Comparison between Flame Atomic Absorption and Microwave Plasma Atomic Emission Spectrometers in the analysis of gold content

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Abstract

The present work aims to compare the reading techniques of Flame Atomic Absorption and Microwave Plasma Atomic Emission Spectrometry. A total of 10 certified samples with the gold levels specified were chosen. After quantifying the gold content in the sampels of interest, the results were transcribed into tables, where the relative error of each of the samples in relation to the certified values and the coefficient of variation of the three aliquots of each standard were also calculated. The study certified the high rate of gold recovery through the Fire Assay and revealed the better performance of MP-AES in relation to FAAS under the reading conditions established by the authors, according to the existing scientific literature. It is concluded that the MP-AES has enough potential to be an alternative, or even to replace instruments commonly used in the quantification of elements, such as gold, provided that more studies emerge to test and prove its superiority.

Keywords: Gold, Fire Assay, Spectrometry, MP-AES.

1. Introduction

The use of gold dates to very ancient times, it is not known for sure how it started, but the first evidence of its large-scale manufacture was revealed by modern archaeologists, who discovered highly sophisticated objects of art and jewelry, dating back to around 3000 BC, in Sumerian tombs in Mesopotamia (Macdonald, 2007).

Nowadays, the demand for this metal continues to grow, whether for technological requirements, economic value retention and even for aesthetic reasons, since, for years, a large part of its demand was concentrated in the jewelry industry (Wanderley , 2015). Thus, in order to make efficient use of a certain area to be explored, a strategic plan is needed that can identify the profit potential, thus making companies in this sector look for methods that analyze the mineral content in localized areas of interest (Calaes, 2006; Kirkemo et al., 1998).

The Fire Assay is considered one of the oldest, most traditional and reliable techniques to identify gold content in a sample, having undergone few modifications over time, except for higher quality reagents and improvements in melting and reading techniques, increasing, then, the reliability of the results (Clark et al., 1998). The technique, according to Clark et. al. (1998), consists of a series of high temperature treatments and melts (hence the name Fire Assay), separations and solubilizations in acid solutions and posterior reading in analytical precision devices.

Considering the reading techniques available on the market, Flame Atomic Absorption Spectrometry (FAAS) is one of those traditionally used because it is able to quantify an analyte of interest (in this case, the concentration of Gold) in seconds (Slavin, 1994). However, in recent years, Microwave Plasma Atomic Emission Spectrometry (MP-AES), a relatively new technique, has gained prominence in different studies due to its high sensitivity and stability combined with the ability to read several elements that may be of interest to the user (BALARAM, 2020).

In view of this scenario, the question that guided the present study arose: As the demand for analysis of the gold content is in great ascendancy, due to the high appreciation of this noble metal, how does the results obtained by the FAAS and MP-AES techniques compare?

Therefore, the present work aimed to know and compare the results achieved by these reading techniques, one already used traditionally, and another relatively new in the laboratory market. This study is justified by the possibility of filling a gap in existing knowledge on the subject, in addition to being able to contribute to research institutions and industries focused on this sector, which seek to innovate in techniques, or even improving the reliability of the results obtained in instruments already used traditionally.

2. Material and Methods

2.1 Historical Context of Gold and Experiments

Gold is considered one of the first metals to be explored, as it was found dissociated from other elements and, in addition to having an appearance that caught the attention of ancient peoples, it was easy to handle. Due to its high density, it was easily separated from other materials of little use. As exploration worsened over the years, mining was extended to fewer rich deposits to meet the global demand for the mineral (Wanderley, 2015; Macdonald, 2007; Habashi, 2016).

Comparing the accuracy and economics of sample analysis methods is widely discussed in the literature. This work focuses on the comparison between FAAS and MP-AES methods for gold analysis. More diversified research in terms of compared materials has already been carried out, as shown in Table 1, where Balaram et al. (2014) performed a comparative analysis of the accuracy of element analysis, considering both methods, including for gold.

