Method Guide: 40689

The Analysis of Environmental Materials by Atomic Absorption Spectrometry

Key Words

- AAS
- Environmental
- Atomic Absorption Spectrometry
- Overview

Introduction

In the field of laboratory analysis, environmental applications have long been a number one priority for many laboratories.

The present concerns about global warming, and the desire to clean up the environment for the benefit of everyone, have produced many new pieces of legislation governing the permitted discharges into waters, the air and on to the land. This increased level of legislation is being enacted by various authorities with a number of key agencies, such as the Environmental Protection Agency in America and the EEC Committees in Europe, leading the way. Such legislation places a responsibility on every organisation to monitor the condition of the local environment and to measure their impact upon it. This, in turn, has meant that there has been a major requirement for instrumentation and methodology capable of implementing the new regulations.

One of the main instrumental techniques that has had a leading role in the analysis of environmental samples is Atomic Absorption Spectrometry (AAS). As a technique, it possesses the right combination of performance and ease of use to carry out the analytical tasks and is priced at a level within the range of many laboratories.

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1) Introduction:

Major sources of pollution come from many of our day-today activities, such as Farming, Industry, Transportation and Urban sites. The effects of these activities impact on the three main areas of our environment; the land, the water and the air. For example, consider the mining and metal processing industry. The mining activity can add pollution to the air (in the form of dust), to the water (in the form of washings from ore processing) and the land (in the form of mining waste heaps). Metals production introduces fumes and particulate to the air and land and produces waste water which flows into the surface water layers.

Environmental pollution is monitored in a number of ways and this has resulted in a wide variety of sample types being supplied for analysis. This list shows the main types:

Biological - serum, urine, tissue.
Waters - sea, fresh, waste.
Plant materials
Soils, sludges and sediments
Airborne particulates

As a result of this variety of sample types, a number of different sampling and preparation techniques have to be used.

Pollution legislation generally specifies certain element concentration levels which it considers to be representative of pollution in the different sample types.

This means that any analytical technique must possess a sensitivity at least equal to, but preferably better than, these levels before it is suitable for use in environmental analysis. As legislation changes it is more often the case that these limits are further reduced. Tables 1 and 2 shown here indicate the applicability of AAS for the different chemical elements and the main sample types characteristic of environmental applications.

ELEMENT	EEC MAC	TECHNIQUE
Magnesium	50,000	FAAS (2.2)
Sodium	150,000	FAAS (3.7)
Potassium	12,000	FAAS (0.9)
Aluminium	200	GFAAS (0.21)
Iron	200	FAAS (4.3)
Manganese	50	GFAAS (0.06)
Copper	3,000	FAAS (4.5)
Zinc	5,000	FAAS (3.3)
Silver	10	GFAAS (0.04)
Arsenic	50	HGAAS (0.05)
Cadmium	5	GFAAS (0.02)
Chromium	50	GFAAS (0.025)
Mercury	1	HGAAS (0.15)
Nickel	50	GFAAS (0.16)
Lead	50	GFAAS (0.07)
Antimony	10	HGAAS (0.27)
Selenium	10	HGAAS (0.27)
Barium	1,000	FAAS (3.0)

Table 1: List of Maximum Allowable Concentrations for drinking water in µg/L, (Council for European Communities Journal), showing the technique (and its detection limit in µg/L in parentheses). FAAS = Flame AAS, GFAAS = Graphite Furnace AAS, HGAAS = Hydride Generation AAS.

From these lists it can be seen that Atomic Absorption can measure the legal limits for toxic metals such as As, Cd, Pb and Hg in most sample types. The use of Hydride techniques can improve the performance for hydride forming elements such as As and Se.

ELEMENT	CLP D.L.	GFAAS D.L.
Aluminium	200	0.21
Antimony	60	0.4
Arsenic	10	0.53
Beryllium	5	0.003
Cadmium	5	0.02
Chromium	10	0.025
Cobalt	50	0.17
Copper	25	0.29
Iron	100	0.18
Lead	3	0.07
Manganese	15	0.06
Nickel	40	0.16
Selenium	5	0.8
Silver	10	0.04
Thallium	10	0.5

Table 2: Comparison of the EPA Method 200.9 required detection limits (µg/L) and the Zeeman GFAAS detection limits (3 σ µg/L) for water analysis

2) Features of the AA Series System:

The Thermo Scientific iCE 3000 Series range of AA spectrometers includes configurations which can be used specifically for environmental use.

