A Procedure for the Improvement in the Determination of a TXRF Spectrometer Sensitivity Curve

Leonardo Bennun*[†] and Vilma Sanhueza**

*Departamento de Física, Universidad de Concepción, Concepción, Edmundo Larenas s/n, Concepción, Chile
**Instituto de Geología Económica Aplicada (GEA), Universidad de Concepción, Concepción, Edmundo Larenas s/n, Concepción, Chile

A simple procedure is proposed to determine the total reflection X-ray fluorescence (TXRF) spectrometer sensitivity curve; this procedure provides better accuracy and exactitude than the standard established method. It uses individual pure substances instead of the use of vendor-certified values of reference calibration standards, which are expensive and lack any method to check their quality. This method avoids problems like uncertainties in the determination of the sensitivity curve according to different standards. It also avoids the need for validation studies between different techniques, in order to assure the quality of their TXRF results.

Introduction

Total reflection X-ray fluorescence (TXRF) is a relatively new surface multi-elemental analysis technique used for the ultra-trace analysis of particles, residues, and impurities deposited on smooth surfaces. Within a relatively short period of time, TXRF has become one of the most widely used techniques in determining trace levels of surface metallic contamination introduced by a variety of semiconductor processing procedures. The method is applied for elemental analysis[1] for both the quantitative and qualitative determination of elements with $Z > 13$; it is efficient and fast and requires only minute specimen quantities. It has been employed in a variety of disciplines, including biology,[2] physics,[3] biomedicine,[4] chemistry,[5] archaeology,[6] medicine,[7] geology,[8] and many others.

TXRF is basically an energy dispersive X-ray fluorescence (XRF) technique in a special geometry. An incident beam impinges upon a sample at angles below the critical angle of external total reflection for X-rays, resulting in reflection of almost 100% of the excitation beam photons. Due to its unique configuration, the main advantage of TXRF over conventional XRF is reduced background measurement by elimination of sample scattering, resulting in increased elemental measurement sensitivity: detection limits are on the order of 10^{-8} g/g.

TXRF has become a widespread method for measuring surface metal contamination on silicon wafers. For quantification, TXRF requires reference samples; the answers one obtains are only as good as the standards used to calibrate the instrument. Since the approaches to making and using these reference samples have significantly varied among TXRF manufacturers and users worldwide, there exists some confusion about the quantification of TXRF. This paper summarizes a method for the best TXRF quantification, when the calibration is made using pure substances.

The usual characterization of a TXRF spectrometer follows a well-established experimental sequence, which determines the relative intensity of different elements in the measured spectrum, at equal concentration: the sensitivity curve. The standard sequence considers these steps: i) A set of reference multi-elemental solutions must be prepared, where the concentrations of the included elements should be known as well as possible, as is depicted in Fig. 1. ii) These artificially prepared samples are measured with the spectrometer, and the abundance of each line is determined, as in depicted in Fig. 2. iii) The obtained information is processed in order to obtain the relative abundance of intensities of different elements referred to one in particular (the internal standard). In the sensitivity curve representation, any element can be chosen as internal
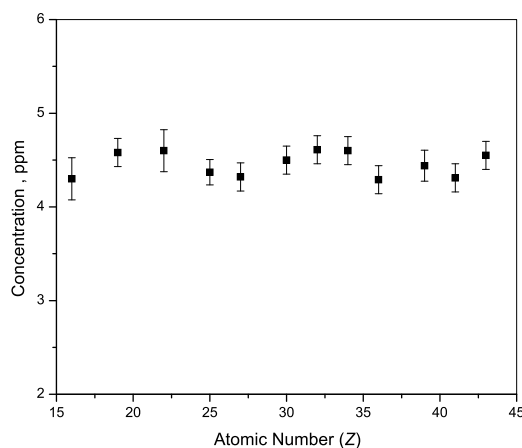

Fig. 1   A set of reference multi-elemental solutions prepared with well known concentrations, in order to determine the sensitivity curve of a TXRF spectrometer.