The experiment by Balaram et al. (2014) can be analyzed as: *"accurate and reliable analytical techniques and methodologies possessing high sensitivity and selectivity, coupled with convenience and economy and applicable to real world situations, are required for geochemical studies. Quantitative analysis of major, minor, and some trace elements were performed in several geochemical reference samples using a new microwave plasma-atomic emission spectrometry (MP-AES) technique. A range of rock, soil, sediment, and water reference materials were chosen to evaluate the performance of this technique. The detection limits for several elements were found to be in the 0.05 to 5 ng/g range, which those of an ICP-AES technique but were much superior to FAAS. Precisions of ≤3% RSD were obtained for minor and ≤6% RSD for trace elements with comparable accuracies for most determinations. The results obtained indicated that MP-AES is a suitable atomic emission spectrometry technique for the accurate determination of major, minor, and selected trace elements required in geochemical studies".*

Table 1. Detection Limits for Different Elements by MP-AES in Comparison With Other Popular Analytical Techniques (FAAS, ICP-AES, and ICP-MS)

Elements	Detection Limits (ng/mL)			
	FAAS	MP-AES	ICP-AES	ICP-MS
P	50,000	33	30	0.1
Zn	1	2.8	1	0.04
Au	6	1.8	20	0.005
Ag	1	0.5	1	0.005
Pt	40	4.5	-	0.005
Pd	-	3.8	-	0.01
Cd	0.5	1.4	1	0.005
Be	2	0.1	0.1	0.012
Al	30	0.6	3	0.01
B	1000	1.3	1	0.012
Mn	1	0.25	0.4	0.005
Ta	-	-	-	0.0003
Mg	0.1	0.12	0.1	0.020
Bi	20	24.4	-	-
Ti	50	7.9	0.5	0.004
Nb	-	-	-	0.001
Cu	1	0.6	1	0.005
Hf	-	-	-	0.001
Zr	-	10	-	0.007
Ni	4	1.3		0.01
Sc	-	-	5	0.009
Y	-	0.4	-	0.003
Mo	30	1.5	3	0.08
Fe	5	1.6	2	0.500
Pb	10	2.1	10	0.0012
Sr	-	0.1	0.06	0.001
Ga	-	-	-	0.002
Cr	2	0.4	2	0.005
Ca	1	0.05	0.02	0.4
Na	0.2	0.12	3	0.05
Ba	-	0.2	0.1	0.01
Li	0.5	0.01	0.3	0.01
K	1	0.65	20	0.5

ICP-MS detection limits (27).
ICP-AES detection limits (28).
F-AAS detection limits (25).
MP-AES detection limits by this study.

Source: (Balaram et al., 2014)

Taking this analysis as a reference, a comparative analysis was carried out considering the methods used by a Brazilian company in operation, which works with the FAAS and MP-AES methods for specific analysis of gold.

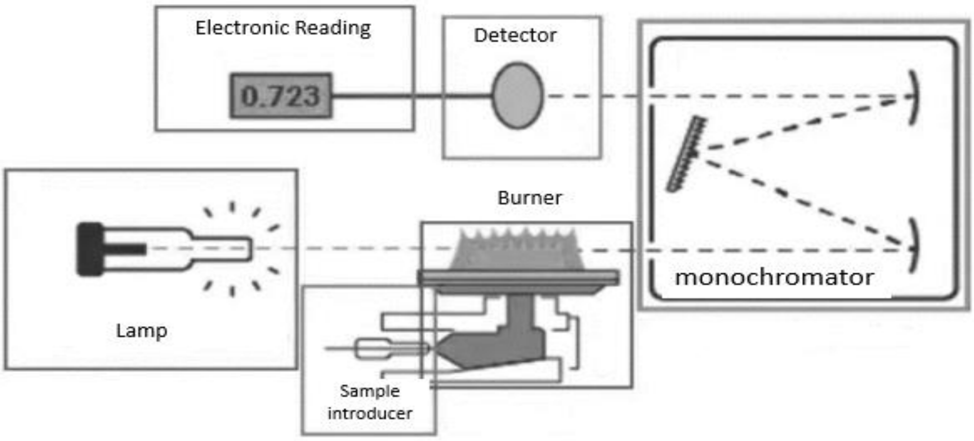
2.2 Flame Atomic Absorption Spectrometer (FAAS)

Atomic absorption is an optical atomic spectrometric technique launched commercially in the mid-1960s and is still widely used on an industrial scale. It is considered a successful analysis method because it has a precise detection limit for samples at lower concentrations. It involves electromagnetic radiation, which can be absorbed by the atoms of the chemical constituents of the analytes and is based on the quantification of fine-line spectra that arise from the electronic transition (Lajunen & Peramaki, 2007; Csuros & Csuros, 2016).

