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FLAME OR FURNACE AA (ATOMIC ABSORPTION) - WHICH TECHNIQUE SHOULD I USE IN MY LABORATORY? A BASIC OVERVIEW OF ELEMENTAL ANALYSIS

Florina RAICU, Constantin VLAGIOIU, Niculae TUDOR

Faculty of Veterinary Medicine, 105 Splaiul Independentei, Bucharest, Romania

Corresponding author email: stratoneflorina@yahoo.com

Abstract

If in a laboratory elemental analysis (heavy metals) on solutions is being performed, there are a couple of very efficient spectrometric techniques that can be used. Flame and Furnace Atomic Absorption (AA) is one of them. This article aims to highlight the applicability of both techniques (Flame Atomic Absorption Spectroscopy "FAAS" and the other one that is Graphite Furnace Atomic Absorption Spectroscopy "GFAAS") that are being used in the analysis of animal and non-animal food samples. For obtaining a relevant pieces of information in order to help the analyst, it is useful to make a parallel between the two AA techniques. This parallel is obtained by objectively answering to a series of questions to make sure that the chosen technique is the best from different point of views (type and number of samples, the type of the analyzed element, the time allocated for each analysis etc.) The defining elements include understanding the operating principles of each mentioned technique (FAAS and GFAAS), their strengths and their weaknesses (spectral interferences, background effects, matrix effects).

***Key words**: applicability, FAAS, GFAAS, parallel, spectral interferences, background effects, matrix effects.*

INTRODUCTION

If in a laboratory elemental analysis (heavy metals) on solutions is being performed, there are a couple of very efficient spectrometric techniques that anyone could use. This article aims to draw a parallel between FAAS (Flame Atomic Absorbtion Spectroscopy) and the GFAAS (Graphite Furnace Atomic Absorption Spectrometry) techniques.

Picking the most effective tool for this job can sometimes be an intimidating task, especially because of the different levels of capabilities. In fact, every single technique may be able to perform a particular analysis at acceptable levels of accuracy and precision (Cordos et al., 1983).

However, by appraising the corresponding strengths and weaknesses of each of the techniques, particularly as they may apply to the practical and performance requirements of the analysis, it is possible to build a balanced basis for taking the best decision (Seely et al., 2009).

MATERIALS AND METHODS

Understanding how the methods work

In order to intelligently choose between these sure techniques - FAAS and GFAAS, for comparison purposes it is helpful to have a general understanding of basic principles and specialized details of each of the elemental analysis instruments (Walker, 2014).

Principles of analysis in spectroscopy

Spectroscopy is a name given to a category of preliminary techniques and procedures which surveys and appraise the effect of intake or emission of energy by chemical analysis of a sample exposed to qualitative and / or quantitative.

The spectroscopic analysis is planted on the synergy between electromagnetic waves and matter. The purpose of spectroscopy is to obtain information from a spectrum about the sample, information such as: internal format, configuration, content, dynamics (Lajunen, 2004).

Classification of spectroscopic methods

1. Atomic Spectroscopy:
    - Atomic Absorption Spectroscopy (AAS/OAS);
    - Atomic Emission Spectroscopy (AES/OES);
    - Atomic Fluorescence; Spectroscopy (AFS);
    - Roentgen Spectroscopy;
    - Electron Spectroscopy (XRS);
2. Molecular Spectroscopy/Mass spectroscopy (MS);
3. Spectroultraviolet-visible (UV/Vis);
4. Spectroscopy for ultrashort time;
5. Spectroelectrochemistry;
6. Laser Spectroscopy;
7. Astrospectroscopy (French et al., 1990).

Atomic spectrometry - principle

Atomic spectrometry is based on the changeover of the sample to level of free atoms by a process of atomization, which takes place in an atomization cell, followed by shelling with optical radiation, having a wavelength well-defined radiation that is emitted by a primary radiation source and sent to the atomization source.

The emission of spectral lines is caused by a passage from a higher energy level to lower energy one. The absorption is the reverse process. Spectral lines for which one is the ground state energy level are called resonance lines. From the analytical point of view, a great importance is represented by resonant lines arising from transitions between the ground state and the first excited level, which are generally the most intense.

The emission spectroscopy or atomic absorption analysis applies, most often, for metallic elements. Atomic absorption spectroscopy is based on absorption of radiations (Christian et al., 1970).

The atomization in Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is a part of the UV-VIS and optical methods. It relies on the measurement of the radiated power which is absorbed by a population of free atoms. Evaporating and atomizing techniques which imposed in AAS are: flame and electrothermal evaporation. In case of using the flame, we have flame atomic absorption spectrometry (FAAS) and for electrothermal evaporation, we speak about electrothermal evaporation atomic absorption spectrometry (ETV-AAS). Regarding the electrothermal evaporators, the graphite furnace is noticeable, being symbolized as GFAAS technique.

