

# Developments and trends in inductively coupled plasma mass spectrometry and its influence on the recent advances in trace element analysis

V. Balaram

*A brief introduction to the various instrumental methods such as atomic absorption spectrometry, X-ray fluorescence spectrometry, neutron activation analysis, inductively coupled plasma atomic emission spectrometry, thermal ionization mass spectrometry, etc. are presented highlighting their relative merits and demerits. The history and developments of inductively coupled plasma mass spectrometry (ICP-MS) and its advantages and limitations over other multi-element instrumental techniques are reviewed. Extended capabilities by hyphenating ICP-MS to various other well-known sample introduction techniques such as flow-injection, electrothermal vapourization, chromatographic methods and laser ablation are discussed in brief. The recent development of high resolution multi-collector double-focusing magnetic mass spectrometer with inductively coupled plasma at atmospheric pressure as source is also discussed. Some of the areas where more developments can be expected in future are suggested.*

RECENT developments in basic material research, environmental studies, quality control protocols in most industries, etc., have placed new demands on the field of metal analysis. Detection and accurate estimation of almost all the elements in the periodic table at ng/ml or  $\mu\text{g/ml}$  range has become an important requirement in the fields of both basic and applied research<sup>1-4</sup>. For example, in the environmental analysis field, the number of regulated elements is becoming more and more and the required levels are moving down to lower levels. Regulations that are being established by many countries for the inorganic contaminants in water and food-related materials, the increased awareness of the importance of trace elements in foods and the element speciation have created demands mainly for increased sample throughput and for lower levels of detection. Earth scientists working on geochemical problems need to determine relative and absolute abundance of the elements present even at trace and ultra-trace levels in a variety of rocks and minerals, with the object of discovering principles governing their distribution and migration<sup>5</sup>. Precise estimation of isotope ratios of certain elements such as Sm, Nd, Pb, U, etc., at very low concentrations is important for applications such as radiogenic dating of rocks, ore deposits and in very accurate estimation of certain elements by isotope dilution method. There is also a need to characterize a variety of materials for trace metal impurities in several industries. The semiconductor industry, for example, requires determination of several trace elements in pure materials.

As the density of the circuitry increases and the geometry shrinks, the need for pure and purer materials increases. The R&D laboratories at the chip manufacturers are working on the needs of one or two generations into the future because the pace of development accelerates so fast. Most of the other industries need their finished products to be analysed for the presence of trace metal impurities. For example, analysis of trace elements in copper is of great significance in electronic industry, where properties of copper may be severely affected by the metal contaminants at levels even below part per million concentrations ( $\mu\text{g/g}$ ). The need for purer and purer reagents for the R&D laboratories, very often requires checking of the common mineral acids and other laboratory reagents for the contamination by certain elements at ultra-trace levels (for example, Rb, Sr, Sm, Nd, Pb, U, etc., for geochronological studies). Finally, the role of trace elements in human health and disease<sup>6</sup> is an area of immense interest for it is known that over a quarter of elements in the periodic table are essential to life. Thus, highly precise and accurate estimation of several elements at very low concentrations is required in a variety of fields such as geological, industrial, nuclear, environmental and biomedical. Most often, the sample volumes are relatively small and analytical requirements relatively high requiring very highly sensitive instrumental techniques for their analysis.

## Methods for the analysis of elements

From the turn of this century there has been an analytical revolution with succession of a series of analytical

V. Balaram is in the National Geophysical Research Institute, Hyderabad 500 007, India



instruments with multielement capabilities. The dominant instrumental analytical techniques available currently for qualitative identification and quantitative estimation of most elements in the periodic table include atomic absorption spectrometry (both flame and graphite furnace AAS), X-ray fluorescence spectrometry (XRF), neutron activation analysis (both instrumental and radioanalytical NAA), thermal ionization mass spectrometry (TIMS), spark source mass spectrometry (SSMS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Most of these are capable of carrying out rapid multielement analysis at  $\mu\text{g/ml}$  levels, except for AAS which can detect and determine one element at a time. Other disadvantages of AAS (both flame and flameless) include the limited concentration range (requiring multiple dilutions to get a signal of appropriate intensity on scale) and the sequential nature of most systems. The fact that only one or two elements can be determined at a time is the major reason which caused its decline in favour of ICP-AES, which was made available in the mid-1970s. Though ICP-AES provides multielement detection for most elements at sub  $\mu\text{g/ml}$  level, there are numerous limitations resulting from complex spectra and matrix interferences. XRF which started in the mid-1950s is a popular analytical technique in both research and industry for the estimation of major and minor elements in several matrices such as rocks, alloys, etc. This technique suffers from drawbacks such as, interferences, very high detection limits for several trace elements in the above matrices, and also this technique cannot handle solutions. One of the main strands of analytical advancement was the development of neutron activation analysis (NAA). Although the principles of NAA had been understood since the publication of Hevesy and Levi's<sup>7</sup> work in 1936, the full potential of the technique was realized only during the 1960s after the development of high resolution gamma-ray detectors<sup>8</sup>. It is a nondestructive technique and offers multielement capability, together with relatively good levels of sensitivity ( $\mu\text{g/ml}$  levels). The need for a nearby reactor often precludes the consideration of NAA. If such a facility exists, the technique can be valuable. However, a greater disadvantage of NAA is the production of radioactive waste apart from having matrix interference effects. However, the radiochemical separation (RNAA) overcomes many matrix interference problems and offers low detection limits (sub  $\text{ng/ml}$  levels). But it involves many long drawn separation procedures which may carry the potential of delivering a high dose of radiation to the analyst. Thermal ionization mass spectrometry (TIMS) is a well-established method for measuring both radiogenic and nonradiogenic isotope ratios. Isotope ratio measurement of elements such as neodymium and strontium is routinely accomplished to high levels of precision and accuracy. But certain elements cannot be analysed by this technique as the

efficiency of thermal ionization decreases with increase in their ionization potentials. Further disadvantages of thermal ionization include, the extensive sample preparation and prolonged analysis times. TIMS is also applicable to elemental analysis. Very high precisions are attainable using the isotope dilution method, though this is limited to elements with more than one naturally occurring isotope. Though in recent years multicollector systems for parallel collection of several isotopes have been perfected, and offer enhanced efficiency and drift compensation, TIMS is not suited to the routine analysis of samples in large numbers.

During the last 15 years, considerable attention has been paid to the development of yet another and more powerful analytical tool called inductively coupled plasma mass spectrometry (ICP-MS) by the combination of plasma ion source with mass spectrometry techniques, which has revolutionized elemental analysis and has become widely accepted as a powerful tool for trace and ultratrace elemental and isotopic analysis. Thus, evolution of instrumentation continues with the latest method being ICP-MS.

