Design, fabrication and performance evaluation of a 22-channel direct reading atomic emission spectrometer using inductively coupled plasma as a source of excitation

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Abstract. The indigenous design, fabrication and performance evaluation of a polychromator, using inductively coupled plasma (ICP) as a source of excitation, are described. A concave holographic grating is used as the dispersing element and a Paschen–Runge mount is chosen to focus the spectra over a wide range along the Rowland circle. Twenty-two exit slits, mounted along the circle, precisely correspond to the wavelengths used for determination of up to twenty elements present in the plasma. Radiations emerging from the exit slits are detected by photomultiplier tubes placed behind them. The photomultiplier signal is recorded by an electronic system consisting of an integrator and a PC-based data acquisition system. The performance of the spectrometer has been evaluated with an ICP excitation source. Synthetic standards in deionized water containing a mixture of twenty impurities have been analysed. Typical determination limits observed for elements range from sub-ppm to ppm levels. All the elements present as impurities can be detected simultaneously. It is also observed that each element has a different emitting region in the ICP flame for which the maximum signal to the background is obtained. The determination limits obtained corresponding to these zones are the lowest. A study of the sensitive emitting zones for several elements has been carried out and the results are demonstrated by photographs of the ICP flame. The study will help in achieving the minimum value of determination limit for an impurity element.

Keywords. Spectrochemical analysis; atomic emission spectrometer; inductively coupled plasma.

1.   Introduction

Optical emission spectrometry (OES) is widely used in the analysis of various trace elements. Electrically generated flames, i.e. plasma, have proved that simultaneous multi-element analysis can be successfully carried out with better determination limits and precision than before (Fassel 1978). This is mainly due to the introduction of inductively coupled plasma (ICP) (Greenfield *et al* 1975; Boumans 1976; Greenfield 1976; Barnes 1978; Robin 1982; Boulos 1985) as the excitation source for the emission spectrometry. In recent years, ICP-OES has become a technique for the analysis of solution samples because of the following features.

 (i) High signal-to-background ratio gives lower determination limits.
 (ii) Large concentration linear dynamic range of about 4 to 5 orders is available and therefore analysis of ppb to percentage level is possible with good accuracy.
(iii) Stability of the plasma flame provides high precision in the analysis.
(iv) The plasma is capable of exciting all the elements present in the sample simul-taneously without any interference of coexisting elements.
 (v) Speed of analysis is high.

   Therefore it was decided to take up the project of indigenous design and fabrication of a direct reading spectrometer to be used with inductively coupled argon plasma as the source of excitation. Twenty elements, namely Mo, Cr, Zn, Cd, Be, Co, B, Mn, Fe, Mg, Pb, Si, Ga, Ni, Al, Sn, Ti, Cu, Zr and Ca, can be selected for multielement analysis.

2.   Design of polychromator

Several types of mounting (Harrison 1955) using a concave grating as a dispersing device are available in literature. The Paschen–Runge (Sawyer 1951) type of mounting was chosen to suit our requirements for the following reasons.

 (i) The spectra are focused sharply along the Rowland circle and this mounting has a wider spectral range.
(ii) The spectral region around the grating normal is the best because of uniform dispersion and the least amount of astigmatism.

   Holographic type of diffraction grating was chosen to reduce the amount of stray radia-tions and ghost images. Figure 1 shows a schematic optical arrangement of a poly-chromator consisting of a concave grating used in the Paschen–Runge mount, entrance slit S and exit slits $S_1, S_2, S_3, \ldots S_n$. When the entrance slit is illuminated by a spectral source, the spectrum is focused sharply along the Rowland circle. The Rowland circle is defined as a circle tangential to the concave grating and of diameter R, where R is the radius of curvature of the concave grating. The entrance and exit slits are fixed on the Rowland circle in order to obtain sharp spectral lines corresponding to various wavelengths. The concave grating is also fixed rigidly with respect to entrance and exit slits. The directions of the diffracted radiation are given by the following equation

