TECHNICAL NOTE

Atomic Absorption

Baseline Offset Correction (BOC)

One of the key components of Stabilized Temperature Platform Furnace (STPF) technology is the use of integrated peak area. It permits accurate quantitation versus aqueous standards even when the sample matrix causes changes in the timing or shape of the analyte peak absorption signal. For example, Figure 1 shows the signals obtained with similar concentrations of lead in a simple aqueous matrix and in a blood sample. Although there are significant differences between the peak height measurements for the two samples, the peak area measurements are in good agreement. In order to obtain accurate quantitation with aqueous standards for such analyses, peak-area measurement must be used.

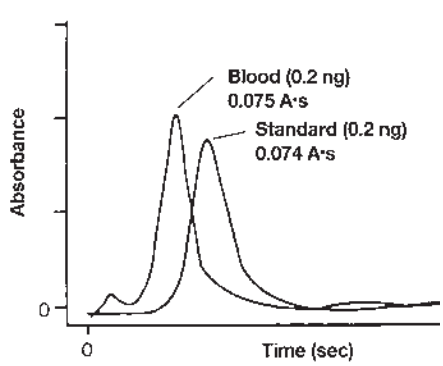

Figure 1. Effect of matrix on peak height and peak area measurements.

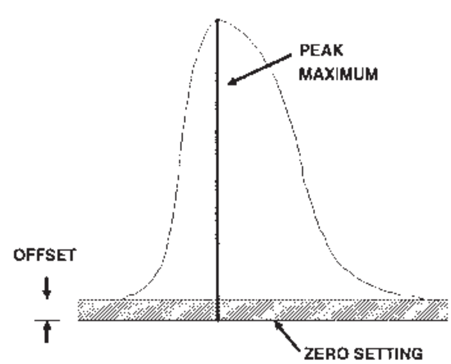

Figure 2. Effect of baseline offset on an integrated absorbance reading.

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Small baseline offsets can occur over time with even the most sophisticated atomic absorption (AA) instruments. The effects of such offsets are normally not seen with flame sampling, as individual determinations are performed very quickly and instrument zero settings are typically checked or reset at reasonable intervals. However, other sampling techniques, including mercury/hydride generation and graphite furnace analysis, not only require longer analysis times – they also typically have a relatively long delay between the start of an analysis and the start of the actual measurement period. These longer analysis times increase the probability that a small baseline offset may occur.

Figure 2 illustrates the relative effect of a baseline offset. The magnitude of the offset has been exaggerated for improved visualization. If the offset is greater than zero, the results will be erroneously high. If it is less than zero, the integrated measurement will be erroneously low.

If peak-height measurements are used, small offsets generally have little impact on the accuracy of the measurement. In contrast, when integrating a signal over a specified time period (i.e., peak-area measurement), even a small offset can introduce significant error as the offset is added to the integrated signal at each point in the measurement cycle. The data in Table 1 permit an estimation of the impact of a baseline offset on peak-height and peak-area measurements using typical analytical parameters.

***Table 1.* Comparison Of Baseline Offset Impact on Peak-Height and Peak-Area Measurements**

Measurement type	Signal	Error caused by 0.001 A baseline shift*
Peak height	0.086 A	1%
Peak area	0.106 A•s	5%

*Assuming 5 sec. integration time

In this instance, the baseline offset is 0.001 A. Such variation is common, even with the best double-beam optical systems. With peak height, only a single measurement is used, that of the peak maximum. The impact of the baseline offset is 0.001 A out of a total signal of 0.086 A or a 1% error. For peak area, the cumulative baseline offset is 0.005 A•s (5 s x 0.001 A), which corresponds to an error of 5% of the corrected AA signal [0.005/(0.106-0.005)]. The cumulative effect of an uncorrected baseline offset can have a significant impact on the accuracy of integrated peak-area measurements.

Ideally, correction for such baseline shifts should be automatically applied immediately before initiating a measurement cycle. Most systems rely on an automatic-zero control for such adjustments, and that control is also used to compensate for blank readings. With furnace or mercury/hydride sampling, an automatic-zero control can compensate for baseline offsets at the start of the measurement or it can be used for blank correction and baseline offset before the analysis begins. It cannot correct for baseline offsets just prior to a measurement *and* maintain blank correction at the same time, however.

PerkinElmer AA instruments and HGA or THGA graphite furnaces include the unique ability to automatically compensate for small baseline offsets using a supplementary technique called Baseline Offset Correction (BOC). With BOC, an integrated peak-area measurement is made immediately prior to the analytical measurement. The time-averaged BOC reading is then used to apply any necessary correction at each point in the measurement cycle. The effect of any baseline offset is automatically eliminated and, since the zero setting has not been changed, automatic blank compensation is maintained.

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