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### THE STRUCTURE OF PHOSPHATE ROCK

#### STUDY OF THE SILICIC ACID CONTENT

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In the course of our investigations into the structure of phosphate rock, reported by us once before on the occasion of the ISMA Technical Conference in Madrid (1), we also gave some attention to the silicic acid content of the phosphate. The cause of this study was the wish to find an answer to the following problems:

- 1) Practical experience has shown that for the production of superphosphate, Florida land-ponce phosphate today generally has to be ground much finer than before and that suitability for acidulation may vary considerably from lot to lot. This behaviour of the ponce phosphate is obviously connected with the fact that with advancing refinement of processing techniques in Florida an increasing proportion of very fine phosphate particles is recovered from the matrix. This proportion of fine flotation concentrate differs from mine to mine and fluctuates between the limits of 60 to 90%. It is greater in the high grades than in the low ones. According to one theory the need for grinding the fine flotation material especially fine is due to a silica coating of the phosphate grains, and this silica coating has to be destroyed by grinding before a successful acidulation with sulphuric acid can take place.
- 2) Fluorine evolution in the course of superphosphate production has already been the subject of several reports (2,3,4). Under practical working conditions generally only a proportion of 20 to 35%, according to the type of phosphate rock, of the fluorine contained in the rock is volatilized. Whynes and Dee (2) confirm that the fluorine evolution takes place quantitatively in the form of  $\text{SiF}_4$ , which means that the hydrofluoric acid produced primarily during the decomposition of fluorapatite reacts in the first place with

silicic acid to form  $\text{SiF}_4$ . They found that the evolution of fluorine is not improved through the addition of finely ground sand, or even of precipitated silica. The same was found by Delomenie (3) for quartz and kiessolguhr. From this behaviour of silicic acid he concluded: "It must therefore be allowed that the silicate content of the natural phosphates and above all, the type of silicates they contain have a great influence on the formation of silicon fluoride. The silicon fluoride and its derivative, fluosilicic acid, seems to be mainly derived from certain natural silicates in the rock which are easily acidulated, and the acidulation of these silicates by sulphuric acid is helped by the hydrofluoric acid resulting from the acidulation of the calcium fluoride." - Such silicates occur above all as clays (montmorillonite) and feldspar. But there is also the possibility that certain amounts of silica may be part of the crystal lattice itself. Attention is drawn in this connection to the wide field of thermally produced silicophosphates in whose crystal lattice the  $\text{PO}_4^{3-}$  ion can largely be substituted by  $\text{SiO}_4^{4-}$  ion.

In order to clarify the problems indicated we endeavoured to develop an as exact as possible method for the determination of the quartz content of phosphate rock in order to be able to differentiate between "Quartz- $\text{SiO}_2$ " and "Silicate- $\text{SiO}_2$ ". By applying this method to various sieve fractions of the rock phosphate in ground and unground state it was tried to prove the presence of a silica coating of the surface.

The investigations have so far only been carried out on two types of phosphate rock: the bulk was pebble phosphate whilst as a reference material Taiba phosphate was used. The latter seemed particularly suitable for the following reasons:

- a) Like pebble phosphate it is of sedimentary origin but differs from it through the ease with which it can be ground and acidulated.
- b) It is by comparison with similar phosphates particularly pure. As a result no interference through by-products (gang, matrix) need be expected.

#### Complete analysis

For the investigation one fairly large sample of each of the two rock phosphates was taken from store. The complete analysis gave the following results:

T A B L E I

	Type of rock phosphate	
	<u>pebble</u>	<u>Taiba</u>
P <sub>2</sub> O <sub>5</sub>	34.92%	37.46%
CO <sub>2</sub>	2.22%	1.55%
F	3.84%	4.15%
SiO <sub>2</sub>	6.25%	2.98%
SO <sub>3</sub>	0.64%	0.08%
CaO	48.38%	50.97%
MgO	0.08%	-
Fe <sub>2</sub> O <sub>3</sub>	1.09%	0.97%
Al <sub>2</sub> O <sub>3</sub>	0.99%	0.78%
K <sub>2</sub> O	0.11%	0.06%
Na <sub>2</sub> O	0.33%	0.12%
Acid insoluble residue (excl. SiO <sub>2</sub> )	0.46%	0.40%
H <sub>2</sub> O (moisture)	0.29%	0.23%
Loss on ignition (excl. H <sub>2</sub> O + CO <sub>2</sub> )	2.37%	1.40%
	<u>101.97%</u>	<u>101.15%</u>
-C for F	1.62%	1.75%
	<u>100.35%</u>	<u>99.40%</u>

The pebble phosphate contains app. 88%, the Taiba phosphate 94% of fluorcarbonate apatite. It is a remarkable fact that in spite of its lower carbonate content Taiba phosphate can be more readily acidulated than pebble phosphate. It seems to us that this too is an indication that the silica content which is nearly double in pebble phosphate is connected with the ease of acidulation.

