

Thin layer chromatographic study of Indian bauxites

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Thin layer chromatography (TLC) has been used for the detection and separation of Al^{3+} , Fe^{2+} , Si^{4+} and Ti^{4+} in bauxite. Thirty bauxite samples of different geological origin have been studied to identify the optimized chromatographic systems capable of selective separations of the constituents. Binary and ternary separations of Al^{3+} , Fe^{2+} , Ti^{4+} and Si^{4+} in bauxite were realized with chromatographic systems comprising various combinations of silica gel G, silica gel H and microcrystalline cellulose coated plates and aqueous mobile phases consisting alkali salt solutions, formic acid and hydrochloric acid etc. The chromatographic system consisting of silica gel H and mixture of 10% aqueous solutions of sodium chloride and formic acid in 8:2 (v/v) ratio was found to be the ideal combination for the analogous separation of Al^{3+} , Fe^{2+} and Ti^{4+} in bauxites. The efficacy of optimized chromatographic system has been investigated by monitoring reproducibility of R_F values and spot compactness with respect to change in bauxite geology, sample concentration and change of mobile phase composition. Chromatograms of the cations were quantitatively evaluated by scanning densitometry in comparison with wet analysis method.

Keywords: Bauxite, TLC, Separation of Al^{3+} , Fe^{2+} , Si^{4+} and Ti^{4+}

Bauxite is a general term applied to a variety of rock like materials containing hydrous aluminium oxide minerals mixed with impurities such as silica, iron, titanium, phosphorous, alkalies etc. with low organic components of natural origin. Though more than sixty chemical constituents in bauxite have been reported¹, Al_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 , and loss on ignition (LOI) generally constitute 99% of bauxite composition. The change in concentration ranges of major constituents in bauxite is decisive for its classification as well as utilization in metallurgical and non-metallurgical applications. The major metallurgical application of bauxite is in the production of aluminium and bauxite is considered as the most economical ore for the commercial production of hydrated aluminium oxide generally called alumina hydrate by Bayer chemical process that accounts 80-90% of bauxite consumption².

India is endowed with large reserves of bauxite containing various impurities, which to a great extent restrict their use in the refractory, abrasive and chemical industries etc. The major bauxite deposits of India are spread across the central Indian as well as east and west costal states and they are grouped into five major geological-geographical groups such as (i)

Eastern Ghats, (ii) Central Indian, (iii) West Coastal (iv) Gujarat and (v) Jammu & Kashmir bauxites. The chemical, mineralogical and physico-mechanical properties of these groups widely vary depending upon the parent rock composition, mode of origin, geomorphological position and duration as well as the age of bauxite formation. The nature and concentration of naturally occurring mineralogical phases in bauxite is significant in the formulation of Bayer plant parameters like caustic concentration, digestion pressure, caustic consumption as well as the quantum of red mud (bauxite tailing) generation. The alumina R&D centers and plant laboratories generally employ conventional wet chemical analysis and instrumental analytical methods^{3,4} like X-Ray fluorescence analysis (XRF) for the determination of oxide concentrations such as Al_2O_3 , Fe_2O_3 , SiO_2 , TiO_2 , and LOI in bauxite.

Chromatography is a simple separation technique generally practiced in various analytical laboratories. The major chromatographic studies relevant to bauxite and related materials reported in the past engrossed the identification of organic acids in Bayer liquors by gas chromatography-mass spectrometry (GC-MS)⁵ and ion chromatography (IC)

determination of anions^{6,7}. Very recently, thin layer chromatographic (TLC) studies of inorganic constituents in bauxite appeared in the literature^{8,9}. These studies highlighted the quantitative TLC-titrimetric and TLC-spectrophotometric determination of Al^{3+} , Fe^{2+} and Ti^{4+} in bauxite. These procedures are invariably time consuming and involve scraping stationary phase from the chromatograms followed by solvent extraction of the analyte from the adsorbent materials. It greatly restricts the utilization of TLC for routine quantitative studies. However; the introduction of optical scanning densitometry has contributed the much needed impetus to consider TLC as reliable quantitative analytical tool and presently TLC-densitometric procedure is widely in use for acquiring accurate and reproducible quantitative data of constituents present in various matrices¹⁰⁻¹⁴.

Considering the interdisciplinary and wide analytical utilization of chromatography techniques, in the present study TLC-scanning densitometric evaluation of four major inorganic constituents present in Indian bauxites has been done.

