Thermal Desorption Technical Support

Note 85: GC/MS data analysis using ClearView™ reprocessing software: Dealing with common ions

Keywords

GC/MS, Total ion chromatogram (TIC), dynamic background compensation (DBC), background ion, interference elimination

Introduction

ClearView software is a standalone GC/MS data reprocessing product developed by ALMSCO International, the detection division of Markes International Ltd. ClearView removes background-related mass ions from the chromatographic data using a dynamic background compensation (DBC) algorithm *i.e.* the compensation adjusts automatically as the level of background interference varies throughout a run. The software can distinguish and eliminate any interference that occurs at a rate which is ten times or more slower than the base width of chromatographic peaks. Typical GCMS interference removed by ClearView includes column bleed, air/water background, 'humps' of unresolved sample components and extended solvent tails. ClearView generates a second reprocessed data file for each run. The original data files are left intact, so there is no risk of data loss. The original files can be used for comparison with the reprocessed data if required.

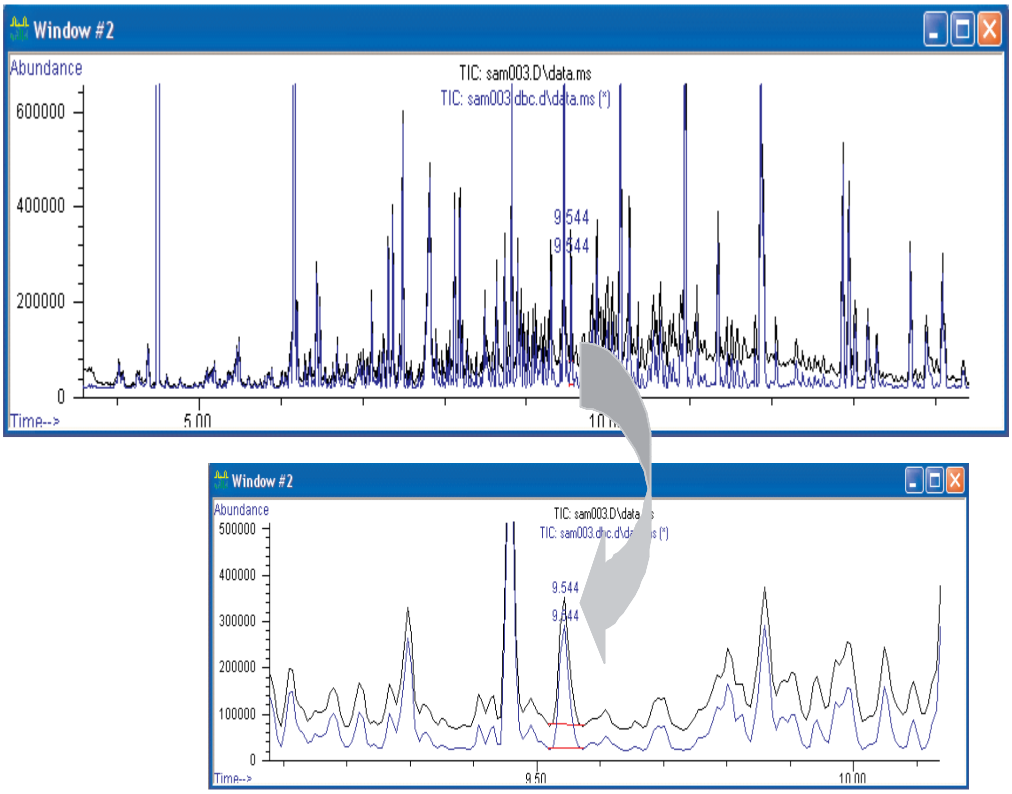
Alternative static background subtraction techniques remove a fixed abundance of ions - normally based on background levels at one particular time/scan point in the total ion chromatogram (TIC). However this can be detrimental to the fragmentation pattern of some real peaks and may, under certain circumstances, even remove trace peaks from the TIC entirely.

