Determination of Major, Minor and Trace Metallic Constituents in Sillimanite: Comparative Evaluation of EDXRF and D. C. Arc Carrier Distillation AES

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ABSTRACT: An attempt was made to determine the major, minor and trace levels of common metallic constituents in sillimanite minerals. Direct current arc atomic emission spectrometry (D. C. Arc AES) and energy dispersive X-ray fluorescence spectrometry (EDXRF) were used for the comparative evaluation. Al and Si were found to be present as major matrix elements, whereas Na, Pb, Tb, Mn, V, Ti, Ca, Mo, Ba, Y, Ni and Nb were present in the range of 20-900 $\mu\text{g g}^{-1}$. The methodologies were developed by using standards made with a mixture of SiO_2 and Al_2O_3 in (1:1) concentration. Multipoint standardization was carried out to establish the calibration curves for each analyte. The methodologies were validated using synthetic samples. The statistical t-test was performed in order to understand the reliability of the data obtained by EDXRF and D. C. Arc AES with a 95 % confidence limit and 8 degrees of freedom. The F-test was also performed to understand the variance of the measurements.

INTRODUCTION

Sillimanite is a polymorph of aluminosilicate metamorphosed sedimentary rock, having a bipyramidal orthorhombic crystal structure.¹⁻³ The chains of Al-O octahedra along the z-axis linked sideways by chains of alternating Si-O tetrahedra are the main features of the sillimanite crystal. Due to the ability of the refractory mullite phase blended with the characteristics of high strength and resistance towards drastic physical and chemical stress even at high temperature, more than 90% of this mineral is being used in the manufacture of non-basic high alumina refractories, metals, glass, ceramics and cements.⁴⁻⁶ In the critical areas of the furnace, for steel degassing chambers, soaking pits, auxiliary pouring, and equipment used in the iron and steel industries these are the main consumers of sillimanite. Apart from refractory applications, the calcinated mineral is widely used in the fabrication of high-tension insulators, electrical ceramics, ceramic

tile, honeycombs, high-temperature insulation, glass melt additives, and production of aluminium oxides, Si-Al alloys, and metallic fibers.⁷⁻¹⁰ However, this variety of application and the high temperature physical, chemical and mechanical properties of sillimanite are highly influenced by the quality of the minerals, i.e., the presence of other elements, which also depends on the origin of the mineral.^{11,12}

Tripathi *et al.* have investigated how the additive TiO_2 can modify the mechanical properties of sillimanite by densification affecting the high temperature flexural strength of the aggregates.¹³ Gill *et al.* developed the Adaptive Neuro-Fuzzy Inference System-based simulation for understanding the material removal rate using stationary ultrasonic drilling by sillimanite-based ceramics.¹⁴ Tripathi *et al.* have also reported that ZrO_2 additives on sillimanite improved the resistance characteristics for the thermal shock of the material.¹⁵ Goergen *et al.* investigated the

rheological characteristics and deformation-induced polymorphic transformation in sillimanite.¹⁶ The mineral was reported to have a wide range of applications and many studies have been published on the physical, thermal, mechanical, and phase change as well as other characterizations of this mineral.

However, not much has been reported on its elemental characterization. Venkateswarulu *et al.* used proton-induced X-ray emission for trace level determination of coastal sand, including sillimanite, which was found to contain more than 20 analytes, including Sc, Zr, Ga, Br, Mo, Nb, Ce, La, and Dy.¹⁷ Pophare and Umathay reported the geochemical characterization of lithologies to understand the history of tectonic evolution, chemical homogeneity / heterogeneity in the light of major, minor, trace and rare earth element chemistry.¹⁸ A combination of inductively coupled plasma atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry (AAS) has also been reported to be useful for the determination of analytes in mineral samples, such as Al, Ca, Mg, Cr, V, Si, Fe and Ti.¹⁹ A combination of neutron activation analysis and ICP-AES was used for the elemental characterization of serpentine of Indian origin, which also has high potential for nuclear shielding material.²⁰ Sometimes, major, minor and trace constituents might have a detrimental influence on the quality of the mineral and hence, its application. For elemental characterization, a simple, rapid, multi-elemental, non-destructive, requirement of a small sample size, precise and reliable analytical technique is required. Ideally, it is exceedingly difficult to have all of these favorable characteristics in a single analytical technique. Moreover, a reference material available for the reliable characterization of the mineral is often not available.²¹

