تحليل النحاس والزنك في سبيكة النحاس باستخدام تقنيات ICP-OES, AAS, SEM

د. مـروة مصطفي محمد أبورويص - كلية هندسة الموارد الطبيعية العجيلات
جامعة الزاوية.
د. هناء أحمد سيف النصر بن حمد – كلية العلوم- جامعة عمر المختار

الملخص :

الهــــدف من هذه الدراسة هو تحليل سبائك النحاس وإجـــــراء تقييم معملي واحد لجميع التقنيات لمعرفة ما إذا كانت هـــذه الطرق يمكن أن تحصل على نتائج موثوقة مقارنة بالقيم المعتمدة لكل عنصر.

تم تحليل عينات من سبائك النحاس الأصفر لتحديد تركيز العناصر مثل النحاس والزنك. وتم إذابة 10 ملغ من العينة في 1 مل من (aqua regia) (3 حمض الهيدروكلوريك : 1 حمض النيتريك) وتركها لمدة 24 ساعة حتى الذوبان الكامل ، ثم نقلها إلى دورق حجمي 100 مل ، ويتكون من Millipore H_2O عالي النقاوة لإنتاج أنواع مختلفة من التركيزات.

من بين النتائج المتحصل عليها منحنيات المعايرة لكل عنصر من عناصر العينة النحاسية خطية للغاية ($R_2 = 0.999$) باستخدام تقنيات مختلفة.، بالإضافة إلى ذلك ، يمكن أن تعطي تقنية ICP-OES نتيجة أكثر موثوقية ودقة من الطرق الأخرى

Analysis of Cu and Zn in brass alloy by using ICP-OES, AAS, SEM techniques

Marwa Mustafa Aborways
Department of Petroleum Engineering, College of Natural Resources, Zawia University
E-mail: m.aborways@zu.edu.ly

Abstract

The objective of this study was to analyze brass alloy and perform a single laboratory evaluation of all techniques to see if these methods can obtain reliable results compared to the certified values for each element. Samples of brass alloy were analyzed to determine the concentration of elements such as Cu and Zn. Sample was weighted (10 mg) and then was dissolved in 1 ml of aqua regia (3 HCl: 1 HNO_3) and left for 24 hours until complete dissolution then transferred into a 100 ml voltumetric flask and made up with ultrapure Millipore H_2O to produce different types of concentrations. Clearly, has been found that the calibration curves for each element of brass sample is extremely linear ($R_2 = 0.999$) by using different techniques. In addition, the ICP-OES can give a more reliable result than other methods.

Keywords: *brass, copper, zinc, ICP-OES, AAS, SEM.*

Introduction:

Cu-Zn alloy (brass) is widely used as an industrial because of its excellent characteristics such as high corrosion resistance and non-magnetism. In addition, brass is relatively resistant to stains and is often used for decorative purposes. By far the best-known composition used has 30% by weight of zinc and is called Cartridge brass, which is best known for its applications as door knobs, bullet cartridge, and tubes, decorative accents in homes, musical instruments and ornaments [1-4]. Copper and Zinc are usually found together in nature, so it is necessary to measure them in the presence of each other. Copper is an important element for human life, with a suggested daily dose of about 2 mg and toxic only in high doses > 15 mg per day, the taste and effects of corrosion. The permissible limits of Cu^{+2} are equal to 2 mg/L in the European Union as well as Zinc has a wide range of application [5][6].

On the whole, brass and bronze are alloys of copper. They are solid solutions or mixtures of copper with another metal. The main difference between brass and bronze is that brass is composed mainly of Copper and Zinc while bronze is mainly Copper and Tin [7]. Brass has a yellow colour, a little like gold. It occurred in prehistoric times, long before zinc was discovered, by the fusion of Copper with calamine, a Zinc ore. The Zinc content of brass varies from 5 to 45 per cent, creating a wide range of metals, each with unique characteristics [2]. The determination of traces of Zinc and Copper is important in metallurgy and environmental analytical chemistry, and there is a growing need for procedures with high sensitivity and selectivity, as these elements play an important role in the fields of biological science, industrial chemistry and medicine. As a result, several methods developed and introduced to analyze bronze and brass. [8].

