Abstract

A simplified guide is presented to assist in the understanding of detector specifications and to show how to relate them to the specific analysis to be performed. Sensitivity specifications should be detector-response unit independent and should relate to the signal-to-noise (S/N) ratio of the detector. The test compound and the data rate should be given. If the dynamic range is claimed to be linear, some indication of how much the response/amount varies over the entire range should be available. Selectivity values should reference the test compounds used.

Introduction

Instrument specifications provided by different vendors should help a scientist choose the product that will best meet his needs. Unfortunately, there are few standards for creating specifications, so it can often be difficult to make direct comparisons.

Detector specifications are particularly important because the detector performance can determine whether an analysis can be performed successfully or not. The major questions involve sensitivity, linearity, selectivity, and repeatability. Repeatability is a function of many system parameters, including injection technique, column bleed, and flow stability. Because detector repeatability cannot be determined independently of other system factors, usually only detector sensitivity and linearity are specified.

Unfortunately, there is still variability in how these are specified. Organizations such as ASTM (American Society for Testing and Materials), the US EPA (United States Environmental Protection Agency), and various national testing organizations in many countries have created standards for detector specifications. Instrument manufacturers may use these methods to test detectors during development, but usually the method is modified to allow easy testing in customer labs and during production. ASTM methods for the thermal conductivity detector (TCD) and flame ionization detector (FID), for example, call for gas standards and/or dilution apparatuses that are not readily available.

Detector Sensitivity

Detector sensitivity should be specified as a minimum detectable level (MDL) or as a measure of the S/N ratio for a specific injected sample amount. These measures are more useful than a simple response/mass value because they include information about the system noise. This is important because amplifiers can increase the apparent response (area or height per gram), but they also increase the noise. Similarly, setting an upper limit on noise is not appropriate because there may be operating conditions in which the noise is large, but the signal increase is proportionately larger, so overall the detector performance is improved.
Both MDL and S/N ratio provide a measure that is independent of the detector electronic units. While the pA measurement of the FID does reflect the number of ions generated, other detectors may have several detection modes, resulting in different units. The original TCDs measured the voltage change across the filament as an indication of filament temperature changes. The current Agilent TCD maintains the filament at constant temperature and measures the change in voltage required to do this. The units reported are still volts, but they are not the same kind of volts as in the original measurement scheme. Similarly, the electron capture detector (ECD) originally provided a current measurement. The Agilent pulsed ECD applies a pulsed voltage across the cell and changes the frequency of the pulsing so that a constant current is maintained. The units for this ECD are Hz (pulses/s). With such different mechanisms for signal transduction, it is important to specify detector performance in a manner that is independent of the detector units.

MDL is peak-width independent, but the data rate or filter bandwidth should be specified. The S/N ratio assumed to represent the MDL should also be given. Usually, S/N = 2. This information allows a user to estimate his detection limit (DL) under his specific separation conditions. MDL units depend on the detector type. The two types are mass flow detectors of which the flame detector is an example, and concentration detectors such as the TCD. Mass flow detectors respond to the mass of a compound in the detector at a given time and the MDL units are mass/time. Concentration detectors respond to the concentration of the compound in the detector sensing volume (not the sample) and their MDL units are mass/volume. The response of mass flow detectors is not dependent on flow; the response of concentration detectors is dependent on flow. Some detectors that are concentration detectors are designed with sweep gases and small cell volumes so that they are not very dependent on column flow and these can be treated as “pseudo” mass flow detectors. The Agilent micro electron capture detector (µECD) is an example.

For mass flow detectors, MDL is calculated by measuring the noise and the area of a peak of known injected mass. Assuming the noise is measured in suitable detector units (pA for the FID) and the area in detector units multiplied by time units (pA-s for the FID), the MDL at S/N = 2 is given by:

\[ \text{MDL} = \frac{2 \times \text{noise} \times \text{amount injected}}{\text{area}} \]  

For the FID, if the amount is in pg (10^{-12}g), the MDL will be in pg/s.

For concentration detectors, MDL has a flow term and is given by

\[ \text{MDL} = \frac{2 \times \text{noise} \times \text{amount injected}}{\text{area} \times \text{flow through detector cell (mL/s)}} \]  

If the amount is in pg, the MDL will have units of pg/mL. Inspecting this, one might conclude that increasing the flow decreases the MDL. But increasing the flow dilutes the sample, so the area will decrease with increasing flow. Thus the value of the denominator changes little with flow leaving the MDL to change as the noise changes with flow. Typically noise increases with increasing flow so MDL also increases.