In view of these limitations, a combination of two distinct multi-elemental analytical techniques has been used for the determination of the metallic constituents in sillimanite at major, minor and trace levels. EDXRF, being rapid and non-destructive in nature, is capable of the estimation of major and minor levels of the constituents.²²⁻²⁶ However, this technique is totally incapable of trace level determination and of the determination of analytes having low Z values (B, Be, Li, *etc.*). On the contrary, D. C. Arc carrier distillation AES is the work horse for the determination of minor and trace level metallic constituents in powder samples used in a variety of industries, including the nuclear industry, where the trace level determination of impurities is very critical.²⁶⁻²⁹ However, this analytical technique is not suitable for major elements, is destructive in nature and associated with poor precision. Moreover, a plasma-based AES technique requires dissolution of the sample into a homogeneous solution, which is indeed difficult for geological samples.^{30,31} So, a combination of analytical techniques not only covers a wide range of analytes, but also gives the confidence in the values obtained by both techniques.³²⁻³⁴ A statistical evaluation is mandatory to demonstrate the reliability and precision of the analyses; therefore, the statistical 't-test' and 'F-test' were performed.^{35,36}

EXPERIMENTAL

Materials. Multielemental standard solutions and individual Specpure solutions of the analytes were used in the present investigation (E-Merck, Germany). High purity Al₂O₃ and SiO₂ powder was procured from Sigma Aldrich (USA) and AgCl from SPEX Industries (USA).

Instrumentation. The EDXRF spectrometric investigation was carried out using the Jordan Valley EX3600M spectrometer. The instrument has a stabilized X-ray tube and Rh as the X-ray source. The X-ray irradiation was carried out in normal air atmosphere and at room temperature. The Si (Li) detector, coupled with a multichannel analyzer, was used as the detection system.³⁷ The maximum resolution of the instrument can be quoted as 0.139 keV at Mn-K α (5.9 keV). Prior to analysis, the samples and standards were ground well to make a completely homogeneous powder with a large surface area. An amount of 500 mg of the powder were put on a Teflon sample holder assembly. The EDXRF instrumental parameters were optimized for the present investigation and are summarized in Table 1.

D.C. Arc carrier distillation AES. Direct current arc carrier distillation atomic emission spectrometry was carried out using a D.C. Arc AES (Arcos FHS12 ICP-AES) instrument procured from Spectro Arcos, Germany.^{38, 39} The instrument has a dual excitation source in the form of D.C. Arc and inductively coupled plasma (ICP). The array of the charge coupled device (CCD) is used as the detection system. The sample introduction assembly, cup type anode, made of high purity graphite with ASTM designation E-130-66 type S-2, was used along with the cylindrical cathode having one sharp side and a cylindrical pedestal, all made of high purity graphite.⁴⁰ Table 1 summarizes the instrumental parameters used in the present case.

Table 1. The Optimized Experimental Parameters for EDXRF and D. C. Arc AES Instruments

Parameter	Value
EDXRF	
Station no.	12-Cu
Filter	4-Fe
Emission current, μ A	100
High voltage, kV	17
Present time, s	100
Atmosphere	Air
Energy, keV	40
Throughput	High
Colorimeter	None
D. C. Arc AES	
Optical Mounting	Paschen-Runge
Type of grating	Holographic
Density of grooves in dispersion element, /mm	1800
Wavelength range, nm	130-800
Resolution (FWHM) of the spectrometer	0.01 nm from 130-450 nm 0.02 nm from 450-800 nm
Thermal isolation	30 $\pm$ 1°C
Detector	CCD with linear array of 3684 pixels in each single array

