A CRITICAL EXAMINATION
OF
QUARTZ, TRIDYMITE AND CRISTOBALITE:
THE ESTIMATION OF FREE SILICA.

BY

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SUMMARY

I. The introduction records the various theories on the aetiology of silicosis and pneumokoniosis with reference to the pathological and chemical aspects of the changes brought about in the lungs by small silica particles.

A survey is also given of physical and chemical analytical techniques for the estimation of the free silica content of rocks and dusts.

2. Detailed investigation of one chemical method, that of Trostel and Wynne, has shown it to be suitable, after modification, for the analysis of Stirlingshire coal-measure rocks.

However, the high experimental losses occurring during the analysis of small particles preclude its use for the determination of the quartz content of airborne dusts.

3. The examination of the physical method of Differential Thermal Analysis has shown it to be influenced by the presence of a layer of non-quartz silica,which is not estimated,on ground quartz particles.

The properties of this layer have been investigated and it has been concluded that it is of relatively constant thickness and density independent of the particle size of the quartz. The proportion of layer to quartz in airborne

dusts is considerable and prevents the use of this method, as it stands, for their analysis. During rock analysis this method suffers some loss in accuracy due to the presence of the non-quartz layer but suggestions are made to produce at least a partial recovery of the loss and also to make the method practicable for dust analysis.

4. The presence of this non-quartz layer has been shown to interfere with the X-ray analysis for quartz in dusts.

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PART I INTRODUCTION

A. Silicosis and Pneumokoniosis

This inquiry into the methods of estimation of free silica in rocks and dusts was undertaken as part of a wide scheme of physiochemical studies of siliceous and allied dusts. These studies were related to the investigation of pneumokoniosis and silicosis in particular, since the aetiological agent of the latter disease is known to be finely divided silica.

Pneumokoniosis - a term applied to various diseases of the lung caused by the inhalation of small dust particles in such occupations as coalmining - is one of the most serious industrial diseases of modern times and claims many victims from the coalmining industry in this country. In I947, for example, the number of cases certified as suffering from the disease was 3,779 (I), 0.5% of the total number of workers in that industry. This disease is caused by the inhalation of airborne dust particles, which after lodging in the lung tissues cause pathological changes which gradually incapacitate the lungs. Silicosis - pneumokoniosis due to the inhalation of particles of silica - producing first irritation and fibrosis is characterised in the later stages by nodular fibrosis, which eventually coalesces, completely disabling the lung. Because of methods of dust suppression silicosis is now slow in establishing itself, as in the Rand gold mines (2) where it does not usually become apparent in less than 18 to 20 years, but it is still often associated with tuberculosis in advanced cases.

Silicosis has been recognised as a disease amongst mineworkers and masons for centuries. Agricola (3) noticed the coughing and breathlessness of miners in the Carpathians, and reference has been made by Dimerbrock, 1649 (4) to the shortness of breath and rigidity of chest of granite workers in the same district.

The first information concerning the aetiology of silicosis was produced by Peacock (5) in 1861, and Greenhow (6) in 1865, who examined the lung tissue from sufferers and isolated 'sand' from which they concluded that the condition was caused by the inhalation of large quantities of dust. The mechanism of the disease however was not suggested. At first workers in this field were inclined to believe that the abrasive qualities of the dust were responsible for the tissue destruction since the mineral particles were seen microscopically to have very sharp edges. Haldane (7) and Mavrogordato (8) gave further support to this theory by publishing conclusions from the study of the pathogenic effect of dusts used for stone dusting in mines. They concluded that since they were soft, powdered clay, shale, and chalk were harmless while the hard gritty substances like crushed granite, flint, and ganister would be dangerous and give rise to the reaction in the lungs.

It soon seemed doubtful if this was the true explanation and in I9I8 Lanza (9) suggested that the pathogenicity of the dust could be connected with its chemical composition since the most dangerous dusts contained the largest amounts of silica. He also drew attention to the small size of the particles in the lungs. They were 2 to 5 microns or less. The action of silica in the production of the disease was further emphasised by the results of experiments by Gye and Kettle (I0) in I922. They injected silica subcutaneously into animals and thereby produced characteristic lesions in the body tissue. These workers also established that the tubercle bacilli proliferated rapidly in the necrotic areas round the silica particles.

Further convincing evidence against the 'Mechanical Theory of Silicosis' was produced in I923 by Gardner (II) who showed that hard sharp particles of silicon carbide did not produce the typical quartz reaction in animal lungs. These results strengthened the 'Chemical Theory' as did the corroborative work of Sayer (I2) in I925 who suggested that dusts high in free silica were the most injurious and that the solubility of silica in body fluids might injure the lung tissues by a poisonous action.

Results obtained by Heffernan (I3) in I926 seemed at first to contradict the previous work but eventually proved to be of fundamental importance in the support of the modern solubility theory. He showed that a dust containing 84% silica and I6% clay with some organic matter did not produce silicosis in the lungs of workers breathing it, and concluded that some constituents of the dust were exerting an influence on the toxic properties. This is one of the first references to the idea of the suppression of the toxicity of silica by some minor constituents of the dust and as such is notable.

Another important suggestion was made by Kettle (I4) in I926 when he favoured the theory that the silica in dissolving in the lung fluid formed colloidal silicic acid which acted as the cell poison producing necrosis and eventually fibrous tissue. He further suggested that silica itself promoted the growth of the tubercle bacilli and not the presence of fibrous tissue or the lymphatic stagnation caused by the dust.

This theory was elaborated in I929 by Heffernan (I5) in his 'Colloidal Theory' which held that silica particles, crystalline, cryptocrystalline or amorphous are engulfed by phagocytes in the alveoli of the lung and conveyed to the pulmonary lymphatic channels where they remain in the lymphatic nodes. The surface of the silica inside the cell is hydrated forming colloidal silica at the expense of the protoplasmic fluid of the phagocyte which dies. This process is retarded if the quartz is protected by a layer of clay, carbon or similar material and is accelerated in the presence of alkali. After the phagocytes die the action spreads to the surrounding tissue cells.

Work carried out in I932 by Kettle (I6) clearly emphasised again the role of siliceous dusts in the production of silicosis. By injecting mice with suspensions of siliceous dusts he produced necrosis of the cells while injections of non-siliceous dusts had no effect and these dusts remained at the site of introduction. It was also shown that the non-siliceous dusts did not aid the establishment of tubercular infection. Kettle further strengthened the solubility theory by showing that a covering of iron oxide rendered toxic quartz quite innocuous.

The <u>Solubility Theory of Silicosis</u> was finally substantiated when Policard (I7) in I933 observed that body cells were poisoned by dissolved silica and that the cells so treated did not disintegrate and disappear, as normally, but seemed to be mummified.

Much work has been carried out by King and others whose results in general continue to support the solubility theory, in that dusts producing dissolved silica at the greatest rates, quartz and flint, were the most pathogenic. Further support was produced by the solubility suppression experiments which produced a substantial decrease in the toxicity of the dusts. Aluminium added in small amounts to quartz used in animal experiments by Denny, Robson and Irwin (I8) was also found to retard the development of silicosis. King, Wright, Ray and Harrison (I9) have repeated these experiments and shown that in the lungs of rats exposed to an atmosphere heavily laden with quartz dust a retardation and a possible prevention of the development of silicotic lesions could be achieved by the addition of 2% aluminium powder.

Denny, Robson and Irwin in I939 (20) observed that the additions of small percentages of metallic aluminium to a quartz dust almost completely inhibited the solubility of the quartz. X-ray studies and also a staining technique using aurine tricarboxylic acid which is adsorbed by the aluminium hydroxide showed that the suppression of the solubility was due to adsorption of a layer of an hydrated aluminium oxide on the surface of the quartz particles.

Results of a contradictory nature have of course been produced such as those obtained from '20 Angstrom' silica. This silica produced as a condensate from glass furnaces causes no fibrotic reaction and is highly soluble. King (2I) found similar results with that particle size. King suggests that this excessively high solubility means a quick elimination from the body which is too rapid to allow the establishment of the usual fibrotic reaction. On the whole, however, the mass of information being produced today is still in support of the solubility theory of silicosis and the contradictory results merely stress the complicated nature of the processes occurring in the lungs during the solution of silica in the presence of other minerals.

In recent years the Medical Research Council has sponsored an investigation into the disease of pneumokoniosis as it appears in South Wales coalworkers. Since in coalmines the quartz content of the airborne dust is seldom greater than 4% (22) they have come to the conclusion that the gross overloading of the miners' lungs with coal dust may be a factor in the production of the fibrosis (23).

Jethro Gough in I947 (24) in his paper emphasises that in simple pneumokoniosis of coalworkers in South Wales the amount of fibrosis is small and that the important change is focal emphysema. This he suggests may be due to dust accumulation interfering mechanically with the function of the lungs. Rogers (25) and Heppleston (25) also agree that the mechanical interference is due to inert dust accumulation in the lungs.

In I946 Policard (26) stated that cells containing silica in the lungs become hypertrophic and join together to form agglomerations of 50 to I00 microns in diameter which fill the alveolar cavities. Their protoplasm also seems to be mummified. These agglomerates destroy the function of the alveoli they fill and so the ventilation of the corresponding area of the pulmonary lobule is affected and the area becomes atelectatic. Atelectasis leads to fibrosis. This theory tends to support that from South Wales suggesting that the gross overloading of the lung with dust probably produces the condition of pneumokoniosis.

Concerning the size of particles causing silicosis Policard in I946 and Drinker in I925 studied the size distribution of particles, by size frequency, in phagocytic cells and found that about 53% were of I or 2 microns diameter (26). Particles larger than 5 microns are very rare in dust cells (26).

King (2I) suggests that to produce silicosis in animals there must be a certain range of particles and to get the condition most rapidly the size should be lower than I micron and larger than 20 A.U. He refers to work by Tebbens, Schulze and Drinker who have drawn attention to the extremely rapid development of silicosis produced by particles of I micron or smaller.

Watson (27) has shown that the particle size analysis of dusts produced by drilling and blasting are remarkably similar when particles above 0.2 microns (the limit of light field microscopy) are considered. Below 0.2 microns, however, election microscopy has revealed great differences, there being more than four times as many particles below 0.I microns in the drilling dust as in that produced by blasting. Hatch and Pool (28) have found in a sample of airborne dust from a rock crushing shed, ten times as many particles by dark field microscopy as were noticed by light field microscopy. Drinker and Hatch (29) report the production of IO^{I2} particles below 0.8 microns per minute by ordinary pneumatic rock drilling.

Petrological studies (30) of the shales of the anthracite and bituminous mines show an increase in the anthracite area of the amount of secondary quartz and mica while hydrated ferric and aluminium oxides are less evident in anthracite shales than in bituminous shales. There is then a correlation between the presence of secondary quartz in South Wales shales and the pneumokoniosis incidence.

It is concluded that silicosis is produced by the inhalation of small particles of silica below 2 microns in diameter which are produced in large numbers by rock drilling operations. Solubility and or adsorption processes are assumed to account for the actual mechanism. Pneumokoniosis however is still unexplained, there being two theories; gross overloading of the lung with coal dust, or a modification of the toxic action of the low silica content of the dust by other constituents.

B. The Determination of The Free Silica in Rocks and Dusts.

Since it has been shown conclusively that free silica in rocks can produce a silicotic reaction in the lungs of animals any scheme of research into the disease must have at its disposal methods of analysis by which the free silica content of rocks and airborne dusts can be estimated. Many methods have been suggested and will be discussed below.

Physical Methods.

Physical methods of analysis estimate quartz only and are based on the differentiation of quartz from other minerals by differences in crystal structure or some other property such as refractive index, density and relative infusibility.

Optical methods using refractive index as the differentiating criterion (31) (32) are suitable for some well defined rocks but are not generally useful because of inaccuracies when applied to the examination of shales and dusts where the small size of the individual mineral particles makes observation and measurement difficult.

Salazar and Silverman (33) and Boguslavskii (34) have recently published physical methods of analysis. Salazar and Silverman pass the dust samples through a controlled flame, fusing all the minerals but the free quartz. The fused airborne dust is then collected by electrostatic precipitation and analysed microscopically. This seems a complicated procedure with many opportunities for inaccuracies and since it depends on the microscope for the final analysis it will suffer from the particle size effect. Boguslavskii's method in which the quartz stained with auramine is examined by luminescence microscopy is open to the same criticism.

Two methods of analysis based on properties of the quartz crystals are those of X-ray diffraction and Differential Thermal Analysis. X-ray diffraction is perhaps the most widely used physical method for the analysis of rocks and dusts for free quartz (35) (36) (37) (38). The accuracy claimed for this method varies with different apparatus and workers ± 5% (35) (37) (38) and I0 to 20% if the dust is under 2 microns in size (39). These claims do not compare favourably with the slower chemical method of Rabson (5I) who gives analysis results giving a ± 2.5% error. Any effect due to the particle size of the quartz seems to have been neglected until Wilchensky (40) recently suggested that it may be considerable.

Differential Thermal Analysis (hereafter referred to as D.T.A.) is based on the change in crystal structure from

α quartz to β quartz at 574°C. (4I) (42) (43) (44) (45). The accuracy claimed is ± I% (I04) and this method has been suggested for use in the analysis of airborne dusts (72). One important feature of this method is the non-interference by other minerals - a defect possible even in X-ray methods (37).

Chemical Methods.

Chemical methods of analysis are methods of 'Rational Analysis' in which an attempt is made to break down the rock minerals and remove their decomposition products leaving quartz as a residue. The individual methods differ mainly in the reagents employed (a) to bring about the mineral decomposition and (b) to remove the decomposition products.

Various acid reagents have been recommended for use in the decomposition of mineral silicates, e.g. sulphuric acid (46) and sodium metaphosphate (47), the liberated silicic acid being removed by alkali solutions. Hydrofluosilicic (48) and hydrofluoboric acids (49) have also been suggested and are interesting because their reaction products are soluble in the acid solution, no alkali extraction being necessary to remove them. Potassium pyrosulphate has been recommended by Trostel and Wynne (50) for the analysis of refractory clays, by Rabson (5I) for the analysis of airborne dusts in the Witswatersrand, and also by Florentin (52) for rock analysis. One of the most recently published methods (Durkan's) (53) requires the use of phosphoric acid to decompose the silicates and dilute hydrofluoric acid to remove the decomposition products.

It appears that all chemical methods of analysis have two basic inaccuracies. The first is due to minerals which are resistant to the decomposition reagents and so appear with the quartz in the analysis residue. The presence of these minerals requires the application of a correction factor.

The second inaccuracy is that produced by the increase in the rate of solubility with a decrease in particle size. During the analysis this causes a loss of quartz mainly in the acid or alkaline extractions used to remove the mineral decomposition products (46) (5I) (53) (54) (55). Some methods such as Shaw's (46) merely apply a single correction factor for all dusts below 5 microns in diameter and others, Line and Aradine (49) and Knopf (48), while having a factor for quartz ground below a I00 U.S. mesh sieve have not investigated the loss on dust of airborne size. This has been shown to be considerable (54) (55).

Durkan (53) gives a table of correction factors for

THE EFFECT OF PARTICLE SIZE ON THE ANALYSIS LOSS

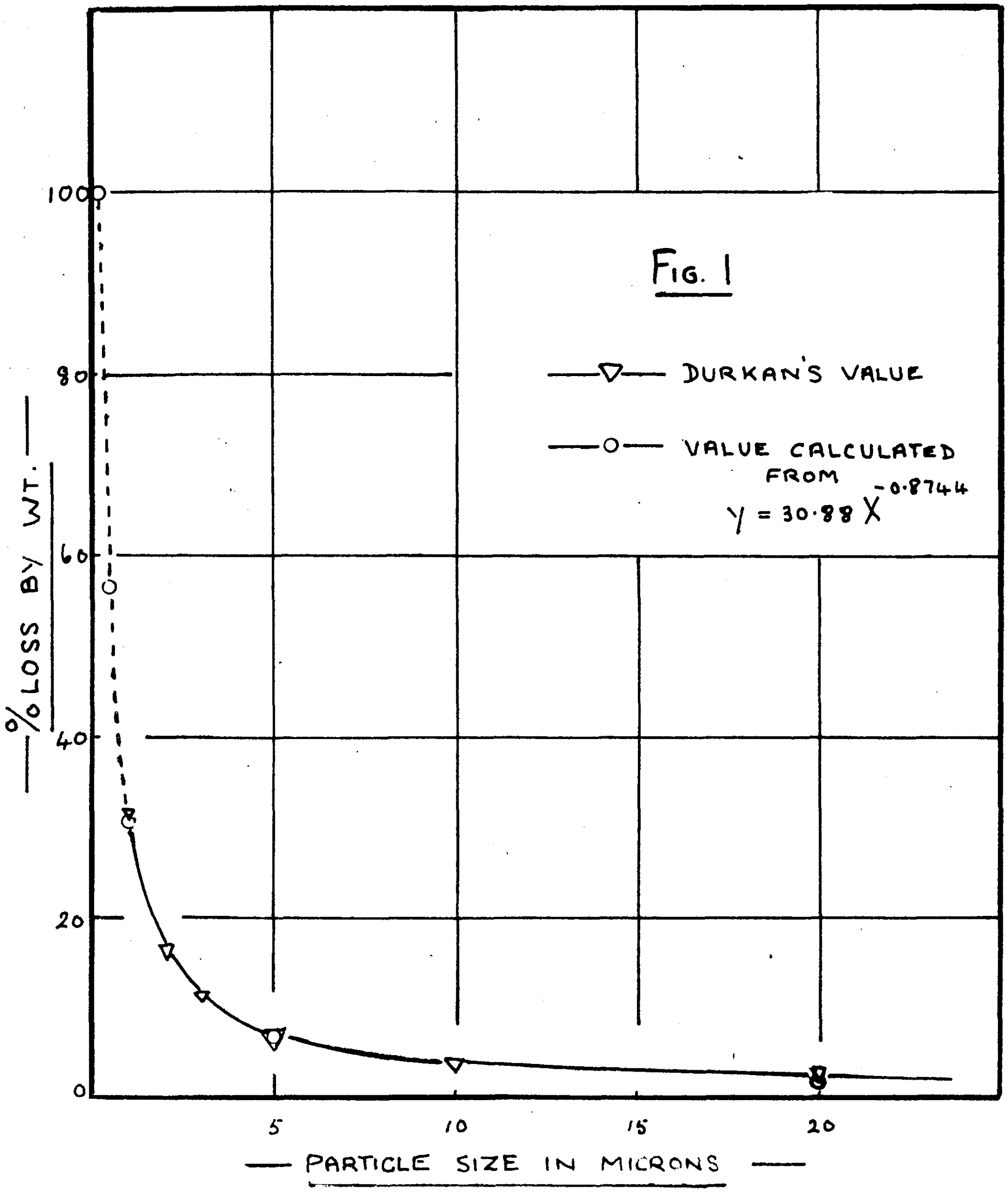


FIG. 1

TABLE I.

The Average Particle Sizes of the Quartz Content of Ten Airborne Coalmine Dusts.

Rank of Coal	Sample No.	Av. particle size in µ	% below I.2 µ by number	% below I.2 µ by weight
Anthracite	2SI	I.I	68.0	38
	IDI	I.0	7I.3	-
	2RI	0.9	78.6	-
	2NI	0.8	78.7	-
Steam	2UI	0.8	79.3	-
	ITI	0.9	75.6	-
Bituminous	IAI	0.7	86.8	-
	ICI	0.6	89.8	-
	IBI	0.5	94.0	66
	IB2	0.6	90.6	-

dusts of various sizes and from these values Fig. I has been derived. It shows that the percentage of a one micron diameter, quartz dust lost during analysis is 32% when double treatment is used. An equation was derived to fit this curve approximately and several values calculated. These are shown on the graph. The percentage loss for particles of 0.5 microns in diameter is found to be about 57% and an I00% loss would occur with particles of between 0.2 and 0.3 microns diameter.

Calculations from figures given by King (56) showing the particle size distribution of the quartz in several airborne dusts collected from South Wales coalmines indicate that the average particle size and also the percentage below I.2 microns in diameter can vary considerably (Table I). For the purposes of these calculations the amounts of the dusts designated as below 0.2 microns were arbitrarily assumed to be 0.05 microns and those greater than 3 microns to be 5 microns.

Deliberation on (a) the variation in the average particle size of these dusts (0.5 to I.I microns), (b) the large experimental losses (30 to 60%) over this particle size range, and (c) the fact that on average 50% by weight of the dusts was below I.2 microns in size (Table I), forced us to the conclusion that only a chemical method which estimated the loss of quartz during the analysis would be suitable for accurate work on airborne dusts. This conclusion removes from consideration all known methods but one, that of Rabson (5I) who estimates the quartz lost in solution by a colorimetric method.

