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Current Calibration Practices for Flame Atomic Absorption Spectrometry - 1. Initial Results from a Survey

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Current Calibration Practices for Flame Atomic Absorption Spectrometry
Part 1. Initial Results From a Survey

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Information about 309 different routine analyses by flame atomic absorption spectrometry has been obtained from a questionnaire survey. The information is analysed according to the methods of overcoming interferences, the methods of curve fitting and the reasons for choosing a particular calibration method. The results indicate that most methods suffer from interference effects and that the addition of matrix modifiers or the matching of standards is the most popular approach to overcoming these effects. Manual curve fitting procedures are still widely used and 5-point calibrations are the most used. No clear cut reasons for choice of calibration strategy emerge from this preliminary analysis of the returns to date.

Any analytical procedure that uses an instrument for the measurement stage will only give accurate results if a reliable calibration procedure is used. As all quantitative procedures use at least a balance or a burette as the instrumental stage, no analytical method can give results the reliability of which is independent of the reliability of the calibration procedure. This is particularly true for flame atomic absorption spectrometry (FAAS), as the instrument response is a complex function of operating parameters and sample composition. In general, calibrations are curved over the working range, the shape depending on both the analyte element and other components of the sample.

As selection of the appropriate calibration strategy is an important part of the analyst's range of problem solving skills, it is surprising that little space is devoted to the topic of calibration in instrumental text-books. Even more surprising is the superficial treatment of the topic in text-books concerned specifically with analytical atomic absorption spectrometry. This includes those which purport to adopt "a practical approach."

For some reason, it appears to be taken for granted that all analytical chemists, including student analytical chemists, know all about calibration strategies. To some extent, with the advent of microcomputer data handling facilities as integral parts of the current generation of atomic absorption spectrometers, constraints have been introduced on the choice of calibration procedure. Once a particular instrument has been selected, then so has the curve fitting algorithm, assuming that the analytical chemist wishes to make use of the considerable time saving features and convenience factors that the use of computerised data acquisition and manipulation facilities brings.

In order to assess the extent to which various calibration procedures are used by practising analytical atomic spectro-scopists and to gain information concerning the factors affecting the choice of calibration strategy when dealing with real samples and of the impact of microcomputers, a questionnaire survey of all UK members of the Atomic Spectroscopy Group (ASG) of the Analytical Division, Royal Society of Chemistry, has been conducted. Some preliminary findings are reported and discussed here.

Experimental

Questionnaire

The first version of the questionnaire was sent to members of the committee of the ASG as a pilot survey. Comments and suggestions received from this pilot survey were incorporated into the final version of the questionnaire, which is shown in Fig. 1.

As can be seen from Fig. 1, the questionnaire is divided into a number of sections. These request information about: (1), analyte element, sample type and dissolution procedure (if the sample is not a liquid); (2), treatment of samples following dissolution such as might be used to overcome or compensate for interference effects; (3), the pre-treatment of standards; (4), instrument operating parameters (including sample presentation) and optimisation; (5), method of data acquisition; (6), the fitting of a curve to the calibration data; and (7), any other relevant information. This version was distributed to the 794 UK members of the ASG.

Results and Discussion

So far, 98 questionnaires have been returned, representing information on 309 different analyses. At this stage only information concerning the approach to overcoming interferences, the number of calibration points and the curve fitting method, and the reason for choosing a particular calibration

method is presented and discussed. A full analysis of all of the information will be given in a later publication.

Approaches to Overcoming Interferences

The results of section 2 of the questionnaire are given in Fig. 2. From this it can be seen that almost one third of the analyses reported as routine were considered not to have any interferences present and samples were analysed against suitably diluted stock aqueous solutions of the appropriate simple metal salts. About a quarter of the total had some form of reagent addition in the sample pre-treatment as a means of suppressing interference effects. The reagent most often added in this group was classified as a releasing agent, though with a substantial number being classified as ionisation suppressants.
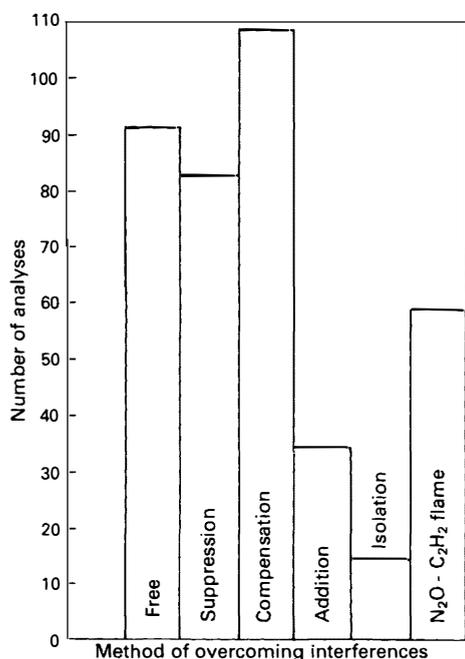

