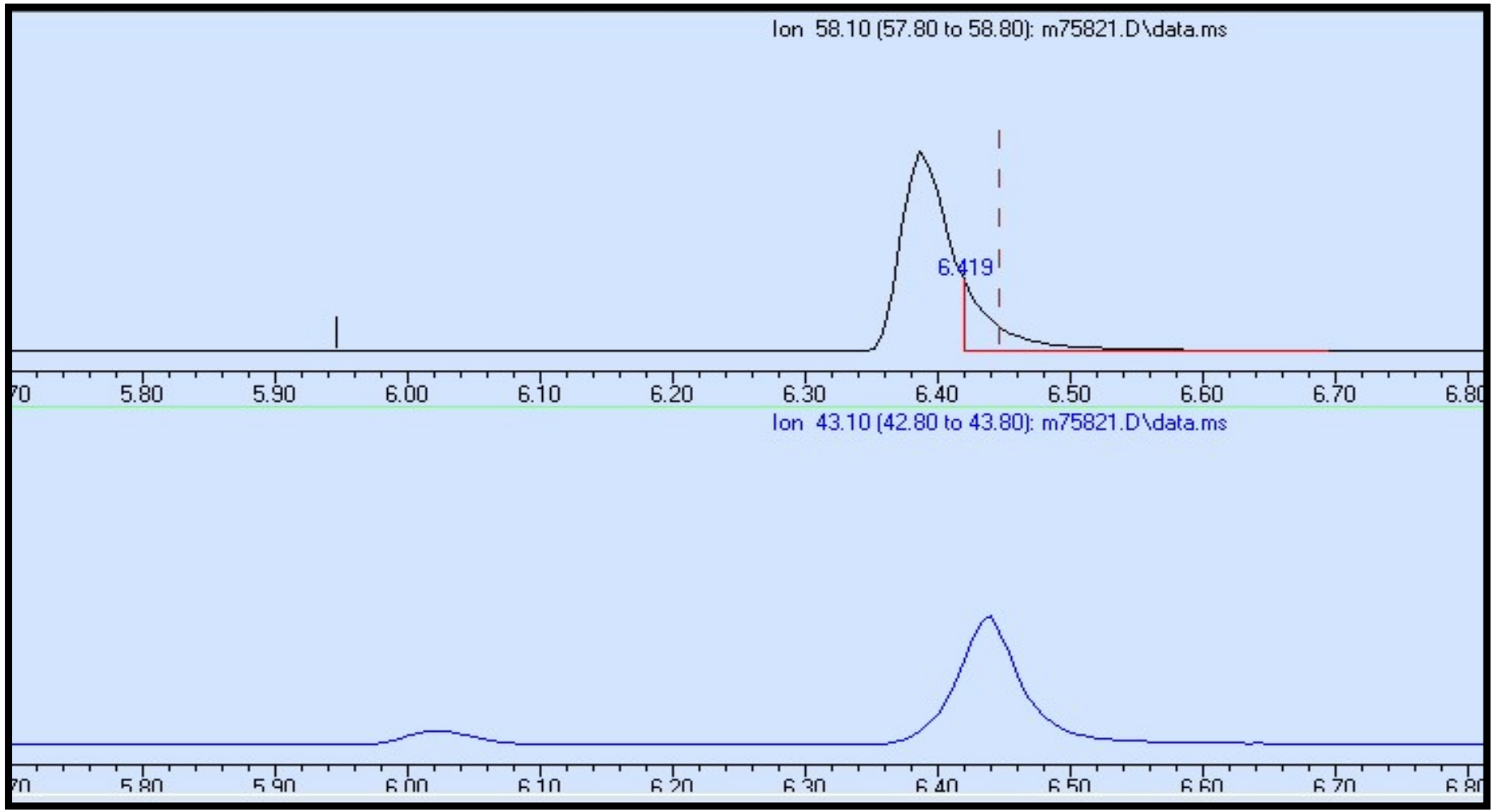
<u>Methacrylonitrile</u>: A false positive sample hit closely matches an isomer of 2-methyl-2-pentene, based on the NIST library search results shown below.



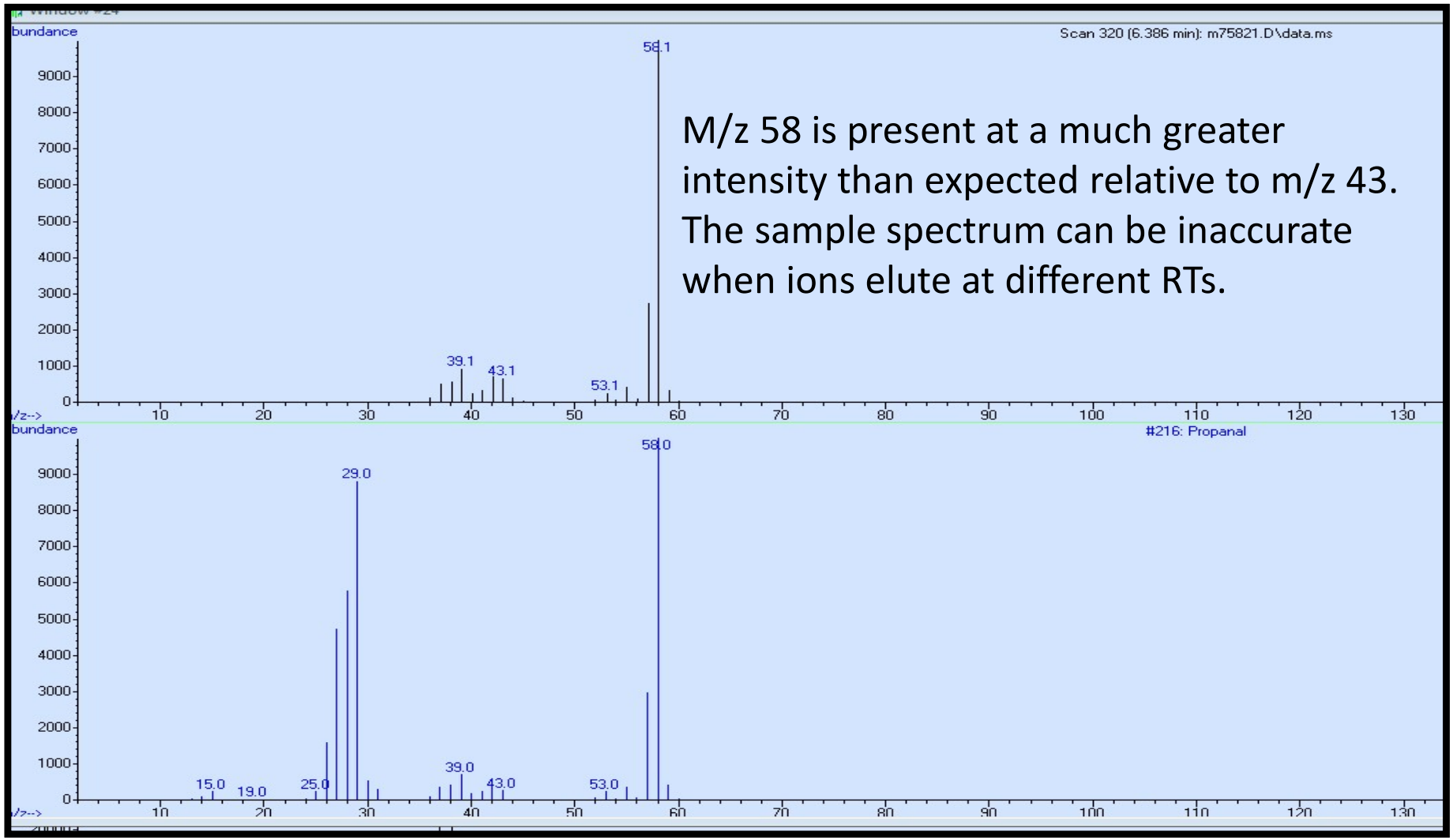
<u>Problem solution</u>: When checking a candidate target compound hit in QEdit, note any extraneous ions (m/z 55, 56, 69, and 84). Methacrylonitrile should display ions 51, 52, 66, and 67. If unsure of the spectrum match for a target compound, perform a forward library search to see if the extraneous ions indicate another compound. Also check the NIST spectrum.



