

An Extensive Review for Recent Advancement in Fluorspar Test Method by WDXRF

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ABSTRACT

The current review paper illustrated the invention in estimation of Fluorspar method; it is commonly used for slag making in steel industry, glass manufacturing and high purity acid grade in nuclear process. In the last centuries significant research efforts have been done for the analysis of fluorspar on industrial basis but still CaF_2 has been analyzed by classical method and no quick method is available. Fluorspar mainly consists of SiO_2 , CaO , Al_2O_3 , BaO and CaF_2 . At present, we have developed X-ray fluorescence method and in current review we emphasize and compare the mineralogical contents of fluorspar estimated by conventional method and new advance method.

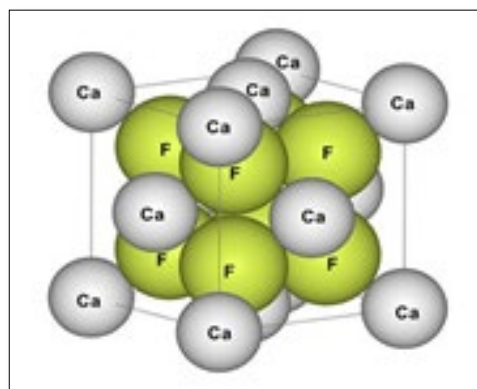
Keywords: CaF_2 , WDXRF method Conventional method, CS analyzer

INTRODUCTION

History and etymology

Fluorite is Latin word noun, fluo, means continuous with flow like water flow. In verb present as fluor or fluere, is stated as flow. The CaF_2 is utilized as flux in steel making process to increase the fluidity of slag or we can say decrease the viscosity. Calcium fluoride melts at 1676 K. The word flux extracted from Latin word noun fluxes. German scientist Agricola having expertise in philology, mining and metallurgy termed as fluorspar as Neo Latinization of the German Flussespar from Flusse (stream, river) and "Spar" (meaning a nonmetallic mineral akin to gypsum, spærstån, spear stone, belong to name crystalline (Picture 1) [1,2].

Fluorite is called as fluorspar is a halide consists of CaF_2 . Calcium fluoride is an isometric mineral with a cubic structure with octahedral and other complex isometric shapes are not occasional. CaF_2 is a colorful mineral having with visible ultraviolet light and it is used as ornamental and lapidary. Fluorite is commonly used in industry as a source of flux for smelting, glasses production and enamels. High quality CaF_2 grades are used a source of fluoride for HF acid manufacturing. It is also used source as intermediate fluorine containing fine chemicals. By using fluorite prepared low dispersion lenses for far ultraviolet region mostly used in microscope and telescopes.



Picture 1. Structure I [3].

Calcium fluoride inorganic compound consist of calcium and fluorine having formula CaF_2 and F-centrally coordinated with 04 Ca^{2+} centers [4]. Crystalline samples of CaF_2 are mostly colorless and some are deep color due to F-presence in center. The few crystal presence in numerous ionic compounds with CeO_2 , ZrO_2 , etc.

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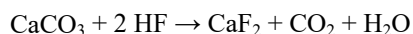
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Occurrence

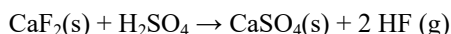
Fluorite is broadly presence mineral in huge deposits in much area. Significant occurrence areas in China, Germany, Austria, Switzerland, England, Norway, Mexico and both the Province of Ontario and Newfoundland and Labrador in Canada. Large deposits also occur in Kenya in the Kerio Valley area within the Great Rift Valley. In Pakistan, Fluorspar is majorly present in Loralai, etc.

APPLICATION, SOURCE OF FLUORINE AND FLUORIDE

High purity grade is manufactured by combination with calcium carbonate and hydrofluoric acid [5].



Fluorite is a main source of hydrogen fluoride [6]; it is commonly used for the production of wide range of materials. HF is evaluated from mineral by the reaction with concentrated sulfuric acid.



The produced HF is converted into fluoride, fluorocarbons and produced different materials. In 1990s annually production of CaF_2 is five billion kilogram. There are three main type of natural fluorspar used in industries. Metallurgical grade fluorite (60-85% CaF_2), Ceramic grade fluorite (85-95% CaF_2) and highest grade, "acid grade fluorite" (97% or more CaF_2), accounts for about 95%.

