Advanced instrumental techniques for the analysis of trace metals released from steel industry with special reference to use of ICP-AES

SULOCHANA CHAUDHURI AND H.D. PANDEY

Environment Laboratory, Research & Development Centre for Iron & Steel
Steel Authority of India Limited, Ranchi - 834 002, India

ABSTRACT

Uncontrolled emissions from steel industries can produce multi-dimensional impacts on the environment, including those due to release of trace metals. Certain metals present even in trace concentrations pose serious environmental problems in the surrounding biosphere. Consequently, a precise, accurate and rapid instrumental technique is required to monitor levels of heavy metals in various emissions released by steel plants. The paper reviews the various instrumental techniques employed for such assessments. A comparison of the various techniques reveals that ICP-AES, despite its limitations in sample preparations, offers a very reliable and powerful tool for heavy metal analysis. Its usefulness is discussed with reference to some of the studies carried out in the Environment Laboratory of SAIL (R&D) on air and water samples from some SAIL steel plants.

INTRODUCTION

An integrated iron and steel industry processes massive quantities of diverse materials and correspondingly generates a large amount of pollution in the surrounding air, water and soil. Suspended particulate matter, both non-respirable and respirable (< 0.5 μm) represent the most common form of metallic air pollution[1]. Other physical forms include liquid droplets (mists) and vapours. Dust released in huge quantities from sinter plant, blast furnace, steel melting shop and raw material handling plants, contains heavy metals many of which could be toxic. Steel processing technology requires a considerable amount of water for use in cooling as well as processing. Water used for contact cooling of various machinery and for cleaning and scrubbing operations may contain large quantities of toxic metals. Water is also used to transport solid wastes as slurries from different steel processing units. Ultimately all waste water is discharged through plant outfalls into receiving water bodies which may be used by the general public.

The large quantity and variety of wastes generated during the various processing steps involved in steel manufacture are generally dumped onto the ground or pits. Heavy metals from these dumps can leach into the soil and eventually reach underground water, adversely affecting both with the passage of time. Therefore, uncontrolled emissions of air, water and generation of slid wasters from the steel industry can seriously influence human, plant and aquatic species through metallic discharge alone.

The intake of some metals even in trace quantities either in aqueous form or associated with dust is often detrimental to human health[2-4], The human tragedy, recently unfolded in large areas of West Bengal as due to arsenic pollution is an episode worth mentioning in this context. It, therefore, becomes important that release of toxic metals by any industry including steel industry are accurately assessed. Furthermore, with environmental laws becoming more and more stringent, it is imperative that source emission inventory for every industry also be generated. In the case of suspended particulate matter, certain metals, which volatilise and preferentially condense back onto the finer fraction causing enrichment of those metals can be used to trace the emission source. If enough number of elements can be quantified in the finer sized fractions, the enrichment profile becomes unique for the source and can be used to fingerprint it. Data from this can then be used for receptor models which can relate composition of atmospheric aerosols to emission sources. Receptor models based on enrichment factors and also chemical mass balance are already in use abroad[5,6].

USE OF ADVANCED INSTRUMENTAL TECHNIQUES

Often, the concentrations of metallic pollutants are very low and analysis must be carried out by highly sensitive instrumentation. A large variety of samples are invariably involved in a complex industry like the steel industry, hence there is a need for instrumentation which can analyse quickly without sacrificing accuracy.

For collection of particulate matter, several types of filter materials have been used. These include glass fibre, cellulose, organic membranes, metal membranes and graphite. Generally, cellulose and glass fibre filters are used with high volume (Hi-vol) samplers[1,6]. The choice of filter depends on the targeted elements, sampling situation and the analytical techniques used to determine the collected trace elements. If required, filter samples are acid digested to bring the metals into solution. Industrial effluent samples are generally acidified to bring total metals into solution[7] and then pre-concentrated before analysis.

