

Capabilities of a photodiode array based system for cataloguing the atomic emission spectra of the inductively coupled plasma*

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Abstract—This paper describes a photodiode array based system and discusses its capabilities for cataloguing the atomic emission spectra emitted from an inductively coupled plasma. Dynamic range and line coverage are assessed and compared with those achievable with Fourier transform spectrometry.

1. INTRODUCTION

THAT A comprehensive atlas of spectral line information would be a useful addition to the fundamental reference data for the inductively coupled plasma (ICP) seems obvious. Not so obvious are the relative adequacies of the various possible experimental approaches for collection of the spectral data. Where does the capability for measuring weaker and weaker lines become pointless or, more importantly, cost prohibitive in terms of equipment, time, and personnel? A general review of this question and the possible experimental approaches for cataloguing the ICP emissions would be valuable but, unfortunately, it is outside of the scope of this workshop/compendium. We summarize in this report a few details of this subject consisting of preliminary observations made with a photodiode array (PDA) based system for documentation of the ICP spectral emissions. In addition, we briefly review several relevant aspects of Fourier transform spectroscopy (FTS) as a means of collecting ICP spectral atlas data.

2. PHOTODIODE ARRAY BASED SYSTEM: DYNAMIC RANGE

The PDA based system allows rapid collection of the extensive data required for spectral compilations of atlas scope. This system, with a one meter spectrometer, also provides essential spectral resolution, line coverage, and dynamic range capabilities for the task. Details of the experimental facilities employed for the preliminary studies described here are listed in Table 1.

For this preliminary assessment we have obtained ICP spectra for iron over the wavelength range of 192–293 nm. It is well known that iron emits a line-rich spectrum and, indeed, the ICP iron spectrum obtained in this study fits that description. The high number density of iron lines provides a ready means for comparison of the spectral line coverage of the photodiode array data with published spectral line data. Comprehensiveness of line coverage is an important consideration for an ICP spectral line atlas because of its relevance to the identification of spectral interference problems. And because the majority of spectral interferences arise from weak lines of concomitant elements present at high concentrations, a measurement system appropriate for atlas compilation must demonstrate an ability for detection of weak lines.

We have chosen to examine the capabilities of a PDA based spectrometric system for the atlas compilation because of the speed with which it can collect the large amount of necessary data. An example of the spectral data available from a single diode array interval is shown in Fig. 1. The 1024 pixel array covers approximately 6.5 nm at this 260 nm wavelength. Figure 1

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Table 1. Experimental facilities and operating conditions

Monochromator	McPherson M2051, 1 m focal length. Holographic grating, 3600 grooves/mm. Entrance slit width: 20 μ m
ICP	Plasma-Therm HFS 5000D, 27 12 MH: 1100 W forward power
Outer Ar flow	16 l/min
Intermediate Ar flow	1 l/min only for starting plasma
Aerosol carrier Ar	1 l/min
Source observation zone	Height zone of 5 mm centered at 15 mm above the load coil with 2:1 image reduction from ICP to photodiode array
Nebulizer	Pneumatic cross flow with a solution uptake rate of 1.5 ml/min
Sample	Fe, 1000 mg/l
Detector	Princeton Applied Research, Model 1453 photodiode array, 1024 elements, unin- tensified. Array cooled to 5°C. Model 1461 detector interface linked to DEC 11/34 computer. Total signal accumulation time per measurement: 100 s