Many methods for its determination have been described in literature, such as ICP-OES technique was used to determine the composition of these modern bronzes through samples which they collected from the art. Two sets of data were observed which including high Zinc brass and low Zinc bronze [9]. In fact, a long time ago foundries very secretive about the alloys (solutions and coatings) that they used, to prevent other smelters from producing a superior product, suggesting that the composition of the alloy might be enough to recognize the origin of a sculpture from its alloy.[10]

Atomic absorption spectroscopy (AAS) is an elemental analysis technique which is used to determine the presence of metals such as Fe, Cu, Al, Pb, Ca, Zn, Cd in liquid samples. Also, it is one of the most important instrumental methods for analyzing metals and some metalloids, because it can be possible to determine the concentrations of 62 different metals. The basis of atomic absorption spectroscopy is the absorption of discrete wavelengths of light by ground state, gas phase free atoms. Free atoms in the gas phase are formed from the sample by an atomizer at high temperature. In addition, AAS is used routinely to determine the ppb and ppm concentration of most metals.[11][12].

When objects and samples need to be examined, but are too small for the resolution range of the human eye, microscopes are normally used, and this field of scientific technology is known as microscopy, which is divided into three branches: scanning probe, electron and optical microscopy. Therefore, an optical microscope is made up of a support, sample stage, lighting equipment that is appropriate, and a single lens and attachments or a series of lenses and equipment for imaging. Recent technological enhancements have led to the development of the digital microscope, which involves the use of a charged coupled device (CCD) camera that can focus on the sample. Therefore, as a computer screen is used to display the image, microscopy eyepieces are not required [13] [14].

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The aim of this study was to analyze brass samples and then compare the results obtained from various methods such as ICP-OES, AAS AND SEM. After that, a validation of the best method for the purpose of this study will be carried out to see whether we can obtain a reliable result from the method and compare these results with those samples that have been previously used for the calibration curve as known samples. These will then be compared with the composition of each element, such as copper and zinc from the unknown samples.

Material and Methods:

All reagents and chemicals used were of analytical reagent grade. The glassware was washed with deionized water and dried. Elements of the stock solutions (Cu and Zn) were prepared at 100 ppm. Working solutions were obtained by diluting the stock solution with deionized water. Aqua regia (75% v/v HCl), (25% v/v HNO_3) was used without further purification to digest samples of brass.

Sample Preparation and Calibration:

A calibration is necessary for quantitative analysis by comparing the measured values of standards with the known concentrations; then the concentration of the samples can be determined. The calibration of the ICP-OES instrument was carried out before each run and two sets of ICP-OES standards solutions were measured before testing the unknown bronze and brass samples to produce a best-fit calibration curve based on three replications at each concentration for each selected element. One set with Cu and Zn in 3% v/v HNO_3 1000 ppm of each stock solution of Cu and Zn. 50 ppm was prepared by mixing 5 ml of each standard solution with 2 ml of nitric acid concentration diluted with deionized water to reach 100 ml in a volumetric flask ; seven standards solutions were prepared with the following concentrations (10 , 5 , 1 ppm, and 500, 100 , 50 , 10 ppb) and blank acid , which consisted of 3%(v/v) as a background subtraction .ICP-OES was used to generate calibration curves, to look at the sensitivity of the method to each element and compare between the intensities of each emission lines against the concentration.

After all the calibration curves for the ICP-OES standard were generated, the known sample (high tensile brass) was analyzed. Sample was weighed (measuring on average 10 mg) and placed in conical 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.
- 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 voltumetric flask.
- The sample was shaken to assure homogeneity of the solution.
- Five standards from this solution were prepared (0.1, 0.2, 0.5, 0.7 and 1) ppm for a set of standards (Cu and Zn).
- After that, other standards for (Cu, Zn) were prepared to the following concentration (2, 4, 6, 8 ppm and 10, 20, 30, 40 ppb) to obtained better results.
- These concentrations were made up with water.

Standard addition method (Cu and Zn).