(1) Dual atomiser system, consisting of a combination of the VP100 Continuous Flow Vapour system and EC90 Electrically Heated Vapour cell, together with a GFS35Z Zeeman Furnace System.

(2) When equipped with the Furnace Autosampler and the appropriate vapour autosampler, the system is capable of fully automated analysis for both vapour and furnace elements. This includes overnight, unattended analyses.

(3) Auto change-over between vapour and furnace analysis carried out by software means only, no manual intervention required.

(4) Easy to use, Wizard-driven software to simplify operation and including comprehensive QC facilities and printout options.

(5) Optional high sensitivity mercury accessories permit mercury perfomance down to µg/L levels.

(6) Validator and Validator$_{plus}$ accessories enable systems to be validated as part of a regulatory compliance programme.

Figure 1: Complete Thermo Scientific iCE 3500 System

3) Environmental Analysis in practice:

We will now break down a typical analysis into its separate parts and consider the main factors which must be borne in mind at each stage of the procedure.

(a) The sampling phase

This is the most important phase of an analysis, and often the one most poorly carried out. It must be remembered that any mistakes made at this stage can ruin the excellence of all the stages that follow. There must be a sampling strategy in place which is carefully thought out and takes into account all the known possible sources of error.

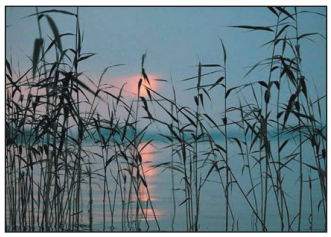
There are two main considerations which are absolutely vital to the success of any analysis:

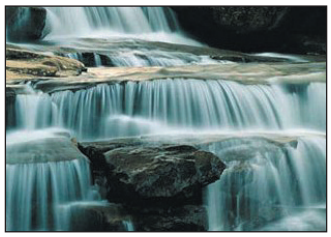
(1) The sample taken must be representative of the whole sample.

(2) The sample containers must be clean.

As an example of point 1, consider the sampling of waters where the following factors must all be considered:

- the influence of tides in seawater sampling.
- the proximity of tributaries or sewage outfalls when sampling river water.
- the possibility of noncontinuous discharge of effluents into a river.
- the presence of cold and warm layers in lakes.
- the fact that still tapwater can contain erroneously high metal concentrations which are not seen in a flowing sample.
- the disturbance of sediments in a river or lake bottom caused by the action of taking the sample.
- that rainwater composition varies with the type of weather, the season and even the time of day.





Another example is from the biological field. When using human hair as an indicator of exposure to toxic materials, it must be remembered that the concentration levels in normal hair increase the closer one moves to the root of the hair. Similar differences occur in plant materials, where element concentration levels in old wood can be totally different to those in the growing tip.

Now moving on to point 2. Sample containers can produce negative, or positive, errors in trace metal analysis by either of two actions.

Firstly, they can add contaminants by leaching or surface desorption of material already present on the container walls. This may be residues of a previous sample or from detergents used to clean the container. In addition, materials used in manufacturing the sample container itself may be a problem. For example, zinc compounds used as mould release agents in manufacturing are a notorious source of contamination in new containers.

Secondly, loss by surface adsorption can reduce the apparent concentration of elements in a sample. This is particularly true of certain plastic materials, such as low density polyethylene, and glass.

Laboratory containers, whether glass or plastic (this includes polyethylene, polypropylene or fluorocarbon) should always be washed first with a detergent solution that does not contain high levels of metal compounds. It is important to remember that certain detergents can contain high levels of metals, such as zinc and sodium, which remain bound to container walls even after flushing with clean distilled or deionised water. Glassware is often cleaned with a chromic acid wash because it is a powerful cleaning agent for removing organic material. However, the chromium persists in glassware for a long time, even after thorough washing with water, and is a major source of contamination.