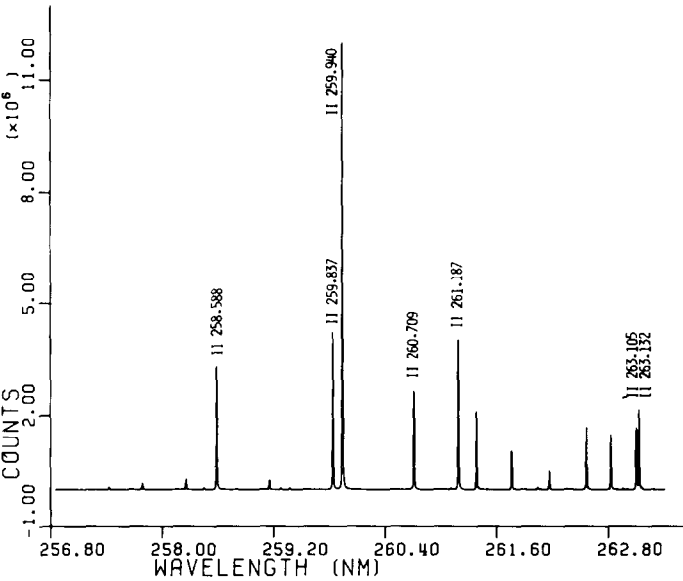


Fig 1. Iron spectrum in the 260 nm region, obtained from a single 1024-diode array interval.

reveals only the strongest iron lines in this region because its linearly-scaled intensity axis has, at best, a practical dynamic range of about 100. To show a larger dynamic range either the linear scale needs to be expanded or a different type of scale needs to be employed. Figure 2 shows the data of Fig. 1 but with the intensity scale expanded by a factor of 2000. Even at this large expansion much of the low intensity detail is very line like with noise and pixel-to-pixel variations in sensitivity accounting for only the lowest level details. Such a large scale expansion is generally unsatisfactory because it produces a very crowded spectrum and additional plots are required to show intermediate and high intensity lines. A plot of the same data with a logarithmic intensity scale is shown in Fig. 3. The logarithmic scale satisfactorily represents lines of strong, intermediate, and weak intensities all on a single plot. Examination of the logarithmically scaled plot provides us with a measure of the line coverage capabilities of the photodiode array. For this purpose let us first focus on the spectral region indicated by the circle in Fig. 3. This region is expanded in Fig. 4 and with the aid of the KELLY tables [1] 22 iron lines have been identified in this 1.0 nm region. Kelly lists 34 lines (from atoms and

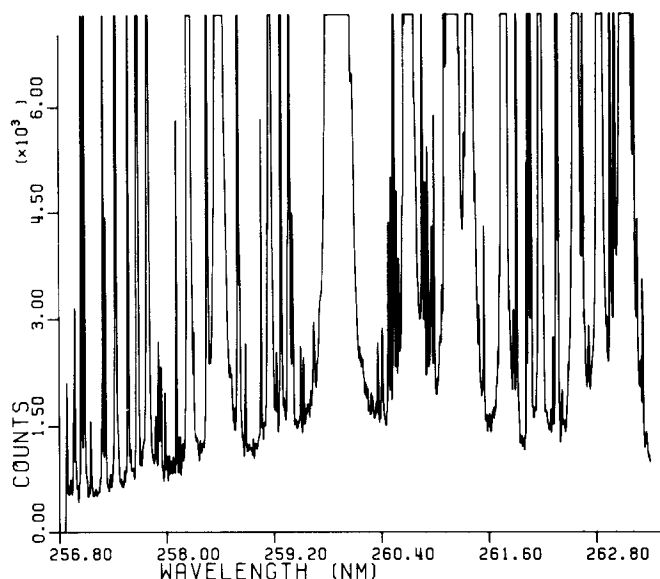


Fig. 2. Same data as Fig. 1 but with the intensity scale expanded by a factor of 2000 to show weak line details.

