

The Porestructure and Texture of a Fluka Chromatographic Alumina Gel.

M.AFZAL AND M.KHAN

*Department of Chemistry,
Quaid-i-Azam University, Islamabad, Pakistan.*

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Summary: The porous nature of Fluka Chromatographic alumina gel 5016 A, has been investigated by adsorption/condensation processes and electron microscopy. The gel is very porous having 63% porosity. Its free water content at 150°C was found to be 2.28% and bound water content at 1000°C was 3.66%. The total pore volume as determined by fluid displacement method is $0.497 \text{ cm}^3 \text{ g}^{-1}$. Its specific surface area as determined by water vapour adsorption is $236 \text{ m}^2 \text{ g}^{-1}$. The greater portion of the surface area and pore volume occurs in small and transitional pores, with average pore radii (hydraulic) of 21 \AA . Heat treatment does not harm the physical structure of the system if the temperature is below 800°C. The surface area and pore volume are lower in comparison with the silica gel ($383 \text{ m}^2 \text{ g}^{-1}$ and $0.62 \text{ cm}^3 \text{ g}^{-1}$) investigated earlier.

Introduction

Alumina gels are widely used for adsorption and catalytic processes. They are used commercially in adsorption chromatography. Pore structure plays an important role in this operation [1-5]. In physical adsorption, especially at higher relative pressure, the behaviour and amount of adsorbate to be adsorbed depends upon the pore structure; hence the adsorption is directly related to the size and shape of the pores, in addition to other factors. The physical nature of the system has been studied by adsorbing various adsorbates and by S.E. Microscopy. The structure of these gels is not simple and the adsorption isotherms could not accurately be interpreted by the Kelvin equation (cylindrical pore model). Therefore the results presented in this paper are analysed through a modelless method originally introduced by Kieselve [6].

Experimental:

The alumina gel used is whitish in colour and is manufactured by Fluka AG, Chemische Fabrik CH. 9470 Buchs; it is designated as Aluminum Oxide Fluka basic type 5016 A, for chromatography. All the reagents used were of high quality analytical grade. Glacial acetic acid (M.Wt. 60.05, Density = 1.06 g cm^{-3}) was manufactured by Merk. Resublimed iodine was manufactured by Bandoengsche Kminefabriex, Holland N.V. Maarsse.

Determination of free water, bound water and densities was carried out as described earlier [7], except that the bound water was determined in covered crucibles to avoid spurring of the fine powder, at temperature $>400^\circ\text{C}$. For all experimental observations, the gel was heated at 500°C

for 1 hour and cooled in a desiccator.

The total pore volume was determined from the geometrical and true volumes. The specific surface area was calculated from the water vapour adsorption isotherm (at 298 K.)

Iodine was adsorbed at 301 K from different concentrations of iodine in potassium iodide aqueous solution in 1:11 (12/K1) ratio. The solutions were kept in dark for 45 hours.

Glacial acetic acid was adsorbed at 305 K from different aqueous concentrations.

The mercury density was determined using a mercury pycnometer.

For electron microscopy the sample was sprayed onto double-sided adhesive Cellotape, which was fixed on a circular sample disk. It was then adjusted in the holder, evacuated and rotated in such a way that it could be properly scanned by electrons from the electron gun. Micrographs were taken by a polaroid camera at 50X magnification, under the mini scan Hitachi Akashi electron microscope at the Biology department, Quaid-i-Azam University.

Bulk densities and dehydration experiments were performed in the usual way.

Density drifts were measured after 15 and 24 hours.

Results and Discussion:

The specific surface area was calculated from the water adsorption isotherm (Fig.1) with the help of Kieselev's equation

$$S = \frac{1}{\gamma} \int_{a_s}^{a_h} \frac{RT \ln P/P_0}{da}$$

The terminology is the same as given in our earlier paper [7]. The surface area comes out to be $236 \text{ m}^2 \text{ g}^{-1}$ and the result is given in table-1. The isotherm is a type IV of BDDT classification [8]. It has an prominent inflexion point at low pressure, leading to a confusion in locating point "B", hence the monolayer amount was not detectable. Therefore BET method was not applied. The type IV isotherm is initially a type II, which becomes modified at high pressure where the adsorption is effected by pore sizes, representing internal surface area of the system. Kieselev's method is a better technique for surface area determination of porous structures with any pore shape.

