

Original article

Using ICP-OES, SEM and Polarography Techniques to Determination of Lead and Tin in Brass alloy

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ABSTRACT

Aims. The objective of this study was to analyses brass (Pb, Sn) and then make an evaluation between all the results obtained using different methods (ICP-OES, SEM and polarography) to see if these methods could obtain reliable results compared with the certified values for each element. **Methods.** Known sample of brass was analyzed to determine the concentration of elements (Pb and Sn), and three brass samples were collected from a shop. These samples were weighed (10 mg) and then dissolved in 1ml aqua regia solution (3:1 HCl and HNO₃ respectively): after 24hours the solutions were diluted by factor 100-200 dilution to prepare different concentration ranges. **Results.** In this study, it was found that, for each element of different brass samples, the calibration curves were very linear and the results obtained from this study using various methods are reproducible and have been repeated three or four times in a single lab validation. **Conclusion.** It can be concluded that the results of SEM were very close to compositions of each element when compared to standards. In addition, polarography method has given very good results for lead in unknown sample. Also, the tin result was very reliable; this result was not expected using different techniques, due to the small amount of tin compared with different method. The limits of detection are in the range of ppm for Pb and Sn elements for ICP-OES.

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INTRODUCTION

Many objects in our daily lives are made of alloys, which are explored to create new materials and enhance their properties. The most important copper alloy is brass. The copper-zinc alloy is known as "yellow" due to its yellow color. It is attractive, highly corrosion resistant, and simple to deal with. Additionally, brass is more durable than bronze, a copper-tin alloy [1-3].

In particular, brass is also made with the addition of lead; however, it is necessary to reduce the amount of lead in the material point of view of the adverse effects on the environment and humans [4]. The addition of small amounts of tin (1-6 wt%) and zinc (1-35 wt%) improve the susceptibility of the alloy of copper and has the advantage of producing sculptures that are harder, stronger and more corrosion resistant to oxidation than copper alone. They also lower the melting temperature required for fusion, but by weight, Zn is less efficient than Sn for creating liquid copper. Furthermore, the addition of a small amount of tin to a copper-zinc alloy greatly increases its resistance to dezincification, consequently alloy additions affect the colour of copper. For instance, increasing the amount of Sn makes patination easier [5].

The analysis of bronze and brass based on the bulk composition of the item is a fundamental tool for analysis and study of ancient archaeological finds. Bronze is generally 88% copper and 12% tin although there are different bronze alloys such as commercial bronze and Architectural bronze which contain 57% copper, 3% lead, and 40% zinc but, as they contain zinc, they could be described as brass alloys [6].

Many analytical methods can be used to determine trace metal in brass one of them ICP-OES which used for the analysis of a small sample of brasses made of up to eight elements in samples of 100 µg. They found accurate results were obtained by repeating the analysis with ICP-OES which involve much complex operating condition but the result of Lead and zinc were exposed to have spectral interference with a small amount of copper, and lead was known to have spectral interference with copper and zinc. Correction of lead was more significant at low concentrations [7-9].

Different methods reported for the characterizing of brass alloys dispersed with graphite such as a lead-free brass alloys. This used a powder metallurgy process which is used as a raw material with a mean practical size of 40 μm and was prepared using a Cu60-Zn40 brass ingot by water atomization without using any additional elements. Thermo gravimetric analysis (TG) was used to investigate the thermal behavior of the powder because of the change in the weight of the brass, and the heating range was 0.03 K/s in Ar gas atmosphere from room temperature up to 1273K. Spark plasma was also used with 30% machining speed graphite with 0.5 mass% and 83% UTS compared with leaded 80/20 brass it was found that the preparation of powder metallurgy affects the graphite particle contents and the process conditions [10].

In this method have been conducted an analysis of alloy fragments. The sample was reduced and dissolved in 25% aq HNO₃ for ICP and argon plasma and then a 1-m polychromator was used. After that, the sample was introduced into the system and modified with the installation of a cloud chamber, removable flashlight, and corrosion-resistant nebulizer. This new method has been used to analyze metals and standard reference materials, has been able to analyze very small volumes and is faster. However, this method when applied to the first detection limits was poorer, with the spray directed by a factor of about 62 compared to those with permanent methods of sample introduction [7].