### History and development of ICP-MS

Gray<sup>9</sup> was the first to demonstrate the potential of the plasma source mass spectrometry in 1975. He used a direct coupled plasma (DCP) and showed that strong signals could be obtained with low-background levels, so that detection of elements in  $\mu\text{g/ml}$  region was possible in aqueous solutions. Although these results were encouraging initially, they also revealed the limitations of the DC plasma used. The gas temperature of about 3500 K was too low to provide adequate sample volatilization, dissociation and ionization of the elements, especially those with ionization energies above 8 eV. Microwave-induced plasma (MIP) was also rejected on the basis of its low-gas temperature and ICP was considered the most suitable. These historic observations by Gray followed by the pioneering work<sup>10-14</sup> by him at the University of Surrey along with Alan Date, at British Geological Survey, UK; R. S. Houk, from Iowa State University at Ames, USA and Don Douglas, at Sciex, Canada in the subsequent years have brought about the development of this powerful analytical instrument. The major innovation in the design of ICP-MS is the interface between the ICP and the quadrupole mass spectrometer. Here, ions produced in the plasma at atmospheric pressure are transported into the quadrupole mass analyser held under ultra-high vacuum through a differentially pumped vacuum system which is not technically simple. The first commercial instruments were introduced in 1983 by two firms, namely V.G. Isotopes (now FI Elemental Analysis, UK) and Sciex Inc. (now Sciex-Perkin Elmer, USA). Perhaps a reflection of the success



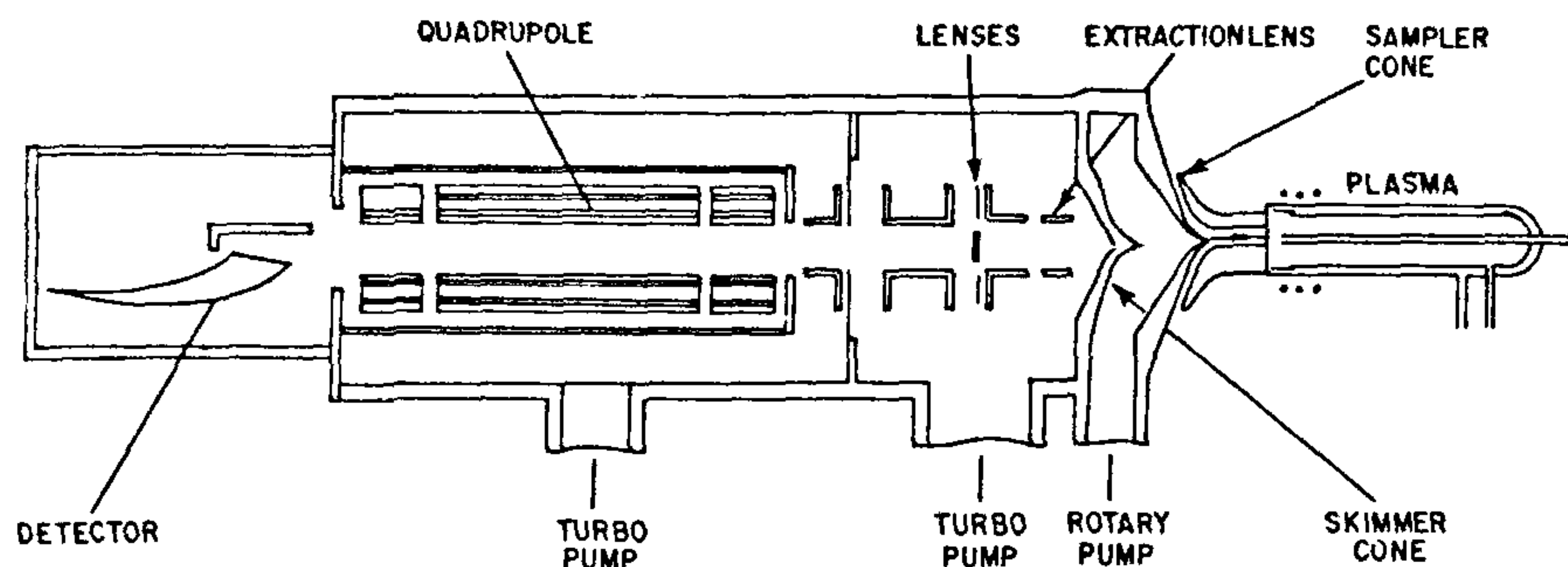


Figure 1. A schematic of plasmaquad system.

is that more than ten firms are manufacturing and marketing this particular instrument world-wide today. Efforts are also on at BARC<sup>15</sup>, Bombay in India to produce this instrument indigenously. Though there are several hundreds of instruments installed in chemical laboratories all over the world, there are only two ICP-MS instruments in India at present. One instrument (Elan 250, Sciex, Canada) is at the Indira Gandhi Centre for Atomic Research, Kalpakkam and the other (VG Plasmaquad, FI Elemental, UK) at the National Geophysical Research Institute, Hyderabad. Though these two instruments were procured mainly for the analysis of nuclear and geological samples respectively, they have also been continuously utilized by several other groups in the country working on a range of disciplines such as geochemical, environmental, water, biological and metallurgical fields since the last eight years.

Over the last decade, ICP-MS has been well established as a powerful tool for simultaneous multielement analysis. The low detection limits, high sample throughput, small sample quantities required for analysis, element versatility (major, minor, trace and ultra-trace) and isotopic capabilities are some of the important features which have made ICP-MS an excellent spectroscopic technique for the analysis of a variety of materials.

### System outline and the principle

Configuration<sup>16</sup> of the instrument consists of three basic units: i) a conventional argon ICP operating at temperatures of 6000-9000 K with a nebulizer, spray-chamber, work coil and associated power supplies, ii) a conventional quadrupole mass spectrometer and associated data collection electronics, which permit rapid scanning of the selected mass range between 0 and 300 amu (atomic mass units), and iii) an interface unit consisting of two water-cooled nickel cones, each containing a small orifice at the centre, which allow sampling of the plasma gases and transfer of the ion-beam into the mass spectrometer.

The principle of ICP-MS can be understood with reference to the schematic diagram given in Figure 1. Samples in the form of solution are introduced through

the peristaltic pump at a rate of about 1 ml/min into the central region of the plasma at atmospheric pressure with the help of a nebulizer and a water-cooled spray-chamber system. The sample is heated to a temperature of approximately 9000 K in the plasma, resulting in a series of processes involving desolvation, vaporization, dissociation, atomization and ionization<sup>17</sup> (Figure 2) in the 'analytical zone' of the ICP. At this temperature, chemical interference effects are insignificant, and essentially all atoms are ionized to a very large extent (majority of the elements in the periodic table are expected to ionize to the extent of about 90% in ICP). The efficiency of ionization in the argon plasma as calculated by the Saha equation<sup>18</sup> shows that the formation of singly charged ions is very efficient in argon plasma and over 54 elements are expected to be ionized with an

