



**GOLD ESTIMATION IN GEOLOGICAL SAMPLES USING ENERGY  
DISPERSIVE X-RAY FLUORESCENCE SPECTROSCOPY**

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GOLD

X-RAY FLUORESCENCE ANALYSIS

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SEDIMENTS

LI-DRIFTED SI DETECTORS

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QUANTITATIVE CHEMICAL ANALYSIS

SAMPLE PREPARATION

INDIA

SENSITIVITY

PLUTONIUM 238

AMERICIUM 241

X-RAY SOURCES

TRACE AMOUNTS

**Abstract:**

Gold concentration in Indus river sediments have been estimated using energy dispersive X -ray fluorescence (EDXRF) spectrometry. To get the best possible detection sensitivity, optimisation of sample preparation procedure and exciting radiation was done. Physical preconcentration procedure of panning of heavy minerals has been employed. Samples were dissolved in aqua regia to homogenize the distribution of gold. For obtaining an optimum excitation sensitivity, radioisotope sources of various energies as well as a low powerlaboratory built transmission type Mo X-ray tube have been used. L shell X-rays of gold have been used for qualitative analysis. For quantitative estimation, a combination of single element fundamental parameter method and scattered radiation standardisation method was used. The sensitivity of our EDXRF spectrometer for gold is around 50 ppm.

## 1 Introduction:

Ultra trace quantities of gold in river sediments of Kashmir valley have been reported by Geological Survey of India /1/ but no detailed quantitative mapping of the region is available to establish its economic importance. We, in collaboration with J & K state Geology & Mining department, have undertaken to study the gold deposits in the Indus river sediments of the Ladakh region. Gold concentration present in these sediments is much below the detection limits of the usual chemical methods and only techniques like neutron activation, atomic absorption and X-ray fluorescence can be successfully used. Due to very low concentration of gold in geological samples (- ppb), preconcentration is still required. Neutron activation analysis (NAA) has a good detection sensitivity for gold (- 0.1 ppm) but requires a high flux neutron source in the form of a research neutron reactor or a high activity  $^{252}\text{Cf}$  neutron source and thus requiring a large infrastructure which is available only at limited places. Energy dispersive X-ray fluorescence spectroscopy is, on the other hand, a powerful technique for multielement detection in trace concentrations, having limits of detection for most of the medium and high atomic number elements in the range of a few ppm.

The estimation of gold using EDXRF spectroscopy is usually done by photo-ionization of K shells of gold present in the sample using high energy excitation source /2/. The high energy excitation X-rays (- 100 KeV) are obtained from radioisotopes or high voltage X-ray tubes. The K series characteristic X-rays of gold thus emitted are detected by a Ge(Li) or a Hyper pure Ge detector. In the present study we have used L series excitation of gold and detected L series characteristic X-rays using a Si(Li) detector. The K series lines were not used because of non availability of a high energy X-ray source and poor detection sensitivity of Si(Li) detectors for higher energies (> 30 KeV).

## 2 Sample Collection and Sample Preparation:

Gold from gravel deposits or bed rocks gets washed away by river water and because of its high density gets enriched in river sediments at places where the water velocity is low such as in regions of confluence or obstruction regions of big boulders or where terracing is observed due to annual cyclic change in water discharge rates. The samples of Indus river sediments of Ladakh region of J & K state were collected from such areas where maximum gold deposition is expected.

About 50 Kg of sample was collected from each site and pan concentrated to - 100 grams by density separation. The pan concentrate is quite heterogeneous in gold distribution because it is present in the form of specks. For homogenisation, the simple procedure of sample grinding could not be used in the present case because of the highly malleable nature of gold and thus chemical treatment of the sample was essential. The sample was dissolved in aqua regia ( $\text{HCl} + 3 \text{HNO}_3$ ) and evaporated to dryness on a waterbath. To remove excess of the acid present in the residue, it was mixed with water and evaporated to dryness several times.

