APPLICATION OF CIRCULAR THIN-LAYER CHROMATOGRAPHY IN THE ANALYSIS OF PAKISTANI MINERALS

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Analysis of ten Pakistani minerals, haematite, magnesite, bentonite, dolomite, gypsum, baryte, bauxite, stibnite, cuprite and chromite was carried out qualitatively by circular thin-layer chromatography. The results thus obtained were compared with the results obtained by emission spectrographic analysis of the same samples. The results are comparable and the circular thin-layer chromatography can be applied safely for routine qualitative analysis of minerals and provides another method for analysis in the laboratory.

Introduction

The different techniques which have been already used for analysis of minerals are emission spectrography, polarography, chemical analysis and chromatographic methods. Facilities of spectrographic and chromatographic methods for qualitative work were available and so these two methods were selected for the analysis of minerals. Thin-layer chromatography was selected for two basic reasons; firstly, the technique is very simple and selective; secondly, a modification of this technique has recently been introduced by Hashmi *et al.*[1,2] relating to the method of Meinhard and Hall[3] for micro-circular thin-layer chromatography. Hashmi *et al.*[1,2] developed an analytical scheme which includes about forty cations for detection and confirmation. This scheme is based upon seperation of cations into five different groups by means of solvent extraction,[4] with modification to include more cations. The groups of cations are analysed subsequently by circular thin-layer chromatography. The method is simple and the development of a chromatoplate is complete within 2 minutes. The results are reproducible.

Samples were analysed qualitatively with the help of circular thin-layer chromatography and results were compared with those obtained by emission spectrograph,

Experimental

(a) *Circular Thin-Layer Chromatographic Analysis*

Reagents.—All reagents were of analytical grade; aluminium oxide D-5, CAMAG, with 5%$CaSO_4$, as binder; silica gel D-O, CAMAG, without binder; spray reagents (see Table 2).

Apparatus.—Circular thin-layer chromatographic apparatus;[1] applicator, CAMAG, Switzerland; glass plates (20×10 cm); levelling table; all-glass sprayer; hot-air blower; spotting capillaries; separating funnel; Agla micro-syringe.

Procedure.—Five g alumina D-5 or silica gel D-O was mixed with 16.0 ml distilled water in a pestle and mortar. The slurry thus formed was placed in the applicator, which was pre-adjusted to produce layers of 250μ thickness. Thoroughly cleaned and dried plates were passed through the applicator in succession and coated plates were left over at room temperature for 24 hr. Dried plates in this way were used throughout the analysis.

