Automating the method of standard additions in flame atomic absorption spectrometry for the analysis of steels

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Introduction
Atomic absorption spectrometry (AAS) is a comparative technique. The standards used to calibrate an AA instrument must closely match the samples, both chemically and physically. Samples with complex, or hard to match matrices can be measured by the method of standard (or analyte) additions. The purpose of this method is to minimize physical and chemical differences between samples and standards. The calibration standards are made up by first spiking aliquots of the sample with varying amounts of the element to be measured and then diluting to a constant volume. The signals of the standards are measured and plotted against the added analyte. The graph is then extrapolated to determine the concentration of the element in the sample, as shown in figure 1.

Figure 1: An example of a standard additions calibration graph. Usually no more than four points are measured using manual calibration standards. SIPS can calibrate using 11 points.

Automation
There are commercial off-line dilution systems that can prepare standards for both normal calibration and standard additions. Varian’s SPS-5 Sample Preparation System is such a device. When using the method of standard additions the prepared standards have to be measured and then the calibration graph must be produced. If the graph does not satisfy the criteria for linearity, the standards must be re-made and re-measured. Thus to automate the method of standard additions there must be a dynamic interaction to enable on-line preparation of standard addition calibration solutions.

Figure 2: A schematic sketch of the SIPS-20 showing the computer controlled pumps.
The Varian SIPS-20, shown in figure 2, is the first commercial system capable of performing on-line both a normal calibration and the more complicated standard addition calibration. The SIPS-20 is a dual peristaltic pump system under precise computer control. One pump is used for sample solution and the other for a bulk standard solution. The nebulizer draws up diluent from a reservoir. The pumps can accurately introduce solutions into this diluent stream. The procedure SIPS follows for calibration by the method of standard additions is described below and summarized in Figure 3.

**Figure 3: A flow-chart showing the system checks SIPS uses for the automatic calibration of a flame AAS instrument using the method of standard additions.**  
*LRR is the linear reading range*

First, the two pumped sample-streams have to be matched or calibrated so the amount of analyte added to the sample is known accurately. The bulk standard solution is pumped through each of the tubes in turn and the pump speeds ratioed so the signals are matched. This calibration is performed at the start of each method. The method can also be set to rematch the pump speeds and tubes at recalibration or reslope or both.

Second, a critical value, the linear reading range (LRR) of the calibration, must be determined. This procedure determines the signal at which the calibration starts to deviate from linearity. The SIPS generates a normal calibration graph. As each calibration point is measured a very rigorous test of linearity, the chi-squared test, is applied. The signal of the calibration point with the maximum allowed deviation (the default chi-squared test value is 0.0002) sets the LRR. The default flame methods have an LRR absorbance value appropriate for each element. The LRR value can also be determined and stored during method development or even at the start of a method in an autorun.

Third, the system ensures the calibration is within the linear reading range (LRR). The calibration solutions (the sample and the bulk standard) are presented. The sample pump and the analyte pump are set at the maximum allowed rate respectively, which generates the top standard. If the resultant signal exceeds the LRR, the pump speeds are reduced automatically until this important condition is met. This reduced speed is called the initial dilution factor (IDF).

All the necessary checks have been done and the instrument is now ready to perform a calibration using the method of standard additions and thus determine the level of analyte in an unknown sample. Both pumps are stopped so the signal of the diluent can be measured (the Reagent Blank). The sample pump speed is then fixed at the IDF. The analyte pump speed is progressively altered to spike the sample with varying amounts of analyte and the respective signals measured. The analyte pump is then stopped to measure the signal of the sample only. The calibration graph (Figure 1) is plotted and the level of analyte in the sample calculated.

Some protocols (such as the US EPA) require that periodic QC Spike recovery measurements be performed to check the validity of a calibration graph. A QC Spike is a sample solution with a known quantity of analyte added. The purpose of the QC Spike is to assess what potential interferences are present. The QC Spike test passes if the measured spiked sample concentration is within 15% of the sum of the unspiked sample and spike added concentrations. A low recovery value indicates that interferences may be present. If the QC Spike test fails, the sample should be re-determined using the method of standard additions. The SIPS-20 can spike the sample on-line to perform the QC Spike recovery test, which saves a considerable amount of laboratory work and time. In addition, if the QC Spike recovery test fails, the user can specify a “Switch to Standard Additions” error action. The SIPS-20 will then automatically re-determine that sample using the method of standard additions.