[†] To whom correspondence should be addressed.
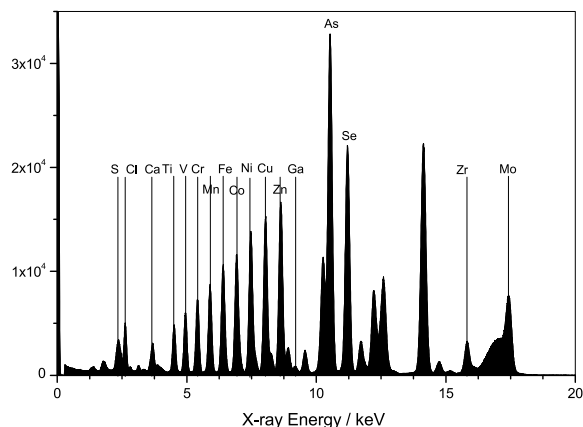E-mail: bennun@yahoo.com

Fig. 2   The spectra of the artificially prepared samples are measured with the spectrometer, and the abundance of each line should be determined.
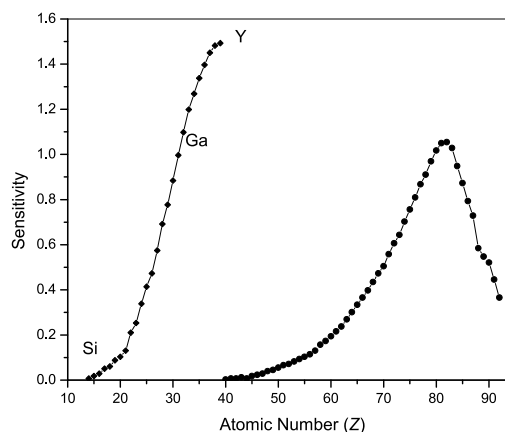

Fig. 3   Typical TXRF spectrometer sensitivity curve. This figure was provided by the fabricant. Different symbols are used for the K-lines (◆) and the L-lines (●).

standard. A typical sensitivity curve is shown in Fig. 3.

In order to undertake the quantification of an unknown sample the procedure starts with the measurement of the sample with the TXRF spectrometer (step ii), the obtained results are affected by the calibration curve (step iii) in order to finally obtain the element's concentration in the sample; a kind of inverse procedure is done. The exactitude of the sensitivity curve impacts the quality of the results when analyzing any unknown sample.

The determination of a TXRF spectrometer sensitivity curve is affected by a set of uncertainties. Some of them can not be avoided (like the statistical fluctuations of the measured signals), and other can be avoided with careful procedures which should be considered in order to assure the quality (the accuracy and precision) of the results. For example, the preparation of artificial reference solutions (other than being time consuming, these should be done by specialized technicians) may be affected by a set of possible errors; a sequence of them can be described as:

1. a) The certified value of the reference calibration standard for a given element A, has a concentration uncertainty, that is, the concentration is expressed as: $C_A \pm \Delta C_A$. b) The volume extracted from that standard solution, which is usually diluted, also has an uncertainty, which can be expressed as: $V_{SA} \pm \Delta V_{SA}$. c) The total volume of the final multi-elemental artificial solution has also an uncertainty, $V_t \pm \Delta V_t$.

2. When a mixture of the reference calibration standards is done, the impurities from a given standard (A with little amounts of B as impurities) would modify the expected concentration of B in the final mixture and *vice versa*. Actually, that problem considers the complete interaction between the set of elements that compose the multi-elemental calibration solution prepared.

3. When a mixture of the reference calibration standards is done, the atoms of one element may produce the precipitation of other atoms (if the mixture produced a non-soluble material). Moreover, some atoms may produce the loss of others *e.g.* if a standard substance is a chloride and it is mixed with another standard that contains NO_3H, the chlorine escapes as HCl when the specimen is dry.

4. If a multi-elemental sample is produced, the measured spectrum increases its complexity, and the adjustment of the registered signals becomes more complex, increasing also the probabilities to produce errors in the intensity of the computed signals.

5. If a standard is produced from a solid sample, it is always delicate to define the amount of water present in the stoichiometry of the substance. That is, there is an uncertainty in the amount of mass of the used elements.