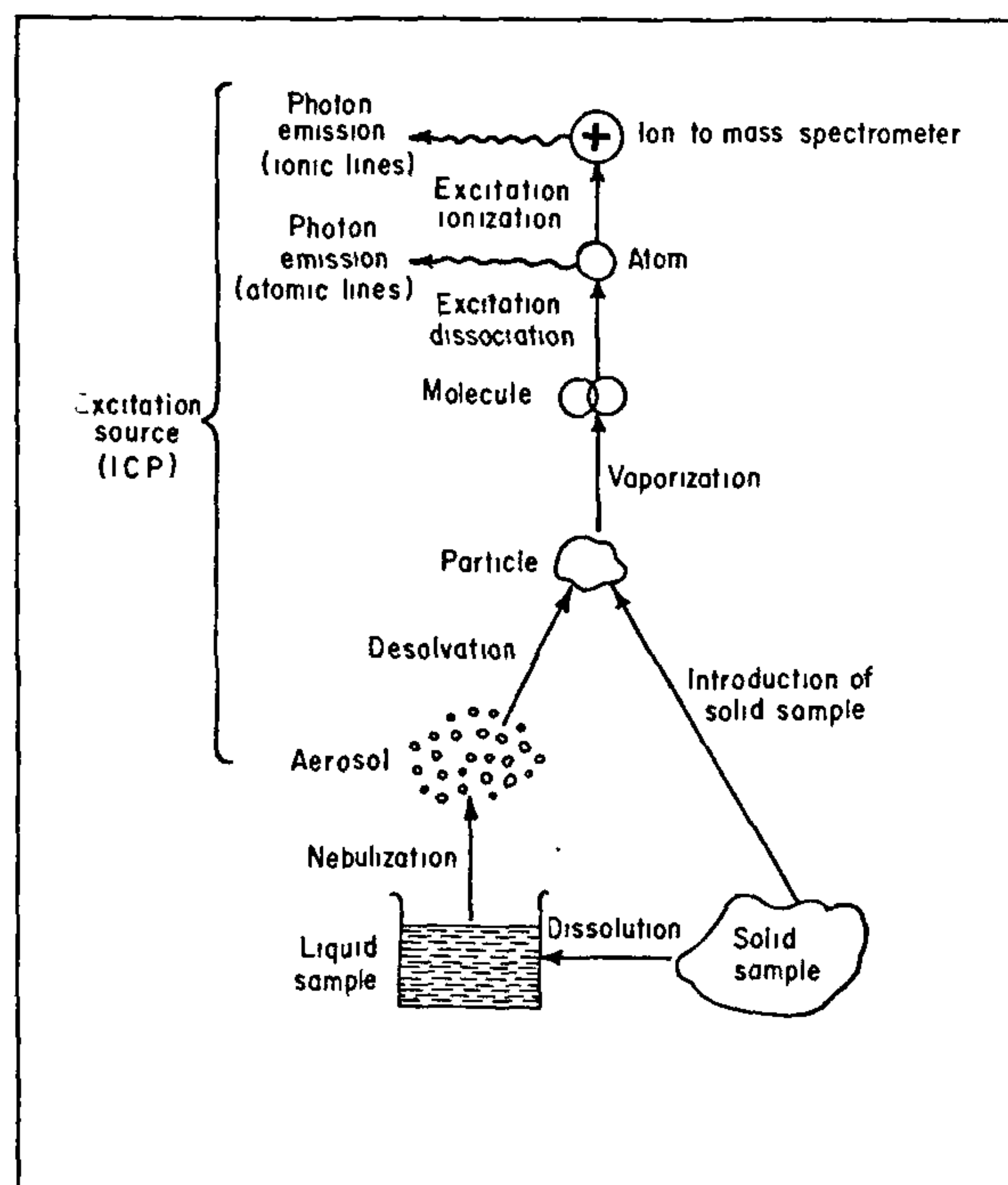


Figure 2. The chain of events leading from sample to the formation of ions.



efficiency of 90% or more<sup>16</sup>. A fraction of the positively charged ions produced in the plasma is transported through a narrow aperture of the sampler cone<sup>19</sup>. Here the plasma beam expands at supersonic speeds because of vacuum conditions (1 mbar) and is sampled by the skimmer cone. The ions and the plasma gas pass into a further high vacuum region ( $1 \times 10^{-4}$  mbar) and pass through a system of electrostatic lenses which extract the positively charged ions and focus them in a form suitable for transmission through the quadrupole mass spectrometer which is kept in a very high vacuum region ( $2 \times 10^{-6}$  mbar). The mass spectrometer transmits only ions of a particular mass to charge ratio, any neutral species accompanying the plasma gases would be taken away from the system by the vacuum pumps. This minimizes the ion-molecular collisions in the system. After mass isolation, the filtered ions pass into the detector system. An ion-detector system consisting of a channel electron multiplier is used in pulse-counting mode, to register the transmitted ions and generate a signal for every ion impinging upon its surface which will be amplified further. Since the number of registered ions from a given isotope, of course depends directly on the concentration of the relevant isotope (element) in the sample, quantification is straightforward. Design of the ion-optics makes the sampled ions to take a curved trajectory around a central photon stop eventually to be counted by an off-axis detector. This arrangement suppresses photon noise as the detector is also sensitive to photon radiation from ICP<sup>16</sup> and produces a low background signal of only around 25 counts per second as against a count rate of about 1 lakh for a 50 ng/ml solution of a monoisotopic element like rhodium. Detection limits, mainly influenced by the relative abundance of the isotope selected for analysis for most elements are currently in the range 0.01 to 0.1 ng/ml (for example, the detection limits of rare earth elements in Table 4). These detection limits are obtainable under multielement operating conditions. For many elements, even better detection limits can be obtained if operating conditions for the plasma, ion optics and mass analyser are optimized exclusively for one element or a few elements of similar mass.

### Performance characteristics and applications

The instruments constructed to date employ quadrupole mass analysers which yield essentially better than unit mass resolution over a mass range up to 300 amu. The analyser can scan very rapidly the entire useful mass range (0–240 amu) or a selected mass window of interest. A mass spectrum is normally obtained by many such repeat scans (say 100) which may take around 60 sec. This process of mass scanning is very rapid, and the instrument can obtain a spectrum for the entire mass