Experimental Procedure

Apparatus

Chromatographic trials were performed with glass plates (7×2.5 , 10×10 , $15 \times 3 \text{ cm}^2$) coated with suitable adsorbents. Systronics (India) pH meter model 335 was used for all pH measurements. The photometric measurements were carried out with a Dual Wavelength Scanning Densitometer equipped with Quanta Scan Software (Model CS-9301PC). UV detection of spots was achieved by fluorescence viewing cabinet and UV lamp (Spectroline, USA, Model M-10 and ENF-280/FE).

Chemicals and reagents

Silica gel G, ethyl alcohol, sodium formate, potassium ferrocyanide, aluminium sulphate, ammonium molybdate, sodium molybdate, acetic acid, silicon standard solution (E. Merck, India), titanium chloride, tiron, aluminon, microcrystalline cellulose (Loba, India), formic acid, sodium chloride, silica gel H, H_{254} (Qualigens, India), pre-coated silica gel H and G plates (Analtech, USA) were used. Other reagents used were of analytical grade.

Test solutions

Preliminary chromatographic studies were carried out with 1% reference standards prepared in double distilled water from ammonium ferrous sulphate,

potassium titanium oxalate and aluminium sulphate salts. Standard silicon solution (1 mg/mL) was used as received.

Chromatographic system

Various combinations of stationary and mobile phases comprising silica gel G, silica gel H, microcrystalline cellulose, and alumina; aqueous salt solutions, organic and mineral acids were used for the chromatographic separation of bauxite constituents. Chromatographic system containing mixed mobile and stationary phases were prepared by mixing individual phases in different ratios. The nature of stationary and mobile phases used for the study is summarized in Tables 1 and 2.

Detection reagents

Al^{3+} was detected by spraying TLC plates with 0.05% aqueous aluminon (tri-ammonium aurin tri-carboxylate; $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_9$), Fe^{2+} by 0.1% potassium ferrocyanide ($[\text{K}_4\text{Fe}(\text{CN})_6]$) and Ti^{4+} by 0.50% tiron (Yoes reagent; $\text{C}_6\text{H}_4\text{Na}_2\text{O}_8\text{S}_2$) respectively. Si^{4+} was detected by spraying 1% ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ or sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) on semi dried plates.

Table 1—Details of stationary phases used for the study

Symbol	Composition
S ₁	Alumina
S ₂	Microcrystalline cellulose (Cellulose)
S ₃	Silica gel G
S ₄	Silica gel G-60
S ₅	Silica gel H
S ₆	Silica gel HF ₂₅₄
S ₇	Silica gel GF ₂₅₄
S ₈	Silica gel G Impregnated with 1% sodium formate
S ₉	Silica gel G-60 Impregnated with 1% sodium formate
S ₁₀	Silica gel H Impregnated with 1% sodium formate
S ₁₁	Silica gel HF ₂₅₄ Impregnated with 1% sodium formate
S ₁₂	Silica gel H Impregnated with 1% sodium formate
S ₁₃	Silica gel H impregnated with 1% sodium chloride
S ₁₄	Silica gel H + Silica gel G (1:1, 1:2, 2:1, 3:7, 7:3, 1:9, 9:1)
S ₁₅	Silica gel H + Cellulose (1:1, 1:2, 2:1, 3:7, 7:3, 1:9, 9:1)
S ₁₆	Silica gel G + Cellulose (1:1, 1:2, 2:1, 3:7, 7:3, 1:9, 9:1)
S ₁₇	Silica gel G-60 + Cellulose (1:1, 1:2, 2:1, 3:7, 7:3, 1:9, 9:1)

