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CHINA CLAY—A SORBENT FOR THIN-LAYER CHROMATOGRAPHY

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SUMMARY

China clay has been developed as a sorbent for thin-layer chromatography. It has the following characteristics:

(1) It is easier to disperse in water and has a shorter development time than equivalent silica gel systems.

(2) It is less active than silica gel and can therefore resolve certain mixtures to a greater extent than silica gel.

(3) The clay is very versatile in the number and type of mixtures it is able to separate.

(4) The interaction between sorbent and solute appears to be similar to silica gel systems.

INTRODUCTION

A number of minerals have been used as sorbents in thin-layer chromatography (TLC). These include hydroxylapatite for proteins¹, activated bleaching earth for alcohols² and talc for Digitalis glycosides³. For more general applications activated bentonite⁴ and calcined kaolinite⁵ have been used.

The present conventional sorbent for TLC is silica gel, which is a three-dimensional open network of primary particles of hydrated silica. The surface areas of silica gel can be as high as 1,000 m²/g. The adsorption depends on the polarity in the solvent of the solutes and the degree of activation of the sorbent. STRAIN⁷ and KLEIN^{8,9} describe at some length, what is known about the chromatographic process for silica gel.

HAER¹⁰ has outlined a very plausible mechanism for silica gel which probably applies to china clay. He states that the activity of a silica gel is affected by the percentage of adsorbed water. Activity is at a maximum of 4% and decreases as the active sites are blocked up to 20% water. Below 4% the activity again decreases as the hydroxyl groups responsible for the hydrogen bonding are removed. Temperatures required to do this are in excess of 1100°. The reason given is that hydroxyl groups responsible for hydrogen bonding are being driven off.

As a similar result is obtained with china clay, but with different percentages

TABLE I

ANALYSIS OF SORBENTS USED

	<i>Silica gel</i> ^a (%)	<i>China clay</i> (%)
<i>Particle size distribution</i> ^b		
> 30 micron	93	96
> 10 micron	31	24
> 5 micron	22	7
< 2 micron	16	—
< 1 micron	7	—
<i>Minerals present</i>		
Silica	87	5
Kaolin	—	57
Mica	—	22
Felspar	—	3
Calcium sulphate hemihydrate	13	13

^a The silica gel was produced by May and Baker Ltd., Dagenham, Great Britain.

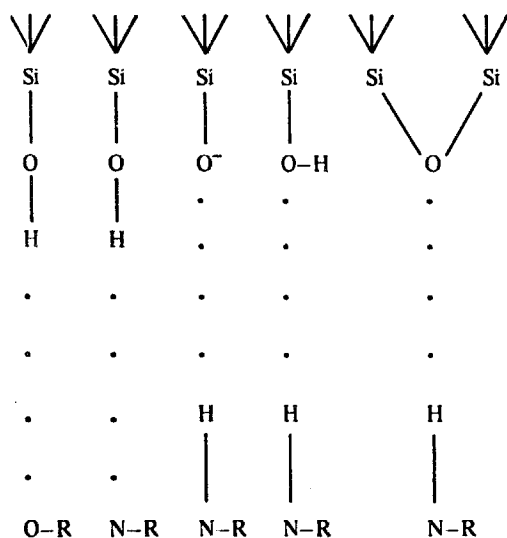
^b The distribution was determined by the ANDREASEN sedimentation method⁶.

of water, and as similar groups are available for the reaction, it is reasonable to suppose that a similar mechanism occurs.

HAER's figures are given below:

RANDERATH¹¹ states "that the adsorbents used are mainly oxides or hydrated oxides. The adsorbed substances are polar or polarisable compounds and are bound to the adsorbent by the same electrostatic forces which hold the crystal lattice together. The "active centres" consist mainly of edges, cracks, corners and defects in the surface at which there are more or less uncombined ions." Large crystals of clay are especially suitable in this respect.

Kaolin is an unsymmetrical structure with one silica and one hydrated alumina layer, combining in a single unit three oxygen layers thick. With large particles (10 μ) the crystals are stacked one on top of another (see Fig. 1). The many defects and chips can be seen. There is no room for penetration of ions or small molecules



