Journal of Scientific & Industrial Research

Vol. 13, No. 10, OCTOBER 1954

IN THIS ISSUE

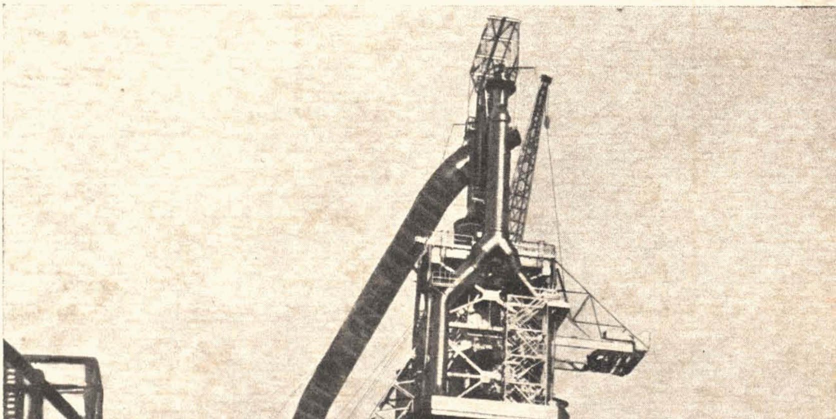
- Properties of mortars from ancient buildings
- Electron diffraction study of silver films on rock salt
- Effect of shape on the voids content of sized powders
- Biosynthesis of vitamin C during germination
- Detection of rape and mustard oils
- Preparation of cation exchange membranes

SECTION A : GENERAL

For Contents see page A3

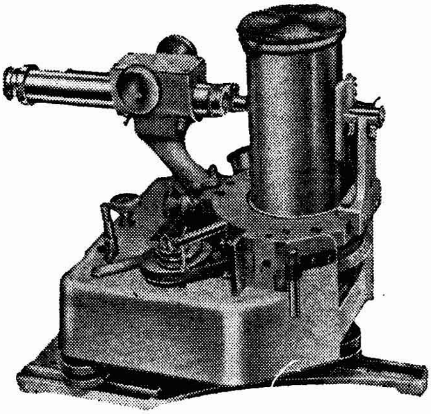
SECTION B : RESEARCH PAPERS

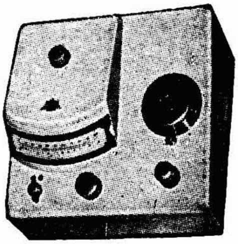
For Contents see page A37

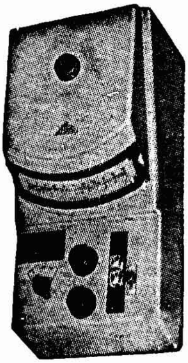


PUBLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
NEW DELHI

J. sci. industr. Res., Vol. 13A, No. 10, Pp. 455-506; & Vol. 13B, No. 10, Pp. 673-748. October 1954







Journal of

Scientific & Industrial Research

Vol. 13A, No. 10, OCTOBER 1954

CONTENTS

COVER PICTURE

The picture on the cover shows the blast furnace designed and built at the Tata Iron & Steel Co. Ltd., Jamshedpur. The furnace, which recently went into operation, is the largest in the east with a capacity of 1,000 tons a day. (*See* page 497.)

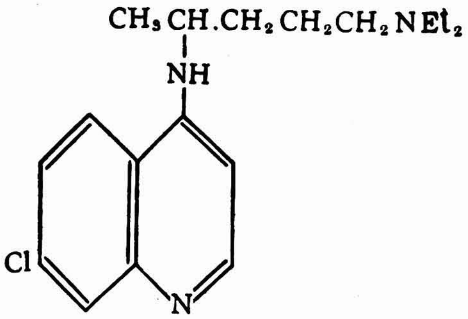
The JOURNAL OF SCIENTIFIC & INDUSTRIAL RESEARCH *is issued monthly.*

The Council of Scientific & Industrial Research assumes no responsibility for the statements and opinions advanced by contributors.

The Editorial Board in its work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists working in various parts of India.

Communications regarding contributions for publication in the JOURNAL, *books for review, subscriptions and advertisements should be addressed to the Editor,* JOURNAL OF SCIENTIFIC & INDUSTRIAL RESEARCH, *Old Mill Road, New Delhi* 2.

ANNUAL SUBSCRIPTION: Rs. 15 (inland); 30 sh. (foreign). SINGLE COPY: Rs. 2 (inland); 4 sh. (foreign)


CH₃CH.CH₂CH₂CH₂NEt₂
NH
Cl
N

Precision Instruments for
RESEARCH & INDUSTRY

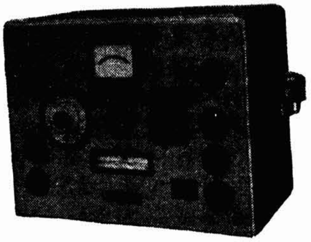


FIG. 1

Multi-Dekameter, Type DK 06 (Fig. 1), for the measurement of the dielectric constant and the dielectric loss in a frequency range of 100 kc. to 20 Mc. with great accuracy. This instrument is specially valuable for measurements of the dielectric constant and the dielectric loss over a wide frequency range in liquids and solid materials. An approved instrument in the research on the behaviour of colloidal and polymer molecules.

NF-Dekameter, Type DK 05, a precision measuring bridge with amplifier, null detector and continuous visual indication (cathode-ray tube) for the determination of the dielectric constant and the dielectric loss over a frequency range from 30 c. to 100 kc. The NF-Dekameter can be specially recommended for the electrotechnical industry as it allows to carry measurements at the important frequencies of 50 c., 800 c. and 1000 c.

Both the instruments, Type DK 05 and Type DK 06, permit complete examinations over a frequency range 30 c. to 20 Mc.

Multi-Megohmmeter, Type MOM I, an instrument for measuring the surface and volume resistivity (up to 10^{14} ohms) in insulating and plastic materials. Measurements can be carried out up to 1000 volts. This instrument, which is mainly employed in the industry for rubber and insulating and plastic materials, also allows studies on the electric breakdown with direct current. It is indispensable in the production of plastics, condensers, cables and wires.

Precision Measuring, Type WBR (Fig. 2), of latest construction with the Logarithmic Amplifier, Type TAV (with built in 1000 c. generator), serves for the precise determination of the electrical conductivity and electrical resistance with a maximum accuracy of ±0.02 per cent in connection with the Logarithmic Amplifier.

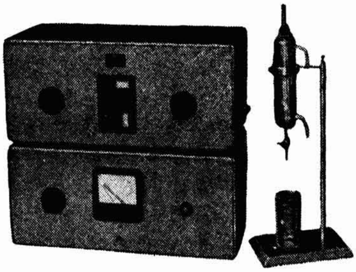


FIG. 2

The conductimetric analysis may also be carried out with this instrument with great accuracy.

For measuring with direct current it is necessary to use a battery (4 to 6 volt) and galvanometer.

MANUFACTURED BY

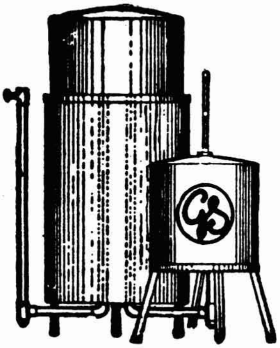
WISSENSCHAFTLICH TECHNISCHE WERKSTATTEN
GERMANY

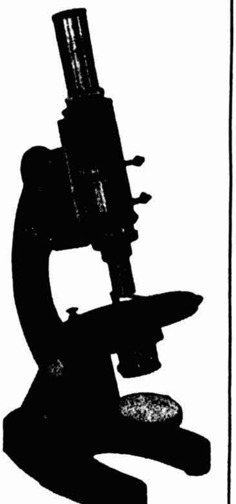
Available Ex-stock from Exclusive Agents in India

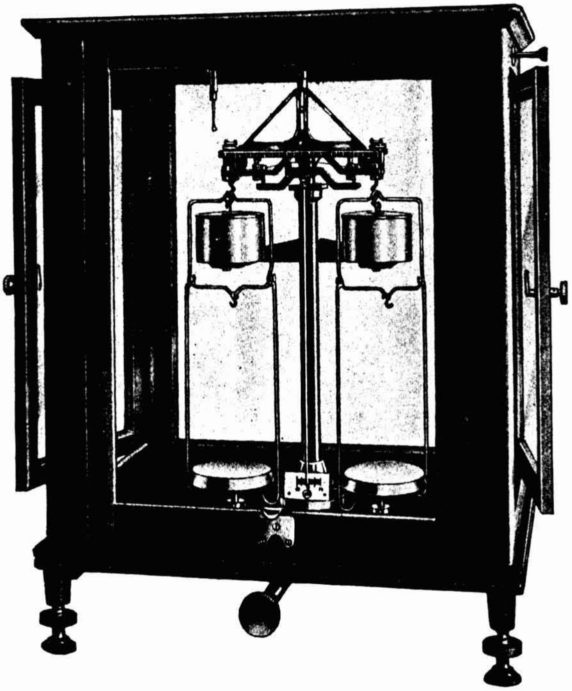
TOSHNIWAL BROS. LTD.

Head Office:
198 JAMSHEDJI TATA ROAD
BOMBAY

Branch Office:
3/30 MOUNT ROAD
MADRAS


GS





SERPINA

Standardised 4 mg. total alkaloids of Rauwolfia serpentina (Benth) per tablet

- Made from specially processed, blended, tested roots of Rauwolfia serpentina (Benth)
- A safe Hypotensive and Cardio-vascular sedative of precise therapeutic value.
- Uniformity of action controlled by biological and chemical assay.
- The pioneer, product endorsed by 20 years of clinical observation and research.
- Available in all the five Continents.

LITERATURE & SAMPLES FROM

THE HIMALAYA DRUG CO., 251, Hornby Road, Bombay 1.

THE POPULAR BOOK DEPOT

(Registered)

LAMINGTON ROAD, BOMBAY 7

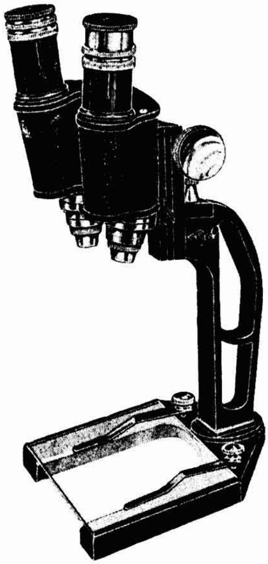
announces arrival of ALL TITLES published by

THE BUTTERWORTH SCIENTIFIC PUBLICATIONS, LONDON

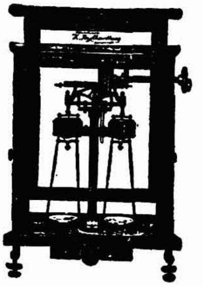
	Rs.	as.
Metallurgy of the Rarer Metals, No. 1 — Chromium (SULLY) (1954) ...	**26**	**4**
Metallurgy of the Rarer Metals, No. 2 — Zirocnium (MILLER) (1954) ...	**33**	**12**
JONES — Instrument Technology, Vol. I — Measurement of Pressure, Level, Flow and Temperature (1953)	**26**	**4**
Corrosion — A series of papers reprinted from ' Research ', Vol. 5 (1952-53) ...	**4**	**8**
WALLACE & MARTIN — Insecticides and Colonial Agricultural Development — 6th Symposium of the Colston Research Society held in the University of Bristol, 23-27-3-1953-1954 book	**22**	**8**
PILBOROUGH — Applied Heat and Heat Engines (1954)	**26**	**4**
E. M. GOODGER — Petroleum and Performance in Internal Combustion Engines (1953)	**24**	**6**

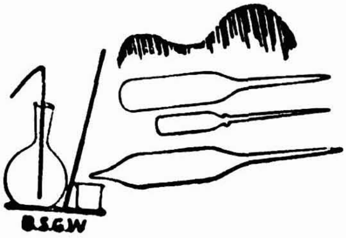
ASK FOR COMPLETE CATALOGUE OF BUTTERWORTH'S

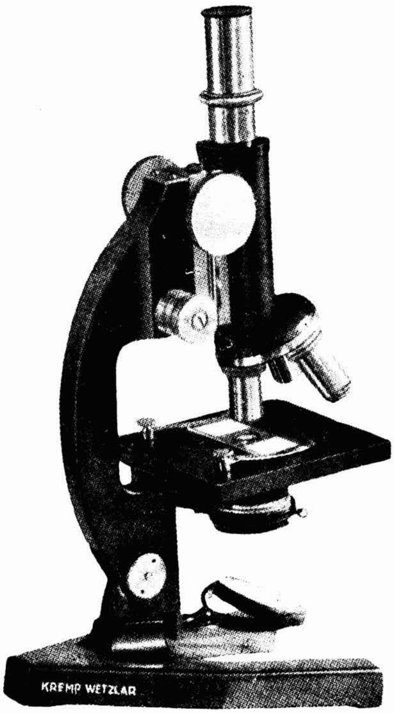
For scientific books it's POPULAR

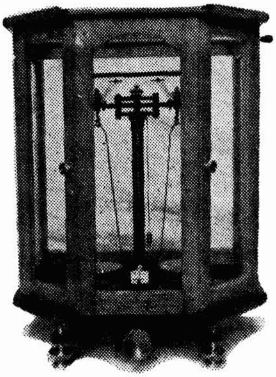


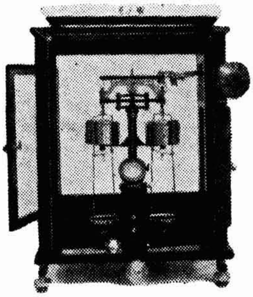
BINOCULAR DISSECTING MICROSCOPE

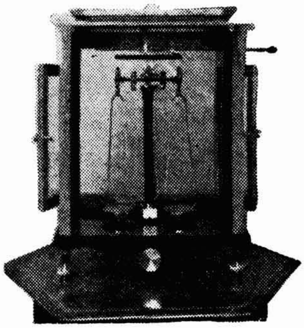


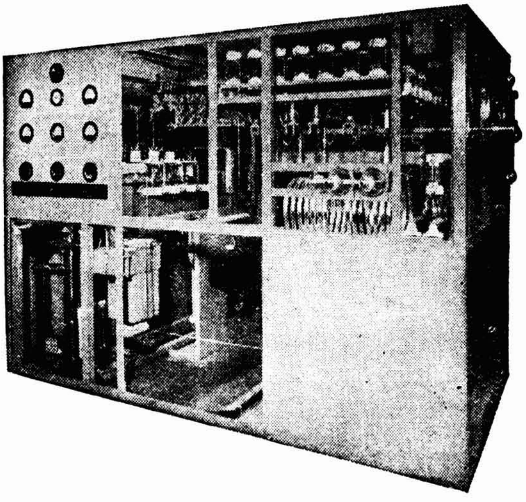

BSGW


KREMP WETZLAR









FIVE

reasons for using

'ANALAR' REAGENTS

1 They conform to published standards of purity.

2 Their labels show maximum limits of all likely impurities.

3 They are packed under carefully controlled conditions.

4 Their use eliminates 'reagent errors'.

5 They are standard analytical materials in laboratories undertaking important and responsible work.

THE BRITISH DRUG HOUSES LTD.
B.D.H. LABORATORY CHEMICALS GROUP
POOLE ENGLAND

BRITISH DRUG HOUSES (INDIA) LTD.
P.O. BOX 1341 BOMBAY.
Branches at: CALCUTTA, DELHI, MADRAS

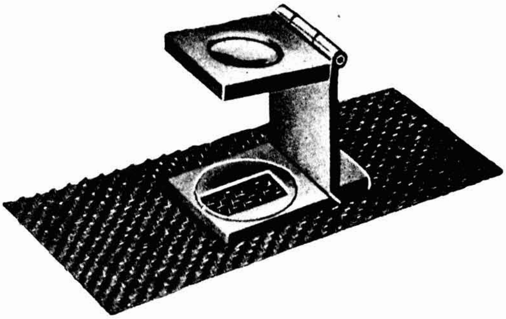
QUICKFIT & QUARTZ Ltd.

The pioneers in the field of interchangeable ground glass apparatus offer:

Various Types of Distillation Assemblies
General Utility Sets
High Vacuum Stopcocks
Expansion and Reduction Adapters
Semi-micro Distillation Sets
Standard Ground Glass Joints
Ball and Socket Joints with Clips
Soxhlet Extraction Apparatus
Conical Spherical Adapters
Stadler Stills

Available from stock :

UNION SCIENTIFIC SYNDICATE
POST BOX No. 2484
52-58 BABU GENU ROAD
BOMBAY 2
Tel : 28465 Gram : **PETROLIUM**



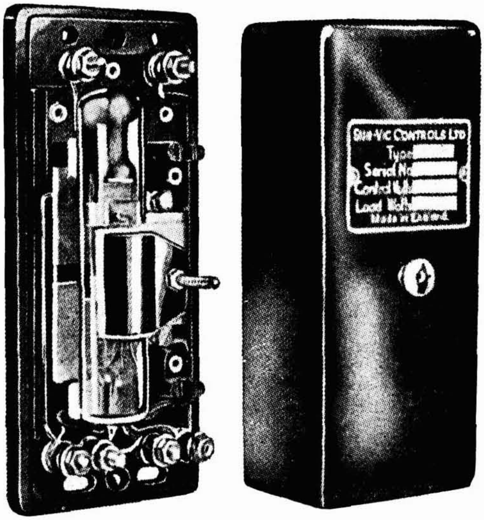
Accurate Wire Screen is required to solve your Screening, Grading or Filtering operation.

●

DIRECT IMPORTERS OF WOVEN WIRE MESH AND PERFORATED METALS

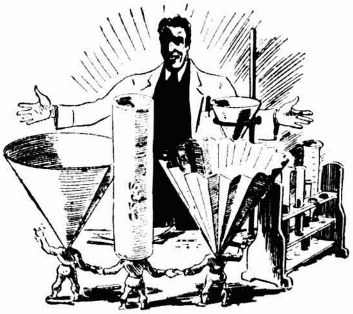
STANDARD METAL CO.

Props.: B. C. GUIN & CO. LTD.
101 NETAJI SUBHAS ROAD
CALCUTTA 1



SUN-VIC CONTROLS LTD
Type
Serial No
Control Volts
Load Watts
Made in England

THIS TRADEMARK MEANS RELIABILITY



WHEN THE RESULT OBTAINED CREATES A DOUBT . . .

Particularly in cases where chemical analyses yield unexpected results, you must be absolutely certain that the results obtained are correct, because the materials used and the means adopted by you in the analytical procedure were perfectly reliable. This confidence is assured whenever you use "S & S" filter papers.

By continuously developing our methods of production and tests we are bringing out in co-operation with the scientists, more and more analytical filter papers year after year, which, on account of their uniformity and dependability on their essential properties, are highly esteemed all over the world.

CARL SCHLEICHER & SCHÜLL · DASSEL/KR. EINBECK

Sole Indenting Agents in India

FILTER PAPER

BIVA'S LIMITED

WOODBURN PARK
CALCUTTA 20

For

Scientific — Medical — Industrial
LABORATORY EQUIPMENT

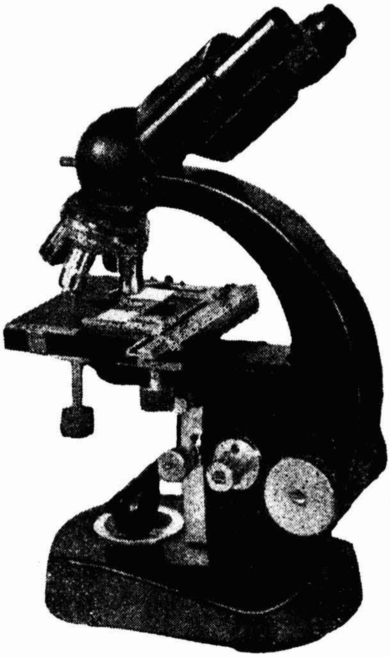
Beck Kassel Microscopes and Binoculars
'Nedoptifa' Phase-Contrast Microscopes
Memmert Ovens and Incubators
Paul Keiner Laboratory Glassware
Metrohm *p*H Meters and Stirrers
Bosch Balances, Rotofix Centrifuges
Laboratory Stirrers and Shaking Apparatus
Intra Hot-Air Sterilizers, etc., etc.

CONTACT:

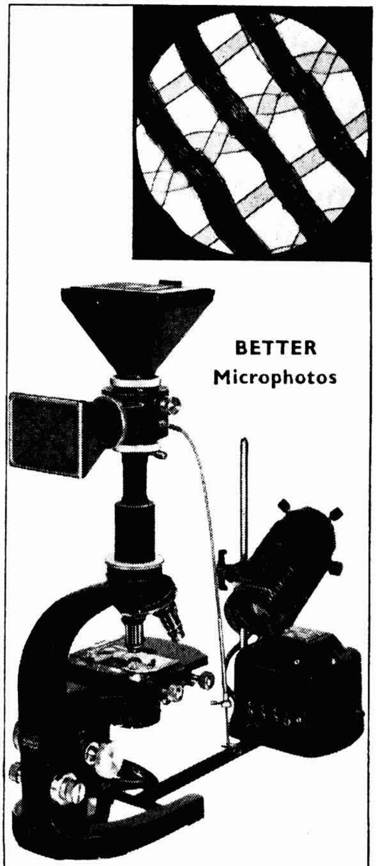
J. T. JAGTIANI

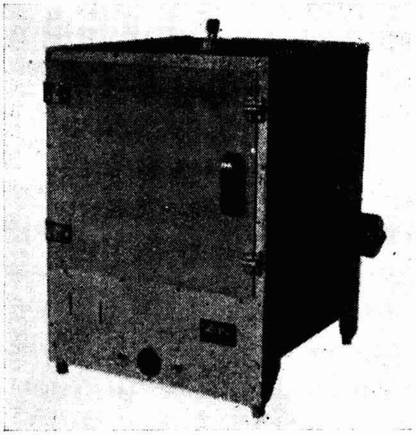
National House, 6 Tulloch Road, Apollo Bunder,
BOMBAY 1

Post Box 332 Grams: FACMARE Phone: 35229

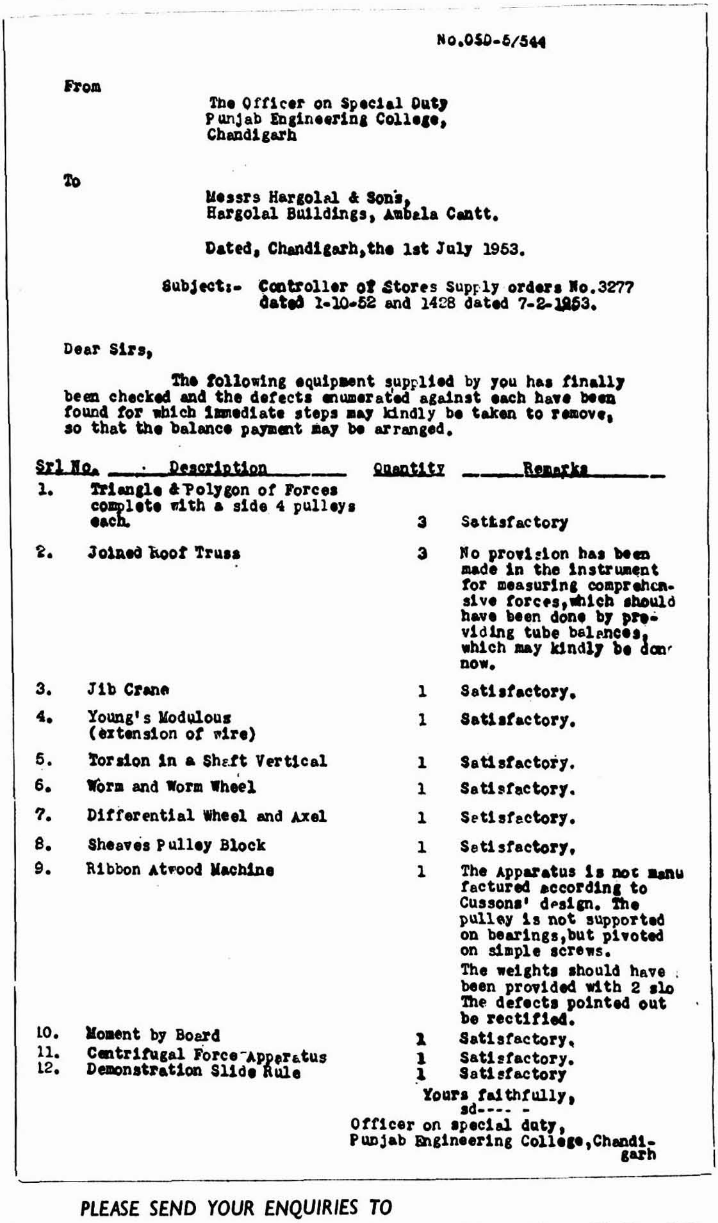


SP/JTJ/1


BETTER
Microphotos




Paharpur Works
G.E.C.
THE GENERAL ELECTRIC COMPANY OF INDIA (MANUFACTURING) LTD.



No.OSD-5/544

From

The Officer on Special Duty
Punjab Engineering College,
Chandigarh

To

Messrs Hargolal & Sons,
Hargolal Buildings, Ambala Cantt.

Dated, Chandigarh, the 1st July 1953.

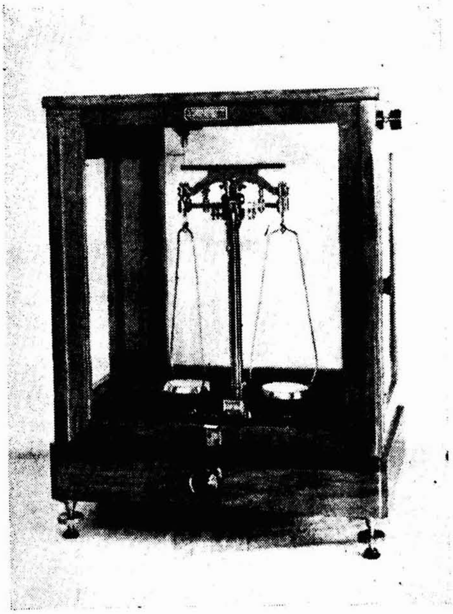
Subject:- Controller of Stores Supply orders No.3277 dated 1-10-52 and 1428 dated 7-2-1953.

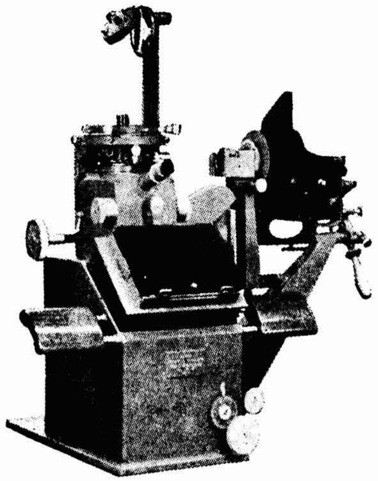
Dear Sirs,

The following equipment supplied by you has finally been checked and the defects enumerated against each have been found for which immediate steps may kindly be taken to remove, so that the balance payment may be arranged.

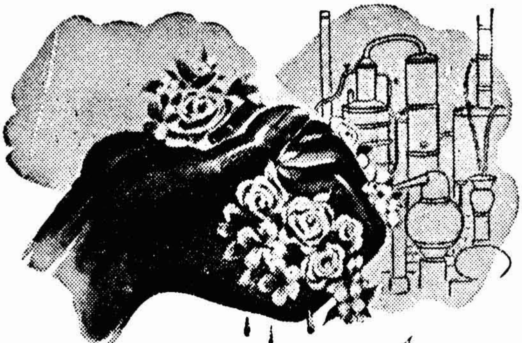
Srl No.	Description	Quantity	Remarks
1.	Triangle & Polygon of Forces complete with a side 4 pulleys each.	3	Satisfactory
2.	Joined Roof Truss	3	No provision has been made in the instrument for measuring comprehensive forces, which should have been done by providing tube balances, which may kindly be don now.
3.	Jib Crane	1	Satisfactory.
4.	Young's Modulous (extension of wire)	1	Satisfactory.
5.	Torsion in a Shaft Vertical	1	Satisfactory.
6.	Worm and Worm Wheel	1	Satisfactory.
7.	Differential Wheel and Axel	1	Satisfactory.
8.	Sheaves Pulley Block	1	Satisfactory.
9.	Ribbon Atwood Machine	1	The Apparatus is not manufactured according to Cussons' design. The pulley is not supported on bearings, but pivoted on simple screws. The weights should have been provided with 2 slo The defects pointed out be rectified.
10.	Moment by Board	1	Satisfactory.
11.	Centrifugal Force Apparatus	1	Satisfactory.
12.	Demonstration Slide Rule	1	Satisfactory

Yours faithfully,
sd---- -
Officer on special duty,
Punjab Engineering College, Chandigarh





VICKERS PROJECTION MICROSCOPE
Magnification : 30x to 4740x




Index Glass
MADE BY
Sigcol

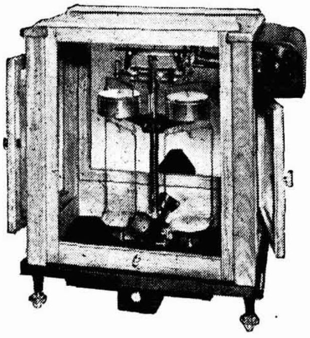
STANTON *Leadership*

The design and construction of every modern Precision Balance manifests the influence that STANTONS have exerted during the past few years

STANTON were first with:

- **Synthetic Sapphire (Corundum) planes.**
- **Full weight-loading balances in Britain.**
- **Balances with a special application — e.g. Gas Density Determination, Thermo Recording Work, Remote Control Work.**

STANTON *now present 2 new models*

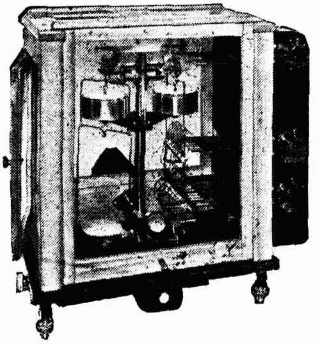


Model A.D.6

Capacity: 200 *g.*
Sensitivity: 0.1 *mg. per half division*

This aperiodic, projection-reading balance provides for external weight-loading of fractions up to 1 g. by means of a single dial. The new graticule reads direct up to 100 mg., resulting in greater weighing speed and less fatigue.

Fully descriptive illustrated folder on request



Model B.A.4

Capacity: 200 *g.*
Sensitivity: 0.1 *mg. per half division*

This balance represents another contribution by Stanton towards greater balance room efficiency. Only four dials give weight-loading up to 200 g. — Graticule reads direct up to 100 mg., and complete weighing can thus be made in twenty to thirty seconds.

For full details write to:

MARTIN & HARRIS Ltd., Savoy Chambers, Wallace St., Fort, Bombay • Tel : 30073

STANTON PRECISION BALANCES

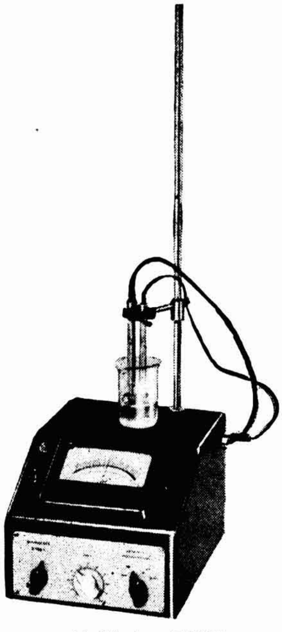
STANTON INSTRUMENTS LTD., LONDON, W.1

An efficient team in

POTENTIOMETRY, CONDUCTOMETRY, POLAROGRAPHY, COULOMETRY, etc.

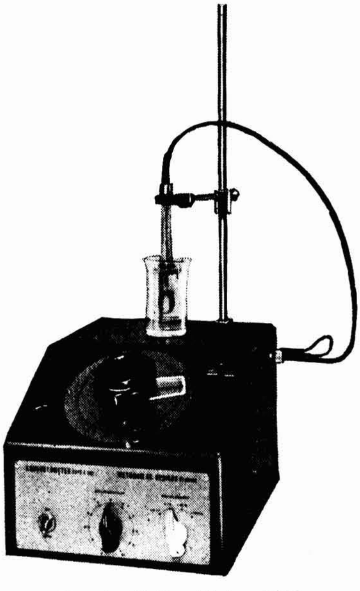
There is a "METROHM" instrument for every application. "METROHM" specialities include pH Meters, pH Controllers and Recorders, Conductivity Meters, Conductivity Controllers and Recorders, Conductometric and Potentiometric Titration Apparatuses, Polarometers, Coulometers, Salinometers and many others.

The novel facilities offered by "METROHM" instruments are
VERSATILITY, ACCURACY, DEPENDABILITY, SIMPLE OPERATION, SPEED,
STURDINESS & INGENIOUS ACCESSORIES



pH Meter E150A

An inexpensive direct reading instrument, entirely line-operated, suitable not only for most of the pH problems arising in the laboratory, but also for a good many applications in the plant itself. Good performance, simple operation and versatility are the features which have led to its great popularity and widespread use.



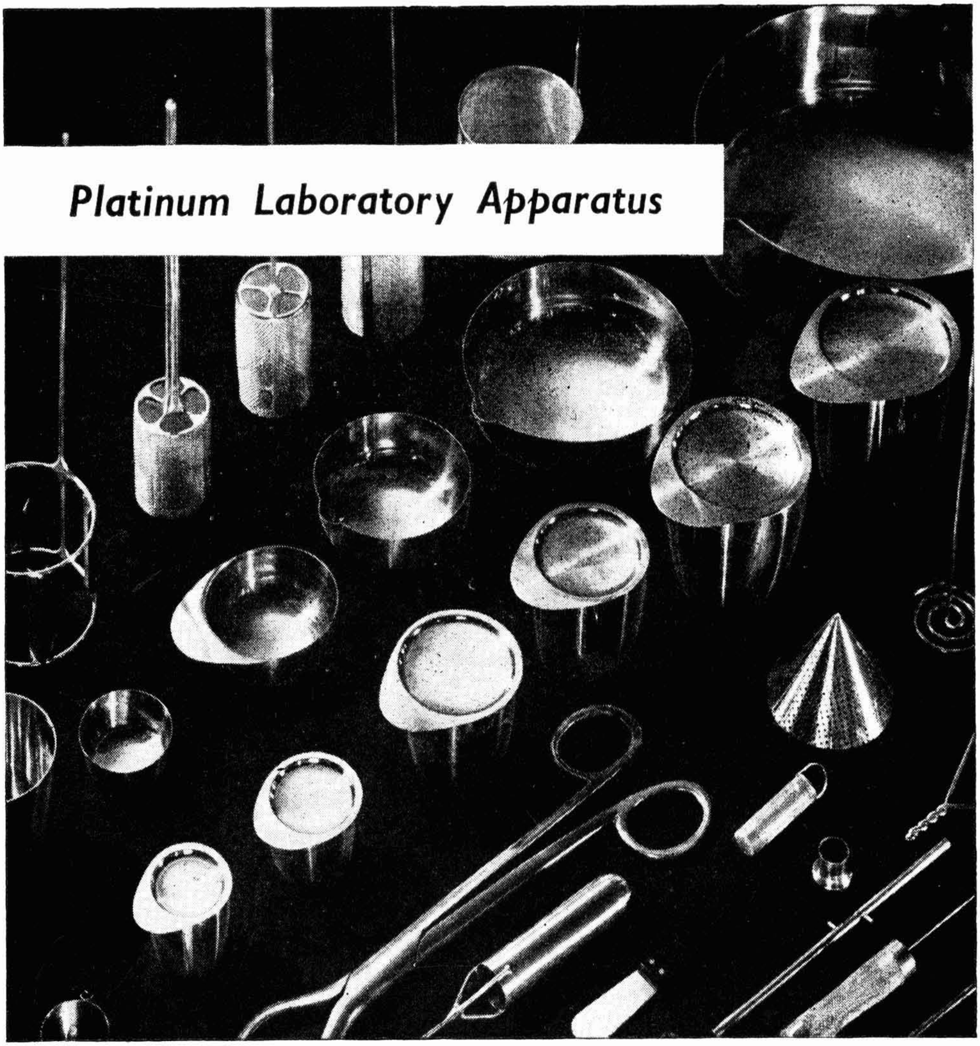
Conductivity Meter E182

A precision instrument for measurement of electrolytic resistances in a simple way, a.c. mains operated, employing a bridge circuit with magic eye. Total range 40-1,000,000 ohms. No need for phase compensation as polarizing capacity is generally small. Accuracy, ± 1 per cent of full scale range.

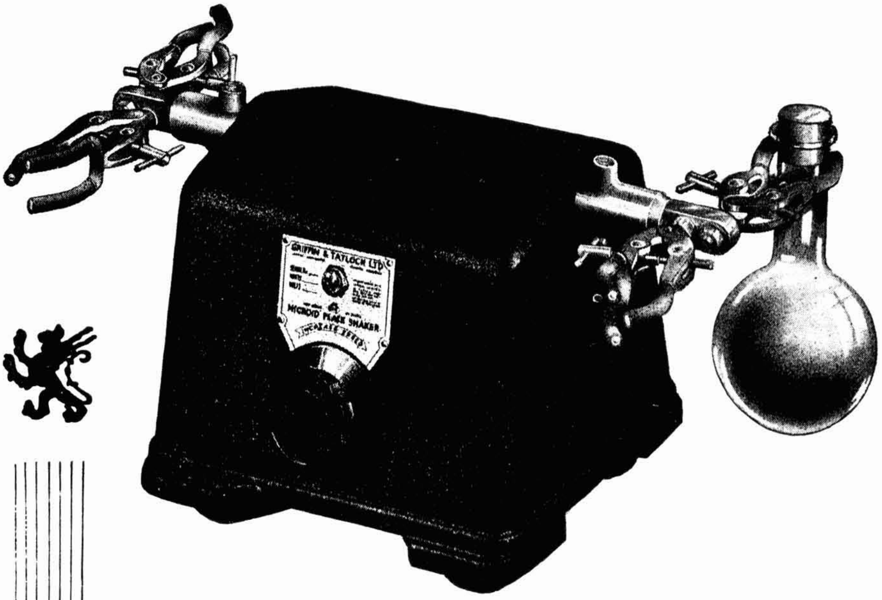
Available ex stock from Exclusive Agents

KAY ORR BROTHERS

P 36 ROYAL EXCHANGE PLACE EXTENSION, CALCUTTA 1



INDEX TO ADVERTISERS


GRIFFIN & TATLOCK LTD
MICROID FLASK SHAKER

Engineering Research in India

IT has been often stated in the context of industrial advancement that what is of first importance is not more scientific research, but the application of what is known. This implies that immense resources of scientific knowledge lie untapped by industry and that for sound and sustained economic development, science, engineering and industry should be brought into intimate partnership.

Scientific research by itself does not give rise to new industries and new products. The results achieved in the laboratory have to be translated into workable economic projects; the tools and equipment required for operating laboratory processes have to be designed and fabricated; and the " know-how ", by which is meant the knowledge required for the effective application of new ideas or processes, has to be worked out. The provision of these requirements for research utilization comes within the domain of technologists and engineers — design engineers, process engineers, production engineers, chemical engineers, and others versed in basic engineering sciences. Engineering is as vital to industry as science, and the need for engineering development is as urgent as the need for scientific development. For harnessing new ideas to productive industry, engineering research should be promoted on a bold and imaginative scale.

Development in engineering calls for a body of knowledge derived from different branches of science and there is urgent need for enlarging research in basic sciences. Intensive research should be initiated in fundamental engineering sciences, e.g. applied mechanics, elasticity, thermodynamics and heat transfer, and talented youth should be encouraged to pursue studies in basic engineering subjects and a climate for discovery and invention should be created. Money spent on research in basic sciences is a safe investment which will pay handsome dividends.

Under an assignment from the Director, Scientific & Industrial Research, Mr. V. Cadambe, Head of the Division of Applied Mechanics and Materials, National Physical Laboratory of India, New Delhi, has recently completed a survey of the progress of research in various branches of engineering and of the facilities for engineering research available in educational and research institutions in the country. The object of the survey was to collect the basic data necessary for formulating an integrated programme of engineering research. A report containing the results of the survey, together with the recommendations, has been published by the Council of Scientific & Industrial Research*.

The report draws attention to the various fields of engineering which have not received adequate attention and emphasizes the view generally held that research effort in engineering is incommensurate with India's natural resources, size and population. The report points out that in countries which are industrially advanced, engineering research has made great strides and that research is pursued with increasing tempo by co-operative research associations of industry, private research organizations, laboratories sponsored by government, universities and industries. In India there are but few co-operative research associations to undertake research for industries. All the universities are not equipped for undertaking engineering research. Out of 45 universities and technological institutions in the country, 6 offer engineering courses

---

**Engineering Research in India*, by V. Cadambe, Council of Scientific & Industrial Research, New Delhi, 1954, pp. xii + 114.

at the postgraduate level; in 16, limited facilities are available in one or two fields; in the remaining 23, there are hardly any facilities for research. Research in civil and communication engineering is being carried out in government establishments and in national laboratories and it is in these fields, particularly in hydraulics and irrigation, that India has made substantial and noteworthy contributions. In other fields of engineering — mechanical, electrical and aeronautical — only a beginning has been made.

In addition to listing engineering problems which need research and investigation, the report has made a number of suggestions of a general character for furthering engineering research and for the development of basic engineering industries. The setting up of a Research Committee on Applied Mechanics under the Board of Engineering Research and the organization of research laboratories for mechanical engineering, electrical machinery and hydro-electric power plant, steam power plant, machine tools, water pollution, automobile engineering, aeronautical engineering, nautical engineering and shipbuilding, gas turbines, industrial machinery and plant, and cement concrete testing have been recommended. As research and development in aeronautical engineering is expensive and beyond the scope of universities, technological institutions and national laboratories, it is suggested that work in this field should be the concern of the Government. The establishment of regional laboratories and workshops to help the development of small-scale and cottage industries and formation of consumers' organizations to undertake work relating to standardization of engineering materials and products are recommended. Emphasis has been laid on liaison between industry and research establishments, engineering museums and technical library and information services.

The survey has emphasized the need for action. Engineering research and industrial progress are interrelated and it is necessary to recognize this mutual dependence in the formulation of plans for the economic development of the country. It is to be hoped that the facts revealed by the survey will receive due attention and that they would be utilized for formulating an adequate programme of engineering research.

Board of Scientific & Industrial Research, Thirty-third Meeting, New Delhi

THE thirty-third meeting of the Board of Scientific & Industrial Research was held in New Delhi on 14 Sept. 1954. The meeting of the Governing Body of the Council was held on the following day. The Prime Minister, Shri Jawaharlal Nehru, presided.

The following new schemes were sanctioned by the Governing Body on the recommendation of the Board:

1. *Linear time of flight mass spectrometry*: DR. B. D. NAGCHAUDHURI, Institute of Nuclear Physics, Calcutta
2. *Photomicrography of brain cells*: MAJ. R. B. DAVIS, Hospital for Mental Diseases, Ranchi
3. *X-ray and optical studies on collagen*: DR. G. N. RAMACHANDRAN, Madras University, Madras
4. *Development of auto-engines for using power alcohol as fuel*: PROF. R. G. P. S. FAIR-

BAIRN & MR. G. L. BANERJEE, Bengal Engineering College, Howrah

5. *Properties of capillary held liquids*: DR. B. R. PURI, Punjab University College, Hoshiarpur

6. *Substitution of ammonium sulphate in processes involving sulphuric acid*: MR. D. K. PATWARDHAN, Banaras Hindu University, Banaras

7. *Production of itaconic acid by fermentation*: DR. K. RAMACHANDRAN & DR. HUSAIN ZAHEER, Central Laboratories for Scientific & Industrial Research, Hyderabad (Dn.)

8. *Some biological aspects of fluorine*: DR. D. NARAYANA RAO, Medical College, Trivandrum

9. *A unit for testing cancer-producing and cancer-inhibiting substances*: DR. V. R. KHANOLKAR, Indian Cancer Research Centre, Bombay

10. *Survey of Rewa sillimanite*: DR. R. S. MITHAL, Banaras Hindu University, Banaras

11. *Polymerization of Δ^3 carene from Indian turpentine oil from Pinus longifolia*: DR. L. M. YEDDANAPALLI, Loyola College, Madras

12. *Cultural and chemical studies of vetiver roots and oils*: DR. D. R. DHINGRA, H.B. Technological Institute, Kanpur

13. *Chemistry of plant chromosomes*: MR. A. K. SHARMA, Calcutta University, Calcutta

14. *Metabolic degradation products of 8-aminoquinolines*: COL. JASWANT SINGH, Malaria Institute of India, Delhi

15. *Setting up of a Pharmacological Research Unit at the G. S. Medical College, Bombay*

16. *Chemical investigation of Indian medicinal plants*: DR. T. R. GOVINDACHARI, Presidency College, Madras

17. *Medicinal and essential oil yielding plants*: DIRECTOR, CINCHONA DEPARTMENT, Ootacamund

18. *Development of free piston compressors*: DR. N. S. NANDESWARAYA, Indian Institute of Technology, Kharagpur

19. *Physical properties of gelatinous substances*: DR. A. M. SRIVASTAVA, Allahabad University, Allahabad

20. *Ultrasonic absorption in liquids*: DR. G. S. VERMA, Allahabad University, Allahabad

21. *Study on plasticity and its relation to other physical and chemical properties of Indian clays*: DR. D. LAHIRI, Calcutta University, Calcutta

22. *Utilization of blast furnace slag*: DR. D. LAHIRI, Calcutta University, Calcutta

23. *Influence of allotropic forms of silica upon the maturing and firing characteristics of white-ware bodies and glazes, etc.*: DR. S. S. DAS, Banaras Hindu University, Banaras

Pilot plant for optical glass — The Governing Body of the Council recommended that a pilot plant for the production of about 5 tons of optical glass per annum should be set up at the Central Glass & Ceramic Research Institute, Calcutta. The plant will not only help to meet part of the demand for optical glass but also help the country to keep abreast of developments in the production techniques of this important material. The Council recommended that the Government of India be requested to make available a sum of Rs. 5 lakhs towards capital and Rs. 2 lakhs per annum towards recurring expenditure to the Central Glass & Ceramic Research Institute, Calcutta, for this purpose.

Institute of Biophysics — The Council have constituted a Committee consisting of Dr. B. C. Roy (*Chairman*) and Dr. Jivraj N. Mehta, Prof. M. N. Saha, Dr. D. S. Kothari, Dr. V. R. Khanolkar, Dr. A. L. Mudaliar and Dr. S. S. Bhatnagar (*Members*) to examine the possibility of setting up a Biophysical Research Institute in India and to prepare detailed proposals for consideration of the Council. In the meantime, the Council approved the setting up of a Nucleus Centre of Biophysical Research at the Central Drug Research Institute, Lucknow, in collaboration with the Lucknow University.

Indian Ephemeris and Nautical Almanac — The Council accepted a proposal to publish an Indian Ephemeris and Nautical Almanac. The former would be a source book to the *Panchang* makers and would give impetus to the study of astronomy in the country. The Almanac would provide useful training in computational and numerical methods, and will serve as an essential prelude to the compilation of complete Nautical and Air Almanacs.

Calendar Reform — Prof. M. N. Saha, Chairman, Calendar Reforms Committee, presented the Experimental Calendar for the five year period 1954-55 to 1958-59. The Council decided that this should be published at the earliest date and circulated to elicit public opinion.

Investigations on Rauwolfia — A Sub-committee consisting of Prof. K. N. Kaul, Col. S. S. Bhatnagar, Rev. Father H. Santapau and Dr. K. Biswas has been constituted to inquire into (i) the present condition of availability, plantation and cultivation of *Rauwolfia serpentina*, (ii) restrictions on the export of the plant and its extracts, and (iii) possibility of preparation of useful intermediates which could be exported.

Symposium — The Council approved a proposal to hold a symposium on Alloy Steel Industry in India at the National Metallurgical Laboratory, Jamshedpur.

Indian Science Congress: 42nd Session, Baroda

A HEAVY PROGRAMME OF SCIENTIFIC DISCUSSIONS, symposia and popular lectures has been planned for the forthcoming session of the Indian Science Congress to be held at Baroda during the week 1-8 January 1955 under the Presidentship of Prof. S. K. Mitra. Besides scientists from all parts of India, the following distinguished visitors from abroad are expected to attend: Prof. Paul Karrer (Switzerland), Prof. T. Watanabe (Japan), Prof. P. A. M. Dirac, Sir Henry Dale, Dr. H. A. Krebs (U.K.), Dr. D. V. Bronk (U.S.A.) and Dr. Siegbahn (Sweden).

There are 38 topics scheduled for discussion in the various sections of the Congress. These include: Statistical methods in genetics and plant breeding; Modern trends in analytical chemistry; Origin of saline deposits in India with special reference to Rajasthan; Minerals in soils and clays; Effect of growth-promoting substances on crop production; Blood grouping in relation to castes in India; Plant introduction as an aid to improvement of food and fodder plants; and Design and manufacture of electrical instruments in India.

The following evening discourses on popular scientific subjects have been planned: Curare and curare alkaloids by Prof. Paul Karrer; Volcanic eruptions; and Geological studies of damages caused by atomic bombs in Hiroshima and Nagasaki by Prof. T. Watanabe; Symmetry in the atomic world by Prof. P. A. M. Dirac; and Science and its social relations by Prof. A. R. Wadia.

An exhibition of instruments, apparatus and equipment will be organized during the session.

Enquiries as to accommodation and local arrangements may be addressed to the Local Secretaries, 42nd Indian Science Congress, M. S. University of Baroda, Baroda.

CHARACTERISTICS OF THE IONOSPHERE OVER CALCUTTA

S. S. Baral, R. K. Mitra, A. K. Saha,
M. R. Kundu, S. Datta & S. Ray

Ionosphere Laboratory, Institute of Radio Physics & Electronics, University College of Science, Calcutta

Fig. 1 shows the monthly average diurnal variation of the ordinary ray critical frequency of region F_2 ($f^\circ F_2$) and also similar variations of the heights of maximum ionization (hpF_2) and the bottom ($h'F_2$) of the F_2 layer during July 1954. The $f^\circ F_2$ variation curve has been compared to that predicted three months before. The percentage of the total number of occasions during routine observations when the critical frequency for the sporadic E layer (fE_s) was greater than 3, 5 and 7 Mc./s. has been plotted for the different hours in Fig. 2. Table 1 gives the median values for the different ionospheric parameters for July 1954.

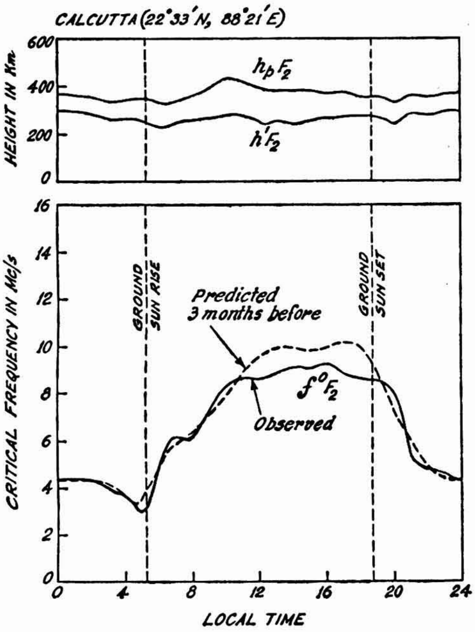


Fig. 1 — Monthly mean ionospheric characteristics for July 1954

Fig. 3 gives the mean M.U.F. predictions for transmissions to different distances via F_2 region over Calcutta during October 1954.

The intensity and frequency of occurrence of E_s ionization were very high during

TABLE 1 — MONTHLY MEDIAN HOURLY VALUES

(*July* 1954)

Time*	$f^\circ F_2$ Mc./s.	hpF_2 km.	$h'F_2$ km.	$f^\circ E$ Mc./s.	fE_s Mc./s.	$(M3000)F_2$
00	4·40	375	300			2·70
01	4·25	360	300			
02	4·40	360	300		5·60	
03	4·05	330	270		5·20	2·95
04	3·70	330	240			
05	3·05	360	240			
06	4·80	330	240		3·15	2·95
07	6·10	330	255		7·15	
08	6·40	360	255		5·30	
09	6·50	390	270		4·45	2·50
10	8·25	450	285		7·20	
11	8·95	450	300		5·60	
12	8·65	390	240		5·90	2·60
13	8·90	390	240		5·20	
14	9·05	390	240		4·65	
15	8·95	390	240		4·85	2•55
16	8·95	375	263		4·60	
17	9·25	390	240		4·05	
18	8·90	330	270		4·60	2·80
19	8·60	360	263		4·95	
20	8·30	323	240		4·30	
21	5·35	345	270			2·85
22	4·80	360	285			
23	4·65	360	300			

*Time: 90° East Meridian Time (U.T. + 6 hr.)