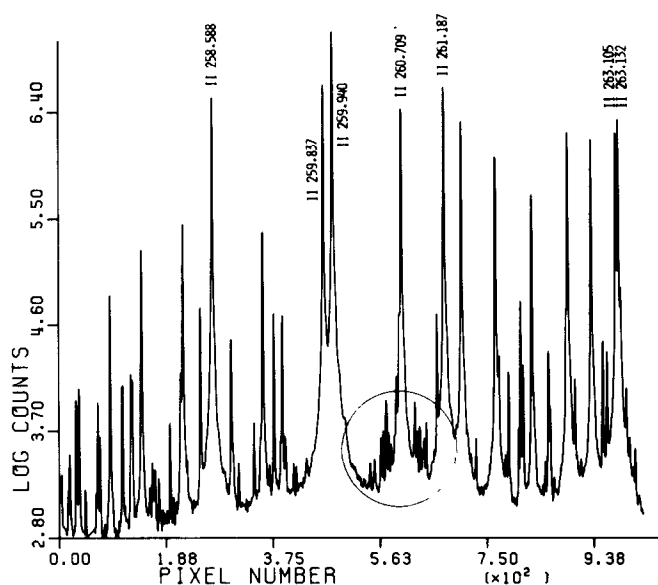


Fig. 3. Same data as in Figs 1 and 2 but with a logarithmically scaled intensity axis to represent the large dynamic range capability of the photodiode array detector. The circled area is explained in the text and expanded to show greater detail in Fig 4.

singly charged ions) in this region so there are still 12 listed lines that are not well defined in our data for this small wavelength region. This missing lines generally fit into two categories: very weak lines (mostly atom lines) and weak ion lines in close proximity to strong lines. What is significant, however, in terms of line coverage is that the weakest identified line, Fe I 260.355 nm, exhibited a net intensity of about 950 counts, while only 0.4 nm away, the strong Fe II 259.940 nm line had an intensity of 1.2×10^7 counts. A visual inspection of Fig. 4 suggests that an intensity of one-half that of the Fe I 260.355 nm line, or about 500 counts, could still be distinguished from the background noise. Thus, this example demonstrates a dynamic range of the PDA based system of approximately 25 000. Additional cooling of the PDA and employment of a 14 bit A/D (12 bit used in present work) may allow modest improvements in this dynamic range figure. (Operation of the detector at -15°C rather than

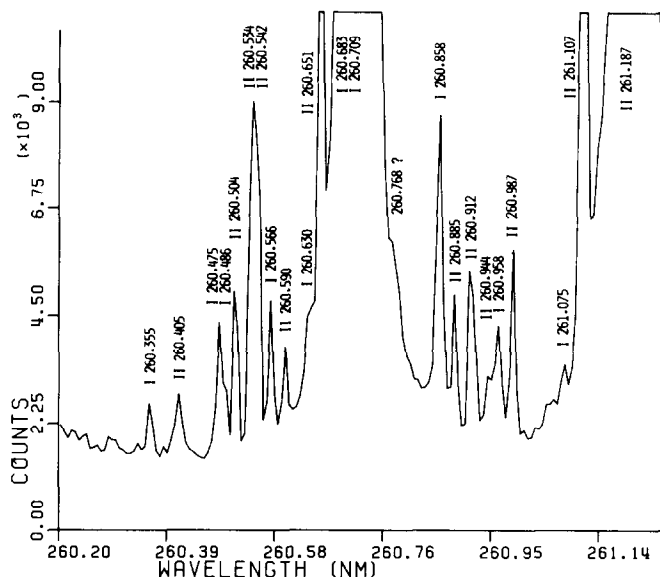


Fig. 4 Expansion of circled area of Fig 3 showing details of weak line emission in the vicinity of strong iron lines.

5°C reduces the dark current by a factor of approximately 8. A 14 bit A/D will allow the same count to be achieved in one-quarter of the measurement time with the potential for diminishing the effects of drift on the blank corrected data.)

3. PDA BASED SYSTEM VS FOURIER TRANSFORM SPECTROMETRY

A comparison is appropriate here between this photodiode array dynamic range and that achievable with Fourier transform spectroscopy (FTS). Instrumentation for FTS in the ultraviolet region has recently become commercially available and a powerful, high-resolution FTS system is nearing completion at the Los Alamos National Laboratory as discussed by PARSONS and PALMER elsewhere in these Proceedings [2]. The FTS technique possesses some very significant advantages for ICP atomic emission spectroscopy, particularly in terms of wavelength accuracy, spectral resolution, simultaneous wavelength measurement, and throughput (Jacquinot's advantage) [3, 4]. A potential problem with the FTS technique for ICP atlas work lies, however, in the multiplex disadvantage, in which the noise from intense features (either from the test element or from features in the ICP background) is distributed throughout the measured spectrum. In an examination of the noise characteristics of an ICP-FTS system, MARRA and HORLICK found that the plasma noise was not distributed uniformly throughout a spectrum but exhibited some regional dependence on the distribution of spectral features [5].

