

## Counting Statistics of Uranium Determination by X-Ray Fluorescence Spectrometry

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**Summary:** The procedure has been explained to evaluate the equipment performance by repeated measurements of energy dispersive X-ray fluorescence signal of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> uranium solution in 3 mol L<sup>-1</sup> of HNO<sub>3</sub>. Standard statistical models were applied to the data. The Poisson distribution function  $[F(X)^P]$  and Normal distribution function  $[F(X)^N]$  were found to be 1.0197 and 1.0049 respectively, which are quite near to the ideal value of unity. Linearity range for uranium determination by XRF was found to be up to  $1.47 \times 10^{-2}$  mol L<sup>-1</sup> of uranium, with regression coefficient "R<sup>2</sup>" of 0.998 under the optimized instrumental parameters.

Keywords: Counting statistics, Uranium determination, EDXRF.

### Introduction

In analytical measurement systems that is based on observing the radiation emission is subjected to some degree of statistical fluctuation particularly in X-ray fluorescence spectrometers where the peaks and background intensities are measured sequentially/simultaneously. These inherent fluctuations represent an unavoidable source of uncertainty in the measurement and often could be predominant source of imprecision or error [1-5]. The values of the counting statistics fall into two categories. The first, to check the normal functioning of counting equipment by multiple measurements of a definite quantity of an analyte where as the second deals with the inherent statistical uncertainty which estimates the precision associated with a single experimental measurement. The specific models being employed for checking the normal functioning of the counting equipment are Poisson distribution and Normal distribution. Here a set of measurements is recorded under identical experimental conditions and by applying the statistical models, the internal variation is quantified. Any abnormal amount of fluctuation detected could indicate malfunctioning of some part of the counting system. To assign the precision to the measurement, the relative standard deviation is to be calculated/computed.

Uranium is one of the elements of prime importance in nuclear cycle and its accurate online quantification is prerequisite of some processes. Different analytical methods such as fluorimetry [6], inductively coupled plasma mass spectrometry and electroanalytical techniques [7], spectrophotometry [8, 9] and X-ray fluorescence spectrometry are available for elemental determination at trace and

ultra trace levels in nuclear fuel materials [10-13]. The X-ray fluorescence spectrometry is a well established technique for the quantification of metals in a wide variety of solid and liquid samples not only as an analytical tool for a research laboratory but also for quality control purposes [12]. Being a multielemental technique it may be used for simultaneous determination of major and minor elements in the sample.

The present study deals with the measurement of precision in the determination of uranium in aqueous solution by X-ray fluorescence spectrometer (XRF), to estimate the behavior of error with counting time under the prevailing experimental conditions. This will also provide necessary tools for evaluating the quality of results obtained by energy dispersive X-ray fluorescence (EDXRF) analysis.

### Results and Discussion

Application of X-ray fluorescence spectrometry for quantitative measurements of an element inherently includes emission and counting of X-ray photons. The performance of the measuring unit for the estimation of this random phenomenon can be evaluated by the application of statistical models where as the errors and standard deviation achieved reflects the confidence in the measured procedure. Therefore, the equipment performance of X-ray fluorescence spectrometer was checked for the determination of uranium by recording the repeated signals of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> of uranium solution in 3 mol L<sup>-1</sup> of HNO<sub>3</sub>, employing the optimized instrumental parameters given in Table 1. A total of 94 measurements were recorded and presented in Table 2.

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Table-1: Optimized parameters used for the determination of uranium by XRF.

Parameters	Values
X-ray tube	Ag
Voltage	25 kV
Current	0.1 mA
DC Mode	ON
Spinning mode	ON
Counting time	100 second
Gain	20 ev/ch
Window levels	
i. Lower level	13340 eV
ii. Upper level:	13820 eV

Table-2: Replicate measured intensities (Counts) of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> of uranium solution by XRF arranged in ascending order.

