



Cultural Heritage Conservation
and Environmental Impact Assessment
by Non-Destructive Testing and Micro-Analysis

Edited by René Van Grieken & Koen Janssens

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Quantitative analysis of ancient metal artefacts by means of portable energy-dispersive x-ray fluorescence spectrometers: a critical review

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ABSTRACT: Field portable energy-dispersive x-ray fluorescence (FP-EDXRF) spectrometers are becoming a standard tool for non-destructive analysis of metals. This article discusses the major issues related to the infield use of such equipments. The quantitative analysis of alloys is in principle possible with some restrictions due to the measuring conditions. The difficulties for a quantitative analysis and some evaluation of instrumental error are presented. Finally, the possibility to use such systems for the assay of ancient gold artefacts is shortly discussed.

1 INTRODUCTION

Quantitative analysis by means of FP-EDXRF spectrometers is becoming a very common and powerful tool in the investigation on ancient metal artefacts; its use, however, opens some methodological problems that are worthwhile discussing because they are in some aspects object of controversies (Van Grieken & Markowicz 1993, Cesareo et al. 2000, Marucco & Stankiewicz 1998).

The metal artefacts and, more in general, materials connected to the metallurgical activity are present in large amounts in museums and scientific collections all over the world. The use of this large experimental material is an important prospective for the archaeometallurgist, who needs experimental verification of his theoretical hypothesis (Giardino 1998). Unfortunately these materials cannot be moved from museums and sites where they are stored, because of conservation and safety reasons. The use of movable instrumentation, i.e. that can be used at the museum (or in site), can solve this problem, creating however new issues concerning its correct use and limitations.

The large use of portable systems is a general trend in all technological areas and, in part, in research (Sackett & Martin 1998). Their practical and economical advantages are evident, allowing, thanks to a greater level of automation, to reduce expenses for personnel and materials and to increase responsiveness. This has been true also in the field of conservation and, in a lesser extent, in archaeometry, in which the principal advantage resides in the possibility to perform a greater number of measurements, thus investigating a large number of different artefacts or performing many measurements on the same one.

The most common disadvantage is the larger risk of obtaining less accurate results (and a lower reproducibility level), due to the fact that the procedures can be better controlled in laboratory. Another point to remark is the need to employ well skilled personnel and a well scheduled plan of work, since the risk to do many useless measurements is larger when using simple instruments as are frequently the portable ones.

The traditional laboratory procedures operate in a remote mode: sampling and analysis phases are well separated in time and in space; the only unwanted consequence of this is to underestimate experimental conditions that could influence the results of the analysis (e.g. contamination, unknown microstructure, etc.). With a mobile system, the above mentioned phases take place in the same site, and frequently within a very short time. This fact can help the use of a more flexible

and effective measurement program, especially when the degree of automation of the instrument is very high.

In the case of a non-destructive measurement some additional problems arise, mainly coming from the potential inhomogeneity of the artefact structure and matrix. In the case of FP-EDXRF spectrometers, these limitations are mainly connected to the finite penetration of emitted x-rays and to the changes in the geometrical efficiency that can hardly be taken fixed when the artefact is examined in a non-destructive way (Gigante & Cesareo 1998).

There have been many important developments in the construction of FP-EDXRF instrumentation in the last decade, mainly due to the availability of small and portable x-ray tubes and non-cryogenic detectors similar, in performance, to the traditional cryogenic ones (Cesareo et al. 1992, Cesareo 2000).

Another remarkable contribution to the in-field use of the EDXRF technique has been the development of software specifically engineered for in-situ acquisition and data analysis, and further data managing.

2 DETERMINATION OF METAL ALLOYS COMPOSITION THROUGH XRF ANALYSIS

The determination of metal alloys composition is one of the most significant problems in which XRF techniques have successfully been employed. The principles on which these techniques are based are the following:

- (a) The elements constituting the alloy produce one (or more) x-ray emissions within the energy range the spectrometer can analyse
- (b) The spectrum of the exciting source is well known
- (c) The coefficients describing absorption and subsequent emission of x-rays by the metallic sample are known (fundamental parameters)
- (d) The approximation of infinite thickness sample is fulfilled
- (e) The detector's physical efficiency and the spectrometer's geometrical efficiency can be determined
- (f) The sample has a perfectly smooth surface; thus the geometry of the measurement can be taken fixed.