Acetone has a mass spectrum that has common ions with hydrocarbons. M/z 43 and 58 ion chromatograms should maximize at the same retention time and exhibit intensities in roughly a 2:1 ratio. Any extraneous ions should be accounted for. In this example, the RT for ion 43 does not line up with that for ion 58, and a library search indicates two separate compounds.

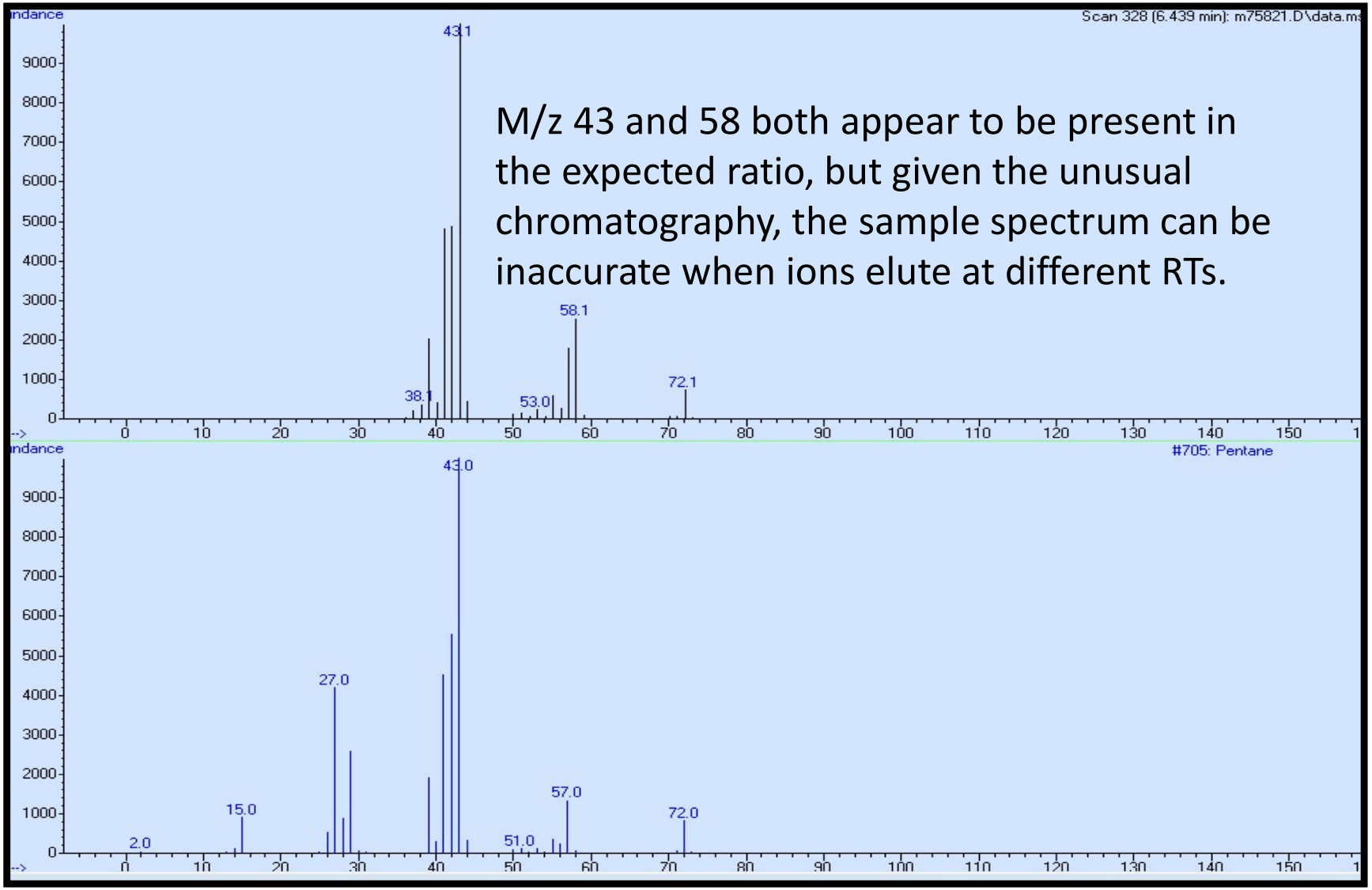


M/z 58 is the first eluting peak at 6.39 minutes, and a library search of this peak matches propanal, not acetone.



M/z 58 is present at a much greater intensity than expected relative to m/z 43. The sample spectrum can be inaccurate when ions elute at different RTs.

