Curve Correction in Atomic Absorption

Application Note

Atomic Absorption

Authors

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Introduction

The Atomic Absorption technique ultimately produces an output measured in optical units – typically, in absorbance units. The operator must somehow convert this absorbance to concentration units in order to obtain the analytical result.

The absorbance would ideally be linear with concentration if the Beer-Lambert Law could be applied exactly, but in practice there is always some deviation. Even within a limited concentration range, calibration curvature is the rule rather than the exception.

Some of the causes of this curvature are controlled by the instrument design or by the experimental conditions used. The degree of curvature for nickel at the 232.0 nm wavelength, for instance, is controlled by the spectral bandwidth chosen on the monochromator, because the curvature arises from overlap of a nearby non-absorbed line in the nickel spectrum. At practical instrument settings, it is not possible to eliminate this curvature completely.

There are also more fundamental causes for calibration curvature, relating to the degree of overlap in the Voigt profiles of the emission and absorption lines. Curvature from such causes is not under the control of the operator, and since it varies from element to element, it cannot be completely removed in instrument design.

Thus it is not possible to avoid the curvature, and various curve-fitting devices have been developed to compensate for the curvature and produce calibrated concentration output from atomic absorption instruments.

Naturally, recent efforts in this direction have been aided by computer and microcomputer technology. The problem is to produce a suitable mathematical algorithm which matches the natural calibration curve as closely as possible, so that after initial set-up the concentration can be computed numerically from the measured absorbance.

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Investigations

In investigating suitable algorithms, we first considered the known practical constraints:

1. The algorithm must be accurate within 1% or better, to be of practical use. Even by manually drawing a calibration graph, we found we could achieve almost 1% accuracy, and the algorithm would need to be at least as good as this to avoid introducing systematic errors into the result.
2. The algorithm must be accurate for all elements, bander all practical conditions. Thus we considered both gentle and severe curvatures, whether instrument-related or more fundamental, as part of the same mathematical problem.
3. The algorithm must be accurate for all atomizers and all measurement modes. We commonly measure equilibrium absorbance signals from a flame atomizer or peak signals from a furnace, and in each situation an accurate concentration output is needed.
4. The algorithm must be accurate over a wide dynamic range in concentration. The total dynamic range in atomic absorption is only about 4 orders of magnitude, and to further restrict this range with a limited curve-correction formula would be a severe disadvantage.
5. The algorithm must achieve this accuracy with a limited number of standards. "A blank and three standards" is a well-established analytical prescription, and it would be a significant practical advantage if this prescription could be followed. It is also desirable to allow less accurate but more convenient calibration with 1 or 2 standards, and more accurate calibration with perhaps 5 standards.

   For more than 5, the labor in preparation and maintenance of standards becomes too great to be justified for most work.

With these constraints in mind, we established the shape of the curve in detail for a number of extreme and intermediate cases, ranging from silver determinations in the flame where the calibration was almost exactly linear up to 2.0 absorbance, to arsenic determinations where (under the extreme conditions applied) the calibration curved towards an asymptote at about 0.6 absorbance so that every concentration above 400 µg/mL produced almost the same absorbance.

In this paper we will concentrate on the results obtained for nickel at 232.0 nm. This is an important practical example, and it also represents one of the most stringent tests of the various computation algorithms. The curvature is quite severe, and the severity depends on the instrumental conditions so that different degrees of curvature are likely in different laboratories.

For nickel, we prepared 21 accurate standard solutions covering the range up to 50 µg/mL. The calibration points fall on curves as shown in Figure 1.

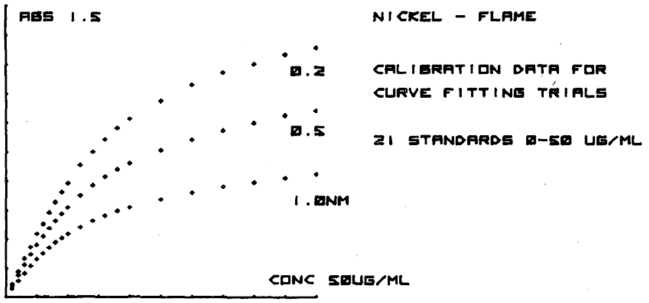

Figure 1.

At this stage we assumed no knowledge of the causes for curvature; we were concerned only with the shape of the curve.

We first considered simple mathematical functions as approximating curves (Figure 2).

