

Thin-Layer Chromatography of Aluminium: Quantitative Densitometric Determination of Fe^{2+} , Ni^{2+} , Cu^{2+} , and Si^{4+}

P.A. Mohamed Najar*, R.N. Chouhan, J.U. Jeurkar, S.D. Dolas, and K.V. Ramana Rao

Jawaharlal Nehru Aluminium Research Development and Design Centre, Amaravati Road, Nagpur, India—440 023

Abstract

Thin-layer chromatography in combination with scanning densitometry is used as a tool for the quantitative determination of some impurity and additive elements in aluminium. Microgram levels of iron, silicon, copper, nickel, titanium, magnesium, manganese, and zinc present in a high concentration aluminium matrix is detected, and selective separations of some of these elements are achieved on silica gel H layers developed with a mobile phase containing aqueous sodium chloride solution. The quantitative determination of iron, silicon, nickel, and copper are obtained from the densitometric evaluation of chromatograms and are compared with the respective optical emission spectral analytical data.

Introduction

Metals are considered as one of the distinct classes of inorganic mixtures of highly concentrated solid solutions in which low concentrations of various residual impurities, additives, and alloying elements are present. Aluminium is one of the most widely used light metallic elements for industrial and domestic applications. Commercially available aluminium is 99% pure; generally, the residual impurities in raw materials of metal production contribute impurities like iron and silicon in primary aluminium. Aluminium alloys are made by the deliberate addition of specific quantities of impurities, like copper, silicon, magnesium, manganese, zinc, titanium, and occasionally nickel, chromium, etc., to the metal melts during melting operations for imparting special properties, like hardness, durability, etc. The quality checkups of aluminium melt in smelter plants is generally carried out by emission spectroscopy (1) and wet analytical methods in combination with instrumental techniques like atomic emission spectroscopy and inductively coupled plasma (ICP) and ICP–mass spectrometry (MS).

Bauxite is the principal ore of aluminium, and recently, thin-layer chromatography (TLC) has been used in combination with

titrimetry and spectrophotometry for the quantitative estimation of its major constituents [viz., Al_2O_3 , Fe_2O_3 , SiO_2 , and TiO_2 (2,3)]. Application of TLC in combination with scanning densitometry was also reported (4,5) for quantitative analysis of Indian bauxites. Because TLC has not been used extensively for metal analysis, in this paper, a TLC-densitometric method developed for aluminium metal analysis and quantitative determination of Si^{4+} , Ni^{2+} , Cu^{2+} , and Fe^{2+} is discussed.

Experimental

Chemicals and reagents

Sodium formate, sodium chloride, potassium ferrocyanide, aluminium sulphate, nickel sulphate, copper sulphate, manganese sulphate, zinc acetate, magnesium chloride, sodium molybdate (E. Merck, Worli, Bombay, India), microcrystalline cellulose, silicon standard solution (Merck, Germany), dimethylglyoxime, sodium chloride, silica gel H, 8-hydroxy quinoline, and hydrochloric acid (Qualigens, Worli, Bombay, India) were used. Other reagents used were of analytical grade.

Instrumentations

Systronics (India) pH meter model 335 was used for all pH measurements. Photometric measurements were carried out by Shimadzu (Koyoto, Japan) make UV–vis Spectrophotometer (Model 1601) and a dual wavelength scanning densitometer (Model CS- 9301PC) equipped with Quanta Scan Software

Test solutions

Reference standards (1%) were prepared in double distilled water with the respective salts. Standard silicon solution (1 mg/mL) in alkaline medium was used as received. Aluminium test samples (1%) were prepared by dissolving commercially available primary and alloy aluminium samples in 15 mL, 10% sodium hydroxide. The complete dissolution of the sample was ensured with heating the mixture at $100^\circ\text{C} \pm 2^\circ\text{C}$ followed by gradual addition of 20 mL, 1:1 HNO_3 . The resultant clear solution is made up with double distilled water and preserved in

* Author to whom correspondence should be addressed: email najarp@hotmail.com.

polyethylene flasks for chromatographic studies.