As a result, several analytical techniques have been used to characterize the surface and body of the helmet and to determine the elemental composition of the metal mass of 62 modern sculptures in bronze. The sculptures in this study are largely a copper alloy made up of two main elements zinc and tin [11-13].

The objectives of this study was to analysis and determine the content of lead and tin by precise methods such as ICP-OES, SEM and polarography in brass alloys. Afterwards, a validation of the best technique for the purpose of this study will be carried out to see if we can find a reliable technique and compare these results with samples that were previously used for the calibration curve with known samples.

METHODS

Reagents

All reagents and chemicals used were of analytical reagent grade. High- purity concentrated Hydrochloric acid (HCl) 75%, Nitric acid (HNO₃) 25% was used without further purification to digest samples of brass. The element of stock solutions (Pb and Sn) used for calibration was prepared at 100 ppm.

Standard preparation in general

From 100 ppm stock solutions of Pb and Sn standard were prepared by placing different concentrations with a pipette into 100 ml voltametric flasks. The concentration of tin was prepared in the 100 ml voltametric flask and was made up with deionised water, whereas lead needs the addition of 1 ml of HCl before being made up with water to get better results. The instruments were run firstly with blanks then the standards and finally the brass solution.

Sample preparation and calibration

10 mg sample was prepared in a 10 ml polypropylene tube instead of glass, because it leads to different results if maintained over time in glass. If the solutions are left in the glass, the sample will stick in the wall of glass leading to the loss of the sample and the concentration being different. 1 ml of aqua regia rather than acid was added to 10 mg of brass sample which was in a conical tube because Sn is not very easily soluble. The tube was put in a stand pipe. Then, this tube left for 24 h for complete dilution. After dissolution, 3% aqua regia and ultra-Millipore water was added for further dilution, the mixture of the brass sample with further dilution was placed in the 100 ml voltametric flask.

More stock standard solutions were prepared from lead and tin in the following concentration, for lead (2.5, 5, 10, 15 and 20) ppm in 100 ml voltametric flask and for tin (50, 100, 200, 300 and 400) ppm in 50 ml voltametric flask and blank solution which was equipped by adding 1 ml of aqua regia in 100 ml voltametric flask, these concentrations were made up with water.

Sample Collection Unknown

Different samples from a collection of stores consisting of this ancient brass were investigated for this study. Each sample was weighed at 10 mg and placed in a 10 ml conical polypropylene tub and dissolved into a solution of 1.0 ml aqua regia (75 % HCl and 25 % HNO₃) and left for 24 hours for complete dissolution. After dissolution, samples were further diluted with 3 ml aqua regia and then diluted by a factor of 100 dilutions in order to be within the detection limit of the instrument, which was used to prepare diluted samples. The calibration curves were run using standards made from the stock solutions.

From the result there are problems associated with keeping samples in glass because this leads to different results if they are kept over time. We have tried to run them on different days, using the same solution and applying different methods. However, when the solutions were kept in plastic flasks the results were close to the result we obtained without keeping the solutions. This means that, if the solutions are left in glass, the sample will stick in the wall, which leads to loss of sample and then the concentration will be different.

RESULTS AND DISCUSSION

Meanwhile, calibration is required for quantitative analysis by comparing the measured values of standards with known concentrations, and so that the concentration of the samples can be determined. Therefore, the ICP-OES instrument calibration was performed before each run and two sets of standard solution were measured by ICP-OES before the test sample of the brass because they are known to produce a calibration curve that fits on the basis of repetitions when each concentration of each selection has been done. ICP-OES was used to generate standard curves to analyze the sensitivity of the method for each item and compare the intensities of individual emission lines against the concentration.

Calculation

After drawing the calibration curve the equation of this linear calibration curve was used to calculate the concentration in ppm, then that was used to calculate the weight percentage of each element to be analyzed, as shown in the following results, the known brass sample was analyzed by ICP-OES technique. To calculate the percentage of Lead using ICP-OES.

