

An Evaluation of An Inductively Coupled Plasma (ICP) Emission Spectrometer

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Key words: ICP; resettability; reliability; spectral interference; SD; RSD.

RINGKASAN

Prestasi satu spektrometer pancaran yang berjenis Plasma Berganding secara Aruhan (ICP) telah dikaji dari segi kepersisan monokromator, kestabilan penjana ICP, dan had-had pengesanan. Kajian-kajian ini menunjukkan bahawa prestasi sistem analitik ini adalah sama dengan spektrometer yang memberikan catitan langsung dengan serentak. Kebersihan bagi monokromator, pelaras ketinggian suluh serta kestabilan unit sumber disahkan.

SUMMARY

The performance of an Inductively Coupled Plasma (ICP) emission spectrometer was evaluated in terms of its monochromator resettability, ICP generator stability and detection limits. The studies showed that the analytical system exhibited similar performance to simultaneous direct reading spectrometers. The reliability of the monochromator, torch height adjustor and the stability of the source unit were confirmed.

INTRODUCTION

In the past few years there has been an increasing application of inductively coupled plasma (ICP) as an excitation source for optical emission spectrometers (Greenfield, 1975; Barnes, 1978; Fassel, 1978). Most of the analytical systems using this technique resorted to polychromators as the optical unit (Barnes, 1979). These direct reading simultaneous polychromators had the advantage of providing for simultaneous determination of an excess of 20 elements. The limitation occurred when matrix composition varied and when semi-qualitative analysis was required. A majority of polychromators therefore incorporated a scanning monochromator for this reason (Lowe, 1980). The extension of such a development in emission spectrometers was the introduction of sequential scanning monochromators which are computer-controlled and capable of multielement determinations. Several of these sequential scanning ICP emission spectrometers have recently been evaluated (Spillman, 1976; Ediger, 1979; Floyd, 1980; Nippus, 1980).

In this paper, the performance of a sequential system in terms of monochromator resettability, ICP generator stability, spectral interference and detection limits was evaluated.

EXPERIMENTAL

Instrument

A Labtest Equipment Co. Model 710 Plasmascan sequential emission spectrometer was used. The operating conditions are summarised in Table 1. The standard software supplied with the system comprises general routines like Create File, Wavelength Calibrate, Peak Find, Calibrate and Run Unknowns. These routines are self-explanatory.

Monochromator Performance

The monochromator performance was evaluated using two methods. The first method was to use the Peak Find routine to 'peak' two elements Ca(3933.66A) and Mn (2576.10A). Ten sets of readings were taken and the standard deviation (SD) for each element wavelength was calculated. In the second method, three elements (Ca, Mn and Na) were used. Relative standard deviations (RSD) for each element using 1.0 $\mu\text{g cm}^{-3}$ solutions were calculated for ten 10-second integration runs at each wavelength of interest. The RSD's for ten 10-second integration scans using the autorun routine were also computed.

Torch Height Adjustment

The instrument has an electronically controlled torch height adjustment. The torch heights

¹ This is a modified version of a paper presented at the First Asian Pacific Chemical Congress, April, 1981, Singapore.

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TABLE 1
Operating Conditions

<i>Monochromator</i>	: 0.75 m Czerny-Turner Monochromator	
<i>Wavelength Range</i>	: 1700 – 3100 A	2nd Order
	: 3100 – 8000 A	1st Order
<i>Liner Dispersion</i>	: 3.7 A/mm	2nd Order
	: 7.4 A/mm	1st Order
<i>R.F. Generator</i>	: 27.12 MHz, 2000W rating, operated at 1.2W forward power, 5W reflected power	
<i>Nebuliser System</i>	: Pneumatic modified Babington type, (G.M.K.) using a 10 roller Gilson Peristaltic Pump.	
<i>Ar Flow Rates</i>	: Sample 0.6 dm ³ /min	
	: Coolant 12 dm ³ /min	
<i>Nebuliser Gas Pressure</i>	: 300 Kpa	
<i>Solution Uptake Rate</i>	: 2 cm ³ /min	
<i>Observation Height</i>	: 15 mm, unless otherwise stated.	
<i>Slits</i>	: Entrance	20 μm
	: Exit	110 μm

were set using a ten-turn potentiometer with dial settings. Each turn in the potentiometer gave a 4.7 mm change in observation height from the top of the coil to the viewing aperture. The SD of ten measurements after each torch height adjustment was determined. The resettability of torch height at two observation zones were evaluated using 1.0 μg cm⁻³ solution of Mn.

