

# DEVELOPMENT OF X-RAY FLUORESCENCE-BASED METHODOLOGY FOR QUALITY CONTROL OF ZARI USED IN SILK SARIS

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## **Abstract**

The traditional Kancheepuram silk sari still maintains its appeal, and has a significant market share. Gold-coated silver thread (zari) is used in this sari. The quality, and hence the price of the sari, is dependent on the composition of the zari. Until now there has been no qualified method of assessing this. This paper presents an X-ray fluorescence-based method of assessing the zari.

## **Key words:**

zari, sari, X-ray, fluorescence

## **1. Introduction**

India has a rich cultural tradition. There are many works of art which represent this, including the Kancheepuram silk sari. A sari is a long single-piece garment worn by women. This traditional sari still maintains its appeal, and contributes to a significant market share in handloom textiles. The incorporation of gold-coated silver thread (zari) is the specialty of these saris. For the same reason, these saris command a higher price range. Since noble metals are involved in the making of these saris, there is a need for stringent quality control to safeguard the buyer's interests. So far, the quality control has been done by using time-consuming conventional chemical analysis. Also, being destructive in nature, conventional chemical analysis can be used to assess silver thread on a sampling basis only, and cannot be used for finished saris. Thus there is a need to develop a suitable non-destructive technique to analyse the chemical composition of the zari in sari form.

Among the chemical analysis methods, the X-ray fluorescence-based (XRF) technique is the most suitable for such non-destructive applications. Different XRF systems/configurations are available, each designed for a specific purpose.

## **2. XRF Analysis for Zari**

The XRF technique provides specific analysis of elemental concentration without regard to chemical combinations. In general, the sample is irradiated with X-rays, either from an X-ray tube or a low-level radioisotope. This radiation excites the elements in the sample, causing them to fluoresce and emit their own characteristic X-rays. The X-rays can be identified either by their wavelength or by their energy. The X-ray intensity is a measure of concentration of the element in the sample.

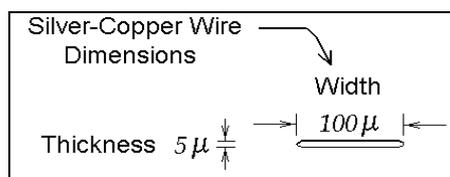
While adopting the XRF technique for the elemental analysis of zari specimens, the important factors that influence the analysis are the composition of the specimen, the energy resolution of the detector, the configuration of the X-ray source, the specimen and the detector, and the efficiency of the XRF peaks of the elements of specific interest, namely silver, copper and gold.

### **2.1 Composition of Zari**

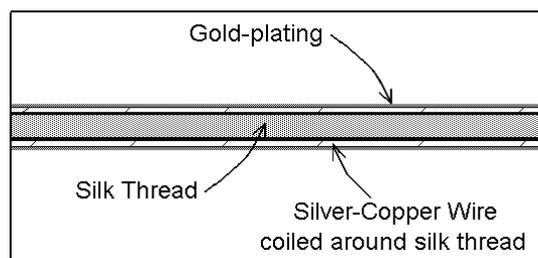
For quantitative analysis, the XRF technique needs a set of standards which cover the range of chemical composition of the samples to be analysed. Apart from the chemical composition, the physical shape of the sample also plays an important role. Not only the shape, but also the texture (whether the zari is in thread form or woven into the fabric) of the standards should be same as that of the sample. If they differ in physical form, the chemical analysis is likely to be incorrect. Thus, for each

of the physical form/texture of the specimens, even if their chemical composition is the same, we need a different set of standards. In this context, it is pertinent to note how the zari thread is made.

The feed material for making zari is a 25-micron diameter wire made of silver-copper alloy. This wire is flattened to a width of 100 microns by rolling in a flattening machine. Figure 1 shows a schematic diagram of the cross-section of the silver wire after flattening. The flattened strip is coiled around a silk thread of the required denier, in a spinning machine, to obtain a silver thread. This silver thread is electro-plated with gold to obtain the gold-thread. This is chemically polished and further flattened with light rollers. Figure 2 shows a schematic diagram of the cross section of the gold-thread (gold zari)<sup>1</sup>. 'Back-of-the-envelope' calculations indicate that the thickness of the silver-copper wire coiled around the silk thread is approximately 5 microns, and the thickness of the gold film is approximately 0.04 microns.