Table 2—Details of mobile phases used for the study

Symbol	Mobile phase	Composition
M ₁	Hydrochloric acid	1, 3, 5, 7, 9%
M ₂	Sodium chloride	10%
M ₃	Ammonium chloride	10%
M ₄	Formic acid	1%
M ₅	Formic acid	2%
M ₆	Formic acid	3%
M ₇	Formic acid	4%
M ₈	Sodium hydroxide	0.1, 0.5, 1%
M ₉	Formic acid + 10% Sodium chloride	(1:9, 9:1, 1:1) v/v
M ₁₀	Formic acid + 10% Ammonium chloride	(1:9, 9:1, 1:1) v/v
M ₁₁	Formic acid + 10% Dimethylformamide	(1:9, 9:1, 1:1) v/v
M ₁₂	Formic acid + 10% Glycerol	(1:9, 9:1, 1:1) v/v
M ₁₃	Formic acid + 1% Sodium chloride	(1:9, 9:1, 1:1) v/v
M ₁₄	Formic acid + 1% Sodium formate	(1:9, 9:1, 1:1) v/v
M ₁₅	1% Formic acid + 1% Ammonium chloride	1:9 v/v
M ₁₆	1% Formic acid + 1% Sodium hydroxide	1:9 v/v
M ₁₇	0.1% Formic acid + 0.5% Sodium hydroxide	1:9 v/v
M ₁₈	0.1% Formic acid + 0.1% Sodium hydroxide	1:9 v/v
M ₁₉	0.1% Formic acid + 0.1% Sodium hydroxide	1:1 v/v
M ₂₀	0.1% Formic acid + 0.1% Sodium hydroxide	7:3 v/v
M ₂₁	0.1% Formic acid + Saturated Sodium chloride	1:9 v/v
M ₂₂	1% Formic acid + Saturated Sodium chloride	1:9 v/v
M ₂₃	10% Formic acid + Saturated Sodium chloride	1:9 v/v
M ₂₄	2.5% Formic acid + Saturated Sodium chloride	1:9 v/v
M ₂₅	5% Formic acid + Saturated Sodium chloride	1:9
M ₂₆	0.4% Formic acid + Saturated Sodium chloride	7:3
M ₂₇	0.4% Formic acid + 10% Sodium hydroxide	1:9
M ₂₈	2.5% Formic acid + 10% Sodium chloride	1:9
M ₂₉	10% Formic acid + 10% Sodium chloride	(3:7, 1:3, 2:8) v/v
M ₃₀	10% Formic acid + 10% Barium chloride	(1:9, 2:8, 3:7) v/v
M ₃₁	10% Formic acid + 10% Potassium bromide	(1:9, 1:3, 1:1) v/v
M ₃₂	10% Formic acid + 10% Sodium sulphate	(1:9, 9:1, 1:1) v/v
M ₃₃	10% Formic acid + 10% Potassium chloride	(1:9, 1:3, 1:1) v/v
M ₃₄	10% Formic acid + 10% Sodium nitrate	(1:9, 9:1, 3:7) v/v
M ₃₅	10% Formic acid + 10% sodium acetate	(1:9, 9:1, 3:7) v/v

Bauxite sample stock

Bauxite sample (1 g) was weighed and transferred into a clean 500 mL beaker. The sample was made wet with few drops of double distilled water. The sample slurry was homogenized with 80 mL acid mixture containing 35% HCl: 70% HNO₃ : H₂SO₄ (1:1 v/v) in the ratio 3:1:4. The contents in the beaker were digested on hot plate at 100 ± 5°C for 45 min. Precipitated silica in the solution was separated by filtration through Whatman No.40 ash less filter paper and subjected for alkali fusion. Fused silica was dissolved in double distilled water containing dilute HCl (1:1 v/v) and made up to the mark in polyethylene flask.

The approximate chemical composition of bauxite samples collected from various mining locations in India has been determined by wet analysis method¹⁵⁻¹⁸ (Table 3).

Sample purification

Test solution of bauxite sample (1%) stock containing Al³⁺, Fe²⁺ and Ti⁴⁺ prepared by the standard method was evaporated on a hot plate to ensure the removal of acids. The dried sample was dissolved in double distilled water containing few drops of dilute HCl (1:1, v/v) and made up to 100 mL in a standard flask for chromatographic study. Appropriate dissolution of purified sample was made according to the requirement and nature of studies carried out.

Preparation of TLC plates

TLC plates were prepared by mixing 1:3 (w/v) silica gel (G or H) or 1:4 (w/v) microcrystalline cellulose and double distilled water. The slurry obtained was shaken mechanically for 5 min after which it was spread as 0.25 mm layer on to 20 × 3.5 cm²