Integration Times

The computer software required that an integration time be defined for each element file. A 1.0 μg cm⁻³ solution of Mn was used to establish an optimum integration time with respect to RSDs. At each integration time entered, counts for 10 runs were recorded and the RSD was calculated. Integration times of 1, 2, 4, 8, 10, 20, 30 seconds were entered consecutively after each set of ten runs.

Observation Height

The signal to background ratio (I_n/I_b) was measured at various heights for Cu, Ca, Cr, Zn, Ni, Fe, Co, Mn, Na and K. Except for Mn and K, the concentration of each element studied was 10.0 μg cm⁻³. The concentrations for Mn and K were 1.0 μg cm⁻³ and 1000 μg cm⁻³ respectively.

Detection Limits

Detection limits and signal to background ratios (I_n/I_o) using 1.0 μg cm⁻³ solution of six elements were determined. Detection Limits were calculated using the equation recommended by the 'ICP Detection Limits Committee' (1979).

$$DL = 3 (RSD)_b \times \frac{C}{SBR}$$

where C = concentration used'

SBR = Signal to background ratio at C

(RSD)_b = relative standard deviation of the blank solution.

Interferences

The effects of spectral interferences on six elements were determined using 1000.0 μg cm⁻³ solutions of a selected list of elements. Each 'interference element' was aspirated into the plasma, after setting the monochromator to the analytical wavelength of the 'interfered element'.

The nature of the interference of Co and Fe on Cu was studied and interference corrections were then computed.

Calibration Curves

Calibration curves for six elements in the range 1.0 μg cm⁻³ to 1000 μg cm⁻³ were computed.

Standard Solutions

All standard solutions, except Zn, were prepared from A.R. grade nitrate of the elements in 1% nitric acid. Zn metal was dissolved in nitric acid and the strength was adjusted to 1%. A 1% nitric acid was used as blank. This was to eliminate any possible matrix effects.

RESULTS AND DISCUSSION

Table 2 shows the results on the evaluation of the monochromator performance. The SD for each wavelength obtained from the Peak Find routine was within ± 0.04Å. There was no significant difference between the RSD's of the 1.0 μg cm⁻³ solution calculated from ten 10-second integration runs and the RSD's of ten 10-second integration scans using the auto-run routine.

The results indicate that the monochromator was sufficiently resettable to give reproducible analytical values. Similar scanning monochromator systems have reported SD for wavelength resettability of ± 0.04Å (Floyd *et al.*, 1980; Nippus, 1980).

AN EVALUATION OF AN ICP EMISSION SPECTROMETER

TABLE 2
Monochromator Resettability

Element	Wavelength (A)	Peak Found (A)	Mono Setting (A)	SD	
Ca	3933.66	3933.24	3933.24	± 0.04A	
Mn	2576.10	2576.05	5152.10	± 0.01A	
SD calculated from 10 peak find routines					
Element	Wavelength (A)	Peak Found (A)	Mono Setting (A)	RSD	RSD (Scan)
Ca	3933.66	3933.25	3933.25	0.0127	0.0209
Mn	2576.10	2576.05	5152.10	0.0128	0.0080
Na	5889.95	5889.56	5889.56	0.0171	0.0132

Note: RSD calculated from 10 ten-second integrations using $1.0 \mu\text{g}/\text{cm}^3$ solutions.

The results of the torch height adjustment are given in Table 3. There is no significant difference in the RSD for each torch height setting. The RSD of ten 10-second integrations at a fixed torch height was 8.70×10^{-3} . Since the torch height was resettable with precision, the system allowed for studies of effect on signal to background ratios with varying observation heights.