An important feature of ClearView is that it preserves all of the mass ions contributing to chromatographic peaks even if the fragmentation pattern/spectrum of the peak contains ions which are common to the background. This key feature is shown in two examples below. In both cases detailed comparison of the peak data in original and reprocessed data files verifies that ClearView accurately eliminates only that proportion of common ions due to the background. The proportion of the common ion due to the peak is not affected.

Example 1: ClearView reprocessed data for a common mass ion 43 amu

Figure 1 shows the effect of ClearView processing for a complex hydrocarbon sample. Mass ion 43 is ubiquitous within this type of sample and typically originates from the fragmentation ion $C_3H_7^+$. The raw data shown in the black trace have been compensated, and the resultant reprocessed data are shown overlayed in blue. Within the sample a test compound has been identified at 9.544 minutes as dodecanal. This is highlighted in the lower trace.

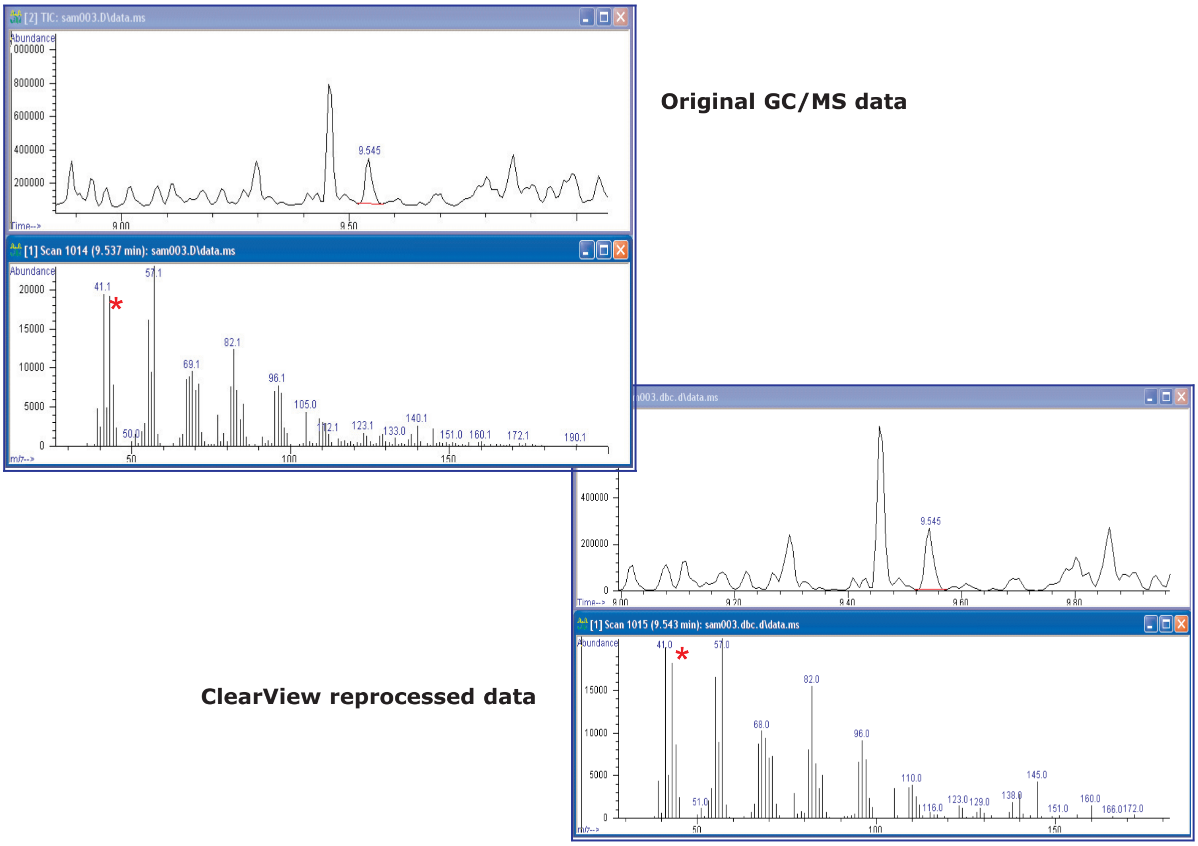
Confirmation of mass 43 within the dodecanal peak for both the original and ClearView reprocessed data is shown in figure 2 (red asterix). The abundance of mass ion 43 is higher in the original data as this includes the additional contribution from background response.