Because noise measurements are a part of the MDL calculation, it is important to understand how they are made. Noise should be measured under “normal” operating conditions, with a column connected and carrier gas on. FID electrometer noise or drift (flame off), for instance, will not provide much indication of how the detector will perform in practice because major sources of noise are not included in this measurement. Noise typically has a high frequency component (electronic in origin) and lower frequency components that are referred to as wander and drift. Wander is random in direction but at a lower frequency than the short term electronic noise. Drift is a monotonic change in signal over a period that is long compared to the wander and electronic noise. These are shown in Figure 1. Terms like “short” and “long” are relative to the width of the chromatographic peaks. In general, one should measure noise over a period of time that is about 10 times the peak width at half height (or 10 times the area/height ratio for a Gaussian peak). Measuring for longer times can over-estimate noise; shorter times may underestimate noise.
Once the time period for the noise measurement is determined, an area of baseline that is free of obvious background or sample peaks should be chosen for the measurement. One good method uses seven segments and measures the peak-to-peak noise of each segment after the drift is removed. This is done by calculating the deviations of the data points from the linear regression line through the points. The difference between the maximum and minimum deviations from this line is the peak-to-peak noise for that segment. It is recommended that the segments be contiguous and have 10 percent overlap. This is illustrated in Figure 2. The average value of the noise of the seven segments is a good representation of the detector noise.

Figure 1. Different components of noise.

Figure 2. Noise measurements for seven overlapping segments that are 10 times the width at half height of the two peaks. The amplitudes of the peaks are two times larger than the average peak-to-peak noise. Both peaks are clearly detectable. The apparent difference in peak size results from the location of Peak 1 in a wander minimum and Peak 2 on a wander maximum. This is why quantitative precision requires a greater S/N ratio than simple detection.
Electronic noise usually is a function of the absolute signal. That is, the higher the signal, the higher the noise. If there is a high background signal due to system contamination from dirty gases or high column bleed, the noise will be higher than for low background conditions. In general, noise is proportional to the square root of the signal so a decrease in background signal by a factor of 4 will decrease the noise by a factor of 2. It may be necessary to add gas purifiers to the supply lines, to condition the column and to allow detectors that have not been heated recently to “bake off” contaminants before the specified performance can be achieved.

The detector MDL value can be related to the minimum detectable sample concentration for a given chromatographic method. For mass flow detectors, the calculation is given by:

\[
c_i = \frac{A}{Hv} \text{MDL} \quad (3)
\]

Where:

\(c_i\) is the minimum sample concentration that can be detected for a given component.

\(A\) and \(H\) are the area and height of that component at some convenient sample concentration.

\(v_e\) is the volume injected corrected for split ratio if appropriate\(^1\). MDL is the specified value.

For a Gaussian peak, \(A/H\) is approximately equal to the peak width measured at half height so that value can be used instead.

As an example, here is the calculation of minimum sample concentration for a peak that is expected to be 2 s wide (half height) on the FID. In this case, we need one additional piece of information and that is the relative amount of carbon in the compound of interest. If our compound is n-hexadecane (C16), for instance, it has 0.85 grams of carbon for every gram of C16. If the FID MDL is 2 pgC/s, then the MDL for C16 is \((2/0.85)\) pg/s of C16 or 2.35 pg/s. Using these values and assuming a 1 µL injection (no split), we have:

\[
c_i = \frac{(2\text{ s})(2.35\text{ pg/s})}{1\ \mu L} = 4.7\ \text{pg/µL} = 4.7\ \text{ng/mL} \quad (4)
\]

If the density of the solvent is 0.7 g/mL, then this is equivalent to \(6.7 \times 10^{-9}\) g/g or 6.7 ppb (w/w).