Lajunen & Peramaki (2007) classify the operation of the Atomic Absorption Spectrometer in three steps: 1) Creation of a steady state of atoms freely dissociated through a heat source; 2) Passage of light of a specific wavelength, corresponding to the energy required to excite an electron from the atom, through the flame; 3) Measurement of absorbance, that is, the amount of light absorbed by atoms as they move to the excited state. After this process, the measured absorbance will be used to calculate the concentration of the element of interest in a solution, based on a calibration chart with predefined solution concentrations.

Figure 1 depicts the working scheme of a flame atomic absorption spectrometer, which has: a sample introduction system, which transports and pulverizes the solution to obtain a homogeneous flow of fine drops; a burner and its associated gas supply, Ar-Acethylene or Nitrous Oxide-Acethylene, to perform the atomization of the analyte; the light source, hollow cathode lamp coated by the element of interest, which produces a beam at the characteristic wavelength of the specific element; a monochromator, used to collect light containing different wavelengths and isolate a narrow band; a detector, responsible for converting the electrical signal emitted by the light from the output slit of the monochromator, making it possible to quantify the absorbance; an equipment control software, which performs the statistical analysis of the results, saves the device settings and generates the reports (Hill & Fisher, 1999).

Figure 1: FAAS Operation Scheme



Source: (Agilent Technologies, 2021)

2.3 Microwave Plasma Atomic Emission Spectrometer (MP-AES)

MP-AES is a detection technique that uses a plasma source at extremely high temperatures to excite the atoms of the analyte of interest to the point of emitting light photons with characteristic wavelengths of a given element, so that it is possible to quantify them (BALARAM, 2020). It is a recent developed analytical tool that has been gaining more and more prominence in the laboratory market due to its ability to simultaneously detect more than one element and have a lower operating cost compared to other instruments with similar objectives (Balaram et al., 2014; Akcil, 2019).

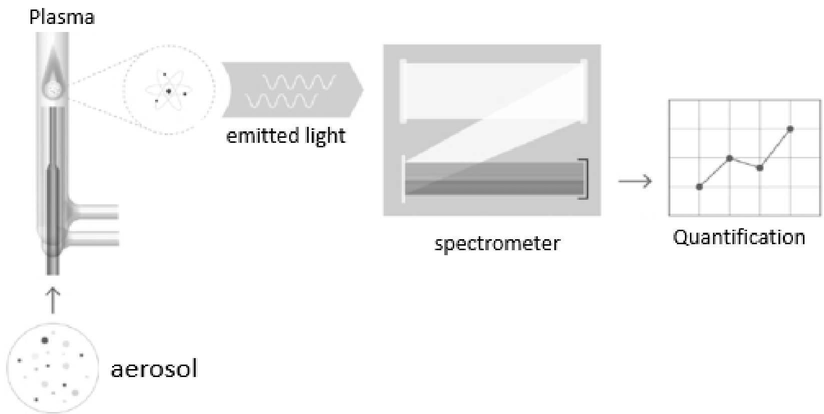
Balaram et al. (2014) says that the atomic emission source has a relatively high temperature, close to 5,000K, so it is an excellent excitation generator for the atomic emission spectrum, resulting in more reliable detection limits and linear dynamic range for most of the atomic emission spectrums. The nitrogen, used to supply the plasma flame, comes from a generator that uses a source of compressed air under specific conditions, which eliminates the need to use flammable gases in the reading process (COOMBS, 2021).

The working process of the MP-AES, represented in Figure 2, is similar to that of the FAAS: an aerosol source is created from a solution of the analyte, using a nebulizer and a spray chamber. This is then introduced into the hot plasma, decomposing and atomizing the elements of interest. Atoms, in continuous excitation, emit light at wavelengths specific to each element, as they return to lower energy states.