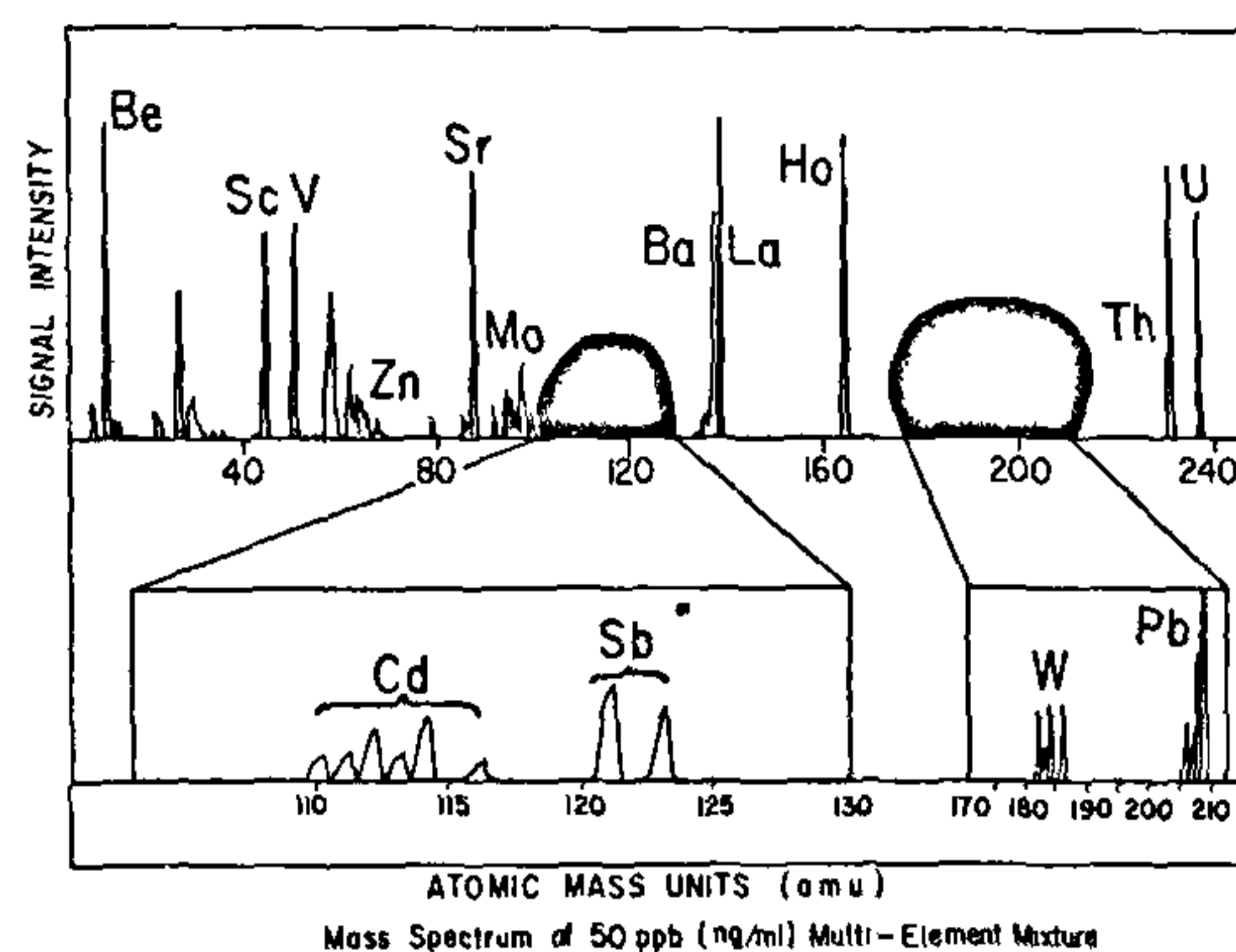


Figure 3. Mass spectrum of 50 ppb (ng/ml) multielement mixture

range of  ${}^7\text{Li}$  to  ${}^{238}\text{U}$  in about 1 min. One such spectrum is shown in Figure 3 for a 50 ng/ml multielement solution, the position of the peak in the spectrum reveals the nature of the element (isotope) in the sample and the height of the peak its concentration. By comparing the mass peaks with those observed for a standard solution run under identical conditions, exact concentrations of different elements in any sample can be precisely calculated after making proper blank and interference corrections by an on-line computer. In place of mass scanning, peak jumping can also be used for data acquisition. Despite early claims that ICP-MS was relatively free from interferences<sup>12</sup>, many workers noticed several kinds of interferences such as matrix effects either exclusively or in conjunction with a particular application<sup>20, 21</sup>. Evans and Giglio<sup>22</sup> have presented a comprehensive review of interferences in ICP-MS. Recently, Burton and Horlick<sup>23</sup> developed a graphically oriented data base of spectral interferences in ICP-MS, such as isobarics, oxides, doubly charged species, background- and matrix-dependent species, etc. This program is called 'MS Interview' which runs on a Macintosh Computer and helps the user to broadly assess the interference problems in ICP-MS. The most important limitation of this technique is nontolerance to high total dissolved solids in the sample solution. More than 0.4% of total dissolved solids cause clogging of the sampler and skimmer cones. For all practical purposes running of 0.1% solutions is recommended for obtaining reasonable long-term stability<sup>24</sup>. Others include the potential interferences from the background and sample matrix, periodic drift in the signal, space-charge and mass discrimination effects, etc. A few of these problems are minimized by the use of internal standardization<sup>25</sup>, matrix-matching standards<sup>26</sup>, addition of chemical modifier<sup>27</sup>, isotope dilution<sup>28</sup>, etc. during analysis.

The advantages of ICP-MS include: (i) very low detection limits which are considerably better than XRF and ICP-AES<sup>26</sup>, (ii) much wider elemental coverage than by AAS or INAA, (iii) capability of doing multielement



## GENERAL ARTICLES

**Table 1.** Trace element data on hornblende mineral reference sample, JH-1 (Geological Survey of Japan) obtained by ICP-MS (at NGRI) in comparison with the values obtained by other popular analytical techniques together with certified values

Element	Values (µg/g)	Technique	Certified values*	Element	Values (µg/g)	Technique	Certified values*	Element	Values (µg/g)	Technique	Certified values*
Sc	82	XRF	231	Y	12	ICP-AES	—	Tb	0.52	INAA	—
	73	ICP-AES			13	FE			0.46	ICP-MS	
	74	FE			14	XRF					
	81.4	INAA			12.22	ICP-MS					
	71.27	ICP-MS									
V	225	FE	630	Zr	42	FE	—	Dy	2.6	GRAV	—
	242	XRF			51	XRF			2.89	ICP-MS	
	272	ICP-AES			86	ICP-AES					
	229.93	ICP-MS			51	ICP-MS					
Cr	617	ICP-AES	53	Nb	3.6	FE	—	Er	1.2	GRAV	—
	625	GRAV			4.6	XRF			1.2	ICP-MS	
	630	INAA			24	ICP-AES					
	669	XRF			3.36	ICP-MS					
	623.71	ICP-MS									
Co	51	GRAV	56	Ba	106	GRAV	—	Lu	0.20	INAA	—
	51.6	INAA			109	XRF			0.13	ICP-MS	
	55	XRF			169	ICP-AES					
	52.11	ICP-MS			112.37	ICP-MS					
Ni	9	GRAV	9	La	7.5	ISE	—	Hf	1.46	INAA	—
	11	XRF			7.6	INAA			1.16	ICP-MS	
	18	ICP-AES			8.18	ICP-MS					
	9.66	ICP-MS									
Zn	67	XRF	62	Ce	17	GRAV	—	Ta	0.24	INAA	—
	92	INAA			17.20	INAA			0.22	ICP-MS	
	130	ICP-AES			19.23	ICP-MS					
	64.26	ICP-MS									
Ga	9	XRF	—	Nd	11.4	INAA	—	Pb	3	XRF	—
	7.36	ICP-MS			12	FE			2.56	ICP-MS	
					11.27	ICP-MS					
Rb	12	ICP-AES	12	Sm	3	INAA	—	Th	1.54	INAA	—
	14	FE			3.42	ICP-MS			1.57	ICP-MS	
	15.4	XRF									
	14.09	ICP-MS									
Sr	152	FE	155	Eu	0.85	GRAV	—	U	0.6	INAA	—
	154	XRF			0.90	INAA			0.46	ICP-MS	
	306	ICP-AES			0.94	ICP-MS					
	156.05	ICP-MS									

GRAV = Gravimetry, XRF = X-ray fluorescence spectrometry; ICP-AES = inductively coupled plasma atomic emission spectrometry; ICP-MS = Inductively coupled plasma mass spectrometry; FE = Flame emission spectrometry; INAA = Instrumental neutron activation analysis  
\*The values obtained by ICP-MS (at NGRI) are average of six values. Analytical data on ICP-AES, XRF, FE, INAA and GRAV are by N Imai, Geological Survey of Japan (personal communication, 1994).