Original GC/MS data

After ClearView processing

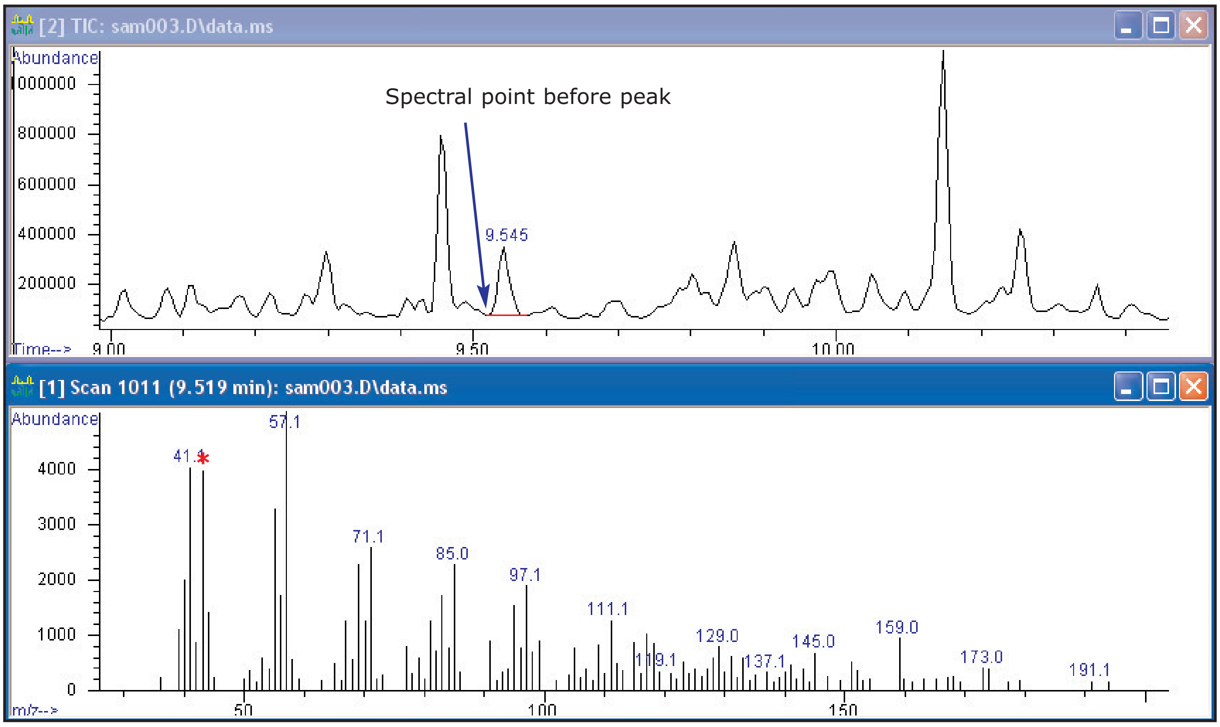
Figure 1: Test compound eluting at 9.544 minutes (dodecanal) containing common mass ion 43



Original GC/MS data

ClearView reprocessed data

Figure 2: Expanded portion of the TIC from both the original and ClearView reprocessed data files with the corresponding apex spectrum of the dodecanal component in each case. Mass ion 43 is highlighted



Spectral point before peak

Figure 3: Fragmentation pattern immediately before dodecanal indicating common mass ion 43

Figure 3 shows the fragmentation pattern of the baseline immediately before the dodecanal peak at 9.519 minutes. This is to confirm that mass 43 is common to both the peak of interest and the background.

