

## STUDIES IN THE PROPERTIES OF HEAT INSULATING BUILDING MATERIALS

### Part 1.—Mixtures of Cement and Rice-Husk Ash

A. K. M. AHSAN ULLAH, MUBARAK AHMAD AND ABDUL HAMID CHOTANI

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

THE flow of heat across the walls, roofs, and other partitions in a building is a factor of considerable importance in the design of houses, and other structures, in order to maintain a comfortable temperature with a minimum of expense. This is particularly so in case of factories and offices, where the temperature should be kept within definite limits to obtain maximum efficiency from the workers. For all such temperature control, the thermal properties of the building materials used are of prime importance. A study has therefore been carried out to evolve suitable compositions for building materials from locally available resources with particular reference to thermal insulation and mechanical strength.

Rice-husk is available in large quantities in the rice growing belts of Pakistan, and is at present mostly used as fuel in the rice husking industry. Occasional attempts have been made to utilize it as a component in the production of certain building materials. In Pakistan, for example, Messrs Gammon (Pak), Ltd., have used blocks made of cement and rice husk under the name "Feather-crete" for insulating the shell construction roofs at Fauji Textile Mills, Jhelum. These blocks were made in 2'×2'×1" size, using a 3:1 ratio by weight of cement and rice husk, the mixing water containing 4% sodium silicate. The thermal conductivity of this type of block was determined in the Building and Road Research Laboratory, Punjab P.W.D., Lahore, and was found to be  $0.13 \times 10^{-3}$  c.g.s. unit. A disc of 10.0 cm. diameter, 2.5 cm. thick, made to the same specifications, was also tested in the Central Laboratory for its thermal conductivity, and a value of  $0.15 \times 10^{-3}$  was obtained, as against the tabulated values,  $0.11 \times 10^{-3}$  for cork, and  $0.5 \times 10^{-3}$  for wood, which goes to show that the incorporation of rice husk imparts very good insulating properties to cement blocks. However, the structural strength of the cement-rice-husk blocks is low and, therefore, they cannot be designed to take any appreciable stress. There is also the danger of organic decay of the rice husk.

It was felt that a possible way out of these difficulties might be the substitution of rice-

husk by the ash left after burning the material as a fuel, on account of the tough and cellular structure of its particles. This idea found a certain measure of support in the fact that rice-husk ash has actually been successfully incorporated in the production of clay bricks.<sup>1</sup>

### Measurement of Conductivity

In order to explore this possibility a systematic study has been made of the performance of cement and rice husk ash blocks of various compositions extending from 5:1 upto 1:20 of the two components by volume. For the measurement of thermal conductivity, the samples were made as discs 10 cms. in diameter and 2.5 cms. thick. The coefficient of thermal conductivity of such a disc can be measured by using Lee's disc method (fig. (1)), wherein the sample (in the form of a disc of area 'A' and thickness 'd') is placed between a cylindrical steam chest and a metal disc freely suspended in the atmosphere. The equilibrium temperature,  $\theta_E$ , of the disc has been obtained by a new method developed in these laboratories, namely by plotting  $\delta\theta/\delta t$  against  $\theta$  and extrapolating to  $\delta\theta/\delta t=0$ . This technique has the advantage of considerably saving time. The coefficient of thermal conductivity is calculated by means of the formula:—

$$K = \frac{d}{A} \times \frac{\theta_E - \theta_{\text{ambient}}}{\theta_{\text{steam}} - \theta_E} \times E(A + A')$$

where A=area of cross-section of disc, A'=area of cylindrical surface of metal disc, E=its emissivity.

The emissivity is obtained by measuring the free cooling curve of the disc and calculating

$$\frac{\delta\theta}{\delta t} / (\theta - \theta_{\text{ambient}}),$$

$$\text{whence } E = \frac{m s}{2A + A'} \left\{ \frac{\delta\theta}{\delta t} / (\theta - \theta_{\text{ambient}}) \right\}$$

where m=mass of the metal disc,

s=specific heat of the metal.

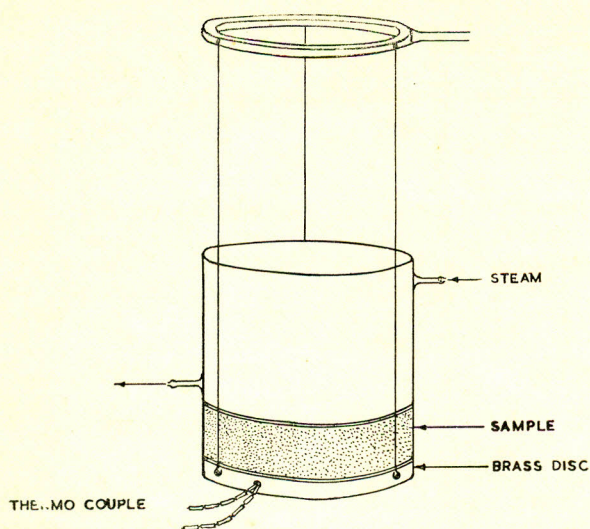


Fig. 1 (a).

A simple way of obtaining the correction to be applied for the heat lost from the exposed cylindrical surface of the sample has been worked out, which consists in repeating the measurement with a sample of twice the thickness. If  $K_1$  and  $K_2$  are the two measured values of  $K$ , the correct value of  $K$  is given by  $K_{\text{corr.}} = K_1 + 1/2 (K_1 - K_2)$  to a good approximation. The detailed theory and experimental verification of this will be given in a separate communication.

### Results Obtained

The experimental results of the thermal conductivity measurements on the discs of cement rice husk ash are shown in table (1) together with the measured densities and tensile strengths of the discs. The densities were obtained by weighing the disc and calculating its volume from its dimensions. In the table,  $K$  is the heat in gram calories transmitted per sq. cm. of cross-section per unit thickness (cm.) per second for each  $1^\circ\text{C}$ . difference of temperature. The estimated error of the experimental values is  $\pm 0.02 \times 10^{-3}$ . The tensile tests were carried out on special briquettes of one inch square effective cross-section made in accordance with British Standard Specifications No. 12/1947, the samples being tested after curing for seven days.

In table (2) are given for comparison the thermal conductivities of a few of the commoner building materials, of which Nos. 1 and 2 have been measured in this laboratory.

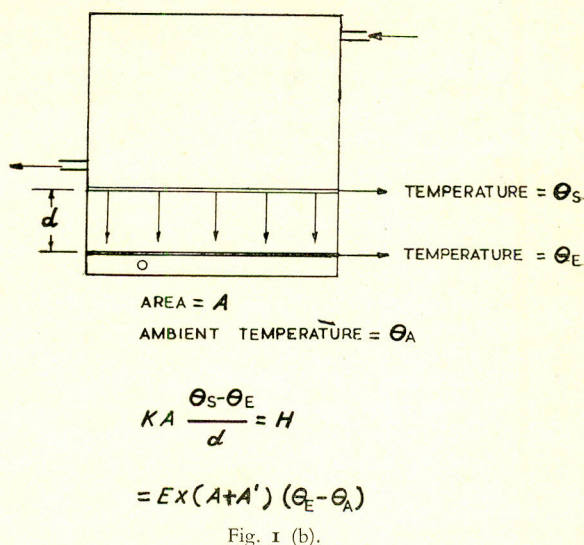


Fig. 1 (b).