$$\sin i + \sin \theta_n = \lambda_n/d \qquad (1)$$

where i is the angle of incidence, θ_n is the angle of diffraction, λ_n is the wavelength of radiation and d is groove spacing of the grating. The signs of the angles i and θ_n are opposite when they lie on different sides of the grating normal.
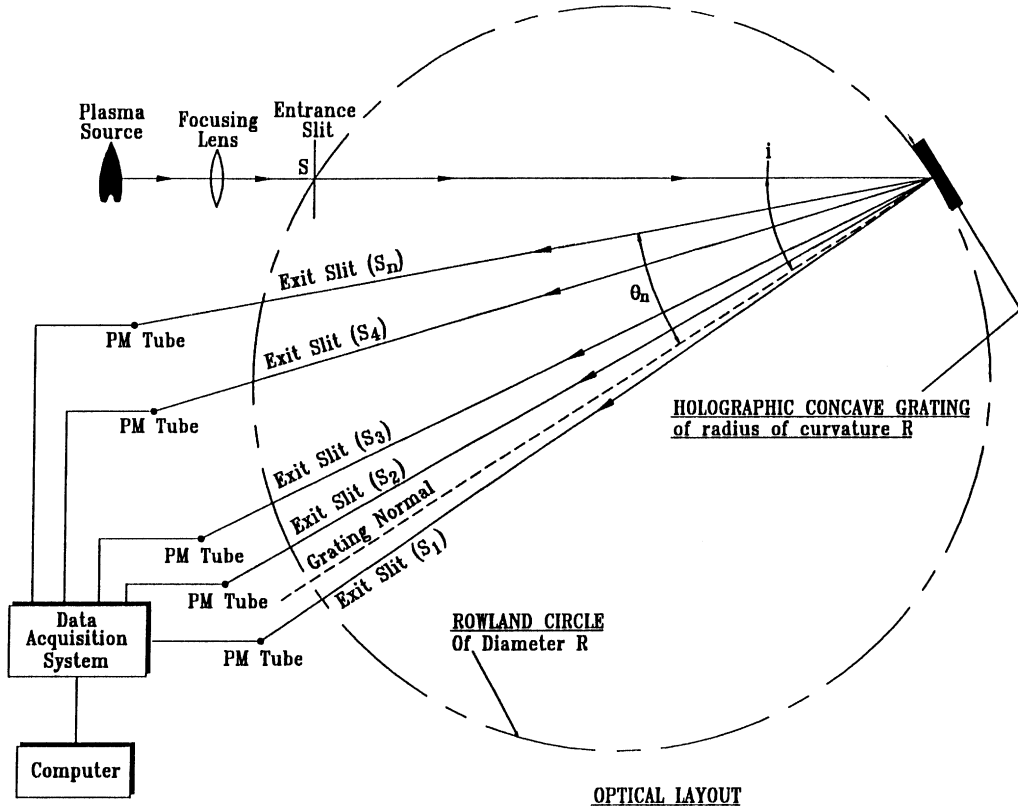
Figure 1. Schematic optical arrangement of a polychromator using concave grating in Paschen–Runge mount.

We have chosen an angle of incidence of 33° for a concave grating of frequency 2550 grooves/mm and radius of curvature 1.0 m to cover a spectral range of 2000 Å to 4000 Å in the first order. The diffracted spectra are focused sharply on the Rowland circle of diameter 1.0 m. Exit slits corresponding to the desired spectral lines are fixed precisely on the Rowland circle at the calculated positions.

3. Calculations of the exit slit positions for various wavelengths

The schematic diagram of the Rowland circle consisting of concave grating, entrance slit S and exit slits $(S_1, S_2, \ldots S_n)$ is shown in figure 1. The distance of the nth exit slit S_n from the entrance slit S along the Rowland circle is given by

$$\text{Arc } SS_n = \frac{(i - \theta_n)^0 R \pi}{180^0}. \tag{2}$$

If the angle of incidence i is given, then the angle of diffraction θ_n is calculated for the given groove spacing d and specific wavelength λ_n from (1). Arc SS_n is then calculated from (2) for a known value of R. Table 1 gives a set of calculated values for the exit slit positions corresponding to the wavelength of the characteristic emission lines of various elements.