For rock analysis this method and technique can be used but being a micromethod it necessitates the use of platinum crucibles, a centrifuge and a microbalance which would become bottlenecks in routine laboratory analysis. It was decided therefore to investigate the application of the method suggested by Trostel and Wynne (50) for "The Determination of Free Silica (quartz) in Refractory Clays" to the analysis of coal-measure rocks. Sauzéat (57) states that this method should not be used for rock analysis owing to the resistance of felspars to the potassium pyrosulphate fusion. However this is a failing with all chemical methods which it is hoped can be allowed for without much loss of accuracy. The chemical reactions used in the Trostel and Wynne method of analysis are similar to those used by Rabson although the methods were produced independently. The Trostel and Wynne method is so similar and simple in technique that it was investigated for the analysis of coal-measure rocks to test the applicability of both methods.

Differential thermal analysis has been investigated both on its own account as a physical method and as a check on the chemical method. It was chosen for its simplicity of technique and apparatus, which is very cheap compared with that for X-ray analysis - the only alternative.

[illegible]

[illegible] analysis con[illegible]

[illegible]

(1) fusion of [illegible] rock samp[illegible] potassium pyrosulphate in vitreous silica crucible under [illegible] controlled conditions

(2) solution of the excess pyrosul[illegible] the soluble products in water and

(3) [illegible]tion of the mixture with [illegible]tion of caustic soda, the filtration of the soli[illegible] from the alkaline solution and its washing with [illegible] hydro[illegible] acid [illegible] the [illegible], aluminium [illegible] compounds [illegible]eased by the decomposition of the ro[illegible]als. The residue is quartz and any undecomposed [illegible]

[illegible]

PART 2 The Estimation of the Free Silica Content of Rocks by the Trostel and Wynne Method.

Introduction

Outline of Method

The Trostel and Wynne method of analysis consists basically of:-

(I) fusion of the ground rock sample with potassium pyrosulphate in vitreous silica crucibles under controlled conditions

(2) solution of the excess pyrosulphate and the soluble products in water and

(3) extraction of the mixture with a solution of caustic soda. The filtration of the solid residue from this alkaline solution and its washing with water and hydrochloric acid removes the silicon, aluminium and iron compounds released by the decomposition of the rock minerals. The residue is quartz and any undecomposed minerals.

Felspars are known to be resistant (50) (5I) (57) to this treatment and the following additional experimental steps are used to apply a correction to compensate for their presence (58). If the analysis residue is twice evaporated to dryness with hydrofluoric acid in the presence of sulphuric acid the felspars are decomposed and their silica volatilised off with the quartz, leaving potassium sulphate and aluminium oxide. Twice the weight of this evaporation residue gives the weight of orthoclase felspar present. The accuracy of this correction has been investigated and will be discussed.

Scope of work.

The investigation of this analytical method was designed to indicate its suitability for the estimation of the free silica in coal-measure rocks. To this end the effect of resistant minerals had to be fully investigated. This was done by determining (I) the number of pyrosulphate fusions required to give optimum decomposition and the efficiency of the decomposition of coal-measure minerals

(2) the accuracy of the method in the presence and absence of resistant minerals

(3) the error introduced if the resistant mineral is not orthoclase felspar, as assumed.

The effect of particle size on the accuracy of the analysis was investigated and a 'quartz loss' correction evaluated for quartz ground to pass a 200 B.S. sieve.

Finally the percentage error of this adapted method was estimated from ten analyses of a standard mixture.

Definitions.

Throughout this thesis the words and phrases below are used with the meanings given.

I. Free Quartz: Silica existing as quartz.

2. Free Silica: Silica existing as quartz and or amorphous, opaline and chalcedonic silica.

3. Arithmetic Mean Deviation (A.M.D.): The average of the arithmetic deviations of a number of results from their average.

4. Percentage Arithmetic Deviation: The A.M.D. as a percentage of the average of a number of results.

5. Percentage Error: The A.M.D. as a percentage of the true value.

Practical Procedure.

Analytical Technique.- for the analysis of refractory clays (50).

(a) 0.5 g. of the dried material ground to pass an I50 (Tyler) sieve is weighed into a vitreous silica crucible and

(b) fused thoroughly with I0 to I5 g. of potassium pyrosulphate.

The fusion is started at a low temperature to prevent loss of sulphur trioxide and finished at I,000°C but not more. The heating should be stopped before salts have begun to crystallise out.

(c) The cooled fusion products are dissolved in I50 to 200 c.c. of hot water in a 400 c.c. Pyrex beaker.

(d) To this warm solution is added about I2 g. of sodium hydroxide pellets, one or two at a time.

(e) The suspension is then digested for ½ hr. on a hot plate at 85° to 90°C.

(f) The quartz residue is filtered off quickly, using a close texture paper and is washed,

I0 times with hot water
5 to I0 times with hot I:I hydrochloric acid
5 times with hot water

(g) After ignition in a tared platinum crucible it is weighed.

(h) To the residue is added 2 drops of I:I sulphuric acid and IO c.c. of 48% hydrofluoric acid (Analar). If the residue after evaporation exceeds 0.00I g. it is discarded and the analysis repeated.

Discussion on Procedure.

For all the experiments the materials were ground to pass a 200 B.S. sieve (76 microns) instead of the recommended I50 (Tyler) sieve (I04 microns). This was done because differential thermal analysis and this chemical analysis could only be compared if the particle sizes of the materials used are similar. A 240 B.S. sieve (66 microns) is recommended for differential thermal analysis.

It was found advantageous to mix the ground rock thoroughly with about two thirds of the powdered potassium pyrosulphate and place the last third as a layer on top of the mixture. This helped to prevent small aggregates of particles from floating on the surface of the fused pyrosulphate where optimum decomposition would not take place. Twelve grams of potassium pyrosulphate were used in every case.

The fusion was carried out by heating the crucible over a low bunsen flame till the pyrosulphate fused and frothing had ceased (I0 to I5 mins.). The temperature was then raised to a red heat for the remainder of the half hour. This was done gradually to prevent excessive loss of sulphur trioxide.

An individual sandbath over a bunsen burner was found to be quite suitable for the extraction. As stated in the original paper the temperature should be kept between 85°C and 90°C. If it is above 90°C there is excessive attack on the quartz and if below 85°C incomplete removal of the decomposition products.

The filtration was always carried out through Whatman No. 42 ashless filter paper.

The final hydrofluoric acid evaporation residue was not discarded but subjected to another evaporation and this residue weighed to enable the calculation of the resistant mineral correction.

Preparation of Materials.

All materials unless otherwise stated were ground by hand in an agate mortar to pass a 200 B.S. sieve and dried before use.

The mixtures I, IA, 2 and 2A were made up from quartz, orthoclase, ferric oxide and kaolin. A base mix of 75% kaolin and 25% ferric oxide was made up and used in the

TABLE 2.

Standard Quartz Mixtures

Component	Mixture No.			
	I	IA	2	2A
Quartz	25.0%	25.0%	75.0%	75.0%
Orthoclase	0.0%	5.0%	0.0%	5.0%
Base Mix	75.0%	70.0%	25.0%	20.0%

mixtures as shown in Table 2.

The quartz - Lochaline sand (referred to as L.A.S.) (a white 99.6% silica sand) (59) - after grinding to pass a 200 B.S. sieve was repeatedly extracted with concentrated hydrochloric acid to remove compounds of iron and aluminium present as impurities. The quartz was then found by hydrofluoric acid evaporation to be 99.9% silica.

The ferric oxide and kaolin (both laboratory reagents) were chosen for the base mix because their decomposition products would be similar to those obtained from rock minerals.

The orthoclase (60) was a good sample of the clear mineral free from colouring impurities.

The quartz and cristobalite (6I) samples 99.9% and 99.8% silica respectively were separated into the size ranges 50 to 70 microns and 3 to 5 microns by water sedimentation. This method was used because sieving does not remove the fine particles efficiently. The reasons for using those particular size ranges are given later.

The standard mixture for the percentage error determination was obtained by mixing together quartz 40.0%, orthoclase 5.3%, ferric oxide I3.3% and kaolin 4I.4%.

Samples of shales and sandstones from two pits in Stirlingshire, Plean and Redding Collieries, were ground

[illegible] above [illegible]
ments. The rock types, sample numbers, and sources [illegible]
given in Table 3. Tourmaline, rutile, hornblende, [illegible]
[illegible]ese, kaolin (mineral) samples were ground simil[illegible]

TABLE 3.

[illegible] Mechanical Work.

This consisted of many repetitions of the [illegible] operations with [illegible] as required [illegible] individual investigations

Source of Rocks.

Rock Type	Sample No.	Colliery of Origin
Shale	5	Plean
"	I2	Plean
Sandstone	3	Plean
"	I5	Redding

to pass a 200 B.S. mesh sieve and used in several experiments. The rock types, sample numbers, and sources are given in Table 3. Tourmaline, rutile, hornblende, orthoclase, kaolin (mineral) samples were ground similarly.

Experimental Work.

This consisted of many repetitions of the analytical technique with single or double fusions as required for the individual investigations.

TABLE 4.

Percentage Decomposition with Number of Fusions.

Rock	No. of Fusions	Fusion Residue as % of rock
Shale (No. 5)	I	23.I
	2	2I.2
	3	2I.5

Experimental Results and Conclusions

The number of pyrosulphate fusions required to give optimum decomposition.

Since it was known that some minerals were resistant to the pyrosulphate fusion and that different minerals would have different decomposition rates it was considered necessary to determine the number of fusions required to bring about optimum decomposition. Samples of shale No. 5 ground in an agate mortar to pass a 200 B.S. sieve were subjected to one, two and three fusions, each one being followed by an alkali extraction as detailed in the published method of analysis. Table 4 gives the fusion residues calculated as a percentage by weight of the original shales.

It seems that in the case of shale No. 5 the decomposition is not completed with a single fusion but is with two fusions. There is no significant difference between the percentage decomposition for two or three fusions.

Two fusions were also found to be necessary for the optimum decomposition of a non-coal-measure sedimentary rock. Unless otherwise stated two fusions have been used in all the work reported.

TABLE 5.

Comparison of Mineral Decompositions

Mineral	Shaw Decomposition	Trostel & Wynne Decomposition
Tourmaline	15.5%	84.2%*
Rutile	29.8%	99.4%
Hornblende	35.0%	11.8%*
Orthoclase	7.7%	4.1%
Kaolin	90.7%	90.6%*

The efficiency of the decomposition of coal-measure minerals.

Felspars are only slightly attacked by fusion with potassium pyrosulphate (50) (5I) and are also the chief resistant minerals found in the residue from the analysis of coal-measure rocks by Shaw's method of estimation of free silica (46). The efficiency of the attack by pyrosulphate fusion on certain minerals whose decomposition by Shaw's method is also incomplete has been investigated. Of seventeen minerals examined by Shaw eleven were found to be decomposed by the sulphuric acid treatment to an extent greater than 90% decomposition. Out of the remaining six the four with the lowest percentage decomposition were chosen together with kaolin - an easily decomposed mineral - and subjected to analysis with two fusions and alkali extractions. Table 5 compares the decompositions obtained.

(x)The residues from tourmaline, hornblende and kaolin either appeared to be quite different from the original mineral or this was seen to be impure, e.g. the residue from kaolin consisted of hard clear grains. For these reasons the figures given in the table cannot be quoted as the percentage decomposition values for the appropriate minerals. Tourmaline and rutile are decom-

TABLE 6.

Accuracy of Analysis.

Mixture No.	Uncorrected Quartz Content	Felspar Corrected Quartz Content	Actual Quartz Content
I	25.6%	24.9%	25.0%
IA	30.2%	24.6%	25.0%
2	74.3%	73.9%	75.0%
2A	79.3%	74.2%	75.0%
Quartz	99.I%	98.8%	I00.0%

posed to a markedly increased extent, hornblende and orthoclase to a lesser extent.

These results emphasise the need for a correction factor to compensate for the presence of resistant minerals in the final quartz residue. The absence of iron oxide in the residues in many analyses suggests the absence of partly resistant minerals like hornblende and tourmaline. This corroborates the observation by Shaw (46).

The accuracy of the method in the presence and absence of resistant minerals.

This investigation was carried out on several mixtures I, IA, 2 and 2A made up as previously described (page 26).

Table 6 shows the results obtained by analysis with one pyrosulphate fusion. The correction applied for the presence of felspar is that already mentioned (page 2I).

From this table of results several points of interest emerge:-

I. The loss on the quartz sample was I.2%.

2. There has been no significant attack on the felspar.

3. No substantial error is introduced by the application of the correction.

4. The 'felspar corrected' results lie within I.0% of the true value.

TABLE 7.

Comparison of Actual and Corrected Analysis Results.

Actual Quartz Content	Av. Corrected Quartz Content	Difference
25.0%	24.8%	0.2%
75.0%	74.I%	0.9%
IOO .0%	98.8%	I.2%

5. A small insoluble non-volatile residue from the reagents is giving a 'felspar residue' from the quartz.

Further examination of the corrected and actual values shows (Table 7) that the differences between them is proportional to the amount of quartz present.

If an allowance is made for the quartz lost, in proportion to the amount present the results lie within 0.5% of the true value. From this set of experiments it is shown that under the conditions of the analysis the attack on quartz is not negligible and must be allowed for in accurate analysis, especially since two fusions and alkali extractions will be used in practice and not one, as in the above experiments. To conclude, it has been found that for this method as for others, two corrections must be applied even for rock analysis - the 'resistant mineral' correction and the 'quartz loss' correction.

The effect of the particle size of quartz and cristobalite on the analysis losses.

Since it was thought possible that a fraction of the quartz dust produced in rock drilling might be converted to cristobalite at the high temperatures reached by the individual particles - some appear as white hot sparks -

THE EFFECT OF PARTICLE SIZE ON THE ANALYSIS LOSS

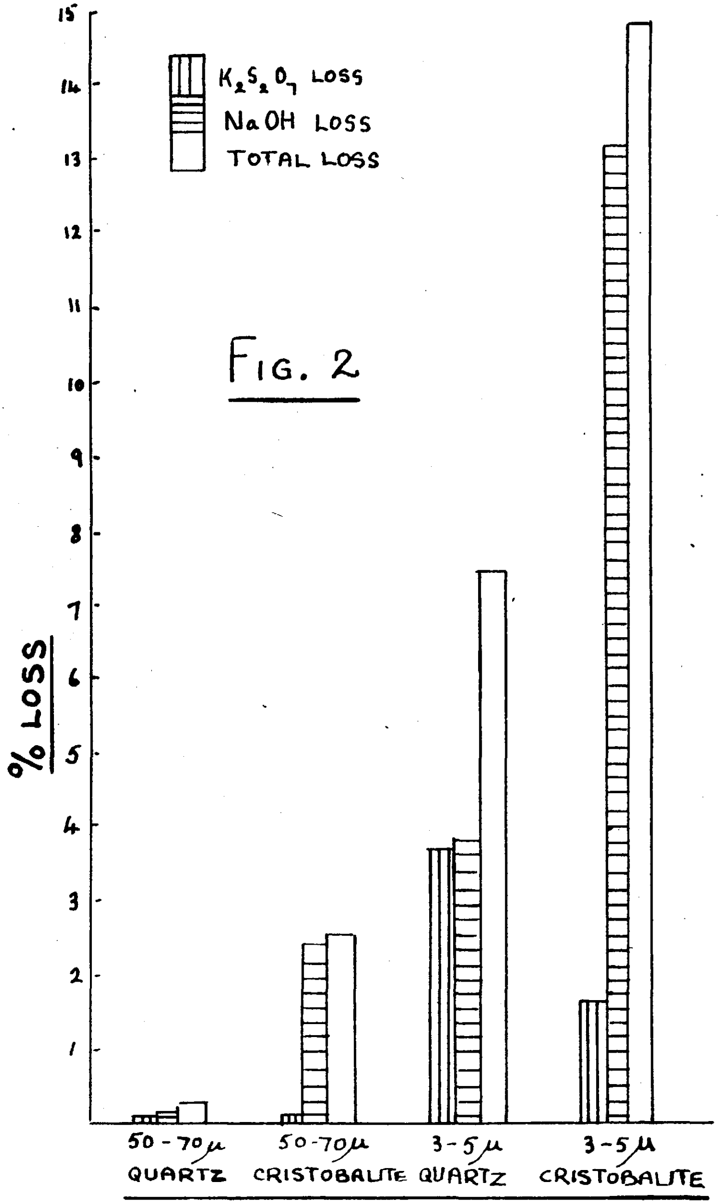


FIG. 2

this inquiry resolved itself into the examination of the losses incurred in the two main parts of the analysis, the fusion and the alkali extraction, by quartz and cristobalite.

Particles of both quartz and cristobalite of 50 to 70 microns and 3 to 5 microns in diameter were used. These size ranges were chosen to represent approximately ground rock and airborne dusts respectively. The 3 to 5 micron particles are of a size which can be filtered from liquid suspensions by a No. 42 Whatman paper, thus removing the need for a centrifuge and the possible decrease in accuracy due to loss of material during transfer to and from the centrifuge tubes.

Three samples of each dust were examined. The losses during the single fusion and the alkali extraction were estimated by finding the total loss and subtracting from it, that occurring during a further alkali extraction. This extraction loss may be smaller than the first extraction which means that the fusion loss may be slightly larger than the true value.

The averages of each three results are given in the histogram in Figure 2, which shows:-

I. The great increase in the total losses from the 3 to 5 micron particles compared with those from the

50 - 70 micron particles for both quartz and cristobalite.

2. The larger total losses for cristobalite compared with quartz in both size ranges.
3. The difference in the relative values of the fusion and alkali extraction losses in both quartz and cristobalite.

Detailed examination of the results shows that the total losses for the 50 - 70 micron quartz are small (0.25%) but that those for cristobalite are ten times larger, so that the presence of cristobalite in a rock would give low free silica results. For quartz particles 3 to 5 microns in diameter the total losses are much higher (7.5%) and a large correction factor for the quartz loss in airborne dusts becomes a necessity. Cristobalite again has a larger analysis loss, being twice that of the quartz.

In both size ranges of quartz particles the losses in the fusion and in the alkali extraction are approximately equal. However for cristobalite the fusion loss in each case is small compared with the high alkali extraction loss which accounts for 90% to 95% of the total. It would appear that cristobalite is much more soluble in the relatively cold alkaline environment than in the hot acid

TABLE 8.

Quartz Loss Values

Sample No.	Av. Loss
I	I.8%
2	3.0%
3	3.3%
4	3.0%
5	3.2%
Av. of 2, 3, 4 & 5	3.I%

environment while quartz is equally soluble in both. This is possibly due to the unstable nature of cristobalite at low temperatures, it being a high temperature modification of silica.

The Trostel and Wynne method of analysis cannot be used with accuracy for the estimation of the free silica content of mixtures of quartz and cristobalite since these polymorphic forms of silica cannot be differentiated chemically. The evaluation of a 'silica loss' factor is thus impossible.

The 'quartz loss' value of rock crystal ground to pass a 200 B.S. sieve.

The 'quartz loss' value for use in routine analysis was obtained by analysing several samples of rock crystal separately ground by hand in an agate mortar to pass a 200 B.S. sieve. Duplicate analysis on each sample gave the average results in Table 8.

Great care was taken to prevent excessive comminution of the particles below 200 B.S. mesh in Sample No. I, by grinding for very short periods (about I5 seconds); with the other samples no special care was taken.

The results indicate that this different grinding procedure has produced a difference in the quartz loss value - a 42% reduction. It appears that if no special care is taken with the grinding a fairly constant 'quartz loss' value is obtained. The average value of 3.I% will be used to calculate the correction for all future analytical results. The quartz loss correction is applied by adding to the felspar corrected result a fraction of 3.I% in proportion to the amount of quartz present.

The estimation of the error introduced if the resistant mineral is not felspar.

As has been found in South Wales (I05), the resistant mineral in the fusion residue may not be orthoclase felspar. If this is so a new correction factor should be calculated from the chemical formula of the mineral or more accurately from an analysis of the residue. To estimate the error introduced in the analysis of Stirlingshire coal-measure rocks by the assumption that the resistant mineral is felspar, samples of two shales and two sandstones were analysed and the resistant mineral corrections calculated as coming from both felspar and muscovite. Muscovite was chosen because a mica was seen to be present in the shale and since it is a mineral of low silica content (47%). Orthoclase felspar is a mineral of high silica content (65%). The corrected free silica values are compared in Table 9.

TABLE 9.

Comparison of Corrected Results.