Table 3—Chemical composition of Indian bauxites used for the study

Sl.No.	Bauxite	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	LOI	CaO
1	Jamnagar`1 (GJ)	28.56	9.98	5.58	2.09	32.04	20.48
2	Jamnagar`2 (GJ)	24.48	14.77	3.10	2.73	31.46	20.49
3	Jamnagar`3 (GJ)	35.70	36.33	0.74	3.83	21.28	0.87
4	Jamnagar`4 (GJ)	56.61	3.99	1.92	2.90	32.08	2.03
5	Jamnagar`5 (GJ)	40.29	30.34	2.46	2.55	23.50	0.89
6	Kutch`1 (GJ)	52.02	11.57	3.12	3.66	28.70	0.99
7	Kutch`2 (GJ)	57.12	4.79	2.36	4.53	31.00	0.87
8	Sabarkantha`1 (GJ)	48.45	11.17	2.10	10.63	27.40	0.44
9	Sabarkantha`2 (GJ)	51.51	12.77	1.96	5.40	27.70	0.28
10	Jabalpur`1 (MP)	51.15	7.38	1.66	9.01	28.49	Nil
11	Jabalpur`2 (MP)	42.84	15.36	11.84	7.32	21.36	Nil
12	Jabalpur`3 (MP)	51.00	7.98	3.78	7.96	27.57	Nil
13	Jabalpur`4 (MP)	56.61	7.18	0.72	9.41	25.01	Nil
14	Katni`1 (MP)	18.87	45.51	19.98	3.37	11.67	Nil
15	Katni`2 (MP)	43.86	20.76	2.52	7.09	23.34	Nil
16	Raigarh (MP)	54.48	8.97	0.30	7.53	27.11	Nil
17	Shivpuri (MP)	30.60	41.12	2.98	3.89	19.85	Nil
18	Bastar (CH)	65.79	4.39	0.80	3.60	24.63	Nil
19	Raigad`1 (MS)	56.61	7.18	1.18	4.24	29.38	Nil
20	Raigad`2 (MS)	56.61	3.98	1.20	5.40	31.31	Nil
21	Raigad`3 (MS)	49.47	16.36	1.34	3.54	28.40	Nil
22	Kolhapur (MS)	43.35	23.15	2.54	4.36	24.98	Nil
23	Ratnagiri (MS)	56.10	3.59	5.62	3.89	30.18	Nil
24	Sindhudurg`1 (MS)	33.15	37.52	4.90	3.83	20.18	Nil
25	Sindhudurg`2 (MS)	47.43	17.56	1.24	5.29	27.34	Nil
26	Panchpat Mali`1 (OR)	40.29	31.14	1.58	3.25	22.84	Nil
27	Panchpat Mali`2 (OR)	39.01	29.74	6.02	2.87	21.66	Nil
28	Panchpat Mali`3 (OR)	40.03	29.54	4.97	2.97	21.78	Nil
29	Panchpat Mali`4 (OR)	43.01	26.35	3.41	2.55	24.05	Nil
30	Panchpat Mali`5 (OR)	55.08	8.98	0.96	3.50	29.13	Nil

GJ: Gujarat, MP: Madhya Pradesh, MS: Maharashtra, OR: Orissa, CH: Chattisgarh; LOI: Loss on ignition

polished glass plates. The plates were dried in room temperature and activated at $100 \pm 5^\circ\text{C}$ for 1 h in an electric oven. The activated plates were stored in vacuum chamber until used.

Impregnated plates were prepared by mixing silica gel G or silica gel H with the impregnating reagents in place of double distilled water under the same experimental conditions which were used for non-impregnated plates.

Chromatography procedure

Approximate 10 μL test solution was applied using a micropipette about 3.0 cm above the lower edge of TLC plates. The spots were dried at room temperature and the plates were developed in developing chambers containing mobile phase by ascending technique. The chambers were prepared in advance for pre-saturation with the mobile phase vapors. In all experimental runs the mobile phase ascend was fixed

at 10 cm from the point of sample application. The developed plates were dried again and the sample constituents were visualized as coloured spots by spraying with suitable detection reagents. The visualized spots were characterized on the basis of their respective R_F values, calculated from the equation $R_F = R_L + R_T / 2$ where R_L is the R_F of leading front and R_T is the R_F of trailing front of each spot.

Compound identification by TLC

For the compound identification and separation of the cations of interest, a synthetic mixture of Al^{3+} , Fe^{2+} , Ti^{4+} and Si^{4+} was prepared from their respective 1% salt solutions. Approximately 10 μL of the solution was loaded on the chromatographic plate coated with silica gel G or H and microcrystalline cellulose. A sample mixture was prepared by mixing 1% aqueous salt solutions of Al^{3+} , Fe^{2+} and Ti^{4+} in the ratio 5:2:1 (v/v/v). A 10 μL sample mixture was

loaded on TLC plates made of silica gel G and silica gel H varieties (Table 1). The plates were developed with various mobile phase combinations (Table 2) and the mobility of cations were recorded for realizing separation possibilities of Al^{3+} , Fe^{2+} and Ti^{4+} . The developed plates were partially dried in room temperature and the spots were detected by spraying 0.01% aluminon for Al^{3+} , 0.10% potassium ferrocyanide for Fe^{2+} and 0.5% tiron for Ti^{4+} . Si^{4+} was detected on microcrystalline cellulose developed with 5% hydrochloric acid by spraying 1% sodium molybdate. The individual group of ions (Al^{3+} , Fe^{2+} , Ti^{4+} , Si^{4+}) was detected on separate plates. The R_F values recorded for all the four ions in their mixture were similar to their individual R_F values under the same experimental conditions.