**Figure1.** Schematic diagram of the cross section of the silver wire after flattening



**Figure2.** Schematic diagram of the cross section of the gold-thread

The elements of primary interest in zari are silver (0 to 55%), copper (20 to 55%) and gold (about 0.6%). Silk thread contributes to the remaining part, approximately 25%. Silk comprises the bulk of the volume of zari thread.

A quantitative compositional analysis of zari includes the following processes: (1) establishing the percentage of silver and copper, and (2) establishing the thickness of gold. A compositional analysis of silver and copper in zari is presented in this paper. Therefore, the objective of this study is to arrive at a suitable XRF system configuration and a suitable procedure.

### 3. XRF Systems and the options

In its most sensitive configuration, the XRF technique is used in many analytical laboratories. In its portable configuration, the XRF technique is used on shop floors and in fields, for applications such as identifying the alloy of machine tools and industrial components, and also in gold assessment of jewellery.

We can classify the XRF systems into two types: wavelength-dispersive and energy-dispersive. Wavelength-dispersive systems are essentially X-ray spectrometers. The wavelength of the characteristic fluorescent X-rays is taken into consideration while identifying the element. Energy-dispersive systems are multi-channel analyser-based systems. The energy of the characteristic fluorescent X-rays is taken into consideration for identifying the element. Generally wavelength-dispersive systems have better resolving capability, and are mostly used for quantitative analysis. Further variations are available depending on the type of X-ray source and detector used, and on the configuration employed.

The elements of interest are in the major (Ag and Cu) or minor (Au) range, but not in the traces. Keeping cost considerations in view, a wavelength-dispersive laboratory system, with its high sensitivity, is not recommended.

Three systems with different possible energy-dispersive XRF configurations were studied. They are: (1) standard X-ray tube-based system (Phillips make) (2) radio isotope-based system with detachable

<sup>1</sup> We have not made any specific effort to study or record the microstructure of the zari thread. It suffices to approximate the cross-section to understand its role in XRF analysis.

probe (Asoma make), and (3) X-ray tube-based system with collimated beam (Röntgenanalytik/Quantum make). In all these systems, the detector is either a proportional counter or a semiconductor detector, since the XRF peaks of silver, copper and gold are well separated.

### **3.1 Standard X-Ray Tube-Based System**

The sample has to be accommodated in a cell. Sample changers accommodate a number of cells in a tray for automated analysis. One of the major problems in using such a tube system for zari analysis is to keep the zari thread in the sample cell for analysis. In practice, this proves to be rather tricky. The thread either gets uncurled and settles at the rim of the cell, or changes its shape in the course of analysis. Thus the area of the zari thread exposed to X-rays varied from count to count. This has led to wide fluctuations in the X-ray count, sometimes by up to 200%. Alternatively, the thread has to be shredded into pieces to receive uniform X-ray irradiation, but such an approach would defeat the purpose of this study - i.e. to find an NDT technique for chemical analysis. A sample standard, to suit the sample cell, was designed to ensure the integrity of the X-ray count.

With this system, analysis cannot be done on an actual sari, unless a part of the sari is cut and put into the sample cell.

### **3.2 Isotope-Based System**

This is a portable system with a handheld probe. This can be conveniently used to analyse the composition of the zari at different regions of the sari. The window of the hand-held probe of the isotope-based system is 25 mm in diameter. Therefore any object whose effective surface area is less than this window will not employ the complete flux of X-rays from the isotope source. Therefore, a separate sample standard was designed in order to analyse the zari thread.

### **3.3 X-Ray Tube-Based System With Collimated Beam**

Here a fine focused X-ray tube is used. The X-rays are collimated through a collimator. Usually, a TV camera is aligned in line with the X-ray beam. This will help in viewing the area being analysed. Thus point-by-point measurements are possible with this system. We used a 300  $\mu\text{m}$  collimator.