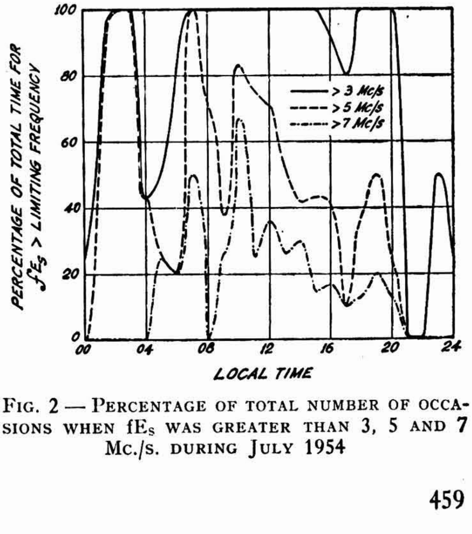


Fig. 2 — Percentage of total number of occasions when fE_s was greater than 3, 5 and 7 Mc./s. during July 1954

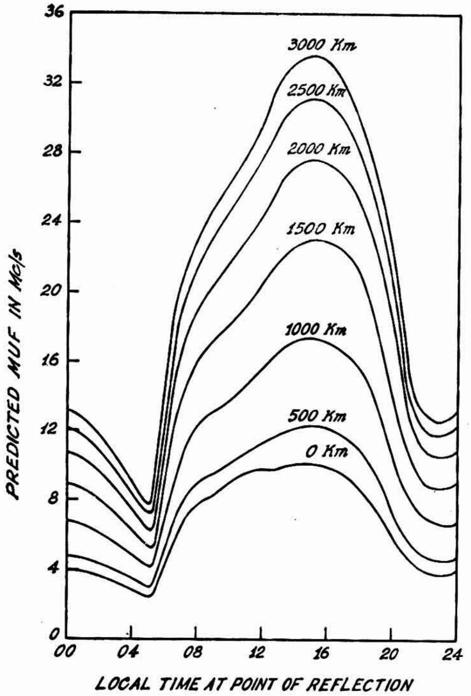


FIG. 3 — PREDICTED M.U.F. FOR TRANSMISSION TO DIFFERENT DISTANCES VIA F_2 REGION OVER CALCUTTA DURING OCTOBER 1954

July 1954. The normal E region characteristics could not be observed on most of the days due to the blanketing effect of the E_s ionization. The behaviour of the F_2 region was normal.

CHARACTERISTICS OF THE IONOSPHERE OVER AHMEDABAD

K. M. KOTADIA, R. G. RASTOGI & R. M. SHERIFF

Ionospheric Research Station, Physical Research Laboratory, Ahmedabad

FIG. 1 shows the diurnal variations of the monthly median critical frequencies of the ordinary waves reflected from E, F_1 and F_2; Fig. 2 shows the variations of the height of maximum electron density and of the minimum virtual heights of the different regions. Table 1 gives the monthly median values of the various parameters for E, E_s,

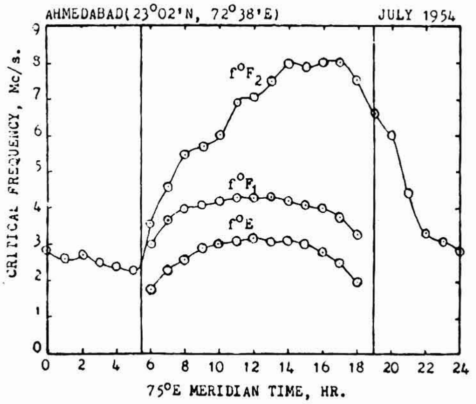


FIG. 1 — DIURNAL VARIATION OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

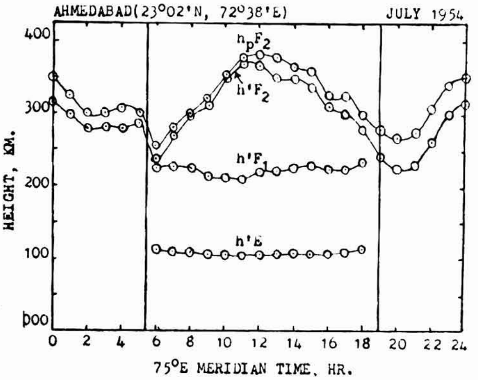


FIG. 2 — DIURNAL VARIATION OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

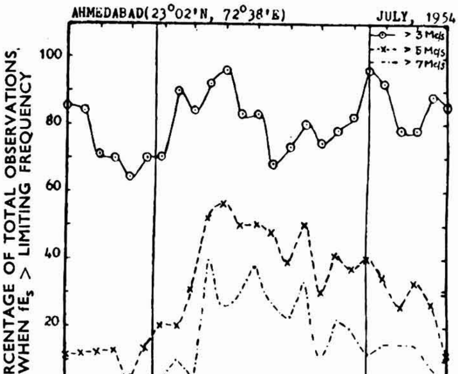


FIG. 3 — DIURNAL VARIATION OF OCCURRENCES OF SPORADIC E LAYER WHEN fE_s WAS HIGHER THAN 3, 5 AND 7 Mc./s.

TABLE 1 — IONOSPHERIC DATA, AHMEDABAD, JULY 1954

(Tabulated hours 75°E. Meridian Time)

TIME hr.	MEDIAN VALUES								NO. OF OCCURRENCES OF Es WITH			TOTAL NO. OF DAYS FOR WHICH Es DATA ARE AVAILABLE
	$f^\circ F_2$ Mc./s.	h_pF_2 km.	$h'F_2$ km.	$f^\circ F_1$ Mc./s.	$h'F_1$ km.	$f^\circ E$ Mc./s.	$h'E$ km.	fE_s Mc./s.	$fE_s >$ 3 Mc./s.	$fE_s >$ 5 Mc./s.	$fE_s >$ 7 Mc./s.	
00	2·8	350	317	—	—	—	—	3·8	22	3	1	26
01	2·6	325	300	—	—	—	—	3·6	21	3	—	25
02	2·7	300	280	—	—	—	—	3·9	17	3	1	24
03	2·5	303*	282	—	—	—	—	3·7	16	3	—	23
04	2·4	307*	280*	—	—	—	—	3·5	14	1	—	22
05	2·3	300	292	—	—	—	—	3·8	16	3	1	23
06	3·6	255	237	3·0*	225*	1·8*	112*	4·0	14	4	1	20
07	4·6	283	270*	3·7	227	2·3	110	4·0	18	4	2	20
08	5·5	300	297	4·0	225	2·6	110	4·8	16	6	1	19
09	5·7	320	312	4·1	215	2·9	107	6·0	23	13	10	25
10	6·0	356	350	4·2	212	3·0	106	6·6	22	13	6	23
11	6·9	377	370	4·3	210	3·1	105	6·3	20	12	7	24
12	7·1	380	367	4·3	220	3·2	107	6·1	20	12	9	24
13	7·5	377	350	4·3	220	3·1	106	6·9	17	12	7	25
14	8·0	365	350	4·2	225*	3·1	107	5·3	19	10	6	26
15	7·9	360	337	4·1	230	3·0	107	6·0	19	12	8	24
16	8·0	325	310	4·0	225	2·8	107	4·7	20	8	3	27
17	8·0	325	300	3·8	225	2·5	110	5·1	21	11	6	27
18	7·5	300	280	3·3	235	2·0*	115*	4·2	22	10	5	27
19	6·6	280	242	—	—	—	—	4·3	24	10	3	25
20	6·0	268	225	—	—	—	—	4·0	24	9	4	26
21	4·4	275	230	—	—	—	—	3·7	21	7	4	27
22	3·3	307	260	—	—	—	—	3·8	21	9	4	27
23	3·1	340	309	—	—	—	—	4·2	23	7	2	26

*Median based on observations less than ten.

F_1 and F_2 regions and the frequencies of occurrence of E_s during hourly observations when fE_s was higher than 3, 5 and 7 Mc./s. and the diurnal variation of the percentage occurrences of E_s is shown in Fig. 3.

The median critical frequencies of F_2 in July 1954 were higher during day and lower during night than in the previous month, and there were practically no changes in $f^\circ F_1$ and $f^\circ E$ from those in the previous month. All the critical frequencies in this month were lower than in July 1953, noon median $f^\circ F_2$, $f^\circ F_1$ and $f^\circ E$ being less by 0·9, 0·1 and 0·2 Mc./s. respectively.

Although the intensities of the sporadic E layer decreased slightly, the frequencies of its occurrence showed a slight increase over those in the previous month, but both of these were higher than in July 1953. Intense and long-duration blanketing type of E_s was observed on 1, 9, 17, 29 and 31 July 1954.

A Continuous Radio Wave Method of Studying Travelling Disturbances in the Ionosphere

B. RAMACHANDRA RAO & E. BHAGIRATHA RAO
Ionosphere Laboratories, Andhra University, Waltair

THE first wind measurements were carried out in early days by making visual observations of the drift of exceptionally bright noctilucent clouds seen at an altitude of about 80 km. In recent years radio techniques have come to play an important part in the study of winds in the ionosphere. Manning and his collaborators[1] developed a new meteoric echo method for studying winds in the upper atmosphere which is based on the measurement of Doppler frequency shift imparted by the ionospheric wind to CW reflections from meteoric ionization columns. Systematic wind measurements have been made by Mitra[2], Kroutkrammer[3], and others, using the spaced receiver technique which involves the use of three high gain pulse receivers placed at the corners of a right-angled triangle for receiving pulse transmissions from a nearby transmitter and reflected from the E region. Records of signal strength variation of the first-hop echo, as a function of time at each of the locations, showed marked time displacements which enabled the calculation of wind velocity and direction. The spaced transmitter method developed by Munro[4] employs three transmitters working on the same frequency and placed at the corners of a right-angled triangle. The first-hop echoes from the F region received at one of the locations are recorded simultaneously. It has been observed that a travelling disturbance produces a clearly defined pattern in the record due to change in the positions of the echoes from the F region and that these patterns have a definite time difference of occurrence at all the three spaced points. Measurement of these time differences enables the determination of horizontal velocity and direction of the travelling disturbance. Recently a CW method of studying horizontal movements of disturbances in the F_2 region of the ionosphere was reported by Somayajulu[5]. This method involves the identification of three equally spaced peaks in the record of signal strength of a distant continuous wave transmitter produced by a travelling wave passing over all the three points of single and double-hop reflections at the ionosphere. This method gives only the component of the velocity in the transmitter-receiver direction. It is difficult to find out the direction of movement from the nature of the peaks observed in such records. Another method of determining wind movements in the ionosphere by using CW transmissions from two distant transmitters was reported by us[6] recently and full details of this investigation are presented here.

Principle of the method

The principle involved in this new method can briefly be explained as follows. It is well known that simultaneous records of time variation of signal strengths of two distant short wave transmitters radiating on two different frequencies do not in general show any similarity. However, under certain conditions, when the transmitters are separated by a short distance, and the frequencies of the radiations are very nearly equal, prominent similarities having time displacements are seen occasionally in both the records. Such prominent variations in signal strength are explained as due to a travelling disturbance passing over any one of the points of reflection and enhancing the signal strength by focussing effect. If this travelling disturbance passes successively over both the points of reflection, two almost identical and prominent peaks will be noticed in both the records with a time displacement equal to the time taken for the disturbance to travel the distance between the two single-hop reflection points in the ionosphere, which is half the distance between the transmitters. Measurement of these time differences in a number of records enables us to calculate the component of the velocity of the travelling disturbance along the line joining the transmitters and also estimate the general direction of its movement by knowing the time sequence of occurrence of these peaks in both the records.

Experimental details

The equipment used for this investigation consists of two communication receivers, two mirror galvanometers, a recorder and a driving mechanism. Communication receivers Hallicrafters model S 40A and Eddystone model 504 were used for this purpose. Two mirror galvanometers which are suitably supported on a rigid base attached to a wall were connected in series with the S-meters of each of the receivers. The galvanometers were suitably damped to eliminate fast period fading as the expected similarities are of long duration type. Light from two galvanometer lamps, mounted rigidly on the wall and vertically above the galvanometer, was allowed to fall on the galvanometer mirrors by using two right-angled prisms and focussed on the drum of a recording camera after reflection. The recording camera consists of a light-proof box in which a drum of length 4·5 in. and circumference 14 in. was supported horizontally on two ball bearings and rotates in a vertical plane. On one side of the recorder there is a window with a fine horizontal slot of 7 in. length for permitting the light beams from both the galvanometers to be focussed on the drum. The shaft of the drum was connected to a clock-work mechanism for rotating it at the rate of one revolution per hour.

Results

CW transmissions from All India Radio at Calcutta and Radio Pakistan Dacca station radiating on 7·210 Mc. and 7·150 Mc. respectively were chosen for this investigation as these stations are separated by a distance of only 240 km. and their frequencies of transmission are very close to each other. Incidentally, it was noticed that Dacca and Calcutta stations are very nearly in a line with Waltair. Using the continuous wave recording equipment described above, simultaneous records of the signal strength variations of these transmissions, received at Waltair, were obtained during the afternoon and evening hours. Hourly records were taken daily from 12.00 to 13.00 hr. I.S.T. and from 17.00 to 18.00 hr. I.S.T. during the months of May-June 1953. In the afternoon, however, the Calcutta station record was taken for 45 min. as the transmission from Calcutta starts from 12.15 hr. I.S.T. From the critical frequency data published by All India Radio Research Department, it was inferred that the propagation takes place via the E or E_s region in the afternoon and via the F region in the evening hours of the observations. It was found that out of about fifty records taken on these stations, more than half have shown reasonably prominent peaks in the Dacca record which reappeared in almost identical form in the Calcutta record after a time interval of 8-13 min. Very often in the same record, an appreciably larger number of similar peaks are observed. Only very few of the afternoon records showed significant evidence of travelling disturbances, whereas most of the evening records showed large number of similar peaks. A complete analysis has been made of all the records and the results obtained for the components of the velocities of travelling disturbances are presented separately for the afternoon and evening records. In Table 1 are presented the time displacements of similarities in the records and velocity components of travelling disturbances calculated on the assumption that transmission takes place by way of single-hop reflection at the ionosphere. A typical record obtained on 13 June 1953 is reproduced in Fig. 1 to illustrate the types of peaks which are identified as due to a travelling disturbance. It can be easily seen from this record that all the peaks a, b and c and the curvatures between them in the Dacca record are reproduced almost identically but with a slight difference in amplitude in the Calcutta record, after a constant time interval of 8·5 min., giving a value of 14 km./min. for the velocity component of

TABLE 1 — CALCUTTA-DACCA 41 METRE BAND

(*Distance*, 240 *km.*; *time*, 12.00-13.00 *hr.*)

SL. No.	DATE	TIME INTERVAL min.	VELOCITY COMPONENT km./min.
1	21-5-53	12·50	9·6
2	26-5-53	8·00	15·0
3	2-6-53	8·25	14·8
4	11-6-53	13·00	9·2
5	13-6-53	8·50	14·0
6	14-6-53	6·00	20·0
7	16-6-53	13·00	9·2

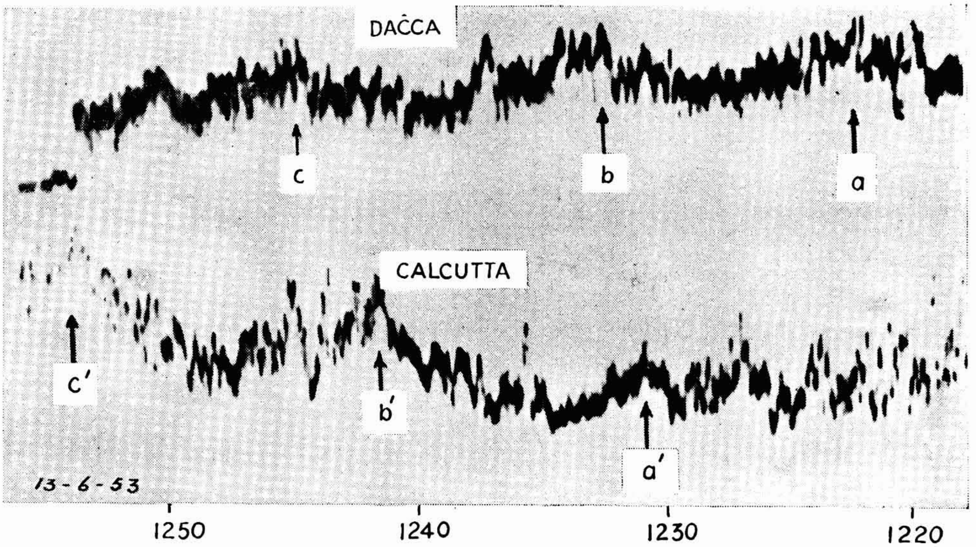


FIG. 1 — SIGNAL STRENGTH RECORD OF CALCUTTA AND DACCA STATIONS SHOWING THE EFFECT OF A TRAVELLING DISTURBANCE MOVING IN A SOUTHERLY DIRECTION

the travelling disturbance. Except for one or two cases, where the velocities are found to be high, the values for the velocity components for the most of the records are found to be in the range of 9-15 km./min. As the similarities occur earlier in the Dacca records, it may be inferred from Fig. 1 that the general trend of movement is from Dacca to Calcutta. Almost all the records have shown that this is the general direction of movement, as the similarities occur always earlier in the Dacca records.

Table 2 gives the values for the time displacements of the similarities noticed in the evening records along with the velocity components. When two or more sets of similarities, having different time displacements, are seen on the same record, they are noted separately in the table as due to travelling disturbance A and B and the velocity component for each is presented separately. As the main contribution for the signal strength at the receiver is due to first-hop reflection, the second hop being weak, all the prominent similarities are attributed to the effect produced by travelling disturbance on the first-hop reflection points. The velocity components obtained from these records range from 7 to 20 km./min. The direction of the travelling disturbances in all these records except the one taken on the 24 May 1953 are from Dacca to Calcutta which is the same as that for the afternoon records. To show the case of reversal of movement, this record is reproduced in Fig. 2. The peaks a, b, c and the curvature between them in the Calcutta record reappear almost similarly as a', b' and c' in the Dacca record after a time delay of 13 min. The velocity component along Calcutta-Dacca line for this case comes out as 9·2 km./min.

TABLE 2 — CALCUTTA-DACCA 41 METRE BAND

(*Distance*, 240 *km.*; *time*, 17.00-18.00 *hr.*)

SL. No.	DATE	TYPE OF SIMILARITIES	TIME INTERVAL min.	VELOCITY COMPONENT km./min.
1	20-5-53	A	5·75	20·8
2	21-5-53	—	12·90	9·2
3	22-5-53	—	7·00	17·1
4	23-5-53	A	9·75	12·3
		B	8·00	15·0
5	24-5-53	—	13·00	9·2
6	25-5-53	—	9·50	12·6
7	26-5-53	—	12·00	10·0
8	29-5-53	A	9·50	12·6
		B	9·25	12·9
9	30-5-53	A	7·50	16·0
10	31-5-53	—	11·50	10·4
11	1-6-53	—	11·20	10·7
12	2-6-53	—	10·00	12·0
13	4-6-53	A	5·75	20·8
		B	8·50	14·0
14	5-6-53	—	13·50	8·9
15	13-6-53	A	6·00	20·0
		B	6·50	18·4
16	15-6-53	—	17·00	7·1
17	18-6-53	—	16·00	7·5
18	19-6-53	—	11·00	11·0
19	24-6-53	—	13·00	9·2

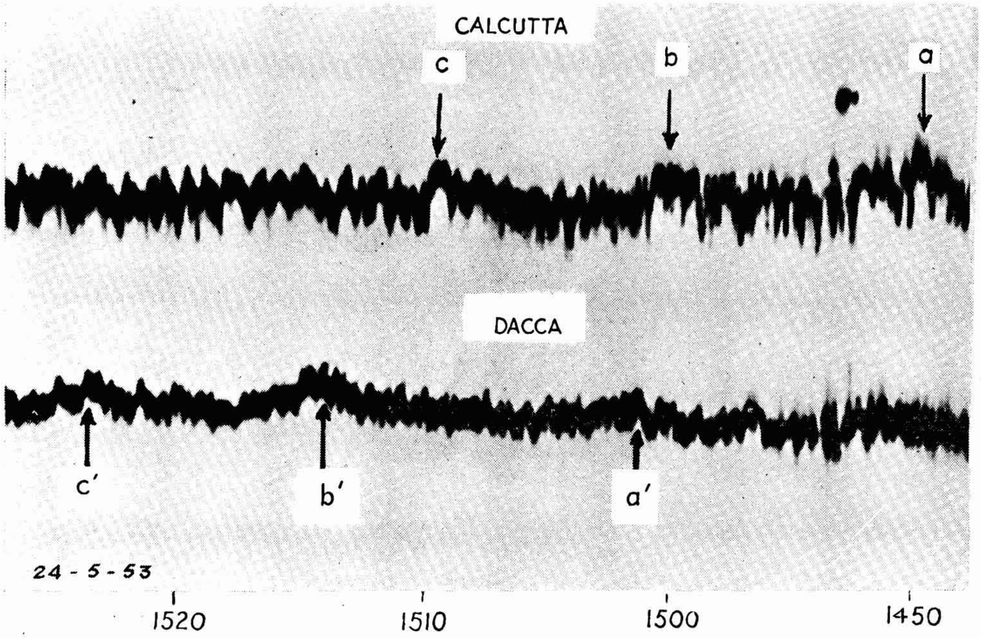


FIG. 2 — SIGNAL STRENGTH RECORDS OF CALCUTTA AND DACCA STATIONS SHOWING THE EFFECT OF TRAVELLING DISTURBANCES MOVING IN A NORTHERLY DIRECTION

Discussion

The method employed here is based on the assumption that there are travelling disturbances in the ionosphere of large dimension which can travel over long distances without any change of form. In the Dacca-Calcutta transmission paths employed in the present investigation, the travelling disturbance has to cover only a distance of 120 km. between the first-hop reflection points. In his extensive investigations on travelling disturbances in the F_2 region, Munro has shown that disturbances which travel over such distances are not uncommon.

Simultaneous records taken on A.I.R. stations of Madras and Mysore on the 49 metre band and Ceylon, Madras on the 49 metre band did not reveal the presence of these travelling disturbances, which may probably be attributed to the fact that these stations are separated by a large distance and are not in a line with the receiving station. It is known that disturbances travelling over such large distances are quite uncommon from the work of Munro.

From the available data of the critical frequencies, it may be said definitely that the afternoon transmissions from Calcutta and Dacca are received via the E layer or the sporadic E. There is no possibility of the existence of disturbances in the E layer which can travel over such large distances without any change of form. As such, the few observed evidences in the afternoon records must be attributed to the sporadic E clouds which are known to travel over large distances without appreciable change. This will also explain the reason why such occurrences are very few in the afternoon records and very large in number in the evening records when the reception is due to the reflections at the F_2 layer.

The velocities obtained in this investigation are actually velocity components along the line joining Dacca and Calcutta, which is 45° east of north. There is good agreement between the observed range of velocity components of 9-20 km./min. for the F region with the values of 5-10 km./min. observed by Munro, considering the fact that the component velocities will always be higher than the actual velocities. The two station method presented here is, therefore, inadequate and will not furnish the full information as to the actual value of velocity and direction of movement of the disturbance.

Very high values of velocities obtained in some records may be due to oblique direction of travel of the winds. But such high values are not common, most probably because the wind movement is predominantly in the Dacca-Calcutta direction. This may also be due to the fact that the travelling waves producing the similarities in the records may not be having a large lateral extent to pass over both the points of reflection when travelling in an oblique direction.

All the records have shown that the general direction of movement of the travelling disturbance is always from Dacca to Calcutta, with the single exception of only one record reproduced in Fig. 2, which showed reversal of direction. If we take into account the fact that wind movements in the northern and southern hemispheres are in opposite directions, the predominantly southerly wind direction observed in the investigation is in good agreement with the general northerly wind direction observed by Munro for the months of May-June. Observations made by Somayajulu for the months of June-November also indicated general southerly movement of winds.

In this investigation, though we have identified the prominent similarities in the records as due to travelling disturbances in the ionosphere, no attempt has been made to obtain information on the nature and shape of the disturbances. In fact, it is rather difficult to draw any conclusion on this aspect, using the meagre data on the shape of the similarities in the records. Recently Munro[7] has obtained some useful information on the shape of a travelling wave from a study of Z and X shape patterns of the h′-t records.

Simultaneous study of transmissions from three distant transmitters is being taken up with a view to extend the usefulness of this method to yield full information on the actual wind velocities and directions.

References

1. MANNING, L. A., *Proc. Inst. Radio Engrs.*, **38** (1950), 887.
2. MITRA, S. N., *Proc. Inst. elec. Engrs.*, **96**(III) (1949), 441.
3. KROUTKRAMMER, *Arch. Elekrt, Vebertrag,* **4** (1950), 133.
4. MUNRO, G. H., *Nature*, **162** (1948), 866.
5. SOMAYAJULU, Y. V., *Nature*, **172** (1953), 818.
6. RAMACHANDRA RAO, B. & BHAGIRATHA RAO, E., *Nature*, **172** (1953), 819.
7. MUNRO, G. H., *Proc. roy. Soc.*, **219** (1953), 447.

Studies in the Properties of Mortars Obtained from Ancient Buildings in India: Part I—Chemical Composition

H. L. UPPAL & RAGHBIR SINGH

Irrigation & Power Research Institute, Punjab, Amritsar

QUITE a large number of hydraulic structures, historical buildings, bridges and causeways on highways and railroads have been constructed in India in the past. These works have stood the test of time, and even after the lapse of several centuries are still sound and intact. Indigenous materials of construction such as hydraulic lime and *surkhi*, *kankar* lime, sand and *surkhi* and allied materials have been used in these structures as portland cement was introduced in India only in 1923. Even after the manufacture of portland cement in the country, many works were carried out with indigenous building materials. When there is an acute shortage of portland cement, the attention of the Government and private agencies is drawn to the necessity of exploring indigenous resources of building materials and putting them to use on a scientific basis so that they may be employed in place of portland cement wherever possible. It is not necessary to use portland cement in all types of constructions. Excepting large hydraulic works such as high dams and weirs, indigenous material could serve the same object equally well as portland cement. Krishnaraja Sagar and Hire Bhaskar dams in Mysore, and Lloyd, Bhaudarbara and Mals dams in Bombay have been constructed with hydraulic lime and *surkhi* and have withstood the test of time very well indeed. It is well known that when *kankar* lime-*surkhi* mortar along with certain ingredients such as gypsum is ground to the same fineness as cement, it produces a mortar as strong with age as that with portland cement.

It is essential, however, that standard specifications should be laid down for the indigenous building materials based on their chemical composition, the proportion of ingredients necessary to give a strong mortar, etc. The use of indigenous material for construction purposes has to be put on a scientific basis, and their manufacture undertaken on a large scale, each process in the manufacture being scientifically controlled, so that the use of these materials is both efficient and economical.

It is, therefore, of interest to collect data regarding the composition of the material used in ancient structures. A knowledge of the composition of the mortars employed in such structures and their properties is invaluable in preparing standard specifications for these materials. With this object in view, mortars from buildings of ages varying from one to five hundred years were collected from different parts of India and analysed for their chemical composition, viz. percentage of calcium oxide, silicon dioxide, magnesium oxide, alumina and iron oxide. The results show the process of evolution of *kankar* lime and hydraulic lime mortars during this period.

Several aspects of the problem have been investigated. This part deals with the evolution of chemical composition of the mortars employed during the past few centuries.

Source of mortar samples

The rest-houses for pilgrims known as "Bungas" — annexes of the Golden Temple, Amritsar — are fairly old buildings with reliable records of dates of erection* (TABLE 1).

TABLE 1 — SOURCE AND AGE OF MORTAR SAMPLES

LAB. REG. No.	SOURCE	AGE years
1192	Bunga Ghannhiya Sardaran	209
1132	Bunga Jassa Singh Ramgarhia	198
1139	Bunga Anup Singh Mazhbi	179
1133	Bunga Qabuliyewalan	179
1134	Bunga Mazhbi Sikhan	176
1140	Bunga Ram Singh Gyani	175
1136	Bunga Sardaran Solahwale	167
1191	Bunga Sardaran Barkiwala	163
1131	Bunga Sodhi Anandpurian	160
1193	Bunga Gadduwalian	160
1143	Bunga Singhpurian	150
1144	Bunga Sardaran Jahlawalian	142
1145	Bunga Sardaran Majithian	140
1137	Fourth Storey of Baba Atal Sahib	132
1198	Bagh Cave (Madhya Bharat)	1500
1199	Mandhu Fort (Madhya Bharat)	500

Age computed as in the year A.D. 1954.

Mortars mixes of *kankar* lime and other materials of the same type were used in them. Mortar samples from these "Bungas", and two other samples, 500 and 1,500 years old, from Madhya Bharat were also collected and analysed.

Chemical composition

The chemical analyses of the mortar samples for calcium oxide, silicon dioxide, total alumina and ferric oxide and magnesium oxide, and loss in weight on ignition were determined in the usual way and the results are recorded in Table 2.

For comparison, seven samples of good *kankar* lime now in use and which possess good tensile strength were similarly analysed. The tensile strength attained by such samples of *kankar* lime after proper calcination and curing under wet sand for 10 days, 28 days, 3 months and 6 months was also determined. The results are given in Table 3.

For arriving at the probable composition of the original dry *kankar* lime or allied cementing materials used in these mortars, the percentage of various oxides was computed on the assumption that ignition loss, which is mainly due to water of hydration taken up by silicates and aluminates of calcium and magnesium and to atmospheric carbon dioxide absorbed through aeration, was nil. Another assumption made is that the ignition loss in the original dry mortar is 5 per cent. This assumption permits an approximate comparison of the old *kankar* limes with good *kankar* limes in use now, since 5 per cent ignition loss is the specified limit in good *kankar* limes, and it is not wholly invalid to assume, for

---

*Giani Gyan Singh, *Agaz Shahr-i-Amritsar*.

TABLE 2 — CHEMICAL COMPOSITION OF MORTARS

LAB. REG. No.	AGE years	LOSS ON IGNITION %	SiO_2 %	R_2O_3 %	CaO %	MgO %
1192	209	38·04	25·56	9·60	24·54	2·14
1132	198	30·84	27·24	7·80	31·42	0·93
1139	179	27·60	27·08	7·98	31·92	3·79
1133	179	24·00	31·28	10·10	31·57	2·26
1134	176	34·24	25·24	9·24	28·66	2·12
1140	175	34·08	27·44	10·36	24·74	2·93
1135	167	32·88	27·88	8·68	27·05	2·59
1191	163	27·24	33·16	10·68	27·07	1·65
1136	160	12·90	48·38	17·42	16·56	2·45
1193	160	28·52	37·76	11·30	16·97	2·68
1143	150	33·26	33·08	8·72	21·41	3·24
1144	142	29·78	30·28	10·00	24·64	4·11
1145	140	32·88	32·56	9·22	21·92	3·17
1137	132	23·44	37·00	11·94	24·86	2·43

TABLE 3 — ANALYSIS OF GOOD *KANKAR* LIME SAMPLES

LAB. REG. No.	LOSS ON IGNITION %	SiO_2 %	R_2O_3 %	CaO %	MgO %	TENSILE STRENGTH, lb./sq. in.			
						10 days	28 days	3 months	6 months
8	21·72	38·04	11·14	23·95	4·92	157	274	320	370
197	20·04	42·24	13·98	22·13	0·83	117	254	347	457
200	21·64	38·70	12·00	24·94	1·66	124	291	354	438
214	24·88	34·56	10·64	23·40	6·29	149	278	344	459
204	20·52	40·66	13·94	19·70	5·14	161	292	361	469
198	17·40	42·84	10·88	24·70	3·66	123	293	362	552
213	23·60	33·32	13·28	22·69	6·66	204	315	373	485

TABLE 4 — CHEMICAL COMPOSITION OF SET MORTAR SAMPLES

LAB. REG. No.	5% IGNITION LOSS BASIS				NO IGNITION LOSS BASIS			
	SiO_2 %	R_2O_3 %	CaO %	MgO %	SiO_2 %	R_2O_3 %	CaO %	MgO %
1192	39·26	11·68	40·77	3·29	41·33	12·29	42·92	3·46
1132	38·40	10·99	44·30	1·31	40·42	11·57	46·63	1·38
1139	36·31	10·72	42·88	5·09	38·25	11·28	45·10	5·37
1133	39·51	12·76	38·79	3·94	41·59	13·43	40·83	4·15
1134	36·75	13·45	41·71	3·09	38·68	14·16	43·91	3·25
1140	39·80	15·01	35·94	4·25	41·89	15·80	37·84	4·47
1135	40·00	12·46	38·82	3·72	42·11	13·11	40·87	3·91
1191	43·28	13·98	35·56	2·16	45·56	14·72	37·45	2·27
1136	54·20	19·51	18·54	2·75	57·05	20·54	19·52	2·89
1193	52·20	15·53	23·45	3·71	54·96	16·45	24·69	3·90
1143	47·28	12·46	30·62	4·64	49·78	13·12	32·22	4·88
1144	41·67	13·77	33·90	5·66	43·86	14·49	35·69	5·96
1145	46·26	13·10	31·15	4·49	48·69	13·79	32·79	4·73
1137	46·11	14·88	30·98	3·03	48·54	15·66	32·61	3·19

TABLE 5 — CHEMICAL COMPOSITION OF GOOD *KANKAR* SAMPLES

LAB. REG. No.	5% IGNITION LOSS BASIS				NO IGNITION LOSS BASIS			
	SiO_2 %	R_2O_3 %	CaO %	MgO %	SiO_2 %	R_2O_3 %	CaO %	MgO %
8	46·30	13·56	29·16	5·98	48·73	14·27	30·68	6·30
197	50·68	16·77	26·55	1·00	53·35	17·65	27·95	1·05
200	47·56	14·74	30·65	2·05	50·06	15·52	32·26	2·16
214	43·84	13·50	30·69	7·97	46·15	14·21	31·25	8·39
204	48·62	16·67	23·56	6·15	51·18	17·55	24·80	6·47
198	49·58	12·59	28·59	4·24	52·19	13·25	30·09	4·47
213	41·68	16·61	28·38	8·33	43·87	17·49	29·87	8·77

purposes of comparison, that any ignition loss in excess of 5 per cent in the analysis of set mortars may be due either to water of aeration or to atmospheric carbon dioxide absorbed through aeration. The computed values are given in Table 4.

Similar data were computed for seven good *kankar* lime samples. The values are given in Table 5.

Computations of age as in the year A.D. 1954 were made and, on the basis of respective ages, the fourteen "Bungas" and Baba Atal Sahib were placed in eight age groups with an interval of ten years between each sample (TABLE 6). The averages of percentages of calcium oxide, silicon dioxide and total alumina and ferric oxide on no ignition loss basis for each of

TABLE 6 — AVERAGE CHEMICAL CHARACTERISTICS OF SET MORTAR SAMPLES

PERIOD	APPROXIMATE AGE years	NO. OF SAMPLES EXAMINED	CHEMICAL COMPOSITION, NO IGNITION LOSS BASIS			LIME/SILICA RATIO	HYDRAULIC MODULUS
			CaO %	SiO_2 %	R_2O_3 %		
High lime period	210	1	42·92	41·33	12·29	1·112	0·968
	200	1	46·63	42·42	11·57	1·234	1·080
	180	3	43·28	39·51	12·96	1·173	1·008
Falling lime period	170	3	38·72	43·19	14·54	0·932	0·798
Low lime period	160	2	22·10	56·00	18·50	0·423	0·363
Moderate lime period	150	1	32·22	49·78	13·12	0·693	0·612
	140	2	32·24	46·28	14·14	0·793	0·687
	130	1	32·61	48·54	15·66	0·719	0·619

these age groups were determined, and on the basis of these averages, lime-silica ratio and hydraulic modulus as the average chemical characteristics of the mortars were determined. The results are given in Table 6.

In calculating the hydraulic moduli of *kankar* lime samples, a further assumption was made, i.e. the average molecular weight of total alumina and ferric oxide was 120. This assumption was calculated to reduce the error in the final results to the minimum, since the usual percentages of these two constituents in mortars approximate to this value. Graphs (FIGS. 1 and 2) for calcium oxide, silicon dioxide, alumina and ferric oxide contents and for hydraulic moduli and lime-silica ratios of these mortars were plotted on this basis.

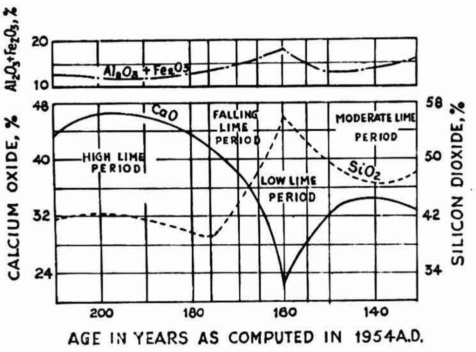


FIG. 1 — STAGES IN THE EVOLUTION OF GOOD *kankar* LIME AND ALLIED MATERIALS

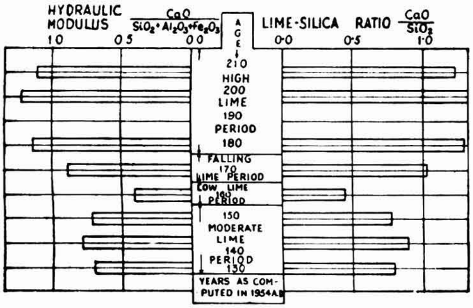


FIG. 2 — CHEMICAL CHARACTERISTICS OF *kankar* LIME AND ALLIED MATERIALS AT DIFFERENT STAGES IN THEIR EVOLUTION

As it was impossible to carry out proper strength tests, visual and sensory examination of the samples was the only means for judging the relative strengths of the mortars. Mortars which could be detected as distinctly argillaceous or calcareous showed poor strength on being subjected to mild pressure between fingers. The results tally fairly well with the results of chemical analysis.

Two mortar samples from Madhya Bharat were also analysed to see if they could provide a background to the evolutionary process in the case of *kankar* lime. The results of chemical analyses are recorded in Table 7.

The limiting values worked out for various constituents in set mortars and good *kankar* lime are recorded in Table 8.

It may be observed from Table 8 that the average oxide composition is the same for set mortars and good *kankar* lime. The extreme limits for percentage oxide composition in good *kankar* fall well within the range of that for set mortars. This shows that our criteria for good *kankar* limes based on oxide composition are supported by the durability of the structures built in olden times employing these mortars.

Another interesting conclusion which emerges from these studies is the gradual betterment of the mortars used over a period of 80 years, i.e. the period elapsing between

TABLE 7 — CHEMICAL COMPOSITION OF MORTARS FROM MADHYA BHARAT

OXIDE COMPOSITION %	LAB. REG. NO. 1198 (1500 YEARS OLD)			LAB. REG. NO. 1199 (500 YEARS OLD)		
	Actual analysis	5% ignition loss basis	No ignition loss basis	Actual analysis	5% ignition loss basis	No ignition loss basis
Loss on ignition	3·12	5·00	0·00	23·20	5·00	0·00
SiO_2	80·08	78·86	83·01	27·48	34·30	36·11
R_2O_3	11·88	11·70	12·32	18·12	22·62	23·81
CaO	3·82	3·76	3·96	27·17	33·92	35·70
MgO	0·69	0·68	0·71	3·33	4·16	4·38
Total	99·59	100·00	100·00	99·30	100·00	100·00

TABLE 8 — LIMITING VALUES FOR DIFFERENT CONSTITUENTS IN *KANKAR* LIME AND MORTAR SAMPLES

OXIDE COMPOSITION (NO IGNITION LOSS BASIS) %	SET MORTAR	GOOD *kankar* LIME	AVERAGE SET MORTAR	AVERAGE GOOD *kankar* LIME
SiO_2	38-57	44-53	48	49
R_2O_3	11-21	13-18	16	16
CaO	20-47	25-32	34	29
MgO	1-6	1-9	4	5

the use of mortar Nos. 1192 and 1137. The evolution of good *kankar* lime seems to have proceeded on a process of selection, poor samples being discarded after empirical trials.

Of greater interest is the gradual improvement observed in the mortars used during this period, as reflected by their oxide composition.

Figs. 1 and 2 illustrate clearly the four distinct periods in the evolution of mortars. Prior to A.D. 1780, the general belief seems to have been that high lime contributed to good strength of mortars. In this period, calcium oxide content, hydraulic modulus and lime-silica ratio are high in the mortars, whereas silicon dioxide and total aluminium oxide and ferric oxide contents are markedly low. The 500-year old sample from Madhya Bharat shows the same trend with respect to calcium oxide and silicon dioxide content and hydraulic modulus and lime-silica ratio. After A.D. 1780, the realization seems to have dawned that high lime in mortars resulted in poor strength and we see the beginning of a period (A.D. 1780-90) in which calcium oxide, hydraulic modulus and lime-silica ratio of the mortar show a fall while there is an appreciable rise in silicon dioxide and total aluminium oxide and ferric oxide content. The fall is sharp in the next ten years, probably as a reaction to the earlier high lime period, and the calcium oxide content, hydraulic modulus and lime-silica ratio of mortars touch an all-time low; the silicon dioxide and total aluminium oxide and ferric oxide contents are too high to confer good strength to the mortars.

The fourth is the moderate lime period (A.D. 1800 onwards). The vagaries of the three earlier periods are remarkably absent and the chemical composition of mortars shows a constancy within the limits of good *kankar* lime. The chemical characteristics of hydraulic modulus and lime-silica ratio of mortars do not show an unsatisfactory trend. The composition of *kankar* limes of this period is such as is likely to give good strength.

Tests carried out on a 1,500-year old sample of set mortar from Bagh Cave in Madhya Bharat showed that the mortar disintegrated under slight pressure and has very little strength due to the excessive use of argillaceous matter in the form of burnt clay of terra-cotta colour and small quantity of lime. This was probably the initial period in the evolution of mortars when it was not known that *surkhi* with lime develops cementing properties due to pozzolanic action.

Studies on Natural Fats: Part XI — The Restricted Random Distribution Rule & Glyceride Structure of the More Saturated Natural Fats

A. R. S. KARTHA
Maharaja's College, Ernakulam*

THE calculation of glyceride structure of natural fats from component acid composition[1] was based on the even distribution rule of Hilditch[2] which has been defined as follows: " (1) When a given fatty acid A forms about 35 per cent of the total acids (A + X) in a fat, it will occur at least once (GAX_2) in practically all the triglycerides. (2) If it forms about 35-65 per cent, it will occur twice (GA_2X) in any given triglyceride molecule in some instances, and of course more frequently the higher the proportion of this acid. (3) If it forms 70 per cent or more, the remaining fatty acids (X) can at most only form mixed glycerides (GA_2X), and the excess of A then, and broadly speaking then only, appears as a simple triglyceride GA_3. (4) A minor component acid which forms much less than about a third of the total fatty acids (15 per cent or less) will not occur more than once in any triglyceride molecule, and of course not at all in many of the triglyceride molecules."

The basis of these computations was purely empirical and had no bearing on the manner in which the glycerides are assembled by natural processes in the fat depots. The details of the methods of calculation[1] which gave results most comparable with the glyceride composition determined by fractional crystallization were: " (a) Arithmetical calculations could be applied only to fats which contained not more than 3, or in some special cases 4 major component acids, and could not be used to calculate the glyceride structure of nut oils, milk fats, marine animal oils, etc., which contain more than 3 major component acids. (b) The method of computation which found most frequent application was the following: The oleic acid (or sometimes other major component unsaturated acid) was divided among the rest of the mixed acids in proportion to the amounts of the latter, and then combined arithmetically with each according to maximum heterogeneity principle (e.g. to give oleo-dipalmitin and palmito-diolein, etc.), and any mono-oleoglycerides were then recombined on maximum heterogeneity principle. (c) When oleic acid greatly predominated over the other acids (none of which exceeds in amount 10 per cent of the total fatty acids), the calculation in (b) simplified into taking each minor component combined with two oleic acid groups (e.g. palmito dioleins, etc.). (d) In a few instances in which a major component saturated acid was accompanied by small proportions (less than 5 per cent of the total acids) of homologous saturated acids, it was found best first to allow for these minor components as mixed glycerides with an acid group of each of two major component acids and subsequently to partition the balance of oleic acid among the remaining acids (e.g. cottonseed oil, virola and kombo fats). This method of calculation leads to different proportions of the different glyceride types in fats of the same saturated acid and GS_3 contents, depending on the proportions of different saturated acids. (e) In a number of cases where the above methods did not succeed in reproducing the observed results, e.g. the palm oils, shea butter, Hodgonia fat, etc., it was found that the observed proportions of GS_3 and/or GU_3 are about the same as or half that expected on the

---

*Present address: Indian Agricultural Research Institute, New Delhi.

principle of random distribution. When GS_3 and GU_3 are about the same as that expected according to chance distribution the fat will evidently be obeying complete random distribution. (f) In higher land animal depot fats, arithmetical partitioning of oleic acid did not reproduce the observed proportions of mixed glycerides in any case. Here the approximate proportions of GS_3 are ascertained graphically from the saturated acid content and after allowing for the acids in the GS_3 on an approximate basis of 60 per cent palmitic and 40 per cent stearic, oleic acid is partitioned between the remaining saturated acids."

No method of calculation is available for deducing the proportions of the different glyceride types directly from the component acids and any other data. When the S and U are taken as types (G, S, U, and A stand for the glyceryl, saturated acid, unsaturated and azelaic acid radicals respectively in this paper), the calculations tend to maximum heterogeneity and the results obtained are quite different from those found experimentally for vegetable fats with S contents between about 20 and 50 per cent. Since it is generally considered that the main difference between the different fatty acids is whether they are saturated or unsaturated, this is a serious drawback for the even distribution rule and the suggested methods of computation.

Hilditch has observed[3] " that it is somewhat illogical to postulate profound constitutive differences in different groups of natural fats, the elaboration of which is presumably due to the same or broadly similar conditions of enzyme systems, temperature and so on ". When our knowledge of glyceride structure of natural fats becomes more precise, it may be possible to simplify these methods of computation so that a single set of formulae will give the detailed glyceride structure of any natural fat irrespective of biologic source or number and nature of component acids, and that the method of calculation would not be purely empirical as in the computations outlined above.

The experimental data on which the even distribution rule is based are the following: (a) The glyceride composition determined by fractional crystallization of vegetable fats of the palmitic-stearic-oleic-linoleic type fatty acid composition having S content less than about 60 per cent[4]. Determination of the glyceride type composition of these fats by methods not involving crystallization have, however, given widely varying results in many cases[5]; (b) determination of the GS_3 contents of a number of vegetable fats containing more than 85 per cent saturated acid content by the method of Hilditch and Lea[6]. This method has since been shown to be not accurate[7]. Further, the GS_3 contents of this type of fat as required by even or chance distribution is approximately the same so that this cannot be a positive support for the even distribution rule. There are very few vegetable fats with saturated acid content between about 60 and 85 per cent mols; and (c) the glyceride composition of a few marine oils containing less than about 30 per cent saturated acids, determined by crystallization[8], also appeared to support the rule.

On the other hand, several classes of natural fats appeared to contain GS_3 approximately as required by chance distribution even when the S content was less than about 85 per cent mols. The ruminant milk fats usually contain GS_3 as required by chance[9], and depot fats of higher land animals contain GS_3 to nearly the same extent[9]. Certain marine animal oils containing large proportions of myristic and lower saturated acids also show GS_3 content approximately as required by chance[10]. Considering these facts, it looks more probable that the vegetable fats containing more than 85 per cent saturated acids also tend to contain GS_3 as required by chance distribution than by even distribution.

It has been shown elsewhere[11] that the processes by which fatty acids are assembled into triglycerides in the natural fat depots do not support the even distribution rule. The evidence summed up is as follows: " The esterification of the fatty acids into triglycerides is effected by the lipases. Evidence has been reported in the literature that plant or animal lipases do not show any specificity towards α or β-hydroxyl of the glycerol. Plant lipases, e.g. ricinus lipase, do not show any specificity towards any fatty acid except that they do not react with acids of less than seven carbon atoms in the chain. Adipose tissue lipase shows the same characteristics as pancreas lipase, and shows increased rates of action as chain length of acids decreases in the saturated series; in the case of unsaturated acids of same chain length, reactivity increases as number of double bonds present increases. The action of lipases, either plant or animal, is reversible and when the fats are in reversible equilibrium with reactants as well as products of reaction for appreciable lengths of time, conditions of a dynamic equilibrium will prevail and all effects of specificities in rates of action with different fatty acids will ultimately be nullified. In plant depots, e.g. seeds, it has been shown that fatty acids are being continuously synthesized and esterified simultaneously during the whole period of maturing of the seeds. Animal fat depots always show the presence of active lipase. Thus, dynamic equilibrium prevails during the formation of both animal and plant fats. In the presence of dynamic equilibrium only simple chance or random distribution can prevail excepting in the presence of some type of super-imposed restraint on the unspecific activity of lipase." This restraint must be of the nature of inability of lipase to synthesize, and since the action of lipase is reversible, and also to hydrolyse particular glycerides or classes of glycerides. Alteration in random distribution will then be the effect of this restriction, and the alteration effected will have the nature of a limited, or in other words, of a directed random distribution, and the nature and extent of alteration effected will depend entirely on the nature and extent of restriction imposed on simple random distribution due to the above restraint and on no other factor.

Experimental evidence has been reported in the literature[11] which shows that lipase reacts freely with all triglycerides which are liquid, but does not react with any triglycerides in the solid state, e.g. tristearin at room temperature. Since the action of lipase is reversible, it is reasonable to assume that lipase cannot synthesize glycerides in the solid phase as well. This assumption receives strong support from the study of the GS_3 contents of natural fats in relation to their component acid composition and melting points[12]. Laboratory esterification of fatty acids and glycerol cannot be brought to any state of completion as happens in fat depots and hence it is not possible to adduce experimental proof to this point in the laboratory. So far this is the only limitation to the entirely unspecific action of lipase in esterification of fatty acids to triglycerides under conditions prevailing in the natural fat depots during fat formation. If this assumption is correct then the fatty acids in natural fats are likely to be distributed according to simple chance distribution when conditions favour this, or according to restricted or directed random distribution consequent on inability of lipases to synthesize or react with solid phase glycerides when simple chance distribution tends to result in the formation of high melting and sparingly soluble glycerides above certain minimal values for particular fats. In the usual types of natural fats only the GS_3 derived from the higher saturated acids are sufficiently high melting and sparingly soluble to be present in the solid phase under conditions prevailing in fat depots, and this would lead to the following salient features regarding their glyceride type composition: (a) Fats with less than about 25 per cent saturated acid content, where GS_3 required according to chance is less than some 2 per cent and is hence small should contain all other glyceride types in proportions as required by chance; (b) fats where GS_3 required according to chance is higher than that actually present should show GS_2U content higher than that required by chance; (c) GSU_2 content of no natural fat could be above about 45-46 per cent; and (d) GU_3 contents of fats with less than about 50 per cent S content would be near about that required according to chance.

The data obtained by crystallization methods on the proportions of GS_2U, GSU_2 and GU_3 in different natural fats of varying saturated acid contents[4,9] do not show these features and hence the actual mechanism effecting the assembly of the fatty acids into triglycerides in the natural fat depots remained unknown.

The fractional crystallization method makes the basic assumption that the fractions into which a fat is separated by crystallization will contain only two adjacent glyceride types. Above about 5°C., the melting point of the highest melting isomorphous form of triolein, it is almost certain that only GS_3, GS_2U and GSU_2 will crystallize out of solution[13]. In case of higher saturated acids most of the GS_3 will be thrown out of solution at 25°-26°C.[14]. However, appreciable amounts of GS_2U can remain in solution at 5°C. due both to their normal solubility and due to intersolubility effect exerted by the dissolved liquid glycerides[13]. On further cooling the GS_2U may be thrown out simultaneously with higher melting forms of GU_3 so that the fractions obtained in the range of *c.* 5° and −25° to −30°C. may actually contain varying proportions of GS_2U, GSU_2 and GU_3 while they will be calculated as mixtures of GS_2U with GSU_2 or GSU_2 with GU_3 depending on the S content of the fractions and this will lead to apparently lower amounts of GS_2U and GU_3. No methods were so far available to determine the glyceride type composition of such fractions. Because of this source of error, the extent of which cannot be easily estimated, attention was given to the possibility of developing methods for determining GS_2U and GSU_2 contents of fats without involving the crystallization principles at any stage. This ultimately led to the working out of the azelaoglyceride estimation method of determining GS_2U and GSU_2 contents in fats where the saturated acids are limited to myristic and those above, and the unsaturated acids present give azelaic acid on oxidation[7,15].

The glyceride type composition of a good number of natural fats from vegetable and animal sources has been determined by this method[5]. The results obtained were different from those obtained by crystallization in most cases where the saturated acid content was less than 40-45 per cent mols. The salient features of the new results are[16]: (1) Whereas fractional crystallization had not shown the presence of any GS_2U in fats with less than about 22 per cent saturated acids, the present method showed appreciable amounts of GS_2U in these; (2) in natural fats where S content was less than about 25-30 per cent, and hence GS_3 required according to chance distribution was small, the proportions of the other glyceride types present were nearly that required by chance; (3) in cases where the values obtained by this method differed from crystallization values, the difference always consisted in higher values for GS_2U and GU_3 and lower values for GSU_2 when determined by the azelaoglyceride method; (4) the present results never showed a GSU_2 content higher than 46-48 per cent mols. for any natural fat; and (5) GU_3 contents of fats with less than about 50 per cent S content were nearly the same as those required by chance distribution when determined according to the present method.