Metallurgical grade has been used traditional as flux; ceramic grade is used in the manufacturing of glass, enamels and cooking utensils. Acid grade used to make hydrogen fluoride and hydrofluoric acid and traditionally by reaction with fluorite with H_2SO_4 [7,8].

ESTIMATION OF FLUORSPAR BY DIFFERENT SCIENTIST

Calcium fluoride contents were determined by EDTA in iron tailings. The samples were prepared by diluted acetic acid to leach calcium carbonate. The contents of CaF_2 consist of two parts one fluoride contents were illustrated by zirconium xylenol orange by spectrometer after CaF_2 was filtered according to these values concentration of CaF_2 were calculated and other practice of CaF_2 by leaching as precipitating with leaching aluminum chloride solution for titration calcium indicator used as indicator EDTA standard titration solution was used to determine for precipitation of CaF_2 in KOH medium. Therefore CaF_2 contents were calculated by values. This illustrated method was simple, rapid, précised and recovery could meet the requirements in the CaF_2 determination the standard deviation was less than 1% and recovery 99-101% [9].

The invented method is for the quantitative determination of calcium fluoride by EDTA titration. Take 0.2-0.50 g sample material into beaker then added HCl and boric acid solution

heat and dissolved for 20-40 min filter sample and collecting filtrate wash precipitates present beaker cool and added water. If barium is present in sample <0.2 wt%, it is precipitating out taking out 10-20% filtrate in beaker with 80-100 ml water and used triethanolamine with KOH to maintained pH grater then 13 and titrate with EDTA standard solution in the presence of mixed indicator. In case of barium grater then >0.2 wt%, aliquot 10-20% of filtrate in beaker adding 40-50 ml introduce 2-5 drops sulfuric acid and boil 10-20 min and hold grater then 8 h and collect filtrate in another beaker washing the original beaker ppt and maintained filtrate volume 80-120 ml and add triethanolamine maintained pH by using KOH grater then 13, titrate with EDTA with mixed indicator.

In first step weight 0.20-0.30 g and 0.40-1.20 g samples material in two beakers then add HCl- H_2SO_4 solution hold at room temperature for 40-60 min and shake 3-50 min till ppt fully dispersed, 1-3 drop phenolphaline indicator and adding KOH the reddish color this process continue till HCL reddish color disappears, transfer solution in volumetric flask and fill with water and hold for 8 h then pipette out 30-50% and repeat same procedure after end of titration calculate non calcium fluoride calcium content in sample by using two volume difference and weight difference of sample materials. The mixed indicter is mixture of calcium, European Pharmacopoeia Reagent and potassium chloride. The invented method has precise and CaF_2 calculated values are authentication.

Fluorite powder directly analyzed by XRF after pressed pellet combination with spectroscopy, the total content of Ca and content of Fe_2O_3 , P, SiO_2 and K_2O as well as carbon present in sample analyzed by IR absorption spectrometer and carbon content calculated as CaCO_3 then CaF_2 calculated content in fluorite. For estimation of unknown samples the working curve was made using nine certified reference material the method is accurate and further verification an accuracy standard (GBW07254) was used to test accuracy and precision of method and found results satisfactory [10].

Analysis of fluorspar by traditional method after separating calcium carbonate and calcium fluoride it takes longer time and not suitable for production but accuracy of results from this method is very high. The publisher was illustrated two methods, alkali fusion and acid leaching method. The operation analyzing results of this method was very easy and short time for completion of analysis and observed that results were accurate and it could be used for quick analyzing before production.

The fluorite standards prepared in group and samples with binder formed in the form of pressed pellets method. These press pellets analyzed by x-ray fluorescence spectrometer and obtained liner regression line. Curves after deduction of enhanced absorption and spectral line overlap interference determine the content of pressed pellet by using curve and

calculate the fluorite by analysis of the corresponding relation of spectral line intensity and concentration. The standards samples and binder after sieving 300 mesh formed press pellet by using palletizer. This creative method is rapid and accurate and can reduce the estimation cost and enhance the detection limits. [11].