analysis, unlike AAS with which we can estimate only one element at a time<sup>29</sup>, (iv) considerably faster sample throughput at a rate of one sample in 3 min for the analysis of over 30 elements<sup>30</sup> and (v) the unique capability of providing a very rapid semiquantitative survey analysis for over 70 elements in an unknown sample<sup>31</sup>. Fulford and Quan<sup>32</sup> have studied the basic characteristics

of negative ions such as F<sup>-</sup>, C<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and S<sup>-</sup> in ICP-MS in the negative ion mode and revealed that they do not originate directly from the plasma but rather from electron capture or reaction downstream of the free jet expansion. They also indicated the possibility of sensitive detection of halogens, especially fluoride, which makes this mode particularly attractive where halogens are of

**Table 2.** Concentrations of various trace elements (ng/ml) in NIST 1643c, a water reference sample, obtained by ICP-MS (at NGRI) in comparison with certified values

Element	ICP-MS value*(ng/ml)	Certified value† (ng/ml)
Be	22 91	23 2
B	118 75	119 00
V	32 07	31 4
Cr	20 29	19 00
Mn	35 79	35 1
Fe	105 34	106 9
Co	23 98	23 50
Ni	61.01	60 60
Cu	22 00	22 30
Zn	75 11	73.90
As	81 48	82 10
Se	12.49	12.70
Rb	11 30	11 40
Sr	266.26	263 60
Mo	102.54	104 30
Ag	2 13	2 21
Cd	12.18	12 2
Ba	50.02	49 60
Tl	8 02	7 90
Pb	34 70	35.30
Bi	12 40	12 00

\*Average of three estimations.

†National Institute of Standard and Technology Certificate, Standard Reference Material 1643c, Trace Elements in Water, 1991.

**Table 3.** Concentrations of gold and some platinum group elements determined by ICP-MS (at NGRI) in a platinum ore reference sample, SARM-7 (Council for Mineral Technology, South Africa) in comparison with certified values

Element	Value obtained by ICP-MS (µg/g)*	Certified values† (µg/g)
Ru	0 41	0 43
Pd	1 55	1 53
Ir	0 06	0 074
Pt	3 67	3 74
Au	0 32	0.31

\*Average of three determinations

†Govindaraju, K., *Geostand Newslett*, 1994, 18, 1-158

specific interest. Other advantages include isotopic analysis capability, relatively few interference effects, linear dynamic range for about 5-6 orders of magnitude, etc.

ICP-MS technique has been applied virtually to all types of samples, including geological<sup>24,33</sup>, marine<sup>34</sup>, biological<sup>35</sup>, nuclear<sup>36</sup>, freshwater<sup>37</sup>, sea water<sup>38</sup>, metallurgical<sup>39</sup>, environmental<sup>31</sup>, petroleum products<sup>40</sup>, etc. There also have been a few instances of measuring trace elements by ICP-MS at pg/g levels in ultra-pure acids<sup>41</sup>. Although some samples like water could be aspirated directly, pretreatment

is required in most cases. The trace element data obtained at our laboratory (Tables 1-3) on the hornblende mineral, water and precious-metal ore reference samples by ICP-MS demonstrate the potentials of ICP-MS in comparison with other popular analytical techniques. The methods used for sample preparation and other details are presented elsewhere<sup>26,31,42,43</sup>. The measurement precisions obtained on various trace elements are better than 5% relative standard deviation (RSD) with comparable accuracies.

### Extending the capabilities of ICP-MS

ICP-MS was basically designed for multielement analysis of aqueous samples. In order to achieve accurate, reliable and sensitive results, especially when the concentrations of analyte elements in the original material or the prepared solution are too low to be determined directly by ICP-MS, or when matrix elements interfere with the determination, preconcentration and separation techniques are needed. In recent times, efforts have been successfully made to extend its capabilities by simple hyphenations to other techniques<sup>44</sup>. Some of them are discussed in the following:

#### *Flow-injection method*

Alternative sample introduction technique such as the flow injection analysis (FIA) when used in combination with ICP-MS is found to be very useful in agricultural, biochemical, clinical, pharmaceutical and environmental fields where smaller amounts of samples are available for analysis. This involves the injection of a discrete sample plug into a nonsegmented carrier stream. The sample moves into carrier stream from injection point to the ICP. A major limitation of ICP-MS is its sensitivity to the matrix (spectroscopic and nonspectroscopic interferences, clogging by solid deposition, etc.). When FIA preconcentration/separation techniques are employed, the analytes can be selectively separated from the bulk of the matrix<sup>45</sup> before injecting into ICP. The advantages include high throughput and minimal sample consumption. An example of effective utilization of FIA-ICP-MS is the estimation of very low levels of Cr, Ni and Pt in urine samples<sup>46</sup>.

#### *Electrothermal vaporization*

Another alternative is to couple an electrothermal vaporization (ETV) unit to ICP-MS. ETV can be carried out using a metal filament or a heated graphite tube. Microlitre amounts of sample are injected into the tube, dried and then rapidly heated to approximately 3000°C to vaporize the sample, which is then transported to the ICP by using a carrier gas-flow. Rapid quadrupole scanning combined with multichannel data acquisition



allows the resultant transient signals to be captured and analysed<sup>47</sup>. This results in decrease of interference effects and improved sensitivity<sup>48</sup>. One interesting example of this technique is the determination of Os in geological materials<sup>49</sup> as it is very difficult to estimate Os in geological samples by solution nebulization.

### *Slurry nebulization*

Although ICP-MS is designed for the analysis of solutions, it can be applied to solids if they are finely ground and suspended in water. Williams *et al.*<sup>50</sup> published a feasibility study of analysing slurry concentrations of 0.05 g per 100 ml of tetrasodium pyrophosphate as dispersing agent for finely ground (<3 µm) sample particles. Slurries of up to 1% w/v can indeed be nebulized using a high-solids nebulizer<sup>51</sup>. This approach is particularly useful for samples which are hard to dissolve<sup>52</sup>.

### *Coupling with chromatographic techniques*

Although many of the analytical techniques available today, including ICP-MS, are capable of determining elements at very low levels, most of them yield information only of total levels. Though ICP-MS can provide isotopic information, it cannot distinguish between different oxidation states of an element. At present there is an increasing demand to quantify the form or oxidation state of trace elements in a wide variety of samples. This is often termed metal speciation. Such information is very important to environmental scientists and toxicologists<sup>6</sup>. One of the most promising approaches to obtain trace metal speciation information is by combining an appropriate chromatographic technique to ICP-MS. Because of chromatography's separation power, coupling it to ICP-MS provides speciation capability. High-performance liquid chromatography (HPLC) is ideal as it employs solutions<sup>44</sup>. In general, the mobile phase must be selected carefully to prevent clogging of the interface, extinguishing of the plasma, etc. Low levels (a few per cent) of organic solvents in water can easily be tolerated by increasing the power and water-cooling the spray chamber (to condense and drain out as much solvent as possible). For higher levels, addition of oxygen to the plasma is required to burn out the carbon. By interfacing liquid chromatographic system with ICP-MS Huang and Jiang<sup>53</sup> have been able to accurately determine mercury species (total mercury and methyl mercury) in Dogfish Muscle reference material. Houk *et al.*<sup>54</sup> also used ion-pair reversed-phase HPLC to separate various cationic species of Hg and Pb in human urine.