Examination of grain fractions

The uncrushed phosphate samples were each divided into 9 grain fractions, above 50 $\mu$  through dry screening on the screening machine and below 50 $\mu$  through elutriation in 1/100 n ammonia solution. An average sample of each grain fraction was finely ground and its total silicic acid content determined by the boric acid/hydrochloric acid method. Quartz determinations were carried out on the ground, as well as on the unground grain fractions. We used for this purpose the X-ray

method mentioned both by Delomenie (3) and Fauvargue (5). Since some difficulties had here to be overcome we shall describe our working method in some detail.

### Quartz analysis by X-ray diffraction

#### 1. Method

For the analysis a Philips-diffractometer with recording Geiger counter was used. Cu-K $\alpha$ -radiation was applied. The difficulties in the X-ray analysis consisted in the preparation including pulverization of the material. In order to accomplish some degree of accuracy in the analysis a certain grain size which depends on the absorption of the material under test must not be exceeded. Otherwise there is no guarantee that the number of particles in reflecting position on the surface of the specimen corresponds to the average for the specimen. Excessive grain sizes lead to fluctuations in the interference intensity from one specimen to the next. Alexander, Klug and Kummer (6) stipulated for their Geiger counter and for plane specimen surface, similar to the one used by ourselves, with a permissible mean error of 1%, a permissible upper limit for quartz crystallites of app.  $5\mu$ . Von Engelhardt (7) calculated for the absolute analysis of quartz a permissible maximum grain size of app.  $1\mu$ . We have attempted to fit our specimens into the order of magnitude of  $1\mu$ . A series of Taiba phosphate samples was reduced to a grain size of below  $2\mu$  through repeated elutriation of the particles below  $4\mu$ , and pulverizing of the coarser ones. The result was a marked improvement in the reproducibility of our results. At the same time however we found that the results suggested a higher quartz content. Excessive pulverizing of the two-phase mixture of aggregates of very small primary particles of phosphate on the one hand and of coarser, as well as harder, quartz on the other hand (other components of rock phosphate can in this connection be ignored) leads to an apparent increase in quartz content, which may possibly be explained by assuming that a portion of the softer phosphate has been powdered so finely that X-rays could no longer detect it as crystalline material.

A more advanced pulverization of the phosphate, compared with quartz, could possibly also lead to a kind of "coating" with phosphate fines of the coarse quartz grains, and so to a seeming diminution of the quartz content. On this subject too we carried out a number of experiments: we sprinkled the surface of the preparation with water, glycerine or alcohol, but we were unable to obtain any definite results. Neither could the possibility of a preferred orientation be excluded. A loosening of the surface as described by von Engelhardt (7) did not improve our results. Von Engelhardt recommends solving the question as to whether there exists a preferred orientation through rotation of the preparation surface in relation to the X-ray beam. This is only practical however on the assumption that there are no changes in interference intensity through non-homogeneous distribution, i.e. if the preparation particles are sufficiently small. Since in our experiments we were unable to meet this requirement for the reasons described earlier, the possibility of establishing a preferred orientation with sufficiently finely powdered particles would here have only been of theoretical interest.

We decided on a compromise regarding the powdering of the samples since it was of over-riding importance to find a method of analysis which would allow the analysis also of certain fractions in unground condition. We were content therefore in the case of ground samples to reduce them to a particle size of  $< 60\mu$  so as to attain conditions roughly comparable with the non-ground samples. Since the individual results showed strong fluctuations a series of 12 specimens was prepared of each sample. In the interpretation of the results we eliminated the two extreme values and took the mean value of the remaining 10 values. This method of examining series of tests corresponds to ten-fold increase of the specimen surface and was therefore likely to lead to better results. Whether or not it would be useful with regard to this particular problem could only be seen in the course of the investigation. Chemical analyses afforded the means of checking.

