A new approach of sample preparation of Wavelength Dispersive X-ray Fluorescence (WDXRF)

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Abstract: In this article we give special attention to current WDXRF users about the sample preparation methods. We report two new methods (Mylar and Matrix) methods for the sample preparation which is quite useful in XRF spectroscopy. Blood and water samples have been analysed by these methods. Various low and high Z elements have been detected by these methods.

Keywords: WDXRF, Matrix, Mylar Method.

I. INTRODUCTION

In these days, X-ray fluorescence (XRF) spectroscopy is more powerful and accurate method used to study the unknown concentration, chemical effects, intensity ratio's, cross-sections, thickness and other parameters of the compounds and elements given in the periodic table. It has proved to be a versatile tool to measure Geological, Archaeological, Biological, Material Science, Powder, Solid and liquid samples [1]. Most of the X-ray fluorescence (XRF) techniques also fulfil with these multi-elemental capabilities. The non-destructive qualitative and quantitative studies of the various elements have also been studied with these analytic techniques with different methods and sample preparation. The basic principle of XRF technique is to excite the given sample/specimen using X-ray beam to produce ionization in the inner shells of the atoms present in the sample due to photoelectric and Compton effect. Major technique can be classified to measure the characteristic of X-ray emission spectra is Wavelength dispersive X-ray fluorescence (WDXRF). In order to analyse the photon atom interaction, each and every part of the technique like detection system, exciting source, low noise preamplifier and amplifier system and processing system is well known.

II. X-RAY TUBE BASED WDXRF EXPERIMENTAL SETUP

The S8 TIGER WDXRF spectrometer (situated at Panjab University Chandigarh) is one of the most commonly used for elemental analysis applications. It can be measured elemental concentration ranging from few ppm to nearly 100%. For excitation of single and multiple target elements Rh anticathode X-ray tube is used. The spectrometer is usually automatically operated at voltage of 60 kV and current of 40 mA. The K x-ray of Rh from anticathode X-ray tube can efficiently excite the characteristic $K\alpha$ fluorescent line for elements in the range of $5 \leq Z \leq 50$ and $L\alpha$ lines in the range of $50 \leq Z \leq 92$. The breumstralung part of incident flux from X-ray tube can also excite the K x-rays lines of some high Z elements. Furthermore, for maintaining a temperature X-ray tube is cooled by deionised water using a chiller. The sample chamber is consisted of 31 sample positions and all samples can be loaded simultaneously and measured sequentially. Analyses were performed under helium atmosphere to avoid powder loss in the analytical chamber, which may occur under vacuum conditions.

The system offers the most flexible and compact beam path. In combination with the high performance X-ray tube and advanced analyzer crystals, this compact beam path gives highest intensity and analytical speed.

Figure 1: Picture of WDXRF setup located at Panjab University Chandigarh.

The calibration functions have been selected out of the calibrations implemented by the software of X-ray spectrometer S4 («SPECTRAPLUS», 2002). The S8 TIGER can analyse all elements from Beryllium to Uranium in a wide variety of sample types. The total time-to result was 113 s, including loading, evacuation, analysis and reporting of the results. The peak acquisition time was optimized using the built-in Spectra Plus® software interface, which calculates the time necessary to achieve an average selected detection limit. The acquisition time varies, therefore, among elements as well as among concentrations of a given element (i.e., the lower the concentration, the greater the time). To avoid any excessively long acquisition times, a maximum time was set for each element, which varies from 30 to 100 s. The background measurement times have been fixed manually, generally at 10 s, except for a few trace elements. The overall measurement time is about 40 min per sample (i.e., 36 samples/24 h). The higher resolution of WDXRF provides advantages in reduced spectral overlaps, so that complex samples can be more accurately characterized. In addition, with high resolution backgrounds are reduced, providing improved detection limits and sensitivity.
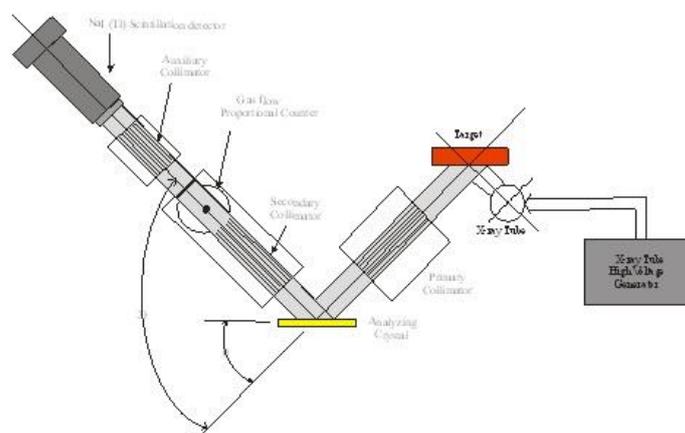

Figure 2: Schematic diagram of WDXRF setup.

