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Target Compound Analysis

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OPTIMIZE

TARGET COMPOUND ANALYSIS

Introduction and Objective

We sometimes lose sight of the fact that all of that QC information really is in support of our main task as GC and GC/MS analysts: the generation of high quality data reports. When you think about it - clients bring samples to labs for two pieces of information: what environmental pollutants exist in this sample (qualitative analysis) and how much of such pollutants are present (quantitative analysis). All of the supplemental information contained in data packages (the QA/QC section) is only meaningful if the “what and how much” information is accurate. I have seen many a lab whose data package contains 100% passing surrogates, spikes and internal standards, but whose data was wrong because the analysts did not know how to reduce and interpret data. They reported analytes that weren’t present (false positives) and failed to report analytes that were present (false negatives).

The problem with data interpretation is that you can’t give “cut and dry” instruction on how to do it. By its definition, it’s interpretive - i.e. certain guidelines can be given to interpret the data but ultimately the results reported by the lab boil down to the technical opinion of the GC/MS analyst or data reviewer.

In this issue I’m going to give my recommendation for the guidelines when performing both target and non- target compound analysis.

Think of the data interpretation as 4 separate processes as follows:

1. Qualitative analysis of target compounds (i.e. which target compounds are present?)
2. Quantitative analysis of target compounds (i.e. how much is present?)
3. Qualitative analysis of non-target compounds (i.e. which non-target compounds are present?)
4. Quantitative analysis of non-target compounds (i.e. how much is present?)

I’ll give you the guidelines I use for doing these 4 tasks. Before we begin, let me say that there are really two “mistakes” that data interpreters/processors should guard against:

- False positives - reporting compounds that aren’t really present
- False negatives - failure to report compounds that are really present

Should either of these two mistakes occur, all of the QC in the world won’t atone for it. This is a far bigger mistake than what labs usually guard against - which is worrying about minimal differences in quantitation. Many labs consider data to be good because % RSDs in their curves are low but, in actuality, this isn’t that big of a deal…or at least it shouldn’t be. Yes, you want linear curves but does it really matter if you report Naphthalene present at 50 ppb and it’s really 40 ppb? Isn’t it far more important that you were actually able to detect Naphthalene in the sample rather than missing it? I feel it is far better to be able to detect what is (and what isn’t) in the sample than get hung up on getting your % RSDs from 15% to 10%. This is just my opinion.

Sometimes, after what I call “due diligence” (i.e. a thorough, systematic and technically sound approach to data interpretation), two equally competent mass spectroscopists may arrive at different conclusions. For example, let’s say you have a complex matrix which yields a “busy” chromatogram (i.e. many non-target compounds). You suspect that a target analyte has co-eluted with a non-target compound. You review the data and determine that the target analyte in question is indeed present and you report it. Your co-worker, just as competent as you, reviews the same data and concludes that the target analyte in question is actually absent and hence should NOT be reported. In his mind, you have reported a false positive, because the target analyte isn’t present. However, since you have done “due diligence” and provided you have data to support your conclusion, then all that exists in an honest difference of opinion and not necessarily a false positive.

Using Enviroquant

Firstly, what is Enviroquant? Enviroquant is a set of macros (Agilent programs - or more specifically a list of commands) designed to automate environmental analyses. Purchasers of the Agilent Chemstation who do not perform environmental analyses oftentimes skip loading the Enviroquant module entirely. If Enviroquant is set up optimally (I love the word “optimize” and all of its derivatives), it will help the analyst quantitate faster and more accurately as well as assist in qualitative analysis. This will free up the analyst to perform the interpretive work.

Loading the Method You Want All the Time

OK - Let's assume you've opened up EDA (Environmental Data Analysis) by double clicking the EDA icon. You have the choice of either having the last method that was accessed loaded or some other default method that will load all the time.

To have the last method that was accessed loaded, proceed as follows:

File\EDA Configuration...brings up a dialog box and you click "Automated Method/Data file"

Thus, when you open EDA it will automatically load the last method and the last data file that was accessed.