After a whole series of experiments designed to answer the question of the most favourable method of preparation we eventually settled for the following: The powder was mixed into a stiff paste with alcohol and applied to the specimen holder of the diffractometer. When the mass was nearly dry the excess material was carefully removed with a sharp razor blade so that as near perfect as possible a surface was produced. Here the fact that the mass hardened during drying proved to be an advantage. With this method of preparation we hoped to avoid a possible preferred orientation coating as well as a separation during preparation. The reproducibility of the apatite interference which is a measure of the effectiveness of the method of preparation was very good. For the evaluation of the X-ray diagrams the intensity of the strongest quartz interference (101) was compared with that of the adjacent apatite interference (002). We limited ourselves to measuring only the amplitude of the interferences. In view of the fluctuations of the quartz interference planimetric measurement would have been no improvement. We refrained from admixing a standard reference material, a method described by Klug and Alexander (8) and also by Fauvarque (5), because the standard material has to be very finely divided and complications would have arisen when using it with the unground fractions.

To calibrate the apparatus, first of all mixtures of Taiba phosphate and quartz were measured. For this purpose, the fraction 0.35 - 0.60 mm, ground to less than  $60\mu$  was used, because it was plentiful and, according to the chemical analysis, particularly poor in  $SiO_2$  (1.16%). The admixed quartz had been elutriated to a particle size of below  $30\mu$ . The results of these measurements have been reproduced (Fig.1) in the attached calibration curve. The calibration curve intersects the ordinate at an intensity ratio  $\frac{\text{quartz}}{\text{apatite}} = 0.14$  which represents a very fair agreement with the result of the test series which for this fraction was 0.16. Moreover if the value of 0.14 is applied to the calibration curve itself a value of 1.3%  $SiO_2$  is found for the Taiba fraction which is in very good agreement with the result of the chemical analysis. When applying the calibration curve to the result obtained with pebble phosphate it was taken into account that the diagram of pebble phosphate shows somewhat less sharp, lower, interferences than that of Taiba phosphate.

2. Results

a) Taiba phosphate

The results obtained in the examination of Taiba phosphate have been summarized in the following table 2 :

T A B L E 2  
Taiba phosphate

Fraction	Diameter equivalent $\mu$	Proportion weight %	% SiO <sub>2</sub>		
			chemically (ground)	by X-ray analysis (ground)	analysis (unground)
1	> 600	0.99	0.68	0.6	0.4
2	600 - 350	16.2	1.16	1.3	0.8
3	350 - 200	26.3	2.01	2.4	1.0
4	200 - 105	32.1	3.22	2.8	3.0
5	105 - 60	16.8	4.47	4.2	3.5
6	60 - 35.6	6.20	4.08	3.3	4.0
7	35.6 - 11.2	1.11	2.05	2.1	1.5
8	11.2 - 3.6	0.18	2.09	+	1.3
9	< 3.6	0.42	1.60	0.7	0.8

+ The quantity was insufficient for a second X-ray.

Comparing to begin with the three SiO<sub>2</sub> values with each other there is remarkably good agreement between "chemical analysis, ground" and "X-ray analysis, ground". But also the values found in the X-ray analysis of the unground samples are on the same level in view of the lower measuring accuracy to be expected. This leads to the conclusion that the silica in Taiba phosphate is present essentially in the form of quartz. Only in the finest fractions (<11 $\mu$ ), which are however quantitatively of little importance, the X-ray analysis gave dearly smaller values which indicated a small content of very fine silicate (clay) particles.

As to the question of a possible silica coating of the grain surface the result gives no clear answer. On the assumption of such a silica coating the silica content should increase with diminishing particle size owing to the relatively larger surface. This applies in the present case down to a particle size of 60 $\mu$  and in this range is also found the bulk of the phosphates (92%). Below 60 $\mu$  however the SiO<sub>2</sub> content decreases rapidly. A further point against the silica coating of the surface is also the fact that the X-ray analysis

values of the unground samples throughout are not higher than those of the ground ones.

b) Pebble Phosphate

The following table 3 contains the values found for pebble phosphate:

