

# AAS - A TOOL FOR MONITORING TRACE METALS IN ENVIRONMENT

CHANDRA SEKHAR K.\*

## INTRODUCTION

Rapid industrialisation coupled with geochemical alterations posed a major threat to environment. Pollution of air, soil and water with both organics and inorganics is a matter of great concern, however, the non-degradable persistent trace metals are the most pressing problems of present decade. They are the most insidious pollutants because of their non-biodegradable nature and property to effect all forms of ecological systems. Owing to their toxicity and ill-effects on living being the present day scientists and researchers have developed interest in the amounts, origin and fate of certain elements. For example certain trace elements such as cadmium, chromium, mercury, lead and vanadium are of great concern because of their toxic effects on plants, animals and humans. Essential trace elements, such as chromium, vanadium, manganese, iron, cobalt, copper and zinc are indispensable for the growth and survival of mankind. From the point of view of toxicity metals can be classified according to the following three criteria: non-critical, toxic and very toxic. Classification of elements according to toxicity and availability is given in Table-1. The impact of heavy metal contamination in biosphere is slowly being recognised as a potential health hazard not only to human beings but almost all the major industries are also affected by trace elements imbalances. For instance the presence of silica in boiler feed water at 30 to 1000 ppm level leads to appearance of scale forming silicates which reduces the heat transfer from boiler.

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\* Scientist, Analytical Chemistry Division,  
National Metallurgical Laboratory, Jamshedpur - 831 007

Continuous monitoring of trace elements is becoming more important from pollution point of view. Pollution monitoring and control of these metals of environment significance need analytical techniques capable of detecting low concentration of these metals which are generally present in micro and submicro quantities. The instrumental methods which are most widely used for determination of trace metals are emission spectroscopy, X-ray fluorescence neutron activation analysis and *atomic absorption spectrophotometry*(AAS). These instruments are highly sensitive, but most of them except AAS are not suitable for atmospheric samples.

### **A HISTORY OF ATOMIC ABSORPTION SPECTROMETRY**

**Early History** : Optical spectroscopy can be traced to 1672, when *Newton* observed that sunlight could be separated into colours upon passage through a prism. Indeed, the word spectrum comes from *Newton's* attempt to describe the ghostly appearance of dispersed sunlight. The first person to observe spectral features other than simple colours was *Wollaston*, who in 1802 described (but made no attempt to explain or characterize) numerous dark lines in the sun's spectrum. Starting in 1817, *Fraunhofer* carefully mapped these lines that bear his name and designated some of the more prominent ones by letters, starting with A at the red end of the spectrum. Even today, one sees reference to the sodium D lines, using *Fraunhofer's* original designation. His observations also laid the groundwork for spectral observations in astronomy. *Fraunhofer* noted that light from Venus looked much like that from the Sun but that light from the bright star, *Sirus*, had a very different spectrum.

*Kirchoff* and *Bunsen* explained the origin of *Fraunhofer* lines in a classic series of papers published in 1859 and 1860. They not only explained that *Fraunhofer* lines were caused by atomic absorption in

the Sun's atmosphere; they also established the general laws of emission and absorption of light and described the conditions needed for earthbound analytical observations using flames in both emission and atomic absorption. Flame analysis became common in Bunsen's lab, and several new elements were discovered by spectral analysis in the early 1960's. However, the full analytical potential of both flame emission and atomic absorption remained unexploited for many years.

**Modern History :** There were several distinct periods, in the *thumbnail* history of flame AAS covering nearly four decades.

In the induction period (1955-62) Atomic absorption - the technique that soon would revolutionize elemental analysis - was ignored by nearly all practicing analytical chemists. *Walsh* and a mere handful of people down under developed the method and demonstrated its utility time and time again and still people stayed away in droves. *Walsh* traveled extensively, trying to promote AAS, and was often frustrated by his inability to generate wide interest. His American friends have not let him forget that he once accurately described the United States as a country 'underdeveloped' in AAS.

From 1962 through 1969 explosive growth ("fun time") occurred as AAS caught on and surged to the forefront of elemental analysis. "*Fun time*" because during this period AAS symposia were spiced by frequent (usually polite) arguments about the best sources and atomizers. New techniques and applications were suggested almost as rapidly as most could follow. During the fun time, detection limits were a source of great pride and it seemed that nearly every conference paper included a claim to have established a new record in the quest for zero. A discussion of interferences were sure to spark instant debate; many researchers argued that AAS was much less prone than atomic emission to effects from chemical interferences.

