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A comparison of six commercially available curve fitting algorithms for calibration in flame atomic absorption spectrometry (FAAS) has been made. Programs using the algorithms were written in BASIC for a microcomputer and, where possible, tested against the commercial version. Calibration curves for magnesium, chromium and nickel produced by the algorithms were compared, on the basis of the sum of squares of the percentage deviations and its root mean square, with each other and with linear interpolation and manual fitting. The standard deviations of the goodness of fit parameters were calculated to indicate significant differences between the fits obtained. With the exception of the simple parabola, linear interpolation and manual methods, which were significantly poorer, the algorithms performed similarly. In general the errors in curve fitting were well below 5% for the commercial algorithms.

Keywords: *Calibration; flame atomic absorption spectrometry; curve fitting*

With the introduction of automatic data handling techniques, several curve fitting algorithms have appeared for calibration in AAS.[1] As the processes that cause the bending of the calibration curve are numerous,[2] many different models for the curve have been used.

De Galan *et al.*[3] have compared the use of manually drawn graphs, polynomials of degrees one to four, a rational function (as used by Perkin-Elmer) and a cubic spline function. Miller-Ihli *et al.*[4] compared linear, cubic spline and Stineman interpolation methods with linear and quadratic functions and a rational function (as used by Baird Atomic), fitted by a least-squares procedure. Both of these rational functions are described later.

In this paper, a comparison is presented of the existing algorithms that are commercially available, using typical calibration data. The algorithms are compared with each other and with two additional techniques: (*i*) linear interpolations[4] and (*ii*) graphical plots by three colleagues using various manual curve fitting methods.

Experimental

Calibration and Test Data

Nickel, chromium and magnesium were chosen as test elements, as these three elements give characteristically different calibration curve shapes. The calibration for nickel was curved over the absorbance range 0–0.8 and asymptotic to absorbance 0.8. The calibration for chromium was initially linear but curved towards an asymptote at absorbance 1.2. The calibration for magnesium was virtually linear over the absorbance range 0–1.2.

Eight standards, including a blank, were made up for each element, by serial dilution of 1000 mg l⁻¹ stock solutions (BDH Chemicals Ltd.), using calibrated glassware. These were then presented to either a Shandon Southern A3300 or a Pye Unicam SP90A atomic absorption spectrometer. An air - acetylene flame was used and operating conditions were optimised for maximum sensitivity. The output was monitored with a Philips PM 8251 chart recorder. The standards were aspirated, in order of increasing concentration, several times to account for drift. The blank was aspirated between each standard, and the blank absorbance value subtracted from each standard absorbance value. The calibration data points were distributed evenly along each curve enabling compari-

sons to be made between each element for four and five point calibrations. All seven standards (the blank being excluded) were used to calculate a parameter for "goodness of fit" in each instance.

Goodness of Fit Parameters

The parameters suggested by Miller-Ihli *et al.*,[4] namely the sum of squares of the percentage deviations (SSPD), equation (1), and its root mean square (RMSPD), equation (2), were used

$$SSPD = \sum_{i=1}^{N} \left(\frac{C_c{}^i - C_k{}^i}{C_k{}^i} \times 100 \right)^2 \quad \dots \quad \dots \quad (1)$$

$$RMSPD = \left(\frac{SSPD}{N} \right)^{\frac{1}{2}} \quad \dots \quad \dots \quad \dots \quad (2)$$

where $C_c{}^i$ is the *i*th concentration calculated by the algorithm, $C_k{}^i$ is the *i*th actual concentration and N is the number of data points tested.

As the percentage deviation for a blank ($C_k{}^i = 0$) is infinite, only seven data points ($N = 7$) were used in the tests.

To give an indication of any significant difference between algorithms, calculations of the standard deviations (SD) of the parameters were made using equations (3) and (4) (derived from the rules for the propagation of random errors[5]), assuming 1% relative standard deviation in $C_c{}^i$ and 0% relative standard deviation in $C_k{}^i$.

$$SD_{SSPD} = 10^4 \left\{ \sum_{i=1}^{N} \left[\frac{0.02\,C_c{}^i(C_c{}^i - C_k{}^i)}{(C_k{}^i)^2} \right] \right\}^{\frac{1}{2}} \quad \dots \quad (3)$$

$$SD_{RMSPD} = \left(\frac{1}{N} \right)^{\frac{1}{2}} \frac{SD_{SSPD}}{2(SSPD)^{\frac{1}{2}}} \quad \dots \quad \dots \quad (4)$$

Algorithms and Programs

The eight different algorithms and calibration methods tested are summarised in Table 1.