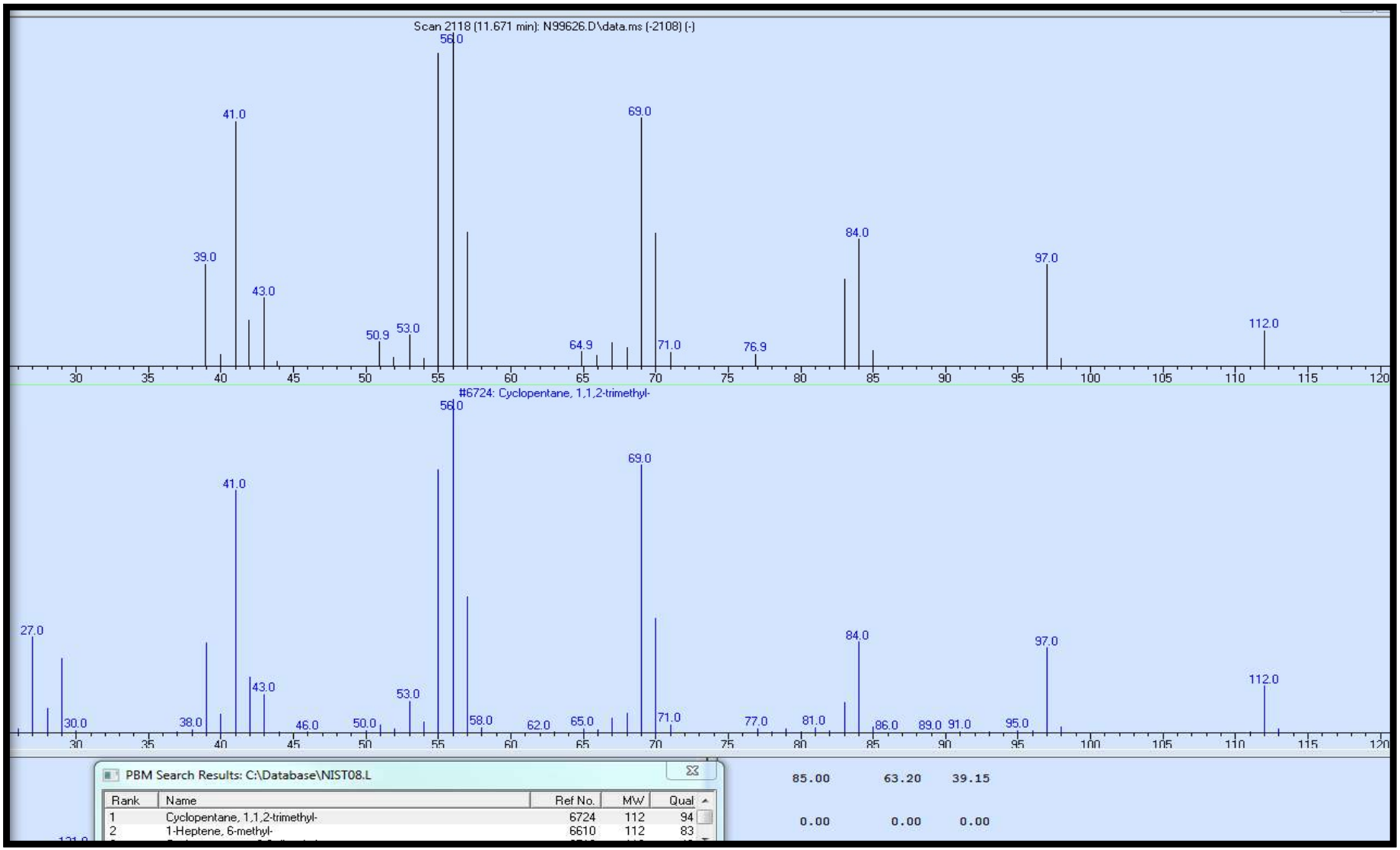
M/z 43 is the second eluting peak at 6.44 minutes, and a library search of this peak matches an isomer of pentane, not acetone.



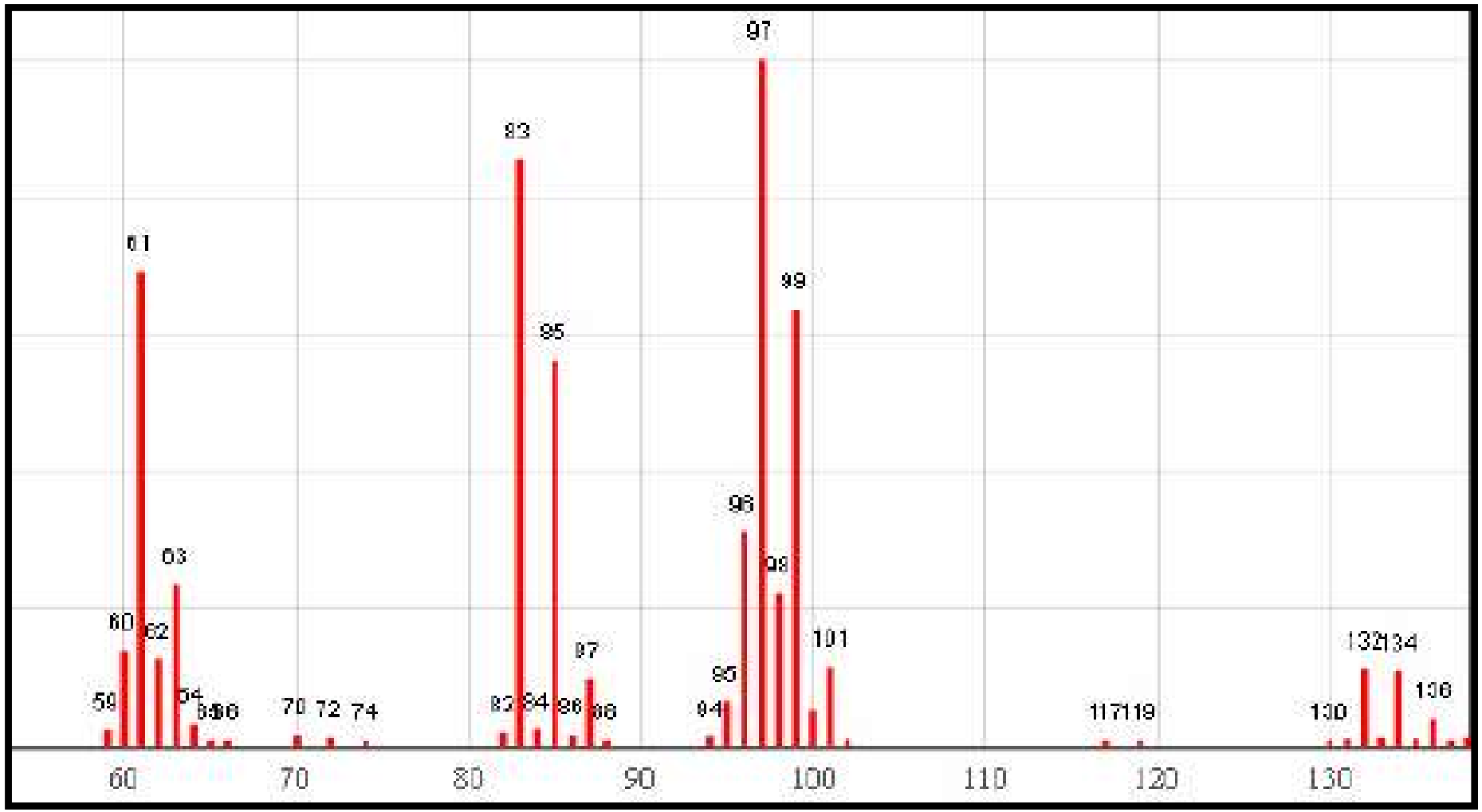
Problem solution: When checking a candidate target compound identification using QEdit, be on the lookout for potential coeluting sample components. A casual look at the sample spectrum might suggest that acetone m/z ions 43 and 58 are in the correct ratio. However, since the two ion peaks elute at distinctly different retention times, this indicates that two separate components are contributing to the ion signals.