If you want some other default method that will load all the time, then you have to single right click the EDA icon on your desktop. Then left click "Properties". Look in the box labeled "target". You will see in that command line something like the following:

C:\HPCHEM\MSEXE\MSDA.EXE 1 ,envorphinit 'C:\HPCHEM\1\methods\envdef.m', envinit.mac

Replace whatever file is listed with the .m (stands for method) with the method you want. For example, if you always process using method called ecsbna2.m, then replace just that portion in the runstring as follows:

C:\HPCHEM\MSEXE\MSDA.EXE 1 ,envorphinit 'C:\HPCHEM\1\methods\ecsbna2.m', envinit.mac

What to Do if the Y Axis Scale is Not Legible

On some systems, when you draw a total ion chromatogram, the Y axis will sometimes be truncated because the default font in the Agilent software does not fit properly on the screen. To remedy this, you need to change the font. In the command line (the command line is the white space just below the lime green strip at the bottom of the screen) type the following:

FONTAXIS="COURIER"

The word COURIER should appear in the lime green bar to indicate that Courier is now the font being used. The click Int\ Draw Chromatogram and it will redraw the chromatogram using the courier font which fits nicely on the screen. Your graphics printouts will also have the courier font. During your data processing, the font may revert to the default, so simply type the above command and redraw the chromatogram and you will correct the problem. After you type FONTAXIS="COURIER" in the command line, you can highlight it by clicking and dragging then hitting CNTL + C (control C, which means copy) then, rather than retyping FONTAXIS="COURIER", you can hit CNTL + V (control V, chich means paste).

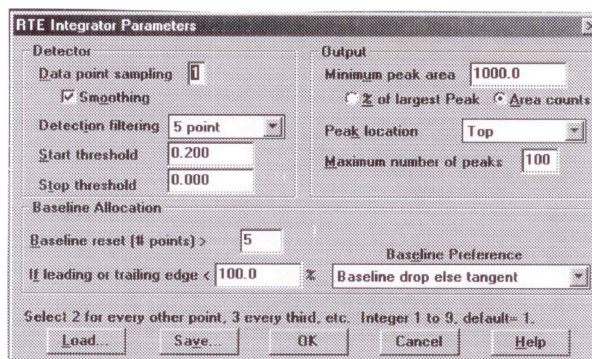
Understanding the RTE Integration Parameters

One of the most useful features of Enviroquant if that is the integration parameters and other settings, which we will discuss, are optimized, the software can quantitate and properly identify every analyte on your target list with no manual integrations necessary. In fact, when I set up mass spec methods during my consulting years, I wouldn't rest until every compound in all 5 points could be integrated and properly identified without any manual integrations or # signs.

The # sign means that the ion qualifiers are out of specification.

The first thing you have to do is set the default integration settings in RTEINT.P. Later on I will show you how to make every compound specify that integration file (or any other file you desire).

Click on Int\Integration Parameters and it will open a dialog box like the one below:



Settings that Ferry considers essential:

- Data point sampling: you see the number 1 in the box above. That means the system will include every point when integrating. If a number 2 were entered, it would use every second point when integrating. I use a setting of 1 for this parameter because, in my experience, it has been the most reliable.
- Smoothing: when checked, a smoothing algorithm is applied to help improve the ability to integrate the whole peak. I always activate the smoothing feature because, in my experience, it does indeed help to improve the integration.
- Detection filtering: it can be set to 5 point, 7 point, or 9 point. The lower the point setting, the more likely they system is to separate shouldered and unresolved peaks into two separate peaks rather than one larger peak. I use a setting of 5 point for this parameter because, in my experience, the other 2 settings seldom integrate the way I want them to integrate.

- Start threshold: it's also called the slope sensitivity. The range is from 0.001 to 100. The default is 0.200. Like the detection filtering, it is used to separate shouldered and unresolved peaks into two separate peaks rather than one larger peak. I have found two settings very useful:

  0.200 often separates shouldered and unresolved peaks into two separate peaks

  0.020 often integrates shouldered and unresolved peaks as one peak

  Obviously with a range of 0.001 to 100 we could spend all year discussing the options but the 0.200 ot 0.020 choices have worked well for me in the past.

- Stop threshold: the range is from 0 to 100. The default is 0. The larger the number, the more efficient the integration routine is in picking up area at the end of a tailing peak. If your peaks are Gaussian (symmetrical), then set it to 0. If you have a few peaks that tail, then a setting of 10 often works and you can write a custom integration file with a large stop threshold just for those peaks.

- Minimum peak area. I see no sense in using the "% of largest peak" setting. Instead, look at your low level standard areas and pick an area count setting commensurate with that.