Other method for estimation of calcium fluorite as CaC_2 with diluted acetic acid. CaF_2 cannot dissolved in acetic acid therefore sample was treated with acetic acid and insoluble material filtered by filter paper then introduced potash solution till pH attain 13 or greater than 13. CaC_2 was determined by EDTA titration method. Insoluble filtered material and filter paper was burned in platinum crucible and added mixed flux with boric acid melt at 950°C than acidify and added potash solution till pH 13 or greater and analyze CaF_2 with EDTA titration. The RSD value of CaC_2 was 0.064 and 0.01916% and CaF_2 RSD value observed 0.6285 and 0.8357%.

Fluorspar contents like CaF_2 , SiO_2 , Al_2O_3 and total iron (TFe) are calculated by XRFS. The samples were prepared by 1 g of sample and fusion mixture KNO_3 (0.2 g), 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 of 3 drops of 150 g/L^{-1} LiBr solution, the mixture was fused at 1050° for 20 min. after cooling the 4 components were estimated. Samples present with reductive substance the fusion method should be modified. $\text{Li}_2\text{B}_4\text{O}_7$ put in the platinum crucible after melting coated on inner wall of crucible at lower and bottom side. After cooling, KNO_3 and Li_2CO_3 added to the crucible and peroxide at low temperature and fused sample as same procedure. The melt sample was used for detection of 4 components. Working curve prepared and used for estimation of results. Four samples were analyzed by said method and giving results has consistency with results [12].

Review on new published paper “Quantification of Metallurgical Flux by Wavelength Dispersive X-ray Fluorescence” this advance test method was developed for the quantification of fluorspar (CaF_2) along with other present ingredients especially trace elements like Ba, Sr, P and Mg. All above reported abstract showed that few methods are invented in which analysis of fluorspar has carried out partially and did not emphasize on complete chemistry of fluorspar. It can only analyze Si, P, K, Na and other elements Ca soluble and total were analyzed by classical methods.

The current established method can analyze necessary elements by WDXEF and carbon was analyzed by carbon sulphur analyzer as well as presence of CO_2 as CaCO_3 was confirmed by using ATR-FTIR and XRD method.

EXPERIMENTAL

Estimation of minerals XRF

WD-XRF- Philips Axios Max, 3KW Rhodium tube as X-ray generator along with crystals, channels and collimator mask was used for creation of application and analyze standards and unknown samples. Carbon was analyzed by CS-800 (Eltra) analyzer [12].

STANDARDS AND CALIBRATION

Initially calibration lines of SiO_2 , Ca, P, SrO, BaO, Fe_2O_3 were developed in WDXRF with known chemical composition of primary standards as well as synthetic standards and same standards except synthetic standards were utilized for carbon development calibration line in CS-800 analyzer. The following primary standards were used for calibration of lines 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 as well as utilized 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) for synthetic standards (**Table 1**).

SAMPLES OCCURRENCE AND COMPOSITION

40 samples were collected by random sampling from different locations of Pakistan Jurassic Loralai limestone of Gadebar, Daman Ghar, tor Thana, Wategam, Mekhtar, Balao, Mahiwal areas of Loralai District. 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 (**Picture 2**). 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.



Picture 2. Collected from Pakistan vicinity [13].

Table 1. Estimated and certified reference standard values (% average of 03 results) by WD-XRF [13].

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)

JK S9 and JK S10 were used for estimation of SiO₂, Al₂O₃ and Fe₂O₃

* 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

N.R: Not Reported; Certified Reported Value in (-----)

Homogeneity of samples through grinding method, grinding time, mesh size, pelletized force binder type and ratio. After said process samples passed through 150 μm and oven dry at 105°C for 24 h and observed lose 0.001-0.10%.

CARBONATES CONFIRMATION BY VOLATILIZATION, ATR-FTIR AND XRD PROCEDURE

CaF₂ mineralogy having major compound of CaCO₃ with respect to other carbonates. This was confirmed by

volatilization method at different temperatures. The decomposition temperatures showed that calcium carbonate is present as main constituent as well as presence of CaCO₃ was confirmed by Thermo Nicolet iS5 FTIR (**Figure 1**) with ZnSe (refractive index 2.67) [14-19]. Mineralogy of compounds was determined by Expert Pro XRD instrument which confirmed (**Figure 2**) the presence of CaCO₃ instead of other compounds [20]. Carbon analyzed for estimation Ca by mathematical calculation by IR method (**Figure 3**).

