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Der Chemica Sinica, 2011, 2(5): 211-219



**Pelagia Research
Library**
ISSN: 0976-8505
CODEN (USA) CSHIA5

Sample preparation for trace element analysis by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS): An overview

Nabil Ramadan Bader

Chemistry Department, Faculty of science, Garyounis university, Benghazi, Libya

ABSTRACT

Sample preparation is an important step in chemical analysis process. The present article gives an overview of recently most used techniques in sample preparation for graphite furnace atomic absorption spectroscopy. Sample decomposition techniques, separation and pre-concentration methods of the target analyte(s) have been discussed.

Keywords: Sample preparation, GFAAS, decomposition, separation, pre-concentration.

INTRODUCTION

There are four main steps in chemical analysis process, sampling, sample preparation, measurement, and data analysis. Sample preparation was probably the single most neglected area in analytical chemistry relatively to the great interest in instruments. While the level of sophistication of the instrumentation for analysis has increased significantly, a comparatively low technical basis of sample preparation often remains.[1]

Nowadays, Sample preparation and development of methods became a growing field along with instrumental improvements. There are drastic improvements in the detection power of measurement techniques used.[2]

The principal objectives of sample preparation for residue analysis are; isolation of the analytes of interest from as many interfering compounds as possible, dissolution of the analytes in a suitable solvent and pre-concentration. In an analytical method sample preparation is followed by a separation and detection procedure.

The selection of a 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.[3]

Liquid samples can be generally introduced for analysis directly and without any prior treatment. The major problem associated with work with solutions is their collection and storage. If measured concentrations satisfy the principal criteria of the spectroscopic method used (sensitivity, dynamic range) and possible interferences are under control, the analysis of solutions may be performed automatically with all modern atomic spectroscopic systems.

If the sample is viscous, such as blood, or colloidal (milk), then it is necessary to dilute the sample with an appropriate solvent. Usually water or dilute nitric acid are employed for this purpose. Surfactants, such as Triton X-100, are added to some samples to lower surface tension and promote through mixing of the diluted sample.[4]

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. In case of solid samples, many steps are required, including sampling, sub-sampling, grinding, and dissolution. 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.[3]

It is possible to analyze solids directly by using the atomic spectroscopy, but this is not the preferred approach.[1]

DISCUSSION

A. Decomposition techniques

Acid digestion or wet decomposition

Acid digestion involves the utilization of mineral or oxidizing acids and an external heat source to decompose the sample matrix in open or closed vessels. The choice of the acid or the combination of the acids depends upon the nature of the matrix to be decomposed.

Wet decomposition has been performed in open systems for many years: Teflon beakers when using HF or glass tubes or beakers on hot plates or aluminum blocks. Open systems are useful for relatively "easy" samples such as food or agricultural, but generally unsuitable for some samples that require lengthy dissolution times of 1–24 h. Other concerns are that they tend to be time consuming and result in evaporative loss of volatile metals and the risk of contamination.[5] Nitric acid is used as oxidant alone or in combination with other acids or sometimes with hydrogen peroxide.[6-8] In addition, hydrofluoric acid can be used in combination with nitric acid for the total decomposition of silica containing organic matrices.[9] Nitric acid is popular because of its chemical compatibility, oxidizing ability, availability, purity, and low cost.[10] Cautions must be considered when using nitric acid alone or in combination with other reagents in the decomposition of organic matrices because of the ability of nitric acid to react with alcohols and aromatic rings forming explosive compounds. If the sample contains high -OH functionality it is best to pre-treat the sample with concentrated sulfuric acid which will act as a dehydrating agent. The use of nitric acid is not recommended for digestion of highly aromatic samples.[11] The closed vessels have been currently used for digestion in order to improve the oxidation efficiency and to reduce the time of digestion, and it has been successfully used for digestion of different types of samples. In closed systems high pressures allow boiling at higher temperatures and often leads to complete dissolution of most samples.[5, 10]

The advantages of the closed system, as compared with the open system are: No volatilization of elements, reduced reagent quantities, and no contamination from external sources.[12]

There are some problems associated with wet digestion like incomplete solubilization of the sample and the possible co-precipitation of the analyte with the precipitate formed in the digestion mixture. The best known example is co-precipitation of lead on calcium sulphate precipitates formed when a sample high in calcium is digested with a mixture containing sulphuric acid.[2]

Microwave Assisted Extraction (MAE)

In principle, only samples or solvents containing dipolar materials or microwave absorbents can be affected by microwaves which heat the extraction body from inside to outside in a very short time, much different from the common heating methods. The acceleration is resulted from the fast and uniform heating feature.[13,14] Basically, two types of MAE system can be used, an open-focused or a closed vessel system. A closed-vessel offers a special way to regulate the extracting temperature by simply adjusting the vessel pressure. The closed digestion technique involves placing the sample in a vial (or bomb), usually constructed of a fluorinated polymer, such as polytetrafluoroethylene (PTFE) or perfluoro alkoxy (PFA). After adding the digestion reagents, the bomb is tightly sealed and placed in the microwave oven for irradiation by microwave energy.[15-17]