The All-Important INIT CAL Menu

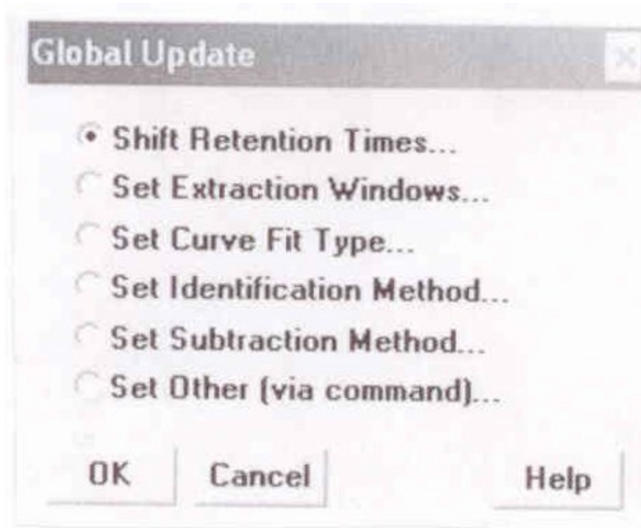
Next I will address techniques to streamline the calibration process. I have seen instances where if the previous calibration responses aren't cleared than the recalibration process will glitch. Here is a sure fire way to be sure the system is recalibrated properly.

1. Load your method
2. Load the mid-level standard (let's assume it's 50 ppb for illustration)
3. Calculate and generate report to the screen
4. QEDIT to ensure proper integration and peak identification. Whenever possible, you should write custom integration files as needed to properly integrate all compounds so as to minimize the need for manual integration.
5. Init Cal/Clear Calibration Responses (NOT clear calibration levels)
6. Init Cal/Update Levels (update retention times, responses and ion qualifiers)
7. Calculate and generate report (you should get exactly 50 ppb with a Q value of 100 for every analyte - if not, repeat steps 3 through 7). Verify that any isomers haven't been misidentified (i.e. the xylenes, dichlorobenzenes, etc).

   This is a key step because if you have a perfect single point with retention times and ion qualifiers updated and all other responses cleared out, it paves the way for the other calibration points to be added systematically and properly.

   Note that you update retention times and ion qualifiers with the mid-level point only. All other points are used solely to update responses.
8. Load each of your other points.
9. Calculate and generate report
10. QEDIT to ensure proper integration and peak identification-manually integrate as needed or better yet write a customized integration file for any compound that Enviroquant cannot integrate properly on its own.
11. Init Cal/Update Levels (update responses ONLY)
12. Repeat steps 8-11 for all remaining points
13. Init Cal/Response factors to printer
14. Save method

Next I'm going to discuss the Global Update Dialog box, which is a powerful feature of Enviroquant that I seldom see used by most analysts. Click Init Cal/Global Update. **It brings up the following dialog box whose settings will be used globally (i.e. in EVERY compound). If you want to change the global setting for specific compounds, you have to do that manually**



The Shift Retention Times entry is almost never useful so I won't waste any time addressing it.

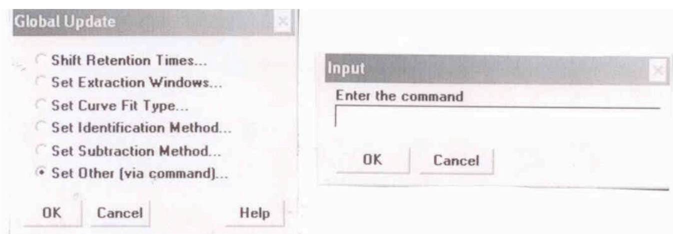
The Set Extraction Windows is a very useful parameter especially if you have installed a new column or are developing a method. By setting the extraction window wide it can help the system locate peaks when the retention has changed. For normal situations, when the retention times are known and constant, I use a setting of 1 min.

For Set Curve Fit you usually use "Averaged Response Factor" but some regulatory agencies allow other curve fits.

For Identification Method you usually use "meets qualifiers, best RT". In fact, I use that 100% of the time because I've never seen where any of the others do a better job at peak recognition.

For Subtraction Method you usually use "No Subtraction" but in some cases Extended are quant works better especially if you have irregular peak shape (Benzoic Acid for instance).