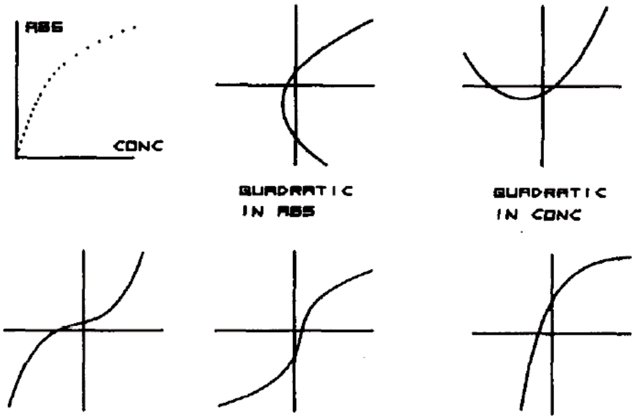

Figure 2.

All of these would be fairly easy to compute, although the quadratic and cubic polynomials expressed with concentration as the variable would require iterative computation to convert a measured absorbance into an unknown concentration after calibration.

Results

Now, using the nickel results at 0.5 nm bandwidth as a typical example, let us examine the performance of these algorithms.

The "quadratic in abs", $c = P + Qa + Ra^2$, is not generally satisfactory (Figure 3).

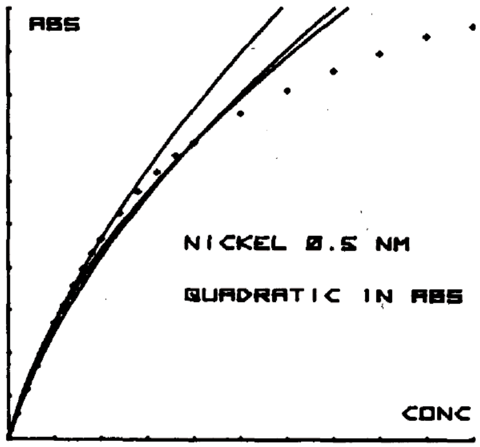

Figure 3.

If the concentration range is small, a good fit can be obtained with well-chosen standards, but this will only apply if the operator has detailed knowledge of the behaviour of the curve in advance. For this nickel example we could not obtain a satisfactory fit above 15 µg/mL so that two-thirds of the possible working range must be sacrificed.

The "quadratic in conc", $a = P + QC + Rc^2$, is a better fit (Figure 4).

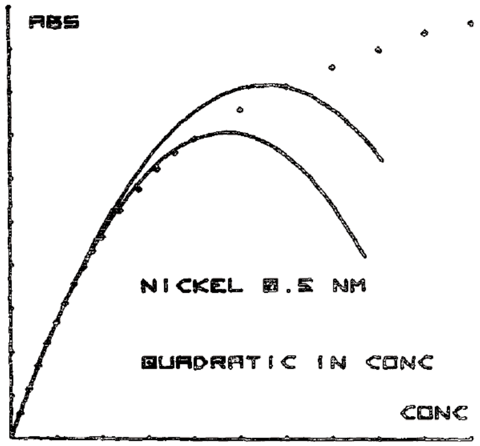

Figure 4.

There are, however, two obvious problems. The working range is again limited, and because the turning point of the parabola is so close there is a risk of misinterpretation. When a measured absorbance can correspond to two quite different computed concentrations, errors are almost certain.

A cubic polynomial is better still. The "cubic in abs", $c = P + Qa + Ra^2 + Sa^3$, can certainly be useful for this curve (Figure 5).

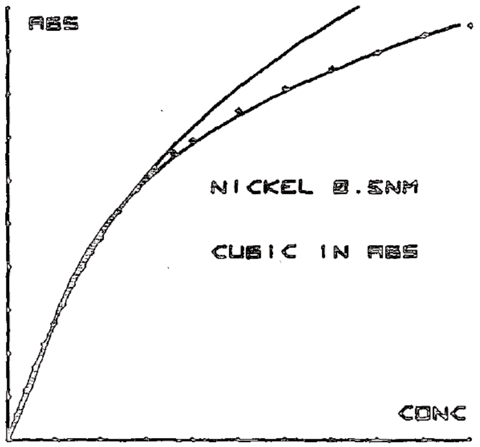

Figure 5.

For more gentle curves, this approximation is excellent, but for a fairly severe curve such as this, there is a compromise. If the curve fits well at the top of the range there are errors at the bottom, and vice versa.

The "cubic in conc" polynomial, $a = P + QC + Rc^2 + Sc^3$, can avoid this problem. With the correct choice of standards, a good fit can be achieved throughout the range (Figure 6). Again, however, there are possible turning points within the range if the wrong standards are used, and beyond the last standard the results are doubtful. For example, if the last standard used was 40 µg/mL the error at 45 µg/mL could be as much as 10%. By using more standards it is possible to refine either of these cubic approximations. Least-squares regression, for example, produces a curve such as that shown in Figure 7 (using 10 standards).