Although almost all reported MAE methods were conducted off-line, on-line approaches have been shown to be possible.[18-20] Microwave-assisted sample preparation techniques are becoming widely used in analytical laboratories all over the world.[21,22]

Combustion

Combustion (Dry ashing) or oxidation is usually performed by placing the sample in an open vessel to remove the organic portion of the sample by thermal decomposition, normally in the presence of an ashing aid, using a muffle furnace. Typical ashing temperatures are 450 to 550°C at atmospheric pressure for 1 to 6 h. The analyte is then extracted from the ash with a mineral acid. The degree of volatilization loss is a limiting factor and depends on the applied temperature, the form in which the analyte is present in the sample, and the chemical environment in the ashing stage.[23] Losses of volatile elements (Hg, As, Se, Cd, Pb, Tl) may occur. Losses of analyte may also occur due retention of analyte in the ash.[4] Oxidizing reagents may be used as ashing aids in order to prevent the volatilization of analytes and also to speed up the ashing process. High-purity magnesium nitrate and magnesium oxide are commonly used for that purpose.[23] Low-temperature ashing involves treatment of the sample at about 120 °C using activated (singlet state) oxygen.

The most important advantages of the ashing are the ability to decompose large sample sizes and dissolving the resulting ash in a small volume of acid, and the need for little or no reagents.[23] In general, combustion methods have been replaced by wet decomposition procedures for most analyses by GFAAS. [3,4]

Fusion

Fusion procedures are well suited for the dissolution of samples that can not be dissolved by other procedures (e.g., geological samples).[4] Fusion is the dissolving of a sample using a molten inorganic salt, generally called a flux, as the solvent. This flux dissolves the sample and, upon cooling, results in a solid mass that is then soluble in a liquid reagent. The dissolving power of the flux is mostly due to the extremely high temperatures (usually 300 to 1000°C) required to render most inorganic salts molten.

The flux must be present in a fairly large quantity in order to be successful and the measurement of the analyte must not be affected by this large quantity. While a flux may be an excellent solvent for difficult samples, it will also dissolve the container to some extent, creating contamination problems and increase the blank level, making the technique unsuitable for many GFAAS analyses.[4,24]

Platinum crucibles are commonly used, but nickel, gold, and porcelain have been successfully used for some applications. Probably the most common fluxes are sodium carbonate (Na_2CO_3), lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), and lithium metaborate (LiBO_2). Fluxes may be used by themselves or in combination with other compounds, such as oxidizing agents (nitrates, chlorates, and peroxides). Applications include silicates and silica based samples and metal oxides. The acidic flux potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$) may be used for difficult metal oxides.[24]

Matrix Modifiers

Matrix modifiers are often used to control interferences during the measurement process in GFAAS. These are chemicals added to the sample to assist in the separation of the analyte from the matrix prior to atomization such that the interference is not present at the time of atomization.[24] For volatile elements, a chemical modifier serves to reduce the volatility of the analyte or to increase the volatility of the matrix.[25] Higher pyrolysis temperature can be used to vaporize more matrix components and therefore, minimize scatter and molecule formation in the atomization step in the analysis.

Modifiers may introduce some problems for real sample analysis. They may require the use of a higher atomization temperature, which may reduce the characteristic mass due to higher rate of diffusion from the tube. The analyte may condense with the chemical modifier in cool regions of the graphite tube. Additionally, the presence of the modifier may produce spectral interference. Common modifiers are magnesium nitrate, ammonium dihydrogen phosphate, diammonium hydrogen phosphate, nickel nitrate, and palladium nitrate alone or in combinations.[4]

Water

The most basic requirement of any analytical laboratory is a good water supply. High quality deionized water is essential for trace element analysis by GFAAS. A number of water purification systems are commercially available. Further purification using sub-boiling distillation unit may be necessary for extremely low levels of concentrations.[4,11]

Direct analysis of solid samples

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 procedure. 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. The availability of appropriate calibration standards of similar composition to the samples analyzed. 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 is depends on the nature of the sample. For good results, it is necessary to produce a homogenous slurry. Converting the sample into powder with small particle size ($< 10\mu\text{m}$) is required.[4]

B. Trace element separation and pre-concentration

Liquid- liquid extraction

Solvent extraction separation is based on the differences in the solubility of elements and their compounds in two immiscible liquid phases. Usually, the initial phase is an aqueous solution and the second phase is an organic solvent immiscible with water.