Chromatography of bauxite samples

Chromatography was performed with TLC plates loaded with 10 μL solutions of bauxite samples under the same experimental conditions described for compound identification with synthetic sample. Well resolved compact spots of Al^{3+} , Fe^{2+} and Ti^{4+} were obtained on silica gel H plates developed with mobile phase (M_{29}) mixture of 10% aqueous formic acid and 10% sodium chloride in 2:8 (v/v) ratio. Si^{4+} was detected on cellulose plates developed with mobile phase M_1 (5%). The detection efficiency and separation possibilities of all the cations were confirmed with that present in bauxites of various geological origins.

Densitometry

TLC-scanning densitometric evaluation of Al^{3+} , Fe^{2+} , Ti^{4+} and Si^{4+} in bauxite was carried out by spotting 1-4 μL bauxite solution of known composition on TLC plates (10 \times 10 cm^2) coated with suitable adsorbents depending on the nature of cations. The plates were developed with the mobile phase selected. Trial plates for each samples loaded were run simultaneously to locate the exact position of analyte spots. After chromatographic development, the plates were partially dried in room temperature and the spots were detected by spraying respective chromogenic reagents. The individual ions *viz.* Al^{3+} , Fe^{2+} , Ti^{4+} , Si^{4+} were detected on separate plates and the spots were subjected for densitometric scanning with deuterium source at the scanning rate of 20 mm s^{-1} at the respective λ_{max} values (530-520 nm for Al^{3+} , 628-520 nm for Fe^{2+} , 410-400 nm for Ti^{4+}

and Si^{4+}) in ascending and descending concentrations. The beam size was 6.04 \times 1.0 with a pitch 0.04 (Delta Y)

Results and Discussion

The chromatographic behaviour of major constituents in thirty bauxite samples of different geological origin as well as varying chemical composition have been examined on selective chromatographic systems (S_1 - S_{17} / M_1 - M_{35}) comprising formic acid, sodium chloride, sodium formate, sodium acetate, sodium nitrate, potassium chloride, potassium bromide, silica gel G, G-60, Silica gel GF₂₅₄, H, HF₂₅₄ and microcrystalline cellulose etc. The reported TLC studies on bauxite^{8,9} revealed limited information on the chromatographic characteristics of bauxite constituents. Therefore the present work has been undertaken with the basic chromatographic studies of Indian bauxites followed by quantitative densitometric determination of major inorganic constituents at optimized chromatographic conditions.

Optimization of chromatographic system

A detailed study has been carried out with one thousand and five hundred chromatographic systems deduced from various combinations of stationary (S_{1-17}) and mobile phases (M_{1-35}) listed in Tables 1 and 2. The preliminary TLC studies revealed that the differential migration of three metallic cations can be induced with the appropriate selection of mobile phases containing combinations of aqueous salt solutions (NaCl, NaBr, CH_3COONa , HCOONa , KCl, Na_2SO_4 , NaNO_3 , BaCl_2 etc.) and formic acid.

The suitability of acidic, basic and neutral stationary phases for bauxite constituents was separately studied with different combinations of mobile phases. It has been noticed that the bauxite constituent show low mobility (R_F) on alumina layers (S_1) possibly due to its basic nature. Al^{3+} , Fe^{2+} and Ti^{4+} show high R_F values and identical mobility pattern with chemically neutral cellulose layers (S_2). Further, due to identical R_F values, spots of Fe^{2+} and Al^{3+} appeared diffused on cellulose layers developed with different mobile phase combinations. Presence of concentrated formic acid in the mobile phase has resulted varying mobility of Fe^{2+} and Al^{3+} with moderate R_F on alumina layers. It is also noticed that the presence of formic acid improve compactness of Al^{3+} spots on cellulose layers. However, higher

concentration of HCOOH in the mobile phase hindered the detection of Ti^{4+} on both alumina and cellulose layers. Since the efficiency of basic and neutral adsorbents was found inadequate for achieving practical separation of Al^{3+} and Fe^{2+} as well as the detection of Ti^{4+} , further studies were carried out on adsorbents with acidic characters viz. silica gel G, Silica Gel G-60 (with gypsum binder, silica gel H (without binder), silica gel HF₂₅₄ (with UV-active fluorescent indicator) etc. In order to find the best stationary phase capable of resulting mutual separation of Al-Fe-Ti, irrespective of bauxite geology among silica gel varieties, representative bauxite samples of different geological origin viz. central Indian, east costal, west costal and Gujarat regions has been separately assessed as shown in Fig. 1.

