

Quantification of Metallurgical Flux by Wavelength Dispersive X-Ray Fluorescence

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Abstract

This work illustrates the quantification of Fluorspar, it is commonly used during metallurgical operations as flux. In general practice it is quantified by conventional method for verification of mineralogy and grades by using 2-3 analysts and days respectively. By using conventional method analyst can estimate CaF_2 , CaO , SiO_2 , MgO and R_2O_3 (mixed oxides) except SrO , BaO , and P etc. due to trace low quantity. At present a new strategy / opportunity has been developed for fast, less interfering and low cost for all type of CaF_2 as pressed pellet by wavelength dispersive X-ray fluorescence (WD-XRF). For verification of such strategy, a series of calibration lines were established by certified reference materials (CRM's) and synthetic standards. Matrix effects were corrected by applied Fundamental Parameters (FP) model. In current methodology CaCO_3 was calculated after analysis of total carbon (C) through Infra red combustion method. All estimations were done in dried samples after removal of moisture. CaF_2 was calculated by applying mathematical formulation. The presence of CaCO_3 instead of other carbonates like MgCO_3 , BaCO_3 , Na_2CO_3 and K_2CO_3 etc were confirmed by XRD, ATR-FTIR, and Volatilization method as well as compared with conventional analysis results and results were validated by using ISO-17025 protocol.

Keywords: CaF_2 ; WD-XRF; XRD; ATR-FTIR; IR method

Introduction

Fluorspar is a cubic has a wide variety of applications [1-5]. It crystallizes as isometric cubic habit halide minerals in the form of calcium fluoride. Octahedral and more complex isometric forms are not uncommon. Element substitution for the calcium cation often includes certain rare earth elements, such as yttrium and cerium. Iron, sodium, and barium are also common impurities. Some fluorine may be replaced by the chloride anion.

Each unit cell is packed with eight F atoms and four Ca atoms and it was felt worthwhile to study the bonding between calcium and fluorine atoms (Figure 1). In the case of fluorites, though studies on thermal vibrations, extinction, etc. have been carried out by researchers [6-12] the clear evidence of the bonding between metal atoms and the fluorine atoms has not been studied.

The cube samples of fluorspar were detected by XRFS, sample was prepared by fusion of Li_2CO_3 (1.0 g) and $\text{Li}_2\text{B}_4\text{O}_7$ (5.0 g) in a Pt crucible and after addition three (03) drops of 150 g/L, LiBr solution. The mixture was fused at 1050°C for 20 min. The melt after cooling to room temperature was used for estimation of the 4 components CaF_2 , SiO_2 , Al_2O_3 and total iron (TFe) by XRFS [13].

Calcium fluoride sample and group of standards with binder by using press powder and analyzed by an X-ray fluorescence spectrometer. Linear regression line was used for detection of samples and standards. The standards and to-be-tested sample pellets are pressed by the steps of sep. mixing the fluorite standard and to-be-tested samples with the binder, grinding, sieving with a 300-mesh sieve and pressing into a pellet using a pelletizer. The inventive method is rapid and accurate and can reduce the detection cost and improve the detection efficiency [14].

Fluorite powder was directly pressed into pellet, the total content of Ca and the contents of Fe_2O_3 , P , SiO_2 and K_2O were all analyzed with X-ray fluorescence spectrometry. Furthermore, the carbon content of the pellet was analyzed with IR absorption spectrometry. Based on the carbon content in the pellet, the calcium content as CaCO_3 was calculated. Then the CaF_2 content in fluorite were obtained. This method is simple and accurate. A working curve Calibration curve

was made using nine certified reference material and used to test the method. In addition, the No 5# in the certified reference material series (GBW07254) was used to test the accuracy and precision of the method and the results are satisfactory [15]. Some accepts of wavelength dispersive X-ray determination of fluorine content in various matrices was estimated by Boča et al. [16]. Generally, the energy-dispersive X-ray fluorescence spectra are plotted as an equi-energy interval with the constant energy resolution. On the other hand, the wavelength-dispersive X-ray fluorescence spectra are usually measured with an

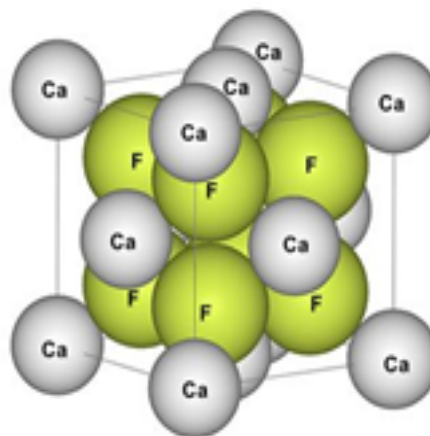


Figure 1: Structure of Fluorspar.

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equi-angle interval supposed the constant angular resolution. When the wavelength axis of wavelength-dispersive X-ray fluorescence spectra is converted into energy, the intensity should be also corrected [17].

Occasionally suggested yet rarely performed X-ray fluorescence (XRF) spectrometry of fluorine seems to fail systematically in yielding reliable quantitative results for rocks and soils. Repeated analyses reveal continuously drifting fluorescence intensities for fluorine, boron and chlorine. Typically, an increase, but in few cases also a decrease, over X-ray exposure time is observed [18].

In present attempt, the investigations were carried for the estimation and validation of all type and grades of Fluorspar. The main purpose was reduction in analysis time frame and toxicological effects with respect to classical method and analysis of minor elements which are difficult to examine accurate and precisely by classical method due to mineralogical effects and low in quantity. The potential of invented method was reconfirmed by using different primary standards, classical analyzed results and the presence of CaCO_3 (calcite) instead of other alkaline carbonates was verified by decarbonation, XRD and ATR-FTIR technologies.

Materials and Methods

Sampling location and geological study area

The CaF_2 samples were collected from different vicinity of Pakistan for verification and classification of grades and invention of methods. Fluorite deposits have been found for the first time in the Jurassic Loralai limestone of Gadebar, Daman Ghar, tor Thana, Wategam, Mekhtar, Balao, Mahiwal areas of Loralai District, Balochistan Maran, Pad Maran and Dilband areas of Kalat district (Figures 2 and 3).

The first largest deposit of fluorite (over 0.1 million ton) are located in Dilband and in its vicinity in Kirthar foldbelt. The second largest deposit of 6750 tons of green fluorite is in Mula-Zahri Range of Kirthar foldbelt. The third largest deposit of fluorite is found in Loralai district and its vicinity in Sulaiman foldbelt.

The fluorite of Loralai area occurs as veins and as disseminated grains along faults and fractures which is hosted by the Jurassic Loralai limestone forming the anticlinal core. Fluorite has many colors such as pink, blue, light-grey, green and light-yellow (Figures 4a-4d). Chemical analysis shows CaF_2 varies from 95.20-95.40%, CaCO_3 from 3.20-3.40% and SiO_2 from 1.40 - 1.44%. Average weight % concentration of Ca is 49%, F is 45%, SiO_2 is 2.30%, CuO is 0.5%, Al_2O_3 is 2%, Fe_2O_3 is 0.08% and LOI is 1.47%. This type of fluorite can be used for acid preparation and also as gemstones. High grade ore (over 96% CaF_2 and less than 5% SiO_2) is mined from Maran and Dilband areas while low grade ore with less than 85% CaF_2 and high SiO_2 content is found at Pad Maran. The total production of fluorite during 1994-95 was about 1000 tones. Mining of fluorite is in progress in the Mekhtar (Balao, Inde, Sande and Zhizhghi), Tor Thana and Zarah areas. The estimated reserves are about 50000 tons. Attractive gem quality fluorite crystals are found in light-green, yellow and light-blue colors from Mekhtar, Wategam Zarah of Loralai district. It is also suggested that the Jurassic strata especially limestone of Kirthar and Sulaiman foldbelts and adjoining western indus suture Zone seems to be significant for further fluorite prospecting Latitude and Longitude (29° North, 66° East (est.)). Neighbouring regions, Quetta district, Baluchistan Pakistan, Zhob District Balochistan province is the main producer of fluorite in Pakistan.



Figure 2: Fluorite deposits have been found at the areas of Loralai District.

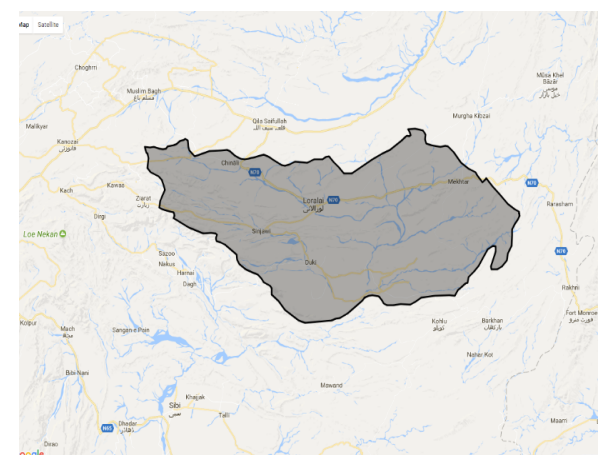


Figure 3: Fluorite deposits have been found at the areas of Kalat district.

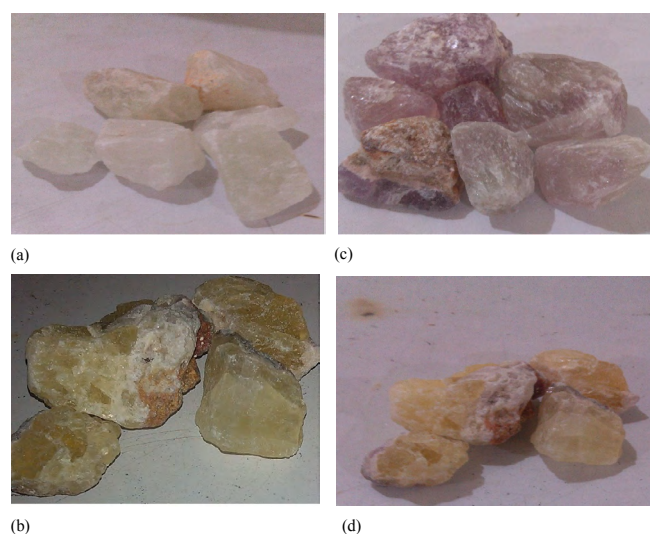


Figure 4: (a-d) Sample of different types of Fluorite collected from Pakistan Vicinity.