Under these hypotheses it is possible to reduce the analytical problem to the solution of a system of non linear equations, using an iterative procedure. These equations describe the functional relationship existing between the measured quantities, i.e. the relative intensities of the different elements' peaks, and the weight fraction of each element constituting the alloy. The equation for each element is:

$$I_i = I_0 G K_i A_i w_i$$

with

$$K_i = \tau(E_0) \left(1 - \frac{1}{J_i}\right) \omega_i f_i \epsilon_i \quad (1)$$

and with

$$A_i = (\mu(E_0) \operatorname{cosec} \psi_1 + \mu(E_i) \operatorname{cosec} \psi_2)^{-1}$$

with:

f_i : probability of emission of the line

G: geometrical efficiency of the spectrometer

I_0 : intensity of the incident beam

J_j : jump ratio

N : number of elements in the sample

w_i : weight fraction of the i -th element

ϵ_i : detector's efficiency for the emitted photons' energy E_i

$\tau(E)$: partial absorption coefficient for the photoelectric effect

ω_i : fluorescence yield

$\mu(E)$: mass absorption coefficient of the sample for the energy E

$\mu_i(E)$: mass absorption coefficient of the i -th element for the energy E

ψ_1 and ψ_2 : angles of incidence and emission

with

$$\mu = \sum_{j=1}^N \mu_j w_j \quad (2)$$

In the above list of parameters, some coefficients are known with a good degree of approximation, such as the absorption coefficients; some others depend on the spectrometer, such as angles and efficiencies. These last ones can only be determined approximately when the sample does not have a smooth and flat surface or the pointing device is not accurate enough. The search for a solution of the system is made through the above mentioned iterative method that allows a quick determination of the best possible w_i , taking into account that the measured intensities (or intensities ratios) are affected by a statistical error and the given parameters are known with an uncertainty. This produces systematic biases on the values. Using a set of reference samples it is possible to determine the best value for the empirical parameters (x-ray tube intensity and geometrical and detection efficiency) (Piorek & Pasmore 1993). It is worth noting that the above equations are for a monochromatic exciting source; the use of a polychromatic beam, as is that generated by an x-ray tube, implies integration on energy spectrum of the source. The determination of the error produced by the application of the iterative method become consequently more complex, and the error itself can be considered as the result of two contributions. The first one is due to fluctuations in the beam intensity integral (and it can be treated as due to the fluctuations of a monochromatic source), the second is due to the shift in the exciting spectrum caused by variations in the voltage applied.

It is possible to use the ratios of the peak areas relative to that of the major alloy constituent. In this way it is implicit the assumption that the sum of the weight fractions equals unity.

Similar approaches to quantitative analysis are commonly found in environmental sciences; i.e. in the field of quantitative evaluation of heavy metals, systems have been developed which yield satisfactory results in the process of soil control. With the scope of such controls, some procedures have been outlined that give way to results which are retained trustworthy, in the typical working conditions of the field. Similarly, there are systems available for the analysis of metal in the industry (Metorex); in this case also standard procedures have been defined.

All of these systems imply the possibility of obtaining satisfactory quantitative results with the use of radioisotopic sources, which do present an intrinsic stability.

3 INSTRUMENTATION

A typical FP-EDXRF spectrometer is mainly composed of:

- an x-ray tube
- an x-ray detector with its electronics
- a multichannel analyser.

We have experienced a rapid evolution of these components in the last decade, starting from the developments of HgI₂ x-ray detectors in the early nineties of the last century (Cesareo et al. 1992). Now the situation seems to be going toward a stabilisation with a landscape of possible choices that fulfil the peculiar requirements of principal applications offering suitable solutions.

Table 1. Characteristics of small-size, portable x-ray tubes according to the element or elements to be analysed.

Element interval	Anode material	Anode voltage (kV)	Current (mA)	X-ray spectrum and peak/ BS* ratio
Sodium-chlorine	Calcium (K-lines)	8-10	0.1-1	3.7 keV peak BS ($\approx 1/1$)
	Tungsten (L-lines)**	13-15		8.4, 9.7 and 11.3 keV peaks
Potassium-yttrium (K-lines)	Molybdenum (K-lines)	30	0.1-1	17.5 keV peak BS ($\approx 0.2/1$)
Cadmium-uranium (L-lines)				
Potassium-barium (K-lines)	Tungsten (K-lines)	40	0.1-1	Practically only BS
Heavy elements (L-lines)				

* Bremsstrahlung.