The programs were written in BASIC for a Sharp MZ700 microcomputer, which incorporates a plotter - printer for the production of graphs and "hard copy" of results. The basic curve fitting program described by Miller[6] was modified to produce the required algorithms.[7-14] Where possible the results from these algorithms were compared with results from the appropriate commercial instrument. The comparison of

Table 1. Summary of algorithms

Equations* used and method of curve fitting	Manufacturers who have adopted the algorithm	Name assigned to algorithm in Fig. 1
$C = a + bA + cA^2$, solved for three data points or fitted by least squares for more data points. Coefficients reduced for less than three data points	Baird Atomic (Data-comp system)	Baird Quadratic
$A/C = a + bA + cA^2$, fitted as above	Baird Atomic (Alpha-star system)	Baird Rational
$C = aA + bA^2 + cA^3$, fitted as above	Instrumentation Laboratory	IL Cubic
$C = (k_1A + k_3A^2)/(k_2A - 1)$, if the top standard absorbance is within 15% of that predicted by the bottom standard, k_3 is set to zero. When the number of standards is three or less, the equation is solved with the appropriate number of coefficients. Otherwise the equation is fitted by least squares	Perkin-Elmer	PE 3 Coefficient PE 2 Coefficient
$A/C = a + bA + cA^2$ solved for each set of three calibration points	Varian Associates	Varian Rational
$C = a + bA + cA^2$. A straight line is calculated between the blank and lowest standard. A quadratic is then applied between the next two data points, a third point being calculated using extrapolated slopes	Pye Unicam	PU Quadratics
$C = a + bA$, solved for every two points	—	Linear Interpolations

* Where C is concentration, A is absorbance and a, b, c, k_1, k_2 and k_3 are coefficients to be found during the fitting procedure.

Table 2. Calibration and test data

Data used for calibration		Nickel		Chromium		Magnesium	
4 point	5 Point	Concentration/ $mg\,l^{-1}$	Absorbance	Concentration/ $mg\,l^{-1}$	Absorbance	Concentration/ $mg\,l^{-1}$	Absorbance
X	X	0	0	0	0	0	0
X	X	5	0.198	5	0.296	0.1	0.092
		10	0.317	10	0.510	0.3	0.283
	X	20	0.472	15	0.696	0.4	0.384
X		30	0.560	20	0.824	0.5	0.484
	X	40	0.617	30	1.002	0.7	0.656
		50	0.662	40	1.140	1.0	0.926
X	X	60	0.701	50	1.198	1.3	1.156

the Pye Unicam SP9 algorithm showed that it was not the same as the one written for the microcomputer, so the SP9 computer was used for subsequent experiments. Adjustment of the burner height was used to produce the required absorbance values. The other algorithms written for the microcomputer showed no significant difference from those used in commercial instruments.

Results and Discussion

The calibration data used is shown in Table 2 and the RMSPD values and their standard deviations are presented as output from the microcomputer in Fig. 1. Values for the associated SSPDs are not given, as they varied by powers of ten, and can easily be calculated from the RMSPD values. The large value for the Perkin-Elmer three-coefficient fit to the four point magnesium calibration is due to the curve becoming discontinuous and asymptotic to absorbance 0.6, as shown in Fig. 2. In this instance, the commercial algorithm[11,12] would choose the two-coefficient version of the function.

Clearly, a quadratic function (Baird Quadratic) does not provide a satisfactory model for calibration curves, except when the curve is virtually linear. A parabola can produce the required asymptote but will also give curvature at the blank level where, in practice, the calibration is often linear.

The results for the manual plots are the average RMSPD and SD_{RMSPD} values for the three analysts involved. Although these average parameters compare favourably with those of the computer fitted algorithms, individual results varied and no one person was consistent. Linear interpolation only appears to be useful if curvature is slight, or if many calibration points are employed.

As might be expected, all the algorithms perform well for the situation in which the calibration is nearly linear but differences become apparent as curved calibrations are encountered. It is interesting to note that fitting a curve by eye is no better, and often worse, than fitting by computer.

There are several ways in which the goodness of fit of a curve to a set of points can be assessed. A commonly used parameter for straight lines is the correlation coefficient. However this tends to give values close to unity if the fit is good for higher absorbances and concentrations even if the fit is poor further down the calibration curve. In addition, it cannot be used for algorithms that either solve equations explicitly for a number of data points, or use interpolation methods.

The sum of squares of the percentage deviations and its root mean square are thus more appropriate measures of the goodness of fit as they can be used for all types of algorithm if intermediate data points are used between calibration points. These parameters represent the fit over all of the curve and, being based on percentage deviations in the concentrations, are unbiased towards any part of the curve. The RMSPD represents the likely error in the concentration, calculated by the algorithm, due to the curve fitting method. The parameter used by Knegt and Stork[15] is very similar but is based on the absorbance values rather than concentration values. This does not give any indication of the error in concentrations due to the curve fitting method.