Some of the most commonly used techniques for trace element analysis of airborne particulate matter and other solid materials like wastes and solid are discussed below. A number of these can also be used for analysis of effluent discharges. The

Table-1 : Analytical detection limits (ng/m³) of various techniques for trace elements associated with airborne particulate matter[29-31]

	Flame AA	Graphite tube AA	ICP	INAA	Graphite spark AES	XRF
As	20	0.5	40	4	10	0.75
Cd	0.2	0.02	2	-	2	13
Co	0.8	0.15	3	0.025	0.5	2
Cr	2	0.3	1	0.25	0.1	2
Cu	1	0.25	1	5	0.05	2
Fe	10	1.0	5	0.02	0.3	3
Hg	0.1	-	200	0.1	1	7
Mn	1	0.1	1	0.6	0.03	2
Ni	4	1.5	6	20	0.1	1
Pb	2	0.2	8	-	0.1	5
Zn	0.2	0.004	1	1	1	1

AA - Atomic absorption spectrometry; ICP - inductively coupled plasma spectrometry; INAA-instrumental neutron activation analysis; AES - atomic emission spectrometry; XRF - X-ray fluorescence

Table-2 : 1991-1992 Threshold limit values for metals in the work environment adopted by ACGIH[6]

Metal	From of exposure	TWA mg/m³
As	metal & soluble compounds (1980)	0.2
Cd	dusts & salts (1976)	0.05
Co	dust & fume (1987)	0.5
Cr	metal & salts (1981)	0.5
Cu	fume (1977)	0.2
	dust & mists (1986)	1
Fe	salts (1986)	1
Hg	skin contact	
	alkyl compounds (1980)	0.01
	all forms except alkyl vapour (1982)	0.05
	aryl and inorganic compounds	0.1
Mn	dust & compounds (1988)	5
Ni	metal (1991) [used to be 1 mg/m³ 1976]	0.05*
Pb	inorganic dust & fumes (1986)	0.15
Zn	as oxide fume (1976)	5
	as oxide dust (1976)	10

*Confirmed human carcinogen; Threshold limit values represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse health effects. Time weighted averages (TWA) are average concentrations for a normal 8-hour workday and 40 hour work-week to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

analytical techniques are divided into two categories : those which require no pre-treatment of the sample but can analyse metals directly from the sampling filter in the case of particulate matter and those which require acid digestion before sample analysis.

Analytical methods requiring no pre-treatment of the sample

X-ray spectrometry involves using X-rays to bombard the metal resulting in the emission of secondary or fluorescent X-rays characteristic of the irradiated metal. The intensity of these secondary emissions can give a quantitative measure of the metal. The method is rapid, non-destructive and applicable to almost all elements in the periodic table. Numerous elements can be analysed simultaneously and results are comparable to those obtained by INAA[8] and atomic absorption analysis except some light elements below atomic number 8 [9,10]. Since only small sample quantities are required, inter-element effects encountered in bulk samples are not very significant in the case of particulate matter analysis[11] but should be accounted for in analysis of solid waste e.g. fly ash[12]. However, the capital investment in equipment and personnel is high.

Instrumental neutron Activation Analysis (INAA) is probably the most power-ful non-destructive tool for precise determination of extremely low levels of trace elements. The sample is irradiated with neutrons causing the formation of different isotopes of the elements in the sample, or conversion to isotopes of neighbouring elements. Many of these isotopes are radioactive, and measurement of their activity allows quantitative analysis of the elements in the sample. Simulateous determination of up to 35 elements in suspended particulates can be done with high precision, sensitivity and accuracy. Limits of detection compare favourably with emission spectrographic and conventional atomic absorption methods[13]. Particles can be analysed directly on the sampling filter. However, the procedure is time consuming[14] with irradiation facilities expensive and scarce.

Methods involving sample pretreatment

Atomic absorption spectrometry (AAS) has been used extensively for the elemental analysis of airborne particulates[15]. The light source, a hollow cathode tube in which the cathode is coated with the metal to be determined, emits light at discrete wavelengths. Introduction of the sample into the flame causes absorption of some part of the incident light. The reduction in beam intensity is a measure of the quantity of element in the sample. Flame techniques generally have detection limits from 0.1 to 10 ng/m^3, depending on the species[6]. Double beam instruments, where the ratio of sample beam to a parallel reference beam is measured, allow a limit of detection several times lower than that attainable with a single beam. Flameless atomisers which use a graphite tube instead of a flame have increased sensitivity by three magnitudes[1,16]. With this

method, all metals and semi-metals can be analysed. Matrix effects are common and must be taken into account. The basic limitation of the method is that only one element can be analysed as a time as each element required the cathode lamp to be changed. Hence it is time consuming and for a large number of elements, sample quantity becomes critical. Moreover, a large inventory of hollow cathode lamps need to be maintained.

