# Instrument Zero and Blank Reading on the SpectrAA Instruments

## Application Note

Atomic Absorption


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## Introduction

To zero a spectrometer properly, two steps must be carried out:

1. Set the instrument zero. This is the reference point against which all other analytical signals will be measured. This is properly performed under the instrument's normal operating conditions. In the case of flame operation, for example, the instrument must be allowed to reach thermal equilibrium with the pure solvent (usually water) being aspirated as a "rinse" before being zeroed.
2. Set the analytical zero using an analytical blank solution. The blank (or control) solution should be aspirated to measure the baseline analyte level. Under ideal conditions, the blank would have no analyte contamination and thus have zero absorbance. In practice, such contamination may occur and the resultant absorbance values must be corrected for in subsequent measurements.

The following is a description of the various stages of a SpectrAA instrument's operation. While in some instances these are valid for any spectrometer (although older models tend to combine the above two steps), the SpectrAA instrument's strength is in providing analytical blank information in the normal operating procedure. Finally although ABSORBANCE mode is discussed, the same is true for EMISSION mode.


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## Instrument

A double-beam spectrometer using a photomultiplier (PM) tube measures the signals of the sample beam (S), reference beam (R) and the PM tube's 'dark' current (D). A single beam instrument measures only sample and dark signals. The Zeeman instrument acts as a double beam with background on (or background only), and as a single beam with background off. The transmittance (T) is calculated by:

$T = (S-D)/(R-D)$

The S-D and R-D measurements are made automatically by instrument electronics. The transmittance (T) is processed by software to give a reading appropriate to the instrument's setting (for example, a log conversion to calculate absorbance).

Note: The emission from the flame is also determined for every measurement cycle, but is ignored for the purposes of this discussion.

## Instrument Zero

This is a one second integration, which determines the zero offset (IZ). Ideally, this integration should be carried out under normal operating conditions with no analyte in the sample path. The measured zero offset is then subtracted from all subsequent readings, and is used to compensate mainly for constant factors such as beam balance and the partial blocking of the light beam by a furnace workhead. The absorbance value displayed in the upper left comer of the screen will show 0.000 after this operation.

## Blank Readings

When the SOLUTION TYPE is set to BLANK and a reading taken, the instrument measures the value of the blank solution offset (BL) which will be subtracted from subsequent readings. This offset is always measured with respect to the last instrument zero or blank as measured in the current element program and becomes the displayed result (see numerical values in Table 1). In the case where a program is being developed or a program with no stored calibration results is recalled, a default value of 0.0 is used. Total correction (TC):

$TC = IZ+BL$

If more than one replicate is used, statistical calculations including the mean of the blank readings are performed for the selected measurement mode (integration, peak height, peak area, or PROMT in the Flame instrument) of the SpectrAA. The SpectrAA also records the value of the last replicate of the blank absorbance for use in measurements modes other than the one currently selected. This means that, during method development, another measurement mode can be tried without re-measuring the blank.

The mean of the replicate blank readings is then treated as the new zero. That is, if the blank solution is read as a sample, the displayed absorbance value is dose to zero. If a new blank is aspirated, it will be measured with respect to the previous blank. If the new blank has a higher level of analyte, then its absorbance will be shown as positive. Lower levels of analyte will give a negative absorbance. The calibration results page reminds the user that the blank absorbance value is a zero point by showing zero in the concentration column, regardless of the absorbance value, next to BLANK (see numerical values in Figure 1).

## Signal Graphics

The Signal Graphics page displays instrument zero and blank absorbance values. During instrument zero a line is drawn along the zero absorbance axis. (Note that changes made during method development such as turning background correction on or off may visually affect the vertical position of the next instrument zero trace). Readings made on blank solutions will be offset from the zero line if there is some absorbing analyte. This offset is equivalent to the blank absorbance value. If the blank solution is subsequently re-measured as a sample, the value shown in the upper left corner of the screen will be close to zero, but the signal trace will still be offset by the current blank absorbance value, thus reflecting its true absorbance level.