Rock.	Free Quartz: Residue Mica	Free Quartz: Residue Felspar.	Difference	% Difference	Felspar as % of rock.
Shale No.12	30.9%	30.3%	0.6	2.0%	3.0%
Shale No. 5	19.7%	19.3%	0.4	2.1%	2.0%
Sandstone No. 3	72.3%	72.2%	0.1	0.1%	0.8%
Sandstone No.15	94.4%	93.7%	0.7	0.8%	3.8%
Av. Value	-	-	0.5	1.3%	2.4%
Max. Value	-	-	0.7	2.1%	3.8%

These results show that calculating the resistant mineral in these rocks as felspar when it may be muscovite reduces the free silica by on average I.3% of its value with a maximum reduction of 2.I%.

It is of interest to note that the average resistant mineral content of the rocks when calculated as felspar is only 2.4% with a maximum of 3.8%.

The adapted Trostel and Wynne method of analysis appears to be accurate enough for the analysis of Stirlingshire coal-measure rocks assuming the resistant mineral to be orthoclase. If it is found that the amount of resistant mineral increases much and is not felspar a new correction factor should be determined.

The arithmetic mean deviation and percentage error of the adapted method for the analysis of a standard mixture.

Since the two inaccuracies in the method have been successfully compensated by applying correction factors it was considered advantageous to have a figure indicative of the accuracy of the adapted method.

This was done by estimating the A.M.D. from the results of ten analyses of a 40.00% quartz mixture made up as detailed in the materials section (page 28). Double fusions were employed and the corrections for 'resistant

TABLE 10.

A.M.D. of Adapted Trostel & Wynne Method on Standard Mixture.

No.	Fusion Residue as % of original weight.	Arith.Dev. from Av.	Resista Mineral Residue as % of Fusion Residue.	Arith.Dev. from Av.	Free Quartz Corrected.	Arith.Dev. from Av.
1	44.5	0.2	6.5	0.4	40.0	0.1
2	43.7	0.6	6.3	0.2	39.4	0.7
3	44.6	0.3	5.9	0.2	40.5	0.4
4	44.4	0.1	6.4	0.3	39.9	0.2
5	44.7	0.4	6.8	0.7	39.8	0.3
6	44.3	0.0	5.2	0.9	40.8	0.7
7	44.4	0.1	5.7	0.4	40.5	0.4
8	44.0	0.3	6.3	0.2	39.7	0.4
9	44.3	0.0	5.7	0.4	40.4	0.3
10	44.4	0.1	6.5	0.4	39.9	0.2
Av.	44.3	0.2	6.1	0.4	40.1	0.4

minerals' and the 'quartz loss' were applied. The results are given in Table IO.

If the fusion residue (quartz and felspar) is corrected for the quartz lost the average value becomes 45.5%. Now the average free quartz content as estimated is 40.I% and if to this is added the felspar content of 5.3% it becomes 45.4% showing that the attack on the felspar during analysis is negligible and is smaller than that on the quartz.

The average free quartz value from the ten results is 40.I% with an A.M.D. of 0.4, i.e. equivalent to a percentage A.M.D. of ± I.0%, and since the average is so close to the true value it is equivalent to a percentage error of ± I.0%. The table of results shows that the maximum deviation in these estimations is 0.7 which is equivalent to a maximum percentage error of ± I.8%. The error in these two cases appears to be due to manipulative inaccuracies.

In estimation No. 2 some of the material has been lost either during the fusion or during the washing of the fusion products since the fusion residue weight is low, with an arithmetic deviation of three times the A.M.D..

Sample No. 6 seems to have lost material during the hydrofluoric acid evaporation since its evaporation residue is low, with an arithmetic deviation twice the average. If these two maximum error samples No. 2 and No. 6 are ignored the percentage error is reduced to ± 0.8% with a maximum error of ± I.0%.

A comparison of the A.M.D. of the fusion residue and the hydrofluoric acid residues reveals that a greater deviation of the results occurs after the acid evaporation showing that extra care is required for this operation.

Time required for duplicate analysis.

One estimation in duplicate with two fusions and two alkali extractions can be done in two and a half days while two estimations in duplicate can be done in three days.

The analysis loss of chalcedony.

During the differential thermal analysis for the free quartz content of the rock samples previously examined by the adapted chemical method discrepancies were discovered between the results. Those from the physical method were on average 6.6% low. This difference could be explained by the presence of some form of silica other than quartz which is the only form determined by differential thermal analysis in the temperature range used. Petrological examination of sandstone No. I5 revealed the presence of chalcedony - a cryptocrystalline form of silica - which is not estimated by differential thermal analysis. The behaviour of chalcedony during chemical analysis was investigated.

A sample of chalcedony was ground to pass a 200 B.S. sieve and subjected to the adapted chemical analysis. The loss was found to be 33.5%. The purity of the chalcedony as estimated by hydrofluoric acid evaporation before and after analysis was 98.8% and 98.9% silica respectively showing that there had been no preferential removal of the impurity.

The most important conclusion to be drawn from this experiment is that the Trostel and Wynne method does not only estimate the free quartz but also two thirds of the chalcedony present which means it gives a low estimate of the free silica and a high estimate of the free quartz.

Summary of conclusions.

After a consideration of the results obtained from the experimental work carried out on this chemical method of analysis the following are the conclusions. These conclusions apply to the method, adapted as described, when used for the analysis of Stirlingshire coal-measure rocks.

I. To obtain optimum decomposition two pyrosulphate fusions are necessary.

2. When this method is used two corrections must be employed, one to compensate for quartz lost and the other for the presence of pyrosulphate resistant minerals.

3. When these factors have been applied to results from the analysis of a standard quartz mixture the percentage error is within ± I.0%.

4. During the analysis of Stirlingshire coal-measure rocks it was found that if the resistant mineral was muscovite and not felspar, as is assumed for the derivation of the correction factor, the results tended to be low, with an average percentage error of - 2.0%.

5. One estimate in duplicate can be done in two and a

half days and two estimations in duplicate in three days. This fairly short time and the simplicity of the technique recommend this method above those of Shaw (46) and Durkan(53).

6. Mixtures of quartz and cristobalite cannot be analysed accurately since it is impossible to evaluate a correction for the combined quartz-cristobalite loss. Cristobalite has a higher loss than quartz, the relative losses varying with particle size. The smaller the particle size the closer become the results.

7. This method estimates two thirds of any chalcedony present.

PART 3: The Estimation of the Quartz Content of Rocks and Dusts by Differential Thermal Analysis.

Introduction.

Methods of thermal analysis, used for many years in the study of the structural changes taking place in heated metals, are based on the measurement of the heat evolved, or absorbed, when the material undergoes physical or chemical changes on being heated or cooled.

Many workers have employed thermal analysis (62) (63) (64) (65) and differential analysis (4I) (42) (43) (44) (45) (66) (67) (68) (69) (70) (7I) in the examination of minerals, clay minerals in particular. In this field thermal analysis has become very useful for differentiating between clays in complex mixtures (45).

Differential thermal analysis, hereafter referred to as D.T.A., is a thermal analysis technique in which the temperature of the test material is measured relative to that of an adjacent inert material by thermocouples connected in opposition and embedded in the test and inert materials. The evolution or absorption of heat in the test sample causes a difference in temperature between it and the inert sample which produces a difference in E.M.F. between the thermocouple junctions. The experimental results are obtained from measurements of this difference in E.M.F..

Trombe (4I), Berkelhamer and Speil (42) and Grimshaw, Westerman and Roberts (43) have all published D.T.A. techniques for the estimation of quartz and the work carried out by the author follows a paper by Roberts (72) - "A Positive Method for the Determination of Free Silica in Dusts". The technique used is that suggested by Roberts in his earlier papers (70) (45).

As has been mentioned in Part 2 chemical methods of analysis for free silica are rendered inaccurate by

(I) the presence of resistant minerals and

(2) the increased solubility of quartz particles of small size. Grimshaw, Westerman and Roberts (43) have carried out a large number of tests upon mixtures of quartz with a variety of diluents which have so far failed to show that the accuracy of the analysis under their experimental conditions is influenced by the environment of the quartz. They have also shown that quartz samples from different sources give similar thermal effects. Therefore this analysis is specific to quartz and is not interfered with by other minerals.

The influence of the particle size of quartz on its thermal effect has not to date been examined and Roberts

(72) while putting forward his method as being suitable for the analysis of dusts states that their independence remains to be proved. He suggests however that since the thermal effect from clays has been proved to be independent of particle size there is good reason to assume this also applies to silica minerals. However in the discussion after the delivery of another paper Roberts (43) made the statement:- "It has recently been stated that if quartz is ground below one micron it loses its crystal form and its X-ray spectrum". This would appear to mean that the grinding of quartz to this size destroys its crystallinity and also therefore its ability to undergo the α - β phase change. It would not then be estimated by D.T.A.; a serious situation when about 50% by weight of the quartz in an airborne coalmine dust has an average particle size of approximately one micron (page I8).

The conclusions drawn from the literature are that D.T.A. for quartz is free from interference from other minerals and may or may not be free from interference from the effect of the particle size of the quartz.

The work carried out on D.T.A. consists of an investigation of the accuracy of the method when applied to the analysis of rocks and a detailed investigation of the effect of particle size on the thermal effect of quartz.

Description of Apparatus.

General Description.

The apparatus used in this investigation is based on that described by Roberts (45). Briefly the principal components are:-

I. A specimen cell consisting of a thin walled refractory container with two similar compartments into which are packed the test and inert materials in which the thermocouples are embedded.

2. A refractory block into which the specimen cell fits. This block is made in two halves and when assembled is cylindrical in shape except for one square end which locates the block in the furnace tube.

3. The furnace, a refractory tube, round which the heating element is wound, in a square aluminium case packed with asbestos wool.

The use of refractory in contrast to metal materials in the construction of the apparatus confers on it important advantages (43). Since the thermal conductivity of refractory is much lower than that of metal the heat transfer between the test sample and the surrounding material is slower. This produces a larger and more sharply defined temperature difference when the endothermic or exothermic change occurs in the test sample. Secondly, for the same reason, the mass of refractory cools more evenly and prevents local cold spots which might cause a drift of the zero or base line of the cooling curve (as will be explained later). The test is carried out during cooling of the samples since

(I) the cooling rate is more reproducible than the heating rate which is difficult to control;

(2) the drift of the zero line of the thermal curve is reduced to a minimum and is linear. It can then be allowed for by extrapolation.

The third benefit of refractory materials is that the thermocouple leads passing through the block do not need to be insulated.

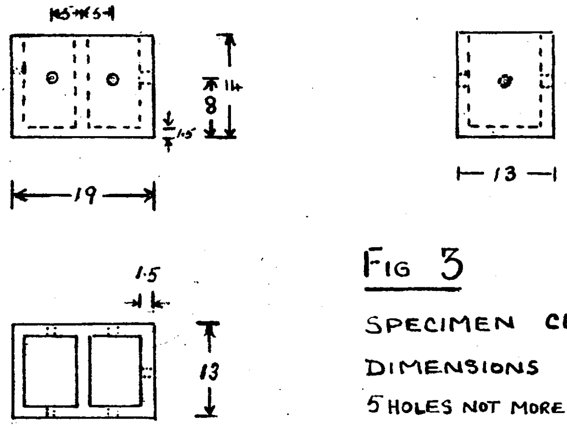


FIG 3

SPECIMEN CELL

DIMENSIONS IN M.M.

5 HOLES NOT MORE THAN 1·6 MM. DIA.

Detailed Description.

A. Specimen Cell.

The first specimen cells used were manufactured industrially (73) from zircon / zirconia refractory bound with ethyl silicate. The wall thickness of I mm. suggested by Roberts (45) was increased to 2 mm. to suit the convenience of the manufacturers. Unfortunately these cells were very friable, so much so that with continued movement the thermocouple wires gradually enlarged the holes in the walls till the shifting position of the thermocouple junctions produced inaccuracies in the results.

Specimen cells are now being produced in alumina or mullite (74) to designs approved by Roberts. These cells do not suffer from the above mentioned fault. Their dimensions are shown in Figure No. 3.

B. Refractory Block.

A refractory block was made to the design of Roberts by casting a block of refractory cement 5½" long by 2½" square in a wooden mould, without the application of pressure as recommended. A satisfactory block was obtained.

A thick paste was compounded from I400 g. of fine grained alundum cement (grade c.c. 60) (74), I40 g. kaolin

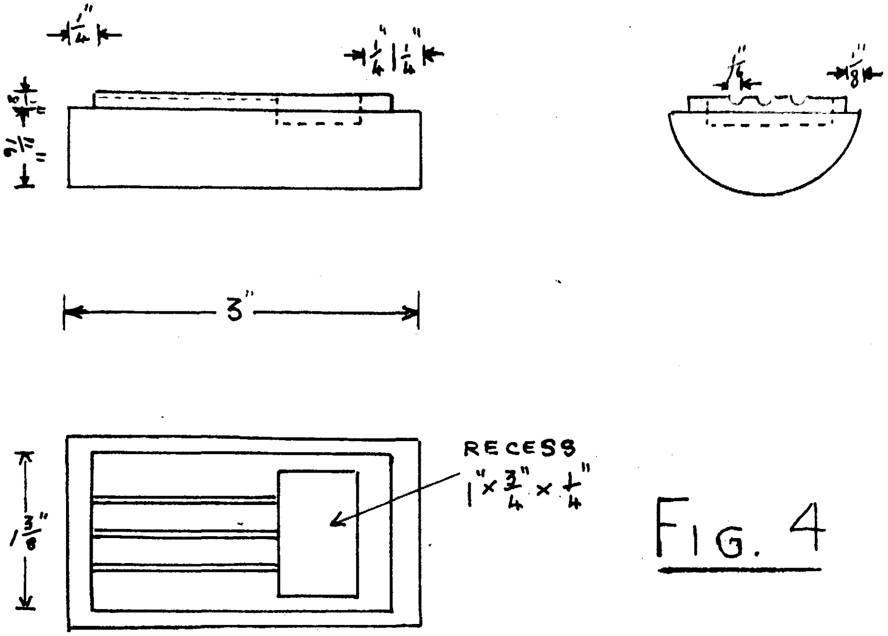
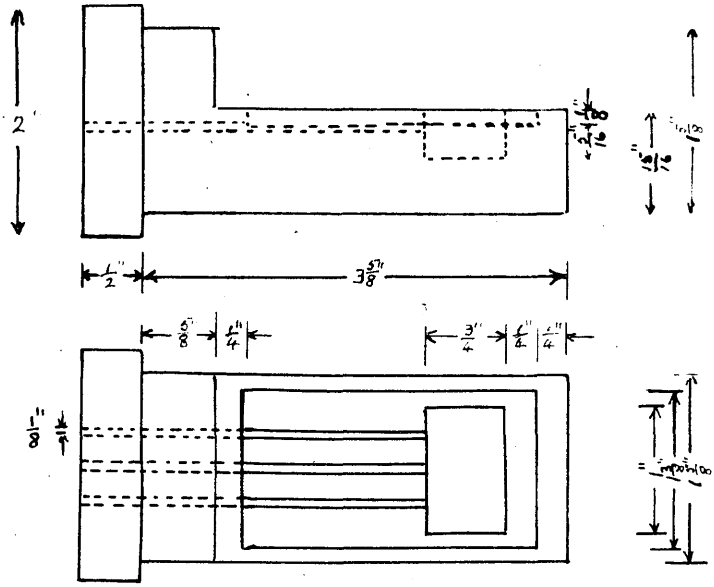


FIG. 4



REFRACTORY BLOCK

and 300 g. of water and placed in three or four separate portions in the wooden mould. Each portion was 'dumped' and 'squashed' to express as much as possible of the occluded air before the others were added. The block was allowed to dry at room temperature for I week. It was then dried at 37°C for 2 days, I00°C for I day and II0°C for 2 days before it was shaped by hand to form the bottom half of the refractory block (Fig. No. 4). Another block, half the depth, was moulded, dried, and shaped to form the top half of the block. After a final shaping of the outside curved surface of the assembled block it was fired at I200°C for 6 hours in a gas fired furnace. A second block made industrially (74) was obtained later.

C. Furnace.

The furnace built round a mullite tube (I $\frac{15''}{16}$ internal diameter $\frac{3''}{16}$ wall thickness and 7" long), and wound to II ohms resistance with I8 S.W.G. nichrome wire as suggested (45), burned out at 6 amps. It was decided when rewinding to reduce the amperage required by winding the furnace tube with 22 S.W.G. (2.523 ohms / ft.) nichrome wire to a resistance of 50 ohms. An I00 ohms double tube resistance in series controlled the D.C. supply. The furnace case was made from $\frac{1''}{32}$ thick aluminium and the ends from $\frac{3''}{8}$ thick Sindanyo. The heating element was wound on the central

FIG. 5. THERMOCOUPLE — CIRCUIT —

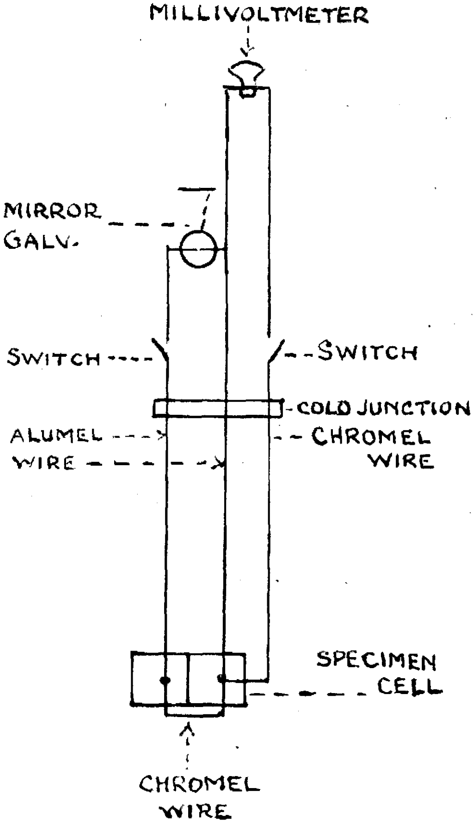
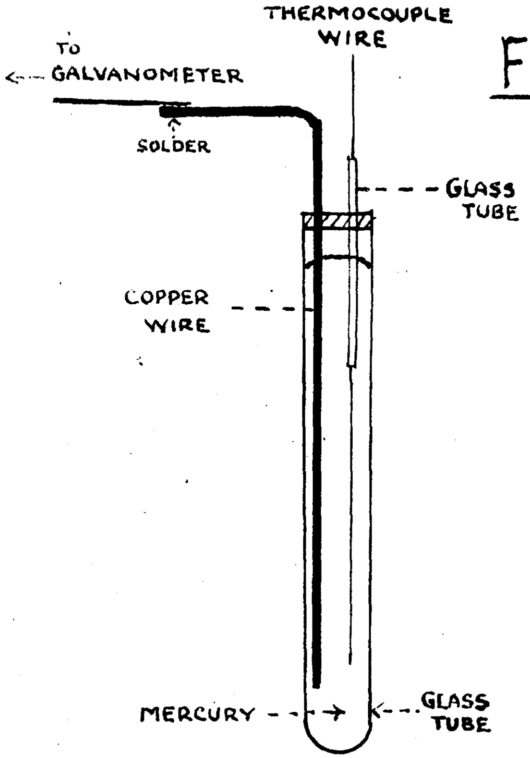


FIG. 6.



— COLD JUNCTION —

5 ins. of the tube and coated with refractory cement. The packing used was asbestos wool.

D. Thermocouples.

The thermocouples 26 S.W.G. chromel-alumel wires (75) were cut and soldered as shown in Fig. No. 5. Enamelling silver solder (m.p. 800°C) (76) was used to solder the joins after the wires had been assembled in the cell. Borax is a suitable flux but must be carefully removed by boiling in water otherwise it gradually corrodes through the wires while in use.

A Dewar Flask filled with ice and water was used to hold the cold junction. Easy dismantling and assembly of the thermocouple circuits during use was obtained as shown in Fig. No. 6. By the arrangement of switches and thermocouples shown (Fig. 5) it is possible to measure the E.M.F. produced by the difference in temperature between the inert and test samples.

E. Galvanometer.

A Cambridge millivoltmeter graduated 0 to 40 millivolts was used to give a measure of the inert sample temperature. The E.M.F. produced by the difference in temperature between the test and inert samples was measured by the deflection on a d'A rsonval mirror galvanometer.