The very existence of spectral interferences in AAS was vigorously denied by proponents of the technique. The confusion concerning interferences can perhaps be best conveyed by quoting from a publication of the period.

*"Atomic absorption spectroscopy does not suffer from chemical interference but (the) presence of large amounts of anions and cations can cause pronounced effects on absorption"*

In other words, it is not the chemicals, but those blasted anions and cations that cause the problems. This is an indicative of the confusion that prevailed during the 'fun time'.

By 1969 most misconceptions about AAS had been resolved, and 1969-76 was a period of relative stability (i.e. relative to that of the previous years). AAS put on its work clothes and began to generate data for other fields. Spectral interferences, although relatively rare, were acknowledged, and chemical interferences were known to be primarily function of the atomizer, not the mode of observation. Research was still being done, and improvements were still being made but with a slower pace compared to growth period. Automated background correction systems for AAS were available and, in an important advance, the nitrous oxide-acetylene flame had nearly doubled the number of elements to which AAS was applicable. The evolution of AAS was essentially complete.

In about 1976 the revolution in solid-state electronics began to make an impact on chemical instrumentation, and there appears to be no end in sight. Instrument throughput and, to a lesser extent, instrument capabilities have been enhanced whereas much of the tedium of routine analysis has been removed.

### A BRIEF HISTORY OF FLAME AAS

1955	Method described independently by Walsh and by Alkemade and Milatz
1955-62	The induction period-development down under while United States remains an "under developed country"
1962-69	Explosive growth the "fun time"
1969-76	Relative stability-AAS puts on its work clothes
1976 -present	Electronic revolution microprocessor and computer enhancement of instrumental capabilities

### TECHNIQUE

Atomic absorption is based on the absorption of photons by an atomic vapour in ground state. When an atom absorbs a photon, one of the outer shell electrons is transferred to an excited energy level. The wave length at which absorption occurs is characteristic of the element and the degree of absorption is a function of concentration of atoms in the vapour. The absorption lines of most elements lie between 190nm to 850 nm.

Arrangement of an AAS consists of the following parts: spectral source of hollow cathode lamp, atomizer, flame (single slot burner), monochromator, radiation detector, amplifier and read out, and other facilities like signal integrator, scale expansion and curve corrector, etc.

In an AAS, in addition to the flame in which the sample is atomized and burnt, there is special source as *hollow cathode lamp* which emits the characteristic light of the element to be analysed. Amount of absorption of the characteristic light of the element (to

be analysed) in the flame is measured. Sensitivity of an AAS depends upon the absorption of the characteristic line in the flame or the number of ground state atoms in the flame. At the normal temperature of the flame, the number of ground state atoms are  $10^2$  to  $10^{10}$  orders more than the number of atoms in the excited state. Atomic absorption technique is most *selective* because of the nature of resonance (selective) absorption of the characteristic line of the element in the groundstate atomic vapour of the element present in the flame. Background noise is reduced by employing hollow cathode lamps modulated at a suitable frequency and an amplifier tuned exactly to this frequency.

#### **SAMPLE COLLECTION FOR POLLUTION STUDIES**

**Air Pollution :** It is necessary to distinguish between general air pollution and specific air pollution. Pollution encountered in almost urban and industrial zones, primarily as a result of combustion processes, which include carbon monoxide, sulphur dioxide, oxides of nitrogen, oxidants, hydrocarbons, suspended particulates and lead, is general pollution. The latter type arises primarily from identified industrial sources and may include specific gaseous and particulate pollutants, such as chlorine from caustic soda factories, iron oxide from steel mills, cotton dust from textile mills and so on. Table-II gives details of sources of particulate emissions.

For the examination of air, a distinction is made between gaseous metals or metallic compounds and particulate matter such as dust, flyash, and aerosols. The various forms of aggregations require differing collection and sample preparation techniques. While the physical chemical examination of gases down to the trace range is nowadays generally well under control, the analysis of airborne dust and aerosols, dust from emissions, and smoke or fog presents considerable difficulties.

Dust particles in air are generally collected by filtration techniques with a twenty-four hour collection time, Coarse dust particles that settle out are collected in containers over a 4-week period and measured by weighing. Glass fibre filters permit a large air throughput, but because of the highly fluctuating element blank values, this type of filter is more suitable for the gravimetric determination of the airborne dust concentration rather than for the elemental analysis of airborne dust. Due to their low and constant metal blank values, cellulose membrane filters are excellently suited for multielement determinations using the most varied analytical techniques. Elements like Pb, Cd, Fe, Zn and other elements can be determined by extracting the filters with acid, or by low temperature or oxygen plasma ashing of the filter and taking up the residue in acid, and nebulizing the solution into the flame.