Buffer solution

Acetate buffer of pH ~ 6.98 was prepared by dissolving 25 g ammonium acetate in 50 mL hot distilled water, followed by the addition of glacial acetic acid (~ 3 mL). The mixture was diluted to 100 mL in standard flask.

Detection reagents

The weight/volume concentration and composition of detection reagents used for the study are shown in parenthesis, in the Determination of impurity levels in aluminium section, where ever applicable.

Chromatographic system

The chromatographic system chosen for this study was a combinations of S_1 (silica gel H) with aqueous salt solutions of M_1 (sodium chloride) and M_2 (sodium formate) as well as S_2 (microcrystalline cellulose) with M_3 (hydrochloric acid).

Chromatography

Preparation of TLC plates

TLC plates were prepared by mixing 1:3 (w/v) silica gel 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 a 0.25-mm layer on polished glass plates (3 × 15 cm² for qualitative studies and 10 × 10 cm² for quantitative studies). The "silica gel" plates were dried at room temperature and activated at 100 ± 5°C for 1 h in an electric oven. The activated plates were stored in a vacuum chamber until used. The experimental conditions remain the same for the preparation of cellulose plates where the activation temperature is 60–80°C.

Procedure

Standard chromatographic procedures (6–8) have been used for sample application on TLC plates; chromatogram development, visualization of separated constituents, and characterization was based on the respective retention factor (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.

Qualitative studies

Separation of metal ions

For the separation, 1% solutions (pH 6.65) of a synthetic mixture containing of Al^{3+} , Fe^{2+} , Si^{4+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Ti^{4+} , Ni^{2+} , and Mg^{2+} were prepared. Approximately 5 μ L of the solutions of aluminium and salt solutions were loaded on the chromatographic plates (3 × 15 cm²) coated with S_1 and S_2 . Chromatography was performed for achieving the detection of impurity elements and observing their migration trend from the point of sample application. The chromatographic system comprising S_1 and 10% M_1 was found capable of detecting Fe^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , Ti^{4+} , Ni^{2+} , and Mg^{2+} . The R_f values recorded for all the ions in their mixture were similar to their individual R_f values under the same experimental conditions.

Determination of impurity levels in aluminium

Solution of standard aluminium samples (10 mL) were mixed

with 10 mL acetate buffer (pH 6.98). This solution (5 μ L) was loaded on TLC plates (3 × 15 cm²) coated with S_1 and S_2 and developed with M_1 . The buffer addition was made for ensuring reproducibility of R_f values and stability of spot color. The impurity elements in the sample were detected (Figure 1)

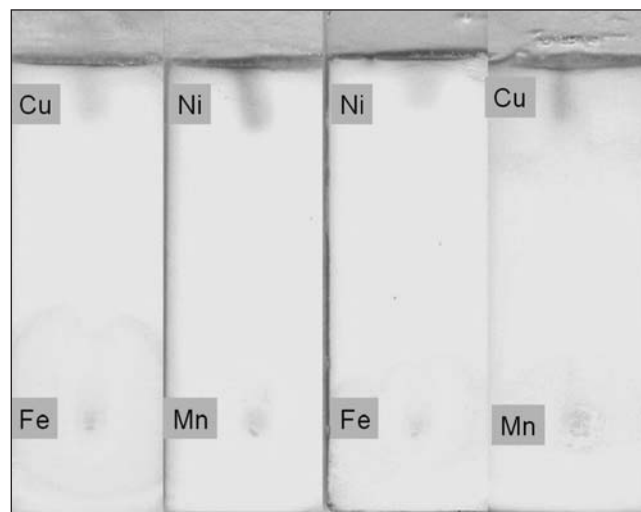


Figure 1. Chromatogram showing qualitative separation of Ni^{2+} , Mn^{2+} , Cu^{2+} , and Fe^{2+} in aluminium alloys (chromatographic system—silica gel H: 10%