Analytes	Detection limit ($\mu\text{g g}^{-1}$)		Sensitivity (counts/ $\mu\text{g g}^{-1}$)		Precision (% RSD)		Regression coefficient (χ^2)	
	EDXRF	D. C. Arc AES	EDXRF	D. C. Arc AES	EDXRF	D. C. Arc AES	EDXRF	D. C. Arc AES
Na	30	5	28	41	8.2	18	0.9987	0.9991
Pb	45	10	23	37	6.3	16	0.9976	0.9935
Tb	50	10	20	37	5.1	20	0.9996	0.9966
Mn	25	5	31	40	4.9	17	0.9951	0.9985
V	40	20	24	31	5.2	19	0.9932	0.9997
Ti	45	20	21	30	6.6	20	0.9996	0.9948
Ca	35	5	22	43	5.9	18	0.9937	0.9985
Ba	50	10	19	39	6.7	14	0.9991	0.9993
Mo	50	40	18	32	7.4	16	0.9960	0.9921
Y	50	40	19	35	7.3	15	0.9999	0.9928
Ni	40	5	22	44	5.9	19	0.9966	0.9948
Nb	40	10	21	38	6.3	20	0.9934	0.9998
Zn	40	5	20	45	5.9	18	0.9901	0.9996
Eu	30	80	30	40	7.7	19	0.9908	0.9930
Al	35	5	24	43	4.9	18	0.9956	0.9922
Si	40	20	20	35	5.5	17	0.9914	0.9987

In case of EDXRF, the powder was put into the Teflon sample chamber, which had a transparent mylar bottom window. A schematic of the sample introduction system is shown in Fig. 1(b).

Method optimization and validation. Table 2 shows a comparative evaluation of the analytical performance. For D. C. Arc AES, the following lines were chosen: Na 588.9 nm, Pb 283.3 nm, Tb 321.890 nm, Mn 257.6 nm, V 318.5 nm, Ti 498.1 nm.

Ca 396.8 nm, Ba 455.404 nm, Mo 202.0 nm, Y 371.029 nm, Ni 305.0 nm, Nb 210.943 nm, Zn 213.5 nm, Eu 393.048 nm, Al 308.2 nm, and Si 288.1 nm. Similarly, for EDXRF, the following analytical lines were chosen: Na 1.041 keV, Pb 10.549 keV, Tb 6.273 keV, Mn 5.899 keV, V 4.952 keV, Ti 4.510 keV, Ca 3.690 keV, Ba 4.466 keV, Mo 17.478 keV, Y 1.924 keV, Ni 7.477 keV, Nb 2.169 keV, Zn 8.367 keV, Eu 5.849 keV, Al 1.487 keV and Si 1.740 keV. In EDXRF, the detection limits (DL) for Mn were found to be lowest among all of the analytes and was equal to 25 $\mu\text{g g}^{-1}$, while for Na and Eu it was 30 $\mu\text{g g}^{-1}$; for Ca and Al it was 35 $\mu\text{g g}^{-1}$; for V, Nb, Si, Zn, and Ni it was 40 $\mu\text{g g}^{-1}$; for Pb and Ti it was 45 $\mu\text{g g}^{-1}$; and for Tb, Ba, Y, the DL was found to be the highest at 50 $\mu\text{g g}^{-1}$.

However, in case of D. C. Arc AES, the detection limit was much lower than that obtained by EDXRF. For Na, Mn, Ca, Ni and Zn, the DL was at 5 $\mu\text{g g}^{-1}$; for Pb, Tb, Ba, Nb at 10 $\mu\text{g g}^{-1}$; for V, Ti, Si at 20 $\mu\text{g g}^{-1}$; and for Mo, Y at 40 $\mu\text{g g}^{-1}$. For Eu, the DL was at 80 $\mu\text{g g}^{-1}$. In case of D. C. Arc AES and due to the formation of the highly refractory oxides by Eu, V, Ti, Mo, Y and Si, their volatility to reach the arc was very poor and hence, their DL was also poorer compared to the other analytes in the matrix. The DL for Si was calculated in the Al_2O_3 matrix only, while for Al it was calculated in the SiO_2 matrix.

The standard deviation values were calculated based on 10 replicate measurements using Equation (1) as follows:

$$s = \sqrt{\sum_n \frac{(x_i - \langle x \rangle)^2}{n-1}} \quad \text{Eq. (1)}$$

where s is the standard deviation, x_i is each replicate value, $\langle x \rangle$ is the average of 10 replicate measurements, and $n-1$ is the degree of freedom.