After the detergent wash, the containers should then be rinsed thoroughly in distilled or deionised water, followed by rinsing with a (1 + 1) solution of nitric acid. The acid is used to strip any metals adhering to the walls of the container. Another distilled water wash should be followed by a (1 + 1) solution of hydrochloric acid. A final distilled wash is made before the container is hot-air dried.

We will now consider some of the more important analyses. The single most important analysis concerns water - there are currently more water samples analysed than any other single type.This is a very convenient sample for AAS because it is already liquid. Solid samples cannot, in general, be analysed directly by AAS.

(b) Water analysis : The pre-treatment phase

Before a sample is collected, the kind of data required at the end of the analysis must be defined. For instance, in water analysis, is it the soluble metals or the suspended solids or a total analysis that is required? When analyzing soil samples, is it the available metals that are to be analysed or the total.

Taking water analysis as an example and with soluble metals to be measured, the following procedure is used.

The water must be filtered through a 0.45µm membrane filter as soon as possible after collection. It is normal to use the first 50 - 100 mL of sample to rinse the apparatus and discard the filtrate. The required sample volume is then collected. Acidification with (1 + 1) nitric acid to pH 2 or less is used to stabilise the metal content. Normally 3 mL of (1 + 1) nitric acid per litre of sample should be sufficient.

If the suspended solids content is required, basically the same initial procedure is used. The difference is that the filter containing the suspended solids is retained and stored in a suitable container. No preservation is needed.

For a total analysis, the whole sample is acidified with (1 + 1) nitric acid to pH 2 or less, preferably at the time of collection. The sample is not filtered.

A relatively new technique that shows great promise for water analysis is on-line pre-concentration. The basis of the method involves the preparation of small mini-columns containing an ion-exchange material. These are taken to the sampling site where known volumes of the sample are drawn through the column, trapping the required elements. The columns are sealed and taken back to the laboratory where the trapped metals are eluted using a small volume of eluent. Concentration factors of 10 – 20 times can be achieved, an added benefit which improves the ultimate detection limits attainable. Columns can be stored for several weeks before carrying out the analysis.

(c) Water analysis : Treatment and analysis

For soluble metals analysis, the filtered and acid-preserved samples can often be analysed as received. If a precipitate forms during storage, it must be re-dissolved by adding acid and/or heating. It is normal practice to analyse samples against matrix matched standards.

The suspended solids held on the filter paper must be solubilised before analysis. This is carried out in the following manner. Place the filter membrane in a suitable clean beaker and add 4 mL concentrated nitric acid. A cover is placed over the beaker and it is heated gently to dissolve the membrane. The temperature is raised to digest the material, continuing until the contents are reduced to low volume. After cooling, another 3 mL of concentrated nitric acid is added and the beaker covered again. Heating is continued until digestion is completed and the contents are then reduced to about 2 mL. The contents are cooled and 10 mL of (1 + 1) hydrochloric acid plus 15 mL of distilled water are added for every 100 mL in the final sample volume. The metals are re-solubilised by heating for 15 minutes, then the contents are cooled and washed into a volumetric flask. Any remaining insoluble material is filtered off, if necessary, and the contents of the flask are made up to volume.

In the case of the total analysis, the preserved sample is heated with an additional 3 mL. of concentrated nitric acid and evaporated to near dryness. It is important that the sample is not boiled or heated to dryness. After cooling, a further 5 mL of concentrated nitric acid is added and the sample re-heated to reflux the acid. The sample is heated, with the addition of more acid as necessary, until the digestion is complete. From this point onwards the finish is the same as for the suspended solids.

(d) Water analysis : Results

Water analysis is carried out and measured against a number of criteria, which tend to be different in different parts of the world. There is presently no universally accepted list of limits but the most commonly used values for natural waters are those published by the USEPA in America. Table 3 shows the guide figures for the different types of natural waters and the typical detection limits which can be obtained when using the appropriate AA technique.

ELEMENT	RIVER	SEA	RAIN	AA D.L.
As	2	3	< 0.3	0.05 *
Ba	20	30	70	0.5
Cd	0.1	0.1	0.5	0.02
Cr	1	0.05	7	0.025
Cu	3	3	30	0.3
Fe	100	10	1000	0.18
Hg	0.07	0.03	0.01	0.15 *
Mn	15	2	60	0.06
Ni	10	2	10	0.16
Pb	3	0.03	50	0.07
Sb	1	0.5	2	0.26 *
Se	0.2	0.4	< 1	0.27 *

Table 3: Natural levels of elements in natural waters. All figures are in µg/L. AA detection limits are for the graphite furnace, apart from those shown with a * which are hydride performance figures.

