TXRF

Analysis of Red and White Wines

Application Note # XRF 444

Introduction

The analysis of trace elements is an important tool for assuring the quality of wines. Several elements such as As, Br, Cd and Zn [1,2] are detrimental to human health. It is therefore necessary to routinely determine whether their percentage in a wine lies within the legally allowed limits. Trace element analysis also is a valuable tool for the identification of a wine's origin and other verification purposes.

Among the most common analytical techniques that are applied in wine analysis are ICP-MS [3] and ICP-OES [4]. Unfortunately these methods are labor and cost intensive. Pretreatment by way of classical wet digestion procedures with strong and concentrated acids or UV irradiation with an oxidant is required in order to remove the organic matrix of samples. Additionally, time consuming calibration routines are prerequisites for the identification and quantification of each element. Finally, when conventional XRF systems are used, samples need to be preconcentrated due to the systems' lack of detection sensitivity [5]. A first successful approach for wine analysis by synchrotron radiation TXRF (SRTXRF) was made in 2003 [6].

This report describes the analysis of 14 different red and white wine samples (Table 1) using the TXRF spectrometer S2 PICOFOX. Part one is concerned with the suitability of S2 PICOFOX for this type of application; part two discusses the accuracy of the trace element analysis of wine standards.

Table 1
Analyzed wine samples

No.	Variety/Region	Vintage	Country of origin
	Red wines		
1	Navarra	2003	Spain
2	Dornfelder	2003	Germany
3	Merlot	2003	France
4	Pinot Noir	2003	France
5	Cabernet Sauvignon	2003	Chile
6	Spätburgunder	2003	Germany
7	Rioja	2003	Spain
8	Shiraz	2004	USA
	White wines		
9	Riesling	2003	Germany
10	Silvaner	2003	Germany
11	Pinot Grigio	2003	Italy
12	Müller-Thurgau	2003	Germany
13	Semillion / Chardonnay	2003	Australia
14	Chenin Blanc / Chardonnay	2004	South Africa

Part I — Trace element analysis

Instrumentation

A S2 PICOFOX – automatic version – with an integrated 25-disc sample changer was used for all analyses. The S2 PICOFOX works with an air-cooled metal-ceramic X-ray tube (Mo anode) and a maximum power of 50 Watt. The energy resolution of the incorporated XFlash® silicon drift detector with an active area of 10 mm^2 is below 160 eV (FWHM @ Mn Ka, 1 kcps).

The complete S2 PICOFOX system has a compact size of only 450 x 590 x 300 mm and weighs 37 kg. Its power consumption is low with 190 Watt.

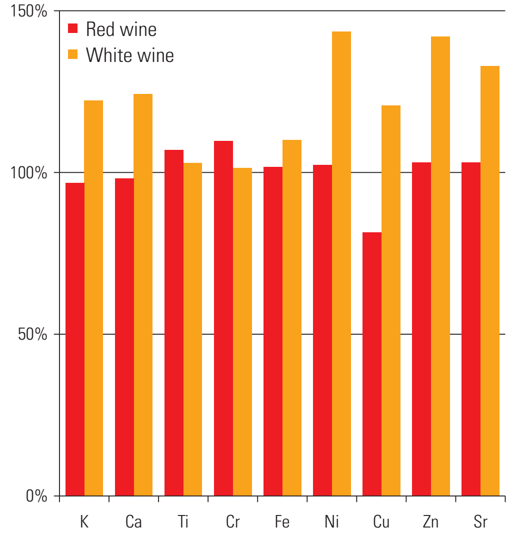

Figure 1

Recovery of the element concentrations of a control solution measured by TXRF

Sample preparation and analysis

The analytical accuracy of the S2 PICOFOX was proven with two control samples of 12 vol % ethanol, which contained different amounts of standard solutions.

For the elemental analysis of wines, 14 bottles of wine were acquired at various supermarkets and German wineries (Table 1). 10 µl of an internal standard solution (Ga, 100 mg/l) were added to a sample aliquot of 1 ml and homogenized. 5 µl of this solution were then applied onto a quartz glass carrier and carefully dried on a heating plate. The TXRF analysis required no futher sample pretreatment. The wine samples were analyzed in triplicate for 1000 seconds each.

Results

The deviation between measured and nominal values of the control solutions was distinctly below 10 %. The published Mn content was below the detection limit due to the overlap of the $K\alpha$ peak with the strong $K\beta$ peak from Cr. This was irrelevant for the wine sample analyses, because the Mn and Fe results were in the same concentration range, while Cr was not detectable.