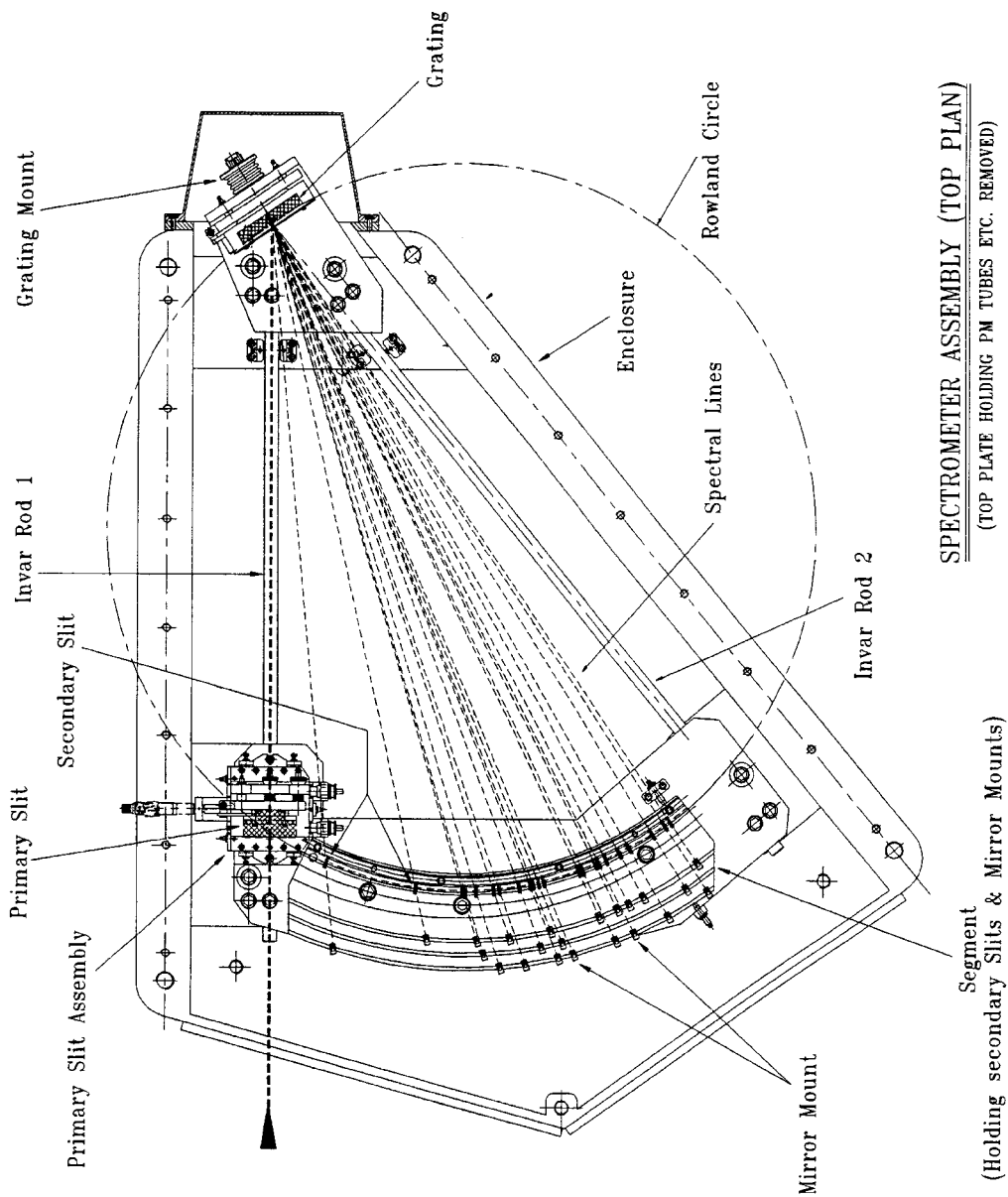**Table 1.** Calculated exit slit positions for various wavelengths.

Position	Element	Wavelength (Å)	Arc SS_n (mm)	$d\lambda/dl$ (Å/mm)
1	Mo	2020.00	605.50	3.920
2	Cr	2055.52	596.44	3.920
3	Zn	2138.56	575.26	3.918
4	Cd	2288.02	537.14	3.917
5	Be	2348.61	521.68	3.913
6	Co	2432.00	500.37	3.909
7	Blank	2477.00	488.85	3.906
8	B	2497.77	483.53	3.900
9	Hg	2536.50	473.61	
10	Mn	2576.10	463.46	3.895
11	Fe	2599.40	457.47	3.880
12	Mg	2802.69	405.08	3.862
13	Pb	2833.07	397.21	3.858
14	U	2865.00	388.93	3.852
15	Si	2881.58	384.63	3.832
16	Ga	2493.00	368.65	
17	Ni	3050.82	340.47	3.810
18	Al	3082.16	332.24	3.794
19	Sn	3175.02	307.76	3.771
20	Ti	3234.00	292.13	
21	Cu	3247.54	288.53	3.721
22	Zr	3496.21	221.70	3.587
23	Hg	3650.20	179.49	
24	Ca	3968.47	89.70	3.473

4. Focusing of the spectrum

The concave grating is illuminated by focusing the mercury source of radiation on the entrance slit of the polychromator. The diffracted light of various spectral lines from ultraviolet to visible radiation is focused sharply along the Rowland circle. The Rowland circle mount is placed such that its curved plane coincides with the Rowland circle. In order to determine the exact position of the Rowland circle, several sets of mercury spectra are photographed by pasting a photographic film along the curved plane of the Rowland circle mount at its different positions. Sharpness of the spectral lines is examined on each recorded photographic film by a magnifier. When the curved plane of the Rowland circle mount coincides with the exact position of the Rowland circle, the recorded spectra remain sharp from 2000 to 4000 Å. After determining the correct position for the sharp spectra, the Rowland circle mount is locked at this position.