As it has now been shown that mass ion 43 is present in both background and peak, a key test will be to examine the original and ClearView reprocessed data files using extracted ion 43. If ClearView reprocessing has eliminated part of the mass ion 43 contributing to the peak this will immediately show up as a reduction in peak height or area in the reprocessed data. Figure 4 shows such an overlayed plot with a (negative) y-axis offset for the original data to allow the 2 peaks to be overlayed exactly.

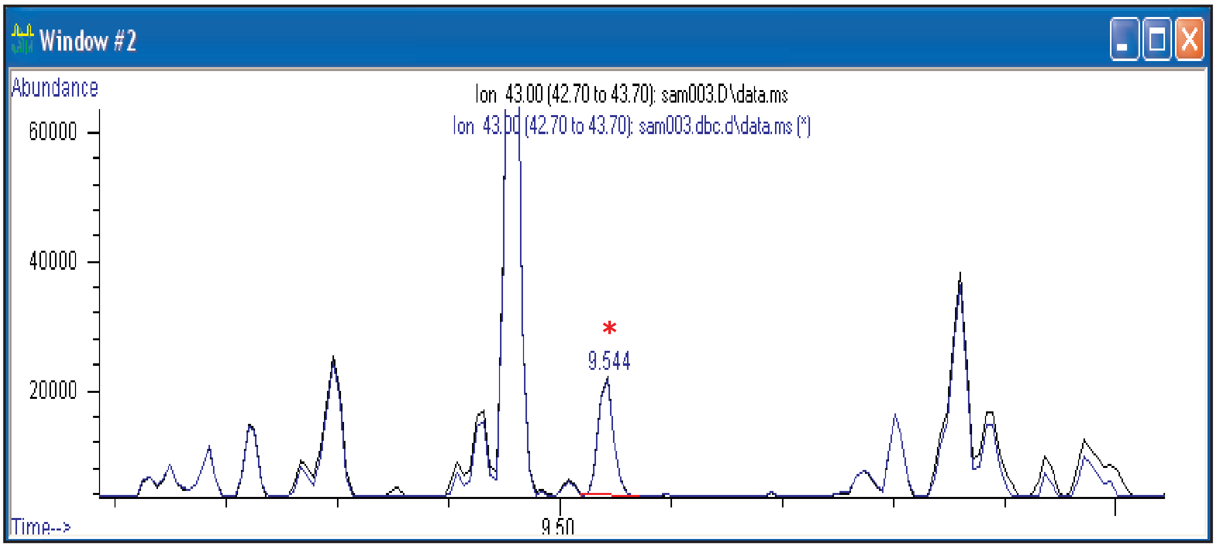


Figure 4: Extracted ion chromatograms (EIC) (mass 43) for the original (black) and ClearView reprocessed (blue) data files – adjusted along the y-axis such that the dodecanal peaks can be overlayed and compared directly

The extracted mass ion 43 peak is identical in both sets of data clearly indicating that ClearView reprocessing has not over (or under) compensated for background contribution of mass 43.

Example 2: ClearView reprocessed data for a common mass ion 55 amu

This example (figure 5) shows a trace landfill odour gas standard analysed using thermal desorption (TD)-GC/MS with a thick-film, high-bleed column. TIC data is shown both before (blue) and after (black) ClearView reprocessing.

ClearView has a dramatic effect in this case; eliminating the interference from column bleed, simplifying integration, improving spectral purity and enhancing the signal to noise ratio (sensitivity).

This is an extreme case of background compensation and therefore a good example of assessing the effect of ClearView on a mass ion that is common to both the compound and the baseline. A test peak at 18.101 minutes was identified as butanethiol containing the mass ion 55 amu. Figure 6 shows the apex spectra for this peak before and after ClearView processing and the library spectra for Butanethiol to confirm the presence of mass 55.