Optical emission spectrometry techniques rely on the emission of electromagnetic radiation in the visible/ultra violet regions of the spectrum by atoms and ions after electronic excitation in electrical discharges. An electric arc or spark will cause volatilization, dissociation and electronic excitation of atomic species present. Each element is characterised by the wavelength of emitted radiation and intensity of spectral lines can be used for quantification. Relative precision is 3 - 10%[17]. However, a major limitation of the technique lies in making the sample conducting before use. The use of plasma as excitation source offers a much wider applicability and precision and is, therefore, fast replacing arc/spark spectrometry.

In plasma emission spectrometry, electronic excitation is brought about by means of taking a gas like argon to a temperature of 6,000 K. The plasma attained has a substantially better signal stability and thus analytical precision. Two types of plasma sources are available commercially - (i) the DC plasma jet which is based on DC-arc discharge and, (ii) the increasingly popular inductively coupled plasma torch (ICP) which uses radio frequency to maintain the plasma [1,17]. Simultaneous and sequential multi-element analysis at high precision and low limits of detection can be done and it is possible to analyse a number of elements in a short time interval. Relative precisions are in the range of 0.05 - 2%. The high temperature ensures that virtually all compounds are broken down into their constituent elements. Background interferences are reduced, and when they do occur, correction can be easily determined and incorporated into the built-in software[18]. However, the equipment is bulky and higher investment in capital cost and personnel is required.

Since the targeted elements to be determined are at such low levels, a major consideration in choosing a particular method is its detection limit for the elements in question. Table-1 gives a comparison of the analytical detection limits for selected trace elements by the various instrumental techniques discussed above. The table, compiled from several sources presents the detection limits expected during analysis of real sample[6]. Taking into account the limitations and advantages of the above methods, ICP-AES is seen to offer quick, reproducible and accurate analysis, even though some time has to be spent in appropriate sample preparation.

Inductively coupled plasma - Atomic emission spectrometer (ICP-AES)

The ICP-AES system available in the environment laboratory is the Applied

67

Research laboratories Model 3410 "Minitorch", so named because the plasma torch generated is much smaller in size than conventional ICP torches and requires relatively less argon to sustain it.

The ICP-AES system has been extensively used to develop methods to monitor trace elements in air, water and solid wastes. The methods developed have been used to analyse ambient air and water samples collected from a variety of sources e.g. steel plants, iron-ore mines and municipal areas. Some solid wastes from different steel plants have also been analysed to study leaching characteristics of certain heavy metals. For collection of suspended particulate matter, the ASTM D 4096 High Volume Sampler Method was employed[19]. Samples were collected for a four hour period using a Hi-vol sampler on pre-weighed Whatman EPM 2000 glass fibre filter papers. The samples were acid digested to bring targeted elements into solution[20-22]. Digestion was carried out in Teflon PFA vessels using a CEM MDS-2000 Microwave sample preparation system, according to USEPA SW-3051 Sediments/Soils microwave digestion[23] programmed schedule. The extracts were vacuum filtered and made up to 30 ml. Before analysing the samples using ICP, inter-element interferences were determined and interference co-efficients incorporated into the analysis procedure if required. Calibration curves generated using ultra-pure metal (supplied by VHG Labs, U.S) were used for quantification.

The analytical method for trace elements in water is essentially the same, but sampling and sample preparation is different[7]. The sample is collected in plastic bottles, acidified and concentrated on site. The volume is made up to 50 ml before analysis by ICP.