Iodine adsorption gives a clear type II isotherm (Fig.2) of BDDT classification. The type II isotherm is generally obtained for adsorption on non porous solids or solids with only external surface area. The specific surface area from iodine adsorption was found to be $186 \text{ m}^2 \text{ g}^{-1}$, calculated as below:

Point "B" was located on the isotherm, and used to calculate the mono-layer amount. It is 186 mg g^{-1} of gel, and was incorporated in the following formula to get the surface area.

$$SS = \frac{X_m}{M} \times N \times AM$$

Where

SS = Specific surface area.
 X_m = Amount of iodine in g adsorbed per g of gel.
 M = Molecular weight of iodine.
 N = Avagadro's number.
 AM = Cross-sectional area of an adsorbed iodine molecule.

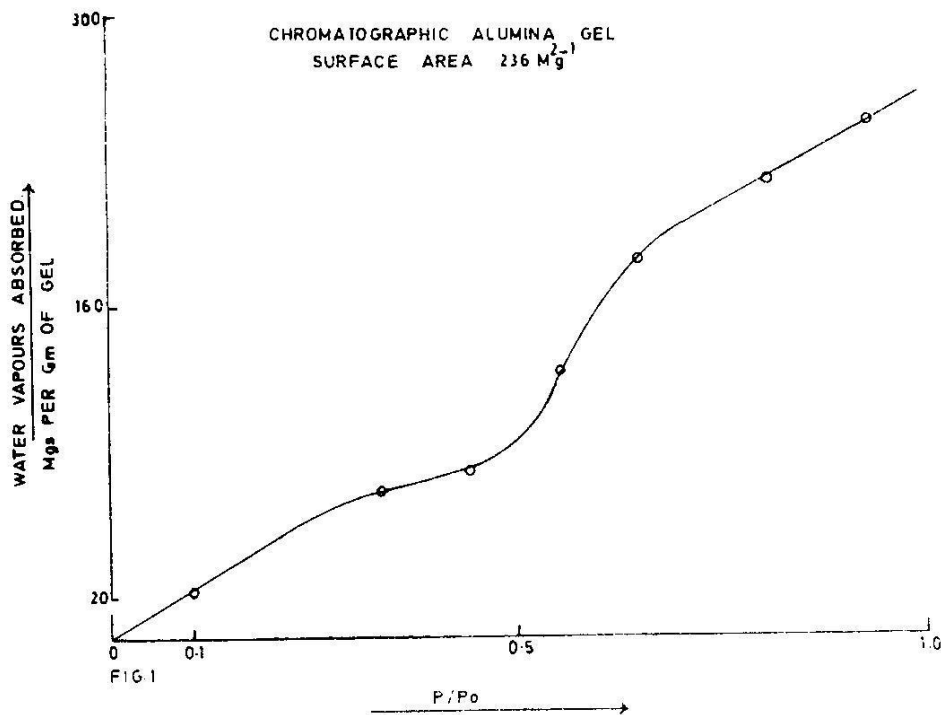
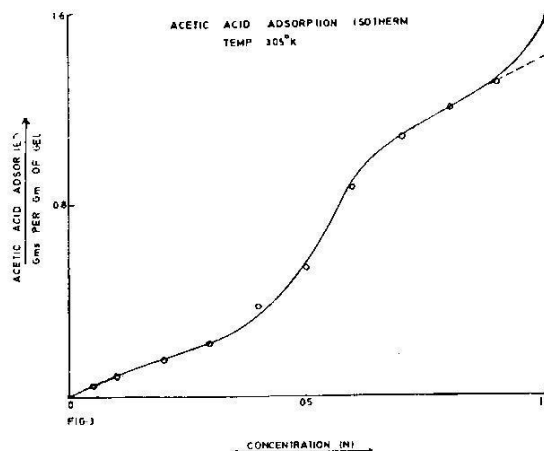
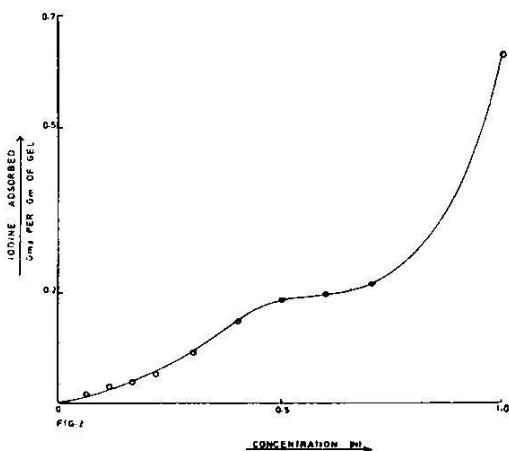


