



(MINI-REVIEW ARTICLE)



Comparative study of spark-optical emission spectroscopy and x-ray fluorescence spectroscopy for quantitative analysis of ferrous and non-ferrous alloys

Sumaira Nosheen *, Muhammad Irfan, Muhammad Nouman, Farzana Habib, Badaruddin Soomro, Bilal Waseem, and Mubashar Akram

Pakistan Institute of Technology for Minerals & Advanced Engineering Materials (PITMAEM), PCSIR Labs Complex Ferozpur Road Lahore, Pakistan.

Publication history: Received on 10 December 2020; revised on 20 December 2020; accepted on 22 December 2020

Article DOI: <https://doi.org/10.30574/ijrsra.2020.1.2.0038>

Abstract

Electrical spark-optical emission spectroscopy (OES) has been used for over 50 years for the direct analysis of alloys in the steel industry. This method has undergone continual improvement over time, but conventional OES can barely reach the new specification limits required for some critical steel alloys. As part of a continuous improvement process, instrument manufacturers, academic and industrial researchers are now showing a particular interest for x-ray spectroscopy (XRF) as an alternate and/or complementary approach for the analysis of steel alloys, mainly precious metals. In this work, by using the same optical mounting (i.e. same spectrometer model with the same spectral lines), we have directly compared the analytical performances of these two sources. By comparing the calculated concentrations obtained with these two sources using the same samples and the same standards, we show that in general the two sources give comparable quantitative results for major, minor and trace elements. The precision obtained with XRF is improved by a factor of two when compared to traditional spark Optical Emission Spectrometer. The results obtained in this work establish OES as a potential method for the quantitative analysis of steel alloys in different industries.

Keywords: Spectroscopy, Emission Spectrometer; Xray Fluorescence Spectrometer; Metallic Alloys, Precious Metals

1. Introduction

In research and development, the word completed is not frequently used and supposed that there is requirement for research always and commonly it is said to be a dead-end street. So, a question may be raised: Is it still possible, necessary and beneficial to perform research in fields like atomic emission spectrometry? In contrast to what non-analysts think, research cannot be confined to the use of an analytical method, as erudite as it might be. It is also analogous with computers meaning the usage of complex software does not mean that we are computerists. [1]

One of the simplest questions that an analyst can query about the chemical characterization of a sample is, 'which element are present and at what concentrations?' As there are 92 elements and millions of different molecules present in nature, distinguishing among the elements is a much easier task than segregating among molecules. However, the elemental composition of the sample is often an important part of the information required to assess the properties [2]

The most commonly employed techniques for the elemental analysis are based on spectroscopy. As cleared from the name, the technique employs electromagnetic radiations (light) that is absorbed or emitted by the atom of sample material. In this way progressive information of respective material can be attained both in terms of quality and quantity. [3] Optical emission spectroscopy using arc and spark excitation (Arc Spark OES) is the preferred method

* Corresponding author: Sumaira Nosheen

Pakistan Institute of Technology for Minerals & Advanced Engineering Materials (PITMAEM), PCSIR Labs Complex Ferozpur Road Lahore, Pakistan.

for trace metal analysis to determine the chemical composition of metallic samples. This process is widely used in the metal making industries, including primary producers, foundries, die casters and manufacturing. Due to its rapid analysis time and inherent accuracy, arc spark optical emission spectroscopy systems are most effective in controlling the processing of alloys. Arc spark spectrometers can be used for many aspects of the production cycle including incoming inspection of materials, metal processing, quality control of semi-finished and finished goods and many other applications where a chemical composition of the metallic material is required. However, there are some shortcomings or limitations of the spark spectrometers that the technique is based on destructing sample surface making it non suitable for precious metals [4]. Precious metals can be measured by various analytical procedures including gravimetric analysis, titration, spectrometry, inductively coupled plasma-optical emission spectrometry (ICP) and X-Ray Fluorescence Spectrometers (XRF) [5-7].