TYPICAL D.T.A. CURVE

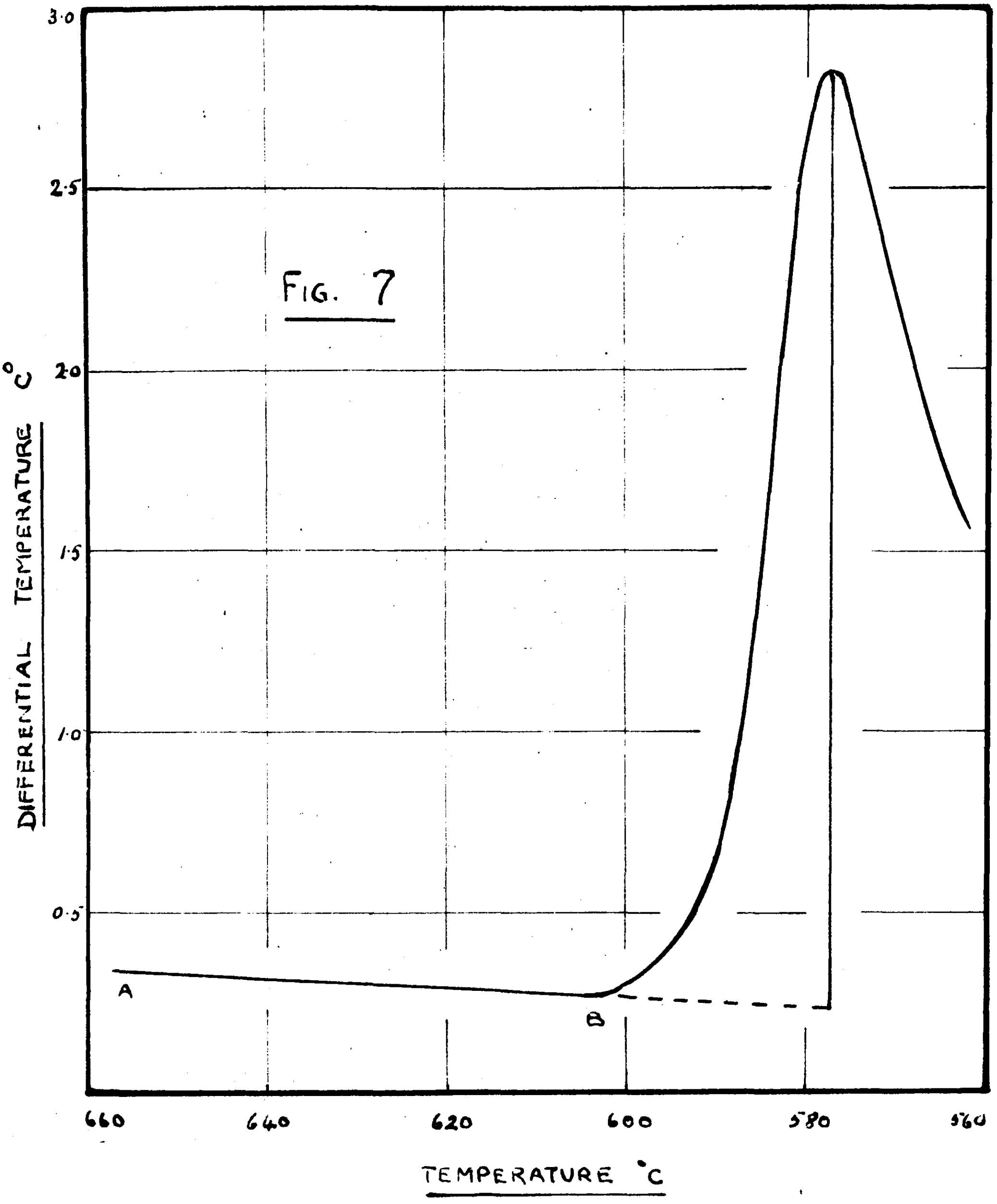


FIG. 7

Outline of Method.

A weighed amount of test sample is carefully packed into the 'one-wire' cell compartment and a weighed sample of fine inert material is packed into the other. Alumina was recommended as an inert material by Roberts. Finely ground chromatographic alumina (77) was used in the present work. After assembly in the furnace and the connection of the thermocouple circuits, the temperature is raised to 700°C. The current is then switched off and the furnace allowed to cool. Measurements of the temperature of the inert sample and test sample are begun at 650°C and continued at fifteen second intervals until 550°C. From the results a thermal curve is drawn. A typical curve for pure quartz crystal is shown in Fig. No. 7. The drift is represented by the line A_B which ideally should be horizontal. Extrapolation as shown establishes the base of the thermal curve and precisely defines the 'peak height'. It has been shown by Roberts (43) that a linear relationship exists between the percentage of quartz present and the observed thermal effect. If a calibration graph is drawn for a set of thermocouples it is possible to estimate the quartz content of a sample from a knowledge of the peak height of the thermal curve.

Theoretical Considerations.

The thermal curve as used by Roberts and others for clay analysis is obtained by plotting the temperature difference between the test and inert samples against the temperature of the test sample. The position of the peak of this curve is indicative of the decomposition temperature. This is unaffected by the amount of the clay present as it would be if the temperature difference was plotted against the inert sample temperature (45). Useful as this procedure is for the identification of clay minerals it is not required for the analysis of quartz. This means that the temperature difference can be plotted against the temperature of the inert material.

Since samples of similar quartz content will give constant temperature differences between test and inert samples the E.M.F.s produced by one set of thermocouples will be constant. Now as the deflection from a suspended coil galvanometer is proportional to the E.M.F. across it, it follows that the deflection in centimetres can be substituted for the temperature difference between the samples and plotted against the inert sample temperatures.

It has been shown that the cooling curves (millivolts against time) of the inert material are all parallel straight lines which means the temperature is varying linearly with time. Therefore it should be possible to substitute time readings for those of the inert sample temperature in the thermal curve, which would then be the graph of deflection in centimetres against time.

This deduction has been proved correct. The calibration curve, peak height against quartz content, for a set of thermocouples was a straight line passing through the origin. The peak heights were measured from deflection against time curves.

Much time is saved in the calculation of the results by this modification.

Experimental Technique.

Preliminary Experiments.

Numerous preliminary experiments were carried out on this apparatus to establish the practical technique. The conclusions from their results are given below with others gathered during the whole of the work on D.T.A.

(A) Heating Current.

A current of at least 2.I amperes (250 volts) is required to heat the furnace and contents above 700°C. At this amperage the heating time is 2 hrs. This can be reduced to I hr. by increasing the current to 2.4 amps. Further reduction can be obtained by using 2.6 amps. but above this is not recommended in case the heating element should burn out.

(B) Background temperature difference.

Soon after the heating current is switched off, the furnace being at 700°C, a difference in temperature between the inert and test samples occurs, causing a deflection on the mirror galvanometer. This deflection reaches a maximum in 4 to 5 minutes and then begins to fall. Over the temperature range during which analysis readings are taken the graph is linear but at an angle to the X-axis. This is the drift of the linear portion of

— CONSTANT PEAK HEIGHT —

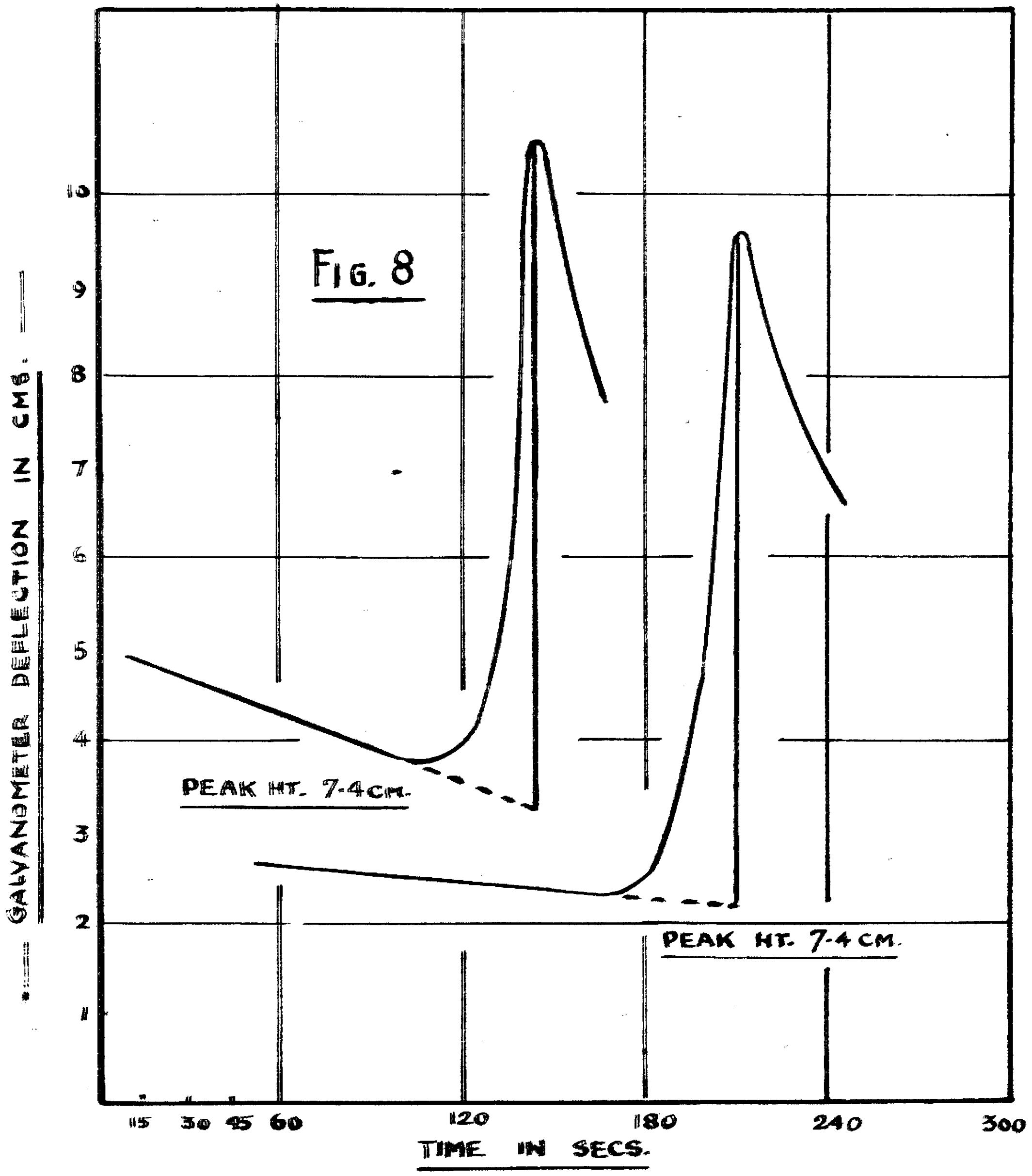


FIG. 8

the D.T.A. graph mentioned by Roberts and is invariably present.

(C) Effect of difference in packing.

The angle to the X-axis of the linear portion of the D.T.A. curve varies from sample to sample of one material and is apparently influenced by differences in the packing of the sample in the specimen cell. However as shown by Roberts (43) extrapolation corrects this difference giving constant peak heights from one material (Fig. No. 8).

(D) Irregularities in the linear portion of the D.T.A. curve.

If the linear portion of the curve deviates much from a straight line especially when the deviation is next to the peak the result is suspect, since it is not known whether this condition influencing the readings has changed, ceased, or is still operating. When the graph has returned to the straight line before the peak, as often happens, the result is probably satisfactory. Duplicate results should always be carried out with a new sample of material.

(E) Reproducibility of results.

Results can be 'reproduced' within ± I% of their average. Duplicates normally lie within this range and if not are usually well outside it. If this happens a third result should be obtained and the doubtful one discarded.

This 'reproducibility' is concordant with the 'accuracy' of ± I% claimed by Roberts.

(F) Moisture in dusts.

All powders used must be dry otherwise the moisture evaporates suddenly when placed in the hot furnace and blows open the powder bed. This also occurs if a dry powder packed in the specimen cell is placed in a hot refractory block and is presumably due to sudden air expansion. Therefore all powders should be dried and the specimen cell placed in a cool refractory block.

(G) Removing the test sample.

Great care must be taken not to disturb the inert sample when removing the test sample from the specimen cell. For accurate analytical work it is better to replace the inert alumina each time.

(H) Reproducibility of cooling rate.

It was discovered that the inert sample cooled at the same rate on all occasions. This made it unnecessary to take readings of the inert sample during the test. As explained earlier (page 62) it made possible the substitution of time readings for the inert sample temperature readings in the D.T.A. curves.

Standard Analytical Procedure.

The practical details are given here in full because of their importance in such a sensitive method of analysis.

Preparation of Materials.

(a) Inert material.

All the work carried out in this investigation was done using alumina from one sample of chromatographic alumina, (77) ground to a fine powder, for 24 hours in a porcelain ball mill. Portions of this were dried and kept in a desiccator until required.

(b) Standard quartz.

This material was used to calibrate the thermocouple sets. Absolutely clear rock crystal (78) was powdered in an iron mortar to pieces below $\frac{1}{8}$ in. diameter. These were heated with hot concentrated hydrochloric acid until the iron from the mortar was completely removed.

The $\frac{1}{8}$ in. pieces were then ground by hand in an agate mortar to pass a 200 B.S. sieve. 100g. was prepared in this way. Further extraction with acid was not carried out as this would have resulted in the loss of the fine particles. The silica content by hydrofluoric acid evaporation was 99.9%.

Standard quartz mixtures were made up from the inert alumina and this standard quartz. Each mixture was made up as required in the quantity required. To serve as a check on the weighing duplicate results were taken from separately compounded mixtures.

Mixtures containing 20% quartz were found to give galvanometer deflections of I2 - I4 cms. and since the scale can be read easily to I mm. this was considered to be sufficiently accurate I mm. in I30 mm. i.e. ± 0.8%. All high-silica sandstone materials for analysis were made up to 20% mixtures and if the deflection was below 5 cms. a 40% mixture would be used. Shales were analysed without dilution.

This procedure gave as standard conditions as could be obtained over many analyses.

(c) Rock samples.

Unless otherwise stated all samples of rocks analysed were ground to pass a 200 B.S. sieve.

Assembly of Apparatus.

(a) Packing of cell.

It was found convenient to weigh the materials onto watch glasses and to transfer them with a small brush to the specimen cell placed on a glass plate. The powders were carefully tamped down to ensure proper packing about the thermocouples. The glass plate retrieved any material spilled.

The zircon / zirconia specimen cells held 0.800 g. of material and the alumina cells 0.500 g.

(b) Assembly of block and location in furnace.

After the cell and thermocouple leads had been placed in position the powder beds were again tamped down in case movement had disarranged the thermocouple leads. The assembled block was placed in the furnace and clamped in position. The clamp served to hold the block centrally in the furnace tube which helped prevent local overheating resulting in a large drift of the zero or base line of the D.T.A. curve.

Further movement of the thermocouple leads in the block and cell was prevented by clamping them in a retort stand clamp just outside the refractory block. This also prevented accidental contact. The ends of the thermocouples were cleaned with fine emery paper before insertion in the mercury of the cold junction.

Measurement of the thermal effect.

A current of 2.4 to 2.6 amps. was used to heat the furnace until the temperature of the inert material gave a reading of 30 mV. on the millivoltmeter. The current was then switched off and the furnace allowed to cool until the millivoltmeter reading was 27 mV.. At this point the millivoltmeter was switched out and the mirror galvanometer switched in. The first reading was taken after 30 secs. and further readings at I5 sec. intervals till after the phase change deflection. The maximum deflection due to the quartz was also noted.

The results were plotted, galvanometer reading in centimetres against time in seconds, to give the D.T.A. curve from which the peak height is measured.

Calibration of thermocouple sets.

Since the calibration curve, peak height against percentage quartz content was found to be a straight line through the origin. The sets were calibrated against 20% quartz mixtures and all further determinations calculated by simple proportion without reference to calibration curves.

[illegible]ale 4 I2.2% I9.[illegible]

x Average of Duplicate results.

TABLE II.

Comparison of D.T.A. and Trostel and Wynne Analysis Results.

Rock Sample	Thermocouple Set Number	Free Quartz Content DTA x	Free Quartz Content T&W x	Difference
Redding Roof (A)	I	87.6%	93.7%	6.I%
" "	4	86.9%	-	-
" (B)	5	80.0%	88.8%	8.8%
" "	6	80.4%	-	-
Plean Roof	4	67.7%	72.2%	4.5%
Plean Shale	4	I2.2%	I9.3%	7.I%
Average	-	-	-	6.6%

x Average of Duplicate results.

The Determination of the Free Quartz Content of Coal-measure Rocks.

To test the reliability of the chemical method of analysis the quartz contents of several rocks previously analysed by the modified Trostel and Wynne method were estimated by D.T.A.

The sandstones were ground to pass a 200 B.S. sieve and diluted with inert alumina to give 20% mixtures. The shales were analysed undiluted.

The results in Table II show two important facts.

I. The reproducibility of the results from different thermocouples is still below the ± I% accuracy claimed for the method.

2. The values obtained by the chemical analysis are seen to be larger than those from D.T.A. by an average of 6.6%.

A qualitative petrological examination of the Redding Roof (A) showed the presence of small amounts of chalcedonic silica. As previously stated a sample of chalcedony (98.8% silica) lost a third of its weight during the chemical analysis. When analysed by D.T.A. this chalcedony gave a reaction equivalent to 2% quartz mixture. This figure agrees with I to 4% found by Berkelhamer (79).

The fact that chalcedony is not estimated by D.T.A. means that since it may be found in rocks of high free quartz content (80) the free silica value of such rocks will be higher than that obtained by D.T.A. This probably accounts for the low free quartz results obtained by Roberts (43) from Welsh quartzites. They were all below 85% quartz. He suggested it might be due to the presence of amorphous or colloidal silica.

This non-estimation of chalcedonic silica is important if the method is being used in silicosis research because chalcedony is toxic and can produce silicotic reactions in animals (Gardner (8I)).

Table II shows that the percentage difference between the chemical and D.T.A. results is very high with samples of low quartz content like the Plean shales and so D.T.A. would be very inaccurate when used to analyse such rocks.

The Influence of Particle Size on The Differential Thermal Analysis of Quartz.

Introduction.

Since the average particle size of the quartz in Welsh coalmine airborne dusts is less than one micron (Table I) , the influence of particle size on the thermal effect of quartz as measured by D.T.A. must be decided. Roberts states that the temperature at which the peak of the thermal curve occurs is not altered by the particle size of the clays (45) and that the small particles will lose their heat more quickly than the larger particles causing the thermal curve to return to the base line more quickly. The following experiment was carried out to remove any doubt about the effect of particle size of quartz.

Experimental.

Pure quartz (70 to 300 microns) was prepared from large quartz crystals. These were ground by hand in an agate mortar and then repeatedly sedimented from water to remove the fine particles. The product, 99.9% silica, (70 to 300 microns) was then ground for I7 hours in a mechanically operated agate mortar. After heating at II0°C for 4 hours to remove moisture this dust was analysed by D.T.A. and found to have a quartz content of 50.5%. This proves that the reduction of the particle size of quartz has an effect on its differential thermal analysis.

There are two possible explanations for this effect, either the particle size, as such, is influencing the heat transfer conditions or the quartz particles have been altered to some degree by grinding. It has been mentioned by Roberts that on grinding below I micron, quartz loses its X-ray pattern (43). Since solubility experiments (82) have shown that ground quartz particles are covered by a layer more soluble than the core, the second explanation was favoured.

The effect of grinding on quartz particles was then investigated.

The Effect of Grinding on Quartz Particles.

Introduction.

Beilby (83) showed by microscopic techniques that the polishing of any crystalline substance produces on the surface "a film which is in many respects, essentially different from the general body underneath it". He postulated that during the process of polishing a thin surface layer of the crystal is melted and flows as a liquid over the surface, covering the abrasion marks. This layer was also shown to have a higher solubility than the crystalline core and was present on a large number of crystalline surfaces, metal and non-metal. Quartz he mentioned in particular as being an example of a hard material capable of being highly polished. He further suggested that "the grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves the transformation of, at any rate, a part of the substance into the vitreous condition".

Beilby concluded that the layer was amorphous but Hamburger in 1932 (84) showed that the polished surface films of crystalline materials consist of lamellae of levelled sub-microscopic crystallites and that from the surface of such films inwards to the core the physical structure of the material shows a gradual change. Finch in 1937 (85) showed that polishing resulted in flow on single calcite crystal surfaces and that the polish layer is crystalline and integral in structure with the underlying crystal when the surface is a cleavage plane. If the polished surface is steeply inclined to all cleavage planes it is vitreous and gradually crystallises with heating.