Table-1: Experimental values of the physical parameters of the alumina gel.

S.No.	Parameter	Value
1.	Free Water (150°C)	2.28%
2.	Bound Water (1000°C)	3.66%
3.	True density (Boiling water)	3.38 g cm^{-3}
4.	Specific Surface area (Water)	$236 \text{ m}^2 \text{ g}^{-1}$
5.	Specific Surface area (Iodine)	$186 \text{ m}^2 \text{ g}^{-1}$
6.	Total Pore vol	$0.497 \text{ cm}^3 \text{ g}^{-1}$
7.	Micropore vol	$0.262 \text{ cm}^3 \text{ g}^{-1}$
8.	Macropore/Transitional	$0.235 \text{ cm}^3 \text{ g}^{-1}$
9.	Average Pore radius	21 \AA
10.	Total Pore length	$8.92 \times 10^{11} \text{ cm g}^{-1}$
11.	Bulk Density (Loose)	0.92 g cm^{-3}
12.	Bulk Density (Packed)	0.996 g cm^{-3}
13.	Porosity	63%



The iodine surface area is lower than the surface area determined by water vapours. This can be explained on the basis of different packing arrangements of different molecules on the adsorbent surface. Alternatively, the size of iodine molecules (cross sectional area = 40 \AA^2) may hinder their entry into the pores whereas the water molecules (cross sectional area = 10.8 \AA^2) can easily go in.

Acetic acid adsorption gives a mixed type III and V isotherm (Fig.3) on the BDDT classification. This type of isotherm cannot be used for surface area estimation because it is difficult to find out when the monomolecular layer is completed. Initially the isotherm is a type III but tends to be type V in the intermediate concentration range. At higher concentrations it again becomes a type III, where it approaches the saturation line asymptotically. This suggests that both internal and external surface areas exist in the system. The existence of external surface area can be inferred from the iodine and acetic acid adsorption isotherms (Fig.2 & 3), where the internal surface area in the given alumina gel is formed by intimate contact (packing) of the

powder particles. This packing is not disturbed in the case of water vapour adsorption - which shows capillary condensation at high pressure, representing internal surface area. In the case of iodine and acetic acid adsorption, the gel is brought in contact with the solution and the fine particles are dispersed throughout the liquid medium. Therefore iodine and acetic acid are mostly adsorbed at the available surface of the individual particles. Moreover the large size of iodine molecules (cross sectional area = 40 \AA^2) may hinder their entry into the pores, so that they adsorb largely on the available external surface. The iodine and acetic acid isotherms turn upwards because of bulk condensation on the external surface area. The iodine surface area is therefore lower than the water surface area.

The total pore volumes were calculated by the density method and the results are given in table-1. Micropore volume was obtained from the water vapour isotherm by applying Gurvitsch's rule. Macropore volume was obtained by subtraction. The average pore radius was calculated to be 21 \AA . The pore size distribution