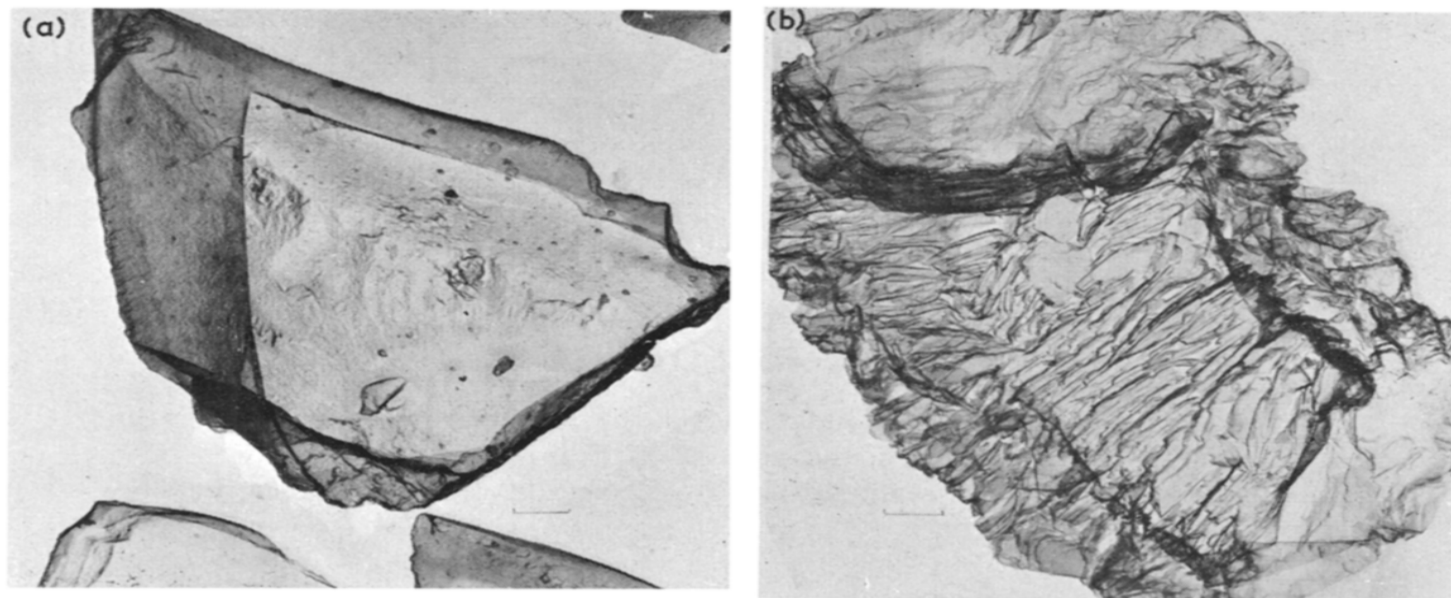


Fig. 1. Electron micrographs of (a) silica gel; (b) china clay. Scale marker = 1μ .

between the sheets, so chromatographic activity (unlike silica) must be confined to the edges.

CHARACTERISTICS OF THE CLAY LAYER

All the work done so far on china clay layers indicates that the mechanism is similar to that involved with silica gel layers. The evidence is as follows: (1) Materials separate in similar orders on clay and silica gel. (2) Similar solvent systems may be used with both sorbents. In the case of the clay, the system must have a lower eluting power to obtain similar R_F values. (3) Adsorbed water has a great effect on the activity of the plate. Calcined clay has no chromatographic activity and plates kept in the laboratory for more than a few days show a greatly reduced activity due to water blocking the active sites.

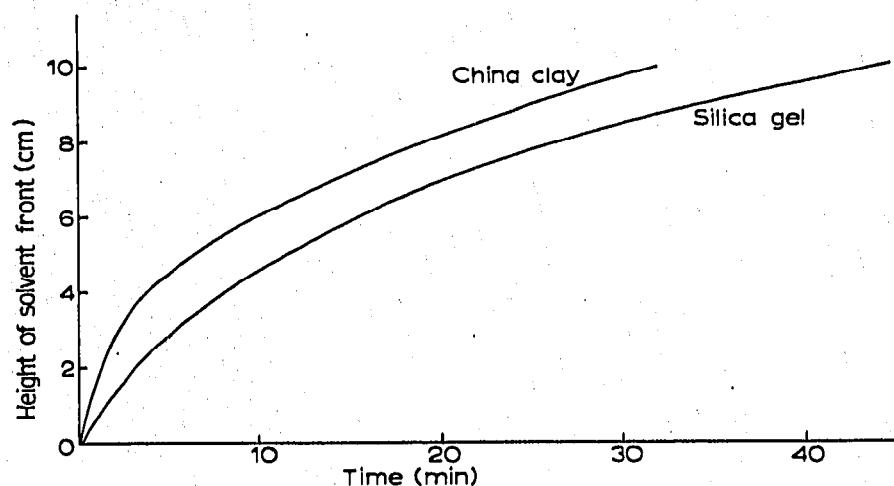


Fig. 2. Relative rates of solvent rise. Solvent: ethanol.

EXPERIMENTAL

The clay containing 13% w/w plaster of Paris was mixed with twice its weight of water (better layers can often be obtained if 4% w/w of anhydrous sodium carbonate is added to the water), using a plastic spatula in a small beaker. Mixing time was maintained at less than 2 min. After coating, the plates were allowed to dry in air before being transferred to the oven for half an hour at 80°. The plates were not activated in any way.