## **4. Calibration**

Ten zari specimens with varying silver and copper proportions were considered. These samples were taken from a batch of zari material that had already been analysed through wet chemical analysis<sup>2</sup>. The range of silver is from traces to 55% (of the total weight of the thread specimen which includes silk). The range of copper is from 20 to 55%. These specimens are used as standards for calibrating the concentration against XRF intensities. The XRF count used is corrected for background and inter-elemental interference.

Calibration curves were obtained for silver ( $L_{\alpha}$ ) and copper ( $K_{\alpha}$ ). Generally, the relationship between elemental concentration and measured X-ray intensity is hyperbolic. If the correction factors are reliable, this hyperbola starts at the origin and terminates at the pure element point. Actually, these curves are part of a family of hyperbolae that link the origin and the pure element point. The X-ray absorption characteristics of the sample matrix will determine which hyperbola the XRF response will follow. Since the concentration range of the elements of interest, namely silver and copper, is large, the calibration curve should fit to a hyperbola. Typical calibration curves are shown in Figures 3 and 4. These are obtained using the isotope-based system.

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<sup>2</sup> The wet chemical analysis was done by M/s. Tamil Nadu Zari Ltd. The weight percentage of silk thread was found by burning the specimen. The residue was analysed for its silver content. The rest of the composition was attributed to copper.

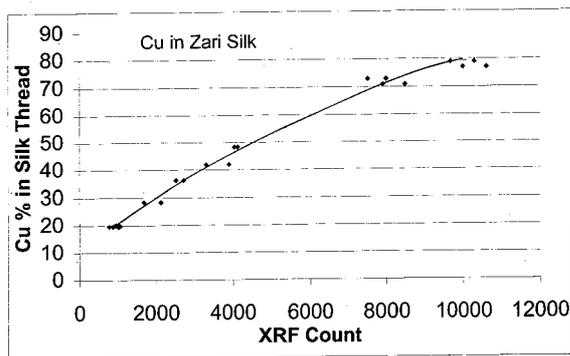


Figure 3. Calibration Curve for Copper

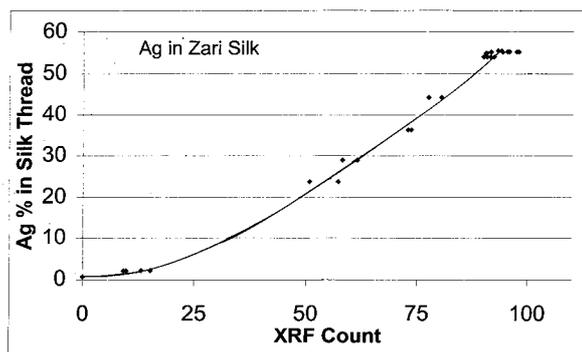


Figure 4. Calibration Curve for Silver

## 5. Results

Using these curves, we are able to estimate the silver and copper content to an accuracy of 2%. Typical results are shown in Tables 1 to 3. Tables 1 and 2 show the estimations obtained with various XRF systems for silver and copper respectively. The XRF-based estimates are in good agreement with the estimates based on wet chemical analysis. **It may be noted that these calibration curves are not universal, but specific to a given XRF system.**

Table 1. Comparative analysis of zari thread for silver using different XRF systems

Sample No.	Ag (Given)	Ag (Calculated) using isotope based system	Ag (Calculated) Using tube system with collimator	Ag (Calculated) Using tube system without collimator
1	44.30	43.40	44.00	42.67
2	28.93	28.47	29.30	30.77
3	36.26	36.63	36.70	37.24
4	23.75	24.00	23.40	23.95
5	2.07	2.07	1.90	3.78
6	0.69	0.69	0.30	0.67
7	0.67	Below detection limit	0.40	0.36
8	2.16	2.16	1.90	3.19
9	54.00	53.5	54.40	55.29
10	55.21	56.75	55.30	56.68

Table 2. Comparative analysis of zari thread for copper using different XRF systems