### Discussion of Results

As was to be expected from the cellular structure of the rice husk ash, the thermal conductivity of the samples containing large quantities of this ash is very low, the value for the ash being about  $0.15 \times 10^{-3}$ . This last value was obtained by filling a Petri dish with the ash, levelling the free surface with a glass plate, and then measuring the  $K$ -value of this composite sample and correcting the result for the effect of the glass bottom of the dish. (Since the loose ash is very compact, the result will not be very different even if the ash is packed in the dish under considerable pressure.) This value is about twice that for air. However, the introduction of large quantities of ash in the sample results in a very marked lowering of the tensile strength, so that a compromise is to be sought at some intermediate composition. The measurements of table (1) are shown graphically in the three curves of figure (2). The curves for tensile strength and density show a monotonous decrease with increasing ash content according to expectation, whereas the graph for the thermal conductivity shows an anomalous behaviour insofar as it has an intermediate minimum followed by a maximum. The density curve seems to be made up of two straight lines, separated by a rather sharp bend at approximately 90% by volume of rice husk ash. This suggests that, in certain ranges of composition, there is perhaps a special interaction between the three components *viz.*, cement, water, and rice husk

TABLE 1

Sample No.	Proportions cement : rice husk ash by vol.	Vol. % of rice husk ash	Measured density g./c.c.	Wt. % of rice husk ash	$K \times 10^{-3}$	Tensile strength lbs/in <sup>2</sup> .
1.	1:0	0.0	2.00	0.0	0.68	375
2.	5:1	16.7	1.93	2.0	0.53	320
3.	2:1	33.3	1.73	5.0	0.47	290
4.	1:1	50.0	1.53	10.0	0.42	250
5.	1:2	66.7	1.32	17.0	0.47	185
6.	1:3	75.0	1.35	23.1	0.50	190
7.	1:4	80.0	1.25	28.6	0.49	160
8.	1:5	83.3	1.20	30.3	0.43	150
9.	1:6	85.7	1.07	37.4	0.41	140
10.	1:8	88.9	1.08	44.4	0.42	80
11.	1:10	90.9	0.87	50.0	0.36	—
12.	1:15	93.8	0.67	60.0	0.27	~0
13.	1:20	95.2	0.68	66.6	0.26	
14.	0:1	100.0	0.20	100.0	0.15	

TABLE 2

Serial No.	Material	K-Value as determined in the Laboratory ( $\times 10^{-3}$ )	K-Value, as obtained from the literature ( $\times 10^{-3}$ )
1.	Cement : ordinary sand (1:3 by wt.) 12.5% water	$0.77 \pm 0.03$	
2.	Cement (local)	$0.68 \pm 0.03$	
3.	Wood	- - -	0.5
4.	Cork	- - -	0.11
5.	Cotton wool	- - -	0.06
6.	Air (still and dry)	- - -	0.06

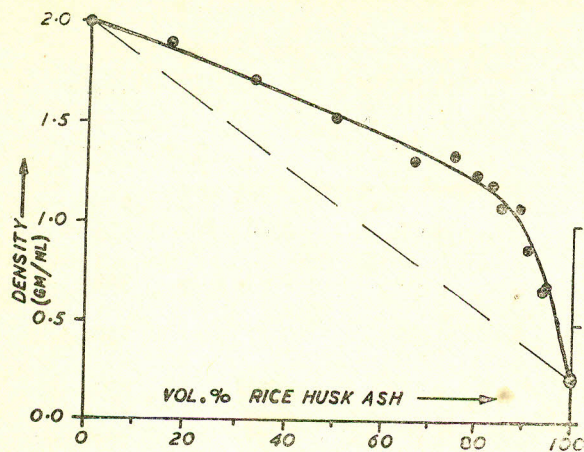


Fig. 2 (a).

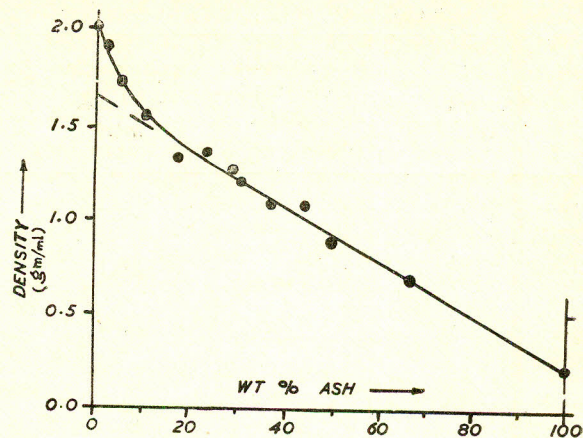


Fig. 3.

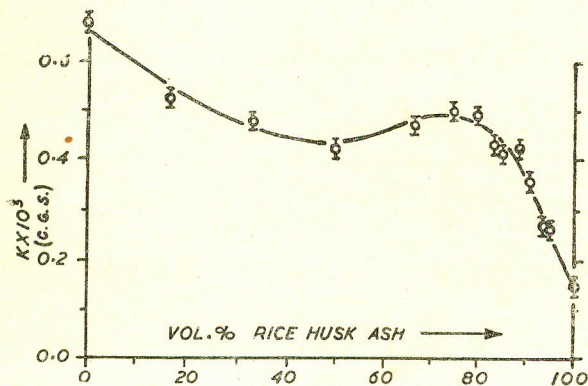


Fig. 2 (b).

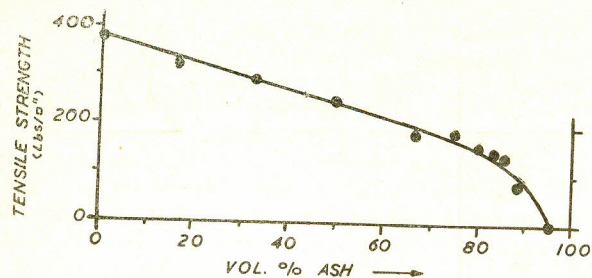


Fig. 3 (c).

ash. It is hoped that a discussion of the theoretical aspects of this will be given in detail in part II of this paper. It is interesting to note that if the density curves are replotted using composition by weight as the abscissa, as in fig. (3), the resulting graph approximates

to a straight line, except for the initial part, which lies somewhat above the extrapolation of this straight line.

The curve for thermal conductivity is particularly interesting in that there exists a minimum at about 50% by volume of ash. The importance of this lies in the fact that this composition of rice husk ash and cement has a good tensile strength value of 250 lbs. per square inch (cf. about 300 lbs./sq. inch for cement concrete), while the K-value is  $0.42 \times 10^{-3}$ , or 60% of the value for cement and cement concrete. This is particularly significant because we can thus obtain a material with a strength comparable with cement concrete and about twice its heat insulation. The cost also will not be materially affected, because the rice husk ash required is about 50% by volume amounting to only 10% by weight. The cement consumption can be further cut down by using mixtures of cement, sand, and rice husk ash in suitable proportions, which are being worked out in these laboratories. Such a material could be used with advantage as a surface plaster in hotter climates and even as a structural material in place of cement concrete.

If a material of very low conductivity is needed (*e.g.*, for air conditioning, etc.) it will be necessary to use rather high percentages of rice husk ash, around 60% by weight for  $K=0.2 \times 10^{-3}$ . Apart from the economic unfeasibility of this, there is the added disadvantage that such a composition has a very low tensile strength, cf. figure 2(c), which would limit its use to non-weight bearing structures like partition walls.

Thus it is seen that the anomalous behaviour shown by the thermal conductivity curve for various compositions of cement and rice husk ash furnishes a building material of considerable practical utility, with the added advantage of a high resistance to fire and insect attack. The theoretical explanation of the anomalous minima and maxima in the thermal conductivity curves involves detailed discussion of the structure of the constituents and their interaction during setting, which will form the subject matter of Part II of the present paper.

### Acknowledgements

Grateful acknowledgement is made to Mr. H.T. Bellamy, I.C.A. Ceramic Expert, for the reference to News Review and for helpful discussions.

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## PRELIMINARY EXAMINATION OF CLIFTON SAND

M. AZEEM\*

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

**W**HEN rocks and minerals are broken down, either by natural or artificial agencies, the products are classified as gravels, sands, silts, and clays, the term sand being usually applied to the material of diameter between about  $1/20$  mm. and 2 mm. In certain shore and river sands, the heavier rock-forming minerals like garnet, tourmaline, rutile, pyroxenes, iron ore, etc., get concentrated as a result of current action, and economically valuable deposits may then be obtained. The black and lustrous coastal sand from Clifton beach seems to be of the latter kind. As a result of preliminary investigations carried out at the Central Laboratories, it was found that nearly 50% of this sand is acid soluble and the insoluble portion is micaceous in appearance, as against the usual run of sands, which consist of about 90% silica. In view of the high mica content of the sand and its large acid soluble fraction, which might prove a significant source of rare elements, a detailed chemical investigation of the Clifton beach sand has been undertaken. The present paper deals with the results of the

analysis and the concentration of certain constituents of these sands.