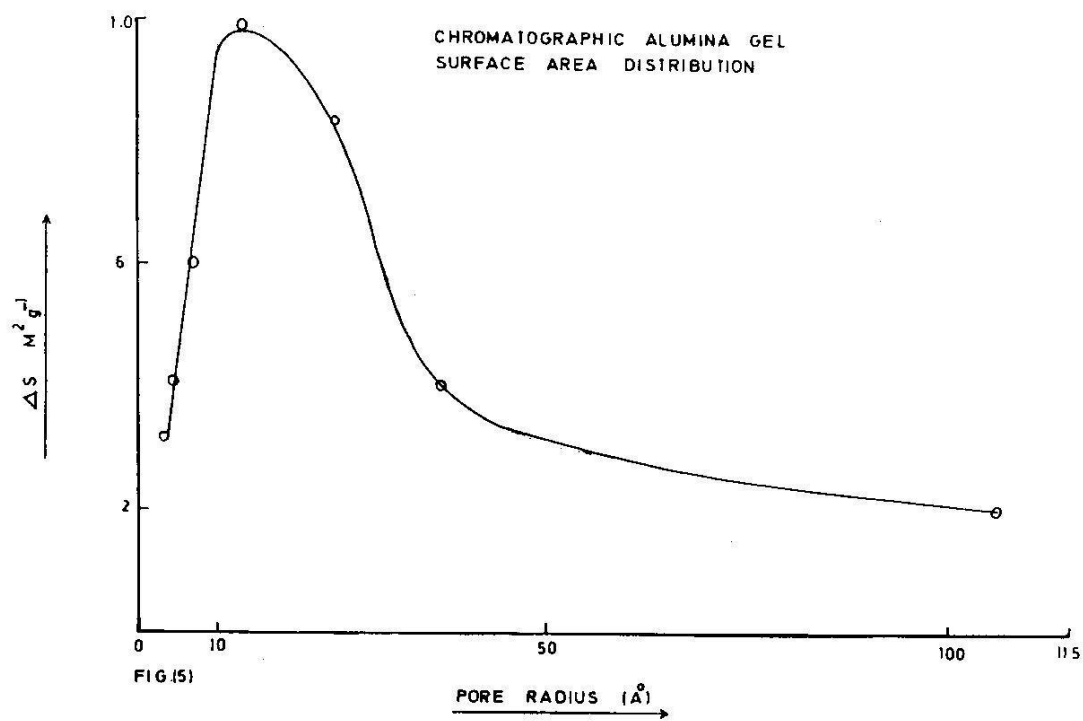
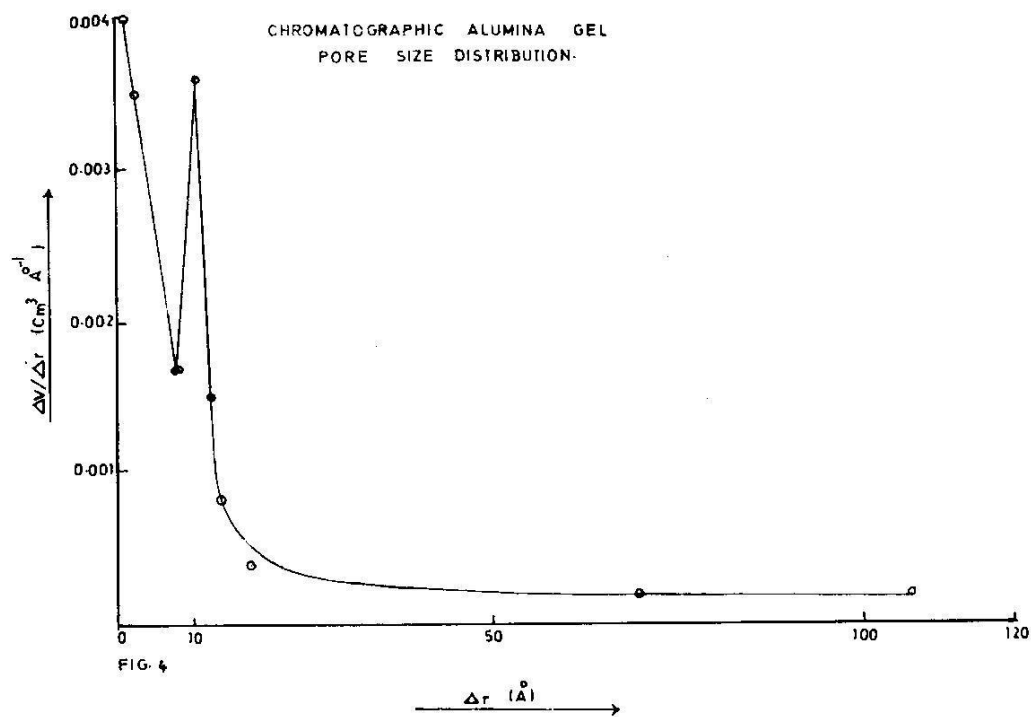




Fig.6-a: S.E. micrograph showing the size and shape (structure) of the alumina gel, at 50 x magnification.