Fig. 2. Numbers of analyses classified by the approach used to overcome interference effects

Several determinations had both releasing agents and ionisation suppressants added, although the questionnaire did not allow a distinction between the use of two separate reagents or a dual purpose reagent such as lanthanum. Only one analysis was reported in which a protecting agent was used. Just over one third of the analyses were described as compensating for interferences by being carried out against standards matched to the samples with respect to some or all of the matrix components. Some analyses used a combination of reagent addition and matrix matching. Just over one tenth of the analyses used the standard additions method and about 5% involved a separation step in which the analyte was isolated from other matrix components. Just under one fifth of the analyses made use of the nitrous oxide - acetylene flame, although only half of these involved the use of the addition of an ionisation suppressant. Another interesting feature was that several analyses were performed with reagent addition to the samples but not to the standards and some with reagent addition to the standards but not to the samples. A few analyses were performed with the instrument deliberately optimised for "minimum interference" and several others were apparently performed with the instrument optimised for both "minimum interference" and "maximum sensitivity."

To some extent, the balance that appears from a study of this section of the questionnaire depends on the sample matrix and the elements determined. The influence of sample type on the choice of method of dealing with interference effects will be examined more closely in a later report. The elements

determined could be grouped into four categories based on number of determinations. In order of decreasing popularity these are Ca, Cu, Pb and Zn, followed by Al, Cd, Fe, Mg, Na, then K, Mn, Li, Ni, and lastly Ag, Au, Co, Cr, Pt, Sn.

Curve Fitting to Calibration Data

The numbers of calibration points used are shown in Fig. 3(*a*) for the normal calibration method. The lower sub-division of each group shows the number of manually fitted curves (either ruler or flexicurve) that were reported for each group. The remaining calibration curves for each group were fitted by using a computer based method. The most popular number of calibration points was 5. The number of additions used in the standard additions mode is shown in Fig. 3(*b*) with the same sub-division as described above.

The use of the atomic absorption instrument's integral computer for curve fitting only accounted for just under one half the total analyses reported (144 analyses described by 42 respondents). Thirty respondents (83 analyses) indicated the use of the ruler and 15 respondents (52 analyses) used a flexicurve. A few respondents reported using both ruler and flexicurve and a few reported using both a manual and a computational based method. Nine respondents were using their own computer interfaced to the instrument (22 analyses) and 10 respondents were using a computer not interfaced to the instrument (27 analyses).

This part of the questionnaire did not cover all possible methods as some respondents were unable to indicate any method at all. From the additional comments made, these respondents were either using an instrument with a hard-wired "curve linearisation" facility or were using a single standard and a simple proportion calculation on a "pocket" calculator.

A suspected "outlier" has been omitted from Fig. 3(*a*). One respondent indicated the use of 25 calibration points together with a manual curve fit method, the over-all strategy being selected for speed.

Choice of Calibration Method

Table 1 shows the breakdown of the analyses reported by number of calibration points used with respect to the criteria speed, precision and accuracy. Table 2 shows a similar breakdown of the method adopted to deal with interference effects. No clear pattern emerges from these tables, although there is a slight tendency to the diagonal relationship of the high numbers that might be expected.

Table 1. Numbers of analyses classified by number of calibration points and reason for choosing the calibration method

Number of calibration points	Speed	Precision	Accuracy
1	21	1	12
2	21	4	18
3	27	25	56
4	28	8	28
5	33	29	43
6	2	1	—
7	—	—	—
8	—	2	2