The analysis of geological samples by EDXRF is complicated by matrix effects and sample inhomogeneity. These effects were neutralised largely by diluting the samples with cellulose in equal weight proportions. The drawback of matrix dilution method is that if the elements to be detected are present in very small concentrations, there is a danger of diluting these elements below the detection limits of the spectrometer. However, we had to use this method to suppress the strong absorption of Au L X-rays by the predominant iron matrix. The acid free residue was mixed with cellulose and homogenised in an agate mortar and pestle. A few milligrams of this mixture was pelletized using a hydraulic press at 25 tonnes/sq.inch pressure.

### 3 Experimental Technique:

The gold analysis was carried on our EDXRF spectrometer /3/ comprising of a cooled Si(Li) detector coupled to a Canberra series 85 pulse height analyzer (Figure 1). The Si(Li) detector has an active area of  $30 \text{ mm}^2$  and a thickness of 4 mm. The resolution of the detector is 155 eV at 5.9 KeV. For excitation of characteristic X-rays from the sample we used various low energy radioisotopes (Table I) and a laboratory built low power transmission anode type Mo X-ray tube. The excitation spectrum from X-ray tube is fairly monochromatic (Mo K lines) with a low continuum background (Figure 2). As the level of gold concentration in the samples was not known apriori the samples were analysed using various excitation sources and with various dilution factors for the sample.

The photoelectric absorption cross-section varies as  $E^{-3}$  above the absorption edge and hence the excitation efficiency decreases very fast with the increase of the excitation energy above the absorption edge of the element to be detected. Thus for monoenergetic excitation, the maximum excitation efficiency is achieved if the excitation energy is near the absorption edge of the line of interest. To excite the L X-rays of gold (9-13 KeV), we first used a 30 mCi  $^{238}\text{Pu}$  radioisotope source which emits U L X-rays (15-17 KeV). This source appeared to be the best suited for the present analysis on the basis of above mentioned criteria. A representative X-ray spectrum acquired for 6000 secs is shown in Figure 3. It was observed that for longer counting times, the Compton scattered U  $L_1$  peak, which is usually very low in intensity, interferes with the weak Au  $L\beta$  line. Hence the presence of gold in the sample could not be ascertained using  $^{238}\text{Pu}$  excitation source though it had good excitation efficiency for gold L lines.

To overcome this problem, a low power transmission type X-ray tube having a Mo target was used. This tube gives essentially monoenergetic X-rays of 17.4 KeV Mo K line. This excitation energy has fairly good excitation efficiency as it is not very far from the Au L shell absorption edge (11-14 KeV). Also, the excitation flux from the X-ray tube is two orders of magnitude higher compared to that of radioisotope excitation leading to higher detection sensitivity for Au L lines. The X-ray tube was operated at 35 KV, 150  $\mu$ A and counting rates were kept around 3000 counts per second. The spectrums were acquired for 2000 secs. A representative spectrum of the sample is shown in Figure 4. It is observed from Figure 4 that a peak corresponding to Au L $\alpha$  energy has developed at 9.7 KeV but no corresponding Au L $\beta$  peak is seen. The intensity of Au L $\alpha$  and Au L $\beta$  should normally be of the same order but as the Au L $\beta$  energy falls on the Mo K $\alpha$  Compton tail, it is possible that the Au L $\beta$  peak gets smeared in the high background in this region. To substantiate this argument, a blank sample similar in composition to the unknown sample was run for 2000 secs. This spectrum was treated as a background spectrum. On top of this spectrum Au L $\alpha$  peak was allowed to build up from a pure gold sample for a time such that the same integral counts were obtained in the Au L $\alpha$  peak as were obtained from the unknown sample. As expected, the associated Au L $\beta$  peak merges in the tailing Compton background and no peak feature is observed at Au L $\beta$  energy (11.4 KeV).