Fluctuations in measured signals can be diminished by increasing the spectrum acquisition time or by analyzing bigger mass samples.

The standard sensitivity curve determination may produce serious discrepancies (up to 100% relative)[9] when other standards are analyzed as though they were samples. These self-inconsistencies, which could be attributed to the standards used, can be avoided with the procedure reported here.

Other sources of possible errors should also be taking into account, when working with the TXRF technique.[10]

Finally, we want to stress that, when a set of reference multi-elemental solutions is prepared in order to obtain the TXRF sensitivity curve (where the concentrations of the included elements are known as well as possible), we are also assuring a given relation between different kinds of atoms (*e.g.* in a 5 ppm Fe and 5 ppm Cu solution, there are 1.1379 Fe atoms per 1 atom of Cu). We would like to stress that, when a pure substance is diluted, the proportion in the solution between the atoms that form the substance is perfectly defined (if the purity of the substance is good). No solution preparation procedure can define with such exactitude the proportion between atoms of the involved elements. Moreover, when the spectrum of the sample is acquired, the purity of the substance can be verified. In the following, we describe a method for obtaining the sensitivity curve of a TXRF spectrometer, obtaining the best accuracy, by the use of pure stoichiometric samples.

Theoretical Considerations

The basic equation for TXRF for a thin film is given by:[11]

$$I_i = K_i I_0 N_0 \sigma_i w_i m_i / A_i \tag{1}$$

where the intensity of the line originated by the element i, I_i, is written in terms of the following parameters: K_i which depends

on experimental geometry and energy detection efficiency; I_0 that stands for the intensity of the excitation source; the Avogadro's number N_0; m_i which represents the mass surface density of the element i with atomic number Z_i; atomic mass A_i; the element i collision cross section σ_i; the photon emission probability per ionization ω_i.

Because the solution does not deposit homogeneously on the reflector, changes in the value of $I_0 m_i$ are produced, which result in significant variations of the total counts in different depositions of the same sample. To avoid this uncertainty, an internal standard is artificially added to the solution in a well-defined concentration. It should be an element not originally present in the sample. In the data processing, the concentrations of the original unknown elements are made in reference to the concentration of the added standard.

If a small amount of the element j is added to the original sample, the relationship between intensities becomes:

$$\frac{I_i}{I_j} = \frac{K_i \sigma_i \omega_i m_i / A_i}{K_j \sigma_j \omega_j m_j / A_j} \tag{2}$$

Since the ratio m_i/m_j is the same as the ratio between the concentrations of these elements in the solution (C_i/C_j), Eq. (2) can be written:[12]

$$\frac{I_i}{I_j} = \frac{S_i C_i}{S_j C_j} \tag{3}$$

where $S = K\sigma\omega/A$ is the sensitivity, either of the analyte element, i, or of the internal standard, j. In order to determine the concentration of the element i, Eq. (3) can be expressed as:

$$C_i = \frac{S_j I_i}{S_i I_j} C_j \tag{4}$$

In order to determine the concentration C_i, from Eq. (4) we observe that the relative sensitivity calibration (S_j/S_i) must be a known value for a set of elements of analytical interest.

Reference solutions are necessary to perform the calibration. Each one of them must contain several elements with well-determined concentrations, as was described in the Introduction. Because an internal standard common to the solutions is required by this method, at least one element must be present in all samples. From the spectral analysis point of view, it is possible to introduce any element as the internal standard in a particular standard solution.

If the sensitivity curve will be obtained from the measurement of pure substances, then Eq. (4) can be reordered as:

$$\frac{m_i}{m_T} = \frac{S_j I_i}{S_i I_j} \frac{m_j}{m_T} \longrightarrow A_i \#At_i = \frac{S_j I_i}{S_i I_j} A_j \#At_j \tag{5}$$

Where $\#At$ is the number of atoms either of the element i or j, and m is the mass of a given element (i or j) or the total mass (m_T) of the sample. The relative sensitivity can be expressed as:

$$\frac{S_j}{S_i} = \frac{A_i \#At_i}{A_j \#At_j} \frac{I_j}{I_i} \tag{6}$$

The relationship between atoms, $R = \#At_i/\#At_j$ is obtained from the known stoichiometry of the used pure substance.