Many respondents indicated that their choice of calibration was made for reasons of: both speed and accuracy; accuracy and precision; speed, accuracy and precision; and occasionally speed and precision. This is the reason for the rather flat distribution along the rows. Respondents obviously felt that, as far as a choice of calibration strategy was concerned, "speed" and "accuracy" were not necessarily mutually exclusive. It is difficult to avoid the impression that respondents interpreted this section as asking reasons for choosing flame atomic absorption spectrometry. Some respondents commented that the reasons for choosing a particular calibration method were a
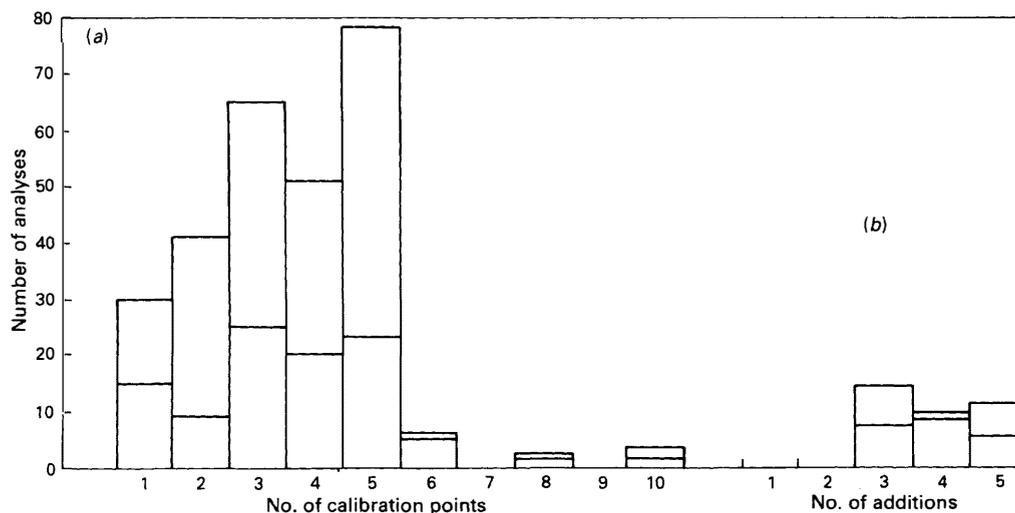
Fig. 3. Numbers of analyses classified by the number of calibration points. (a), Normal calibration curves; (b), standard additions method

judicious balance of all three criteria listed. One other criterion was proposed by a few respondents, namely "simplicity." This might be interpreted as a compromise between speed and accuracy. One or two commented that the choice of calibration strategy depended on the particular problem to be solved. While this is true, the questionnaire sought information about analyses that were considered routine, and thus the decision about the calibration strategy to be adopted should have been taken some time ago, presumably at the time the method was being developed and evaluated.

Table 2. Numbers of analyses classified by method of approach to dealing with interference effects and reason for choosing the calibration method

Approach to dealing with interferences	Speed	Precision	Accuracy
No pre-treatment	53	23	45
Matrix modification	59	27	72
Matrix matching · · ..	40	29	65
Standard additions · · · ·	7	6	16
Matrix isolation · · · ·	9	11	14

It is possible that a clearer picture will emerge concerning the choice of calibration strategies when the types of sample and elements sought are classified as well.

Conclusions

The extent to which conclusions can be drawn and generalisations formulated from the results presented here is limited. Firstly, the target sample (members of the ASG) might not be representative of the entire population of AAS users, and

secondly, the sub-sample of questionnaires returned could also be unrepresentative. In addition to these limitations, some shortcomings in the questionnaire became apparent when respondents interpreted the questions in different ways. For example, it is clear that not everyone agrees on what constitutes an "addition" in the standard additions method. Some respondents who indicated n additions in section 2, indicated n calibration points in section 6; some indicated $n + 1$ calibration points. It would probably have been sensible to ask about the strategy used for drift correction and re-calibration. Also, to include, in section 6, a question concerning the use of hard-wired curve-linearisation facilities.

It appears that, as far as routine analyses are concerned, the most frequently determined elements are calcium, copper, lead and zinc. Over two thirds of such analyses involve attempts to overcome interference effects, but of these attempts the standard additions method does not feature to any extent. The same comment can be made about techniques such as solvent extraction, co-precipitation, etc. The use of the nitrous oxide - acetylene flame accounts for about one fifth of routine analyses but the use of an ionisation suppressant with this flame type is by no means automatic. Five calibration points is the most popular number to use, and the use of ruler and flexicurve to draw the calibration curve is still widespread.

The use of instruments' integral computers does not dominate the picture yet.

The survey continues; anyone wishing to participate should contact the authors for a copy of the questionnaire.