Newest revisions to 8260 and 8270 – SIM and full scan. One of these things is not like the other!

As regulatory agencies push action limits lower and lower, laboratories have had to move to increasingly more sensitive methodologies for analyses in order to meet their clients' needs. One of the methodologies commonly used is selected ion monitoring (SIM). Gas chromatography (GC)/mass spectrometry (MS) SIM is particularly attractive because it can be performed using the same analytical instrumentation the lab is already using for the full scan methods for volatiles (8260) and semi-volatile analyses (8270) and can increase analytical sensitivity for the target compounds by a factor of 10 to 100. SIM is different from traditional full-scan analysis in that only selected masses of interest for each target compound are monitored, rather than scanning across a range of 200 to 500 masses covering all of the target compounds. SIM can provide excellent specificity and sensitivity because of this focus on a few narrow mass windows specific to each of the target compounds.

Laboratories typically use EPA Methods 8260C (volatile organics) and 8270D (semi-volatile organics) from SW-846 (Test Methods for Evaluating Solid Waste: Physical/Chemical Methods), which allow for the use of SIM as an acceptable modification to full scan analyses. However, the criteria specified in these versions of the methods are only applicable to full scan analysis, including the criteria required for identification and confirmation of the target compounds. While much of the methodology, including GC operating conditions and programs and calibration procedures for SIM, is the same as that used for full scan analyses, the acquisition of mass data for SIM is different, as are the criteria for identification and confirmation of the target compounds. The current revisions of these methods commonly used by the laboratory do not fully address the specifics of proper acquisition and identification for analysis of samples in SIM mode.

In June of 2018, the EPA released Update VI to SW-846, which included revisions 8260D and 8270E. Analytes not previously included in the method and the use of GC/MS/MS (GC triple quadrupole MS) were added, and changes were made to the sections describing blanks (Section 9.5). Guidance for using hydrogen as a carrier gas (Appendix B), as well as other changes were also introduced. The most notable revision was the inclusion of more detailed guidance for SIM analyses. In addition to the guidelines specified in Methods 8260C and 8270D (dwell times, accounting for mass defects, etc.), the newest revisions to these methods, 8260D and 8270E, now include the following acquisition and calibration guidelines:

- At least two ions should be monitored for each target analyte, and the mid-point of the calibration curve is used to establish ion ratio criteria for each compound. The ratios of primary and secondary ions are the only qualitative tool available in SIM runs (other than retention time [RT]), which increases their importance in confirmation of proper target compound identification.

- All monitored ions must be correctly integrated in order to achieve accurate ion ratios. The primary/secondary ion ratios and the reference mass spectrum should be updated from the mid-point ICAL standard

For analyte identification, the following guidance was added:

- The relative intensities of the qualifier ion(s) (i.e., secondary characteristic ions, or additional monitored MS/MS transitions) should agree within 30% of the relative intensities of these ions in the reference spectrum. The reference mass spectrum used for this comparison should be generated by the laboratory using the conditions of this method (typically a mid-level calibration standard).

There is a lot of gray area in the method text that allows laboratories to take a variety of approaches to this methodology and the way it is employed. ddms routinely performs third-party data validation where SIM is used. Based on issues we routinely encounter with these data, we would like to offer some food for thought.

We see that many laboratories do not correctly (or just do not) establish ion ratios. For SIM, ion ratios provide the confirmation that the identified peak is attributable to the target compound. Laboratories often compare SIM data to full scan reference spectra to confirm component identification in samples. Because SIM and full scan data are not the same and will not give the same abundances, comparing the SIM data to full scan reference data is not appropriate. If the reference standards aren't acquired under the same conditions as the samples, SIM in this case, you are not supporting your data accurately. Instrument software that normalizes mass peaks from SIM to match full scan spectra are NOT true raw data. Newer instrumentation and software that allow acquisition of so-called "simultaneous" full-scan and SIM data can present their own challenges if not well understood and used appropriately.

Many laboratories ensure that the primary ion is properly integrated, but don't ensure that all ions monitored are properly integrated in order to establish correct ion ratios. Inaccurate integration will result in incorrect ion ratios which, in turn, may affect identification of target compounds in samples. During validation, the ion ratios for compounds in the sample are compared with the established acceptance limits. An ion ratio outside this window may indicate a possible interference with a high or low bias, or even an incorrect identification (false positive). The sample results may require qualification as presumptively present (N) and/or estimated (J).

Laboratories should be using a mid-level standard to establish the target ion ratios and the acceptance windows. But, the laboratory should also look carefully at the ion ratio across the range of the calibration concentrations to make sure that they are using acceptance windows for the ratio that will

give them accurate identification at low and high concentrations as well. PAHs (polycyclic aromatic hydrocarbons) are a class of compounds often analyzed by SIM in order to meet very low project action limits. PAHs have limited characteristic masses, and they should be examined very carefully to be sure that confirmation is supported at lower concentrations.

Many PAH compounds share the same characteristic ions. With the push to reduce analysis time, chromatographic peaks are increasingly compressed and mass peaks shared between multiple analytes may overlap. The laboratory must ensure that they are acquiring sufficient data over the entire peak and that peaks are adequately resolved to give accurate and consistent integration. It goes without saying that one must always be mindful of signal to noise ratio (S/N) for these selected masses.

Because data generated using SIM are used to meet project or regulatory action limits at very low concentrations, the importance of properly, accurately, and defensibly executed SIM analysis is critical. Many states, New York and New Jersey among them, offer certification for revisions 8260D and 8270E, but many laboratories have not upgraded to these revisions yet. Even with the improvements in the methods and with the improvements in the instrumentation and software available to the laboratories, good laboratory practice and the ground rules for mass spectrometry must be front and center for data quality and defensibility.

For more information, contact:
ecsteam@ddmsinc.com