Detemination of Major Elements in Soil Sample Using XRF Technique

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ABSTRACT

The soils of the Himalayas are under constant threat because of increase in urbanization. The study was aimed to assess the fertility status of the soils and then to estimate the environmental risk associated with elevated levels of environmentally major elements.

The objectives of this paper are-

- *Determination of major elements like Na, Mg, Al, Si, P, Ca, Ti, Mn, and Fe as oxides in sediment samples using XRF technique.*
- *To estimate the analytical performance of the technique.*

This task provides for high precision determinations of 10 major elements as oxides wavelength dispersive x-ray fluorescence (WDXRF).The accuracy achievable by it is unsurpassed by any other instrumental technique. The error of determination is typically 0.5% relative error or less for major elements at crustal abundance levels. This technique has a long history of providing precise and accurate results to various programs in the Geological Discipline. The method is well proven for analyzing all types of rocks, soils and most types of minerals.

Keywords: *Minerals, XRF, WDXRF.*

INTRODUCTION

X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analysis of rocks, minerals, sediments, fluids and composition of layers and coatings.

The XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis. XRF has the advantage of varying non destructive multi-elemental fast and cast-effective. Furthermore it provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from a 100% to few parts per million (ppm). Its main disadvantages is that analysis are generally restricted to elements heavier than fluorine it requires only a minimum of sample preparation.

METHODOLOGY

The complete work is composed of several components as follows-

- Collection of sediment samples from the field.

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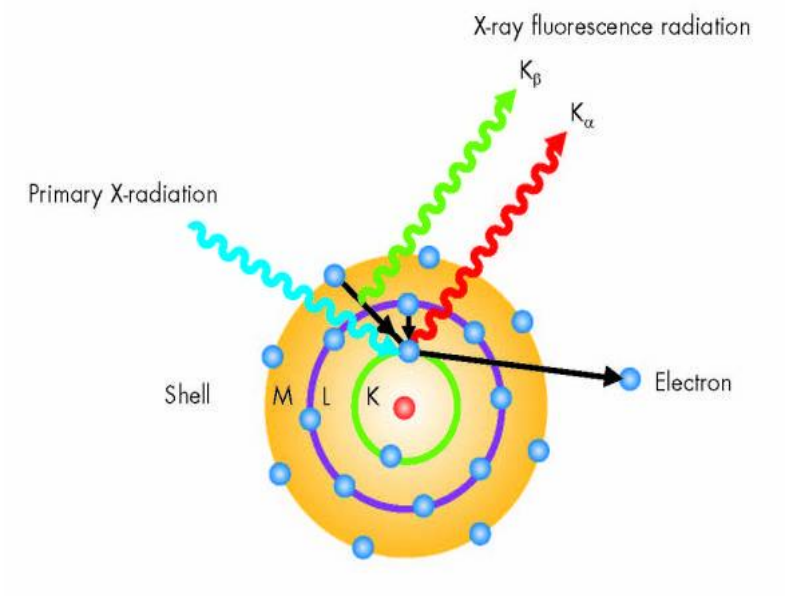
- Processing of samples comprising of sieving, pulverizing and storing properly in labeled bottles.
- Determination of loss on ignition (LOI) using muffle furnace at 900^0C.
- Samples were prepared as pressed pellets.
- Analysis of the samples by XRF.
- Processing of analytical data and study of technique performance parameters such as minimum detection limit (MDL), accuracy and precision.
- The performance of XRF techniques was evaluated for determination of ten major elements in the following using sixteen sediment samples-
- H-47,H-48,H-49,H-50,H-51,H-52,H-53,H-54,H-55,H-57,H-64,H-90,H-92,H-95,H-96,H-97

XRF analysis was performed on pressed power pellets using wavelength dispersive x-ray fluorescence system i.e. SIEMENS STS 3000…

PRINCIPLE OF XRF TECHNIQUE

An inner shell electron is excited by an incident photon in the x-ray region. During the de-excitation process, an electron is moving from a higher energy level to fill the vacancy. The energy difference between the two shells appears an x-ray, emitted by the atom the x-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis).

A typical XRF spectroscopy arrangement includes a source of primary radiation (usually radioisotope or an x-ray tube) and equipment for detecting the secondary X-rays.



ANALYTICAL PROCEDURE
SPECIMEN PREPARATION TECHNIQUE
LOSS ON IGNITION (LOI)

LOI is considered as essential parameter for a quality XRF analysis. By ignoring LOI, the total cannot be used as a measure of the accuracy of the analysis.