The difference in the values between the two methods could be due to two reasons, namely various proportions of GS_2U remaining behind in mother liquors containing varying quantities of GU_3 in cases where the temperature of crystallization was *c.* 0°C. and above, and various proportions of GU_3 being precipitated along with GS_2U and GSU_2 at temperatures between 0° and −30°C. Both these phenomena have now been experimentally demonstrated[13]. Distearo-olein is insoluble in acetone at 0°C., but in presence of GU_3 appreciable amounts of the former were found to remain in solution at 0°C. Still larger proportions of GS_2U may be expected to remain in solution at 0°C. in acetone in the crystallization of natural fats because the GS_2U present in these will be mixtures with lower melting points and greater solubilities. This gives us an idea of the effect of component glyceride and acid composition on the amount of separation obtainable by crystallization, and also substantiates the first point. The second point[13] is substantiated by the analysis of a less soluble fraction obtained by crystallizing a groundnut oil from acetone containing 10 per cent acetic acid between −15° and −18°C. The fraction contained 28 per cent mols. of saturated acids. This was not, however, a mixture of 84 per cent GSU_2 and 16 per cent GU_3 expected according to the assumptions underlying crystallization methods, but contained 17 per cent GS_2U, 32 per cent GU_3 and 51 per cent GSU_2. The soluble fraction obtained in the above crystallization contained 33 per cent GSU_2 and 67 per cent GU_3, and hence the results demonstrate the second source of error in the crystallization methods.

The proportions of different glyceride types determined by azelaoglyceride estimation methods in the series of natural fats with S content varying from about 8 to about 99 were characteristic in a new manner: they were related in the same manner to the proportions required according to simple chance distribution. The relationship thus discovered, termed the rule of glyceride type distribution in natural fats, is briefly stated as follows[12]: " The glyceride type distribution of any natural fat is obtained by interchanging according to chance one-third the saturated acids represented by the difference between the actual GS_3 content and the GS_3 content required according to chance, with the unsaturated acids in the other glyceride types as required according to chance, without allowing the formation of any further GS_3." According to this when GS_3 chance is the same as GS_3 actuals, the difference between the two vanishes: hence no interchange is necessary in such cases and the proportions of the different glyceride types present will be the same as those required by chance. The rule has been found to be obeyed by all vegetable and animal fats so far examined[12]. Fats which contain large amounts of GS_3, e.g. land animal depot fats, and vegetable fats containing large proportions of myristic and lower saturated acids obey the rule in the same way as the palmitic-stearic-oleic-linoleic type vegetable fats containing practically no GS_3. The views of Hilditch that it is illogical to postulate the existence of profound constitutive differences between different groups of natural fats which are produced by the same or broadly similar conditions of enzyme systems, temperature, etc. (loc. cit.), are thus substantiated by the present results which indicate that most probably all natural fats are constituted on the same fundamental basis, at least as regards their glyceride type distribution.

It has already been mentioned that the only restriction imposed on the completely non-selective action of lipase in the esterification of the natural fats is its inability to react with or synthesize solid phase glycerides[11]. The component acids of natural fats are usually such that the tri- and di-unsaturated glycerides are usually liquid at the habitat temperatures of the depots; the mono-unsaturated glycerides are under the same conditions, liquids or low melting solids readily soluble in the liquid tri- and di-unsaturated glycerides, and only the GS_3, when derived from higher chain length acids, have melting points appreciably higher than the habitat temperatures. These are characterized also by very sparing solubility in liquid triglycerides, and hence only these can, under any conditions, exist as separate solid phase insoluble in liquid fractions of the fats. Thus GS_3 is the only glyceride type whose synthesis up to the proportions required by chance can be restricted in the natural fat depots. On this assumption it follows that the only way by which the mixture of fatty acids synthesized in the depots can be completely built up into triglycerides is by random interchange of one-third the saturated acids in the difference in value between GS_3 actuals and GS_3 chance, with unsaturated acids from the other glyceride types, without allowing the formation of any GS_3 beyond the limits permitted by the melting point and solubility of the GS_3 formed by random esterification from the saturated acids present. Such a mechanism of esterification provides the explanation for the relationship between the actual and chance proportions of glyceride types in natural fats as represented in the rule of glyceride type distribution. The mechanism of esterification of fatty acids thus arrived at has been termed *the restricted random distribution rule or theory**.

A study of the detailed glyceride structure of some of the more saturated natural fats in the light of the restricted random distribution rule is attempted in this paper. Since in the esterification of natural fats there appears to be no other restriction to chance distribution than limitation of GS_3 formation in cases where the saturated acids are of too high molecular weights, and hence would produce too high melting GS_3, the mathematical derivation of the detailed glyceride structure of any natural fat according to restricted random distribution is easily done. The factors determining the extent of limitation of GS_3 formation has been discussed in detail elsewhere[11] and depend mainly on character of biologic source, component acid composition and habitat temperature. Depending on these each fat depot appears to be characterized by a specific maximum melting point of fat synthesized. This maximum limit of melting point permissible will vary to some extent with habitat temperature in the same depot, but is apparently not affected by any other factor so far as our present knowledge goes. A good amount of evidence has recently been presented by the author[14] showing that natural fats containing proportions of GS_3 lower than chance values will show melting points lower than those of the corresponding chance distributed fats, and this forms further support for the restricted random distribution rule.

The natural fats fall into three broad groups on the basis of their glyceride structure: those showing no limitation of GS_3

---

*The author is grateful to Dr. R. J. Vander Wal, Research Division, Armour & Co., Chicago, for suggesting this term.

formation; those showing some limitation of GS_3 formation; and lastly those showing high limitation of GS_3 formation and in which GS_3 actuals is less than about 10 per cent of GS_3 chance. In fats showing no limitation of GS_3 formation, simple chance or random distribution prevails and the proportions of the different glyceride types as well as individual glycerides are those required according to chance distribution rules.

In fats showing limitation of GS_3 formation the proportions of the different glyceride types follow the glyceride type distribution rule. Since there is no restriction in interchange of any radicals between GS_2U, GSU_2 and GU_3, the different saturated and unsaturated acids will be distributed in the same ratio in these three glyceride types. Hence, the proportions of the individual glycerides constituting any one of the above glyceride types will be those required according to chance if we regard each of the glyceride types separately.

When in a natural fat showing appreciable limitation of GS_3 formation a number of different saturated acids of differing chain lengths and melting points are present, there can be preferential elimination of the higher melting and less soluble GS_3 which will naturally be derived from the acids of higher chain lengths. This selective elimination can operate only in the last stage of GS_3 formation[11], i.e. during esterification of GS_2OH to GS_3, and hence when only one or two saturated acids are present and their molecular weights are not very much different, any selective elimination effected will be too small to produce appreciable or even measurable deviation from chance distribution in the structure of the individual glycerides composing the GS_3, though the amount of the latter present may differ appreciably from that required according to chance. This is supported by the approximate analyses reported by Hilditch and colleagues on the composition of GS_3 fractions from a number of ox, buffalo and sheep depot fats[17] and palm oils[18].

In cases where the fat contains a number of saturated acids and at the same time shows high limitation of GS_3 formation, the GS_3 present can show measurable selective elimination of higher chain length acids as has been demonstrated by the results of Hilditch and colleagues on the composition of GS_3 fractions from a number of low melting vegetable oils of the palmitic-stearic-oleic-linoleic type fatty acid composition[19]. The amount of GS_3 present in such cases is reduced to less than 10 per cent of that possible according to chance distribution, and the proportions of GS_3 actually present are very small so that the selective concentration of lower acids in such cases is of little practical significance. Hence, we come to the following conclusions: (1) In all natural fats proportions of individual glycerides in GS_2U, GSU_2 and GU_3 types are those required according to chance distribution considering each type separately; and (2) in fats showing little or no limitation of GS_3 formation the proportions of individual glycerides composing the GS_3 will be those required according to chance considering this type separately; in fats showing high limitation of GS_3 formation and having a series of saturated acids, the proportions of individual glycerides calculated in this manner will give an approximation to those present.

A single set of formulae will thus be able to give the detailed glyceride composition of any natural fat from the component acid composition and GS_3 content alone.

Calculation of glyceride type composition from GS_3 and S contents — If S and U be the molar proportions of saturated and unsaturated acids per cent in a fat, then the proportions of different glyceride types required according to chance are the following:

$$GS_3 \text{ chance} = 100 \times (S/100)^3$$
$$GU_3 \text{ chance} = 100 \times (U/100)^3$$
$$GS_2U \text{ chance} = 3 \times 100 \times (S/100)^2(U/100)$$
$$GSU_2 \text{ chance} = 3 \times 100 \times (S/100)(U/100)^2$$

In practice GS_2U and GSU_2 can be calculated in a much simpler way. If $S-GS_3$ chance be X and $U-GU_3$ chance be Y, then

$$GS_2U \text{ chance} = 2X-Y \text{ and}$$
$$GSU_2 \text{ chance} = 2Y-X$$

Theoretical derivation of formulae for calculating actual GS_2U, GSU_2 and GU_3 contents when GS_3 actuals is less than GS_3 chance has been described in detail elsewhere[11]. In practice the calculations can be made much simpler by the following procedure:

Let the difference between GS_3 chance and GS_3 actuals be A. Then A/3 is the S to be interchanged according to chance with unsaturated acids represented by 2/3 GSU_2 chance + GU_3 chance. The proportions of acids interchanged in GU_3 will then be $A/3 \times GU_3$ chance/GU_3 chance + 2/3 GSU_2 chance. The amount of GU_3 consequently converted to GSU_2 will be $3 \times A/3 \times GU_3$ chance/GU_3 chance + 2/3 GSU_2 chance. Hence GU_3 actuals will be GU_3 chance$-A \times$ GU_3 chance/GU_3 chance + 2/3 GSU_2 chance distribution.

Thus we get GS_3 actuals and GU_3 actuals. Let $S-GS_3$ actuals be X' and $U-GU_3$ actuals be Y'. Then

GS_2U actuals $= 2X'-Y'$ and
GSU_2 actuals $= 2Y'-X'$

Calculation of detailed glyceride structure — According to the restricted random distribution rule the proportions of individual glycerides are dependent on the proportions of the different glyceride types and the component acid composition only and no other factors. Let the proportions of different saturated acids be $s_1, s_2, s_3 \ldots s_n$ so that $s_1 + s_2 + s_3 + \ldots s_n = S$, and the proportions of the different unsaturated acids be $u_1, u_2, u_3 \ldots u_n$ such that $u_1 + u_2 + u_3 + \ldots u_n = U$.

Proportions of fully saturated glycerides will be as follows:

$G(s_1)_3 = GS_3 \text{ actuals} \times (s_1/S)^3$
$G(s_1)_2s_2 = 3 \times GS_3 \text{ actuals} \times (s_1/S)^2(s_2/S)$
$Gs_1s_2s_3 = 6 \times GS_3 \text{ actuals} \times (s_1/S)(s_2/S) \times (s_3/S)$

Similarly also for individual GU_3 glycerides.

GS_2U glycerides are calculated as follows:

$G(s_1)_2U = GS_2U \text{ actuals} \times (s_1/S)^2$
$Gs_1s_2U = 2 \times GS_2U \text{ actuals} \times (s_1/S)(s_2/S)$

Similarly also for GSU_2 glycerides.

Further differentiation of disaturated glycerides is as follows:

$G(s_1)_2u_1 = G(s_1)_2U \times u_1/U$ and
$Gs_1s_2u_1 = Gs_1s_2U \times u_1/U$, and similarly also for GSU_2 glycerides.

The above calculations are common for all natural fats irrespective of their biologic source or component acid composition or changes induced in fats by differences in environments. The proportions of the glyceride types estimated by azelaoglyceride methods in nearly 30 natural fats has established the validity of the calculations up to the glyceride type composition stage[16]. Further confirmation of the rule depends on the proportions of individual glycerides in different natural fats. According to methods at present available, the determination of individual glycerides has to depend, at some stage or other, on fractional crystallization, and resolution attained by crystallization is at best only partial. In case of GS_3 mixtures direct fractional crystallization is the only possible method; further complications being that melting points of mixed GS_3 glycerides from higher saturated acids are very close to each other, and so also the tendency shown by individual GS_3 glycerides to form eutectic mixtures with each other.

According to the present rule the mean molecular weight of the saturated acids in the GS_2U and GSU_2 types must be the same. This has been shown to be the case in a number of vegetable fats containing only traces of GS_3 by comparing the S from the GS_2A-GSA_2 fractions obtained from precipitated magnesium salts, with the S from the purely GSA_2 fractions obtained from the soluble magnesium salts in the azelaoglyceride separation of products of acetic acid-acetone-permanganate oxidation of fats[5].

It has been indicated previously that the error introduced in the fractional crystallization of fats is largely due to the presence of GU_3, and that when amounts of GU_3 present are rather small, the error also becomes smaller. It has also been mentioned that when the ratio of GU_3 to GS_2U reaches a value of 5 or above, crystallization is not able to effect much separation of the GS_2U at all, and that the maximum amount of GU_3 which can be detected by this method is probably only 4/5 of that actually present[13]. We can conclude from this that when in a fractional crystallization GU_3 found to be present is about 4/5 of that possible according to the glyceride type distribution rule, the maximum limit of separation would have been reached. Further, when the difference between the GU_3 found by crystallization and that required according to the glyceride type distribution rule is small, say not more than about 3-5 units per cent, the proportions of the individual glycerides calculated from the crystallization data would be very nearly correct. In the more saturated fats containing above about 40 per cent mols. of S, the proportions of GU_3 required to be present according to the present rule are well below 10-15 per cent in general, and when crystallization shows the presence of GU_3 in amounts differing by not more than 3-4 per cent from the values required according to the present rule, the proportions of other glyceride types and also of the individual glycerides should be capable of being predicted with reasonable accuracy by calculations according to the restricted random distribution rule discussed above.

The detailed glyceride structure of a number of natural fats containing more than about 40 per cent saturated acids have been worked out by Hilditch and his colleagues, and others. A comparison is now made of the results obtained by them experimentally and the values calculated theoretically according to the present method from the component acid composition and GS_3 contents reported by these workers for their samples. The values obtained by the crystallization method will be the maximum limits for GSU_2 and minimum limits for GS_2U and GU_3; the calculated values should be lower than the experimental values for GSU_2 and higher for GS_2U and GU_3 if they differ from the latter. The experimental and calculated (the latter enclosed within brackets) values for a series of natural fats are given in the sequence. In these calculations, following the practice of Hilditch, small quantities of homologous saturated acids accompanying major component saturated acids are classed along with the latter. Thus, when small quantities of myristic acid accompany palmitic acid they are classed as palmitins and so on unless otherwise stated. All unsaturated acid radicals are termed oleins, and U mentioned as oleic acid except where mentioned. In a number of instances the reported fatty acid composition does not agree with the overall glyceride composition given, and in most of such cases the former has been corrected, the individual acids being proportionately stepped up or down as required, so as to agree with the latter.

Vegetable fats

(1) *Mimusops heckelii fat*[20] — Component acids: palmitic, 5; stearic, 37; and oleic, 58 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 1 (1); distearo-olein, 27-31 (32); stearopalmito-olein, 7-3 (9); stearodiolein, 46-41 (36); palmitodiolein, 9-14 (5); and GU_3, 10 (17) per cent mols.

(2) *Shea butter*[21] — Component acids: palmitic, 6; stearic, 40; and oleic, 54 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 4 (4); distearo-olein, 35 (33); stearopalmito-olein, trace (10); stearodiolein, 45 (35); palmitodiolein, 10 (5); and GU_3, 5 (13) per cent mols.

(3) *Palm oil, Bassa*[22] — Component acids: palmitic, 43; stearic, 4; and oleic, 53 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 6 (6); dipalmito-olein, 31 (36); palmitostearo-olein, 10 (7); palmitodiolein, 41 (34); stearodiolein, nil (3); and GU_3, 12 (14) per cent mols.

(4) *Hodgsonia fat*[23] — Component acids: palmitic, 42; stearic, 9; and oleic, 49 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 3 (3); dipalmito-olein, 33 (38); distearo-olein, nil (3); palmitostearo-olein, 27 (16); palmitodiolein, 24 (25); stearodiolein, nil (7); and GU_3, 13 (9) per cent mols.

(5) *Garcinia morella fat*[24] — Component acids: palmitic, 1; stearic, 48; and oleic, 51 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 46 (50); palmitostearo-olein, nil (3); stearodiolein, 47 (34); palmitodiolein, 4 (1); and GU_3, 1 (10) per cent mols.

(6) *Palm oil, Cameroons*[22] — Component acids: palmitic, 51; stearic, 4; and oleic, 45 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 8 (8); dipalmito-olein, 43 (48); palmitostearo-olein, 11 (7); palmitodiolein, 32 (28); stearodiolein, nil (3); and GU_3, 6 (6) per cent mols.

(7) *Shorea robusta fat*[25] — Component acids: palmitic, 5; stearic, 44; arachidic, 6; and oleic, 45 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 41-45 (42); palmitostearo-olein, 8 (10); arachidostearo-olein, 14-10 (14); sterodiolein, 25-21 (22); palmitodiolein, 5 (2); arachidodiolein, 4-8 (3); and GU_3, nil (4) per cent mols.

(8) *Allanblackia stuhlmanii fat*[26] — Component acids: palmitic, 3; stearic, 52; and oleic, 45 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 1 (1); distearo-olein, 66 (60); stearopalmito-olein, trace (7); stearodiolein, 33 (27); palmitodiolein, trace (1); and GU_3, 0 (4) per cent mols.

(9) *Allanblackia parviflora fat*[27] — Component acids: palmitic, 3; stearic, 53; and oleic, 44 per cent mols. Experimental and

(calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 60 (61); stearopalmito-olein, 7 (7); stearodiolein, 29 (24); palmitodiolein, 3 (2); and GU_3, nil (4) per cent mols.

(10) *Vateria indica fat*[28] — Component acids: palmitic, 14; stearic, 44; and olein, 42 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 45 (42); dipalmito-olein, 7 (4); stearopalmito-olein, 17 (26); stearodiolein, 16 (18); palmitodiolein, 13 (6); and GU_3, nil (2) per cent mols.

(11) *Garcinia indica fat, I*[24] — Component acids: palmitic, 3; stearic, 56; and oleic, 41 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 1 (1); distearo-olein, 68 (69); stearopalmito-olein, 8 (8); stearodiolein, 20 (19); palmitodiolein, 1 (1); and GU_3, 2 (2) per cent mols.

(12) *Garcinia indica fat, II*[29] — Component acids: palmitic, 7; stearic, 54; and oleic, 39 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 4 (4); distearo-olein, 58 (60); dipalmito-olein, nil (1); stearopalmito-olein, 15 (15); stearodiolein, 21 (17); and GU_3, nil (1) per cent mols.

(13) *Cacao butter*[30] — Component acids: palmitic, 26; stearic, 35; and oleic, 39 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 19 (26); dipalmito-olein, 6 (15); stearopalmito-olein, 52 (39); stearodiolein, 12 (10); palmitodiolein, 9 (7); and GU_3, nil (1) per cent mols.

(14) *Phulwara butter*[31] —Component acids: palmitic, 59; stearic, 3; and oleic, 38 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 8 (8); dipalmito-olein, 62 (66); palmitostearo-olein, 7 (5); palmitodiolein, 23 (20); stearodiolein, trace (1); and GU_3, nil (1) per cent mols.

(15) *Allanblackia floribunda fat*[27] — Component acids: palmitic, 2; stearic, 60; and oleic, 38 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 2 (2); distearo-olein, 76 (78); stearopalmito-olein, 5 (5); stearodiolein, 16 (14); palmitodiolein, 1 (nil); and GU_3, nil (1) per cent mols.

(16) *Borneo tallow*[32] — Component acids: palmitic, 20; stearic, 43; and oleic, 37 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 5 (5); distearo-olein, 40 (37); dipalmito-olein, 8 (8); stearopalmito-olein, 31 (34); stearodiolein, 13 (11); palmitodiolein, 3 (5); and GU_3, 0 (0) per cent mols.

(17) *Kombo fat*[33] — Component acids: lauric, 9; myristic, 63; palmitic, 2; and unsaturated acids ("oleins"), 26 per cent mols. Experimental and (calculated) glyceride structures: trimyristin, 21 (24); dimyristolaurin, 17 (10); dimyristopalmitin, nil (2); other GS_3, nil (2); lauromyristo-olein, 10 (10); dimyristo-olein, 33 (33); palmitomyristo-olein, 3 (3); myristodiolein, 16 (14); laurodiolein, nil (2); and GU_3, nil (1) per cent mols.

(18) *Irvingia barterii fat*[34] — Component acids: lauric, 43; myristic, 49; and oleic, 8 per cent mols. Experimental and (calculated) glyceride structures: trilaurin, nil (8); trimyristin, nil (11); dilauromyristin, 31 (27); laurodimyristin, 48 (33) per cent mols.; and rest mono and disaturated glycerides.

(19) *Virola fat*[33] — Component acids: lauric, 18; myristic, 73; palmitic, 4; and oleic, 5 per cent mols. Experimental and (calculated) glyceride structures are trimyristin, 43 (39); laurodimyristin, 31 (29); dilauromyristin, 1 (7); lauromyristopalmitin, 10 (3); dimyristopalmitin, nil (6); oleodimyristin, 3 (12); and other disaturated glycerides, 12 (3) per cent mols.

Animal fats

In calculating the glyceride structure of animal fats, all C_{16} and lower acids have been taken as palmitic acid following the procedure of Hilditch. The actual proportions of palmitic acid in these fats are appreciably lower than the values used for calculation since appreciable amounts of unsaturated C_{16} and C_{14} acids occur in these over and above a usual 3-5 per cent of myristic acid. A greater margin is hence to be allowed for the proportions of dipalmitoglycerides thus calculated than in the case of vegetable fats where the proportions of palmitic acid used for calculation are practically the same as the proportions actually present.

(20) *Pig back fat*[35] — Component acids: palmitic, 33; stearic, 14; and oleic, 53 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 5 (5); oleodipalmitin, 5 (22); oleodistearin, nil (4); oleopalmitostearin, 34-27 (18); palmitodiolein, 53-46 (27); stearodiolein, 0-7 (11) and GU_3, 10-3 (13) per cent mols.

(21) *Sheep back fat*[36] — Component acids: palmitic, 37; stearic, 15; and oleic, 48 per

cent mols. Experimental and (calculated) glyceride structures: GS_3, 5 (5); dipalmito-olein, 13 (27); distearo-olein, nil (4); palmito-stearo-olein, 36-29 (23); palmitodiolein, 39-46 (23); stearodiolein, 0-7 (10); and GU_3, 0-7 (8) per cent mols.

(22) *Pig perinephric fat*[35] — Component acids: palmitic, 35; stearic, 18; and oleic, 47 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 9 (9); dipalmito-olein, 9 (21); distearo-olein, nil (6); palmitostearo-olein, 39-34 (22); palmitodiolein, 35-40 (23); stearodiolein, 0-5 (11); and GU_3, 3-8 (8) per cent mols.

(23) *Sheep perinephric fat*[36] — Component acids: palmitic, 32; stearic, 27; and oleic, 41 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 14 (14); dipalmito-olein, 5 (16); distearo-olein, 7-2 (11); stearopalmito-olein, 42-41 (27); palmitodiolein, 24-25 (15); stearodiolein, 1-13 (12); and GU_3, 0-7 (5) per cent mols.

(24) *Ox, English*[37] — Component acids: palmitic, 39; stearic, 23; and oleic, 38 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 17 (17); dipalmito-olein, 15 (22); distearo-olein, 2 (8); palmito-stearo-olein, 32 (26); stearodiolein, 11 (9); palmitodiolein, 23 (14); and GU_3, nil (4) per cent mols.

(25) *Ox, Calicut*[38] — Component acids: palmitic, 41; stearic, 28; and oleic, 31 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 28 (28); dipalmito-olein, 11 (19); distearo-olein, 2 (9); palmito-stearo-olein, 41-38 (25); palmitodiolein, 14-17 (10); stearodiolein, 0-3 (7); and GU_3, 0-3 (2) per cent mols.

(26) *Ox, Bombay*[38] — Component acids: palmitic, 50; stearic, 26; and oleic, 24 per cent mols. Experimental and (calculated) glyceride structures: GS_3, 36 (36); dipalmito-olein, 18 (24); distearo-olein, nil (7); palmito-stearo-olein, 35-34 (25); stearodiolein, 0-1 (1); palmitodiolein, 10-11 (7); and GU_3, 1-0 (nil) per cent mols.

The above results show that in the case of the more saturated fats, where due to the absence of any large amounts of GU_3 crystallization is likely to give more or less accurate results, the proportions of individual glycerides recorded by this method show good agreement with those calculated according to the restricted random distribution rule from GS_3 content and component acid composition alone. It should be remembered in particular that the same formulae are used for all the fats irrespective of biologic source or number and nature of component acids. This forms further support of the restricted random distribution rule.

Summary

Methods of calculating detailed glyceride structure of natural fats from the fully saturated glyceride (GS_3) content and component acid composition according to the restricted random distribution rule are described. According to this rule the glyceride structure of all natural fats are calculated in the same manner irrespective of biologic source or fatty acid composition. The proportions of the different glyceride types in a series of natural fats determined by the azelaoglyceride analysis methods agree closely with those calculated according to the rule from the GS_3 and saturated acid contents. The proportions of different individual glycerides determined by the crystallization method in a series of natural fats containing higher than about 40 per cent saturated acids show good agreement with those calculated according to the present methods.

References

1. Hilditch, T. P. & Meara, M. L., *J. Soc. chem. Ind. Lond.*, **61** (1942), 117.
2. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 16.
3. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 301, 237.
4. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 231-87.
5. Kartha, A. R. S., *Studies on Natural Fats* (published by the author), 1951, Vol. 1, 6-54.
6. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 256-61.
7. Kartha, A. R. S., *Studies on Natural Fats* (published by the author), 1951, Vol. 1, 6-29.
8. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 288-94.
9. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 297-337.
10. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 295-97.
11. Kartha, A. R. S., *Studies on Natural Fats* (published by the author), 1951, Vol. 1, 84-110.

12. Kartha, A. R. S., *Studies on Natural Fats* (published by the author), 1951, Vol. 1, 67-84.
13. Kartha, A. R. S., *J. sci. industr. Res.*, **13A** (1954), 273.
14. Kartha, A. R. S., *J. sci. industr. Res.*, **11A** (1952), 354; **12A** (1953), 504.
15. Kartha, A. R. S., *J. Amer. Oil Chem. Soc.*, **30** (1953), 280.
16. Kartha, A. R. S., *Studies on Natural Fats* (published by the author), 1951, Vol. 1, 54-84.
17. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 316.
18. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 281.
19. Hilditch, T. P., *The Chemical Constitution of Natural Fats* (Chapman & Hall, London), 1947, 274.
20. Atherton, D. & Meara, M. L., *J. Soc. chem. Ind. Lond.*, **59** (1940), 95.
21. Green, T. G. & Hilditch, T. P., *J. Soc. chem. Ind. Lond.*, **57** (1938), 49.
22. Hilditch, T. P. & Maddison, L., *J. Soc. chem. Ind. Lond.*, **59** (1940), 67.
23. Hilditch, T. P., Meara, M. L. & Pedelty, W. H., *J. Soc. chem. Ind. Lond.*, **58** (1939), 26.
24. Hilditch, T. P. & Murti, K. S., *J. Soc. chem. Ind. Lond.*, **60** (1941), 16.
25. Hilditch, T. P. & Zaky, Y. A. H., *J. Soc. chem. Ind. Lond.*, **61** (1942), 34.
26. Hilditch, T. P. & Saletore, S. A., *J. Soc. chem. Ind. Lond.*, **50** (1931), 468T.
27. Meara, M. L. & Zaky, Y. A. H., *J. Soc. chem. Ind. Lond.*, **59** (1940), 25.
28. Rao, C. V. & Rao, M. N., *J. Indian chem. Soc.*, **20** (1943), 298.
29. Vidyarthi, N. L. & Dasa Rao, C. J., *J. Indian chem. Soc.*, **16** (1939), 437.
30. Hilditch, T. P. & Stainsby, W. J., *J. Soc. chem. Ind. Lond.*, **55** (1936), 95T.
31. Bushell, W. J. & Hilditch, T. P., *J. Soc. chem. Ind. Lond.*, **57** (1938), 48.
32. Hilditch, T. P. & Bushell, W. J., *J. Soc. chem. Ind. Lond.*, **57** (1938), 447.
33. Atherton, G. & Meara, M. L., *J. Soc. chem. Ind. Lond.*, **58** (1939), 353.
34. Collin, G. & Hilditch, T. P., *J. Soc. chem. Ind. Lond.*, **49** (1930), 138T.
35. Hilditch, T. P. & Pedelty, W. H., *Biochem. J.*, **34** (1940), 971.
36. Hilditch, T. P. & Zaky, Y. A. H., *Biochem. J.*, **35** (1941), 940.
37. Hilditch, T. P. & Paul, S., *Biochem. J.*, **32** (1938), 1775.
38. Hilditch, T. P. & Murti, K. S., *Biochem. J.*, **34** (1940), 1301.

Flood Control

THE RECENT FLOODS, WHICH HAVE WROUGHT devastation in north-eastern India, have focussed the attention of the Government on the urgent need for adequate control measures. A comprehensive programme of flood control has been formulated. As an immediate measure, construction of revetments, spurs and embankments is to be started on selected sites and collection of hydrological and other data regarding maximum water levels and other characteristics of the rivers in the region is to be undertaken. This will be followed by channel improvements. The long-term phase of the programme envisages measures such as construction of reservoirs on tributaries of certain rivers. The total cost of the measures is roughly estimated at Rs. 175 crores.

To ensure implementation of the approved schemes by the States, State Flood Control Boards are being constituted in U.P., Bihar, West Bengal and Assam. It is the duty of these Boards to assess the flood problem in their areas, collect data, prepare comprehensive flood control schemes for the States and indicate priorities.

For controlling the floods in the Ganga and the Brahmaputra and their tributaries, the Government of India have set up two River Valley Commissions. The Central Water & Power Commission as the technical agency of the River Commissions will prepare an integrated plan for each river basin on the basis of data supplied by the States.

A Central Flood Control Board has also been constituted on which the Union Ministry of Irrigation & Power and the State Boards are represented. The Central Board will consider the schemes submitted by State Boards and draw up a national flood control programme. The Central Board will be assisted by a technical committee consisting of experts in flood engineering, soil conservation and agriculture. Experts from other countries and ECAFE will also be invited to assist this committee whenever necessary.

REVIEWS

BETWEEN US AND HUNGER, by C. Maya Das (Oxford University Press, Bombay), 1954, pp. ix + 157. Price Rs. 10

The author of this handy publication, who is the retired Director of Agriculture, Uttar Pradesh, has behind him thirty-one years of experience in the science and practice of agriculture. Apart from this long experience, he has had the privilege of being an onlooker of the game in which he had been an active participant. He is, therefore, eminently fit to write a book of the kind under review.

Mr. Maya Das states, in the preface, (1) that the book is intended to help those who are deeply and sincerely interested in seeing India free from hunger and want, (2) that a brief analysis is attempted of the major causes of the present-day affairs by attempting to present a true picture of the country's present economic situation, and (3) that a way is indicated whereby the fundamental obstacles to increased production can be overcome.

A feature of our economic and social problems — particularly of agriculture — is that we have conclusions with too little or no data and data without conclusions. The result is that too often our policies, plans and programmes rely on borrowed wisdom and experience from other countries. Consequently, we often experience disconcerting failures. Witness, for example, the Grow More Food (G.M.F.) Campaign, the failure of which Mr. Maya Das admits.

One would, therefore, expect to find in a book written by an expert and published in the year 1954, a critical examination of the situation, sifting of facts from fallacies, fancies and fads, and suggestions of ways and means of dealing with some of the most difficult problems of the day. In this expectation the reader will be sorely disappointed, because the book does not live up to the promise of the preface.

In chapter one, attention is drawn to the gravity of the food situation by stating that during the period intervening between 1943-44 and 1950-51, the overall cereal production had fallen from 602·5 lb. per acre to 479·7 lb. per acre. During this period the area under cereals increased by about 20·4 million acres and this period coincided with the G.M.F. drive. This is, as usual, attributed to increased acreage, drought and deluge, lack of fertilizers and manures, damage by insects, rodents and other pests. There is nothing new in this diagnosis of the causes which have always been with us. Not a word is said about the huge difference in the production figures of the Ministry of Food and Agriculture and of the Central Statistical Department of the Government of India. This is a crisis in responsibility for statistical data and has not been considered. Also, nothing has been said about the recent statements of increase in production to the point of self-sufficiency and even of export, and how the ryot is affected. When the ministers say that the food position is satisfactory do they mean comparatively easy conditions or absolute improvement with real exportable surpluses?

A more precise accounting showing how we have reached the present position, by surveying and analysing the data, emphasizing the imperfections, ambiguities and assumptions in our policies and programmes, would have been helpful in educating the reader.

In chapter four, the problem of surplus cattle is dealt with. There will be general agreement with the author when he says, that not only in beauty of form but in their economical feeding habits and in their resistance to disease, our best herds are unsurpassed. Evidence of this is seen in the fact that several countries keep Indian cattle for breeding purposes. Mr. Maya Das continues and says that we are left with a surplus population of about 50 per cent (89 millions out of 177·5 millions) of our cattle, which are useless either for milk production or for draft purposes, and which are a drain on the available fodder and grain supplies. He suggests segregation and sterilization as remedies.

Frequent and persistent statements of any kind soon assume the status of truth just as custom assumes a legal status in the eyes and ears of law. Are cattle really surplus to the needs of our country? Or are they considered surplus because they are useless for work or milk? Have they reached that condition through hereditary degeneration or environmental deterioration from lack of food and fodder? These are questions which have not been answered.

The grazing nuisance of cultivated crops by rural cattle and the roaming of cattle in towns and cities should not be construed as an indication of their being surplus to the needs of the country, but should be seen either as surplus to the *individual* owner or as being due to his warped civic sense or both.

The food production problem and the cattle problem are closely linked up. Cattle are inefficient as milkers and workers because there are not enough food and fodder for them; adequate food and fodder cannot be grown because cattle are inefficient. That is a vicious circle characterizing the present situation. Mr. Maya Das attributes it to the encroachment of cultivation on village commons and fodder and grazing resources. He does not indicate where and how this vicious circle can be broken. On the other hand, he advocates in other chapters wasteland reclamation and development by land development corporations or syndicates with a system of bullock *cum* machine combination, and does not say how the cattle fodder problem is to be solved.

Sterilization is suggested by Mr. Maya Das as one of the effective means of reducing cattle population. He relies on artificial insemination which is possible to manage with very few stud bulls. It is difficult to see how the adoption of this practice will solve the problem. Whatever may be the means in which cows are impregnated, the overall situation will be still the production of equal numbers of cow and bull calves. Could it be assumed that because semen from good stud bulls is used, good cow and bullock calves are invariably produced? The food position being what it is, will there not be useless and surplus cattle? There are other considerations in respect of artificial insemination. Could it be assumed that in our large-scale schemes of artificial insemination we are using the semen of *proved* bulls? Mr. Maya Das does not discuss this important aspect of the problem, the consequences of which are not the same to us as in the western countries. In those countries, if a cow or a bull which is the product of artificial insemination does not come up to the standard, the animal will still be useful as a beef animal. It is not so with us. Again, while discussing the problem of surplus cattle, Mr. Maya Das has not made any reference to the resumption of crossing Indian cows with foreign bulls. Past experience in this line over a period of thirty years had been unhappy, and there are many knowledgeable and experienced people who doubt the wisdom or expediency of the resumption of this type of cross-breeding.

In chapter ten, the problem of " mechanization, the land and the bullock " has been discussed. At the outset Mr. Maya Das has asked the question whether the tractor has or has not an essential place in the drive for increased food production. He has placed emphasis on undeveloped and under-developed areas, and has advocated bullock *cum* tractor run farms which should be worked by State-aided and commercially worked land development corporations.

For us in India mechanization of agriculture presents both opportunities and obstacles. The introduction of mechanization depends on whether opportunity outweighs the obstacle or vice versa. Mr. Maya Das has dealt with only opportunities and has ignored difficulties. It will be useful to consider a few of the latter.

Two or three years ago, Mr. Maya Das told the U.P. Zamindari Abolition Committee that the double crop area in U.P. could be extended through mechanization and mechanical cultivation. This idea he has elaborated and expanded in the book under review. In U.P. as in other parts of India, the area under double crop is determined primarily, if not solely, by the water facilities available; and where they are available the large majority of ryots do take advantage of it. For instance, during the quinquennium 1939-40 to 1943-44, the U.P. districts of Banaras, Jaunpur, Ghazipur and Allahabad had under double crop 66 to 90 per cent of the area of their farms, and that under the existing peasant agricultural systems and practices. Further extension through mechanization and mechanical tillage may be possible in isolated areas and particular instances, but there is no information whether mechanization of the areas that are now double cropped would be attended by better results. The discussion by Mr. Maya Das does not throw light on this question.

The introduction of mechanization into undeveloped areas and into under-developed areas (which have already established systems and practices of agriculture) should satisfy two conditions. Firstly, it should result in increased yield per acre; secondly, it must reduce the cost of production per acre. That means mechanization should be accompanied by increased production with reduced cost per acre of such production. What we sorely need today is increased production per acre and not increased production per man (which is the criterion for western countries).

Looking at the problem from this point of view there is no evidence that better tillage with tractors and their implements would increase yield per acre. All the available evidence points in the other direction. Experiments in different parts of India, spread over a period of fifty years, show that deeper and better cultivation than is done with the country plough with implements involving soil inversion is unnecessary as a routine practice, and may even result in the slow but steady fall in yields. British and American experience in recent decades shows that mechanization while increasing the output per man, has not been accompanied by a corresponding increase in output per acre.

In extensive farming under mechanization, the law of diminishing returns will operate earlier than in small-scale agriculture. That is because mechanical operations will be governed by the cost of working the mechanical equipment. Therefore, the efficiency (the number and methods of ploughing for the production of a good seed bed) will be in the proportion of costs to operations. Where tractors, implements, spare parts, fuel and lubricating oils have to be imported, the total cost will permit cultivation only to the extent of optimum efficiency and consequently the yield per acre will only be the optimum and not the maximum. Supplementary bullock cultivation may improve the soil and seed-bed conditions, but here comes the cost of maintaining both tractors and bullocks, and that requires serious consideration by the farm administrators.

There is no evidence that the present low yields are due to small holdings and/or to primitive techniques. Nor is there evidence that mechanical *cum* bullock farms would be better proposition from the points of view of economics and increased production. Here, as in the other chapters of the book, there is lack of objective analysis and discussion supported by convincing data and experience.

B. VISWA NATH

SILTING OF RESERVOIRS, Central Board of Irrigation & Power Publication No. 1, by A. N. Khosla (Manager, Government of India Press, Simla), 1953, pp. xxi + 206

The author has collected in this book available data on the river valleys in India, the Nile valley and the important river valleys of U.S.A. Reference is also made to the silt studies conducted in Japan.

Intensive research in North India on the silting of reservoirs and associated problems started with the investigation and design of the multi-purpose river valley projects such as the Damodar, the Mahanadi, the Sutlej (Bhakra-Nangal) and the Kosi projects. The Punjab before partition and Bombay already possessed research stations at Lahore, Malikpur and Khadakwasla; these laboratories were easily switched on to the investigation of the silt problem. The studies of the suspended matter in the Nile have been in progress for quite a number of years; such studies in U.S.A. have been very much more recent starting perhaps in a significant measure from the date of investigation of the Boulder Dam.

It is here relevant to observe that while in North India dams of magnitude have had a real start only after the advent of independence, States like Hyderabad, Mysore, Madras and Travancore had even from the closing years of the nineteenth century advanced in the design and construction of dams. In fact, the last century had to its credit the Periyar reservoir with a dam 176 ft. high in the year 1895. Its storage is 8,000 million cu. ft. The silt problem has been investigated in great detail in the case of South Indian reservoirs.

The silt problem itself is a very complicated one and has a multitude of aspects. There is the suspended load which can be determined fairly accurately; there is the bed silt whose correct estimation is still baffling engineers; there is the natural formation of deltas in the plains of river valleys. Similar deltas would be forming now at the heads of reservoirs due to the dropping of silt where the rapidly flowing rivers meet the more stagnant upper end of reservoir storage; there is the problem of density currents, the low level sluices passing the whole of the incoming silt; there is the problem of the margins gradually filling up; there is also the problem of silt getting consolidated by further accretion of silt on top and, thereby, its interference with the storage capacity growing somewhat less with time, etc.; there is also the question of the silt content varying with floods, flashy or otherwise, and synchronizing or not synchronizing with the flood peaks. Snow-fed rivers behave differently from those purely rain-fed and there are rivers fed both by snow and rain. How the construction of dams leads to the formation of a delta above them and how existing delta formation can afford approximate data to enable us to forecast the growth of delta above dams have all been fully worked out in the report of the dam projects in South India. These elaborate methods will be found in the volumes on Kistna reservoir project and in the literature developed for the Ramapadasagar project. With all these factors the problem of silt study becomes very complex.

The law of diminishing returns has progressively encroached into the region of irrigation and the construction of dams. The early British period perhaps saw a good deal of activity in the construction or restoration of small reservoirs which are better called tanks. Such works were comparatively cheap and brought in returns of 6 per cent (even up to 10 per cent and occasionally more) on the capital outlay. And now when the living index has shot up we find that the only device open to increase irrigation and stabilize supply is by the construction of medium and high dams. While, for finding food by increasing the irrigated area and insuring crops against drought, dams need the highest priority, a welfare state has to be equally alert in the matter of advancement of education, and improving the standard of life of the common man. It has been a problem to find adequate funds for river valley and other equally urgent undertakings, but with foreign aid and deficit financing a satisfactory solution is being found. Naturally, therefore, every rupee spent on river valley multi-purpose projects has to be made to go as long a way as possible, and one of the ways in which it can be done is to assess the loss in the useful reservoir storage due to silting. So, this problem of silting of reservoirs is a burning problem, and any reasonable expenditure in regard to this should justify itself perhaps not in the immediate but in the long run. It will be one of the ways in which the future generation can be taken care of. In chapter II of Khosla's book the reservoirs dealt with are comparatively small ones and may not actually give comparable data applicable to large reservoirs. This is not so in chapter III where the Mahanadi and Kosi rivers have been dealt with.

Khosla's book has attempted to reduce all data to a common denominator, namely that for every 100 sq. miles of catchment the silt delivered by a river is of the order of 79-100 ft. acres. This information is useful for one who has to rush through his design of a reservoir. The best method of estimating the silt accretion in a reservoir is to arrive at the progressive variation in their capacities. There are adequate instruments, such as the echo sounder, etc., to take rapid soundings of reservoirs and we have also enough mechanical and electrical calculators and it should not be impossible to organize parties as in the Geological Survey of India or the Survey of India, etc., and send them out with enough equipment for making observations in important rivers and gather useful data in the matter of the progressive silting of reservoirs as a whole and in sections. A circulating party going from reservoir to reservoir or taking up a few reservoirs each year can do this advantageously. Further research on these lines seems to be called for in the silting of reservoirs.

N.R.

RESERPINE (SERPASIL) AND OTHER ALKALOIDS OF *Rauwolfia serpentina*: CHEMISTRY, PHARMACOLOGY AND CLINICAL APPLICATIONS, edited by Roy Waldo Miner [Annals of the New York Academy of Sciences, **59** (1954), pp. 140]

This monograph is the result of a conference on reserpine and other alkaloids of *Rauwolfia serpentina*. The large number of authors contributing to the monograph and the diversity of the topics are indicative of the growing interest on the subject. The table of contents of this monograph reveals the vast developments in the chemistry of different alkaloids of *Rauwolfia serpentina*, their pharmacodynamics and their varying role in essential hypertension, neuropsychiatric and other clinical conditions.

The book contains 12 papers which were presented at the conference.

The first paper by Prof. E. Schlittler deals with the chemistry of rauwolfia alkaloids including reserpine. After reviewing the previous work done in this field by various investigators the author observes that originally the active material was thought to be in the non-alkaloid fraction of " oleoresin ". However, when modern isolation techniques such as counter-current distribution and chromatography were applied to this material, an active alkaloid was isolated which was given the name reserpine (MUELLER, SCHLITTLER and BEIN, *Experientia*, 1952, **8**, 338). Prof. Schlittler, in this paper, has discussed the constitution of this alkaloid in detail. A number of analogues of reserpine have been prepared in order to study the effect of variations in the molecule upon physiological activity, but in no case was any compound found which had a higher degree of sedative or blood pressure effect than reserpine.

There are four papers dealing with pharmacology and endocrine aspect of pharmacology of reserpine. The findings of Bein regarding the effects of the alkaloid on central nervous system and cardiovascular system have been confirmed. The alkaloid is effective both orally and parenterally and in either case there is a latent period of 1-2 hours. The alkaloid produces sedation but the animal can always be aroused and the E.E.G. records show a natural pattern in contrast to the sleep pattern as seen in barbiturates. It has been suggested that the site of action is the hypothalamus. The drug appears to bring about parasympathetic preponderance as evidenced by meiosis, relaxation of nictitating membrane, bradycardia and augmentation of secretory and motor activity of the gastro-intestinal tract. This parasympathetic preponderance is possibly of central origin.

Reserpine causes moderate fall of blood pressure which develops gradually after intravenous injection. The mechanism of action is primarily a decreased peripheral resistance which is again explained by parasympathetic preponderance. All evidence at present seems to indicate that the site of action is the hypothalamus.

Indications of delayed action of reserpine and such observations as weight gain in patients on continued administration of the drug suggest that the drug may have some influence on endocrine glands. Further, the hypothalamus, which is believed to regulate in some way the pituitary hormones, appears to be the chief site of action of reserpine; theoretically, therefore, it could be expected to mediate widespread actions through the endocrine system. In view of these facts endocrine aspects of the pharmacology of reserpine have been investigated and reported here by Gaunt *et al.* (p. 22). Reserpine appears to interfere with estrous cycle and reproductive capacity of female rats even in small doses; in large doses it inhibits androgen secretion in the males. The significance of these findings is difficult to interpret at present. Reserpine also appears to have no inhibitory action on the release of anti-diuretic hormone of the anterior pituitary. Like many other nonspecific stress stimuli the compound causes mild stimulation of adrenal cortex. Reserpine also prevents hypertension caused by humoral stimuli, e.g. hypertension caused by chronic cortisone treatment.

The remaining papers deal with clinical applications of reserpine. The two main pharmacological actions of the drug, e.g. lowering the blood pressure and the sedative and tranquillizing influence, have led to the trials of the reserpine in the following conditions: (i) hypertension, (ii) neuropsychiatric conditions, (iii) gynaecological conditions, and (iv) geaiatrics. As many as seven reports on the use of reserpine and other alkaloids in hypertension are included in the present volume. The drug has been given a fair trial on a representative group of patients comprising all types of hypertension. It is considered to be a useful and moderately potent hypotensive agent. Its effect is slowly established. In small continued doses it is well tolerated. Given alone, its main effect is to control the subjective symptoms accompanying high blood pressure. Its usefulness appears to be in combined therapy where more potent agents such as azamethonium or hydrazin-ophthalazine are used for immediate effects in severe hypertensives and rauwolfia alkaloids are then continued for maintenance therapy. Reserpine alone is useful in cases with mild hypertension of short duration. It was also found to be a safe and mild hypotensive agent for elderly patients. In the opinion of majority of the workers the main side effects are nasal congestion, depression, muscle aches and, with larger doses, gain in weight and diarrhoea. These symptoms are not annoying and decrease with continued administration. No serious side effects have been encountered.

Reserpine has also been tried by intravenous route for inducing immediate effects, and it has been found to be satisfactory for this purpose but the effect does not last long. It has been suggested that reserpine degrades as a result of metabolism to a yohimbine-like substance having sympatholytic properties. Some authors have compared the crude alkaloids of *Rauwolfia serpentina* with reserpine and, according to Wilkins (p. 36) and Freis and Ari (p. 45), the crude alkaloids and reserpine have practically identical effects upon the arterial pressure and pulse rate, and the side effects of the two are also practically identical. Wilkins, however, says: " perhaps other active principles which are known to be present in Rauwolfia may be clinically beneficial. We have not yet closed our minds to this possibility."

The sedative properties of rauwolfia in the form of extract and isolated alkaloid in different types of neuropsychiatric conditions have been reported by Dr. Kline of Columbia University (p. 107). About 600 patients have been treated and rauwolfia has proved to be an effective sedative for use in mental hospitals. Rauwolfia reduces anxiety and obsessive-compulsive drives and overcomes excessive inhibition and reticence. Considerable research, however, would be necessary to determine the exact indications of the drug in the treatment of psychoneurosis.

A report on the use of rauwolfia in certain gynaecologic condition in which psyche plays a contributing role is also included in this volume. The drug appears to be useful in conditions like menstrual molimina, in constant tension states, in frigidity and in women complaining of menopausal syndrome. The evaluation of the effect of reserpine are, however, based upon observations on a small group of cases.

Regarding the clinical use of reserpine in geriatrics, Raymond Harris (p. 95) is of opinion that in addition to the effect of this drug on hypertension, it is of value in allaying the nervousness, insomnia and states of excitement which frequently afflict the elderly patient.

There are only a few of the many biological and therapeutic potentialities of the drug, which provide an impetus and challenge for further investigations. The reviewer is convinced that we are entering a fertile field which will bear a rich harvest. This monograph will serve a useful purpose if it provides a stimulus to new ideas.

N. N. De

FIBRES FROM SYNTHETIC POLYMERS, edited by Rolland Hill (Elsevier Publishing Co. Ltd., London), 1953, pp. xv + 554. Price 95*s*.

Modern synthetic fibres have excited the interest of scientists and laymen alike. The position occupied by natural fibres till now is threatened by rapid developments in synthetic fibres. Synthetic fibres assure an inexhaustible source of supply of our requirements of textiles in peace and war.

The present volume, sixth in the series on high polymers published by Elsevier, presents an authoritative and up-to-date account of the fundamental principles in the theory and practice of fibre formation. In such a compilation where not less than eighteen specialists from universities and industry have contributed on the different aspects of a vast subject, a considerable amount of repetition is unavoidable. It is equally difficult to maintain absolute uniformity and balance between theoretical discussion and technological details. The editor is to be congratulated for his efforts in presenting widely scattered useful information in a book form and this volume together with Elsevier's earlier volume on *Physics and Chemistry of Cellulose Fibres* covers the whole subject in a convenient and compact form.

The subject is developed under four main sections, covered by 20 chapters, dealing with the synthesis of fibre forming polymers, structural relationships, spinning processes and their properties and applications.

The first section gives a concise account of the kinetics and energetics of polymerization and poly-condensation reactions. The preparation of fibre-forming vinyl polymers, polyamides, polyesters, poly-urethanes, etc., is described in three separate chapters. A brief survey of the future trends in the development of fibres from a large number of less-known organic polymers is also presented.

A complete knowledge of the molecular weight, molecular weight distribution and molecular structure is essential to the understanding and production of fibres with specific properties. This valuable aspect of the subject is well covered in the second section so ably written by C. W. Bunn. The correlation between amorphous and crystalline parts in a fibre and their influence on the physical properties of the fibre is neatly presented. This section provides an interesting reading both for a polymer chemist and an X-ray worker.

The third section presents an interesting and informative account of the spinning of fibres by melt extrusion and by wet and dry spinning processes. There is a separate chapter devoted to thermodynamical treatment of the solution behaviour of polymers and this is an essential prerequisite for a proper understanding of fibre-forming techniques. Some of the salient features associated with spinning processes such as influence of stretch, formation of the primary skin, air velocities in dry spinning, cold drawing, etc., are adequately dealt with.

The last section deals with the properties and applications of synthetic fibres. The low moisture regain, high tenacity, high elasticity, chemical resistance and resistance to bacteria and insects make them suited for many special applications. A passing reference to the knitting and weaving properties of the fibres is also made. The concluding chapter is devoted to problems involved in the dyeing of these fibres and deals with the difference in their behaviour from cellulosic fibres.

Each chapter has a brief list of references but the inclusion of a suitable bibliography recommended for further reading would have been of immense help to the reader. The present volume is a useful reference book for physicists and chemists alike and should be particularly valuable to those engaged in textile research. The book is well printed and has a nice get-up.

S. L. KAPUR

SELECTED CHAPTERS FROM MODERN INORGANIC CHEMISTRY, by K. K. Dole (Dastane Brothers' Home Service Ltd., Poona), 1953, pp. viii + 634. Price Rs. 13/12

The author has succeeded to a great extent in condensing a large amount of information available on a number of topics in advanced inorganic chemistry within the 600 pages of the book. Although the book is not meant to be a text-book on inorganic chemistry, it is a useful and suitable guiding supplement to students preparing for their B.Sc. and M.Sc. degree examinations.

MATA PRASAD

PUBLICATIONS RECEIVED

ELEMENTS AND ATOMS IN GREEK AND INDIAN THOUGHT, by N. S. Subramanya Sastry (published by the author), 1954, pp. 74, price Rs. 3/8

TECHNICAL AID TO FOOD INDUSTRIES, edited and compiled by G. T. Kale, R. C. Bhutiani, N. V. R. Iyengar, V. Balu & A. N. Sankaran (Central Food Technological Research Institute, Mysore), 1954, pp. xvi + 270, price Rs. 5

ISOTOPIC TRACERS, by G. E. Francis, W. Mulligan & A. Wormall (University of London, London), 1954, pp. xvi + 306, price 37*s*. 6*d*. net

BREAD — THE CHEMISTRY AND NUTRITION OF FLOUR AND BREAD WITH AN INTRODUCTION TO THEIR HISTORY AND TECHNOLOGY, by Lord Horder, Sir Challes Dodds & T. Moran (Constable & Co. Ltd., London), 1954, pp. vii + 186, price 18*s*.

STAINLESS IRON AND STEEL, Vol. II, by J. H. G. Monypenny, edited by F. C. Thompson (Chapman & Hall Ltd., London), 1954, pp. xii + 330, price 55*s*.

PETROLEUM MICROBIOLOGY: AN INTRODUCTION TO MICROBIOLOGICAL PETROLEUM ENGINEERING, by Ernest Beerstecher, Jr. (Elsevier Publishing Co. Ltd., London), 1954, xv + 375, price 55*s*.