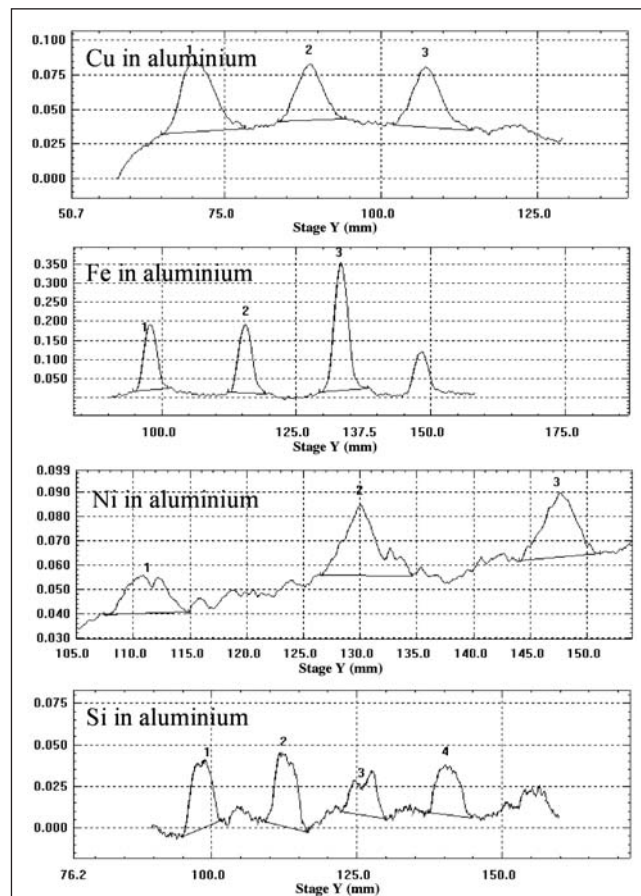


Figure 2. Schematics of densitometric scanning of impurity elements in aluminium. (Multiple peaks of each element indicate scanning at different sample concentration).

by spraying respective chromogenic reagents. Fe^{2+} gave blue colored spot with 0.5% potassium ferrocyanide ($[\text{K}_4\text{Fe}(\text{CN})_6]$) and Cu^{2+} appeared as dull yellow with sodium diethyl dithiocarbamate ($\text{C}_2\text{H}_{10}\text{NNaS}_2 \cdot 3\text{H}_2\text{O}$). Ni^{2+} produced a pink spot while spraying 1% alcoholic dimethylglyoxime ($\text{C}_4\text{H}_8\text{N}_2\text{O}_2$). Mn^{2+} was detected as light brown spot by spraying 2M aqueous NaOH -30% H_2O_2 , 1:1 (v/v). Zn^{2+} appeared as red spot when spraying 0.1% dithizone ($\text{C}_{13}\text{H}_{12}\text{N}_4\text{S}$) in carbon tetrachloride. The fluorescent yellow spot of Mg^{2+} in the sample was identified by spraying 1% 8-hydroxy quinoline ($\text{C}_9\text{H}_7\text{NO}$) in ethanol. The detection of Si^{4+} was achieved on S_2 . The sample solution was loaded on S_2 pre-developed with 10% sodium molybdate ($\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$) followed by spraying 10% (v/v) hydrochloric acid. Si^{4+} was detected as bright yellow spots. The plates were developed with 2% (v/v) of M_3 .

Quantitative studies

The quantitative determination of Fe^{2+} , Si^{4+} , Cu^{2+} , and Ni^{2+} in aluminium was carried out by scanning densitometry. Fe^{2+} and Cu^{2+} were separated on silica gel H coated TLC plates, and for their determination, a set of standard sample solutions (1.0%, 1.5%, 2.0%, and 2.5%) were prepared by dissolving an aluminium sample diluted with acetate buffer (pH ~ 6.98) in a 1:1 (v/v) ratio. Calibration curves were constructed for the determination of Fe^{2+} and Cu^{2+} by loading 5 μL of the solutions (1.775, 2.662, 3.55, 4.435 μg Fe^{2+} , 1.00, 1.500, 2.00, 2.500 μg Cu^{2+}) on TLC plates coated with silica gel H ($10 \times 10 \text{ cm}^2$) at 2 cm above from the lower edge by using micropipette. For Ni^{2+} , sample solutions were prepared by dissolving a master alloy sample containing 0.5% Ni^{2+} in HCl (1:1 v/v). Appropriate dilutions were made to get sample solutions containing 2.500, 3.750, 5.000, and 6.250 μg Ni^{2+} . The sample solutions were loaded on the TLC plates and developed with 10% NaCl solution, and the ions were detected (R_f : Fe^{2+} : 0.01, Ni^{2+} : 0.96, Cu^{2+} : 0.94) on separate TLC plates and subjected to densitometric scanning. The Fe^{2+} spot appears blue and scanned at 628 nm, Cu^{2+} spot was dull yellow and scanned at 410 nm, and the bright pink spot of Ni^{2+} was scanned at 525 nm. The chromatogram of Si^{4+} was prepared by