The relative standard deviation was calculated in Equation (2) as follows:

$$\% \text{RSD} = \frac{s}{\langle x \rangle} \times 100 \% \quad \text{Eq. (2)}$$

Since 's' was a function of $\langle x \rangle$, therefore, to avoid such contribution, the precision values were expressed as % RSD. The RSD for all of the analytes in EDXRF were found to be less than 10%, while for D. C. Arc it was in the range of 15-20%. The major issue for the poor precision was reported to be due to arc wandering.

For EDXRF, the linear dynamic range (LDR) for Na, Mn, Ca, Ba, Ni, and Al was found to be in the range between their DL and 10,000 $\mu\text{g g}^{-1}$. For Si and Al, it varied from their DL up to 40%. Beyond that, the calibration curves were found to deviate from linearity. For the rest of the analytes, the LDR varied from their DL to 5000 $\mu\text{g g}^{-1}$. However, for D. C. Arc AES, the calibration curves were found to be sigmoid in nature and hence, log intensity vs. log analyte concentration was used in order to achieve the LDR. Na, Mn, Ca, Ni, Pb, Tb, Ba, Nb, and Zn were found to have LDR from their DL to 500 $\mu\text{g g}^{-1}$; whereas for V, Ti, Si, Mo, Y, and Eu, the LDR varied from their DL to 800 $\mu\text{g g}^{-1}$.

Table 3 summarizes the validation of the developed analytical methodologies using synthetic samples. In synthetic sample 1, on the matrix $\text{SiO}_2\text{-Al}_2\text{O}_3$ (1:1) mixture, aliquots of multi-elemental aqueous standards were added in such a way, so that the final concentration in the powder samples would be 100 $\mu\text{g g}^{-1}$, while for the synthetic sample 2 it was 200 $\mu\text{g g}^{-1}$. In case of Mo, Y, V, Ti, etc., their corresponding metal oxides are highly refractory in nature; hence, they have a poorer DL. The estimations of most of the analytes were within the acceptable limits, and the data obtained by both techniques were also comparable. The mean of the replicate measurements in both sides was found to fall within the expected mean (added values). This observation apparently indicates that there is no determinate error/bias during replicate measurements. The observed ranges are due to random error. The confidence intervals for D. C. Arc AES were found to be wider in comparison to EDXRF.

Table 3. Analysis of Synthetic Samples Prepared by $\text{Al}_2\text{O}_3\text{-SiO}_2$ in 1:1 Ratio as Matrix

Analytes	Synthetic sample 1			Synthetic sample 2		
	As prepared	EDXRF	D. C. Arc AES	As prepared	EDXRF	D. C. Arc AES
Na	100	94±6	85±15	200	185±18	220±30
Pb	100	103±8	110±20	200	190±15	218±35
Tb	100	97±8	98±15	200	211±18	180±30
Mn	100	96±9	111±18	200	215±20	175±34
V	100	108±9	92±16	200	188±16	230±40
Ti	100	99±8	96±17	200	190±15	215±35
Ca	100	104±8	100±18	200	193±18	170±35
Ba	100	97±8	93±15	200	209±15	190±30
Mo	100	105±9	104±18	200	201±16	205±35
Y	100	100±10	90±17	200	185±17	210±30
Ni	100	101±8	99±17	200	190±18	225±35
Nb	100	98±9	109±15	200	196±18	172±33
Zn	100	108±7	102±15	200	190±15	220±35
Eu	100	95±8	110±20	200	205±19	180±35

Table 4. A Comparative Characterization of Sillimanite by EDXRF and D. C. Arc AES

Analytes	EDXRF ($\mu\text{g g}^{-1}$)	D. C. Arc AES ($\mu\text{g g}^{-1}$)	ICP-AES ($\mu\text{g g}^{-1}$)
Na	60 $\pm$ 3	50 $\pm$ 9	54 $\pm$ 3
Pb	780 $\pm$ 30	850 $\pm$ 120	600 $\pm$ 30
Tb	450 $\pm$ 20	370 $\pm$ 70	400 $\pm$ 20
Mn	400 $\pm$ 20	330 $\pm$ 60	380 $\pm$ 20
V	260 $\pm$ 15	250 $\pm$ 40	260 $\pm$ 10
Ti	500 $\pm$ 30	600 $\pm$ 90	540 $\pm$ 20
Ca	320 $\pm$ 15	280 $\pm$ 50	290 $\pm$ 20
Ba	170 $\pm$ 10	200 $\pm$ 40	180 $\pm$ 10
Mo	73 $\pm$ 5	65 $\pm$ 10	68 $\pm$ 4
Y	50 $\pm$ 5	50 $\pm$ 8	48 $\pm$ 3
Ni	50 $\pm$ 4	52 $\pm$ 4	50 $\pm$ 3
Nb	50 $\pm$ 7	50 $\pm$ 4	51 $\pm$ 3
Zn	BDL	10.0 $\pm$ 0.9	9.9 $\pm$ 0.4
Eu	30 $\pm$ 2	BDL	27 $\pm$ 1
Al	29%	22%	26%
Si	14%	12%	13.5%