** Possibly with a transparent anode.

3.1 X-ray tubes

A great variety of x-ray tubes of various types (maximum voltage, current, anode), sizes and cost are currently available for EDXRF analysis, depending on the problem, and more specifically on the element or elements to be analysed. Leaving out analysis of traces, which requires high-current tubes with proper secondary targets, low-power x-ray tubes (with selected anodes) are generally adequate. They may be chosen primarily as a function of the atomic number of the elements to be analysed. Table 1 gives a survey of useful EDXRF tubes (Oxford, EIS) for analysis of any element.

A low size, low power W-anode x-ray tube working up to 50 kV, 0.1-0.3 mA is adequate for analysis of all elements of interest in any matrices with the exception of trace elements. Working at low voltages (15-20 kV) and at high voltages (35-40 kV) respectively, this tube is able to excite low atomic number elements such as S and Cl, or elements from Ca to Pb. In Figure 1 is shown a small x-ray tube with its pointing device (two collimated laser beams) which helps the user in the localization of the excitation area.

The advantage in using an x-ray tube, rather than a sealed radioisotopic source, is in the possibility to collimate the beam in a small area. A capillary collimator can also be employed in conjunction with the x-ray tube, to collimate the beam into sub mm² areas.

3.2 X-ray detectors

The typical, high-resolution x-ray detector was traditionally the nitrogen cooled Si or Ge detector, with an energy resolution of about 150-200 eV at 5.9 keV.

In the last decade, small size thermoelectrically cooled semiconductor detectors have become available, such as HgI₂, Si-PIN, SDD and CZT (Cesareo et al. 1992, Huber et al. 1995, Fiorini et al. 1997).

These detectors are cooled to about -30°C by means of a Peltier circuit, and are contained in small size boxes also including a high quality preamplifier and the Peltier circuit.

- HgI₂ detectors were the first to be constructed, and currently have an energy resolution of about 180-200 eV at 5.9 keV, and an efficiency of about 100% in the whole range of x-rays.
- Si-PIN detectors, with a Si thickness of 300 μm , exhibit an energy resolution of 160-200 eV, and are useful up to about 30 keV, because the efficiency is decreasing at energy larger than 15 keV, due to the limited thickness.
- SDD (Si-drift) detectors have a Si thickness of 300 μm , and an energy resolution of about 150 eV at 5.9 keV. They are able to work also at high counting rates.
- CZT detectors have a thickness of 2 mm and an efficiency of about 100% in the whole x-ray range. The energy resolution is about 300 and 700 eV at 5.9 and 59.6 keV, respectively.

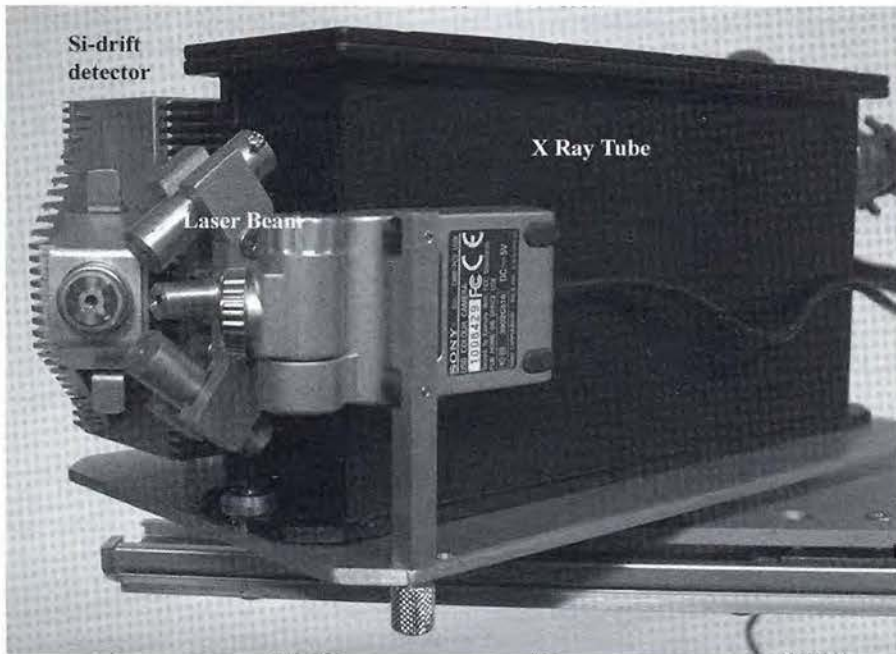


Figure 1. FP-EDXRF instrumentation (EIS s.r.l., Rome, Italy): detector, x-ray tube and pointing device.