5. Precision positioning of the exit slits and the photomultiplier tubes

A thin steel plate of width 45 mm and length 556 mm is taken for making vertical slots along the length of the plate. Calculated exit slit positions for 24 wavelengths are marked vertically on the strip and slots of width 25 mm and length 20 mm are cut. These slots act as secondary apertures for exiting radiations. The plate of secondary apertures is fixed on front side of the Rowland circle mount to stop unwanted radiations so that radiations of 24 wavelengths only are allowed to pass through the vertical slots. This is done by measuring

SPECTROMETER ASSEMBLY (TOP PLAN)
(TOP PLATE HOLDING PM TUBES ETC. REMOVED)

Grating

Grating Mount

Invar Rod 1

Secondary Slit

Primary Slit

Primary Slit Assembly

Rowland Circle

Enclosure

Spectral Lines

Invar Rod 2

Mirror Mount

Segment
(Holding secondary Slits & Mirror Mounts)

Figure 2. Plan of the poly-chromator.

the intensity of mercury lines (2536.5 and 3650.2 Å) which pass through the slots, numbers 9 and 23, of the secondary aperture. The line intensity is measured by a photomultiplier tube (PMT) placed behind the slots. These lines can also be observed visually by an uranium glass filter or a fluorescent paper. The secondary aperture is then locked in position on the Rowland circle mount. The next step is to fix the exit slits of width $100\,\mu$m at the calculated positions. The exit slits must be strictly vertical and parallel to the ruling lines of the grating and the entrance slit. For this purpose hollow cathode lamps corresponding to all the elements are used as sources of monochromatic radiations of specific wavelengths. For example, if we want to fix the exit slit for a boron line, the entrance slit is illuminated by a hollow cathode lamp of boron. The radiation of boron wavelength (2497.77 Å) is taken through the vertical slot number 8 and its intensity is measured by the photomultiplier tube. The exit slit of width $100\,\mu$m is now mounted on the groove made into the Rowland circle mount. The exit slit is moved laterally in steps of a few microns to maximise the intensity of the signal measured by the photomultiplier tube. The exit slit is made vertical by means of precision rotating screws. When the maximum amount of intensity is received by the photomultiplier tube, the exit slit is locked in position. Similar procedure is used for fixing the remaining exit slits using different hollow cathode lamps. Photomultiplier tubes for elements such as Ca, Hg, Zr, Cu, Al, U, Mn and Mo, and the blank are then fixed directly behind the exit slits in the space available on the base plate of the instrument. Photo-multiplier tubes for the remaining elements are mounted on the ceiling of the top cover plate of the instrument. In this case, strips of cylindrical mirror of radius of curvature 50 mm are mounted behind the exit slits and their orientation is kept such that the radiations from the corresponding exit slit are focused on the photomultiplier tube. Two channels are set aside corresponding to the Hg lines. These two channels are useful for initial alignment and focusing of the spectral lines. The output of each photomultiplier tube
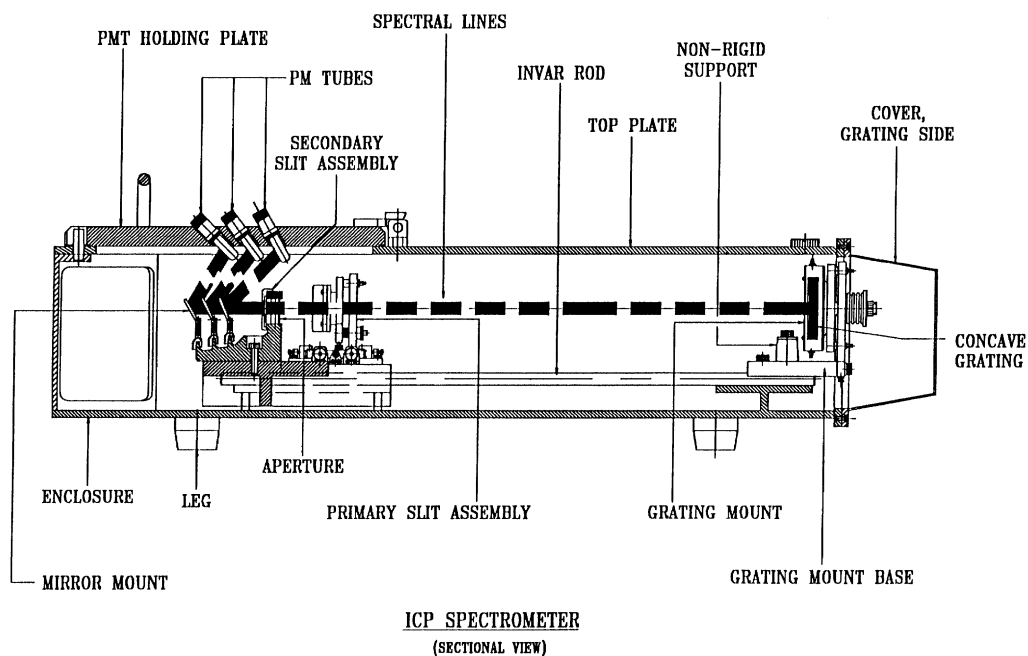
Figure 3.   Side view of the polychromator.