That brings us to the last entry "Set Other (via Command)". Here's where you need to know the commands and variables in order to use this feature. I will tell you the 4 commands that I think you will find most helpful. See the dialog box below:



= =

Command: Amt_Units$

What it does: Sets the units of concentration that appear on the quant report

How to use: Type the following in the box:

Amt_Units$ ="ug/L" to have ug/L appear.

Other examples are Amt_Units$="ng/uL" or Amt_Units$="ppb" This setting is case sensitive. Remember to use the quotation marks.

= =

Command: Unc_tp

What it does: Sets the % window for ion qualifier to either absolute or relative

How to use: Type the following in the box:

Unc_tp=0 (sets the % to relative)

Unc_tp=1 (sets the % to absolute)

For example, let's say the compound is 1,4-Dichlorobenzene. The quant ion is 146 and Qualifier #1 is ion 148 at 72% and Qualifier #2 is ion 111 at 40%. But you have to allow a certain window. You're not going to get exactly 72% of ion 148, you will get about 72%. So, you can either set the window to absolute or relative. If you use 20% absolute, for example, the window would be 52-92%. If you use 20% relative, the window would be 58-86 (20% of 72=14 so the window is plus/minus 14).

I suggest that you ALWAYS use relative percentage. The reason being is that by using relative percentage, the software sets the window to an appropriate range based on the size of the qualifier. I like to use 50% relative. So it takes the expected % and sets the window 50% below to 50% above.

Examples:

Qualifier ion % relative to Quant ion	Window used in RELATIVE setting
80	40%-120% of quant ion
50	25%-75% of quant ion
20	10%-20% of quant ion
10	5%-15% of quant ion

As you can see, the window widens and shrinks in an appropriate manner commensurate with the Qualifer ion % relative to Quant ion. Another benefit of the relative setting is that the window can NEVER include a negative number. Take those same 4 ions and let's examine the window if a 20% absolute window is used.

Qualifier ion % relative to Quant ion	Window used in ABSOLUTE setting
80	60%-80% of quant ion
50	30%-70% of quant ion
20	0%-40% of quant ion
10	-10%-30% of quant ion

As you can see, the smaller ions include 0 and even negative numbers at the low end of the range! This is illogical and thus should NEVER occur in your method. Stick with RELATIVE setting and your ranges will always be correct.

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Command: Q1_Pu, Q2_Pu, Q3_Pu - qualifier ion uncertainty in %

What it does: sets the % window for each qualifier ion

How to use: Type the following in the box:

Q1_Pu=XX (sets the % uncertainty to XX%)

Examples:

- Q1_Pu=50 (sets the % uncertainty of Qualifier
#1 in all compounds to 50%)

- Q2_Pu=60 (sets the % uncertainty of Qualifier
#2 in all compounds to 60%)

- Q3_Pu=50 (sets the % uncertainty of Qualifier
#3 in all compounds to 50%)

Note: You must do each qualifier separately as a separate command.

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Command: TgtEvents$ - target ion integration mode

What it does: sets the target integration events file for all compounds

How to use: Type the following in the box:

TgtEvents$ =”rteint.p” to have rteint.p as the integration file for all compounds. To check to see if done correctly, go into Init Cal\Edit Compounds. Check out any compound. Go to page 3. Look at the bottom left of the screen and you should see rteint.p entered under Integration Parameter File next to Tgt. Remember to use the quotation marks.

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Below is an example of a properly set Page 1.

Name 1,4-Dichlorobenzene Concentration Units ng/uL

Retention Time Information

Ret Time 10.000

Extract signals from

- 1.000 + 1.000 Min %

This is 9.000 to 11.000 min

Ref Spec Name SAV11

Signals to Be Used for Quantitation

Quant signal Target Ion

	m/z	Relative Response	% Uncert Rel
Tgt	146.00	100.0	
Q1	148.00	71.70	50.00
Q2	111.00	39.50	50.00
Q3	75.00	40.00	50.00

Quantitation Parameters

Quant type Target compound

Measure response by Area

Ident by Meets qualifiers, Best RT

Maximum number of hits 5

Subtraction No subtraction

Calibration Information

Curve Fit Avg of Response Factors

Linear term:

RF Rel Std Dev:

Prev Next Plot Page 2 Page 3 OK Cancel Help

NOTE: If the system cannot detect a compound, DO NOT arbitrarily drop the small ions. This is a terrible way to force the system to detect compounds. If the system cannot detect small ions the way it should, you should find out why and correct it. This is a troubleshooting issue, not a software issue!