Sample No.	Cu (Given)	Cu (Calculated) using isotope-based system	Cu (Calculated) Using tube system with collimator	Cu (Calculated) Using tube system without collimator
1	28.36	29.50	28.00	32.36
2	41.87	41.44	42.20	44.71
3	36.18	34.84	35.80	33.63
4	48.31	48.31	48.60	48.59
5	70.88	71.65	70.50	56.00
6	77.00	78.5	77.30	80.07
7	78.89	78.21	79.30	87.30
8	72.90	72.25	72.70	56.53
9	20.00	20.00	20.10	23.05
10	19.59	19.56	19.60	18.00

### 5.1 Effect of Texture

When the zari thread to be analysed is in thread form or on a bobbin, the X-ray beam (300  $\mu\text{m}$  diameter) sees the zari alone. However, when the zari to be analysed is woven into the sari, the zari thread (approximately 100 to 150  $\mu\text{m}$  width) may not utilise the beam completely. The X-ray beam (300  $\mu\text{m}$ ) sees not only the zari but also the surrounding silk thread. In order to study this, different parts of the sari with different designs were analysed and compared with individual thread analysis.

**Table 3.** Analysis of different parts of Kancheepuram zari silk sari using X-ray tube-based system with collimator

Sample No.	Nature of zari silk sari part	Silver# (%)	Copper# (%)
1	Border	48.12 $\pm$ 0.40	25.45 $\pm$ 0.38
2	Pallo	49.25 $\pm$ 0.26	24.85 $\pm$ 0.70
3	Body lining (horizontal)	40.67 $\pm$ 0.86	32.15 $\pm$ 0.77
4	Zari thread cut from the sari	50.37 $\pm$ 0.64	23.37 $\pm$ 0.59

# Average of 4 Values

Table 3 shows the results obtained on different parts of a Kancheepuram zari silk sari with a 300- $\mu\text{m}$  collimated X-ray beam. The effect of texture may be noticed if we observe the Ag-Cu composition of the zari thread woven into the sari. The design density of the zari thread (i.e. the area percentage of the X-ray beam covering the zari thread) in the border and pall region is higher compared to that in the body-lining region. Accordingly, the estimates in the border and pall regions are closer to the individual zari thread estimates. The use of a slit collimator (say, 100  $\mu\text{m}$   $\times$  500  $\mu\text{m}$ ) can minimise the error in estimation, even in regions of low design density. The increase in Cu in the fabric, compared to that in the thread form, may be caused by enhanced X-ray emissions in this region by the woven silk or the colour dye.

### 6. Conclusion

Among the three configurations studied, the standard X-ray tube-based system with a broad beam is not suitable for analysing zari, due to difficulty in handling the specimen. The isotope-based system is suitable for analysing zari in spindle/bobbin form, and also in the saris themselves. However, it cannot be used for studying individual threads, since the isotope source gives a broad and divergent beam. Also, while analyzing saris, the design density of the zari may influence the estimates. The isotope source strength decreases gradually, which requires frequent revision of the analysis parameters and also needs periodic replacement of the source. The X-ray tube-based system with a collimated beam of 100  $\mu\text{m}$  is the most suitable system for quality control of the zari. This system, with a custom-made sample chamber design, can be used for analysing the zari in any form (thread, spindle or bobbin), as well as zari saris.

### Acknowledgements

*We would like to thank TIFAC, DST for suggesting TNZL, Kancheepuram to get the expertise from IGCAR for this developmental work. We are thankful to Shri A. Eugene and Shri S. Selvam (the immediate past and present Managing Directors) and Shri S. Kuppusamy of TNZL for their active involvement and for providing us with necessary samples and data on wet chemical analysis. We are grateful to Dr. Deepak Bhatnagar, DST and Dr. R.M. Krishnan, CECRI, Karaikudi for their support and encouragement. We express our sincere gratitude to Dr. R. Chidambaram, Chairman TIFAC and Principal Scientific Advisor to the Government of India for his keen interest. Some of the experimental work has been carried out with the help of Mr. Musale, Quantum, Mumbai, and the same is acknowledged.*

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