In complex cases, check the ion chromatograms of characteristic ions.

1,1,2-Trichloroethane exhibits a chlorine isotope pattern that is rarely misidentified. In this case, extraneous ions are present and the chlorine isotope pattern is poorly matched. A library search indicates a hydrocarbon.



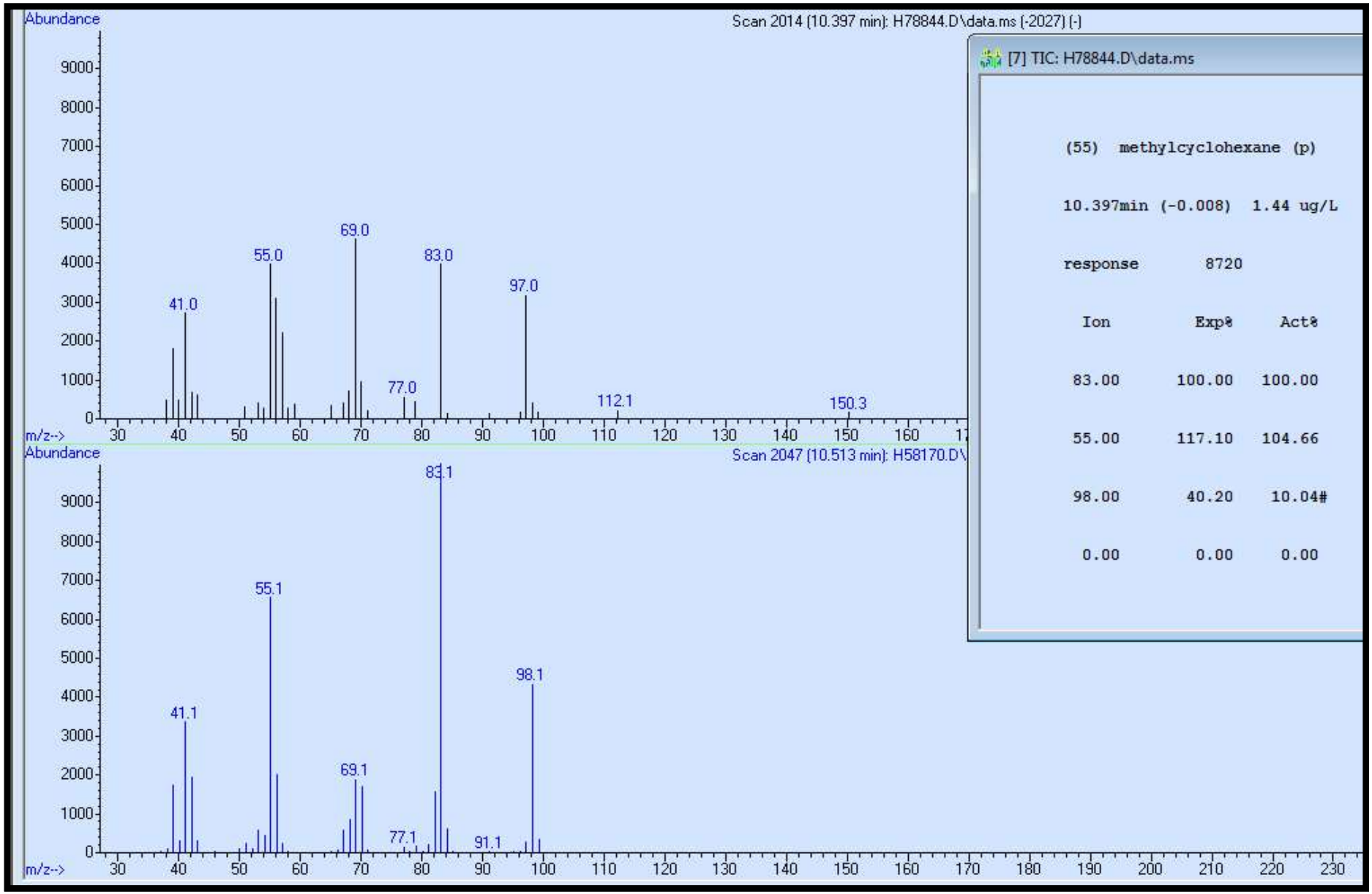
1,1,2-Trichloroethane NIST library spectrum. Ion fragments "m" and "m+2" represent isotopic abundances of chlorine. Ion fragments having 1 chlorine atom display a 3:1 ratio (61:63). Ions with two chlorines are roughly in a 3:2 ratio (63:65 & 97:99). Ions with 3 chlorines (132:134) are roughly a 1:1 ratio.