The main inorganic compounds in the wine samples contained K, Mg, P, Cl and Ca. Elements only included in minor amounts were Fe, Zn, Rb and Sr, while Ni, Cu, Br, Ba and Pb were only present in trace amounts (Figure 2). All the detected elements were present in

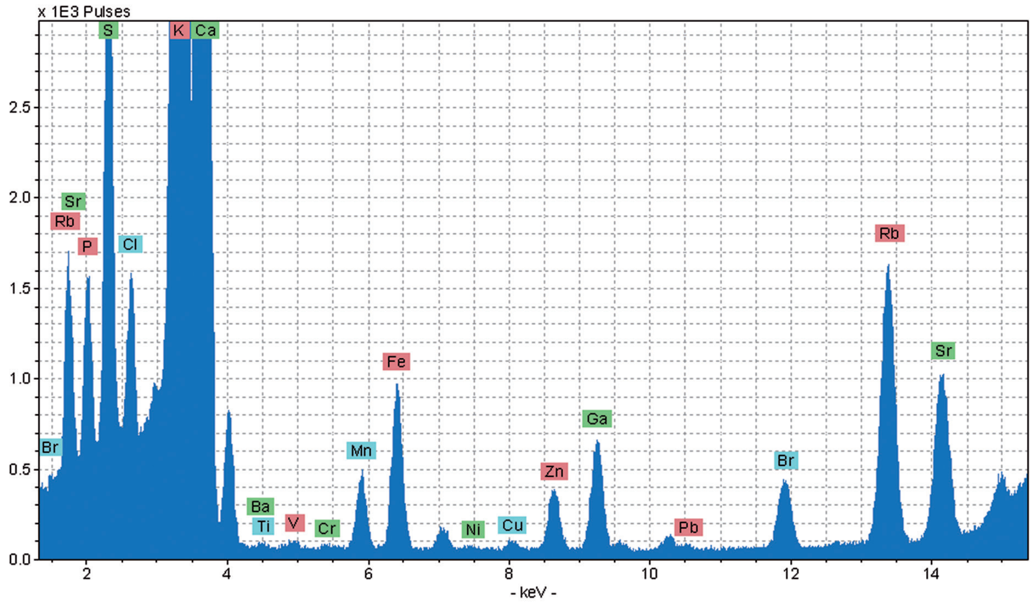

Figure 2

Typical TXRF spectrum for wine samples (sample no. 9) amounts that were clearly below the legally allowed limits.

The detection limits for all elements except for Mg are in the range of 10 to 1000 µg/l (Figure 3). Cd could not beanalyzed, because it can only be detected by its Lα-line at 3.133 keV, which has an overlap with the strong K Kα-line.

Recent measurements with the optimized S2 PICOFOX with "High Efficiency Modul" (see lab report DOC-81-EXS-078) improved the detection limits by a factor of about 5.

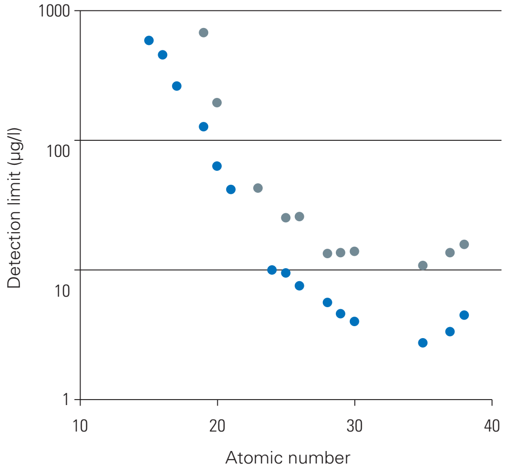

Figure 3
Detection limits for wine analysis achieved by the TXRF spectrometer S2 PICOFOX (grey dots – standard, blue dots – high efficiency modul)

Conclusions

This study clearly demonstrates the efficient use of the TXRF spectrometer S2 PICOFOX for trace element analysis of wine samples. The analytical results showed distinctly individual distribution patterns for each analyzed wine sample. The results could therefore be used for a regional characterization of wine samples.

