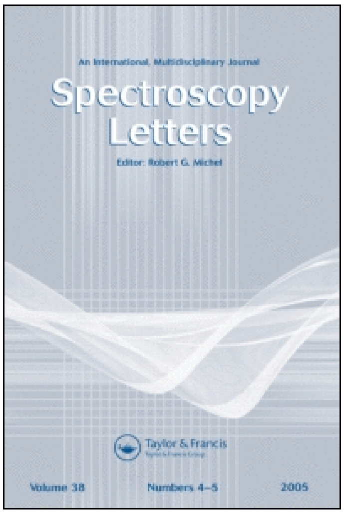

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Preliminary Studies IK Echelle Flame Spectroscope

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PRELIMINARY STUDIES IN ECHELLE FLAME SPECTROSCOPY

KEY WORDS: High-resolution, Echelle, Flame Spectroscopy.

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INTRODUCTION

It has recently been stated[2] that "flame photometry can scarcely equal the freedom from spectral interference of atomic absorption until monochromators with effective bandpasses of ca. 0.02 Å (i.e. half-band width of absorption line) become generally available." Resolution of at least this order is now attainable with the aid of instrumentation based on the echelle grating, with none of the disadvantages normally associated with conventional ultra-high resolution monochromators.

The echelle grating, which was developed by Harrison[3,4] some twenty years ago to answer this very need, consists of a series of ruled wedges, generally 8-80 mm^{-1}, arranged in such a way that the inclined grating resembles a series of steps. The optical system is arranged such that the incident light is nearly normal to the steep side of the wedge. Order overlap is avoided by preliminary dispersion with a low resolution prism or grating. The resulting spectrum is thus a two-dimensional array in which vertical displacement is indicative of the grating order, and horizontal displacement indicates wavelength within each order. For more detailed information the original references should be consulted[3-7].

The principal advantages of the use of the echelle as a dispersive system in analytical spectroscopy are that it provides spectral resolution which could otherwise be obtained only with a much larger conventional monochromator system, and that the intensity of the resolved spectral line is very much greater than that which could be obtained with a simple monochromator of comparable resolution. So far these advantages have been put to excellent use primarily in astronomical studies[8-11], where physical size is often particularly important. Thus, for example, small echelle systems in rockets have been used in solar spectral studies[8]. Echelle instruments have also been employed in the investigation of the Zeeman effect[12], line structure[13], and isotope ratio studies[14], where very high resolution is essential. Our preliminary investigation, which we believe to be the first in echelle flame spectroscopy, indicates that the virtual specificity of echelle emission spectroscopy is directly comparable to that of atomic absorption spectroscopy, and that molecular band interferences, in particular, are virtually non-existent. Moreover, in view of the fact that even with high background flames such as the turbulent oxy-acetylene flame used in the present investigation, line to background ratios are improved by more than one order of magnitude compared to typical emission spectrometers, excellent detection limits should be readily obtainable with a suitable detector-readout system.

In this publication we wish to report some preliminary observations on the use of the echelle in analytical flame spectroscopy, with particular reference to the effect of high-resolution on concentration-intensity relationships.

INSTRUMENTATION

The system used consists of a SpectraSpan Model 101 Echelle Spectrometer (Spectrametrics, Inc., Burlington, Mass.) fitted with a Beckman total consumption burner. The instrument is fitted[15] with an echelle grating in a Czerny-Turner mounting and a quartz prism. The dispersion of the system was estimated to be 0.48 Å mm^{-1} at 2,000 Å and 1.2 Å mm^{-1} at 5,000 Å, with a free spectral range of 18 Å and 100 Å respectively at these wavelengths. Spectra over the entire UV-visible range were photographed with exposures of less than one minute on 4" x 5" Polaroid Type 57 film rated at 3,000 ASA. A slightly fuel rich turbulent oxy-acetylene flame was used throughout this investigation.

RESULTS AND DISCUSSION

A brief preliminary investigation of the determination of sodium showed that strong self-reversal of the sodium lines at 589.00 nm and 589.59 nm was clearly visible at high sodium concentrations both photographically and also by manual photoelectric scanning. A clear indication of this is obtained from the calibration curves shown in Figure 1. Using entrance and exit slits of 25 µ and 100 µ respectively, the intensity at the line center decreases with increasing sodium concentration above 250 ppm. If, however, measurements are made at the half-intensity and quarter-intensity points on the emission profile obtained by nebulizing a 20 ppm sodium solution, the effect of reversal on the calibration curve is less pronouned, primarily as a result of the narrower absorption profile of the atoms in the cooler outer mantle of the turbulent flame. If the dimensions of the entrance slit are increased, see Figure 2, the extent of reversal becomes less pronounced when measurements are made at the line center, until eventually a typical emission calibration curve such as that shown in Figure 2C is obtained. It should be pointed out, however, that even under these conditions, the spectral resolution at this wavelength is still appreciably better than 1 Å. As expected, the depth of the reversal 'well' was found to decrease with increasing slit width at a given concentration. The results obtained for sodium indicate that by using an echelle monochromator, excellent detection limits should be attainable by atomic absorption spectroscopy using either continuous or flame sources, and these are at present under investigation.

The calibration curves obtained for manganese showed the same trends as those described above for sodium. The spectrum of the manganese triplet obtained using 100 µ slits is shown in Figure 3, and the calibration curves for manganese at the peak and half-intensity points on the emission profile from a 100 ppm manganese solution are shown in Figure 4.