In recent years the need for fast determination of precious alloys composition stimulated the proposals of different alternative techniques for caratage determination, among which the X-Ray fluorescence spectrometers are worth mentioning [8]. In this paper, both OES and XRF techniques will be compared on the basis of principle and applications with respect to ferrous and non-ferrous alloys.

2. Description of Emission Spectra in Spark Emission Spectrometer

Emission spectra were first utilized in analytical chemistry as they were simpler to detect than absorption spectra. Flames, arcs, and sparks are all classical radiation sources. The spectra emitted from the sample due to provision of high energy in form of high voltage arc/spark is measured with the aid of optical system inside the chamber. The lay out of the optics is designed in such a way to split the radiations in single beam before entering detectors i.e. photomultiplier tubes. The recommended unit of these wavelength is nanometer. Other units including Angstrom and microns are also employed in some cases. The range of the spectra is between 200-800 nm for emission spectrometer. The quantity of radiations emitted is used to calculate the percentage concentration of any element in the base metal.

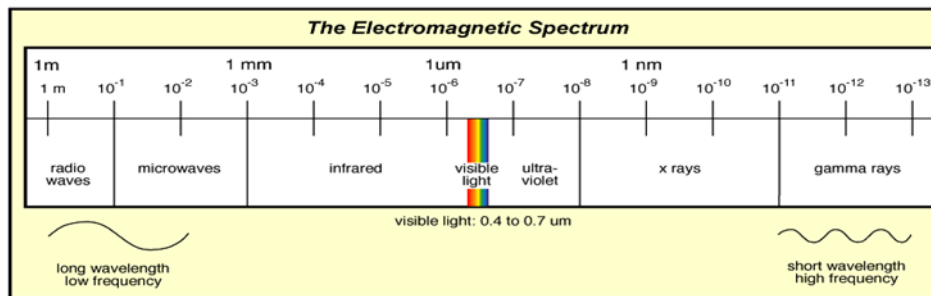


Figure 1 Electromagnetic spectra [9]

2.1 Entrance slit and Gratings

The entrance slit selects the part of radiation emitted by the sample which will join the grating. It is 0.02 nm. wide and 6 mm. high. Resolving power of the instrument, which should be theoretically equal to the product of the total number of grating lines and the diffraction order, practically is less than this value because it is not a infinitely narrow slit, but it has a finite width. The narrower the slit, the smaller the background. But it is a nonsense adopting infinitesimal width slits, because of the diffraction caused by the slit itself. Moreover if the entrance slit is too much narrow, continuous adjustments will be necessary to keep it aligned with the exit slits. Dispersion, that is separation of radiation in its monochromatic components, is made by a concave grating. The grating is a dispersive means characterized by very thin and equally-spaced lines engraved on a reflective surface. If the slit width and the distance between the lines have the same size order as incident radiation wavelength, the grating gives rise to dispersion, that is separation of radiation in monochromatic components. Principle quantities which characterize optic system are dispersion and resolving power. Dispersion, or better, reciprocal linear dispersion D , gives rise to the difference, usually expressed in \AA , between wavelength of two spectral lines which appear 1mm separated. Then lower dispersion is (in absolute value), easier identification and analysis of spectral lines. As a consequence, a better dispersive power allows us to cover a more limited spectral range (because of the dimension of the instruments) in comparison with the spectral range analyzed by a worse dispersion grating [10].

2.2 Exit Slits

Every monochromatic image of the entrance slit is sharply reproduced on Rowland circle. These are consisted of small photoengraved plates set on the circle. Their function is isolating spectral lines belonging to the elements selected for analysis allowing photomultipliers, situated immediately behind, to receive light coming out through the slits. Photomultipliers are put just behind the slits, if there is room enough, otherwise these are set elsewhere and radiation join them by a mirrors system. Exit slits are 0.06 -0.09 mm wide, that is higher than entrance slit, to allow little displacements of the spectrum without compromising radiation collecting. Mobile exit slits have been almost completely abandoned for more than one reason, among which thermic and optic instability and their high cost. Fixed photoengraved exit slits, on the contrary, have high stability and you can dispose as many as you need, depending on how many elements you want to analyze.