is fed to a data-acquisition system consisting of an electronic integrator and a personal computer. The intensities of radiation of all the channels are measured simultaneously in the form of intensity counts and are displayed on the computer screen. Figures 2 and 3 show the plan and the side view of the instrument indicating the complexity of mounting of the exit slits and photomultiplier tubes in the limited volume of space inside the instrument.

## 6. Signal detection and data acquisition system

Radiation intensities from various channels are converted to electrical signals by means of a set of photomultiplier tubes. Basically, the data-acquisition system (DAS) consists of hardware which accepts the electrical signals for further processing and software to operate the hardware for acquiring the data in the required form. Further processing is done through the computer to calculate the calibration coefficients for the standards. These calibration coefficients are then used to determine the quantities of the elements present in the sample based on the intensity data acquired from the sample. The data acquisition hardware operates under the control of a personal computer which in turn is governed by the data acquisition software. A digital I/O card forms the link between the personal computer and the data acquisition hardware. The integrator produces an integrated output from the PMT current, while averaging out the effects of random noise. It operates either in integrate or in reset mode. Four such integrators are incorporated in a printed circuit board and six such boards are used to provide 22 integrators for the 22 channels and two integrators for standby purpose. The control circuit performs functions such as resetting all the integrators initially, starting integration in all the channels simultaneously, setting the required channel for overflow detection and data acquisition, discharging a particular capacitor when its output voltage crosses the threshold of the overflow detection comparator and resetting all the integrators at the end of integration.

A 12-bit successive approximation type analog to digital converter (ADC) along with overflow detection circuit performs digitization of the integrated analog signal and helps to achieve the required dynamic range of six decades.

A menu-driven user-friendly software has been developed in Turbo pascal to perform data acquisition and processing tasks.

## 7. Application and performance testing using ICP as a source of excitation

The instrument has application for multielement analysis (up to 20 elements) using ICP as a source of excitation. Figure 4 shows an ICP torch assembly schematically. The ICP source is an ''electrical flame'' generated by a high power (1 kW) radio frequency (RF) generator. The power from the RF generator at a frequency of 27.12 MHz is coupled to a load coil through which an argon gas jet is made to flow. The RF power in the load coil is absorbed by the argon gas, which is converted to argon plasma. The sample in the form of a liquid solution is introduced into the carrier argon gas. Minute aerosol particles of the sample are produced in the plasma due to the passage of the sample solution through a nebulising needle. The temperature of the plasma is about 6000 to 10000 K, which is maintained by the inductive power transfer from the load coil. The atoms in the sample introduced into the plasma by the argon gas flow are excited into neutral and ionic states and radiate in the form of complex spectra characteristic of each element in the sample. The sample is introduced into the flame to detect the presence of a certain element B (say).
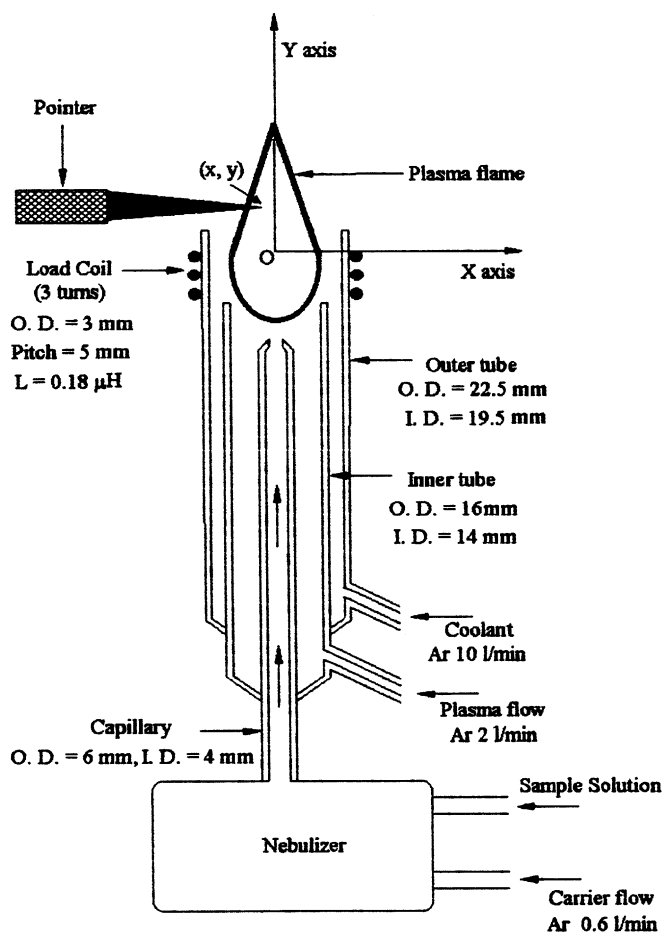
Figure 4.   Schematic diagram of ICP torch assembly used as a source of excitation.