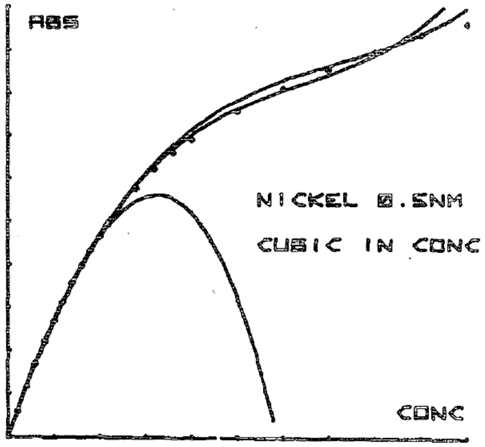

Figure 6.

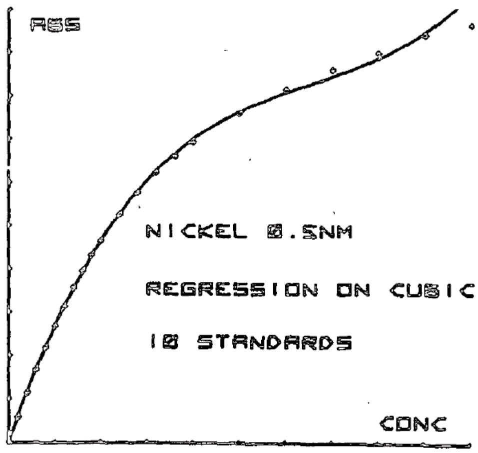

Figure 7.

The nature of the least-squares approach is to produce the largest benefit with the largest numbers, and here the curve does indeed fit well at higher absorbance.

However, a cubic function is inescapably cubic, and as in this example it will always give errors above the last standard. If anything, the errors are worse using the regression because the lower part of the curve has been forced into a particular shape which emphasizes the rate of change beyond the last standard.

An exponential function has sometimes been recommended for curve fitting in AA, because conceptually the curve seems to approach an asymptote. For nickel the fit is quite good (Figure 8).

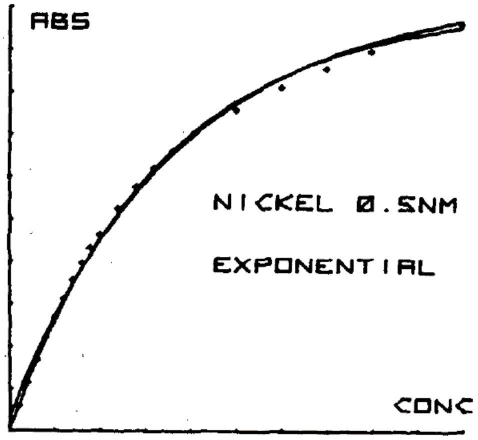

Figure 8.

Over a limited range, the exponential is a good approximation, but only two calibration points can be used, and over a wider range the fit between the calibration points suffers.

To improve this, one instrument company has published a modified exponential function based on transmittance rather than on absorbance data. There is a benefit (see Figure 9). Again, however, only two standards are used and the fit is not good over a wide range, at least for our data.

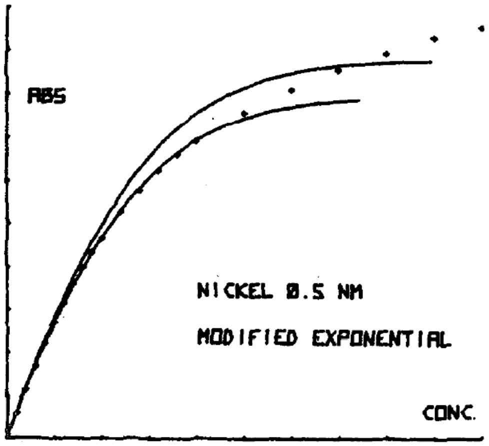

Figure 9.

A New Method

After considering all of these approximations, we concluded that none were wholly satisfactory. All of them are useful in a small working range, but over a wider range all of them have one disadvantage or another, causing inaccuracies. We concluded that the natural calibration graph (absorbance against concentration) could not be approximated well enough without more complex mathematics.