The plasma emission is directed to a scanning monochromator, and the wavelength of interest is captured on a CCD (Charge Coupled Device) detector, which measures the spectra and sends the information to the software of the instrument. The operating system will then quantify the concentration of the analyte through the intensity and compare its emission with the known concentrations of the same element, plotted on a calibration curve (BALARAM, 2020).

Balaram (2020) states that the fact that the MP-AES performs the sampling and quantifies the analyte in an isolated environment minimizes the chances of external factors, such as temperature and unwanted particles, influencing the destabilization of the device, while the FAAS has a partially open chamber. The author also argues that MP-AES provides a faster determination of elements and eliminates the need for time-consuming dilutions, and, consequently, decreases the possibility of human error during analysis at higher concentrations due to the greater dynamic range.

Figure 2: MP-AES working diagram



Source: (Agilent Technologies, 2021)

2.4 Methods

The development of the present work consisted, firstly, in the formulation of the guiding question: how does the results of the analyzes obtained by the FAAS and MP-AES techniques compare? The process described in this study was carried out following the work instructions used in the daily life of the company used in this research, which describe and standardize the activities to be carried out.

After choosing the reference method, 10 standards were chosen with certified contents between 0 and 50ppm in triplicate, totaling 30 samples to be analyzed. Thirty grams of each sample was weighed on a precision scale with a deviation of +- 0.001g and they were placed in properly identified plastic bags. One hundred and seventy grams of Flux was added to each container that stores the sample. The flux is composed by 35.61% of Sodium Carbonate, 9.92% of Borax, 49.98% of Litargyrium, 3.65% of Silica, 0.80% of Wheat Flour and 0.04% of pulverized silver nitrate. Its constitution may vary according to the properties of the sample to be analyzed. Still at this stage, a space containing only 170g of Flux, called White, was added to the sequence, to later compensate any interferences that could contaminate the samples. After homogenization, the samples were placed in refractory crucibles and placed in a gas oven at 1,150 ºC for 1 hour. After the time necessary for all the samples to melt, they were removed from the ovens and placed in proper molds to cool and the analyte of interest to be deposited at the bottom of them.

The formed lead buds were separated from the slag, weighed and placed in cupels. The button weighing process occurs because the cupels can absorb up to 65g of lead, therefore, buttons that exceed this value will need to be divided and placed in different containers. The cupels were placed in an electric oven at 950 ºC and removed after about 1 hour and 20 minutes, which is the average time required to absorb all the melted lead and only remain the silver pearl.

The beads were transferred to test tubes, which were positioned on a grid, where they received acid attacks. Using a volume dispenser, 1 mL of nitric acid with 65% PA diluted at 50% v/v was added to the tubes, and then the tube grid was placed in the water bath until the beads of silver were opened into the solution, requiring no more than 5 minutes for the process. After verifying that all the beads were properly opened, 1 mL of 37% PA hydrochloric acid was added and the grid was placed in the water bath again, now for 15 minutes, for total solubilization of the gold concentration in the solution. After the time, the samples were placed for a brief cooling and 8 mL of deionized water was added. The total volume of the solutions, 10 mL, was taken to the homogenizer for about 8 minutes to then proceed to the reading step.

The reading process occurs in a similar way in both FAAS and MP-AES. Firstly, calibration curves were made with predetermined linear points. In the case of FAAS, two curves were constructed: one for low concentration, and the other for high concentration. The low concentration curve will have points of 0.5; 1; 2; 5 and 10 ppm of gold, with QCs, which are reference points of the curve, used to measure the stability of the device for each number of samples read, in the ranges of 9; 4 and 0.4 ppm. The high concentration curve has points of 10; 20 and 30 ppm, with QCs of 25 and 9 ppm. If the sample read exceeds the low curve detection capability, a new reading will be taken at high. If it exceeds the 30 ppm of the high curve, a dilution will be made for the reading to be performed and, later, the correction will be made in the calculation of the real concentration. The need to use two different calibration curves is due to standard reasons.