NOTES & NEWS

Recovery of tin from tinplate scrap

TIN IS USUALLY RECOVERED FROM tinplate scrap either by dissolving out the metal by chlorine and obtaining tin chloride, or dissolving it by treatment with alkali and electrodepositing it from the alkaline solution. A third method, in which tin is obtained as tin oxide, is to treat the scrap with a hot solution of an alkali and precipitate tin from the solution as tin oxide with the help of an oxidizing agent.

In view of the high price of tin *c.* Rs. 9,000 per ton, and the fact that India depends entirely on imported tin, the recovery of metallic tin from tin scrap is important, and methods which yield metallic tin from the scrap should be preferred. Of the above methods, the electrolytic method seems to be best suited for the recovery of tin metal from scrap but it has many disadvantages. The anode material does not dissolve at a sufficiently rapid rate to maintain the concentration of tin salt during electrolysis, absorption of carbon dioxide by the alkali hinders the formation of alkali stannate and the slimy deposit of tin formed is difficult to work up. In view of these drawbacks, attempts were made to employ an electrochemical method for the recovery of tin from scrap. In this method, tin scrap is treated with chlorine and the metal deposited from tin chloride solution electrochemically by means of a metal, such as aluminium, which is more electro-negative than tin. The normal electrode potential of aluminium is 1·24 V. at 25°C. as compared to 0·14 for tin at the same temperature.

The crude tin deposit obtained in this process is a flocculent mass which can be easily skimmed off. The deposit on melting in a crucible, using a cover of ammonium chloride, gave tin metal of high purity (nearly 100 per cent). The recovery of tin from scrap containing 0·6 and 0·86 per cent tin was 86·9 and 83·5 per cent respectively.

In order to verify whether the incomplete recovery of tin from the scrap was due to incomplete reduction of tin chloride by aluminium, a solution containing 11·7 g. of tin and 6·4 g. of iron per litre was treated with aluminium as in the previous experiment. The residual solution after separating the tin deposit was analysed for tin and iron. Analysis of the residual solution showed 0·1 g. tin and 5·8 g. of iron in it. The deposit was melted as before to obtain the metal. The recovery of tin was 82·9 per cent and the purity of melted tin was also nearly 100 per cent. This experiment showed that aluminium brings about almost total reduction of tin salt in the solution and that very little iron was deposited with it. The loss of tin observed in both cases is most probably due to losses during melting of the deposit. Further work on this process is in progress.—B. CHATTERJEE, *Bengal Engineering College, Howrah, West Bengal.*

Anodizing and colouring of aluminium

A NUMBER OF PROCESSES EMPLOYING chromic acid, sulphamic acid, oxalic acid, ortho-phosphoric acid, boric acid, or sulphuric acid are used in commerce for anodizing aluminium. An improved process, based on sulphuric acid process, has been developed in the Applied Mechanics Division of the National Physical Laboratory of India, New Delhi. The process is cheaper and easier to work and gives satisfactory results.

The surface of the article is thoroughly cleaned free from dirt, greese, etc., and suspended in a bath whose temperature is controlled between 80° and 90°F. The article acts as the anode. A suitable lead sheet is used as a cathode. The voltage in the beginning is set at 10 V. d.c. and slowly raised to 14-18 V., where it is kept constant for 20-40 min. till the desired surface is obtained. As a result of a series of experiments, satisfactory operating conditions (TABLE 1) have been found.

The deposit obtained in expt. 1 takes a fast colour in dye solution and the deposit obtained in expt. 4 is most receptive to dye. The film deposits obtained in expts. 3 and 5 are more resistant to corrosion.

After the oxide film has been formed the article is washed thoroughly in clean running water and passed on to the dyeing tank if required or the film is sealed by dipping in hot water.

After anodizing, the article is dipped in a suitable dye solution for *c.* 10-15 min. at 160°-80°F. The *p*H of the solution is kept constant during this period by the addition of acetic acid; for obtaining bright and lustrous films, addition of sodium chloride is recommended. Operating conditions that have been found satisfactory for the dyeing of the films with different dyes are given in Table 2.

TABLE 1

EXPT. No.	ANODE	H_2SO_4 SOLN. %	VOLTAGE V.	TIME min.
1	Aluminium parts	20	15	30-35
2	do	20	17	30-32
3	do	20	18	25-30
4	do	15	14	45-50
5	do	15	18	35-40
6	Aluminium alloy	20	16	25-30
7	do	20	18	20-25

TABLE 2

DYE	CONC. OF DYE g./l.	*p*H OF BATH	TEMP. OF BATH °F.	TIME min.	SHADE OBTAINED
Alimax red	1·0	4·5	175-80	10-15	Crimson red
do	0·5	4·5	170-75	10-15	Light red
Alimax blue	1·0	4·4	160-70	12-15	Light blue
do	2·0	4·4	170-80	15-20	Deep blue
Alimax green	1·5-2·0	4·2	170-75	15-20	Black
do	0·5	4·0	160-75	10-15	Green
Alimax yellow	1·0-2·0	3·8	160-70	12-15	Yellow
Alimax orange	0·5	4·0	160-70	12-15	Orange
Alimax black	1·0	4·0	160-70	12-15	Blue black

After dyeing, the article is washed thoroughly and passed through the setting tank. A 5 per cent solution of nickel chloride at *c.* 200°F. is used for setting. The dyed article is immersed in this solution for 15-20 min. and swilled in water.

The anodized and dyed film on the object so obtained can withstand considerable wear and tear and does not develop cracks during bending, unlike the best enamel coating.

Copper plating and oxidizing

INVESTIGATIONS ON VARIOUS aspects of copper electroplating and oxidizing have been conducted in the Applied Mechanics Division of the National Physical Laboratory of India, New Delhi, with a view to making the practical plater familiar with the techniques of the processes.

In commercial copper plating two types of baths are generally used: the alkaline or cyanide bath and the acid copper bath. One of the successful alkaline bath formulations contained: cupro-cupric sulphite, 4·5 oz.; potassium cyanide, 7·0 oz.; water, 1·0 gal. The best operating conditions were 2-4 V. at a current density of 3-5 amp./sq. ft. at 120°F. Another successful alkaline copper bath formulation contained: copper-cyanide, 4·0-4·5 oz.; potassium cyanide, 5·5-6·0 oz.; sodium carbonate, 0·75-1·0 oz.; water, 1·0 gal. Optimum operating conditions were 3-4 V. at a current density of 5-10 amp./sq. ft. and a temperature of 90°F.

The cyanide baths are generally unstable and the more so at higher temperature, hence great care should be taken to maintain the bath at as low a temperature as possible. The accurate control of free cyanide content of the bath is very important. Blistering of the deposits noticed sometimes can be minimized by swilling the article in cold and boiling water alternately, or by heating the article to *c.* 130°-50°C. and quenching in water while still hot.

The main constituents of an acid copper bath developed are: copper sulphate, 28-32 oz.; sulphuric acid, 6-8 oz.; and water, 1·0 gal. Other addition agents were added according to the plating rate and the type of deposit required. Addition of glue (0·25-0·35 oz./gal.) gives smooth and fine grained deposits; phenol (0·15 - 0·20 oz./gal.) gives hard and smooth deposits useful in electro-typing; and thiourea (0·0015-0·0025 oz./gal.) and molasses (0·10-0·15 oz./gal.) give soft and semi-bright deposits which can be buffed to a bright surface.

The solution is somewhat susceptible to organic impurities and care should be taken to prevent the contamination of arsenic salts, because rough, brittle deposits are produced with black or brown streaks. The free acid content of the bath should be accurately checked.

The oxidizing process involves the production of a film of sulphide on copper plated articles. Oxidizing salts are mostly imported at present. A new oxidizing salt, successfully developed in the laboratory consisted of sulphur, 38-42 parts; potassium hydroxide, 20-25 parts; and sodium hydroxide, 30-40 parts. Sulphur is melted in a crucible and the mixture of potassium and sodium hydroxides is added slowly with stirring. When effervascence starts heating is slowed down and after some time flowers of sulphur are formed with evolution of heat. It is cooled and stored in airtight bottle. The efficiency of the salt deteriorates on keeping.

For oxidizing, fresh solution is made by dissolving 1-2 oz. of the oxidizing salt in 1 gal. of water. The article after plating and swilling is dipped in the solution at 100°-120°F. After a few minutes when it attains blue black colour, the article is taken out, swilled and relieved wherever necessary and lacquered. The finish obtained compared favourably with that obtained with imported brands of oxidizing salts as regards appearance, lustre, adhesion to the metal and adhesion of the lacquer to the oxidized surface.

A substitute for " Easy Flo " silver solder

SILVER SOLDERS ARE USED FOR joining fine instrument parts. In order to fill up small fillets and minute crevices, the solders should have low melting point and good flow characteristics. A variety of silver solders are available commercially but few of them have these properties. The commercial solder " Easy Flo " which is imported is expensive. Investigations were, therefore, carried out in the Applied Mechanics Division of the National Physical Laboratory of India, New Delhi, to develop solders having the desirable qualities. As a result of these studies two grades of solders were developed for use with ferrous and non-ferrous metals and alloys:

(1) Silver 50 parts, copper 24-26 parts, zinc 18-20 parts and tin 5-7 parts; this solder is suitable for use with ferrous and non-ferrous metals and alloys; and

(2) Silver 50 parts, copper 22-24 parts, zinc 18-20 parts, tin 4-6 parts and phosphorous 0·5-2·0 parts for use with non-ferrous metals and alloys.

These solders melt at *c.* 635°C. and their flow point is 645°C. They are ductile at *c.* 120°C. and hence can be made in all the common forms such as thin sheets, wires, strips, etc. The proprietary materials available in the market are mostly imported ones and contain cadmium which is not produced in this country while the metals used in these solders are available in plenty.

The low melting point and flow temperature of these solders reduce the danger of warping of the work piece during welding. It is not affected much by thermal changes and its strength and ductility are very slightly reduced during welding. The joints obtained are strong and leak-proof. The manufacture of these solders does not involve any complicated equipment which can be prepared in any workshop. The cost of the solder works out to *c.* Rs. 30 or less per pound whereas the imported solder costs *c.* Rs. 75 a pound.

Extraction of sugarcane wax

ATTEMPTS HAVE BEEN MADE FROM time to time in India to work out a process for the commercial extraction of sugarcane wax from sugar factory press mud. The only sugar factory in India extracting cane wax from press mud on a commercial scale is at Ravolgon, Bombay State.

Work on the large scale extraction of cane wax was initiated in 1939, by Dr. M. Narasinga Rao and co-workers in the Chemical Technology Laboratories, Andhra University. The work now in progress in these laboratories, under the direction of Dr. M. Narasinga Rao, relates to the design of a commercial extractor for recovering sugarcane wax from press mud. As a preliminary step, the study of solvent flow through a bed of press mud of known particle size range has been undertaken.

A weighed quantity of press mud was extracted with carbon tetrachloride when 9 per cent wax (iod. val., 58·6; sap. val., 173·2) on the weight of press mud was obtained. A glass percolator (1¾ in. diam.) was packed with dried and powdered press mud (particle size range, 3/8-3/16 in.) by random dense method. A simple device developed in this laboratory was used to feed the solvent at constant rate from the top of the percolator. The bed was maintained at the required temperature by means of an electrical heating coil outside the percolator.

Carbon tetrachloride was fed at a known rate and the percolate was collected in 50 cc. batches. The time for collecting each batch and the viscosity and specific gravity of the extracts were determined. The solvent was evaporated and the wax left over was weighed and analysed for its iodine and saponification values.

In one experiment, the extraction was carried out in two stages. Press mud (200 g.) was extracted at a temperature of 37°C. and a solvent flow rate of 4·5 cc./min. Six samples of 50 cc. each were collected. The temperature of extraction was then raised to 55°C. keeping the flow rate constant, and 6 more samples were collected. In another experiment the extraction was carried out throughout at 55°C. The residual cake in each case was analysed for its wax content by extracting it repeatedly with carbon tetrachloride.

The results obtained in these studies show that the wax extracts in the two stages of the first experiment differ in specific gravity and viscosity. The specific gravity of the extracts in the first 6 batches was greater than that of the extracts in the second 6 batches. The viscosity of the extracts in the second 6 batches was greater than that of the first 6 batches. The iodine values of the first 6 batches was higher than that of the second lot indicating that most of the unsaturated constituents (in this case oleic acid portion of the oil fraction) in the total waxy matter are preferentially extracted first. The wax obtained in the second lot of extracts had a higher melting point indicating a partial separation of true wax from oil. The viscosities and densities of the extracts were used as guides for correlating the pressure drop and hence the solvent flow conditions through the bed of press mud.

In this type of extraction — extraction under conditions which vary continuously — the wax content of the extract and the press mud and the composition of the wax at each stage vary continuously and affect the flow rate of the solvent through the bed of press mud.

Further investigations on these aspects as well as the correlation of the results obtained for the purpose of commercial extractor design are in progress.— K. R. K. SARMA, K. SATYANANDA RAO, V. SUBBA RAO & C. VENKATESWARLU *Chemical Technology Laboratories, Andhra University, Waltair.*

Storage of *Kamala* Seeds

Kamala SEEDS WHICH CONTAIN A drying oil should be stored properly in order to prevent their deterioration and spoilage of the oil contained in them. The work described in this note reports the results of studies on the effect of storing fresh *Kamala* (*Mallotus philippinensis*) seeds for a period of one year on the oil contained in them. The results have shown that the seeds can be stored in tins or gunny bags without much deterioration for 6 months.

Fresh and sound *kamala* seeds were packed in tin containers and in small gunny bags (12 in. × 6 in.). The weight of seeds packed in each tin or bag was 650 g. The tins were filled to their capacity with this quantity of seeds. The tins and bags were stored in a well-ventilated room. During storage, the temperature of the room varied between 20°-35°C. and the relative humidity between 25-80 per cent. The seeds were stored for different intervals in tins and bags, and their physical condition noted at the end of every 2 months. The condition of the seed kernels was also noted. Seeds (100 g.) of fresh as well as stored samples, were crushed and extracted with ether in a Soxhlet apparatus and the extracted oil was examined for its acid[1] and saponification values and kamlolenic acid content[1].

The seeds stored in bags were mouldy after 2 months storage. The seed kernels, which are white in the fresh seed, turn brown after 6 months storage. The percentage of seeds, which turned brown after 12 months storage was 30-35. Seeds stored in tins were free from mould growth but a few small reddish brown insects made their appearance after 8 months storage. About 20 per cent of the seeds were found damaged by the insects after 12 months storage, but a few of the seed kernels were found to have turned brown after 6 months storage.

There was no appreciable loss in the oil content of the seeds stored in bags and tins. The oil content of fresh seeds and of seeds stored in bags and tins after 12 months storage being 37·6, 36·5 and 35·6 per cent respectively.

The acid value of the oil obtained from the seeds gradually increases on storage. It is somewhat more in the case of seeds stored in bags and less in the case of those stored in tins. The acid values of oil from fresh seeds and from seeds stored in bags and tins for 6 and 12 months were 12·1, 14·8 and 15·3; and 12·1, 16·9 and 13·4 respectively.

No appreciable variation was observed in the saponification values of oil from fresh seeds and stored seeds. The values for oil from fresh seeds and from seeds stored in bags and tins for 12 months were 198·5, 198·9 and 197·0 respectively.

The kamlolenic acid content of the oil from the seeds was observed to fall gradually on storage. It is more in the case of seeds stored in bags than for those stored in tins. The values for fresh seed and seed stored for 6 and 12 months in bags and tins were 64·6, 57·2 and 56·2; and 64·6, 54·1 and 58·0 per cent respectively.

The results show that *Kamala* seeds can be stored in gunny bags or tins without undergoing appreciable deterioration for about 6 months. The seeds stored in bags deteriorate more quickly than those stored in tins.

The authors are thankful to Mr. I. M. Qureshi, Silviculturist, Bombay State, for the supply of fresh *kamala* seed. They are also grateful to the Indian Meteorological Department, Poona for supplying relative humidity data for the period the work was in progress. S. C. GUPTA & J. S. AGGARWAL, *National Chemical Laboratory of India, Poona.*

---

1. GUPTA, S. C., GUPTA, S. S. & AGGARWAL, J. S., *J. Amer. Oil chem. Soc.*, **31** (1954), 287.

New phosphate minerals

TWO MORE NEW PHOSPHATE MINERALS — tavorite and barbosalite — have been discovered in the Sapucaia pegmatite mine in Minas Gerais, Brazil. Three other minerals, recently described in the mineralogical literature, were named frondelite, faheyite, and moraesite. Tavorite and barbosalite are intimately intergrown secondary phosphate minerals that occur with many other phosphate minerals in the pegmatite.

Tavorite is a hydrous lithium ferric phosphate, the ferric analogue of montebrasite with which it is isostructural. The mineral occurs as a yellow, very fine grained aggregate with a mean index of refraction of 1·807 and a specific gravity of 3·29. The chemical analysis shows the following percentages: Li_2O, 7·64; FeO, 2·39; MnO, 1·47; Fe_2O_3, 42·57; P_2O_5, 39·78; H_2O+, 5·76; and H_2O-, 0·40. The formula, as derived from the chemical analysis, is $(Li_{0·90}, Fe^{II}_{0·06}, Mn^{II}_{0·04}) Fe^{III}_{0·94}(PO_4)_{0·99} (OH)_{1·13}$ as compared with the ideal formula $LiFe(PO_4)(OH)$. X-ray powder data show principal d-spacings at 3·045, 3·285, 4·99, 4·68 and 2·474A.

Barbosalite is a hydrous ferrous ferric phosphate, the ferric analogue of scorzalite. The mineral occurs in black, nearly opaque grains and masses that may be very fine-grained aggregates. Thin grain edges are dark blue green with evident pleochroism. The apparent mean index of refraction is 1·810, and the specific gravity is 3·60. The chemical analysis, recalculated to 100 per cent after subtracting admixed tavorite, is FeO, 13·12; MnO, 2·82; Fe_2O_3, 41·70; P_2O_5, 37·54; and H_2O, 4·92 per cent. Its ideal chemical formula is $Fe^{II}Fe^{III}(PO_4)_2(OH)_2$. X-ray powder data indicate principal d-spacings at 3·361, 3·313, 4·84, 3·239 and 2·327A. The mineral is structurally identical with a synthesized compound described by Gheith as ferrous ferric lazulite and both are closely related to, but have a larger cell size than, scorzalite.

Tavorite and barbosalite are examples of complete substitution of trivalent iron for aluminium in known mineral structures [*Science*, **119** (1954), 739].

Solar battery

A SOLAR BATTERY EMPLOYING A cadmium sulphide crystal has been developed by the Air Research and Development Commands, U.S.A. Electrodes—one of silver and the other of indium—are attached to the opposite sides of the crystal and a motor or battery included in the circuit. A wafer thin scale (4 × 15 ft.) fitted into the roof of a house can supply enough current to operate lights and all other electrical appliances of an average house. In the experimental model, an $\frac{1}{8}$ in. contact area produced current $\frac{1}{3}$ V. [*Science Newsletter*, **65** (1954), 389].

Lead sulphide cell

A NEW PHOTOCONDUCTIVE LEAD sulphide type cell (61SV), introduced by Mullard Ltd., is characterized by extreme sensitivity to infra-red radiation, a high speed of response, a high signal to noise ratio, small size and robustness. It is capable of detecting very small temperature variations in low temperature sources down to 100°C. situated at distances of 100 yd. or more and can, therefore, be used for controlling and monitoring the work in radio-frequency heating and similar industrial set-ups where the detection of temperature or temperature changes without actual contact with the work is required. Another application of the cell is in the monitoring of gas, oil-fired and pulverized fuel furnaces, where it is used to follow the temperature fluctuations rather than the luminosity of the flame. It can also be used in burglar alarms, infra-red telephony, industrial and astronomical spectroscopy, gas analysis and rapid measurement of humidity [*Chem. Age*, **70** (1954), 1112].

Ionic pump

A SIMPLE AIR PUMP WITH NO moving parts and which can produce a vacuum as high as one billionth of normal atmospheric pressure has been developed by scientists at the General Electric. The pump, which is known as ionic pump, may eventually simplify exhaustion of radio tubes and other vacuum tubes. Streams of oil or mercury vapour employed in other type of pumps are not required in this pump.

One form of the pump consists of a circular stainless steel box, about 2 in. in diam. and 1 in. thick. The box is supported between the poles of a powerful Alnico permanent magnet, and is connected by means of a tube to the vessel from which gas is to be exhausted. Inside the box is a tungsten ring, connected to the positively charged side of the high-voltage circuit which supplies the pump. The metal walls of the box are connected to the negative side of the circuit. Sides of the pump are lined with carbon plates.

Exhaustion of air to *c.* 0·0001 atm. is accomplished with an ordinary mechanical pump. Then the ionic pump is connected to the vessel and exhaustion continued. Electrical forces break up the gas atoms into ions of positive charges which are attracted towards the negatively charged pump walls. On the way they are absorbed by the carbon plates and the desired vacuum is reached. The absorbed gases can be driven out of the carbon by simply heating the whole pump. The ionic pump works on practically all gases and it could be used for pumping out all systems where a high vacuum is desired [*J. Franklin Inst.*, **257** (1954), 527].

Colour X-ray photographs

A SYSTEM FOR TAKING COLOUR X-ray photographs is described which is based on the fact that different materials absorb X-rays differently. The colour X-ray photographs show more detail than those obtained by ordinary X-rays. By taking three ordinary X-ray pictures of a part of the body, each time using a different wavelength, and then combining these pictures by projecting them through different coloured filters, a single multicoloured image or photographic print results.

In locating a given element in a body, the body is alternately X-rayed by frequencies slightly higher and lower than the characteristic absorption of the element. The difference in intensity is essentially a measure of the element alone. A typical application would be the use of an iodine tracer inserted in the body to map out a particular organ. In ordinary X-ray pictures, the blackening from the tracer might not be noticeably different from that of the surrounding body, but the colour pictures would show it up [*J. Franklin Inst.*, **257** (1954), 531].

A new peroxy acid

PEROXYTRIFLUOROACETIC ACID, the most reactive peroxy acid known, has been synthesized by adding trifluoroacetic anhydride to 90 per cent hydrogen peroxide in a chlorinated solvent (methylene chloride, chloroform, ethylene dichloride, etc.). Peroxytrifluoroacetic acid is used for the oxidizing conversion of olefines to α-glycols, anilines to nitrobenzenes, and nitrosoamines to nitramines.

In olefine oxidations, the resulting hydroxytrifluoroacetates are hydrolysed by methanolysis to α-glycols. Thus, 1-pentene gives 1, 2-pentanediol (77 per cent); cyclohexane gives *trans*-1, 2-cyclohexanediol (82 per cent). In addition to obtaining good yields, another advantage is that reactions are carried out under essentially anhydrous conditions, permitting ready isolation of water-soluble glycols. This peroxy acid is about the only method available for oxidizing nitrosoamines to nitramines. Yields are nearly quantitative. In aniline oxidations, yields are likewise high [*Industr. Engng. Chem.*, **46** (1954), 17A].

Flame-proofing of fabrics

TETRAKIS (HYDROXYMETHYL) phosphonium chloride (THPC), $(HOCH_2)_4PCl$, in combination with a few chemicals, has been found to impart permanent flame resistance to cotton fabrics. THPC is produced by the reaction of phosphine with formaldehyde and hydrochloric acid. The THPC treatment offers, among other advantages, compatibility with water-repellency treatments. The latter may be applied after treating, or may be incorporated into the processing solution and applied in one padding and curing operation. After 15 typical launderings, little or no loss occurs, and the fabric will pass the standard vertical flame test. Materials treated with THPC solutions are also glow-proof.

THPC reduces the tear strength of fabrics somewhat, but application of a softener restores the tear strength of many fabrics about equal to that of untreated goods. In some cases tear strength has even been improved by this combined treatment. Fabrics treated with THPC resins show improved crease resistance. The same treatment imparts considerable resistance to shrinkage. It also makes the fabric mildew or rot resistant. Samples of THPC-treated fabrics buried in the soil retained 85 per cent breaking strength after 112 days exposure; untreated specimens retained only 3 per cent strength after 10 days.

A typical resin-forming solution contains 15·8 per cent THPC, 9·5 per cent trimethylolmelamine, 9·9 per cent urea and 3·0 per cent triethanolamine. During polymerization, hydrochloric acid is split out of the THPC molecule. Urea is employed in the formulation primarily to tie up this free acid, to protect the cotton from acid tendering. Some of the urea reacts with THPC to become part of the polymer, some of it decomposes during the curing process. Triethanolamine stabilizes the solution. Fabrics may be processed on a continuous basis, or they may be treated batchwise. In either case they are first padded in the resin-forming solution (passed through an oversized wringer roll) and then dried promptly at *c.* 185°F. The fabric then goes through a series of processes which include curing, washing, softening and final drying.

The degree of flame resistance depends on the amount of resin put into the fabric, and on fabric construction. For most purposes, a resin pick-up of 10-20 per cent by weight is adequate [*Industr. Engng. Chem.*, **46** (1954), 15A].

Production of vitamin B_{12}

INVESTIGATIONS CARRIED OUT TO determine suitable operating conditions for the industrial production and recovery of vitamin B_{12} produced by the fermentation of a satisfactory substrate by *Streptomyces olivaceus*, NRRL B-1125, are described.

Satisfactory yields of vitamin B_{12} are obtained in aerated and agitated, submerged-culture fermentations of a medium containing 4·0 per cent of a mixture of distillers' solubles and extracted unheated soyabean meal, 1·0 per cent dextrose, 0·5 per cent calcium carbonate, 0·1 per cent soyabean oil or other suitable antifoam agent, and cobalt chloride ($CoCl_2.6H_2O$) at a concentration of 2-10 p.p.m. The medium may be sterilized batchwise in steel or stainless steel vessels by maintaining it for 1-2 hr. at a temperature of 250°F., or continuously at 325°F. with a retention time of 13 min.

Inoculum for the fermentation is prepared from medium containing 0·5 per cent steep liquor solids, 0·5 per cent dextrose, and 0·1 per cent soyabean oil or other suitable antifoam agent. This medium is batch-sterilized at 250°F. for 1 hr. at *p*H 7·0 and inoculated with 1-2 per cent by volume of a culture of *S. olivaceus*. The seed culture is aerated for 48 hr. at 80°-85°F.

The sterile medium in the production fermentor is inoculated with 5 per cent by volume of seed culture. Vigorous mechanical agitation is employed and sterile air at the rate of $\frac{1}{4}$-$\frac{1}{2}$ volume per minute per volume of medium is passed through the medium. The temperature of the fermenting medium is controlled at the range of 78°-82°F. After 72 hr. the *p*H of the liquor is reduced to 5·0 with sulphuric acid, and 100 p.p.m. of sodium sulphite is added. The liquor is then evaporated to a syrup of 20-25 per cent solids content at 150°F. or below. The syrup is then drum dried, using steam pressures varying from 20 to 60 lb./sq. in. gauge.

Vitamin B_{12} concentrates produced by this process are estimated to cost 2·7 cents/mg. of vitamin [*Industr. Engng. Chem.*, **46** (1954), 843].

Production of fatty alcohols

THE NEW HIGH PRESSURE HYDROGENATION plant of Marchon Products Ltd., Whitehaven, England, which has recently gone on stream, has been designed for maximum flexibility and can make fatty alcohols from vegetable oils, tallow, fatty acids, or fatty acid esters. The plant, which runs as a continuous unit, can conveniently be divided into five main sections, each of which can be operated separately.

The first section is concerned with the manufacture of the copper chromite catalyst and hydrogen is produced in the second section. In the third section, the fatty acid esters are manufactured by reacting together fatty alcohols and fatty acids.

Hydrogenation of the esters is carried out in the fourth section. The esters are mixed with requisite amount of catalyst to form a paste. This paste is pumped by special pumps at a pressure of 4,000-5,000 lb./sq. in. into stainless steel lined autoclaves. Hydrogen in excess, compressed to the same pressure, is fed with the ester into the autoclaves and the reaction converting the ester into fatty alcohols takes place at around 300°C. The excess hydrogen is then separated off in a high-pressure separator, cleaned, recompressed, and recycled to the incoming hydrogen stream. The mixture of fatty alcohol and catalyst is reduced to atmospheric pressure. The catalyst is removed by filter pressing and the crude clean lauryl alcohol pumped to intermediate storage tanks. About 90 per cent of the recovered catalyst is recycled.

In the fifth section, the crude alcohols pass to a fractionating column which consists of a boiler and distillation tower packed with rings. The fractionating tower is so designed that it can produce any specific fatty alcohol of over 99 per cent purity. Half the final product alcohol then goes back to the ester plant for the production of the initial ester, the other half going to the aluminium storage tanks [*Chem. Ind.*, (1954), 775].

Rice enrichment

IN RECENT YEARS INCREASING attention is being paid to developing methods for conserving or improving the nutritional value of rice while, at the same time, retaining the characteristics which render it acceptable to the majority of rice consumers.

The artificial enrichment of rice with selected minerals and synthetic vitamins raised problems not encountered in the enrichment of wheat flour and bread, owing to the discrete nature of the rice grain and the usual procedures for washing and cooking rice prior to consumption. A method of rice enrichment, which was designed to overcome these problems and which has been introduced into the Philippines, was developed by Messrs Hoffman-La-Roche of Basle, Switzerland, and Nutley, N.J., U.S.A.

Manufacture of enriched rice " premix " — The process of manufacture is as follows: Highly milled (white) rice of good quality is used for the preparation of " premix ". The raw materials needed for the manufacture of " premix " are: thiamine hydrochloride, niacin, sulphuric acid, corn syrup, iron pyrophosphate, talc, corn protein, distilled pine resin, stearic or palmitic acid, and ethyl alcohol. Suitable concentrated solutions of thiamine and niacin are prepared, according to the concentration required in the premix, and the correct volume of the mixed solutions is sprayed through a perforated pipe on to the rice as it is slowly rotated in a trumbol. After the last traces of vitamin solution have been blown out of the pipe by compressed air, the rice, which has absorbed the vitamin solution, is dried by passing warm air into the trumbol. When the rice is dry, half the total quantity of coating solution is sprayed on the rice which is again dried. A weighed quantity of finely powdered iron pyrophosphate is then thoroughly mixed with the rice, and the remainder of the coating solution is sprayed on and the rice again dried. The coating solution consists of a solution of zein and fatty acid (palmitic or stearic acid) and pine resin dissolved in alcohol. After the coating has been applied and the rice is dried, the finished product, now known as Premix Rice, is discharged from the trumbol and packed in suitable bags. For consumption, one part of " premix " is mixed with 199 parts of ordinary rice. The mixture, known as enriched rice, contains per lb. 2·0, 16·0 and 13·0 mg. of thiamine, niacin and iron respectively. Since the protective coating, which is insoluble in cold water, is applied to the grains after the addition of nutrients, the latter are protected from being dissolved out while washing. Thus, while washing losses of thiamine from highly milled rice vary from 27·9 to 63 per cent, those from " premix " are 7·9-18 per cent only.

Cost of enriched rice — The cost of " premix " is estimated at 64 cents per kilo and the cost of enrichment works out to about 44 cents per kilo excluding the cost of rice. The cost of vitamins and chemicals represents about 47 per cent of this or about 20 cents per kilo. The cost of enrichment per caput per annum in the Philippines has been estimated at 42 cents and excluding the rice base, 29 cents per caput. In practice the cost becomes a little higher if the price charged by the mills for adding premix to rice is considered.

Cost of plant — The cost of the premix plant owned by National Rice & Corn Corporation is estimated at $ 21,737 including the cost of installation. The operating capital necessary for this plant is estimated at $ 138,000.

On the basis of 300 working days, each of one single 8-hr. shift, the plant will produce 680,396 kg. of premix per annum. This quantity of premix is sufficient to enrich rice for 1·04 million people, on the assumption that the intake is 131·4 kg. of rice per caput per annum. An increase in production could be achieved without difficulty by running two or even three 8-hr. shifts during each 24 hr. Continuous operation over the 24 hr. would give an output of just over two million kilograms of premix per annum (300 working days).

Clinical findings — Premix was introduced on an experimental scale in seven municipalities on the Manila Bay side of Bataan Province in the Philippines in 1948, and on a commercial basis in 1951. The benefit accruing from this experiment has been assessed by comparing statistics from three surveys undertaken by W.H.O. and F.A.O. in 1948, 1950 and 1952 which include information on diet of normal subjects and beriberi patients, and clinical examination of patients. Biochemical results obtained from blood specimens of persons examined in 1948 and re-examined in 1950 are shown in Table 1.

The increase in mean value of haemoglobin, whole blood thiamine, and urinary thiamine excretion in 1950 as compared with the 1948 figures indicates an increase

TABLE 1

	1948 MEAN	1950 MEAN	DIFFERENCE
Haemoglobin, g./100 cc.	10·9	12·9	+2·0
Blood thiamine, μg./100 cc.	3·5	4·3	+0·8
Serum protein, g./100 g.	6·7	6·8	+0·1
Serum ascorbic acid, mg./100 cc.	0·49	0·4	−0·01
Serum vitamin A, μg./100 cc.	42·3	35·0	−7·3
Serum carotene, μg./100 cc.	48·4	74·0	+26·6
Urinary thiamine, μg./g. creatinine	0·65	253·0	+188·0

in the dietary intake of iron and thiamine which can be associated with the consumption of enriched rice during the period between the surveys.

Beriberi mortality rate also showed a marked drop of about 50 per cent in 1949 and 1950 (*Rice Enrichment in the Philippines, F.A.O. Nutritional Studies, No.* 12, 1954).

Gas-liquid chromatography

A NEWLY DEVELOPED GAS-LIQUID chromatographic apparatus enables a complete analysis of, say, motor spirit in *c.* 3 hr., whereas the same separation by the normal fractional distillation procedure takes three weeks. The speed and efficiency of this method make it more convenient than fractional distillation method and more foolproof and reliable than infra-red spectroscopy.

Two columns packed with kieselguhr are used in the apparatus: one is loaded with 0·5 mg. of the liquid to be analysed, and the other is for the balance. Both are enclosed in a thermostatically controlled jacket, and pure dry nitrogen is passed down both columns at an equal and steady rate. Analysis of the constituents as they emerge from the bottom of the column takes place in an ingenious density meter. It is in the form of a balanced bridge, the nitrogen stream from each column being divided into two in the channels of a Perspex block. Between the two halves of the bridge is a chamber in which an electrically heated element radiates heat equally on to two sensitive thermocouples. When a very slight difference in density occurs between two nitrogen streams, there will be a slight displacement through the detector chamber and the amount of heat falling on the two thermocouples will no longer be equal. By attaching these thermocouples to an ordinary pen recorder, it is possible to obtain a plot resembling those obtained by liquid-liquid chromatography or electrophoretic separation. As with these, each peak is specific, and the area under the peak is directly proportional to the quantity of substance present in the mixture.

The sensitivity of the instrument is remarkably high: 0·06 μg. of amyl alcohol can be detected per ml. of nitrogen — 1 part in 10,000.

Of particular importance is the fact that the nature of a substance can be deduced by the rate at which it passes through the column. Thus in plots of retention time against number of C atoms, homologues lie along a straight line; the higher the degree of chain-branching, the lower the retention time; and if figures for two different stationary phases are compared, it is possible to obtain a very good idea of the composition and structure of an unknown substance [*Chem. Age,* **70** (1954), 1193].

Gas chromatography

GAS CHROMATOGRAPHY, A NEW technique developed, has been employed in the analysis of volatile substances. Partition of the volatile substances is effected between a gas and a liquid which is adsorbed upon a substance such as charcoal or kieselguhr. The apparatus consists of an adsorption column of narrow bore tubing packed with kieselguhr saturated with a non-volatile liquid (dinonyl phthalate). The tube is surrounded by a vapour jacket so that the column may be maintained at a convenient temperature and the sample, which may be as small as 0·01 cc., added to the top of the column through a rubber serum cap from a micrometer syringe. The sample is carried through the column by a controlled stream of oxygen-free nitrogen, separating into zones as it passes. On emergence from the end of the column it is fed to a detector. This may utilize any one of the properties of the vapour-saturated nitrogen stream; the method which has been developed most successfully so far, uses thermal conductivity. The nitrogen gas passes a controlling manometer, a small rotameter and one side of a thermal conductivity cell before reaching the column. Upon leaving it the gas is returned to the other side of the cell which consists of two electrically heated platinum wires passing axially through holes drilled in a nickel block. The wires form two arms of a Wheatstone bridge and the out-of-balance voltage from the network is amplified and used to drive a pen recorder.

The process is controlled by adjusting the temperature of the vapour jacket which should be high enough to permit the complete passage of the sample within a reasonable time, but not too high so that the separation of the most volatile components is impaired. The record appears as a continuous line, peaks in the height of this line form the time axis corresponding to separate constituents of the mixture. The concentration of each component is indicated to an accuracy of ±1 per cent by the height of the peaks.

Detection by the thermal conductivity cell has the disadvantage of inability to separate components having similar adsorption properties and thermal conductivities and being unsuitable for the detection of labile substances owing to the necessity of employing heated wires [*Chem. Prod.,* **17** (1954), 237].

Determination of ammonium and potassium

THE MAIN INTERFERING IONS IN the determination of potassium by precipitation as potassium tetraphenylboron are caesium, rubidium and ammonium. Caesium and rubidium are likely to be present only in special cases, but ammonium and potassium are often found together in analytical operations. The methods so far in use for their individual determination are either time-consuming or expensive. A new method for the simultaneous determination of ammonium and potassium has been developed based on the reaction of ammonium salts with formaldehyde. The precipitation is effected in the presence of a good excess of formaldehyde and alkali.

The solution containing *c.* 10-20 mg. of potassium is neutralized to methyl-red indicator and treated with 10 cc. of 30 per cent formaldehyde which has been neutralized with 0·05N sodium hydroxide to a phenolphthalein end point. The liberated acid is then titrated with 0·05N sodium hydroxide in the usual way; 1 ml. 0·05N sodium hydroxide = 0·902 mg. of NH_4.

To the test solution, requisite amount of formaldehyde is added so that its concentration in the solution is 2·0-2·5 ml. per mg. of ammonium ion present. Sodium hydroxide is then added until the alkalinity of the solution is *c.* 1N. The solution is next heated to the boiling point and then a 0·2 per cent solution of the reagent (tetraphenylboron) is added dropwise with constant stirring. The precipitate appears after a few ml. of reagent have been added; after cooling it is filtered off and washed first with a saturated aqueous solution of the potassium salt, and then with a little water. The filter paper and precipitate are returned to the same beaker and acetone is added (*c*. 20-25 ml. of acetone for *c*. 20 mg. of potassium).

After adding 1-2 ml. of 2N acetic acid, 1 ml. of 0·1N potassium bromide solution and 2 drops of eosin solution, titration is carried out with 0·05N silver nitrate. Near the end of the titration the filter paper is stirred well with a glass rod.

From the total amount of silver nitrate consumed the amount of potassium bromide added is deducted; 1 ml. of 0·05N silver nitrate = 1·955 mg. of potassium [*Industr. Chem.*, **30** (1954), 348].

Measurement of radio isotopes in tissues

A NEW METHOD IS DESCRIBED FOR the measurement of radio isotopes (both β and γ emitting) in tissues in which rapid disintegration of entire organs of moderate-sized animals and of entire bodies of smaller species is possible. Formamid, when added to freshly prepared homogenates of the tissues, gives a clear colloidal solution even at room temperature. This solution is rapidly liquid-counted at infinite thickness employing the end-window Geiger counter.

Tissues or whole animals are first broken in a Waring blendor and an aliquot passed through Potter-Elvehjem homogenizer. Ten cc. samples of the homogenate are poured into volumetric flasks, an equal volume of formamid added, and measurements taken in 30 cc. beakers at constant distance from the counting tube. An inexpensive and portable rate meter, such as the 1615B, serves adequately and the direct readings facilitate the running of a large number of samples. A duplicate sample of the colloid prepared in water serves as the standard for all measurements.

Standard deviations from average calculated values were ±2·2 per cent for P^{32}, ±1·9 per cent for Y^{90} and ±3·1 per cent for Au^{198} [*Science*, **119** (1954), 739].

Rapid screw-thread pitch measurement

A TECHNIQUE RECENTLY DEVeloped at the U.S. National Bureau of Standards has proved satisfactory for rapid and accurate measurement of the lead of both straight-thread and tapered ring gauges. The new technique makes use of a device consisting of an adjustable sine plate on which the gauge to be tested is mounted, and a carriage which travels on accurately machined ways to move a ball-point probe in and out of the mounted gauge. The lead determination involves measurement of the movement of the carriage through the use of a glass scale graduated in increments of 0·050 in. over a range of 4 in. The glass scale moves with the carriage, and the position of the scale is observed with a microscope having four reticle graduations, each equivalent to 0·01 in. on the scale. A scale graduation is brought into apparent coincidence with the nearest reticle graduation by rotating a plane parallel plate of optical glass in the optical path of the microscope. This parallel plate constitutes a kind of " optical micrometer ", that is, the shaft on which it rotates carries a graduated drum having 200 divisions for each 0·01 in. of apparent motion of a scale graduation. This gives a least reading of 0·00005 in. and permits estimation of fifths of divisions. The scale is accurate to ±0·00002 in. in 1 in. and ±0·00004 in. in 4 in. [*J. Franklin Inst.*, **257** (1954), 492].

New recording thermo-balance

A NEW RECORDING THERMO-balance, air-damped and suitable for a total load of 100 g. is described. For " thermo " work the balance is surmounted by a bifilar nichrome-wound furnace of 2 in. internal bore which is silica-lined and arranged with a removable top. The furnace is designed for use with an inner silica sheath when it is desired to heat the charge in a gas atmosphere. It is counterbalanced with its own low voltage transformer and may be raised or lowered over the charge. Its position above the balance renders convection currents inoffensive and the provision of heat radiation shields between the furnace and balance makes the effect of stray radiation negligible. Its bifilar winding prevents field effects when magnetic or conductive materials are heated. Built-in P.A.M. temperature controller is provided and programme control can be fitted if required.

The object to be tested may be placed on either the lower pan or on a silica platform located in the furnace and mounted on a silica rod which rises from the top of the rear suspension piece. Furnace temperature and change of weight are followed simultaneously on a twin pen electronic recorder fitted above the balance and in front of the furnace. The curves are thus seen at eye level and are both shown by continuous lines side by side. The twin pens are power driven by servo-motors and receive their information from a platinum-rhodium/platinum thermocouple and a capacity follower plate located over the balance beam. This plate faithfully follows every minute movement of the beam and has no direct or mechanical contact with it. Thus, the balance may be arranged for either 1 mg. sensitivity or for one-tenth mg. sensitivity with the same proportional accuracy of scale. The instrument once set will reproduce and record time, temperature and weight changes for periods up to several days [*Atomics*, **5** (1954), 195].

Tablet disintegration test apparatus

A SIMPLE MECHANICAL DEVICE TO carry out the B.P. tablet disintegration test is described. The apparatus has proved satisfactory for routine use.

The test-tubes in which the disintegration tests are carried out are mounted radially on clips on a rotating disc in a shallow cupboard maintained at 37°C. The cupboard is enclosed by a Perspex panel and the progress of the disintegration can be followed all the time through this observation door. The disc is rotated at a speed which allows the tablets to fall slowly through water and the method of inversion ensures that the tubes turn over evenly and that the tablets are not knocked about.

In use the cupboard is allowed to attain a steady temperature and test-tubes with B. 24 ground glass stoppers containing the tablets are filled with water at 37°C., leaving a small air space. The motor is then switched off, the tubes placed in the clips and the apparatus restarted. The progress of the disintegration can then be followed continuously or a timing clock can warn the operator after any desired interval of time. The results obtained are reproducible and agree with those obtained by manual methods [*J. Pharm. Pharmacol.*, **6** (1954), 496].

Symposium on the River Hooghly

A SYMPOSIUM ON THE RIVER Hooghly was held on 10 July 1954, under the auspices of the Science Club of Calcutta. Dr. N. K. Bose, Director, River Research Institute, West Bengal, was in the chair. Dr. B. C. Roy, the Chief Minister, West Bengal, inaugurated the symposium.

The problems of the River Hooghly which have been causing concern are: (1) increasing salinity of its waters; (2) decreasing navigability; (3) large-scale contamination of its waters due to the growth of industries along the banks of the river; and (4) control of the intake floats in connection with the drinking water supply of the city on account of the strong high and low tides.

These problems led to a careful survey of the River Hooghly. As the Ganges gradually moved out of its original course to further north, the Bhagirathi-Hooghly, which used to carry a great deal of inland water from the Ganges and the rivers above Calcutta, has now ceased to flow. As a result, except for a month or so during the rains, the Hooghly maintains no connection with the Ganges. The silting up of the mouth of the Hooghly from the tides on account of a perennial current of inadequate strength has become a serious problem, both from the point of navigation as well as keeping down the salinity of the waters of the river. Further, much water-logging has occurred in Nadia and Murshidabad districts with great damage to arable lands. Occurrence of sand dunes in Malda by silting has caused the bed of the river to rise higher and higher, with the result that the embankments are submerged on occasions, and the agricultural lands are covered with saline water. For the same reason of preponderance of sand dunes, the tidal rivers of the Sunderbans have been so frequently breaching the protective embankments that it has become very difficult to keep these in repair.

Dr. S. C. Deb dealt with " Sedimentation and Geophysics of the Gangetic Delta ". The area now forming the course of the River Hooghly consisted of an extensive lake or marshy land, into which the rivers like Damodar were discharging their waters and as these boggy lands silted up, drainage channels came into existence. The River Hooghly was probably one of such channels which was subsequently captured by the Ganges after it had broken through the Rajmahal barrier about half a million years ago. A study of the sediments in the area around River Hooghly would provide information on the best way of tackling the problems of the river.

Shri S. P. Sarathy dealt with the navigability of the River Hooghly. The seaward approaches to and from Calcutta are navigable with difficulty and pilotage has now become compulsory. The Hooghly receives upland water supply during the monsoon months but during the rest of the year it depends entirely on the tidal water for navigation. Even for this condition to continue, the channel has got to be kept open to a navigable depth by constant dredging. Maintenance of a perennial head-water supply will check the shrinkage in the volume of water in the upper reaches of the river above Calcutta.

Dr. Hora pointed out that a survey carried out in 1954 revealed that the waters of the River Hooghly were saline up to a distance of 100 miles above Calcutta.

Concluding, Dr. N. K. Bose observed that the proposed Ganga barrage at Farakka alone offered a permanent solution of the problems connected with the River Hooghly. The construction of the barrage would lead to a discharge of 20,000 cusecs of water through the Bhagirathi, making it navigable for vessels of 6 ft. draught up to some distance from Kalna, which forms the tidal limit of the river. The perennial discharge in the river will improve the navigability within the tidal reach. As a result of the discharge, the drainage condition and the consequent fertility of the lands in the area will improve. The barrage will also prevent the flow back of waters from River Hooghly into the low-level main Ganga channel through the upper reaches of the Bhagirathi.

New blast furnace at Tisco

A MODERN BLAST FURNACE WITH A rated capacity of 1,000 tons per day recently went into operation at the Tata Iron & Steel Co. Ltd., Jamshedpur. The furnace, the largest in Asia, has been designed and built in India.

The furnace dimensions are: height, 227 ft. 6 in.; volume, 32,064 cu. ft.; hearth diam., 22 ft. 6 in. The design of top gas offtakes and downcomers is entirely of new type. It is a vertical 4 × 2 × 1 system with 3 bleeder valves at the top. This allows a large area at each point of entry. The downcomers are connected centrally with a 36 ft. diam. dust catcher so as to promote uniform distribution of gas leaving the stock columns and to reduce flue dust loss thereby effecting a saving in coke and consumption of ore per ton of pig iron. A venturi system provided in the hot blast main helps to achieve a uniform temperature of the blast entering the tuyeres.

A pug mill provided under the dust catcher prevents the fine flue dust flying about during dumping.

World Census of Agriculture

THE FIRST OF THE THREE VOLUMES of a World Census of Agriculture compiled by the United Nations Food & Agriculture Organization is expected to be published by the end of 1954. The other two volumes are expected to be out in 1955 and 1956 respectively. The census will cover agricultural statistics for 63·3 per cent of the land surface of the globe (the U.S.S.R. and China excluded) and covers territories inhabited by 67·6 per cent of the world's population.

The first volume of the census will summarize statistical methods used for the census, the second will tabulate the data for each country, and the third will make a comparison of each country's statistics and analyse, on a regional or worldwide basis, the principal elements such as utilization of land, tenure, agricultural workers, crops and stock breeding (*Unesco Features*, 13 August 1954).

A.S.T.M. Annual Meeting

THE 1954 ANNUAL MEETING OF the American Society for Testing Materials was held during 13-18 June at Chicago. Thirty-six technical sessions were held at which were presented 110 technical papers covering various aspects of engineering materials. The proceedings also included 600 meetings of the technical committees. Sixty-five new specifications and tests were approved and revisions in 229 existing tentatives and standards were acted on. This brings the total number of A.S.T.M. Standards to 2,120.

Of the 36 technical sessions held, 12 comprised six symposia on timely material subjects. The balance were devoted to groups of papers on specific subjects or were report sessions. The symposia covered coal sampling; temperature stability of electrical insulating materials; odour; permeability of soils; effect of cyclic heating and stressing on metals at elevated temperatures; and methods of lasting building constructions. Other groups of papers concerned such subjects as testing; bituminous materials; fatigue; soils, effect of temperature; concrete; creep; concrete, cementitious materials; plastics; and impact testing. A special session entitled " What Standards Mean to Us " was also held. The session was in the form of a round table discussion with formal presentation by a prominent panel.

The Marburg Lecture was delivered by Harold F. Dodge (Bell Telephone Laboratories), the subject of the lecture being " Interpretation of Engineering Data ". Francis M. Howell (Aluminium Research Corporation) delivered the Gillet Lecture on " Fatigue of Aluminium ".

Nickel Bulletin

THE JULY-AUGUST ISSUE OF *The Nickel Bulletin*, comprising the double summer number, contains abstracts of technical and patent literature on a wide range of subjects.

The current interest in exploitation of relatively low-grade metal bearing ores is reflected in two reports on extraction of nickel in U.S.A. Other items in the nickel section include investigations of analytical procedure, and the development of nickel cathodes for electronic tubes.

The electrodeposition section refers to reports by the American Electroplaters' Society and the American Society for Testing Materials on exposure tests of plated coatings, and on methods of porosity testing, with special reference to proposed modification of the salt-spray test.

The non-ferrous literature includes a report on the properties of nickel silver strip of various compositions, and details of tentative A.S.T.M. specifications for nickel-tin bronzes.

In the constructional steel field reference is made to review of literature on high-strength, low-alloy steels, to reports on composition and treatment of nickel-containing steels for gudgeon pins, and to hot-working dies of nickel-molybdenum steel.

The section relating to heat and corrosion resisting materials contains a series of papers on the influence of cycling of temperature and load, on the behaviour of materials at high temperature, and reports on the critical evaluation of tests for determination of susceptibility to intercrystalline corrosion, and of methods for identification of sigma phase. Other items of interest in this section relate to the creep properties of copper-nickel alloys; tests on improved materials for superheaters; stress-relief treatment of austenitic welds; nickel-chromium-boron facing alloys, and the use of nickel-clad steel for containers in tanker vessels transporting caustic soda.

The bulletin is supplied free of charge and can be had from the Mond Nickel Co. Ltd., Technical Office, 1 Forbes Street, Fort, Bombay.

Corrosion Technology

THIS NEW PUBLICATION WAS started in March 1954 as a supplement to *Chemical & Process Engineering*, and is now published as a separate journal from June 1954. The journal is intended to give practical and impartial advice on the control and prevention of corrosion in all its forms. Corrosion problems are dealt with under the following heads: Corrosion-resistant plant and equipment; Resistant metals, plastics, rubber, graphite, carbon, ceramics and other materials; Protective coatings and finishes; Corrosion inhibitors; Protective packaging; Metal pre-treatments; Cathodic protection; Engineering and design, etc. Work in the corrosion research laboratories of the world will be surveyed in a special series of articles. In addition, corrosion problems relating to specific industries will be dealt with in articles by experts in those industries.

Inventions in the field of corrosion are regularly reviewed. International progress in the fight against corrosion is reviewed in a separate section " Corrosion Research Round-up ".

The journal is published monthly by the Leonard Hill Technical Group, Stratford House, Eden Street, London N.W.1. The annual subscription is 40*s*.

Announcements

THE FOLLOWING OFFICE-BEARERS have been elected to the *Council of the Geological, Mining and Metallurgical Society of India* for the session 1954-55: *President*, Mr. M. K. Ray (Achipur); *Vice-Presidents*, Mr. J. N. Mukherjee (Calcutta) and Mr. W. B. Metre (Digboi); *Joint Secretaries*, Prof. N. N. Chatterjee (Calcutta) and Prof. N. L. Sharma (Dhanbad); *Treasurer*, Prof. P. C. Datta (Calcutta).

Norman L. Mochel, Manager, Metallurgical Engineering, Westinghouse Electric Corp., was elected President of the American Society for Testing Materials for the year 1954-55.

The 1955 Annual Meeting of the American Society for Testing Materials will be held from 26 June to 1 July in Atlantic City.

INSTRUMENTS AND APPLIANCES

NEW MINIATURE LABORATORY

A compact and portable semi-micro organic unit, comprising 61 components from the Quickfit & Quartz range of interchangeable laboratory glassware has been designed by Norwood Technical Institute, London. The aim is to meet the problem of providing adequate room for laboratory equipment.

