

## **Sample preparation for atomic spectroscopic analysis: An overview**

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### **ABSTRACT**

*Sample preparation is an important step in chemical analysis, from time and reagent consuming point of view and from the probability of errors. In the present article, types of samples, problems associated with sample preparation, and sample preparation for most used atomic spectroscopic techniques, FAAS, GFAAS, ICP, and XRF have been discussed.*

**Keywords:** Sample preparation, Atomic spectroscopy, decomposition, separation, pre-concentration.

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Analysis by atomic spectroscopic methods practically always necessitates a simple or more complex preparation of the sample. These steps of sample preparation are generally the most critical part of analysis because they are responsible for the most errors.[1-3]

In an analytical method sample preparation is followed by a separation and detection procedure. Only a few direct methods allow the introduction of the sample without any preparation. In these cases the lack of reliable calibration is the major problem. On the other hand, sample preparation allows the separation and/or pre-concentration of analytes and makes possible the use of several determination methods.

Sample preparations involve digestion, extraction and preparation of the analytes before the analysis, so this step is time limiting, requiring *ca.* 61% of the total time to perform the complete analysis, and is responsible for 30% of the total analysis error. Nowadays, the goals to be reached are the best results, in the shortest time, with minimal contamination, low reagent consumption and generation of minimal residue or waste.[1]

In atomic spectroscopy the sample normally is found in one of two forms: solid or liquid. The liquid phase seems to be the easiest form in which to handle the sample, but some requirement for filtration is required. However, the inherent lack of sensitivity of many spectroscopic techniques and the need to carry out determinations at lower and lower levels means that invariably some form of pre-concentrations is required. If the sample is in a solid form, the normal requirement is to convert it into the liquid form although it is possible to analyse solids directly by using atomic spectroscopy, but this is not the preferred approach.[1, 4] The principal objectives of sample preparation for residue analysis are; dissolution of the analytes in a suitable solvent, isolation of the analytes of interest from as many interfering compounds as possible, and pre-concentration.

The selection of a sample preparation method is dependent upon: (1) the analyte(s), (2) the analyte concentration level(s), (3) the sample matrix, (4) the instrumental measurement technique, and (5) the required sample size.

### **Contamination and Losses**

The major problem in preparing samples for trace analysis is the risk of contamination. Contamination is associated with several probable causes, i.e. the grade of reagents used, sample storage container, steps of digestion or dilution of the sample and their previous history, and human intervention.

Losses are a particularly significant problem in trace analysis. Container surfaces, for example, may present a significantly large area on which the analyte can be adsorbed. At higher levels such a small absolute loss would have little effect on the concentration but at trace levels a large proportion of the analyte may be stripped from the solution.[5,6]

### **Samples**

Samples analyzed may be divided into those which are already in an aqueous solution (e.g. various water samples, beverages, blood, serum, and urine.), in other liquid form (e.g. oils, fuels, and organic solvents.) or in solid form (e.g. soils, sediments, plants, animal tissues, metals, and plastics.). Solid samples may contain a high proportion of organic matter (e.g. plants, animal tissues, and plastics.) or have more inorganic composition (e.g. soils, sediments, and metals.). For routine analysis by atomic spectroscopic techniques, which are all dedicated to work with aqueous samples, the analysis of other liquids must be adapted and the solids are generally converted into a solution by an appropriate dissolution method.[2]

There are two large categories of analytical matrices: organic and inorganic samples. The inorganic samples incorporate soil, inorganic substance, sediment, clay and metal. The organic or carbon-based samples include biological, polymeric, petrochemical and pharmaceutical samples. Organic samples can be solubilized on a dry or wet basis, and in an open or closed system. These methods guarantee the elimination of organic material and the quantitative recovery of the analyte in the solution.[1]

In case of solid samples, many steps are required, including sampling, sub-sampling, grinding, and dissolution. The risk of contamination is higher than in the case of liquid samples. [6]

In the following, sample preparation for the most used atomic spectroscopic techniques will be discussed.

### **Flame atomic absorption spectrometry (FAAS)**

Flame atomic absorption spectrometry (FAAS) is a mature analytical method, which is present in almost any analytical laboratory as a working horse for elemental determinations of elemental metals. [7]

Aqueous samples can be generally introduced for analysis directly and without any prior treatment. The only major problem associated with working with solutions is their collection and storage. Concerning atomic spectroscopic analysis itself, no particular precautions have to be taken. Non-aqueous samples can sometimes be run directly, but this depends significantly on their viscosity. In FAAS analysis, the viscosity should be similar to that of water for which most nebulizers are designed. Only some organic solvents, such as ethanol or methyl isobutyl ketone, are often used for dilution of organic liquids, the major drawback, encountered with these techniques is the dilution factor, which reduces the metal content per unit volume.[6] Standards can be prepared in the pure solvent. Elements in organic solvents usually give an FAAS analysis response similar to that given by the same element in aqueous solution.

Solid samples are usually analyzed by dissolving the sample to form a liquid solution that can be introduced into the flame or furnace. Dissolution can be accomplished by mineral acid digestion (wet ashing), fusion of solids with molten salts and dissolution of the fusion bead, dry ashing of organic solids with acid dissolution of the residue, combustion in oxygen bombs, and other procedures too numerous to mention. The main disadvantage of acid dissolution is the risk of loss and contamination particularly at ppm and ppb levels of analyte.