Therefore, we searched for some transformation of the data which would produce more easily-handled curves. Graphical trials on several possible transformations revealed that a plot of a/c against a, or c/a against c, produced pseudo calibrations which had very desirable properties. We chose the a/c against a plot as the basis for a new calibration algorithm using the parabolic rational function $a/c = P + Qa + Ra^2$. For brevity we call this the 'rational method'. Looking at the data for nickel, we can see how this data transformation works (Figure 10).

In place of the natural calibration curves, we have new curves with interesting properties. Where the normal calibration is almost straight (at low absorbance), the transformed data follows almost a straight line. The transformed data has no particular physical meaning, but it does allow us to approximate the calibration with very simple mathematical functions. Indeed, a straight line is a good fit to the upper part of these transformed curves (at higher absorbance) and using a parabola the fit is even better.

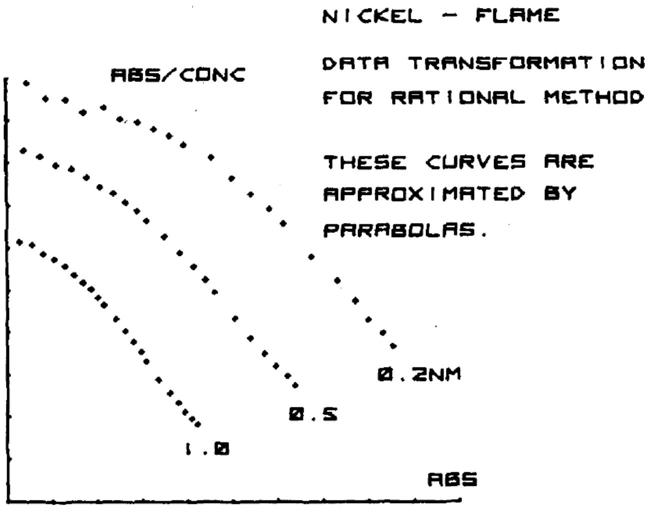

Figure 10.

Applying the rational method to these nickel calibrations, and plotting the results in the more familiar absorbance-concentration co-ordinates, the fit is obviously very promising (Figure 11).

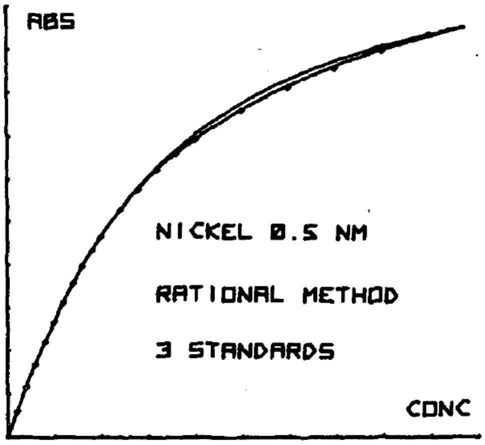

Figure 11.

The errors are less than 1% even over this wide range if three calibration points are suitably chosen. Even with badly chosen standards the errors are quite small. For these examples the standards were at 5, 20, 50 µg/mL (good fit) and at 2, 5, 50 µg/mL (worse fit but not a natural choice of calibration points). These curves genuinely possess the characteristics of real calibrations; a benefit which, as we have seen, cannot be claimed for the earlier approximations.

Over a limited concentration range (say 3 orders of magnitude), two or three standards are quite sufficient with this algorithm (Figure 12).

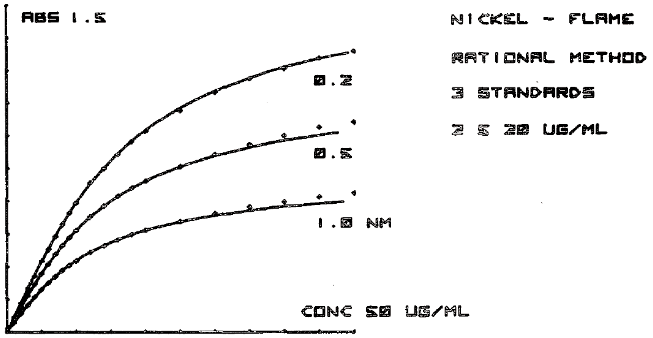

Figure 12.

As we can see, errors do appear above the top standard, but these errors are generally quite small. There is no systematic deviation as there is with the earlier cubic approximations, for example.

The calibration range can be extended to the fourth order of magnitude by suitable choice of three standards, as seen above, but for maximum accuracy over the wider range it is better to add a fourth or even a fifth standard (Figure 13).