A variety of high-efficiency nebulizers such as Mistral nebulizer<sup>55</sup>, ultrasonic nebulizer<sup>54</sup>, direct injection nebulizer<sup>56</sup>, hydraulic nebulizer<sup>57</sup> and recycling nebulizer<sup>58</sup> have been successfully employed together with

ICP-MS to realize the full potential of the technique. For example, memory effects associated with conventional pneumatic nebulization were found to be drastically reduced with direct injection nebulization<sup>56</sup>.

### *Laser ablation*

For the analysis of high-purity materials, such as high-pure metals, semiconductors, etc., sample treatment must be kept to an absolute minimum. This requirement has led to the development of a technique called laser ablation-ICP-MS (LA-ICP-MS). Gray<sup>59</sup> demonstrated the feasibility of laser ablation for solid sample introduction to ICP-MS for the first time in 1985. Laser ablation is an attractive alternative sample introduction technique to dissolution, particularly for handling geological materials<sup>60</sup>. A pulsed Nd:YAG laser is used to ablate solid samples held within an ablation cell. The laser is focused onto the surface of the solid sample, and controlled laser pulses of a millisecond duration vapourize the analyte material. The microparticulate cloud produced is carried by a stream of argon gas to the ICP torch and subsequently ionized within the plasma followed by mass spectrometric analysis. It is of particular importance to the nuclear, semiconductor, mineral and ceramic industries where information on several trace elements at µg/g and ng/g levels are needed without dissolving the sample. This technique can also provide very rapid semiquantitative analysis of materials of completely unknown composition<sup>61</sup>. LA-ICP-MS also offers the possibility of producing spatial information on element distribution at micrometer scale in solid materials<sup>62</sup>. This technique has also been applied to the characterization of spent nuclear fuels and to study the isotopic distributions of fission products and actinides in fuel pellets<sup>63,64</sup> and conductive (e.g. alloys powders) and nonconductive powder samples<sup>65</sup> (e.g. calcium sulphate and titanium dioxide powders for industrial use).

### *High resolution-ICP-multiple collector mass spectrometry (HR-ICP-MC-MS)*

ICP-MS equipped with quadrupole mass analysers has been applied to the measurement of isotope ratios<sup>60</sup>. It is currently not possible to achieve precisions better than 0.1% RSD in routine analysis. This is not sufficient for geochronological studies and nuclear purposes. An unique instrument with ICP as source and incorporating a double focusing magnetic sector mass analyser equipped with multiple ion collectors has been recently developed<sup>66</sup>. The isotopic components were measured simultaneously which allowed high precision and high accuracy isotope ratio analysis (better than 0.01% RSD) which were comparable to those exhibited by TIMS<sup>67</sup>. It is also demonstrated recently that by combining laser ablation with HR-ICP-MC-MS, the isotopic composition



**Table 4.** Detection limits ( $3\sigma$  values) of rare earth elements obtained by ICP-MS, LA-ICP-MS and HR-ICP-MS in comparison with those obtained by other well-established multielement analytical techniques

Element	XRF ( $\mu\text{g/g}$ )*	ICP-AES ( $\mu\text{g/ml}$ )*	INAA ( $\mu\text{g/g}$ )*	ICP-MS ( $\text{ng/ml}$ )**	LA-ICP-MS ( $\mu\text{g/g}$ ) <sup>†</sup>	HR-ICP-MS ( $\text{pg/ml}$ ) <sup>‡</sup>
La	1.17	0.044	0.83	0.010	0.11	0.0014
Ce	1.10	0.145	2.50	0.015	0.13	0.002
Pr	1.03	0.065	—	0.010	0.13	0.001
Nd	0.87	0.085	7.70	0.050	0.12	0.0058
Sm	0.77	0.031	0.17	0.036	0.11	0.005
Eu	0.73	0.005	0.08	0.017	0.14	0.003
Gd	0.67	0.035	6.5	0.012	0.12	0.005
Tb	0.67	—	0.15	0.009	0.17	0.0008
Dy	0.63	0.011	—	0.024	0.14	0.002
Ho	0.60	0.010	2.83	0.010	0.16	0.0005
Er	0.57	0.019	—	0.028	0.14	0.002
Tm	0.57	—	0.57	0.009	0.17	0.0008
Yb	0.57	0.004	0.23	0.025	0.18	0.002
Lu	0.50	0.004	0.17	0.008	0.16	0.0009

\*ref. 70; \*\*ref. 24; <sup>†</sup>ref. 77; <sup>‡</sup>ref. 74, —not available.

of solids can be measured directly to similar superior levels of precision and accuracy even for those elements such as W, Sn, Te, Mo, etc., which are difficult to ionize by thermal ionization<sup>68</sup>. High resolution ICP-MS offers detection limits better than 0.1 pg/ml in aqueous solutions for several elements. Table 4 gives the detection limits obtained by HR-ICP-MS for rare earth elements in comparison with those obtained by other multielement analytical techniques. We can see that the detection limits obtained by HR-ICP-MS are better by several orders of magnitude. This is a powerful analytical tool, especially when complex matrices like geological, ceramic, biological, sea water, etc. are investigated. Such matrices not only suffer from many spectral interferences such as isobaric overlaps, interferences from molecular ions, doubly charged ionic species, etc., which are well known but also from numerous unexpected spectral interferences which may additionally arise because of the complexity of these matrices and confuse the spectral interpretation. High resolution mass spectrometers keep the analyst free from most of the significant problems from spectral interferences in real samples while simultaneously improving sensitivity<sup>69</sup>. At least three firms, viz. FI Elemental Analysis, Winsford, UK (PlasmaTrace); Jeol Ltd, Tokyo, Japan, (JMS-Plamax1); and Finnigan MAT, Bremen, Germany (ELEMENT) have launched high resolution instruments during 1993.

### Future directions

New developments in ICP-MS instrumentation and applications are advancing the understanding and the utility of the technique. The following are some of the areas where striking improvements can be expected in future.

i) During the nebulization of the samples, experience<sup>70</sup> has shown that approximately only one in one million ions sampled actually reaches the detector. This astonishing inefficiency of the present instruments suggests that further refinement of the design of the interface and ion-optics will improve the sensitivity further. Space-charge effects are thought to be a major cause of ion loss in ICP-MS. Briefly, as the beam leaves the skimmer cone it encounters the electric field of ion lens and the electrons are stripped away. The current from the ions remaining in the beam is far too high for the lens to tolerate so that the ion beam explodes, resulting in loss of ions. Active research is going on in this direction to minimize these effects. One firm (Hewlett-Packard, USA) has eliminated the need for a photon stop by mounting the quadrupole and detector off axis. An omega lens is used to bend the ion beam into the entrance aperture of the quadrupole. By this arrangement it is claimed that the new design has achieved a very high ion transmission with minimal space-charge effects, resulting in very low background and high sensitivity compared to the conventional systems<sup>71</sup>.