The coastal sand from Keamari to Korangi, a stretch of about 10 miles, is black in appearance, but on close examination it was found to contain black and white lustrous platy particles in addition to calcareous and siliceous material.

The acid soluble fraction contains a large proportion of iron (about 20%) beside an average of about 3% of aluminium, 5% of magnesium, and  $1\frac{1}{2}$ % of titanium. The sand, moreover, shows a marked degree of radioactivity, which has been traced to a thorium content of about 0.02% on the basis of whole sand. It also contains about 0.4% of lithium and 0.3% of rubidium, which are distributed over both acid soluble and acid insoluble fractions. A proper mineralogical survey of the area at various depths including the shallower parts of the sea coupled with suitable methods of concentration, such as floatation and magnetic separation, could ultimately prove Clifton sand to be a valuable asset to the country. The technique of magnetic separation appears to be particularly attractive because a single pass through the separator

\* Now at the Argonne National Laboratory, Lemont, Ill, under a training programme of the Atomic Energy Commission of Pakistan.

has been found to double the concentrations of iron, titanium, thorium, in the magnetic and of lithium in the non-magnetic fractions.

### Chemical Analysis

Random samples of the sand drawn from the surface down to depths of about three ft. were analysed using both chemical and physical methods. In preliminary assays the percentage composition of the major constituents of the sand was found to be as noted in table I.

TABLE I.—COMPOSITION OF CLIFTON SAND

Moisture	..	I—2%
Material soluble in dilute HCl (10%)	.. ..	24.80—26%
Fraction soluble in HCl under pressure includes that dissolved by cold dilute HCl (10%)		47—50%
Micaceous material obtained from $K_2S_2O_7$ fusion	..	43.8%—45%
Mica (by calculation)	..	10.1%—11%
Biotite and similar materials		45.5%—47%
Silica sand and dust	..	15%—16.17%
Calcareous material (calculated on the basis of loss in weight due to the evolution of carbon dioxide on addition of HCl)	.. ..	20—22%

It will be seen that while the percentage of silica is remarkably low, that of the calcareous matter is exceptionally high. This feature of the sand and its general composition would seem to justify its descriptions as a mineral. Mica was identified under a polarizing microscope, while physico-chemical methods were used for identifying biotite and lepidolite. The calcareous material does not appear to originate from the weathering of limestone, which is abundant around the Karachi coast, but rather from the accumulation of the minute shells of dead sea-organisms as shown by microscopic examination (plate I).

The semi-quantitative estimation of mica was carried out by the following method. About one gram of the sand was fused with  $Na_2CO_3$  and then extracted with HCl, the silica content being determined in the usual manner. The total quantity of silica so obtained is the sum of that obtained from mica, biotite, lepidolite, and silica present as such

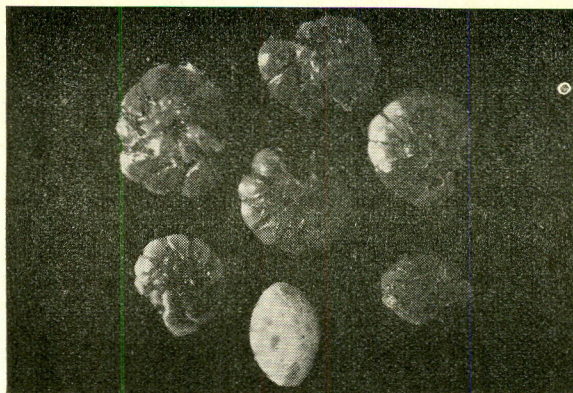


Plate I.—Micro-photograph of non-magnetic fraction.

in the sand. Another sample of the sand (about one g.) was fused with potassium pyrosulphate and extracted with HCl; the residue was then thoroughly washed with distilled water until free from chloride. The mica remains unattacked<sup>3</sup> and the residue obtained is a mixture of mica and silica ( $SiO_2$  formed due to the decomposition of biotite and lepidolite, together with  $SiO_2$  originally present). The difference between the two values gives the quantity of mica present in the original sand.

Qualitative analysis of the sand showed that it contains fair quantities of titanium, and lithium, in addition to iron, aluminium, calcium, magnesium, sodium, potassium, and silica and traces of thorium. These elements were estimated by the methods noted below:

1. Iron            Volumetric    Dichromate.
2. Titanium      Colourimetric Pertitanic acid.
3. Aluminium   Gravimetric    As oxide.
4. Calcium        —do—          As carbonate.
5. Magnesium    —do—          As pyrophosphate.
6. Silica          —do—          Using hydrofluoric acid.
7. Lithium        —do—          As sulphate.
8. Thorium        (a) Geiger Counter.  
                      (b) X-ray fluorescence analysis.  
                      (c) Qualitatively as oxalate.

A detailed account of the chemical constituents of the sand is given in tables (II to IV).

### Spectroscopic & X-ray Analysis

The presence of lithium was confirmed by spectro-chemical analysis. The results of the chemical analysis were confirmed and supplemented (with special reference to thorium and titanium) by *fluorescent X-ray* analysis. (Plates II-A & B). The X-ray analysis also shows the presence of rubidium and strontium to the extent of 0.3% which could not, however, be detected chemically. Peaks corresponding to lithium, aluminium, and silicon are not observed in the X-ray spectrometer record,

because these elements, being of low atomic weight, do not give characteristic X-radiation strong enough to be recorded with the usual apparatus. A rough estimate of the abundance of the elements was made from the peak heights. It is seen to be in substantial agreement with the chemically estimated values (table III).

### Geiger Counter Analysis

Finally, the presence of the radioactive constituent was confirmed by means of Geiger counter measurements, and a quantitative

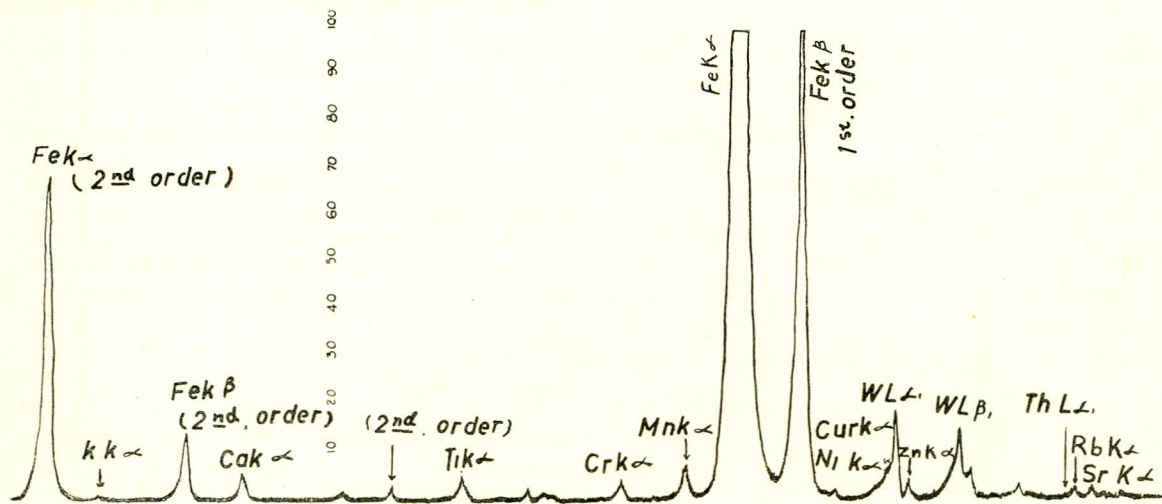


Plate II A.—X-Ray spectrograph of the sand.