RESULTS

Ethanol was taken as the standard solvent in this series of experiments. Layers 400 μ thick (to overcome the thickness effect) of china clay and silica gel were used. The china clay reached the standard height of 10 cm in 30 min, whereas the silica gel took 45 min (Fig. 2).

Effect of layer thickness on rate of solvent rise

TRUTER¹² has determined the effect of thickness on the rate of solvent rise with silica gel and shown that above 250 μ any further increase in layer thickness had little or no effect. The experiment was repeated with china clay, using ethanol. All five experiments were run together in a large tank with a corresponding decrease in degree of saturation of atmosphere. Results are shown in Table II. From these

TABLE II

EFFECT OF LAYER THICKNESS ON RATE OF SOLVENT RISE

Thickness (μ)	Solvent height (cm)			
	2	5	7	10
50	3 min 0 sec	16 min	20 min	60 min
100	2 min 50 sec	15 min	29 min	45.5 min
200	2 min 40 sec	15 min	27 min	41 min
400	2 min 40 sec	15 min	27 min	43 min

results the solvent height after 40 min can be measured. They show that with layers thicker than 200 μ , there was no further increase in the rate of rise of the solvent.

Rates of rise of various solvents

The development times of thin-layer chromatograms are determined by the rate of rise of the solvent system concerned. These were measured for the following solvents of differing eluting powers: benzene, ether, chloroform and ethanol. The results were comparable to those obtained by TRUTER¹³.

The eluting powers of solvents

The lists given by TRAPPE¹⁴ for silica gel apply equally well for clay.

TABLE III

 $R_f \times 100$ VALUES OF DESAGA THREE-DYE MIXTURE

Mobile phases: (A) carbon disulphide; (B) toluene-heptane (1:1); (C) cyclohexane.

Compounds	A		B		C	
	China clay	Silica gel	China clay	Silica gel	China clay	Silica gel
Butter Yellow	92	01	80	01	85	0
Sudan Red G	50	0	40	0	39	0
Indophenol Blue	22	0	25	0	50	0