550	648	683	705	728
571	649	683	705	731
576	649	684	707	736
605	654	684	707	737
607	655	685	708	738
611	656	686	709	740
613	659	687	713	741
616	661	691	714	743
626	662	691	716	747
626	665	691	717	751
631	668	692	718	754
632	671	693	719	754
636	672	694	720	757
636	675	694	722	760
638	676	699	725	762
643	677	701	726	764
644	679	701	726	776
645	682	701	726	791
647	682	702	727	-

To calculate the precision related to uranium determination by X-ray fluorescence spectrometry, a sample of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> uranium solution in 3 mol L<sup>-1</sup> of HNO<sub>3</sub>, was exposed for ten times. The counting time of signal measurement was fixed as 100 seconds. The statistical calculations of the data have been compiled and shown in Table-3. The relative standard deviation (RSD) value was found to be 1.627%, which is well within the acceptable limit of  $\leq 3$  %.

The signal stability or the behavior of the standard deviation was checked by counting the sample of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> of uranium solution for different time intervals. The counting time was varied from 10 to 500 seconds and the results are graphically represented in Figure 2, which is a plot of counting time verses determined percent error. It is clear from the Figure 2, that the percent error was decreased from 6.9 to less than 1.0 % with the increase in counting time. Similar results were observed for solutions with  $1.26 \times 10^{-3}$  mol L<sup>-1</sup> and  $2.10 \times 10^{-3}$  mol L<sup>-1</sup> of uranium where the percent error decreased from 4.2 to 2.15 and 2.15 to 0.4 % respectively.

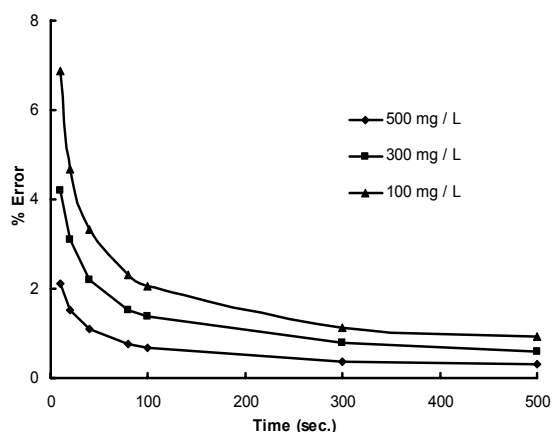


Fig. 2: Variation of counting error with time.

The perusal of the data indicates that the percentage error at the exposure time of 100 sec. is in the range of 1.2 to 0.4% for the concentration range of 100 to 500 mg/L, respectively. With further increase in counting time the variation in error was insignificant, therefore, a counting time of 100 sec. was considered suitable for stable, reliable and accurate measurement of uranium signal and was used in all the subsequent measurements.

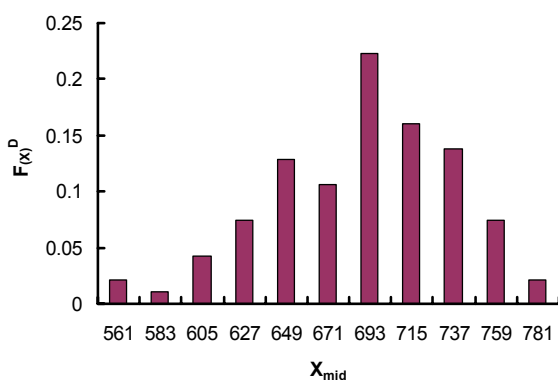
#### Application of the Statistical Models

The statistical models discussed in section "treatment of data", were applied to the measured intensity data of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> of uranium solution in 3M HNO<sub>3</sub> for equipment checking and the results complied are given in Table 4. Mid-class values ( $X_{mid}$ ) were plotted against Distribution function  $\Sigma F(x)^D$ , Poisson-distribution function  $F(x)^P$  and Normal distribution function  $F(x)^N$  data and are shown in Fig. 3-5 respectively. The determined values of  $\Sigma F(x)^D$ ,  $\Sigma F(x)^P$  and  $\Sigma F(x)^N$  were found to be 1.0002, 1.0199 and 1.0011 respectively and are quite near to the ideal value of unity, indicating smooth functioning of the equipment and the expected statistical error due to the instrument is negligible. The width of the bar in Poisson distribution function curve (Fig. 3) shows the internal fluctuation of the data within each class. This internal variation within a specific class is determined by variance, which is the square of standard deviation and reported in the last column of Table-3. The determined relative standard deviation was found to be 1.627 %. The precisions of 2.3 and  $\leq 3.0$ % have been reported for the determination of uranium in phosphoric acid [8] and thorium matrix [9, 11], respectively.