TABLE 3
Torch Height Resettability

Torch Height	RSD (Fixed)	RSD (Changed)
20 mm	*	7.67×10^{-3}
10 mm	8.70×10^{-3}	7.73×10^{-3}

Note:
RSD calculated from 10 ten-second integrations using $1.0 \mu\text{g}/\text{cm}^3$ Mn solutions.
Measured resettability of torch height is ± 0.01 mm.

The graphical representation of RSD against varying integration time using a $1.0 \mu\text{g cm}^{-3}$ solution of Mn is given in Fig. 1. The minimum integration time should be not less than 10 seconds if RSD was not to be sacrificed. Similar sequential scanning systems had used 2-second integration times without reporting their RSD. (Hoult, 1980).

The changes in signal to background ratio (I_n/I_b) at various observation heights for the elements studied are shown in Fig. 2 and 3. The results illustrate that each element had an optimum observation height which may or may not be identical to each other. These results are characteristic of ICP systems. (Barnes, 1978, 1979). In simul-

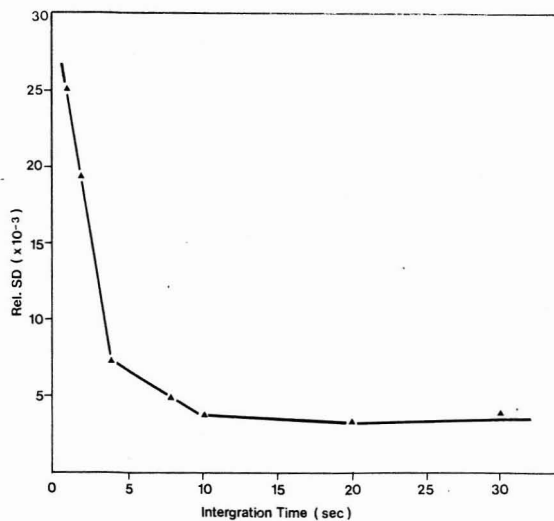


Fig. 1. RSD at various intergration times.

taneous direct reading spectrometers, compromised observation heights were necessarily used.

Sequential scanning spectrometers, however, need not have this limitation. In routine analysis, a compromised height (15 mm) was selected for the sequential instrument. However, when low detection limits were required, the optimum height was set for that particular element.

Table 4 gives the detection limits, signal to background ratios, and RSD's for each $1.0 \mu\text{g cm}^{-3}$ solution of the six elements under study. Most elements showed RSD levels within 1%. The (I_n/I_b) values were higher than anticipated, but the detection limits were not lower than those estimated by Wing *et al.*, (1979).

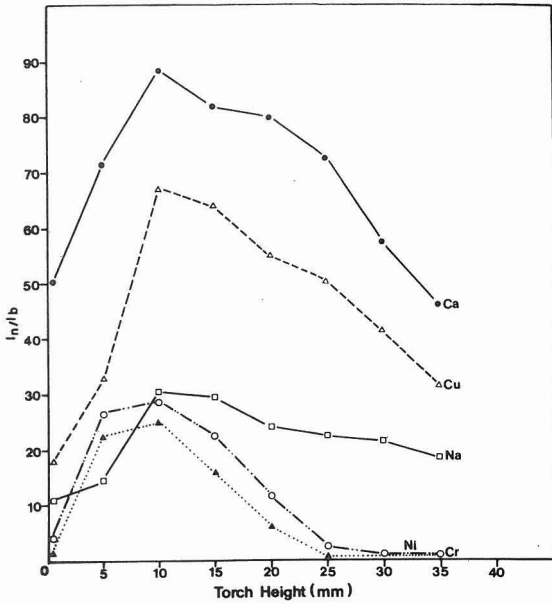


Fig. 2. I_n/I_b at various torch heights.

Table 5 summarises the results of interference studies. These results show significant interferences from Cu and Ni on Zn (2138.56A); Fe on Co (2388.92Å) and Co and Fe (2382.04A). These spectral interferences were not unexpected since Cu (2138.51A) and Ni (2138.58A) lines have been reported (Parsons *et al.*, 1980). Similarity two Co lines (2382.33A and 2381.75A) were within $\pm 0.30A$ from the Fe wavelength used. Moreover, Parsons *et al.*, (1980) also indicated the Fe (2388.39A) interference on Co at 2388.91A.