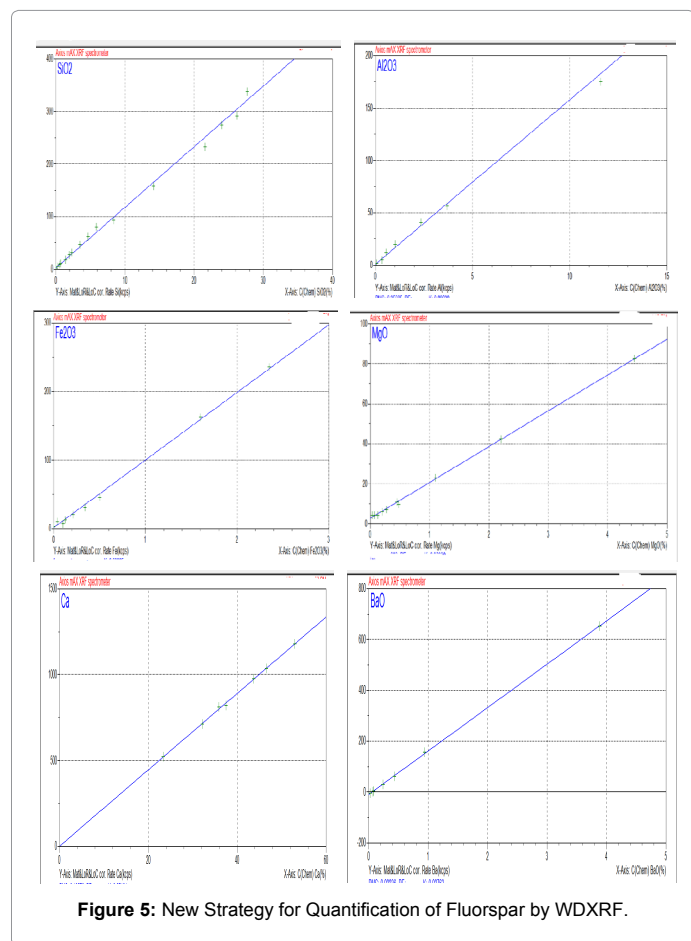


Figure 5: New Strategy for Quantification of Fluorspar by WDXRF.

Experimental

Methods

Standards and samples preparation technique: Fluorspar is universal flux used during steel production for slag making. At present variety of fluorspars were analyzed by new strategy received from different country regions. Sample preparation technique is the essential part of precise and accurate development of application. Therefore, estimations of unknown samples and certified reference materials were prepared under specified conditions. These conditions were adopted for homogeneity of the samples like grinding method, grinding time, mesh size, pelletized force, time, binder type and ratio of binder. Nevertheless, before making final pressed pellets the samples were properly pulverized below 150 μm , Tyler 100 and kept in oven for loss on drying at 100-110°C for 24 hours and same procedure for drying was applied with standards and observed loss in the range of 0.001 to 0.1%. Each dried standards and samples were mixed with 0.75 g wax (binder) in zirconium grinding bowl mill for 240 second and applied 30 to 40 KN force for one minute in aluminum cup (dia 40 mm) for uniform pellets, Herzog semi automatic press was used for said purpose.

Standard materials: Calibration lines plays important role for the development of application and achievement of precise results. In present investigation, to minimize the matrix affects during initial stage of application a series of primary standards (CRMs) i- JK S9, ii- NCS DC 14023, iii- NCS DC 14025, iv- NCS DC 62003a, v- HJ-CGL 101, vi- UNS LAB Fluorite FM, vii- ICRM-5132-89, viii- JK S10, ix- BCS

392 have been used including in-house synthetic standards which were prepared by combination of high purity analytical reagents of silica (SiO_2), calcium oxide (CaO), calcium fluoride (CaF_2), aluminum oxide (Al_2O_3), magnesium oxide (MgO) and ferric oxide (Fe_2O_3).

Wavelength dispersive X-ray fluorescence spectrometer: WD-XRF- Philips Axios Max was used in current method for the estimation of major and minor mineralogy of CaF_2 . This instrument can be used for the determination of beryllium (Be) to uranium (U) and the level of concentrations varying by using appropriate signal and composite crystals [19]. The system used to have 3 KW Rhodium tube as X-ray generator along with other supporting determinators like channels, crystals, detector and collimators mask, initially the instrument parameters and system setup were selected as per need. After setup selection run maximum concentration samples with respect to each element for determination of angles and then adjusted analysis time, LLD (lower limit of detection) and applied background correction of each element as per requirement then same were used for pulse height distribution (PHD) determination.

Instrument operating conditions: For achievement of accurate results, the instrument operating conditions were set as conductivity 0-500 μS , internal water flow 3.5-5 L/min, external water flow 1-4 L/min, Instrument Cabinet temperature 29.85-30.10°C, Vacuum level 0-100 Pa, Detector Gas Flow 0.5-3 l/h, X-ray tube cooling water 12-20°C and Gas Cylinder Pressure 600-1300 hPa.

Carbon sulfur analyzer calibration and estimation

Preparation of calibration standards: A series of standards were prepared by using primary standard ICRM-5132-89 having carbon content 1.41% and diluted with the help of lithium tetra borate and made series of standards of total carbon. Lithium tetra borate dried at 700°C before used.

Carbon sulfur operating mechanism: CS-800 (Eltra) analyzer was used for estimation of carbon in standards and samples, before estimation of unknown samples the instrument was calibrated with different ranges of CRMs. The said instrument is microprocessor-based instrument it can estimate a wide range of measurements, simultaneously estimate the carbon and sulfur content in metals, ores, ceramics and other inorganic materials. During this process the carbon and sulfur present in sample are oxidized to CO_2 and SO_2 and detected by infrared (IR) cell. The concentrations of unknown samples were determined relative to calibration standards. To reduce interferences from instrument drift, reference measurements of primary standards were used for verification of machine and maintained accuracy of range prior to analysis of samples.

Volatilization procedure: CaF_2 mineralogy is the major combination of CaCO_3 instead of other carbonates, for verification and presence of CaCO_3 (calcite) the volatilization tests were performed in tube furnace in the presence of helium gas with different temperatures and evaluate the loss and presence of different carbonates, for the confirmation few CRMs and samples were tested at 450, 550, 600 and 700°C [20,21]. After said temperatures decarbonation volatilization test was not performed due to loss of fluorine at higher temperature [22].

Attenuated Total Reflection-FTIR (ATR-FTIR) for carbonates: The Fourier-transform infrared spectroscopy (FTIR) is used for recording of spectrum in the range of 4000-400 cm^{-1} . Infrared measurements may perform in transmission, reflectance or attenuated total reflection (ATR) mode. For the study of different variety of materials as per their characteristics can be identifying by using different FTIR

techniques. In daily research work the majority of people use the surface technique is attenuated total reflection (ATR), it can be used for the determination of liquid and dried pain films [23,24]. The most of bending and skeletal vibrations are absorb in $1500\text{--}650\text{ cm}^{-1}$ region, it causes small an electronic effect in the molecule direct to large shifts. A molecule of spectrum has a hundred of absorption bands are present, but there is no need to allocate the majority of bands. These spectra just like a fingerprint of the molecule and this region is named as fingerprint region [25].

When material is placed on crystal the IR beam penetrates the thin layer of the sample surface and losses the energy, causing the attenuated total reflection. In this technique the good contact between the sample and crystal is important [26].

The depth of penetration of the IR beam on sample depends on the IR radiation angle of incidence, redaction wavelength and refractive index of the crystal and samples. The internal reflection technique is commonly used for the nondestructive estimation of solids, powders and liquid. In current study the Thermo Nicolet is 5 FTIR with ZnSe (refractive index 2.67) was used for the investigation of fluorspar fingerprints. In present case the instrument was operated at 4 cm^{-1} resolution and results detected after 32 scans.

X-Ray Diffraction (XRD) analysis: The CaF_2 mineralogy was determined by using X-ray Powder diffraction instrument PW3040/60 (Philips diffractometer, XPERT-PRO) and unit operating at 40 kV and 30

mA using the Cu K α radiation). The diffractograms were automatically matched with ICDD software. Mineralogy was determined with dried samples and evaluated the present Compounds.

Results and Discussion

XRF instrument parameters

Before construction of calibration lines, the instrument parameters were selected as per requirement Table 1 shows the selection of crystals, Collimator, detector and power (combination of mA and KV) of X-ray tube. After selection of elements, angles and PHDs of each element were measured through synthetic and CRMs materials then applied offset background of channels, background calculated time and other parameters for each element. Initially, the background was estimated and subtracted from the peak area before calculation of the net peak areas. These parameters were applied to all elements as per requirement. The subtractions some time introduce large error of analysis for small peaks and gives error especially in case of minor elements (Table 2).

XRF calibration with certified reference materials

In the current study various certified reference materials (CRMs) of fluorite were used during calibration and validation of application. For extension of lines the few CRMs were diluted with the help of lithium tetra borate ($\text{Li}_2\text{B}_4\text{O}_7$) and few synthetic standards prepared as per fluorspar constituents. The main mineralogy of fluorspar is consisting

Channel	Line	Crystal	2d nm	Collimator (μm)	Detector	KV	mA
Al	KA	PE 002	0.8746	300	Gas flow	24	125
Si	KA	PE 002	0.8746	300	Gas flow	24	125
Fe	KA	LiF 200	0.4027	300	Scintillator	60	50
Mg	KA	PX1	5.0181	300	Gas flow	24	125
Ca	KA	LiF 200	0.4027	150	Gas flow	30	100
Ba	KA	LiF 200	0.4027	300	Scintillator	60	50

Table 1: Instrument parameters and system setup.

Channel	Offset Bg1(2T)	PHD (LL)	PHD(UL)	CSE%	Peak Time (s)	Channel	Background Time (s)	Start angle (*2T)	Angle Height (*2T)	End angle (*2T)	Step Size (*2T)	Scan time (s)	Back ground coefficient	Sensitivity (Kcps)	Abs. Error %
$\text{Al}_2\text{O}_3/\text{Al}$	2.3936	22	78	0.108	60	AlBg1	12	142.44	144.92	147.44	0.05	25	0.4958	3.35	0.005
SiO_2/Si	2.3152	24	78	0.047	60	SiBg1	04	106.62	109.17	111.62	0.05	25	0.1716	15.66	0.002
$\text{Fe}_2\text{O}_3/\text{Fe}$	0.9456	15	78	0.069	60	FeBg1	12	56.50	57.54	58.51	0.04	10	1.5855	8.52	0.003
MgO/Mg	2.2830	19	78	0.204	60	MgBg1	18	20.23	22.82	25.23	0.05	50	0.4598	1.09	0.010
CaO/Ca	-1.0258	32	73	0.013	60	CaBg1	10	112.05	113.12	114.05	0.04	10	24.705	234.3	0.001
BaO/Ba	-0.8856	31	73	0.023	60	BaBg1	18	10.03	10.97	12.05	0.04	10	49.165	91.34	0.001

Table 2: Parameters for each element applied during application formation.