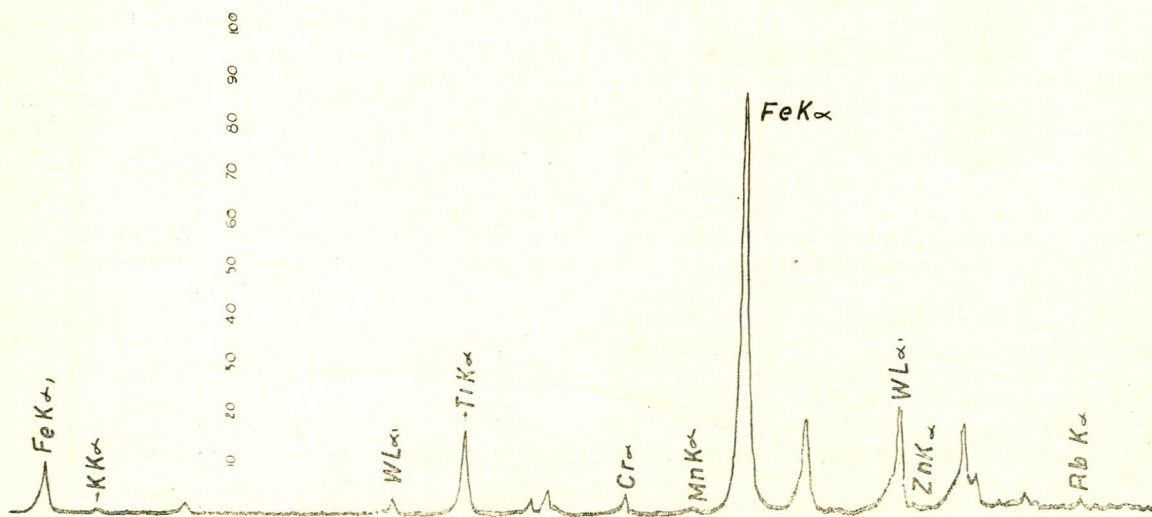


Plate II B.—X-Ray spectrograph of the sand.

estimate of thorium was made by comparing the radioactivity of the sand with standard radioactive samples. These standards were prepared as homogeneous mixtures of  $\text{CaCO}_3$  with thorium nitrate and uranyl acetate by successive dilutions of thorium nitrate and uranyl acetate, respectively, with  $\text{CaCO}_3$ .

The method adopted for estimating the radiation given off by the sand was essentially to surround the counter tube by an annulus of the sand. Two tubes of transparent plastic with different diameters, closed at one and open at the other, were fitted into each other coaxially. The Geiger counter tube was inserted into the inner tube (plate III) and five readings of background counts of five minutes duration each were taken. Then the annular space between the plastic tubes was filled with a weighed quantity of the sand, and the number of counts obtained in several five-minute intervals was again recorded.

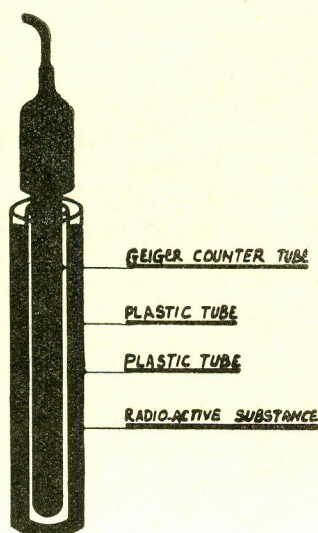


Plate III.

The tube was emptied and the background counts recorded as before. The overall average background counting rate and also the average rate with the sand in the tube was calculated, the difference being the extra counts per minute due to the radioactive material in the sand.

This procedure eliminates the error due to a possible variation in the background rate, and enables the extra counts (due to the sand)

to be estimated to an accuracy of about 10% of the quantity measured. The counts for the standard materials were determined as in the case of sand. The weights of the various materials taken were nearly equal, varying from 70 to 75 grams. Since the standard contains a known quantity of thorium, the thorium content of the sand is readily estimated from the ratio of the counting rates.

Assuming that the radio-activity is distributed over a stretch of beach about 70 miles long, one furlong wide and about three and a half feet deep, it should contain approximately 30,000 tons of thorium, 800,000 tons of titanium and up to 50,000 tons each of lithium and rubidium. It is true that the sand is a low-grade source of these elements, but, in view of the growing importance of radioactive reserves and other rare elements in Pakistan, this source may not be insignificant. It will not be out of place to mention here that Atomic Energy Commission of America has announced a programme under which by-products containing as little as .05% uranium or thorium are considered as possible source materials.<sup>4</sup>

Further, the techniques of mineral dressing have developed to such an extent in recent times, that it may not be an impracticable proposition to recover these elements from poor sources such as Clifton sand. Out of a variety of available techniques, the following methods have been tried with this sand, particularly for the concentration of titanium, thorium and lithium.

### Water Classification

The densities of the minerals of titanium and thorium are between four and five, whereas those of biotite, mica, calcareous material, lithium and rubidium ore are between 2.6 and

TABLE II.—ANALYSIS OF THE FRACTION OF THE SAND SOLUBLE IN HYDROCHLORIC ACID UNDER PRESSURE

(Values are the percentages of the cations calculated on the basis of whole sand)

Lithium	..	..	0.35
Magnesium	..	..	2.7
Aluminium	..	..	1.7
Calcium	..	..	7.1
Titanium	..	..	0.66
Iron	..	..	9.4
Thorium	..	..	Traces.



3.2. It was expected that with simple water classification, biotite, mica, lepidolite silica, and calcareous material would flow over, while thorium, and titanium minerals would sink to the bottom of the classifier, but the two fractions did not show any appreciable difference in their titanium and radioactive contents: the Geiger counter readings for both fractions were the same within the limits of experimental error.

TABLE III.—COMPARISON OF QUANTITATIVE ANALYSIS BY CHEMICAL MEANS AND A ROUGH QUANTITATIVE ESTIMATE FROM FLUORESCENT X-RAY ANALYSIS

(The values refer to the percentage of the elements present in the sand)

Element	Total sand		Micaceous material obtained after treatment of sand with HCl under pressure.	
	Chemical analysis	X-ray analysis	Chemical analysis	X-ray analysis
Lithium .. ..	0.35	—	—	—
Magnesium .. ..	2.8	—	0.31	—
Aluminium .. ..	5.1	—	7.1	—
Silicon .. ..	18.3	—	34.3	—
Calcium .. ..	7.3	5.0	0.24	—
Titanium .. ..	0.9	0.9	0.4	0.7
Chromium .. ..	not estimated	0.6	—	0.2
Manganese .. ..	not estimated	0.4	—	0.06
Iron .. ..	9.7	10.0	0.6	0.5
Nickel .. ..	—	0.2	—	—
Copper .. ..	—	0.06	—	—
Zinc .. ..	not estimated	0.04	—	0.05
Rubidium .. ..	not estimated	0.3	—	—
Strontium .. ..	not estimated	0.3	—	—
Thorium .. ..	Traces*	0.01	—	—

\* Geiger counter measurements of table IV-√ 0.024% thorium.

Note: The low value for calcium as estimated from the X-ray record is probably due to calcium carbonate being in the form of granules, which are liable to loss during the preparation of the sample.

TABLE IV.—X-RAY COUNTS RECORDED WITH THE GEIGER COUNTER

	Back-ground	0.015% Uranyl acetate	0.1% Thorium nitrate	Clifton sand	Magnetic fraction	Non- magnetic fraction
Total counts per minute ..	6.0±0.5	27.7±1.1	23.3±1.1	16.0±0.8	19.3±0.8	13.4±.7
Counts after subtraction of background ..	—	21.7±1.2	17.3±1.2	10.0±0.9	13.4±0.9	7.4±0.8
Equivalent radioactive con- tent	—	0.014% Uranium	0.42% Thorium	0.024% Thorium	0.033% Thorium	0.018% Thorium

### Electromagnetic Separation

When the sand is passed through an electro-magnetic classifier operating at a rather large flux density, the magnetic fraction is black in colour, and is found to contain silica, mica, lepidolite, and calcareous material.