The above calculation leaves out one significant factor and that is the data rate used. Suppose the MDL is specified at a data rate of 5 Hz. This data rate is appropriate for peaks that are between 1.5 s and 3 s wide at half height. These peaks will have from 15 to 30 data points across them from baseline to baseline.\(^2\) This provides the chromatographer with the ability to detect peak shape problems while it delivers the best minimum detectable level for those peaks and excellent area and retention time (RT) repeatability. More data points increase the noise without adding information. For our example peak, 5 Hz is the correct data rate and no further correction is needed to estimate minimum sample concentration from the MDL. If the peaks become four times narrower, the data rate should be increase to 20 Hz. The peak height will be four times what it was before and the noise will increase as the square root of the ratio of the data rates:

\[
\frac{\text{Noise (20 Hz)}}{\text{Noise (5 Hz)}} = \sqrt{\frac{20}{5}} = 2 \quad (5)
\]

Thus the S/N for the same sample amount will increase by a factor of \(4/2 = 2\). This means that the sample concentration that gives a minimum detectable peak is 2.35 pg/µL. Similarly, chromatography that produces wider peaks will result in higher minimum detectable sample concentrations because the noise decreases more slowly than the peak height. The effect of changing the chromatographic conditions (and thus peak width) is given by:

\[
\frac{S_1/N_1}{S_2/N_2} = \frac{\text{width}_2}{\text{width}_1} \quad (6)
\]

This assumes that the data rate is changed as the peak width changes. This relationship can be added to our calculation for sample minimum concentration:

\[
c_i = \frac{A}{Hv} \text{MDL} \sqrt{\frac{\text{analysis data rate}}{\text{MDL data rate}}} \quad (7)
\]

\(\text{For a Gaussian peak, if } t_b \text{ is the RT and } w_{1/2} \text{ the width at half height, then 98% of the peak area will be contained in the time window from } t_b - w_{1/2} \text{ to } t_b + w_{1/2}. \text{ The signal at } t_b + w_{1/2} \text{ will be 2.5% of the peak height higher than the baseline value. If } A/H \text{ is chosen as the peak width measure, then the window from } t_b - A/H \text{ to } t_b + A/H \text{ will contain } \approx 98\% \text{ of the area and the signal will be } \approx 2\% \text{ of the peak height above the baseline value at the time } t_b + A/H.\)\\

\(1\) The effective volume injected is given by:

\[
v_e = \frac{v}{1 + SR}\]

where \(v\) is the volume injected and SR is the split ratio.

\(2\) For a Gaussian peak, if \(t_b\) is the RT and \(w_{1/2}\) the width at half height, then 98% of the peak area will be contained in the time window from \(t_b - w_{1/2}\) to \(t_b + w_{1/2}\). The signal at \(t_b + w_{1/2}\) will be 2.5% of the peak height higher than the baseline value. If \(A/H\) is chosen as the peak width measure, then the window from \(t_b - A/H\) to \(t_b + A/H\) will contain >98% of the area and the signal will be <2% of the peak height above the baseline value at the time \(t_b + A/H\).
It should be remembered that this represents the concentration at which a 1-µL injection will give a peak that is twice higher than the noise. For accurate quantitation, the peak usually needs to be at least four to five times larger than the MDL.

A detector specified by S/N ratio for a given amount injected can be easily compared to one specified by MDL using the above calculations. The FID in our example would give S/N = 2 for 4.7 pg injected when the peak was 2 s wide and detected at 5 Hz. If another FID were specified as having S/N = 20 for 50 pg, then one could see that the performance is very close with the first having S/N = 20 at 47 pg. However, this would only be a valid comparison if the peak widths were similar. If the second FID were tested with a peak that was significantly different, the S/N value would need to be adjusted to take that into account.

The calculation for concentration detectors includes a flow term. This flow is the total flow through the detector and includes the column flow and any makeup flow. Because of the unique design of the Agilent Technologies TCD, the detector flow also includes some of the reference flow. The detector flow for this TCD can be approximated by:

\[ F_{\text{COR}} = \frac{0.4}{60} (F_{\text{MU}} + F_{\text{COL}} + F_{\text{REF}}) \left( \frac{T_{\text{DET}}}{T_{\text{AMB}}} \right) \] (8)

Here \( F_{\text{COR}} \) is the flow through the detector cell in mL/s, \( F_{\text{MU}}, F_{\text{COL}}, \) and \( F_{\text{REF}} \) are the makeup gas flow, column flow and reference flow respectively in mL/min, and measured at room temperature, \( T_{\text{AMB}}. \) \( T_{\text{DET}} \) is the detector temperature. Both temperatures are in degrees Kelvin.