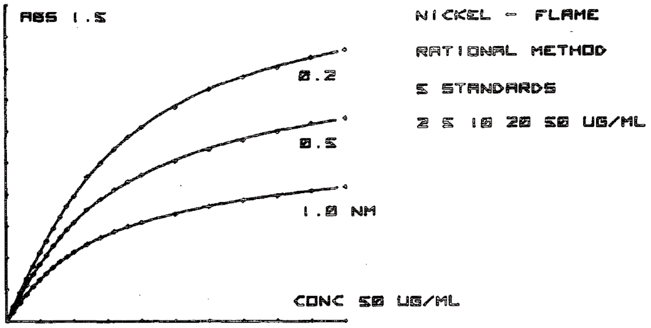

Figure 13.

With five standards, a choice arises: least-squares regression on a single curve, or generation of a family of overlapping curves. Least-squares regression works best when there is a statistically significant number of calibration points, but for four or five standards we prefer to generate a family of overlapping parabolas. This method provides an excellent fit to the actual calibration and allows for the fact that the rational method transformation does not always provide a simple curve. There is a degree of S-shape in the curve at high absorbance which is best approximated by taking a family of parabolas rather than one.

This rational method is very successful for a large variety of curves. The most severe curve in our trials was for arsenic under extreme instrument conditions which resulted in the calibration curving almost to an asymptote at about 0.6 absorbance (Figure 14).

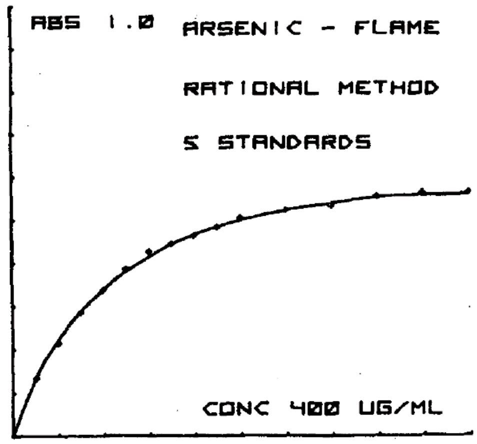

Figure 14.

With five standards, even this curve could be accommodated. In practice, of course, it is not feasible to use such a calibration at high concentration because the absorbance difference between 350 and 400 µg/mL is almost zero. Over a more limited range the curve can be accommodated with three standards.

Where the curvature is not so severe, three standards are almost always sufficient (Figure 15).

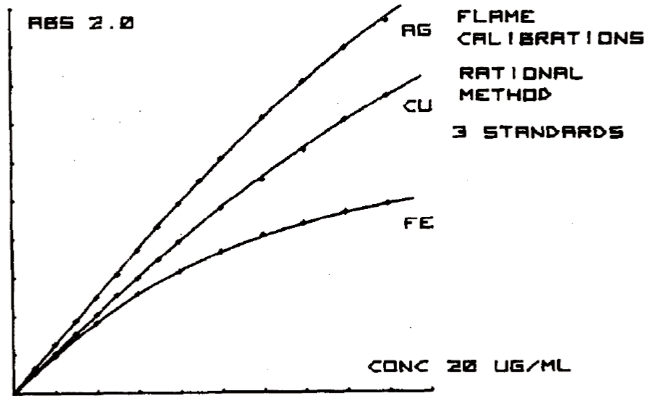

Figure 15.

For silver and copper there is little curvature and almost any approximation is good; the rational method is no exception. For iron, which is an example of moderate curvature typical of a large class of elements, the fit with three standards is excellent (the absorbance scale here has been extended to 2.0 absorbance, so that the curvature for iron appears to be exaggerated).

The same excellent fit is obtained using other atomizers. For peak height or peak area results in the graphite tube atomizer, or with vapor generation methods, the fit is excellent. Even flame emission results can be accommodated, in spite of the fact that self-absorption (the major cause of curvature in flame emission) produces fundamentally different curves which would not be expected to match the same algorithm as the atomic absorption curves.

This new algorithm has been chosen as the calibration method for our atomic absorption products.

We feel that this new rational-method algorithm will provide consistently better results than any previous method. It is very quick in computation, involving no iterations or approximations (unlike exponential methods).

It fits exactly at each calibrating point (unlike regressions methods), and for all of the elements in our study the accuracy was better than 1% at all points with any rational choice of standards. It allows the entire working range to be used up to about four orders of magnitude, and it allows for all types of calibration curvature regardless of the cause.

This “Varian Instruments At Work” was originally published in August 1977 as a “Lecture Transcript”. The rational method algorithm described here has been used in all Varian AA instruments produced since then and the method has consistently proved its accuracy and fidelity.

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