24 hours after the sample solutions were prepared as usual, the solutions of the sample were diluted in water, this solution was made up to a volume of 100 ml.

A new solution of 1/50 dilution of sample was prepared from this solution. 1 ml of the first solution was without adding any standard, put into a 50 ml voltumetric flask with 3 ml aqua regia then made up with water.

The second one was prepared by taking 1/50 into voltumetric flask, adding 1 ml (Cu 100 ppm) and 1 ml (Zn 100 ppm). This solution was made up with water that gives 2 ppm concentration and 4 ppm was prepared by adding 2 ml from 100 ppm (Cu, Zn) into the 50 ml voltumetric flask. 6 ppm and 8 ppm were made in the same way by adding 3 ml and 4 ml from 100 ppm copper and zinc into a 50 ml voltumitric flask. These solutions which had been prepared were made up with water. After being prepared all these standards were run on ICP-OES to determine each element in the brass from low concentration to high concentration.

Sample collection unknown:

Three samples from a collection of stores consisting of these 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 % HNO_3) 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

Result and discussion:

At the first, known and unknown brass samples were analyzed by ICP-OES, ASS, and SEM to choose the best technique. ICP-OES analysis gives good agreements with the concentrations of Copper and Zinc in the certificate. The concentration of Copper obtained (53.3%) and Zinc (35%) whilst in certificate they were (58.5%) and (35%) respectively as shown in **Table 1**. This means that the ICP-OES is very accurate in determining these elements. Also, AAS has given good results for Cu and Zn. Comparing the results of the two methods (ICP-OES, AAS), it appears that the ICP-OES give the best results when compared to AAS. Whilst the results of determination Cu in unknown brass sample by using ICP-OES and AAS are similar, especially for the copper percentage as shown in **Table 2**. As can be seen, the brass alloy results indicate that the concentration of Copper is the highest percentage, whitest for the Zinc was found a small amount by ICP-OES. **Table 2** shown that the amount of Zinc calculated by using AAS (39.1%) is considered bigger than the normal percentage of Zinc in brass alloy, while the amount of Zinc found by using ICP-OES (37.7%) was nearly the same amount. The analysis by AAS was not very reliable when compared with the composition of each element of the standards, even though the calibration curve for each element was presented in linear curves in previous AAS results. This method was used to analyze brass for two elements which are Copper and Zinc.

Element s	Standard (%)	ICP-OES (%)	AAS (%)	SEM Weight (%)	LOD by using AAS	LOD by using ICP-OES
Cu	**58.5**	**58.3**	**58.4**	**52.02**	**0.309**	**0.174**
Zn	**35.8**	**35.7**	**35.8**	**34.12**	**0.0292**	**0.0329**

Table 1: The results of (Cu and Zn) obtained by three techniques on the brass alloy comparing with its percentage from the certificate.

Elements	Standard (%)	ICP-OES (%)	AAS(%)	SEM Weight (%)	LOD by using AAS	LOD by using ICP-OES
Cu	**58.7**	**57.5**	**57.6**	**46.56**	**0.359**	**0.487**
Zn	**38.5**	**37.7**	**39.1**	**39.74**	**0.0143**	**0.05**

Table 2: The results of (Cu and Zn) which obtained by three techniques in brass alloy comparing with its percentage from the certificate.

By comparing these two methods, ICP-OES proves to be less time-consuming, this is because the ICP-OES elemental analysis can be performed more quantitatively in a short period of 1 minute with a little more of the solution (0.5-1.0 ml). ICP-OES also has wide linear dynamic ranges, good sensitivity, and limited spectral and chemical interferences, and low detection limits (for most elements are in the range of ppm). AAS is not very sensitive and it only can run one element at a time (time-consuming), also we need the follow- cathode lamp for each element.