Analysis of actual sample. Table 4 summarizes the analytical results for sillimanite. The elements Na, Pb, Tb, Mn, V, Ti, Ca, Ba, Mo, Y, Ni and Nb as estimated by both techniques were found to be present at minor or trace level. Also, 5 $\mu\text{g g}^{-1}$ B (249.7 nm) and 8 $\mu\text{g g}^{-1}$ Be (234.4 nm) were detected by D. C. Arc AES, while they could not be detected by EDXRF. Even though both D. C. Arc and EDXRF were used to estimate Al and Si as major elements, negative bias is expected for D. C. Arc AES and hence, the EDXRF data (29 % Al and 14 % Si) were more reliable. A 10 $\mu\text{g g}^{-1}$ Zn (213.5 nm) was also estimated by D. C. Arc AES; however, it could not be detected by EDXRF as the detection limit was estimated as 40 $\mu\text{g g}^{-1}$ for Zn (K_{α}) by EDXRF. On the other hand, 30 $\mu\text{g g}^{-1}$ Eu was estimated by EDXRF using its L_{α} ; however, it could not be detected by D. C. Arc AES. This was attributed to the formation of the highly refractory oxide Eu_2O_3 , resulting in poorer DL for Eu (80 $\mu\text{g g}^{-1}$) by D. C. Arc AES. the elements Na, Mo, Y, Ni and Nb were found to be present in the concentration range of 45-80 $\mu\text{g g}^{-1}$; Ba, Ca, V, Mn, Tb were present in the concentration range of 150-450 $\mu\text{g g}^{-1}$; while Pb and Ti were found to be more than 500 $\mu\text{g g}^{-1}$. The results obtained by both techniques were in good agreement.

Statistical evaluation. The analytical results were subjected to statistical evaluation for their variation in terms of the Student's t test using Equation (3):

$$\mu = \langle x \rangle \pm \frac{s.t}{\sqrt{N}} \quad \text{Eq. (3)}$$

where μ is the theoretical mean, t is the t value.

Based on null hypothesis, there is no difference between the mean values obtained for each analyte in both techniques as shown with Equation (4):

$$H_0^{\text{null hypothesis}} = H_{D.C.Arc AES} = H_{EDXRF} \quad \text{Eq. (4)}$$

Alternatively, the mean values are different, i.e., as shown with Equation (5):

Fig. 2 Student t-test for the analysis of sillimanite samples for the metallic constituents by D. C. Arc AES and EDXRF technique.

Fig. 3 F-test for the analysis of sillimanite samples for the metallic constituents by D. C. Arc AES and EDXRF technique.

$$H_1^{\text{Alternative to null hypothesis}} = H_{D.C.Arc AES} \neq H_{EDXRF} \quad \text{Eq. (5)}$$

The 't' values were calculated with the degree of freedom 8 ($t_{expt}^{8,95\%}$) and with a 95 % confidence level (Fig. 2). Since $t_{expt}^{8,95\%} < t_{critical}^{8,95\%}$, the null hypothesis was found to be true. The variation in analytical results was within statistical variation and acceptable with 95 % confidence level.

Similarly, the F-test was also carried out at degrees of freedom 10 with a 95 % confidence level. In accordance with null hypothesis, Equation (6) shows:

$$S_{D.C.Arc AES}^2 = S_{EDXRF}^2 \quad \text{Eq. (6)}$$

where the terms correspond to the variance of the specific techniques.