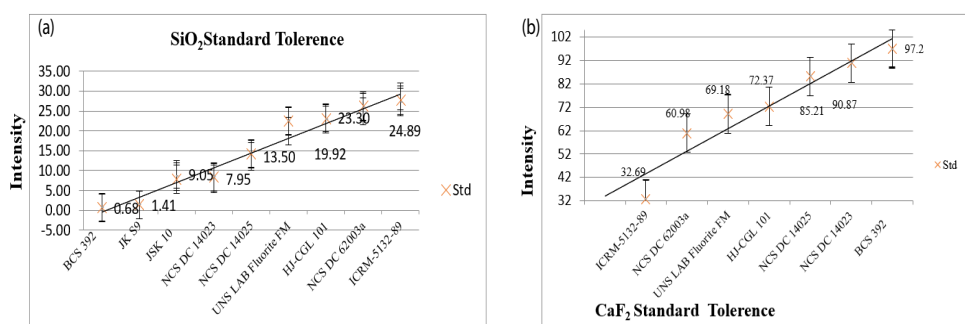


Figure 6: (6a and 6b) standard tolerance of Fluorspar standards samples.

Compound/ Channel	Intercept of Regression Line	Slope of regression line	Root mean Square value	K factor
Al ₂ O ₃ /Al	-0.05	0.064	0.356	0.200
SiO ₂ /Si	-0.2055	0.087	0.847	0.232
Fe ₂ O ₃ /Fe	-0.0131	0.010	0.043	0.080
MgO/Mg	-0.15	0.055	0.040	0.067
CaO/Ca	0.015	0.045	0.44	0.072
BaO/B	0.058	0.0058	0.022	0.028

Table 3a: Calibration coefficient for WD-XRF application.

Element	Alpha for Al ₂ O ₃	Alpha for SiO ₂	Alpha for Fe ₂ O ₃	Alpha for MgO	Alpha for BaO	Lo (C) for SiO ₂	Lo (C) for MgO	Lo (C) for Al ₂ O ₃	Lo (C) for Fe ₂ O ₃	Lo (C) for Ca	Lo (R) for Al	Lo (R) for Ca	Lo (R) for Ba
Al	-0.2194	-0.1976	0.6217	0.8306	1.6005	-0.0154	-0.696	-	-	0.0041	-	0.0305	0.0039
Si	0.9249	-0.0716	0.6438	0.8179	1.7244	-	-	-0.0214	0.5738	-	1.355	-	-
Mg	-0.3119	-0.2501	0.5955	-0.3429	1.2185	-	-	-	-	-	-	-0.2014	-
Fe	-0.8024	-0.7829	-0.6103	-0.8208	0.8475	-	-	0.0014	-	-	-	-	-
Ca	-0.0905	-0.011	-0.1748	-0.1562	0.8922	-0.0427	-	-0.1439	-0.1675	-	-	-	-
Ba	-0.7844	-0.7643	0.3948	-0.7936	3.9321	-	-	-	-	0.0019	-	-	-

Table 3b: Theoretical matrix correction coefficient values.

S.#	Std Name	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	MgO	Ca (Total)	BaO	Carbon by Combustion method	CaO By C	CaF ₂ By CaO
1	JK S9	-	1.21 (1.4)	(N.R)	2.33 (2.2)	(N.R)	(N.R)	0.024	0.112 (N.R)	-
2	NCS DC 14023	(N.R)	7.92 (8.35)	0.11 (0.124)	(N.R)	46.37* (N.R)	(N.R)	0.002	0.011 (N.R)	91.76 (90.87)
3	NCS DC 14025	(N.R)	13.66 (14.15)	0.192 (0.209)	(N.R)	43.98* (N.R)	(N.R)	0.002	0.011 (N.R)	85.74 (85.21)
4	NCS DC 62003a	3.64 (3.69)	26.59 (26.20)	2.36 (2.35)	0.30 (0.18)	31.27* (N.R)	(N.R)	0.10	1.77 (1.17)	60.10 (60.98)
5	HJ-CGL 101	2.55 (2.35)	23.23 (23.01)	0.299 (0.34)	0.030 (0.021)	36.80 (37.32)	(N.R)	0.06	0.28 (N.R)	71.18 (72.37)
6	UNS LAB Fluorite FM	0.27 (0.329)	20.27 (22.59)	0.45 (0.496)	0.043 (0.036)	36.24 (35.89)	3.89 (3.89)	0.10	0.467 (N.R)	69.79 (69.18)
7	ICRM-5132-89	11.12 (N.R)	27.94 (27.68)	(N.R)	4.47 (N.R)	21.17 (N.R)	(N.R)	1.41	6.58 (N.R)	32.10 (32.69)
8	JK S10	0.553 (0.54)	8.21 (7.8)	0.084 (0.11)	0.40 (0.30)	(N.R)	(N.R)	0.001	0.005	-
9	BCS 392	(N.R)	0.73 (0.67)	(N.R)	(N.R)	50.22* (N.R)	0.46 (0.37)	0.102	0.476	97.49 (97.2)

Table 4: N.R=Not Reported, Certified Reported Value in (-----). JK S9 and JK S10 were used for estimation of SiO₂, Al₂O₃ and Fe₂O₃. *In CRMs, Total Calcium are not reported. Hence, total Ca was calculated theoretically by taking Ca from CaF₂ and CaO respectively and validated from classical method. + MgO calculated by classical method

of SiO₂, Fe₂O₃, MgO, CaCO₃, CaF₂ as well as BaO, P, S, Na and K. The calibration lines were illustrated against concentration v/s intensity (Figure 5) then applied theoretical correction coefficient for correction in lines and observed calibration coefficients of each element. In current application the maximum concentration range, lower limit of detection (LLD) of each element, slope of regression line, intercept of regression line and other parameters were generated during application development are mentioned in Tables 3a and 3b.

WD-XRF estimated CRMs

Standard samples were analyzed as test samples after development of application for verification and re-confirmation of known standard value (Figures 6a and 6b). The re-estimated certified reference value shows the accuracy of application present in Table 4.

Estimation of CRMs and samples by classical method

The same standards and samples were used for the estimation by of Al₂O₃, MgO, total Ca, Ca (Soluble), SiO₂, CaF₂ (by difference of total and soluble Ca) and R₂O₃ (Fe₂O₃, Al₂O₃ etc.) by ASTM-E-815 and ASTM-E-1506. BaO is difficult to estimate by conventional method (Tables 5 and 6).

Error comparisons from standards

Comparison illustrated the accuracy of current method and classical method in Table 7. Both observed values were nearest to each other and showed that current method is precise and accurate with respect to conventional method and assay to operative and demonstrative.

Calibration and analysis of carbon

The total carbon of CRM's and unknown samples were analyzed by combustion method (Figure 7). The standard reference material (ICRM-5132-89, C=1.41%) was used for calibration with different dilutions showed the linearity and regression factor was $R^2=0.999$ (Table 8). The above-mentioned CRMs were used for the validation of carbon analyzer. The theoretical carbon value was calculated by CaCO_3 present in standards. The accuracy of carbon estimated value directly effects on value of CaF_2 (Table 9).

Calculation for conversion

The following factors were used for calculation during development of application for conversion of elements:

$$\text{Total Ca to CaF}_2 = [\text{Total Conc ("Ca")} - (\text{Conc ("C")} \times 4.665) \times 0.715] \times 1.95$$

Apply factors during application development,

- C to $\text{CaO}=4.665$,
- $\text{CaO to Ca}=0.715$,

- Ca to $\text{CaF}_2=1.95$.

Alkali metal decarbonation

The presence of calcite in CaF_2 instead of other carbonates was examined at different temperatures (Table 10). The values showed that the initially loss in samples and standards was in small quantity and the maximum loss was observed at 700°C as shown in Figure 8. At 450°C the observed loss is less than the other temperatures value it confirmed the absence of MgCO_3 [27].

Mineralogical phase evaluation by XRD

The XRD patterns of Fluorspar powdered samples were illustrated in already characterized through WDXRF and classical method with the help of Expert Pro for the evidence of alkali carbonates, OH, apatite group of compounds and presence of calcium fluorite. The observed patterns are mentioned in Figures 9a-9c. The observed peaks were characterized and theta θ values with software library and illustrated the present mineralogy are similar with natural compounds of CaF_2 and the presence of calcite peak in diffractograms describe and confirm the presence of CaCO_3 instead of other alkaline carbonates and the

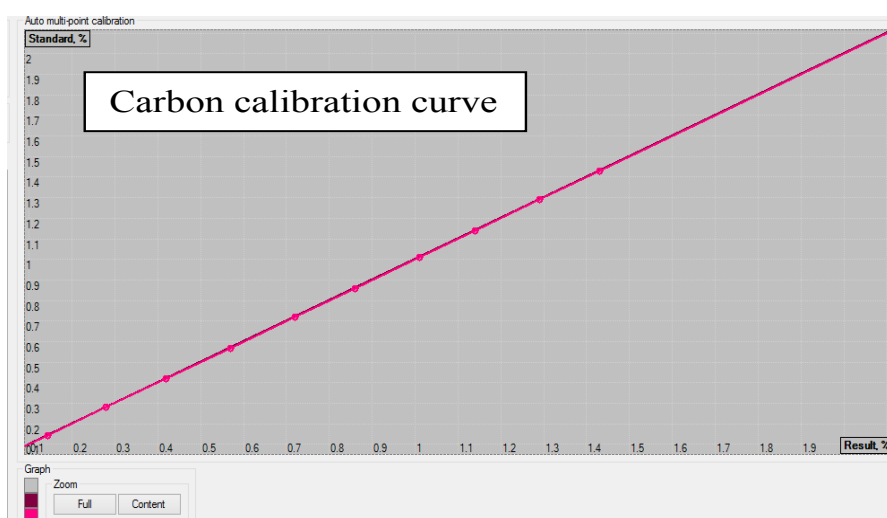


Figure 7: The total carbon of CRM's and unknown samples were analyzed by combustion method.

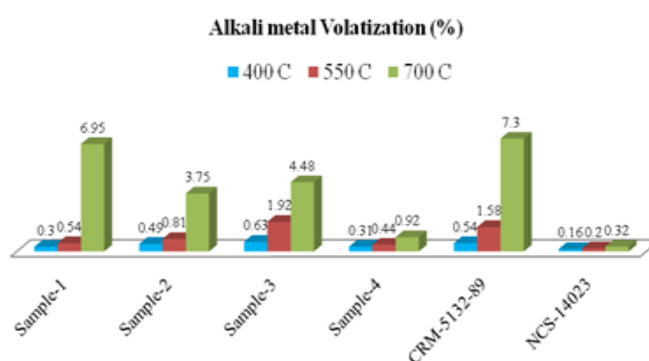


Figure 8: The loss in samples and standards with maximum loss was observed at 700°C .