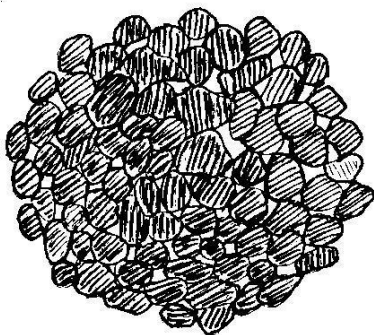


Fig.6-b: S.E. micrograph interpretation showing arrangement of the gel particles at 50 x magnification.

- Dashed area is occupied by the particles.
- Blank area gives rise to voids.

(Fig.4) and the surface area distribution (Fig.5) were obtained by analysis of the water vapour isotherm (Fig.1).

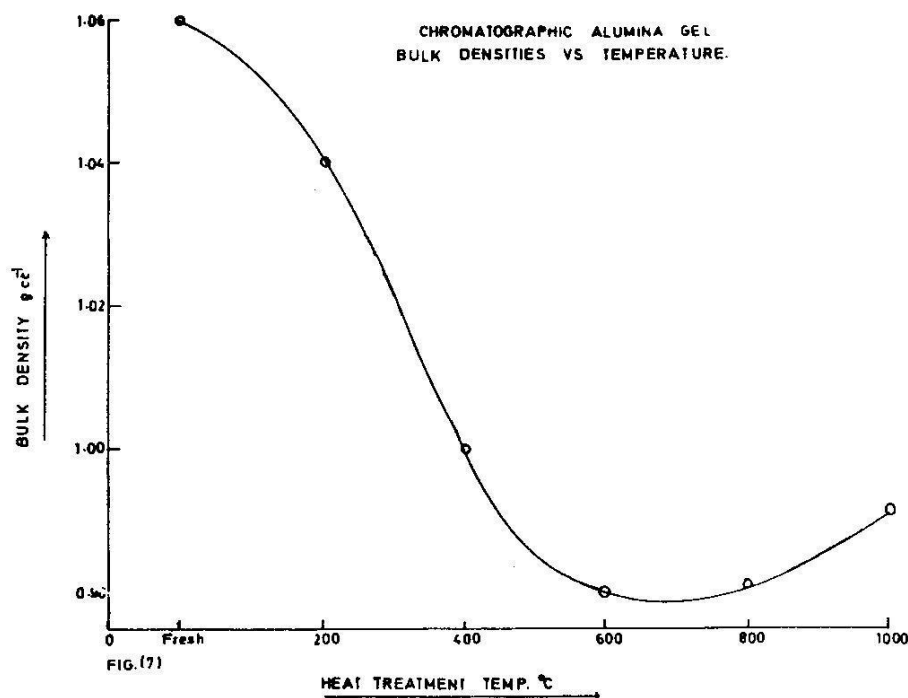
These results show that a large portion of the pores have radii $\leq 24 \text{ \AA}$, which contained major part of the specific surface area. The high porosity (63%) of the gel is explained as being the percent void volume out of the total geometrical volume. Here the geometrical volume (0.7936 cm^3) is large enough in comparison with the true volume (0.2958 cm^3) resulting in a high ratio of the void volume to the geometrical volume - thus giving high porosity.

Density drifts were measured in order to obtain some deep insight into the structural system. The first density reading was taken after 10 minutes followed by readings after 15 and 24 hours. The experiment was performed in order to understand the diffusion of water and mercury into the interior of the capillaries. The results are given in table-II. The drifts seem to be the results of one or all of the following reasons [9].