The alternative hypotheses are shown in Equation (7) and (8):

$$S_{D.C.Arc AES}^2 \neq S_{EDXRF}^2 \quad \text{Eq. (7)}$$

$$F_{expt} = \frac{S_{D.C.Arc AES}^2}{S_{EDXRF}^2} \quad \text{Eq. (8)}$$

$F_{critical}$ was 2.98, while the experimentally determined F values were found to be well below the critical value (Fig. 3) and hence, the methods are precise.

Fig. 4 (a) shows the concentration ranges of the analytes present in different sillimanites, while Fig. 4 (b) depicts the same for the major elements of Al and Si. For Na, Mo, Y, Ni, and Pb, where the concentration range was found to be 50-60 $\mu\text{g g}^{-1}$; for Ba it was in the range 170-190 $\mu\text{g g}^{-1}$; for Ca and V it was 250-260 $\mu\text{g g}^{-1}$; for

Fig. 4 Concentration range of major, minor and trace elements present in sillimanite collected from the different regions.

Mn the variation was $350\text{--}390 \mu\text{g g}^{-1}$. In the case of Tb, Ti and Pb, the concentration range was $450\text{--}500 \mu\text{g g}^{-1}$, $510\text{--}590 \mu\text{g g}^{-1}$, and $750\text{--}880 \mu\text{g g}^{-1}$, respectively. The Al concentration was found to vary between 24–30%, while Si was found to vary within 12–18%.

CONCLUSIONS

Analytical methodologies were developed for the determination of major, minor and trace metallic constituents in sillimanite using the AES and XRF techniques. The $\text{Al}_2\text{O}_3\text{--SiO}_2$ (1:1) powder mixture was used to prepare the multipoint standards. The DLs were found to be poorer in case of EDXRF. For Eu and other analytes, which form highly refractory oxides, the DL was poorer with D. C. Arc AES. For Na, Mo, Y, Ni and Nb, the DLs were found to be in the concentration range from $45\text{--}80 \mu\text{g g}^{-1}$; for Ba, Ca, V, Mn, Tb in the concentration range from $150\text{--}450 \mu\text{g g}^{-1}$; Pb and Ti were found to be more than $500 \mu\text{g g}^{-1}$. The t_{critical} was found to be more than $t_{\text{experimental}}$, revealing the reliability of the data. The F-test revealed that the variance was within the allowed statistical limit.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- H. Yang, R. M. Hazen, L. W. Finger, C. T. Prewitt, and R. T. Downs, *Phys. Chem. Miner.*, 1997, **25**, 39–47. <https://doi.org/10.1007/s002690050084>
- M. T. Vaughan and D. J. Weidner, *Phys. Chem. Miner.*, 1978, **3**, 133–144. <https://doi.org/10.1007/BF00308117>
- D. R. Peacor, R. C. Rouse, and E. S. Grew, *Am. Mineral.*, 1999, **84**, 1152–1161. <https://doi.org/10.2138/am-1999-7-818>
- S. Kumar, S. K. Das, and P. K. Dasgopdar, *Ceram. Int.*, 2003, **29**, 139–144. [https://doi.org/10.1016/S0272-8842\(02\)00095-0](https://doi.org/10.1016/S0272-8842(02)00095-0)
- M. Vijay, P. V. Ananthapadmanabhan, K. Ramachandran, G. Hiremath, C. B. Mathai, B. Nalini, and B. C. Pillai, *Int. J. Refract. Met. H.*, 2013, **36**, 174–178. <https://doi.org/10.1016/j.ijrmhm.2012.08.012>
- A. Tomba, M. A. Camerucci, G. Urretavizcaya, A. L. Cavalieri, M. A. Sainz, and A. Caballero, *Ceram. Int.*, 1999, **25**, 245–252. [https://doi.org/10.1016/S0272-8842\(98\)00031-5](https://doi.org/10.1016/S0272-8842(98)00031-5)
- G. G. Lepezin, S. A. Kargopolov, and V. Yu. Zhirakovskii, *Russ. Geol. Geophys.*, 2010, **51**, 1247–1256. <https://doi.org/10.1016/j.rgg.2010.11.004>
- S. Sharma, T. Nanda, and O. P. Pandey, *Tribol. Int.*, 2018, **123**, 142–154. <https://doi.org/10.1016/j.triboint.2017.12.031>
- M. M. S. Al Bosta, K.-J. Ma, and H.-H. Chien, *Infrared Phys. Technol.*, 2013, **60**, 323–334. <https://doi.org/10.1016/j.infrared.2013.06.006>
- P. Kumar, M. Nath, A. Ghosh, and S. Tripathi, *Trans. Nonferrous Met. Soc. China*, 2016, **26**, 2397–2403. [https://doi.org/10.1016/S1003-6326\(16\)64329-7](https://doi.org/10.1016/S1003-6326(16)64329-7)
- B. L. Dutrow, C. T. Foster JR, and D. J. Henry, *Am. Mineral.*, 1999, **84**, 794–805. <https://doi.org/10.2138/am-1999-5-615>
- B. W. Evans and C. V. Guidotti, *Contrib. Mineral. Petrol.*, 1966, **12**, 25–62. <https://doi.org/10.1007/BF02651127>
- H. S. Tripathi and G. Banerjee, *J. Euro. Ceram. Soc.*, 1998, **18**, 2081–2087. [https://doi.org/10.1016/S0955-2219\(98\)00149-6](https://doi.org/10.1016/S0955-2219(98)00149-6)
- S. S. Gill and J. Singh, *Expert Syst. Appl.*, 2010, **37**, 5590–5598. <https://doi.org/10.1016/j.eswa.2010.02.054>
- H. S. Tripathi, S. K. Das, B. Mukherjee, A. Ghosh, and G. Banerjee, *Ceram. Int.*, 2001, **27**, 833–837. [https://doi.org/10.1016/S0272-8842\(01\)00037-2](https://doi.org/10.1016/S0272-8842(01)00037-2)
- E. T. Goergen, D. L. Whitney, M. E. Zimmerman, and T. Hiraga, *Tectonophysics*, 2008, **454**, 23–35. <https://doi.org/10.1016/j.tecto.2008.03.010>
- P. Venkateswarulu, C. Kasipathi, K. Srinivasa Rao,