From the graph the equation is $Y = 106.51x + 42.477$ (Table 1)

When $y = 535.2$

$$535.2 = 106.51x + 42.477$$

$$X = 4.63 \text{ ppm} \times 10 = 46.3 \text{ } \mu\text{g} / 1000 = 0.0463 \text{ mg}$$

$$\% \text{ of Pb in brass sample} = \frac{0.0463}{9.86} \times 100 = 0.47\%$$

This was used to calculate the percentage in weight for both elements (Pb and Sn) in known and unknown samples.

Table 1. Values of Lead standards obtained by ICP-OES

Concentration of Pb standards (ppm)	Intensity Cts/S
0	31.92
2	263.7
4	465.2
6	694.2
8	899.1
10	1096
Brass sample	535.2

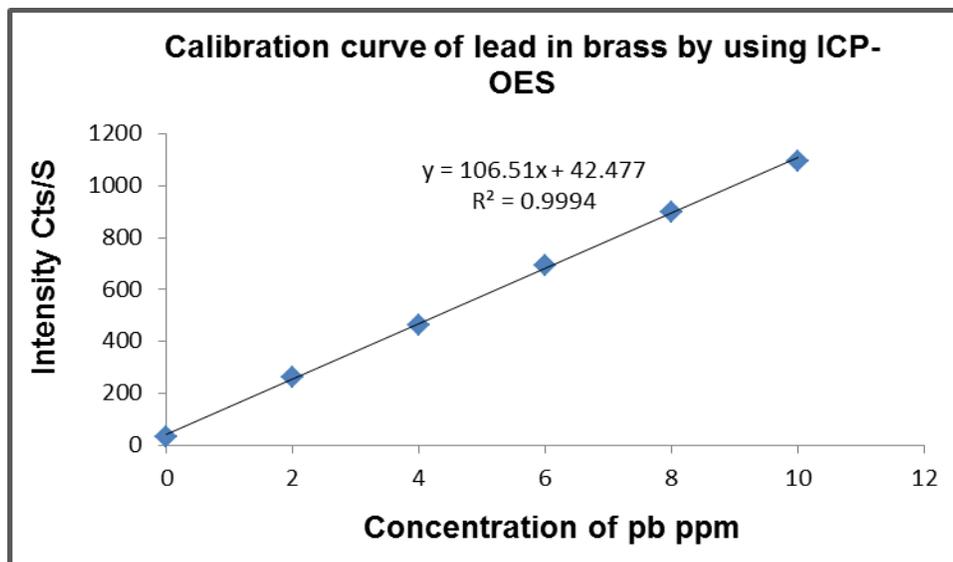


Fig 1. Plot of intensity against concentration by using ICP-OES.