Table-3: Statistical calculations of replicate measurements of  $4.201 \times 10^{-4} \text{ mol L}^{-1}$  uranium solution by XRF.

S. NO.	Counting time (Sec)	UL $\alpha$ Line intensity, I (counts)	Deviation $d = x_i - \bar{X}$	Deviation square $d^2$ (Variance)
1	100	1595	-9	81
2	"	1580	-24	576
3	"	1629	+25	625
4	"	1566	-38	1444
5	"	1568	-36	1296
6	"	1603	-1	1
7	"	1623	19	361
8	"	1620	16	256
9	"	1635	31	961
10	"	1627	23	529

$N=10$        $\bar{I} = \frac{\sum I}{n} = 1604$        $\sum d^2 = 6130$   
 $\frac{\sum d^2}{(n-1)} = 681.11$   
 $\sigma = \sqrt{\frac{\sum d^2}{(n-1)}} = 26.10$   
 $RSD = \frac{\sigma}{\bar{I}} = 0.01627$   
**% RSD = 1.627**

Fig. 3: Variation in distribution with  $X_{mid}$ .

#### Calibration Curve

For quantitative estimation of uranium, intensities of the calibration standards were recorded using optimized instrumental conditions (Table-1). The concentration of uranium was varied from  $2.101 \times 10^{-3}$  to  $1.47 \times 10^{-2} \text{ mol L}^{-1}$  in  $3.0 \text{ mol L}^{-1}$  of nitric acid solution. The variation of XRF signal with the change in uranium concentration is reproduced in Table-5. The calibration curve is shown in Fig. 6, which is a plot of XRF intensity versus uranium concentration. To obtain an empirical relationship for uranium determination, least square fitting was done on the calibration standards. The best regression coefficients come out to be 1.46 and 124 for slope and intercept respectively, with  $R^2$  value of 0.998. The straight line equation for uranium determination in  $3 \text{ mol L}^{-1}$  of  $\text{HNO}_3$  under the optimized instrumental parameters was found to be  $y = 1.46x + 124.0$

where  $x$  = uranium concentration ( $\text{mol L}^{-1}$ ) and  $y$  = number of counts

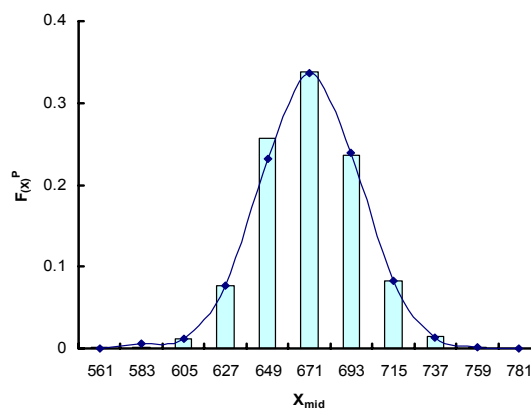
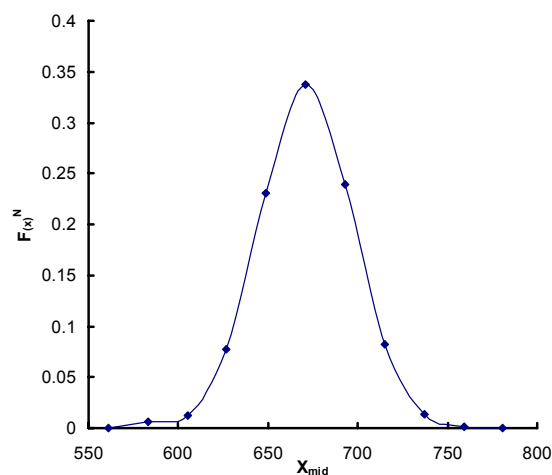
Fig. 4: Poisson distribution as a function of  $X_{mid}$ .Fig. 5: Normal distribution curve for multiple determinations of  $100 \text{ mg L}^{-1}$  of uranium solution by XRF.