Part II – Accuracy of the trace element analysis of wine standards by TXRF

Among numerous chemical parameters, the analysis of trace elements is of crucial importance for the quality control in wine production. Four elements are of particular importance:

- Calcium (Ca): Calcium can make wine perishable through calcium tartrate deposits.
- Copper (Cu): An excess of copper ions can lead to the formation of an unsightly haze (casse) in finished wine.
- Iron (Fe): Involved in casse formation (along with copper), iron ions can contaminate wine through contact with exposed iron (non-stainless steel) surfaces.
- Potassium (K): Excessive potassium contributes to higher pH-value in wines. It can also potentially lead to tartrate instability. Some countries therefore have official limits for how much a wine is allowed to contain.

Depending on the existing quality and legal regulations concering a country's wines, additional analysis and control of redundant trace elements is necessary.

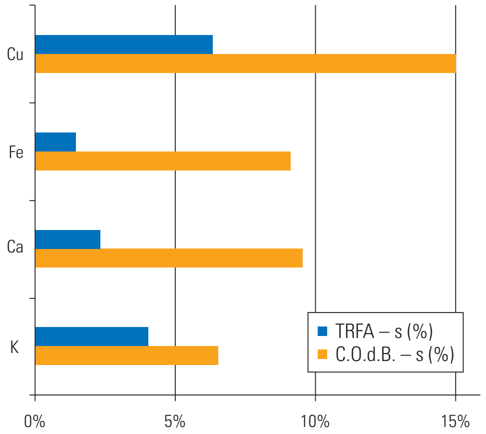

Figure 4
Results of the reproducibility measurements by TXRF and comparison of the standard deviation with the certified values of the wine reference standard (blue – standard deviation TXRF, orange – standard deviation certified values)

Part two of this report describes how a series of four wine standards were measured in order to prove the accuracy and reproducibility of the S2 PICOFOX TXRF spectrometer.

Samples

The reference samples for this study were obtained from the Centre Œnologique de Bourgogne. Four wine samples obtained in sealed glass ampoules were available for test measurements.

Sample preparation and analysis

The addition of 5 µl Vanadium standard solution (Merck, 1 g/l) is recommended for the preparation of wine samples. In order to test the reproducibility of this preparation technique, 10 samples of each of the 4 wine reference standards were prepared and analyzed using a measurement time of 1000 seconds.

Results

The results of the test measurements are summarized in Table 2. The TXRF analysis results for K, Ca, Fe and Cu were consistent with the certified values of all 4 wine reference standards. With the exception of Cu in the reference standard No. 1, all relative standard deviations were below 5 %. This can be explained with the Cu concentration being close to the detection limit. The result indicates a very good reproducibility – especially if the fact is taken into account that the deviations of the certified values were between 5 and 15 % (Figure 4).

Since the TXRF analysis method used by S2 PICOFOX easily allows the simultaneous analysis of numerous elements, the concentrations of further elements, namely P, S, Cl, K, Mn, Ni, Zn, Br, Rb, Sr and Pb were analyzed simultaneously.

Summary

The analysis of four wine reference standard samples has demonstrated that the TXRF benchtop spectrometer S2 PICOFOX provides accurate and reproducible results of trace elements in wine samples.

In comparison to other analytical techniques such as AAS and ICP-OES TXRF analysis with S2 PICOFOX has many advantages:

- Straightforward sample preparation without dilution or digestion procedures.
- No need for external calibrations, as quantification is achieved through internal standards.
- Simultaneous analysis of all detectable elements.
- As a benchtop system S2 PICOFOX makes mobile usage possible and does not need external media.

	n = 10	TXRF [mg/l]	s [mg/l]	Ref. [mg/l]	s [mg/l]
No.1	Ca	62	1.0	63	6
	Fe	1.98	0.03	2.2	0.2
	Cu	0.20	0.01	0.2	0.03
No. 2	K	553	19	562	50
	Fe	7.91	0.13	8.3	0.3
	Cu	0.46	0.02	0.52	0.06
No. 3	Fe	3.01	0.06	3.1	0.2
No. 4	K	981	13	920	60
	Ca	102	1.5	110	12

Table 2

Reproducibility measurements of wine reference standards from the Centre Œnologique de Bourgogne

References

[1] The International Office of Vine and Wine (OIV): Compendium of international methods of analysis of wine and musts.

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[5] Anjos, M. J. et al. (2003): EDXRF analysis of red and white wines from Brazil. X-Ray Spectrom. (in press).

[6] Anjos, M. J. et al. (2003): Trace element determination in red and white wines using total-reflection X-ray fluorescence. Spectrochimica acta Part B, 58, 2227-2232.

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Order No. DOC-A81-EXS044, Rev. 2.1 © 2015 – 2025 Bruker Nano GmbH, Am Studio 2D, 12489 Berlin, Germany.

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