Ray (86) during experiments on the heat of solution of various forms of silica in hydrofluoric acid showed that the heat of solution of quartz ground for a long time was greater than that of quartz dust produced by a short grinding treatment and also that the heat of solution of vitreous silica was greater than that of either. His conclusion was that the prolonged grinding had converted some of the quartz to a vitreous silica. He calculated from the heats of solution that 31.2% of the quartz had been vitrified and from a consideration of the change in density that 25.7% had been vitrified.

These results of Ray's were criticised by Sosman (87) who concluded that the observed reduction in density was caused by "some unrecognised factor" and not by grinding. He quotes the work of Johnston and Adams (88) who obtained no reduction in density with decrease in particle size. They however did not specify grinding times and their particle sizes are relatively large, the smallest being from 20 microns to the limit of vision. Also this finest dust was obtained by sedimentation from water and no mention is made of precautions taken to recover the finest particles from the water. Sosman suggested that the reduction in density might be due to agate worn off the mortar during grinding.

There would appear to be no doubt that ground quartz will have on its surface a disturbed layer and from the previous experiment it appears that this layer has lost its crystallinity since it no longer gives the α to β quartz change on which D.T.A. is based.

In view of the somewhat controversial results it was decided to confirm Ray's work and to examine the ground product for the presence of cristobalite and tridymite; two high temperature silica modifications. Since the surface flow is due to high local temperatures (89) (90) it was thought possible that cristobalite and tridymite might be formed although this change is normally slow.

It was also decided to investigate the abrasion of the mortar during quartz grinding, and to correlate if possible the grinding time, specific surface, and quartz

TABLE I2.

Silica Contamination of Alumina Ground in Agate Mortar.

Grinding Time	Silica content of dust
4 hr.	5.3%
I8 hr.	7.2%

TABLE I3.

Silica Contamination of Garnet Ground in Agate Mortar.

Grinding Time	Silica Content of dust	Average	% A.M.D.
0 hr.	40.I%	40.I%	± 0.8%
	40.6%		
	39.9%		
	39.6%		
2 hr.	40.2%	40.I%	± 0.6%
	40.3%		
4 hr.	39.8%		
	40.4%		
I7 hr.	39.7%		
	40.0%		

content of the resultant dust.

The abrasion loss from a mechanical agate mortar.

It seemed possible that since agate is chalcedonic silica and as such is not estimated by D.T.A. at least some of the decrease in the 'quartz content' of quartz after grinding might be due to agate ground off the mortar. This idea is reinforced by a consideration of the relative hardness of agate and quartz. Quartz has a hardness of 7 on the Mho scale and agate about 6 (92), 6.5 (93). The mortar could be scratched by quartz - a test of relative hardness.

To clarify the situation it was decided to estimate the amount of silica ground off the mortar during different grinding periods so that an allowance could be made in later density or quartz determinations for the presence of agate in the ground material. Two six gram samples of fused alumina, 99.7% pure and hardness 9 (92), were ground in a mechanical mortar for 4 and I8 hours respectively. The silica content of the alumina before and after grinding was estimated by evaporation with hydrofluoric acid. Contamination of alumina with abraded agate is confirmed by the result given in Table I2. This was not unexpected since there was a large difference in hardness between the minerals.

Unfortunately it was impossible to obtain a non-siliceous mineral of a hardness of 7, the same as quartz, in a pure enough state. Of the siliceous minerals available the purest were almandine garnets (iron-aluminium garnets $Fe_3 Al_2 (SiO_4)_3$) of hardness 6.5 to 7.5 (94). The hardness of the garnets used was assumed to be between 7 and 7.5 since they scratched quartz.

To give a more homogeneous material the garnets were ground by hand in an agate mortar to pass a 90 B.S. sieve. During the quartz grinding experiments 4 g. had been used. So, to keep the volume of material constant 6 g. of garnet (S.G. 4.0) were used. After grinding, the garnet dust was dried and the total silica content estimated by a volumetric method (95).

Duplicate estimations of the silica content of the garnets before and after 2, 4 and I7 hours grinding were carried out. The results, Table I3, show very conclusively that no silica from abraded agate has appeared in the ground garnet.

The effect of grinding on the density of quartz.

The following experiments were carried out to check Ray's observations.

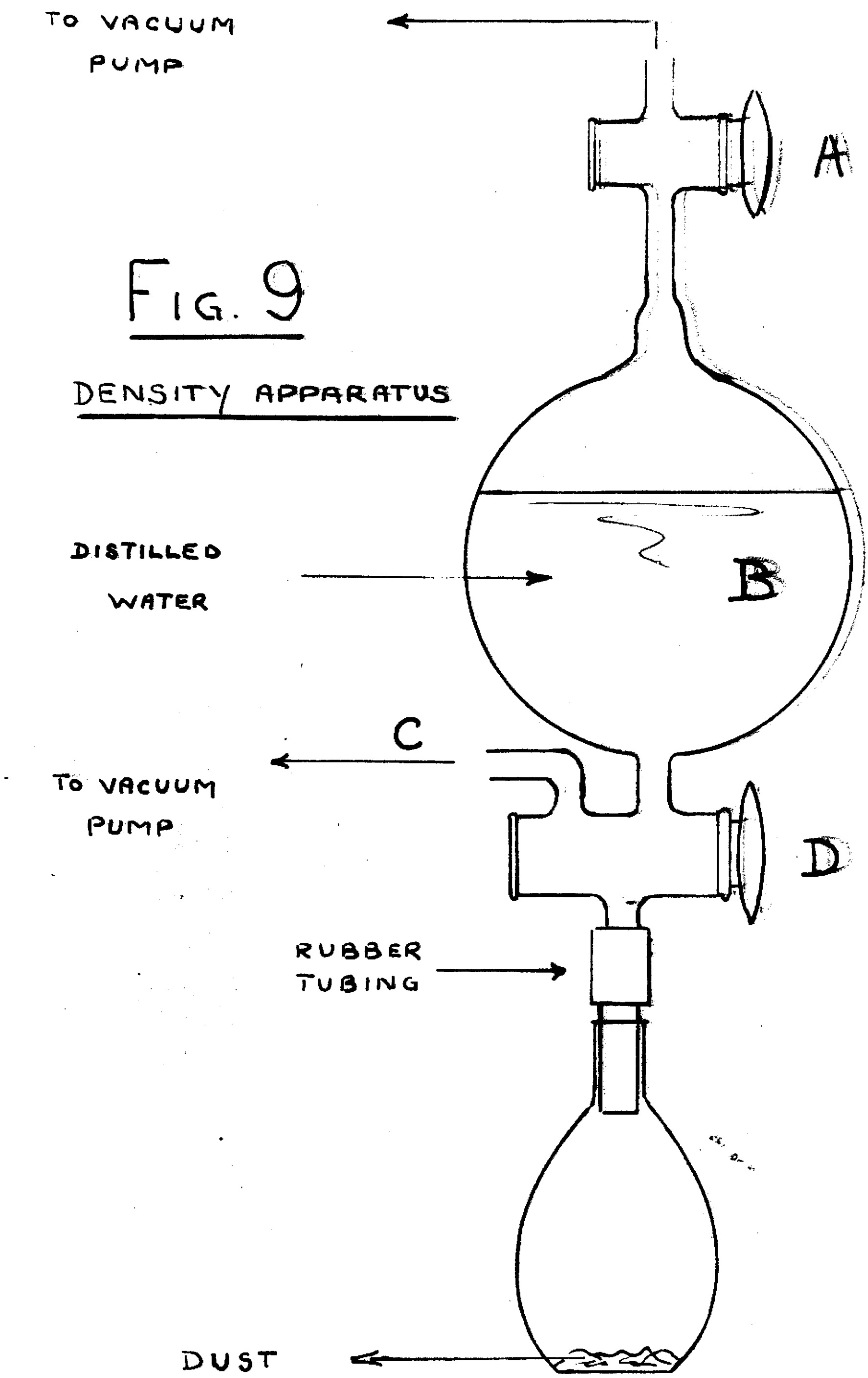
Experimental.

(a) Materials.

I. Quartz dust 70 to 300 microns diameter was prepared

FIG. 9

DENSITY APPARATUS



from large quartz crystals specially selected for their transparency and freedom from contamination. These were ground by hand in an agate mortar and the dust prepared by repeated sedimentation from water to ensure complete removal of the finer particles. The silica content was found by hydrofluoric acid evaporation to be 99.9%.

2. Vitreous silica dust 300 to 600 microns was prepared from Transparent Vitreosil (74) containing 99.8% silica. This was ground in a steel roller mill, sieved and the 50 to 70 B.S. sieve fraction sedimented from water. Microscopic examination of the particles showed the presence of occasional occluded air bubbles.

(b) Density Measurement.

The apparatus shown in Fig. No. 9 was used to estimate the densities of the quartz before and after grinding. The liquid and dust were brought together under vacuum to promote complete wetting of the dust without the presence of air bubbles. Distilled water in the bulb (B) was deaerated by opening stopcock (A) to the vacuum pump for 30 minutes. The air was then removed from the dust in the density bottle through the side arm (C). When this was completed the stopcocks (A) and (D) were opened and the density bottle half filled with the deaerated water. The vacuum pump was then connected to the

TABLE I4.

Densities of Quartz and Vitreous Silica after Grinding.

Material	Silica Modifications Present	Density at I8°C	Experimental Error
Quartz (70-300μ)	Q. No C or T	2.648 (2.649)*	± 0.2I%
Quartz (I7hr. ground)	Q. No C or T	2.550	± 0.I2%
Vitreous Silica (300-600μ)	No Q or C or T	2.20I (2.203)*	± 0.I4%
Vitreous Silica (I7hr. ground)	No Q or C or T	2.230	± 0.25%

* - Figures in brackets after Sosman (87)

Q - Quartz

C - Cristobalite

T - Tridymite

Density figures after Clelland (82).

side arm (C), and the air removed again for 20 minutes. The bottle was detached and filled completely with deaerated water. The densities of 0.5 to 1.0 g. of dusts were measured at 18°C by the normal procedure and the results are reported to three decimal places with an estimated experimental error of not greater than about ± 0.25% of the measured density.

Since high surface temperatures have been shown to be produced during grinding and polishing processes (89) (90) (91) it was considered possible that cristobalite and tridymite with densities of 2.33 and 2.28 respectively might be present in the surface layer as well as vitreous silica. The quartz and vitreous silica dusts were therefore analysed by D.T.A. for the presence of cristobalite and tridymite (appendix).

Results and Conclusions.

The results shown in Table 14 indicate the absence of cristobalite and tridymite in ground quartz and vitreous silica. When it was discovered that the density of vitreous silica had increased with grinding it was examined for quartz by D.T.A. None was found. Solubility results (82) also showed an increase in the solubility of vitreous silica after grinding which would suggest that the layer on these silica dusts may not be truly vitreous.

The density of quartz has been shown to decrease with grinding for I7 hours and this cannot be due to the production of cristobalite and tridymite or to the presence of agate from the mortar.

The increase in density of vitreous silica might possibly be caused by the opening up of occluded air bubbles. However these results as a whole confirm Ray's results.

Further Investigations of Ground Quartz and its Surface Layer.

Introduction.

Briefly summarising the situation at this stage, we have suggested that when quartz suffers prolonged grinding it has produced on its surface a layer of silica of a form other than quartz, tridymite or cristobalite. It may be vitreous, polycrystalline or both. In any case it is not estimated by D.T.A. and so does not give the α to β quartz change. We have also shown that the density of this layer is less than that of quartz.

To elucidate the nature of this layer which could be responsible for the 'apparent quartz loss' in D.T.A., samples of rock crystal were ground for 2, 4, 7, and I7 hours in a mechanical agate mortar and the quartz contents of the dusts were determined by D.T.A. Their densities and specific surfaces were also measured to correlate if possible the quartz loss with time of grinding, change in density and with change in specific surface. If the quartz particle is covered with a non-quartz layer the proportion of this layer should increase with an increase in surface area, i.e. with a decrease in particle size which will occur with progressively longer grinding periods.

The density and quartz content measurements were carried out as previously described and the specific surface by the method of Lea and Nurse (96) (Appendix).

Materials.

The base material for these experiments was the fines collected from the disintegration in a roller mill of large pieces of pure rock crystal. The crushed quartz was extracted repeatedly with hot concentrated hydrochloric acid until all the iron from the roller mill had been removed. The powder was then sedimented several times from water to remove the finer particles leaving quartz of a particle size I00 to 400 microns.

Specific surface of ground quartz.

Experimental details.

Since about 6 g. of material were required for the surface area measurement, two lots of 4 g. each, were ground for each time period to keep the grinding results comparable with previous experiments. The dusts produced were dried for 4 hours at II0°C and kept in a vacuum desiccator. The specific surface measurements were carried out first, because during its estimation the dust is not altered or contaminated in any way and can be used after

TABLE I5.

The Effect of Grinding on the Specific Surface, Density and 'Quartz Content' of Rock Crystal.

Grinding Time in Hours.	Specific Surface cm^2/g.	Calculated Average Particle Size	Density	Quartz Loss
0	-	250 µ	2.664	0.0%
2	9,350	2.4 µ	2.640	32.7%
4	I0,450	2.2 µ	-	34.5%
7	II,800	I.9 µ	-	37.5%
I7	I7,500	I.3 µ	2.606	50.5%

EFFECT OF GRINDING ON SPECIFIC SURFACE AND QUARTZ CONTENT

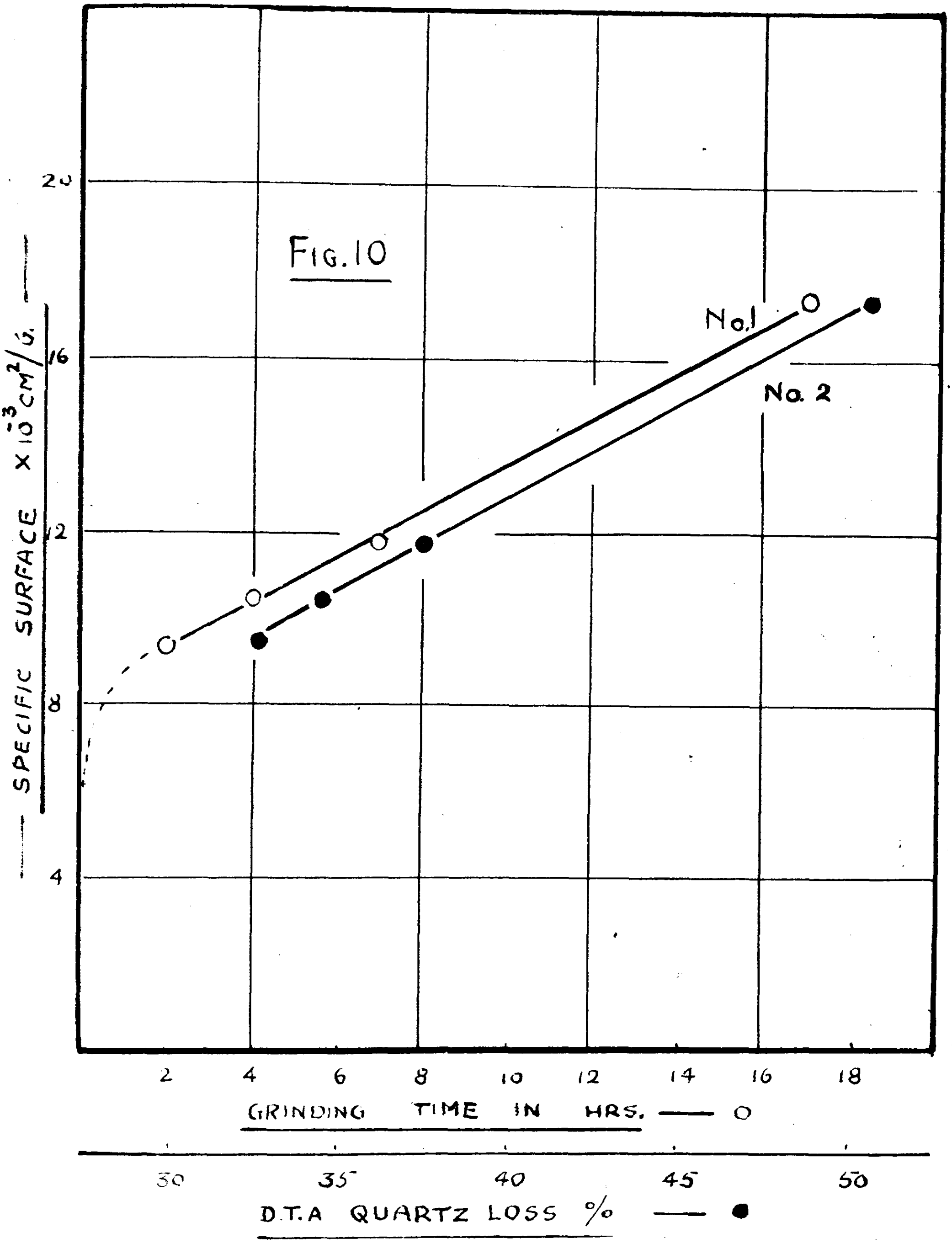


FIG. 10

CHANGE OF SPECIFIC SURFACE WITH PARTICLE SIZE

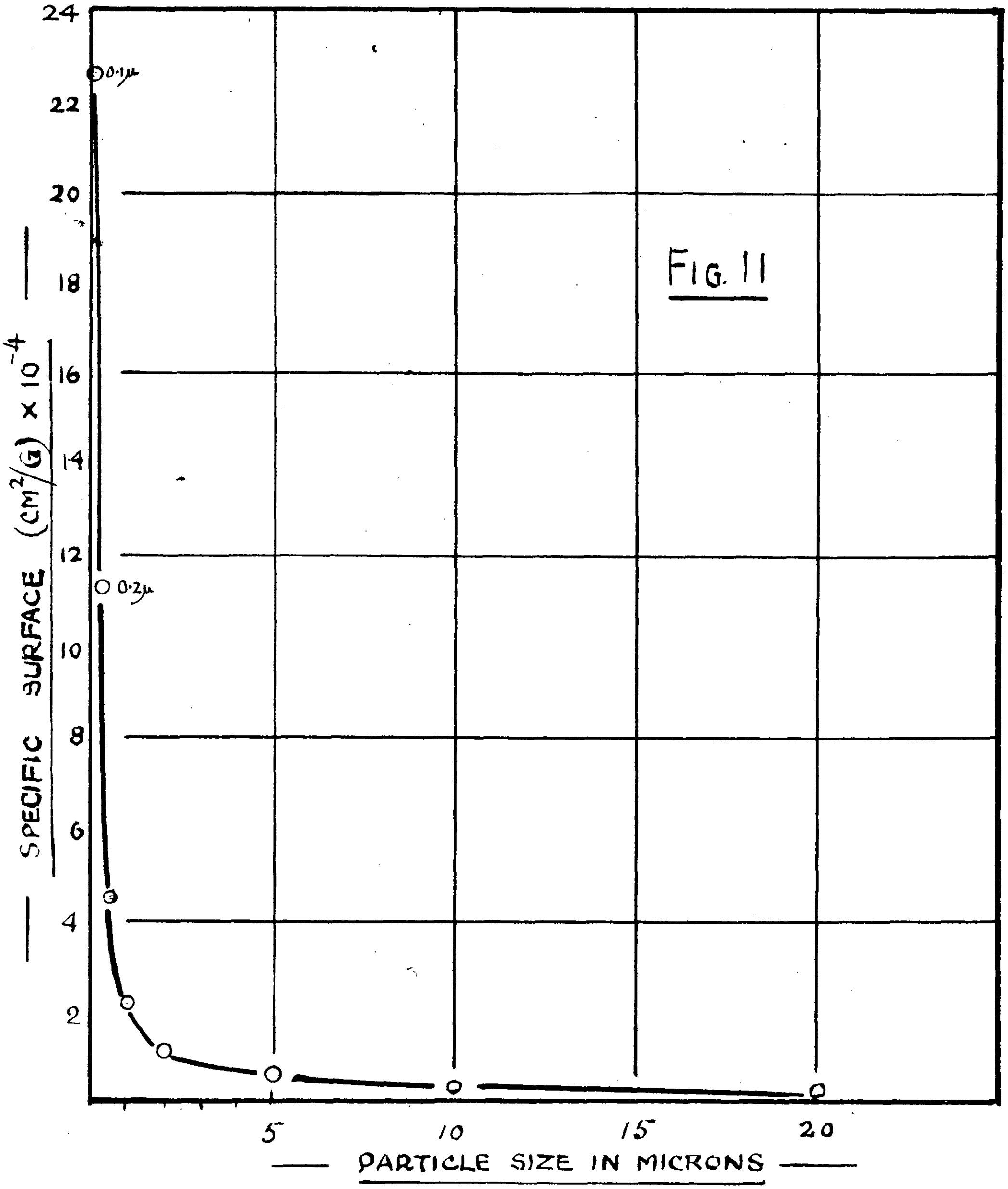


FIG. 11

drying for the quartz content and density determinations.