The study revealed that silica gel H (S₅) and silica gel HF₂₅₄ (S₆) were the two best options for bauxite analysis in comparison with silica gel G varieties in terms of optimum reproducibility of R_F values as well as spot compactness of the cations. During this study, it was also observed that the chromatographic systems containing silica gel (H or G) as stationary phase and 10% aqueous alkali salt solutions and 10% formic acid in the mobile phase are essential for achieving desirable resolution of Al, Fe and Ti in bauxite samples. The ternary separation of Al-Fe-Ti in bauxite was found possible only when the binary mobile phase contained at least 5 - 20% HCOOH depending on the dilution of salt solutions in the binary system. The reproducibility and repeatability of R_F values of the cations were verified with different bauxite samples loaded on plain (S₅) and impregnated

silica gel H (S₁₂) varieties with the mobile phase containing 10% aqueous solutions of NaCl and formic acid (8:2 v/v) as shown in Fig. 2. Change in R_F values of Al^{3+} and Fe^{2+} were noticed with change in chemical composition of bauxite sample, however, Ti^{4+} remained at the point of sample application with R_F close to zero. Presence of 1% sodium formate as impregnating reagent in silica gel H had slightly lowered R_F values of the cations but not affected the ternary separation. The studies are repeated with change in concentration of sample as well as change in concentration of HCOONa. The change in chemical composition of bauxite has very little effect on the mobility of cations (Fig. 3) and this establishes the efficiency of the chromatographic system. The increase in concentration of HCOONa (Fig. 4) in the stationary phase was found to progressively decrease the R_F of Al^{3+} and Fe^{2+} and the spot compactness was found directly proportional to the HCOONa concentration.

Based on the above studies, it has been concluded that the chromatographic system containing silica gel H as stationary phase and mixture of 10% aqueous solutions of sodium chloride and formic acid in 8:2 (v/v) as mobile phase was the best chromatographic system suitable for the TLC study of Al^{3+} , Fe^{2+} and Ti^{4+} in bauxite. Similarly the chromatographic system containing microcrystalline cellulose and 5% hydrochloric acid was chosen for the analysis of Si^{4+} . The optimized chromatographic conditions as shown in Table 4 were derived and the quantitative densitometric analysis of Al^{3+} , Fe^{2+} , Ti^{4+} and Si^{4+} in bauxite was carried out.

