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Improvements in the Measurements of Characteristic Concentrations in Continuum Source Atomic Absorption Spectrometry

Sir: In a previous paper (*1*), we described and demonstrated the operation of a continuum-source high-resolution wavelength modulated atomic absorption spectrometer (CEWM-AA) and compared its characteristic concentrations (In accordance with IUPAC recommendations, the term "characteristic concentrations" is used to mean the "concentration giving an absorbance of 0.0044".) and detection limits to conventional line-source atomic absorption. Although the detection limits for seven of the nine elements tested were better than conventionally background-corrected line source results, the characteristic concentrations were somewhat poorer. This note reports improved measurements which demonstrate that the characteristic concentrations of CEWM-AA are more nearly equal to those of line-source AA than had been previously thought.

The new measurements differ from those previously reported (*1, 2*) in several ways: (a) stray light due to the partial overlap of the light from adjacent orders was discovered to have affected the previous measurements and has now been eliminated; (b) smaller slit widths are used; (c) in the previous comparison of line vs. continuum source characteristic concentrations, the two instruments being compared utilized burners of different design, which may have influenced the comparison; (d) the method of calculating absorbance from the output of the lock-in amplifier in the previous CEWM-AA measurements depended on the value of a waveform correction factor whose derivation was based on several simplifying assumptions (*3*), whereas the present measurements are based on direct photocurrent measurement not involving a lock-in; and (e) the same *entrance* slit width was used in both line and continuum source measurements in the present work in order to avoid an error due to the inhomogeneous distribution of absorbing atoms across the light beam, while in the line source measurements the *exit* slit width was increased in an effort to bring the spectral bandpass as close as possible to the value recommended for line source measurements.

The present measurements differ from those of Keliher and Wohlers (*2*) because of points (a) and (e) above, neither of which were considered by these workers, and because the present data were obtained at a 25-μm slit width even at wavelengths below 230 nm, where Keliher and Wohlers used a 10-μm slit in that region. We have found that, although the 10-μm slit gives better characteristic concentrations, alignment difficulties and poor signal-to-noise ratios make this slit width impractical for actual analytical work. Another difference is that the monochromator used in the present work has been fitted with a refractor plate wavelength modulator, whose defocusing effect might be expected to increase the effective spectral bandpass to a slight extent.

As a result of these improvements, we feel that the characteristic concentration comparisons reported here are more nearly correct than those previously reported (*1*).

EXPERIMENTAL

The instrumentation was set up as described previously (*1*), except that an improved version of the Spectrometrics Model 102 echelle spectrometer was used. This new version is provided with a set of precision, interchangeable slits from 25- to 200-μm width. Because of the improved quality of the slits and slit mounting blocks, it proved to be practical to use the 25-μm slits, whereas in previous work (*1*) this slit width had caused alignment difficulties and excessive light losses. As would be expected, the characteristic concentrations improve if the slit width is reduced (*4*). The detection limit, on the other hand, theoretically does not change (*5*). More important, the new spectrometer is provided with an order-sorter prism with a larger base and greater dispersion. This results in more complete separation of adjacent orders and reduces order-overlap stray light, a problem peculiar to echelle monochromators which was not suspected or corrected for in previous work (*1, 2*).

In order to avoid differences in flame optimization and burner design from interfering with characteristic concentration comparisons, line-source characteristic concentrations were measured on the same flame and optical system as the CEWM-AA system, except that the wavelength modulation was disabled. Since only *comparisons* of characteristic concentrations were sought, no attempt was made to optimize burner and flame conditions, which were the same for both line and continuum source measurements. The burner system used (i.e., Varian-Techtron AB-41 with 10-cm standard air–acetylene burner head) and the conditions of burner position and gas flow rates, were matched as closely as possible to the previous work (*1, 2*).

Continuum source characteristic concentrations were measured both with wavelength modulation, taking I and I_0 from an oscilloscope presentation of the modulated photosignal, and without wavelength modulation, using a nanoammeter to measure the dc photosignals. Both methods gave the same characteristic concentrations.

RESULTS AND DISCUSSION

Of the several potential sources of error listed above, only stray light (a) seems to be significant. The stray light resulting from the partial overlap of adjacent orders is a problem unique to the echelle spectrometer. In the two-dimensional spectrum produced by the echelle (*6*), light intensity falling in the orders immediately above and below the measured order may become a source of stray light if the slit height is large enough to allow appreciable overlap of the adjacent orders. Since a continuum source is used in CEWM-AA, there will always be appreciable light intensity at all wavelengths in the adjacent orders.

Previous measurements of stray light (*1*) were done by the ASTM method (*7*), which cannot detect near stray light of this type. As usual, the stray light, being unabsorbed by the analyte, worsens characteristic concentration. However, the improved model of the echelle spectrometer used in the present work reduces this difficulty by providing greater order separating dispersion. Nevertheless, characteristic concentration is still significantly poorer at the largest slit height, as shown by the Zn analytical curve in Figure 1. The previously reported characteristic concentration measurements (*1*) were performed at a slit height which gave an order overlap equivalent to that at a slit height of 500 μm on the present instrument. The data presented here were obtained at 300 μm, a compromise between characteristic concentration and light intensity.