When the detector cell volume is much smaller than the peak volume,\(^3\) the minimum sample concentration that can be detected is given by:

\[
c_i = 2 \left( \frac{400 \text{ pg/mL}}{1 \mu L} \right) \left( \frac{0.4}{60 \text{ s/min}} \right) (40 \text{ mL/min}) \]

\[
= \frac{(273 + 300) ^\circ K}{(273 + 25) ^\circ K} \left( \frac{5}{5} \right) \] (10)

\[
= 410 \text{ pg/µL} = 0.41 \text{ ng/µL} = 0.41 \mu g/mL
\]

For the solvent in the FID example, this can also be expressed as 580 ppb (w/w).

Since many TCD samples are gas samples, it is also useful to calculate the minimum sample concentration for those samples. The process is similar, but the usual concentration units are mole percent or ppm (v/v or mole/mole). The total number of moles injected can be calculated from:

\[
n = \frac{pV}{RT} \] (11)

Where:
- \( p \) is the sample loop pressure in atmospheres
- \( V \) is the loop volume in mL
- \( T \) is the sample temperature in °K
- \( R \) is the ideal gas constant, 82 mL-atm/mol-°K.

The minimum detectable concentration (in pmol/mL) is obtained by dividing the MDL by the molecular weight of the analyte. It should also be noted that the large sample volumes (0.1–2 mL) may require the use of relatively high sampling flows to avoid excessive peak width due to sample load time. For packed columns, the carrier flow rate is usually sufficient: for capillary columns, use of a split inlet with appropriate split ratio can maintain peak efficiency but at a cost of sensitivity. Two examples are given.

1. Packed column, 30 mL/min column flow, 1 mL sample loop, propane sample (44 g/mol), makeup gas (MUG) = 2 mL/min, Ref = 45 mL/min, detector at 200 °C, peak width (half-height) 20 s, sample loop at 25 °C, 1 atm. With this wide a peak, the data rate can be set to 0.5 Hz which is 1/10 of the original data rate.

2. Capillary column, 2 mL/min, 1.0 mL sample loop, propane sample, split ratio = 20, MUG = 6 mL/min, Ref = 15 mL/min, detector at 200 °C, peak width 4 s, sample loop at 25 °C, 1 atm. A suitable data rate for this peak is 2 Hz or two-fifths of the original data rate.

\( ^3 \) Peak volume ~ 2(\( V_{\text{COR}} \))\( F_{\text{COR}} \). For our example, this is about 5.3 mL (>3.0 µL cell volume)

\( ^4 \) This is with He carrier/detector gas and a 5 Hz data rate. The TCD responds to the difference in thermal conductivity between pure carrier gas and carrier gas with analyte. If the compound under test has a thermal conductivity significantly different from propane or if a different carrier gas is used, the MDL will be different.
Using the relationship:
\[
\frac{\text{mol C}_3}{\text{mol injected}} = \frac{[R] / [T_e] / [\text{MDL}]}{w_{1/2} / v_e / \text{molecular wt C}_3} \cdot F_{\text{COR}} \tag{12}
\]

one gets for each case:

1. Minimum sample mole fraction C\(_3\) =

\[
\frac{[82 \text{ mL}]}{\text{mol}^2 \text{K}} \cdot \frac{[298 \text{ °K}][400 \text{ pg}]}{\text{mL}^2} \cdot \frac{10^{-12} \text{ g}}{\text{pg}} \cdot \frac{0.5 \text{ Hz}}{5 \text{ Hz}} \cdot \frac{0.81 \text{ mL}}{\text{s}} = 1.1 \times 10^{-6} = 1.1 \text{ ppm}
\]

2. Minimum sample mole fraction C\(_3\) =

\[
\frac{[82 \text{ mL}]}{\text{mol}^2 \text{K}} \cdot \frac{[298 \text{ °K}][400 \text{ pg}]}{\text{mL}^2} \cdot \frac{10^{-12} \text{ g}}{\text{pg}} \cdot \frac{2 \text{ Hz}}{5 \text{ Hz}} \cdot \frac{0.26 \text{ mL}}{\text{s}} = 3.0 \times 10^{-6} = 3.0 \text{ ppm}
\]

The higher minimum sample concentration with the capillary system comes not from the relative detector sensitivity, but from the fact that the effective injection volume is about 0.05 mL versus 1 mL for the packed column. This is necessary to avoid peak broadening due to the sample loading time. The user can trade off sample volume, DLs, peak width, and resolution to optimize his analysis. Again, narrower peaks usually give lower DLs (better sensitivity). With a concentration detector, however, the flow term must be considered when using higher flows to decrease peak widths.