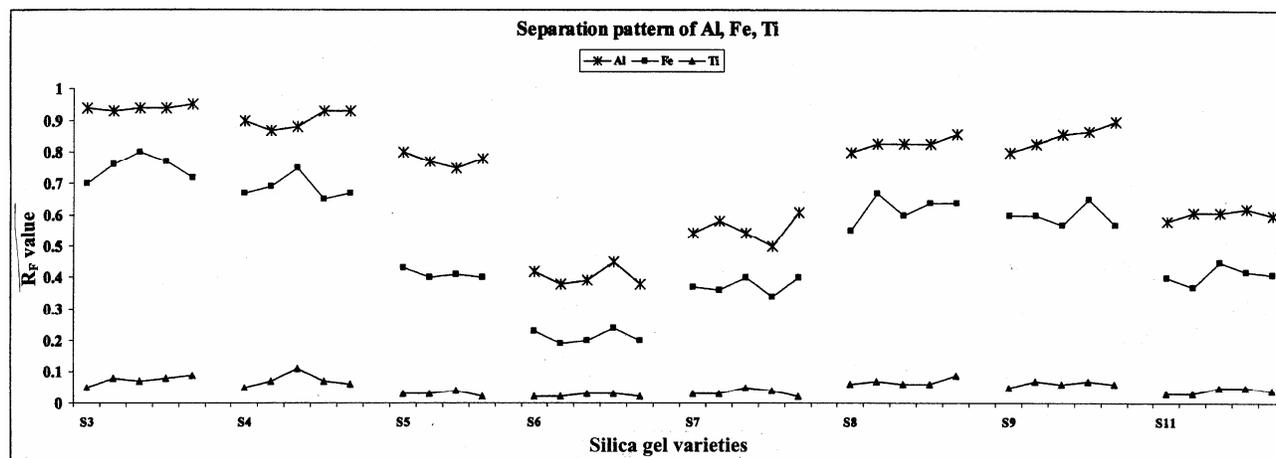


Fig. 1—Separation of Al, Fe and Ti in Indian bauxites on Silica gel varieties

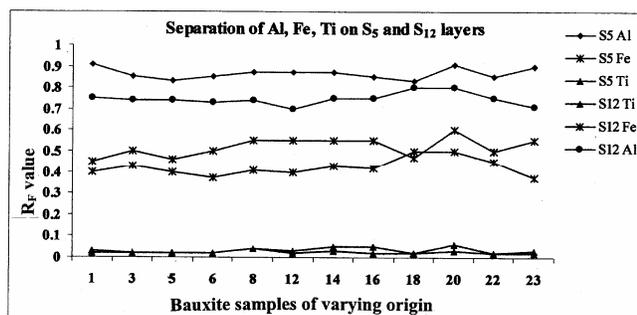


Fig. 2— R_F values of Al, Fe and Ti on plain and impregnated Silica gel H layers

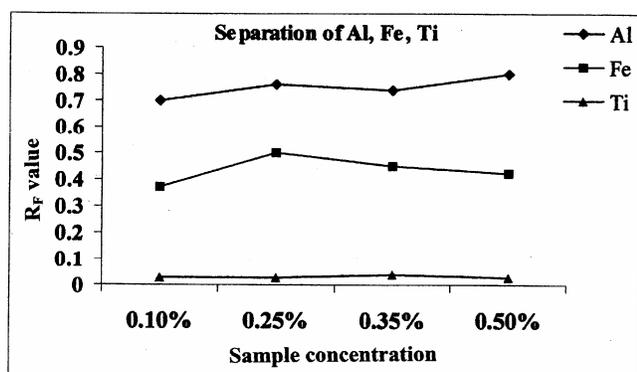


Fig. 3—Variation of R_F with change in sample concentration on S_{12}

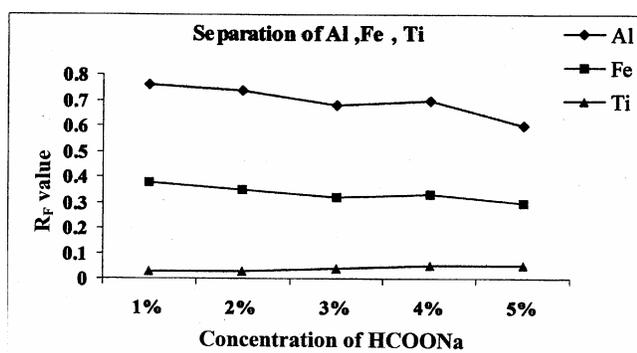


Fig. 4—Variation of R_F values with increase in concentration of HCOONa

Scanning densitometric analysis of bauxite constituents

A set of fourteen bauxite samples of various geological origins (East coast, west coast, Gujarat, Central India) was used for the densitometric evaluation. Chromatography of the samples was carried out at optimized chromatographic conditions as shown in Table 4. The calibration curves were constructed for individual cations (Al^{3+} , Fe^{2+} , Ti^{4+} and Si^{4+}) at their respective λ_{max} values by spotting 10 μ L

Table 4—Optimized conditions for quantitative TLC analysis of bauxite

Densitometry of bauxite constituents (Al, Fe, Ti, Si)	
Item	Parameter
Sample nature	Acid digested
Concentration	0.01-0.50%
Sample loading volume	1- 4 μ L
Potassium ferrocyanide	0.10% aqueous
Aluminon	0.01% aqueous
Tiron	0.50% aqueous
Sodium molybdate	0.50% aqueous
Silica gel H	For Al, Fe, Ti
Microcrystalline cellulose	For Si
Solid liquid ratio for slurry	1:3 (w/v)
Plate size	10 \times 10 cm^2
Slurry volume for plate coating	10 mL
Coating layer thickness	Approx. 2-3 mm
Plate activation temperature	100 \pm 5 $^{\circ}C$
Plate activation time	60 \pm 5 min.
Sample loading temperature	30 ~40 $^{\circ}C$
10% NaCl + 10% HCOOH	8:2 (v/v)
Mobile phase volume	10 mL
Mobile phase ascent	7 cm

samples of bauxite sample solutions of different concentrations, i.e 0.1, 0.5, 1, 2, 4, 8, 10% of Al^{3+} , Fe^{2+} , Ti^{4+} , Si^{4+} in ascending and descending concentration ranges. Concentration of cations present in the samples was estimated by measuring the peak area of respective cation. The percentage error was calculated with respect to the concentration of constituents in the samples and the concentration value was obtained, after densitometry, by using the equation:

$$E = \frac{A-B}{B} \times 100$$

where E = % error; A = % composition of constituent in the sample; B = % value of constituent in the standard.