MP-AES needs only one calibration curve, with points at 0.1; 0.5; 1; 5; 10; 25; 50; 100; 300 and 500 ppm and QCs in the ranges of 0.4; 4 and 40 ppm. If the sample exceeds the detection capacity of the curve made, its dilution will be necessary, so that the device can perform the reading within the predetermined range. The MP-AES performs the analyte reading at 2 wavelengths already identified as element-specific and exports the most optimized result to the control software. To construct these curves, the certified Gold Standard 1,000 ppm was used as a matrix and the necessary concentrations of each point of the curve were diluted in volumetric flasks.

After reading the calibration points, the system of each device calculates the coefficient of determination of the regression (R^2), to numerically express the percentage of the variation of the analytical signal obtained by the variation of the concentration of the analyte. The closer to 1, the more accurate the representation by the equation of the line obtained in the regression.

The sampling process in the FAAS is performed manually, while that of the MP-AES is done in a completely automated way, requiring only the configuration of the device by a properly instructed analyst. In both equipment, the collected sample has readings performed in triplicate, and the result generated is an arithmetic mean of the three values obtained.

After the devices determined the readings of each sample of interest, the values were placed in a table, in which the concentration values in ppm (parts per million) or g/t (grams per ton) were calculated, through the equation (1):

$$\text{Concentration } (ppm) = (\text{Readings} \times V(mL) \times D\text{ilution}) / \, Mass\ (g) \quad (1)$$

where Reading is the value obtained by the devices, *V* is the total volume of the solution in which the analyte is found, Dilution is the number of times the sample can be diluted for the curve to be able to detect the absorbance value and has a default value of 1, and Mass is the amount of sample weighed at the beginning of the process.

The results obtained will be presented in a table format for critical evaluation and comparison of values presented in each device, together with the reference concentrations of each sample. The analytical curves will also be represented graphically, together with their regression coefficient for each one of them.

3. Results

This study revealed the efficiency of Fire Assay combined with modern analytical techniques, since the gold recovery rate is almost 100%, which justifies its use as an industry standard process for obtaining and quantifying precious metals. It is essential to analyze a potential exploration source and obtain reliable results in order to guarantee the quality and value of the area of interest.

Analyzing the objective of the work, which is the comparison between the two reading instruments, there are some considerations that indicate the best performance of the MP-AES, such as the detection limit of the calibration curve used. Table 2 below shows the calibration curves and their respective R^2 values. The results as shown in Tables 3 and 4 indicate that Standard 1, with the lowest gold concentration value among all analyzed, did not obtain an acceptable relative error for any of the three aliquots in the FAAS, since the calibration curve constructed for the instrument cannot detect samples below 0.5 ppm. Karlsson et al. (2015) highlights the better yield and accuracy of MP-AES in samples with lower concentrations.

Table 2: Results obtained in calibration curves of reading instruments

MP-AES			FAAS		
Method Concentration	Intensity	R^2	Method Concentration	Intensity	R^2
242.795 nm			Low curve		
0	0	0.9998	0	0.0004	0.9999
0.1	1,254.6		0.5	0.0116	
0.5	6,155.2		1	0.0236	
1	12,294		2	0.0474	
5	61,658		5	0.1150	
10	119,720		10	0.2259	
274.825 nm			High curve		
10	4,126	0.9998	0	0.0001	0,9997
100	42,920		10	0.1324	
300	122,450		20	0.2575	
500	207,580		30	0.38	

Source: (Authors,2022)

Another point to note is the ability of MP-AES to determine several chemical elements in just one run, using different wavelengths, while FAAS can quantify only one specific element per analysis. This characteristic of the MP-AES, as corroborated by Ozbek et al. (2019), gives prominent advantages to it, due to the lower cost per analysis, speed and simplicity. Table 3 shows the values already calculated from the samples in FAAS.

The MP-AES also excelled in the stability of the device in keeping the results stable with just one reading of the calibration curve during the process. During the experiment, the FAAS lost the calibration of the curve built in the middle of the quantification of the samples, causing the results shown to come out much below or above the predicted. A new calibration was performed, and the reading continued normally until the end.

Another data observed was the reading speed in each of the instruments. While the MP-AES operates in a fully automated way, the FAAS, as it does not have an automatic sampler, requires a trained analyst to read the analytical curve and the samples. The time spent to perform the quantification of all analytes was higher in FAAS.