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Procedure- dried samples are ignited to quantify their volatile contents (mainly H_2O and CO_2etc) which cannot be analyzed by XRF. The standard procedure is as follows –

- Pre-ignite the alumina crucibles (to be used) for at least 15 min.
- Allow them to cool for 10min before commencing weighing
- 5gm powder of each sixteen samples used was taken in these separate alumina crucibles respectively and their weight was measured. The crucibles were then kept in furnace at a temperature of 900^0C for about two hours; so that the whole moisture forms this powder samples got removed.
- After the removal of moisture the crucible with powder samples are again weighed and either LOI is calculated.

Calculation of LOI

% Loss on Ignition = Loss or Gain in Wt. Powder * 100 Original Wt. of Powder

POWERED AND PELLETS

This is the most convenient sample preparation technique with reasonably good precision and accuracy in results. Powders can be used as such or they can be briquette under suitable pressure. Binders may be added in some cases to make the pellet durable. The disadvantage of this technique is that it can solve the heterogeneity problem. Particle size effects can also occur if sample is not properly powdered. Grinding may induce trace level contamination. Surface effects influence low atomic number analysis.

Major elements in silicate rock are usually determined by XRF using pressed powder pellets. The sediment samples from different areas is dried in oven to remove moisture and then sieved in mechanical shaker up to 108m which are again pulverized to 75m in powdering machine.

Pressed pellets from the powdered rock simples are made as follows; 5g of sample powder are mixed with 2-3drops of polyvinyl alcohol solution. Now the pellets are made in a hydraulic pressure machine by applying 17tones load (approximately). Finally the pellets are kept in a hot box (600-700^0C) for overnight to drive off the excess water from the binder. Pressed pellets can be analyzed the spectrometer without further preparation.

REFERENCE STANDARDS

Reference standards are standardized objects or substances which are used as a measurement bases for similar objects or substances. Reference standards are also used as calibrators (e.g., particle count, melting point, standardization of titrants and as blanks and controls).Reference standards are used mainly in all analytical procedures. Several reference standards were used in analysis of major elements in sediment samples in the present exercise.

S.N.	Name of Reference Standard	Description	Producing Agencies
1	GXR-2	SOIL	USGS,U.S.A
2	GXR-6	SOIL	USGS,U.S.A
3	SO-1	SOIL	CCRMP,CANADA
4	GSS-1	SOIL	IGGE,CHINA
5	GSS-4	SOIL	IGGE,CHINA
6	GSD-9	SEDIMENT	IGGE,CHINA
7	GSD-10	SEDIMENT	IGGE,CHINA

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Accuracy

Accuracy is the degree of closeness of closeness of a measured or calculated quantity to its actual (true) value. Accuracy is closely related to precision. Also called reproducibility or repeatability, the degree to which further measurements or calculations show the same or similar results.

Accuracy indicates proximity to the true value, precision to the repeatability or reproducibility of the measurement.

Errors

Error is the difference between the true value and the measured value error is expressed as the ratio **(m -T)/ T* 100**

Error can be classified into three categories

(i) Statistical error
(ii) Systematic error
(iii) Error due to sensitivity of instrument

The error of a determination is the inverse of the accuracy, i.e.; smaller the error greater is the accuracy.

The magnitude of deviation of the individual values from the arithmetic mean 'm' of all is a measure of the precision of measurement. More is the deviation, less is the precision

Minimum Detection Limit

Lowest concentration that can be measured with a precision of 50% or the concentration level above which it is possible to say with confidence that the element is present.

Precision

Relative standard deviation is useful for comparing the uncertainty between different measurements of varying absolute magnitude. The RSD is calculated from the standard deviation s, and is commonly expressed as parts per thousand (ppt) or percentage %.

RSD = (s/x) *1000 ppt
RSD % =(s/x)*100

ANALYSIS OF UNKNOWN SAMPLES

Sixteen samples were used as unknown. Sample processing was done in similar way as in case of standard samples. These were analyzed in similar operating condition using the same parameter set as in case of standard reference samples.

RESULTS

- For major elements in sediment we found the % deviation between analyzed and recommended values by using the standard reference samples GSS-1, the result of accuracy calculations are given in table.

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ELEMENTS	AV	RV	DIFF	%DEV
Na2O	1.61	1.66	-0.05	-3.01
MgO	1.88	1.81	0.07	3.86
Al2O3	14.21	14.2	0.01	0.07
SiO2	63.22	62.6	0.62	0.99
P2O5	0.17	0.17	0	0
K2O	2.57	2.59	-0.02	-0.77
CaO	1.62	1.72	-0.01	-5.81
TiO2	0.8	0.81	-0.01	-1.23
MnO	0.22	0.23	-0.01	-4.34
Fe2O3	5.23	5.19	0.04	0.77

- In case of major elements to estimate precision the standard reference samples GSS-1 are analyzed five times and corresponding standard deviation, RSD are calculated. Sample processing is done in identical manner in each case.