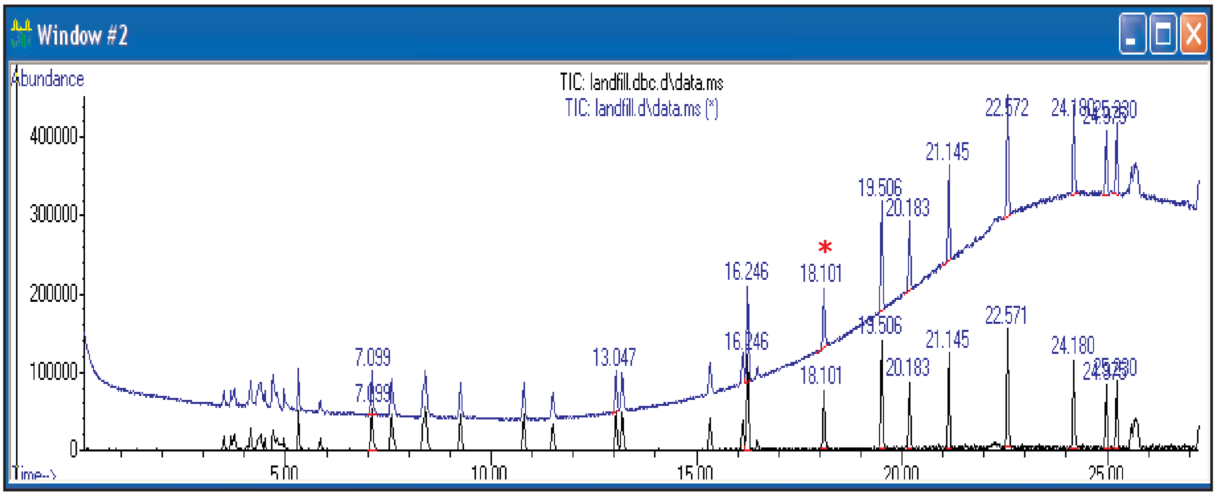
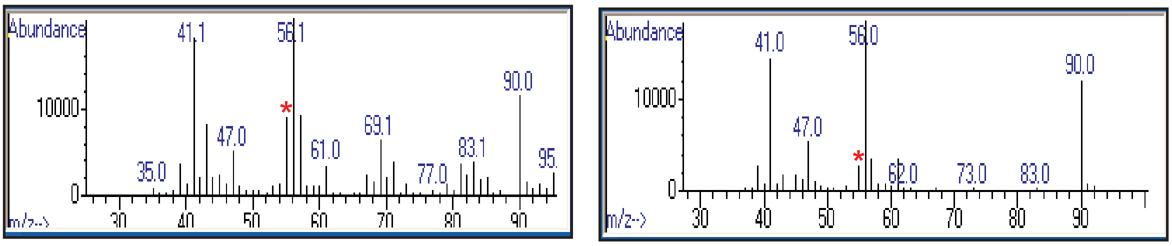
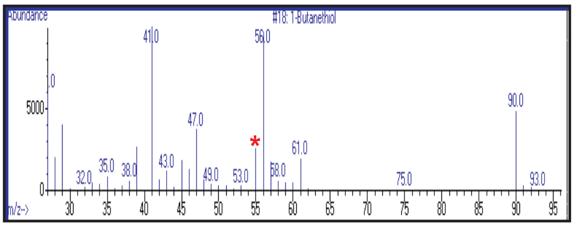


Figure 5: Landfill odour standard analysed using a high-bleed column, shown before and after ClearView reprocessing



A) Butanethiol apex spectra *BEFORE* ClearView processing

B) Butanethiol apex spectra *AFTER* ClearView processing



C) Butanethiol spectra from NIST library

Figure 6: Butanethiol apex spectrum (A) from the original data file, after ClearView reprocessing (B), and library spectra (NIST05) (C)

To confirm the presence of mass ion 55 in the background, baseline spectra were taken immediately before and after the peak (see figure 7). Mass ion 55 is clearly visible in each case.