loading 5- μL solutions (0.0103, 0.015, 0.0206, and 0.0257 μg Si^{4+}) on cellulose plates predeveloped with 10% sodium molybdate, followed by spraying with 10% hydrochloric acid for the color development. The yellow-colored spot appeared on the TLC plate was directly scanned (without development) at 395 nm for the determination of Si^{4+} . From the peak area corresponding to the concentration range of cations (Figure 2) loaded on the TLC plates, calibration curves were constructed, and the concentration of Fe^{2+} , Si^{4+} , and Cu^{2+} in the standard aluminium samples was determined. Repeated trials were carried out with standard samples A, B, and C in order to check the reproducibility and accuracy of the results. Master alloy samples and utensil samples were used for the determination of Ni^{2+} . The peak area corresponding to the cations present in unknown samples were determined by the simultaneous loading of standard (Sample A) and sample solutions (Samples D, E, and F) side by side on the same TLC plate, and chromatography was performed under the same experimental conditions described for standard sample. From the peak area of standard and sample spots, the recovery percentage of unknown cations of interest was determined. The composition of some metal samples used for the study is shown in Table I.

Results and Discussions

The chromatographic behavior of impurity elements in 10 aluminium samples were examined on selective chromatographic systems comprising formic acid, sodium chloride, sodium formate, silica gel H, and microcrystalline cellulose. Considering the difference in compositional variations of aluminium matrices (alloys), selective chromatographic systems were used for both qualitative and quantitative studies. The results of these studies are summarized in Table II–VI and Figure 1–3.

Nature of sample

To study the effect of sample composition on the mobility (R_f) of impurities in aluminium, chromatography was performed with aluminium samples of different chemical composition under the same experimental conditions ($\text{S}_{1,2}$ - $\text{M}_{1,3}$). The R_f values recorded for Fe^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} , Mg^{2+} , Ni^{2+} , Si^{4+} , and

Table I. Optical Emission Spectral Analysis of Aluminium Samples Used for the Chromatographic Study

Constituent	% Composition of constituents in metal					
	A	B	C	D	E	F
Si	0.41	0.28	0.35	0.22	0.38	0.22
Fe	0.71	0.75	1.55	0.30	0.15	0.63
Cu	0.40	0.24	0.31	0.17	0.002	0.20
Mn	0.28	0.34	0.21	1.71	0.001	0.046
Mg	0.17	0.14	0.15	1.14	0.51	0.031
Zn	0.70	0.21	0.52	0.004	0.001	0.27
Ni	0.016	0.026	0.022	0.002	0.002	0.010
Cr	0.029	0.025	0.032	0.001	0.0005	0.0037
Ti	0.012	0.019	0.11	0.001	0.013	0.0017
V	0.005	0.0063	0.004	0.002	0.005	0.0022
Al	97.10	97.89	96.50	96.39	98.89	98.39

Table II. R_f - R_f Value of Impurity Elements in Aluminium

Sample	Chromatographic system (S_1 - M_1)* and (S_2 - M_3)†
Primary aluminium	Fe (0.04-0.0) Si (0.98-0.90)*
Copper alloy	Fe (0.05-0.0) Cu (0.95-0.88)*
Magnesium alloy	Fe (0.03-0.0) Mg (0.05-0.00)†
Manganese alloy	Fe (0.04-0.0) Mn (0.99-0.93)*
Silicon alloy	Fe (0.04-0.0) Si (0.95-0.89)†
Utensil sample 1	Fe (0.03-0.0) Ni (0.96-0.90)*
Utensil sample 2	Fe (0.03-0.0) Zn (0.99-0.91)*

* R_f - R_f of the leading front of the spot and R_f - R_f of the trailing front.
 † The R_f - R_f values shown are average of five consecutive trials in each chromatographic system.