RESULTS AND DISCUSSION

Permissible limits have to be considered whenever assessment is carried out. Table-2 gives work zone Threshold Limit Values - Time Weighted Averages (TLV-TWA) for some metals, as adopted by American Conference of Governmental Industrial Hygienists (ACGIH)[24]. Table-3 gives minimum National Standards (MINAS) as laid down by Central Pollution Control Board (CPCB) for Industrial effluent discharges into inland surface water.

Over the last five years ICP-AES in-house developed methods have been used to analyse plant effluents at IISCO, DSP[25] and also in the MIOM-KIOM complex. Some typical results for samples collected from DSP and IISCO during 1992-93 are given in Figs.1 & 2. The arithmetic average trace metal concentrations over the eight month period was calculated for each outfall to give an idea of time integrated values. For IISCO that meant an average of five data points for two
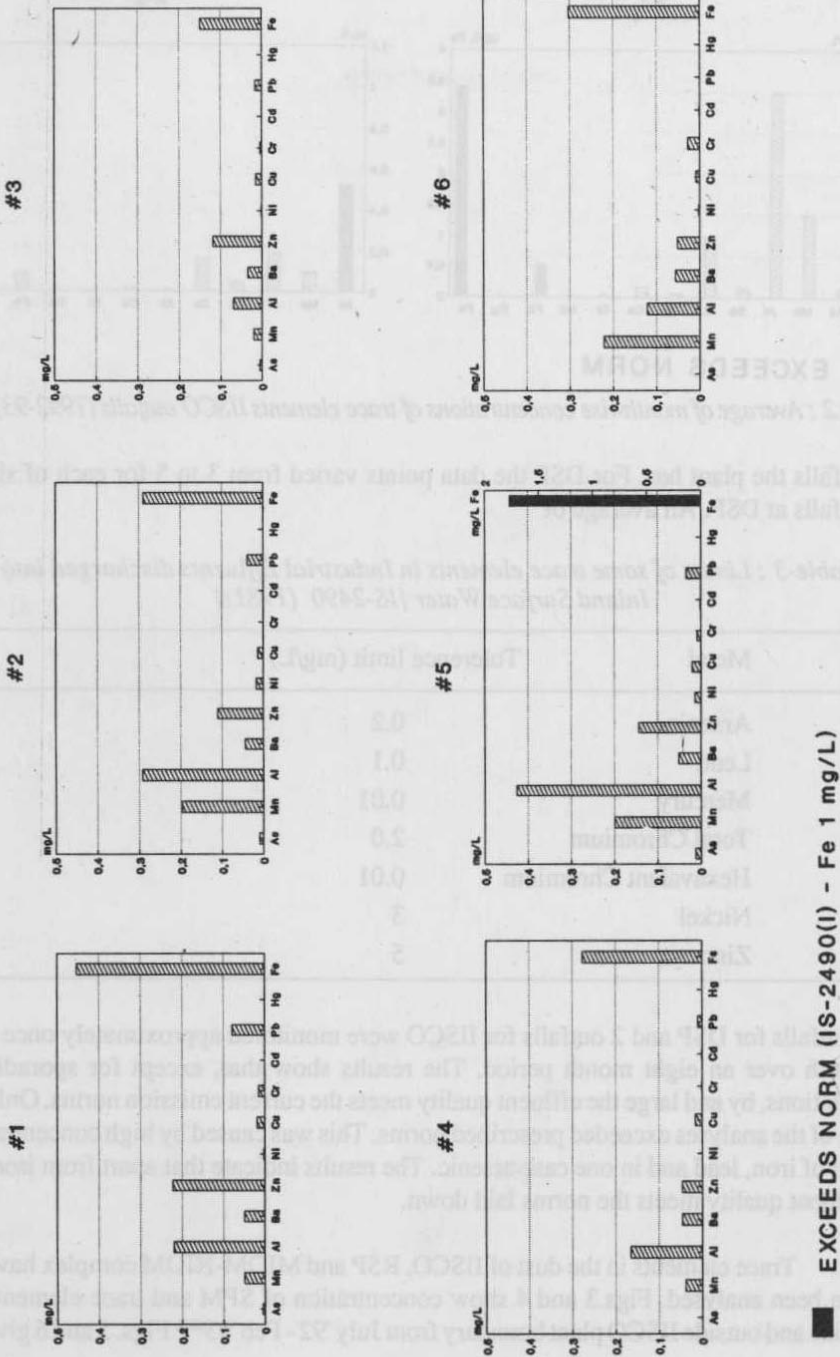
Fig.1 : Average of monthwise concentrations of trace element DSP outfalls (1992-93)