Elements	MEAS.1	MEAS.2	MEAS.3	MEARS.4	MEAS.5	AVG	S.D	%RSD
Na2O	1.61	1.61	1.61	1.61	1.61	1.61	0	0
MgO	1.88	1.89	1.88	1.89	1.89	1.89	0.01	0.53
Al2O3	14.21	14.23	14.22	14.22	14.21	14.22	0.01	0.07
SiO2	63.32	63.18	63.18	63.19	63.25	63.22	0.06	0.09
P2O5	0.17	0.17	0.17	0.17	0.17	0.17	0	0
K2O	2.57	2.57	2.57	2.57	2.57	2.57	0	0
CaO	1.63	1.62	1.62	1.63	1.63	1.63	0.01	0.61
TiO2	0.8	0.8	0.8	0.8	0.8	0.8	0	0
MnO	0.22	0.22	0.22	0.22	0.22	0.22	0	0
Fe2O3	5.23	5.24	5.23	5.24	5.24	5.24	0.01	0.19

- Term sensitivity is qualitatively used to refer the detection limit of a technique. The sensitivity of a technique refers to the slope of the calibration curve plotted as concentration versus intensity and measured.

Elements	2ϴPeak	Net intensity	Time (sec) used	Conc (%)	MDL
		Peak	for DL calculation		
Na2O	24.982	0.9007	700	0.38	0.009
MgO	20.688	7.462	300	1.54	0.009
Al2O3	144.55	64.2618	300	12.27	0.022
SiO2	144.558	161.791	200	49.28	0.054
P2O5	141.279	1.4336	700	0.11	0.003
K2O	136.874	77.2493	300	3.35	0.005
CaO	113.279	21.3677	300	1.05	0.005
TiO2	86.319	14.1178	600	0.71	0.002
MnO	63.118	2.8233	400	0.042	0.008
Fe2O3	57.519	233.1741	200	9.34	0.004

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- The analyzed value of all elements in sample treated as unknown was satisfactory.

SDMNT	Na2O	MgO	Al2O3	SiO2	P2O5	K2O	CaO	TiO2	MnO	Fe2O3	SUM	LOI
	%	%	%	%	%	%	%	%	%	%	%	%
H-47	0.78	1.91	12.2	72.3	0.09	2.16	1.63	0.65	0.06	4.31	96.1	4.09
H-48	0.42	1.97	13.7	67.8	0.09	2.15	1.59	0.68	0.06	4.62	93.1	4.3
H-49	0.72	1.67	14	70.5	0.08	2.39	0.49	0.66	0.07	4.55	95.1	3.65
H-50	0.74	1.48	12.6	73.6	0.08	2.12	0.42	0.64	0.07	4.42	96.2	2.79
H-51	0.65	1.57	12.5	68.8	0.12	1.97	0.78	0.65	0.11	6.99	94.1	4.56
H-52	0.72	1.48	14.2	72.2	0.07	2.37	0.37	0.79	0.07	4.48	96.8	3.19
H-53	0.8	1.5	13.1	73.2	0.08	2.18	0.59	0.66	0.08	4.98	97.2	3.31
H-54	0.82	1.4	11.6	76.5	0.09	1.87	0.56	0.67	0.07	4.84	98.4	3.04
H-55	0.83	1.41	9.4	78.3	0.09	1.85	0.67	0.67	0.08	5.09	98.4	2.63
H-57	0.87	0.96	7.63	82.3	0.08	1.31	1.09	0.5	0.05	2.78	97.6	2.08
H-64	0.97	1.12	7.93	79.1	0.09	1.31	1.61	0.79	0.09	4.66	97.7	3.18
H-90	0.88	1.28	9.39	78	0.07	1.47	1.47	0.58	0.06	3.68	96.9	3.54
H-92	0.93	1.37	10.7	77.7	0.07	1.72	1.29	0.59	0.06	3.62	98.1	3.76
H-95	1.21	1.2	8.87	79.6	0.08	1.42	1.67	0.58	0.06	2.57	97.3	3.94
H-96	0.97	1.43	10.6	74.3	0.09	1.64	1.97	0.6	0.06	3.03	94.7	3.16
H-97	1.05	1.33	8.86	75.3	0.08	1.58	2.61	0.61	0.06	2.82	94.3	4.37

CONCLUSION

We analyze different standard samples and determine the precision and accuracy of the XRF spectrometer.

- Precision of analysis is best for the elements like Na2O, K2O, P2O5, TiO2 and MnO in case of reference sample GSS-1 if the conc. Of any elements is close to DL then the precision become poor.
- It is observed that accuracy is best for elements $A1_2O3$ measured in reference sample GSS-1. This is shown by low % deviation. The elements like SiO_2 and Fe_2O_3 have good accuracy as shown by lower % deviation. While the CaO has worst accuracy and P_2O_5 has no deviation i.e. best accuracy.

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