Despite observing Au L $\alpha$  peaks and reasoning the absence of Au L $\beta$  line using X-ray tube and  $^{238}\text{Pu}$  radioisotope excitation, we wanted to have an independent positive test which could unambiguously confirm the presence of gold. For this purpose we changed the excitation energy to 22 KeV using a  $^{241}\text{Am}$  radioisotope of 500 mci and a secondary target of silver. The secondary source geometry for sample excitation is shown in Figure 5. The secondary target of silver has a backing of tungsten which gives rise to a background of W L lines. The background W L $\beta$  (9.670 KeV) line overlaps with the Au L $\alpha$  peak (9.711 KeV). To suppress the W L X-ray background, we used a backing of



lead as a collimator. A spectrum acquired for 5000 sec, using  $^{241}\text{Am}$  - Ag secondary target with a lead collimator, is shown in Figure 6. This spectrum clearly shows the presence of Au L $\alpha$  and L $\beta$  peaks thereby confirming the presence of gold in these samples. However, the excitation energy with this source is very far from the absorption edge energy for Au L lines and hence the counting statistics is poor. Furthermore, Au L peaks are surrounded by comparatively intense Pb L $\alpha$  and Pb L $\beta$  peaks originating from the collimator which leads to large errors in estimating background below the weak gold L lines. Thus using 22 KeV excitation energy, the presence of gold was established qualitatively.

#### 4 Quantitative Estimation:

For the quantitative estimation of gold present in the sample we have used the Au L $\alpha$  peak intensity observed using low power Mo X-ray tube excitation. The procedure adopted by us for quantitative estimation of gold in the sample is a combination of the single element standard fundamental parameter method /4/ and the scattered radiation standardisation method /5/. The detailed analysis was performed on Norsk Data ND-540 Computer system.

The intensity, I, of the fluorescent X-ray peak as detected by the X-ray spectrometer is related to the mass of the element present in the sample and is given by

$$I = I_0 G \tau \left[ 1 - \frac{1}{J} \right] \omega \epsilon T f m A \quad (1)$$

where

$I_0$  is the incident excitation photon flux on the sample,

G is the geometrical constant,

$\tau$  is the photoelectric mass absorption cross-section,

J is the jump ratio,

$w$  is the fluorescent yield,  
 $T$  is the transmission of fluorescent radiation in its path,  
 $e$  is the detector efficiency for the fluorescent energy,  
 $f$  is the fractional intensity of the X-ray line under analysis,  
 $m$  is the mass of the unknown element, and  
 $A$  is the absorption correction term.

For intermediate thick samples, the absorption correction term can be written as

$$A = \frac{1 - \exp[-(\mu_i \operatorname{cosec} \varphi + \mu_f \operatorname{cosec} \psi) \cdot M]}{(\mu_i \operatorname{cosec} \varphi + \mu_f \operatorname{cosec} \psi) \cdot M} \quad (2)$$

where

$\mu_i$  is the total mass absorption at incident energy,  
 $\mu_f$  is the total mass absorption at fluorescent energy,  
 $\varphi$  &  $\psi$  are the average angles of incident and fluorescent radiation with respect to the sample surface, and  
 $M$  is the total mass of the sample.

The incident photon flux  $I_0$  should remain constant during the analysis of whole set of samples. However, there are minor variations in the photon flux from the X-ray tube. These variations have been taken care of by using Compton normalised incident and fluorescent X-ray peak intensities.

Though the X-ray tube emits Mo K X-rays (i.e. Mo K $\alpha$  and Mo K $\beta$ ), we assume the excitation to be essentially monoenergetic with the incident energy being the weighted average of Mo K $\alpha$  and Mo K $\beta$  lines. In fundamental parameters approach for quantitative analysis, the tabulated values of photoelectric absorption cross section /6/, jump ratios /7/ and fluorescent yields /8/ are used for the evaluation of equation (1). The only unknown factor in eq. (1) is  $I_0 G$  which was determined by running a single element standard. We have used

synthetic mercury standards. The mercury standards were prepared by mixing dilute mercuric chloride in a mixture of  $\text{SiO}_2$  and cellulose. The concentration range for Hg was kept between 150 to 200 ppm.