Results and conclusions.

Table I5 gives the results obtained in all the experiments. The 'quartz loss' referred to is the percentage by weight of the quartz destroyed during grinding. Fig. No. IO shows the graph of specific surface against grinding time (No. I). This has two points of interest; firstly the extremely rapid change of specific surface with grinding times under I hour duration and secondly the straight line portion indicative of a regular change with time. The steepness of the initial part of the curve will be mentioned again later. The specific surface increases very rapidly to a value of 9,000 sq.cm./g., equivalent to an average particle size of about 2.5 microns, and from then on at a regular rate in direct proportion to the grinding time. It appears that as soon as grinding commences the large particles are broken and abraded to produce gradually increasing amounts of very small particles of large specific surface. Thus the powder becomes much more heterogeneous in size with a rapidly increasing specific surface because the specific surface of particles begins to increase rapidly at about 2 microns diameter (Fig. No. II). At 9,000 sq.cm./g. the dust has become much more uniform in size again and any further change in specific surface is at a much slower uniform rate and is possibly mainly due to the abrasion rather than breakage of the particles. It is expected that the particle diameter about which this change takes place will be dependent on many variables:-

(I) The coincidence of the pestle and mortar surfaces.

(2) The speed of rotation and oscillation of the mortar and pestle.

(3) The pressure applied between the mortar and pestle.

Since the 'quartz loss' plotted against specific surface gives a straight line (No. 2 Fig. IO) the 'quartz loss' is in direct proportion to the specific surface and the grinding time. This suggests that the particles are covered with a layer of constant thickness. One corollary of the above hypothesis is that it should be possible to produce from quartz, by grinding, a particle which has no quartz structure and whose diameter will be twice the layer thickness.

Density of layer on ground quartz.

Table I5 shows again that the density of quartz decreases with grinding and that there has been a significant reduction even after 2 hours grinding. Ray (86) calculated from his density results that 25.7% of the quartz ground for I5 hours had changed to vitreous silica. Table I5 reveals that the quartz loss as measured by D.T.A. in quartz ground for I7 hours is 50.5% and that not even the quartz loss for 2 hours grinding is as low as 25.7%. A value of I2.5% altered quartz was obtained by Ray's method of calculation from the density results for I7 hours ground quartz in Table I5. A wide discrepancy is apparent. An extract of Ray's paper follows:-

"Unground silica sand density	2.638
I5 hr. ground " " "	2.528
Crushed silica glass "	2.208

". . . .The difference between the densities of unground silver sand and silica glass is 0.43 and of silver sand unground and ground is 0.II; i.e. 25.7% of the material is converted to the vitreous state".

During these and other calculations it was considered to be more accurate to calculate these values assuming a change in volume in the formation of the layer.

I.e. Vol. of layer + Vol. of core = Vol. of particle ——(I)

If the weight of the particle is assumed to be I00 and the layer to be Wl then the weight of the core is (I00-Wl).

Equation (I) becomes

$$\frac{Wl}{Dl} + \frac{I00 - Wl}{Db} = \frac{I00}{Da} \qquad \text{——(2)}$$

Dl = Density of layer. Db = Density before grinding.

Da = Density after grinding.

Using equation (2) Ray's result became 22.4% and the author's 9.2%. It was noticed that the density reduction found by Ray was 0.II while that found by the author was 0.058 - about half.

The estimation of the moisture content of an undried sample of this dust showed it to contain I.2% water, the presence of which would give a final reduction in density of 0.I0 - almost the same as Ray's. Since Ray dried his dusts well it is suggested that either they became wet again or, as is more likely, the grinding was much more severe producing a dust with a larger specific surface and non-quartz content. There is still a large difference in the value of the quartz destroyed as measured by D.T.A. and calculated from the density.

The only solution appears to be that the density of the layer is not 2.20I but 2.55 as calculated from equation (2) and the D.T.A. result. The calculated density of the layer on the quartz ground for 2 hours is 2.59. It would appear that the layer on quartz is not completely vitreous, at least, and the density would suggest that it is chalcedonic in character.

The thickness of the layer on ground quartz.

To estimate the thickness of the layer on ground quartz, samples of different particle sizes, prepared by different means, were analysed by D.T.A.

Materials.

I. Quartz ground for 2 hours in an agate mortar (from above experiments).

2. Quartz ground for I7 hours in an agate mortar (from above emperiments).

3. Lochaline sand 5 to I0 microns(ground in a porcelain ball mill.)

4. Lochaline sand less than I micron(ground in a porcelain ball mill.)

Calculation.

Let r = radius of core.
T = thickness of layer.
R = radius of particle.

Then volume of particle Vp $= \frac{4}{3}\pi R^3$

and volume of core Vc $= \frac{4}{3}\pi r^3$

$\therefore$ volume of layer $= \frac{4}{3}\pi (R^3 - r^3)$

$$\therefore \frac{\text{Vol. of layer}}{\text{Vol. of particle}} = \left(\frac{R^3 - r^3}{R^3}\right) = I - \frac{r^3}{R^3}$$

i.e. Vol. of layer as fraction of total Vol. $= \frac{Vl}{Vp} = I - \frac{r^3}{R^3}$

$$\therefore \quad \frac{r}{R} = \sqrt[3]{I - \frac{VI}{Vp}}$$

$$\therefore \quad r = R\sqrt[3]{1 - \frac{Vl}{Vp}}$$

But thickness of layer $= R - r = R - R\sqrt[3]{1 - \frac{Vl}{Vp}}$

i.e. Thickness of layer $= R\left(1 - \sqrt[3]{1 - \frac{Vl}{Vp}}\right)$ —— (3)

From the D.T.A. results for quartz content and the densities of quartz, and the ground particles, the ratio of the volume of the layer to the volume of the particle can be calaulated.

E.g. the following results were obtained for the quartz ground for 2 hours.

Quartz content by D.T.A. = 67.6%

Density of particles = 2.640

Density of original material = 2.664

Av. particle size = 2.42 microns (calculated from specific surface)

$\therefore$ Vol. of quartz $= \frac{67.6}{2.664}$ and Vol. of layer $= \frac{32.4}{Dl}$

Vol. of particle $= \frac{100}{2.640}$

$$\therefore \frac{67.6}{2.664} + \frac{32.4}{Dl} = \frac{100}{2.64}$$

$\therefore$ Vol. of layer $= \frac{32.4}{Dl} = 37.88 - 25.37 = 12.51$

$$\therefore Dl = \frac{32.4}{12.51} = 2.59$$

TABLE I6.

Thickness of Non-quartz Layer.

Sample	Av. Particle Size μ	Percentage Layer by weight	Thickness of Layer in μ.
5 to IOμ L.A.S.	6.7	II.7%	0.I4
Rock Crystal	2.4	32.4%	0.I5
"	I.3	50.5%	0.I4
< I μ L.A.S.	0.8	60.0%	0.II
Average	-	-	0.I4

$$\frac{Vl}{Vp} = \frac{12.51}{37.88} = 0.3302$$

$$\therefore \text{Thickness of layer} = 1.21\left(1 - \sqrt[3]{1 - 0.3302}\right) \text{ microns.}$$
$$= 0.15 \text{ microns.}$$

Since it had been shown that the density of the layer on the material ground for I7 hours was 2.55 the above calculation was repeated using 2.50 as the density of the layer instead of 2.59. This increased the thickness to only 0.I6 microns. Thus a relatively large change in density has little effect on the thickness as calculated. Layer densities of 2.50 and 2.60 were assumed for the less than I micron and 5 to I0 micron particles respectively. This was done because density determinations from these dusts would have been inaccurate because of porcelain impurities.

The results (Table I6) indicate that the thickness of the non-quartz layer on all quartz particles is 0.II to 0.I5 microns and is independent of the mode of production and the particle size.

The calculations of layer density and thickness are based on the assumption that the decrease in the D.T.A. quartz content after grinding is due wholly to the production of this non-quartz layer and not to the reduction of the quartz particle size as well. To clearly substantiate the above conclusions this was investigated as shown below.

The effect of particle size on the Differential Thermal Analysis of quartz.

The effect of the particle size, as such, and not in combination with that of the layer was investigated by extracting several quartz dusts with hydrofluoric acid which process was traced by D.T.A. The results clearly show the removal of the non-quartz layer.

The D.T.A. apparatus was calibrated with quartz of average particle size approximately 250 microns. The particles were all in the range I00 to 400 microns. It can be shown by calculation that the weight of the layer on this material is below I% of the total weight so that it will have no measurable effect on the D.T.A. whose reproducibility is ± I%.

Lochaline sand 5 to I0 microns in diameter was extracted for 5 minutes with 40% hydrofluoric acid after which the D.T.A. quartz content had been raised to equal that of the calibrating material; i.e. from 88% quartz to I00% quartz. This dust was chosen because it is closely ranged and contains no fines with large amounts of layer. The result shows that particles less than I0 microns give the same deflection as those of 250 microns. This seemed to suggest that particle size has no effect. It might be however that the effect is only apparent with particles of very small size.

Rock crystal ground for 4 hours of average particle size 2.4 microns (calculated from specific surface) was extracted for I0 minutes with 20% hydrofluoric acid then 5 minutes with 40% acid after which it was found that the quartz content had been raised from 65% to I00%.

Lochaline sand less than I micron in size was extracted with 40% hydrofluoric acid but the reaction was much too vigorous. Ten per cent acid was then used.

An evaporation of this less than I micron Lochaline sand with hydrofluoric acid in the presence of sulphuric acid revealed a residue which could only be derived from porcelain ground off the ball mill. The residue which was assumed to be alumina and potassium sulphate amounted to 4.2% of the dust. Hard porcelain is made from I part quartz, 2 parts clay and I part felspar, (97) and if the evaporation residue is assumed to be from a similar material the amount of porcelain in the dust will be 7%. The less than I micron Lochaline sand will then have a maximum quartz content of 93%.

The initial D.T.A. analysis of this material showed a quartz content of 33%. After 20 minutes extraction with I0% hydrofluoric acid this was increased to 74% while a 2 hour extraction increased this to 8I%. A further I0 minute extraction with 20% acid removed all the quartz and left the porcelain residue.

Assuming this original material is 33 parts quartz and 67 parts non-quartz (60 non-quartz silica and 7 porcelain) if all the non-quartz silica is removed by extraction a dust of composition 33 parts quartz and 7 parts porcelain i.e. 82% quartz, would be obtained. This means the highest quartz content which can be measured is 82%. Since a value of 8I% has been obtained this suffices to prove when considered with the previous results that particle size in itself, that is divorced from the non-quartz layer which normally covers all particles, has no effect even with very fine particles less than I micron in diameter.

The variation of the 'quartz content' of quartz ground to pass a 200 B.S. sieve - the calibration standard.

Since it has been shown that quartz samples of different particle size have different quartz contents, and since the specific surface against grinding time curve Fig. I0 NO. I is so steep in its initial portion it was thought probable that quartz ground below 200 B.S. mesh would

TABLE I7.

The 'Quartz Content' of Quartz Samples Similarly Ground to Pass a 200 B.S. Sieve.

Sample No.	Quartz Content	Arithmetic Deviation	A.M.D.	%A.M.D.
I	82.5	I.4	± 0.9	± I.I%
2	84.I	0.2		
3	85.0	I.I		
Av.	83.9	0.9		

TABLE I8.

The 'Quartz Content' of Quartz Samples Differently Ground to Pass a 200 B.S. Sieve.

Sample No.	Quartz Content	Arithmetic Deviation	A.M.D.	%A.M.D.
I	82.5	2.7	±2.0	± 2.4%
2	84,I	I.I		
3	85.0	0.2		
4	89.0	3.8		
Av.	85.2	2.0		

contain a considerable percentage of non quartz layer.

The apparatus was calibrated with rock crystal of 250 microns average particle size whose layer content is not detected by D.T.A. Four samples of this quartz were ground to pass a 200 B.S. sieve and analysed by D.T.A. The results are given in Tables I7 and I8.

Results and Conclusions.

Samples I, 2 and 3 were ground with special care and give results (Table I7) with a percentage deviation of ± I.I%.

Sample 4 was ground for a very short time, about I5 seconds, and had a 'quartz content' of 89% which increased the percentage deviation to ± 2.4% (Table I8).

Such differences in quartz content will also occur in the quartz of rocks ground for analysis. These results do not support the claim of ± I% accuracy put forward by Roberts.

The Effect of the Layer on the Estimation of Quartz by X-ray Analysis.

Introduction.

The quartz content of airborne dusts has been estimated by the powder technique (35) (36) (37) (38) but no reference was made to the effect of particle size on the

THE EFFECT OF PARTICLE SIZE ON THE RELATIVE INTEGRATED INTENSITY

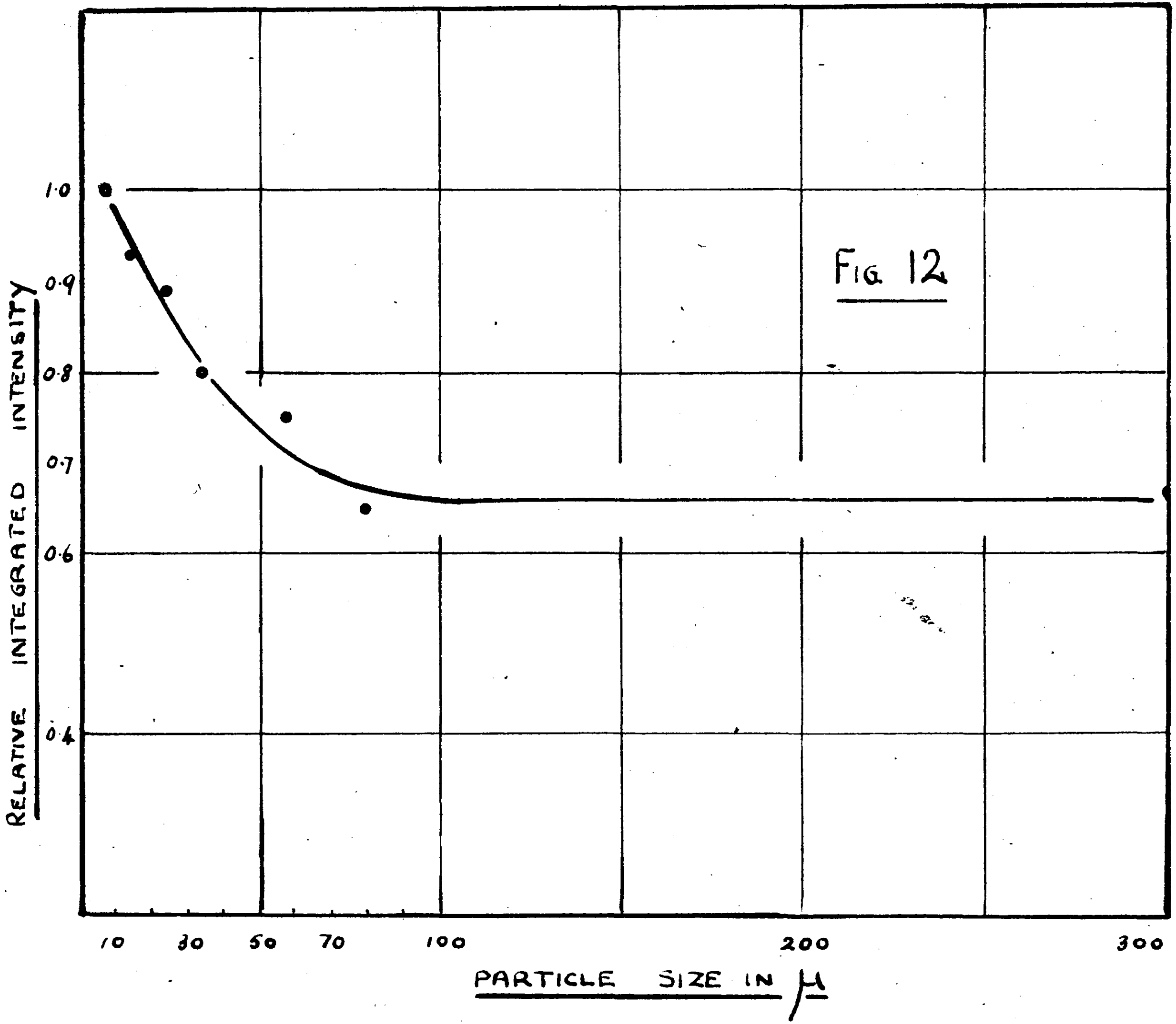


FIG 12

accuracy of the analysis. This is claimed in several papers to be ± 5.0%.

Lonsdale (99) states that crystallites of a size less than IOO A.U. (0.0I microns) give X-ray reflections which become broadened with decreasing size whether the crystallites are arranged to form a single mosaic crystal, a fibre or a powder. The broadening of the line will result in a decrease in intensity. This effect would appear to be of little consequence since the weight of such particles in an airborne dust will be very small.

Recently however Wilchensky (40) has published results on the effect of the crystal and particle size on the diffracted power. He indicates that large effects are produced by particles larger than 7 microns. Fig. No. I2 shows the magnitude of these effects on the relative integrated intensity from particles of iron of different particle sizes. The relative integrated intensity from particles of 7 microns has been taken as unity and all others calculated relative to it. The magnitude of the effect is sufficient to interfere with the X-ray analysis of ground rocks if these are not previously ground below 5 microns.

<u>Experimental.</u>

The effect of the presence of the layer on ground

TABLE 19

Intensity of X-ray Lines.

Quartz Sample	Microphotometer Galvanometer Deflection in cms.				Average
5 to 10 µ (88% quartz)	7.6	7.2	6.2	8.6	7.4
5 to 10 µ (100% quartz)	8.9	10.2	8.4	9.4	9.2

quartz was investigated by taking back-reflection powder photographs of the following quartz dusts whose quartz contents had been measured by D.T.A.

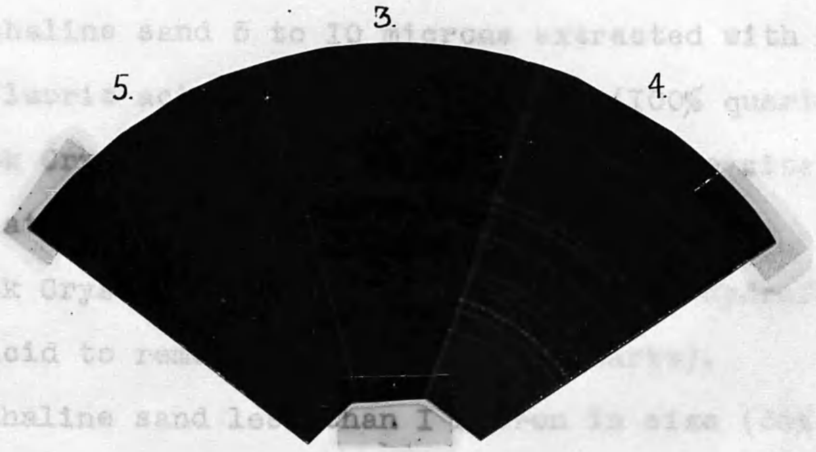
I. Lochaline sand 5 to I0 microns with layer (88% quartz).

2. Lochaline sand 5 to I0 microns extracted with hydro-
fluoric ac (I00% quartz).

3. Rock Cr [illegible]
La

4. Rock Crys hydrochloric
acid to rem artz).

5. Lochaline sand les han I ron in size (38% quartz).



Results and conclusions.

The photographs obtained were very faint due presumably to underexposure and so microphotometer galvanometer readings could only be obtained from the first bright lines of the 5 to I0 micron dusts. These are given in Table I9. A print of the photographs of dusts 3, 4, and 5 show the differences in line intensities.

From Table I9 it appears that the intensities of the lines of the unextracted dust have been reduced roughly in proportion to the decrease in quartz content. This is also shown qualitatively in the photographs. If there was any particle size effect, according to Wilchensky, the intensity of the lines from the less than I micron dust should be quartz was investigated by taking back-reflection powder photographs of the following quartz dusts whose quartz contents had been measured by D.T.A.

I. Lochaline sand 5 to I0 microns with layer (88% quartz).

2. Lochaline sand 5 to I0 microns extracted with hydrofluoric acid to remove the layer (I00% quartz).

3. Rock Crystal 2.2 microns average particle size (calculated from specific surface) (66% quartz).

4. Rock Crystal 2.2 microns extracted with hydrofluoric acid to remove the layer (I00% quartz).

5. Lochaline sand less than I micron in size (36% quartz).

Results and conclusions.