ii) The normally operated nebulizers deliver only 1–2% of the sample to the plasma. This fraction can be increased roughly by an order of magnitude by using ultrasonic nebulizers as they produce smaller, more uniform droplets and is generally not prone to blockage and so is more efficient than pneumatic nebulizers<sup>72</sup>. Striking advances have already been made in this direction and some more may follow in future.

iii) Another effective way of minimizing the interference effects is to reduce the water load to the ICP by using the multiple desolvation<sup>73</sup> steps at  $-80^{\circ}\text{C}$  for a continuous flow ultrasonic nebulizer. It has been observed that oxide and other polyatomic interferences were reduced by several orders of magnitude.



iv) As already discussed, one of the most effective methods of overcoming spectral interferences is to use high resolution ICP-MS, using a double focusing mass analyser to enable mass measurements at very high resolution (50,000 approx., the resolution is typically defined as  $P = M \Delta M$ , where  $\Delta M$  is the width of the peak at mass  $M$  at 5% of the peak height). At present these systems are finding applications in precise determination of stable isotopes and isotope ratios in geological and environmental studies<sup>74</sup>.

v) One of the prominent areas of research in ICP-MS in recent times is the use of mixed gas plasmas<sup>75</sup> (addition of small amounts of oxygen or nitrogen or hydrogen to argon, or use of xenon or helium plasmas). The mixed gas plasmas have two major advantages in ICP-MS; reduction of polyatomic interferences and direct analysis of organic materials<sup>76</sup>. Use of helium as plasma gas is important because of its very high first ionization potential (24.5 eV) which exceeds that of argon (15.75 eV). Thus greater excitation and ionization of analyte ions is expected with the plasma. This is particularly important for sensitive estimations of elements such as halogens which are not efficiently ionized in argon plasma. Hence they are determined in negative ion mode in conventional ICP-MS.

Since its commercial introduction in 1983, ICP-MS has proved to be a versatile and powerful technique for handling routine analytical problems involving both elemental and isotopic analysis in a wide variety of matrices. By coupling alternative sampling techniques such as laser ablation, the ICP-MS technique is able to solve many analytical problems, not possible by other instrumental methods. Currently ICP-MS is a subject of very active research in the field of inorganic analytical chemistry and the instrument will continue to be an important asset to any chemical laboratory. The developments in ICP-MS, LA-ICP-MS and HR-ICP-MS are expected to address both the technical and operational limitations of the present systems, eventually leading to more reliable, robust and low-cost instruments.

1. Ehrlich, H. L., *Geomicrobiology*, Marcel Dekker, New York, 1990, p 646
2. McLaren, J. W., in *The Handbook of Inductively Coupled Plasma Mass Spectrometry* (eds Jarvis, K. E., Gray, A. L. and Houk, R. S.), Blackie, USA, 1992, p 265.
3. Emery, D. and Robinson, A., *Inorganic Geochemistry. Applications to Petroleum Geology*, Blackwell, London, 1993, p 254
4. Martin, M. H. and Coughtrey, P. J., *Biological Monitoring of Heavy Metal Pollution* (ed Mellanby, K.), Applied Science, London, 1992.
5. Rollinson, H. R., *Using Geochemical Data Evaluation, Presentation, Interpretation*, Longman, England, 1993, p. 17.
6. Tolg, G., in *Metal Compounds in Environment and Life* (ed Merian, E.), Science and Technology Letters, Middlesex, UK, 1992
7. Hevesy, G. Von and Levi, H., *Nature*, 1936, **137**, 185.
8. Gordon, G. E., Randle, K., Goles, G. G., Corliss, J. B., Beeson, M. H. and Oxley, S. S., *Geochim Cosmochim Acta*, 1968, **32**, 369-396
9. Gray, A. L., *Analyst*, 1975, **100**, 289-299
10. Gray, A. L., *Dyn Mass Spectrom*, 1978, **5**, 106
11. Gray, A. L. and Date, A. R., *Dyn Mass Spectrom*, 1981, **6**, 252-266
12. Gray, A. L. and Date, A. R. *Analyst*, 1983, **108**, 159.

13. Houk, R. S., Fassel, V. A., Flesch, G. D., Svec, H. J., Gray, A. L. and Taylor, C. E., *Anal Chem*, 1980, **52**, 2283-2289.
14. Douglas, D. J. and French, J. B., *Spectrochim Acta*, 1986, **B41**, 197-204
15. Natarajan, V. and Rama Rao, V. V. K., Proceedings of the Sixth National Symposium on Mass Spectrometry, Dehradun, 1993, pp 367-372.
16. Houk, R. S., *Anal Chem*, 1986, **58**, 97A-105A.
17. Moore, G. L., *Introduction to Inductively Coupled Plasma Atomic Emission Spectrometry*, Elsevier, Amsterdam, 1989, pp 1-130
18. Boumans, P. W. J. M., *Theory of Spectromechanical Excitation*, Hilger and Watts, London, 1966, Chapter 7
19. Gray, A. L. F. Z., *Anal Chem*, 1986, **324**, 561-570
20. Vaughan, M. A. and Horlick, G., *Appl. Spectrosc.*, 1986, **40**(4), 434-445
21. Tan, S. H. and Horlick, G., *Appl Spectrosc*, 1986, **40**(4), 445-460.
22. Evans, E. H. and Giglio, J. J., *J. Anal. Atom. Spectrom*, 1993, **8**, 1-18
23. Burton, L. L. and Horlick, G., *Spectrochim. Acta*, 1992, **B47**, E1621-E1627
24. Balaram, V., *J. Indian Chem Soc*, 1991, **68**, 600-603.
25. Balaram, V. and Saxena, V. K., Proceedings of the First International Conference on Plasma Source Mass Spectrometry, Durham, UK, 1988, abstract, p 44
26. Balaram, V., Anjaiah, K. V. and Reddy, M. R. P., *Analyst*, 1995, **120**, 1401-1406.
27. Goossens, J., Vanhaecke, F., Moens, L. and Dams, R., *Anal. Chem Acta*, 1993, **280**, 137-143
28. Longerich, H. P., *At Spectrosc.*, 1989, **10**, 112-115
29. Balaram, V. *Geophys. Res Bull.*, 1988, **26**, 1-7
30. Balaram, V., Manikyamba, C., Ramesh, S. L. and Anjaiah, K. V., *At Spectrosc*, 1992, **13**, 19-75.
31. Balaram, V., *At Spectrosc.*, 1993, **14**, 174-179.
32. Fulford, J. E. and Quan, E. S. K., *Appl Spectrosc.*, 1988 **42**, 3.
33. Jarvis, K. E., *J. Anal. At Spectrom*, 1989, **4**, 563-570
34. Nagender Nath, B., Balaram, V., Sudhakar, M. and Pluger, W. L., *Marine Chem*, 1992, **38**, 185-208.
35. Vanhoe, H., Vandecasteele, C., Versieck, J. and Dams, R., *Anal Chem. Acta*, 1991, **244**, 259-267
36. Vijayalakshmi, S., Krishna Prabhu, R., Mahalingam, T. R. and Mathews, C. K., *At Spectrosc.*, 1992, **13**, 61-66
37. Vanhecke, F., Vandecasteele, C. and Dams, R., *Anal. Lett.*, 1992, **25**, 919-936
38. Kato, Takunori, Nakamura, S. and Morita, M., *Anal. Sci.*, 1990, **6**, 623-626
39. Luck, J. and Siewers, U. F. Z., *Anal Chem*, 1988, **331**, 129-132
40. Alswaidan, H. M., *Anal Lett*, 1994, **27**, 145-152
41. Paulsen, P. J., Beary, E. S., Bushee, D. S. and Moody, J. R., *Anal. Chem*, 1988, **60**, 971-975.
42. Balaram, V., Ramesh, S. L. and Anjaiah, K. V. F. J., *Anal. Chem.*, 1995 (in press).
43. Balaram, V., Hussain, T. S. M., Uday Raj, B., Charan, S. N., Subba Rao, D. V., Anjaiah, K. V., Ramesh, S. L. and Ilangoan, I., *J. Geochem. Explor.*, 1995 (in press)
44. Beauchemin, D., *Trends. Anal. Chem*, 1991, **10**, 71-77.
45. Ruzicka, J. and Fresenius, Z., *Anal. Chem*, 1988, **329**, 653
46. Plantz, M. R., Fritz, J. S., Smith, F. G. and Houk, R. S., *Anal. Chem*, 1989, **61**, 149.
47. Denoyer, E. R., *At Spectrosc*, 1991, **12**, 215-224.
48. Whittaker, P. G., Lind, T., Williams, J. G. and Gray, A. L., *Analyst*, 1989, **114**, 675.
49. Gregoire, D. C., *Anal Chem.*, 1990, **62**, 141
50. Williams, J. G., Gray, A. L., Norman, P. and Ebdon, L., *J. Anal. At Spectrom.*, 1987, **2**, 469-472.
51. Ebdon, L., Foulkes, M. E., Parry, H. G. M. and Tye, C. T., *J. Anal. At Spectrom*, 1988, **3**, 753.
52. Jarvis, K. E., *Chem Geol*, 1992, **95**, 73-84.