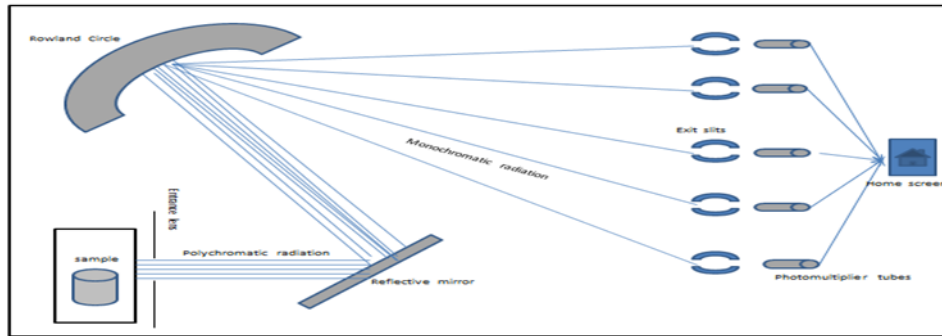


Figure 2 Schematic View of Optical Emission Spectrometer

3. X-ray fluorescence (XRF) spectrometry

Atomic fluorescence in flames was first studied by Nichols and Howes. They described the fluorescence of Ca, Sr, Ba, Li, and Na in a Bunsen flame in 1923. The first analytical atomic fluorescence spectrometer based on the studies of Bagder and Alkemade, was constructed by Winefordner and his co-workers in 1964. X-ray fluorescence (XRF) is a technique based on the effect that high energetic X-radiation excites at a specimen of an elemental mixture lower energetic X-lines specific for the present elements. The source that provides photons of sufficient energy to carry this out is termed as primary radiation. It is, most times, an X-ray tube in which electrons are accelerated from the cathode to the anode by a high voltage. High-energy quantum radiations are generated by interaction with the anode material. These radiations are led to the sample, in which the interaction generates a second X-ray beam, called secondary radiation, that is detected and conveniently quantified. Each element emits its unique characteristic secondary X-rays, the energy of which is related to the analyte concentration, the sample matrix, and excitation and detection conditions [11]. The XRF technique has many advantages; it is fast, accurate, non-destructive and has a limit of detection in the range of few parts per million (ppm) of most elements. For these reasons, the XRF analysis method is widely used in many fields such as metallurgy industry, geology and mineralogy, food industry and environmental management. The analysis of steel is useful for various purposes, such as the inspection of raw materials, intermediate product and end products, process control in iron, steel manufacturing and quality control. The sample preparation for XRF is relatively simple that require less time consumption and effort. For example, when the solid sample is homogeneous then it needs only polishing to be ready for analysis.

The working principle is based on the excitation of the sample atoms high-energy X-rays, followed by the emission of characteristic photons with a certain energy, well correlated to the atomic number Z of each element (Moseley's law). The determination of the energy (or wavelength) of the emitted photon allows qualitative analysis and the determination of the number of emitted characteristic photons allows quantitative analysis. The fundamental physical principle of X-ray fluorescence is described in the article about the theory of X-ray fluorescence spectroscopy.

3.1. Excitation Source

X-rays excite the atoms of the sample to emit radiation. The radiation is measured by a semiconductor detector. The pin hole diaphragm provided in the unit concentrates the exciting X-rays on one spot of the sample. The scanning of the sample will result in displaying the concentration on the screen.