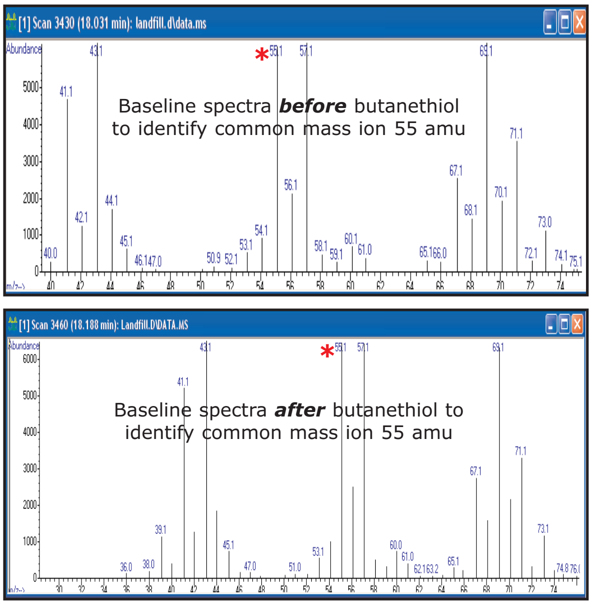


Figure 7 Baseline spectra before/after Butanethiol peak identifying mass ion 55 amu

As in example 1, the extracted ion chromatogram (EIC) (mass 55) data, original and ClearView reprocessed, can be compared for butanethiol. Any reduction in mass 55 ion abundance in the reprocessed data will be immediately evident by overlaying and comparing peak areas/heights (See figure 8).

By overlaying and off-setting the original data downwards, such that the butanethiol peak in the original data exactly overlays that in the reprocessed data (figure 9), it is immediately evident that the peak areas/heights are identical, even in close-up.

Moreover, it should be noted that the abundance of mass ion 55 in butanethiol is relatively small and any over- or under-compensation for the background contribution, by ClearView, would have a significant and obvious impact on the extracted ion peak area/height. From the flatness of the EIC baseline, it can be seen that ClearView is accurately compensating for mass 55 in the background but without impacting the contribution of mass 55 to the butanethiol peak.

Figure 10 shows the baseline fragmentation pattern in the ClearView-reprocessed data immediately before/after the butanethiol peak. The low y-axis 'abundance' scale and complete absence of mass ion 55 confirms how well ClearView is compensating for background interference.

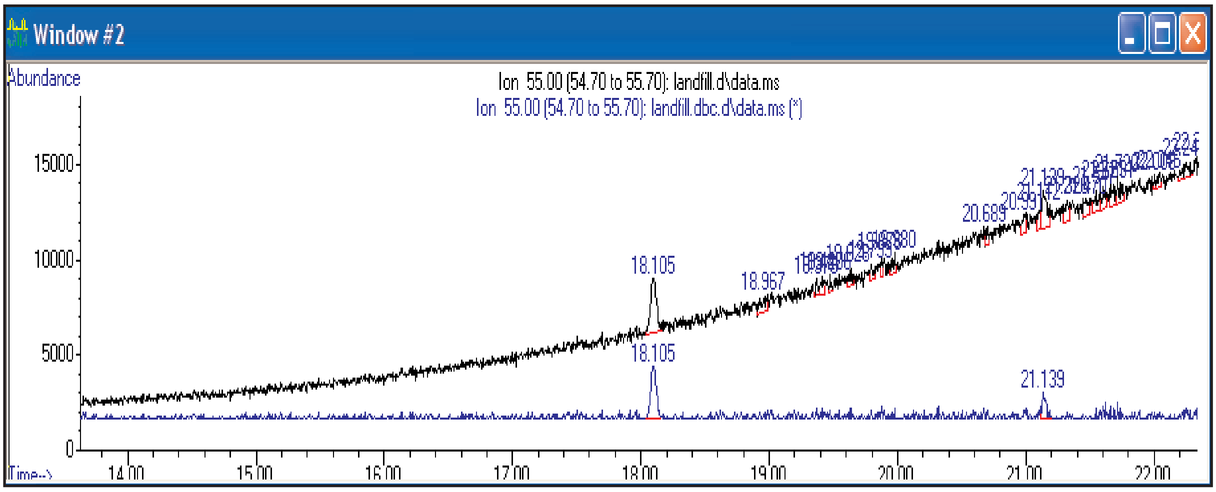


Figure 8: Overlaid original (black) and ClearView reprocessed (blue) EICs for mass 55 amu