#1   #2
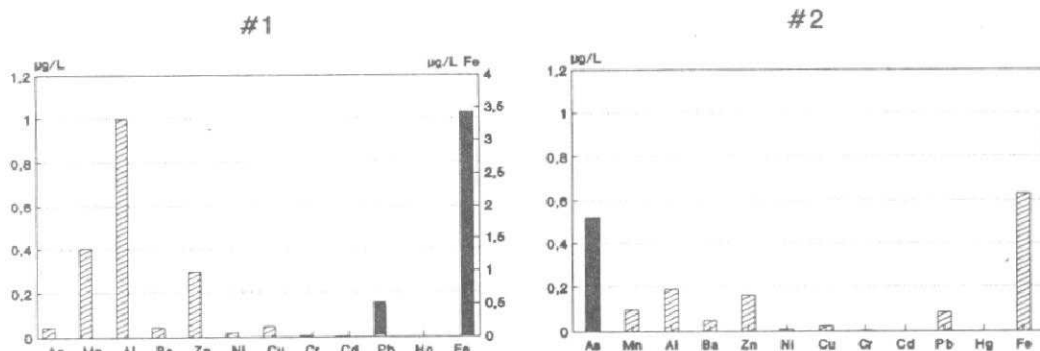
■ EXCEEDS NORM

Fig.2 : Average of monthwise concentrations of trace elements IISCO outfalls (1992-93)

outfalls the plant has. For DSP the data points varied from 3 to 5 for each of six outfalls at DSP. An average of

Table-3 : Limits of some trace elements in Industrial Effluents discharged into Inland Surface Water [IS-2490 (1981)]

Metal	Tolerence limit (mg/L)
Arsenic	0.2
Lead	0.1
Mercury	0.01
Total Chromium	2.0
Hexavalent Chromium	0.01
Nickel	3
Zinc	5

5 outfalls for DSP and 2 outfalls for IISCO were monitored approximately once a month over an eight month period. The results show that, except for sporadic violations, by and large the effluent quality meets the current emission norms. Only 3% of the analyses exceeded prescribed norms. This was caused by high concentration of iron, lead and in one case arsenic. The results indicate that apart from iron, effluent quality meets the norms laid down.