- R. Venkateswara Rao, and T. R. Rautray, *Inst. Sci. Technol.*, 2013, **41**, 406-427. <https://doi.org/10.1080/10739149.2012.757739>
18. A. M. Pophare and R. M. Umathay, *Gond. Geol. Magz.*, 2009, **24**, 123-130. <https://doi.org/5542712cocf23ff716835d44>
19. R. Radhamani, P. Murugesan, A. Premadas, and P. K. Srivastava, *Talanta*, 2007, **71**, 1932-1938. <https://doi.org/10.1016/j.talanta.2006.08.031>
20. A. Sengupta, B. Rajeswari, R. M. Kadam, and R. J. Kshirsagar, *J. Radioanal. Nucl. Chem.*, 2012, **292**, 903-908. <https://doi.org/10.1007/s10967-011-1535-7>
21. J. E. Gagnon, B. J. Fryer, I. M. Samson, and A. E. Williams-Jones, *J. Anal. At. Spectrom.*, 2008, **23**, 1529-1537. <https://doi.org/10.1039/B801807N>
22. A. Mohapatra, T. R. Rautray, V. Vijayan, R. K. Mohanty, and S. K. Dey, *Aquaculture*, 2007, **270**, 552-558. <https://doi.org/10.1016/j.aquaculture.2007.04.023>
23. Z. L. L. Yeung, R. C. W. Kwok, and K. N. Yu, *Appl. Radiat. Isotopes*, 2003, **58**, 339-346. [https://doi.org/10.1016/S0969-8043\(02\)00351-2](https://doi.org/10.1016/S0969-8043(02)00351-2)
24. H. Matsunami, K. Matsuda, S. Yamasaki, K. Kimura, Y. Ogawa, and Y. Miura, *Soil Sci. Plant Nutr.*, 2010, **56**, 530-540. <https://doi.org/10.1111/j.1747-0765.2010.00489.x>
25. G. M. Marcazzan, M. Ceriani, G. Valli, and R. Vecchi, *X-ray Spectrom.*, 2004, **33**, 267-272. <https://doi.org/10.1002/xrs.719>
26. N. Pathak, V. C. Adya, S. K. Thulasidas, A. Sengupta, T. K. Seshagiri, and S. V. Godbole, *At. Spectrosc.*, 2014, **35**, 17-24.
27. A. Sengupta and V. C. Adya, *At. Spectrosc.*, 2013, **34**, 207-215.
28. B. Rajeswari, S. Pathak, Sk. Jayabun, N. Pathak, M. Mohapatra, A. Sengupta, and R. M. Kadam, *At. Spectrosc.*, 2019, **40**, 221-226. <https://doi.org/10.46770/AS.2019.06.004>
29. S. Pathak, Sk. Jayabun, B. Rajeswari, N. Pathak, M. Mohapatra, A. Sengupta, and R. M. Kadam, *At. Spectrosc.*, 2019, **40**, 215-220. <https://doi.org/10.46770/AS.2019.06.003>
30. T. H. Bell and C. Cuff, *J. Metamorph. Geol.*, 1989, **7**, 425-447. <https://doi.org/10.1111/j.1525-1314.1989.tb00607.x>
31. T. H. Bell and M. J. Rubenach, *Tectonophys.*, 1983, **92**, 171-194. [https://doi.org/10.1016/0040-1951\(83\)90089-6](https://doi.org/10.1016/0040-1951(83)90089-6)