S.#	Std Name	SiO ₂	Ca (Total)	CaO	CaF ₂	R ₂ O ₃
1	JK S9 (slag)	1.49	N.P	N.P	N.P	31.47
2	NCS DC 14023	8.06	46.69	0.19	90.77	0.16
3	NCS DC 14025	13.74	43.89	0.11	85.59	0.32
4	NCS DC 62003a	26.09	32.32	1.23	61.31	6.4
5	HJ-CGL 101	23.15	37.39	0.28	71.35	2.66
6	UNS LAB Fluorite FM	22.75	35.99	0.56	69.4	0.78
7	ICRM-5132-89	27.94	20.39	6.75	32.4	12.92
8	JK S10 (slag)	7.67	N.P	N.P	N.P	0.67
9	BCS 392	0.79	49.55	0.5	95.93	-

N.P=Not possible, ASTM method applicable for Fluorspar not for slag.

Table 5: Estimated certified reference standard values (%) by conventional methods.

Sample #	SiO ₂ Mean	SD	RSD	Uncertainty U _A	CaO	SD	RSD	Uncertainty U _A	R ₂ O ₃	SD	RSD	Uncertainty U _A	CaF ₂	SD	RSD	Uncertainty U _A
1	13.34	0.020	0.150	0.012	2.24	0.021	0.924	0.0120	2.59	0.021	0.800	0.012	81.30	0.153	0.188	0.088
2	6.87	0.021	0.303	0.012	14.03	0.061	0.434	0.0351	1.34	0.017	1.293	0.010	70.35	0.025	0.036	0.015
3	7.27	0.021	0.286	0.012	12.68	0.025	0.198	0.0145	1.18	0.021	1.759	0.012	71.82	0.025	0.035	0.015
4	11.85	0.047	0.399	0.027	2.58	0.020	0.772	0.0115	2.54	0.010	0.392	0.006	81.23	0.189	0.233	0.109
5	7.87	0.032	0.408	0.019	7.51	0.015	0.203	0.0088	1.30	0.015	1.169	0.009	79.83	0.032	0.040	0.019
6	17.63	0.026	0.150	0.015	3.36	0.010	0.297	0.0058	4.36	0.021	0.478	0.012	73.93	0.032	0.043	0.019
7	30.08	0.100	0.332	0.058	5.61	0.015	0.273	0.0088	5.36	0.031	0.571	0.018	56.41	0.010	0.018	0.006
8	10.28	0.021	0.202	0.012	2.13	0.012	0.543	0.0067	2.50	0.015	0.610	0.009	84.39	0.026	0.031	0.015
9	19.36	0.021	0.108	0.012	4.49	0.015	0.340	0.0088	5.09	0.017	0.340	0.010	69.80	0.021	0.030	0.012
10	11.18	0.026	0.237	0.015	2.80	0.017	0.619	0.0100	2.77	0.010	0.361	0.006	83.06	0.044	0.052	0.025
11	17.44	0.026	0.152	0.015	3.46	0.015	0.442	0.0088	4.52	0.010	0.221	0.006	74.57	0.036	0.048	0.021
12	11.00	0.153	1.397	0.088	3.24	0.015	0.470	0.0088	2.40	0.015	0.635	0.009	82.62	0.031	0.037	0.018
13	28.74	0.050	0.175	0.029	5.25	0.015	0.291	0.0088	6.14	0.021	0.339	0.012	58.52	0.026	0.045	0.015
14	16.85	0.044	0.259	0.025	3.58	0.023	0.646	0.0133	3.63	0.015	0.420	0.009	75.19	0.026	0.035	0.015
15	16.45	0.023	0.140	0.013	3.58	0.015	0.427	0.0088	6.75	0.012	0.171	0.007	70.93	0.026	0.037	0.015
16	7.87	0.031	0.388	0.018	4.40	0.032	0.725	0.0186	1.92	0.021	1.086	0.012	83.78	0.021	0.025	0.012
17	10.79	0.032	0.298	0.019	4.30	0.087	2.014	0.0500	2.61	0.026	1.018	0.015	81.44	0.021	0.026	0.012
18	9.81	0.031	0.311	0.018	3.31	0.218	0.010	0.0058	2.22	0.015	0.686	0.009	83.98	0.021	0.025	0.012
19	2.13	0.026	1.248	0.015	0.73	0.021	0.021	0.0120	0.82	0.012	1.414	0.007	95.51	0.025	0.026	0.015
20	N.D	-	-	-	4.92	0.021	0.021	0.0120	N.D	-	-	-	85.44	0.031	0.036	0.018
21	N.D	-	--	-	0.55	0.010	0.010	0.0058	N.D	-	-	-	98.88	0.026	0.027	0.015
22	N.D	-	-	-	1.12	0.020	0.012	0.0067	N.D	-	-	-	97.28	0.021	0.021	0.012
23	N.D	-	-	-	0.18	0.015	0.010	0.0058	N.D	-	-	-	97.81	0.031	0.031	0.018
24	9.26	0.025	0.272	0.015	11.19	0.025	0.025	0.0145	3.11	0.015	0.490	0.009	69.19	0.026	0.038	0.015
25	17.23	0.021	0.121	0.012	15.65	0.029	0.029	0.0167	6.61	0.020	0.303	0.012	50.52	0.015	0.030	0.009
26	3.99	0.108	2.63	0.061	0.34	0.015	0.010	0.0058	0.44	0.010	2.273	0.006	94.67	0.021	0.022	0.012
27	12.76	0.038	0.297	0.022	2.58	0.012	0.012	0.0067	2.14	0.021	0.974	0.012	81.28	0.015	0.019	0.009
28	16.72	0.038	0.226	0.022	0.45	0.015	0.010	0.0058	5.01	0.042	0.827	0.024	77.84	0.015	0.020	0.009
29	12.99	0.025	0.194	0.015	0.67	0.010	0.010	0.0058	1.32	0.015	1.151	0.009	85.60	0.021	0.024	0.012
30	8.66	0.032	0.371	0.019	1.01	0.042	0.006	0.0033	1.20	0.020	1.653	0.012	88.21	0.010	0.011	0.006
31	7.07	0.121	1.701	0.070	12.3	0.153	0.153	0.0882	0.91	0.017	1.903	0.010	71.13	0.020	0.028	0.012
32	8.45	0.026	0.313	0.015	9.41	0.015	0.015	0.0088	2.39	0.017	0.725	0.010	74.80	0.012	0.015	0.007
33	8.84	0.036	0.407	0.021	2.91	0.015	0.015	0.0088	1.62	0.020	1.235	0.012	85.77	0.015	0.018	0.009
34	8.94	0.015	0.171	0.009	10.75	0.020	0.020	0.0115	3.04	0.015	0.499	0.009	71.78	0.015	0.021	0.009
35	6.58	0.036	0.547	0.021	2.80	0.021	0.021	0.0120	1.54	0.015	0.996	0.009	88.61	0.017	0.020	0.010
36	10.22	0.026	0.259	0.015	10.86	0.020	0.020	0.0115	3.01	0.044	1.439	0.025	69.70	0.010	0.014	0.006
37	10.22	0.093	0.910	0.054	7.82	0.017	0.017	0.0100	3.25	0.020	0.613	0.012	75.94	0.015	0.020	0.009
38	9.43	0.040	0.428	0.023	11.22	0.010	0.010	0.0058	3.24	0.015	0.470	0.009	72.85	0.012	0.016	0.007
39	13.0	0.136	1.041	0.078	7.29	0.127	0.017	0.0100	3.41	0.021	0.611	0.012	71.33	0.010	0.014	0.006
40	N.D	-	-	-	0.10	0.001	0.008	0.0046	1.82	0.015	0.838	0.009	97.01	0.010	0.010	0.006
41	0.34	0.006	1.715	0.003	0.10	0.010	0.009	0.0049	1.67	0.010	0.602	0.006	96.72	0.010	0.010	0.006
42	4.12	0.003	0.739	0.018	1.17	0.015	0.015	0.0088	1.17	0.026	2.281	0.015	92.45	0.015	0.017	0.009
43	7.30	0.115	1.589	0.067	4.71	0.021	0.021	0.0120	2.24	0.010	0.444	0.006	83.16	0.015	0.018	0.009
44	0.32	0.006	1.786	0.003	0.10	0.010	0.012	0.0067	1.52	0.021	1.367	0.012	97.92	0.006	0.006	0.003
45	N.D	-	-	-	0.11	0.006	0.012	0.0067	1.52	0.006	0.378	0.003	95.63	0.015	0.016	0.009

Table 6: Quantitative estimation of samples (% Average of 03 results) by classical Methods. * N.D=Not determined

S.#	Std Name	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂		CaF ₂	
		WDXRF	WDXRF	WDXRF	Classical Method	WDXRF	Classical Method
1	JK S9	-	-	-0.19	-0.09	-	-
2	NCS DC 14023	N.R	-0.014	-0.43	0.29	0.89	-0.1
3	NCS DC 14025	N.R	-0.017	-0.49	0.41	0.53	0.38
4	NCS DC 62003a	-0.05	-0.01	0.39	0.11	-0.88	0.33
5	HJ-CGL 101	0.2	-0.04	0.22	-0.14	-1.19	-1.02
6	UNS LAB Fluorite FM	-0.059	-0.046	0.32	-0.16	0.61	0.22
7	ICRM-5132-89	N.R	N.R	0.26	-0.26	-0.59	-0.29
8	JSK 10	0.01	-0.026	0.41	-0.13	N.R	
9	BCS 392	N.R	N.R	0.06	-0.1	0.29	-1.27

Table 7: Error comparison from standards.

S. No	Standards (%)	% Observed Value	% Accuracy
1	0.14	0.136	97.4
2	0.28	0.278	99.28
3	0.42	0.424	100.55
4	0.56	0.556	100.0
5	0.70	0.703	101.42
6	0.84	0.845	100.59
7	0.98	0.98	100.0
8	1.12	1.125	100.44
9	1.26	1.26	100.0
10	1.41	1.42	100.0

Table 8: % accuracy of Carbon after dilutions of standard.

S. No	Standards	% Standard calculated Value	% Observed Value	% Accuracy
1	NCS DC 14023	0.0024	0.002	83.33
2	NCS DC 14025	0.0024	0.002	83.33
3	NCS DC 62003a	0.38	0.38	100
4	HJ-CGL 101	0.0876	0.088	100
5	UNS LAB Fluorite FM	0.0354	0.035	100
6	ICRM-5132-89	1.41	1.41	100
7	BCS 392	0.10	0.10	100

Table 9: Primary standards (Carbon value) for validation of application.

fluorine is present in single phase compound as CaF₂. The morphology of CaF₂ also present for information at different scan ranges [28].