A practical example is given in Figure 1. A SpectrAA-30A Flame instrument was used to generate some sample data. Solutions aspirated were distilled water (0 µg Cu/mL), 1 µg Cu/mL (1 ppm) and 5 µg Cu/mL (5 ppm). The values printed out are reproduced along with a screen print of the associated signal graphics traces. The screen traces were subsequently labeled for identification.

| SAMPLE | CONC | %RSD | MEAN ABS | READINGS |
|---|---|---|---|---|
| BLANK | 0.000 | | 0.146 | 0.146 |
| SAMPLE 1 | 0.494 | 0.0 | 0.494 | 0.494 |
| SAMPLE 2 | -0.146 | 0.0 | -0.146 | -0.146 |
| BLANK | 0.000 | | -0.146 | -0.146 |
| SAMPLE 3 | 0.144 | 0.0 | 0.144 | 0.144 |
| SAMPLE 4 | 0.637 | 0.0 | 0.637 | 0.637 |
| SAMPLE 5 | -0.000 | 0.0 | -0.000 | -0.000 |

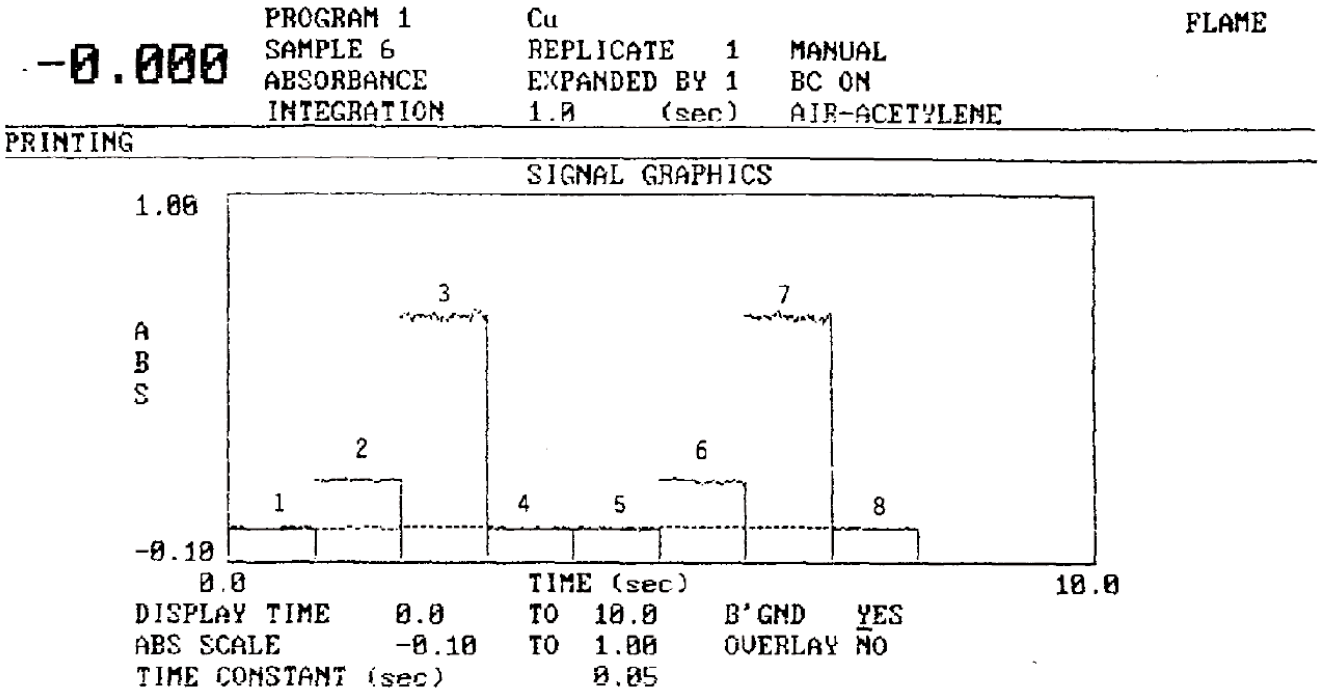


*Figure 1. Manually generated readings with a screen print of the associated Signal Graphics page by aspirating the following solutions: water (traces 1,4,5,8); 1 µg Cu/mL (traces 2,6); 5 µg Cu/mL (traces 3,7).*
*Trace 1 is an INSTRUMENT ZERO.*
*Traces 2 and 5 are BLANKS.*

The signal graphics traces display the absorbance signals obtained after the instrument zero offset has been subtracted from the readings. Note that since no correction for the blank solution offset has been applied, the uncorrected values can be read off using the graphics cursor. These are listed in Table 1.

Unlike the signal graphics traces, the values printed out (in Figure 1) are corrected for the blank absorbance signals. The first blank reading was performed while aspirating the 1 µg Cu/mL solution. The measured offset is 0.146 absorbance units. The second blank reading was performed while aspirating distilled water. The absorbance was measured as 0.146 which means the current offset is now zero. How these offsets affect the digitally displayed values of the samples is summarized in Table 1.