T A B L E 3  
Pebble Phosphate

Fraction	Diameter equivalent $\mu$	Proportion weight %	% SiO <sub>2</sub>		
			chemically (ground)	by X-ray analysis (ground)	analysis (unground)
1	> 3500	11.9	5.18	4.4	-++
2	3500 - 1120	28.6	4.98	4.3	-++
3	1120 - 350	36.1	7.98	7.8	3.7
4	350 - 105	22.2	6.32	5.7	3.5
5	105 - 60	3.62	5.65	5.4	13.0
6	60 - 35.6	0.18	9.40	8.4	11.2
7	35.6 - 11.2	0.21	6.83	5.2	6.3
8	11.2 - 3.6	0.08	4.90	-+	3.1
9	< 3.6	0.06	3.74	-+	1.4

+ The quantity was insufficient for a second X-ray

++ Too coarse grained

In the case of pebble phosphate the results are much less clear cut. The fact immediately noticeable is that practically the entire material (99%) is coarser than 105 $\mu$ . If the values of "chemical analysis, ground" and "X-ray analysis, ground" are compared it is found that although the values run somewhat parallel, the X-ray values are definitely lower. The weighted mean for the chemical values is 6.40%, for the X-ray value on the other hand 5.9%.

The bulk of the silica in pebble phosphate exists therefore in the form of quartz whereas a smaller portion (~10%) is present as silicate, again largely in the finest fractions.

In contrast to the Taiba phosphate we find in the pebble phosphate under test among the various grain sizes for the ground samples two maxima, one of app. 8% at 350 - 1120 $\mu$  and a second of app. 9% at 35 to 60 $\mu$ .

The X-ray analysis of the unground samples also gave in this instance considerably deviating values which on the whole lie below those of the ground samples. Only for the fractions



of 105 - 60 $\mu$  and 60 - 35 $\mu$  the values of 13 and 11% are considerably higher. Unfortunately this finding can hardly be considered evidence for a silica coating of the surface since these two fractions together only amount to 0.8% and quantitatively are therefore of no significance. To sum up it may be said of the X-ray analysis that it has given us useful values concerning the quartz content. Although there are some indications of a silica coating of the surface no certain proof could be obtained from the examination of the unground particles.

#### Microscopic examination

Finally we tried to approach the problem of silica coating by microscopic methods. When fractions rich in silica are examined under the microscope the transparent clear quartz grains are noticed immediately in contrast to the phosphate particles which in the transmitted light appear black to dark brown. In pebble phosphate the proportion of quartz grains is clearly higher than in Talba phosphate. Although no quantitative analysis has so far been carried out through counting of the particles within the various grain fractions visual evidence shows clearly that the bulk of the silicic acid in both phosphates exists in the form of inconspicuous quartz particles.

If a drop of hydrochloric acid (5%) is brought onto the slide the quartz particles remain unchanged. In the phosphate grains on the other hand solution phenomena immediately appear to start from the outside edge: the dark grains assume a bright lining which continuously grows until finally the whole grain has become transparent except for a residual "haze". This process can be clearly observed in the micrographs of fig. 2 and 3 which show two successive stages of solution. Fig. 4 finally shows in 50 x enlargement the residual structure of the grain in the upper right hand corner.

The delicate haze-like structure which is left behind after solution of the phosphate material in hydrochloric acid, still fully retaining the shape of the original grain but disintegrating into tiny bits on touch, is quite obviously a silica skeleton. It seems therefore that with regard to the quartz content of phosphate rock we have to distinguish between inconspicuous quartz grains (sand) originating from the matrix, and a skeleton formed through silica coating during the course of development of the phosphate grain.

The complexity of the results obtained in X-ray analysis, especially in the case of pebble phosphate, is apparently due to the fact that the two quartz portions, sand and silica skeleton, are differently distributed among the grain fractions. The renowned drop of the quartz content in the finer fractions, unexpected at a first glance, may be due for instance to the admixed sand being coarser by nature than the phosphate particles. A further point worth considering is that the silica coating cannot assume unlimitedly high values but reaches a limit value after covering the internal surface or filling up the micro-cavities. Attention is drawn in this connection to the work by Hill, Caro and Wieczorek (9,10) investigating the internal surface of phosphate rock. For further advance in this field a method of analysis is needed which differentiates between the two quartz forms. Work on the development of such a method is in progress.