The determination limit for each element depends on the zone of the ICP flame focused on the entrance slit. In addition, the operating parameters (Scott *et al* 1974; Boumans & de Boer 1975; Berman & Mclaren 1978; Fassel 1978) like aerosol flow rate, power of the RF generator and frequency etc. can be selected for simultaneous multielement analysis with minimum interference effects, wide linear dynamic range and good detection limits. In order to determine the sensitive emitting zone, the ICP flame is focused on the entrance slit of the polychromator. The photocurrent generated by the PMT is measured by an electrometer connected to this channel. The ICP flame is moved up and down, and from left to right in order to obtain the maximum signal-to-background ratio. This is the zone which emits the maximum radiation and gives the lowest possible value of the determination limit for this element. Standards of B (say) dissolved in deionized water with concentration in the range of $0.01\,\mu g/ml$ to $10.0\,\mu g/ml$ are prepared and injected into the plasma flame. Intensity counts are measured for various concentrations of the standards and a curve of concentration versus intensity is plotted for the B channel to find its determination limit as shown in figure 5. The plot of figure 5 can be used to determine the concentration of boron present in the unknown sample. The same procedure is repeated for
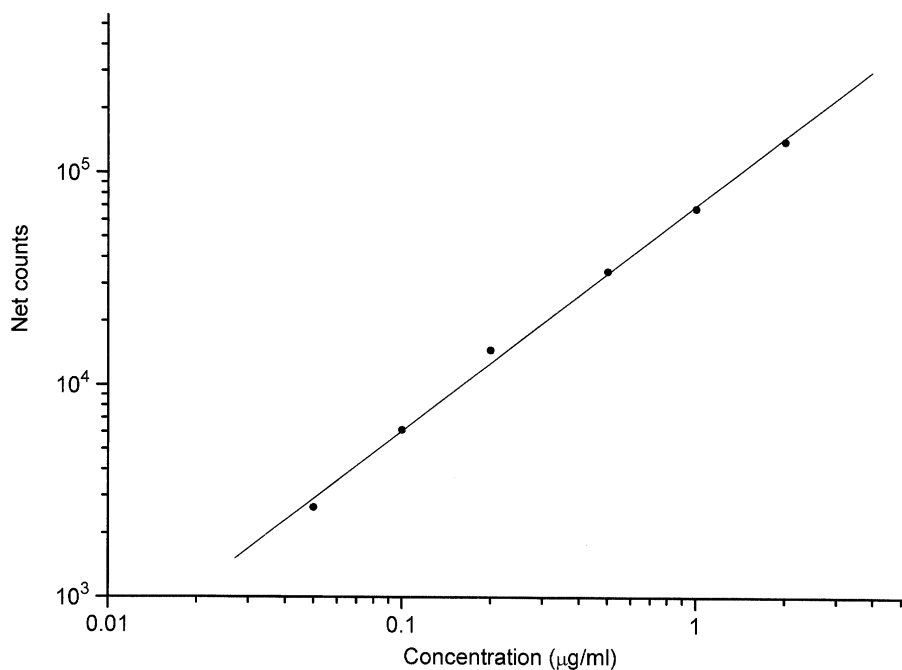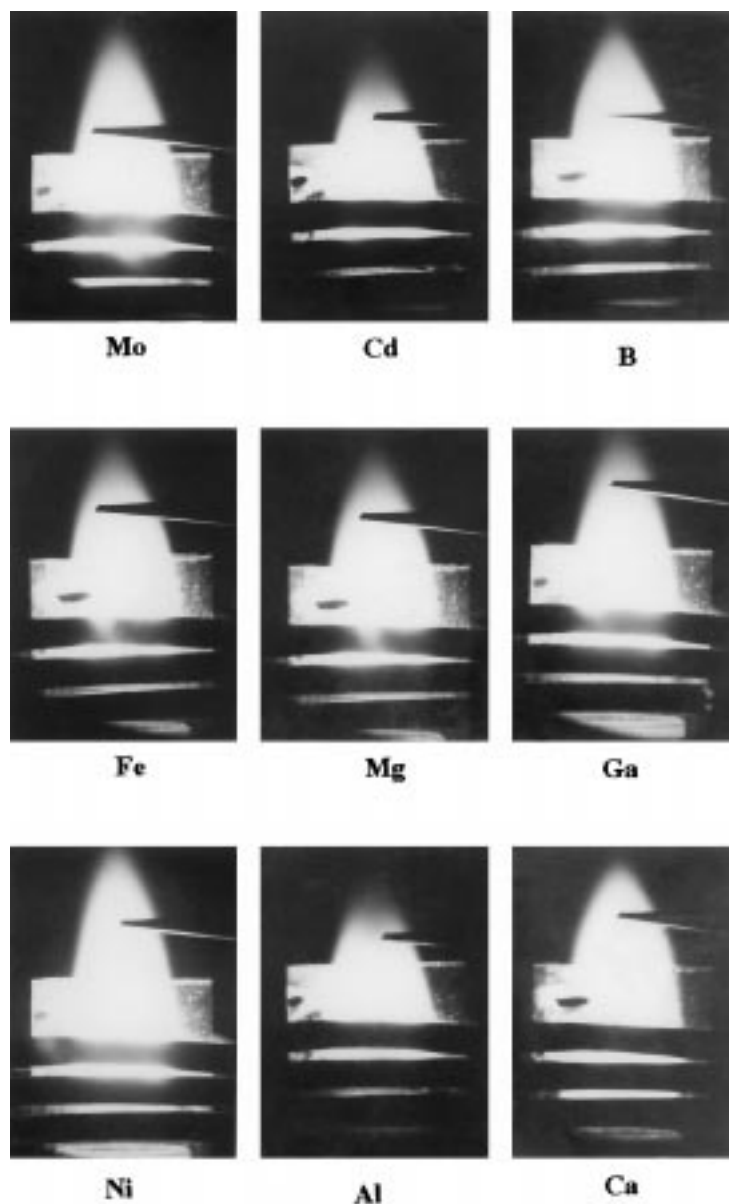
Figure 5. Calibration plot of boron element showing the concentration versus intensity counts obtained for the single element analysis.