FTIR evaluation by ATR method

Qualitative analyses of any compound having different chemical constituents are characterized by frequencies and their characteristics. For this purpose, FTIR and XRD may be help for evaluation. In powdered samples the variety of FTIR techniques may be used for the analysis of surface. The most common technique is attenuated total reflection (ATR) (Figures 10a and 10f). In present study the ATR-FTIR was used for the presence of CaCO₃ in fluor spar, for said purpose four (04) samples and two (02) standards NCS DC-14023 and ICRM-5132-89 were selected (Table 11). The presence of bands of infrared spectrum of the Ca-CO group stretching of carbonates on the 713, 875 and 1418 -1473 cm⁻¹ it shows the absorption bands of CaCO₃ (Calcite) [29,30] and correspond to the different elongation bands of C-O. The 1418-1473 cm⁻¹ wave numbers are the in-plane bending, 875 cm⁻¹ wave number is the out-plan bending and 713 cm⁻¹ wave number is an asymmetric stretching region [31]. The bands at 912-935 cm⁻¹, 1000-1011 cm⁻¹, 1031-1033 cm⁻¹, 1081-1187 cm⁻¹ are belongs to SiO₂ (quartz),

these are also confirmed by the presence of XRD results [32].

The strong band observed in few samples and standards at 3642-3650 cm⁻¹ belongs to the O-H bonds (water group) to the hydroxide and characterized as water of crystallization [33]. Moreover, the bands at 777-795 cm⁻¹ related to presence of CaF₂ [28].

Pressed Specimen Analysis Instead of Fused Bead

The said application was especially designed for all categories of fluor spar in pressed pellet specimens. Fluorine has low molecular weight and melting temperature. Because of low molecular weight of fluorine in most of the geological sample's possible losses of fluorine before calcinations and decomposes during 825°C-1330°C [34] due to evaporation before calcinations temperature it is futile to estimate by fused bead sample.

Fatal Impact on method

In the presence of other carbonates like Mg, Na, Ba, etc. instead of CaCO₃, the current application will quantify the concentration as total carbonates, and the application has limitations to differentiate the separate carbonates as well as fatal impact on estimation of CaF₂. But the estimated results through different techniques show that the natural occurring fluor spar has CaCO₃ and the other carbonates are present in small quantity. Therefore, the developed method has no fatal impact on determinations of CaF₂ mineralogy.

Invented method specificity

The method specificity was study by using the standards used for development and classical method for validation of application with different primary and synthetic standards concentrations. Measurement time of all elements including background correction time was 340 second. The peaks of each element showed that no specific peak overlaps demonstrating the method specificity.

Linearity and application range

Measurements of each element spectral data collected from standards were fit in linear calibration mode. The net intensity of each element was used for linear corrections and matrix absorption effects were corrected by applying fixed alpha correction method. Therefore, the Fundamental Parameter model was used for correction coefficients of each element (Tables 3a and 3b).

Method validation

Verification and implementation of new method in industry commonly use the powerful tool is Method validation. In current method the tools used for validation were standard deviation, recovery (R, %), relative percent difference (RPD, Eq. (1)), instrument detection

S.#	Temp°C	Sample-1	Sample-2 (%)	Sample-3	CRM-IARM 5132-89	CRM NCS DC-14023
1	400	0.30	0.49	0.63	0.54	0.16
2	550	0.49	0.81	1.92	1.58	0.20
3	700	6.95	1.92	4.48	7.3	0.32

Table 10: Volatilization measurements of alkaline earth carbonates.

S. No	Peaks cm ⁻¹										
15	692	793	878	911	935	1000	1031	1115	1187	1433	
3	688	712	777	875	913	1002	1033	1092		1418	1455
16		712	795	875	912	1001	1032	1091		1418	
19	695		871	877		1011			1437	1457	1473
(5132-81)	694	712	728	795	875	1009				1436	
(NCS-4023)			777	796				1081			

Table 11: ATR-FTIR Evaluation.

limit (IDL), limit of quantitation (LOQ), method detection limit (MDL) and uncertainty (U_a), have been executed as significant part of the data which might be expressed the importance of biases at different concentration levels.

$$RPD = 100 \times (\text{Value2} - \text{Value1}) / (\text{Value2} + \text{Value1}) / 2 \quad (1)$$

Al₂O₃, SiO₂, Fe₂O₃ and CaF₂ in the synthetic and certified reference materials and samples were verified using the optimized methods. Both of the mean concentration and standard deviation (SD) of the observed value for three replicates (n=3), %R, RSD, RPD have been used for accuracy measurement. IDL (expressed as 3 × SD), MDL (expressed as t × SD, where t (n-1, 1-α=0.95); t=2.92), and LOQ (expressed as 3 × SD) and uncertainty (U_a) were also estimated.

The recovery %R was the ratio of the observed concentration (C_{obs}) of estimated elements achieve by the optimized analytical procedure to the concentration at a reference level (C_{ref}).

The recovery was used to test the significant departure from unity and to prove the specificity of the method optimization [35]. Therefore, it was a good practice for ion method validation to estimate R that checked sample to control bias at random duplicate within-run precision [36]. Therefore, it was a good practice for ion method validation to estimate R that checked sample to control bias at random duplicate within-run precision [37].

IDL was used to communicate the elements present concentration identical to the electric signal of the WDXRF. Principally, this is the smallest signal that can be distinguished from the background noise of the instrument and is always laid below the MDL but does not necessary use for compliance data reporting [38]. Furthermore, it was executed to refer to the precision of the technique and the sensitivity of the instrument.

The other valuable detection limit is MDL that served statistically in human health protection and was typically used to evaluate data [38]. Otherwise, MDL is expressed as a minimum concentration of a substance that can be measured and reported with 99% confidence [38].

Even MDL does not take into account the effects of high or low bias in a series of measurements due to matrix interferences, but it was used in the current work to accomplish a relative measure of the performances of the two methods (WDXRF and classical methods for CaO, SiO₂, Al₂O₃, and CaF₂ etc. measurement) for the determinations of these elements in calcium fluoride in different synthetic and reference

standards and unknown samples. LOQ which is a function to three factors: matrix, method, and analyst specificity [39].

This value is 03 × SD away from the mean as mentioned [26]. The sample concentration value (expressed as mean) that is found greater than LOQ was termed in the region of quantitation, while the concentration that belongs to the range LOQ ≥ mean ≥ IDL was expressed to be in the region of detection. Thus, LOQ was used in this study to verify a permissible limit of detection and to illustrate the smallest concentration of the element that can be consistently measured by each analytical process.

Quantification of uncertainty relevant data was analyzed considering the uncertainty associated with measurement in accordance with the EURACHEM/CITAC guide [40]. This procedure was implemented since ion analysis requires high quality of analytical data. In this work, the Guide “Measurement uncertainty arising from sampling” has been entirely adopted to facilitate the practical implementation of the technical procedure [41]. Moreover, the application of this guide clearly referred to the sources of uncertainty through the sampling, which were heterogeneous (or inhomogeneous), these were [42]. Effects of specific sampling strategy. Effects of sampling process on the sample composition of studied metals.

Therefore, present study approach to provide a practical approach for evaluating contents in CaF₂ using the concept of measurement uncertainty that enhanced both: The optimization of the analytical procedure. Design control of a sampling plan based on the repeatability of sample contribution, the application of the analytical measurement uncertainty described by EURACHEM/ CITAC was achieved. To define the stability of reading point of the ion concentration, it was decided to check the uncertainty (U_A). This term was determined through the analytical applications which were directly connected to the lack of homogeneity during sample collection.

The results of the replication process of the analytical methods based on the contents in the artificial/ synthetic reference standards. Table 12 showed good recovery values which referred that the effect of standards matrix and sample homogeneity was very critical and proved matrix influence with any of the optimized methods. Moreover, no significant difference was observed between the results obtained by the tested and the reference comparative outcomes of the reference sample for each procedure. The recovery test and the relative findings of the statistics of value had indicated a good sensitivity. On the other hand, Table 12 had defined RPD percent's, low limits of IDL, MDL, and LOQ of the optimized methods.

RSD (%) values were observed in samples ranged from 0.1-2.71% and 0.0059-0.23 and in reference materials ranged from 0.027-0.73 and 0.016-0.033 for the determinations of SiO₂ and CaF₂ measured by the same classical method. The same samples and reference standards were analyzed by WDXRF and observed RSD (%) ranged in reference substance 0.014-0.047 % and 0.043-0.82, for the estimation of CaF₂ and SiO₂ respectively. In samples the RSD (%) values were estimated ranged in SiO₂ 0.058-5.21 and CaF₂ 0.04-0.28 (Figures 11a and 11e).

Precision and accuracy of application was depending upon the reproducibility of each element results. The accuracy of the method was investigated by determining the % accuracy standards with known number of different elements (Table 12).