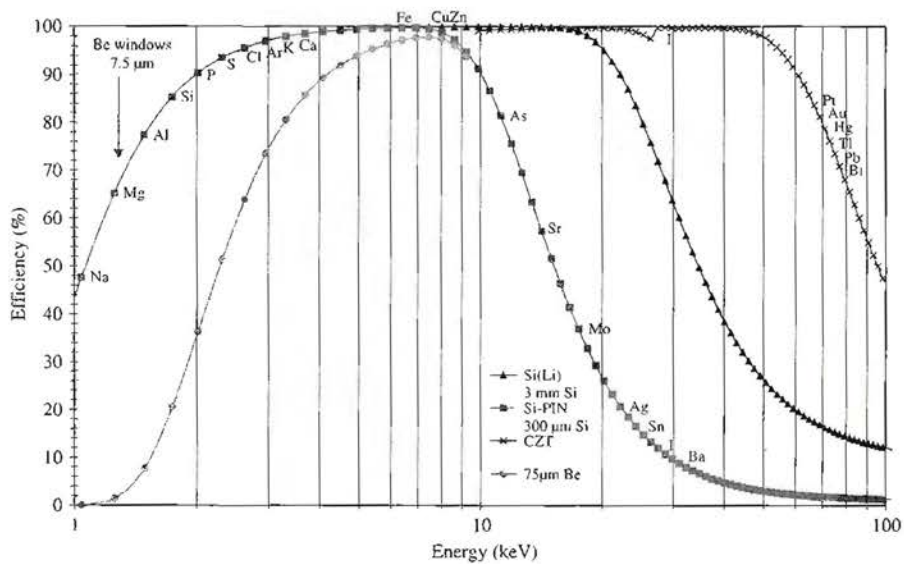


Figure 2. Efficiency of Si(Li), Si-PIN and CZT detectors.

In Figure 2, the efficiency of a Si(Li) detector is compared with that of two thermoelectrically cooled detectors: (a) a 300 μm thick Si detector (SDD or Si-PIN), (b) a 3 mm thick CdZnTe detector.

A summary of the useful Peltier-cooled detectors is given in Table 2.

Table 2. Comparison between the performance of various x-ray detectors: Si(Li), HPGe, Si-PIN, HgI₂, and SDD having an area of 10, 30, 7, 5 and 3.5 mm² respectively.

	Si(Li)	HPGe	Si-PIN	HgI ₂	Si-drift
Energy resolution (FWHM at 5.9 keV)	140	150	170	200	155
Useful energy range (keV)	1–50	1–120	2–25	2–120	2–25
Efficiency*	0.008	0.025	0.0055	0.004	0.003
Shaping time (μs)	6–12	6	12	12	2
Cooling system	Liquid nitrogen	Liquid nitrogen	Peltier	Peltier	Peltier

* At 1 cm from a point source.

4 POSSIBLE EXPERIMENTAL ERRORS AND THEIR RELEVANCE IN EDXRF MEASUREMENTS

One of the basic aspects of a campaign of measurements is the possibility to indicate the precision of the results, which is associated with the statistical dispersion that one finds when considering the results of multiple measures. One also needs to investigate the accuracy of the data and, consequently, the reproducibility of the experimental procedure.

There are several possible causes of errors in an EDXRF measurement, namely the statistical error (due to the physical processes of spectrum generation in the tube and of signal formation in the detector), the calibration error (which produces a systematic rather than a randomly distributed effect), errors due to inhomogeneities in the object in analysis, and more errors associated with the measuring system as a whole. The latter are due to instrumental instabilities and to the geometry of the measure, which greatly affects the results, especially when dealing with artefacts having a rough surface.