Mg²⁺, etc. revealed that the compositional variations does not affect the binary separations viz., Fe–Cu, Fe–Ni, Ni–Mn, Cu–Ni, Mn–Cu, and Si–Mg. Repeated trials show reproducible R_f values (Table II) under the same experimental conditions.

Effect of pH

pH of the sample and mobile phase play an important role in the detection and mobility of the cations. A high R_f value (R_f varies from 0.85–0.98) was observed for Ni²⁺, Cu²⁺, and Zn²⁺, with the S₁–M₁ system. Fe²⁺ and Mn²⁺ remained at the point of sample application and resulted binary separations. It was noticed that a decrease in pH of the sample or mobile phases (addition of acids 1% formic, hydrochloric or nitric acids) harm the separation possibility due to tailing of Fe²⁺ from the point of sample application ($R_L - R_T \leq 0.30$, where R_L is the R_f of leading front of the spot and R_T is R_f of trailing front of the spot). Also, the presence of acid in the mobile phase adversely affected detection of Ni²⁺ and Cu²⁺. Detection and separation of Mg²⁺ was largely affected by the pH variation of the sample. Neutral or slightly basic pH (pH ~ 7.5–8.0) was found to be

Table III. Detection Limits of Cations in Aqueous Salt Solutions and Aluminium Samples

Sample	Detection limit in ppm*			
	Fe	Ni	Ti	Si
Potassium titanium oxalate			2.50	
Ferric chloride	2.40			
Nickel chloride	2.00			
Sodium silicate standard solution				3.50
Aluminium alloys	4.00	5.00	5.50	5.00
	0.50 [†]			

* Average of five consecutive trials under standard chromatographic conditions.
[†] Without development of TLC plates.

Table IV. Optimized Experimental Conditions*

Sample preparation				
Densitometry				
Element	Concentration	pH	Volume	λ_{\max} (nm)
Fe ²⁺	0.50%	6.68	05.0 μ L	628
Cu ²⁺	0.50%	6.68	05.0 μ L	410
Ni ²⁺	1.00%	0.50	05.0 μ L	530
Si ⁴⁺	1.00%	0.30	05.0 μ L	390
Chromatography				
Element	System	Chromogenic reagents		
Fe ²⁺	S ₁ –M ₁ 10%	Potassium ferrocyanide 0.10%		
Cu ²⁺	S ₁ –M ₁ 10%	Sodium diethyl dithiocarbamate 0.01%		
Ni ²⁺	S ₁ –M ₁ 10%	Dimethylglyoxime 0.01%		
Si ⁴⁺	S ₂ –M ₃ 05%	Sodium molybdate and HCl 10.0%		

ideal for the detection with C₉H₇NO. The detection and stability of yellow molybdosilicate was achieved in the pH range of 0.7–0.95. The sample solution needs to be acidified to pH 0.3–0.4 prior to loading on TLC plate in order to achieve the detection of Si⁴⁺.

Limit of detection

The detection limits of Al³⁺, Fe²⁺, and Ni²⁺ were determined by spotting different volumes of standard aluminium sample solutions on TLC plates (S₁) followed by development of the plates with mobile phases 10% M₁. The procedure was repeated with successive lowering of sample concentration loaded on TLC plates until no peak was observed during the scanning of the spot by a densitometer at the respective λ_{\max} values. For Si⁴⁺ the trials