The same situation largely applies for drinking water but Tables 1 and 2 (shown earlier) represent the figures currently used within Europe and the USA.

Moving on to other types of environmental samples, we will consider their main characteristics.

4) Airborne particulate analysis:

There are many sources of airborne particulate, such as waste incineration and welding activities to name but a few. Waste incineration has caused a much higher awareness of the problems caused to the environment, on the one hand solid wastes are reduced by up to 90 % but on the other hand new waste products like dust are created.

Samples are commonly collected by sucking known volumes of air through a glass fibre or membrane filter. The volume of air used depends on the level of contamination and the elements being measured. A high volume set-up with a 20 - 25 cm wide filter typically has collection times (for a flow rate of 75 m^3h^{-1}) of 1 hour for contaminated urban air and up to 12 hours for clean rural atmospheres. A number of portable, battery-powered samplers are available for personal monitoring at the workplace. Using 25 mm glass fibre filters, a flow rate of about 2 litres/min is used. This type of sampler is also used for sampling at sites where no mains electricity is available. An alternative for use at large installations, such as power stations or incinerator chimneys, is the cascade impactor or electrostatic filter. Two types of sample are, therefore, generally available - particles held on a membrane filter or loose powder taken from a cascade impactor or the like.

Where samples are mainly metals, as in welding fume, and collected using personal samplers, the usual dissolution procedure is to use simple acid digestion. The metals involved define the procedure used. For Cr, Cu, Fe, Mn, Ni, Zn, Ag, Cd, Pb, Au, B, Ba, Bi, Ca, Mg, Sr and V the filters are simply digested in 10 mL of concentrated nitric acid. For Al, Be, Co, Mo and Ti the filters are digested in 10 mL of a 50:50 mixture of nitric and hydrochloric acids. After digestion the samples are heated at 140 °C to near dryness and then re-solubilised to a final volume of 10 mL with 0.1 % nitric acid.

METAL	EXPOSURE LIMIT (8 HOURS) MG.M³	AIR VOLUME SAMPLED (LITRES)
Al	5.0	180
B	10.0	60
Be	0.002	500
Cd	0.025	280
Cu	0.2	90
Cr	0.5	90
Fe	5.0	150
Mn	1.0	22
Ni	1.0	90
Pb	0.15	180
Ti	5.0	100
Zn	5.0	100

Table 4: List of airborne particulate exposure limits (according to 91/332/EEC and 96/94/EC

Table 4 shows the current limits for exposure measured over an 8-hour working day, together with the approximate volume of air which needs to be sampled in order to get a measureable signal.

For samples containing a high ash content, dissolution schemes developed for the analysis of siliceous materials are generally used. Increasingly the use of microwave digestion is becoming the preferred technique. By using a sealed vessel and heating it in a microwave oven, it is possible to considerably shorten the dissolution time. There are a number of commercially available laboratory microwave systems which are specifically designed for use with the corrosive chemicals used in dissolution procedures. Typically a sample treated by the traditional pressure digestion method requires about 50 minutes of heating whereas the microwave takes about 6 minutes. The USEPA has certified some of its methods (often these become the standard methods elsewhere in the world) with microwave dissolution.

The results shown below in Table 5 are for an Urban particulate, NBS SRM1648, prepared using microwave dissolution.

METAL	CERTIFIED VALUE	FOUND
Al	3.4 +/- 0.11	3.60
Fe	3.91 +/- 0.10	3.32
Pb	0.655 +/- 0.008	0.579
Zn	0.476 +/- 0.014	0.434
All results in % weight		
Cd	75 +/- 7	77.3
Cu	609 +/- 27	603
Mn	860	666
Ni	82 +/- 3	84
V	140 +/- 3	112
All results in mg/g		

Table 5: Analysis results obtained for NIST SRM1648

5) Analysis of soils and sediments:

A serious source of long-term pollution results from the common practice of disposing of urban solid wastes by burying them in landfill sites. Similarly, the use of some sewage sludges for agricultural purposes can cause problems, both by contamination of the crops and also of surface and groundwater. Toxic elements in these materials are leached out slowly with time by the action of rainwater percolating down through the layers. The result can be severe contamination of underlying soil and groundwater, with the consequent risk to extracted water supplies. The metals found in the groundwater depends on a number of factors but the ultimate aim of the analysis is to simulate the natural leaching action of rain in order to estimate the available metals content. This is normally done by taking a known weight of waste and leaching it with a dilute acid, typically 0.5 M acetic acid.