The collimator masks are situated between the sample and collimator and serve the purpose of cutting out the radiation coming from the edge of the cup aperture. The maximum angle of divergence of the incident X-rays that fall on the analyzing crystals is limited by the spacing between the collimator plates. The size of the mask is generally adapted to suit of the cup aperture being used. The small spacing between collimator plates decreases the divergence and hence increases the energy resolution. A drawback of small spacing is a decrease in the incident flux that reaches the crystal. A number of parallel radiations passes through the collimators and falls on analyzing crystal. At the crystal, the radiation is diffracted in various directions according to the Bragg law. The WDXRF spectrometer is consisted of three analyzing crystal namely, XS-55, PET, LiF (200) with 2d spacing of 55.4, 8.75 and 4.026 Å respectively. The characteristic lines of different energies emitted from the sample are diffracted into different directions by these analyzing crystals according to their 2d value. Therefore a variety of crystal types with different 2d values is required to detect the whole element in the range of $5 \leq Z \leq 50$. Table shows a list of the common crystal types.

III. SAMPLE PREPARATIONS METHODS

For any technique and for less error, sample preparation is very important to get better results. In WDXRF technique the sample should be in solid, liquid and in powder form. In order to determine the concentration in (rock, chalk etc) low and high Z elements, the sample should be homogeneous (for powder form case). For powder samples, the grain size must be less than 50 μm (micro meter). Different researches used different techniques or methods for the sample preparation. *Gakuta Takahashi* described different methods for the sample preparation. Author used different binders like wax, cellulose and boric acids etc, as a binder which is used to stick the powder samples into the pellets. Author tried to explain various methods like Pressed Powder method and loose powder method. In their study, they also picturized the various limitations like errors, sample stick into the pellets etc during sample preparation. [2]. F. Demir *et al* also described the error occurs during sample preparation. [3] To remove these types of discrepancies, we develop two methods for the sample preparation. One is called Matrix method and other is Mylar method. To detect the low Z elements, we place the powder samples between two thin mylars and rub it so that absorption effect and impurities can be reduced. The other method (matrix method) is to add citric acid in 4:1 as a binder. This method can be applied for any samples. Citric acid is used because it is less contaminated as compared to the other compounds. In our present study, we test our new methods on a blood samples. To do this we collect the blood samples of patient's of different ages. To make self supporting pellets, we add 4:1 citric acid (matrix method) in a blood and then dry the sample at room temperature for 48 hours to make it in a powder form. Then dried blood samples were grounded with mortar and pestle into pellets of 23 mm diameter with pressure of 60 kN/m^2. Highly uniform and durable pellets with thickness ranging from 320 to 350 mg/cm^2 were obtained. Similarly, Jaipur water sample was treated with Mylar method. In this case heat the water sample for 2 hours at boiling point. After 2 hours white residue remains. Now that residue was placed in between two mylars and rub it so that all portion of the mylar were filled with residue sample.

IV. RESULTS AND DISCUSSIONS

The concentration of the various elements of blood samples Cl, K, S, Na, Fe, P, Si, Ru, Ca, Mg, Al, Zn, Cu, Pd, Br and Mo has been presented in Table 1. Similarly elements of (Jaipur water sample) like C, O, Cl, Ca, S, Si, Na, K, Mg, Fe, Br, Sr, Zn, P, Cr, Mn, Cu, Ni and Zr has been given in Table 2. All results given in the table 1 and table 2 are in ppm level. So it is cleared from both the table that WDXRF is capable for analysis low and high Z elements.

Here p1-p3 represents blood samples and S1 represents water sample. The instrument error is of ±5 %.

Elements	P1(ppm)	P2(ppm)	P3
Cl	7597	7195	7767
K	4146	4053	3832
S	2800	2640	2377
Na	2423	2398	2793
Fe	1825	1618	1151
P	576	597	581
Si	118	133	233
Ru	111	128	180
Ca	165	335	360
Mg	50	126	141
Al	52	78	77
Zn	54	60	59
Cu	33	45	39
Pd	260	281	144
Br	37	----	----
Mo	124	118	----

Table 1: Concentration of the various elements of blood samples Cl, K, S, Na, Fe, P, Si, Ru, Ca, Mg, Al, Zn, Cu, Pd, Br and Mo.

Elements	S1(ppm)
C	396300
O	262000
Cl	6400
K	3900
Fe	2400
S	2100
Na	1600
Gd	900
P	600
Pd	200
Si	200
Ca	100
Mg	95
Al	70
Zn	64
Br	41
Cu	26

Table 2: Concentration of the various elements of blood samples C, O, Cl, Ca, S, Si, Na, K, Mg, Fe, Br, Sr, Zn, P, Cr, Mn, Cu, Ni and Zr.

V. CONCLUSION

In the past decades, the significant technologies and ideas developed to make WDXRF apparatus become more powerful tool for elemental analysis, chemical effects, scattering process, intensity ratio, cross section and other parameters. But for better results best sample preparation is required. Matrix and Mylar methods are reliable to make best sample preparation for solid, liquid and powder samples. The advantages of these methods are the significant improvement in sensitivity of the detector. With these new methods low and high Z elements have been detected from blood and water samples. In the future, we investigate the role of these elements in blood and water samples. To sum up, we expect that with further improvements in sample preparation so that accurate and precise results will come out.

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