Table 2. Observed determination limits for various elements in single element analysis using the atomic emission spectrometer.

Element	Determination limit (μg/ml)	Coordinates of the sensitive zone of ICP flame (x, y) (mm)
Mo	0.2	(-3.61, 9.82)
Cr	0.25	–
Zn	0.1	–
Cd	0.1	(-0.05, 9.87)
Be	0.05	–
Co	2.5	(-2.53, 9.94)
B	0.05	(-1.39, 11.67)
Fe	1.0	(2.88, 14.58)
Zr	0.5	–
Si	2.0	(-2.19, 12.75)
Ga	1.0	(-1.23, 16.73)
Pb	5.0	–
Sn	5.0	(4.10, 16.12)
Al	0.5	(0.69, 11.28)
Mn	0.5	–
Mg	0.1	(-1.38, 13.89)
Ca	0.1	(-0.39, 13.35)
Ti	0.5	(-0.46, 12.13)
Cu	0.1	–
Ni	1.0	(-0.83, 15.87)

Figure 6. Photographs of the ICP flame showing the sensitive analytical zones for achieving the lower determination limits for various elements. The sensitive analytical zone is shown by the tip of the pointer for each element as indicated under the photograph.

the remaining 19 elements to estimate their determination limits, by focusing the different corresponding sensitive zones of the ICP flame on to the entrance slit. Determination limits for various elements using this procedure have been obtained and are listed in table 2 along with the position of the corresponding sensitive zone of the ICP flame. It is observed that the sensitive emitting zones of the ICP flame corresponding to different elements are
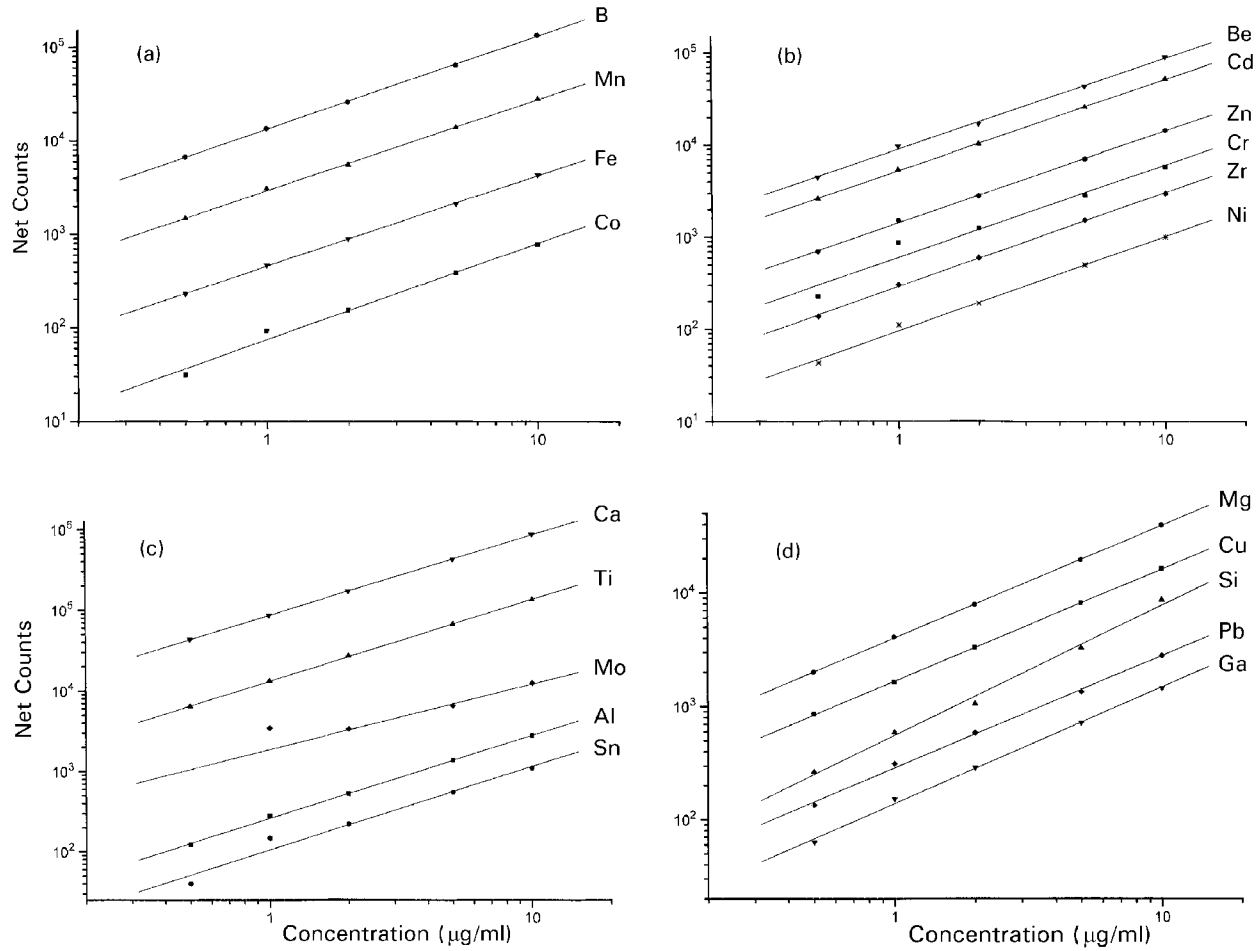
Figure 7. Calibration plots of 20 elements showing the concentration versus intensity counts obtained for the multielement (20 element) analysis.

different. These sensitive zones for the elements have been determined and are recorded in the photographs shown in figure 6. Sensitive emitting zones for the various elements are indicated by the tip of the pointer.