Table V. Densitometric Determination of Impurity Elements in Aluminium Alloys

Peak area*	Comparative data of densitometry with OES [†]			
	% Composition		Error	
	Spectral Densitometry	analysis	% Error	Average
Fe²⁺				
478.15	0.710	0.712	0.28	1.62
519.54	0.768	0.758	1.31	
995.21	1.508	1.559	3.27	
Cu²⁺				
312.43	0.418	0.405	3.20	2.68
197.32	0.253	0.242	4.54	
231.98	0.310	0.311	0.32	
Ni²⁺				
42.61	0.012	0.012	0	1.51
28.40	0.008	0.008	0	
82.95	0.023	0.022	4.54	
Si⁴⁺				
178.77	0.461	0.412	10.62	3.99
108.52	0.283	0.280	1.070	
134.69	0.356	0.357	0.280	

* Peak area measurement is average of three consecutive trials.
[†] OES = optical emission spectroscopy.

Table VI. Optimized Conditions for the Preparation of TLC Plates*

Preparation of silica gel H coated TLC plate	
Solid liquid ratio	1:3 (w/v)
Plate size	10 × 10 cm ²
Slurry volume	10 mL
Layer thickness	~ 2.5 mm
Activation temperature	100 ± 5°C
Plate activation time	60 ± 5 min

* The experimental conditions remain the same for cellulose plates where the solid liquid ratio is 1:4 (w/v) and activation temperature is 60–80°C.

were carried out on S_2 , pre-developed with sodium molybdate followed by development with 3% M_3 as well as without development of the TLC plate. The accuracy and reproducibility of the limits of detection were confirmed with different aqueous salt solutions of respective cations and aluminium alloy samples. The details of the study are summarized in Table III

Densitometry

In order to achieve the accuracy and reproducibility of densitometric determination of impurity elements in aluminium samples, modifications were made in the routine detection and development procedures. With respect to the impurity elements of interest, the spot was detected on pre-developed plates, or the plates were developed with mobile phases containing a specific concentration of respective detection reagents to ensure consistency in R_f during the repeated trials, least spot diffusion, and effective separation (Figure 3). In certain cases, the spot mobility was controlled with selective addition of buffers.

For the determination of Fe^{2+} and Cu^{2+} , the sample solution was neutralized with acetate buffer (pH 6.98) prior to loading on TLC plates, and the chromatogram containing Fe^{2+} (R_f 0.0) and Cu^{2+} (0.96) has been subjected for densitometry (Figure 3). The optimized experimental conditions used for sample preparation and chromatography for the densitometric determination of Fe^{2+} , Cu^{2+} , Ni^{2+} , and Si^{4+} are summarized in Table IV.

Chromatography has been performed with aluminium samples of varying chemical compositions under the optimized

experimental conditions. The concentration of Fe^{2+} , Cu^{2+} , Ni^{2+} , and Si^{4+} in the samples was determined from the corresponding peak areas (Figure 2). The percentage error was calculated with respect to the concentration of the elements loaded on the TLC plates. The densitometric result obtained was well in the range of optical emission spectrometric (OES) data as shown in Table V. In order to ensure the accuracy of densitometric data, reproducibility of major chromatographic parameters were repeatedly studied under various experimental conditions.

The laboratory-made TLC plates were prepared in optimized experimental conditions (Table VI) for achieving consistency in R_f values, spot size, and development time.

Conclusion

The reported TLC method devoted to the analysis of aluminium metal permits the separation and determination of various impurities (Si^{4+} , Ni^{2+} , Cu^{2+} , and Fe^{2+}) within 15 min, which allows a high throughput of samples. The method was run for several months in the laboratory under different experimental conditions and has clearly proven its reliability, irrespective of chromatographic variations, with respect to humidity and temperature. Because of the accuracy in densitometric determination with spectral analysis for a great number impurity elements in aluminium, this method has an evident interest for *in situ* routine metal analysis of bulk samples, viz. scrap classification for segregation and recycling of industry rejects such as scrap, chips, and dross for secondary aluminium production where the concentration range of major impurity elements or alloying elements are just sufficient for pre-treatment.