An experimental evaluation of some of these errors has been made by estimation of the statistical spread of the results of some sets of $N = 10$ measurements on a metal foil made of 95% Au and 5% Ag; each set of measures was characterized by the sources of errors it could possibly be affected by, and the error was calculated as:

$$S = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} \quad (3)$$

where x_i is the result of the i -th measurement, and \bar{x} is the average of the 10 results.

In order to better evaluate the effect of each kind of error, the different sources have been divided as follows:

1. Instrumental error, due to:
 - a. Detector
 - b. X-ray tube
2. Measurement error, due to:
 - a. Geometry
 - b. Calculation procedures
 - c. Sample inhomogeneity

It is therefore possible, in principle, to calculate the total error as the quadratic sum of the errors due to each possible source:

$$\sigma_{\text{total}}^2 = \sigma_a^2 + \sigma_b^2 + \dots \quad (4)$$

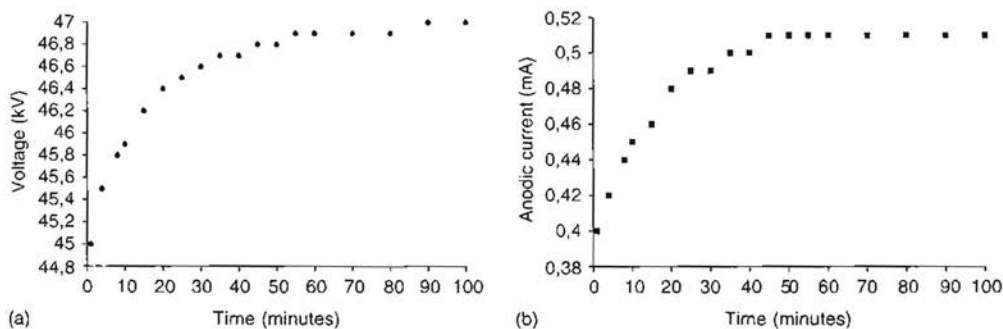


Figure 3. Behaviour of the tube's characteristics during the first 100 minutes after it has been turned on. (a) Voltage ($\tau = 21.5 \text{ s}^{-1}$), (b) Anodic current ($\tau = 13.8 \text{ s}^{-1}$).

The above relation holds only when the contributing errors are independent. Using an FP-EDXRF spectrometer, this condition is not fulfilled, especially for the instrumental causes of error. In this case, the evaluation of the contribution of each source of error can be done only by looking at its effect on the overall error, taking into account that the statistical error sets a lower limit to the precision obtainable.

4.1 Instrumental error

As for the detector, it induces a statistical error due to the Poissonian process of formation of the signal in the detector itself; the relative uncertainty has been found to be $\sigma/N = 1/\sqrt{N}$, where N is the net area of the peak of interest (which was either Ag $K\alpha$ or Au $L\alpha$ in our experiment). The relevance of the counting statistics in terms of resulting error leads to the choice to make long measures (600 s each) in order to enhance the importance of other sources of error.

The x-ray tube can be used in optimal conditions of stability by starting the first measurement about an hour after the system has been turned on; this lets the tube's voltage and current both reach an "equilibrium" value and drastically reduces fluctuations of the measured spectra (see Figs 3a, b).

The instability introduced by the shut-down of high tension is usually less relevant because the current flows continuously in the filament. An error can be induced by the inertia with which the maximum voltage is reached when the tube is turned on again; it is thus advisable to wait a few seconds before starting another measurement. The overall error associated to measurement affected by both the detector and the tube's instabilities has been found to lie in the range 0.5–3.0% of the weight fraction (calculated from the measured peak areas through the fundamental parameters approach).

4.2 Measurement error

The geometry of the measurement, if considered fixed, induces a systematic bias on the results. On the other hand, repositioning of the sample has a direct effect on the spread of the results; if done with a certain care, repositioning does not greatly influence the overall error which still lies in the range 0.5–3.0% of the weight fraction. A less careful (manual) repositioning causes the error to be for the most part due to geometry; its overall value varies greatly and goes up to about 20% of the weight fraction. The latter is the case when one can choose to calculate the concentration of each element in the alloy using the peak ratios, i.e. the ratios between the net areas of the peaks of interest and the area of a peak chosen as a "reference" (typically the Au $L\alpha$ for gold alloys). The use of peak ratios allows to diminish the dependence on the geometrical factor and thus to reduce the influence of repositioning, yielding errors smaller than about 3.0% on the weight fraction.

