



# Analytical performance of benchtop total reflection X-ray fluorescence instrumentation for multielemental analysis of wine samples



Rogerta Dalipi<sup>a</sup>, Eva Marguí<sup>b,\*</sup>, Laura Borgese<sup>a</sup>, Fabjola Bilo<sup>a</sup>, Laura E. Depero<sup>a</sup>

<sup>a</sup> Department of Mechanical and Industrial Engineering, University of Brescia, 25123 Brescia, Italy

<sup>b</sup> Department of Chemistry, University of Girona, Campus Montilivi, 17071 Girona, Spain

## ARTICLE INFO

### Article history:

Received 18 September 2015

Received in revised form 1 April 2016

Accepted 6 April 2016

Available online 8 April 2016

### Keywords:

TXRF

Wine

Multielemental analysis

Mo X-ray tube

W X-ray tube

## ABSTRACT

Recent technological improvements have led to a widespread adoption of benchtop total reflection X-ray fluorescence systems (TXRF) for analysis of liquid samples. However, benchtop TXRF systems usually present limited sensitivity compared with high-scale instrumentation which can restrict its application in some fields.

The aim of the present work was to evaluate and compare the analytical capabilities of two TXRF systems, equipped with low power Mo and W target X-ray tubes, for multielemental analysis of wine samples. Using the Mo-TXRF system, the detection limits for most elements were one order of magnitude lower than those attained using the W-TXRF system. For the detection of high Z elements like Cd and Ag, however, W-TXRF remains a very good option due to the possibility of K-Lines detection.

Accuracy and precision of the obtained results have been evaluated analyzing spiked real wine samples and comparing the TXRF results with those obtained by inductively coupled plasma emission spectroscopy (ICP-OES). In general, good agreement was obtained between ICP-OES and TXRF results for the analysis of both red and white wine samples except for light elements (i.e., K) which TXRF concentrations were underestimated. However, a further achievement of analytical quality of TXRF results can be achieved if wine analysis is performed after dilution of the sample with de-ionized water.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The analysis of wine is of great interest, since it is a common alcoholic beverage widely consumed around the world. It has been demonstrated that the daily consumption of wine, contributes significantly to the dietary intake of elements like Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni or Zn which are considered essential for humans [1]. Anyway, an excessive intake of some of the elements mentioned above or of other potentially toxic elements like As, Cd and Pb may be harmful for human health [2]. On this basis, it is obvious that elemental analysis of wine is important for wine-making industry and consumers. In fact, wine constituents are rigorously regulated by International Organization of Vine and Wine [3] and European Commission [4]. Moreover, due to the high complex matrix, the elemental analysis of wine is a challenging task for analytical chemists.

Atomic spectrometry techniques such as inductively coupled plasma-mass spectrometry (ICP-MS) [5–8], ICP atomic emission spectrometry (ICP-OES) [9,10], electrothermal atomic absorption spectrometry (ETAAS) [8,11] and flame atomic absorption spectrometry (FAAS) [12] have been widely used for elemental analysis of wine.

Another possibility is the use of total reflection X-ray fluorescence spectrometry (TXRF). TXRF is a well established analytical technique for multi element determination in various types of samples, especially liquids and powdered, or micro samples [13]. To perform analysis under total-reflection conditions, samples must be provided as thin films. For liquid samples, this is done by depositing 5–50  $\mu\text{L}$  of sample on a reflective carrier and subsequently drying of the drop. The TXRF system exploits that, at very low glancing angles of the primary X-ray beam ( $\approx 0.1^\circ$ ), X-ray photons are almost completely absorbed within thin specimens. Therefore, the high background that would generally occur due to scatter from the sample support is absent leading to improved detection limits at  $\mu\text{g L}^{-1}$  level [14]. In the last decades, some papers have been published about wine analysis by TXRF [6,15–22]. These studies are mostly focused on wine contamination from exogenous sources during the wine manufacturing process [15,16,18], wine classification for growing areas [19,20] or production stages [21]. According to Anjos and Castiñeira, matrix effects can be neglected when using TXRF for wine analysis, so only a minimal sample pretreatment is necessary [6,15]. Some other advantages of this technique over ICP-MS are the possibility to get simultaneous multielemental information about the wine sample, the low amount of sample required to perform the analysis and the possibility to get quantitative results without external calibration. Usually, quantitative analysis of wine samples by ICP techniques entails the use of matrix-matched standards for calibration

\* Corresponding author.

E-mail address: [eva.margui@udg.edu](mailto:eva.margui@udg.edu) (E. Marguí).