The absorption correction term, A, was calculated using an iteration procedure. In the zeroth iteration the whole matrix was assumed to be a mixture of cellulose and  $\text{FeCl}_3$  and absorption correction terms for elements detected were calculated. The concentration of detected elements thus obtained were included in the next iteration for absorption correction. The iteration process was continued till concentration of various elements detected became constant.

This quantitative estimation method was tested for synthetic standards of mercury and accuracies in the range of - 10% were obtained.

##### 5 Results and Conclusions:

Table II gives the concentration of Au for the four samples undertaken for the present study. The concentration values given in table II corresponds to gold values as obtained in the residue after acid digestion of the sample. This study shows that the gold concentration in Indus river sediments lie in the range of 0.3 to 0.5 grams per ton.

After running these samples it was realized that iron forms the major matrix in these samples. Thus considerable matrix absorption effects are expected. The sample was diluted with a cellulose matrix for reducing absorption effects but this method reduced the detection sensitivity of gold in the samples. To overcome these problem it will be worthwhile if the pan concentrated sample is first treated with HCl to remove the major iron content. This procedure is planned to be used in the detailed exploration study with a large number of samples.

In conclusion, the present study outlines a procedure for the gold estimation in river sediments on a routine basis using the EDXRF spectrometer. Mo target transmission type X-ray tube gives optimum excitation sensitivity. However for the confirmation of the presence of gold, a qualitative run using 22 KeV excitation is desirable, as using this excitation both gold  $L\alpha$  and  $L\beta$  lines can be observed.

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Figure Captions:

Figure 1 : Block diagram of the EDXRF spectrometer.

Figure 2 : Output X-ray spectrum of the laboratory built transmission anode X-ray tube.

Figure 3 : A representative X-ray spectrum of the sample using  $^{238}\text{Pu}$  excitation source with an acquisition time of 6000 seconds.

Figure 4 : A representative X-ray spectrum of the sample using Mo X-ray tube excitation with an acquisition time of 2000 seconds.

Figure 5 : Annular source geometry and the source - secondary target geometry used for radioisotope excitation.

Figure 6 : A representative X-ray spectrum of the sample using  $^{241}\text{Am}$ -Ag secondary excitation with an acquisition time of 6000 seconds.

**TABLE-I:** Various radioisotope excitation sources available, source strength, half life, principal emission energies and the range of elements that can be analyzed with good sensitivity.

Source	Strength (mCi)	Half life (Yrs.)	Energies (KeV)	Range of Elements
$^{55}\text{Fe}$	30	2.7	5.9 (Mn K)	Si to V (K Lines)
$^{238}\text{Pu}$	30	89.6	12-16 (U L)	Ca to Se (K Lines)
$^{241}\text{Am}$ (filtered)	100	458	59.6	Zr to Gd (K Lines) Pb to U (L Lines)
$^{241}\text{Am}$ - Cu Target	500	458	8.0 (Cu K)	Ca to Fe (K Lines)
$^{241}\text{Am}$ -Ag Target	500	458	22 (Ag K)	Ca to Tc (K Lines) W to U (L Lines)

TABLE II : Concentration of Gold in the pellet and the residue

Sample	Gold Concentration (ppm)	
	Pellet	Residue
G1	478	884
G2	150	298
G3	205	404
G4	135	269



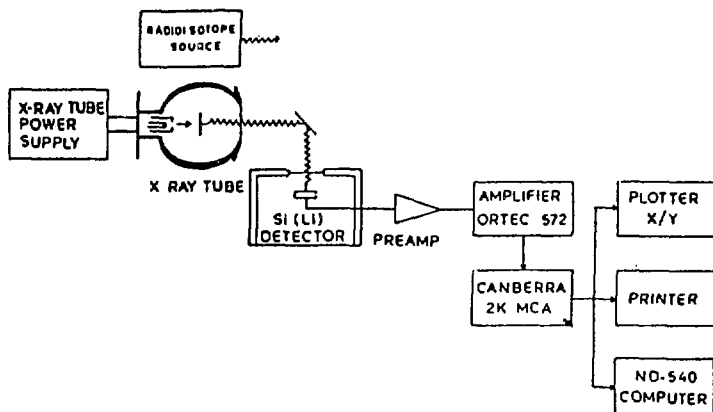


Figure 1 : Block diagram of the EDXRF spectrometer.