**Industrial effluent :** Suspended matter in the sample is first separated, or if it contains any of the elements to be determined, it must be homogenized and dissolved or extracted with nitric acid. In extreme cases, the solid matter is centrifuged off and treated separately as sludge. Clear or clarified water is acidified to about 1% with nitric acid and can be aspirated in the atomic absorption spectrometer without further treatment in the concentrations ranges present can be handled. Samples with a high suspended solids content must be digested by heating with nitric acid for 30 min. Calibration standards should also be acidified 1% with nitric acid if the concentrations are too high and alternative line can be used or solutions are brought within the best range by dilution with deionized water also acidified with 1% of nitric acid. If the concentrations are too low, the sample may be evaporated to a lower volume, or the wanted metals extracted into an organic solvents.

**Sludges** : Sludges containing organic matter are wet or dry-ashed like other organic matrices and taken up in mineral acid. If the inorganic residue contains siliceous material, the silica can either be removed with hydrofluoric acid and perchloric acids or the residue completely solubilized by a method generally applicable to silicates. Alternatively, sludges and sediments can be extracted for heavy element analysis with hydrochloric/nitric acid mixtures. This is effective for several elements including cobalt, copper, chromium, iron, manganese, nickel, lead and zinc.

### "SHORT CUTS" IN AAS

Over recent years, the demands placed upon AAS have increased steadily. The fact that speed and simplicity are much improved compared to the methods of thirty years ago is no longer relevant. It is appropriate at this point to consider the 'shortcuts' which allow for more rapid use of flame spectroscopy, and possibility of saving time. They are :

- 1) Sample preparation, including separation and/or preconcentration
- 2) Addition of releasing agents or ionisation buffers
- 3) Dilution to an appropriate approximate concentration
- 4) Instrument warm-up and optimization
- 5) Finding approximate concentrations if not already known
- 6) Routine use, including data processing

**Errors from losses and contamination** : Because of the inherently low limits of detection of AAS, dilute solutions are used not only for determining substances at trace levels, but also for determining major constituents at dilutions where the effects of interferences are reduced or eliminated. This advantage of working with dilute solutions, however, is unavoidably associated with errors due to losses (mostly due to adsorption), contamination from reagents, and contamination from the walls of the containers. In the past, these sources of

errors have been relatively unimportant except for the most sensitive chemical methods. An insidious type of loss results from the adsorption of metallic ions from dilute solutions on the walls of the container. These losses, which may or may not be significant for a particular determination, will depend on the pH of the solution, the concentration of the ionic species present, and the history of the container surface. To avoid losses of this type of AAS procedures, frequent use is made of a "master" standard solution from which dilute solution are made that are not stored more than two weeks.

Polyethylene is evidently one of the best container materials because of its low metallic content and the nonpolar nature of its surface. Many of the common elements (Mn, V, Ba, Mg, etc.) can be stored in polyethylene containers in concentrations of only 3 ppm for at least one year without loss. The pH of the solution should be low enough to prevent hydrolysis of the metallic ions, and a pH of 2 or less would be best.

**Contamination :** Contamination becomes a problem when elements are determined at concentration levels below approximately 0.01 per cent. At the 0.01 percent (100 ppm) concentration level, there are about 10,000 atoms present for each atom of the element to be determined (if they have the same atomic weight). Because of the overwhelming preponderance of other substances present, relatively large quantities of reagent chemicals are required to dissolve the sample; in addition, the solution is exposed to relatively large surface areas of the containers during the processing of the sample.

Reagent-grade acids contain traces of metals (Table-III), some of which originate from the glass bottles used for storage. Although the concentration of each of the metals present is specified to be below the 1 ppm level, the acids used must be included in a study

of reagent blanks. This source of contamination may be significant, as in the dissolution of 1 g of a sample that requires 15 ml of acid. For example, a contaminating metal when present at the 1 ppm level in the acid (sp.g. 1.3) will contribute a blank (20 ug) equivalent to 20 ppm in the 1-g sample.