All the calibration curves of standard solution for Cu and Zn 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 with both ICP-OES and AAS techniques (**fig**1-4)

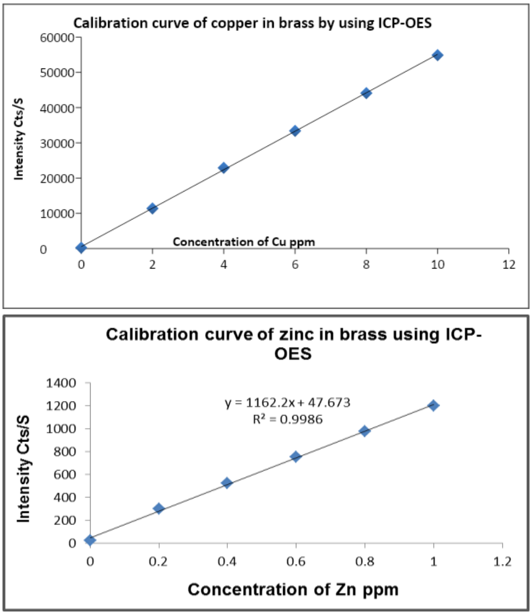

Fig1: Plot of intensity against concentration for ICP-OES.

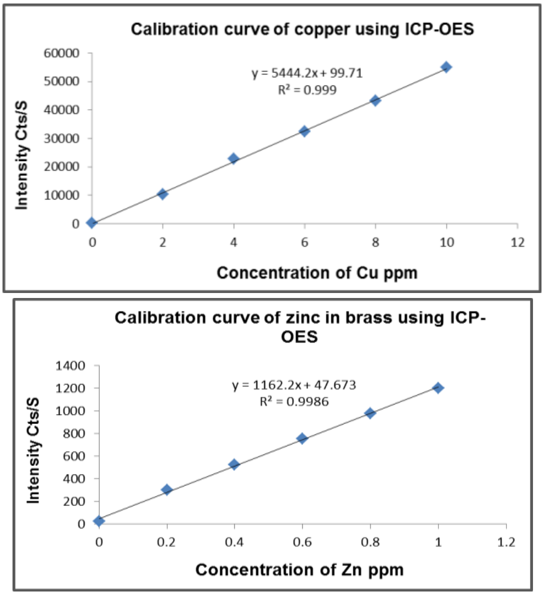

Fig2: Plot of intensity against concentration by using ICP-OES.

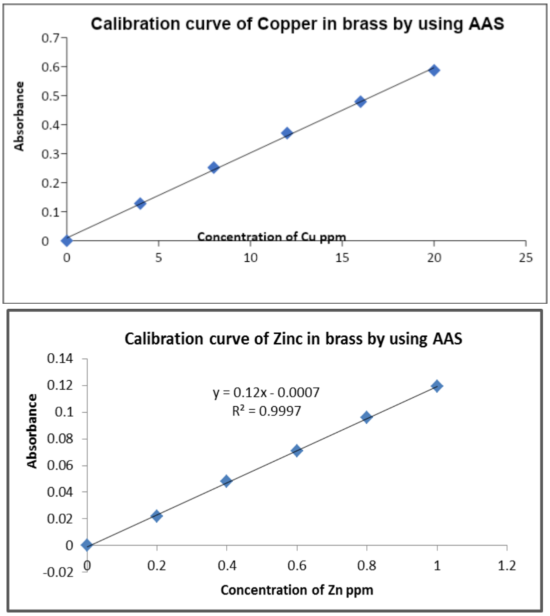

Fig3: Plot of absorption against concentration by using AAS.

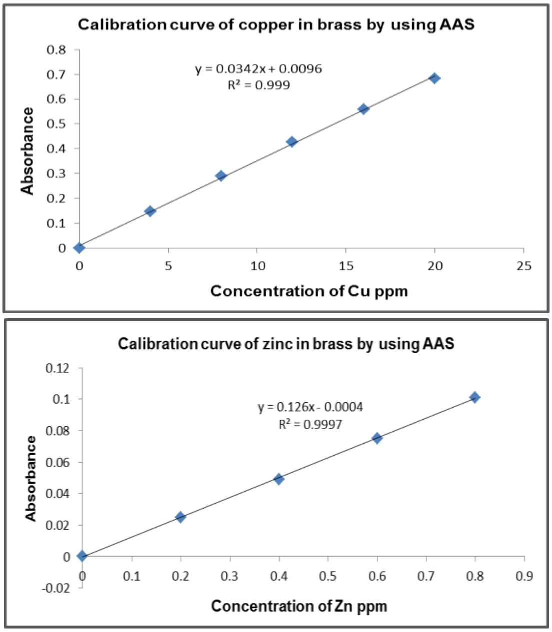

Fig 4: Plot of absorption against concentration by using AAS.