*Table 1. Comparison of Screen Trace and Blank Corrected Absorbances in Figure 1*

| | | | Signal (Abs) | | |
|---|---|---|---|---|---|
| Trace | Read as | Solution | Screen trace | Digital display | Comments |
| 1 | INSTR'MT ZERO | water | 0.000 | 0.000 | offset = 0.000 |
| 2 | Blank | 1 ppm Cu | 0.146 | 0.000 | offset = 0.146 |
| 3 | Sample 1 | 5 ppm Cu | 0.640 | 0.494 | corrected value (0.640–0.146) |
| 4 | Sample 2 | water | 0.000 | -0.146 | corrected value (0.000–0.146) |
| 5 | Blank | waler | 0.000 | -0.146 | new off set calculated (0.146–0.146 = 0.000) |
| 6 | Sample 3 | 1 ppm Cu | 0.144 | 0.144 | corrected value (0.144–0.000) |
| 7 | Sample 4 | 5 ppm Cu | 0.637 | 0.637 | corrected value (0.637–0.000) |
| 8 | Sample 5 | water | 0.000 | -0.000 | corrected value (slight noise effect) |

# Operation

## Flame

1. Automatic run–Auto-sampling
   When a program is recalled, the programmable sample changer (PSC) drives the probe to the rinse position and aspirates the rinse to allow the burner to be in a stable operating condition. Instrument zero is measured ("READING" appears very briefly in the screen message line). The probe is driven to the sampler's BLANK position and blank solution aspirated and measured. The displayed blank absorbance will not necessarily be zero. Regardless of the actual absorbance, this reading is the reference zero for further measurements.
2. Automatic run–Manual Sampling
   The program is recalled, but no instrument zero is done as the instrument cannot assume the correct solution is being aspirated. The operator should aspirate a clean rinse solvent and press INSTR'MT ZERO key, then aspirate a blank solution and measure the blank absorbance value.
3. Manual Operation–Manual Sampling
   (as used for Table 1)
   In method development, the situation is identical to the automatic run/manual sampling case. Note that the PSC is not designed for manual operation.

## Furnace

1. Automatic run–Automatic sampling
   When a program is recalled, the instrument automatically does an instrument zero without heating the tube. The Zeeman system will also activate the magnet during the measurement period. Blank solution is then injected and readings performed as for the equivalent flame case (Flame, case 1).
2. Automatic run–Manual sampling
   As for equivalent flame case above (Flame, case 2) the instrument cannot assume the sample beam is free from blockage. The operator should press the INSTR'MT ZERO key at the start of a program before making any measurements.
3. Manual operation–Automatic sampling
   The operator can press INSTR'MT ZERO key at any point. START GTA key allows the programmable sample dispenser (PSD) to be used for calibration on the blank solution.
4. Manual Operation–Manual Sampling
   As for the furnace manual operation/automatic sampling case above (3), except the solution must be injected manually before START GTA key is pressed.

For a summary of the operation information, refer to Table 2.

*Table 2. Sequence of Events in a SpectrAA Automatic Run (No user intervention needed with a sampler)*

| | Instrument | | Result of | Action required with |
|---|---|---|---|---|
| Step | Flame | Furnace | event | manual sampling |
| 1 | Recall program | Recall program | Blank values cleared | |
| 2 | Aspirate rinse | No action | Instrument zeroed | Press INSTR'MT ZERO key |
| 3 | Aspirate blank | Inject blank | Blank level set | Press READ key |
| 4 | Aspirate solutions | Inject solutions | Corrected values taken | Press READ key |

## Conclusion

Operation of the SpectrAA instruments differs from the older series instruments only in the information supplied. By measuring instrument zero and blank absorbance separately, the SpectrAA series allows the operator to monitor the level of blank absorbance. The blank mean absorbance value is used to correct all subsequent sample measurements to reflect the actual analyte absorbance. A nonzero blank absorbance is therefore no cause for concern, unless the values are higher than expected indicating a chemical problem such as contamination or matrix interference effects.

## Appendix

Programmable Gas Control Unit

The SpectrAA–30/40P is equipped with a programmable gas control unit (PGCU) and this is automatically 'zeroed' at appropriate stages. The PGCU is 'zeroed' by equalizing acetylene pressures on both sides of the flow rate transducer and measuring its effective zero flow offset. This occurs whenever INSTR'MT ZERO is pressed in manual operation or every time BLANK is measured during calibration, recalibration or reslope in an automatic run.

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