Acknowledgments

The authors thank Dr. J. Mukhopadhyay, Director JNARDDC, for his constant encouragement, useful suggestions, and permission for publishing the work. The Science & Technology Wing, Ministry of Mines, Government of India is acknowledged for financial support to the project on "Development of rapid analytical procedures for bauxite and semi-quantitative analysis of scrap aluminium".

References

1. K. Grjotheim and B.J. Welch. *Aluminium Smelter Technology—A Pure and Applied Approach*, 2nd ed. Aluminium-Verlag, Dusseldorf, Germany, 1988, pp. 251–61.
2. A. Mohammad and S. Hena. Inducement of a new micellar mobile phase for thin-layer separation and quantitative estimation of aluminium (III) in bauxite with preliminary separation from Iron (III) and titanium (IV). *Sep. Sci. Technol.* **39**: 2731–50 (2004).
3. P.A. Mohamed Najar, J.U. Jeurkar, and K.V. Ramana Rao. Thin layer chromatographic study of bauxite: Detection and separation of major constituents and quantitative estimation of co-existing Al^{3+} ,

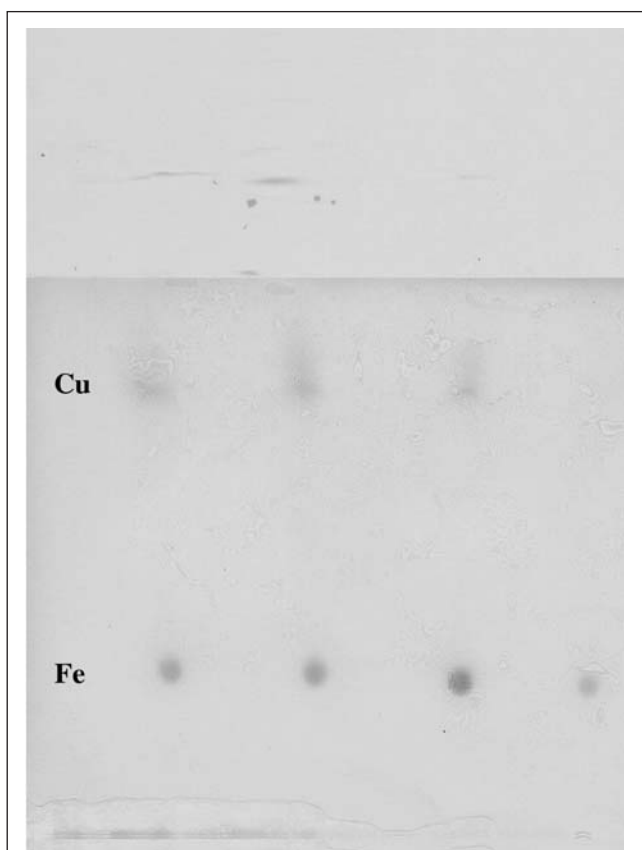


Figure 3. Separation of Fe^{2+} and Cu^{2+} under optimized experimental conditions for densitometric evaluation (Chromatographic System—Silica gel H:

- Fe²⁺, and Ti⁴⁺. *Chinese J. Chromatogr.* **23(5)**: 555–61 (2005).
4. P.A. Mohamed Najar, J.U. Jeurkar, and K.V. Ramana Rao. "A new analytical technique for detection, separation and quantitative estimation of constituents of bauxite". In proceedings of *Status of Bauxite, Alumina, Downstream Products and Future Prospects at XVI the International Committee for Study of Bauxite, Alumina and Aluminium* (ICSOBA). Nagpur, India, November 28–30, 2005, pp. 257–61.
 5. P.A. Mohamed Najar and K.V. Ramana Rao. "Thin layer chromatography of bauxite: Instrumental characterization and quantification by scanning densitometry". In the Proceedings (CD-Volume) of *Annual Meeting and Exhibition at Alumina and Bauxite Symposium of The Minerals, Metals and Materials Society* (TMS). San Antonio, TX, 2006.
 6. *Thin-Layer Chromatography—A Laboratory Handbook*, 2nd ed, E. Stahl, Ed. George Allen & Unwin, Ltd. London, UK, Springer-Verlag, Berlin, Heidelberg, New York, NY, 1969, pp. 52–85.