   Several standards containing mixtures of 20 elements dissolved in deionised water with concentrations in the range of $0.5\,\mu g/ml$ to $10\,\mu g/ml$ were prepared for multielement simultaneous analysis. These standards were also analysed using the indigenously developed instrument. Calibration plots for simultaneous analysis of a mixture of 20 elements are shown in figure 7. It may be pointed out here that in the case of simultaneous analysis of samples containing mixtures of many elements, it is possible to reach the lowest possible determination limit only for one element by focusing the sensitive zone of that element on the entrance slit. In the present analysis, the sensitive zone of the ICP flame corresponding to the element boron was focused on to the entrance slit to meet our requirement of lower determination limit for boron.

8. Results and discussion

Table 2 lists the determination limits for single-element analysis for various elements as determined by the ICP-AES instrument developed indigenously. The determination limit given in $\mu g/ml$ is a measure of the sensitivity of the technique in determining the concentration of a particular element in the sample. The lowest value of determination limit for any one element is possible only when a specific zone of the ICP flame is focused on the entrance slit of the polychromator. These observations will guide the user in selecting the proper zone in the ICP flame for achieving the lowest value of the determination limit for the particular element of interest under analysis. The determination limits of all the elements in simultaneous multielement analysis are higher than those shown in table 2 except for the element for which the sensitive zone of the ICP flame is focused on the entrance slit. The element which will have the lowest possible determination limit can be chosen by using the corresponding sensitive zone in the ICP flame for analysis.

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