## Discussion of results

On summarizing the results of our experiments with regard to the problems posed at the beginning, we should like to stress that our work is not yet finished and that more intensive research is required. On the basis of present results the following statements can be made:

- 1) In the two phosphates under examination, Taiba and Florida pebble, silica is present mainly in the form of quartz.
- 2) Whereas in Taiba phosphate silica in the form of silicate could be detected only in the finest fractions the average content of silicate-SiO<sub>2</sub> in pebble phosphate was app. 0.5%.
- 3) Quartz occurs in two forms: as coarser, inconspicuous particles (sand) and as a skeleton which envelops and penetrates the phosphate grains. The quantitative ratio between these two quartz forms could not yet be determined.
- 4) The difficulties experienced in the grinding and refining of the pebble phosphate concentrate referred to at the beginning may be explained according to the available results by a complete silification of the smaller grain sizes. Since the silica penetration starts at the outside and proceeds towards the inside it is natural that the smaller grain sizes are more strongly silica impregnated than the bigger ones.
- 5) The presence of SiO<sub>2</sub> in the apatite lattice could so far not be established. The reactive silicate believed to be present by Delomenie, which contributes to the fluorine evolution in superphosphate production, is in fact probably very finely divided skeleton silica. A further proof for this lies in the fact that the Taiba phosphate examined by us contains no appreciable quantities of silicate, yet gives a fluorine evolution of 20% during superphosphate production.

The X-ray analyses have been carried out in the Institute of Mineralogy of the University of Göttingen. We are much obliged to Prof. Gorrans for valuable advice, and in particular for permission to carry out the X-ray analysis in his Institute.

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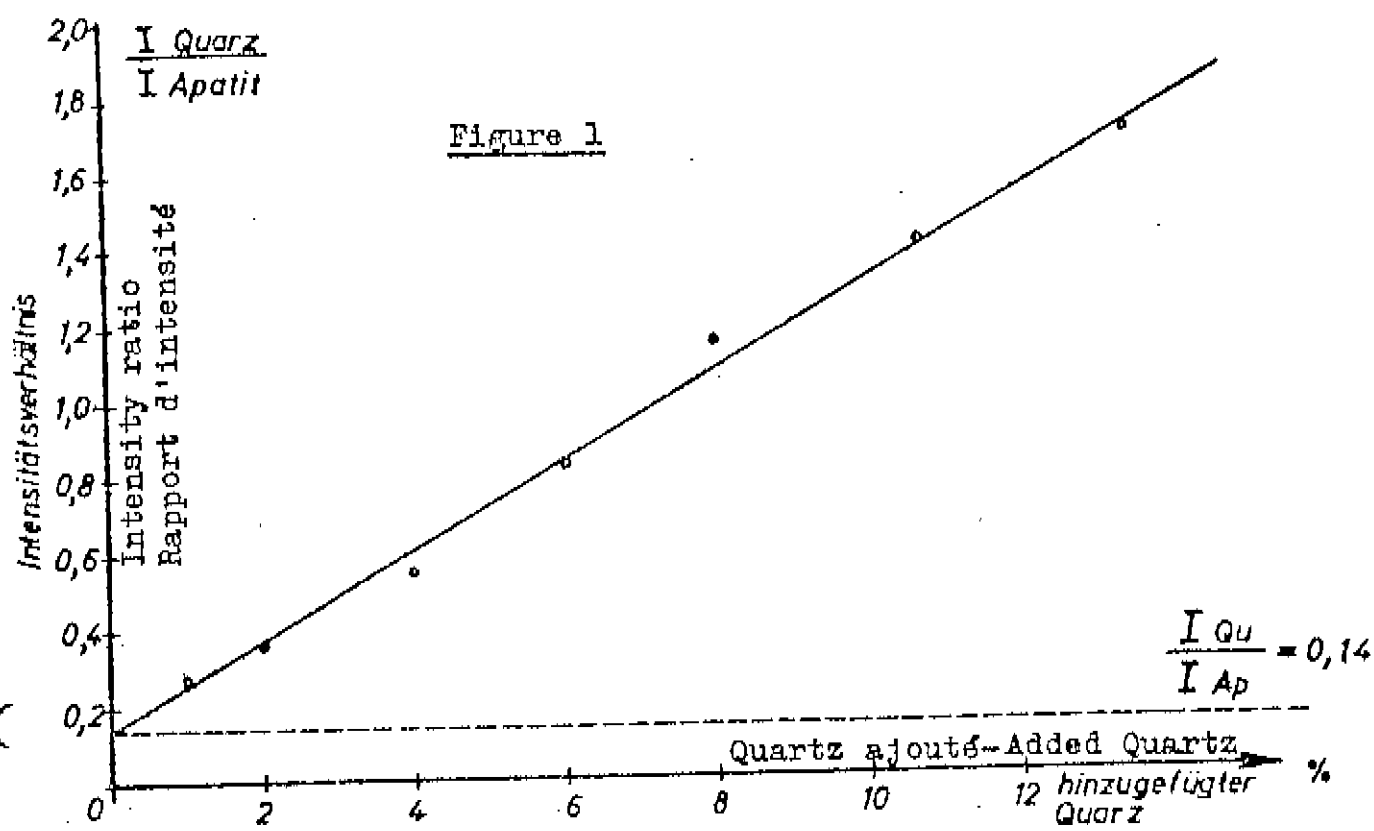