We can notice from Eq. (6), that the relation between atoms ($\#At_i/\#At_j$) can be considered without error ($\Delta R = 0$). The same consideration can be used for the relationship between the atomic mass A_i/A_j. The only source of errors in Eq. (6) is

Table 1 Substances selected to determine the TXRF spectrometer sensitivity

Compound	Elements determined	Compound	Elements determined
$KMnO_4$	Mn/K	SO_4Mg	S/Mg
$FeCl_3$	Fe/Cl	SO_4K_2	K/S
$CuSO_4$	Cu/S	$CuCl_2$	Cu/Cl
$ZnCl_2$	Zn/Cl	$K_2Cr_2O_7$	K/Cr
Cl_2Sr	Cl/Sr	K_2CrO_4	K/Cr
KCl	K/Cl	KBr	K/Br
ClCu	Cu/Cl		

produced by the statistical fluctuations of the registered signals (I_i and I_j) which can be diminished as much as we want by increasing the spectrum acquisition time or by analyzing bigger mass samples.

Experimental

The TXRF analytical system used in this study is an S2 PICOFOX Bruker spectrometer that is enclosed in a suitably designed X-ray biological shield. The system includes a) an X-ray metal-ceramic tube, with a molybdenum target, working at 50 W of maximum power, at 50 kV and 1.5 mA, air-cooled; b) a multi-layer monochromator; c) a Peltier-cooled high resolution XFlash® Silicon Drift Detector, which does not need a liquid nitrogen cooling system, with 10 mm^2 active area, and energy resolution <160 eV at 100 kcps (Mn K_α line, 5.9 keV).

The S2 PICOFOX TXRF spectrometer is a versatile instrument for trace element analysis of different kinds of samples. It is completely independent of any cooling media and therefore applicable for on-site analysis. Further benefits of the S2 PICOFOX are the simple calibration routine, the absence of matrix or memory effects and the ability for multi-element analysis.

Sample preparation

The TXRF system offers almost no sample preparation, so it does not require time-consuming digestion by hazardous chemicals. In contrast to AAS/ICP instrumentation, the S2 PICOFOX is suitable for almost all sample types such as liquids, suspensions, filters, particles and body fluids.

It is necessary to select many substances with known stoichiometry and high purity with at least two elements suitable to be determined with the technique with $12 < Z < 41$, K-lines. One solution for each one of the chemical substances to be analyzed was prepared. They were made with use of a solvent that may be dried by evaporation by the use of an IR lamp (bidistilled and then deionized water was used). A volume of 10 μL of the sample solution was deposited with a micropipet on a 30-mm-diameter quartz reflector and dried by an IR lamp. A set of 13 different compounds (see Table 1) were used. None of the compounds presented particular handling hazards. Commercial reagents (Merck) were used as supplied. For low Z substances, containing S, K, Cl, *etc*., solutions with concentrations of 30 – 50 ppm were made. Solutions containing heavier elements were made in the range of 10 – 20 ppm.

For each compound, an irradiation and data collection time of 500 s was preset for all samples, and two measurements were performed for each one.
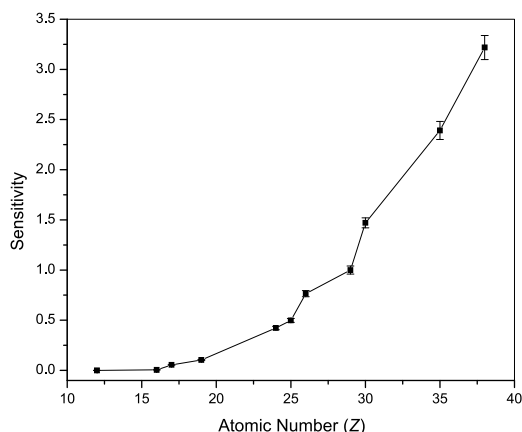
Fig. 4   Sensitivity curve for K-line X-ray emissions determined by the proposed method. Copper was selected as the internal standard.