**Table 1**  
Instrumental characteristics and measurement conditions for TXRF and ICP-OES analysis of wine samples.

Instrumental characteristics	Benchtop TXRF spectrometers (S2 PICOFOX, Bruker AXS Microanalysis)	
	Mo system	W system
Anode	Mo	W
X-ray tube	Air-cooled metal ceramic	Air-cooled metal ceramic
Maximum power	40 W	50 W
Optics	Multilayer monochromator (17.5 keV)	Multilayer monochromator (35 keV)
Detector	Silicon drift detector, Area: 30 mm <sup>2</sup> , FWHM: 139.43 eV (Mn K $\alpha$ )	Silicon drift detector, Area: 10 mm <sup>2</sup> , FWHM: 146.72 eV (Mn K $\alpha$ )
Filter	Mo 10.00 $\mu$ m	Ni 50.00 $\mu$ m
Sample changer	Manual version for single samples	Automatic version with cassette for up to 25 samples
Atmosphere	Air	Air
Voltage	50 kV	50 kV
Current	750 $\mu$ A	1000 $\mu$ A
Measuring time	600 s	2000 s
Instrumental characteristics	ICP-OES spectrometer (Agilent ICP-OES 5100-SVDV)	
Element (wavelength)	K (404.721 nm), Ca (317.933 nm), Mn (257.610 nm), Fe (238.204 nm), Ni (231.604 nm), Cu (327.395 nm), Zn (213.857 nm), Rb (780.026 nm), Sr (407.771 nm), Pb (217.000 nm)	
RF Power	1200 W	
Plasma gas flow rate	12 L min <sup>-1</sup>	
Plasma configuration	Axial	
Nebulizer type	Concentric	
Wavelength selector	Polychromator	
Detector	Silicon based multichannel array detector CCD (Charge Coupled Device)	

purposes in order to overcome matrix effects [7]. In the case of TXRF, quantification can be performed directly by internal standardization, and thus, the quantification procedure is faster and easier. Moreover, with the recent development and commercialization of benchtop systems, which do not require cooling media or gas consumption for operation, TXRF analysis is also cost-effective compared to other atomic spectroscopic techniques. Nevertheless, benchtop TXRF systems usually have limited sensitivity in comparison with high-scale TXRF instrumentation, which can restrict application in some fields. Most of the contributions published so far dealing with the analysis of wine samples by TXRF analysis were performed using large-scaled systems [15,16, 18–20]. The aim of the present contribution is to evaluate the real analytical capabilities of low power benchtop TXRF instrumentation for multielemental analysis of wine samples.

In a recent paper [17], we have explored the capabilities of a benchtop TXRF system, equipped with a low power Mo X-ray tube, for routine multi-element analysis of Italian wines. However, commercial TXRF systems can be equipped with both, Mo and W X-ray tubes and for this reason in the present contribution we have evaluated and compared the possibilities of both TXRF systems, in order to demonstrate the real possibilities of benchtop TXRF systems for the analysis of wine samples.

## 2. Experimental

### 2.1. Reagents and solutions

Stock solutions of 1000 mg L<sup>-1</sup> (ROMIL PrimAg<sup>®</sup> Mono-component reference solutions) of interesting elements were used to prepare standard solutions. Ultrapure de-ionized water, used for dilution of stock solutions, samples and preparation of alcoholic synthetic solution (12% ethanol v/v), was obtained from a Milli-Q purifier system (Millipore Corp., Bedford, Massachusetts). ICP multielement standard solution IV (23 elements in 6% nitric acid, Merck KGaA, Darmstadt, Germany) was used to prepare the reference solutions in 12% ethanol v/v matrix. Silicone solution in isopropanol (Serva GmbH & Co, Germany) was used to coat all the quartz glass disc reflectors in order to obtain a hydrophobic film before deposition of liquid samples droplets.

### 2.2. Samples and synthetic alcoholic standards

#### 2.2.1. Wine samples

Nine different Italian wine samples (seven red and two white) were provided by 'Istituto Zooprofilattico Sperimentale della Lombardia e dell'Emilia Romagna' of Brescia, Italy. All the wine samples come from a control sampling of commercial wines of the Emilia Romagna Italian Region.

#### 2.2.2. Synthetic alcoholic standards

Since no certified reference materials (CRMs) for trace elements determination in wine are available, limits of detection (LOD) for both TXRF systems were evaluated using a synthetic alcoholic solution. Absolute ethanol was added to ultrapure de-ionized water in order to obtain a final alcohol concentration similar to that of a typical wine (12% v/v). The alcoholic solution was added to the ICP multielement standard solution IV to prepare a reference solution with concentrations of 10 mg L<sup>-1</sup>. Gallium was chosen as internal standard (IS) for quantitative analysis of other elements.

#### 2.2.3. Spiked wine samples

The evaluation of the accuracy was performed in a red wine sample by a spiking procedure. The target elements were Ca, Ni, Cd and Pb. Four aliquots were taken from the wine sample solution with a defined volume (about 200  $\mu$ L). In the first aliquot was not added any standard solution ( $c_0$ ), while the other two aliquots were spiked with a fixed small volume (20  $\mu$ L) of a standard solution (aqueous solution) containing the analyte elements (Ca, Ni, Cd, and Pb) in different concentrations ( $c_1$  and  $c_2$ ). The final solutions were thoroughly mixed to ensure homogeneity. The influence of the sample matrix on the accuracy was also evaluated by spiking the red wine sample after it was diluted in the ratio 1:1 with ultrapure de-ionized water.

### 2.3. Sample preparation for TXRF analysis

The best sample preparation conditions for wine sample analysis by TXRF were carefully evaluated (see Section 3.1). Finally, the selected conditions for wine analysis were as follows: sample solutions were prepared by weighing 1 mL of each wine sample and adding the

Download English Version:

<https://daneshyari.com/en/article/1239659>

Download Persian Version:

<https://daneshyari.com/article/1239659>

[Daneshyari.com](https://daneshyari.com)