

Understanding “Brackish” Integration

► **Introduction:** What is “brackish integration”? Although the main application of this type of peak integration involves the analysis of brackish and saline samples, it can be used for other reasons as well. These include exclusion of area due to baseline noise from the area of the peak being integrated, accommodating samples exhibiting mismatch with the carrier (occurs with digestion methods most often), and of course, in the analysis of saline samples. These situations are discussed in more detail below.

► **Examples:**

Exclusion of noise from the integration:

Figure 1 below is a zoomed in section of the baseline in a trace level method for phenol. **Figure 2** shows the difference in what is integrated with and without brackish integration.

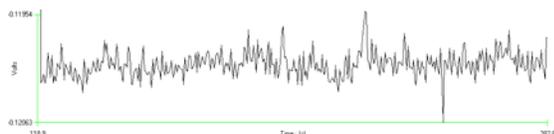


Figure 1: Noise in a baseline

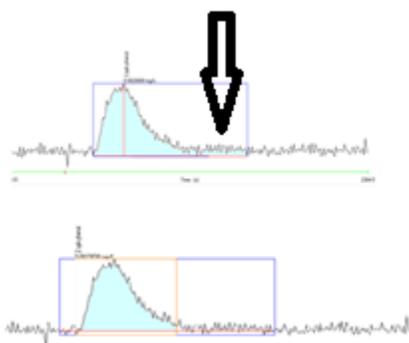


Figure 2: Brackish integration prevents area that is not related to the sample from being integrated. This is not as important for methods with higher analytical ranges, as the contribution from noise is

negligible. But for trace level analyses, this area can be significant- even though it is not due to the analyte.

Sample/Carrier Mismatch. A second situation in which this type of integration is sometimes used is to deal with a sample/carrier matrix mismatch. This situation arises most often in methods involving a digestion. **Figure 3** below shows a peak, obtained with injection of a sample with a sample matrix that does not quite match that of the carrier:

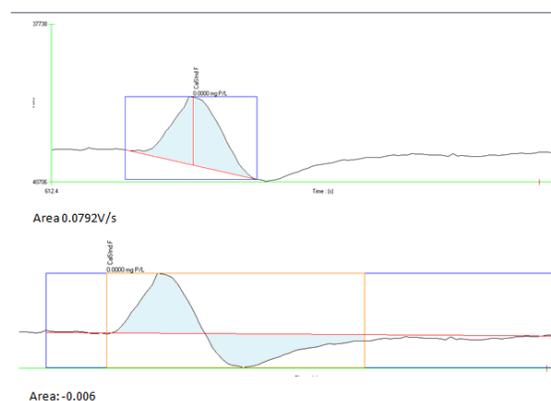


Figure 3: Matrix mismatch

By using the brackish integration feature, area below the baseline of the peak is considered as negative. When added to the positive area, the value is nearly zero.

Brackish/seawater samples. Finally, in the case of brackish and seawater, the existence of a Refractive Index (or RI) when a saline sample is injected into a DI water carrier is actually exploited.

The refractive index that results provides a response that does not comprise a “typical” peak, and where only part of the response produced is related to analyte concentration. **Figure 4** below diagrams this effect when the sample contains no analyte. In this

case, the positive and negative areas are essentially equal:

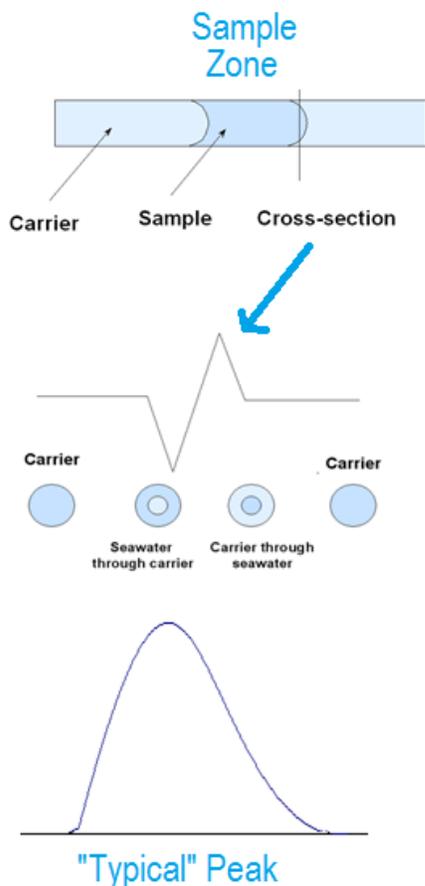


Figure 4: Brackish versus "Typical" FIA peak

Injection of a very large sample volume allows the portion of the peak due to analyte to be seen. Using brackish integration, the non-analyte related dip and peak of the RI can be ignored. This approach is actually used to maximize sensitivity for trace level methods.