Table 3: Results obtained in FAAS

Pattern	Reference Value (Ppm)	Calculated Value (Ppm)			Relative Error (%)			Coefficient Of Variation
		1	2	3	1	2	3	
1	0.0032	0.011	0.009	0.009	226.00%	189.90%	186.42%	5.95%
2	0.769	0.699	0.715	0.708	9.16%	6.97%	7.90%	0.97%
3	1.75	1.611	1.767	1.686	7.96%	0.98%	3.67%	3.79%
4	4.14	4.222	4.21	4.247	1.97%	1.69%	2.58%	0.37%
5	8.97	9.065	9.155	9.13	1.06%	2.06%	1.79%	0.42%
6	12.95	13.842	13.595	13.757	6.89%	4.98%	6.23%	0.75%
7	19.92	20.415	20.219	20.807	2.48%	1.50%	4.45%	1.19%
8	23.97	25.046	24.951	24.966	4.49%	4.09%	4.16%	0.17%
9	30.94	32.281	32.117	32.582	4.33%	3.80%	5.31%	0.60%
10	51.12	54.759	53.053	54.839	7.12%	3.78%	7.27%	1.52%

Source: (Authors,2022)

Table 4 shows the results obtained in the MP-AES.

Table 4: Results Obtained in MP-AES

Pattern	Reference Value (Ppm)	Calculated Value (Ppm)			Relative Error (%)			Coefficient Of Variation
		1	2	3	1	2	3	
1	0.0032	0.0033	0.0035	0,0033	1.10%	7.01%	3.00%	2.38%
2	0.769	0.673	0.708	0,684	12.51%	7.91%	11.10%	2.15%
3	1.75	1.57	1.684	1,657	10.30%	3.78%	5.34%	2.97%
4	4.14	4.033	3.994	4,263	2.59%	3.53%	2.97%	2.90%
5	8.97	9.013	8.983	9,08	0.48%	0.14%	1.23%	0.45%
6	12.95	13.261	13.012	13,429	2.40%	0.47%	3.70%	1.30%
7	19.92	19.843	19.945	20,109	0.38%	0.12%	0.95%	0.55%
8	23.97	23.575	23.596	23,613	1.65%	1.56%	1.49%	0.07%
9	30.94	30.821	30.501	30,794	0.38%	1.42%	0.47%	0.47%
10	51.12	51.984	50.082	51,778	1.69%	2.03%	1.29%	1.66%

Source: (Authors,2022)

The operating cost of each instrument is another factor to be considered. While the FAAS uses gases such as acetylene and nitrous oxide to feed the flame for atomizing the analytes, the MP-

AES uses nitrogen, from a generator fed by compressed air, to operate the plasma. Therefore, when compared, the operational and maintenance costs of the MP-AES are lower than those of the FAAS, as discussed by Teodoro et al. (2013), for not using flammable gases, a fact that also contributes to greater safety in the laboratory environment, a savings, estimated by company processes at approximately 10% for the presented experimental context in terms of materials and machinery costs.

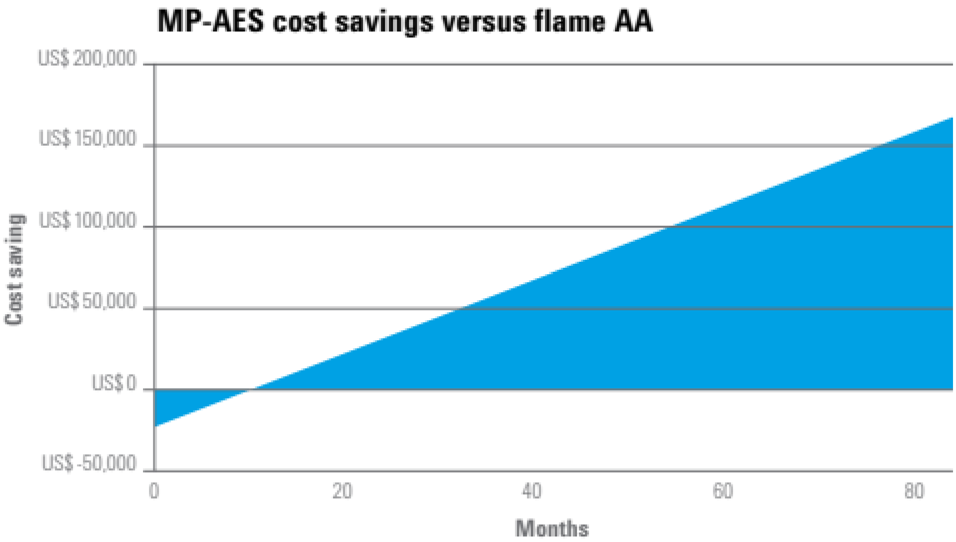
In terms of costs, we have two possible analyses: firstly, the estimate that the manufacturer presents, and secondly, the savings that were obtained in this experiment. The first analysis can be supported by the graph in Figure 3, where equipment manufacturer Agilent demonstrates the savings possible over months of using the AES MP