The SEM results obtained from the analysis of known brass samples are presented in **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 and AAS results. 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 two elements from SEM which were scanned from 700-800µm for Cu. However, the only element which was anywhere close to the CRMs was zinc, which obtained results of (34.12%) while the certificate gave (35.8%).

Sample	**% Standards Cu**	**% Cu**	**% Standards Zn**	**% Zn**
known brass sample	**58.5**	**52.02**	**35.8**	**34.12**
Unknown brass sample	**58.7**	**46.56**	**38.5**	**39.74**

Table 3: Results of known and unknown brass sample using SEM

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 (see figures 5 and 6). The results were not very good using the SEM method because the result obtained for Zn was too high compared with standards reference materials. In addition, the Copper result obtained was very low 46.56% compared with the expected results (58.7%).

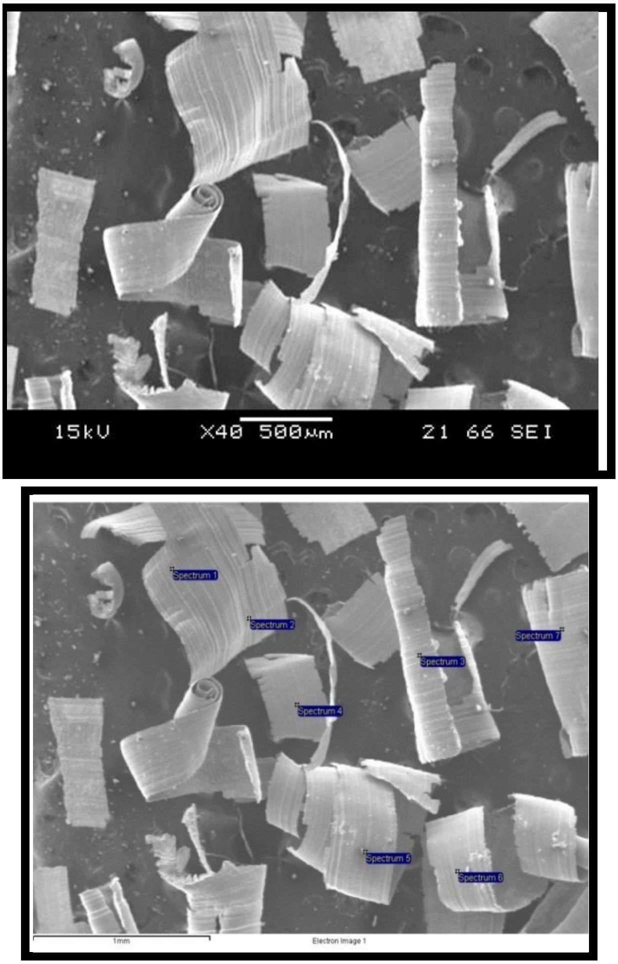

Fig5 :SEM image and SEM electronic image for known sample.