Figure 5 below shows a diagram, and an actual example of this effect. **Please note:** The extent and effect of the Refractive Index does vary, depending upon the wavelength of the analysis and the analyte concentration. For example, in the case of orthophosphate, measured at 880nm, the effect is

more pronounced than it is for nitrate, measured at 520 or 540nm.

An added advantage in these methods is that DI water, not artificial seawater or low nutrient seawater, is used for the carrier as well as in the preparation of standards. Because the FIA is fast, the salt effect (differences in reaction rate and/or response of a chemistry in a saline matrix) is also minimized.

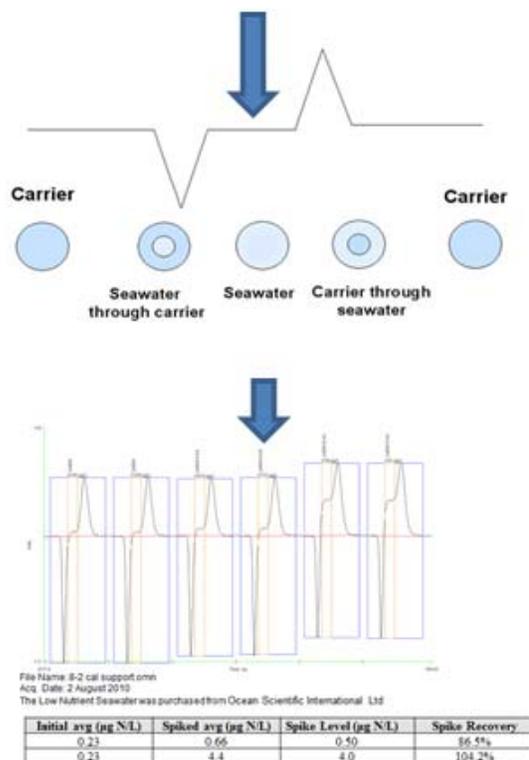


Figure 5: Brackish peaks and integration

Determination of the best integration window for saline samples:

It is best to run a calibration (even if it is one replicate of each level) with each tray. In this way, if there are aberrations in timing, reanalysis is much more easily done. Recipe for artificial seawater (used in setting brackish integration parameters):

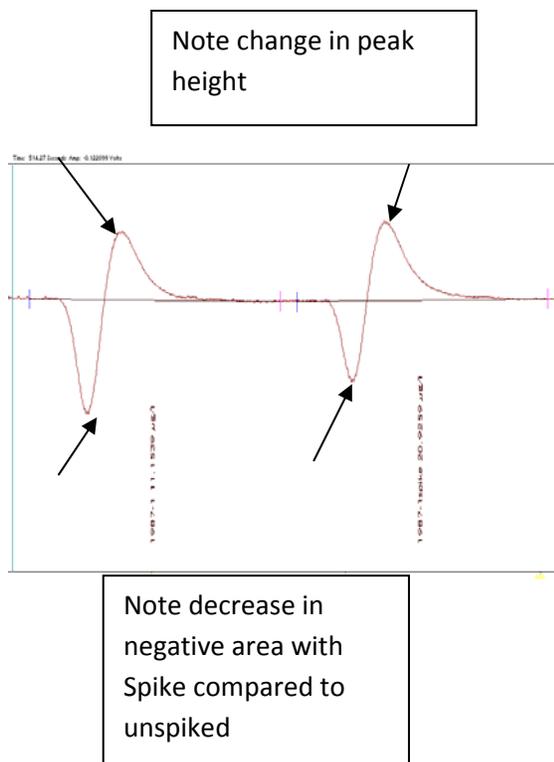
To a 2L flask containing about 1000 mL of DI water, add 58.6g NaCl (sodium chloride), 18.8g MgSO₄·7H₂O (magnesium sulfate heptahydrate), and 0.44g NaHCO₃

(sodium bicarbonate). Dilute to the mark, and stir to dissolve.

Please Note: It is unlikely that the ASW blank will give a reading of zero, due to the presence of analytes (such as PO₄) at some level in the stock chemicals.

Recovery of the analyte spiked into the ASW, using the "blank" as an initial value, will give a spike recovery value, and aid in setting integration.

Diagram of a seawater sample, both spiked and unspiked (with 10 ppb P as PO₄)



will make the determination of integration parameters simpler.

- 4) **In addition to samples and spikes, a standard of known concentration should be included.** The value for this standard should be very near to its known value with the chosen integration parameters.
- 5) Spike recoveries in seawater matrix should be no worse than 80-120%, and will ideally be in the range of 90-110%. In artificial seawater, they should be generally in the range of 90-110%.

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- 1) **Decrease in amount of negative area may need to be considered** in the integration parameters, and a portion of this area may need to be included in the integrated section of the peaks. (1/2 is a good place to begin).
- 2) **Increase in peak height should also be used as a guide** in choosing integration start and stop times.
- 3) If a calibration (1 rep of each standard) is run along with spiked and unspiked samples, this