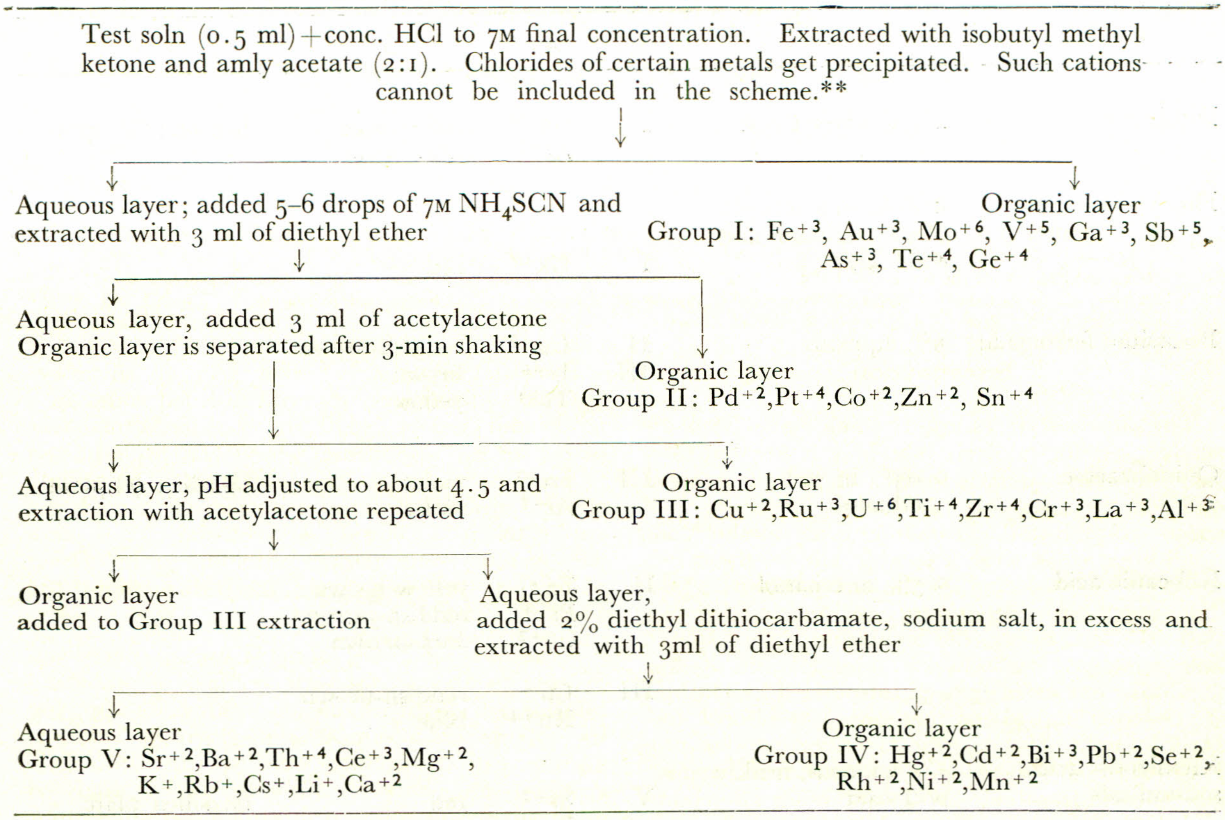
A solution of 4–5% mineral was prepared according to Scotts[5] standard method of preparing solution for chemical analysis. Then by applying the solvent extraction scheme given in Table 1, all the cations present were divided into I–V groups. The cation solutions were analysed qualitatively for different groups by circular thin-layer chromatography. About 1μl of the group solution was applied on the thin adsorbent layer and the spot was dried with the help of hot air blower. The developing chamber with the specific solvent (Table 3) in it was placed on the spot and then developed by irrigating pipette, with the same solvent as one in the developing chamber. The developed plate was sprayed with the chromogenic reagent of that group, and the coloured rings thus developed presented the analysis of that group. The cations were identified by the colour and R_f value of different rings. All the groups were analysed in this way and the results are summed up in Table 4.

(b) *Emission Spectrographic Analysis*

Hilger medium quartz spectrograph was used for spectrographic analysis. Graphite electrodes of the arc system were cleaned and the arc was struck by applying electric potential to the electrodes. After necessary alignment of optical and recording system, the spectrum of the arc of electrodes was recorded on a photographic plate.

The experiment was repeated with another set of graphite electrodes, lower one carrying the mineral sample and recording the emission spectra of each mineral on a photographic plate. Analysis

TABLE 1.—SOLVENT EXTRACTION SCHEME OF CATIONS.*



Test soln (0.5 ml)+conc. HCl to 7M final concentration. Extracted with isobutyl methyl ketone and amly acetate (2:1). Chlorides of certain metals get precipitated. Such cations cannot be included in the scheme.**

Aqueous layer; added 5–6 drops of 7M NH_4SCN and extracted with 3 ml of diethyl ether

Organic layer
Group I: Fe^{+3}, Au^{+3}, Mo^{+6}, V^{+5}, Ga^{+3}, Sb^{+5}, As^{+3}, Te^{+4}, Ge^{+4}

Aqueous layer, added 3 ml of acetylacetone
Organic layer is separated after 3-min shaking