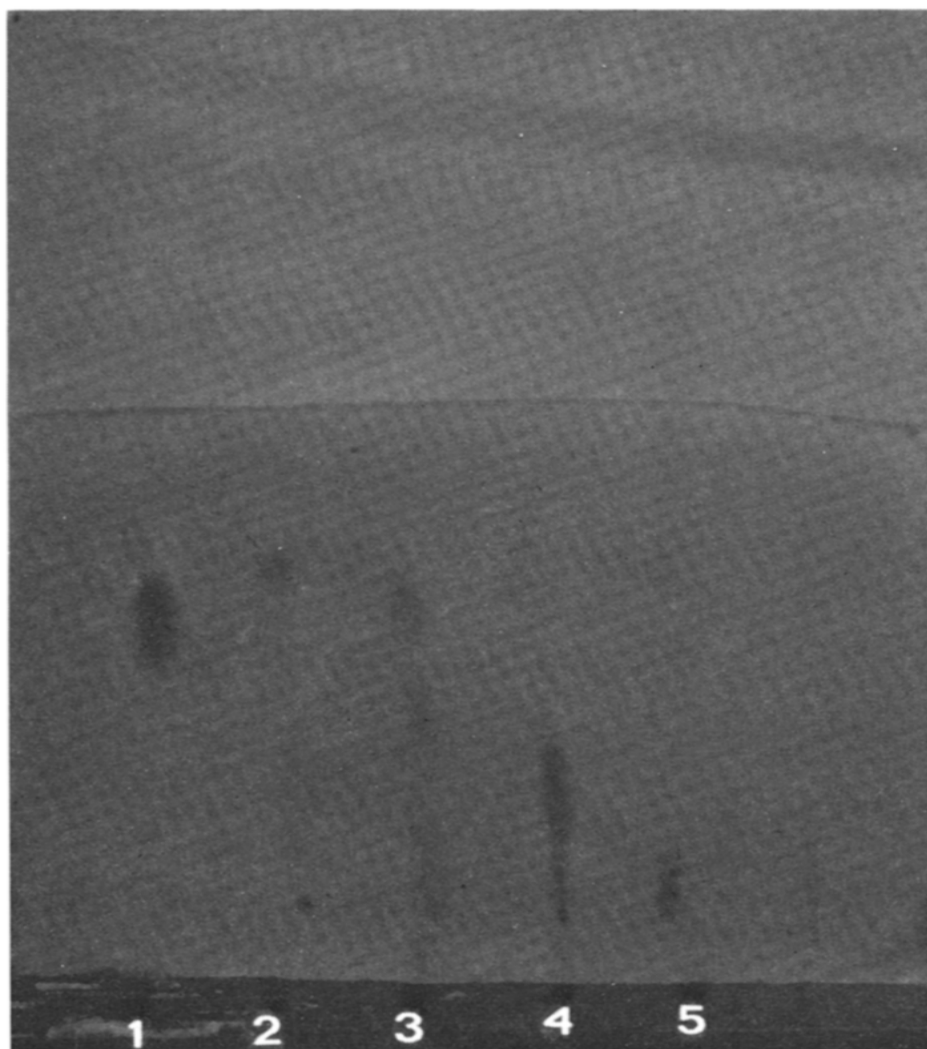


Fig. 3. Photograph of a separation on china clay. 1 = Methyl Red; 2 = Thymol Blue; 3 = B.D.H. universal indicator; 4 = Methyl Orange; 5 = Phenol Red. The spots are somewhat overloaded to aid the photographer. The solvent front was only run 6 cm.

TABLE IV

 $R_F \times 100$ VALUES OF WATER-SOLUBLE INDICATORS

Mobile phase: ethyl acetate-ethyl alcohol-ammonia (12:3:1).

Compounds	China clay	Silica gel
Phenolphthalein	97	85
Methyl Red	57	12
Cresol Red	29	—
Methyl Orange	21	10
Thymol Blue	75	20
Phenol Red	08	20

^a Universal indicator and full range indicator separated to a larger extent on clay than on silica gel.

TABLE V

 $R_F \times 100$ VALUES OF DRUGS

Mobile phase: diethyl ether-chloroform (10:1).

For detection the plate was placed in a jar containing solid iodine.

Compounds	China clay	Silica gel
Phenacetin	95	40
Paracetamol	70	25
Caffeine	45	30
Acetylsalicylic acid	20	streak

TABLE VI

 $R_F \times 100$ VALUES OF AMINO ACIDS

Mobile phases: (A) chloroform-ethanol-ammonia-water (20:20:5:2); (B) butanol-acetic acid-water (4:1:1). The solvents were used in a satisfactory two-way separation.

Detection: ninhydrin followed by 5% polyvinyl alcohol solution; plates heated to 100° after each application.

Compounds	A		B	
	China clay	Silica gel	China clay	Silica gel
Glycine	25	33	23	18
Alanine	45	43	40	22
Proline	55	33	40	14
Cysteine	25	40	10	09
Leucine	80	60	60	44
Tryptophan	90	66	50	47

TABLE VII

 $R_F \times 100$ VALUES OF SUGARS

Mobile phase: isopropanol-ethyl acetate-water (14:4:1.5).

Detection: 0.5% KMnO_4 dissolved in 0.1 N NaOH ; plate heated at 100° for 2 min to give pale yellow spots.

Compounds	China clay	Silica gel
Glucose	80	63
Sucrose	75	63
Fructose	60	63
Lactose	25	50

TABLE VIII

 $R_F \times 100$ VALUES OF PHENOLS

Mobile phase: heptane-dioxane-glacial acetic acid (45:12:2).

Detection: 0.1 N KMnO_4 dissolved in 0.1 N Na_2CO_3 . Pale yellow spots.

Compounds	China clay	Silica gel
Phenol	90	25
Catechol	70	5
Resorcinol	60	0
Pyrogallol	40	0
Gallic acid	10	0

TABLE IX

 $R_F \times 100$ VALUES OF INDOLE DERIVATIVES

Mobile phase: cyclohexane-carbon tetrachloride-glacial acetic acid (10:10:1).

The slide was placed in a jar containing solid iodine.

Compounds	China clay	Silica gel
Indole	95	20
Anthranilic acid	80	10
Isatin	30	5
Tryptophan	0	0

Examples of separations

(a) *Desaga three-dye mixture, solvent benzene* (Table III). 4% sodium carbonate was incorporated into the clay layer.

(b) *Water-soluble indicators* (Table IV and Fig. 3). The individual dyes were dissolved in a small quantity of alcohol; 4% sodium carbonate was incorporated in the clay layer.

(c) *Drugs*. See Table V.

(d) *Amino acids* (Table VI). Every component of the system has to be fresh to obtain a satisfactory separation of amino acids. The amino acids were dissolved in water containing 10% isopropanol; 3 mg were dissolved in 5 ml of solvent. The atmosphere above the plates had to be saturated with vapour and this was done by lining the tank with filter paper before starting the experiment. The polyvinyl alcohol spray helps to intensify the spots which are best seen by transmitted light.

(e) *Sugars* (see Table VII).

(f) *Phenols* (Table VIII). Phenols must be dissolved in freshly prepared distilled water to prevent oxidation. Even so, the samples should be run as soon as they have dissolved.

(g) *Indole derivatives* (Table IX). As with phenols the solutions must be used when fresh.

CONCLUSIONS

China clay seems to be a useful addition to the range of sorbents suitable for TLC. Separations can be obtained quickly and R_F values are reproducible.

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