The relationship of dynamic range to the FTS multiplex disadvantage has not been explicitly defined. Data are available, however, on the effects of concomitant elements on the background noise and analyte detection limits of the FTS technique. For example FAIRES [4] showed that 100 mg/l Ca elevated baseline noise by a factor of 70 while 1000 mg/l Ca impaired the detection limits of the Ni I 352.45 and Al I 396.15 nm lines by a factor of 122. STUBLEY and HORLICK [6] found that the detection limit for the Zn I 213.86 nm line deteriorated by a factor of 44 in the presence of 500 mg/l magnesium. Their data also showed that ICP-FTS detection limits were as much as 200 times poorer than those obtained from a conventional direct reading ICP system. Hadamard transform spectrometry, like FTS also subject to the multiplex disadvantage, was found by PLANKEY *et al.* to give a dynamic range of about 30 when a strong line was present in the spectrum [7]. Spectra obtained by FAIRES on a high resolution FTS instrument revealed dynamic range values of approximately 800–1600

for wavelength intervals of 0.7–5.7 nm [8].* The above data strongly suggest that the distributed noise of the FTS technique, however it manifests itself, may seriously limit the dynamic range for atlas compilation purposes where information on a wide range of emission intensities is necessary and where regions of weak lines cannot be conveniently isolated from regions of strong lines. As a consequence, much needed information on weak ICP line emission may not be available from FTS generated spectra.

4. PHOTODIODE ARRAY BASED SYSTEM: ASSESSMENT

Returning now to the evaluation of the line coverage capabilities of the PDA system, it is appropriate to emphasize that there are no absolute listings of spectral lines by which the coverage can be judged. Line coverage can be evaluated only by comparison with other comprehensive surveys of spectra. Figure 5 shows a comparison of a portion of a PDA region with a spectrum of a corresponding wavelength region obtained by MICHAUD and MERMET [9]. At 288 nm, this is a region of relatively weak iron emission where the most intense line (288.076 nm) is approximately a factor of 370 less intense than the Fe II 259.940 nm line. There is an excellent correlation of lines between the two spectra except for two lines flagged by Michaud and Mermet with question marks (288.16 and 288.28 nm). These lines, absent in our spectrum, may be spurious silicon and zinc lines. A few additional weak lines become evident when the PDA data in Fig. 5 are replotted with a logarithmic intensity axis as shown in Fig. 6. Some of the additional lines appear as unresolved components on the shoulders of the stronger lines, e.g. on the high wavelength sides of the 287.2382, 287.3401, 287.4172 and 287.8761 nm lines.

A more extensive comparison is shown in Table 2 in which the numbers of lines we have observed in a sampling of regions in the 200–300 nm range are compared with the numbers of