The magnetic fraction gives considerable higher counting rate than the whole sand, about 70% of the original radioactivity being concentrated in this fraction, the rest being in the non-magnetic fraction. This result is rather surprising because monazite is not present in the sand, which is obvious from the X-ray spectrometer record, cerium being absent.

In the light of these observations it would appear that thorium in the magnetic fraction is present as intrusions<sup>5</sup> in the biotite, and the portion in the non-magnetic fraction is probably thorite resulting from the weathering and disintegration of biotite; it cannot be in the form of monazite or thorianite because in the X-ray analysis there is no indication of either cerium or uranium. The titanium appears only in the magnetic fraction (table V), so that its percentage in this fraction is about double that of in the whole sand. On the basis of these results it appears that titanium is either in the form of ilmenite or in combination with biotite.<sup>6</sup>

Further studies directed particularly towards the concentration of titanium, thorium, lithium and rubidium to economic limits, are in progress.

TABLE V.—CHEMICAL ANALYSIS OF MAGNETIC AND NON-MAGNETIC FRACTIONS OF THE SAND

Cations	Magnetic	Non- magnetic
Lithium ..	0.2%	.5%
Magnesium ..	3.4%	Traces.
Aluminium ..	6.6%	4.5%
Silicon ..	15.0%	17.5%
Calcium ..	0.4%	14.7%
Titanium ..	1.7%	Nil
Iron ..	17.2%	1.1%
Thorium ..	0.033%*	0.018%

\*Estimated from Geiger counter measurements.

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## STANDARDIZATION OF MYROBALAN EXTRACTS FOR THE MANUFACTURE OF FOUNTAIN PEN INKS

GEORGE HAHN AND RAFIQUE AHMAD SIDDIQUI

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

THE indigenous manufacture of good-quality fountain pen inks is an important problem for the country, because approximately rupees five lakhs worth of these inks are presently being imported every year. A good ink should possess a number of properties such as good flow, a deep and fast colour, and freedom from corrosive action, sedimentation, and fungal growth. Of these, the last three conditions are critical and largely depend on the concentration and character of the organic acid used in the manufacture of the ink. This acid material is cheaply obtainable from the indigenous nut, *Myrobalan*, which is the name given to the unripe fruit or nuts of various species of the tree, *terminalia chebula*, of which the variety indigenous to Pakistan is known as "hurr". The nuts contain 30-40% tannin of the pyrogallol variety.

On hydrolysis of the aqueous extracts of these nuts, gallic acid solutions are obtained, which can be used in the preparation of inks of the ferrous-polyoxybenzene-complex type. For this, it is necessary to standardise these extracts in order to get a uniform, reproducible tinctogenic value of the ink.

The aqueous extracts of the nuts consist of mixtures of substances so numerous and che-

mically complex that, in our knowledge, there is no reference in the literature to practical methods for their separation or evaluation. The determination of tannin by the standard gelatin method does not afford a true criterion of the value of the product for ink making, and it was considered preferable to use the tinctogenic value itself for standardization.

As gallic acid is the main polyoxybenzene-compound in the myrobalan-tannins it was used for comparison as well as for fixing the optimum conditions under which the iron-complexes were formed.

Theoretically the formation of ferrous-gallic acid-complexes can depend on: (1) the molar ratio of ferrous salt to gallic acid; (2) the pH of the solution; (3) the nature of the buffer used; (4) the time of formation; and (5) the temperature. It is also necessary to fix properly the conditions of the complex formation because the size of the particles in the colloidal solution of the blue iron complex should be within a definite range in order to get comparable tinctogenic values with photo-electric colorimetry. The necessary conditions for maximum sensitivity of photo-electric methods are the use of monochromatic light, the absence of large sized colloidal material in the solution examined, and an optimum thickness of the

absorption cell for maximum accuracy, the second of these conditions being amenable in the present case to only an approximate adjustment.

*Ratio of the reactants:* The colour developed from the equimolar mixture of ferrous-ammonium sulphate and gallic acid increases in intensity with further additions of the ferrous salt solution until a ratio of one part gallic acid to approximately eight parts of ferrous ammonium sulphate is obtained. A slight excess above this ratio does not appreciably vary the intensity of colour (see table IV). The spectral composition of colour is also not affected by small variations in the relative amounts of the reactants, though wide differences in the ratio do produce considerable alteration in the extinction coefficient, as will be seen from table I(a) and (b).

TABLE I(A).—EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate in ml.	Extinction coefficient $E \times 100$
1	0.5	4.0	13.0
2	1.0	8.0	28.0
3	1.5	12.0	54.0
4	2.0	16.0	76.0
5	2.5	20.0	98.0
6	3.0	24.0	111
7	3.5	28.0	118
8	4.0	32.0	122

TABLE I(B)

1	1.0	35.0	39.0
2	2.0	35.0	88.0
3	3.0	35.0	115
4	4.0	35.0	124

TABLE I(C).—EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES AT pH = 5.6

1	2.0	1.0	33.0
2	2.0	2.0	51.0
3	2.0	4.0	62.0
4	2.0	6.0	67.0
5	2.0	8.0	74.0
6	2.0	10.0	84.0
7	2.0	12.0	89.0
8	2.0	14.0	96.0
9	2.0	16.0	pptd.
10	2.0	18.0	pptd.

*pH of the solution:* Both the intensity and the composition of the colour are affected by the pH of the medium (table II and V(a)-(d)), and the stability of the colloidal solution will also depend on this factor. It is therefore essential to fix the optimum pH to which the test solutions are buffered, within the acidic range in order to avoid oxidation of gallic acid.

*Composition of the buffer:* The requirements of a good buffer are a strong buffer-action and non-reactiveness towards the test substances. Both these conditions were best provided by the acetate buffer in the acidic range, while the boric acid-borax buffer of the same pH gave red instead of blue solutions, due to the well known formation of boron complexes with the hydroxylic compounds. (see table II(b)).

*Size of the particles:* A colloidal dispersion of the coloured precipitate changes the colour of the transmitted light and also reflects some of the light. In photo-electric colorimetry, the size of the particle therefore affects the estimation. With variations in the average size of the colloidal particles, there will be corresponding variations in the transmission of light. The size of the particles depends upon the concentration of the reactants, the method and order of mixing, and the time for which the solution is left standing. The preparation of the colloidal solution should be carried out in fair dilution because the sensitivity of the colorimeter rapidly decreases with the increase of extinction coefficient beyond about 0.5.

*Time of standing of the colloidal solution* : The colorimetric reading with a freshly prepared test sample goes on increasing with the time till a stage is reached where the extinction coefficient remains nearly stable for a long time (see table III). The readings have, therefore, been taken after the lapse of the time required for the attainment of the stability. This optimum time is influenced by pH of the medium, concentration of the reactants, and the temperature of the solutions.

Colloidal solutions tend to coagulate on standing, the size of the particles increasing due to the formation of agglomerates. The solutions should not, therefore, be left standing for unduly long periods before readings are taken.

#### *Standardization—Method and Apparatus* :

The "Series of Standards" method was considered to be of advantage, because it does not depend on the applicability of Beers' law. The maximum colouration developed with the known volume of the test substance is compared colorimetrically with a series of standards prepared with the same quantity of iron solution and increasing quantities of pure gallic acid solutions. The value of the unknown is measured against the standard to which it most nearly conforms and is estimated from that standard. When the volume and colour of the unknown sample and the standard are the same, the contents of the test substance in each will be identical, and its concentration in the sample is thus obtained without calculations.

A photoelectric colorimeter is used for observing the extinction coefficient of the various solutions. This apparatus is preferable to the visual method of observation with the Lovibond tintometer on account of its higher accuracy. Table I (c) shows how the extinction coefficient rises correspondingly with the concentration of the iron-complex-solution, while the visual tintometer gives no clear indication of the varying concentration of the iron-complex (Table II (c)). To obtain maximum sensitivity, a selected filter is placed in the path of the light before the photoelectric cell.