Organic layer
Group II: Pd^{+2},Pt^{+4},Co^{+2},Zn^{+2}, Sn^{+4}

Aqueous layer, pH adjusted to about 4.5 and extraction with acetylacetone repeated

Organic layer
Group III: Cu^{+2},Ru^{+3},U^{+6},Ti^{+4},Zr^{+4},Cr^{+3},La^{+3},Al^{+3}

Organic layer
added to Group III extraction

Aqueous layer,
added 2% diethyl dithiocarbamate, sodium salt, in excess and extracted with 3ml of diethyl ether

Aqueous layer
Group V: Sr^{+2},Ba^{+2},Th^{+4},Ce^{+3},Mg^{+2}, K^{+},Rb^{+},Cs^{+},Li^{+},Ca^{+2}

Organic layer
Group IV: Hg^{+2},Cd^{+2},Bi^{+3},Pb^{+2},Se^{+2}, Rh^{+2},Ni^{+2},Mn^{+2}

*The individual metal ions present in each group are given in Groups I—V.

. These include **Ag+, Hg+, Pb+,W^{+6} and traces Tl+. Traces of Pb, remains can be analysed.

TABLE 2.—SPRAY REAGENTS FOR THE LOCATION OF CATIONS.

Reagents	Solutions	Group	Elements detected	Colour	Remarks
1	2	3	4	5	6
Alizarine	Saturated soln. in 96% ethanol	III	Zr^{+4} U^{+6}	violet violet	on silica gel plate
		V	Th^{+4} Ce^{+3} Mg^{+2}	blue-violet blue-violet violet	
			Mg^{+2} Ca^{+2} Th^{+4} Ce^{+3}	red-violet blue-violet blue-violet blue-violet	on silica plate
Dimethylglyoxime	1% in 96% ethanol	IV	Ni^{+2} Mn^{+2}	red brown-yellow	after spray exposure to NH_3 vapours for 15 min.

(*Continued*)

(*Table 2 continued*)

1	2	3	4	5	6
Dithizone	2% in chloroform	I	Ga^{+3}	red-orange	heated after spray
			As^{+5}	red-orange	
Phenyl fluorone	0.05% in a mixture of 96% ethanol and conc. HCl (3:1)	I	Ge^{+4}	red	
Potassium ferrocynide	5% aqueous	II	Cu^{+2}	reddish-brown	
		III	U^{+6}	brown	
			Ti^{+4}	yellow	
Quinalizarine	0.05% in 70% ethanol	III	La^{+3}	violet	on silica gel plate
			Al^{+3}	violet	
Rubeanic acid	0.5% in ethanol	II	Pd^{+2}	yellow-brown	
			Pt^{+4}	reddish-purple	
			Co^{+2}	dark-brown	
		III	Cu^{+}	reddish-brown	
			Ru^{+3}	blue	
Rhodizonic acid, sodium salt	1% aqueous, freshly prepared	V	Sr^{+2}	red	on silica plate
			Ba^{+2}	red	
Sodium sulphide	2% aqueous	IV	Hg^{+2}	tan to black	
			Cd^{+2}	Yellow	
			Bi^{+3}	dark-brown	
			Pb^{+2}	brown	
Sodium cobaltinitrite	Cobaltinitrite* (3 parts) mixed with 1 part of methanol	V	K^{+}	yellow	
			Rb^{+}	blackish-brown	
			Cs^{+}	orange-brown	
Silver nitrate–fluorescein	1% soln. of $AgNO_3$ in water, after short drying followed by 0.1% fluorescein in alcohol	V	Li^{+}	dark-brown	
Stannous chloride–potassium iodide	Dissolve 5g. $SnCl_2$ in 10ml conc. HCl, and dilute to 100 ml with addition of 0.5g KI	I	Au^{+3}	grey to black	
			Te^{+4}	dark-brown	
		IV	Hg^{+2}	Tan	
			Se^{+2}	red	
			Rh^{+2}	yellow	

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*Cobalt acetate $(CH_3COO)_2Co.4H_2O$ (11.0g), lead acetate $(CH_3COO)_2Pb.3H_2O$(16.2g), sodium nitrite (20 g) and glacial acetic acid (2ml) are mixed and the soln is made to 150 ml with water, centrifuged and filtered.