**Benefits of standard additions**

There are, in principle, no compatibility problems between sample matrix and standard because the standards are prepared in the sample. This is correct only if the added standard closely matches the analyte present in the samples chemically and physically.
Limitations of standard additions

The calibration graph must be substantially linear since accurate regression cannot be obtained from non-linear calibration points. It is also essential to obtain an accurate baseline from a suitable reagent blank. The fact that the measured part of the graph is linear does not always mean that linear extrapolation will produce the correct results.

Applying the method of standard additions in flame work has traditionally been very labor-intensive. Every sample type requires its own set of at least four calibration solutions. Operators must be carefully trained to prepare appropriate standards. This includes recognizing if the calibration is non-linear and diluting the standards so the respective signals are in the linear region.

Practical application

Two reference steel samples were used to demonstrate the ability of the SIPS-20 to analyze complex samples by the method of standard additions. These were NIST-348a (National Institute of Science and Technology, Gaithersburg, MD, U.S.A.) and BCS-336 (British Chemical Standards, Bureau of Analysed Samples Ltd, Teesside, England).

Experimental

Instrumentation

A SIPS-20 was used with a Varian SpectrAA-880 atomic absorption spectrometer fitted with a standard Mark VI spray chamber and nebulizer. A Mark VI nitrous oxide-acetylene burner was used for all elements. Molybdenum and chromium were determined using a nitrous oxide-acetylene flame and the rest of the elements by air-acetylene flame.

Reagents and solutions

Standards used were diluted from 1000 ppm AA standards supplied by BDH (Poole, England).

All acids used were AR grade supplied by BDH (Poole, England).

The samples were dissolved using a general method. Samples (0.1000 g) were accurately weighed into beakers and 2 mL concentrated hydrochloric acid (32%) and 1 mL concentrated nitric acid (76%) added. When the reaction subsided, 2 mL of concentrated perchloric acid (70%) was added and the solution warmed until white fumes of perchloric acid appeared or the solutions became reddish-brown.

Warning: Observe all precautions when using perchloric and concentrated acids.

The solution was warmed a further 5 minutes. Distilled water (50 mL) was added and the solution filtered through Whatman #1 filter and diluted to 100 mL. For the determination of molybdenum, 0.5 g of aluminium(III) chloride was added as a chemical modifier.

Table 1 lists the analytical wavelengths and concentration of the bulk multi-element standard used. The operator only has to prepare one suitable diluent solution and one suitable analyte solution for each element. The analyte solution can be multi-element or single-element. The operator specifies in the method the concentration of the bulk standard and the number of standard points required. The operator does not have to prepare the standard solution sets for the samples to be calibrated. Once the bulk solution has been prepared, the number of samples for calibration can be varied without having a significant impact on operator time. This feature alone removes a significant work-load. When the system is started in an autorun, the software sets the initial dilution factor, if required, checks the system and performs the calibration.

Table 1: Wavelength and bulk standard concentrations used for the analysis of steels.

<table>
<thead>
<tr>
<th>Element</th>
<th>Bulk standard concentration mg/L</th>
<th>Wavelength nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>10</td>
<td>240.7</td>
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<tr>
<td>Mn</td>
<td>20</td>
<td>403.1</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>352.5</td>
</tr>
<tr>
<td>Cr</td>
<td>100</td>
<td>428.9</td>
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<tr>
<td>Mo</td>
<td>60</td>
<td>313.3</td>
</tr>
</tbody>
</table>

Results and discussion

The results obtained using the SIPS-20 are shown in Table 2.

Table 2: Results from the analysis of reference steel samples using standard additions and SIPS.
The initial results for molybdenum demonstrate the
effect of not matching the chemical state of the
sample with the analyte\(^6\,^{10}\). Aluminium has been
noted as a releasing agent for molybdenum\(^1\)\(^1\) and
was added here to the samples (because the
sample is pumped at a constant rate).

The method development, sample dissolution and
determinations were all done within a day and all
results, apart from a low-level cobalt value, were
within 5% even for a complex iron matrix. A routine
quality control laboratory can readily adapt this
scheme to suit its samples.

**Conclusion**

Applying the method of standard additions in flame
AAS is tedious to carry out manually. With the SIPS,
this analysis can be automated because the system
is capable of making quite complex decisions.

The SIPS-20 can also automatically perform on-line
dilutions of over-range samples and normal multi-
point calibrations from a single bulk standard.

The SIPS accessories therefore offer real benefits
in the automation of the method of standard
additions in flame AAS.

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