No attempt was made to compare the calibration algorithms with the standards distributed differently along the curve, which may have improved the performance of some algorithms. This would require detailed knowledge of the curve shape, which may not be available in a real analytical situation.
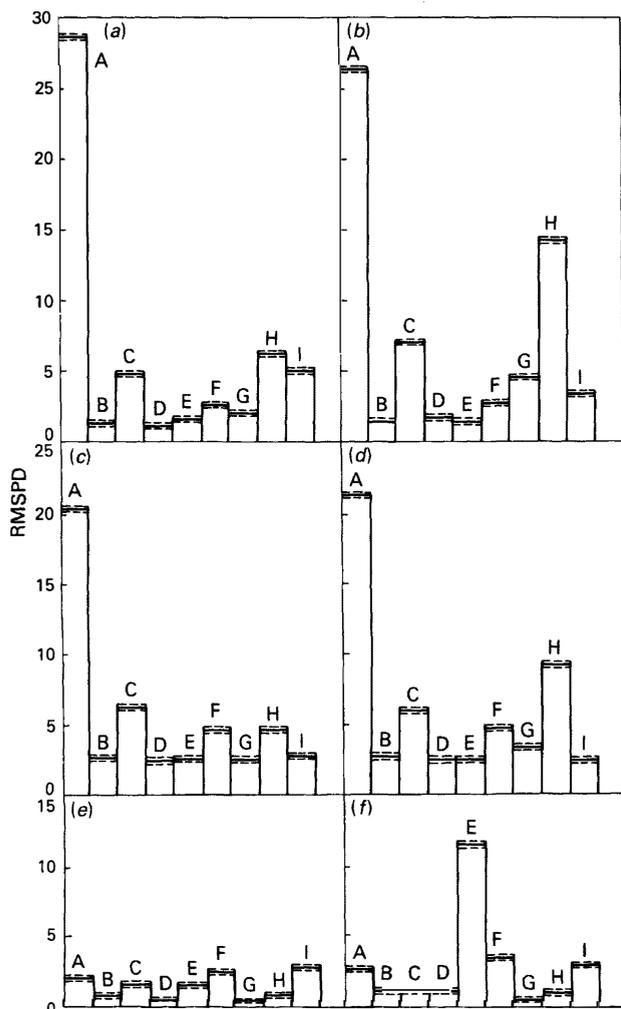
Fig. 1. RMSPD values for each algorithm and element. The dotted lines represent ± half the standard deviations of the values: (a) nickel, 5 point; (b) nickel, 4 point; (c) chromium, 5 point; (d) chromium, 4 point; (e) magnesium, 5 point; and (f) magnesium, 4 point. A, Baird Quadratic; B, Baird Rational; C, IL Cubic; D, Varian Rational; E, PE 3 Coefficient; F, PE 2 Coefficient; G, PU Quadratics; H, Linear Interpolation; and I, Manual
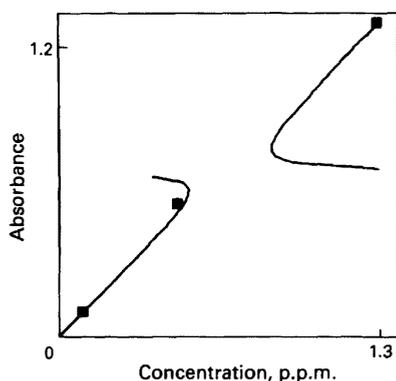
Fig. 2. The discontinuity observed for the four-point magnesium calibration, when fitted with the Perkin-Elmer 3 Coefficient function

Conclusions

It is apparent that the performance of a particular algorithm depends on the shape of the calibration curve. There are situations in which the errors introduced by the poor fit of the calibration function can be quite serious. In such instances, manual plotting of the calibration curve is no better than the computer fitted curves. Given the difficulty of predicting what the shape of a particular element's calibration curve will be for a particular instrument under a particular set of operating conditions, it seems likely that whatever algorithm is used there will always be errors due to the lack of fit. These errors will generally be worse, the fewer the calibration points that are used. As calibration is a non-productive part of an instrument's operating period, there is naturally a tendency to reduce the number of standards required to the minimum. Some improvements in the fits obtained with the various algorithms may be possible if appropriate weighting is given to each calibration point. It is well known that the calibration points are heteroscedastic. One possible way round the errors introduced by fitting curves to a limited number of calibration points is to use an alternative calibration strategy. Two such alternative strategies, based on the use of a microcomputer, are: (a) to produce a continuous concentration - time profile from an exponential dilution flask[16] and to collect, in effect, a very large number of calibration points over the required working range; and (b) to dilute automatically, by a known factor, a concentrated standard to give the same absorbance as the unknown.[17] Neither of these two methods requires any knowledge of what the shape of the absorbance concentration plot is.

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