### **Experimental**

*Apparatus* : The Gallenkamp photoelectric colorimeter was employed for determining the extinction coefficient of the solutions, while the Lovibond tintometer was used for the analysis of colour into its components.

*Material* : Pure gallic acid, acetic acid, sodium acetate, boric acid and borax, supplied by E. Merk, and ferrous ammonium sulphate of B.D.H. quality were used.

*Ferrous ammonium-sulphate solution* : Standard ferrous ammonium sulphate solution of M/40 strength was prepared by dissolving 1.7375 g. of the salt in distilled water and filling up to 250 ml. including 2.0 ml. of 10% hydrochloric acid to keep the solution free from turbidity.

*Gallic acid solution* : Gallic acid solution of M/40 strength was prepared by dissolving 1.1750 g. of gallic acid in distilled water and filling up to 250 ml. with distilled water. Three drops of toluene were added to keep it free from moulds.

#### *Acetic acid — Sodium acetate buffer* :

- (a) *Acetic acid solution* of molar strength was prepared by volumetric standardization method.
- (b) Molar sodium acetate solution was prepared by dissolving 136.0 g. of the salt (with 3 moles of water of crystallization) in distilled water and making up to one litre.

#### *Boric acid — Borax buffer* :

- (a) 12.404 g. of boric acid plus 2.925 g. sodium chloride was dissolved and made up to one litre with distilled water.
- (b) 19.108 g. of borax was also dissolved in distilled water and made up to one litre.

Buffers of various pH values were made from these solutions in accordance with "International Critical Tables" Vol. 1, pp. 81-84.

### **Preparation of the Extract**

The nuts, obtained from the local market, were ground and sifted through a 10-mesh sieve.

One hundred grammes of the sifted powder was packed in a large separating funnel having a cotton plug at the bottom and hot water was allowed to percolate slowly through it. The end of the extraction was determined by the formation of only a negligible blue colour on adding an excess of ferrous ammonium sulphate solution to a few ml. of the extract. Three liters of hot water (at 70°-80°C.) were necessary for the complete extraction of tannin.

*Hydrolysis of the extract* : Five hundred ml. of the extract was refluxed with 25.0 ml. of 10% hydrochloric acid for eight hours to hydrolyze the gallotannin, cf. the method recommended by G. Martin and E.I. Cooke (Industrial Chemistry : Organic, seventh edn., p. 490, 1952, The Technical Press Limited, London).

*Selection of the filter* : The test solution was taken in an observation tube and colorimetric readings with different filters placed in the path of the light were recorded, the maximum reading being observed when filter "608" was used. Filter "608" was therefore employed during all the observations for the colorimetric readings.

TABLE II (A).—pH VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES WITH DIFFERENT BUFFER SOLUTIONS

Cylinder No.	pH of the buffer solution (10.0 ml.)	M/40 gallic acid soln in ml.	Iron solution (M/40) in ml.	pH of the colloidal solution
1	3.6	2.0	2.0	3.6
2	3.8	"	"	3.8
3	4.0	"	"	4.0
4	4.2	"	"	4.2
5	4.4	"	"	4.4
6	4.6	"	"	4.6
7	4.8	"	"	4.8
8	5.0	"	"	5.0
9	5.2	"	"	5.2
10	5.4	"	"	5.4
11	5.6	"	"	5.6
12	6.77	"	"	6.77
13	7.60	"	"	7.60
14	8.08	"	"	8.08
15	8.69	"	"	8.69

(i) *Determination of the optimum pH* : A series of fifteen 100 ml. cylinders were arranged and 10.0 ml. of different buffer solutions of pH values varying from 3.6 to 8.69 were taken. For the pH values from 3.6 to 5.6, acetic acid-sodium acetate buffers, and from 6.7 to 8.69 boric acid-borax buffers were used. Two ml. of M/40 gallic acid solution was added to every cylinder and the volume made upto 60 ml. by adding distilled water. Two ml. of M/40 ferrous ammonium sulphate solution was added to each and the final volume was adjusted to 100 ml. The pH of the solutions was not affected, and still corresponded to the values of the buffers taken in each case (table II(a)).

Tintometer measurements on the fifteen samples showed that the composition and intensity of colour remained practically constant when the pH of the medium was 5.2-5.6. (Table II(b)). In this range of pH values, the blue component increased very slightly while the yellow component remained constant. There was no regularity in the composition and intensity of colour in the pH range 6.70-8.69. The colour of the solutions in this pH range was predominantly red instead of blue, due to the formation of the already mentioned boron complexes.

TABLE II (B).—LOVIBOND VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS-GALLIC ACID COMPLEXES

Cylinder No. of table II(a)	pH of the colloidal solution	Red	Yellow	Blue
8	5.0	( 7.0 ( 6.8	( 8.0 ( 8.0	(11.6 (11.0
9	5.2	( 7.1 ( 7.1	( 8.0 ( 8.0	( 9.2 ( 9.4
10	5.4	( 7.2 ( 7.1	( 8.0 ( 8.0	( 8.6 ( 8.8
11	5.6	( 7.2 ( 7.3	( 8.0 ( 8.0	( 8.3 ( 8.3
12	6.77	( 4.1 ( 4.0	( 3.0 ( 3.0	( 4.8 ( 4.8
13	7.60	(12.4 (12.4	( 6.0 ( 6.0	( 9.6 ( 9.4
14	8.08	(11.2 (11.3	( 7.0 ( 7.0	( 9.0 ( 9.0
15	8.69	( 9.9 (10.1	( 7.0 ( 9.0	( 7.3 ( 7.3

TABLE II (c).—LOVIBOND VALUES OF THE COLLOIDAL SOLUTIONS OF FERROUS-GALLIC ACID COMPLEXES CONTAINING 2 ML. OF M/40 GALLIC ACID SOLUTION

Cylinder No. cf. table I(c)	M/40 ferrous ammonium sulphate solution in ml.	Red	Yellow	Blue
1	1.0	4.4	1.4	5.3
2	2.0	6.5	1.6	6.9
3	4.0	8.0	3.9	10.8
4	6.0	9.2	3.9	11.2
5	8.0	7.1	3.1	9.5
6	10.0	7.0	5.7	11.1
7	12.0	8.0	7.1	12.2
8	14.0	7.5	7.6	11.8
9	16.0	7.0	6.3	10.7
10	18.0	7.0	6.9	10.5

The time required for the full development of colour was longer with solutions at lower pH values. It was visually observed that solutions buffered at pH 5.2 to 5.6 developed strong colour within a minute while solutions at pH values below 4.4 required more than five minutes to develop a colour of similar strength. It was also observed that tendency towards coagulation of the colloidal solutions increased with decreasing pH of the solutions. Colloidal solutions buffered at pH 5.6 were clear even after standing for five days, while solutions at lower pH values had coagulated.

Due to the above considerations, pH 5.6 was considered to be the optimum pH to which all of the test solutions were buffered.

(ii) *Determination of the time of standing:* Colloidal solutions of two strengths buffered at pH 5.6 were prepared: (A) 0.25 ml. of the gallic acid solution mixed with 8.0 ml. of the ferrous ammonium sulphate solution and diluted to 100 ml.; and (B) 0.5 ml. of the gallic acid solution mixed with 16.0 ml. of the ferrous ammonium sulphate solution, and diluted to 100 ml. The colorimetric readings were recorded every five minutes until relatively

stable values were obtained, after a lapse of about 50 minutes (figure 1); the readings increased monotonously in both cases (table III and curves of figure 1).