The structural units of the gel might have been pushed together by contact with liquid. The solid surface

Table-II: Density readings taken after 10 mins., 15 hour and 24 hours to show density drifts. The corresponding physical properties of the gel are also shown.

Time	Mercury Density g cm^{-3}	Water Density g cm^{-3}	Pore Vol g cm^{-3}	Porosity %
1. 10 Minutes	1.262	3.38	0.497	63
2. After 15 Hours	1.39	3.80	0.456	63
3. After 24 Hours	1.63	3.86	0.354	58



might have been deformed or the concerned fluids may have penetrated into the texture with the passage of time.

Our electron micrograph (Fig.6/a) is a bit dim and pictured manually in (Fig.6/b). Micrographs indicate that the gel particles are roughly spherical, arranged in a disorderly way to leave relatively large voids.

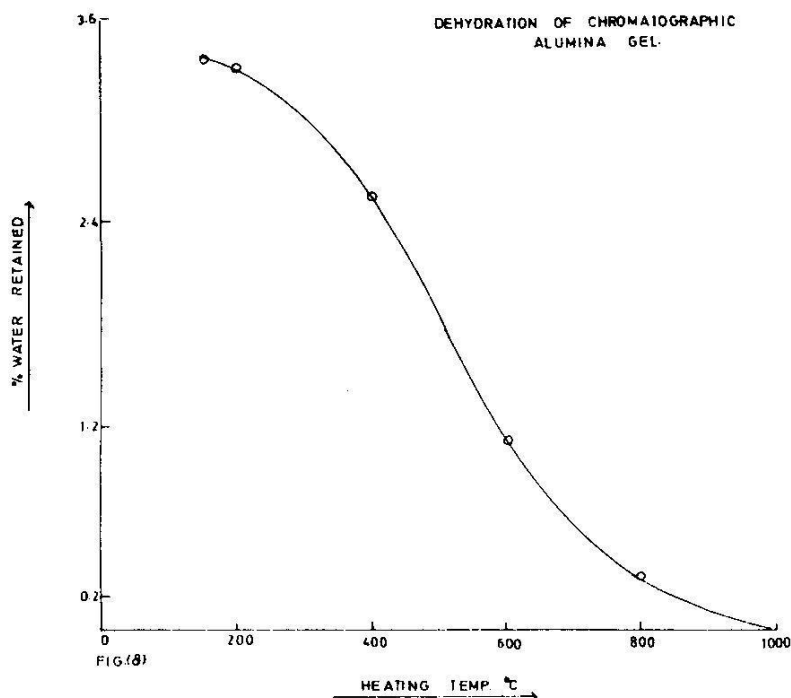
Heat effect on the system was examined in terms of bulk densities and the dehydration process. The bulk densities decrease showing that water is removed with no appreciable change in the physical structure during the course of the heat treatment. However at high temperature (800°C) the grains shrink. The heat effect (below 800°C) on the gel is not harmful. Further it is substantiated by the dehydration curve (Fig.8) with a small slope.

The removal of textural water might have been effected by the covered crucible method, but when the experiments were repeated in the open crucibles at a temperature which would not spurt the powder (e.g. 400°C), the results were nearly the same. Therefore it is reasonable to say that the structural water in alumina gel is lower in quantity if compared with silica and alumina gel is comparatively heat resistant.

Conclusion:

Electron micrographs (Fig.6/a,b) show that the gel particles are roughly spherical indicating no regular order of arrangement. The gel has a large pore structure with an average pore radius of 21 Å. The system has a relatively large void volume with 63% porosity.

Cumulative interpretation of all the isotherms (Fig.1,2 & 3) suggest



that the chromatographic alumina gel is more or less porous with a greater portion of external surface area. This is true for powders. Most of the surface area and pore volume occur in the transitional/small pores.

Bulk densities in the temperature range 200-1000°C, indicate that the structural system is comparatively heat resistant.

The structural units of the gel might have been pushed together by contact with the liquid. The solid surface might have been deformed or most probably the density changes recorded are due to the time-dependent penetration of liquid into alumina. All these phenomena might reduce the free surface energy by adsorption.

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