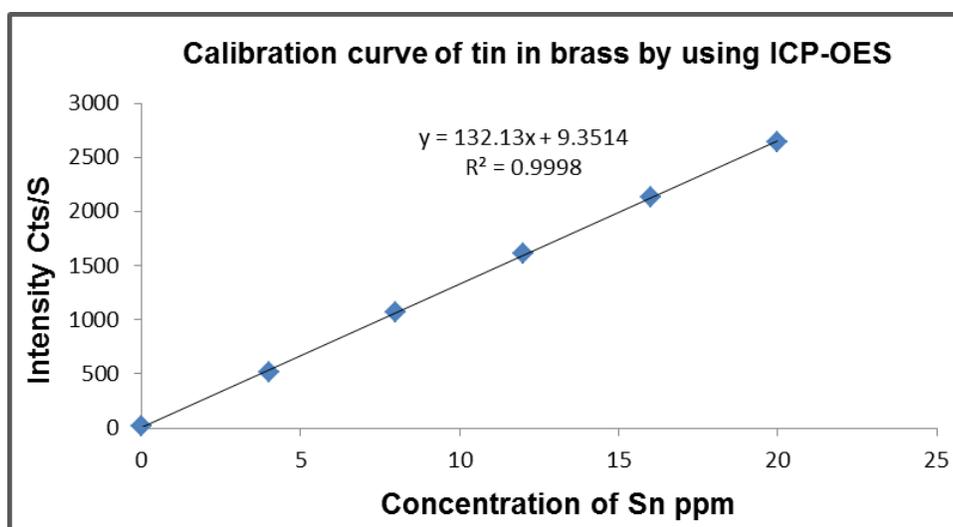


Fig 2. Plot of intensity against concentration by using ICP-OES

The experiments were performed by using external standards, a list of the 2 elements (Pb and Sn) in the known sample in this study were tested by ICP-OES and SEM techniques. A summary of these elements are given in Table 2 for this sample. All the calibration curves of standard solution for two elements were plotted using Excel, plotting the intensity against the concentration (ppm). The graphs we have obtained give a perfect linearity and correlation coefficient close to one.

Replicate analysis of the references and known sample were done under the same conditions but the result we obtained is not very reliable: each time we ran the sample the result for each of them is different when compared with expected standard results; for example, the results for known sample expected are Pb 0.47 % and Sn 0.65 % but the results obtained for each elements are Pb 0.35% and Sn 0.70 %. However, The ICP-OES method showed some errors, since the concentration of lead obtained (0.47%) was higher than the concentration in the certificate (0.35%).

Table 2. The results of (Pb and Sn) which obtained by two techniques in brass alloy comparing with its percentage from the certificate

Elements	Standard (%)	ICP-OES (%)	SEM Weight (%)	LOD by using ICP-OES
Pb	0.35	0.47	11.5	0.322
Sn	0.70	0.65	0.29	0.252

The SEM results obtained from the analysis of known brass samples are presented in the above table 3. It can be seen from the data in the spectrum that the analysis using SEM-EDX reported significantly different from the ICP-OES technique. It was found that the composition of the brass sample was very similar. In contrast, the overall composition displayed that the result we obtained is not very reliable, it is different when compared with expected standard results for all elements from SEM which were scanned from 700-800µm for Pb and Sn respectively. As mentioned earlier some problems may be encountered in analysis by SEM, for instance, cleaning the surface of the SEM is not enough, but the measurements were based on SEM results and standards.

Three samples (unknown) from a collection of store consisting of this ancient brass were investigated for this study. The results obtained from preliminary analysis of brass samples are presented. The experiments were performed by using external standards, a list of the 2 elements (Pb and Sn) in the unknown samples in this study were tested by ICP-OES. A summary of these elements are given in the Table 3. All the calibration curves of standard solution for all elements were plotted using Excel, plotting the intensity against the concentration (ppm). The graphs we have obtained give a perfect linearity and correlation coefficient close to one.

Table 3: The results of (Pb and Sn) which obtained by two techniques in brass alloy comparing with its percentage from the certificate

Sample description	High tensile Brass		Gunmetal		Phosphor bronze	
	Pb	Sn	Pb	Sn	Pb	Sn
Element						
Standard %	2.24	0.27	0.70	9.35	0.064	9.80
ICP-OES (%)	2.13	0.35	0.30	9.5	0.86	9.1
SEM Weight (%)	0.59	0.61	3.56	9.39	-	8.36
LOD by using ICP-OES	0.154	2.71	0.321	0.255	0.175	0.322