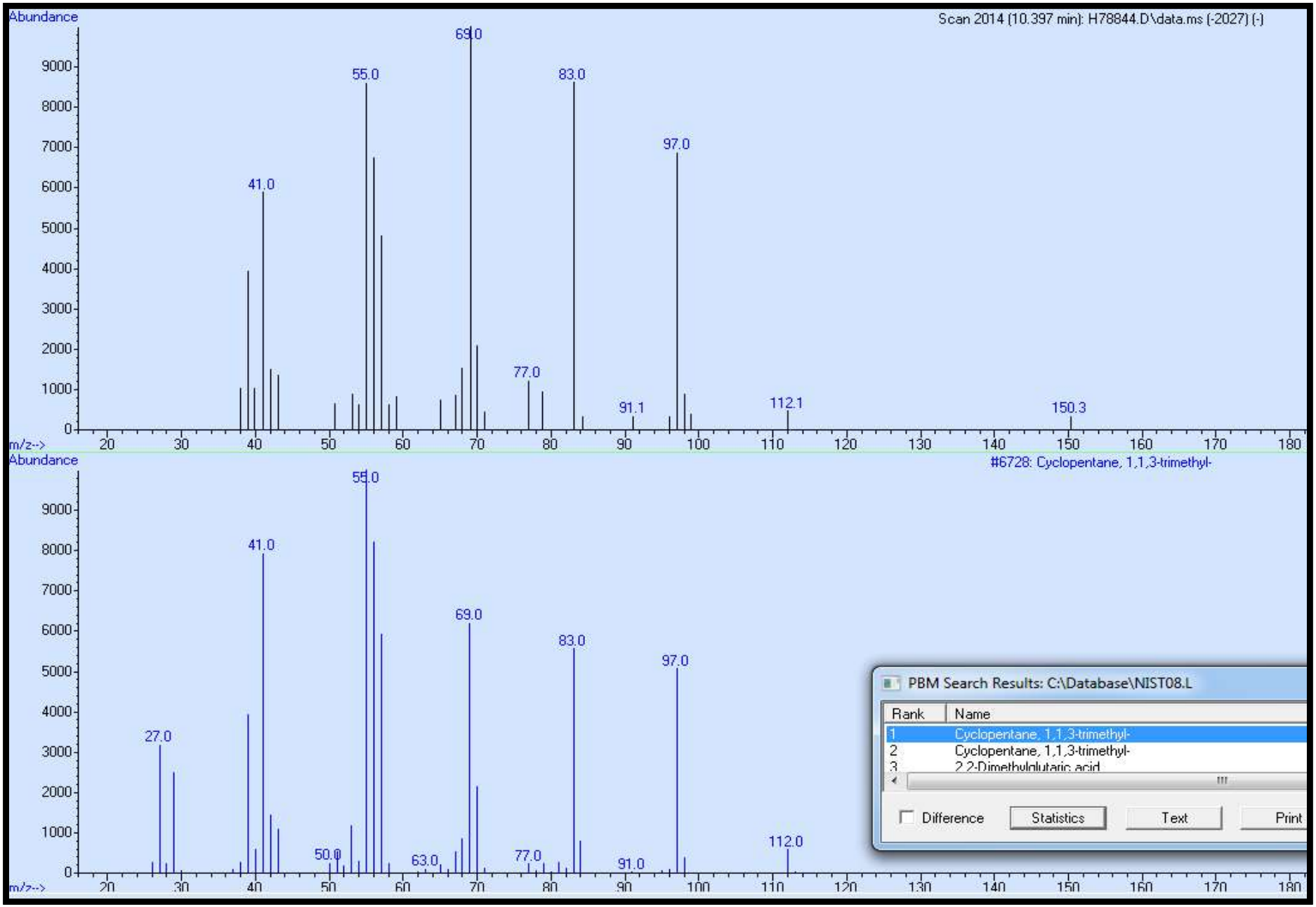
<u>Problem solution</u>: When checking sample spectra for candidate target compound hits using QEdit, look carefully at the m/(m+2) chlorine isotope patterns found in the sample and compare to the ratios from the NIST library spectrum.

Knowledge of the expected natural isotopic abundance patterns for chlorine isotopes should be applied when evaluating candidate target compounds as well as during the evaluation of library search results for tentatively identified compounds (TICs).

Five major ions associated with methylcyclohexane were detected in a sample, but m/z 98 was missing and m/z 97 was an extraneous ion. The sample spectrum was searched against the NIST library and matched a different hydrocarbon compound.

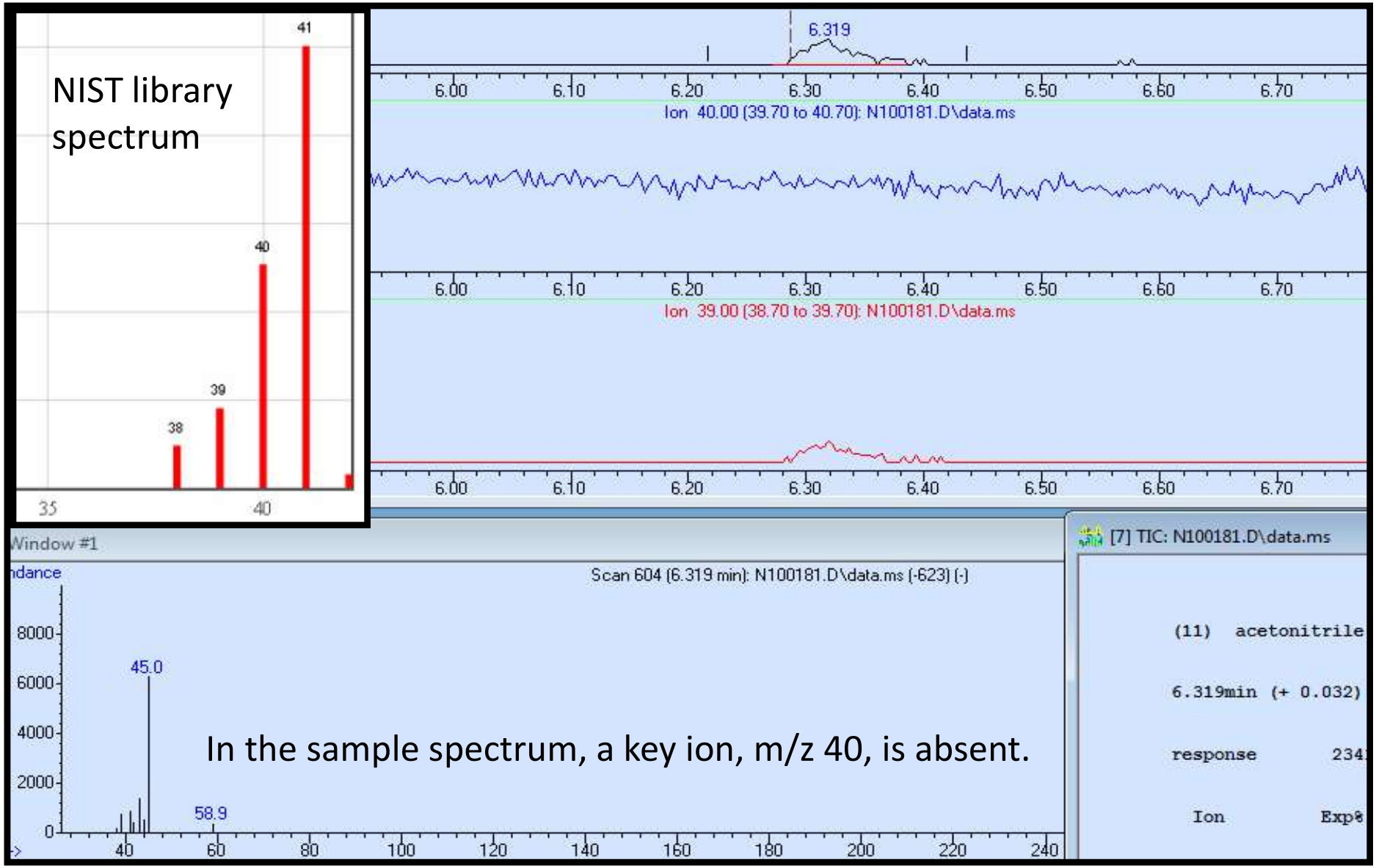


The sample spectrum matches 1,1,3-trimethylcyclopentane.