What to do if the system cannot find and properly integrate a peak and how to create a custom integration file for a specific compound

1. Use INT\Ion chromatogram to extract the quant ion
2. Use INT\Load integration parameters to ensure that RTEINT.P is loaded
3. Make the necessary changes to RTEINT.P based on what you learned in this issue
4. Use INT\integrate until it integrates properly
5. SAVE as " .P" (specify name here)
6. Enter this newly created file on Page 3 of INIT CAL\EDIT COMPOUNDS
7. Go to the apex and double right click - a spectrum appears
8. Type "NORM 100" [RETURN]
9. Type TAB [RETURN]
10. Write down which qualifier ions you wish to use and their percentage and enter that information on Page 1

The CON CAL Menu

The only point I wish to make here is that EACH TIME you run a CCC/SPCC Cal check, you should update the reference spectra. It takes but a minute and is accessed by:

Con Cal\Update Reference Spectra

Quantitating and Reviewing Data

Next let's consider the finer points of the Quant menu bar. I'm sure everyone is familiar with "Calculate and Generate Report" and "Generate Report". But let's look at "Edit Quant Report Options". Look on the bottom right corner of the screen and you will see the following:

Omit Target Compounds that:

- are missed
- have qualifiers out of range

If the "are missed" box is checked off, the quant report will omit, entirely, the names of compounds that were not found. If the "are missed" is unchecked - it will list the compound name and the term "N.D." , for not detected, on the quant report.

If the "have qualifiers out of range" box is checked off, the quant report will omit, entirely, the names of compounds that were found but with ion qualifiers out of range. If the "have qualifiers out of range" box is unchecked - it will list the compound name and then flag such compounds with qualifiers out of range on the quant report with a # sign.

Here's how I use these boxes:

For standards, I expect every compound to be present, so I leave both boxes UNCHECKED. That way if a compound is missed I can easily tell by scanning the quant report for an "N.D." flag. If a compound has ion qualifiers out, the quant report flags it with the # sign so I can correct the problem and requant until ALL compounds are found with NO # signs. For samples, I CHECK both boxes because if the compound is not found or has outlying qualifiers, then I want those compounds left off of the quant report entirely. Some analysts like to CHECK the "are missed" box and UNCHECK the "have qualifiers out of range" box because if the software finds the quant ion of a compound but has qualifiers out, they like to look carefully at the peak in QEDIT and decide for themselves if it is a hit or not. Whatever you choose to do is your own prerogative, I am merely pointing out the options available.

I just mentioned QEDIT in the last paragraph. Let's discuss this feature in detail. You will probably spend more time using QEDIT in the data reduction part of your analysis than any other part of Enviroquant so it is important to know how to use if efficiently. After you have calculated and generated a report, you may QEDIT the data. Click Quant\QEDIT Quant Result to load the QEDIT menus.

At this point, Quick QEDIT should load automatically. It will be a box containing a list of target compounds and should be visible at the top right-center of the screen. It puts an "X" mark next to the target compounds that were found. If Quick QEDIT does not automatically load upon entering QEDIT, you can load it manually by clicking QEDIT\Restart Quick QEDIT.

Here's a tip that may very well save you from getting carpal tunnel syndrome. Let's say you run a standard and want to scroll through every compound for a few seconds ensuring proper identification of isomers and complete integration (a good idea to do especially

when changing flows, columns, or anything else that might cause retention times to shift or peak shape to change). You could double right click the bottom right hand box (the one that lists the compound, RT, area, and ions) and go from compound to compound that way. Of course, that can get very tedious. An easier way would be to click on the CONFIGURE box at the top of Quick QEDIT. That opens a dialog box that allows you to input the number of seconds that will elapse in between each compound as the system scrolls through each one for you. You can stop the automatic timed scrolling anytime by clicking STOP and then resume it by clicking START. I love this feature especially when doing method development. The Quick QEDIT also allows you to QDEL (delete) a compound with a click of the mouse. Once done, click EXIT - the software will confirm that you want to SAVE the changes you made in QEDIT (e.g. re-integrations or re-identifications) and then exit back into the main Enviroquant menu.