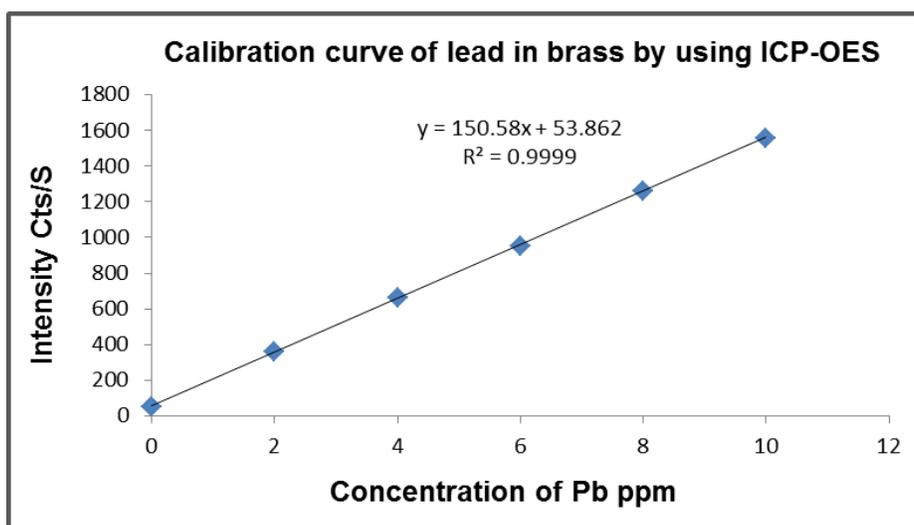


Fig 3. Plot of intensity against concentration by using ICP-OES

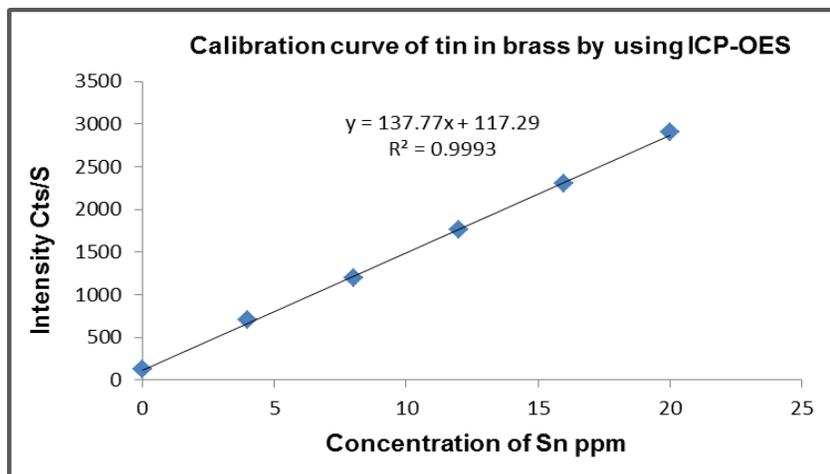


Fig 4: Plot of intensity against concentration by using ICP-OES

The results obtained from the analysis of all unknown samples can be compared in table 3. It was very difficult to decide on the best method to adopt for this investigation because the results have been obtained using different techniques. When compared with the standards, the results were not very reliable but it can be said that the results obtained from SEM were very close to the standards compositions. The result of HTB sample indicate that lead has the same amount of (2.13%) as in the certificate using ICP-OES. Moreover, the amount of tin found by using the same method is larger (0.35) when it should be (0.27). Nevertheless, lead result which obtained by using polarography (2.21%) was nearly close to the expect result (2.24%) as shown in Table 4, that mean polarography the best method to analysis lead in brass sample compared with other techniques ICP-OES and SEM. Table 4 and Figure 5 shows the calibration curve and calculation concentration of lead by using polarography technique.

Table 4: Values of lead standards obtained by polarography

Concentration of Pb standards (ppm)	Peak height
0	-8.98E-10
2	-8.27E-08
6	-2.18E-07
8	-2.76E-07
10	3.65E-07
Brass sample dilute (1:50)	1.465E-07