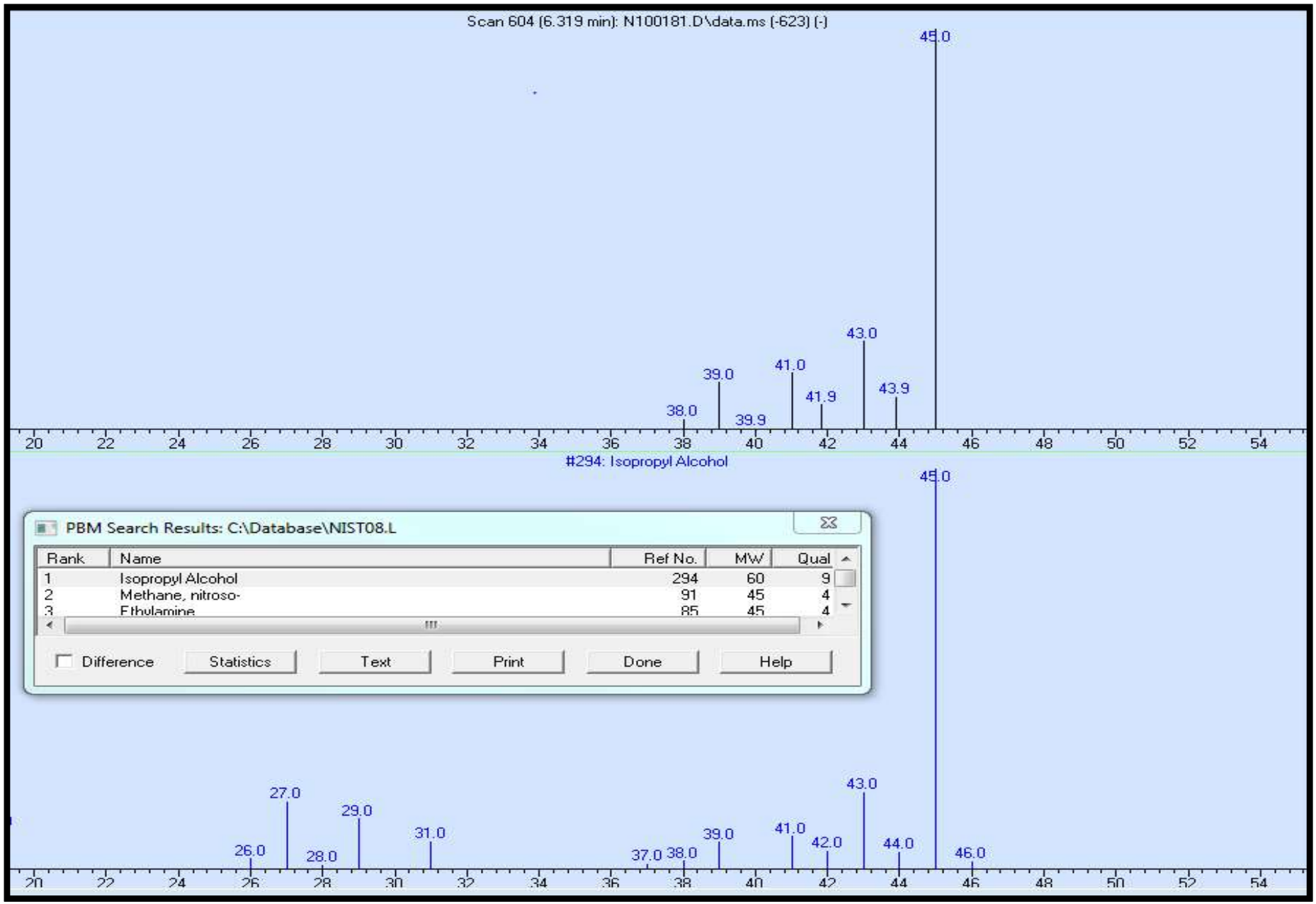


Problem solution: **When checking sample spectra, look for potentially significant missing and extraneous ions. In this example, only one out of the 7 largest ions is absent from the sample spectrum, but the library search results clearly match a different compound.**

Acetonitrile misidentified in a sample. m/Z 39:40:41 ratio does not match NIST library spectrum.



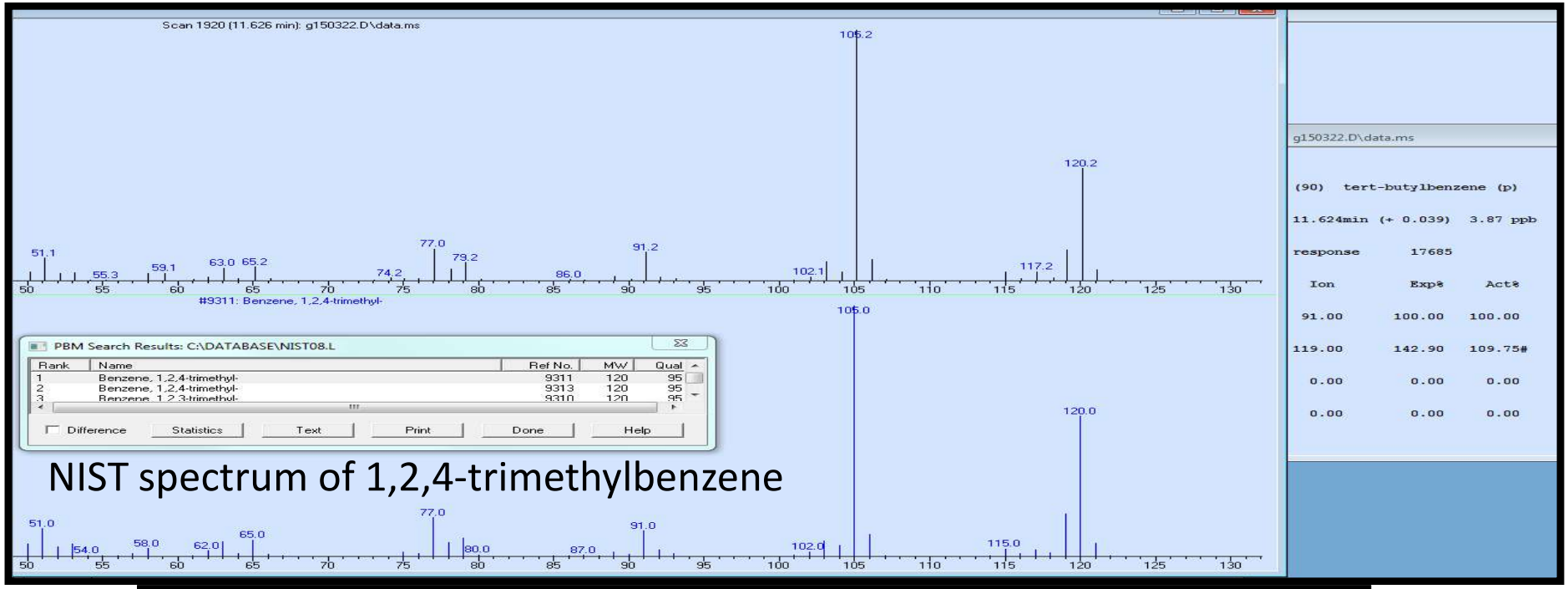
NIST library search matches isopropyl alcohol, not acetonitrile



