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CONVENTIONAL MEASUREMENTS OF SPECTRAL LINE PROFILES FROM HOLLOW CATHODE LAMPS AND INDUCTIVELY COUPLED ARGON PLASMA BY A WAVELENGTH-MODULATION ECHELLE MONOCHROMATOR

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The spectral line profiles of emission lines from hollow cathode lamps and an inductively coupled argon plasma have been measured by using a wavelength-modulation echelle monochromator. The data for the linewidths of Zn, Cd, Fe, Mg and Ca are provided along with a data correction method.

In recent years, an inductively coupled plasma (ICP) has been established as an analytical excitation source of great potential, and extensively applied to the analysis of various samples. In ICP emission spectrometry, the profiles of emission lines from the ICP are of analytical interest in relation with spectral interferences1),2) or excitation mechanisms3)-6). Previous information about the line profiles from the ICP has been obtained by the measurements with a Fabry-Perot interferometer. However, most of these works were performed in terms of the lines over 400 nm because of the difficulty in fabricating dielectric coating especially below 400 nm. Furthermore, the Fabry-Perot interferometer is rather complicated and difficult to adjust and operate stably.

An echelle monochromator was first described by Harrison in 19497). As has been discussed8), it has some significant advantages over conventional monochromators such as high resolution, compactness and ease of use. Therefore, the echelle monochromator has been applied to analytical atomic spectrometry such as emission spectrometry and atomic absorption spectrometry, and also used in line profile measurements of vapor discharge lamps (VDL)9), electrodeless discharge lamps (EDL)10) and hollow cathode lamps (HCL)11),12).

In this paper, the emission line profiles from HCLs and ICP are investigated with an echelle monochromator. The wavelength-modulation technique is employed for a rapid repetitive scanning in a narrow wavelength region.

An echelle monochromator (Model UOE-1 from Kyoto-Koken Co., Japan) equipped with a quartz plate behind the entrance slit for wavelength-modulation was used as an optical dispersion system. The wave form for modulation was sinusoidal and the modulation frequency was 125 Hz. The optical characteristics of the echelle monochromator are given in Table 1.

The emission signal detected by a photomultiplier (PMT; Model R919 from Hamamatsu TV Co.) was amplified with a preamplifier and then acquired at 50 points

Table 1. Some Optical Characteristics of the Echelle Monochromator

focal length	80 cm
groove density	79 grooves mm^{-1}
angle of diffraction	75°58'
order of diffraction at 300 nm	82
reciprocal linear dispersion at 300 nm	0.046 nm mm^{-1}

with a sample-and-hold circuit during each half-cycle of modulation by the trigger pulses from a computer (Model HP85 from Hewlett-Packard Co.). The signal was stored in the computer memories through an A/D converter. In order to improve the precision, one data acquisition process mentioned above was repeated for integration 1250 times for 10 s. The angle of the quartz plate, which determined the wavelength position, was monitored by measuring the modulation wave in the same way as the PMT signal. The line profile was drawn on a X-Y plotter (Model 7225A from Hewlett-Packard Co.).

A plasma torch system and a RF generator (Model HFP2000D) were obtained from Kyoto-Koken Co. and Plasma Therm Co., respectively. A concentric nebulizer was used for sample introduction. The ICP or HCLs (Hamamatsu TV Co.) was imaged onto the entrance slit of the monochromator with a spherical lens (f = 12 cm) at a magnification of unity. The ICP was sustained at 1.1 kW RF power, and observed at 15 mm above the load coil. The Ar flow rates of coolant, auxiliary and carrier gases were 12, 0.8 and 0.9 l min^{-1}, respectively. The copper and zinc HCLs were operated at 5 mA d.c., at which the self-absorption of the emission lines might be negligible[13].

The observed line profiles of Zn I 213.856 nm and Cu I 324.754 nm from HCLs are shown in Fig. 1. As can be seen in Fig. 1, the copper doublet line at 324.754 nm, whose interval is known to be 0.004 nm, is clearly resolved. This result indicates high resolution of the echelle monochromator employed in the present experiment. In the case of Zn I 213.856 nm, the corrected line profile and instrumental function are also shown in Fig. 1. They were obtained by the procedure mentioned below.

The observed FWHM (full width at half maximum) of Zn I 213.856 nm line vs horizontal slit width is shown in Fig. 2. The results in Fig. 2 suggest that the instrumental broadening, which is determined by a instrumental function, is not negligible even at the narrowest slit width. Therefore, the instrumental function must be corrected to obtain the actual FWHM. The actual FWHM was estimated by extrapolating the linear line in Fig. 2, and was 0.00039 nm. Here, if it is

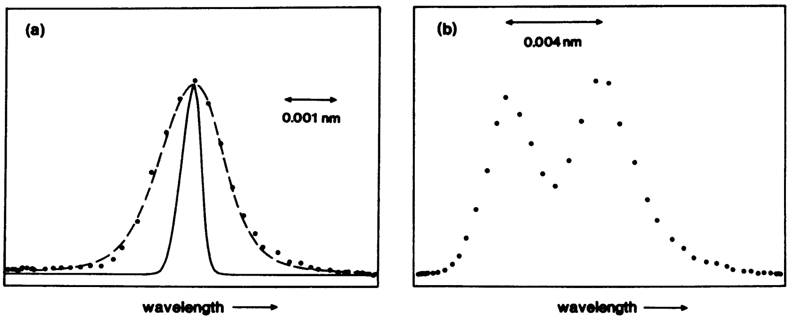

Fig. 1. The observed emission line profiles for (a) Zn I 213.856 nm, and (b) Cu I 324.754 nm from HCLs. Both zinc and copper HCLs were operated at 5 mA. In the case of zinc line, the corrected line profile and instrumental function are also shown as solid and broken lines.

assumed that the FWHM of HCL is determined only by the Doppler broadening 13), the corrected line profile in Fig. 1 is obtained as a pure Gaussian. On the other hand, the computer simulation for the observed profile was made, assuming a usual Voigt function4) In consequence, the instrumental function can be calculated from the simulated profile by the deconvolution technique.