The unit is mounted on a wooden stand, the base of which incorporates two drawers containing test-tube racks for spare apparatus and thermometers. The handles, by which the assembly is lifted, are pierced to form additional test-tube racks. All the components on the assembly are fitted to the board by clips and can easily be removed for cleaning.

Among the apparatus contained on the stand is a test pipette for dispensing reagents and for assisting the evaporation of solvents; a reflux apparatus, with water condenser; melting-point apparatus with stirrer; a continuous extractor for solids; a steam distillation unit with special anti-suck-back device; a fractional distillation unit with a simple air-jacketed column, with fraction collectors mounted to slide to and fro; and a vacuum distillation unit, with a three-way fraction collector. On the end of the unit are two Willstatter filters and a Schwinger filter and flasks; ice bath, with ears to support test-tubes; separating funnel and drip tube; and water inlet and outlet for the entire assembly.

The dimensions of the unit are: the components are mounted on a frame 30 × 18 × 8 in. to form 12 process units; and the whole structure weighs a little less than 14 lb. For the purposes of teaching, this size is considered admirable in that it occupies little space but, at the same time, permits an experiment to be carried out fully. Another advantage is that the use of materials is considerably more economic and the possibility of accidents diminished.

Electric Bunsen Burner

An adaptable piece of equipment which will be welcomed by the modern laboratory is the new "Bunray" electric Bunsen burner developed by Shandon Scientific Co., London. This infra-red reflex burner, which can be used in any position — vertically, horizontally or upside down — combines all the advantage of the Bunsen burner with the good features of electrical heating. It eliminates the danger of explosions through faulty gas connections and provides a cleaner and more concentrated heat source. Following the heating up period of approximately one minute, temperatures up to 800° can be reached, and the heating supply can be adjusted by means of an energy regulator, a sliding rheostat or an auto-transformer. The electric Bunsen burner is 6¼ in. high with a heavy cast iron base which carried on short insulators, the socket into which a 340 watt heating element is plugged. This element is protected against spilling or boiling over by a close-fitting, easily removable quartz sleeve.

A number of small accessories are provided to extend the usefulness of the burner. A hot plate attachment consisting of a cast and machined aluminium plate of 4 in. diameter can be fitted directly into the burner top, and the burner can be converted into a furnace by the use of a crucible attachment. The electric Bunsen burner can also be used as an infra-red lamp for evaporating liquids from watch glasses or planchettes, making it particularly effective in laboratories using radioactive isotopes.

Filler for Heavy Paste

A new heavy-paste filler has been designed and produced by Filling Machines Ltd., Glasgow, to handle tough putty-like materials into collapsible tubes. Filling of such products presents an obvious problem because of the nature of the materials involved. A worm-like extruder is used to eject the material to be handled through a protruding tube on to which the operator fits a collapsible tube. The filled container is pushed off the mouth by the force of the extruded material, and is then closed by the operator.

The new filler is specially designed for use in the paint, chemical and allied industries.

A Universal Clarifier

One of the major problems of wet grinding is that of keeping the coolant clean. Since continuous through flow of coolant is uneconomical, settling tanks have been used for clarification. While the clarified coolant is being pumped off from a level above the settled sludge in the tank, turbulence is caused and this prevents continued settling.

In a new system devised by Philips Electrical Ltd., London, the polluted coolant, on leaving the workpiece, flows into a trough of special filtering material carried on an endless wire mesh conveyer. The medium retains all swart and abrasive dust on its surface but is sufficiently porous to permit a continuous flow of filtered coolant into the sump of the clarifier whence it is pumped back to the grinding head.

As the filtering medium becomes clogged, the liquid level above it rises until a float on its surface actuates a micro-switch which causes a movement of the medium and the presentation of a fresh filtering surface to the liquid.

There are four standard models of this type of clarifier having capacities of 500, 1,000, 1,800 and 3,000 gal. per hour. These approximate flow rates are for normal soluble-oil coolants and depend on the stock removed and on the viscosity of the coolant.

In one practical application of this system to a grinding machine on which the coolant was normally in need of complete change every fortnight, it was found that, after installation of the new equipment, the same coolant was suitable for use for three or four months.

B.D.H. Fine Chemicals

The following new organic and inorganic chemicals have been added: 2:4-Dimethoxy benzaldehyde, N-methyl formanilide, sodium tetraphenyl boron, absolute industrial methylated spirit.

Volumetric Glassware

Notes on Applied Science No. 6, *Volumetric Glassware*; *Scientific Aspects of Design & Accuracy*, published by D.S.I.R., London, describes the scientific requirements on which standards for volumetric glassware must be based and sets out the main features of standardization. Special feature of particular instruments are also dealt with.

The booklet includes sections on the basis of graduation, the construction and verification of apparatus and the dependence of volume delivered on delivery procedure.

BIBLIOGRAPHICAL LIST OF PAPERS PUBLISHED IN SOME INDIAN SCIENTIFIC PERIODICALS, AUGUST 1954

CHEMISTRY

Analytical

Badad, J., Pinsky, A. & Sharon, N., Calculation of total solids in milk of cows in Israel by Richmond's formula, *Indian J. Dairy Sci.*, **7** (1954), 98

Datta, S. K. & Banerjee, G., Estimation of thorium by organic reagents. Part II. 2:4-Dichloro-phenoxy- and guaiacoxy-acetic acids, *J. Indian chem. Soc.*, **31** (1954), 397

Deshmukh, G. S. & Joshi, M. K., Determination of thiocyanate by ceric sulphate, *J. Indian chem. Soc.*, **31** (1954), 413

Laxminarayana, H. & Iya, K. K., Tetrazolium reduction test for quality control of milk, *Indian J. Dairy Sci.*, **7** (1954), 83

Mitra, R. P., Gupta, A. R. & Jain, D. V. S., Polarographic and titrimetric study of acidic silver bromide complex, *J. Indian chem. Soc.*, **31** (1954), 346

Saraswathi Devi, L. (Miss), Bioassay of heavy metals by *Aspergillus niger* — sensitivity of a new strain, *Proc. Indian Acad. Sci.*, **40B** (1954), 1

Biological

Mani, G. S., Srinivasan, M. R. & Ray, S. C., Studies on the production of ghee (clarified butterfat) directly from cream. Part II. The qualitative factors in cream affecting its washability for reduction of serum-solids, *Indian J. Dairy Sci.*, **7** (1954), 69

Narayanan, K. M., Shroff, N. B., Anantakrishnan, C. P. & Sen, K. C., Vitamin A in dairy products. Part II. Vitamin A in curd and ghee from fortified milk, *Indian J. Dairy Sci.*, **7** (1954), 76

Wadhwani, T. K., Constitution of bone salt and tricalcium phosphate. Part I, *J. Indian chem. Soc.*, **31** (1954), 359

Wadhwani, T. K., Constitution of bone salt and tricalcium phosphate. Part II, *J. Indian chem. Soc.*, **31** (1954), 365

Wadhwani, T. K., Mechanism of calcification, *J. Indian chem. Soc.*, **31** (1954), 372

Inorganic

Lal, K. & Singh, G., Action of potassium sulphite on potassium permanganate, *J. Indian chem. Soc.*, **31** (1954), 410

Organic

Baichwal, R. S., Baichwal, M. R. (Mrs.) & Khorana, M. L., Synthesis of β-naphthol derivatives. Part II. 6-Alkyl naphthols and intermediary ketones, *Indian J. Pharm.*, **16** (1954), 90

Baichwal, R. S., Baichwal, M. R. (Mrs.) & Khorana, M. L., Antibacterial properties of β-naphthol derivatives. Part III. Alkyl naphthols, *Indian J. Pharm.*, **16** (1954), 93

Khastgir, H., Mukharjee, S. M. & Bhattacharyya, B. K., Studies in Friedel-Crafts reaction. Part III. Intramolecular cyclization of methyl 2-(β-phenylethyl)-6-methyl-cyclohex-2-en-1-one-6-carboxylate, *J. Indian chem. Soc.*, **31** (1954), 351

Lathrop, E. C. & Nelson, G. H., The chemical composition of some leaf and bast fibres, *Indian Pulp Pap.*, **9** (1954), 27

Mhaskar, V. V. & Banerjee, B. N., Component acids and the probable glycerides of the milk fat obtained from cottonseed-fed buffaloes, *Indian J. vet. Sci.*, **24** (1954), 93

Ranbir Singh, Chemistry of aliphatic thiocarbamides. Part III. N:N′-dimethylthiocarbamide, *J. Indian chem. Soc.*, **31** (1954), 355

Sen Gupta, P. & Bhattacharyya, B. D., Studies in Friedel-Crafts reaction. Part II. Inter-molecular condensation of anisole with methyl 2-methyl-2-carbomethoxy-*cyclo*hex-5-en-1-one-6-acetate, *J. Indian chem. Soc.*, **31** (1954), 337

Sheth, M. C. & Desai, C. M., Chemical examination of the seed oil of *Jatropha glandulifera* Roxb., *J. Indian chem. Soc.*, **31** (1954), 407

Subbaram, M. R., Heterocyclic compounds. Part II. Synthesis of 4-quinazolones with substituents in the 2- and 3-positions, *Proc. Indian Acad. Sci.*, **40A** (1954), 22

Physical

Desai, C. M. & Vaidya, B. K., Action of light on some organic colouring matters. Part III, *J. Indian chem. Soc.*, **31** (1954), 389

Ghosh, B. N., Estimation of true zeta potential of the particles of a diaphragm in contact with a solution of an electrolyte, *J. Indian chem. Soc.*, **31** (1954), 393

Kazi, H. J. & Desai, C. M., Interfacial tension and auto-complex formation in aqueous cupric chloride, *J. Indian chem. Soc.*, **31** (1954), 418

Kazi, H. J. & Desai, C. M., Interfacial tension and complex formation. The system $CoCl_2$-KCl-H_2O, *J. Indian chem. Soc.*, **31** (1954), 415

Kazi, H. J. & Desai, C. M., Interfacial tension and complex formation. The system $CoCl_2$-Na (NH_4 or Li)Cl-H_2O, *J. Indian chem. Soc.*, **31** (1954), 416

Lahiri, D., A study of colours produced by copper oxide in sodaboric oxide glasses, *J. Indian chem. Soc.*, **31** (1954), 377

Mathai, I. M. & Anantakrishnan, S. V., Kinetics of the olefine-bromine reaction. Part VII. The reaction between crotonic and dimethyl acrylic acids and bromine in carbon tetrachloride, *Proc. Indian Acad. Sci.*, **40A** (1954), 47

Pande, C. S. & Bhatnagar, M. P., Formation of complex compounds between urea and alkaline earth halides. Part I. The system $BaCl_2$-$CO(NH_2)_2$-H_2O: Viscosity and conductivity, *J. Indian chem. Soc.*, **31** (1954), 402

Pande, C. S. & Bhatnagar, M. P., Formation of complex compounds between urea and alkaline earth halides. Part II. The system $BaCl_2$-$CO(NH_2)_2$-H_2O: Surface tension and refractive index, *J. Indian chem. Soc.*, **31** (1954), 405

Pati, T., Products of summability methods, *Proc. nat. Inst. Sci. India*, **20** (1954), 348

Rakshit, S. C., Molecular thickness of the stabilizer film in xylene/water emulsions, *J. Indian chem. Soc.*, **31** (1954), 384

Seth, B. R., Generalized singular points with applications to flow problems, *Proc. Indian Acad. Sci.*, **40A** (1954), 25

ENGINEERING

Advani, R. M., Determination of the elements of hydraulic jump, *Irrigation & Power*, **11** (1954), 248

Bhoota, B. V., Essential steps in sewage treatment, *J. Instn. Engrs. India*, **34** (1954), 465

Deshpande, M. V., A universal power circle diagram, *J. Instn. Engrs. India*, **34** (1954), 553

Guha, S. K., Gurdas Ram & Rao, G. V., Vibration characteristics of the Khadakwasla Dam (Poona, India), *Irrigation & Power*, **11** (1954), 239

Joshi, N. S., Design of open channels in rocky cuts: Values of rugosity coefficient, *J. Instn. Engrs. India*, **34** (1954), 479

Thadani, N. M. & Sitaraman, K., Building a mountain railway across the Vindhyas: Construction of the new down line between Budni and Barkhera, *J. Instn. Engrs. India*, **34** (1954), 501

VENKATESAN, M. N., Rapid method of evaluating soil rock densities and percentage compaction on the fill in earth dams, *Irrigation & Power*, **11** (1954), 277

GEOLOGY

PRAMANIK, S. K., Is salt in Sambhar Lake wind-borne from the Rann of Cutch and the Arabian Sea ? *Proc. nat. Inst. Sci. India*, **20** (1954), 265

MATHEMATICS

BAMBAH, R. P., On polar reciprocal convex domains: Addendum, *Proc. nat. Inst. Sci. India*, **20** (1954), 324

BASU, D., On the optimum character of some estimators used in multistage sampling problems, *Sankhya*, **13** (1954), 363

BASU, D. & LAHA, R. G., On some characterizations of the normal distribution, *Sankhya*, **13** (1954), 359

MANN, H. B., A theory of estimation for the fundamental random process and the Ornstein Uhlenbeck process, *Sankhya*, **13** (1954), 325

MANN, H. B. & MORANDA, P. B., On the efficiency of the least square estimates of parameters in the ,Ornstein Uhlenbeck process, *Sankhya*, **13** (1954), 351

PADMAVALLY, K., A generalization of Cantor Bendixon theorem, *Proc. nat. Inst. Sci. India*, **20** (1954), 305

RUSHTON, S., On the confluent hypergeometric function $M(x, y, x)$, *Sankhya*, **13** (1954), 369

RUSHTON, S. & LANG, E. D., Tables of the confluent hypergeometric function, *Sankhya*, **13** (1954), 377

SINGH, V., Appell set of polynomials, *Proc. nat. Inst. Sci. India*, **20** (1954), 341

SINGH, V., On Angelescus polynomials, *Proc. nat. Inst. Sci. India*, **20** (1954), 280

TAWDE, N. R. & LAUD, B. B., On the working of some theories of vibrational transition probabilities, *Proc. nat. Inst. Sci. India*, **20** (1954), 259

METEOROLOGY

PRATAP, R., Atmospheric oscillations at high altitudes and their relation to geomagnetic field variations, *Proc. nat. Inst. Sci. India*, **20** (1954), 252

PHYSICS

AGGARWAL, S. P., Relation between maximum pressure and shot-start pressure, *Proc. nat. Inst. Sci. India*, **20** (1954), 307

BANERJEE, B. K., Study of metal film on glass surface, *Proc. nat. Inst. Sci. India*, **20** (1954), 241

BANERJEE, C. C., Proton-proton scattering at 340 Mev., *Indian J. Phys.*, **28** (1954), 221

BANERJEE, S. B., On the Raman spectra of ethylene dichloride in solutions of different strengths, *Indian J. Phys.*, **28** (1954), 205

BASU, D., Pseudoscalar interaction and proton-proton scattering, *Indian J. Phys.*, **28** (1954), 201

DATTA, S., Accurate determination of the magnetic anisotropies of the hydrated salts of some elements of the iron group, *Indian J. Phys.*, **28** (1954), 239

DUBE, G. P. & SINGH, L. S., On the kinetic energy of fission-fragments from U^{235}, *Indian J. Phys.*, **28** (1954), 227

DUBE, G. P. & SINGH, L. S., On the semi-empirical mass-formula and alpha-disintegration energy in the region of heavy and medium heavy nuclides, *Proc. Indian Acad. Sci.*, **40A** (1954), 37

DUBE, G. P. & SINGH, L. S., On the validity of semi-empirical atomic mass-formula in the region of rare-earth nuclides, *Indian J. Phys.*, **28** (1954), 177

DUTTA ROY, S. K., A new electrodynamic method of measuring magnetic fields, *Indian J. Phys.*, **28** (1954), 183

GHOSH, D. K., On the time of relaxation of some organic molecules in pure liquid state, *Indian J. Phys.*, **28** (1954), 191

GHOSH, K. M., A note on the Karman's spectrum function of isotropic turbulence, *Proc. nat. Inst. Sci. India*, **20** (1954), 336

KHARE, R. C., Instability of non-radial oscillations of centrally condensed stars, *Proc. nat. Inst. Sci. India*, **20** (1954), 326

KHASTGIR, S. R. & SRIVASTAVA, C. M., Origin of R.F. oscillations in A.C. 'silent' discharges, *Proc. nat. Inst. Sci. India*, **20** (1954), 290

MAJUMDAR, K. & VARSHNI, Y. P., Spectroscopic constants of molecules. II. On the vibration frequencies of diatoms of the type XY, *Indian J. Phys.*, **28** (1954), 209

MITRA, S. N. & IYENGAR, V. C., Observation of scatter echoes on high power pulsed transmissions, *Indian J. Phys.*, **28** (1954), 147

MOOKHERJI, A., Microwave method in the study of paramagnetic ions in crystals, *Proc. Rajasthan Acad. Sci.*, **4** (1953), 32

RAMAN, C. V. & RAMDAS, A. K., The structure and optical behaviour of iridescent calcite, *Proc. Indian Acad. Sci.*, **40A** (1954), 1

RAMANNA, R. & IYENGAR, S. B. D., On the distribution of thermal neutrons from a fast neutron source placed at the interface of two media, *Proc. Indian Acad. Sci.*, **40A** (1954), 8

ROY, S. B. & CHAKRAVARTI, R., On the production of charged meson pairs by neutral particles in cosmic rays, *Indian J. Phys.*, **28** (1954), 167

SANTHAMMA, V., Force constants for the BF_3 molecule, *Proc. nat. Inst. Sci. India*, **20** (1954), 245

SEN, K. R., The mechanical characters of jute. (4) Filament surface, *Jute Bull.*, **17** (1954), 102

SIL, N. C., Electron capture by ions passing through gases, *Indian J. Phys.*, **28** (1954), 232

SINGH, S., Target damages by explosive charges with lined conical cavities, *Proc. nat. Inst. Sci. India*, **20** (1954), 274

SREERAMAMURTY, K. & HARANATH, P. B. V., Absorption spectrum of 3-chloro-thionaphthene, *Proc. nat. Inst. Sci. India*, **20** (1954), 318

SUR, P. K. & MAJUMDAR, K., The absorption spectrum of BiBr, *Proc. nat. Inst. Sci. India*, **20** (1954), 235

TIRUMALESA, D. & RAMAKRISHNA RAO, V., Force constants and thermodynamic properties of $TiCl_4$, *Indian J. Phys.*, **28** (1954), 216

TECHNOLOGY

ARAVAMUTHAN, V., Electrolytic production of magnesium metal in India employing dolomite and bitterns as raw materials, *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 45

BANDYOPADHYAY, N. N., Horn plastics. Part II. Horn-phenolshellac composition, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 20

Bandyopadhyay, S. B., Quality of jute and its assessment, *Jute Bull.*, **17** (1954), 86

Bhargava, M. P., Bagasse for writing and printing papers, *Indian Pulp Pap.*, **9** (1954), 37

Bhat, R. V., Wrapping papers, *Indian Pulp Pap.*, **9** (1954), 41

Bhat, R. V. & Singh, M. M., Indigenous cellulosic raw materials for the production of pulp, paper and board. Part XXII. Wrapping papers from *Trema orientalis* Blume, *Indian For.*, **80** (1954), 453

Bose, A. N., Ayan Dutt, J. M. & Saha, M., Studies on extension of storage life of fish by chemical ice, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 30

Chakrabarty, S. R. & Chakrabarty, M. M., The composition and utilization of Indian tea seed oils, *Indian Soap J.*, **20**(1) (1954), 16

Dhawan, C. L., Bahri, J. C. & Gobindpuri, P. S., Surkhi as pozzuolana — Its lime absorption, *Irrigation & Power*, **11** (1954), 285

Guha, S. R. D., Blotting paper, *Indian Pulp Pap.*, **9** (1954), 46

Jatkar, S. K. K. & Mattoo, B. N., Studies on karanja oil. Part I. Extraction of karanjin and pongamol, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 39

Kalbag, S. S. & Kane, J. G., Electrolytic oxidation of soaps, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 1

Kelkar, G. M. & colleagues, Use of non-edible oils in soap making, *Indian Soap J.*, **20**(19) (1954), 13

Kirpal Singh, K., Kapur, N. S. & Mathur, P. B., Further studies on the cold storage of mangoes, *Indian J. agric. Sci.*, **24** (1954), 137

Kirpal Singh, K. & Mathur, P. B., A note on the cold storage of sapotas (*Achras sapota*), *Indian J. agric. Sci.*, **24** (1954), 149

Kothari, P. S., White water and back water, *Indian Pulp Pap.*, **9** (1954), 95

Mehta, T. N., Rao, C. V. N., Rao, B. Y. & Chudgar, N. M., Urea adducts of fatty acids. Part II. Separation of castor oil fatty acids, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 23

Mitra, S. N., Further studies on the relation between crude fibre and non-tender stalk contents of Indian tea, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 49

Mitra, S. N., On the present legal standards for tea, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 51

Narayana Rao, M. & Krishnamurthy, K., Activation of indigenous earths for bleaching of vegetable oils, *Bull. cent. Food tech. Res. Inst.*, **3** (1954), 196

Natarajan, A., Brine purification system in the operation of mercury cells for electrolytic alkali-chlorine, *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 34

Paniker, V., Operation and characteristics of Krebs mercury cells for electrolytic alkali-chlorine, *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 25

Pingale, S. V., Storage of wheat in jute bags impregnated with synergized lindane, *Bull. cent. Food tech. Res. Inst.*, **3** (1954), 198

Puri, B. R., Lakhanpal, M. L. & Gupta, P. C., Preparation of activated charcoal by phosphoric acid treatment, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 35

Ramachandran, S., Rajagopalan, S. R. & Dey, B. B., Hard chromium plating of piston rings, *Bull. cent. electrochem. Res. Inst.*, **1**(3) (1954), 30

Rama Char, T. L., Electroplating: Some recent developments and future possibilities, *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 49

Rama Char, T. L. & Mathur, J., The sulphamate bath for cadmium-zinc alloy plating, *Bull. cent. electrochem. Res. Inst.*, **1**(3) (1954), 27

Ramamurti, K., Pectin from citrus pulp with a note on the preparation of *d*-galacturonic acid from citrus pectin, *Proc. Rajasthan Acad. Sci.*, **4** (1953), 13

Ramaswamy, S., Ramani, R. V. & Subramanyan, N., Materials of construction in the chlorine-alkali industry, *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 62

Sanvordenkar, K. S. & Tendolkar, G. S., Electrodeposition of iron powder, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 13

Saxena, E. R. & Datar, D. S., Extraction of potash from felspar. Part VI. Alteration of felspar by the thermal reaction with sodium carbonate and with sodium sulphate, *J. Indian chem. Soc., Industr. Edn.*, **17** (1954), 44

Sen, K. R., The mechanical characters of jute. (5) Density and gravimetric fineness, *Jute Bull.*, **17** (1954), 133

Seshadri, K., Manufacture of hydrogen peroxide. Part II. *Bull. (India Sect.) electrochem. Soc.*, **3** (1954), 66

Shenoy, B. A., Anodic oxidation of aluminium, *Bull. cent. electrochem. Res. Inst.*, **1**(3) (1954), 35

Sreenivas, A., Calcium carbide, *Bull. cent. electrochem. Res. Inst.*, **1**(3) (1954), 38

Sriramchandramurty, K. & Prabhakara Reddy, P., Ochres: Their properties and utilization, *Ind-Com. J.*, **9** (1954), 197

Tewari, M. C. & Pande, J. N., Testing of wood preservatives. Part II. Boliden salts, *Indian For.*, **80** (1954), 480

Progress Reports

MEDICAL RESEARCH IN INDIA — 1953

THE REPORT OF THE SCIENTIFIC ADVISORY BOARD of the Indian Council of Medical Research for the year 1953 reviews the research activities of the various units of the Council during the past few years. A brief account of the activities of some of the units is presented here.

Nutrition — Determinations of the amino acid contents of proteins of cereals and pulses have shown lysine to be the limiting amino acid in the former and methionine and tryptophane in the latter.

Experiments on the availability of B-vitamins in raw and cooked foods have shown that the whole of vitamin contained in a foodstuff is not necessarily available to the body. Studies on the biosynthesis of vitamin C using radio-isotope C^{14} have shown pyruvic acid to be one of the compounds from which ascorbic acid is formed. Dietary requirement of riboflavin has been shown to be affected by the fat and protein content of the diet, since they influence the intestinal biosynthesis of riboflavin. There is some evidence to show that low level of protein in the diet adversely influences the utilization of riboflavin. Between 1 and 2 mg. of riboflavin meet the requirements of Indian adults living mainly on vegetarian diets. The metabolism and storage of vitamin A have been found to be influenced by the dietary protein. Studies on the mode of action of vitamins have shown that in plasma, vitamin A probably exists in combination with the albumin fraction.

A significant observation has been that the low intake of protein is one of the causes of the lowering of basal metabolic rate. Low-protein diet was also found to considerably reduce the fertility in rats.

A tryptic inhibitor has been isolated from the duck egg white having a twofold action; it interferes in the tryptic hydrolysis of proteins within the intestines and exerts a growth-depressing action independent of its anti-tryptic activity.

Nutritional diseases — Patients of nutritional oedema showed increase in extra-cellular compartment of the body, and a substantial increase in intracellular hydration leading to a considerable reduction of cell solids. Studies on electrolyte metabolism led to the conclusion that defective sodium excretion may not be the primary cause of nutritional oedema. Experiments with rats showed that in starvation the capacity of the liver to inactivate the anti-diuretic hormone was greatly reduced. This observation helps to explain the occurrence of anti-diuretic hormone-like substances in the urine of nutritional oedema cases in quantities larger than in normal.

Field investigations undertaken included several diet and nutrition surveys.

Feeling the necessity of fortifying and enriching some classes of foodstuffs, the Nutrition Advisory Committee has recommended the fortification of *atta* with calcium carbonate, wheat flour with B-vitamins and " toned " milk and vanaspati with vitamin A.

Leprosy — The role of contact in the spread of leprosy has been closely studied and has yielded some interesting results. Among 1,613 contacts, 444, i.e. 27·5 per cent, new cases were discovered. Of the rest, 523, i.e. 44·7 per cent, showed bacilli in the skin with no clinical symptoms. These cases were, however, positive to lepromin. The remaining 646 persons remained both clinically and bacteriologically negative. Of the new cases, 13·7 per cent were observed in 146 contacts in 51 households where only a neutral case existed in each and in which each member of the family was examined. On the other hand, 27·7 per cent arose in 145 contacts in 53 households where there were cases of lepromatous leprosy.

Studies on lepromin reaction have shown it to be an allergic phenomenon, though allergy is not always specific, but may be dependent in some cases on sensitization with other acid-fast bacilli. Investigations into the histology of early lesions of leprosy have established that lepra bacilli enter the body through unbroken skin, particularly during childhood, after repeated contact with a leprosy patient or infective material. The causative organisms seem to have a predilection for migration towards degenerating and regenerating nerve fibrils and the bacilli tend to travel towards the finest twigs in the superficial nerve plexuses. Thus, from the point of view of cutaneous neurohistology, there is no non-neural leprosy either at the inception or during the progress of the disease. With the use of staining technique it was shown that the extent of total damage to the nerve fibrils in the skin was a more reliable index of the pathological change than could be appreciated by clinical tests.

Clinical research — Studies on oral cancer patients have shown a deficiency of vitamins B_1, B_2 and B_{12} in them; the administration of vitamin increases the excretion of oestrogens. A definite fall in vitamin B_{12} excretion on administration of oestrogens in all oral cancer cases has also been recorded.

It has been shown that fibrosis of liver in early stages is a reversible process. A method has been worked out for the chemical estimation of fibrous tissue in diseased liver. Normally, about 3 per cent of dried liver substance is fibrous tissue and unless this increases to about 6 per cent, cirrhosis of the liver is not microscopically diagnosed.

Methionine, cysteine and glutathione have been shown to exert protective action, though to a varying degree, in cases of toxic liver injury.

Some interesting data have been collected from patients of infective hepatitis. In 75 per cent of the fatal cases the white cell count was found to be about 10,000 per cu. mm., whereas 70 per cent of the non-fatal cases had leukopenia or a normal count during the fibrile or pre-ictric stage and shortly after.

Macrocytic anaemia has been shown to be due to folic acid and vitamin B_{12} deficiency, the former playing a major role. Dietary inadequacy, hypersplenism and steatorrhoea are the contributory factors for its relapse. There is no relation between serum iron level and the types of anaemias in pregnancy or the period of gestation. Estimation of serum iron level and the iron-binding capacity of serum have been found useful in differentiating iron deficiency anaemias from familial erythroblastic anaemias.

Rattus has been found to be the main reservoir of *R. orientalis*, the cause of scrub typhus in India. It has been suggested that *Trombicule deliniensis* is the vector for *R. orientalis*. A correlation has been detected between the maximum prevalence of scrub typhus in the rainy season which coincides with the breeding season of *T. deliniensis*.

An epidemic dropsy-like condition was reproduced in rhesus monkeys with the administration of argemone oil both by oral route and by injection — a confirmation of the belief that epidemic dropsy is caused by injestion of argemone-adulterated mustard oil. A simple method has been developed by the Clinical Research Unit, Calcutta, for the isolation of total alkaloids directly from argemone seeds. A test has also been evolved for the detection of argemone oil in animal tissues, body fluids and excreta in very small amounts.

Indigenous drugs — Work on *Cissampelos pareira* has indicated that the plant, which is available in plenty in the lower ranges of the Himalayas, contains an active principle which is as good a smooth muscle relaxant as d-tubcurarine chloride. A glycoside has been isolated from *Thevetia neriifolia* having properties and uses similar to those of digitalis. The Council has sponsored a part of the research on the cultivation of drugs like pyrethrum, *Atropa belladonna*, *Atropa acuminata*, *Digitalis purpurea*, *D. lanata* and *Podophyllum emodi* at the Experimental Drug Farm, Srinagar. A programme has been initiated for the introduction of exotic plants such as *Datura innoxia* from Mexico and *Duboisia* species from Australia as better sources of hyoscyamine, *Urginea scilla* from Mediterranean coasts and *Coriandum sativum*, *Foeniculum vulgaris* from Russia and Germany and *Heliospsis longipes* from Mexico as a source of an active principle " Scoberin " which is two and a half times as toxic as pyrethrin to house-flies.

TIN RESEARCH INSTITUTE, ENGLAND — ANNUAL REPORT FOR 1953

THE RESEARCH WORK CARRIED OUT BY THE INSTITUTE during the year is reviewed under four principle heads: Electrodeposition, Alloys, Tinplate and hot-tinning, and Organotin compounds.

Electrodeposition — Two new alloys, tin-lead and tin-antimony, are being examined as overlays on bearings. Recent work done on the coating of tin on to aluminium by chemical displacement has resulted in the improvement of the control and economy of the operations. The process is widely used for motor car and aeroplane pistons. The plating process for an alloy consisting of two parts of tin and one of nickel has been successfully developed. It gives an attractive ornamental finish for articles made of the common metals. A simple and highly useful plating consists of a coating of three parts of tin and one of zinc.

Tin alloys — Solid bearings containing 30 per cent tin alloyed with a strong aluminium matrix have been made in the laboratory for trials in Italian tram cars. Another alloy containing 20 per cent tin bonded to a duralumin backing has been in experimental use on a number of automotive engines used in cars and trucks. A third alloy containing 15 per cent tin can be bonded to steel backing shells and bearings have been prepared for trials in automobiles. The operation of these bearings and their resistance to fatigue have proved satisfactory in laboratory trials.

Work on the continuous casting of bronze bars and research into improved methods of sand casting have been continued. A new alloy consisting of copper-manganese-tin has been developed. The new alloy is almost white and takes a very high finish and is suitable for rolling, stamping, etc.

Tinplate and hot-tinning — Studies on the formation and structure of the tin-iron alloy layer in tinplate have revealed that the alloy layer affects soldering quality; the quantity of alloy layer, for any given amount of tin, affects corrosion resistance. An investigation of methods for determining the amount of alloy has been completed.

Organotin compounds — The use of dibutyltin compounds as stabilizers for polyvinyl chloride plastics is now firmly established. The same compound is also being used, on a small scale, for stabilizing chlorinated rubber paints. A new class of compounds — trialkyltin and triaryltin — has been found to possess strong biocidal properties. Some of them have the unusual merit of combining extremely powerful fungicidal and insecticidal properties. Among the possible fields of application being explored are agriculture, textiles, wood preservatives and paints.

INDIAN PATENTS

[A few of the Patent Applications notified as accepted in the *Gazette of India*, Part III, Section 2, for August 1954, are listed below.]

Chemicals, plastics, rubber, paints and allied products

48934. Improvements in the manufacture and purification of fatty acids: *A mixture of fatty acids is treated with* 1-5 *times its weight of urea in saturated solution of* 80 *per cent aqueous ethanol, the precipitate is separated from the liquor and the fatty acids are recovered by boiling the precipitate and the mother liquor separately with water* — Achaya, Saletore & Zaheer

50426. Methods of manufacturing 2: 5-dichloro alkali phenolate: *Reacting hexachloro hexane with alkali hydroxide in presence of methanol at* 160°-80°*C.*— N. V. Philips' Gloeilampenfabrieken

49140. Improvements in or relating to viscous or solid substances consisting of an oil compound and method for manufacturing the same: *Heating the oil in the presence of an alkaloid* — Lebret & Padieu

51701. Production of sulphur dioxide from calcium sulphate: *Calcium sulphate is heated with sodium sulphate and bauxite* — (Miss) Osmani, Datar & Zaheer

48499. An improved method for the production of manganese salts from manganese ores, and its application for the regeneration of the spent electrolytic manganese sulphate baths: *Digesting manganese ore with dilute mineral acid and an organic reducing agent* — Council of Scientific & Industrial Research

48938 and 48939. Preparation of substituted amines: *Reductively alkylating a compound of the formula* $R'RN\text{-}Ar\text{-}NHR^2$ *by hydrogenation in the presence of a ketone to a compound of the formula* $R'RRN\text{-}Ar\text{-}NHR^2$.

Reductively alkylating a nitroso compound of the formula $R'RN\text{-}Ar\text{-}NO$ *by hydrogenation in the presence of a ketone to an amine of the formula* $R'RN\text{-}Ar\text{-}NHR^2$ — I.C.I. Ltd.

49164. Process for the manufacture of new pyridazines: *A pyridazine containing a reactive esterified hydroxyl group in the* 3 *and* 6-*positions is reacted with an aliphatic, araliphatic or aromatic alcohol or phenol* — Ciba Ltd.

49407. Process for the production of finely divided oxides: *Mixing gases which together burn to form water, with volatile metal or metalloid compound and causing the mixture thus formed to react in burner flame* — Deutsche Gold-Und Silber-Scheideanstalt vormals Roessler

49457. Method of recovering non-ferrous metals from solutions containing salts thereof: *Prior to gas reduction there is added to the solution an amount of material capable of forming with the dissolved metal a gas-reducible complexion and also powdered metal* — Chemical Construction Corporation

49505. Silica-alumina catalysts and the process of using them: *By mechanically mixing* 3-20 *weight per cent silical hydrogel with* 2-6 *weight per cent alumina hydrosol and drying the mixture at at least* 250°*F.*— Standard Oil Development Co.

49536. Process for the manufacture of aza-cycloalkanes: *By reacting* 2-(*tertiary aminoalkyl*)-*cyclo-alkanones*-(1) *with hydrazoic acid* — Ciba Ltd.

50015. Manufacture of compounds of the azulene series: *By heating monocyclic ten-ring compounds of the alicyclic series having at most one double bond in the ring, to a high temperature in the presence of catalysts* — Ciba Ltd.

51783. Bleaching and hydrogenation of cottonseed oil: *During hydrogenation of cottonseed oil, the final traces of colour are removed by effecting the hydrogenation in presence of active carbon and activated fullers' earth* — Amrit Banaspati Co. Ltd.

52014. Preparation of halogenated rubber: *By the electrolysis of a halogen acid in the presence of stabilized rubber latex for the liberation of the halogen in situ* — Council of Scientific & Industrial Research

48995. Surface coating: *To predetermined base ingredients supplied in a container having a lid is added a measured quantity of pigment from a flexible and compressible envelope by slitting the envelope, removing the lid, introducing the cut end into the container, gripping the opposite sides of the envelope between the upper edge of the container and the edge of the lid and discharging the pigment into the base ingredients by withdrawing the envelope* — G. J. Liebich Co.

50256. Process for the manufacture of novel methyl pyridine compounds: *Reacting the compound* $R'\text{-}NH\text{-}NH_2$ *with a compound of the formula* $R''\text{-}Hal$ *or* $R''\text{-}O\text{-}R''$ *where* R' *stands for* 2-*methyl-pyridine*-4-*carboxylic acid radical and* R'' *stands for an aliphatic, alicyclic, aromatic or heterocyclic carboxylic acid radical* — F. Hoffmann-La Roche & Co. Aktiengesellschaft

50833. Process of preparing calcium carbide: *The oxygen-containing blast is fed at a rate of* 40-100 *m./sec. through annularly arranged tuyeres of a shaft furnace wherein said tuyeres slope downwardly at an angle of* 10°-30° *to the horizontal* — Stamicarbon N.V.

51615. Derivatives of pyrimidine: 4, 5-*Diamino*-6-*mercapto-pyrimidine is prepared by reacting* 4-*amino*-5-*nitro*-6-*chloro-pyrimidine with an excess of ammonium or alkali metal hydrosulphide* — The Wellcome Foundation Ltd.

Chemical processes, engineering and equipment

50324. Process for the recovery of sulphates and iron compounds from solutions of ferrous sulphate and sulphuric acid, especially waste pickle liquor: *Treating with gases containing* NH_3, H_2S *and* HCN *to obtain* $(NH_4)_2SO_4$: $Fe(OH)_2$, *iron cyanide and* $FeSO_4$ — F. J. COLLIN A. G.

51127. Means for handling and transporting pulverulent, granular and like material: *Having a conical casing arranged with nozzles interposed in a conduit transporting the material* — KENNEDY-VAN SAUN MFG. & ENGNG. CORPORATION

48970. Improvements in tubulous vapour generating and superheating units: *Means for adjusting flow of gases through superheater tube bank including at least one closure member extending across the by-pass* — BABCOCK & WILCOX LTD.

51480. Tank and the like structure for transportation of liquids and solids: *Comprising a freight carrying space having double walls at the bottom and on the sides* — JOSEPH-YERVANT MICHEL NAJJAR

50636. Current meters for measurement of stream velocities or the like: *Propeller-driven direct current generator in a streamlined body generates electrical voltages proportional to the stream velocity* — DIRECTOR, INDIAN INSTITUTE OF SCIENCE, BANGALORE

Physics — general

48961. Improvements in or relating to epidiascopes: *Comprising housing with internal lights and their reflectors, optical lens for projecting images and means whereby an object whose image is to be projected is positioned at a wall of the housing opposite the lens* — MUNIR

49386. Permanent magnets and method of manufacturing them: *Particles of magnetic powder composed of crystals of magneto-plumbite structure of at least one compound* $MO_6Fe_2O_3$ ($M = Ba$, Sr *or* Pb) *and in a state of division adapted to favour a* $(BH)_{max.}$ *value of more than* $2{\cdot}3 \times 10^6$ *are united to form a magnetically anisotrope body and heated to a temperature between* 1,150° *and* 1,350°*C.*— N. V. PHILIPS' GLOEILAMPENFABRIEKEN

Food and kindred products

49918. The manufacture of articles of food and confectionery: *Containing a central filling of sugar, liquid glucose and yeast processed under heat and vacuum* — THE K.C.P. LTD.

Drugs and pharmaceuticals

48984. Preparation of relaxin: *Extracting ovaries of pregnant animals, treating with salt and filtering to remove solid material, precipitating crude hormone from the filtrate* — WARNER-HUDNUT INC.

50048. A substitute of agar agar in bacteriolgical media: *Treating " Ispahgol ", botanically known as Plantago ovata, with alkalies, neutralizing the alkali and drying to thin chips or powder* — AGGARWAL

51834. Pharmaceutical preparations containing new pyridazines: *The preparation comprises a diether of 3:6-dihydroxy-pyridazine substituted in the 4 and 5-position with aliphatic, aromatic or araliphatic residues with a pharmaceutical carrier* — CIBA LTD.

49697. Production of penicillins: *Recovering penicillin from aqueous solutions by precipitation with acids or by carrying over the penicillins in the presence of acids from said solutions into organic solvents and separating them by evaporating the solvent* — BIOCHEMIE GESELLSCHAFT MIT BESCHRANKTER HAFTUNG

51699. Manufacture and use of complex iron salts of nitrilo-triacetic acid: *Reacting ferric salt and alkali metal or ammonium salt of nitrilo-triacetic acid, neutralizing the product and evaporating to dryness* — CIBA LTD.

Fuels and lubricants

49015. Process of treating badly swelling and caking coals: *The coal in pulverized and fluidized form is subjected to a flash oxidation at* 675°-800°*F., cooled and separated from the fluid carrier* — KRUPPA & RINCKHOFF

Metals and metal products

51408. Process of manufacturing low alloy steel and steel articles made from said steel, in particular oil wells tubing: *By subjecting steel containing in addition to carbon and iron, silicon, aluminium, chromium and manganese, to a heat treatment comprising an austenite forming step followed by atmospheric cooling and long tempering or annealing at* 500°-700°*C.*— SOCIETE DES ACIERIES DE POMPEY

48884. Production of grey cast iron: *Adding to molten cast iron not only magnesium but also rare earth metal in an amount between* 0·005 *and* 0·02 *per cent by weight of molten iron* — THE MOND NICKEL CO. LTD.

51902. Process for the production of ferro-manganese: *Into pig iron obtained from blast furnace, air enriched with oxygen is blown, the metal and slag separated, slag subsequently treated for obtaining ferro-manganese* — DEMAG AKTIENGESELLSCHAFT

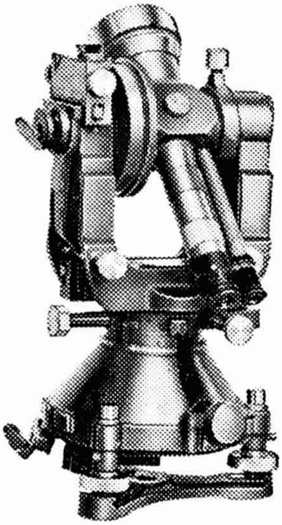
Glass and ceramics

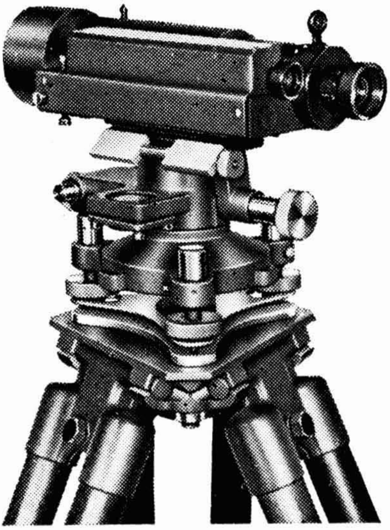
50286. Methods of and apparatus for manufacturing toughened bent glass: *Heating flat glass to its softening temperature and warping itself about a forming member and continually supporting the glass to each side of the bend by yielding plane members* — PILKINGTON BROTHERS LTD.

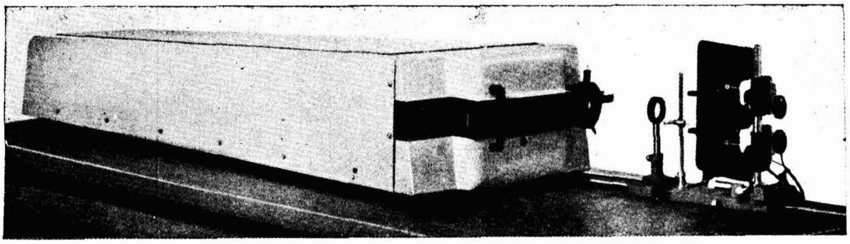
Building materials and methods

50854. Laminated building materials: *Asbestos-felt sheets bonded to one or each side of a rigid heat insulating board* — ROBERTSON THAIN LTD.

51657. Improved means for tensioning reinforcing wires for concrete beams, slabs and other articles: *Reinforcing wires anchored at one end and extending from tubular cavity in the article gripped by wire engaging means adapted to be drawn outwardly by tension applying means and means for maintaining tension until cement grouting fed to cavity sets and hardens* — ROCLA PIPES LTD.







Journal of Scientific & Industrial Research

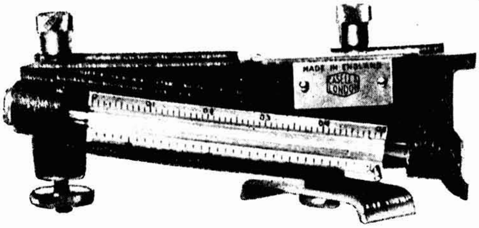
Vol. 13B, No. 10, OCTOBER 1954

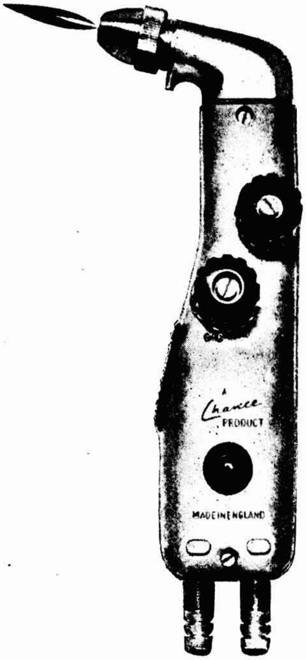
CONTENTS

Letters to the Editor

PUBLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
NEW DELHI

J. sci. industr. Res., Vol. 13B, No. 10, Pp. 673-748. October 1954


MADE IN ENGLAND
CASELLA LONDON


A Chance PRODUCT
MADE IN ENGLAND

Torsional Rigidity of Narrow Bars & Tubes of Twisted Shape

V. CADAMBE & R. K. KAUL
National Physical Laboratory of India, New Delhi

It has been shown that in the case of straight narrow sections, the torque equation contains a term proportional to θ^3 in addition to the Saint Venant's value. On a similar examination, it has been found that in the case of geometrically twisted tubes, the total contribution of the longitudinal stresses is proportional to $(\theta + \phi)^3$ where θ and ϕ are the elastic and initial twists of the tube. In the case of large initial twists, such as in turbine blades and propellers, the total contribution due to the longitudinal normal stresses, therefore, becomes considerable and should be taken into account. A few examples illustrating the application of the theory are presented.

THE solution of the problems of torsion of prismatical bars for uniform twist and without any axial restraint was first given by Saint Venant and has a simple solution. The problem of determining the torsion function $\Phi(x, y)$ is a special case of the second boundary value problem of potential theory which is associated with the name of Neumann, and consists in determining a function Φ that is harmonic in a given region and whose normal derivative is prescribed on the boundary of the region[1]. Such a simple solution shows that the normal stresses σ_x, σ_y and σ_z all vanish along with shear stress τ_{xy} and the remaining two shear stresses τ_{zx}, τ_{zy} produce a warping of cross-section which is uniform along all cross-sections. An assumption made in such a solution is that the distance between any two cross-sections during twist remains unchanged. This assumption is correct for steel and other materials where the maximum shearing stress τ_{max} during torsion is very small in comparison to the rigidity modulus G, and so the maximum longitudinal stress σ_{max} is negligible. But for materials like rubber and narrow thin-walled tubes and bars, this assumption is not correct because the shearing stress during torsion reaches quite a high value and is of the same order as G. In such cases the value of the longitudinal normal stress σ_{max} is no longer small compared to the value of shear stress τ_{max}, and has to be taken into account.

These longitudinal stresses vary from point to point along the cross-section and are given by a parabolic law in the case of a narrow rectangular section. Further, these stresses have the direction of the longitudinal fibres of the twisted strip and are not parallel to each other, but are inclined to the axis of the strip. Their projections on a plane perpendicular to the axis of the twisted bar give rise to a moment which is additional to that developed by Saint Venant's shearing stresses.

It has been shown by Timoshenko[2] that in straight narrow rectangular bars the increase in rigidity above Saint Venant's value, contributed by longitudinal normal stresses, is proportional to θ^3, where θ is the elastic angle of twist in radians per unit length. Following the same procedure the torsional rigidity of geometrically twisted bars is determined on the basis of the assumptions that (1) the initial twist ϕ is very small, and (2) the normal stresses again lie in the direction of the longitudinal fibres of the twisted bar.

Theory

Let the small initial twist of a non-circular narrow prismatical bar be ϕ radians per unit length and the elastic twist θ radians per unit length; $(\theta >> \phi)$ as shown in Fig. 1.

The unit elongation ϵ of a longitudinal fibre AD, under the assumption that the distance between the cross-sections during elastic twist does not change, and for small angles α where $\sin\alpha = \tan\alpha = \alpha$, it is approximately equal to

$$[\sec(\alpha+\beta)-1] \approx \frac{r^2}{2}(\theta+\phi)^2$$

There is, however, a unit longitudinal contraction ϵ_o between the two cross-sections during twist, provided no external longitudinal tensile force is applied to prevent this. Hence, the net unit elongation of fibre AD is

$$\epsilon = \frac{r^2}{2}(\theta+\phi)^2 - \epsilon_o$$

and, therefore, from Hookes law, stress

$$\sigma = E\left\{\frac{r^2}{2}(\theta+\phi)^2 - \epsilon_o\right\} \quad \ldots\ldots \quad (1)$$

These normal longitudinal stresses are inclined to the axis of the bar. The summation of the vertical component of these forces corresponding to these inclined normal stresses is equal to the external force, if any, and since the external force is zero, we have the total normal outward force $P = \iint \sigma . r dr d\Omega$, if $\cos(\alpha+\beta)$ is assumed to be unity. In the case of thin-walled tubes the outward normal force is $\oint \sigma t ds$ where t is the thickness of the thin-walled section and the integration is along the contour.

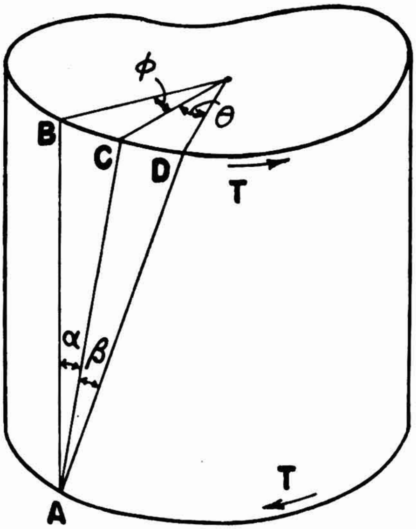


FIG. 1 — A NARROW GEOMETRICALLY TWISTED SECTION UNDER TORQUE T

Substituting the value of σ from eqn. (1), we have the total outward normal force

$$P = E\iint\left\{\frac{r^2}{2}(\theta+\phi)^2 - \epsilon_o\right\} r dr d\Omega$$

In the case of pure torque, outward normal force is zero, therefore

$$\epsilon_o = \frac{1}{2}(\theta+\phi)^2 \frac{1}{A}\iint r^3 dr d\Omega$$

$$\text{and } \sigma = \frac{E}{2}(\theta+\phi)^2\left[r^2 - \frac{1}{A}\iint r^3 dr d\Omega\right] \quad \ldots\ldots \quad (2)$$

These normal longitudinal stresses are inclined to the axis of the bar at an angle $(\alpha+\beta)$. Their horizontal component $\sigma\sin(\alpha+\beta)$ gives rise to a moment $r\,\sigma\sin(\alpha+\beta)$ in each longitudinal fibre of area $A = \iint r dr d\Omega$ and, therefore, the extra torque contributed by the longitudinal stresses is

$$\iint \sigma(\alpha+\beta) r^2 dr d\Omega = (\theta+\phi)\iint \sigma r^3 dr d\Omega$$
$$= (1+\mu)\,G\,(\theta+\phi)^3\left[\iint r^5 dr d\Omega - \frac{1}{A}\left(\iint r^3 dr d\Omega\right)^2\right] \quad \ldots\ldots \quad (3)$$

where $E/G = 2(1+\mu)$.

The torsional rigidity T' due to Saint Venant's shearing stresses τ is $KG\theta$ where K is the equivalent polar moment of inertia for the shaft. This constant K is determined from the torsion function $\Phi(x, y)$ which satisfies the equation $\nabla^2\Phi = -2G\theta$ in domain D under the prescribed boundary condition $\frac{d\Phi}{ds} = 0$ on the boundary C. In the case of tubes or other doubly connected bodies an additional condition to the Neumann problem is the restriction that $\oint_{C_i} \frac{\partial\Phi}{\partial n} ds - 2G\theta A_i = 0$ where A_i is the area of the interior hole bounded by C_i and $i = 1, 2, 3, \ldots, n$.

The value of the constant K has been worked out for a number of known sections. In the case of thin tubular members[3] the membrane analogy can be used successfully and the value of K can be determined from the relation

$$K \approx \frac{4A^2t}{S} \quad \ldots\ldots\ldots \quad (4)$$

where A is the area bounded by the middle line of the tube section and S its perimeter.

In the case of prismatical bars, the value of this constant K can be worked out by rigorous analysis for a few simple sections whereas in the case of more difficult ones, the use of energy method leads to satisfactory results to a first approximation.