(*Table 2 continued*)

(*Table 2 continued*)

1	2	3		4	5
Peroxide–benzidine	Spray with 5% soln of Na_2O_2 in water followed by 1% soln benzidine in glacial acid	III	Cr^{+3}	dark-blue	Exposure to NH_3 vapours
		IV	Mn^{+2}	blue	
Taninc acid	10% in water	I	Fe^{+5} Au^{+3} Mo^{+6} V^{+5}	dull -violet grey-black dark-yellow dark-blue	Heat slightly
Diphenyl carbazide	1% in 96% ethanol	II	Co^{+2} Zn^{+2} Sn^{+2}	red-violet red-violet violet	

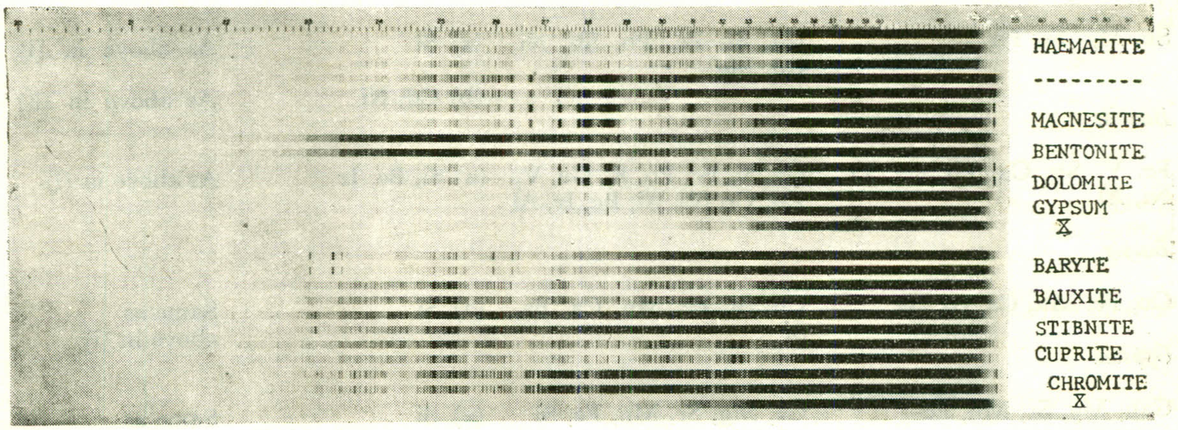

Fig. 1.—Spectrum analysis of minerals.

TABLE 3.—SOLVENTS FOR SEPARATION CATIONS.

Solvent	Composition	Group
A	Acetone, hydrochloric acid (4M) acetylacetone (9.0:0.6:0.4)	I, II
B	Acetone, hydrochloric acid (4M) (9.4:0.6)	
C	Acetone, hydrochloric acid (4M), acetylacetone (9.6:0.3:0.1)	IV
D	Acetone, hydrochloric acid (4M) (9.2:0.8)	V
E	Acetone, hydrochloric acid conc. (9.4:0.6)	V

of each mineral was carried out twice. The results of the ten minerals are shown in Fig. 1. Strips marked X are blank exposures of electrode arc material. The wavelength scale appears on the top of the strip.

The line spectra of each mineral was read with the help of Hilger Spectrum Projector and the principal lines of the spectrum were read with the help of standard tables of different elements. The detected elements are given in Table 4.

Results and Discussion

The results of circular thin-layer chromatographic analysis and spectrographic analysis are presented in Table 4 for comparison. The third column of the table presents metals which were

TABLE 4.—COMPARISON OF RESULTS OF CIRCULAR THIN-LAYER CHROMATOGRAPHY AND SPECTROGRAPHIC ANALYSIS OF MINERALS.