32. A. Sengupta, B. Rajeswari, and R. M. Kadam, *Chem. Selects*, 2020, **5**, 3763-3769. <https://doi.org/10.1002/slct.202000156>
33. A. Sengupta, B. Rajeswari, and R. M. Kadam, *J. Anal. At. Spectrom.*, 2020, **35**, 169-177. <https://doi.org/10.1039/C9JA00321E>
34. A. Sengupta, S. K. Thulasidas, and V. Natarajan, *J. Radioanal. Nucl. Chem.*, 2015, **303**, 2421-2429. <https://doi.org/10.1007/s10967-014-3679-8>
35. G. D. Ruxton, *Behav. Ecol.*, 2006, **17**, 688-690. <https://doi.org/10.1093/beheco/ark016>
36. P. Baldi and A. D. Long, *Bioinformatics*, 2001, **17**, 509-519. <https://doi.org/10.1093/bioinformatics/17.6.509>
37. V. Natarajan, M. J. Kulkarni, N. K. Porwal, B. A. Dhawale, N. S. Hon, S. V. Godbole, and V. K. Manchanda, *Nucl. Instrum. Meth. B.*, 2008, **266**, 3290-3294. <https://doi.org/10.1016/j.nimb.2008.04.011>
38. A. Sengupta, T. Ippili, Sk. Jayabun, M. Singh, and S. K. Thulasidas, *J. Radioanal. Nucl. Chem.*, 2016, **310**, 59-67. <https://doi.org/10.1007/s10967-016-4790-9>
39. A. Sengupta, Y. Airan, S. K. Thulasidas, and V. Natarajan, *At. Spectrosc.*, 2015, **36**, 82-95.
40. L. S. Dale, *Appl. Spectrosc.*, 1974, **28**, 564-568. <https://doi.org/10.1366/000370274774332010>
41. A. G. I. Dalvi, C. S. Deodhar, T. K. Sheshagiri, M. S. Khalap, and B. D. Joshi, *Talanta*, 1978, **25**, 665-668. [https://doi.org/10.1016/0039-9140\(78\)80168-4](https://doi.org/10.1016/0039-9140(78)80168-4)
42. B. F. Scribner and H. R. Mullin, *J. Res. Natl. Bur Stand.*, 1946, **37**, 379-389. https://doi.org/jresv37n6p379_A1b
43. N. K. Porwal, A. A. Argekar, P. J. Purohit, A. G. Page, and M. D. Sastry, *Fresenius' J. Anal. Chem.*, 1990, **338**, 255-258. <https://doi.org/10.1007/BF00323019>
44. I. Mounteney, A. K. Burton, A. R. Farrant, M. J. Watts, S. J. Kemp, and J. M. Cook, *J. Geochem. Explor.*, 2018, **184**, 1-10. <https://doi.org/10.1016/j.gexplo.2017.10.007>
45. J. Rajendran, P. K. Thampi, and G. Balasubramanian, *Anal. Lett.*, 2006, **39**, 2297-2306. <https://doi.org/10.1080/00032710600755587>
46. P. Hannaker and H. Q. Lie, *Talanta*, 1984, **31**, 1153-1157. [https://doi.org/10.1016/0039-9140\(84\)80267-2](https://doi.org/10.1016/0039-9140(84)80267-2)