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COMPARISON OF SENSITIVITY OF ATOMIC-ABSORPTION
AND ATOMIC-FLUORESCENCE SPECTROSCOPY

KEY WORDS: Atomic-Absorption Spectroscopy, Atomic-Fluorescence Spectroscopy, Sensitivity, Detection-limit, Hollow cathode lamps, Electrodeless discharge lamps

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Willis ¹ has commented on an apparent confusion in terminology in recent papers from this laboratory ^{2,3,4} with respect to the detection limit in atomic-absorption and atomic-fluorescence spectroscopy.

As he points out, early workers in atomic-absorption spectroscopy used the words 'Sensitivity' and 'detection limit' interchangeably without exact definition. In one of his own contributions ⁵, the concentration is quoted of metals in solution required to give 1% absorption - corresponding to the maximum noise level ie a detection limit corresponding to 1% at a signal:noise ratio of 1. As Willis indicates, noise levels for hollow cathode lamps are frequently lower than the 1% absorption level. Accordingly the word 'Sensitivity' has been used for the concentration of metals in aqueous solution required to produce 1% absorption of line intensity from the primary source. This gives a fairly true measure of the transition probability for the atomic line, superimposed on the efficiency of the nebulising

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- atomising system. The term 'detection limit' has come to mean the aqueous concentration of metal ions, stated in ppm, required to produce an absorption-signal : system-noise signal ratio of 1 or 2, or whatever ratio the researcher specifies. The detection limit varies from one instrument to another and on a given instrument and flame from one lamp to another, with gain setting, slit-width, scale expansion factor, etc. Willis¹ includes the operator of the instrument, presumably indicating ^{that} / bias also plays an important part in selecting the scale reading. Although the 'detection limit' has some merit in absorption studies, the Sensitivity definition is fundamentally and practically a much more realistic and meaningful term. But, even with good single beam instrumentation it is not a figure that is generally used by most operators as the lowest point on their analytical calibration curve because such a low absorbance value cannot be measured precisely and accurately in most instances. A much more realistic figure would be to select an arbitrary value of 0.01 absorbance unit rather than a percentage, with an odd absorbance value.

'Sensitivity' cannot, unfortunately, be defined in the same way for fluorescence emission signals, but here the noise level is chiefly contributed by the electronics of the detector-amplifier system and, to a lesser extent, by the flame emission at the band pass used. Where there is no scatter or reflection from surrounding equipment, the noise level is independent of the primary source: Consequently, whilst the detection limit in fluorescence is again subject to instrumental variables, as in absorption, it is more characteristic of

the practical sensitivity of the fluorescence method, and there is no better measure of sensitivity to be used at present. (The word 'sensitivity' is used here in normal English usage, N.E.U.)

West and Williams^{2,3} define their detection limit as corresponding to 1% scale deflection at a signal:noise ratio of 2 (Ag) or 1 (Mg). It is difficult to see Willis' objection to this definition of detection limit, which gives an idea of the noise level at maximum gain and slit width, as 1% of the full scale deflection. It is true, however, that in both papers the elementary error was made by referring to 1% absorption as 'detection limit' in AAS, rather than Sensitivity, but the values quoted are defined.

The real test of the sensitivity (N.E.U.) of the AAS and AFS methods is to compare the smallest amounts one can determine reproducibly and accurately. It is not suggested that a term 'determination limit' should be defined, but in our experience, and that of many others, the lower ends of AFS calibration curves commonly correspond to 10 fold lower concentrations than the corresponding AAS curves using the same apparatus which has been designed for absorption measurements. Thus the sensitivity (N.E.U.) of AFS as a technique does, in our experience, prove to be generally superior to that of atomic-absorption where a good line source is available.

Willis says that West and coworkers reached their conclusions concerning the relative detection limits in AFS and AAS - he should of course have said relative sensitivity - by comparing detection limits in AFS with Sensitivities in AAS. There is of course no 'Sensitivity' figure for

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AFS, only the 'detection limit' which is felt to be more characteristic of sensitivity (N.E.U.) in AFS than in AAS. The Sensitivity value for AAS is agreed to be a more appropriate measure of sensitivity (N.E.U.) in AAS. However, even if one argues over the terms to be compared, the calibration curves do bear out our conclusions.

Willis states correctly that we have found microwave excited electrodeless discharge lamps to have higher intensities than, and comparable stabilities to, conventional hollow cathode lamps. He then goes on, incorrectly, to say that the failure of Dagnall, Taylor and West to obtain detection limits in AAS approaching those reported by others using somewhat similar equipment, but with hollow-cathode lamps, is difficult to explain. Here Willis has confused his terminology; we did not quote any detection limits for AAS, only Sensitivities. Certainly the Sensitivities we found with the electrodeless discharge lamps are very similar to those quoted by the manufacturer using hollow cathode lamps. The improvement with electrodeless discharge lamps is probably significant for As, Hg and Se. Willis' observation that we failed to set as good detection limits is, however, completely untenable since we did not determine detection limits.

Lastly, if we compare the Perkin Elmer Model 290 detection limits in AAS quoted by Willis with the AFS detection limits quoted by Dagnall, Taylor and West it will be seen that, in 10 out of the 15 instances where direct comparison is possible, the AFS limits are superior. This occurs despite the fact the Model 290 is designed for atomic absorption measurements and that the instrument we used (also designed for absorption) was non-standard and that an inordinate flame to slit distance of 25 cm had to be used. Much better sensitivity (N.E.U.) ^{could be} realised with correctly designed equipment.

The paper concerned ⁴ explicitly states that it sets out to show that improvised apparatus commonly available in most laboratories may be used to measure atomic fluorescence in conjunction with laboratory prepared electrodeless discharge lamps to good advantage.

On the basis of the above discussion and Willis' own data , clearly his contention that sweeping generalisations were made by Dagnall, Taylor and West cannot be substantiated.

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