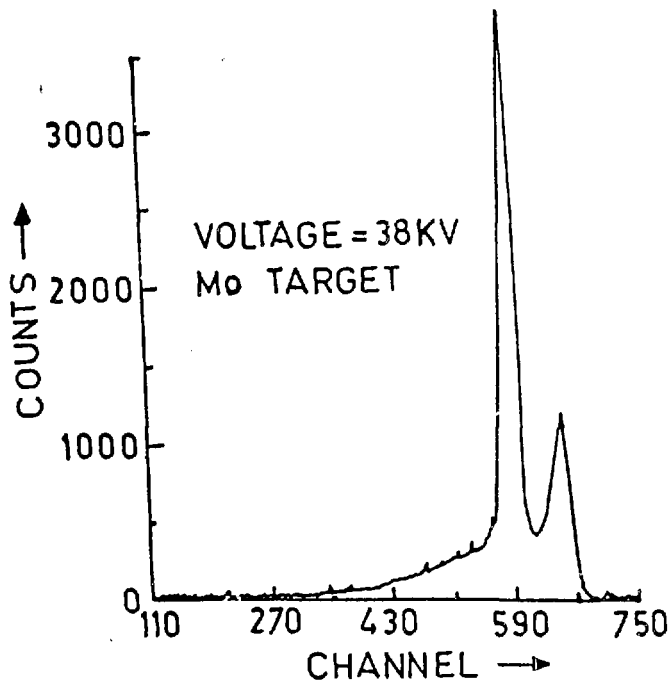


Figure 2 : Output X-ray spectrum of the laboratory built transmission anode X-ray tube.

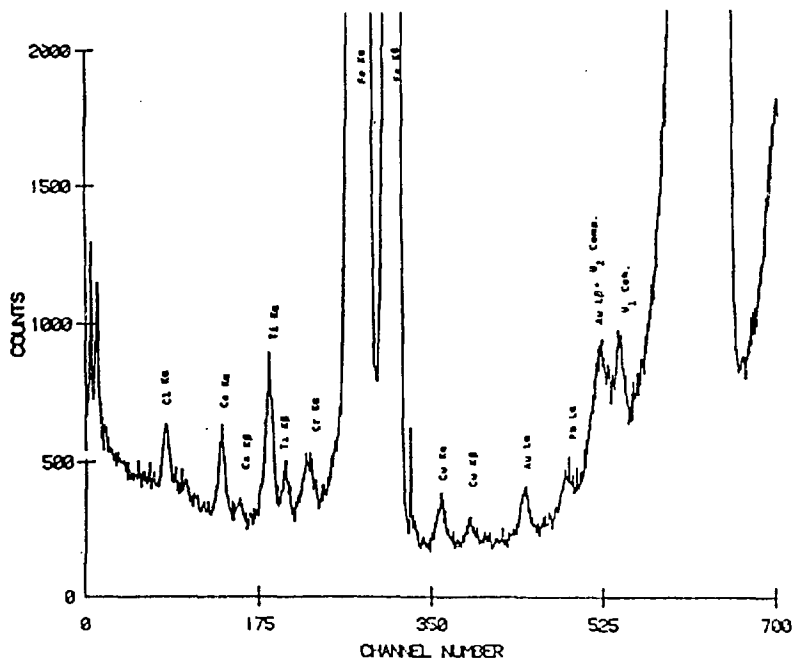


Figure 3 : A representative X-ray spectrum of the sample using  $^{238}\text{Pu}$  excitation source with an acquisition time of 6000 seconds.