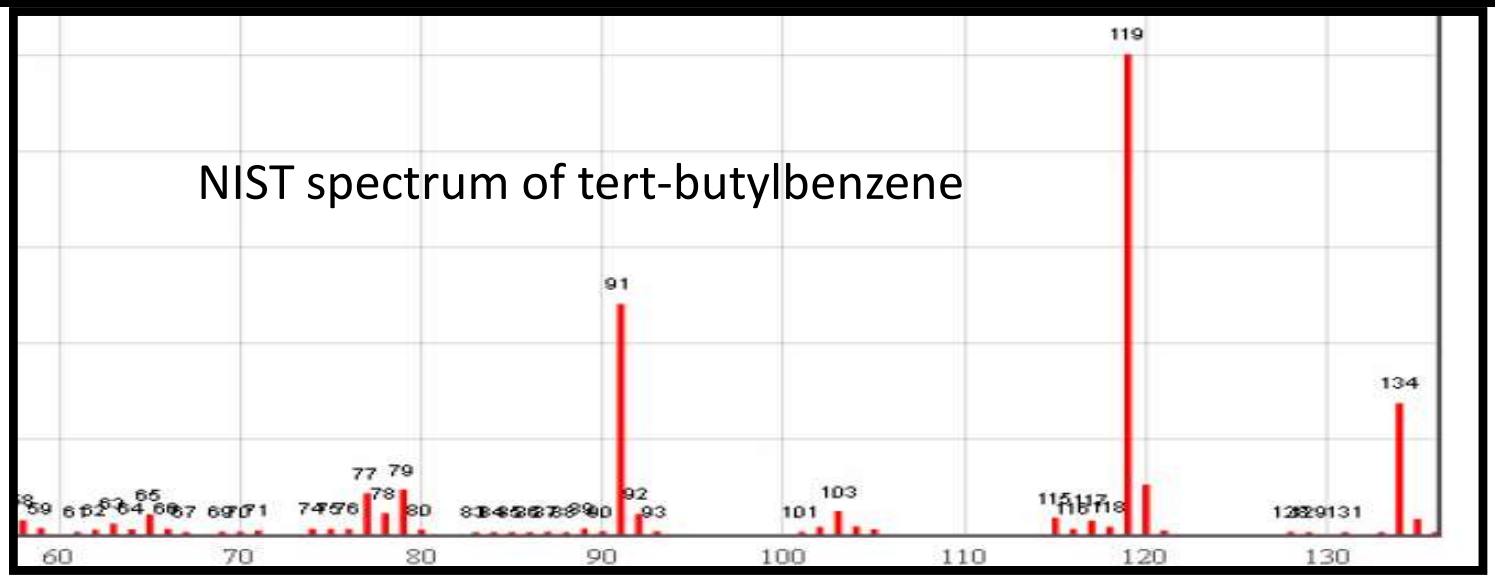
<u>Problem solution</u>: Acetonitrile exhibits a very simple mass spectrum, with ions m/z 39 and 41 common among many hydrocarbons. Therefore, false positives can occur in sample quantitation reports.

When reviewing a sample spectrum for acetonitrile, pay particular attention to m/z 40, which is a more unique ion. The expected ratio of intensities for ions 39:40:41 should be verified.

Tert-butylbenzene misidentified in a sample. Retention time and spectrum match 1,2,4-trimethylbenzene, a target analyte that elutes 0.04 minutes later.