Table-4: Data related to statistical models applied to signal variation of  $4.201 \times 10^{-4}$  mol L<sup>-1</sup> uranium solution. Range = High Class - Low Class

$$791 - 550 = 241$$

$$\text{Class Width} = \frac{\text{Range}}{11} = \frac{241}{11} = 21.9$$

No. of Obs.	No. of Classes	Mean of class (Xmid.)	Frequency (F)	F(x) <sup>D</sup> = F/N	Mean = F(x) <sup>D</sup> × X	Poisson Distribution F(X) <sup>P</sup>	Normal Distribution F(X) <sup>N</sup>
1	550-571.9	560.95	2	0.0213	11.78	0.00142	$3.752 \times 10^{-5}$
2	572-593.9	582.95	1	0.0106	6.41	0.001	0.00641
3	594-615.9	604.95	4	0.0425	26.01	0.0117	0.0125
4	616-637.9	626.95	7	0.0745	46.39	0.0771	0.0770
5	638-659.9	648.95	12	0.1277	83.07	0.2562	0.2311
6	660-681.9	670.95	10	0.1064	71.12	0.3373	0.3372
7	682-703.9	692.95	21	0.2234	154.53	0.2369	0.2393
8	704-725.9	714.95	15	0.1596	114.39	0.0824	0.0826
9	726-747.9	736.95	13	0.1383	101.70	0.0146	0.0139
10	748-769.9	758.95	7	0.0745	56.16	0.0013	0.0011
11	770-791.9	780.95	2	0.0213	16.40	$1.139 \times 10^{-5}$	$6.833 \times 10^{-6}$
			N = 94	$\Sigma F(x)^D = 1.0002$	$\Sigma \text{Mean} = m = 671.48$	$\Sigma F(x)^P = 1.0199$	$\Sigma F(x)^N = 1.0011$

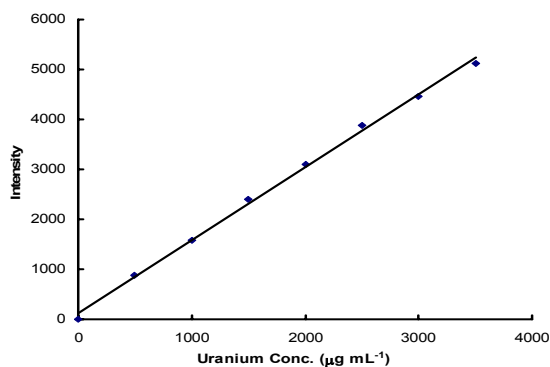


Fig. 6: Calibration curve of uranium determination in 3 mol L<sup>-1</sup> of HNO<sub>3</sub> solution.

Table-5: Variation of XRF signal (Counts) with change in uranium concentration in 3 mol L<sup>-1</sup> of HNO<sub>3</sub> solution.

X <sub>i</sub> (mol L <sup>-1</sup> )	Y <sub>i</sub> (counts)	X <sub>i</sub> Y <sub>i</sub>	X <sub>i</sub> <sup>2</sup>
$2.10 \times 10^{-3}$	880	$4.40 \times 10^5$	$2.50 \times 10^5$
$4.20 \times 10^{-3}$	1590	$1.59 \times 10^6$	$1.00 \times 10^6$
$6.30 \times 10^{-3}$	2395	$3.59 \times 10^6$	$2.25 \times 10^6$
$8.40 \times 10^{-3}$	3108	$6.22 \times 10^6$	$4.00 \times 10^6$
$1.05 \times 10^{-2}$	3885	$9.71 \times 10^6$	$6.25 \times 10^6$
$1.26 \times 10^{-2}$	4470	$1.34 \times 10^7$	$9.00 \times 10^6$
$1.47 \times 10^{-2}$	5115	$1.79 \times 10^7$	$1.23 \times 10^7$
$\Sigma X_i = 1.4 \times 10^4$	$\Sigma Y_i = 2.14 \times 10^4$	$\Sigma X_i Y_i = 5.29 \times 10^7$	$\Sigma X_i^2 = 3.51 \times 10^7$