After extraction the concentration of the metallic complex in the organic phase can then be directly determined by atomic absorption spectrophotometric method. The main disadvantage of liquid- liquid extraction is the large consumption of solvents which is not environmentally friendly aspect.[3]

Co-precipitation

The co-precipitation is used to pre-concentrate the metal ion by formation of insoluble compound. It is used when direct precipitation can not separate the desired analyte due to its low concentration in sample solution. The co-precipitation can be associated with metal adsorption on the precipitate surface or due to metal incorporation onto the precipitate structures. After precipitation the precipitate can be removed by centrifugation and dissolved in acids to be measured by GFAAS. Inorganic or organic substances can be used as co-precipitation agents. The organic agents usually chosen are those able to originate neutral chelates with metallic species. The carrier element, is precipitated to co-precipitate trace elements in sample solutions, copper and zinc are popular, because of their limited negative effects for environment.

Organic co-precipitants, generally dithiocarbamates of bismuth and copper have been widely used as efficient collectors of trace elements.[26,27] Many metal ions from water samples have been pre-concentrated by co-precipitation with hydroxides of iron (III) [28], indium(III) [29], and zirconium [30]. T. Oymak et al. have developed a coprecipitation method using a combination of 2-mercaptobenzothiazole (MBT) as a chelating reagent and copper as coprecipitate carrier was used for the determination of trace Pb(II) and Cd(II) in various food samples by GFAAS.[31]

Cloud point extraction (CPE)

The cloud point extraction (CPE) of metal ions involves the formation of sparingly water soluble chelates with suitable reagents. The method is based on the entrapment of uncharged moiety within a micelle formed by heating the surfactant solution above the cloud point temperature. Cloud point extraction is an attractive technique that reduces the consumption of the solvent, extraction time and the disposal costs.[3,32]

The main parameter to attain a surfactant monomer agglomeration in a micelle-rich phase is the surfactant concentration at the cloud point temperature. The temperature-concentration phase diagram is specific for each surfactant. The effect of additives such as salts and other surfactants also has to be considered.[33,34]

Several ligands, have been used such as 1-(2-thiazolylazo)-2-naphthol (TAN), ammonium pyrrolidinedithiocarbamate (APDC), 8-hydroxyquinoline (Oxine), dithizone, diethyldithiocarbamate (DDTC), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP), and 1-(2-pyridylazo)-2-naphthol (PAN), have been used in cloud point extraction of metal ions.[35]

Organic solvents and surfactants are both compatible with detection by graphite furnace because they stabilize the solution and are completely oxidized before the detection step.[36]

Many metal ions have been determined by graphite furnace atomic absorption spectrometry such as Pt, As, Cd and also speciation analysis of Cr(III) and Cr(VI) after CPE in different kinds of samples.[37-41]

Solid phase extraction (SPE)

The solid phase typically consists of small, porous particles of silica with a bonded organic phase or of an organic polymer, such as crosslinked polystyrene. The extraction can take place in a batch mode in which the solid extractant is intimately mixed with liquid sample solution. In chemical analysis it is more common to pack the solid extractant into a small tube and pass the liquid sample through the tube.[42]

The nature and properties of the sorbent are of prime importance for effective retention of metallic species. Careful choice of the sorbent is thus crucial to the development of SPE methodology.

Solid-phase extraction (SPE) has become increasingly popular in trace elements separation and pre-concentration compared with the classical liquid-liquid extraction method because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the ability to combine with different detection techniques in on-line or off-line mode.[43]

Many types of solid materials such as modified polyurethane foam (PUF) [44], cellulose [45], activated carbon [46], silica gel [47] and micro crystalline naphthalene [48] have been used for pre-concentration of metals. The surface can be modified chemically by chemical reaction or physically by means of adsorption, in order to enhance the selectivity toward certain metal ion or certain group of elements.[49-52]

Saygi et al. proposed a method for speciation of selenium(IV) and selenium(VI) in environmental samples. The method is based on the solid phase extraction of the selenium(IV)-ammonium pyrrolidine dithiocarbamate (APDC) chelate on the Diaion HP-2MG. The preconcentration factor was 100. [53]

A method for the determination of ultra-trace amounts of cadmium by GFAAS after its preconcentration using minicolumns containing silica gel modified by N,N'-Bis(salicylidene)1,3-propylenediamine has been developed by Bader. The limit of detection of the combination SPE with GFAAS lies in the detection limit range of ICP-MS. [54] The method has been applied for determination of Cd in some environmental water samples.

Plant materials can be used as a cheap and low cost material for adsorption e.g. modified corn starch, phosphate treated saw dust, Algal material, and activated carbon derived from tendu leaf. [55,56]

A solid-phase extraction method using zeolite A-4 for the pre-concentration and determination of trace amounts of cadmium in water samples by GFAAS was investigated by Minamisawa et. al. Zeolite A-4 collected cadmium from sample solutions at pH 3.0 – 9.0, and the zeolite A-4 containing cadmium could be dissolved with nitric acid and then injected to the graphite furnace. [57]

Finally, there are many different techniques used for sample preparation specially those for flame atomic absorption spectroscopy are applicable for GFAAS after taking in consideration the concentration level of the analyte. [58-61]

CONCLUSION

There are many different sample preparation techniques for GFAAS. 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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