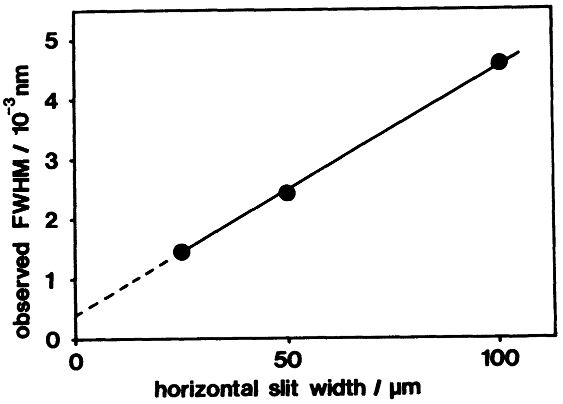

Fig. 2. Dependence of the observed FWHM from zinc HCL on horizontal slit widths. Zinc HCL was operated at 5 mA, and observed at 213.856 nm.

The extrapolated value is the FWHM at the minimum slit width, $\Delta\lambda_{1/2}(S\to0)$. This $\Delta\lambda_{1/2}(S\to0)$ is not the true FWHM of HCL because it is convoluted by other instrumental function, abberation. It is usually difficult to estimate abberation. In the present experiment, the HCL temperature calculated by the $\Delta\lambda_{1/2}(S\to0)$ is 430 K, which is in good agreement with literature value13),14). Therefore, the broadening caused by abberation may be considerably small. Moreover, the true FWHM of HCL may also be smaller than that caused by instrumental function, and so the uncertainty of the true FWHM of HCL does not contribute significantly to the instrumental function. Thus, the $\Delta\lambda_{1/2}(S\to0)$ is assumed to be a true Doppler FWHM. In fact, when the uncertainty of Doppler temperature of HCL is 100 K, the error in instrumental FWHM is only 2 %.

The dotted lines in Fig. 3 show the observed emission line profiles of Zn I 214.856 nm and Cd I 228.802 nm from the argon ICP, along with the simulated and corrected line profiles. With the deconvolution technique using the instrumental function, the actual line profiles can be deduced and are shown as the solid lines in Fig. 3. In the calculation, it was assumed that the instrumental function at any wavelength had the same profile shape except FWHM, and that the FWHM was proportional to the reciprocal linear dispersion of the monochromator. Some observed and actual FWHMs of emission lines from the ICP are summarized in Table 2, where the concentrations of solutions used are also shown in the final column. As can be seen from Table 2, the actual FWHMs of ICP emission lines of Zn, Cd, Fe, Mg and Ca are in the range from 0.0017 to 0.0047 nm. Human and Scott reported the FWHMs of 0.0031 nm for Ca II 393.367 nm, and 0.0027 nm for Sr II 421.552 nm4). The FWHM values obtained in Table 2 are quite reasonable in comparison

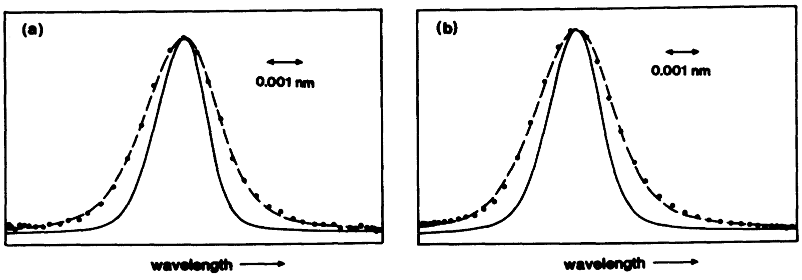

Fig. 3. The emission line profiles for (a) Zn I 213.856 nm, and (b) Cd I 228.802 nm from argon ICP.
● ● : observed line profile, — — : simulated line profile, —— : corrected line profile.

with those reported by Human and Scott. The larger FWHMs for Mg and Ca lines may be attributed to self-absorption in the ICP.

As discussed above, the present wavelength-modulation echelle monochromator system provides satisfactory resolution for the rapid and precise measurements of emission lines from the HCLs and argon ICP. Since spectral interferences are still severe problems in ICP emission spectrometry, the information about the emission line profiles and widths may help to solve or reduce such interference problems. Thus, the wavelength-modulation echelle monochromator is useful for analytical purpose, along with the simultaneous or sequential multielement determination.

Table 2. Observed FWHMs, Actual FWHMs of Emission Lines from Argon ICP, and Concentrations of Solutions

wavelength of line/nm	FWHM/10^{-3}nm observed	actual	concentration of solution/μgml^{-1}
Zn I 213.856	2.5	1.7	10
Cd II 214.438	2.7	1.7	100
Cd I 228.802	2.9	1.9	100
Fe II 259.940	3.6	2.5	100
Mg II 279.553	4.8	3.6	10
Mg I 285.213	6.0	4.7	10
Ca II 393.367	6.1	4.3	10
Ca I 422.673	6.1	4.3	10

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