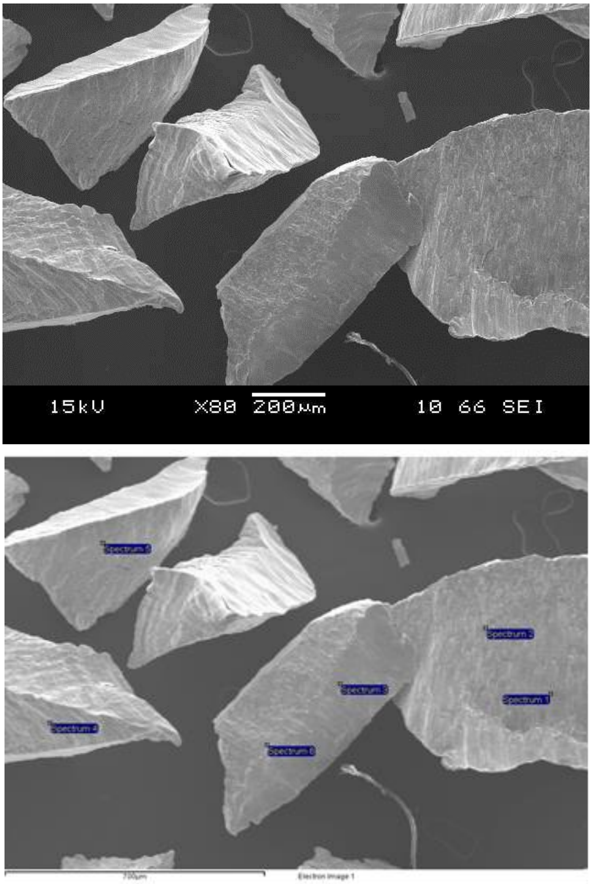

Fig6: SEM image and SEM electronic image for unknown sample.

Conclusion:

This work shows that ICP-OES and SEM techniques are more accurate and faster than AAS in known and unknown samples for measuring trace elements of (Cu, Zn) and their concentration in brass alloy. Although AAS has similar features to ICP-OES, when using ICP-OES there are greater benefits, such as limited chemical and spectral interferences, good sensitivity, wide linear dynamic ranges, and it also offers faster completion and improved detection limits. Whereas, one of the most important results obtained from this study is that the curves were very linear for both elements. In addition, the analysis of unknown samples showed that all samples have been described as a standard in brass, in comparison with samples from the standards.

References:

[1]-Mitic. S. S.; Micic. R. J.; Simonovic. R. M (2009). Determination of traces of copper (II) by spectrophotometer. Food Chemistry, 117. pp. 461–465.

[2] - Fabre, P., Reynes, O. (2010). Determination of Copper and Zinc in Brass: Two Basic Methods. Journal of Chemical Education, American Chemical Society, Division of Chemical Education, 87 (8), pp. 836-837.

[3] -H Yilmaz Atay, G Uslu, Y Kahmaz and O Atay. (2020). IOP Conf.Ser.: Mater. Sci.Eng.

[4]- Okayasu, M., Muranaga, T., Endo, A. (2017). Journal of Science: Advanced Materials and Devices, 2. PP. 128-139.

[5]- Charles W.M Bodar, Marja E.J. Pronk, Dick T.H.M. Sijm. (2005). The European Union Risk Assessment on Zinc and Zinc Compounds: The Process and the Facts. Integr Environ Assess Manag, 1. pp. 301-319.

[6]- M. Ghaedi, K. Mortazavi, M. Montazeroohori, A. Shokrollahi, M. Soylak. (2013). Materials Science and Engineering, 33 .pp. 2338-2344.

[7]- Arvand, M.; Abolghasemi, S.; Zanjanchi, M.A. (2007). Simultaneous determination of zinc and copper (II) with 1-(2-pyridylazo) 2-naphthol in micellar media by spectrophotometric H-point standard addition method. *Analytical Chemistry*, 62 (4), pp. 342-347.

[8]- Brian, K. (1996) *Copper, Silver and Gold*. Reed Library, Australia.

[9]- Marcus, L. Young and Suzanne Schnepp. (2009). A compositional study of modern bronze sculptures. *Anal Bioanal Chem*, 395, pp. 171-184.

[10]- Scott, D. “Copper and bronze in art” the Getty Conservation Institute Los Angeles. 2002.

[11]- Maldonado. J. “Analytical Chemistry for Technicians” (3th Ed). CRC Press, 2003.

[12]- Robinson, J.; Skelly Frame, E.; Frame ll, G. Undergraduate instrumental analysis. 2005.

[13]- Skoog, Douglas A.; Holler, F. James; West, Donald M.(1997). Fundamentals of *Analytical Chemistry*. 7th edition. Saunders College Publishing.

[14]- Lemmer, P. et al. (2008). Light Microscopy with Single Molecule Resolution at the Nanoscale: Applied Physics B, 93, pp. 1-12.