If you make changes and then decide you want to go back to the original data, click QEDIT\Abort Changes and Exit.

If you want to display the reference spectra in the bottom left hand box, click Spectrum\Display Reference Spectra. The reference spectrum for each compound, as obtained when you clicked Con Cal\Update Reference Spectra (mentioned previously), will appear underneath the sample spectrum at the bottom left.

Interpreting the Data After the Run Has Been Made

OK - so how do we go about determining what is present in a sample? First, let me say that we're not always 100% sure a target analyte exists - generally we refer to the confidence as being in the 95%-99% level. This means we are 95%-99% certain that this compound exists. Can we ever be 100% sure? Theoretically not, so the maximum certainty can be expressed as 99%. Maybe if a client tells us that some compound is known to be present, and we are confirming the presence of an analyte, then we can say we are 100% sure. But for this discussion, let's say that when we report an analyte we are somewhere in the 95%-99% confidence range, with our confidence being higher in clean matrices where matches between unknowns and knowns are better than in complex matrices.

Let me give you a checklist of what to do in qualitative analysis of target compounds. But first, before you process any samples, you must do the following:

1. Pass tune check

2. Run your check standard

3. Run your method blank

After running your check standard, you should immediately do the following:

- Update retention times
- Update ion qualifiers
- Update reference spectra

The interpretation of subsequent data is predicated on having the system updated for these 3 items immediately after the check standard has been run. After you run your blank, you are then ready to run samples. Let's say you run a sample and your quantitation report lists a hit for a target compound. This tells you that the system has potentially identified a target compound hit and you should check to determine if it is really a hit or not. What factors do you take into consideration when determining if it is a hit or not? I use any and all of the following pieces of information to determine if the compound is truly present.

Q Value

The "Q" value, as it relates to target compound analysis, is a reflection of how closely the ion ratios matched in your unknown sample as compared to what was specified in your compound list. In general, Q values above 80 often indicate a true hit, and Q values below 50 often indicate a mis-hit. Q values between 50-80 are non-confirming and don't tend to indicate a hit or a mis-hit. These ranges are just guidelines. In general, it is better to skew your data reduction routine towards false positives rather than false negatives. In other words, set your peak/base peak ratio wide so that the system is less likely to miss a compound because the ion ratios are not exactly what they were expected to be. Sometimes, in complex matrices, background interferences can skew the Q value and you want to be sure you don't miss reporting a compound. You can always determine that it was a mis-hit during the data review process, whereas, if you miss a compound that actually is present, you may or may not be able to catch that!

You should always specify at least one qualifier ion. For low level PRQL drinking water matrices (Method 524.2 Rev. 4.0) some labs use only the quant ion if the fragmentation pattern dictates so and a high MDL would arise if a qualifier ion were used. An example of this is 1,1-Dichloroacetone, a compound whose mass spectrum yields the following:

ion 43 - 100%

ion 63 - 5%

ion 83 - 5%

ion 48 - 5%

In order to see the qualifier ions, the 1,1-Dichloroacetone must be run at about 5 times higher than it would need to be run at if just ion 43 were used. But I think it is correct to do this.

CAUTION: If you do only use ONE ion (the quant ion) you will get a Q value of 100 since there are no qualifier ions to be out of range. This is BAD and I advise against it.

Relative Retention Time

Why *relative* retention time you may ask? Why not the absolute retention time? Well, in a clean matrix, it doesn't really matter and you can certainly use the absolute retention time of the "suspected hit" vs. the absolute retention time of the compound in the check standard. This works fine for drinking water and other clean matrices where absolute retention times generally deviate no more than 0.05 minutes. But, what about matrices where the contamination may slightly overload the column, creating a rise or shift in the baseline? In these circumstances, the absolute retention time can become shifted and hence become a less reliable means of determining if a hit is true or not. This problem can be corrected by comparing the relative retention time (RRT) of the "suspected hit" vs. the relative retention time of the compound in the check standard. The RRT is the absolute RT of the compound/absolute RT of the ISTD off of which it quantitates. Using the RRT methods corrects for slight RT drift in complex matrices.