Trace elements in the dust of IISCO, RSP and MIOM-KIOM complex have also been analysed. Figs.3 and 4 show concentration of SPM and trace elements inside and outside IISCO plant boundary from July '92 - Feb '93[26]. Figs. 5 and 6 give
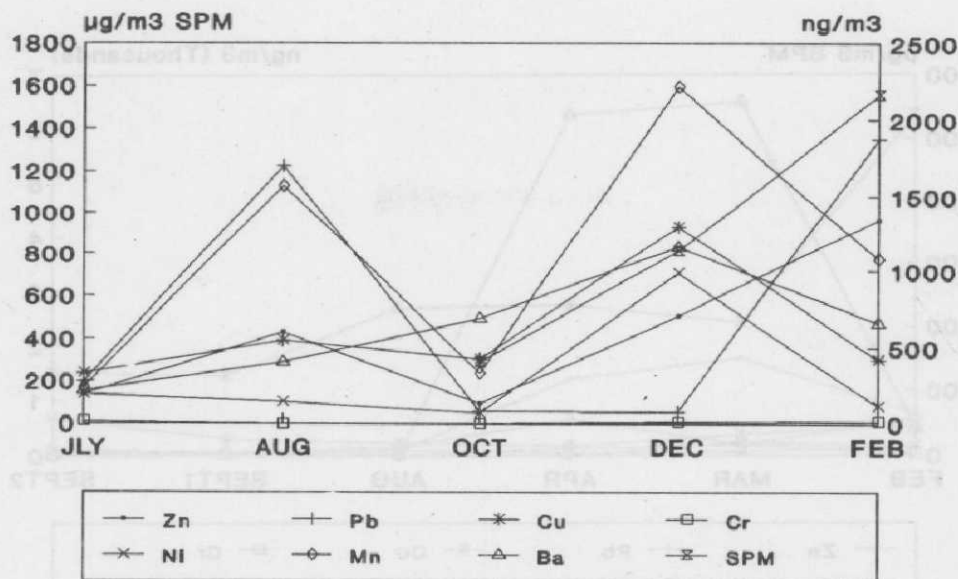
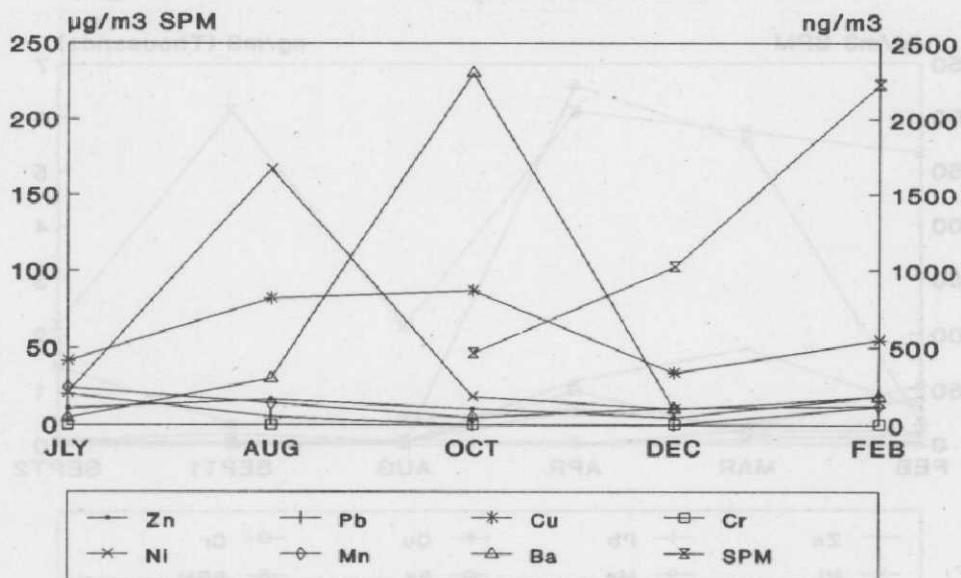Fig.3: SPM & trace element concentration inside IISCO plant boundary July'92-Feb.'93

Fig.4 : SPM & Trace element concentration outside IISCO plant boundary
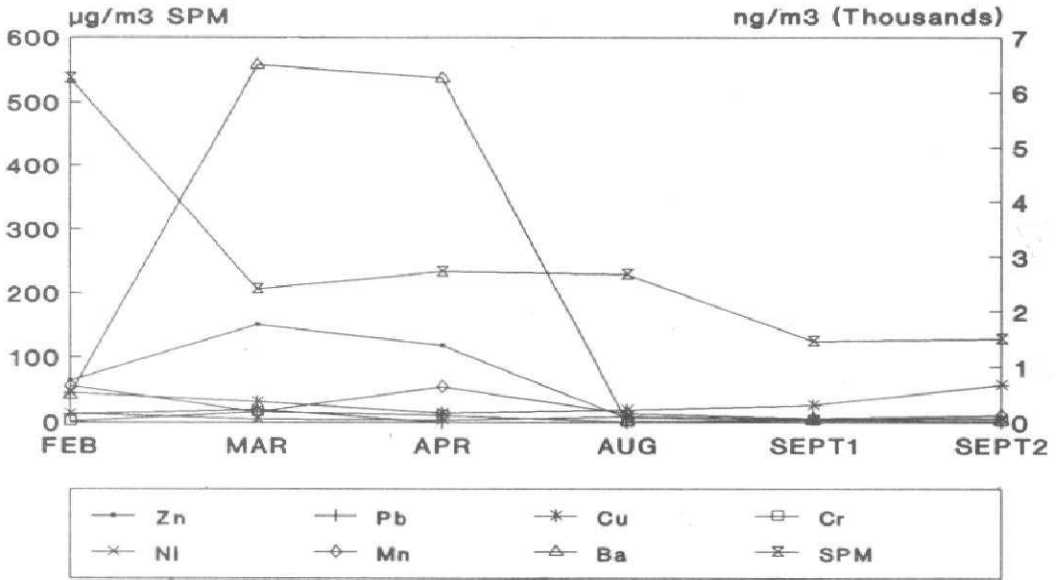July'92 - Feb.'93