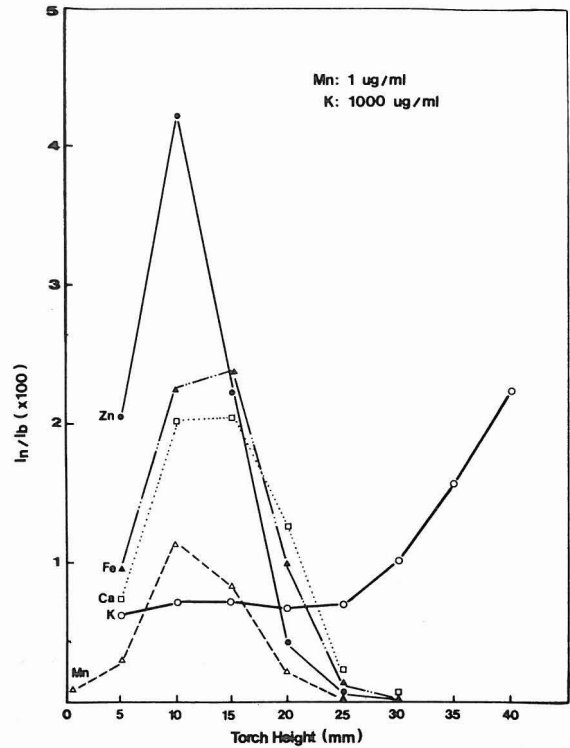


Fig. 3. I_n/I_b at various torch heights.

These spectral interferences can be avoided by selecting another wavelength if the sensitivity of that wavelength is suitable for the element concentration. If spectral interferences cannot be avoided then spectral corrections would be necessary.

TABLE 4
Detection limits

Element	Wavelength (A)	I_n/I_b	$D_L (\mu g/dm^3)$	LQDC	RSD @ 1.0 $\mu g/cm^3$
Cu	3247.54	8.64	3.40	17.00	3.88×10^{-3}
Fe	2382.04	15.08	4.93	24.65	4.36×10^{-3}
Co	2388.92	14.14	7.35	36.75	20.20×10^{-3}
Zn	2138.56	17.75	5.59	27.95	5.97×10^{-3}
Mn	2376.10	81.70	0.29	1.45	8.4×10^{-3}
Na	5889.95	7.25	3.39	16.95	3.95×10^{-3}

Note:

$$D_L = 3(RSD)_b \times \frac{C_o}{SBR} \quad \text{where } SBR = I_n/I_b$$

LQDC = Lowest Quantitatively Determinable Concentration = $5 D_L$

I_n/I_b at 1.0 $\mu g/cm^3$
RSD based on 10 ten-second integrations

AN EVALUATION OF AN ICP EMISSION SPECTROMETER

TABLE 5
Interference Studies

Interfering Element	Apparent Concentration ($\mu\text{g}/\text{cm}^3$) of Interfered Element					
	Cu	Zn	Fe	Co	Mn	Na
Cu	*	7.527	0.036	0.045	0.003	—
Ca	0.021	0.013	0.005	0.013	—	0.119
Cr	0.013	0.155	0.026	0.130	0.258	0.039
Zn	-0.011	*	0.045	0.024	—	0.012
Ni	0.019	3.996	0.156	0.195	0.007	0.074
Fe	0.096	0.572	*	2.915	0.409	0.078
Co	0.054	0.233	2.545	*	0.137	0.496
Mn	0.022	0.541	0.258	0.293	*	0.030
Na	-0.004	0.004	0.005	0.003	—	*
K	-0.007	0.005	0.012	0.003	-0.002	0.779

Note: 1000 $\mu\text{g}/\text{cm}^3$ interfering element on interfered element wavelength.

The interference of Co and Fe on Cu was found to affect parallel shift along the linear calibration of Cu. Table 6 gives the interference corrections. The equation shows that the interference effect was not a linear relationship. Moreover coefficients of the second order polynomial relationship indicated that the actual correction was minimal.