The error induced by calculation procedures is not easy to quantify. It can usually be included in the calibration error, due to the setting that is systematically made before a series of measurements, by using some reference samples. An experimental verification of the variations in the values of the

calibration parameters in repeated measures during a few days has shown that the relative variation is no greater than about 1.5%.

The most significant uncertainty in the quantitative measurement of an alloy's composition during in field measures is obviously induced by the sample itself, which can be inhomogeneous and/or present surface deformations and corrosion layers.

5 MINIMUM DETECTABLE LIMITS OF SILVER AND COPPER IN GOLD ALLOYS

The minimum detectable limit (MDL) of Ag and Cu in a gold alloy has been calculated using the following expression:

$$\text{MDL} = \frac{3\sigma_B}{dN/dC} \quad (5)$$

with σ_B = experimental error on the background, and dN/dC = detection sensibility; this last quantity is estimated by use of a linear fit on a set of 5 data relative to standards containing different concentrations of Ag, Cu and Au. Our portable system yields the following results: $\text{MDL}_{\text{Ag}} = 0.061\%$ and $\text{MDL}_{\text{Cu}} = 0.12\%$.

6 GOLD ASSAYING

Gold assaying by means of non-destructive XRF provides users with a real alternative to traditional gold assaying techniques. The results shown above confirm the possibility to obtain an accuracy of a few tenths of a percent relative to the weight fraction in optimal working conditions, i.e. when the surface of the sample is uniform and smooth. Moreover, the MDLs are satisfactory enough for archaeometric purposes in the case of major alloy constituents. This opens realistic perspectives for field portable analysis of ancient gold artefacts. A campaign on prehistoric jewellery in the Messenian region of the Peloponnesus is under way, in co-operation with Greek researchers. Although not yet published, the results obtained show how it is really possible to use portable systems for this kind of analysis (see Fig. 4).

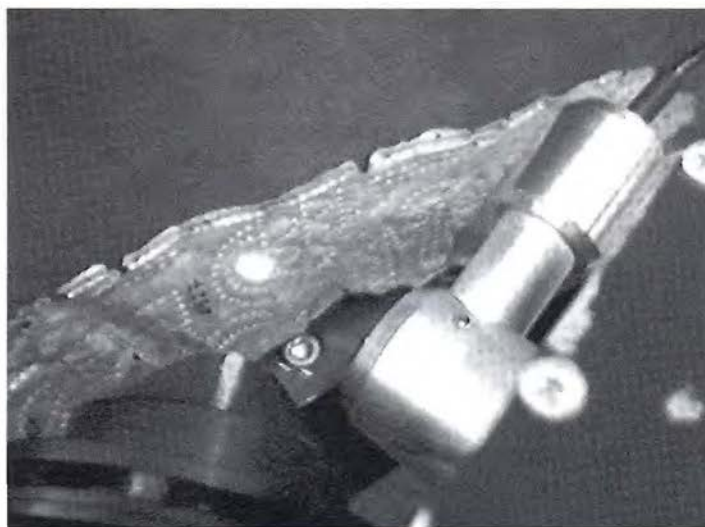


Figure 4. The FP-EDXRF spectrometer during the measurements on Messenian gold artefacts in the 2002 campaign.

7 CONCLUSIONS

A critical analysis of the errors of field portable spectrometers has shown how simple experimental devices make it possible to reach a level of precision better than 3% on the calculated weight fractions.

It has been proven valid a method for the correction of the geometrical efficiency errors, based on the use of a reference peak and the peak ratios.

The errors due to the use of a low power x-ray source, such as those currently available, do not set a strict limit to the possibility of obtaining good precisions. The many measurements made (whose results are partly reported in this article) have shown how, by using some care, the error due to source fluctuations is comparable if not negligible with respect to the statistical one, in most common experimental conditions, in which short counting times can be employed.

Our statement is confirmed by a careful analysis of the results obtainable with portable XRF systems operated with radioisotopic sources, which do not yield significantly better results.

In this review of the possible obtainable results it is worth underlining that the error introduced by the sample itself, due to its inhomogeneities and surface deformation, cannot be easily quantified. In many experimental conditions, such as those of non-destructive analysis, the latter is probably the most relevant source of error.

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