Now the torque T' due to Saint Venant's shearing stresses is additional to that developed by the longitudinal stresses. Adding the two we have the total rigidity

$$T = KG\theta\left[1+\frac{1+\mu}{K}\frac{(\theta+\phi)^3}{\theta}\cdot\left\{\iint r^5 dr d\Omega-\frac{1}{A}\left(\iint r^3 dr d\Omega\right)^2\right\}\right] \quad \ldots (5)$$

In the case of thin-walled sections of constant thickness t we substitute A by tS and the area integral $\iint r dr d\Omega$ by the contour integral $\oint t ds$, leading to the relation

$$\frac{T}{T'}=\left[1+\frac{S(1+\mu).(\theta+\phi)^3}{4A^2\theta}\left\{\oint r^4 ds-\frac{1}{S}\left(\oint r^2 ds\right)^2\right\}\right] \quad \ldots . (6)$$

since for a thin-walled tube the value of K from membrane analogy is $4A^2t/S$.

Applications

The use of the formulae (5) and (6) derived above is illustrated in determining the torsional rigidity of a few narrow tubes and solid sections.

(i) Thin-walled tube of rectangular shape, (2a × 2b).

From membrane analogy Saint Venant's

torque $T' \approx \dfrac{16a^2b^2}{a+b}G\theta t.$

The eqn. (6) reduces to

$$\frac{T}{T'}=\left[1+\frac{1+\mu}{45}\frac{(\theta+\phi)^3}{\theta}a^2\frac{1+n}{n^4}.\right.$$
$$\left.(n^5+5n^4-5n^3-5n^2+5n+1)\right]$$
$$=[1+(\theta+\phi)^3a^2\,Q/\theta]$$

where $Q=\left[\dfrac{1+\mu}{45}\cdot\dfrac{1+n}{n^4}.\right.$

$$\left.(n^5+5n^4-5n^3-5n^2+5n+1)\right]$$

The value of Q is plotted in Fig. 2, curve I, for different values of n and $\mu = 0{\cdot}3$. Such a curve is useful for calculating the value of T/T' for intermediate ratios of $n = a/b$. The effect of initial twist ϕ on T/T' is illustrated in Fig. 3, curve I, for a typical section where $n = 20$ and $a = 1$ in.

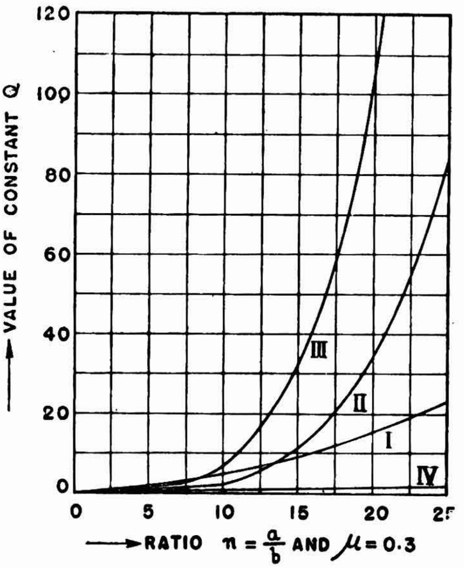


FIG. 2 — RELATION BETWEEN COEFFICIENT Q AND RATIO n.

(ii) In the case of a solid section ($b \times c$) where c is the thickness and b the width, Saint Venant's torque $T' \approx bc^3G\theta/3$.

The rigidity ratio as obtained from eqn. (5) is

$$\frac{T}{T'}=\left[1+\frac{(\theta+\phi)^3}{\theta}b^2Q\right]$$

where $Q = (1+\mu)\dfrac{1+n^4}{60n^2}$ and $n = b/c$.

The value of Q against n is plotted in Fig. 2, curve II. Also the effect of initial twist ϕ on T/T' is illustrated in Fig. 3, curve II, for a typical section, where $n = 20$ and $b = 1$ in. It will be seen from the graph that for higher b/c ratios, the value of Q increases rapidly and even a small degree of geometrical twist will considerably increase the T/T' ratio. For a twisted bar with $n = 20$, $\theta = 0{\cdot}5$ *rad*, $\phi = 0{\cdot}05$ *rad* and $b = 1$ in.; $T/T' = 12{\cdot}5$. Thus, when the effect of longitudinal fibre stress is considered, the torsional rigidity so obtained is 12·5 times higher than Saint Venant's value.

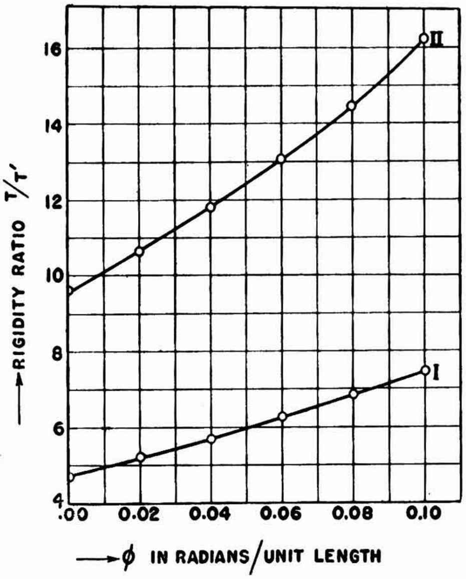


FIG. 3 — EFFECT OF INITIAL TWIST ϕ ON TORSIONAL RIGIDITY RATIO T/T'

(iii) Thin symmetrical solid section bounded by two parabolas $y = c^2 - x^2/a^2$

$$\left[\iint r^5 dr d\Omega - \frac{1}{A}\left(\iint r^3 dr d\Omega\right)^2\right]$$

$$= \frac{64ac^{11}}{525}\left(n^4 - \frac{8}{9}n^2 + \frac{296}{297}\right)$$

where $n = a/c$ and area $A = 8ac^3/3$.

The approximate value of the torsional rigidity factor K was determined by Rayleigh-Ritz[4] method. The value of this constant to a first approximation was determined as

$$K \approx \frac{256}{35}\,\frac{a^3c^7}{3a^2+4c^2}$$

Therefore, T/T' from eqn. (5) is

$$= \left[1 + \frac{1+\mu}{60}\,\frac{(\theta+\phi)^3}{\theta}\,\frac{3n^2+4}{n^6}.\left(n^4 - \frac{8}{9}n^2 + \frac{296}{297}\right)a^4\right]$$

The value of the coefficient Q is

$$= \left[(1+\mu)\frac{3n^2+4}{60n^6}\left(n^4 - \frac{8}{9}n^2 + \frac{296}{297}\right)\right]$$

This is plotted for different values of n in Fig. 2, curve III. If a parabolic section with $n = 20$, $\theta = 0{\cdot}5$ *rad*, $\phi = 0{\cdot}05$ *rad* and $a = 1$ in. is compared with a straight section, the ratio T/T' is found to be 35·5. It will be observed that the increase in T/T' is much more predominant in solid sections as compared to thin-walled hollow sections. This is also clear from the next example.

(iv) Thin symmetrical hollow section bounded by two circular arcs $r^2 = a^2 + b^2 - 2ab\cos\theta$ and of thickness t.

Torsional rigidity factor K from membrane analogy for thin tubular section

$$\approx 4A^2/S$$

$$\approx \frac{4b^4}{a}\sec^{-1}\frac{1}{n}\left[2n^2\cos^{-1}\frac{1}{n} - \sqrt{n^2-1}\right]^2$$

$$\text{and}\left[\oint r^4 ds - \frac{1}{S}\left(\oint r^2 ds\right)^2\right]$$

$$= 4ab^4\left[2n^2\cos^{-1}\frac{1}{n} - 4(n^2-1)\sec^{-1}\frac{1}{n} + 2\sqrt{n^2-1}\right]$$

where $S = 4a\cos^{-1}\frac{1}{n}$.

$$\text{Therefore, } \frac{T}{T'} = \left[1 + (1+\mu)\frac{(\theta+\phi)^3}{\theta}.\frac{\left[2n^2\cos^{-1}\frac{1}{n} - 4(n^2-1)\sec^{-1}\frac{1}{n} + 2\sqrt{n^2-1}\right]}{\left(2n^2\cos^{-1}\frac{1}{n} - \sqrt{n^2-1}\right)^2}\,b^2n^2\cos^{-1}\frac{1}{n}\right]$$

Putting it in the general form

$$\frac{T}{T'} = \left[1 + \frac{(\theta+\phi)^3}{\theta}b^2Q\right]$$

where the values of Q are as given in Fig. 2, curve IV, and

$$Q = (1+\mu).\frac{n^2\cos^{-1}\frac{1}{n}\left[2n^2\cos^{-1}\frac{1}{n} - 4(n^2-1)\sec^{-1}\frac{1}{n} + 2\sqrt{n^2-1}\right]}{\left[2n^2\cos^{-1}\frac{1}{n} - \sqrt{n^2-1}\right]^2}$$

For the same values of n, θ, ϕ and b as used in previous example the value of $T/T' =$ 1·029. This shows that for hollow thin-walled sections the value of T changes very little from T'.

Conclusions

It will be observed that in bars with geometrical twist, the portion of the torque contributed by longitudinal stresses is considerably more than that of Saint Venant's torque. Especially in solid narrow sections this contribution increases with increased angle of geometrical twist and cannot be neglected in analysis. Such curved sections are generally found in turbine blades, propellers, bourdon tubes, etc., and the analysis carried out above will be found useful in the correct determination of the rigidity of such sections.

References

1. Timoshenko, S. & Goodier, J. N., *Theory of Elasticity* (McGraw-Hill Book Co., New York), 1951, 258-62.
2. Timoshenko, S., *Strength of Materials*, Vol. II (Van Nostrand Co. Inc., New York), 1951, 298-304.
3. Timoshenko, S., *Strength of Materials*, Vol. II (Van Nostrand Co. Inc., New York), 1951, 278-82.
4. Sokolonikoff, I. S., *Mathematical Theory of Elasticity* (McGraw-Hill Book Co., New York), 1946, 306-11.

An Electron Diffraction Study of the Structures & the Growth of Silver Films on Rock Salt

A. GOSWAMI*

National Physical Laboratory of India, New Delhi

The epitaxial growth of silver films on rock salt has been studied. The extensive twinning of silver crystals and double twinning phenomenon have been observed. From the latter observation the appearance of (211) orientation of silver crystals along with the main (100) orientation has been explained and a mechanism of the growth of silver film on rock salt suggested.

THE structures of the silver films formed under vacuum on rock salt cleavage faces at high temperatures have been investigated by many workers[1]. Electron diffraction patterns obtained from such films show not only the normal diffraction spots due to the deposited silver crystals having integral hkl values but also the groups of satellite diffraction spots around the normal one, with fractional indices. Kirchner and Lassen[2] thought them to be due to the cross grating effects of octahedral planes but Laue[3-5] showed that these satellite patterns could be explained from the shape of the crystals (form factor) forming the silver film. Menzer[6,7] from the geometrical consideration of the reciprocal lattices, concluded that these abnormal spots were due to the extensive twinning on the four equivalent symmetrical { 111 } types of planes on which face centred metals generally twinned themselves though in some cases the satellite spots might be due to the shape of the crystals. Menzer[8] also suggested a mechanism of the growth of the silver film, in which the initially growing crystal nuclei were thought to be orientated with their { 221 } planes parallel to the cleavage plane of rock salt. These crystals which can have four symmetrical equivalent positions meet and grow together forming interpenetrating lattices and finally bringing the (100) plane of silver film parallel to the (100) face of rock salt. Goche and Wilman[1] in their detailed study did not observe any spots indicating actual twinning and agreed with the view of Menzer about the growth of silver film on rock salt.

---

*Present address: National Chemical Laboratory of India, Poona.

Bru and Gharpurey[9] have observed epitaxial stress effect between the silver deposits and rock salt (110) substrate in their interface leading to the rotational slip of the deposited silver crystals. Similar interfacial stress effect and their subsequent release by rotational slips were first observed by Evans and Wilman[10] by oxidizing single crystal of zinc sulphide and by Goswami[11] in electrodeposited cadmium on Cu (110) face.

The growing of crystal nuclei as was suggested by Menzer with their { 221 } types of planes initially parallel to the (100) face of rock salt and their subsequent rearrangement such that { 100 } planes become parallel to the initial surface by twinning process seems to be less likely, as was pointed out by Bru and Gharpurey[9], for these involve the assumption that initially planes with high indices like { 221 }, { 114 }, { 115 }, etc., can grow more quickly on (100), (110) and (111) faces respectively than those having lower indices. It is rather unlikely that planes with such high indices will have greater tendency to form than those with lower integral values, unless these planes have lattice spacings which are very similar to those of the substrate surface. This is not true in the above cases.

In the present work, a further study has been made on the epitaxial growth of silver films on rock salt at high temperatures by electron diffraction technique and on the basis of the results obtained a mechanism of the growth of silver film has been suggested.

Experimental procedure

Preparation of silver films — Silver metal was evaporated *in vacuo* from a red-hot nichrome wire made into a spiral and deposited at about 340°C. on a freshly cleaved (100) face of a rock salt crystal, placed a few centimeters away. The evaporation of silver was continued for about 10-15 min. till a suitable thickness of film was obtained on the rock salt crystal. The specimen was then cooled, still under vacuum, removed to the R.C.A. EMU3 type of electron microscope and examined under the diffraction condition. The rock salt specimen was initially examined by the electron diffraction technique before depositing the silver film.

Results and discussion

The electron diffraction patterns of a rock salt crystal cleavage face in its two principle azimuths are shown in Figs. 1 and 2.

The elongated diffraction spots as well as the well-defined Kikuchi lines in the patterns show that the cleavage face of the rock salt was perfect, free from disturbed layers and atomically smooth. The diffraction patterns of the deposited silver film taken along the two principle azimuths of the rock salt crystal are shown in Figs. 3 and 4. The patterns consisting of quite sharp and well-defined spots are different in the two azimuths showing that the deposited film was two degree orientated with respect to the substrate rock salt, i.e. the axial directions of silver crystals grew in common orientations with those of the substrate crystal.

The diffraction patterns of the silver film have some interesting features. The main

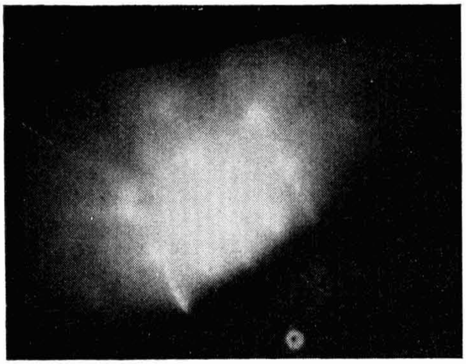


FIG. 1 — ELECTRON DIFFRACTION PATTERN OF ROCK SALT CLEAVAGE (100) FACE; BEAM ALONG [$\bar{1}10$] DIRECTION

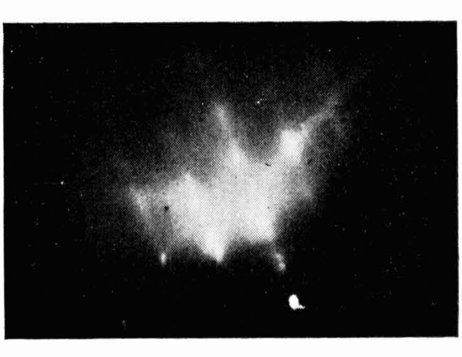


FIG. 2 — ELECTRON DIFFRACTION PATTERN OF ROCK SALT CLEAVAGE (100) FACE; BEAM ALONG [001] DIRECTION

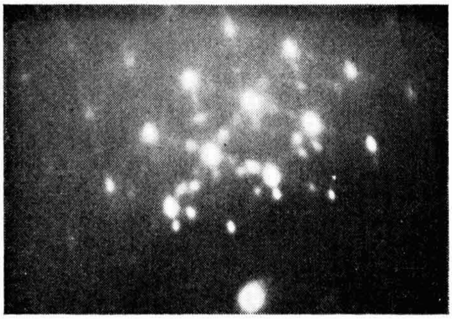


FIG. 3 — ELECTRON DIFFRACTION PATTERN OF SILVER FILM ON ROCK SALT CLEAVAGE FACE; BEAM ALONG [110] DIRECTION

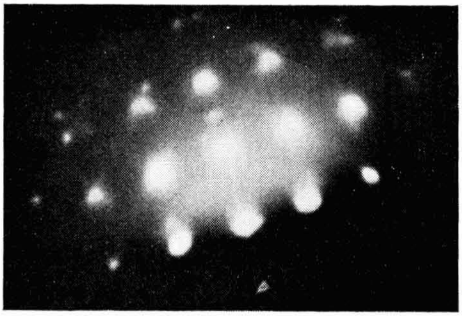


FIG. 4 — ELECTRON DIFFRACTION PATTERN OF SILVER FILM ON ROCK SALT CLEAVAGE FACE; BEAM ALONG [001] DIRECTION

patterns consisting of centred $\sqrt{2}$ rectangular type of spots having strong intensity (FIG. 3) are surrounded by groups of four satellite spots of less intensity, along the four equivalent [111] directions situated at one-third distance from the next strong spot of the main pattern. Similar groups of patterns are also seen though less prominent (FIG. 4), when the beam was along the cube axis of the rock salt. In addition to these spots, there are other diffraction spots, viz. one spot having strong intensity between 400 and 600 diffraction spots in the plane of incidence normal to the shadow edge and also a few others which do not seem to have any relation with either of the above two types of patterns.

The interpretation of the diffraction patterns of the two-degree orientated silver film was done from the consideration of the reciprocal lattices of the silver film. The electron diffraction pattern of any crystal corresponds to the projection of the reciprocal lattices in a plane normal to the beam direction but magnified λL times. When the electron beams are along either the cube or cube face diagonal directions of silver crystals the patterns will be similar to the projection of reciprocal lattices as on the (100) and (110) planes. The patterns will be square or centred $\sqrt{2}$ types of rectangles respectively. Such patterns were observed when the beam was either along the cube or cube face diagonal directions of the rock salt crystal. Hence the orientation of silver film was such that the cube axis of the silver crystal was along the cube axis of the rock salt crystal.

The second orientation was obtained from the diffraction spots appearing in the plane of incidence normal to the shadow edge. It is seen that 200, 400, 600 types of diffracted spots are in the plane of incidence normal to the shadow edge and hence the cube axis of the silver was also normal to the rock salt surface, i.e. (100) plane of silver was parallel to the cube face of rock salt. The orientation of the silver film was thus completely fixed in two directions with respect to the substrate sodium chloride lattice. The third axis is automatically fixed.

The indexing of the patterns is shown in Figs. 5 and 6. The indexed patterns mostly conform to the above orientation with the exception of a few diffraction spots which are considered below. The appearance of groups of four satellite spots having non-integral values of indices along the four symmetrical [111] directions of silver is due to the extensive twinning on the four

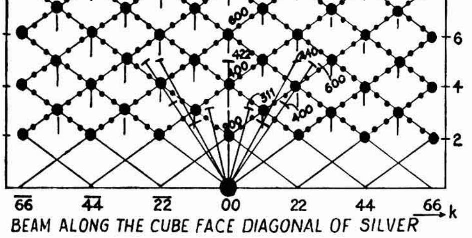


FIG. 5 — INDEXED ELECTRON DIFFRACTION PATTERN (FIG. 3) [●, main spot pattern; •, spot due to twinning]

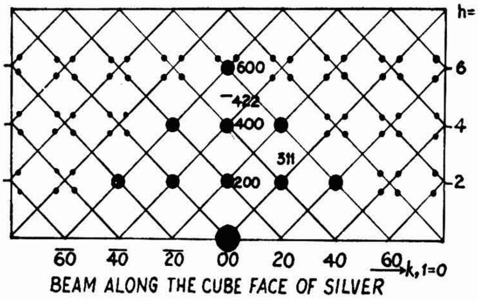


FIG. 6 — INDEXED ELECTRON DIFFRACTION PATTERN (FIG. 4) [●, main spot pattern; •, spot due to twinning]

equivalent symmetrical { 111 } planes of silver as had been explained by Menzer[7,8] and Goche and Wilman[1].

It is further seen that the 422 diffraction spot appears in the plane of incidence, normal to the shadow edge indicating that the film was growing with { 211 } types of planes parallel to the cube face of the rock salt crystal. Further, the occurrence of 311, 200, 440 diffraction spots (FIG. 5) in their abnormal positions, conforming to the (100) orientation (in addition to the normal positions) at angles about 15°, 34° 30′ and 30° respectively from the plane of incidence, seems to be due to the (211) orientation of some of the silver crystals, since the angle between the (211) plane and those above should be 15°, 35° 16′ and 30° 1′ respectively for (211) orientation of the film.

In addition to the above abnormal diffraction spots there are many other diffraction spots, situated just below the normal diffraction spots of silver but elongated towards the shadow edge (FIG. 3; *see* indexed pattern 5), which could not be accounted for from the normal diffraction spots either from silver or sodium chloride or from the probable reaction products silver chloride. Possibly these spots were due to the refraction effects of silver crystals, which grew with definite facets.

Double twinning — The formation of some silver crystals with the { 211 } planes parallel to the cube face of the rock salt, along the main two-degree (100) orientation, is not clearly understood, even from the consideration of the best atomic fitting between the substrate and the deposited lattices. The deposited silver would then have (100) orientation but their cube axis would have been turned through 45°, i.e. the cube axis would have been parallel to the cube face diagonal direction of the rock salt. But such orientation was not found in the present case. On the other hand, the (211) orientation of silver crystal can be easily explained from the phenomenon of double twinning as was observed by the author[11] during the epitaxial growth of cuprous oxide on Cu (110). The presence of many satellite spots indicates the extensive nature of the twinning on { 111 } planes of silver crystals. It is quite possible that some of these twinned crystals may retwin themselves on one of the remaining three { 111 } planes of the twinned crystal bringing a new set of planes parallel to the initial crystal face.

It is seen from Fig. 7 that if a crystal twins on { 111 } planes, the { 221 } and { 114 } planes of the twinned crystals become parallel respectively to the (100) and (110) planes of the initial crystal. But on retwinning on { 111 } planes the { 211 } planes of the second twinned crystal become nearly parallel to (100) plane of the initial crystal. Thus, silver crystals growing initially with (100) orientation may, after some time, show (221) and (211) orientations due to the single and the double-twinning phenomena. The appearance of groups of

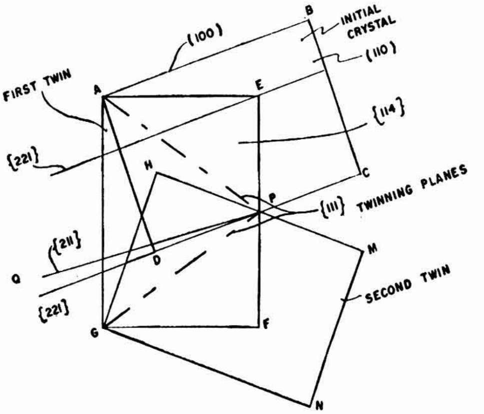


FIG. 7 — FORMATION OF DOUBLY TWINNED CRYSTALS OF SILVER; TWINNING ON { 111 } TYPES OF PLANES [ABCD, original crystal; AEFG, twinned crystal; GHMN, doubly twinned crystal; AP, PG, twinning planes, (111) types; PQ, 211 planes of doubly twinned crystal, nearly parallel to (100) plane of the initial crystal]

satellite spots round the normal diffraction spots shows that the crystals had (221) orientation, though the actual (221) diffracted spot could not be recorded due to the small size of the negative plates. But the appearance of (211) type of orientation, due to double twinning, has been observed in the present investigation.

Growth of silver films — Laue[3-5] in his theory of form factors showed that the formation of crystals with definite facets was possible but he did not clearly explain how the silver film was growing on rock salt with increase in thickness. Menzer's idea of the growth of silver film was that at the initial stage of the film formation crystal nuclei grew with their { 221 } planes parallel to the cube face of silver. With increase in film thickness, the crystal nuclei met and coalesced to form interpenetrating lattices finally forming (100) face of the silver parallel to the cleavage face of rock salt. Goche and Wilman, in their detailed study, also supported the above view of the growth of silver film. This view of the growth of silver film with the initial (221) orientation and finally developing (100) orientation does not seem to be very likely as has already been discussed[9]. On the other hand the growth of the films, the extensive twinning, the double-twinning phenomena, etc., can be easily interpreted by the mechanism that initially crystals of silver grew with their (100) planes parallel to the rock salt cleavage face. Due to the lattice misfits between the substrate and the deposits (about 27 per cent) in their interface, there will be considerable interfacial stress which will cause extensive twinning of deposited silver crystals. Some of the twinned crystals may then retwin themselves bringing { 211 } planes nearly parallel to the rock salt cleavage face.

The above mechanism is quite consistent with the author's observations[11,12] on the growth of two-degree orientated cuprous oxide on Cu (110), where it was found that cuprous oxide initially grew with parallel (110) orientation on Cu (110) but with increase in thickness of the film the crystals of cuprous oxide had a tendency to twin on { 111 } planes, finally bringing { 114 } type of planes parallel to the (110) face of Cu.

Acknowledgement

My best thanks are due to Prof. K. S. Krishnan, Director, National Physical Laboratory, New Delhi, for his encouragement and interest in the work and to the National Institute of Sciences of India for the award of an I.C.I. Fellowship.

References

1. GOCHE, O. & WILMAN, H., *Proc. phys. Soc.*, **51** (1939), 625.
2. KIRCHNER, F. & LASSEN, H., *Ann. Phys. Lpz.*, **24** (1935), 173.
3. v. LAUE, M., *Ann. Phys. Lpz.*, **26** (1936), 55.
4. v. LAUE, M. & RIEWE, K. H., *Z. Krystallogr.*, **95** (1936), 408.
5. v. LAUE, M., *Ann. Phys. Lpz.*, **29** (1937), 211.
6. MENZER, G., *Naturwissenschaften*, **26** (1938), 385.
7. MENZER, G., *Z. Krystallogr.*, **99** (1938), 378.
8. MENZER, G., *Z. Krystallogr.*, **99** (1938), 410.
9. BRU, L. & GHARPUREY, M. K., *Proc. phys. Soc.*, **64A** (1951), 283.
10. EVANS, D. M. & WILMAN, H., *Proc. phys. Soc.*, **63A** (1950), 298.
11. GOSWAMI, A., *Ph.D. Thesis, London University* (1950).
12. GOSWAMI, A., *Symposium on Electroplating and Metal Finishing*, National Metallurgical Laboratory, Jamshedpur (1952), 16.

Effect of Shape on the Voids Content of Sized Powders & Their Binary Mixtures

G. D. JOGLEKAR & N. R. SUBRAMANIAN
Division of Industrial Physics, National Physical Laboratory of India, New Delhi

The factors influencing the packing of powdered materials in general, and of petroleum coke and retort carbon, and their binary mixtures in particular, have been studied. With finer sizes, the cohesive forces binding the particles together become predominant and affect the packing density. In the packing of powders of finer sizes, the fractions composing the powders should be selected on the basis of practical grading trials.

THE subject of the packing of aggregates of powders of different sizes and shapes is of importance in manufacturing processes where compaction of powders into the desired shapes is carried out, such as in the manufacture of ceramic wares, refractory materials, carbon products, powder metallurgy products, etc. The compaction may be achieved either by moulding or by extrusion. The quality as shown by the strength, porosity, permeability, etc., of the finished products depends to a considerable extent upon the particle sizes of the various materials that make up the product. The packing of concrete aggregates by suitable grading and the determination of its bulk density are of considerable importance in civil engineering works and in studies connected with the flow of fluids through granular beds and porous bodies.

Variables

During the past 25 years a number of papers have appeared dealing with the theoretical aspect of this subject, but still the grading of particles is mostly carried out either by empirical formulae or by trial and error methods. This is due to the fact that the solution of this problem purely by mathematical treatment is difficult, as a number of variables come into operation. These variables may be put down as:

(1) Shape of the particles.
(2) Size of the particles.
(3) Orientation of the particles in the container. In the present studies the orientation is of a random nature.
(4) Method of mixing of the particles.
(5) Weight of the particles.
(6) Specific properties of the material such as hardness, density, etc.
(7) Surface condition of the particles.
(8) Shape and size of the container.
(9) Mode and degree of compaction.
(10) Cohesive forces between the particles.
(11) Friction between the particles and the container walls.

The shape of particles and the effects of some of these variables are difficult to ascertain, and, therefore, the best solution is obtained by the method of trial and error, though theoretical studies do help in indicating the changes to be made in the selection of different sizes to achieve the desired result.

Packing of particles with defined geometrical shapes — The shape of particles generally met with in industrial processes is irregular, and in most cases difficult to ascertain correctly. With the same raw materials, the shape of particles may vary with the size and the method of comminution used. In the theoretical approach to the subject, only particles having well-defined geometrical shapes have been studied. Most of the work deals with spherical particles.

In the case of cubes for an arrangement giving maximum packing density and zero voidage, each cube would touch its neighbour in (6 × 4) 24 ways without disturbing the packing density. If the cubes are replaced by square plates every plate would touch its neighbour in (4 × 2) 8 ways. If rectangular plates are used, each plate would touch its neighbour in (2 × 2) 4 ways. This shows that the randomness of getting a dense packing decreases as the shape of the particles departs from a cubical one. In the case of hexagonal and triangular plates giving zero voidage, every plate would touch its neighbouring ones in (6 × 2) 12 and (3 × 2) 6 ways respectively.

In the case of spheres of any one size the densest packing takes place in two types of orientations obtained with the rhombohedral packing. The per cent voidage obtained with spheres in different packing arrangements is given in Table 1[1].

The packing of ellipsoids and cylinders was studied by White and Walton[2]. They have shown that the use of particles of ellipsoidal shape does not appear to reduce the porosity, but particles of cylindrical shape reduce it below that possible with the spherical ones.

It will be seen from Table 1 that the voidage decreases as the number of points of contact increases. If it is desired to reduce the voidage the voids will have to be filled by smaller spheres which will fit into the irregular shaped pockets between the primary spheres without disturbing the arrangement. These spheres may be called the " secondary spheres ". Even with this arrangement a certain voidage will be left and this can be further reduced by ternary, quaternary, and quinary spheres of successively smaller and smaller diameters. The increase in the number of sizes increases the number of the points of contact and thus decreases the voidage. The voidage will be reduced to zero when the number of points of contact becomes infinite, and the solid state is reached.

White and Walton[2] have investigated the decrease in voidage that can take place by using successively smaller and smaller spheres for one rhombohedral system of packing. They have shown that the voids can be reduced from 25·95 to 14·9 per cent by using smaller and smaller spheres up to the quinary stage. Further addition of very fine filler to fill up the remaining voids reduces the voidage theoretically from 14·9 to 3·9 per cent.

TABLE 1 — PER CENT VOIDAGE WITH SPHERES

No.	SYSTEM OF PACKING	POINTS OF CONTACT	VOIDAGE %
1	Cubic	6	47·64
2	Orthorhombic (two orientations)	8	39·55
3	Tetragonal sphenoidal	10	30·20
4	Rhombohedral (two orientations)	12	25·95

The theoretical minimum voidage is obtained only when each sphere goes into its proper place, but such an arrangement is not practically possible. The importance of the theoretical study is only to get some sort of an indication of the proportions of the various sizes which are likely to give low-void mixtures.

Practical studies have been carried out on the packing of lead shots by a number of workers. With the same size of shots, the voidage varies from 37 to 44 per cent. Smith *et al.*[3] have studied the distribution of contacts per sphere and have shown that the number of contacts that generally occur is 8. From Table 1 it will be seen that this corresponds to the orthorhombic system of packing. The voidage obtained with such a system is 39·55 per cent which nearly corresponds to that obtained in practice.

The voidage is generally found to be more for particles having irregular shapes, and the increase in voidage is somewhat proportional to the deviation of the shape of the particles from the spherical one.

Fraser[4] has shown that angularity may either increase or decrease the voidage. Generally it increases the voidage, but in the case of mildly and uniformly disc-shaped particles, there is a decrease.

Container — The theoretical packing densities obtained in the case of spheres in infinite space do not hold good when packing is considered in a container. This is due to the effect of container walls.

Verman and Banerjee[5] have considered the effect of container walls on the packing density of single size or mixture of different sizes of particles, in which each small sized fraction is present in sufficient proportion to fill up the voids produced by the next larger sized fraction. In such a case only the smallest sized fraction is to be taken into account for considering the effect of container walls.

For a cubical container they give a formula:

$$d_n = \left(\frac{n-1}{n}\right)^3 d_o \quad \ldots\ldots\ldots (1)$$

Where dn is the overall packing density in a cubic container having sides n times particle diameter of the smallest sized material and d_o is the characteristic packing density of the particles in the interior of the container which may be considered as specific to the particle shape and size and the mode of packing.

The above equation may be written as

$$d_n = \left(1 - \frac{3}{n}\right)d_o \quad \ldots\ldots\ldots \quad (2)$$

by omitting the higher values of $\frac{1}{n}$ when n becomes sufficiently large. If the error due to the effect of container walls should be less than 1 per cent, it will be necessary to have the sides of the container 300 times the diameter of the packed material.

The perturbing effect of the container walls extends deeper than the layer of particles in actual contact with the walls, and the same authors have modified equation (1) as follows:

$$d_n = \left(\frac{n-1}{n}\right)^3 d_o + \left[1-\left(\frac{n-2}{n}\right)^3\right]\Delta d \quad \ldots \quad (3)$$

where Δd is the change in density due to the perturbing effect only. Brown and Hawksley[6] have shown that this effect extends to a depth of three particles. They have shown that Δd is small in the case of coal particles, indicating thereby that the wall effects for irregularly shaped particles would be less than for spheres. To fit their experimental data on the packing of coal, they have also suggested that the factor $(n-1)$ in equation (1) should be changed to $(n-\frac{1}{2})$. With this modification equation (2) may be written as

$$d_n = 1 - \frac{3}{2n}\, d_o \quad \ldots\ldots\ldots \quad (4)$$

Considering equation (4), the sides of the container will have to be 150 times the diameter of the powder to give an error of 1 per cent.

Frictional forces — From the above discussions it will be seen that the study of the effect of the variation of shape and of container walls is limited to theoretical considerations only. In industrial practice, the particles of materials employed do not have well-defined geometrical shapes. The cohesive forces between the particles and the frictional forces between the particles and the container walls also play an important part. The magnitude of each of these is difficult to judge. The cohesive forces assume great importance as the size of the particles gets finer and finer, and may be the predominant factor governing the packing density.

Range of sizes — Another factor which is of importance is the range of sizes of particles generally used in practice, and this range is limited in most cases. Perhaps the only case where the range is very large is the concrete mixture, where the diameter of the stone may be about 1 in , and that of the cement about 12 μ, and the ratio of the diameters of the two sizes would then be approximately 2,000.

Such large differences between the largest and the smallest diameters do not exist in other industries. In the case of the powder metallurgy products, the size variation is much restricted. The carbon products, in which the authors are interested, also do not have such a wide variation in particle sizes. For most of the industrial products one may take the larger particle size as about 100 μ and the lower size as 2 to 5 μ. In actual practice this range is much narrowed down. It will also be seen that the particle size used is such that the cohesive forces may become more important, and the normal theoretical considerations of packing do not hold good completely.

Materials and methods

The authors were interested in the subject of the packing of petroleum coke and retort carbon powders in connection with their work on the manufacture of carbon products. This study was considered essential to get the products of maximum or desired density, and with the desired texture in the finished products. Efforts were made to get the desired properties by gap grading, as this method was found more suitable than continuous grading.

Materials — The materials taken for study in these experiments were petroleum coke and retort carbon. These were calcined to *c.* 1,200°C. to drive off the volatile matter. The calcined sample of petroleum coke had less than 1 per cent ash, while the retort carbon had *c.* 4 per cent ash. The specific gravity ($-60+70$ size) of the petroleum coke was 2·00 and that of the retort carbon was 1·84. The material was ground in a ball mill, and sieved with the I.M.M. sieves, to get the desired sized fractions. The ground material was treated with a magnetic separator to remove any iron particles that might have come in from the ball mill parts during grinding. The sized fractions were heated at 110°C. for 1-1½ hr. before using them for apparent density determinations to remove the absorbed moisture which might affect the inter-particular forces.

The average figures for the voids per cent obtained for various sized fractions of the petroleum coke and the retort carbon are given in Table 2 and graphically shown in Fig. 1. The −200 mesh fractions were sufficiently closely sized fractions. Their size distribution was studied by the sedimentation method, and the diameter of the predominant size is given in the table. The bag material was obtained by air separation of the powders and had a particle size varying between 5 and 10 µ. The diameter in such cases was the " Stokes diameter " (ds).

The packing densities can be measured either in the loose state or in the compacted state. The former was selected for these studies. In loose packing, minimum degree of compaction is obtained. As it was desired to study the effect of the particle shape on the packing density, the tapping method of compacting was not selected. It was thought that tapping or vibrating in a particular direction, either horizontal or vertical, or a combination of both, may affect the packing due to the shape factor of the particles, the particles being either flaky, angular or spherical.

Apparatus — The apparatus used for measuring the apparent density of powders was similar to that recommended in the A.S.T.M. Specifications on the Standard Methods of Testing Moulding Powders[7]. The apparatus consisted of a measuring cup of 100 cc. capacity. The diameter of the cup was equal to half its height. The funnel used for holding the powder had a cone angle of 40°. The dimensions of the cup and the funnel are given in Fig. 2. The apparatus was assembled as shown in the figure.

TABLE 2 — PERCENTAGE OF VOIDS IN SIZED FRACTIONS OF PETROLEUM COKE AND RETORT CARBON

Size	Average diameter (microns)	Voids %	
		Petroleum coke	Retort carbon
−10+20	952	67·8	54·3
−20+30	530	67·3	55·6
−30+40	370	67·4	55·4
−40+50	285	67·3	56·7
−50+60	233	67·5	—
−50+70	197	67·7	—
−60+70	218	—	56·9
−70+80	170	67·0	56·9
−100+120	116	67·4	58·0
−120+150	95	67·7	58·6
−200	52*	67·8	—
−200	40*	—	64·6
Bag material	5-10*	88·0	84·3

*Predominant size present determined by sedimentation method; diameter, Stokes diameter (ds).

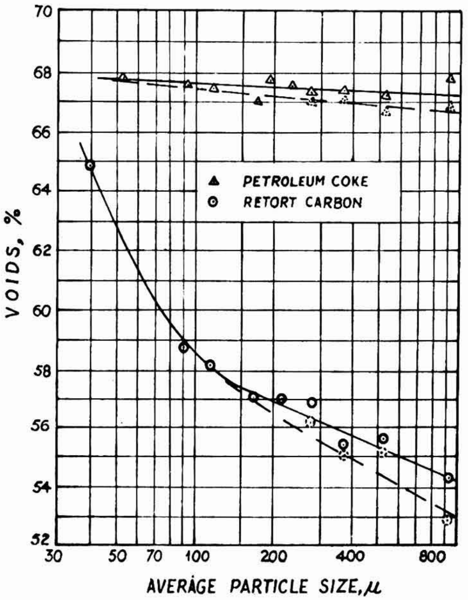


FIG. 1 — VOIDS IN SIZED FRACTIONS

Apparent density of sized fractions — A sample weighing 100 g. was taken from the sized fractions and put in the funnel, the bottom end of which was kept closed with a flat strip. When the sample was poured into the funnel, the flat strip was then removed quickly and the material allowed to fall freely into the cup. When dealing with finer fractions the flow was not continuous, and the material in the funnel was loosened by means of a thin wire. After all the material from the funnel had fallen into the cup, the excess material on the top of the cup was scraped off with a straight edge. In carrying out all these operations, care was taken to see that no jerks were given to the apparatus causing thereby some packing other than the loose one to take place. The material in the cup was then accurately weighed to the nearest 0·10 g. The weight in grams of 1 cc. of powder gave the apparent density of the powder. Generally, minimum of three such readings were taken, and the results averaged out. The variation between individual readings was found to be less than 1 per cent.

Packing density — To obtain the packing density of the material, the apparent density figures were divided by the specific gravity of the material.

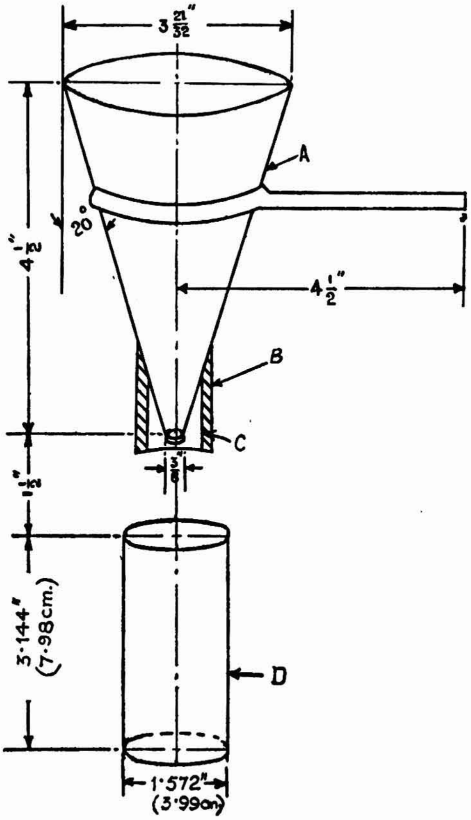


FIG. 2 — APPARATUS FOR APPARENT DENSITY TEST [A, solder $\frac{1}{4}$ in. brass ring around outside; B, solder $\frac{3}{32}$ in. brass tubing, $\frac{3}{4}$ in. I.D.; C, space not to be filled with solder; D, 100 cc. standard liquid measure calibrated to an accuracy of 0·5 cc.]

Voids per cent — When the cup was filled up with the powder, certain amount of voids were left between the particles and between the particles and the container walls. The voids per cent was calculated from the following:

$$\text{Voids per cent} = (1 - \text{packing density}) \times 100$$
$$= \left(1 - \frac{\text{apparent density}}{\text{specific gravity}}\right) \times 100$$

Flow time — The time required for 100 g. of the powder to flow through the funnel of the apparatus used for apparent density determination was noted. In the case of petroleum coke, it could be measured easily up to $-100+120$ mesh fraction. It was about 10 sec. For the next finer fraction, i.e. $-120+150$ mesh fraction, it shot up to about 27 sec., and for still finer fractions it could not be determined.

In the case of retort carbon up to -50 $+70$ mesh fraction, the flow time was about 7-8 sec.; for $-70+80$ mesh fraction it was about 14 sec., and for finer fractions it could not be determined as the powder did not flow freely.

Apparent density of binary mixture — The effect of mixing finer fractions with the rougher ones on the lowering of the voids per cent was studied with these powders. The fixed size was $-10+20$ mesh fraction. Finer fractions in varying percentages were mixed with the fixed fraction and their apparent densities determined and the voids percentage calculated from the average of the apparent density determinations. The various fractions were mixed in the desired proportions on weight basis. To avoid any segregation of the mixed material, a double cone mixer was designed from which the mixed powder could be poured straight into the measuring cup. The cones had the same dimensions as the funnel in Fig. 2. The two cones were spaced by a cylindrical portion.

The details about the mixer are shown in Fig. 3. The fractions were heated at 110°C. for 1-$1\frac{1}{2}$ hr., and requisite quantities of each were put in the conical mixer, the bottom end of which was kept closed by a cork. After filling the mixer, the top end was also closed by a cork and the mixer was then rotated 50 times by hand. After the mixing was over, the cork on the top end was removed. A flat metal strip was put on this end and this end was brought down over the measuring cup. The other cork was then removed, and the metal flat strip was taken away quickly, and the mixed powder allowed to fall freely into the cup. The extra powder was removed with a straight edge and the weight of the mixture determined as in the previous case. When finer fractions were added, it was found necessary to loosen the material in the cone by a thin wire.

The weight in grams of 1 cc. of mixture of the powders gave the apparent density of the mixture. From this the packing density and the voids per cent were calculated. The average voids per cent obtained for petroleum coke and retort carbon with these mixtures are shown in Tables 3 and 4 respec-

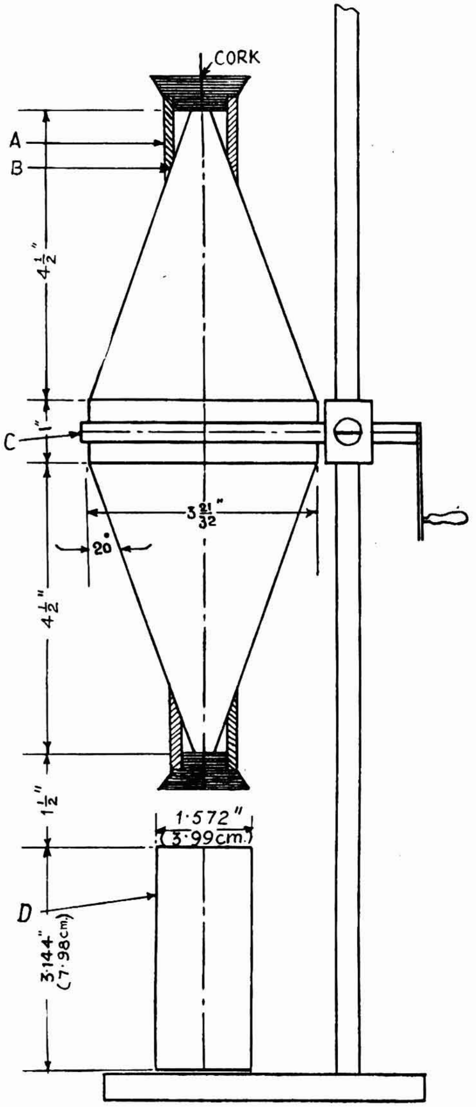


FIG. 3 — APPARATUS FOR APPARENT DENSITY TEST FOR MIXTURES [A, solder $\frac{3}{32}$ in. tubing of brass, $\frac{3}{4}$ in. I.D.; B, space not to be filled with solder; C, solder $\frac{1}{4}$ in. brass ring around outside; D, 100 cc. standard liquid measure calibrated to an accuracy of 0·5 cc.]

tively. The results are shown graphically in Figs. 4 and 5 respectively.

Table 4 does not give figures for voids per cent when the bag material is added to the fixed size. With 5, 10 and 25 per cent of the bag material, the figures for voids per cent are 56·8, 57·6 and 59·8 respectively.

TABLE 3 — PERCENTAGE OF VOIDS IN BINARY MIXTURES OF PETROLEUM COKE

(*Fixed size* −10+20 *mesh fraction; voids* %, 67·8)

SIZE / % VARIABLE SIZE BY WT.	VOIDS %						
	25	40	45	50	60	75	100
−20+30	—	—	—	66·6	—	—	67·3
−30+40	66·7	—	—	66·2	—	66·4	67·4
−60+70	65·0	—	—	64·5	—	65·4	67·7
−100+120	63·9	—	—	62·9	—	64·4	67·4
−120+150	63·2	—	—	62·0	—	64·0	67·7
−200	62·2	58·5	57·8	58·4	59·8	63·4	67·8

TABLE 4 — PERCENTAGE OF VOIDS IN BINARY MIXTURES OF RETORT CARBON

(*Fixed size* −10+20 *mesh fraction; voids* %, 54·3)

SIZE / % VARIABLE SIZE BY WT.	VOIDS %				
	25	40	50	75	100
−20+30	54·2	—	54·8	55·4	55·6
−30+40	53·5	—	53·5	54·0	55·4
−40+50	52·6	52·6	52·8	54·0	56·7
−50+70	51·2	50·7	50·4	52·9	56·9
−70+80	49·8	49·2	49·2	52·8	56·9
−100+120	48·6	46·8	47·3	54·0	58·0
−120+150	48·5	47·4	48·1	53·0	58·6
−200	48·8	47·2	50·2	—	64·6

Discussion

Wall effect — It would be seen from the experimental part of this paper that no corrections for the effect of container walls have been applied in finding out the apparent densities of the powders. The wall effect becomes of appreciable importance if the size of the container is comparable with the size of the particles under study. In mixtures, if the finer fraction is present in sufficient quantity, the size of the finer fraction should be taken into account in evaluating the effect of the container walls.

In Table 5 are given the ratio of the diameter and the length of the measuring cup to the average size of the particle. The experimental variations may be put down as 1 per cent. If the wall effect is smaller or of this order, it may be neglected. In the introductory part, it was stated that if the ratio n = 300, the error would be 1 per cent if Verman's formula is taken into consideration. If the modified formula suggested by Brown and Hawksley is applied, this value for "n" would be 150 for a similar error. It was also stated there that the wall effect for irregularly shaped particles would be less

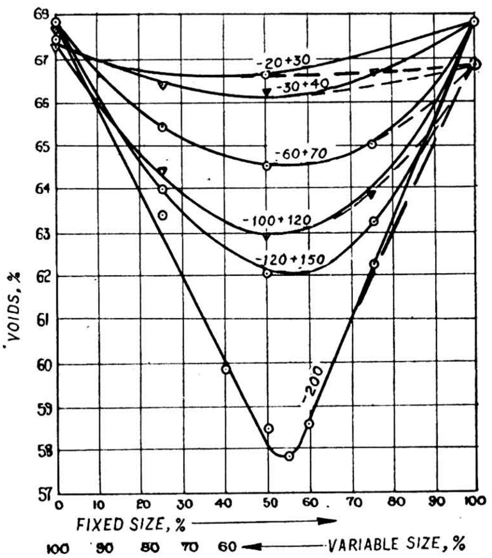


FIG. 4 — VOIDS IN THE BINARY MIXTURES OF PETROLEUM COKE

TABLE 5 — RATIO OF CONTAINER DIAMETER AND HEIGHT TO THE AVERAGE PARTICLE DIAMETER

I.M.M. MESH SIZE	AVERAGE DIAMETER μ	$n_1 = \frac{\text{CONTAINER DIAM.}}{\text{AVERAGE PARTICLE DIAM.}}$	$n_2 = \frac{\text{CONTAINER HEIGHT}}{\text{AVERAGE PARTICLE DIAM.}}$
−10+20	952	42	84
−20+30	530	75	151
−30+40	370	108	216
−40+50	285	140	280
−50+60	233	171	342
−60+70	197	203	406
−50+70	218	183	366
−70+80	170	235	470
−100+120	116	344	688
−120+150	95	420	840
−200	52	767	1534
−200	40	998	1996

than that for spheres. It will be seen from Table 5 that except in the case of −10+20 mesh fraction and perhaps to a certain extent with −20+30 mesh fraction there is no need to apply the wall correction.

In the case of mixtures containing −30+40 mesh or finer fractions, there is no need to apply corrections for the wall effect. As such the figures given for voids per cent in the tables are not corrected for wall effects. However, in Figs. 1, 4 and 5 are shown the corrected values of the voidage by dotted lines. The corrections for wall effect have been calculated by using Verman's formula as modified by Brown and Hawksley.

Voids per cent of sized fractions — It would be seen from Fig. 1 that the voids per cent of the sized fractions of petroleum coke does not vary over the size range studied. With retort carbon (FIG. 1) this is found to increase continuously, and the increase in the voids per cent for sized fractions less than 150 μ is very rapid. The voids per cent for the bag material is not shown in the figure.

The difference in the voids per cent shown by petroleum coke and retort carbon for the various sized fractions will have to be attributed to the shape of the particles. Fig. 6 shows petroleum coke and retort carbon in the lump form. Petroleum coke lumps (bottom) appear spherical while retort carbon lumps (top) appear cubical or platy and to a certain extent angular.

Petroleum coke is obtained in the distillation of petroleum oils as a residue, while retort carbon is obtained in coal carbonization by the deposition of carbon in the upper parts of the retort. Petroleum coke is a soft material and easier to grind than retort carbon which is very hard and abrasive[8].

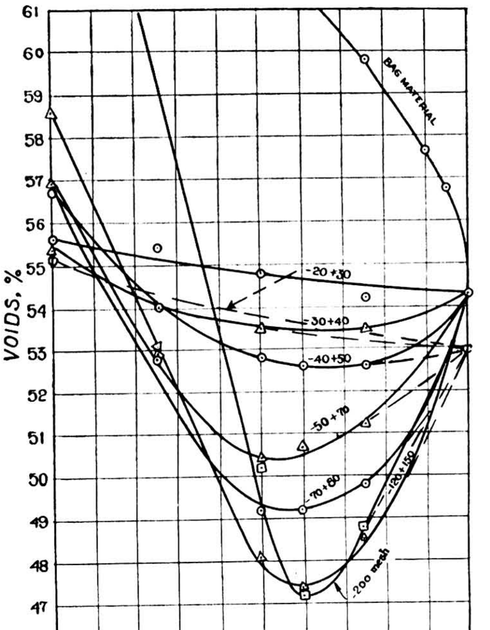


FIG. 5 — VOIDS IN THE BINARY MIXTURES OF RETORT CARBON

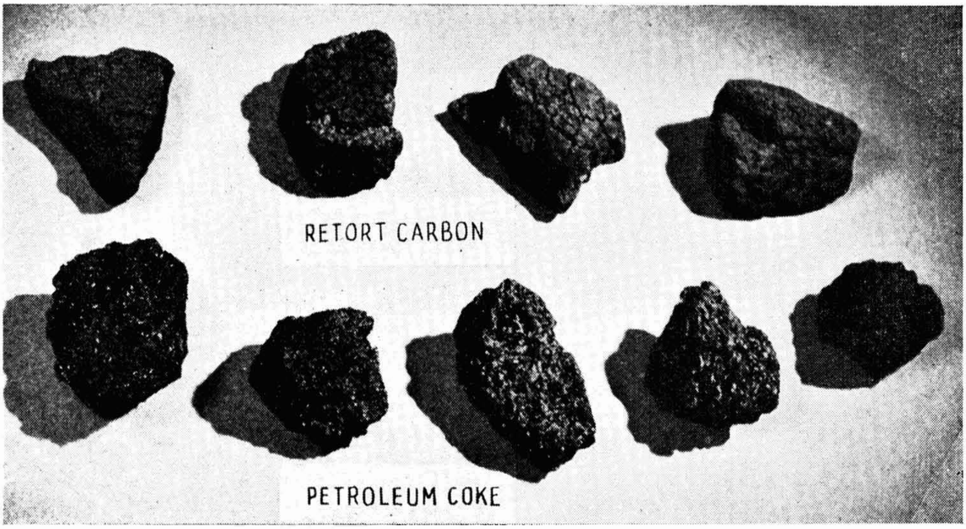


FIG. 6 — PETROLEUM COKE AND RETORT CARBON IN LUMP FORM

In grinding, the edges of particles get rounded off more quickly with petroleum coke than with retort carbon. This is brought out clearly in Figs. 7 and 8, which show the sized fractions of petroleum coke (−30+40 mesh) and of retort carbon (−40+50 mesh). Petroleum coke particles appear spherical, while retort carbon particles appear to be more angular in shape.