TABLE 6
Interelement Correction

$$(\text{Cu})_T = (\text{Cu})_A + f(\text{Fe}) + f(\text{Co})$$

where $(\text{Cu})_T$ = true concentration of Cu

$(\text{Cu})_A$ = Apparent concentration of Cu

$$\text{Now } f(\text{Fe}) = -2.684373\text{E} - 04(\text{Fe}) + 1.070595\text{E} - 08(\text{Fe})^2$$

$$f(\text{Co}) = -2.283135\text{E} - 04(\text{Co}) + 1.463613\text{E} - 08(\text{Co})^2$$

$$\text{Then } (\text{Cu})_T = (\text{Cu})_A + 1.070595\text{E} - 08(\text{Fe})^2 - 2.684373\text{E} - 04(\text{Fe}) + (\text{Cu})_A + 1.463413\text{E} - 08(\text{Co})^2 - 2.283135\text{E} - 04(\text{Co})$$

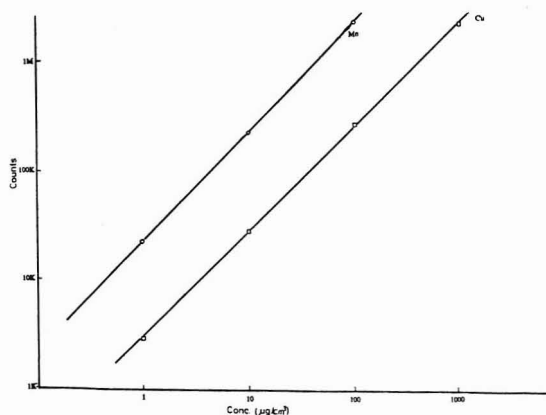


Fig. 4. Calibration curves of Mn and Cu.

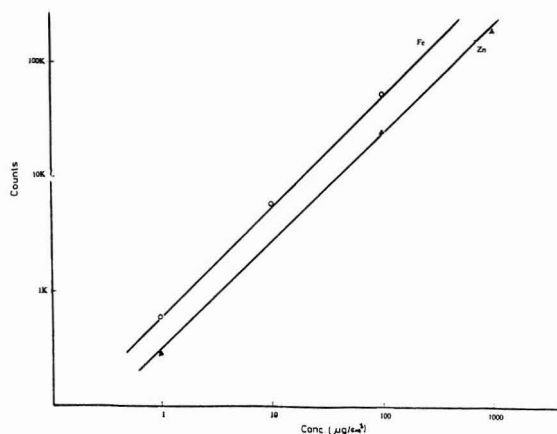


Fig. 5. Calibration curves of Fe and Zn.

Fig. 4, 5 and 6 give the calibration curves for the six elements under study. All the curves illustrate linearity over three to four orders of magnitude as reported by Barnes (1978). A two point calibration routine would, therefore, be sufficient for most elements.

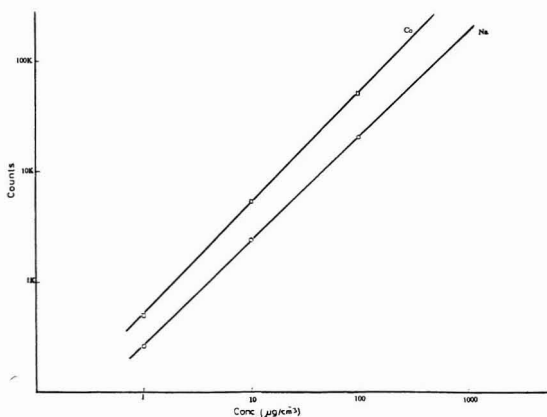


Fig. 6. Calibration curves of Co and Na.

CONCLUSION

Studies on the sequential scanning ICP emission spectrometer show that the analytical system exhibited similar performances to simultaneous direct reading spectrometers. The reliability of the monochromator, torch height adjuster and stability of the source unit were all confirmed.

Data accumulated from these and future studies on spectral interferences will eventually allow for the routine use of the instrument in quantitative analysis.

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(Received 10 September 1981)