Least square line i)  $5.29 \times 10^7 = 3.51 \times 10^7 m + 1.4 \times 10^4 c$   
 ii)  $2.14 \times 10^4 = 1.4 \times 10^4 m + 7c$

## Experimental

### Equipment

Energy dispersive X-ray fluorescence spectrometer XR-500 from M/S Links System, UK, was used. The system was equipped with 860 analyzer and 10 mm<sup>2</sup> × 3 mm deep Si(Li) detector with resolution of 155 eV, was used for measuring the uranium intensity.

### Chemicals

Stock solution of  $2.10 \times 10^{-2}$  mol L<sup>-1</sup> of uranium was prepared by dissolving appropriate

amount of specpure uranium oxide (U<sub>3</sub>O<sub>8</sub>) from Johnson-Methey, in minimum amount of supra pure nitric acid from Merck, and the volume was made up with 3 mol L<sup>-1</sup> of HNO<sub>3</sub>. The standard solutions of the desired concentration were prepared by appropriate dilution of this stock solution immediately before use. All other chemicals/reagents used were of analytical grade and used as such without any treatment. Distilled and deionized water was used throughout this work.

### Procedure

The standard uranium solutions in 3 mol L<sup>-1</sup> of HNO<sub>3</sub> were taken in a flat bottom polyethylene sample bottle (Fig. 1), and presented to spectrometer. Intensity of the uranium solution was recorded as a series of successive measurements (X) under the optimized conditions given in Table 1, at an interval of about five minutes.

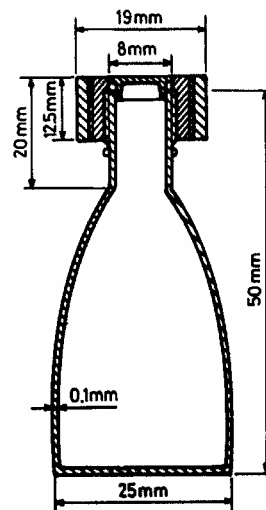


Fig. 1: Polyethylene sampling bottle used for counting.

*Treatment of Data*

The data obtained by certain number of independent measurements "N" of a physical property may be characterized for the applications of statistical models as:

1. Arrangement of the data in ascending order
2. Range = (Highest value of signal – Lowest value of signal)
3. Class - width (C. W) = Range / No. of classes
4. Class limit  
 Class I  $C_{lower} \rightarrow C_{upper}$   
 $X_{min} \quad (X_{min} + C.W)$   
 Class II:  $X_{min} + C.W \rightarrow X_{min} + 2 C.W$   
 " " " "  
 " " " "  
 " " " "
5.  $X_{mid} = (C_{lower} + C_{upper}) / 2$
6. Frequency of data (F): No. of occurrence of value X in a particular class.
7. Frequency distribution function [F(x)<sup>D</sup>] is the relative frequency with which the number appears during the collection of the data and is given as:

$$F(x)^D = \frac{\text{No. of occurrence of value } x}{\text{Total No. of measurements}} = \frac{F}{N}$$

$$\text{For ideal case } \sum_{x=0}^{x=\infty} F(x)^D = 1$$

8. Mean ( $\bar{X}$ ) = F(X)<sup>D</sup> × X<sub>mid</sub>
9. Poisson - Distribution function [F(X)<sup>P</sup>]  
 $F(X)^P = P(X)^P \times C.W.$

$$\text{where } P(X)^P = \frac{1}{\sqrt{2\pi\bar{X}}} \left(\frac{\bar{X}}{X}\right)^X \exp(X - \bar{X})$$