Fig. 2

Whole scale  
=  $670 \mu$

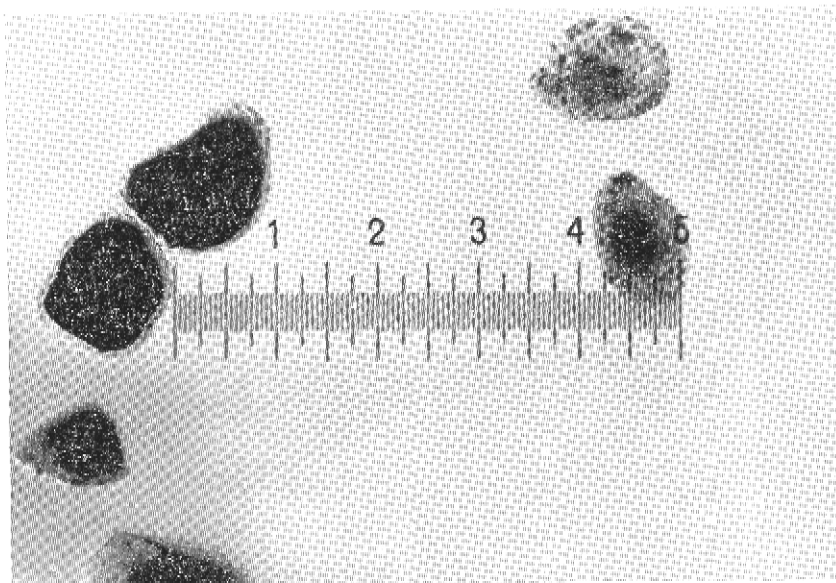


Fig. 3

Whole scale  
=  $670 \mu$

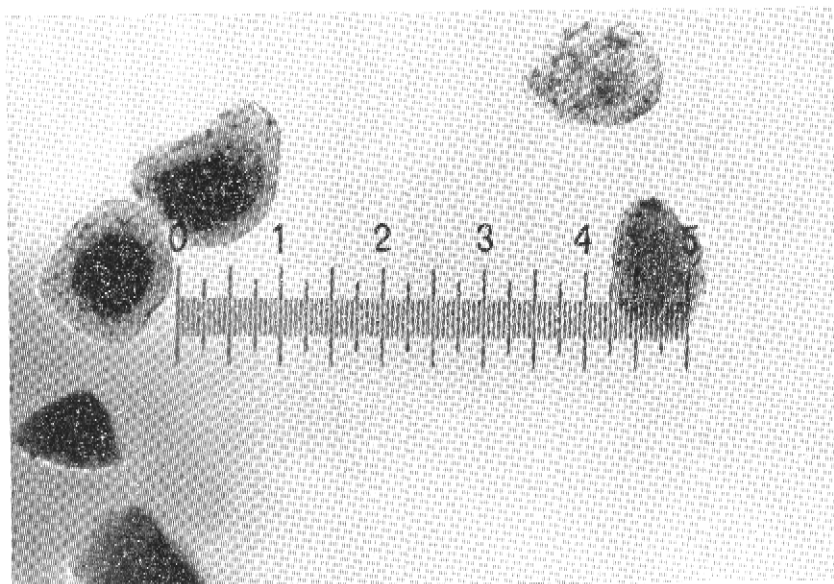


Fig. 4

Whole scale  
=  $125 \mu$