Flame Atomic Absorption Spectrometry (FAAS)

In FAAS method, either an air or a nitrous oxide mixed with acetylene flame is used, for evaporating the solvent and disband the sample into its fundamental atoms. When light from a hollow cathode lamp (selected based on the element to be determined) passes through the cloud of atoms, the destination atoms absorb the light from the lamp. A detector is measuring this, and the information is used to calculate the concentration of that element in the original sample.

If a flame is used, then the excitation temperature reached by a sample is limited to a maximum of approximately 2600°C (with the N2O/acetylene flame). For most of the elements, this is not a problem. Compounds of the alkali metals, for example, and most of the heavy metals such as lead or cadmium and transition metals like manganese or nickel are all atomized with good efficiency with either flame type, with typical FAAS detection limits in the sub-ppm range (French et al., 1990).

However, there are a number of disobedient elements like V, Zr, Mo and B which do not perform well with a flame source. This is because the maximum temperature reached, even with the N2O/acetylene flame, is insufficient to break down compounds of these elements. As a result, flame AAS sensitivity for these elements is not as good as other elemental analysis techniques (Smith et al., 1993).

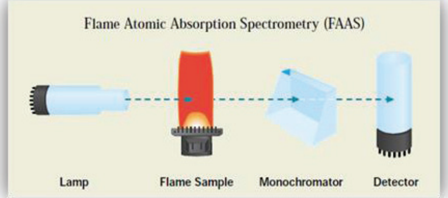


Figure 1. The components of the FAAS (French et al., 1990)

Strengths

- Facile usage;
- Very fast;
- Low cost;
- Relatively few interferences;
- Very compact instrument;
- Excellent performance;
- Robust interface.

Limitations

- Moderate detection limits;
- Element limitations;
- 1-10 elements per determination;
- No screening ability (Lajunen, 2004).

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

This technique is approximately the same as flame AA technique. The difference is that the flame is replaced by a small graphite tube that is electrically heated, or cuvette, which is heated to a temperature up to 3000°C to generate the cloud of atoms.

The higher atom density and longer residence time in the tube improve furnace AAS detection limits by a factor of up to 1000x compared to flame AAS, down to the sub-ppb range. However, because of the temperature limitation and the use of graphite cuvettes, refractory element performance is still somewhat limited (Rains, 2008).

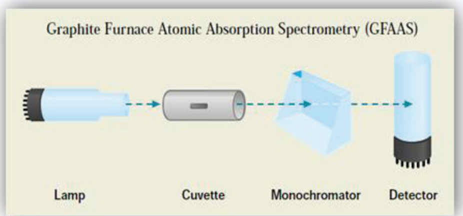


Figure 2. The components of the GFAAS (French et al., 1990)

Strengths

- Very good detection limits;
- Small sample size;
- Moderate price;
- Very compact instrument;
- Few spectral interferences.

Limitations

- Slower analysis time;
- Chemical interferences;
- Element limitations;
- 1-6 elements per determination;
- No screening ability;
- Limited dynamic range (Smith et al., 1993).

Interferences in AAS

This term represents all physical and chemical phenomena which act on the analyte's atoms, resulting in changing the signal, which would be obtained in their absence. If the sample and reference behave differently during measurement, interference will appear.

- Interferences in flame atomization

Spectral interferences in SAA: appear when the resonance emitted by the source line overlaps with an absorption line of another element in the flame, or over a molecular tape.

Physical: originated in the modification of the physical characteristics of the measuring solution (viscosity, surface tension, vapor pressure, temperature).

Chemicals: is the most important category of interference. Interference gets worse, as you increase the temperature difference between dissociation of the original compound, respectively, of the new one. Using the hot flames, as well as addition of salts of metals that form stable compounds with the interfering ion minimize these types of interference. (Cordos et al., 1983).

Interference of ionization: the atoms of analyte are partially ionized burning hot, which causes decreased absorption signal. In the analysis by FAAS working alkaline metal, most often, the flame temperature favors low temperature that increases atomization. Ionization effects can be reduced or eliminated by the addition of both the sample and the calibration standards, an item in excess ionized easier than the analyte.

- Interference in the graphite furnace atomization

Physical: volatility and viscosity affect pipetting solutions into the graphite tube. Surface tension affects the dispersion of the solution inside the oven and, consequently, the analytical response. If there are added surfactants (detergent or a surfactant such as Triton X), their behavior approach to the organic solutions.

Chemical (matrix effects) of the sample and the reagents used for the matrix can affect the dissolution of the analyte signal absorption, leading to a depression or an increase in the analytical response (Rains, 2008).

In GFAAS, chemical interferences due to the effects can cause the formation of stable or volatile compounds in the atomizer. Interference caused by the forming of volatile compounds can be avoided by modifying the matrix. This can be done by: choosing an appropriate temperature for drying-calcination cycle-atomization; adding a reagent in sample and calibration standards (the role of the matrix is to boost the volatility or to convert the analyte in a less volatile compound). In both situations, the change is made to the volatility of the analyte and the matrix to be adequately different to allow their separation in the ashing stage.