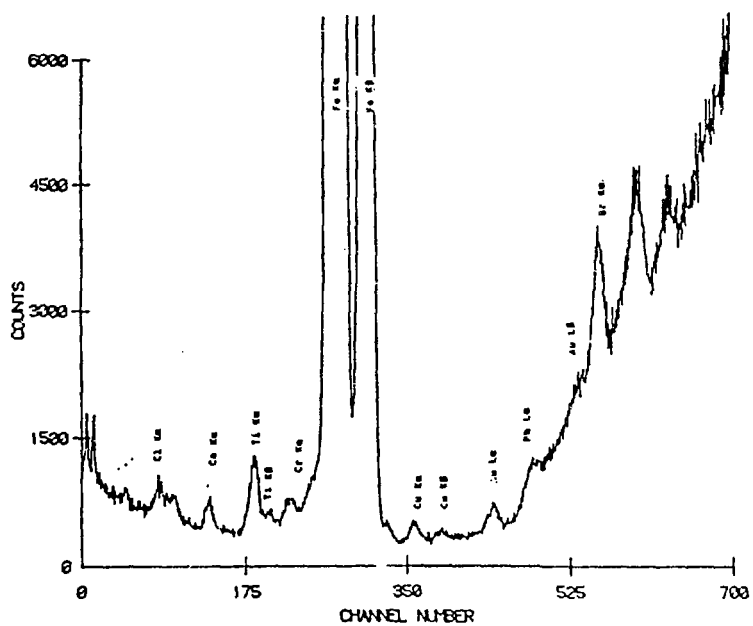


Figure 4 :A representative X-ray spectrum of the sample using Mo X-ray tube excitation with an acquisition time of 2000 seconds.

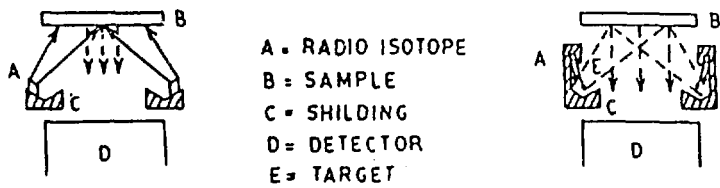


Figure 5 : Annular source geometry and the source - secondary target geometry used for radioisotope excitation.

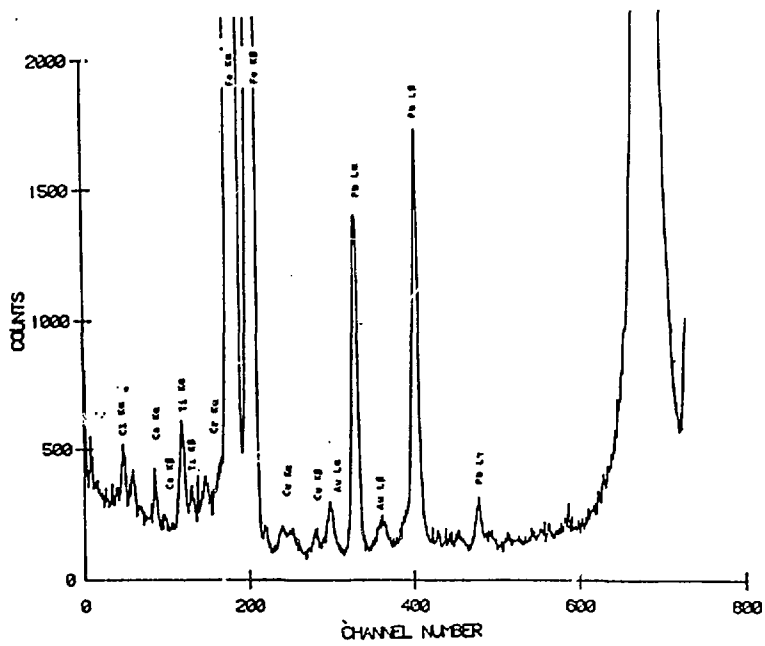


Figure 6 : A representative X-ray spectrum of the sample using  $^{241}\text{Am}$ -Ag secondary excitation with an acquisition time of 6000 seconds.