Detection and quantification limits

The lower limit of detection (LLD) of each element was calculated

S. No.	Element	Std Name	Certified value	Mean value	SD	RSD	Uncertainty U _A	% Recovery	RPD	MDL (at 95 % CL) t=2.92	IDL	LOQ
1	SiO ₂	JK S9	1.4	1.21 ^a	0.01	0.82	0.0058	86.43	-3.61	0.029	0.03	0.03
				1.49 ^b	0.01	0.671	0.0058	106.43	1.56	0.024	0.025	0.024
2		NCS DC 14023	8.35	7.92 ^a	0.2	0.253	0.0115	94.85	-0.01	0.058	0.06	0.06
				8.07 ^b	0.015	0.189	0.0087	96.69	-0.85	0.036	0.037	0.037
3		NCS DC 14025	14.15	13.66 ^a	0.015	0.112	0.0088	96.54	-0.88	0.045	0.046	0.046
				13.75 ^b	0.01	0.073	0.0058	97.17	-0.7	0.024	0.025	0.024
4		NCS DC 62003a	26.2	26.59 ^a	0.015	0.057	0.0088	98.53	1.38	0.045	0.046	0.046
				26.09 ^b	0.007	0.027	0.0041	99.56	-0.11	0.015	0.015	0.015
5		HJ-CGL 101	23.01	23.23 ^a	0.01	0.043	0.0058	99.1	0.23	0.029	0.03	0.03
				23.15 ^b	0.021	0.109	0.0118	100.59	0.15	0.06	0.062	0.062
6		UNS LAB Fluorite FM	22.59	22.27 ^a	0.015	0.075	0.0087	98.58	-0.37	0.045	0.046	0.046
				22.76 ^b	0.013	0.067	0.0072	100.77	0.19	0.036	0.037	0.037
7		ICRM-5132-89	27.68	27.94 ^a	0.02	0.072	0.0115	99.06	0.23	0.058	0.06	0.06
				27.95 ^b	0.008	0.036	0.0047	100.98	0.24	0.024	0.025	0.024
8		JK S10	7.8	8.21 ^a	0.01	0.122	0.0058	95	1.28	0.029	0.03	0.03
				7.67 ^b	0.008	0.13	0.0047	98.33	-0.42	0.024	0.025	0.024
9		BCS 392	0.67	0.73 ^a	0.006	0.795	0.0035	91.78	2.14	0.017	0.017	0.017
				0.79 ^b	0.0058	0.732	0.0072	117.41	4.11	0.036	0.037	0.037
10	Al ₂ O ₃	NCS DC 62003a	3.69	3.64 ^a	0.01	0.275	0.0058	98.65	-0.34	0.029	0.03	0.03
				NR	-	-	-	-	-	-	-	-
11		HJ-CGL 101	2.35	2.55 ^a	0.015	0.6	0.0088	92.15	1.83	0.045	0.046	0.046
				NR	-	-	-	-	-	-	-	-
12		UNS LAB Fluorite FM	0.329	0.27 ^a	0.006	2.112	0.0033	81.82	-8.33	0.017	0.017	0.017
				NR	-	-	-	-	-	-	-	-
13		JK S10	0.54	0.55 ^a	0.015	2.794	0.0088	98.19	-0.46	0.045	0.046	0.046
				NR	-	-	-	-	-	-	-	-
14	Fe ₂ O ₃	NCS DC 14023	0.124	0.11 ^a	0.006	5.413	0.0033	88.71	-2.99	0.017	0.017	0.017
				NR	-	-	-	-	-	-	-	-
15		NCS DC 14025	0.209	0.19 ^a	0.001	0.518	0.0006	91.87	-1.99	0.003	0.003	0.003
				NR	-	-	-	-	-	-	-	-
16		NCS DC 62003a	2.35	2.36 ^a	0.015	0.648	0.0088	99.58	0.11	0.045	0.046	0.046
				NR	-	-	-	-	-	-	-	-
17		HJ-CGL 101	0.34	0.3 ^a	0.002	0.508	0.0009	88.24	-3.13	0.004	0.005	0.005
				NR	-	-	-	-	-	-	-	-
18		UNS LAB Fluorite FM	0.496	0.45 ^a	0.01	2.222	0.0058	90.73	-2.43	0.029	0.03	0.03
				NR	-	-	-	-	-	-	-	-
19		JK S10	0.11	0.084 ^a	0.002	2.381	0.0012	76.36	-6.12	0.006	0.006	0.006
				NR	-	-	-	-	-	-	-	-
20	MgO	JK S9	2.2	2.33 ^a	0.006	0.247	0.0033	94.4	1.43	0.017	0.017	0.017
				NR	-	-	-	-	-	-	-	-

21		NCS DC 62003a	0.18	0.3 ^a	0.006	1.946	0.0033	60	12.19	0.017	0.017	0.017
				NR	-	-	-	-	-	-	-	-
22		HJ-CGL 101	0.021	0.03 ^a	0.001	3.333	0.0006	70	8.82	0.003	0.003	0.003
				NR	-	-	-	-	-	-	-	-
23		UNS LAB Fluorite FM	0.036	0.043 ^a	0.002	3.525	0.0009	83.72	4.43	0.004	0.005	0.005
				NR	-	-	-	-	-	-	-	-
24		JK S10	0.3	0.4 ^a	0.006	1.42	0.0033	75	0.13	0.017	0.017	0.017
				NR	-	-	-	-	-	-	-	-
25		NCS DC 14023	90.87	91.76 ^a	0.02	0.0218	0.0115	99.03	0.25	0.058	0.06	0.06
				90.77 ^b	0.02	0.022	0.0115	99.89	-0.03	0.058	0.06	0.06
26		NCS DC 14025	85.21	85.74 ^a	0.017	0.0243	0.0098	99.38	0.16	0.061	0.062	0.062
				85.59 ^b	0.02	0.0234	0.0115	100.45	0.11	0.058	0.06	0.06
27		NCS DC 62003a	60.98	60.12 ^a	0.022	0.044	0.0125	98.56	-0.32	0.077	0.079	0.079
				61.31 ^b	0.02	0.0326	0.0115	100.54	0.14	0.058	0.06	0.06
28	CaF ₂	HJ-CGL 101	72.37	71.19 ^a	0.008	0.014	0.0047	98.56	-0.41	0.029	0.03	0.03
				71.35 ^b	0.015	0.0214	0.0088	98.59	-0.35	0.045	0.046	0.046
29		UNS LAB Fluorite FM	69.18	69.78 ^a	0.008	0.0143	0.0047	99.13	0.22	0.029	0.03	0.03
				69.4 ^b	0.015	0.022	0.0088	100.32	0.44	0.045	0.046	0.046
30		ICRM-5132-89	32.69	32.12 ^a	0.013	0.0476	0.0072	98.2	-0.44	0.045	0.046	0.046
				32.4 ^b	0.01	0.0309	0.0058	99.11	-0.22	0.029	0.03	0.03
31		BCS 392	97.2	97.5 ^a	0.015	0.0157	0.0088	99.7	0.08	0.045	0.046	0.046
				95.93 ^b	0.015	0.0159	0.0088	98.69	-0.33	0.045	0.046	0.046

a-----WDXRF method, b-----Classical method NR= Not reported in certificate.

Table 12: Method Validation of Invented by Classical method and WDXRF results of CRMs.

S.#	Compound/Channel	LLD (ppm)	Lower Range (%)	Upper Range (%)
1	Al ₂ O ₃ /Al	57.46	0.056	11.80
2	SiO ₂ /Si	12.54	0.36	27.68
3	Fe ₂ O ₃ /Fe	40.46	0.039	2.35
4	MgO/Mg	139.18	0.036	4.45
5	Ca	6.36	23.16	50.22
6	BaO/Ba	16.28	0.035	3.98

Table 13: Application Concentration Range of WD-XRF.

S.#	Test items	Invented method	Proficiency results	Normalized Inter quartile range (%)
1	CaF ₂	95.16	94.43	0.28
2	SiO ₂	1.11	1.46	0.11
3	Total Fe	0.295	0.303	0.015

Table 14: Proficiency and invented method test result.

S.No	Al ₂ O ₃ Mean	SD	RSD	Uncertainty U _A	SiO ₂ Mean	SD	RSD	Uncertainty U _A	Fe ₂ O ₃ Mean	SD	RSD	Uncertainty U _A	MgO Mean	SD	RSD	Uncertainty U _A
1	1.88	0.025	1.34	0.015	13.12	0.097	0.74	0.056	0.51	0.038	7.38	0.022	0.22	0.025	11.62	0.015
2	0.92	0.031	3.31	0.018	7.19	0.031	0.43	0.018	0.30	0.015	5.04	0.009	0.24	0.026	11.02	0.015
3	0.79	0.023	2.91	0.013	7.63	0.021	0.27	0.012	0.31	0.006	1.84	0.003	0.22	0.015	6.84	0.009
4	1.89	0.035	1.86	0.020	11.82	0.025	0.21	0.015	0.58	0.036	6.22	0.021	0.23	0.025	11.10	0.015
5	0.91	0.010	1.10	0.006	7.65	0.035	0.46	0.020	0.24	0.040	17.08	0.023	0.20	0.015	7.51	0.009
6	3.13	0.058	1.84	0.033	17.46	0.030	0.17	0.017	1.04	0.060	5.77	0.035	0.52	0.042	8.06	0.024

7	4.08	0.104	2.55	0.060	29.81	0.025	0.08	0.015	1.14	0.036	3.16	0.021	0.65	0.025	3.85	0.015
8	1.51	0.010	0.66	0.006	10.39	0.031	0.29	0.018	0.84	0.060	7.14	0.035	0.20	0.031	15.53	0.018
9	4.45	0.021	0.47	0.012	19.28	0.031	0.16	0.018	0.54	0.025	4.69	0.015	0.16	0.031	19.50	0.018
10	1.95	0.010	0.51	0.006	11.11	0.032	0.29	0.019	0.49	0.020	4.08	0.012	0.28	0.030	10.71	0.017
11	3.76	0.010	0.27	0.006	17.29	0.010	0.06	0.006	0.65	0.050	7.70	0.029	0.17	0.025	15.10	0.015
12	1.70	0.036	2.12	0.021	10.86	0.021	0.19	0.012	0.58	0.035	6.02	0.020	0.31	0.040	13.18	0.023
13	4.82	0.010	0.21	0.006	28.62	0.031	0.11	0.018	1.08	0.085	7.90	0.049	0.71	0.025	3.56	0.015
14	2.47	0.032	1.30	0.019	16.69	0.021	0.12	0.012	1.04	0.055	5.31	0.032	0.35	0.025	7.12	0.015
15	5.75	0.072	1.26	0.042	16.58	0.021	0.13	0.012	0.73	0.025	3.43	0.015	0.70	0.040	5.80	0.023
16	1.55	0.047	3.06	0.027	7.93	0.021	0.26	0.012	0.27	0.015	5.73	0.009	0.22	0.025	11.62	0.015
17	1.80	0.040	2.22	0.023	10.85	0.026	0.24	0.015	0.63	0.042	6.57	0.024	0.27	0.042	15.61	0.024
18	1.66	0.060	3.64	0.035	9.83	0.015	0.16	0.009	0.41	0.045	10.91	0.026	0.25	0.025	10.20	0.015
19	0.66	0.036	5.46	0.021	2.17	0.025	1.16	0.015	0.08	0.006	6.58	0.003	0.39	0.025	6.40	0.015
20	<0.01	-	-	-	<0.01	-	-	-	<0.01	-	-	-	0.17	0.015	9.17	0.009
21	<0.01	-	-	-	<0.01	-	-	-	<0.01	-	-	-	0.23	0.031	13.48	0.018
22	<0.01	-	-	-	<0.01	-	-	-	<0.01	-	-	-	0.18	0.006	3.27	0.003
23	<0.01	-	-	-	<0.01	-	-	-	<0.01	-	-	-	0.18	0.021	11.35	0.012
24	2.51	0.032	1.28	0.019	9.36	0.031	0.33	0.018	0.51	0.060	11.90	0.035	0.51	0.032	6.26	0.019
25	5.54	0.057	1.03	0.033	17.14	0.042	0.24	0.024	1.04	0.060	5.77	0.035	0.24	0.015	6.45	0.009
26	0.36	0.035	9.85	0.020	3.97	0.110	2.77	0.064	0.07	0.003	3.66	0.001	0.15	0.015	9.96	0.009
27	1.30	0.021	1.61	0.012	12.82	0.026	0.21	0.015	0.80	0.025	3.13	0.015	0.15	0.025	16.41	0.015
28	4.45	0.036	0.81	0.021	16.81	0.046	0.27	0.026	0.38	0.040	10.54	0.023	0.14	0.031	21.31	0.018
29	0.88	0.021	2.36	0.012	12.45	0.439	3.52	0.253	0.28	0.025	9.10	0.015	0.17	0.021	12.49	0.012
30	0.62	0.040	6.55	0.023	8.59	0.020	0.23	0.012	0.57	0.051	9.06	0.030	0.17	0.030	17.65	0.017
31	0.67	0.026	3.95	0.015	6.98	0.015	0.22	0.009	0.10	0.015	15.80	0.009	0.20	0.025	12.80	0.015
32	1.92	0.040	2.11	0.023	8.39	0.064	0.77	0.037	0.28	0.031	11.04	0.018	0.31	0.035	11.21	0.020
33	0.99	0.096	9.74	0.056	8.77	0.036	0.41	0.021	0.48	0.025	5.28	0.015	0.21	0.015	7.16	0.009
34	2.66	0.025	0.95	0.015	8.77	0.015	0.17	0.009	0.25	0.040	15.95	0.023	0.32	0.015	4.82	0.009
35	1.13	0.021	1.85	0.012	6.52	0.025	0.39	0.015	0.24	0.031	12.56	0.018	0.55	0.030	5.45	0.017
36	2.44	0.025	1.03	0.015	10.07	0.059	0.58	0.034	0.54	0.059	10.78	0.034	0.61	0.046	7.51	0.026
37	2.79	0.015	0.55	0.009	10.04	0.045	0.45	0.026	0.32	0.031	9.45	0.018	0.42	0.040	9.70	0.023
38	2.52	0.015	0.61	0.009	9.54	0.031	0.32	0.018	0.55	0.040	7.27	0.023	0.53	0.020	3.77	0.012
39	2.96	0.020	0.68	0.012	12.89	0.042	0.32	0.024	0.31	0.021	6.79	0.012	0.32	0.031	9.65	0.018
40	1.63	0.025	1.54	0.015	<0.01	-	-	-	0.06	0.003	4.95	0.002	0.85	0.074	8.71	0.043
41	1.50	0.031	2.04	0.018	0.31	0.015	4.98	0.009	0.06	0.004	7.10	0.002	0.61	0.025	4.10	0.015
42	0.87	0.015	1.76	0.009	3.91	0.031	0.78	0.018	0.18	0.025	14.24	0.015	0.46	0.020	4.35	0.012
43	1.78	0.025	1.42	0.015	7.22	0.025	0.35	0.015	0.28	0.015	5.39	0.009	0.59	0.025	4.24	0.015
44	1.22	0.021	1.71	0.012	0.26	0.001	0.38	0.001	0.05	0.003	4.63	0.001	0.45	0.046	10.18	0.026
45	1.42	0.038	2.67	0.022	0.06	0.003	5.21	0.002	0.07	0.005	6.76	0.003	0.83	0.020	2.41	0.012

