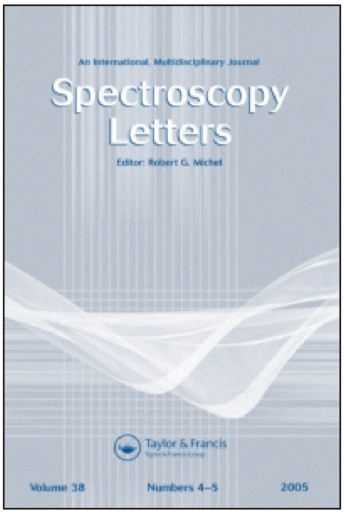

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Comparison of Detection Limits in Atomic Fluorescence and Absorption Spectroscopy

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COMPARISON OF DETECTION LIMITS IN ATOMIC FLUORESCENCE AND ABSORPTION SPECTROSCOPY

KEY WORDS : Detection limits, atomic fluorescence spectroscopy, atomic absorption spectroscopy

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Dagnall, Taylor, and West[1] have recently compared detection limits for a number of metals in atomic fluorescence and absorption spectroscopy and have concluded that "atomic fluorescence measurements using an electrodeless discharge tube are inherently more sensitive than those obtainable by atomic absorption measurements". Likewise West and Williams have compared the two techniques for magnesium[2] and silver[3], using high-intensity hollow-cathode lamps as sources, and have found much lower detection limits in fluorescence than in absorption.

Since there seems to be some confusion about the meaning of the term "detection limit" as used by these authors it seems desirable to clarify the issues involved.

Early workers in the field of atomic absorption spectroscopy[4-7] tended to use the terms "detection limit" and "sensitivity" interchangeably and without giving them any exact meaning. Gatehouse and Willis[8], in an extensive survey of the performance of a simple single-beam instrument, quoted the concentrations of metal in aqueous solution required to give 1% absorption, which corresponded to the maximum noise level found in their equipment. They stressed however that since the noise levels of hollow-cathode lamps for many metals were lower than this, the true detection limit would frequently be less than the concentration giving 1% absorption. Later authors[9,10] pointed out the value of using the word "sensitivity" for the concentration of metal required to give 1% absorption, since this quantity, which is determined by the oscillator strength of the absorbing line and the performance of the atomizing system, serves to indicate approximately the useful working range under ordinary analytical conditions.

The "detection limit" is defined in terms of the signal-to-noise ratio, and is the concentration of metal in aqueous solution required to give an absorption signal equal to (or double, if greater confidence is required) the noise level of the signal from the light source when water alone is sprayed into the flame. In practice, observed detection limits, unlike sensitivities, vary considerably with the instrument and the operator, and are determined principally by the stability of the light source and of the detector-amplifier-readout system. If warranted by the stability of these components, scale expansion may be used to improve the limit of detection, and provision for this is made in most modern instruments.

In atomic fluorescence, as in emission spectroscopy, there is no quantity directly corresponding to the sensitivity in absorption, but "detection limit" is defined analogously as the concentration of metal required to produce a fluorescence signal equal to (or double) the noise level of the emission signal from the flame when water alone is sprayed. The detection limit is largely independent of the signal-to-noise ratio of the radiation emitted by the exciting light source.

West and coworkers[1-3] reached their conclusions concerning the relative detection limits in atomic fluorescence and absorption spectroscopy by comparing detection limits in the former technique with sensitivities in the latter, apparently assuming that absorption values of less than 1% can never be detected. Clearly this method of comparison is misleading, as the detection limit in both techniques must be defined in terms of signal-to-noise ratio, and it is surprising that this simple fact apparently escaped the notice of the reviewers of the above papers.

According to West and coworkers[11,12] microwave-excited electrodeless discharge lamps have much higher intensities and are at least as stable as conventional hollow-cathode lamps. Thus the failure of Dagnall, Taylor, and West to obtain detection limits in atomic absorption approaching those reported by others using somewhat similar equipment but with hollow-cathode sources is difficult to explain. It can only be assumed that the quality of the detector-amplifier-readout

TABLE 1

Detection Limits and Sensitivities in Atomic Fluorescence and Absorption Spectroscopy

Metal	Atomic Line nm	Dagnall, Taylor, & West[1]		Perkin-Elmer Model 290[13]	
		Fluorescence detection limit, µg/ml[a]	Absorption sensitivity, µg/ml[b]	Absorption sensitivity, µg/ml[b]	Absorption detection limit, µg/ml[b,c]
Ag	328.1	0.02	0.10	0.1	0.025
Al	396.1	50[d]	2.0[e]	2.0[e]	-
	309.3	-	-	1.3[e]	0.1[e]
As	193.7	0.13[f]	1.5[g]	2	2
Bi	306.8	1.00[f]	-	2.1	-
	223.1	-	-	0.8	0.1
Cd	228.8	0.0001	0.05	0.04	0.005
Co	240.7	0.04	0.15	0.15	0.015
Cr	357.9	0.05	0.20	0.15	0.015
Cu	324.7	0.03	0.15	0.15	0.0075
Fe	248.3	0.008	0.20[g]	0.15	0.015
Hg	253.7	0.10	6.00[g]	11	1.5
Mn	279.5	0.014	0.10	0.10	0.01
Ni	232.0	0.006	0.20	0.15	0.03
Pb	405.8	0.06	-	-	-
	283.3	0.40	-	0.7[h]	0.035[h]
Sb	217.6	0.08	-	0.7	0.1
Se	196.1	0.16	0.80[g]	2[h]	1[h]
Sn	303.4	0.60	-	-	-
	224.6	-	-	1.2[a]	0.15[a]
Te	214.3	0.06	0.8[g]	0.7	0.15
Tl	377.6	0.20	2.0[g]	-	-
	276.8	-	-	0.45	0.035
Zn	213.9	0.0002	0.05	0.025[h]	0.0075

[a] Air-hydrogen flame.

[b] 10 cm air-acetylene flame.

[c] The detection limits of reference 13 have been divided by 2 to correspond with the signal-to-noise ratio of unity used in reference 1.

[d] Nitrous oxide-hydrogen flame.

[e] 5 cm nitrous oxide-acetylene flame.

[f] Nitrogen-hydrogen-entrained air flame.

[g] 10 cm air-propane flame.

[h] Can be improved in lower-temperature flame.

system was inadequate to do justice to the stability of the light sources. Table 1 shows Dagnall, Taylor, and West's detection limits in atomic fluorescence and sensitivities in absorption together with sensitivities and detection limits for a comparable single-beam commercial atomic absorption instrument[13]. Use of a more sophisticated double-beam instrument allows of considerably lower detection limits in absorption[14].

On the basis of the data in Table 1 it is difficult to sustain the rather sweeping generalizations made by Dagnall, Taylor, and West.

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