Studies regarding modifiers remain dominant as a research field in electrothermal atomization. Often, modifier consists of a mixture of substances, one that acts directly on the matrix and the other on the analyte. In some cases, using the organic modifiers, such as ascorbic acid, lactic acid, citric acid, EDTA, facilitates the reduction of the metal analyte and lowers the temperature of the atomization (Oliveira et al., 2017).

RESULTS AND DISCUSSIONS

It's implausible that a single technique is going to perfectly correspond all of a laboratory's needs. Unless you have lots of space, very skilled staff, and an extra budget, you'll probably have to make some compromises.

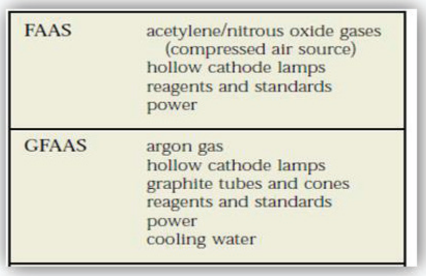
You should look in to the future, and try to anticipate what changes may occur in your analytical requirements. If possible, allow some room for system expansion.

Capital costs

Obviously, because there are a lot of instruments available from different manufacturers, and because so many options and configurations are possible, it is difficult to put absolute values on capital costs. A critical aspect is given by accessories or options, which may add considerably to the purchase price. Practically, you can expect to pay from around $15-20,000 for a base configuration flame AA system. Speaking about the GF-AAS, the costs are at least double (Walker, 2014).

Operating costs

For GFAAS use, your reagents may also need to be enhanced from normal analytical grade to high-purity grade. You'll find major variations in the quantities of common supplies like argon, for instance, consumed during an analysis. GF-AAS only uses about 3.0 L/min of argon (Lajunen, 2004).



FAAS	acetylene/nitrous oxide gases (compressed air source) hollow cathode lamps reagents and standards power
GFAAS	argon gas hollow cathode lamps graphite tubes and cones reagents and standards power cooling water

Figure 3. Specific conditions for the operation of each technique (Lajunen, 2004)

Detection Limits

As principle, based on practice, GFAAS deliver the best detection limits from these two techniques (usually in the sub-ppb range), followed by FAAS (in the sub-ppm range) (Oliveira et al., 2017).

CONCLUSIONS

In order to make a parallel between the two AA techniques, anyone should objectively answer to a series of questions, such as:

Does this method have a *high applicability*?

What are *the sample types* to be analyzed?

What *elements* and *absorption ranges* are required?

How many components will be identified per each sample?

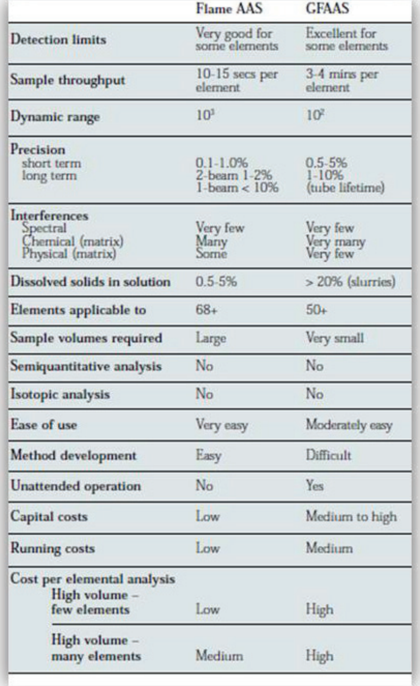
What is the *efficiency* and *precision requirements?*

Are *the analytical demands* likely to differ on a daily basis?

Are there *administrative issues* to take into consideration (e.g.: specific analysis protocol requirements)?

How many samples will be analyzed per day?

<u>*Who*</u> will be performing on the instrument?
What <u>*level of operator's competence*</u> is available?
How much <u>*laboratory space*</u> is available?
And (of course) what is <u>*the available budget*</u>?



	Flame AAS	GFAAS
Detection limits	Very good for some elements	Excellent for some elements
Sample throughput	10-15 secs per element	3-4 mins per element
Dynamic range	10^3	10^2
Precision		
short term	0.1-1.0%	0.5-5%
long term	2-beam 1-2% 1-beam < 10%	1-10% (tube lifetime)
Interferences		
Spectral	Very few	Very few
Chemical (matrix)	Many	Very many
Physical (matrix)	Some	Very few
Dissolved solids in solution	0.5-5%	> 20% (slurries)
Elements applicable to	68+	50+
Sample volumes required	Large	Very small
Semiquantitative analysis	No	No
Isotopic analysis	No	No
Ease of use	Very easy	Moderately easy
Method development	Easy	Difficult
Unattended operation	No	Yes
Capital costs	Low	Medium to high
Running costs	Low	Medium
Cost per elemental analysis		
High volume – few elements	Low	High
High volume – many elements	Medium	High

Figure 4. Summary of elemental analysis techniques (Lajunen, 2004)

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