Data analysis

All data were acquired on PICOFOX. For all quantitative data, the instrument was operated at its normal full power levels with data acquisition times of 500 s. The TXRF instrument used in this study was routinely calibrated.

The interpretation of the spectra and elemental evaluation was performed by the X-ray analysis software program SPECTRA 5.3, released by Bruker and included with the S2 PICOFOX 6.0. Elements are identified in an interactive procedure contrasting operator experience with X-ray library suggestions.

Element abundances in each specimen were derived from X-ray signal intensities by a TXRF quantification sequence. The instrumental sensitivity relative to the chosen internal standard element (copper) is derived using Eq. (6). The sensitivity curve was obtained by analyzing 13 different solutions.

The instrument calibration curve (for K-line X-ray emissions) is reported in Fig. 4, where copper was selected as the internal standard.

Results and Discussion

The set of samples analyzed allowed us to obtain the sensitivity curve, which is shown in Fig. 4. The quality of the results is affected by: 1) the purity of the analyzed substance which was placed on the reflector, and 2) statistical counting errors.

To reduce these sources of error, careful procedures were implemented and the values of the sensitivity shown in Fig. 4 show an uncertainty at most of 4%. The accuracy of the spectrometer calibration is affected by statistical counting, and can be improved by depositing larger sample volumes on the reflector or by longer counting times. For low Z substances, particular care must be taken because of the decreased sensitivity for these elements.

The purity of each substance used was verified after the spectrum of the sample was acquired; then the data were included in the calibration curve.

Impact over accuracy and precision in standard measurements

In order to evaluate the impact of the proposed method over TXRF measurements, first we mention that Fig. 4 includes the magnesium sensitivity. The sensitivity of this low Z element ($Z = 12$) it not easily evaluated with the standard calibration method, because it is very small compared with the sensitivities of the possible elements included in the multielemental solution analyzed. Usually, this element is not reported among the fabricants in the sensitivity curve, so its determination in a given sample can only be qualitative. With the proposed method, in order to evaluate the magnesium sensitivity, the chosen substance should have another low Z element, so both evaluated sensitivities are similar. In this case, we have analyzed a magnesium sulfate ($MgSO_4 \cdot 7H_2O$) solution.

In order to estimate the improvement of the sensitivity calculated using the proposed method over the values obtained from the methods which use commercially available multi-elemental standard solutions, we proposed an experiment and then we compared the results. The purpose is to determine by both methods the relative abundance between two different elements, in a known substance, but considered as incognita. In particular, we have analyzed a $CuCl_2$ salt, which was evaluated first with the standard multi-elemental method. A Merck-VI-02 sample was used as a reference standard. The exact mass relation between Cl/Cu is 1.11. The relation obtained from three independent prepared $CuCl_2$ solutions was 1.02 ± 0.03. In order to evaluate that relation with the proposed method, first we calculated the relative sensitivity $S_{Cu/Cl}$ from another compound, CuCl, which have the same kind of atoms but with different stoichiometry. Then applying Eq. (4), the relationship between concentrations Cl/Cu from the three $CuCl_2$ solutions, was 1.08 ± 0.02.

Usually an absolute TXRF determination is made by the use of an internal standard, which is an element artificially added to the solution in a well-defined concentration. That element should not be originally present in the sample. In the data processing, the concentrations of the original unknown elements are made in reference to the concentration of the added standard. The TXRF determination is affected by set of uncertainties; these include the statistical fluctuations of the measured signals (ε_{sf}), the error of the concentration of the internal standard (ε_{is}), the uncertainties in the sensitivity curve (ε_{sc}), processing the collected X-ray spectra and calculating the net peak areas (ε_p). The overall uncertainty (ε_t) can be evaluated as:

$$\varepsilon_t = \sqrt{(\varepsilon_{sf})^2 + (\varepsilon_{is})^2 + (\varepsilon_{sc})^2 + (\varepsilon_{sf})^2 + (\varepsilon_p)^2} \qquad (7)$$

Each one of the terms of Eq. (7) can be evaluated independently. In particular, the error produced because the addition of the internal standard ε_{is}, can be diminished with careful procedures and should be evaluated in each particular situation, according to the level of experience of the technicians that perform the duties.