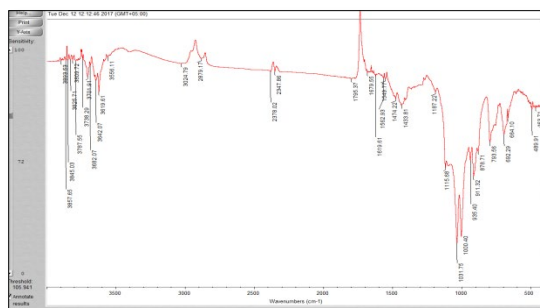


Figure 1. FTIR fingerprints shows presence of CaCO₃ [13].

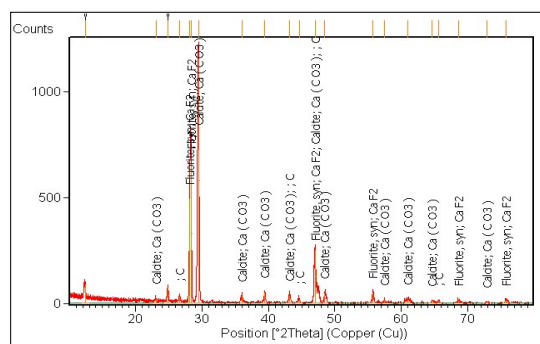


Figure 2. XRD pattern presence of CaCO₃ [13].

RESULTS AND DISCUSSION

Why pressed sample instead of bead sample?

The published application was particularly designed for all type of fluorspar in pressed pellet samples. Fluorine has low molecular weight and decomposes during 825°C-1330°C [21].

Hence due to this possible loss of fluorine may occur during calcinations. So, it is ineffective to estimate by fused bead sample.

Mineralogy by XRD

Fluorspar samples mineralogy were identified by XRD patterns and illustrated the presence of alkaline earth carbonate as CaCO₃ and CaF₂.

FTIR illustrations

The characterized FTIR confirmed the presence of CaCO₃ in fluorspar. The presence of infrared spectrum of the CaCO group stretching of carbonates on 713, 875 and 1418-1473

cm⁻¹ it shows the absorption bands of CaCO₃ (Calcite) [22,23].

Analysis of carbon and CaF₂ calculation

Total carbon in certified reference material were used for calibration after analysis by combustion method and observed regression factor R²=0.999 which shows the linearity of calibration line. Theoretical carbon value was used for calculation of CaCO₃ present in standards samples the accuracy of carbon direct related to CaF₂.

The following conversion factors used during development of application:

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

Apply factors during application development

- i- C to CaO=4.665; ii- CaO to Ca=0.715; iii- Ca to CaF₂=1.95

Significant impact on method

The published application quantify the concentration as total carbonates in the presence of other carbonates such as Mg, Na and Ba, etc., instead of CaCO_3 , the developed method has limitation to distinguish/separate the carbonates attached with alkali and alkaline earth metals other than CaCO_3 and it cause significant impact on method. The analysis by different techniques shows that natural fluorspar has major contents of CaCO_3 with respect to other carbonates. Therefore on the bases of several analytical observations the developed application has no significant impact in the presence of other carbonates in minor quantity on estimation of CaF_2 .

Specificity of invention

The invented method has less background corrections, line overlaps and measuring time with respect to other developed methods and classical estimations. The primary and in-house established standards have no interference to each other. The complete analysis time for standard and sample was just 340 s.

Method validation

The current invented method has been verified by method validation before implementation in industry. For validation different statistical tools such as standard deviation, recovery (R, %), relative percent difference (RPD, Eq. (1)), instrument detection limit (IDL), limit of quantization (LOQ), method detection limit (MDL) and uncertainty (U_a), were used. The same method was verified by classical method and observed that both values were approximately same.

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

Accuracy of fluorspar values

Accuracy of the CaO and CaF_2 directly related to estimation of carbon observed values and values used in calibration of carbon line (**Figure 3**). The accuracy of CaF_2 primary certified standards results is illustrated in terms of bar chart (**Figure 4**).