To obtain some idea of the ultimate resolution of the instrumentation, the mutual interference of the gallium and manganese lines at 403.30 nm and 403.31 nm respectively was investigated. Although, as expected, no clear separation of the lines was obtained, even with a 25 µ entrance slit,

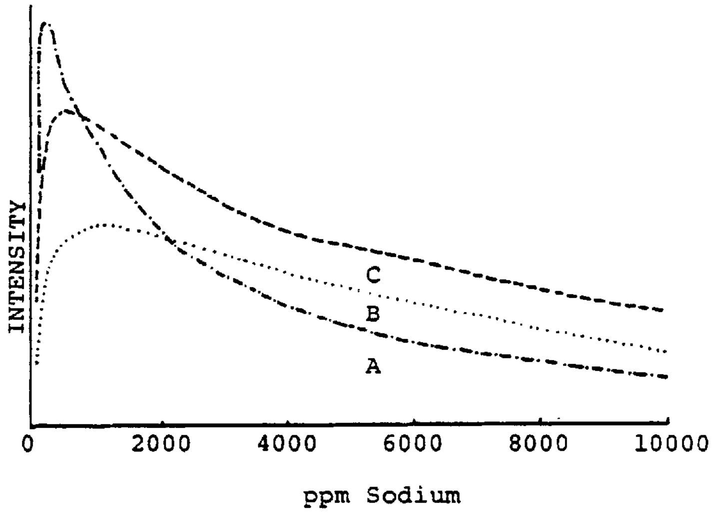

FIG. 1

Calibration curves for sodium at 589.00 nm with 25 μ entrance slit at A) line center, B) 50% line intensity at 20 ppm, C) 25% line intensity at 20 ppm.

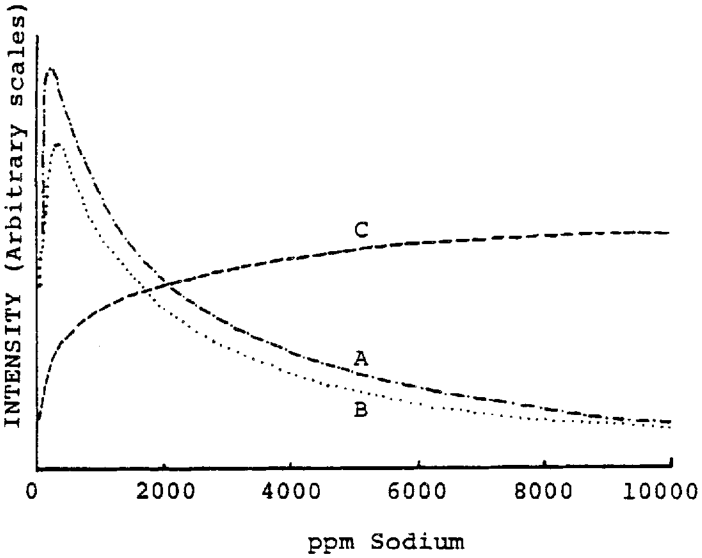

FIG. 2

Calibration curves for sodium at 589.00 nm with A) 25 μ entrance slit, B) 100 μ entrance slit, C) 500 μ entrance slit. All curves are at line center.

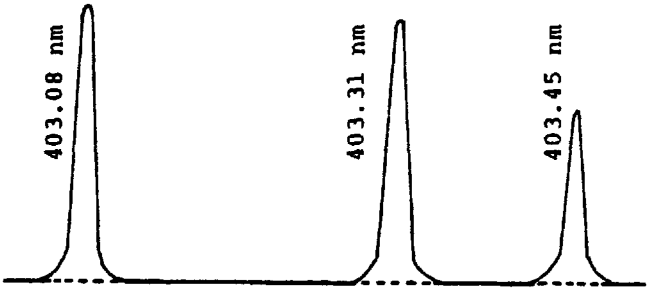

FIG. 3

Photoelectric scan of manganese triplet, using 100 μ entrance slit, showing typical resolution. (1,000 ppm)

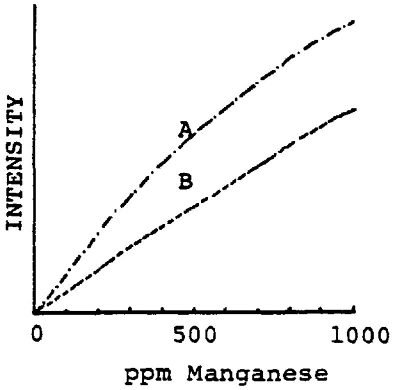

FIG. 4

Calibration curves for manganese at 403.08 nm at A) line center, B) 50% intensity at 100 ppm.

substantial broadening of the 403.31 nm manganese line was clearly visible, indicating the definite presence of gallium, when solutions containing equal amounts of manganese and gallium were aspirated into the flame. In this instance the limitation is the actual physical overlap of these spectral lines, which are separated by only 0.009 nm. This is probably the best documented mutual interference system in atomic absorption spectroscopy, but our results indicate that the interference can be virtually eliminated in echelle spectroscopy by making measurements at a point on the high wavelength side of the manganese 403.31 nm line emission profile.

CONCLUSIONS

The results of this preliminary investigation indicate that the very high resolution attainable with an echelle spectrometer gives to flame emission spectroscopy a virtual specificity previously associated only with absorption and fluorescence techniques, and that even where the latter techniques can furnish greater sensitivity, the echelle spectrometer should prove to be an invaluable tool in the detailed investigation of these phenomena.

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