Conclusion

The procedure proposed to determine the sensitivity curve is simpler and perhaps faster than the standard used method and provides better accuracy and exactitude in the determination of a TXRF sensitivity curve. It simplifies the sensitivity determination of low Z elements, and it avoids the use of vendor-certified values of reference calibration standards, which are expensive and lack any method to check their quality. In this procedure, when the spectrum of the sample is acquired, the purity of each substance is verified independently, that is, the method has a checking procedure. Better purity substances are included and others may be rejected in order to determine the more accurate spectrometer calibration.

This method avoids facing problems like uncertainties in the

determination of the sensitivity curve according to different standards.[12] It also avoids validation studies between different techniques in order to assure the quality of TXRF results. A work has indicated very close agreement between vendor-certified values on TXRF reference calibration standards and the results from an ion beam technique heavy ion backscattering spectrometry (HIBS)[13] which does not require standards for accurate analysis. Other inter-comparison studies have focused on the combination of VPD-DC with TXRF, more specifically on the accuracy of TXRF in the analysis of the micro-droplet residues. In comparison with independent techniques such as ICPMS and GFAAS,[14-16] these studies have reported the tendency of TXRF to underestimate the metallic concentration. Such of studies can be avoided with the appropriate selection of the samples studied.

Acknowledgements

References

1. R. Klockenkämper, "*Chemical Analysis. A Series of Monographs on Analytical Chemistry and Its Applications*", ed. J. D. Winefordener, **1997**, Vol. 140, John Wiley & Sons, New York.

2. M. Piacenti da Silva, O. L. Domingues, A. Ribeiro-Silva, and M. E. Poletti, *Spectrochim. Acta, Part B*, **2009**, *64*, 587.

3. D. Hellin, S. De Gendt, N. Valckx, P. W. Mertens, and C. Vinckier, *Spectrochim. Acta, Part B*, **2006**, *61*, 496.

4. R. Fernández-Ruiz, R. Costo, M. P. Morales, O. Bomatí-Miguel, and S. Veintemillas-Verdaguer, *Spectrochim. Acta, Part B*, **2008**, *63*, 1387.

5. J. Stas, A. Khuder, and J. Karjou, *Appl. Radiat. Isot.*, **2008**, *66*, 450.

6. R. Fernández-Ruiz and M. García-Heras, *Spectrochim. Acta, Part B*, **2007**, *62*, 1123.

7. H. Stosnach and M. Mages, *Spectrochim. Acta, Part B*, **2009**, *64*, 354.

8. F. M. Adebiyi, O. I. Asubiojo, and T. R. Ajayi, *Fuel*, **2006**, *85*, 396.

9. D. Werho, R. B. Gregory, S. N. Schauer, X. Liu, G. F. Carney, J. C. Banks, J. A. Knapp, B. L. Doyle, and A. C. Diebold, *Adv. X-Ray Anal.*, **1998**, *40*, 37.

10. Y. Mori and K. Uemura, *X-Ray Spectrom.*, **1999**, *28*, 421.

11. H. Schwenke, W. Berneike, J. Knoth, and U. Weisbrod, in "*Advances in X-Ray Analysis*", ed. J. V. Gilfrich, C. S. Barrett, T. C. Huang, R. Jenkins, and P. K. Predecki, **1989**, Vol. 32, Plenum Press, New York, 105.

12. A. A. Markowicz, in "*Handbook of X-Ray Spectrometry*", ed. V. Grieken and A. A. Markowicz, **1993**, Marcel Dekker Inc., New York.

13. R. S. Hockett, *Anal. Sci.*, **1995**, *11*, 511.

14. G. Buhrer, *Spectrochim. Acta, Part B*, **1999**, *54*, 1399.

15. J. Wang, M. Balazs, P. Pianetta, K. Baur, and S. Brennan, *Solid State Phenom.*, **2001**, *76 – 77*, 75.

16. D. Hellin, J. Rip, S. Arnauts, S. De Gendt, P. W. Mertens, and C. Vinckier, *Spectrochim. Acta, Part B*, **2004**, *59*, 1149.