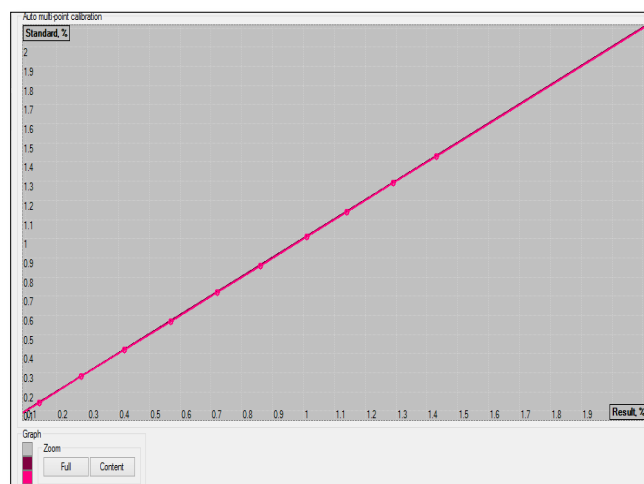


Figure 3. Carbon calibration curve [13].

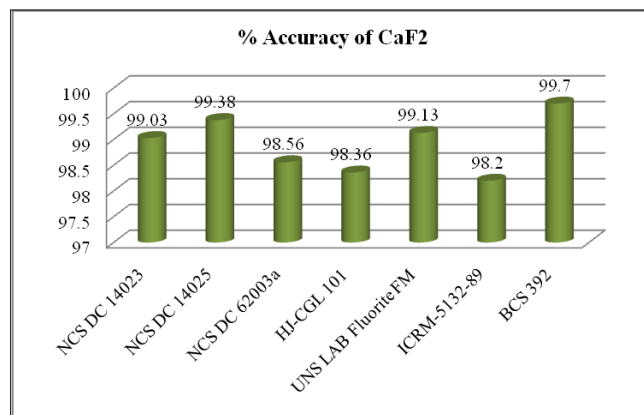


Figure 4. % accuracy of CaF_2 [13].

Method validation and proficiency test results

This commercial method has also verified by the proficiency test method. The proficiency results (Table 2) shows that

invented method is used as commercial for all type of fluoride grades and accurate for determination of CaF₂.

Table 2. Proficiency and invented method test result [13].

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

Novelty of work

How we can say the published work is novel as compare to classical and other published methods? On the basis of significant of current work with respect to non-hazardous, time saving, customer beneficial, industrial application and less error observed values of standards and samples with related classical method and minimum z-score and statistically significant Accuracy and precision of the results obtained through invented method was more consistent as compared to other method due to less human influence.

CONCLUSION

This paper "Quantification of metallurgical flux by wavelength dispersive x-ray fluorescence" was selected as a review of the method advancement in the field of inorganic chemistry.

Before said method the CaF₂ was estimated by classical method as described in American standard testing method (ASTM-E1506) and some other methods have developed for estimation of fluoride by combination with classical and instrumental techniques but still not used in industry.

The published method is advanced methodology for the determination of fluoride by instrumental technique. It is the first step towards the novel development in short term technique, improved performance and less hazardous with respect to classical method. Finally by taking an overview of the current technique it is strong support to analyst with confidence and opportunity towards the new approach in the field of chemistry. At present we have further modify the published method and can analyze complete estimation with WDXRF without using carbon analyzer.