In terms of costs, we have two possible analyses: firstly, the estimate that the manufacturer presents, and secondly, the savings that were obtained in this experiment. The first analysis can be supported by the graph in Figure 3, where equipment manufacturer Agilent demonstrates the savings possible over months of using the MP AES. According to the manufacturer, the initial investment of approximately US$ 50,000 pays off in approximately 12-14 months, generating an increasing, and almost linear, savings, reaching more than US$ 150,000 in return. In agreement with Agilent Technologies (2016), such savings come from: "*No expensive acetylene and nitrous oxide gases, and no danger of flammable gas leaks; No need to plumb multiple gases into the laboratory, making it ideal for remote locations such as mine sites or environmental monitoring stations; No need to order, connect or replace cylinders, reducing your ongoing operating and servicing costs; No transport or manual cylinder handling risks, and no risk of frozen regulators in cold climates; No greenhouse gas emissions —the Agilent 4210 MP-AES has zero fuel-based carbon emissions*".

For the experiment carried out, which was carried out with the number of samples presented, a reference is taken of a company already active in the market in a period longer than the investment process of 12 to 14 months, which represents a presence in the period already of return (as shown in figure 3). In analysis together with those responsible for the company, they were allowed to explain some savings parameters for the experiment carried out, for example:

- An Acetylene cylinder costs BRL 1,600.00 reais, with 20 BAR and two cylinders are used per week for the quantity of samples that were used. However, the MP AES does not need to change cylinders as it only depends on compressed air and the nitrogen generator that is sold in the package.
- Hollow cathode lamps: from time to time (according utilization) they need to be replaced because of their lifespan (their price is between BRL 900.00 and 1,300.00 reais). The plasma generator torch of the MP AES, if handled and sanitized with care, has a durability that still cannot be estimated (it is so long).

Figure 3: MP-AES Savings (Agilent Evaluation)



Source: (Agilent Technologies, 2016)

In a numerical consideration of the values found (as described in tables 2 and 3), it can be seen that among the patterns evaluated, specifically in the analysis of relative error, GAAS obtained extremely high margins, reaching more than 200 times in patten 1 The coefficient of variation of this pattern was the highest found in the entire experimentation process, reaching 5.95% (more than double the highest coefficient of variation found in the MP-AES, which was 2.97%). In addition, the lowest coefficient of variation was obtained by the MP-AES with a rate of 0.07%.

4. Conclusion

Every analytical technique has strengths and weaknesses, and the Microwave Atomic Plasma Emission Spectrometer and the Flame Atomic Absorption Spectrometer are no exception to the rule. The study revealed the best performance of the first in the reading conditions established by the authors. Despite this, FAAS is still highly used by industry and laboratories for its ability to deliver analytical results with satisfactory speed and reliability.

The MP-AES stands out for its multi-element simultaneous reading capability, low operating cost, lower detection limit and greater safety as it does not use flammable gases. Another benefit of this method is that it is a compact instrument and takes up minimal space in the laboratory, making it ideal for small locations and places where the regular supply of flammable gases would be an obstacle. Despite so many advantages, special care must be taken with the granulometry of the solutions: samples with a high rate of total dissolved solids can easily damage the device.

The reading method by MP-AES, despite being new, has been gradually standing out and drawing the attention of academics in the area, who already consider it an acceptable alternative to commonly used techniques, such as FAAS itself. More studies can be done to discover possible interferences in multi-element analyzes to understand the full potential of such a method.

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