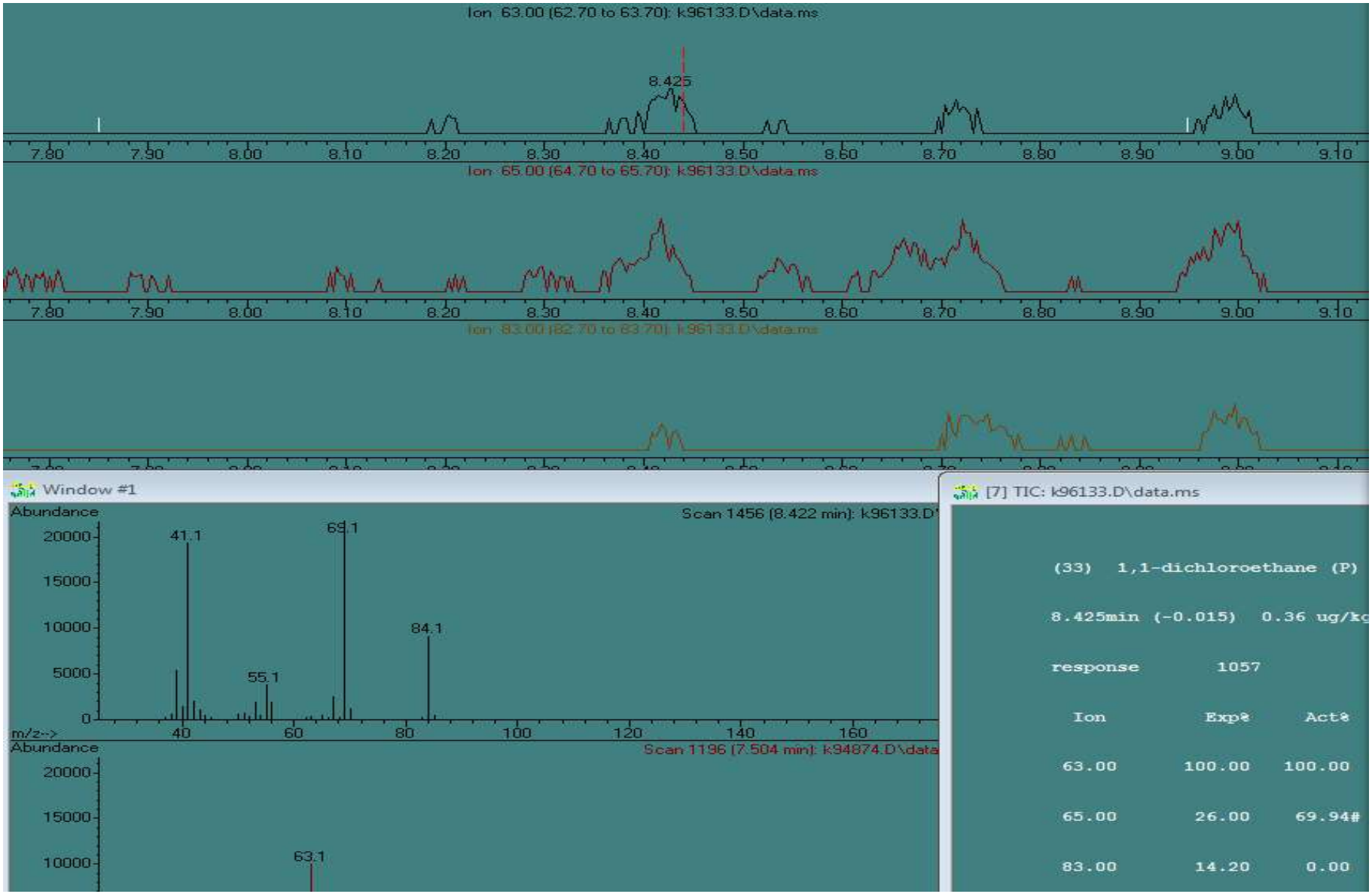
NIST spectrum of 1,2,4-trimethylbenzene



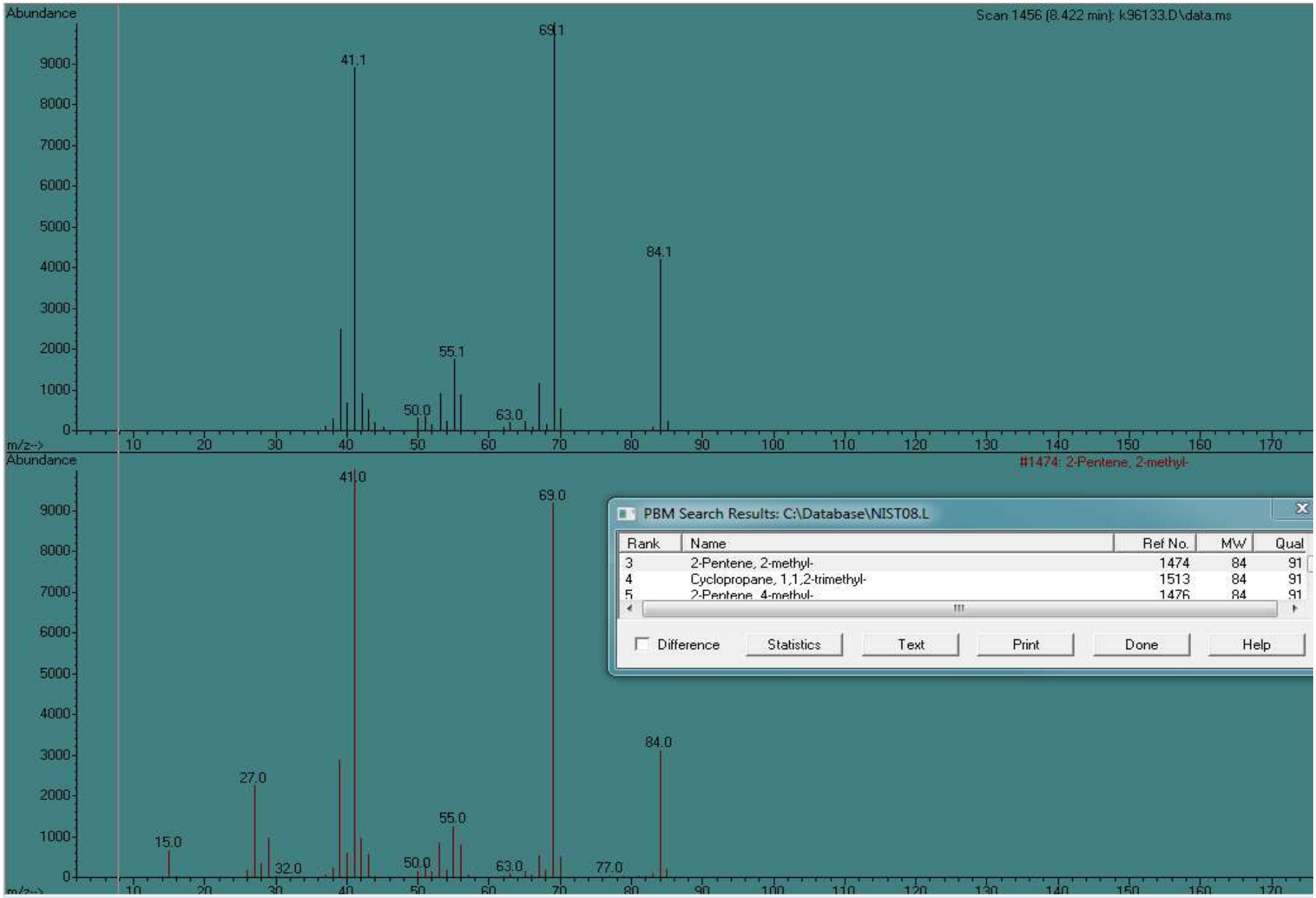
NIST spectrum of tert-butylbenzene

Problem solution: When checking sample spectra, examine all potentially significant missing and extraneous ions. In this example, the molecular ion, m/z 134, was absent and several extraneous ions were confirmed via a library search to match a different target compound. The two target compounds, tert-butylbenzene and 1,2,4-trimethylbenzene, elute only 0.04 minutes apart but can be distinguished by examining all characteristic ions.

1,1-Dichloroethane misidentified in a sample on instrument K. Ions 63, 65, and 83 are minor shared ions from a hydrocarbon.



NIST library search matches spectrum of 2-methyl-2-pentene.



NIST spectrum of 1,1-dichloroethane.