The photographs obtained were very faint due presumably to underexposure and so microphotometer galvanometer readings could only be obtained from the first bright lines of the 5 to I0 micron dusts. These are given in Table I9. A print of the photographs of dusts 3, 4, and 5 show the differences in line intensities.

From Table I9 it appears that the intensities of the lines of the unextracted dust have been reduced roughly in proportion to the decrease in quartz content. This is also shown qualitatively in the photographs. If there was any particle size effect, according to Wilchensky, the intensity of the lines from the less than I micron dust should be darker than the others instead of lighter. Thus it seems that the layer existing on ground quartz particles is also interfering with the analysis of quartz dusts by X-ray methods.

The Refractive Index of the Layer on Ground Quartz.

Introduction.

Since it has been suggested that the layer on ground quartz is vitreous in character (83) (86) the following experiment was carried out to determine whether the refractive index of the quartz had altered appreciably with grinding. The refractive indices of quartz and vitreous silica are I.544 and I.459 respectively (80).

Experimental.

Samples of quartz, less than I micron, I to 3, 3 to 5, and 5 to I0 microns in diameter and a sample of vitreous silica less than 2 microns in diameter were examined in a Vickers Projection Microscope (I6 mm. objective and I0 X eyepiece).

The dust was placed on the microscope slide and focussed on the microscope screen. A drop or two of O - nitroluene, refractive index I.547 was allowed to flow over the field. The effect was noted. If the refractive index of the liquid is the same as that of the immersed mineral, the latter will disappear from sight.

Results and discussion.

On the application of *O* - nitroluene all the quartz dusts disappeared; the vitreous silica dust did not.

Since the less than I micron dust is only 33% quartz it was considered that if the layer on these particles was vitreous they would behave optically more like particles of vitreous silica than like particles of quartz. They should not then have disappeared on immersion in *O* - nitrotoluene. It would appear that the refractive index of the layer is close to that of quartz and not near that of vitreous silica.

Summary of differential thermal analysis results.

All results obtained from D.T.A. are influenced by the fact that ground quartz particles are covered with a layer of silica which does not give the α to β quartz change and so is not estimated by D.T.A.

This layer has been shown to be 0.II to 0.I5 microns in thickness, assuming spherical particles, and to have a density of about 2.55 to 2.59. Its refractive index is close to that of quartz and not near that of vitreous silica. The X-ray analysis of quartz powder has also been shown to be affected by its presence. The fact that it is not estimated by D.T.A. indicates that it could be chalcedony, vitreous silica, cristobalite, or tridymite. The last two have been proved to be absent and the density results suggest that it is chalcedonic in character and not vitreous. This conclusion is strengthened by the appearance of a layer on ground vitreous silica which has a higher solubility than the core (82) and also by the increase in the density of vitreous silica with grinding.

The percentage of the layer in quartz ground to pass a 200 B.S. sieve has been estimated at II% to I7% and has been shown to vary with the grinding time. As this material is used to calibrate the apparatus and since the 'quartz content' of the quartz in the ground rocks will vary similarly an inaccuracy is present which is not consistent with the ± 1% accuracy claimed. An estimate of the accuracy would now be ± 3% for sandstone rocks. Shales however are a different matter since the particle size of the quartz is much smaller than that in sandstones and the percentage of layer on these particles will be higher and unknown.

The analysis of rocks by D T.A. and chemical analysis (Table II) showed that the D.T.A. results were on average 6.6% lower than chemical results and that it was independent of quartz content. This being so, the difference between the D.T.A. and chemical analysis value for the shale was a large proportion (37%) of the free silica content. This may be due to the presence of approximately similar amounts of chalcedony in all these rocks and or the inaccuracy due to the variability of the 'quartz content' of the ground quartz standard and also of the quartz in the ground rocks.

The method as it stands is not suitable for the analysis of dusts, since the percentage of layer on quartz below 1 micron is about 60% and that on the calibrating quartz 15%.

The Nature of The Layer on Ground Quartz Particles and its Effect on Silicosis Research.

It has been shown that ground quartz particles are covered with a non-quartz layer 0.14 microns in thickness and Fig. No. 16 is the graph of the percentage of layer plotted against particle size assuming spherical particles. It shows the high percentage of non-quartz layer which will be present in dusts below 1 micron in diameter. Several references have already been made to the large numbers of such particles produced during rock drilling and grinding (28) (29) and since about 50% by weight of the quartz in an airborne dust may be under 1.2 microns (page 18) it follows that a considerable proportion of this quartz must be in the form of the non-quartz layer. This means that these particles may have properties associated with the disturbed layer and not with quartz and that the results of animal experiments may be due in the main to the properties of the layer.

It has been concluded that the layer on quartz is not wholly vitreous as has been suggested by Beilby but, in agreement with Hamburger and Finch, that it is crystalline in character with a vitreous outer skin (Hamburger) (84), or polycrystalline and vitreous in different places depend-

CHANGE OF % LAYER WITH PARTICLE SIZE

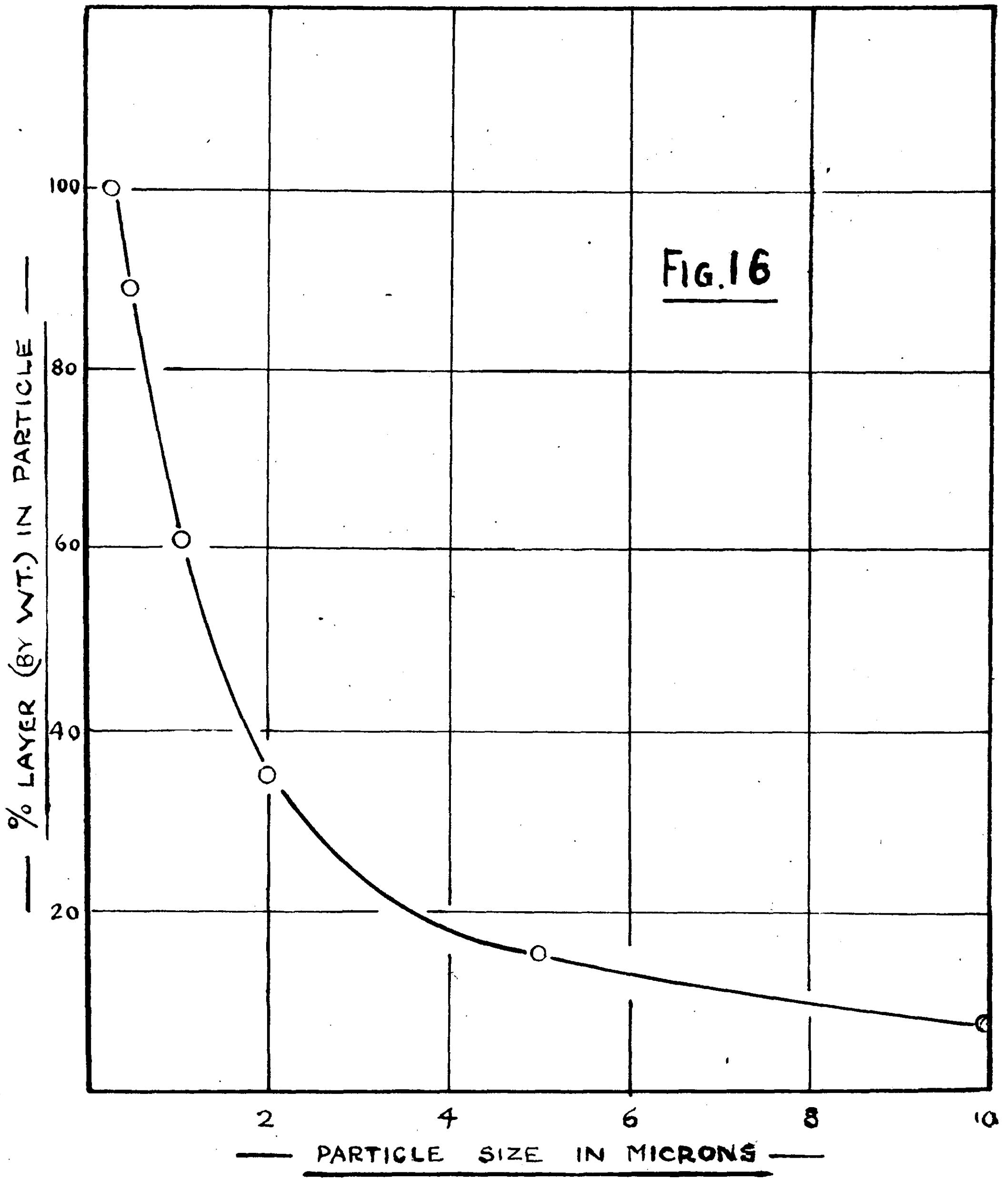


FIG. 16

TABLE 20.

Solubility of Layer.

I Time in Days	2 Total Silica	3 A.M.R. Silica	4 Colloidal Silica
4	4.55	0.64	3.9I
I0	5.85	I.06	4.79
I7	6.28	I.42	4.86
33	7.49	2.I0	5.39
59	8.78	2.90	5.88

Units - mg./I00 ml.

DISPERSION OF SILICA FROM QUARTZ

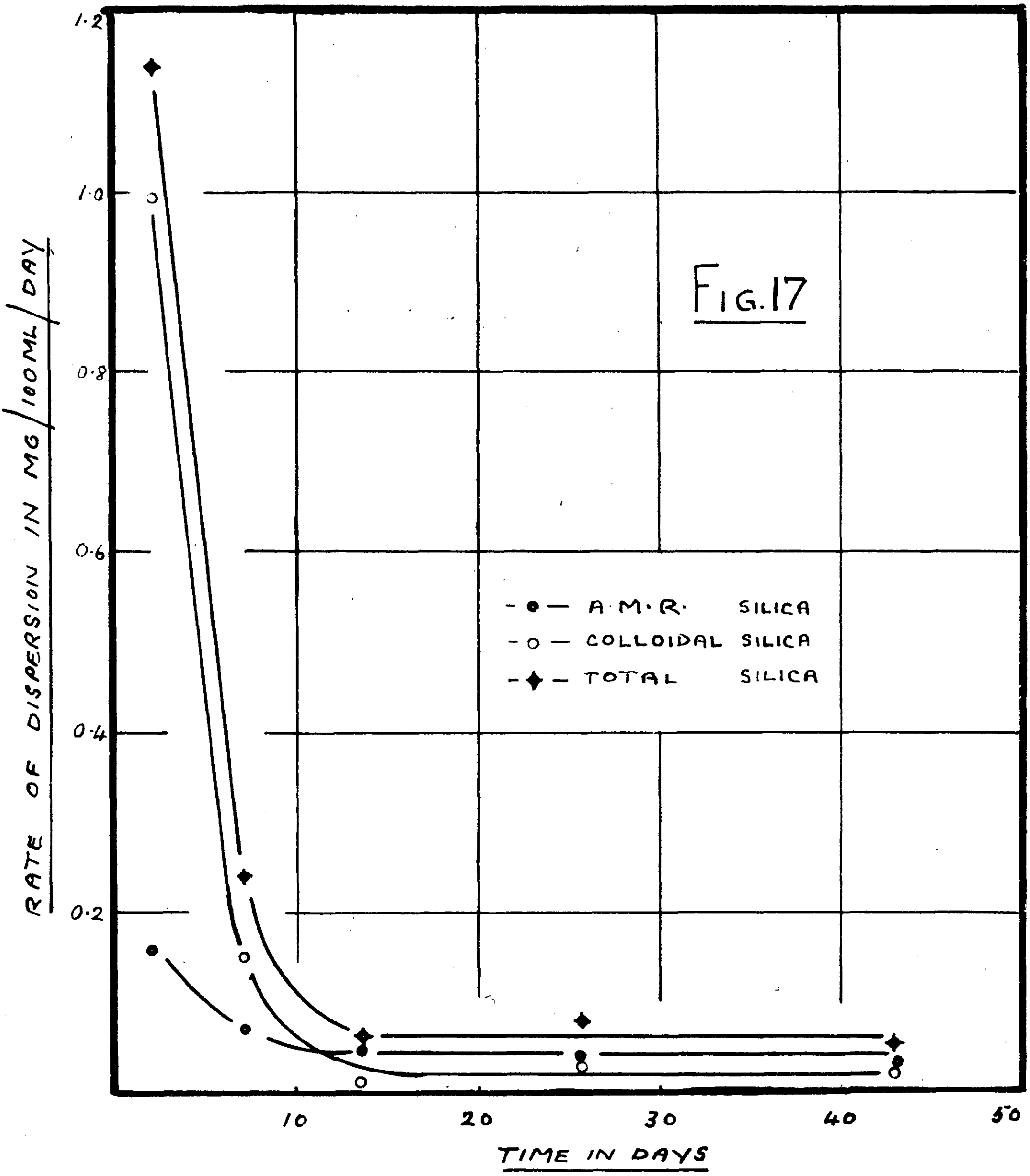


FIG. 17

ing on the presence of cleavage planes in the underlying crystal (Finch)(85). The density of the layer was found to be 2.55 to 2.59. (Chalcedony has a density of 2.59 to 2.64 and vitreous silica 2.20).

Clelland (82) during extractive solubility experiments on quartz particles obtained the results shown in columns 2 and 3, Table 20. The A.M.R. silica - ammonium molybdate reactive silica - is silica in solution which is estimated by colorimetric analysis and the total silica is the total silica leaving the particle. Much of it is in the colloidal form and is not estimated by colorimetric analysis (82). By subtraction, the amount of colloidal silica being dispersed from the particles can be obtained. Fig. No. I7 shows the rate of dispersion of these two forms of silica in mg/I00ml/day from I0 g. of rock crystal 70 - 90 mesh in I00 ml. borate buffer pH 7.5 at 37°C (calculated from Table 20). The main conclusions drawn from the graph and table are:-

I. During the first I0 days a relatively large amount of colloidal silica, 82% of the total, is dispersed in the solvent.

2. After the first I0 days the silica dispersion is constant till at least the 59th day.

3. The rate of dispersion of silica during the first

extraction period of 4 days is I9 times that during the periods from the I0th to the 59th day.

Thus it appears that the layer is producing a large amount of dispersed colloidal silica when in contact with an environment of the same pH and temperature as the lungs of animals. However when the thickness of the layer producing this colloidal silica was calculated, assuming that the total silica dispersed in the first I0 days came from the layer, it was found to be only 0.02 microns and not 0.I4 microns as determined from the D.T.A. and density results. Here was further evidence of an outer skin to the disturbed layer.

The percentage of the outer skin in the layer was calculated to be I7.4% by weight and the density of the whole layer assuming the remainder to be chalcedonic was found to lie within the range 2.5I to 2.55 which compares quite favourably with the 2.55 to 2.59 obtained from D.T.A. and density determinations of quartz before and after grinding.

Nagelschmidt (I06) by X-ray methods has found a non-quartz outer skin on quartz particles approximately I micron in diameter and has shown it to be 0.03 microns thick. Since this skin is not estimated by X-rays it is probably amorphous while the remaining part of the layer could be chalcedony which gives the quartz X-ray spectrum and is not

TABLE 2I.

Specific Surface, % Layer, % to be expected as Colloidal Silica.

Particle diameter in μ	Specific Surface cm^2/g.	% Layer	% as Colloidal Silica
3 to 5	5,660	I8%	3.I%
I	22,640	6I%	I0.4%
0.5	45,280	89%	I5.I%
0.2	II3,200	I00%	I7.0%

estimated by D.T.A.

It would appear that the disturbed layer is approximately I7% vitreous with the remainder cryptocrystalline in nature. This agrees in essence with the conclusions of Hamburger (84) and Finch (85). Colloidal silica appears to be the main dispersed form of the vitreous portion of the layer.

Table 2I gives for quartz of several particle sizes the specific surface, the percentage of layer and the percentage of the particles to be expected as colloidal silica in the solvent.

The application to silicosis research.

"We know that in animals particles between 3 and 5 microns will produce some fibrosis but not a great deal, while particles of the order of I micron will produce a very rapid development of nodular fibrosis in the lungs. Tebben, Schulze and Drinker not long ago published a paper in which they drew attention to the extremely rapid development of silic osis produced by particles of I micron or smaller......."

This is a quotation from King (2I) and in the light of the above experimental results there seems to be a parallel between the production of silicosis and the properties detailed in Table 2I.

The influence of colloidal silica in the production of silicosis has been suggested. Gardner (8I) classed dispersed colloidal silica as the worst of all forms of silica in provoking tissue reactions. Policard (26) cites work by Peissachowitz who obtained only slight reactions in cell protoplasm from silica particles enclosed in a collodion sack. Amor (I07) shows that β silicic acid precipitates protein from pleural exudate and suggests that this may be an important process in the production of silicosis.

The question however remains open and only animal experiments using quartz dust with and without the vitreous outer skin, and the whole layer, can finally close it.

[illegible] ground in a mechanical agate mortar for 2 hours to produce a layer of about 30% on the particles. This would bring the percentage layer onto the linear portion of the graph, No. I Fig. [illegible], where the 'quartz loss' doesn't vary so much with grinding time as it does in short grinding periods.

The same procedure is recommended for the analysis of [illegible] suggested that the calibration standard

Future Work.

Suggestions are given below for the continued investigation of methods of analysis for free silica in rocks and dusts.

Chemical Analysis.

Since the Trostel and Wynne method cannot be used for the analysis of small quartz particles the investigation of Rabson's method (5I) is recommended, particular study to be given to the accuracy of his method of estimation of the quartz lost during analysis.

Differential Thermal Analysis.

To improve the accuracy of the D.T.A. of rocks which is inaccurate because of the presence of varying amounts of non-quartz layer on the quartz in samples of rock and quartz ground to pass a 200 B.S. sieve it is suggested that both the calibrating quartz and the rock samples should be ground in a mechanical agate mortar for 2 hours to produce a layer of about 30% on the particles. This would bring the percentage layer onto the linear portion of the graph, No. I Fig. IO, where the 'quartz loss' doesn't vary so much with grinding time as it does in short grinding periods.

The same procedure is recommended for the analysis of dusts. It is suggested that the calibration standard should be ground to a similar particle size as the dust being analysed; i.e. to have a similar layer content. Alternatively it might be possible to calibrate the apparatus on quartz without a layer and employ a correction for the presence of the layer on the quartz in the ground rock by assuming a layer thickness of 0.I4 microns. This method would of course necessitate the measurement of the average particle size of the dusts being analysed.

X-ray Analysis.

The effect of the layer on X-ray powder techniques should be thoroughly investigated because comparison of the results obtained by this and D.T.A. might give further evidence of the nature of the disturbed layer.

Silica Dispersed from Quartz Particles.

It is considered most important that comprehensive experiments should be carried out concerning the properties of the colloidal silicic acid liberated from the disturbed layer and its effect on the lungs and lung fluids in animals. This could be done by using quartz dusts with and without the non-quartz layer.

PART 4. APPENDIX.

This Appendix contains:-

(I) Detailed descriptions of methods of analysis used during the work described in the previous pages. These were collected here so that as far as possible the sequence of the thesis might be preserved.

(2) An investigation of a method of analysis for Free Silica.

[illegible] the refrac-
[illegible] of the base line
[illegible] due to
local irregularities of the temperature gradient within the sample. A steel block successfully reduces this drift (43).

The analysis was carried out on a heating system since the rate of cooling of the furnace below 300°C was so small as to suppress almost completely the thermal effects due to cristobalite and tridymite.

Since a metal block was being used the thermocouple leads were insulated with fine bore [illegible] tubing as they passed through the block.

[illegible]

The heating rate at constant [illegible]

The Qualitative Estimation of Cristobalite and Tridymite in Dusts.

Grimshaw, Westerman and Roberts (43) describe the use of D.T.A. for the estimation of cristobalite and tridymite. Since they have found that the method as used for quartz is not capable of direct application, because of the presence of double temperature peaks of size varying from sample to sample, the analysis of the dusts detailed below was purely qualitative.

A stainless steel block was used instead of the refractory block because with this the drift of the base line proved particularly troublesome and seemed to be due to local irregularities of the temperature gradient within the sample. A steel block successfully reduces this drift (43).

The analysis was carried out on a heating system since the rate of cooling of the furnace below 300°C was so small as to suppress almost completely the thermal effects due to cristobalite and tridymite.

Since a metal block was being used the thermocouple leads were insulated with fine bore vitreous silica tubing as they passed through the block.

Experimental.

The heating rate at constant amperage of 2 amps. was first shown to be constant then the tests were carried out.

No deflections due to the presence of cristobalite or tridymite were obtained from either ground quartz or vitreous silica, nor was quartz found in ground vitreous silica.

[illegible] ities of [illegible] weight distribution curve and shape or surface factors which may vary with particle size. However in many cases and particularly where the data are required for the estimation of speeds of chemical reactions, it is sufficient to know the specific surface - the surface area per unit weight of the powder.