Calculations of minimum sample concentration from a specification should be used as a guideline and for comparison purposes. The detector specifications are developed for systems in controlled environments with conditioned columns and clean gases. There will be variations in the achievable results based on the quality of gases, cleanliness of the gas supply system, the amount of column bleed, and the nature of the sample components.

**Detector Dynamic Range**

The second important detector specification is its dynamic range. This measures the effective sample concentration range over which the detector can be used. See Figure 3. In this range, the detector response monotonically increases with concentration. Eventually some concentration is reached beyond which the detector is “saturated” and the response no longer increases (or may even decrease) with increasing concentration. Dynamic range is usually defined as the ratio of this maximum sample concentration to the sample concentration that represents the MDL.

A variation on this is the linear dynamic range. Over this concentration range, the detector response per sample amount injected is constant. If a deviation range is given, this is usually the maximum and minimum deviation from the average response. Detectors like the FID and TCD are usually very linear in their response. Other detectors are not as linear, often due to the physics of the response mechanism. The flame photometric detector (FPD) responds to \(S_2^-\) so the area is more linear with the square of the concentration of sulfur compounds. The Agilent \(\mu\)ECD is especially designed to have a linear response even though the response is not intrinsically linear. If the response is not linear, the detector should be calibrated at several concentrations and calibration curves generated from this data should be used to calculate amounts from areas.

Often manuals or data sheets provide plots of area versus injected amount. Because of the large dynamic ranges available, these usually use logarithm scaled axes. Unfortunately, this scaling can make non-linear data appear to be linear. Data is only linear if the slope of the line is 1. A better way to present the data is to plot response/amount (area/gram, for example) on the y-axis and amount on the x-axis. The x-axis can be scaled logarithmically. Figure 3 illustrated the results of the first approach and Figure 4 shows the same data plotted as response/amount versus amount. Clearly, more detail is available from the second plot.

![Figure 3. Plot of area versus amount with both axes scaled logarithmically. The fall off in response at high concentrations is apparent but the rest of the data appears linear.](image-url)
Standard methods for measuring the detector dynamic range often involve connecting the output of a dilution system directly to the detector and monitoring the response with changing concentration. This measures the actual detector dynamic range. A more practical approach involves injecting samples of different concentrations onto the column and measuring the peak area for each concentration level. This is a more practical approach because it does not involve special apparatus and it is more representative of the actual lab practices by which samples will be analyzed. Analysts using capillary columns may actually find that their practical dynamic range exceeds the specified range. This is because the column overloads at the higher concentrations so the peaks broaden, and the maximum concentration reaching the detector for a given sample amount injected is less than it would be without this phenomenon. Of course, the peak broadening significantly reduces the resolution achievable for the separation and also causes large deviations in RTs. In evaluating the suitability of a separation, the analyst will want to test the method with samples that span the expected concentration range to be sure that the separation remains adequate and that the detector response remains in the appropriate range. At times it may be necessary to change to a higher capacity column or to increase the split ratio or the sample dilution. These remedies for the high concentration range often cause the MDL to increase, so compromise may be necessary. With adequate resolution between peaks, a wide dynamic range detector like the FID can actually quantify an impurity peak at 20 pg/nL and the solvent peak (typically about 0.7 mg/µL for hydrocarbons). This represents a useful dynamic range of $3.5 \times 10^7$. This does require a digital data path that can handle the full dynamic range and a data system that supports that kind of data.