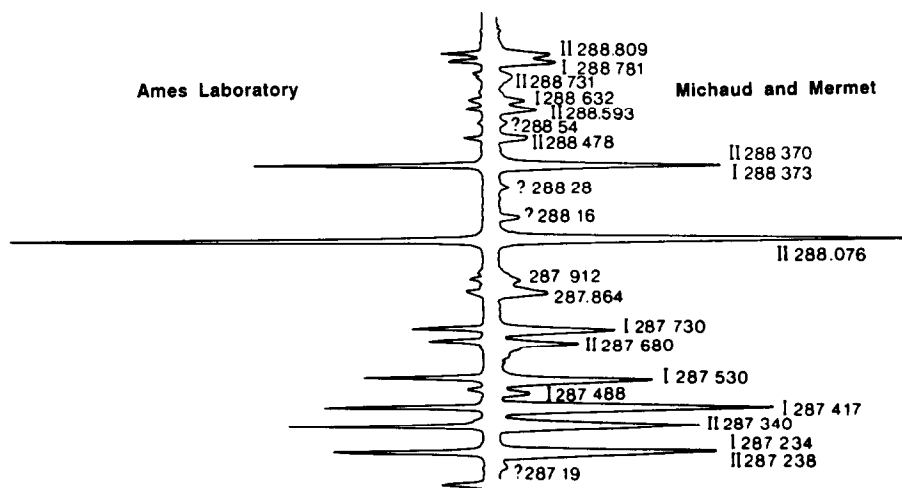


Fig. 5. Correlation of Ames Laboratory photodiode array iron spectrum at 288 nm with data published by MICHAUD and MERMET [9]. Right portion of figure reprinted with permission of authors and Pergamon Journals Ltd.

* See, for example, the following data[8]

Page	Line	Intensity	$\Delta\lambda$
352	Fe I 372.69250 nm	1.30	0.7 nm
352	Fe I 371.99270	1036.15	
311	V I 413.44491	1.05	5.7
311	Sr II 407.77056	1694.10	
311	Hg I 404.65796	1.70	3.1
311	Ca II 393.36537	1512.92	
311	V II 391.43096	0.99	2.1

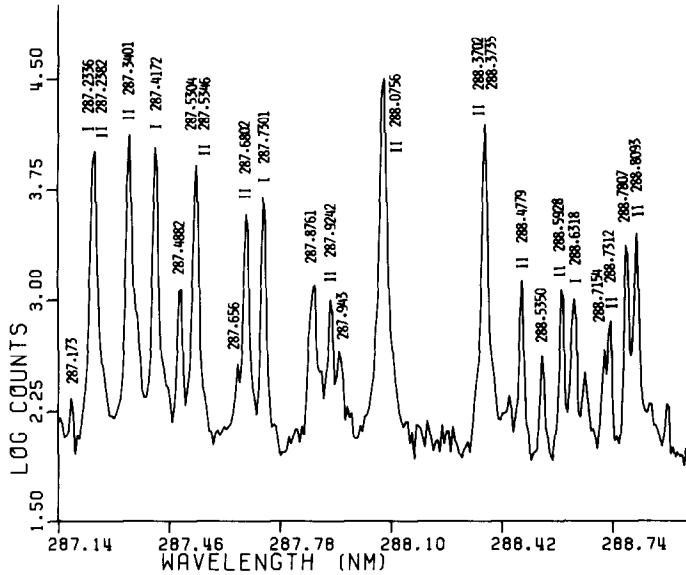


Fig 6 Left-hand portion of Fig 5 iron spectrum replotted with logarithmic intensity scale to show greater detail of weak line emission. The wavelengths were obtained from the MIT tables [10].

Table 2. Comparison of spectral line coverage (lines observed or listed per wavelength interval)

Wavelength region (nm)	MICHAUD				
	Ames Laboratory	and MERMET [9]	MIT [10]	NBS [11]	KELLY 1979 [1]
200–203.501	77	23	2	NA	36
201.704–208.485	123	37	3	NA	67
241 834–248.430	138	66	167	26	292
256.879–263.404	74	72	154	32	169
287.028–293.364	105	91	148	17	154

lines listed in the major wavelength tables. The line counts were obtained from logarithmically scaled plots, like that in Fig. 3, where a peak was counted as a line if it was obviously line like and distinguishable from the background noise. For the two lowest wavelength intervals, we observed more lines than listed in any of the comparison references. It should be noted, however, that the line coverages of the major wavelength tables were severely limited, at the time the data were compiled, by the lack of sensitivity of photographic plates to wavelengths below 230 nm. For the three highest wavelength regions in Table 2 we observed approximately one-half to two-thirds of the lines listed in the KELLY tables [1].

5. CONCLUSIONS

We have shown that the photodiode array detector has a wide dynamic range and, when combined with an appropriate spectrometer provides spectral resolution capabilities comparable to or exceeding those of most commercial ICP systems. Published data suggest that FTS capabilities for documentation of weak spectral lines for atlas compilations may be seriously compromised by the multiplex disadvantage. Direct FTS measurements of dynamic range similar to those described in this manuscript seems appropriate.

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