A percentage recovery of 98% \pm 2% was obtained with respect to the wet analysis data. The study was repeated under identical experimental conditions and the standard deviation in the densitometric measurement with respect to wet analysis data was obtained (Table 5).

Limit of detection

The detection limits of Al^{3+} , Fe^{3+} and Ti^{4+} Si^{4+} were determined by spotting different volumes of bauxite sample solutions on TLC plates (S_5) followed by

Table 5—Scanning densitometric determination of major constituents in Indian bauxites
% Composition of bauxite constituents

Sample No.	Fe ₂ O ₃			Al ₂ O ₃			TiO ₂			SiO ₂			
	DMA*	SD	ERR	DMA*	SD	ERR	DMA*	SD	ERR	DMA*	SD	ERR	
03	36.64	0.054	0.85	35.22	0.342	1.34	3.76	0.890	3.83	1.82	0.75	0.323	0.74
05	30.34	0.531	0	40.50	0.382	0.52	2.61	0.237	2.55	2.35	3.28	1.365	2.46
09	12.71	0.261	0	51.51	0.308	0	5.22	0.235	5.40	2.06	2.18	0.995	1.96
10	7.38	0.018	0	51.15	0.502	0	8.36	0.223	9.01	7.21	1.53	0.309	1.66
11	15.33	0.053	0.19	41.84	0.432	2.28	7.55	0.981	7.32	3.14	10.93	2.055	11.84
12	7.98	0.091	0	50.09	0.678	1.78	7.94	0.086	7.96	0.25	3.76	1.939	3.78
14	20.76	0.018	0	43.86	0.412	0	7.46	0.098	7.09	5.21	2.59	0.456	2.52
15	7.28	0.068	1.39	56.69	0.337	0.14	9.90	0.454	9.41	5.02	0.73	0.898	0.72
16	8.99	0.027	0.22	54.55	0.236	0.13	7.55	0.237	7.53	0.26	0.30	0.987	0.30
18	4.32	0.030	1.59	64.10	0.820	2.56	3.90	0.341	3.60	8.83	0.78	0.887	0.80
21	16.37	0.029	0.06	49.26	0.055	0.42	3.41	0.567	3.54	3.67	1.29	0.336	1.34
20	3.98	0.282	0	56.19	0.071	0.74	5.29	0.459	5.40	2.03	1.20	0.138	1.20
23	3.51	0.103	2.22	55.30	0.077	1.42	3.57	0.119	3.89	8.22	5.48	1.876	5.62
26	31.28	0.297	0.45	39.67	0.301	1.54	3.09	0.043	3.25	4.92	1.43	0.927	1.58

DMA: Densitometric analysis; SD : Standard deviation; WCA: Wet chemical analysis; ERR: Error;

*Each DMA value is average of five consecutive scanning of five different spots of same sample loaded on the TLC plate

development of the plates with mobile phases M₂₉ (2:8 v/v). The procedure was repeated with successive lowering of sample concentration loaded on TLC plates until no peak was observed during the scanning of spot by densitometer at the respective λ_{\max} values. For Si⁴⁺ the trials were carried out on S₂ pre-developed with sodium molybdate followed by development with 5% M₁ as well as without development of TLC plate. The accuracy and reproducibility of detection limit (Al³⁺ 8-12 ppm; Fe²⁺ 3-7 ppm; Ti⁴⁺ 5-7 ppm; Si⁴⁺ 10-15 ppm) were confirmed with repeated trials of ten bauxite samples of different geological origin. The trace level detection of the cations in bauxite samples required dilution of detection reagents i.e 0.01% aluminon, 0.10% potassium ferrocyanide and 0.50% tiron.

Conclusions

The present chromatographic studies on bauxites revealed the possibility of developing a rapid and cost effective quantitative methodology for the analysis of ore samples. The investigations revealed that TLC procedure can be successfully modified and coupled with sophisticated instrumental methods for quantitative determination of trace elements in natural samples. The TLC-Densitometry procedure developed for the analysis of major constituents in bauxite is highly useful for trace level detection of cations including silica in bauxite samples. The analysis procedure developed is simple, faster and can be used as complementary to the existing quantitative wet chemical and instrumental methods of ICP or XRF analysis.

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