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REFERENCES

- Douglas H. "fluorite". Online etymology dictionary. Available at: <https://www.etymonline.com/word/fluor>
- Douglas H. "spar". Online etymology dictionary. Available at: <https://www.etymonline.com/word/spar>
- Hurlbut CS, Klein C (1985) Manual of Mineralogy (after James D Dana)/Cornelis Klein, Cornelius S Hurlbut Jr. 20th Edn, pp: 324-325. ISBN 0-471-80580-7. Available at: <https://trove.nla.gov.au/work/8455391>
- Miessler GL, Tarr DA (2003) Inorganic Chemistry. 3rd Edn. Pearson/Prentice Hall Publisher. Available at: <https://www.amazon.ca/Inorganic-Chemistry-5th-Gary-Miessler/dp/0321811054>
- Aigueperse J, Mollard P, Devilliers D, Chemla M, Faron R, et al. (2000) Fluorine Compounds, Inorganic. Wiley Online Library. Available at: https://onlinelibrary.wiley.com/doi/full/10.1002/14356007.a11_307
- Aigueperse J, Mollard P, Devilliers D, Chemla M, Faron R, et al. (2005). Fluorine Compounds, Inorganic. Ullmann's Encyclopedia of Industrial Chemistry. Weinheim: Wiley-VCH.
- Wiberg E, Wiberg N, Holleman AF (2001) Inorganic Chemistry. Academic Press: San Diego. Available at: <https://www.worldcat.org/title/inorganic-chemistry/oclc/48056955>
- Michael MM (2009) Fluorspar. USGS Minerals Yearbook. Available at: <https://minerals.usgs.gov/minerals/pubs/commodity/fluorspar/myb1-2009-fluor.pdf>
- Yang C, Chaoyan C (2016) Determination of CaF₂ in iron ore tailings by EDTA complexometric titration. Chinese Journal of Inorganic Analytical Chemistry 6: 20-24.
- Xian Y (2014) Analysis of component in fluorite using pressed powder pellet x-ray fluorescence spectrometry combined with infrared spectroscopy. China Inorganic Analytical Chemistry 4: 50-52.
- Ma A, Feng S (2012) Method of measuring component contents in fluorite by applying X fluorescence powder tablet pressing method. Faming Zhuanli Shenqing CN 102809578.
- Li S, Du C, Zhang H (2011) Determination of TFe, SiO₂, P, CaO, MgO in sponge iron by x-ray

- fluorescence spectrometry. *Lihua Jianyan Huaxue Fence* 47: 1162-1164.
13. Akhter N, Mumtaz M, Hussain SS (2018) Quantification of metallurgical flux by wavelength dispersive x-ray fluorescence. *Chem Sci J* 9: 1-17.
 14. Nishikawa M, Batdorj D, Ukachi M, Onishi K, Nagano K, et al. (2013) Preparation and chemical characterisation of an Asian mineral dust certified reference material. *Anal Methods* 5: 4088-4095.
 15. Maitra S, Chakrabarty N, Pramanik J (2008) Decomposition kinetics of alkaline earth carbonates by integral approximation method. *Ceramica* 54: 268-272.
 16. Valverde JM, Perejon A, Medinac S, Perez-Maquedad LA (2015) Thermal decomposition of dolomite under CO₂: Insights from TGA and in situ XRD analysis. *Phys Chem Chem Phys* 17: 30162-30176.
 17. Mazzeo R, Joseph E, Prati S, Millemaggi A (2007) Attenuated total reflection Fourier transform infrared microspectroscopic mapping for the characterization of paint cross sections. *Analytica Chimica Acta* 599: 107-117.
 18. Zhang WR, Lowe C, Smith R (2009) Depth profiling of coil coating using step-scan photoacoustic FTIR. *Progress in Organic Coatings* 65: 469-476.
 19. Stuart (2004) *Infrared Spectroscopy: Fundamentals and Applications B*. John Wiley & Sons, Ltd ISBNs: 0-470-85427-8 (HB); 0-470-85428-6 (PB).
 20. Pandey GC, Kulshreshtha AK (1993) Fourier transform infrared spectroscopy as a quality control tool. *Process Control and Quality* 4: 109-123.
 21. Schmidbaur H (1985) Greenwood VNN, Chemistry of the Elements. Von N. N. Greenwood und A. Earnshaw. Pergamon Press, Oxford 1984, 1542 S., geb. \$ 95.00. - ISBN 0-08-022056-8; Paperback \$34.95: - ISBN 0-08-022057-6. Wiley Online Library.
 22. Meejoo S, Maneeprakorn W, Winotai P (2006) Phase and thermal stability of nanocrystalline hydroxyapatite prepared via microwave heating. *Thermochimica Acta* 447: 115-120.
 23. Ratner B, Hoffman A, Schoen F (2004) *An Introduction to Materials in Medicine*. In: *Biomaterials Science*. 2nd Edn. Academic Press, p: 851.