- 53 Huang, C. W and Jiang, S. J., *J. Anal At Spectrom*, 1993, 8, 681-686.
- 54 Houk, R. S., *et al.*, *Anal Chem*, 1992, 64, 2444
- 55 Walder, A. J., Platzer, I. and Fredman, P. A., *J Anal At Spectrum*, 1993, 8, 19
- 56 Powel, M. J., Quan, E. S. K., Boomer, D. W and Wiederin, *Anal. Chem*, 1992, 64, 2253-2257
57. Jakubowski, *et al.*, *Spectrochim Acta*, 1992, 47, 119-123.
- 58 Chen, *et al.*, *J. Anal At. Spectrom*, 1992, 7, 905-910.
- 59 Gray, A. L., *Analyst*, 1985, 111, 551-556
- 60 Jarvis, K. E., Gray, A. L. and Houk, R. S., *Handbook of Inductively Coupled Plasma Mass Spectrometry*. Blackie, Glasgow and London, 1992.
- 61 Denoyer, E. R., Fredeen, K. J. and Hager, J. W., *Anal. Chem*, 1991, 63, 445A-457A
- 62 Pearce, N. J., Perkins, W. T., Abell, I., Duller, G. A. T and Fuge, R., *J Anal. At. Spectrom*, 1992, 7, 53-57.
- 63 Garcia Alonso, J. I., Babelot, J. F., Glatz, J. P., Cromboom, O. and Koch, L., *Radiochem Acta*, 1993, in press.
64. Alonso, J. I., Garcia, Serrano, J. G., Babelot, J. F., Closset, J. C., Nicolaou, G. and Koch, L., personal communication, 1994.
65. Raith, A and Hutton, R. C. Fresenius, *J. Anal. Chem*, 1994, 349, in press
- 66 Walder, A. J. and Fredman, P. A., *J. Anal. At. Spectrom*, 1992, 7, 571
- 67 Walder, A. J., Koller, D., Reed, N. M., Hutton, R. C. and Fredman, P. A., *J. Anal At Spectrom.*, 1993, 8, 1037-1041.
- 68 Halliday, A. N., Christensen, J. C., Hall, C. M., Jones, C. E., Lee, D. C., Teagle, D., Walder, A. J. and Entwistle, A., *Proc GEOANALYSIS 94 An International Symposium on the Analysis of Geological and Environmental Materials*, Ambleside, England, 1994, C41.
69. Feldman, I., Tittes, W., Jakubowski, N., Stuewer, D. and Giessman, U., *J. Anal At. Spectrom.*, 1994, 9, 1007-1014
70. Hall, G. E. M., *J. Geochem Explor*, 1982, 44, 201-249
- 71 Potter, D., *Int Lab*, 1994, 3, 30-31
72. Clifford, R. H., Tan, H., Liu, H., Montaser A., Zarrin, F. and Keady, P. B., *Spectrochim Acta*, 1993, B48, 1221-1235
- 73 Alves, L. C., Daniel, R., Wiederin, R. O. and Houk, R. S., *Anal Chem*, 1992, 64, 1164-1169
- 74 Yamasaki, S. I., Tsumura, A. and Takaku, Y., *Microchem J.* 1994, 49, 305-318
75. Durrant, S. F. F., *J Anal Chem*, 1993, 347, 389-392.
76. Hutton, R. C., *J Anal. At Spectrosc*, 1986, 1, 259-263.
77. Cousin H. and Magyar, B., *Mikrochim Acta*, 1994, 13, 313-323

ACKNOWLEDGEMENTS. I thank Dr S. M. Naqvi for his valuable guidance and encouragement, Dr Sajid Husain, Analytical Division, Indian Institute of Chemical Technology, Hyderabad, for critical reading of the manuscript and helpful suggestions, Drs S. Nirmal Charan and M. V. Subba Rao (NGRI) for their helpful suggestions.

## Climate change and agriculture – An Indian perspective

Sulochana Gadgil

*In this paper, we examine the major predictions made so far regarding the nature of climate change and its impacts on our region in the light of the known errors of the set of models and the observations over this century. The major predictions of the climate models about the impact of increased concentration of greenhouse gases are at variance with the observations over the Indian region during the last century characterized by such increases and global warming. It is important to note that as far as the Indian region is concerned, the impact of year-to-year variation of the monsoon will continue to be dominant over longer period changes even in the presence of global warming. Recent studies have also brought out the uncertainties in the yields simulated by crop models. It is suggested that a deeper understanding of the links between climate and agricultural productivity is essential for generating reliable predictions of impact of climate change. Such an insight is also required for identifying cropping patterns and management practices which are tailored for sustained maximum yield in the face of the vagaries of the monsoon.*

THE last decade has witnessed a rapid increase in the awareness of global change and triggered widespread apprehension amongst scientists and governments about the implications for their part of the globe. The major facets of global change are changes in climate, the con-

centration of atmospheric constituents (such as CO<sub>2</sub>, CH<sub>4</sub>, etc.), land surface cover (e.g. desertification, deforestation) and biodiversity. The changes in these facets are of concern to us because of the impact on human beings and on resources critical to their survival. On the other hand, the changes in many of these facets have a large anthropogenic component, e.g. deforestation, loss in biodiversity, the increase in CO<sub>2</sub> due to burning of

Sulochana Gadgil is in the Centre for Atmospheric Sciences, Indian Institute of Science, Bangalore 560 012, India