3.2. Detectors

A high-resolution silicon drift detector (SDD) that makes determination of trace and minor elements even more accurate. Adding to that precision is a new ultrahigh count rate. With the same measurement time as prior models, it delivers up to 4X higher intensities. [16]

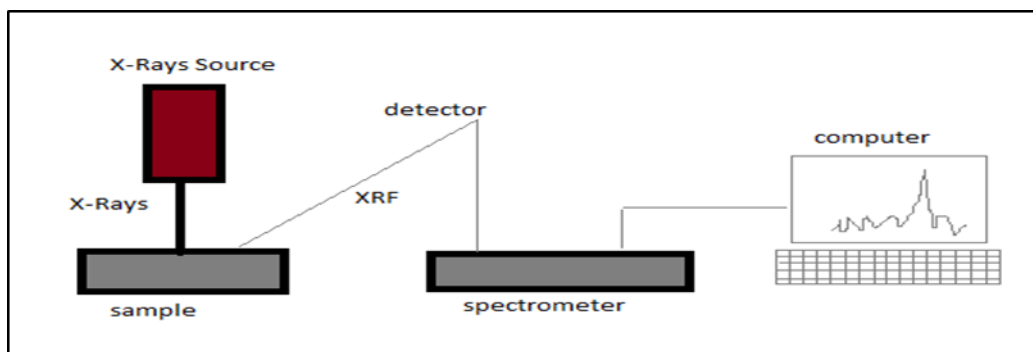


Figure 3 Schematic View of X-Ray Fluorescence Spectrometer

4. Conclusion

There are many challenges which are related to instrumentation, their principle and applications which should be taken into account and solved by R&D teams and Engineers. Until now Emission Spectrometry is considered as fast and reliable technique having applications in the field of primary metals production, foundries and recycling etc. The only discrepancy in this technique is destruction of sample surface. Due to this, precious metals are tested by Xray fluorescence technique. Good accuracy and precision, obtained both in OES and XRF analysis let to indorse these techniques both for determination of the total concentration of elements in metal and alloys.

Compliance with ethical standards

Acknowledgments

The author would like to acknowledge all operators of the OES and XRF laboratories, management of PCSIR, and my colleagues for continuous support at every step.

Disclosure of conflict of interest

The authors declare no conflict of interest for the current paper.

References

- [1] Is it still possible, necessary and beneficial to perform research in ICP-atomic emission spectrometry? J. M. Mermet, J.A n a l. At. Spectrom. 2005; 20: 11 – 16.
- [2] Concepts, Instrumentation and techniques in Inductively coupled plasma Optical Emission Spectrometry, Charles B. Boss and Kenneth J. Fredeen, Perkin-Almer Life and Analytical sciences, third edition, USA.
- [3] Van Loon JC, Barefoot RR. Determiantion of precious metals, selected instrumental methods, J.Wiley. 1991.
- [4] Rouessac F, Rouessac A, Chemical Analysis; J.Wiley. 2000.
- [5] Skoog DA, West DM, Holler FJ, Fundamentals of Analytical Chemistry;7th Edition, Saunders College publishing, 1996.
- [6] M Corsi, G Cristoforetti, V Palleschia, A Salvetti, E Tognoni. A fast and accurate method for the determination of precious alloys caratage by Laser Induced Plasma Spectroscopy, Eur. Phys. J. D 13. 2001; 373–377.
- [7] D Kloos. Proc. 24th Int. Precious Metals Conference. 2001; 17.

- [8] Al-Eshaikh MA, Kadachi A. Elemental analysis of steel products using X-ray fluorescence (XRF) technique. *Journal of King Saud University-Engineering Sciences*. 2011; 23(2): 75-79.
- [9] Hou X, He Y, Jones BT. Recent advances in portable X-ray fluorescence spectrometry. *Applied Spectroscopy Reviews*. 2004; 39(1): 1-25.
- [10] Blank AB, Eksperiandova LP. Specimen preparation in x-ray fluorescence analysis of materials and natural objects. *X-Ray Spectrometry*. 1998; 27(3): 147-160.
- [11] Christina Strel, P. Kregsamer. in *Encyclopedia of Spectroscopy and Spectrometry*. 1999.