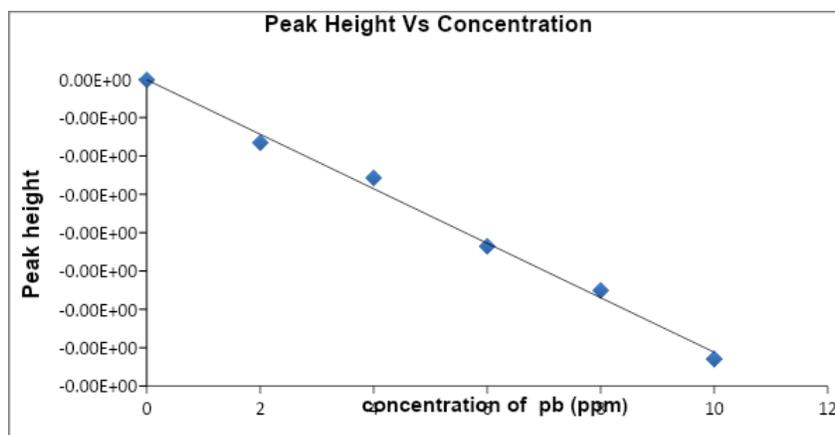


Fig 5. Plot of intensity against concentration by using polarography.

CONCLUSION

This study has investigated the analysis of brass samples, all the methods used have given results that are not very close to standards. Although the results are not very close to the standards, the calibration curve for all the measurements using different instruments was good (linear). So it was very difficult to decide the best technique to be adopted for this research which was the main aim of this study because the results have been obtained using different techniques. By comparison with the standards, the results were not very dependable but it can be said that the results obtained from SEM were very close to compositions of each element when compared to standards. In addition, polarography method has given very good results for lead in unknown sample. Eventually, a number of significant limitations should be considered. Firstly, the sampling methods and errors related to them as mentioned previously, as the transfer of the sample, could result in the loss of the sample, and issues with the preparation of the solution should be taken into account. Secondly, the precision and reproducibility of each technique is located within the measurement standards; when certified values of the samples were carried out using SEM, surface cleaning was found to be a problem of this method.

Disclaimer

The article has not been previously presented or published, and is not part of a thesis project.

Conflict of Interest

There are no financial, personal, or professional conflicts of interest to declare.

REFERENCES

1. Fabre P, Reynes O. Determination of Copper and Zinc in Brass: Two Basic Methods. *Journal of Chemical Education*, American Chemical Society, Division of Chemical Education. 2010;87: 836-837.
2. Yilmaz Atay H, Uslu G, Kahmaz Y, Atay O. *IOP Conf. Ser.: Mater. Sci Eng.* (2020);726.
3. Chang T, Herting G, Goidanich S, Amaya S, Arenas J, Le Bozec N, Jin Y, Leygraf C, Wallinder I. The role of Sn on the long-term atmospheric corrosion of binary Cu0Sn bronze alloys in architecture. *Corros. Sci.* 2019;149: 54-67.
4. Marcus L, Schnepf Y. A Compositional study of modern bronze sculptures. *Anal Bioanal Chem.* 2009;395: 171-184.
5. Lyon S. Corrosion of Tin and its Alloys. *Material Science and Material Engineering.* (2010), 3: 2068-2077.
6. Brian, K. 1996. *Copper, Silver and Gold.* Reed Library, Australia.
7. Carpenter R, Central Res E. Analysis of casework-sized alloy fragments by inductively coupled plasma-optical emission spectrometry(ICP-OES) using discrete nebulization. *Forensic Science International.* 1985;27:165-170.
8. Trampuz Z, Drglin T. ICP-AES comparative study of some late bronze age hoards. *Nuclear Instruments and Methods in Physics Research.* 2005;239:44-50.
9. Pernicka E. Instrumentelle multi-elementanalyse archaologischerr kupfer and bronze artefact. *Ein Methodenvergleich Jahrb, RGZM.* 1984;31: 517.
10. Imai H, Kosaka Y, Kojima A, Li S, Kondoh K, Umeda J, Atsumi H. Characteristics and machinability of lead – free P/M Cu60-Zn40 brass alloys dispersed with graphite. *J Powder Technology.* (2010), 198: 417-442.
11. Pantos E, Kockelmann W, Chapon L. Neutron and X-ray characterization of the metallurgical properties of a 7th century BC Corinthian-type bronze helmet. *Nuclear Instruments and Methods in Physics Research.* (2005) 239 :16-26
12. Zannat T, Ahamed M. J. *Eur. Chem.* 2015;6(2):141-150.
13. Ahmed J, Islam M, Aziz S. *Chem Sci Inter J.* 2019;26(2):1-19.