Retort carbon gives a higher packing density or lower voids than the petroleum coke. As the particles are cubical or platy, these perhaps give a closer packing than the spherical particles of petroleum coke. As the size is reduced, the edges get rounded off slowly and the particles try to approach sphericity, thereby causing a lowering of the packing density or an increase in the voids content.

The cohesive forces in petroleum coke do not increase to cause increase in the voids content up to 50 μ size, though they become predominant at some smaller size to give 88 per cent voids for the bag material. With retort carbon the change in the voids content is very rapid for particles less than 150 μ in size (FIG. 1).

It will be seen from these experiments that measurement of the loose apparent density of sized fractions brings out the variations in the shape of the particles under study. In addition it brings out whether or not any progressive changes are taking place in the shape of the particles as the size gets reduced. The method is simple and inexpensive.

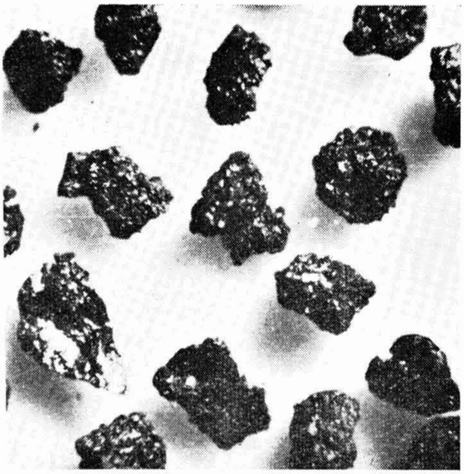


FIG. 7 — PETROLEUM COKE (−30+40 MESH I.M.M.)

Apparent density of binary mixtures — It was stated in the introductory part that the voids could be reduced by adding finer fractions which could fill up the voids. When

FIG. 8 — RETORT CARBON (−40+50 MESH I.M.M.)

finer fractions are added to the coarser ones the porosity gets reduced due to the finer fractions occupying the voids in the matrix formed by the coarser particles. The porosity gets continuously reduced till the finer fractions disturb the matrix of the coarser ones. Beyond this point, the finer fractions form the main matrix, in which the coarser fraction could be considered as embedded. From this limiting point the increased proportion of finer fractions gives increasing porosity till the porosity becomes the same as for the finer fractions.

It would be seen from Figs. 4 and 5 that the maximum reduction in voids takes place for both petroleum coke and retort carbon, when the percentage by weight of the coarse fraction is between 55 and 65 per cent. The shape factor does not seem to influence this percentage very much.

When bag material is added to the coarse fraction, the voids instead of decreasing are found to increase continuously with the increase in the percentage of the finer fraction. Theoretically the material being very fine, one should expect to get very low voids when such fine material is added. But the findings are on the contrary, due to the considerably increased effect of the cohesive forces which cause bridging and keep the particles away. Cohesive forces may also lead to small particles being attached at random to the surface of larger particles; thus disturbing the natural lattice arrangement which the larger particles may have assumed in the absence of smaller ones. The effect would be to push large particles apart and thus increase the voidage.

Decrease in voids per cent of binary mixtures

The per cent reduction in minimum voids over that of the fixed size fraction for the mixtures of petroleum coke and retort carbon is given in Table 6. The minimum voids are taken from Figs. 4 and 5 for petroleum coke and retort carbon respectively. The per cent reduction in minimum voids is plotted against the ratio of the variable size to the fixed size in Fig. 9. The figure shows that with petroleum coke there is a continuous increase in the per cent reduction in minimum voids over the size range studied. With retort carbon this increase continues till the size ratio becomes 0·1. Between size ratio of 0·1 and 0·04 no further increase

TABLE 6 — PERCENTAGE OF REDUCTION IN MINIMUM VOIDS FOR BINARY MIXTURES

(*Fixed size −10+20 mesh fraction*)

VARIABLE SIZE	RATIO = VARIABLE SIZE / FIXED SIZE	% REDUCTION	
		Petroleum coke	Retort carbon
−20+30	0·557	1·9	0·2
−30+40	0·389	2·5	1·5
−40+50	0·299	—	3·2
−50+70	0·229	—	7·2
−60+70	0·207	5·0	—
−70+80	0·179	—	9·4
−100+120	0·122	7·2	—
−120+150	0·100	8·6	12·7
−200	0·055	14·8	—
−200	0·042	—	13·1

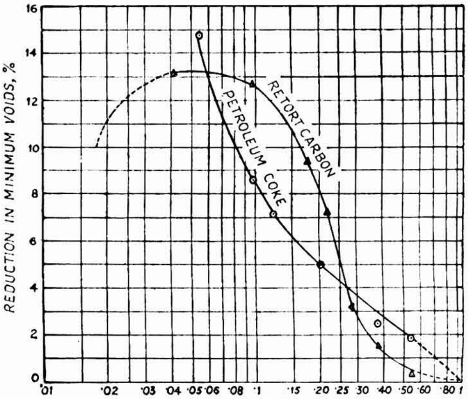


FIG. 9 — REDUCTION IN MINIMUM VOIDS OF BINARY MIXTURES

is obtained. The curve has a tendency to progress further as shown by the dotted line, due to the cohesive forces becoming predominant in this size range. The curve for petroleum coke would show a similar behaviour with finer sized fractions.

It would be seen from this study that it is better to select the various fractions based on practical tests, as the voids content depends upon the shape and size of powders used.

Acknowledgement

We are thankful to Shri R. C. Dhawan and Shri T. Suryanarayanam for taking the photographs and to Shri M. P. Kumarswamy for help in the experimental work.

References

1. GRATON, L. C. & FRASER, H. G., *J. Geol.*, **43** (1935), 785-909.
2. WHITE, H. E. & WALTON, S. F., *J. Amer. ceram. Soc.*, **20** (1937), 155-66.
3. SMITH, W. O., FOOTE, P. D. & BUSANG, P. F., *Phys. Rev.*, **34** (1929), 1271-74.
4. FRASER, H. G., *J. Geol.*, **43** (1935), 938.
5. VERMAN, L. C. & BANERJEE, S., *Nature*, **157** (1946), 584.
6. BROWN, R. L. & HAWKSLEY, P. G. W., *Nature*, **157** (1946), 585.
7. A.S.T.M. Designation D-392-38 (1938).
8. JOGLEKAR, G. D. & SEN, D., *J. sci. industr. Res.*, **4** (1946), 777.

Entrainment of Radiophosphorus (P^{32}) on Copper Sulphide

K. R. KAR & L. KASTURI RANGAN

Department of Chemistry & Department of Physics, University of Delhi, Delhi

During a chemical separation of radiophosphorus (P^{32}) from copper (on which it was deposited electrolytically) by precipitation of copper as copper sulphide, a measurable amount of P^{32} was found to be entrained in the copper sulphide precipitate and could not be removed by washing according to standard analytical procedure. Of the several wash solutions tried alkaline polysulphide solution was found to remove almost completely the entrained P^{32}. The observed effect is presumably due to the formation, in tracer quantity, of a sulphide of P^{32}, and its subsequent entrainment with the copper sulphide precipitate. A mechanism for the formation of such a compound has been suggested.

FOLLOWING the method of Govaerts[1], 2 l. of carbon disulphide contained in a Pyrex glass flask were irradiated with fast neutrons from a 100 mg. ($Ra\alpha+Be$) source for 250 hr. with two copper electrodes (2×1 in.) held inside the liquid with an electric field of 150 V./cm. between them. Most of the radiophosphorus formed by (n, p) reaction in S^{32} was found to be deposited on the electrodes. The copper plates were dissolved in acid, and copper was eliminated as copper sulphide from the mixed acid solution. It was observed that a measurable activity was retained on copper sulphide even after thorough washing according to standard analytical procedure. With a view to recover the entrained material and also to gain an idea as to its nature, the precipitated copper sulphide was washed with different wash liquids. Alkaline ammonium polysulphide solution was found efficient in removing completely the last traces of the active substance from the copper sulphide precipitate. Various possibilities to explain the observed effects have been examined, and it is postulated that a sulphide of phosphorus is formed on the copper sulphide precipitate during the precipitation of copper by hydrogen sulphide. The results of these investigations are discussed in this paper.

Experimental procedure

After irradiation, one of the copper electrodes containing the active deposit was examined by a Geiger-Müller radiation monitor and the activity followed for one month. It was found to decay with a half-life ∼14·3 days, which agrees with the known half-life of P^{32}.

The activity of the copper sulphide precipitate and other samples was measured by taking a known quantity of the sample under an end-window type of G.M. counter. The usual high tension supply, amplifier and recorder were used for detection. The geometry of counting and the masses of the various samples tested were kept identical. The probable error in counting in any of the cases did not exceed ± 10 per cent. The background activity was less than 4 counts per minute.

Isolation of P^{32} — The copper plates containing the active deposit of P^{32} were dissolved in concentrated nitric acid, the excess acid driven out completely and the copper separated from the solution as copper sulphide by passing a stream of washed hydrogen sulphide through the hot original solution. To the filtrate *c.* 80 mg. of sodium ammonium hydrogen phosphate (Analar) was added as carrier and the phosphate was finally isolated as magnesium ammonium phosphate. In one experiment, phosphate carrier was added to the solution even before eliminating copper. This was to examine if entrained activity on copper sulphide could be removed.

TABLE 1 — ENTRAINED ACTIVITY OF COPPER SULPHIDE PRECIPITATE AFTER DIFFERENT TREATMENTS

Expt. No.	Precipitate and mode of treatment	Nett count/hr.
1	CuS washed free from HCl with H_2S water	219
2	CuS washed free from HCl with H_2S water*	189
3	CuS washed with HCl solution	204
4	CuS washed with ammonium nitrate solution	201
5	CuS washed with ammonium phosphate solution	220
6	CuS washed with H_2S saturated ammonium hydroxide solution	105
7	Residual CuS precipitate in (1) filtered, mixed with pre-formed As_2S_3 ppt. and the mixture washed with ammonium polysulphide solution	35
8	About half of the As_2S_3 precipitated from filtrate in (7) was acidified and dried	105
9	The filtrate from (8) evaporated	10

*Carrier (sodium ammonium hydrogen phosphate) added before precipitating CuS.

Copper sulphide precipitate — Identical weights (110 mg.) of copper sulphide treated with various chemical reagents as well as untreated copper sulphide (after thorough washing with H_2S water) were dried and the activities of the samples were measured with the help of the counting unit. The results are given in Table 1.

Discussion

The results given in Table 1 reveal the following points: (1) Copper sulphide precipitate is practically completely freed from the active material when ammonium polysulphide is used as the wash liquid; (2) when a little pre-formed As_2S_3 precipitate was added to the CuS before washing with ammonium polysulphide and the filtrate containing the active material was acidified with hydrochloric acid, almost the entire activity is passed on to the As_2S_3 precipitate; the activity of the acidic filtrate is insignificant; (3) addition of phosphate carrier prior to the precipitation of copper sulphide decreases the activity of the precipitate slightly; (4) washing the precipitate separately with (a) ammonium phosphate, (b) ammonium nitrate and (c) hydrochloric acid is without any effect on the entrained activity on the copper sulphide precipitate. Failure of these solutions to dislodge the active material on the copper sulphide indicates that it is not a case of unspecific adsorption, because it is well known that in such cases substances which are most efficient in displacing adsorbed radio elements are the ions isotopic with those of the radio elements (in this case ammonium phosphate) or the ions containing its chemical homologue[2,3] (ammonium nitrate in this instance). On the other hand, the solubility of the material in alkaline ammonium polysulphide and its subsequent passage to the precipitated As_2S_3, obtained on acidification of the filtrate, can be explained if we assume that in the presence of an excess of hydrogen sulphide, the phosphate ion is converted, though in very small quantities, into thiophosphorus acid (by reduction) or thiophosphoric acid (salts of these acids are known[4]), and these unstable acids next break up into the sparingly soluble P_2S_5 or a lower sulphide of phosphorus (vide precipitation of As_2S_3 from an acidic solution of arsinate[5]) which get adsorbed on the surface of the copper sulphide precipitate. Unlike arsenic, a quantitative precipitation of phosphorus as sulphide does not take place because of its higher electronegativity.

When the copper sulphide precipitate is treated with alkaline polysulphide (expt. No. 7, TABLE 1), the sulphide of phosphorus formed reacts with the precipitate to give the soluble thio salt which passes along with the arsenic into the filtrate, from which it is again deposited over As_2S_3 precipitate on acidification. The little activity that passes on to the last filtrate is presumably due to partial hydrolysis of the phosphate[6]. The mechanism suggested may be represented as below:

$$H_3PO_4 + H_2S \rightleftharpoons H_3PS_4 \text{ or } H_3PS_3$$
$$2H_3PS_4 \longrightarrow 3H_2S + P_2S_5$$
$$P_2S_5 + (NH_4)_2S_x \longrightarrow (NH_4)_3PS_4 \text{ (soluble)}$$
$$(NH_4)_3PS_4 + \text{excess } H_2O \longrightarrow P_2S_5 + H_2S + NH_4OH$$
$$P_2S_5 + \text{excess } H_2O \longrightarrow P_2O_5 + H_2S$$

and also

$$(NH_4)_3PS_4 \text{ on acidification} \longrightarrow P_2S_5 \text{ (deposited on } As_2S_3 \text{)}$$

The dilution of the adsorbed activity on copper sulphide, when inactive phosphate carrier is added prior to the precipitation of copper sulphide, is due to the dilution of the active phosphate.

To test the validity of the suggested mechanism, copper was precipitated from a copper sulphate solution, under otherwise identical conditions, and the freshly formed precipitate, after washing it free from hydrogen sulphide, was added to the same volume of a solution containing the active phosphorus. The precipitate was kept in contact with the active solution for 24 hr. and its activity measured after thorough washing with water saturated with hydrogen sulphide. It is observed that so long as hydrogen sulphide is not bubbled through the solution containing the active material, the activity is not entrained along with the copper sulphide precipitate. The activity of 200 mg. of the copper sulphide sample thus obtained was 29 counts/hr. as compared to 180 counts/hr. for the same weight of copper sulphide precipitated by hydrogen sulphide gas directly from the active solution and washing it as before.

Acknowledgement

Our grateful thanks are due to Dr. N. K. Saha, Reader in Physics, Delhi University, for his kind interest and encouragement during the progress of the work. The work has been done with the financial support of the Atomic Energy Commission, Government of India.

References

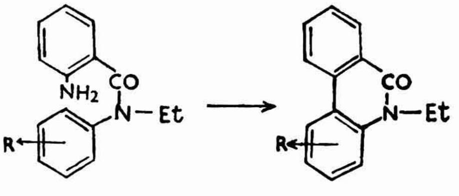
1. GOVAERTS, *Nature*, **141** (1938), 871.
2. OTTO HAHN, *Applied Radiochemistry* (University Press, Cornell), 1936, Chap. IV.
3. BRODA, E., *Advances in Radiochemistry* (University Press, Cambridge), 1950, 11.
4. EPHRAIM, *Inorganic Chemistry* (Gurney & Jackson, London), 1939, 732.
5. EPHRAIM, *Inorganic Chemistry* (Gurney & Jackson, London.), 1939, 735.
6. EPHRAIM, *Inorganic Chemistry* (Gurney & Jackson, London), 1939, 736.

Application of the Pschorr Reaction to the Synthesis of Phenanthridine Derivatives

T. R. GOVINDACHARI & N. ARUMUGAM
Chemistry Department, Presidency College, Madras

The Pschorr reaction has been applied to several 2-amino-N-ethylbenzanilides. The yields (5-19 per cent) of phenanthridones are unsatisfactory.

OF the several methods available for the synthesis of phenanthridine derivatives, the least investigated till recently has been the application of the Pschorr reaction to the synthesis of this ring system. Pictet and Gonset[1] reported the formation of N-methylphenanthridone by heating an aqueous solution of the diazonium chloride prepared from 2-amino-N-methylbenzanilide. Attempts by Richardson, Robinson and Seijo[2] and Noller, Denyes, Gates and Wasley[3] to apply the Pschorr reaction to the synthesis of benzophenanthridones did not succeed. Our interest in the application of the Pschorr reaction to the synthesis of phenanthridine derivatives was stimulated by the work of Hey and Osbond[4] on inter-nuclear cyclization employing the Pschorr reaction. We investigated the application of the Pschorr reaction to the diazonium compounds derived from the following amines: 2-amino-N-ethylbenzanilide, 2-amino-N-ethylbenzo-*o*-toluidide, 2-amino-N-ethylbenzo-*m*-toluidide, 2-amino-N-ethylbenzo-*p*-toluidide, 2-amino-2′-methoxy-N-ethylbenzanilide, 2-amino-3′-methoxy-N-ethylbenzanilide, 2-amino-4′-methoxy-N-ethylbenzanilide, 2-amino-3′-bromo-N-ethylbenzanilide and 2-amino-4′-bromo-N-ethylbenzanilide.



R = H, CH_3, OCH_3, Br

Meanwhile, Heacock and Hey[5] have reported the application of the Pschorr reaction to the synthesis of phenanthridine derivatives. However, all the compounds investigated by us are different from those employed by Heacock and Hey (loc. cit.). In no case could we get yields of the order obtained by these workers. The results of our experiments are presented in Table 1.

An ortho substituent on the ring undergoing cyclization lowers the yield, an observation also made by Heacock and Hey[5] and also supported by the observation that N-methyl-6, 7-methylenedioxyphenanthridone is obtained in 50 per cent yield[6,7], while N-methyl-1-ethyl-6, 7-methylenedioxyphenanthridone is obtained in only 10 per cent yield. Curiously, meta substituents on the ring undergoing cyclization appear to suppress phenanthridone formation completely. Decomposition of the diazonium sulphate by heating in presence of copper

TABLE 1 — N-ETHYLPHENANTHRIDONES

AMINE	PROCEDURE	YIELD %
2-Amino-N-ethylbenzanilide	a	8
	b	7
	c	5
2-Amino-N-ethylbenzo-*o*-toluidide	a	0
	b	5
	c	0
2-Amino-N-ethylbenzo-*m*-toluidide	a	0
	b	0
	c	0
2-Amino-N-ethylbenzo-*p*-toluidide	a	11
	b	5
2-Amino-2′-methoxy-N-ethylbenzanilide	a	13
	b	0
2-Amino-3′-methoxy-N-ethylbenzanilide	a	0
2-Amino-4′-methoxy-N-ethylbenzanilide	a	19
	b	5
2-Amino-3′-bromo-N-ethylbenzanilide	a	0
2-Amino-4′-bromo-N-ethylbenzanilide	a	6
	b	0
2-Amino-N-ethyl-N-phenylbenzylamine	a	0
	b	8

powder generally gave better yields than decomposition with addition of sodium hypophosphite. Diazotization with amyl nitrite offered no special advantage over the ordinary procedure. Pschorr ring closure of the diazonium sulphate obtained from N-ethyl-N-phenyl-2-aminobenzylamine also proceeded in poor yield giving 9, 10-dihydro-N-ethylphenanthridine. The results recorded in Table 1 may be useful in the assessment of the value of the Pschorr reaction for the synthesis of phenanthridine derivatives.

Experimental procedure

N-ethyl derivatives of *o*-, *m*- and *p*-toluidines, *o*-, *m*- and *p*-anisidines, *m*- and *p*-bromanilines were prepared by the following general procedure illustrated in the case of *o*-toluidine.

A mixture of *o*-toluidine (40 g.; 0·37 mole) and ethyl bromide (40 g.; 0·37 mole) was heated under reflux for 2 hr. The reaction mixture which set to a solid mass on cooling was treated with water, and excess ethyl bromide was expelled by boiling the solution. The cooled solution was made alkaline with a concentrated solution of sodium hydroxide and the liberated mixture of bases was extracted with ether. After removal of ether, the oily residue was dissolved in a mixture of concentrated hydrochloric acid (70 cc.) and water (350 cc.). The acid solution was cooled well in ice and treated with a saturated aqueous solution of sodium nitrite (21 g.). The nitrosamine which separated as a dark oil was extracted with ether and the ether extract thoroughly washed with a dilute solution of sodium hydroxide. The nitrosamine obtained after removal of the ether was added gradually to a cold solution of stannous chloride (122 g.) in concentrated hydrochloric acid (140 cc.). Careful cooling was necessary at this stage. The mixture was then made alkaline and steam distilled. The distillate was extracted with ether and the extract dried over potassium hydroxide. Removal of the solvent yielded N-ethyl-*o*-toluidine (17 g.) distilling at 215°.

Preparation of 2-nitrobenzoyl derivatives — The following general procedure illustrated in the case of N-ethyl-*o*-toluidine was adopted in all cases.

A solution of N-ethyl-*o*-toluidine (7·5 g.) in benzene (25 cc.) was treated with a solution of 2-nitrobenzoyl chloride (10 g.) in benzene (25 cc.). A solution of sodium carbonate (50 cc., 20 per cent) was run in with vigorous stirring. The aqueous layer was drawn off and the benzene layer washed successively with dilute hydrochloric acid (25 cc.; 4N) and water. The benzene was distilled off and the residue crystallized from dilute alcohol; yield 14 g.; m.p. 136°.

TABLE 2 — ANALYTICAL DATA FOR 2-NITRO-N-ETHYLBENZANILIDES

COMPOUND	M.P. °C.	NITROGEN	
		Found %	Required %
2-Nitro-N-ethylbenzanilide	99	10·2	10·4
2-Nitro-N-ethylbenzo-*o*-toluidide	136	10·1	9·9
2-Nitro-N-ethylbenzo-*m*-toluidide	106	10·1	9·9
2-Nitro-N-ethylbenzo-*p*-toluidide	90	10·0	9·9
2-Nitro-2′-methoxy-N-ethylbenzanilide	118	9·5	9·3
2-Nitro-3′-methoxy-N-ethylbenzanilide	88	9·8	9·3
2-Nitro-4′-methoxy-N-ethylbenzanilide	66	9·7	9·3
2-Nitro-3′-bromo-N-ethylbenzanilide	89	8·2	8·0
2-Nitro-4′-bromo-N-ethylbenzanilide	137	8·1	8·0

The melting points of the various anilides and the analytical data are recorded in Table 2.

Preparation of 2-amino-N-ethylbenzanilides — The 2-nitro-N-ethylbenzanilides were reduced to the corresponding 2-amino-N-ethylbenzanilides by the following general procedure.

A solution of 2-nitro-N-ethylbenzanilide (10 g.) in alcohol (150 cc.) was reduced at a hydrogen pressure of 60 lb./sq. in. after addition of Adams's catalyst (0·1 g.) in a Paar hydrogenation apparatus. After the reduction was complete, the catalyst was removed by filtration and the filtrate distilled to remove alcohol. The amine was purified by distillation and characterized by the preparation of suitable derivatives.

2-*Amino-N-ethylbenzanilide* was crystallized from alcohol; m.p. 104°-6° (found: N, 12·0; $C_{15}H_{16}N_2O$ requires: N, 11·7 per cent). The benzoyl derivative of the amine melted at 126° (found: N, 8·5; $C_{22}H_{20}N_2O_2$ requires: N, 8·1 per cent).

2-*Amino-N-ethylbenzo-o-toluidide* was a highly viscous oil. The hydrochloride prepared in the usual way and crystallized from absolute alcohol melted at 173° (found: N, 9·9; $C_{16}H_{19}N_2OCl$ requires: N, 9·6 per cent).

2-Amino-N-ethylbenzo-m-toluidide was a viscous oil. The picrate was prepared in the usual way and crystallized from alcohol; m.p. 156° (found: N, 14·8; $C_{22}H_{21}N_5O_8$ requires: N, 14·5 per cent).

2-Amino-N-ethylbenzo-p-toluidide was a viscous oil. The hydrochloride was prepared in the usual way and crystallized from absolute alcohol; m.p. 180° (found: N, 9·3; $C_{16}H_{19}N_2OCl$ requires: N, 9·6 per cent).

2-Amino-2'-methoxy-N-ethylbenzanilide was a viscous oil. The benzoyl derivative prepared in the usual way after crystallization from alcohol melted at 133° (found: N, 7·7; $C_{23}H_{22}N_2O_3$ requires: N, 7·5 per cent).

2-Amino-3'-methoxy-N-ethylbenzanilide— The base crystallized from alcohol melted at 69° (found: N, 10·3; $C_{16}H_{18}N_2O_2$ requires: N, 10·4 per cent). The hydrochloride of the base was prepared in the usual way and crystallized from alcohol; m.p. 170° (found: N, 9·4; $C_{16}H_{19}N_2O_2Cl$ requires: N, 9·1 per cent).

2-Amino-4'-methoxy-N-ethylbenzanilide — The base crystallized from alcohol melted at 102° (found: N, 10·7; $C_{16}H_{18}N_2O_2$ requires: N, 10·4 per cent). The benzoyl derivative melted at 92°-94° (found: N, 7·8; $C_{23}H_{22}N_2O_3$ requires: N, 7·5 per cent).

2-Amino-3'-bromo-N-ethylbenzanilide — The base crystallized from alcohol melted at 109° (found: N, 8·6; $C_{15}H_{15}N_2OBr$ requires: N, 8·8 per cent). The m.p. of the hydrochloride was > 350° (found: N, 7·6; $C_{15}H_{16}N_2OBrCl$ requires: N, 7·9 per cent).

2-Amino-4'-bromo-N-ethylbenzanilide — The base crystallized from alcohol melted at 91° (found: N, 8·5; $C_{15}H_{15}N_2OBr$ requires: N, 8·8 per cent).

The benzoyl derivative after crystallization from alcohol melted at 160° (found: N, 6·5; $C_{22}H_{19}N_2O_2Br$ requires: N, 6·6 per cent).

Preparation of phenanthridones by internuclear cyclization: *N-ethylphenanthridone* — *Procedure (a)* — A solution of 2-amino-N-ethylbenzanilide (2·4 g.) in dilute sulphuric acid (5 cc. concentrated sulphuric acid + 100 cc. water) was cooled in an ice-salt bath and treated dropwise with a solution of sodium nitrite (0·8 g. in 10 cc. water). After stirring for 1 hr. at the bath temperature, the temperature was allowed to rise and the solution was ultimately heated to 70° in a water bath. The heating was stopped when the evolution of nitrogen ceased. A dark brown oil separated at this stage. The solution was cooled and extracted with chloroform. The chloroform extract was repeatedly washed with a dilute solution of sodium hydroxide for removal of phenolic substances and finally with water. Removal of solvent from the dried chloroform extract left a dark brown viscous oil (1·7 g.). The oil was dissolved in dry benzene and chromatographed on an alumina column. The first 300 cc. of the benzene eluate were colourless, after which a yellow zone moved into the eluate. From the first eluate, 0·2 g. of N-ethylphenanthridone was obtained. This was recrystallized from alcohol; m.p. 89° (found: C, 81·1; H, 6·1; N, 6·6; $C_{15}H_{13}ON$ requires: C, 80·7; H, 5·8; N, 6·3 per cent). The eluate from the yellow zone yielded a yellow solid (0·5 g.) melting at 82°. The melting point of this solid was not sharp even after repeated crystallization.

The alkaline wash liquid from the original chloroform extract yielded on acidification a phenol, which melted at 74°-76° after crystallization from dilute alcohol. The yield of phenol was 0·7 g. (found: C, 74·7; H, 6·3; N, 5·2; $C_{15}H_{15}O_2N$ requires: C, 74·7; H, 6·2; N, 5·8 per cent).

Procedure (b) — A solution of 2-amino-N-ethylbenzanilide (3 g.) in dilute sulphuric acid (60 cc., 10 per cent) was cooled and diazotized in the usual way with sodium nitrite (1·3 g., 10 cc. water). The solution was then treated with sufficient sulphamic acid to react with excess sodium nitrite, and then with a solution of sodium hypophosphite (15 g. in 15 cc. water) after addition of a little copper powder. There was vigorous evolution of nitrogen and separation of resinous material. The solution and the resin were repeatedly extracted with chloroform, and the chloroform extract washed with alkali to remove phenolic material. The washed chloroform extract yielded a brownish residue. Chromatographic fractionation yielded N-ethylphenanthridone (0·2 g.; m.p. 89°), the other fractions being uncrystallizable oils.

Procedure (c) — A solution of 2-amino-N-ethylbenzanilide (3 g.) in alcohol (30 cc.) and sulphuric acid (d, 1·8, 1·8 cc.) was treated dropwise with amyl nitrite (36 cc.) at 20°. The solution was then gradually heated to 60° and copper powder (6 g.) added with vigorous stirring. There was vigorous evolution of nitrogen and separation of resinous material. The solution was filtered and the filtrate distilled to remove alcohol. Both the residues were thoroughly extracted with chloroform. The chloroform extract was washed with a dilute solution of sodium hydroxide and then with water. The residue left after removal of chloroform was chromatographed on alumina. The yield of pure N-ethylphenanthridone, m.p. 89°, was 0·15 g. The other fractions obtained were all uncrystallizable oils.

Pschorr reaction with 2-amino-N-ethylbenzo-o-toluidide — Treatment of 2-amino-N-ethylbenzo-*o*-toluidide by procedure (b) yielded a crystalline compound, m.p. 143°-45°, whose analysis, however, did not correspond to that expected for 1-methyl-N-ethylphenanthridone (found: C, 80·1; H, 6·1; N, 6·1 per cent).

3-*Methyl-N-ethylphenanthridone* was crystallized from alcohol and melted at 97° (found: C, 81·1; H, 6·4; N, 5·8; $C_{16}H_{15}ON$ requires: C, 81·0; H, 6·3; N, 5·9 per cent).

1-*Methoxy-N-ethylphenanthridone* was crystallized from alcohol and melted at 117° (found: C, 75·4; H, 5·4; N, 5·4; $C_{16}H_{15}O_2N$ requires: C, 75·9; H, 5·9; N, 5·5 per cent).

3-*Methoxy-N-ethylphenanthridone* was crystallized from alcohol and melted at 138° (found: C, 75·3; H, 5·5; N, 5·4; $C_{16}H_{15}O_2N$ requires: C, 75·9; H, 5·9; N, 5·5 per cent).

3-*Bromo-N-ethylphenanthridone* was crystallized from alcohol and melted at 116° (found: C, 59·6; H, 3·9; N, 4·6; $C_{15}H_{12}ONBr$ requires: C, 59·6; H, 4·0; N, 4·4 per cent).

N-ethyl-N-phenyl-2-aminobenzylamine — A solution of 2-amino-N-ethylbenzanilide (5 g.) in absolute ether (200 cc.) was added gradually to a stirred suspension of lithium aluminium hydride (1 g.) in absolute ether (150 cc.). After stirring for 1 hr., water was added cautiously to decompose excess lithium aluminium hydride. The ether layer was poured off from the sludge of lithium aluminate, dried over anhydrous sodium sulphate and the ether removed. Removal of the ether yielded N-ethyl-N-phenyl-2-aminobenzylamine (4·4 g.) which melted at 65°-67° after crystallization from alcohol (found: N, 12·7; $C_{15}H_{18}N_2$ requires: N, 12·4 per cent). The benzoyl derivative of the base melted at 130° (found: N, 8·5; $C_{22}H_{22}N_2O$ requires: N, 8·5 per cent).

9, 10-*Dihydro-N-ethylphenanthridine* — The above amine was submitted to the Pschorr reaction by procedure (b), and the product isolated by chromatographic fractionation. The oil obtained was converted to a picrate which melted at 210° after crystallization from alcohol (found: C, 57·8; H, 3·9; N, 12·9; $C_{21}H_{18}O_7N_4$ requires: C, 57·5; H, 4·1; N, 12·8 per cent).

Acknowledgement

We thank the Government of India for the award of a scholarship to one of us (N.A.).

References

1. Pictet & Gonset, *Arch. Sci. phys. nat.*, **3** (1897), 37.
2. Richardson, Robinson & Seijo, *J. chem. Soc.*, (1937), 835.
3. Noller, Denyes, Gates & Wasley, *J. Amer. chem. Soc.*, **59** (1937), 2079.
4. Hey & Osbond, *J. chem. Soc.*, (1949), 3164, 3172.
5. Heacock & Hey, *J. chem. Soc.*, (1952), 1508.
6. Forrest, Haworth, Pinder & Stevens, *J. chem. Soc.*, (1949), 1311.
7. Kelly, Taylor & Wiesner, *J. chem. Soc.*, (1953), 2094.

Survey of Anthoxanthins: Part VI—Isolation & Constitution of Neo-sakuranin

(Miss) B. PURI & T. R. SESHADRI

Departments of Chemistry, Lady Irwin College & Delhi University, Delhi

The sakuranin fraction of the bark of *Prunus puddum* has been examined chromatographically and found to contain besides sakuranin (flavanone glucoside) a new chalkone glucoside. This has been isolated. On hydrolysis it yields sakuranetin and 1 mole of glucose and on complete methylation and hydrolysis 2 : 4 : 4′-trimethoxy-6-hydroxy chalkone. The same products are obtained from sakuranin also. The new compound, therefore, is 2 : 4′-dihydroxy-4-methoxy-6-glucosidoxy chalkone and is named neo-sakuranin.

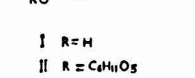
BASED on the general influence of chelation on the comparative stability of flavanone and chalkone structures[1,2], an investigation was started on the occurrence of compounds of this group in plant materials. In Part III[3] of this series it was reported that a new chalkone glucoside is present along with butrin in the extracts of *Butea frondosa* flowers. This compound called iso-butrin was isolated and its constitution established as 4: 3′-diglycoside of butein. Next coreopsin[4], butein-4-monoglucoside, was found to be the predominant entity in many flowers and it underwent partial change into the corresponding flavanone glucoside during extraction. A similar case has further been found to occur in the liquorice root[5]. The real yellow colouring matter of this root is a chalkone glucoside iso-liquiritin, and liquiritin, the flavanone glucoside, is only a transformation product.

Past investigations on the components of the bark of *Prunus puddum* suggested a possible chalkone, flavanone combination occurring in this source also, though it may belong to a slightly different type. Butein and butin are resorcinol derivatives and the flavanone form is not stabilized by chelation. In the present case though the compounds have a phloroglucinol unit making the flavanone structure predominantly stable, the chalkone structure is rendered possible by substitution of one of the 2: 6-hydroxyl groups. The bark of *P. puddum*[6,7] contains a number of components which could be divided into two groups: (1) non-glycosidic, consisting of sakuranetin, genkwanin, prunetin and padmakastein; and (2) glycosidic consisting of padmakastin and sakuranin. The constitution of sakuranin (II) has been established as the 5-glucoside of sakuranetin[8,9] (I). Since in this flavanone derivative the 5-position is occupied, it cannot be quite stable and should be accompanied by the corresponding chalkone glucoside. An examination of the sakuranin fraction by chromatography confirmed this expectation. There was a bright yellow ring visible before spraying whereas sakuranin formed a colourless ring which was visible only after spraying with ammonia.

The chalkone glycoside could be isolated by carefully working up the mother liquor from which sakuranin had been removed. Unlike sakuranin it is deep yellow in colour and readily gives a prominent yellow ring in the paper chromatogram. It is isomeric with sakuranin and on hydrolysis gives the same products, glucose and sakuranetin. The production of a flavanone instead of a chalkone is due to the fact that as soon as the sugar group is removed, the condition favourable for the predominant stability of the flavanone is produced. Determination of the amount of sugar and aglucone has confirmed that it is a mono-glucoside and the colour reactions agree with those of a chalkone structure.

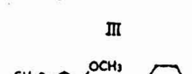
Sakuranin was first isolated by Asahina[8] from the bark of the Japanese cherry tree, *Prunus yedoensis*, and later from *P. serrulata*. It was shown to be a mono-glucoside of sakuranetin. In their later work Asahina, Shinoda and Inubuse[9] showed that sakuranetin was 5: 4′-dihydroxy-7-methoxy flavanone and that the sugar unit was present in the phloroglucinol part, because when sakuranin was heated with barium hydroxide, it gave rise to *p*-hydroxy benzaldehyde and a glucoside of 4-methyl-phloracetophenone. This constitution was confirmed by Zemplen, Bognar and Mester[10] by the synthesis of sakuranin employing 4-methyl-phloracetophenone-2-glucoside tetra-acetate and condensing it with *p*-hydroxy benzaldehyde. The usual method of complete methylation and hydrolysis has not so far been adopted for determining the constitution. These experiments have now been done and the product is found to be 2-hydroxy-4: 6: 4′-trimethoxy chalkone (IV)[1,11,12].

The new chalkone glucoside (neo-sakuranin) has also been studied similarly. Complete methylation has been carried out using dimethyl sulphate and potassium carbonate and the resulting product hydrolysed. 2:4: 4′-Trimethoxy-6-hydroxy chalkone (IV) is obtained as the final product just as in the case of sakuranin itself, thus showing conclusively that the chalkone glucoside carries the sugar group in the 6-position. Hence this new chalkone isomer of sakuranin is given the name of neo-sakuranin (III); the name iso-sakuranin is unsuitable as it may give a wrong impression that it is a glycoside of iso-sakuranetin. Its constitution is further confirmed by the conversion of sakuranin into neo-sakuranin. In the course of their synthesis of sakuranin Zemplen *et al.*[10] obtained in an impure condition the chalkone glucoside as intermediate. This was converted into the flavanone glycoside, sakuranin, by treatment with sodium acetate solution. The purified neo-sakuranin has now been subjected to the same treatment and a good yield of sakuranin has been obtained.

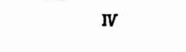


I R=H

II R = $C_6H_{11}O_5$



III



IV

Experimental procedure

Extraction of the bark — The dried bark of *Prunus puddum* (2 kg.) was extracted in the cold according to the procedure described by Narasimhachari and Seshadri[7]. The deep red alcoholic extract was then concentrated (300 cc.) and the concentrate was allowed to stand when after 2 days a deep red sticky solid separated out. This was filtered and the filtrate was extracted repeatedly with hot benzene. The aqueous solution containing the crude glycosides was studied chromatographically. A yellow ring was obtained without spraying, Rf value 0·62; another yellow ring appeared after spraying, Rf value 0·76. The solvent used was water saturated with phenol, temperature 35° ± 1°C., and the spray was of 1 per cent ammonia.

Isolation of sakuranin and neo-sakuranin— The glycosidic solution was saturated with an excess of ether and allowed to stand in an ice chest. After a few days a white crystalline solid separated out. This was filtered and crystallized repeatedly from alcohol when sakuranin appeared in the form of colourless needles sintering at 87°C. and melting at 210°-12°C. In paper chromatography it gave a colourless ring which became yellow after spraying with ammonia, Rf value 0·76. It produced an intense yellow colour with sodium hydroxide, a brown colour with concentrated sulphuric acid, no colour with alcoholic ferric chloride and a green colour with concentrated nitric acid. There was no padmakastin in this sample of bark; similar samples were met with earlier also.

The remaining glycosidic solution was allowed to concentrate in order to remove as far as possible all the sakuranin from it. It was then treated with a solution of neutral lead acetate and the precipitate which contained most of the impurities was filtered off. The filtrate was then treated with a solution of basic lead acetate when a clean bright yellow precipitate was obtained. This was filtered, suspended in alcohol and decomposed with hydrogen sulphide. The precipitated lead sulphide was filtered off and the clean filtrate was allowed to concentrate. In a few days a yellow amorphous solid separated out which even after repeated recrystallization from alcohol appeared in the form of a yellow semi-solid. This was separated, washed with small quantities of alcohol and allowed to stand when it turned crystalline, yellow prisms sintering at 85°C. and melting at 110°-12°C. (decomp.) (found: C, 56·7; H, 5·2; $C_{22}H_{24}O_{10},H_2O$ requires: C, 56·7; H, 5·6 per cent). In circular paper chromatography it gave a marked yellow ring without spraying, Rf value 0·62. A second ring was not obtained on spraying. It produced a deep yellow colour with sodium hydroxide, an orange-red colour with concentrated sulphuric acid, an orange-yellow colour with concentrated nitric acid and a deep brown colour with alcoholic ferric chloride.

Hydrolysis: *Sakuranin* — A pure sample of sakuranin was hydrolysed by boiling with 7 per cent aqueous alcoholic sulphuric acid for 2 hr. On allowing the solution to cool a colourless solid separated out which gave in paper chromatography a colourless ring turning yellow after spraying with ammonia, Rf value 0·20. When the solid was separated and recrystallized from alcohol, it agreed in all its properties with the description of sakuranetin (flavanone).

The aqueous solution was then extracted with ether to remove last traces of the flavanone and neutralized with barium carbonate. The solution was filtered off, concentrated and tested for sugar chromatographically. It produced a ring, Rf value 0·60, indicating it to be glucose [temperature, 34°-36°C., phenol water (9 : 1) as solvent and aniline hydrogen phthallate as spray].

Neo-sakuranin — A pure sample of neo-sakuranin was similarly hydrolysed and tested for aglucone and sugar. It produced a ring corresponding to the flavanone sakuranetin, Rf value 0·21; the chromatography of the sugar indicated it to be glucose, Rf value 0·59.

Quantitative study of the hydrolysis of neo-sakuranin gave the following results: found: glucose, 39·4; dried aglucone, 62·4; $C_{22}H_{24}O_{10}, H_2O$ requires: glucose, 38·6; aglucone, 61·4 per cent.

Conversion of sakuranin into neo-sakuranin — A pure sample of sakuranin (1 g.) was dissolved in aqueous sodium hydroxide (5 per cent) and kept aside for 15 min. It was then acidified with citric acid solution (5 per cent) while cooled in ice. The solution was then evaporated at room temperature in the presence of caustic potash sticks. A yellow solid separated out after a few days. In paper chromatography it gave a prominent yellow ring without spraying, Rf value 0·62, the same as was obtained for neo-sakuranin. After spraying with ammonia no second ring was visible. Even the mother liquor gave the same results, thus showing that there was complete conversion of sakuranin into neo-sakuranin. The colour reactions of the product agreed with those of neo-sakuranin. When recrystallized from alcohol, it first separated as a yellow liquid which finally turned into orange-yellow rectangular prisms. The product sintered at 85°C. and melted at 110°-12°C. (decomp.). The mixed melting point with neo-sakuranin isolated directly from the bark was undepressed.

Conversion of neo-sakuranin into sakuranin — Neo-sakuranin (1 g.) was dissolved in alcohol (5 cc.), water (40 cc.) and crystalline sodium acetate (2 g.) added and the mixture kept in a thermostat at 38°C. for 3 days. The yellowish red solution slowly became paler and sakuranin crystallized out. The change was completed by warming on a water bath for half an hour. The filtered solid crystallized from aqueous alcohol as colourless needles which sintered at 87°C. and melted completely at 210°-12°C. It was identical with sakuranin.

Methylation and hydrolysis of the glycosides: (a) *Sakuranin* — Sakuranin (1 g.) was suspended in dry acetone (100 cc.), treated with an excess of dimethyl sulphate (3 cc.) and anhydrous potassium carbonate (6 g.) and refluxed on a water bath for 120 hr. When there was no more ferric reaction, the excess of acetone and dimethyl sulphate was distilled off. Water was added to the residue to dissolve the potassium salts. Enough sulphuric acid was added to neutralize the potassium salts and then to make it approximately 7 per cent. It was then hydrolysed by boiling for 2 hr. The solution was cooled and extracted with ether. On removing the solvent a yellow solid separated out. It was crystallized twice from rectified spirits when it appeared in the form of lemon-yellow stout prisms melting at 112°-13°C. It dissolved in aqueous alkali forming a yellow solution and gave a red colour with alcoholic ferric chloride. No red or related colour was obtained on reduction with magnesium and hydrochloric acid, but a bright yellow colour was observed when the substance was treated with boric and citric acids in dry acetone solution. All these properties showed the product to be 2: 4: 4′-trimethoxy-6-hydroxy chalkone and a mixed melting point with an authentic synthetic sample[1] confirmed the identity.

(b) *Neo-sakuranin* — A pure sample of neo-sakuranin was similarly methylated and hydrolysed. The product was the same 2: 4: 4′-trimethoxy-6-hydroxy chalkone giving the same colour reactions, melting point and mixed melting point.

References

1. Narasimhachari & Seshadri, *Proc. Indian Acad. Sci.*, **27A** (1948), 223.
2. Seshadri, *J. sci. industr. Res.*, **9A** (1950), 276-81.
3. (Miss) Puri & Seshadri, *J. sci. industr. Res.*, **12B** (1953) 462.
4. (Miss) Puri & Seshadri, *J. sci. industr. Res.*, **13B** (1954), 321.
5. (Miss) Puri & Seshadri, *J. sci. industr. Res.*, **13B** (1954), 475.
6. Narasimhachari & Seshadri, *Proc. Indian Acad. Sci.*, **30A** (1949), 271.
7. Narasimhachari & Seshadri, *Proc. Indian Acad. Sci.*, **35A** (1952), 202.
8. Asahina, *J. pharm. Soc. Japan*, **246** (1908), 259.
9. Asahina, Shinoda & Inubuse, *J. pharm. Soc. Japan*, **550** (1927), 1007.
10. Zemplen, Bognar & Mester, *Ber. dtsch. Chem. Ges.*, **75B** (1942), 1432.
11. Kostanecki & Tambor, *Ber. dtsch. Chem. Ges.*, **37B** (1904), 792.
12. Bargellini, *Gazz. Chim. Ital.*, **44** (1914), 421.

Chonemorphine, the Chief Alkaloid in the Root Bark of *Chonemorpha macrophylla* G. Don: Part II — Alkaline Hydrolysis of Chonemorphine

K. G. DAS & P. P. PILLAY

Department of Applied Chemistry, University of Travancore, Trivandrum

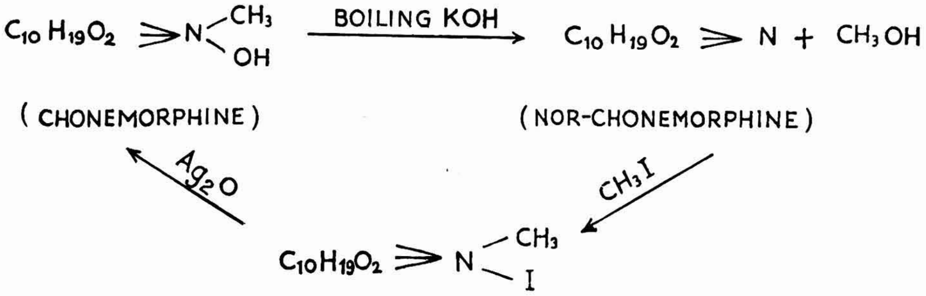
Alkaline hydrolysis of the quaternary alkaloid chonemorphine proceeds quantitatively to give methanol and nor-chonemorphine, which has been identified as a tertiary base. Nor-chonemorphine forms salts and an N-oxide by addition. Chonemorphine can be obtained by the action of methyl iodide followed by silver oxide on nor-chonemorphine.

CHONEMORPHINE has been shown to be a saturated quaternary alkaloid of the formula $C_{11}H_{23}O_3N$, possessing one N-CH_3 group in the molecule. It melts without decomposition at 414°-16°C.[1]. The Hofmann degradation of the alkaloid does not proceed smoothly, while the Emde method leads to the recovery of the unchanged alkaloid. The base is unaffected by boiling with 10 per cent sulphuric acid or with 20 per cent hydrochloric acid. However, by boiling for *c.* 5 hr. with 5 per cent aqueous potash, or better still, by refluxing for 2 hr. with 5 per cent alcoholic potash, chonemorphine is broken down smoothly, presumably quantitatively, into one molecule of methanol and one molecule of a new base which has been named nor-chonemorphine. Methanol formed was not estimated but, after isolation, was oxidized to formaldehyde which was identified by Mulliken's test[2]. Another portion was converted to the 3: 5-dinitrobenzoate, which melted at 107°C. either alone or on admixture with a sample of pure methyl 3: 5-dinitrobenzoate.

Characteristics of nor-chonemorphine—Nor-chonemorphine crystallizes from petroleum ether and appears to be dimorphic, separating in the form of needles or plates. Both the forms melt at 141°-42°C. It is highly soluble in organic solvents, but unlike chonemorphine, it is insoluble in water; $[\alpha]_D^{30°} = +51{\cdot}7°$ in 8·8 per cent chloroform solution. It analyses to the molecular formula $C_{10}H_{19}O_2N$. This formula was confirmed by determining its molecular weight by the Rast method, using camphor as solvent, as well as by the equivalent weights derived from the ignition of the platinichloride and the aurichloride.

In conformity with its expected tertiary nature, nor-chonemorphine forms well-crystallized salts, by addition, on treatment with acids. N-nitroso or N-acetyl nor-chonemorphine could not be prepared. On treatment with hydrogen peroxide in acetone solution, it gave an N-oxide, which remained in an amorphous condition even after purification through the crystalline hydrochloride. It melted between 230° and 235°C. and formed salts with acids. This compound liberates iodine from a solution of potassium iodide and is transformed back to nor-chonemorphine by gentle warming with aqueous sulphur dioxide.

Relationship between chonemorphine and nor-chonemorphine — Since methanol is eliminated by the action of alkali on a quaternary base containing a methyl imino group, with the formation of a tertiary base, it was presumed that the reverse change could be effected through nor-chonemorphine methiodide. This assumption proved correct, for on adding a molecule of methyl iodide to nor-chonemorphine dissolved in petroleum ether, the methiodide crystallized out overnight. Recrystallized from dilute alcohol, it melted at 312°C., either alone or on admixture with an authentic sample of chonemorphine iodide. This was further confirmed by treatment with silver oxide in alcoholic solution. The product obtained was proved to be chonemorphine by determining the mixed melting points of the base and its salts. The structural relationship between the two bases is shown below:



(Nor-chonemorphine methiodide or chonemorphine iodide)

This reaction also confirms the molecular formula of chonemorphine to be $C_{11}H_{23}O_3N$, as it could be synthesized from or degraded to nor-chonemorphine which lends itself easily to molecular weight determination. This smooth and practically quantitative degradation of chonemorphine by boiling alkali is noteworthy as quaternary, methyl ammonium bases usually require more drastic treatment for decomposition, resulting in the rupture of a chain on one side of the N atom (Hofmann's degradation). However, elimination of methanol from the methyl-quaternary bases obtained from a few alkaloids has also been recorded in literature. Among the simpler bases, N-methyl-N-propyl piperidinium hydroxide on heating gives a mixture of N-methyl piperidine and N-propyl piperidine, one being formed by the elimination of propanol and the other of methanol[3]. N-methyl-N-propyl-pyrrolidinium hydroxide behaves likewise. Where there are two different N-alkyl radicals, the alcohol with the smaller alkyl radical tends to be eliminated with greater ease[3]. This is what happens in the case of chonemorphine.

The elucidation of the constitution of chonemorphine thus resolves itself into that of finding the structure of nor-chonemorphine.

Experimental procedure

Action of boiling acids on chonemorphine — Chonemorphine (0·1 g.) was boiled with 5 cc. of 10 per cent sulphuric acid or with 5 cc. concentrated hydrochloric acid for 2 hr. In either case, the alkaloid was recovered unchanged.

Action of boiling alkali on chonemorphine — Chonemorphine (20 g.) was refluxed for 5 hr. with 200 cc. of 5 per cent aqueous potassium hydroxide and then the mixture was distilled, collecting 15 cc. of the distillate in an ice-cooled receiver. The hydrolytic product was then cooled, filtered and washed free of alkali; yield 16·8 g.; calculated 17·1 g.

In later experiments, the hydrolysis of chonemorphine was found to proceed more smoothly by refluxing for 2 hr. with 5 per cent alcoholic potash.

Identification of methanol — The aqueous distillate was saturated with anhydrous potassium carbonate, distilled and 3 cc. of the distillate collected. The distillate smells of methanol, and could be oxidized to formaldehyde by a hot platinum spiral or hot copper oxide. Formaldehyde formed was identified by Mulliken's test. By treatment with 3: 5-dinitrobenzoyl chloride, it gave an ester, which after crystallization from alcohol, melted at 107°C. either alone or in admixture with a sample of methyl 3: 5-dinitrobenzoate.

Nor-chonemorphine crystallizes from petroleum ether usually in the form of needles, but sometimes as plates. Both forms melted at 141°-42°C. It is highly soluble in common organic solvents and insoluble in water. Its molecular weight was determined by the Rast method, using camphor as solvent (found: C, 65·4, 65·7; H, 10·6, 10·8; N, 7·6; mol. wt., 180·5, 181·3; $C_{10}H_{19}O_2N$ requires: C, 64·9; H, 10·3; N, 7·5 per cent; mol. wt., 185). $[\alpha]_D^{30^\circ} = +51{\cdot}7^\circ$ in 8·8 per cent chloroform solution. Nor-chonemorphine was recovered unchanged after boiling with concentrated hydrochloric acid or with 40 per cent alcoholic potash for a few hours.