Soil samples are dried to constant weight at about 110 ºC. It may take as long as 2 days to achieve this. Stones and other debris must be removed before the dried sample is ground in a metal-free mortar and pestle to pass a 100 mesh sieve. Each sample powder is then shaken thoroughly to ensure homogeneity before a known weight of sample is taken for the analysis.

Soil and sediment analyses are good examples of the problems of taking truly representative samples. Sufficient material must be taken to be indicative of the whole site being sampled and then the bulk material must be subdivided to provide the final representative sample. For a total analysis, conventional pressure dissolution or microwave attack are used. Leaching can also be carried out using aqua regia attack. Typically 1 gram of sample is digested with 30 mL aqua regia by boiling to low volume.

After cooling, 25 mL concentrated nitric acid is added and boiled to dryness. The residue is dissolved in distilled water and analysed against standards which have had similar treatment.

The results in Table 6 are for the analysis of a landfill sample and the underlying soil levels measured after an acetic acid leach.

ELEMENT	LANDFILL MATERIAL	UNDERLYING SOIL
Al	12,000	8,800
As	0.1	18
Cd	0.8	0.3
Co	8.4	3.8
Cr	37	18
Cu	430	79
Fe	36,000	14,000
Mn	340	200
Ni	27	24
Pb	140	110
V	5.5	4.9
Zn	420	95

All results in µg/g

Table 6: Analysis of leachate from a landfill site compared to the underlying base soil

ELEMENT	MEASURED	CERTIFIED
Al	49.4 +/- 0.2 %	47.0
Ba	2.92 +/- 0.5 %	2.50
Cd	0.879 +/- 0.3 %	0.90
Cr	57.3 +/- 0.9 %	55.4
Cu	3.98 +/- 0.3 %	3.91
Fe	444 +/- 0.3 %	441
Mn	1.84 +/- 0.1 %	1.87
Ni	0.56 +/- 2.4 %	0.53
Pb	6.38 +/- 0.6 %	6.42
Ti	3.42 +/- 2.3 %	3.50
V	1.10 +/- 0.7 %	0.97
Zn	10.8 +/- 0.7 %	10.6

All results in µg/g

Table 7: Analysis of a wet digested river sediment

The second set of results shown in Table 7 are for a river sediment using the aqua regia treatment.

6) Plant material analysis:

Plant materials are often used as indicators of both airborne and sub-soil contamination. Samples may be root crops, like turnip or beetroot, or leaves of plants, such as lettuce or cabbage.

Roadside vegetation has commonly been used to monitor Pb contamination from vehicle exhausts.

Table 8 shows some typical values for a range of elements in different crops.

PLANT	PART	Cd	Cu	Ni	Pb	Zn
Tomato	Fruit	1	6.8	7.1	2.3	18.5
	Leaf	8.5	10.9	11.1	10.3	24.6
Lettuce	Fruit	5.5	9.4	6.3	2.7	111
	Leaf	5.5	9.4	6.3	2.7	111
Carrot	Fruit	0.92	2.85	2.0	0.92	53.9
	Leaf	1.8	8.8	3.7	8.2	166
Cabbage	Fruit	1.1	5.7	9.7	3.0	58.5
	Leaf	1.1	5.7	9.7	3.0	58.5
Oats	Fruit	0.3	6.0	3.7	0.77	43.1
	Leaf	0.92	15.4	7.7	0.77	93.9
Pea	Fruit	0.15	7.6	6.0	1.5	50.8
	Leaf	0.15	11.1	2.0	6.9	93.9
Total soil		7.4	113.0	81.3	164	318
Extractable (acetic acid)		5.9	17.4	25.6	8.87	73.7

All results as mg/kg dry matter

Table 8: Results for various crops and the soil on which they were grown

We will consider the determination of arsenic and selenium in plant materials using the Hydride technique.