Dissolution is still the most common approach to atomic absorption spectrometry (AAS) analysis of solids. Solid particulates in air, gas and fluid streams can be collected by filtration and analyzed by digesting the filter and the collected particulates.[8]

There are many different techniques which could be used in order to separate and pre-concentrate the metal ions such as chromatography[9-11], solid phase extraction[12-18], cloud point extraction[19-23], and Co-precipitation.[6,24-26]

### **Graphite furnaces atomic absorption spectrometry (GFAAS):**

Electrothermal atomic absorption spectrometry, especially with graphite furnaces, has developed in the past decades to an unrivaled method for ultratrace analyses at an affordable price.

The analytical advantages of GFAAS are that its detection limits are about two orders of magnitude better than either FAAS or ICP-OES (inductively coupled plasma – optical emission spectroscopy) and that very small sample volumes can be analyzed. The entire analytical process is slow, but is completely automated in modern instruments.

There are many different techniques used for sample preparation, especially those for FAAS are applicable for GFAAS after taking in consideration the type and concentration level of the analyte, type of sample, matrix modifier, and instrumentation features.

There is a growing interest in the atomic spectroscopic determination of elements directly in solid samples, without prior preparations to avoid the contamination and/or losses associated with this step. In addition, there is no dilution of the sample, which allows measurement of lower levels of analyte than dissolution procedures. Solid sampling procedures are particularly convenient for GFAAS analysis when only small amounts of sample are available. However, problems may arise because of unrepresentative sub-sampling and enhanced interferences compared with the analysis of solutions.[2]

For many reasons the precision obtained by solid sampling is generally less than that obtained with solution analysis. One reason is the availability of appropriate calibration standards of similar composition to the samples analyzed. Another reason is that the interference effects observed with solid sampling may be greater compared to those with dissolved samples whose matrix is simplified as a result of the mineralization, and finally, sample introduction into the atomizer is less convenient than with dissolved samples.[2]

Instead of dissolution of powdered samples or direct analysis slurry sampling is used in which the material is suspended in a liquid diluent. The liquid depends on the nature of the sample. For good results, it is necessary to produce a homogenous slurry. Therefore converting the sample into powder with small particle size ( $< 10\mu\text{m}$ ) is required.[27-31]

#### **Inductively coupled plasma (ICP):**

The inductively coupled plasma is the most commonly used plasma. Sample preparation methods for ICP analysis of trace metals can be found in many sources. The sample introduction for ICP applications requires that samples be in a liquid form so as to be aspirated through a nebulizer and that suspended solids must be removed to prevent clogging of the nebulizer. Therefore, solid samples such as soils and sludges must first be acid digested to extract the metals of interest from the solids, and the resulting digestate must be filtered, centrifuged or allowed to sit to remove the suspended solids prior to analysis.

Drinking water with turbidity greater than 1NTU (normal turbidity unit) must also be acid digested followed by the removal of suspended solids prior to analysis.[32]

Solid samples can be in the form of fine suspensions in a liquid (slurries). The slurries are introduced into the plasma using a V-type nebulizer. Alternatively, the fine particle can be produced by the ablation of solid with the use of either spark system for conductive samples or a laser for any type of samples.[33]

#### **X-ray fluorescence (XRF):**

X-ray fluorescence (XRF) is a non-destructive analytical technique. For detecting elements at trace levels  $\mu\text{g/g}$  (ppm),  $\text{ng/g}$  (ppb) or even  $\text{pg/g}$  (ppt) with XRF, generally special techniques as well as sample preparation methods have to be used.[34]

For most laboratory XRF equipments, the energy of the emitted X-ray is independent of the chemical state of the element; therefore, XRF is generally considered to be an elemental analysis method.

XRF requires little sample preparation. Both solid and liquid samples can be analyzed. A standard sample holder of an XRF instrument accommodates disks with a diameter of 1-3 cm and up to 1cm high. It can be in the form of polished disks, pellets of pressed powders, liquids, thin films, and particulate material on a filter. Very flat surfaces are required for quantitative analysis. To obtain good quantitative results, the sample must be homogenous and the irradiated surface must be very smooth.[33]

X-ray fluorescence is useful for elements with atomic numbers greater than 4, including metals and nonmetals. For qualitative analysis, no sample preparation is required and the method is generally nondestructive. XRF is used extensively for quantitative determination of elements in alloys and mineral samples, particularly of elements with high atomic weights.

The best solvents are  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , hydrocarbons, and oxygenated carbon compounds, because these compounds contain only low atomic number elements. Solvents such as  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CS}_2$ , and  $\text{CCl}_4$  are undesirable because they contain elements with higher atomic numbers; they may reabsorb the fluorescence from lower-Z elements and will also give characteristic lines for Cl or S.

Organic solvents must not dissolve or react with the film used to cover the sample. Solid samples that can be cut and polished to give a flat surface can be analyzed after polishing. Care must be taken not to contaminate the sample with the cutting tool or polishing compound. For example, cutting a flat piece of polymer with a steel razor blade can result in iron being detected in the polymer sample.

Other solids should be converted to a powder, using a ball mill. The grinding tools must not contaminate the sample, hence boron carbide is often used to contain and grind samples. The sample powder may be pressed or mixed with lithium borate salt, borax, wax, or other suitable binder and formed into a briquette.[35]

## CONCLUSION

There are many different techniques for sample preparation for atomic spectroscopy techniques. The selection of the sample preparation method depends mainly upon the analyte concentration, matrix, instrument operation conditions, costs and the environmental considerations.

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