Fig.5 : SPM & Trace element concentration inside RSP plant boundary
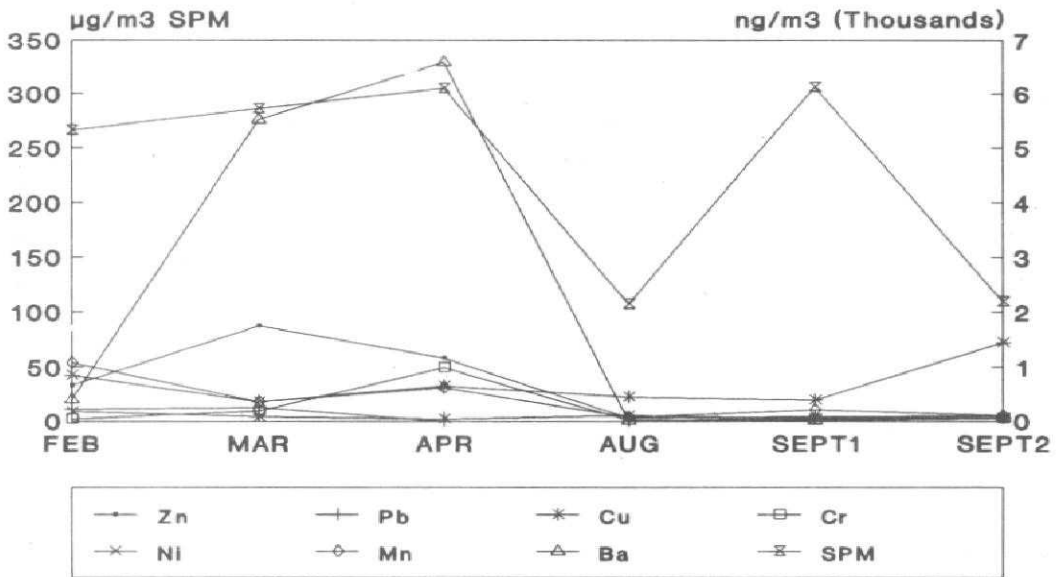*Feb'93-Sept.'93*

Fig.6 : SPM & Trace element concentration outside RSP plant boundary
Feb.'93-Sept.'93

the results of work done at RSP from Feb - Sep. '93. These measurements are for ambient air. Since there are no norms set for metallic compounds in ambient air, comparison has been made only with work zone TWA values and all levels were found to be well within TWA norms. Zinc and barium levels inside the plant tend to rise with SPM, whereas there is no such correlation outside the plant.

The technique has also been applied to study enrichment of certain trace elements for development of receptor modelling for source identification[27,28]. Elemental enrichment due to coal combustion was studied in the fly as samples from captive power plants of BSL and RSP. Samples were fractionated using sedimentation, then digested by microwave and finally analysed by Inductively Coupled Plasma - Atomic Emission Spectrometer. Enrichment was observed in Cr, Zn, Ni, Ba, Pb, Cu and enrichment factors found to vary from 1 to 15 times with greater enrichment in RSP fly ash.

CONCLUSION

A survey of the various analytical techniques available for comprehensive trace metal analysis shows that ICP-AES is notably a suitable system, despite the initial higher investment in equipment and personnel. The instrument available at RDCIS has been used to develop methods to accurately quantify trace metals released into ambient air as well as steel plant effluents. Extensive use of the system has been made to assess emissions from SAIL steel plants. Results obtained were compared with stipulated norms and found to be largely within permissible limits.

REFERENCES

[1]   R.M.Harrison in "Handbook of air pollution analysis", R.M. Harisson & R.Perry Eds., Chapman & Hall, London (1986) pp.215.