The actual sampling procedures for plant materials will vary considerably, depending whether it is a root or foliage sample. Again, taking a representative sample is important. Foliage should be cut, not plucked or torn, at least 3 cm. above the soil level to avoid contamination from the soil itself. A composite sample of at least 25 plants should be taken and this should weigh not less than 1 kg in weight. Materials like roots should be washed free of soil and about 200 g of sample taken.

These samples are then air-dried and ground to pass a 1 mm sieve. A representative sample is then digested in a nitric acid/perchloric acid mixture (with care - there can be a risk of explosion if too much organic material is involved). The digest is then heated in concentrated hydrochloric acid to convert the As and Se to their lower oxidation state (due to the lower sensitivity of the higher states).

Results are shown for As in certified plant foliage materials in Table 9 and for Se in flour in Table 10.

SAMPLE	MEASURED	CERTIFIED
Pine Needles	0.19	0.21
(NIST 1575)		
Spinach	0.13	0.15
(NIST 1570)		

All results in µg/g

Table 9: Analysis of plant materials for As

SAMPLE	MEASURED	CERTIFIED
Wheat Flour	0.19	0.21
(NIST 1567)		

All results in µg/g

Table 10: Analysis of wheat flour for Se

7) Biological Samples:

The range of biological sample can be quite wide, with some available in liquid form (serum and urine) but others are taken as solids (tissue and hair) requiring solubilisation. Biological samples are often taken from workers as part of an Industrial Health programme; typical examples are monitoring workers in plating bath works or people handling toxic materials such as beryllium in the semiconductor industry. Urine is not a good indicator of long-term exposure; blood and blood serum are better.

Tissue and bone are the best indicators but the most difficult samples to obtain.

In the environmental field, tissue from a variety of species is used but a particularly useful indicator of pollution in natural waters, like the sea, and sediments are shellfish.

These filter feeders convert inorganic metals, such as Hg, Pb and Cd, into their organo-metallic forms and these are stored, generally in the fatty tissues. They can amplify natural surrounding levels of pollution many-fold, as shown in Table 11 below. Care must be taken, therefore, when sampling shellfish because the toxic metals are preferentially stored in certain tissues, as shown below in Table 12.

Fluid samples are normally treated by simple dilution but tissue samples require solubilisation by an appropriate wet-digestion procedure.

METAL	AMPLIFICATION FACTOR
Cd	2,260,000 times
Cr	200,000
Fe	290,000
Pb	290,000
Mn	56,000
Mo	90
Ni	12,000

Table 11: Examples of the metal enrichment that can occur in shellfish tissue relative to surrounding waters

SAMPLE TYPE	% OF BODY MASS	Pb CONC (mg/kg)	Cd CONC (mg/kg)
Scallop: Gills	10	52	< 20
Muscle	24	< 5	< 20
Fatty tissue	17	8	2000
Intestine	1	28	< 20
Kidney	1	137	< 20
Gonads	20	78	< 20
Sediment		< 5	< 20
Seawater *		3	0.11

* Seawater results are in µg/L

Table 12: Comparison of trace metal concentrations in shellfish tissue to local seawater and sediments

9) Conclusions:

At the present time, AAS has a leading role in environmental analysis because of its sensitivity for a large selection of elements typically determined by environmentalists. Graphite furnace-AAS continues to be the preferred technique for ppb level determinations of the heavy, toxic metals like Pb and Cd. In addition, hydride techniques provide excellent performance for the semimetals like As, Se and Sb. Finally, a range of specific accessories provide detection limits for Hg down to the ppt level.

The Thermo Scientific iCE 3000 Series has the capability of providing a turn-key solution to many of the analytical problems in this applications field. Its unique combination of Zeeman correction graphite furnace and vapour analysis with electrically heated atomisation cell, all in a very compact dual atomisation spectrometer, can satisfy the requirements of many laboratories in the most cost-effective way.

In addition to these offices, Thermo Fisher Scientific maintains a network of represen tative organizations throughout the world.

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