Table 15a: Quantitative analysis (% Average of 03 results) of samples by WDXRF.

S. No	BaO Mean	SD	RSD	Uncertainty U _A	C Mean	SD	RSD	Uncertainty U _A	CaO By C Mean	SD	RSD	Uncertainty U _A	CaF ₂ By CaO Mean	SD	RSD	Uncertainty U _A
1	0.1	0.003	2.58	0.0015	0.44	0.04	9.26	0.023	2.05	0.06	2.95	0.035	81.62	0.112	0.14	0.065
2	0.04	0.004	9.74	0.0021	2.9	0.04	1.4	0.023	13.77	0.321	2.34	0.186	70.36	0.196	0.28	0.113
3	0.11	0.013	12.34	0.0078	2.7	0.031	1.13	0.018	12.57	0.306	2.43	0.176	71.4	0.103	0.14	0.059
4	0.31	0.01	3.12	0.0055	0.53	0.015	2.9	0.009	2.47	0.051	2.08	0.03	81.48	0.105	0.13	0.061
5	0.28	0.007	2.34	0.0038	1.6	0.071	4.42	0.041	7.46	0.042	0.56	0.024	79.61	0.177	0.22	0.102
6	0.22	0.007	2.99	0.0038	0.73	0.04	5.56	0.023	3.4	0.04	1.19	0.023	73.75	0.136	0.18	0.078
7	0.18	0.007	3.67	0.0038	1.2	0.075	6.29	0.044	5.55	0.045	0.81	0.026	56.83	0.08	0.14	0.046
8	0.39	0.005	1.15	0.0026	0.43	0.045	10.57	0.026	2.03	0.153	7.51	0.088	83.99	0.14	0.17	0.081
9	0.55	0.006	1.12	0.0035	0.94	0.05	5.32	0.029	4.38	0.07	1.6	0.04	69.52	0.081	0.12	0.047
10	0.15	0.005	3.25	0.0029	0.6	0.04	6.77	0.023	2.8	0.098	3.52	0.057	82.99	0.12	0.14	0.069
11	0.1	0.003	2.58	0.0015	0.71	0.04	5.72	0.023	3.31	0.04	1.22	0.023	74.44	0.042	0.06	0.024
12	0.19	0.004	1.86	0.002	0.67	0.055	8.26	0.032	3.13	0.047	1.51	0.027	82.59	0.076	0.09	0.044
13	0.15	0.005	3.39	0.0029	1.09	0.045	4.15	0.026	5.08	0.06	1.19	0.035	58.59	0.045	0.08	0.026
14	0.28	0.005	1.77	0.0029	0.73	0.035	4.83	0.02	3.34	0.095	2.83	0.055	75.04	0.064	0.09	0.037
15	0.04	0.005	11.76	0.0026	0.76	0.047	6.19	0.027	3.54	0.061	1.72	0.035	70.74	0.07	0.1	0.04
16	0.07	0.004	5.23	0.0021	0.94	0.031	3.26	0.018	4.38	0.09	2.06	0.052	83.67	0.214	0.26	0.123
17	0.14	0.004	2.96	0.0023	0.9	0.036	4.01	0.021	4.2	0.035	0.84	0.02	81.13	0.032	0.04	0.019
18	0.35	0.003	0.73	0.0015	0.72	0.057	7.93	0.033	3.36	0.015	0.46	0.009	83.63	0.059	0.07	0.034
19	0.02	0.002	8.62	0.0012	0.15	0.035	23.94	0.02	0.7	0.04	5.75	0.023	95.14	0.05	0.05	0.029
20	3.52	0.005	0.13	0.0026	1.07	0.025	2.36	0.015	4.98	0.031	0.61	0.018	85.57	0.035	0.04	0.02
21	0.04	0.005	12.39	0.0026	0.1	0.025	24.35	0.015	0.57	0.071	12.37	0.041	98.88	0.046	0.05	0.026
22	0.76	0.003	0.35	0.0015	0.23	0.025	11.1	0.015	1.09	0.045	4.15	0.026	97.04	0.07	0.07	0.041
23	1.48	0.003	0.17	0.0015	0.04	0.002	3.95	0.001	0.17	0.006	3.33	0.003	97.65	0.051	0.05	0.03
24	0.8	0.005	0.63	0.0029	2.37	0.06	2.54	0.035	11	0.095	0.86	0.055	68.93	0.072	0.1	0.042
25	0.04	0.004	9.05	0.0023	3.35	0.05	1.5	0.029	15.63	0.067	0.43	0.038	50.13	0.131	0.26	0.075
26	0.02	0.003	15.53	0.0018	0.07	0.006	9.22	0.004	0.33	0.015	4.68	0.009	94.38	0.09	0.1	0.052
27	0.46	0.003	0.66	0.0018	0.54	0.04	7.53	0.023	2.52	0.078	3.08	0.045	81.51	0.071	0.09	0.041
28	0.1	0.004	4.54	0.0025	0.09	0.025	29.04	0.015	0.4	0.061	15.15	0.035	77.67	0.155	0.2	0.09
29	0.05	0.004	7.37	0.002	0.15	0.042	27.15	0.024	0.7	0.021	2.99	0.012	85.74	0.04	0.05	0.023
30	0.05	0.003	5.69	0.0018	0.2	0.04	20.55	0.023	0.93	0.055	5.9	0.032	88.16	0.147	0.17	0.085
31	0.19	0.004	2.08	0.0023	2.61	0.025	0.96	0.015	12.2	0.025	0.21	0.015	70.92	0.046	0.06	0.026
32	0.27	0.003	1.11	0.0017	2.02	0.038	1.88	0.022	9.41	0.055	0.59	0.032	74.55	0.06	0.08	0.035
33	0.15	0.003	2.1	0.0018	0.63	0.035	5.6	0.02	2.93	0.035	1.2	0.02	85.45	0.04	0.05	0.023
34	0.2	0.004	1.79	0.002	2.32	0.035	1.51	0.02	10.82	0.076	0.7	0.044	71.42	0.035	0.05	0.02
35	0.03	0.002	6.79	0.0012	0.58	0.05	8.73	0.029	2.71	0.076	2.82	0.044	88.46	0.07	0.08	0.041
36	0.17	0.004	2.06	0.002	2.33	0.081	3.5	0.047	10.87	0.086	0.79	0.05	69.63	0.055	0.08	0.032
37	0.11	0.004	3.09	0.002	1.65	0.025	1.52	0.015	7.7	0.015	0.2	0.009	75.63	0.04	0.05	0.023
38	0.73	0.031	4.2	0.0176	2.37	0.051	2.17	0.03	11.05	0.075	0.68	0.044	72.71	0.038	0.05	0.022
39	0.15	0.004	2.65	0.0023	1.56	0.04	2.59	0.023	7.28	0.123	1.69	0.071	71.51	0.065	0.09	0.038
40	0.02	0.003	15.1	0.0015	0.02	0.003	17.63	0.002	0.08	0.003	3.35	0.002	96.81	0.045	0.05	0.026
41	0.03	0.004	13.73	0.0024	0.02	0.002	11.76	0.001	0.08	0.003	3.83	0.002	96.57	0.071	0.07	0.041
42	0.05	0.005	8.99	0.0026	0.22	0.031	14.1	0.018	1.03	0.081	7.93	0.047	92.44	0.181	0.2	0.105
43	0.04	0.004	8.04	0.002	1	0.035	3.5	0.02	4.66	0.085	1.83	0.049	82.84	0.17	0.21	0.098
44	0.03	0.007	25.04	0.0041	0.01	0.005	34.99	0.003	0.07	0.025	37.75	0.015	98.3	0.155	0.16	0.09
45	0.02	0.002	8.65	0.001	0.024	0.004	15.02	0.002	0.11	0.021	19.52	0.012	95.93	0.169	0.18	0.098

Table 15b: Quantitative analysis (% Average of 03 results) of samples by WDXRF.

in present application depends upon the background correction time and concentration of each element to be used for calibration line development (Table 13).

Verification of invented method by proficiency test results

The developed method has been also verified by the proficiency test method. The proficiency results (Table 14) showed that invented method is applicable and accurate for determination of CaF₂.

% Accuracy of carbon diluted standards

Series of standards were prepared after dilution of primary standard for carbon calibration line. This line was used for validation of other primary standards and unknown samples. The observed value and linear regression value ($R^2=0.999$) of plotted line of prepared standards show % accuracy of application.