Comparison to Reference Spectrum

As was said earlier, data interpretation ultimately boils down to the subjective opinion of the analyst or data reviewer. Although we can use mathematical guidelines such as Q value or RRT, the background corrected spectrum of the hit needs to be visually compare to the background corrected spectrum of the suspected target analyte. This enables you to see the entire mass spectrum of both the unknown and the known side by side. It is difficult to give specific guidelines for this one - you will get good at comparing spectra with experience. Suffice it to say, however, that you shouldn't call anything a "hit" unless you do this visual comparison.

Maximization Check

Here is a cut and dry one (sort of). If a compound is truly present (even in a complex matrix), the quant ion and qualifiers should pass the maximization check. That is, the selected ion profiles of all the key ions should maximize (reach an apex) **at the same scan**. There are two exceptions when this may not happen:

1. The peak shape is not Gaussian (symmetrical). For example, Benzoic Acid fragments into ions 105, 77 and 122. Often, due to the odd peak shape of this compound, will cause these 3 selected ion profiles to maximize at separate scans...often several scans apart.
2. If the compound elutes very close (but not exactly) in retention time with an interfering peak that has one or more of the key ions for that compound, the hit may fail the maximization check. This is because the selected ion profiles are skewed by the interfering compounds, causing them to maximize at different retention times which would then translate into being different scans.

So, although it is not 100% - the general rule is that passing the maximization check tends to support the presence of the target analyte, and failing the maximization check tends to support the absence of the target analyte (subject to the two exceptions listed).

Library Search

This technique can be employed when you suspect that a target analyte is co-eluting with a non-target analyte. For example, your quant report lists a hit with a moderately high Q value of 75. This is in the range where you're not sure if it is a hit or not. You check the RRT of the hit and it is close to the RRT in the check standard. The maximization check passes. But, when you visually compare the reference spectrum of the check standard to the hit, you notice all kinds of background ions present. For this example, let's say the hit was Naphthalene. Your quant ion is 128. Your qualifiers are 127 and 129 at 15% each. In your spectrum you see all three of these ions plus a whole slew of other ions - such as 43, 57, 71, 105, and 119. The 128 is not even the base peak and the 127 and 129 are only about 12% of 128 - a little less than you expected. Well, there are two possibilities here:

1. Naphthalene is present along with one or more nontarget compounds

OR

2. Naphthalene is absent and the 3 ions indicative of Naphthalene coincidentally are from the non-target compound in the ratio similar to what they are in Naphthalene.

The likelihood of situation 2 arising is far less when you specify 3 or more ions (one quant ion and 2 or 3 qualifiers) in your compound list. Well, how can you tell which of these two situations has occurred? One way is to perform a library search of the hit. If the system identifies a compound that has the 3 ions indicative of Naphthalene in the ratio similar to what they are in Naphthalene, then that would tend to support that possibility #2 has occurred. If the system cannot find any such compound other than Naphthalene with those 3 ions in that ration - that would tend to support possibility #1 above.

It is a good idea to use qualifier ions throughout the mass spectrum if possible - at the low mass end, mid mass range, and high mass range.

Overall Nature of the Sample

Your final piece of information is to consider the overall nature of the sample. Look at the other compounds (both target and non-target) to get a "feel" of the sample. If you are unsure as to whether a hit is truly a target compound - consider the likelihood of this compound being present in this sample. Generally, but not always, compounds alike in chemistry are found together. For example, when you find Benzene, Toluene and Ethyl benzene, you find the xylenes. When you find one PAH, you often find others. When you find one halogenated solvent, you often find others. When you find one branched aromatic (e.g. n-propyl benzene), you often find others. When you find one phthalate ester, you often find others, and so on. Also, consider the source of the sample - was it near a solvent reclamation site? Or an underground storage tank? Is it chlorinated municipal drinking water in which all 4 THM (trihalomethanes) might be found? Has your lab analyzed a sample from this site previously so you can compare results? Answers to these questions often are very useful if your qualitative analysis is borderline and you are on the fence as to whether or not to report a sample.

Think of the data processing activity as a puzzle - with all the bits of information and tools you have at your disposal as pieces to the puzzle. Individually, no one thing may confirm or deny a hit - but collectively you get a sense of whether the compound is present or not.

As far as I am concerned, the main thing is to have a systematic, logical, analytically sound approach to target compound qualitative analysis. Even if others may disagree with your opinion, if you've done your "due diligence" and can substantiate your interpretation, then you've done the best you can.

OPTIMIZE

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