**Selectivity**

The final detector attribute that must be examined is selectivity. This is used to describe what kind of chemicals the detector responds to and how well it ignores other compounds that might interfere. In gas chromatography, detectors are available that demonstrate a wide range of selectivity. Some are essentially universal and respond to all species. The TCD, mass selective detector (MSD) and the helium ionization detector (HID) are examples of universal detectors. The response can vary with compound, but usually not by more than a factor of 10 to 100. The FID responds to almost all organic compounds. Organic molecules without CH$_2$ units (such as formic acid or carbon tetrachloride) do not respond well, but they are exceptions. The FID with its wide linear dynamic range and relatively high sensitivity is a compelling detector for analysis of many organic compounds. It does not respond to non-organics, so things like air peaks are not seen. Other detectors are used because they are selective and respond only to some sample components. The ECD responds to compounds that capture electrons. The relative responses can vary. Simple aromatics are relatively poor responders while highly nitrated or chlorinated compounds generally respond very strongly. Other detectors respond to specific elements in the eluting molecules. The FPD responds to P or S and sometimes As (depending on the filter installed). The nitrogen phosphorus detector (NPD) responds to most N and P containing organic compounds. In addition, the MSD can be run in a mode that allows it to respond only to ions of specific mass to charge ratio. This mode converts it from a universal detector to a selective detector.

Selective detectors often show superior sensitivity as well as selectivity. This makes them especially attractive for determining low concentration components in complex matrices. Sample preparation time may be reduced when the compounds of interest respond to one of these detectors while the major matrix components do not.

Selectivity is usually measured as the relative response for one compound (or element) versus another compound. Usually a hydrocarbon such as octadecane (C18) is chosen to represent the response to C. For element specific detectors, a compound that contains the element(s) of interest

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**Figure 4.** Plot of area/amount vs. area. The amount axis is scaled logarithmically. The average value of area/amount was calculated excluding data for the highest amount. This data indicates that this detector is linear over a range of $3 \times 10^4 \pm 17\%$. 

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is chosen. For the NPD, for instance, Agilent uses malathion as a P-containing compound and azobenzene as a compound containing N. A sample containing known amounts of azobenzene, octadecane and malathion are injected. The concentration of octadecane is much greater than the other components. The selectivities are calculated from:

\[ \text{Selectivity (P/C)} = \frac{\text{Area}_{\text{malathion}}}{\text{Area}_{\text{octadecane}}} \frac{[\text{mass}_{\text{malathion}}][\%P_{\text{malathion}}]}{[\text{mass}_{\text{octadecane}}][\%C_{\text{octadecane}}]} \]  

(15)

\[ \text{Selectivity (N/C)} = \frac{\text{Area}_{\text{azobenzene}}}{\text{Area}_{\text{octadecane}}} \frac{[\text{mass}_{\text{azobenzene}}][\%N_{\text{azobenzene}}]}{[\text{mass}_{\text{octadecane}}][\%C_{\text{octadecane}}]} \]  

(16)

The FPD selectivity can be determined in a similar way. It should be noted, however, that the S selectivity is based on peaks that are separated. This does measure the relative response of S versus C, but it does not address the phenomenon of quenching. S response requires a reaction in the flame to form excited \( S_2 \). This species then emits the light that is detected. This process is quenched by high concentrations of hydrocarbons so the selectivity measures the difference in signal for S versus C molecules independently. Coeluting C molecules will effectively decrease the sensitivity to S. This is true for a pulsed FPD as well as conventional ones.

There are no standards on what compounds to use for testing selectivity. Generally they need to be representative of typical compounds in their class, relatively stable, and well behaved chromatographically.

**Detector Specification for the Agilent 6890N GC**

Sensitivity, selectivity and linearity are very specific measurements, specific to the individual instrument used, the chromatographic method, the analyte and to some extent, the operator. When translated to an instrument specification, the meaning is somewhat modified as it now applies to an entire population of instruments, not one instrument, performing one method, in one laboratory. Agilent uses the noise and signal calculations previously described to measure the DLs of many instruments using the same detector type. The specification for that detector is then set at a level high enough over the average to ensure that every single instrument and detector that arrives at a customer site is able to achieve the specification. This results in a very conservative specification but one that is also achievable with all instruments.

**Conclusions**

Understanding detector specifications and knowing how to relate them to the specific analysis to be performed is an important part of assuring that a gas chromatographic system will be suitable for the analysis. Sensitivity specifications should be detector response unit independent and should relate to the S/N ratio of the detector. The test compound and the data rate should be given. If the dynamic range is claimed to be linear, some indication of how much the response/amount varies over the entire range should be available. Selectivity values should reference the test compounds used.

Although the specification guide may be simplified, the manufacturer should be able to provide detailed procedures describing how the tests were run. These can be used to understand differences in the ways specifications are written and how the specification can be applied to a specific sample or analysis.

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