It is also possible that the overall stray light level of the instrument is increased by reflection and scattering of the primary beam by the refractor plate, which in the present instrument is positioned behind the entrance slit. This possibility was not specifically investigated, but it is probably not a large factor since the characteristic concentrations obtained here are, if anything, better than those obtained by Keliher and Wohlers (*2*), who did not use a refractor plate modulator. In any case, the signal-to-noise and background correction advantages of wavelength modulation (*1*) far outweigh whatever slight degradation in characteristic concentration might be attributable to stray light or spectrometer defocusing.

A comparison of the characteristic concentrations of line and continuum source AA is given in Table I. Since it was suspected that line source characteristic concentrations might

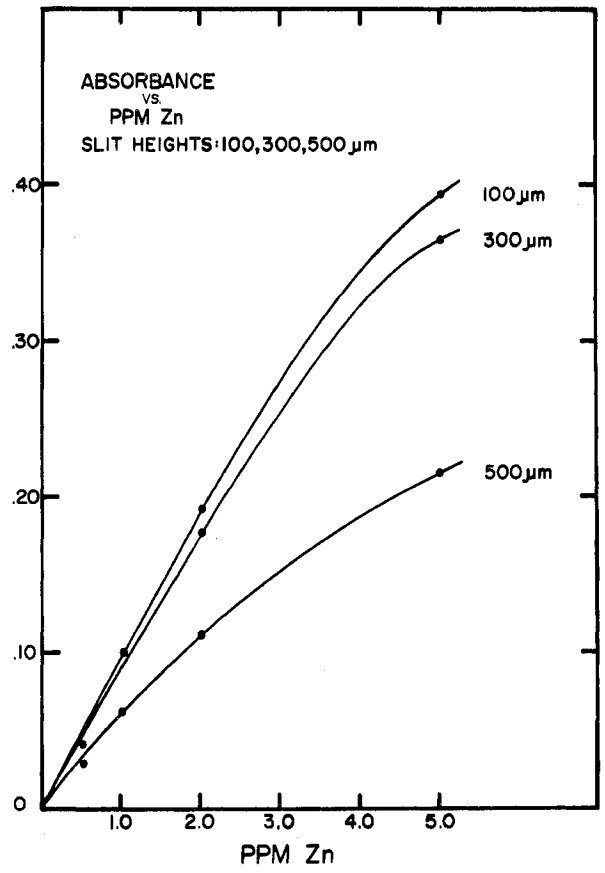

Figure 1. Effect of slit height on the Zn (213.86 nm) analytical curve in an air–acetylene flame

be a function of spectral bandpass, an attempt was made to determine the line source characteristic concentrations at the spectral bandpass usually used in conventional instrumentation. Because of the high resolution of the echelle spectrometer, however, such spectral bandpasses cannot ordinarily be reached even at the largest available slit width. As a rule, characteristic concentration is found either to remain unchanged or to improve as spectral bandpass is decreased. Thus, the line source characteristic concentrations reported here could, in principle, be slightly too good. A brief experimental check, however, showed that this effect was insignificant. The data in Table I show that the continuum source characteristic concentrations obtained here are slightly better than those reported by Keliher and Wohlers (*2*) and by Zander et al. (*1*). Although the differences are of approximately the right magnitude to be accounted for by the order-overlap stray light effect, they might also be due to slight differences in flame conditions and burner position. Compared to line source characteristic concentrations measured under the same conditions, the continuum source characteristic concentrations vary from a factor of 2 poorer (for Zn) to nearly equal (for Ba).

CONCLUSIONS

The usefulness of characteristic concentration as a figure of merit in atomic absorption, as opposed to detection limit, is questionable. We have already shown (*1*) that the detection limits of the CEWM-AA technique are better for most elements than those of conventional background-corrected line source AA. But characteristic concentration comparisons between line and continuum source measurements are nevertheless significant as an indication of how much one can expect to gain by going to an even higher resolution system, assuming that the lower continuum source characteristic concentrations reported here are indeed due to the Beer's law deviation caused by finite source width and assuming that hollow cathode sources represent the ultimate case of negligible source width. The data presented here show that little is to be gained by improved resolution alone.

Table I. Characteristic Concentrations[a] of Line (AAL) and Continuum Source (AAC) Atomic Absorption

		Characteristic concentrations			
Element	Line, nm	AAL, this work[c]	AAC, this work	AAC, Keliher (*2*)	AAC, Zander (*1*)
Zn	213.86	0.025	0.047[e]	...	0.05[e]
Mg	285.2	0.012	0.016	0.020[d]	0.03
Cu	324.7	0.10	0.17	0.20	0.34
Ca	422.7	0.10	0.16	0.20	0.59
Ba[b]	553.5	2.0	2.3	3.5	...

[a] Concentrations, ppm in aqueous solution, which give an absorbance of 0.0044. [b] N_2O/C_2H_2 flame with ionization supressor; all others air/C_2H_2 flame. [c] 25-μm entrance slit, 200-μm exit slit. Hollow cathode lamp current as per manufacturer's recommendation. [d] 10-μm entrance and exit slits; all other AAC data at 25-μm entrance and exit slits. [e] Corrected for far stray light (*1*).

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