Summary

1. After nearer look on the summarize outcomes of fluor spar measurements by XRF and classical methods obtained from

Classical method	Estimation Type	Estimated Duration (Hr)	Main Power	Current Method	Estimated Duration (Hr)	Main Power
MgO, CaO (total), CaO (soluble)	Titration	24 Hrs	04 Personnel	WD-XRF	10 mints	02 Personnel
SiO ₂	Gravimetric					
Fe ₂ O ₃ , Al ₂ O ₃ (R ₂ O ₃)	Gravimetric					
BaO	N.P			By Combustions	10 mints	
Carbon	No need					
CaF ₂	By calculation					

Table 16: Comparisons of classical and WD-XRF estimation method.

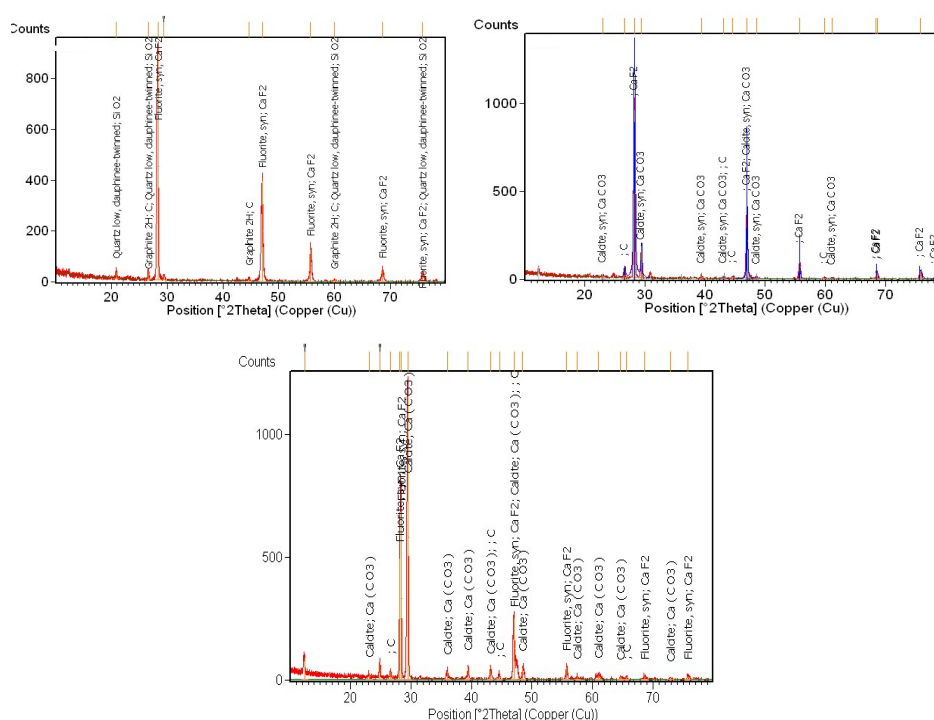


Figure 9: (9a-9c) The XRD patterns shows the fingerprints of CaF₂.

the following indicators (R, RSD, IDL, MDL, and LOQ) as shown in Table 12 and readability data, standard deviation and uncertainty of CRMs and samples. We can conclude that WD XRF is found the best constant readability with least uncertainty.

- The current chosen method for estimation of fluorspar is very rapid and simple than the classical method due to difficult, engagement of 02/03 personnel and time-consuming chemical method.
- The accuracy of the XRF method is depends upon the particle size, sample preparation and linearity of calibration curve.
- The XRF method is validated with the help of certified reference materials which covers all range of fluorspar and validated by number of statistical tools.

Conclusion

In current study, two analytical methods are used for the estimation of Fluorspar, Classical and WDXRF. WDXRF method will be highly smart and easy to use because the suggested analytical procedure required comparatively low-cost equipment, simple to operate, with a minimum

analysis of time and sample size. The instrumental approach pursued in this paper highlighted the importance of suitable sample preparation design to acquired accurate and reproducible results. For validation of XRF method, ISO/IEC 17025 protocol was followed. The drift effects in the optimized method had influenced the precision in long series of measurements. The precision involvement had been monitored using CRMs and verity of samples as shown in Table 12.

In sequence herewith, the development of such instrumental application was successfully guaranteed the principles of comparability and traceability which ensured high levels of analytical quality.

Based on the current method and confirmation the presence of CaCO₃ instead of other carbonates was proved by classical method, volatilization, XRD and ATR-FTIR methods. These findings tabulated and compared with classical method in Tables 15 and 16. In conventional method ASTM standard has no provision for the analysis of MgO, BaO, Al₂O₃ and Fe₂O₃ (in separate manner, ASTM report as R₂O₃). By using XRF method we can estimate major and minor constituents of CaF₂ without any interference. The XRD patterns and ATR results showed the presence of CaCO₃ instead of other alkali carbonates like MgCO₃, Br₂CO₃, Na₂CO₃, and K₂CO₃ etc. Trend analysis of CaF₂ and SiO₂. Figure 12 showed that both results were observed nearest to each

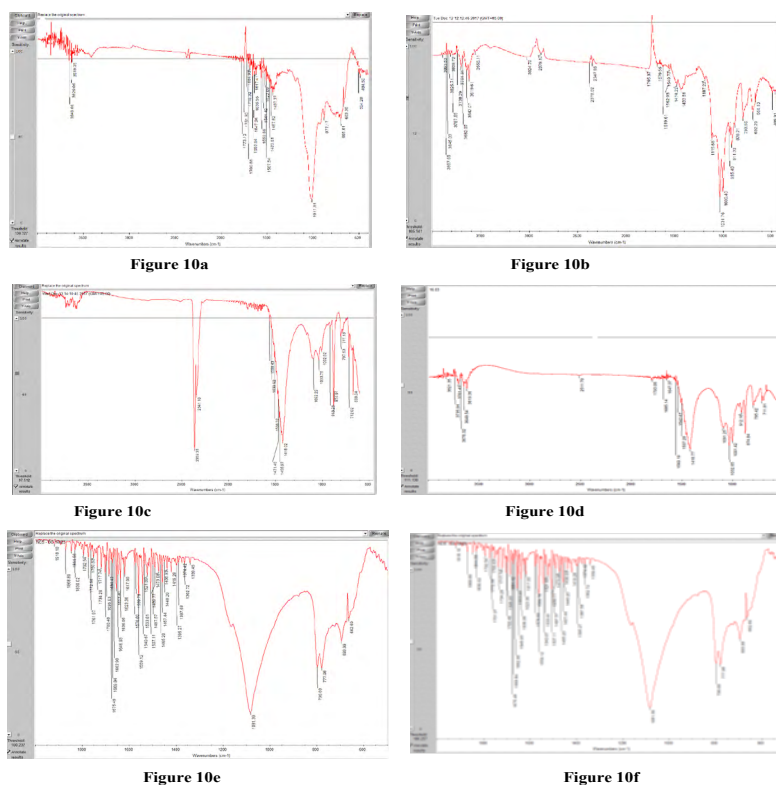


Figure 10: (10a-10f) Fingerprints of CaF_2 .

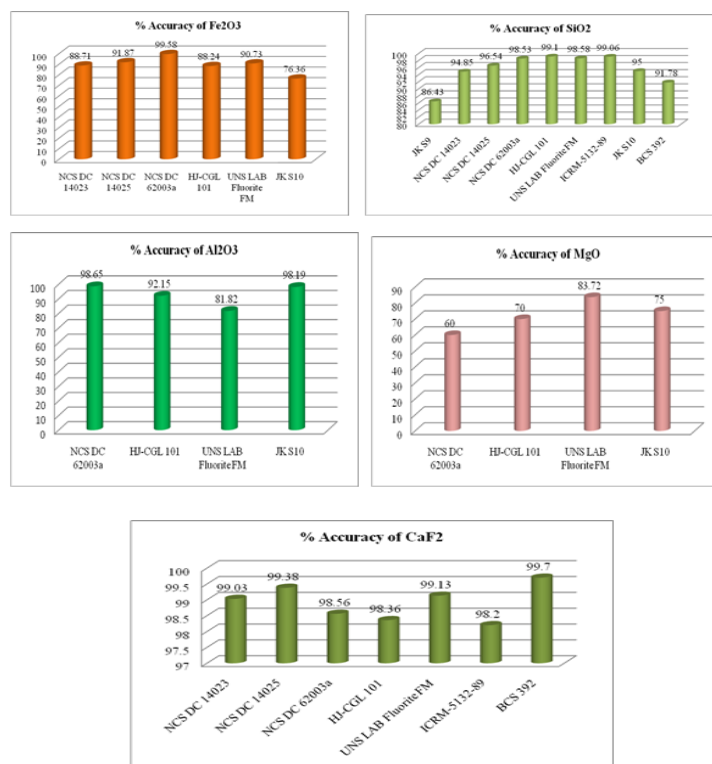


Figure 11: % Accuracy of different compounds with respect to different CRM values.

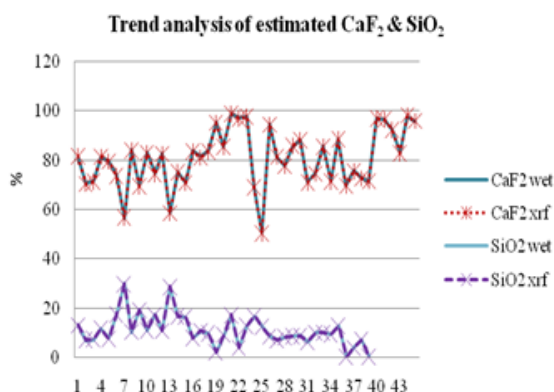


Figure 12: Trend analysis between conventional and WDXRF method of different compounds.

other, accurate and précised. Compatibility of both results showed that we can analyze any type of fluorspar by using invented method to save the human and environment hazards to the earth.

The loss of volatilization depends upon the molecular weight and order of reaction of the materials in case of carbonates the loss will be observed in such protocol, $\text{MgCO}_3 > \text{CaCO}_3 > \text{Na}_2\text{CO}_3 > \text{K}_2\text{CO}_3 > \text{SrCO}_3 > \text{BaCO}_3$ (if all type of carbonates will present in same compound). In current study maximum loss observed at 700 °C it confirmed the presence of CaCO_3 .

On the bases of above examinations, we can conclude that the invented WDXRF method has potential of precision, accuracy, sensitivity, reproducibility and linearity for the determination of CaF_2 and has no fatal impact on method in the presence of CaCO_3 instead of other carbonates because CaF_2 widely found as natural resources and have minimum chance for the presence of other carbonates in large quantity. However, the method is essay, ecological, beneficial, simplicity and could be used for estimation of any type and grade of CaF_2 .

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