Circular TLC analysis	Spectrographic analyses	Cations which could not be found by circular TLC	Remarks
Chromite			
Fe, Cr, Mn, Ca, Mg, Pb, V, Ti, Al, Ni, Co, Sb, Sn, Mo, Zr, Ge, As	Fe, Cr, Mn, Ca, Mg, Pb, V, Ti, Ni, Co, Al, Sr, Na, K, Si, Ir, Ru, Rh, Mo, Sb, Sn, As, Zr, Ce, Ge, W, Ag	(a) Si, Na, Ir, Be, W, Ag. (b) Rh, Ce, Sr, K, Ru	(i) (a) are not included in the scheme (ii) (b) are present below their detectable concentration
Cuprite			
Cu, Mg, Fe, Mn, Pb, Zr, V, Sb, Sn, Co, Ni, Ge, Ca, Cr, Rh, Ce, K, Sr	Cu, Si, Mg, Fe, Mn, Na, K, Pb, Zr, Rh, Ce, Sr, Ag, V, Cr, Sb, Sn, Co, Ni, Ca, Ge, Ir	(a) Si, Na, Ir, Ag	Same as above in (i)
Stibinite			
Sb, Mg, Fe, Pb	Cu, Si, Fe, Pb, Sb, Ni, Cd, Mg	(a) Si	As above in (i)
		(b) Cd, Ni	As above in (ii)
Bauxite			
Fe, V, Sb, Cu, Pb, Ge, Zn, Ni, Al	Cu, Si, Fe, Pb, K, Ge, V, Zn, Cr, Sb, Ni, Be, Ir, Al	(a) Si, Be, Ir	As above in (i)
Baryte			
Cu, Fe, Mn, Ca, Ba, Sr	Cu, Si, Fe, Mn, Ca, Ba, Sr	(a) Si	Same as above in (i)
Gypsum			
Can, Mg, Sr, Mn, Fe	Ca, Mg, Sr, Mn, Fe, Si	(a) Si	Same as above in (i)
Dolomite			
Ba, Ca, Sr, Mn, Fe, Mg, Pb, Zn, Sb, Bi	Ca, Sr, Mn, Fe, Si, Mg, Sb, Bi, Ba, Na, Zn, Pb, Cr	(a) Si, Na	Same as above in (ii)
		(b) Cr	Same as above in (ii)
Bentonite			
Fe, Mg, Mn, Ca, Ge, V, Sb, Sn, Bi, Ti	Si, Mg, Fe, Mn, Ca, Ti, Ge, V, Na, Pb, Cr, Sb, Sn Bi, Co, Ni	(a) Si, Na	As above in (i)
		(b) Pb, Cr, Co, Ni	As above in (ii)
Magnesite			
Ca, Sr, Mg, Fe, Cu, Bi, Sb	Cu, Si, Mg, Fe, Sr, Ca, Cr, Sb, Bi	(a) Si (b) Cr	As above in (i) As above in (ii)
Haematite			
Mn, Fe, Mg, Ca, V, Ge, Sb, Sn, Bi, Ni, Ba, Sr, Pb	Si, Mg, Fe, Mn, Cr, Sb, Sn, Bi, Ni, Ca, Ba, Sr, Na, Pb, W,V,Ge	(a) Si, W, Na	As above in (i)
		(b) Cr	As above in (ii)

not detected by the chromatographic methods. It is clear from the table that most of the cations which were not detected by circular thin-layer chromatography are those, which are not included in the solvent extraction scheme. Only few are those cations which are included in the scheme but cannot be detected due to their very low concentration in the mineral. Thus circular thin-layer chromatography can be used as a standard method of analysis for metal ions from any source. The method is easy, time saving and can be operated upon in the field. The analysis can be carried out in micro quantities.

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