TABLE III—TIME FOR THE CONSTANT VALUES OF THE EXTINCTION COEFFICIENT OF TWO COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES OF DIFFERENT STRENGTHS

Time interval in minutes	Extinction coefficient $E \times 100$	
	Solution A	Solution B
10	45.0	72.0
15	49.5	75.0
20	53.5	76.0
25	55.5	76.5
30	58.0	80.0
35	59.0	81.0
40	60.0	82.0
50	61.5	84.0
60	62.5	85.0
70	63.5	85.5
80	64.5	—

Solution A:—0.25 ml. M/40 gallic acid and 8.0 ml M/40 ferrous ammonium sulphate.

Solution B:—0.5 ml. M/40 gallic acid and 16.0 ml M/40 ferrous ammonium sulphate.

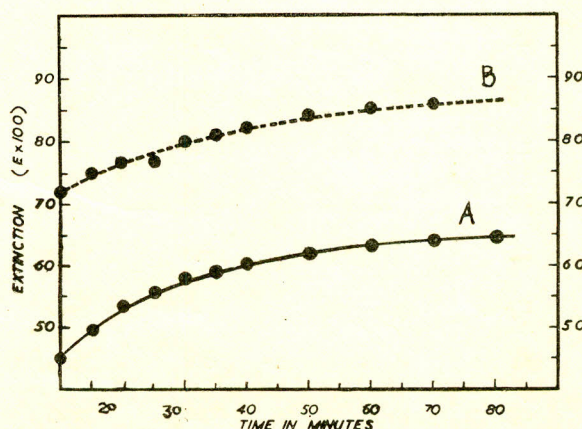


Fig. 1.

(iii) *Ratio of the reactants* : 10.0 ml. of the buffer of pH 5.6 were taken in each of the 19 cylinders of the series. Two ml. of M/40 gallic acid solution was added to each and the volume made upto 60 ml. M/40 ferrous ammonium sulphate solution was added in increasing steps of 1.0 ml. to every cylinder of the series, the volume being then made upto 100 ml.

TABLE IV

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient $E \times 100$
1	2.0	1.0	10.5
2	"	2.0	25.0
3	"	3.0	34.0
4	"	4.0	45.0
5	"	5.0	55.0
6	"	6.0	57.0
7	"	7.0	60.0
8	"	8.0	69.0
9	"	9.0	61.0
10	"	10.0	65.0
11	"	11.0	58.0
12	"	12.0	68.0
13	"	13.0	64.0
14	"	14.0	71.0
15	"	15.0	76.0
16	"	16.0	76.0
17	"	17.0	76.0
18	"	18.0	76.0
19	"	19.0	76.0

The time required for the attainment of the relatively stable colour determined experimentally with the first and the last samples of the series was found to be about 40 minutes. Readings were therefore taken after 50 minutes. The extinction values increased with the increase in the quantity of ferrous ammonium sulphate solution. Samples with more than 15 ml. of the ferrous solution gave nearly constant values. It was found that 1.0 ml. of M/40 gallic acid solution needed at least 7.5-8.0 ml. of M/40 ferrous ammonium sulphate solution to give the maximum colouration at pH 5.6 and temp. = 30°C. (table IV).

Similar experiments were carried out at different pH values, and it was observed that although the maximum readings obtained were influenced by the pH of the solution (lower extinction coefficients in the case of lower pH values), the optimum ratio of the reactants was approximately the same (table V).

TABLE V(A).—at pH=4.4

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient $E \times 100$
1	0.5	1.0	19.0
2	"	2.0	25.0
3	"	3.0	30.5
4	"	4.0	33.5
5	"	5.0	36.5
6	"	6.0	36.5

TABLE V (B).—at pH=4.8

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient $E \times 100$
1	0.5	1.0	30.0
2	"	2.0	37.0
3	"	3.0	40.0
4	"	4.0	41.0
5	"	5.0	41.0
6	"	6.0	41.0



TABLE V (c).—at pH=5.2

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	1.0	40.0
2	„	2.0	42.0
3	„	3.0	43.0
4	„	4.0	44.0
5	„	5.0	45.0
6	„	6.0	46.0

TABLE V (d).—at pH=5.6

Cylinder No.	M/40 Gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	1.0	42.0
2	„	2.0	42.0
3	„	3.0	46.0
4	„	4.0	46.0
5	„	5.0	46.0
6	„	6.0	49.0

(iv) *Standardization of the hydrolyzed myrobalan extract*: Ten ml. of the buffer of pH 5.6 was taken in every cylinder of the series, 0.5 ml. of the extract was added to each, and the volume was made upto 60 ml. M/40 ferrous ammonium sulphate solution was added to each in increasing steps of 2.0 ml. The solutions were mixed slowly with constant stirring.

The first and the last samples of the series were observed colorimetrically at intervals of five minutes. The time required for the full development of colour was nearly 30 minutes. The final readings of the whole series were therefore taken after 40 minutes. The readings were constant at 83.0 with the solutions having 10.0-16.0 ml. of iron solution (table VI (a)).

In another series of eight cylinders 10.0 ml. of the same buffer (pH 5.6) were taken and M/40 gallic acid solution was added in increasing steps of 0.05 ml. The readings were recorded as in the last experiment. The extinction value of the series which corresponded to the extinction value of the extract was noted against the standard with 1.70 ml. of the gallic acid solution (see table VI b). It

TABLE VI (A)

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES OBTAINED WITH HYDROLYZED TANNIN EXTRACT			
Cylinder No.	Hydrolyzed tannin extract in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	0.5	2.0	74.5
2	„	4.0	78.5
3	„	6.0	80.0
4	„	8.0	83.5
5	„	10.0	84.0
6	„	12.0	83.0
7	„	14.0	85.0
8	„	16.0	84.5

TABLE VI (B)

EXTINCTION COEFFICIENT OF THE COLLOIDAL SOLUTIONS OF FERROUS GALLIC ACID COMPLEXES			
Cylinder No.	M/40 gallic acid solution in ml.	M/40 Ferrous ammonium sulphate solution in ml.	Extinction coefficient E × 100
1	1.50	10.0	74.0
2	1.55	„	77.0
3	1.60	„	79.0
4	1.65	„	80.0
5	1.70	„	83.0
6	1.75	„	86.5
7	1.80	„	85.5
8	1.85	„	92.5
9	1.90	„	94.0

follows from this that 0.5 ml. of the hydrolyzed extract is equivalent in its colour value to 1.70 ml. of M/40 gallic acid solution. The strength of the extract in terms of the gallic acid equivalent was thus found to be 16 g./litre, *i.e.*, M/12 approximately.

The accuracy of this method was estimated at 0.05 ml. in 1.70 ml., which means approximately 3% by volume, so that a difference of 0.04 grammes of gallic acid can be detected. Table VI (b) shows that the accuracy can be

improved by interpolation between standards, because an alteration of 0.05 ml. in the volume of gallic acid solution produced 2.5 units difference in the extinction coefficient. On the other hand, there is a drawback in the method, in so far as the size of the particles as well as the stability of the complexes varies uncontrollably over a small range, affecting the accuracy adversely to the extent of about 2%, so that nothing could be gained by improving the accuracy of the measurements beyond that limit.

## STUDIES ON SHARK LIVER OIL

### Part I—Physico-chemical Constants and Vitamin 'A' Content of Liver Oil from Sharks of the Karachi Coast

S. MAQSOOD ALI, S. ABDUL HAQ AND S. MAHDIHASSAN

*Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

**F**ISH liver oils have attained great commercial importance on account of being rich sources of vitamins A and D. In many countries of Europe and America large industries developed and exploited different fishes like cod, halibut, sword-fish etc., for this purpose. During the past few years Pakistan has imported on an average 200,000 pounds a year of low potency fish liver oils at a cost of approximately Rs. 400,000. To this must be added the imports of vitamin concentrates at a still higher cost in foreign exchange. Unfortunately no such industry exists in Pakistan although marine fishes abound along the Karachi and Makran coasts. According to the statistics collected by the Central Fisheries Department, the present landing of sharks has been continuous over a period of years and stands around 10,000 tons per annum. Considerable amount of shark meat is dried, cured and exported from this country, but the liver oil is extracted in a very crude manner, resulting in a dark coloured obnoxious smelling product which is mainly used for smearing fishing boats.