$$\text{For ideal case } \sum F(X)^P = 1$$

10. Normal - Distribution function [F(X)<sup>N</sup>]  
 $F(X)^N = P(X)^N \times C.W.$

$$\text{where: } [F(X)^N] = \frac{1}{\sqrt{2\pi\bar{X}}} \times \exp\left(-\frac{(X - \bar{X})^2}{2\bar{X}}\right)$$

$$\text{For ideal case } \sum F(X)^N = 1$$

*Precision Related to XRF Measurement*

To assign the precision to the measurement made by X-ray fluorescence spectrometry. The standard deviation relative to the mean is relative standard deviation (RSD), which is given by

$$RSD = \frac{\sigma}{\bar{X}}$$

where  $\sigma$  = Standard deviation

$$\bar{X} = \text{Average or arithmetic mean}$$

It is expressed as a fraction or as a percent.

The standard deviation ( $\sigma$ ) is given by:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N} (X_i - \bar{X})^2}{N-1}}$$

and measures dispersion about the mean. The square of standard deviation is the variance ( $\sigma^2$ ) which gives an idea of internal fluctuation of data in a particular class.

The arithmetic mean is given by

$$\bar{X} = \frac{1}{N} \sum_{i=1}^{i=N} X_i$$

The practical significance of standard deviation may be explained as:

The confidence limits are the upper and lower values between which the actual measurement will fall with a certain probability. For an infinitely large number of readings showing a normal distribution the 50% probability error is that where the individual X will lie between  $X \pm 0.67\sigma$ , 68.3% error in X-measurement lies between  $X \pm \sigma$ . Similarly, 95.4 %, 99.7 %, 99.9 % probability means that an individual X values lie between  $\pm 2\sigma$ ,  $3\sigma$  and  $4\sigma$  respectively.

*Least Square Fitting*

It is a normal practice to fit a curve to a set of experimental data to get useful information. The human misjudgment in drawing a smooth curve can be avoided by using the method of least square. According to this method, a curve will be the best fitted to the observed data if sum of squares of deviations between observed values ( $Y_i$ ) and determined values ( $Y_e$ ) from the curve are minimum *i.e.*

$$\sum (Y_i - Y_e)^2 \text{ is the least.}$$

Consider a data, which can be expressed by a straight line equation as:

$$Y_i = mX_i + C$$

where  $m$  = slope of the line and  
 $C$  = intercept

$$\sum (Y_i - mX_i - C)^2 \text{ is least.} \quad (\text{i})$$

Differentiate w. r. t. X

$$2 \sum (Y_i - mX_i - C) - X_i = 0$$

or

$$\sum X_i Y_i - \sum mX_i^2 - C \sum X_i = 0 \quad (\text{ii})$$

Differentiate w. r. t. Y

$$2 \sum (Y_i - mX_i - C) - 1 = 0$$

or

$$\sum Y_i - m \sum X_i - nC = 0 \quad (\text{iii})$$

where  $\sum C = nC$

so we get two equations : as

$$\sum X_i Y_i = m \sum X_i^2 + C \sum X_i \quad (\text{iv})$$

$$\sum Y_i = m \sum X_i + nC \quad (\text{v})$$

These two equations are called normal equations of a least square line. The values of “m” and “c” can be calculated by solving the equation (iv) and (v). Similarly, the parabolic is represented by:

$$Y = a + bX + cX^2 \quad (\text{vi})$$

Since relation (vi) involves three unknowns a, b and c, therefore, three equations are needed to find values of these unknowns. These equations can be derived in a similar way as has been done for least square fitting as:

$$\sum Y_i = na + b \sum X_i + c \sum X_i^2 \quad (\text{vii})$$

$$\sum X_i Y_i = a \sum X_i + b \sum X_i^2 + c \sum X_i^3 \quad (\text{viii})$$

$$\sum X_i^2 Y_i = a \sum X_i^2 + b \sum X_i^3 + c \sum X_i^4 \quad (\text{ix})$$

The values of a, b and c can be determined by solving the eq. (vii) to (ix).

## Conclusion

From the data it was statistically established that the measurement of uranium in solution by XRF is rapid, precise and accurate technique. The determination could be made without any chemical treatment of the sample.

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