Direct adsorption methods tend to be complicated and tedious and for the few results required air permeability methods were considered satisfactory especially since relative values were all that were required to trace the increase in surface area of quartz with time of grinding. Other factors influencing the choice of method were the simplicity of the apparatus and the ease of operation.

Much work has been done recently on the permeability method of fineness measurement by Lea and Nurse (96) Gooden and Smith (100) Rigden (101) Carman (102). They have found that the method gives accurate results for comparatively coarse materials of varying shapes but that

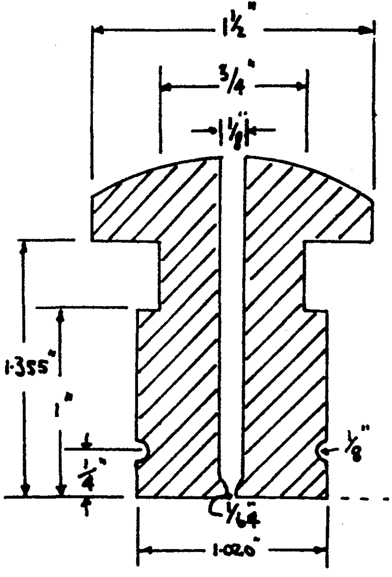
The Determination of the Surface Area of Dusts.

Introduction.

In order to completely specify the granular properties of a powder it is necessary to know the whole size-weight distribution curve and shape or surface factors which may vary with particle size. However in many cases and particularly where the data are required for the estimation of speeds of chemical reactions, it is sufficient to know the specific surface - the surface area per unit weight of the powder.

Direct adsorption methods tend to be complicated and tedious and for the few results required air permeability methods were considered satisfactory especially since relative values were all that were required to trace the increase in surface area of quartz with time of grinding. Other factors influencing the choice of method were the simplicity of the apparatus and the ease of operation.

Much work has been done recently on the permeability methods of fineness measurement by Lea and Nurse (96) Gooden and Smith (IOO) Rigden (IOI) Carman (IO2). They have shown that the method gives accurate results for comparatively coarse materials of varying shapes but that for finer powders the simple theory requires some modifica-



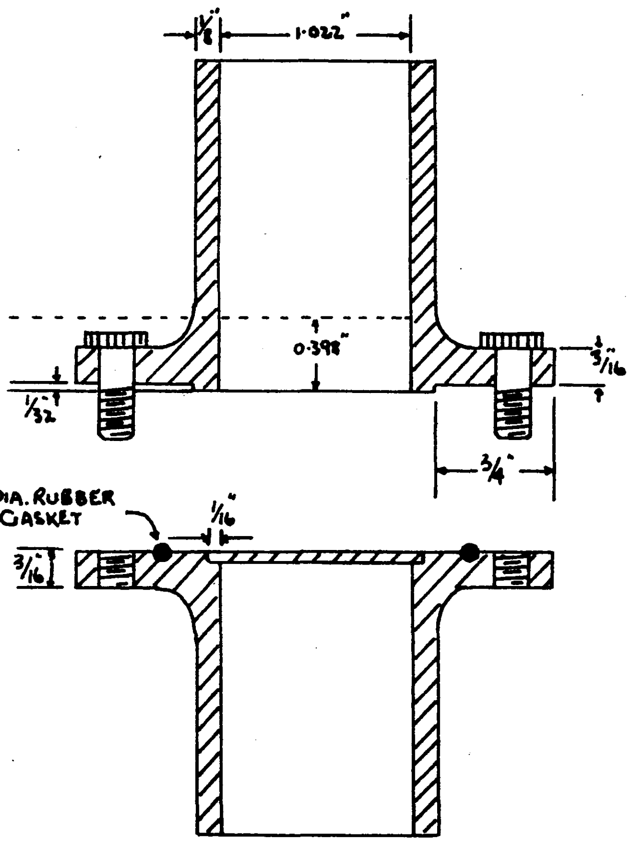
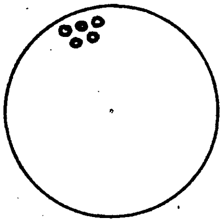


FIG. 13

SCALE: FULL SIZE.

HALF SECTION.

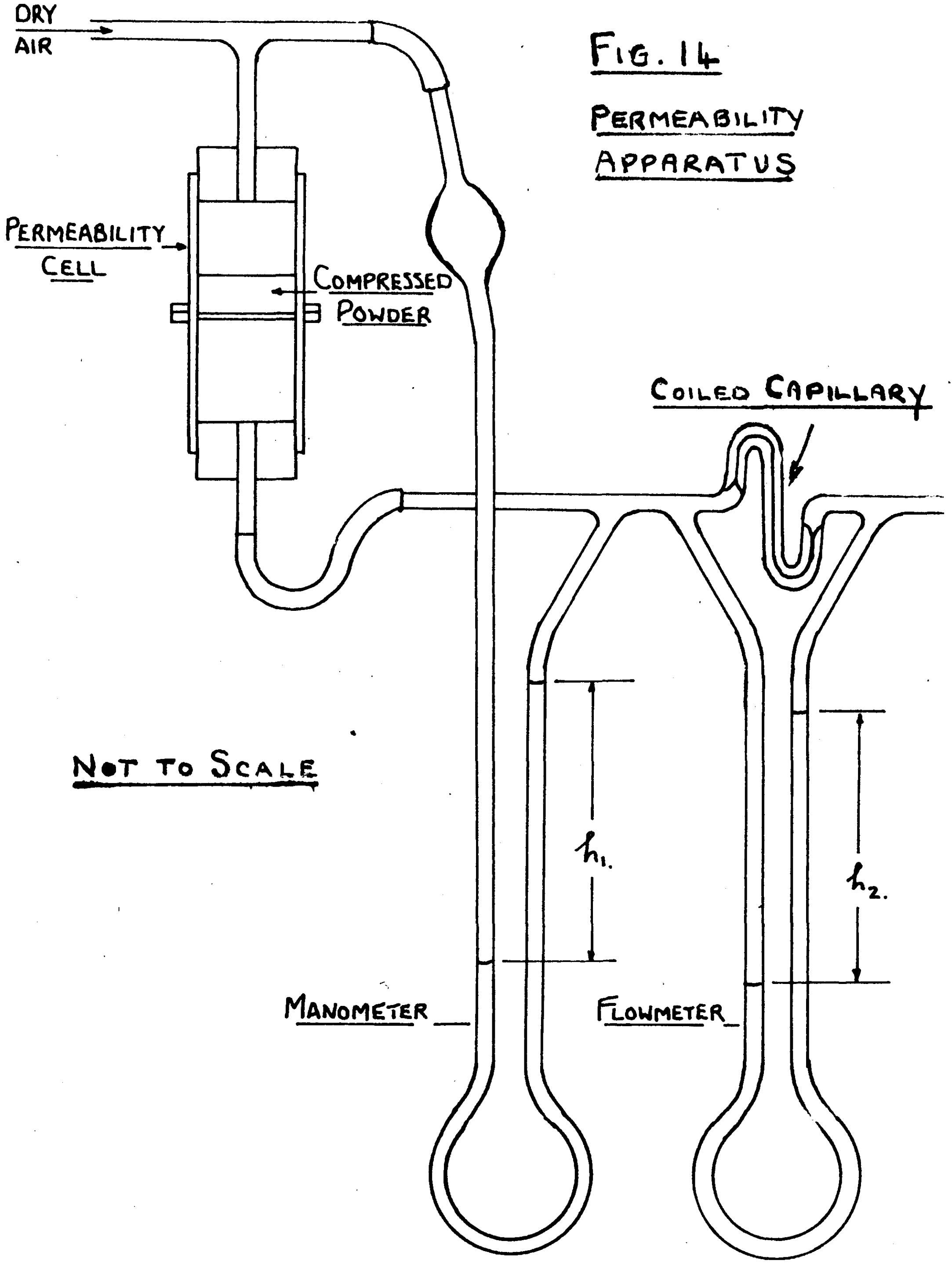
PERMEABILITY CELL



PERFORATED PLATE.
1/16" HOLES SPACED 3/32".

FIG. 14

PERMEABILITY APPARATUS



NOT TO SCALE

tion. Although the absolute figure for specific surface is subject to uncertainty the method has proved to be of much use in comparing the fineness of a diversity of materials. Lea and Nurse (96) state that down to 2 microns the method using air as the permeability fluid, described below, is accurate to ± 5%.

Since it is known that the density of the quartz varies with grinding the effect of this change on the porosity value and on the final specific surface was calculated. Theoretically to keep the porosity at a constant value with a change in density a new weight of material should be packed into the constant volume cell. However the error introduced by a typical drop in density from 2.65 to 2.55 in a dust of I7,400 cm^2/g specific surface amounted to only 4% which was ignored for the purposes of this investigation.

Apparatus.

In the air permeability method devised by Lea and Nurse the powder is compressed to a definite porosity by using a known weight in a special constant volume permeability cell (Fig. No. I3). The air flow through the bed is measured by means of a capillary flowmeter and the pressure across the bed by a manometer (Fig. No. I4). The equation derived for use in the apparatus is:

$$S = \frac{I4}{\sigma(I - \epsilon)} \sqrt{\frac{\epsilon^3 A h_1}{C L h_2}}$$

S = Specific surface in cm^2/g.

ϵ = the porosity

σ = the powder density

C = the flowmeter constant

h_1 = pressure head in cms.

h_2 = flowmeter head in cms.

A = cross sectional area of bed in cms.

L = depth of bed in cms.

Experimental procedure.

6.I206 g. of each of the samples of ground quartz were used giving a porosity of 0.568. This powder was placed in the cylinder and compressed to a bed of fixed dimensions. The plunger was introduced very slowly to allow the air to escape up the central hole. If this operation is hurried dust is lost through the hole.

After compression was completed the plunger was carefully withdrawn by giving it a half turn and extracting it very slowly leaving a level bed of powder. The rubber bungs carrying the glass tubes from the manometers were then carefully inserted as shown in Fig. No. I4. Air, dried and freed from carbon dioxide, was forced through the powder and the values h_I and h_2 read for several rates of flow. The mean values for h_I/h_2 were substituted in the equation and the specific surface calculated.

The results obtained are given in Table 22.

TABLE 22.

The Change in Specific Surface with Grinding.

Grinding Time in hours.	$\frac{h_I}{h_2}$	Specific Surface in cm^2/g	Average Specific Surface
2	I.28	9,550	9,350 ± 2.I%
"	I.I8	9,I50	
4	I.49	I0,370	I0,450 ± 0.7%
"	I.54	I0,520	
7	2.09	II,600	II,800 ± I.7%
"	2.I6	I2,000	
I7	4.39	I7,800	I7,550 ± I.4%
"	4.I6	I7,300	

The Determination of the Total Silica in Rocks. (95)

Introduction.

The total silica content of almandine garnets was estimated before and after grinding in a mechanical agate mortar by this volumetric method of analysis. It was chosen in preference to the classical sodium carbonate fusion - hydrochloric acid evaporation method because:-

(I) it did not require platinum crucibles which resulted in a saving in time,

(2) it is much quicker in itself,

(3) it is more accurate with a lower standard deviation than the classical method.

Analytical Technique.

In no case must more than 60 mg. of silica be present in the portion finally taken for analysis.

Fusion. (I) 7 g. of Analar caustic soda are fused in a 5 cm. diameter nickel crucible. Onto this cooled solid is carefully brushed a weighed portion of ground rock. The caustic soda is gently heated, fused again and heated to a dull red heat during 3 minutes.

Solution. (I) The handwarm crucible is placed in a tall form 500 ml. beaker and covered with a clock glass. Boiling water from the blowing tube of a washbottle is poured into it and the cover glass replaced.

(2) After the vigorous reaction, the beaker sides, clock glass and crucible are washed with hot water. The crucible is rinsed with a little warm dilute hydrochloric acid which is poured into a 500 ml. "iodine flask" graduated at I70 ml.

(3) 20 ml. of concentrated hydrochloric acid is placed in the "iodine flask" and the alkaline fusion solution poured into it with constant swirling.

(4) Heating on a hot plate clears the solution which should not be boiled. The flask is then cooled rapidly and the contents diluted to I70 ml. with distilled water.

(5) 3 g. of pellet caustic soda are dropped into the flask and swirled till dissolved. 8 drops of thymol blue indicator should then be added followed by concentrated hydrochloric acid drop by drop till the colour changes from blue to yellow and just to red. However this last change was difficult to follow in the strong yellow solution so the pH adjustment was done using Johnson's Universal pH papers.

Precipitation. (I) To the flask 8 ml. dilute hydrochloric acid (I:I), 5 ml. dilute acetic acid (I:2) and 30 ml. I0% ammonium molybdate are added and well mixed.

(2) The flask is then heated to 80° to 90°C for I0 to I2 minutes and 40 ml. dilute hydrochloric acid (I:I) and 65 ml. 2% quinoline solution are added with constant swirling.

The flask is reheated to 80° to 90°C for a further 5 minutes. It is then rapidly cooled.

Filtration. (I) A good paper-pulp pad is used. The precipitate is washed twice by decantation with about 25 to 30 ml. of cold water and then transferred to the pad where it is washed 6 times with 30 ml. portions of cold water.

Titration. (I) The precipitate after removal with the pad to the original flask is dissolved in 30 ml. normal sodium hydroxide solution.

(2) A few drops of cresol red - thymol blue indicator are added and the solution titrated with 0.5 normal hydrochloric acid solution till the indicator changes from blue to rose and just to yellow.

(3) A blank test on all reagents should be carried out.

(4) The total silica content is calculated from the expression I ml. N. NaOH = 0.0025I3 g. SiO_2.

Results.

Care must be taken in the use of this method because the presence of phosphates interferes in the estimation.

A test analysis of a rock sample gave the total silica value of 47.4% while the classical method gave 47.3%. Since such good agreement was obtained this method was used to carry out the previously mentioned estimations.

The Estimation of the Free Crystalline Silica in Rocks by the Line and Aradine Method.

Introduction.

This method of analysis (49) was chosen for investigation because of the simplicity of its technique. Basically, it consists of the extraction of a weighed amount of ground rock (less than 100 U.S. mesh) by hydrofluoboric acid at a temperature of 50°C. The extraction liquid is renewed every 24 hours till the rate of loss of the rock residue is constant and approximately 0.34% per day which is the rate of attack on quartz ground to pass an 100 U.S. sieve. Line and Aradine have shown that different minerals have different decomposition rates and it appears that some are not decomposed even after 12 days, (garnet and beryl). This being so the investigation of this method was focussed on the behaviour of sedimentary rocks during analysis and on the behaviour of small quartz particles of a size found in airborne dusts.

Apparatus.

The apparatus consisted of platinum crucibles and a gas heated, water jacketed, oven thermostatically controlled by a mercury regulator. The temperature was maintained at 50°C ± 5° while air was drawn through the oven by a water filter pump. All filtrations and residue washings were carried out on Whatman No. 42 filter paper in glass filter funnels.

Experimental.

Since hydrofluoboric acid made from commercial hydrofluoric acid was found to contain sulphuric acid some hydrofluoric acid was prepared from anhydrous hydrogen fluoride.

The hydrofluoboric acid was prepared by adding 32 g. boric acid to 75 c.c. 48% hydrofluoric acid in a I25 c.c. platinum basin immersed in ice. The solid boric acid was added gradually with constant stirring, each portion being allowed to dissolve before further additions were made. The solution was evaporated to 50 c.c., cooled and filtered through ashless filter paper to give a pale yellow liquid.

Analysis.

(I) 0.5 g. of the ground rock (below an I00 U.S. sieve) is heated to burn off all organic matter and extracted with hot concentrated hydrochloric acid.

(2) The residue is then extracted for 48 hours at 50°C with

I2.5 c.c. hydrofluoboric acid
2.5 c.c. phosphoric acid (S.G. I.39)
5 c.c. 2 M ferric chloride solution,

more ferric chloride being added should the yellow colour disappear.

(3) After cooling the residue is filtered and washed 4 times with normal hydrochloric acid and 5 times with hot water.

(4) The paper and contents are returned to the crucible and ignited. The residue is weighed.

(5) This procedure is repeated till the loss is constant.

(6) The total loss in weight gives the weight of the silicate content of the rock.

(7) This residue is heated with 4 c.c. to 6 c.c. of 48% hydrofluoric acid and a few drops of concentrated sulphuric acid. Careful evaporation is required and is repeated to constant weight.

(8) The loss in weight due to the evaporation is the silica content of the extraction residue and is corrected for the quartz lost during the extraction by applying the following equation

$$\log Yo = \log y - kx \log e \qquad (I03)$$

where Y = mg. of free silica in residue

Yo = " " " originally present.

k = rate of attack = 0.34% / 24 hrs.

x = time of extraction in days.

Results.

The effect of particle size is shown by the fact that the attack by hydrofluoboric acid on quartz below 5 microns in size (separated by air elutriation) is 3.4% per 24 hours i.e. I0 times that for particles ground as for rock analysis. This method cannot then by recommended as it stands for the analysis of airborne dusts.

After I3 days extraction of a sedimentary rock the loss per day exceeded 0.34% indicating the continued presence of a non-quartz mineral. The graph (Fig. No. I5) shows the percentage loss against extraction time and indicates (I) the solution of 92.3% of the rock within 6 days - the time during which most minerals are decomposed - and

(2) the much slower attack on the 7.7% residue. After a further 7 days the analysis was stopped and the result reported as a 'maximum' free silica content of 5.7%. This result agrees with the value of 5.5% obtained later by the modified Trostel and Wynne method. Nevertheless this method was not considered suitable because of the long time required for the analysis.

DURATION OF ANALYSIS BY LINE AND ARADINE METHOD

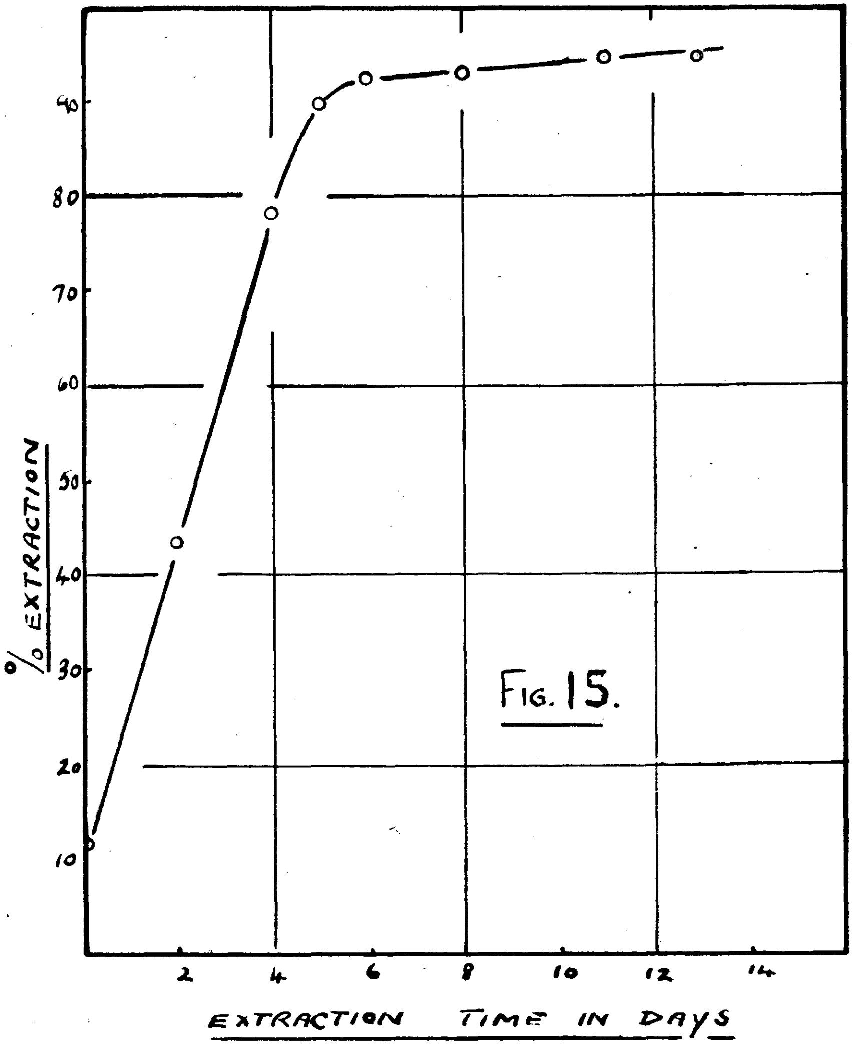


FIG. 15.

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