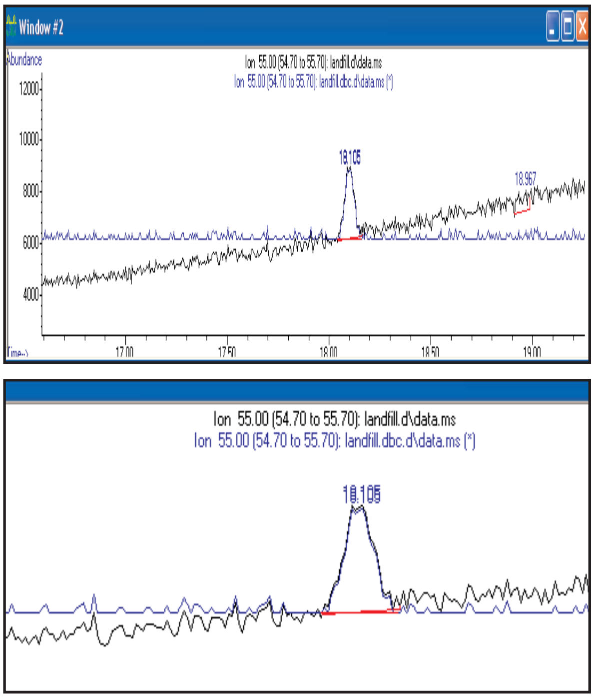


Figure 9: Overlaid and offset aligned EIC (mass 55) data; original (black) and ClearView reprocessed (blue)

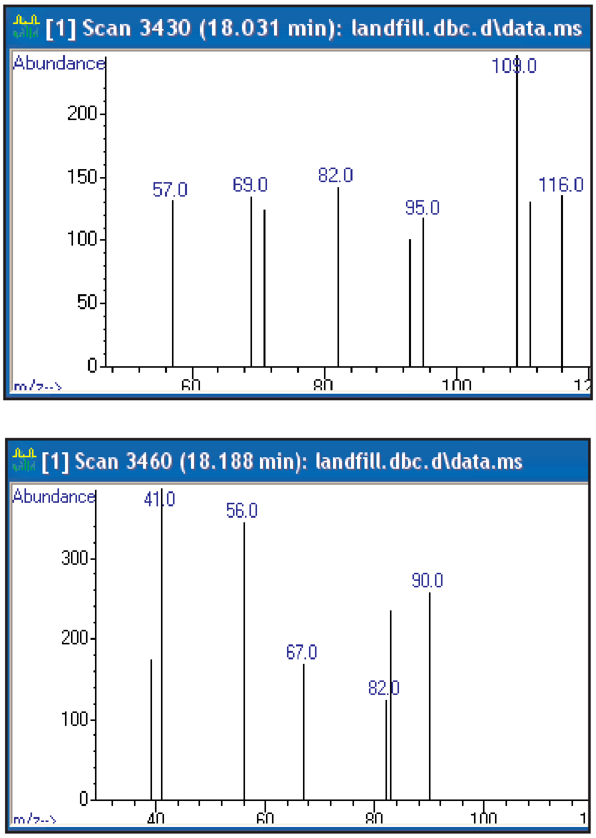


Figure 10: Fragmentation data immediately before/after butanethiol peak after ClearView processing

Summary

The remarkable performance of ClearView in terms of being able to selectively remove background interference from chromatographic data, even when the same mass ion is present in both, has been clearly demonstrated in these two very different examples. In summary, ClearView has been shown to:

- Compensate accurately for chromatographic background even though that background is varying across a run
- Accurately distinguish mass ion contributions to chromatographic peaks and leave these unchanged
- Fulfill both these key functions even when the same mass ion is present in both background and peaks

Trademarks

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