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**Table-1**

Non-Critical			Toxic but vary rare		Very toxic and relatively accessible		
Na	C	F	Ti	Ga	Be	As	Au
K	P	Li	Hf	La	Co	Se	Hg
Mg	Fe	Rb	Zr	Os	Ni	Te	Tl
Ca	S	Sr	W	Rh	Cu	Pd	Pb
H	Cl	Al	Nb	Ir	Zn	Ag	Sb
O	Br	Se	Ta	Ru	Sn	cd	Bi
N			Re	Ba		Pt	

**Table-2**

Industry & Process	Source of emission	Particulate matter
Iron and steel mills	Blast furnaces, steel making furnaces, sintering machines	Iron oxide, dust smoke
Iron foundaries	Cupolas, shake-out making	Iron oxide, smoke, oildust, metal fumes
Non-ferrous metallurgy	smelters and furnaces	Smoke, metal fumes, oil grease
coke manufacture	Oven operation, quenching materials handling	Coal and coke dust coal tars
Acid manufacture	Thermal processes rock acidulating grinding	Acid mist, dust
Portland cement	kilns, driers, material handling system	Alkali and process dusts
Petroleum refineries	catalyst regenerators sludge incinerators	Catalyst dust, ash from sludge

**Table-3****Trace Metal Concentration ( $\mu\text{g}/\text{kg}$ ) in some Acids**

	HCl	HNO <sub>3</sub>	HClO <sub>4</sub>
Ag	0.2	0.1	0.5
Ca	24	30	1.7
Cd	0.5	0.2	4
Cr	0.3	130	18
Cu	1	4	3
Fe	7	55	10
K	10	11	9
Mg	20	-	4
Ni	3	3	0.5
Pb	<1	0.3	16
Sn	<6	1	<1
Zn	4	8	17

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Element	Optimum conditions				Alternative line(nm)	Approximate Equivalent dilution	Remarks
	Wave length(nm)	Lamp current (mA)	Slitwidth(nm)	Flame stoichiometry			
Ag	328.07	4	0.4	air-acetylene	338.29	2	Al, Th, W depress
Al	309.03	10	0.4	Nitrous oxide a cetylene, fuel rich	394.4	2	Add ionization buffer (KCl)
As	193.70	8	0.4	air-acetylene	197.2	2	Hydride genera- tion
Bi	223.1	6	0.4	air-acetylene fuel lean	306.7	3	-
Cd	228.8	6	0.4	air-acetylene fuel lean	326.1	600	Silicates depress
Co	240.7	15	0.2	air-acetylene fuel lean	252.1	2	Transition metals interfere
Cr	357.9	10	0.2	air-acetylene fuel rich	425.4	2	Same oxidation state
Cu	324.8	5	0.4	air acetylene fuel lean	327.4	2	Transition metal interfere
Fe	248.3	15	0.2	air-acetylene fuel lean	271.9	3	Perchloric nitric and Ni depress
Ga	287.4	15	0.4	air-acetylene fuel lean	417.1	2	-

Element	Optimum Conditions				Alternative line(nm)	Approximate Equivalent dilution	Remarks
	Wave length(nm)	Lamp current (mA)	Slitwidth(nm)	Flame stoichiometry			
Hg	253.6	6	0.4	Air-acetylene fuel lean	-	-	Cold vapour generation
Mn	279.5	12	0.2	Air-acetylene fuel lean	280.1	3	Si depress
Mo	313.3	15	0.4	Air acetylene fuel rich	319.4	4	Ca,Fe,Mn,Sr.depress
Ni	232.0	15	0.2	Air-acetylene fuel lean	234.6	4	Excessiron enhances
Pb	217.0	6	0.4	Air-acetylene fuel lean	283.3	2	-
Pt	265.9	15	0.4	Air-acetylene fuel lean	262.8	3	Noble metals effect
Sb	206.8	15	0.2	Air-acetylene stoichiometry	231.1	2	Hydrate generation
Se	196.0	6	0.4	Air-acetylene fuel lean	203.99	3	Hydride generation
Sn	224.6	8	0.2	Nitrous oxide acetylene fuel rich	286.3	2	Cu, Pb, Ni, and Zn interfere
Ti	365.4	15	0.2	Nitrous oxide-acetylene fuel rich	335.5	2	Al, Fe enhance Add ionization buffer
U	358.5	15	0.2	Nitrous oxide-acetylene fuel rich	348.9	3	Add ionization buffer
V	318.5	15	0.4	Nitrous oxide-acetylene fuel rich	385.6	6	Al, Ti enhance Add ionization buffer
Zn	213.9	10	0.4	air-acetylene fuel lean	307.6	7000	Si depress
Zr	360.1	15	0.2	Nitrous oxide acetylene fuel rich	298.5	2	Add ammonium fluoride