In view of the facts stated above systematic investigations on the problem have been taken

up. The present paper deals with the yields and the physico-chemical characteristics of the oils from different species of sharks, and their vitamin A content in relation to age, size and sex of the fish. It may be stated in this connection that the liver oil of sharks found in Indian waters has been studied by Chakarwarty, Sarangdhar, Kini, Setna, Das and others<sup>1-6</sup> but sharks of the Karachi coastal waters have not been paid much attention, and there are only a few isolated references on the yields of their liver oil and its vitamin A content.

In the course of the present studies the following conclusions have been arrived at:—

- (1) The oil extracted from various species of sharks contains from 2000 to 72,000 U.S.P. units of vitamin A per gram with an average of 15,000 U.S.P. units per gram, which is a much higher average than is noted for the liver oil of sharks from any other coastal area of the sub-continent. According to Setna<sup>4</sup> this is perhaps due to the super-abundance of prawns and shrimps on the Karachi coast and the comparative

PHYSICO-CHEMICAL CONSTANTS AND VITAMIN 'A' CONTENT OF LIVER OIL FROM SHARKS OF THE KARACHI COAST

Date of collection	Name of Fish	Sex	Approx. body weight lbs.	Length Ft.	Weight of Liver lbs.	Liver oil %	Vitamin 'A' U.S.P. units per gram.	Free fatty acids as oleic %	Unsaponifiable matter %	Saponification value	Iodine value	Refractive index at 40°C.	Specific gravity at 30°C.
<b>Hammerhead Sharks</b>													
15- 2-56	Hammerhead shark (unidentified sp.)	.. Male	—	—	—	36.5	54,000	0.4	4.7	177.0	150.6	—	—
5- 5-56	Sphyrna malleus. 'Bodher-butther'	.. —	—	3	3.5	21.3	53,300	0.7	—	—	—	—	—
19- 9-56	—do—	.. Female	160	10	16	40.2	11,618	0.1	3.8	175.0	124.0	1.4662	0.9183
23-10-56	—do—	.. Female	15	4	0.7	6.0	18,000	0.2	—	184.0	—	—	0.9173
10- 1-57	—do—	.. Male	160	5.5	6	38.5	72,359	0.13	6.1	183.1	131.2	1.4670	0.9151
13- 2-57	—do—	.. Male	200	12	30	46.0	40,222	0.4	5.7	183.1	—	1.4671	0.9121
5- 6-56	Sphyrna blochii 'Julia mangar, Doka'	.. Male	15	2	0.7	10.0	51,000	0.7	—	—	—	—	—
14-11-56	—do—	.. Female	280	6.5	20	20.6	71,500	1.4	7.7	177.2	129.3	1.4685	0.9165
10- 1-57	—do—	.. Male	14	4	1.2	15.6	18,198	0.13	3.7	184.9	113.0	1.4670	0.9161
<b>Saw Fishes</b>													
1- 2-56	Pristis cuspidatus 'Khanda mangar, Liaro'	.. —	—	—	—	10.6	8,800	0.4	2.7	182.2	151.1	1.4660	0.9191
25- 9-56	—do—	.. Female	120	6	8	33.1	5,640	0.29	3.9	184.0	133.0	1.4662	0.9196
3-11-56	—do—	.. Female	100	7	4.5	24.8	9,227	0.13	2.8	193.1	146.2	1.4660	0.9188
27- 8-56	Pristis zysron 'Kharra mangar'	.. Female	50	5	2	9.5	2,708	0.17	2.5	183.9	—	1.4665	0.9170
4- 9-56	—do—	.. Male	1600	20	160	59.1	8,200	0.1	3.6	185.6	105.0	1.4613	0.9143
25- 9-56	—do—	.. Female	160	9	13	34.8	1,829	0.39	3.7	186.0	142.9	1.4648	0.9176
<b>Skates</b>													
25- 2-56	Rhinobatus granulatus 'Kair, Seroe'	.. Female	—	—	—	36.3	14,000	0.15	2.2	181.0	145.1	1.4664	0.9182
2- 1-57	—do—	.. Female	30	4	1	8.1	7,876	0.09	3.4	172.2	152.0	1.4650	0.9195
1-11-56	Rhynchobatus djeddensis	.. Female	80	5	2	21.3	3,274	0.1	4.7	180.1	131.1	1.4685	0.9220
3-11-56	—do—	.. Female	50	5	1.6	30.0	3,927	0.07	6.0	187.1	113.5	1.4682	0.9212
27- 8-56	Unidentified sp.	.. Female	30	4	2.5	20.2	2,369	0.16	2.1	185.0	—	1.4660	0.9200
<b>Miscellaneous Sharks</b>													
5- 6-56	Carcharias limbatus Small black tipped grey shark. 'Muyyach'	.. Female	80	5	7	38.5	4,100	0.10	1.9	172.0	141.1	1.4640	0.9171
17- 7-56	—do—	.. Male	100	6	10	30.0	19,000	0.13	—	183.0	—	1.4654	0.9188
3-11-56	—do—	.. Female	80	6	4.2	12.9	6,693	0.49	4.17	189.9	121.3	1.4668	0.9193
25- 6-56	Carcharias melanopterus Large black tipped grey shark. 'Kanatyan ; 'hangar'	.. Male	20	2.5	—	23.0	21,300	0.39	4.3	177.0	100.2	1.4668	—
17- 7-56	Rhineodon typicus	.. —	—	—	—	—	—	—	—	—	—	—	—
15-10-56	Whale shark, 'Mohr mangra'	.. Female	30	3.5	2	36.0	2,050	0.16	1.3	185.0	—	1.4593	0.9170
15-10-56	—do—	.. Female	8	3	0.5	10	750	0.19	—	177.1	123.0	1.4635	0.9175
24- 7-56	Galeocerdo arcticus Tiger shark, 'Kari'	.. Male	4	2	35gm.	39.9	7,140	2.4	6.3	180.0	147.0	—	Oil was extracted by means of ether
24- 7-56	—do—	.. Female	4	2	30gm.	41.0	2,300	2.5	10.9	187.1	135.2	—	Oil was extracted by means of ether
15- 2-57	—do—	.. Male	200	10	50	65.5	21,682	0.27	—	192.0	122.0	1.4630	Oil was extracted by means of ether

dearth of this important fish food near Bombay.

- (2) Hammerhead shark (*S. malleus*) is the richest source of vitamin A. Its liver oil contains up to 72,000 U.S.P. units of vitamin A per gram. The yield of oil from adult sharks ranges from 21-46% of the weight of fresh liver. Liver of males have a higher vitamin content than those of females.
- (3) Maturity of the fish and size of the liver have an important bearing on the yield of oil. Large livers weighing 6 lbs. or more yield 30-65% and small livers only 8 to 25% of oil.
- (4) The chemical constants of the oil such as iodine value, saponification value and the percentage of unsaponifiable matter significantly vary with the different species of sharks, whereas physical constants *i.e.*, specific gravity and refractive index show only slight differences. No correlation was found between any of the physico-chemical constants and vitamin A potency. The unsaponifiable matter of the oil has a much lower percentage (1.3 to 10.9%), compared to liver oils of sharks of the Atlantic and Pacific coasts for which it has been recorded upto 90%.

The shark was identified and the necessary data regarding the sex, approximate body weight, the weight of the liver and length of the fish were noted. The liver was brought to the laboratory and after removing blood, gall

bladder etc. was minced in a mincing machine. Weighed quantity of liver was mixed with twice its weight of hot water and digested for about 45 minutes at 80-85°C. The mixture was allowed to stand for some time in a separating funnel. The lower layer of water was removed and the oil along with the liver tissue was centrifuged. The oil thus separated was finally dried over anhydrous sodium sulphate and filtered hot into a tared flask. Vitamin A was determined spectrophotometrically<sup>7</sup> and physico-chemical characteristics of the oil were determined by standard methods and are recorded in the attached table.

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