[2]   V.E. Thomson et.al. J.Air Pollut. Contol Assoc. 35 (1985) pp.535.

[3]   C.W.Sweet and S.J. Vermette : Environ. Sci. Technol, 27 (1993) pp.2502.

[4]   R.A.Goyer in "Toxic effects of metals" C.D.Klassen, M.O. Amdur & J.Doull Eds., Macmillan, New York (1986), pp.582.

[5]   G.E.Gordon : Environ. Sci. Technol., 22 (1988) pp.1132.

[6]   W.H. Schroeder: J. Air. Pollut. Control Assoc., 37 (1987) pp.1267.

[7]   Standard methods for the examination of water & waste water, 18th Edn. A.E. Greenberg, L.S.Clesceri and A.D.Eaton Eds., APHA, AWWA, WEF U.S. (1992) pp.3-1.

[8]   R.H. Hammerle et.al. Anal.Chem. 45 (1973) pp.1939.

[9]   C.L. Luke et al.: Environ. Sci. Technol: 6 (1972) pp.1105.

[10]   J.V. Gilfrich et.al. : Anal.Chem: 45(1973) pp.2002.

[11]   H.D.Pandey, C.D.Mishra and B.Prasad, Proc. of IIM seminar on Impact of Industry on Environment, Ranchi, India June 5-6 (1987) pp.II.1.1

[12]   C.D.Mishra and H.D.Pandey, Proc. of International Sysposium on Residues and Effluents: Processing and Environmental considerations: TMS Annual Meeting, San Diego, California,U.S.March 1-5 (1992) pp.149.

[13]   W.H.Zoller and G.E.Gordon: Anal. Chem., 42 (1970) pp.257.

[14]   R.Dams *et.al*: Anal.Chem., 42 (1970) pp.861.

[15]   J.Y.Hwang: Anal.Chem., 44 (1972) pp.20a.

[16]   J.P. Matousek and K.G.Brodie: Anal.Chem. 45(1973) pp.1606.

[17]   F.W.Fifield and D.Kealey in "Analytical Chemistry", International Textbook Co.Ltd. London (1986) pp.248.

[18]   Applied Research Laboratory 3410 ICP Spectrometer manual, ARL, Switzerland (1989).

[19]   ASTM D 4096-91 Standard method for SPM in Atomosphere (High-Volume Sampler method)

[20]   Standard practice for acid-extraction of elements from sediments using closed vessel microwave heating ASTM D 5258-92, 1992.

[21]   Standard practices for extraction of trace elements from sediments ASTM D 3974-81 (Reapproved 1990).

[22]   D.E.Kimborough and J.Wakakuwa: Environ., Sci Technol. 26 (1992) pp.173.

[23]   CEM MSD Operator's Manual: CEM Corp. U.S. (1988).

[24]   American Conference of Governmental Industrial Hygenists Threshold limit values for chemical substances in the work environment ACGIH, U.S. (1988).

[25]   S.Chaudhuri and G. Chattopadhyay: Proceedings of Pollution control in steel industry, Ranchi, India. Aug.4-5, 1994.

[26]   S.Chaudhuri et.al: Proceedings of 41st Annual Technical Meeting of Indian Institute of Metals, Calcutta, India. Nov.14-16, 1995.

[27]   S.Chaudhuri, G.Chattopadhyay and U.Kumar : Proc. of International Symposium on "Mineral Beneficiation - Recent trends and beyond 2000 AD" Nagpur, India. Oct. 3-4, 1994.

[28]   S.Chatterjee *et.al*: RDCIS Completion report No. R&D 65:02:2436:04:95(1995)

[29]   D.F.S. Natusch et.al. in Air Pollution control Part-III, Measuring & Monitoring air pollutants, W.Strauss Ed., Wiley, New York (1978) pp.217.

[30]   T.G.Dzubay and R.K.Stevens : Environ. Sci.Technol., 9 (1975) pp.663.

[31]   T.G.Dzubay, X-ray fluorescence analysis of environmental samples, Ann Arbor Science, Ann Arbor, MI, U.S. (1977).