Nor-chonemorphine hydrochloride, prepared in the usual manner, crystallizes from hot water in glistening plates, melting at 388°-90°C. The crystals were anhydrous, sparingly soluble in water and very soluble in alcohol (found: Cl, 16·0, 15·9; $C_{10}H_{19}O_2N, HCl$ requires: Cl, 16·0 per cent).

Nor-chonemorphine platinichloride was obtained as a pale pink amorphous powder which chars on heating [found: Pt, 32·8, 32·7; $(C_{10}H_{19}O_2N)_2H_2PtCl_6$ requires: Pt, 32·8 per cent].

Nor-chonemorphine aurichloride was obtained as a pale yellow precipitate, soluble in alcohol and melting at 242°-43°C. (found: Au, 37·6; $C_{10}H_{19}O_2N$, $HAuCl_4$ requires: Au, 37·3 per cent).

Nor-chonemorphine hydroiodide melts at 280°-81°C.

Nor-chonemorphine sulphate melts at 340°-42°C.

Nor-chonemorphine N-oxide — Nor-chonemorphine (0·4 g.), dissolved in acetone (20 cc.) was treated with 5 per cent hydrogen peroxide (1·44 cc., 1 mol.). It was left overnight and then allowed to evaporate *in vacuo*. The amorphous product was dissolved in dilute acetic acid, then the hydrochloride was precipitated with saturated potassium chloride, filtered and recrystallized from hot water. The N-oxide was precipitated from the hydrochloride with ammonia and recrystallized from dilute alcohol; m.p. 230°-35°C. (found: C, 58·8; H, 9·1; $C_{10}H_{19}O_3N$ requires: C, 59·7; H, 9·4 per cent). The oxide liberates iodine from a solution of potassium iodide, but like other N-oxides of the tertiary bases, its hydrochloride does not liberate iodine.

Reduction of nor-chonemorphine N-oxide — The oxide (0·1 g.) was dissolved in dilute acetic acid and sulphur dioxide was passed into it to saturation. The solution was warmed, precipitated with potassium chloride and the solid recrystallized from hot water. Plates melting at 388°-90°C. were obtained, which were proved to be nor-chonemorphine hydrochloride by the method of mixed melting points.

Prior to the finding that chonemorphine could be smoothly broken down by alkali, Hofmann degradation was attempted with unsatisfactory results. Attempts were also made to reduce chonemorphine chloride by the Emde method, using a hot aqueous solution of the salt and sodium amalgam but the alkaloid was recovered unchanged.

Nor-chonemorphine methiodide — To a solution of nor-chonemorphine (0·5 g.) in petroleum ether (5 cc.) was added methyl iodide (0·39 g., 1 mol.). The methiodide which crystallizes out overnight was recrystallized from dilute alcohol. Aggregates of plates were obtained which melt at 312°C. alone or in admixture with a sample of pure chonemorphine iodide.

Chonemorphine from nor-chonemorphine methiodide — The pure methiodide (0·3 g.) dissolved in dilute alcohol was shaken with freshly prepared silver oxide, and kept overnight in the ice chest. It was filtered, concentrated *in vacuo*, cooled and filtered. The crystals obtained after recrystallizing from alcohol melted at 413°-15°C., which was not lowered by mixing with pure chonemorphine. Further, with HCl, chonemorphine ·chloride was obtained.

References

1. Das & Pillay, *J. sci. industr. Res.*, **13B** (1954), 602.
2. Mulliken, *Identification of Pure Organic Compounds* (Wiley, New York), **1** (1916), 168, 171.
3. Von Braun, *Ann. Chem.*, **382** (1911), 5.

Biosynthesis of Vitamin C during Germination: A Study of Certain Related Enzyme Systems

R. A. KULKARNI & A. SREENIVASAN
Department of Chemical Technology, University of Bombay, Bombay

A study of the changes in the enzymic make-up of *müng* seedlings germinated under different conditions has been made with a view to elucidating the postulated role of intermediates of glucose oxidation in ascorbic acid biosynthesis. The observations point to a precursorial role for glucose and its breakdown products. Chloretone treatment inhibits pyruvic oxidase activity without influencing glucose oxidation. A metabolic shunting of pyruvate or other glucose intermediate leading to pathways that result in ascorbic acid elaboration is suggested.

IN previous communications[1-4] it was reported that the elaboration from glucose of ascorbic acid in germinating *müng* (*Phaseolus radiatus*) and in excised *müng* embryos during growth probably occurred via some of the Krebs's intermediates. Recent indications, however, would point to an intact conversion of the glucose molecule into vitamin C in the rat[5,6] and in cress seedlings[6]. The observed stimulatory effects of glyceraldehyde and pyruvate[7] do not, on the other hand, preclude the possibility of a recombination of metabolically derived glucose fragments as an alternate route for ascorbic acid biogenesis in the rat. Glucuronic acid is an established intermediate in the pathway for ascorbic acid biosynthesis[6,8] and could arise from glycerol[9].

Since the process of germination is attended by a variety of changes, enzymic in nature, it was considered that studies by quantitation of certain of the oxidase systems in *müng* seedlings might reveal additional information on the manner of the oxidative synthesis of the vitamin from glucose.

Experimental procedure

Procedures for seed germination, pretreatments and methods of sampling were as described previously[1-4]. Other details, where necessary, are given in the text. Results in every case represent averages of at least duplicate determinations.

Changes in citric acid during germination — Since oxidation of glucose proceeds via the citric acid cycle, it was of interest to study the changes in citric acid content of *müng* seeds during germination in diffuse light or in darkness after overnight soaking in water; in one set the seeds were soaked for this period in 3 per cent glucose solution. Aseptic conditions were ensured as detailed previously. The method employed for citric acid determinations was essentially the pentabromoacetone colorimetric procedure of Pucher *et al.*[10]. The results are given in Table 1.

There is a progressive fall in the values for citric acid with increased sprouting due evidently to greater activity of the enzymes involved in its oxidation. The effects of darkness and of steeping in glucose solution are consistent with their known stimulation of vitamin C synthesis[2].

It was reported earlier[11] that an extract of overnight soaked *müng* seeds enhanced enzymic oxidation of ascorbic acid and that this behaviour of the seedling extract diminished with germination. It has since been ascertained (unpublished data) that this effect is attributable to the citrate ions in the extracts.

Endogenous respiration — The values for endogenous respiration of extracts of 4-day-

TABLE 1 — CITRIC ACID CONTENT OF GERMINATING *MUNG*

GERMINATION IN	CITRIC ACID, G./100 G. DRY WT. AFTER GERMINATION			µL. O_2 UPTAKE/HR./MG. (DRY WT.) OF EXTRACT FROM 4-DAY-OLD SEEDLINGS
	Overnight	3 days	5 days	
Diffuse light	1·45	0·56	0·34	1·0
Darkness	1·60	0·38	0·24	2·1
Glucose pretreated seeds	2·12	0·48	0·27	3·2

old seedlings are included in Table 1 (last column). Samples of seedlings were extracted with ice-cold water and made to volume (1 g./cc.). Extracts were dialysed overnight against water in cellophane tubes inside a refrigerator. The dialysed extract in 1 cc. amount was transferred to the main chamber of a Warburg flask containing 2 cc. of M/5 phosphate buffer, *p*H 7. The centre cup contained 0·2 cc. of 10 per cent KOH solution to absorb carbon dioxide. Oxygen uptake data were recorded during 1 hr. at 37°C. after an equilibration period of 10 min.

Undialysed extracts gave very high oxygen uptake values and hence dialysis was resorted to in this as well as in all other Warburg experiments. This procedure also excluded any probable inhibition due to excess of endogenous substrates. The increased uptake values in extracts of seedlings germinated in dark or after pre-soaking in glucose solution run parallel to the extent of ascorbic acid biogenesis in these cases.

Oxidation of sugars and sugar intermediates — The enzyme studies were carried out using the conventional Warburg procedure. The reaction flasks each contained 3·2 cc. in total volume made up of 0·2 cc. of 10 per cent potassium hydroxide solution in the centre cup with filter paper strip to absorb carbon dioxide, and in the main compartment 1 cc. of the dialysed seedling (4 days') extract, 1 cc. solution of sugars (5 mg./cc.) or the Krebs's intermediates (2 mg./cc.) in the form of sodium salts as substrate and 1 cc. of M/5 phosphate buffer, *p*H 7. Substrate solution was tipped in from the side arm at zero time after 10 min. equilibration in the Warburg bath at 37°C. Corrections were effected for endogenous uptakes (TABLE 2).

Active glucose, succinic, pyruvic and malic oxidase systems are present in the seedling extracts. These are considerably more active when the *müng* seeds are pre-soaked in glucose prior to germination. Germination in the absence of light also reveals the same trend. The activities thus correspond to the extent of elaboration of ascorbic acid under these conditions. Among the other substrates studied were: hexose diphosphate, inositol, sodium glycerophosphate, aspartate, and α-ketoglutarate; oxygen uptakes with these substrates were either small or negligible.

The presence of the active oxidases was confirmed by the study of the additive effects obtained with cell suspensions of a strain of *Escherichia coli*. The organism (a laboratory isolate) was grown at 30°C. in Roux bottles containing 100 cc. of a medium composed of 1 per cent yeast extract, 1 per cent peptone, 0·5 per cent potassium hydrogen phosphate and 0·5 per cent glucose. At the end of 18 hr., the cells were harvested by centrifugation, washed twice with ice-cold 0·9 per cent sodium chloride solution and suspended in phosphate buffer. 0·5 cc. of the suspension was used for enzyme activity measurements along with 1 cc. of dialysed seedling extract (germinated for 4 days in diffuse light) using the substrates studied before (TABLE 2). The final values for oxygen uptake (TABLE 3) were corrected for endogenous respiration.

Inhibition of pyruvate oxidation in chloretone-treated seedlings — The stimulation of ascorbic acid synthesis in *müng* seedlings by chloretone was reported earlier[4]. The effect of such treatment on the above enzyme systems was studied. The seeds were soaked in a solution of chloretone (500 p.p.m.) overnight and allowed to germinate as usual. Dialysed extracts of 4-day-old seedlings were used as source of enzyme and compared for

TABLE 3 — ADDITIVE EFFECTS OF SEEDLING EXTRACT AND *E. COLI* SUSPENSION ON OXIDATION OF SUBSTRATES

SUBSTRATE	μL. O_2 UPTAKE/HR. WITH		
	E. coli	Seedling extract	*E. coli* + seedling extract
Glucose	48	26	75
Succinate	38	14	54
Fumarate	60	20	74
Pyruvate	15	12	30

TABLE 2 — CHANGES IN THE ENZYME SYSTEMS OF GLUCOSE METABOLISM

GERMINATION IN	μL. O_2 UPTAKE/HR./100 MG. (DRY WT.) OF SEEDLING EXTRACT WITH SUBSTRATE						
	Glucose	Fructose	Mannose	Succinate	Fumarate	Malate	Pyruvate
Diffuse light	65·7	18·9	40·6	24·8	26·7	24·4	39·0
Darkness	70·0	21·8	43·2	45·2	113·9	43·0	87·1
Glucose pretreated seeds	112·0	61·5	89·3	73·2	143·5	52·2	90·3

TABLE 4 — EFFECT OF CHLORETONE TREATMENT ON OXIDATION OF SUBSTRATES BY SEEDLING EXTRACTS

SUBSTRATE	μL. O_2 UPTAKE/HR./100 MG. OF SEEDLING EXTRACT	
	Untreated	Chloretone treated
Glucose	65·9	61·4
Succinate	25·1	23·5
Fumarate	27·1	22·2
Pyruvate	36·6	10·0

TABLE 5 — ASCORBIC ACID OXIDASE, PHENOLASE AND PEROXIDASE ACTIVITIES OF SEEDLING EXTRACT

GERMINATED IN	μL. O_2 UPTAKE/HR./MG. (DRY WT.)		PYROGALLOL OXIDIZED IN 5 MIN./MG. DRY WT. (IN TERMS OF COLORIMETER READINGS), PEROXIDASE
	Ascorbic acid oxidase	Phenolase	
Diffuse light	9·0	8·2	3·8
Darkness	8·1	7·4	7·3

activities with similar untreated seedling extracts prepared simultaneously (TABLE 4).

A pronounced inhibitory effect on pyruvate oxidation is observable as a result of chloretone treatment overnight prior to germination of seeds. The inhibition of pyruvate oxidation in chloretone-administered rats has been reported[12]. It is interesting to note that chloretone does not appreciably affect the overall glucose oxidase activity.

Changes in ascorbic acid oxidase, polyphenolase and peroxidase activities — The enhanced formation of ascorbic acid as a result of germination in the dark was partly attributed to the enzyme ascorbic acid oxidase being less active[2,13]. The determinations of ascorbic acid oxidase and phenolase activities of the seedling extracts (1 g./cc.) were carried out manometrically using ascorbic acid and pyrogallol (5 mg. in 1 cc. each, neutralized) as substrates respectively. M/5 phosphate buffers, *p*H 5·8 and 7·3 respectively, were used for ascorbic acid oxidase and phenolase activity determinations. Peroxidase activity was followed colorimetrically[14] using pyrogallol (5 mg. in 1 cc.) in presence of hydrogen peroxide (1 cc. of 0·5 per cent) at *p*H 6·3. The results are given in Table 5.

Extract of seeds germinated in the dark shows less of ascorbic acid oxidase (cf. 2) and phenolase activities, but peroxidase activity is nearly doubled.

Discussion

The enhanced formation of ascorbic acid as a result of germination in the dark was attributed to increased amylolysis as well as partly to the absence of photo-oxidation and to decreased ascorbic acid oxidase activity in these seedlings[13] in contrast to seeds germinated normally, i.e. in diffuse light. Although germination in the dark results in decreased phenolase and ascorbic acid oxidase activities, there is considerable enhancement in peroxidase activity. The significance of this change remains obscure.

The rate of endogenous respiration as well as of the oxidation of various substrates of carbohydrate breakdown by extracts obtained from seeds germinated in diffuse light, in darkness and after overnight soaking in glucose solution, runs parallel to the extent of biogenesis of ascorbic acid under these conditions. Presumably, therefore, these observations would imply that elaboration of ascorbic acid from glucose through breakdown to smaller fragments is at least one route of synthesis of this vitamin in *müng* seedlings. It should be remembered that, unlike in the rat or in cress seedlings, there is a greatly increased elaboration of various enzymes during seed germination concurrently with ascorbic acid synthesis.

The marked inhibition of pyruvate oxidation in the chloretone-treated seedlings takes place without a corresponding effect on the oxidation of glucose or of the other substrates studied. It would seem, although not proved here, therefore, that normal breakdown of carbohydrate is interfered with at the pyruvate stage so that, possibly, more of it is made available for alternate use in ascorbic acid synthesis. A metabolic shunting of pyruvate by blocking of oxidation at the succinate stage through malonate[15] or at the α-ketoglutarate stage through forced transamination by feeding of ammonium chloride[16] is known. That chloretone and other narcotics could uncouple oxidative synthesis of adenosine triphosphate has been suggested[17].

The stimulation by chloretone treatment of ascorbic acid synthesis in the seedlings (cf. 3) is apparently less pronounced than its inhibition of pyruvate oxidation (TABLE 4). This is probably due to the direct toxic effect of the narcotic on growth. It has not been possible to study the effect of pyruvate in presence of chloretone on account of this toxicity to seedlings. The inhibitory effects of added Krebs's intermediates in more than minimal concentrations have been reported earlier[3]. Under normal conditions of germination and, assuming the formation of these intermediates as a prerequisite to vitamin elaboration, their concentrations will at no time reach high levels on account of rapid and continuous mobilization.

References

1. SREENIVASAN, A. & WANDREKAR, S. D., *Proc. Indian Acad. Sci.*, **32B** (1950), 143.
2. SREENIVASAN, A. & WANDREKAR, S. D., *Proc. Indian Acad. Sci.*, **32B** (1950), 231.
3. BHARANI, S. P., SHAH, Y. S. & SREENIVASAN, A., *Proc. Indian Acad. Sci.*, **37B** (1953), 33.
4. BHARANI, S. P., SHAH, Y. S. & SREENIVASAN, A., *Proc. Indian Acad. Sci.*, **37B** (1953), 54.
5. HOROWITZ, H. H. & KING, C. G., *J. biol. Chem.*, **200** (1953), 125.
6. ISHERWOOD, F. A., CHEN, Y. T. & MAPSON, L. W., *Biochem. J.*, **56** (1954), 1, 15.
7. SMYTHE, C. V. & KING, C. G., *J. biol. Chem.*, **142** (1942), 529.
8. HOROWITZ, H. H. & KING, C. G., *J. biol. Chem.*, **205** (1953), 815.
9. DOERSCHUK, A. P., *J. biol. Chem.*, **195** (1952), 855.
10. PUCHER, G. W., SHERMAN, C. C. & VICKERY, H. B., *J. biol. Chem.*, **113** (1936), 235.
11. SREENIVASAN, A. & WANDREKAR, S. D., *Nature*, **165** (1950), 318.
12. ROY, S. C., ROY, S. K. & GUHA, B. C., *Nature*, **158** (1946), 238.
13. SREENIVASAN, A. & WANDREKAR, S. D., *Nature*, **165** (1950), 765.
14. GIBSON, M. R. & MAHER, F. T., *J. Amer. pharm. Ass.*, **40** (1951), 40.
15. LEHNINGER, A. L., *J. biol. Chem.*, **164** (1946), 291.
16. RACKNAGEL, R. O. & POTTER, VAN R., *J. biol. Chem.*, **191** (1951), 263.
17. JOHNSON, W. J. & QUASTEL, J. H., *Nature*, **171** (1953), 602.

A New Antibiotic from a Non-pigmented Strain of *Penicillium notatum* Westling

V. C. VORA, (Mrs.) K. SHETE & A. T. DUDANI*
Central Drug Research Institute, Lucknow

The chemical and antibacterial properties of a new antibiotic isolated from a non-pigmented strain of *Penicillium notatum* Westling are described.

PENICILLIUM notatum strains have been shown to produce various types of penicillins[1], notatin[2] and notalysin[3]. A non-pigmented strain of *P. notatum* Westling (29C), obtained from a sample of local soil, has been found to produce an antibacterial substance, which on testing appears to be different from those already reported in literature. The isolation and properties of this substance are described in the present communication.

Cultural characteristics of the mold 29C

Culture medium — Czapek-Dox agar.

Colony characteristics — Rate of growth restricted; velvety smooth, azonate or faintly zonate growth; margin slightly raised; sporulation moderately heavy and uniform; colour, white in young parts to pale bluish green in older parts; no distinct odour; no soluble pigment in the medium; colony reverse, pale buff to light brown.

Conidial stage — Branched below the sterigmata and metulae, asymmetric, not strongly divaricate, biverticillate. Conidiophore erect arising from the substrate hyphae, branched once, twice or more. No surface markings; smooth.

This strain is characterized by almost globose conidia and absence of pigment. It differs from the typical members of the chrysogenum series in having no yellow pigment and from the oxalium series in not having larger, strongly elliptical conidia. The strain, however, tallies to a large extent with a strain of *notatum*[4].

Growth conditions

The culture was grown on a medium consisting of dextrose, 50 g.; $NaNO_3$, 2·0 g.;

---

*Present address: Central Research Institute, Kasauli.

$K_2HPO_4.3H_2O$, 1·0 g.; $MgSO_4$, 0·5 g.; KCl, 0·2 g.; $FeSO_4.7H_2O$, 0·01 g.; distilled water, 1,000 ml. (*p*H 7·0). The medium was distributed in Roux bottles, 250 ml. in each, and sterilized. The bottles were inoculated with spore suspensions prepared from slants grown on Raulin-Thom agar. After 12 days' incubation at 24°C. the bottles were harvested. The final *p*H was found to be 5·5. The activity of the culture filtrate was tested by the cup-plate method against *S. aureus*, *E. coli*, *Shigella dysenteriae*, *Shigella paradysenteriae*, *S. typhi* and *V. cholerae*.

The addition of various organic supplements like the corn steep liquor, yeast extract, peptone, alone or in combination, did not increase the yield of the antibiotic. Substitution of dextrose with other sugars (sucrose, fructose, lactose and maltose) and starch was also tried. It was found that sucrose gave as good a production of the active compound as dextrose. The optima for *p*H and temperature for the production of the antibiotic were found to be in the range of 7·0-8·0 at 24°-25°C. The mold failed to show any appreciable activity when grown on Raulin-Thom[5], Czapek-Dox[6] and Windling[7] media.

Isolation of active principle

The 12-day-old active culture filtrate was stirred with 1 per cent (w/v) activated carbon (Merck) for 2 hr. and filtered. The filtrate was found to be inactive. The active carbon cake was dried over sulphuric acid and then extracted with chloroform for 14-18 hr. The chloroform extract was dried and filtered. The residue left after the evaporation of chloroform was dissolved in a small amount of absolute alcohol and cooled. A white crystalline substance (A) separated which was found to be inactive. The alcoholic solution after the removal of compound A was evaporated to dryness and the residue dissolved in the minimum amount of water. The water soluble portion retained the activity while the insoluble fraction was inactive. The active fraction was extracted four times with equal volumes of chloroform and then with ether until the ether extract had no visible yellow colouration. The spent mother liquor was evaporated *in vacuo* to dryness and was found to retain a part of the activity. The chloroform extract was found to contain small quantities of compound A and the active principle, while the ether extract contained most of the antibiotic. On evaporating the ether extract, a syrupy residue (compound B) was obtained. The average yield of compound B was approximately 40-45 mg./l.

TABLE 1 — ANTIBACTERIAL ACTIVITY OF THE ACTIVE PRINCIPLE (COMPOUND B)

TEST ORGANISM	MAXIMUM ACTIVITY IN A DILUTION OF
C. diphtheriae	1: 8,000
S. faecalis	1: 4,000
Streptococcus haemolyticus	1: 64,000
Streptococcus viridans	1: 64,000
S. aureus	1: 16,000
E. coli	1: 4,000
Shigella dysenteriae Shiga	1: 32,000
Shigella paradysenteriae Flexner	1: 4,000
S. paratyphi A	Negative
S. paratyphi B	1: 4,000
S. typhi	1: 4,000
Proteus vulgaris	1: 4,000
V. cholerae (Ogawa)	1: 80,000
V. cholerae (Inaba)	1: 30,000
V. cholerae (Rough)	1: 45,000
B. subtilis	Negative

The antibacterial activity of the substance tested by serial dilution method is presented in Table 1.

Physical and chemical properties of compound B

The syrupy substance, when sublimed at 150°-60°C. in high vacuum, gave a yellow-coloured sublimate soluble in water, ether, chloroform and most organic solvents. The substance is stable to heat and remains active for a long time even when stored at room temperature (27°-29°C.).

Compound B does not contain sulphur, halogen or nitrogen.

The aqueous solution of the compound turns pinkish red on standing. In dilute alkali the substance is inactivated. With N sodium hydroxide solution the substance gives at first a reddish purple colour changing through green to bluish green and then to reddish purple again. When heated with zinc dust and hydrochloric acid the solution becomes greenish in colour, but on keeping, the solution changes to pinkish red. The compound gives a blue colouration with ethyl cyanacetate (Craven test)[8] changing through green to brownish red. With Brady's reagent the substance gives immediate turbidity and precipitate on standing. But these precipitates do not seem to be those of a simple phenylhydrazone.

The substance reduces Fehling's solution instantaneously. It decolourizes a strong solution of potassium permanganate and also bromine water. No colouration was observed on addition of a few drops of ferric chloride to the aqueous or alcoholic solution of compound B. It has not been possible to crystallize compound B so far.

Discussion

From the antibacterial and other properties described above it is obvious that compound B is different from penicillin, notatin and notalysin. It is well known that presence of glucose and oxygen[2] in the medium is essential for the antibacterial action of notatin, while the assay broth[9] used for the serial dilution does not contain glucose. Notalysin[10] itself is not antibacterial but it is known to protect penicillin against the action of penicillinase.

Further work on the characteristics of the active compound is in progress.

Summary

A new antibiotic from a non-pigmented strain of *P. notatum* Westling has been isolated. The antibiotic has been tested by serial dilution method and found to be active against a number of micro-organisms. Some general and chemical properties of the antibiotic are described.

Acknowledgement

We wish to thank Prof. S. R. Bose of R. G. Kar Medical College, Calcutta, for the identification of the mold.

References

1. Florey, H. W., Chain, E., Heatley, N. G., Jennings, M. A., Sanders, A. G., Abraham, E. P. & Florey, M. E., *Antibiotics* (Oxford Medical Publications, London), 1949.
2. Coulthard, C. E., Michaelis, R., Short, W. E., Syxes, G., Skrimshire, G. E. H., Standfast, A. E. B., Birkinshaw, J. H. & Raistrick, H., *Nature*, **150** (1942), 634.
3. Hutter, S., *Schweiz. med. wschr.*, **76** (1946), 1138.
4. Raper, K. B. & Thom, C., *A Manual of the Penicillia* (Williams & Wilkins Co., Baltimore), 1949.
5. Oxford, A. E. & Raistrick, H., *Biochem. J.*, **27** (1933), 1473.
6. Birkinshaw, J. H. & Raistrick, H., *Biochem. J.*, **28** (1934), 828.
7. Johnson, J. R., Kidwai, A. R. & Warner, J. S., *J. Amer. chem. Soc.*, **75** (1953), 2110.
8. Craven, A., *J. chem. Soc.*, (1931), 1605.
9. Dudani, A. T. & Agarwala, S. C., *J. sci. industr. Res.*, **11B** (1952), 551.
10. Hutter, S., *C. R. Soc. biol. Paris*, **142** (1948), 560.

Determination of Copper & Arsenic or Antimony in the Presence of One Another

M. R. VERMA & Y. P. SINGH
National Physical Laboratory of India, New Delhi

A simple iodometric method has been developed for the estimation of Cu$^{\cdot\cdot}$ and As$^{\cdot\cdot\cdot}$ or Cu$^{\cdot\cdot}$ and Sb$^{\cdot\cdot\cdot}$ when they are present together. It consists in complexing the solutions with alkali citrate and titration of As$^{\cdot\cdot\cdot}$ or Sb$^{\cdot\cdot\cdot}$ with standard iodine in neutral solution. After completion of the titrations the solution is acidified, when the copper complex breaks down and the iodine equivalent of copper is liberated which can be titrated. The method is rapid and is applicable for a wide range of concentrations of the constituent elements.

DETERMINATION of copper and arsenic, in the presence of one another, is required in materials of the type Paris green, arsenical copper, etc. Copper and antimony may similarly be required to be determined in certain alloy compositions. Methods adopted hitherto for the determination of these elements, when the materials are available in sufficient amount and the constituents present in comparable proportions, may briefly be summarized as under. With arsenic and copper, the method consists in the separation of arsenic as arsenious chloride from the solution by distillation, estimation of the same by iodometric method, and determination of copper in the residue by volumetric or electrodeposition method[1]. Arsenic may also be separated by the addition of ferrous salt[2] leaving copper which can be determined either directly or copper may be estimated by electrodeposition[3] from the mixture without prior separation of arsenic. In an antimony-copper solution, antimony may be determined by oxidation with potassium bromate, and copper determined in the solution iodometrically by buffering the solution suitably, e.g. with sulphosalicylic acid or potassium bifluoride[4]. Buffering may also be effected with a mixture of acetic and sulphuric acids[5]. Such a control of *p*H is necessary, otherwise in strongly acidic solutions, iodides are freely oxidized by pentavalent arsenic or antimony and this makes the determination of copper unreliable[6]. Kolthoff and Cremer[7], and Pochinok[8] suggested a method for the analysis of Paris green in which advantage is taken of the complexing properties of alkali pyrophosphate for copper, when trivalent arsenic can be titrated iodometrically; on treatment of the same with a suitable concentration of the acid, copper liberates an equivalent amount of iodine which can be titrated.

In an earlier communication by Verma and Kapur[9], Kolthoff's method of complexing copper with the pyrophosphate was extended to the determination of iodate ions in the presence of the former. Though successful, this method had the drawback of being slow; it was even slower to work with when extended to the determination of antimony in presence of copper. Swift and Lee[10] and Hume and Kolthoff[11] attempted to determine copper and iodate, bromate, etc., in the presence of one another. A method was finally evolved for complexing copper with potassium citrate and thus making available the anions (bromate, iodate, etc.) for determination iodometrically. Copper from the same solution may be estimated by lowering the *p*H of the solution suitably and titrating the liberated iodine. According to Park[12], complete reduction of copper should be possible in a citrate buffered solution, which is well within the *p*H range in which no interference may be caused by the reoxidation of iodide by pentavalent arsenic or antimony.

In the present communication, an iodometric method has been developed for the determination of copper and arsenic (+3) and copper and antimony (+3) when present together in solutions.

Solutions

Copper solution — About 25 g. of Analar grade copper sulphate was dissolved per litre and its strength determined by iodometric titration against standard sodium thiosulphate.

Antimony$^{(+++)}$ *solution* — 29·15 g. of antimony trioxide (*C.P.* grade) was dissolved in a mixture of hydrochloric acid and tartaric acid, neutralized with sodium hydroxide and volume made to 41. Alternately, 16·7 g. of potassium antimony tartrate were dissolved per litre in water.

The above two solutions were standardized against iodine, which in turn was standardized against standard arsenious acid.

Arsenic$^{(+++)}$ *solution* was prepared by dissolving weighed quantity of A.R. arsenious oxide in alkali and neutralizing free alkali with hydrochloric acid.

Potassium citrate — 324·4 g. of the salt (*C.P.* grade) were dissolved per litre to make an approximately molar solution. The solution was tested for its freedom from reducing matter, particularly its absorption for iodine. Whenever reducing substances were present, the citrate solution was kept in contact with excess iodine solution for 1 hr. and the balance removed.

Acetic acid (*6N*) was also tested for reducing substances in the above manner.

Sulphuric acid (*6N*), *C.P.* grade, was also tested in the above manner.

Sodium bicarbonate was of *C.P.* or reagent grade and substantially free from carbonate.

Iodine solution — Nearly N/10.

Sodium thiosulphate — Nearly N/10; frequently standardized against potassium dichromate.

Experimental procedure

Measured volumes of the solution of copper sulphate and arsenious acid were mixed together and neutralized with sodium bicarbonate or dilute ammonia to incipient precipitation of copper. The solution was just acidified with acetic acid followed by addition of a measured quantity of molar alkali citrate. Excess of sodium bicarbonate was added and the solution titrated with standard iodine solution. The titre was used as equivalent of trivalent arsenic.

At this stage, dilute acetic acid was added to remove excess of sodium bicarbonate followed by about 2 g. of potassium iodide and a mixture of 6N acetic acid and 6N sulphuric acid. The solution was cooled to *c.* 10°C. before the addition of potassium iodide. The iodine liberated was titrated against standard sodium thiosulphate. Since the liberation of iodine is slow, potassium thiocyanate is added towards the end to complete the reaction[13]. The total iodine liberated is equivalent of copper in the solution.

For the estimation of arsenic (in smaller quantities), the determinations were made potentiometrically using the polarized bimetallic system of Willard and Fenwick[14]. Similar procedures were adopted for the determination of antimony in the presence of copper.

During these determinations it was noted that the thiosulphate titre of copper in the presence of potassium citrate was slightly higher than for copper alone. For accurate work, it may be necessary to standardize thiosulphate and iodine solutions against aliquots of solutions containing known quantities of copper or arsenic and antimony to which the requisite amounts of potassium citrate, sodium bicarbonate, acids, etc., have been added.

The results obtained are given in Tables 1-3.

Discussion

From the results recorded in Tables 1-3 it may be seen that copper and arsenic (ous) or copper and antimony (ous) when present in the form of solution can be easily estimated

TABLE 1 — ANALYSIS OF SOLUTIONS CONTAINING ARSENIC AND COPPER

[*$CuSO_4$ solution (Cu^{++}), N/12·16; As_2O_3 solution (As^{+++}), N/13·36; potassium citrate, molar; acetic acid, 6N; sulphuric acid, 6N; standard sodium thiosulphate and iodine solutions used*]

Vol. of arsenic soln. cc.	Vol. of copper soln. cc.	Reagents added	Vol. of iodine cc.	Reagents added	Vol. of thiosulphate cc.	Remarks
—	25	Ammoniacal till blue colour; neutralized with acetic acid; potassium iodide	—	—	23·8 23·8 23·9	—
—	25	Potassium citrate, 25 cc.; ammoniacal till blue colour; acetic acid, 10 cc.; sulphuric acid, 25 cc.; potassium iodide	—	—	24·0 24·1	One cc. of the N/11·58 sodium thiosulphate solution is equivalent to 0·005436 g. of copper
25	—	Sodium bicarbonate (excess)	24·8 24·8 24·7	—	—	—
25	—	Sodium bicarbonate (excess) 25 cc. of potassium citrate solution	24·8	—	—	One cc. of the N/13·26 iodine solution is equivalent to 0·002926 g. arsenic
25	25	Potassium citrate, 30 cc.; excess of sodium bicarbonate	24·8 24·8 24·8	After neutralization of sodium bicarbonate with dilute acetic acid, added potassium iodide followed by sulphuric acid, 25 cc. and acetic acid, 15 cc.	24·2 24·0 24·1	—
25	25	Potassium citrate, 30 cc.; excess of sodium bicarbonate	24·8	Sulphuric acid, 25 cc.; acetic acid, 40 cc.	24·1 24·1 24·2	—
25	25	do	24·8	Sulphuric acid, 25 cc.; acetic acid, 35 cc.	24·2	—
25	25	do	24·8	Sulphuric acid, 28 cc.; acetic acid, 35 cc.	24·2	—
—	25	—	—	Potassium citrate, 30 cc. + sodium bicarbonate; acetic acid till neutralized; potassium iodide; sulphuric acid, 25 cc.; acetic acid, 40 cc.	21·8	Fresh solutions of $CuSO_4$ and As_2O_3 were used; $CuSO_4$, N/13·38; As_2O_3, N/16·41
25	25	Potassium citrate, 30 cc.; acetic acid; sodium bicarbonate	20·2	Acetic acid added till sodium bicarbonate is neutralized; potassium iodide; sulphuric acid, 25 cc.; acetic acid, 40 cc.	21·8 21·85	—
20	25	do	16·2 16·2	Potassium iodide; sulphuric acid, 25 cc.; acetic acid, 40 cc.	21·9 21·8	—
15	25	do	12·1 12·1	Potassium iodide; sulphuric acid, 30 cc.; acetic acid, 45 cc.	21·85	—
10	25	do	8·05 8·10	Potassium iodide; sulphuric acid 30 cc.; acetic acid, 45 cc.	21·8 21·9	—
5	25	do	4·05 4·05	Potassium iodide; sulphuric acid, 30 cc.; acetic acid, 45 cc.	21·85 21·85	—

TABLE 2 — ANALYSIS OF SOLUTIONS CONTAINING ARSENIC AND COPPER

[*The arsenic* (As^{+++}) *and iodine solutions were diluted ten times each and an aliquot of the arsenic solution added to copper solution*; As^{+++}, *N*/164·1; Cu^{++}, *N*/13·38; *standard iodine soln.*; *and* 1 *cc. thiosulphate soln.* = 0·005436 *g. of copper*]

VOL. OF ARSENIC SOLN. cc.	VOL. OF COPPER SOLN. cc.	REAGENTS ADDED	VOL. OF IODINE SOLN. cc.	REAGENTS ADDED	VOL. OF THIOSULPHATE SOLN. cc.	REMARKS
20	25	30 cc. of potassium citrate; sodium bicarbonate	16·5 16·4	Acetic acid added till all sodium bicarbonate were neutralized; potassium iodide; sulphuric acid, 30 cc.; acetic acid, 40 cc.	21·8 21·85	One cc. of N/132·6 iodine solution is equivalent to 0·0002826 g. of arsenic
10	25	do	8·3 8·25	do	21·8 21·8	—
Potentiometric titrations (*by Willard and Ferwick's polarized platinum electrode*)						
—	25	30 cc. of potassium citrate; sodium bicarbonate	0·15	—	—	—
10	25	do	8·60 8·60	—	—	—
5	25	do	4·30 4·30 4·25	—	—	—

TABLE 3 — ANALYSIS OF SOLUTIONS CONTAINING ANTIMONY AND COPPER

[$CuSO_4$ (Cu^{++}), *N*/11·37; *potassium antimony tartrate* (Sb^{+++}), *N*/12·74; *sulphuric acid*, 6*N*; *acetic acid*, 6*N*; *iodine*, *N*/10·35; *and standard sodium thiosulphate soln.*]

VOL. OF Sb SOLN. cc.	VOL. OF Cu SOLN. cc.	REAGENTS ADDED	VOL. OF IODINE SOLN. cc.	REAGENTS ADDED	VOL. OF THIOSULPHATE SOLN. cc.	REMARKS
—	25	Ammonia; acetic acid, 5 cc. cooled in ice water	—	Potassium iodide, 2 g.	22·30 22·25 22·30	—
—	25	Ammonia; acetic acid, 5 cc.; potassium citrate, 25 cc.; sulphuric acid, 15 cc.; acetic acid, 15 cc.	—	Potassium iodide, 2 g.	22·35 22·4 22·38	One cc. of sodium thiosulphate is equivalent of 0·006244 g. of Cu
25	—	Sodium bicarbonate in excess	20·3	—	—	—
25	50	Ammonia; acetic acid, 5 cc.; potassium citrate, 50 cc.; sodium bicarbonate in excess	20·5	Neutralized with acetic acid, and added acetic acid, 30 cc.; sulphuric acid, 30 cc.; potassium iodide, 2 g.	44·6	—
25	25	do	20·4	do	22·5	One cc. of iodine solution is equivalent of 0·005856 g. of Sb
15	25	Ammonia; acetic acid, 5 cc.; potassium citrate, 25 cc.; sodium bicarbonate in excess	12·2	Neutralized with acetic acid, and added acetic acid, 30 cc.; sulphuric acid, 30 cc.; and potassium iodide, 2 g.	22·35	—
10	25	do	8·2	do	22·4	—
5	25	do	4·1	do	22·35	—
2	25	do	1·7	do	22·4	—
25	15	do	20·3 20·25	Neutralized with acetic acid, and added acetic acid, 20 cc.; sulphuric acid, 20 cc.; and potassium iodide, 2 g.	13·45 13·5	—
25	10	do	20·3	do	9·0	—
25	5	do	20·3	do	4·6 4·5	—

by iodometric method; in the initial stages copper is complexed with alkali citrate and the solution kept at *p*H 8·3 by sodium bicarbonate, when arsenic (ous) or antimony (ous) can be titrated easily without any interference from copper. On completion of the reaction, the *p*H is lowered and kept within a suitable range, when the copper complex breaks down making available copper for iodometric determination.

The method has been tried at several levels of concentration of copper and arsenic, and copper and antimony, and has been found to give reproducible and satisfactory results. At very low concentrations of arsenic, it may be titrated satisfactorily in the usual manner, the end point being determined potentiometrically.

The method is being extended to alloys and ores containing these elements.

Acknowledgement

Our thanks are due to Dr. K. S. Krishnan, Director, National Physical Laboratory of India, for his permission to publish this paper.

References

1. *Official Methods of Analysis, A.O.A.C.*, 1950, 50 *et seq.*
2. BULLIVANT, D. J., *Chem. Abstr.*, **36** (1942), 4055.
3. PARK, B., *Industr. Engng. Chem.* (*Analyt. Ed.*) **12** (1940), 97.
4. TANANAEV, I. V. & LITVINENKO, N. S., *Chem. Abstr.*, **35** (1941), 1345.
5. FOOTE, H. W. & VANCE, J. E., *Industr. Engng. Chem.* (*Analyt. Ed.*), **8** (1936), 119.
6. SCOTT, W. W., *Standard Methods of Chemical Analysis* (D. Van Nostrand & Co., New York), **1** (1948), 75.
7. KOLTHOFF, I. M. & CREMER, *Chem. Abstr.*, **16** (1922), 538.
8. POCHINOK, KH. N., *Chem. Abstr.*, **33** (1939), 86.
9. VERMA, M. R. & KAPUR, P. L., *Industr. Engng. Chem.* (*Analyt. Ed.*), **16** (1941), 338.
10. SWIFT, E. H. & LEE, T. L., *Industr. Engng. Chem.* (*Analyt. Ed.*), **14** (1942), 466.
11. HUME, D. N. & KOLTHOFF, I. M., *Industr. Engng. Chem.* (*Analyt. Ed.*), **16** (1944), 103.
12. PARK, B., *Industr. Engng. Chem.* (*Analyt. Ed.*), **3** (1931), 77.
13. HAMMOCK, E. W. & SWIFT, E. H., *Analyt. Chem.*, **21** (1949), 975.
14. KOLTHOFF, I. M. & FURMAN, N. M., *Potentiometric Titrations* (Wiley, New York), 1949, 110.

Estimation of Sodium in Serum & Other Biological Fluids

(Mrs.) ALAMELA VENKATARAMAN
Department of Biochemistry, Haffkine Institute, Bombay

A modified " one-piece " uranyl reagent has been developed for the estimation of sodium in serum and other biological fluids. A simple micro-chemical method is described for the accurate determination of serum sodium.

THE determination of serum sodium for clinical purposes requires a higher order of accuracy than do most blood analyses. Since the range of normal concentration is rather narrow, a departure of probably 4-5 per cent from the normal is of clinical significance. Therefore, any method for the routine estimation of serum sodium to be worth while must be highly accurate.

In most of the micro-chemical methods in vogue now, the sodium is precipitated from the ashed sample or trichloracetic acid (T.C.A.) extract as a triple acetate with uranium and a divalent metal like zinc or magnesium. This is followed by the analysis of the carefully washed precipitate by gravimetric, titrimetric or colorimetric procedures. The triple salt is easily soluble in water but insoluble in excess of the reagent or alcohol. Washing of the precipitate free from the excess of the reagent must be thorough and care must be taken to avoid loss of the precipitate either due to redissolution or mechanical loss during decantation. Most of the modified methods give reliable and reproduceable results in the hands of an expert but they are slow and tedious requiring care and attention. The number of manipulations usually involved not only add to the time consumed but increase the possibility of errors. Scrupulous care is essential when determining small amounts of sodium, as the element is ubiquitous and the chances of including extraneous sodium through laboratory glassware and chemical reagents are manifold.

Flame photometer offers a rapid means of analysis with satisfactory accuracy. However, it has been emphasized that " even the best of such an instrument can give reliable results only when handled by an experienced and competent analyst. No doubt, the instrument saves material and time but the responsibility of the analyst who operates the instrument is in no way reduced. Unstable conditions may cause sudden changes in the performance of the instrument, giving results with errors so large as to make the estimation useless. Frequently, inconsistent readings are obtained due to alterations in gas and oxygen pressures, and fluctuations like these are not easily rectified. The analyst has to keep on the alert for any change in the response of the instrument "[1-4]. Flame photometer is an expensive instrument, out of reach of many clinical laboratories, and, therefore, a chemical method which would be rapid as well as accurate should be welcome.

Consequently, it is necessary to have a method that would (a) involve the minimum number of manipulations, (b) be completed in a short time, (c) require the minimum amount of the uranyl salt which is costly and often not readily available in a pure form, (d) avoid ashing of the serum sample or preparation of portein-free filtrates, (e) not require separation and washing of the precipitated triple salt, and (f) make use of the supernatant liquid for colorimetric estimation.

A thorough study was, therefore, undertaken to develop a " one-piece " reagent in alcohol so that the serum sample could be used directly without preliminary deproteinization.

Very few attempts have been made so far in this direction to use an alcoholic reagent, and to work up the supernatant liquid instead of the precipitate. The use of the supernatant has the decisive advantage of eliminating the processes of washing, weighing, transferring or titrations. A reagent containing 30 g. of uranyl acetate and 150 g. of magnesium acetate per litre of 50 per cent alcohol was introduced by Caley *et al.*[5] who used a T.C.A. extract of serum and measured the volume of the packed precipitate of the triple salt in a special capillary tube. Lindsay *et al.*[6] making use of the same reagent measured nephelometrically the turbidity produced by the precipitated triple acetate. Bradbury[7] and later FowWeather and Anderson[8] using Weinbach's[9] reagent precipitated the sodium from T.C.A. extracts with the addition of alcohol, and measured the loss in the yellow colour of the reagent colorimetrically. Weinbach's reagent, however, consists of a very large excess of uranyl and of zinc acetates per litre of the aqueous solution. Trinder[10] has published a simple method wherein the alcohol concentration in the reagent has been raised to 80 per cent so that the serum proteins could be precipitated along with the triple salt at one stage. The uranium in the supernatant is determined colorimetrically as uranyl ferrocyanide. The concentration of the uranyl radical in the supernatant would be indirectly proportional to the amount of sodium precipitated.

The procedure described in this paper is more or less in line with that of Trinder except for slight variations. The reagent employed by us is, however, of different composition. The original Weinbach's reagent and its later modifications require boiling because of the low solubility of the uranyl acetate. The nitrate, $UO_2.(NO_3)_2 6H_2O$, has a very high solubility and is, therefore, recommended in place of the acetate. Further, some of the samples of the acetate have been found to be completely precipitated in 70-80 per cent alcoholic solution.

Sodium combines with zinc or magnesium uranyl acetate in a definite ratio to give sparingly soluble crystals of the triple salt of the composition $(UO_2)_3$Zn (or Mg) Na $Ac_9 6H_2O$[11]. Although according to the formula only 1 mol. of zinc or magnesium acetate is required for every 3 mol. of the uranyl radical, all the previous workers have, for no obvious reasons, used a very large excess of the zinc or magnesium salt — as much as 30 times the required quantity.

During the course of this study it was found necessary to avoid the zinc salt and use magnesium acetate instead, since in the colorimetric estimation of the uranium as the ferrocyanide, the turbidity developed on standing is due to the white gelatinous precipitate of the zinc ferrocyanide. Using magnesium acetate, satisfactory colour development is obtained when either the precipitated triple acetate or the supernatant is treated with ferrocyanide in dilute acetic acid. The optimum quantity of the magnesium salt for immediate and complete precipitation of the triple acetate has been worked out to be about 5-6 times the quantity actually required by the formula, i.e. 2 mol. of magnesium acetate for every mole of the uranyl nitrate. At this concentration the precipitation of the triple salt is complete within 5-10 min. either at room temperature or in the cold. The " one-piece " reagent described in this paper consists of an 80 per cent alcoholic solution containing 0·02 mol. of uranyl nitrate and 0·04 mol. of magnesium acetate per litre with enough acetic acid to give a *p*H of about 5·0-5·2.

Estimation of uranium — Bradbury[7] and FowWeather and Anderson[8] using Weinbach's reagent[9] measure the loss in the yellow colour of the supernatant solution after precipitation of the sodium. Many colour reactions of uranium are known. Of these, the brown colour of the uranyl ferrocyanide is a highly sensitive test for small amounts of uranium. In the absence of any zinc salt the brown solution is clear for many hours. Table 1 indicates the amount of colour developed with varying amounts of the reagent expressed in terms of galvanometer reading (G) and optical density (D) (*see* under "Procedure" for details). Temperature (5°, 25°, 37°C.) has no effect on the colour development.

TABLE 1 — ESTIMATION OF THE URANIUM IN THE REAGENT AS THE FERROCYANIDE

QUANTITY OF REAGENT ml.	GALVANOMETER READING (G)	OPTICAL DENSITY (D)
0·10	79·0	0·1024
0·15	71·0	0·1487
0·20	62·0	0·2076
0·25	55·5	0·2557
0·30	49·5	0·3054
0·35	43·5	0·3615
0·40	38·5	0·4145
0·45	34·5	0·4622
0·50	30·5	0·5157

Materials and methods

Reagents: *Alcoholic uranyl magnesium acetate* — Uranyl nitrate, $UO_2(NO_3)_2$-$6H_2O$ (10 g.), magnesium acetate ($MgAc_2$-$4H_2O$, 8·6 g.), and glacial acetic acid (30 ml.) are dissolved in water, made up to 200 ml. in a graduated cylinder and diluted to 1 litre with absolute or 95 per cent alcohol*. Two ml. of the stock sodium chloride solution is added to the saturated reagent with reference to the triple salt and the final reagent is preserved in a brown glass-stoppered bottle, preferably in the refrigerator, to avoid evaporation of the solvent.

Stock sodium chloride (*1 ml. = 5 mg. Na*) — 1·270 g. of dry sodium chloride is dissolved in 100 ml. of water. A series of standards containing 100-500 mg. per cent of sodium are prepared by diluting this stock solution.

Potassium ferrocyanide (*10 per cent*) — Fifty g. of $K_4Fe(CN)_6.3H_2O$ are dissolved in 500 ml. of water and stored in a brown bottle. Any precipitated impurities are removed by decantation.

Acetic acid (*1 per cent*) — Ten ml. of glacial acetic acid are added to 1 litre of water.

Glassware — To avoid extraneous sodium from laboratory glassware which are normally cleaned with washing soda, the articles used for sodium determinations are segregated, rinsed with dilute nitric acid and reserved only for this work.

Centrifuge tubes — Centrifuge tubes (15 ml.) can be used for precipitation. In the absence of glass stoppers, glass rods are used for mixing.

Pipettes — A 5-ml. " Exax " bulb pipette should be reserved for measuring the reagent. A few 0·1 ml. blood pipettes are tested for accuracy and confined to this work only. After use they are rinsed with dilute potassium hydroxide solution, dilute nitric acid, flushed with water and dried. One ml. graduated standard pipettes are also reserved for measuring the aliquots of the supernatant and are cleaned by flushing with plenty of water.

Test-tubes graduated at 50 *ml.*— Folin's N.P.N. tubes or 50 ml. volumetric flasks may be used for developing the colour with ferrocyanide. However, it is more convenient and cheaper to calibrate a few big test-tubes at 50 ml.

---

*Care must be taken to specially purify the alcohol obtained from local distilleries.

Colorimeter — Any type of photoelectric colorimeter with suitable filters can be used.

Collection of samples — Care is taken to use specially washed syringes and glassware for the collection of blood samples and the separation of the sera. Hospitals must be advised to separate the sera within an hour of drawing the samples and any haemolysed sample must be rejected.

Procedure — Five ml. of the cold alcoholic reagent is accurately pipetted into each of the centrifuge tubes. To one tube B (sodium blank) 0·1 ml. of distilled water was added, and into the others 0·1 ml. of clear serum or the standard solution is introduced, blowing through the pipette gently. For the sake of greater accuracy different standards are measured with the same pipette, after rinsing. Duplicates were run for both standards and serum samples. The contents are mixed well by inserting a clean glass rod and swirling the tube vigorously for 1-2 min. The tubes are then closed with either rubber caps or corks and left in the refrigerator or a beaker of ice water. After about half an hour the tubes are centrifuged for 2-3 min. and the clear supernatant used for the next stage of colour development. Half ml. of the clear solution is carefully pipetted out into the tubes graduated at 50 ml. and diluted to about 25 ml. with 1 per cent acetic acid. One ml. of potassium ferrocyanide is then added to all the tubes and the volume made up to 50 ml. with 1 per cent acetic acid. The colorimeter blank is prepared with 1 ml. of ferrocyanide in 1 per cent acetic acid. The intensity of the colour was read at a suitable wavelength (400-450 μ) or with suitable filters.

Calibration graph — The concentrations (C) of the standard solutions are plotted against the corresponding galvanometer readings (G) or optical densities (D) or ($D_B - D_S$) and the sodium content of the unknown serum sample is read directly from the graph (TABLE 2). In accordance with modern practice, an analysis is made every time on the standard solution (e.g. 300 mg. per cent) as a basis for calculation. Variations in the daily reading of the sodium blank (B) on the photometer have been very small, within half a scale division. To overcome the error due to even such small variations either in the sodium blank or the standard, calculations may be made as follows.

TABLE 2 — DATA FOR CALIBRATION GRAPH

(0·5 *ml. of clear supernatant used to develop the colour*)

CONC. OF SODIUM mg. % (C)	GALVANOMETER READING (G)	OPTICAL DENSITY (D)*	($D_B - D_S$)†
O(B)	30·5	0·5157	nil
100	36·5	0·4377	0·0780
200	44·5	0·3516	0·1641
250	49·0	0·3098	0·2059
300	54·0	0·2676	0·2481
350	59·5	0·2255	0·2902
400	64·5	0·1904	0·3253
500	78·5	0·1051	0·4106

*Represents the concentration of uranium in the supernatant.

†Represents the concentration of uranium precipitated as the triple salt.

Since the amount of uranium precipitated is directly proportional to or the amount of uranium in the supernatant is inversely proportional to the concentration C_s of sodium added, ($D_B - D_S$) would represent the loss in concentration of uranium in the solution (or the concentration of uranium precipitated as the triple salt) and is proportional to C_S.

$$\text{Thus: } \frac{D_B - D_X}{D_B - D_S} \times C_S = C_X$$

$$\text{i.e. } \frac{\log G_X - \log G_B}{\log G_S - \log G_B} \times C_S = C_X$$

where G_B, G_S and G_X are the galvanometer readings of the sodium blank, standard and the unknown, and D_B, D_S and D_X are the corresponding optical densities.

Discussion

The modified uranyl magnesium acetate reagent and the procedure outlined above have been in use for routine work in this laboratory for the last three years or so. The reagent is extremely stable and only needs protection from evaporation of the solvent. The method is simple and any number of serum samples may be analysed effortlessly. The reagent used has been designed for serum sodium analyses and the concentration of the uranyl salt has been so adjusted that about half the amount of uranium is precipitated by 0·1 ml. of the fluid*. For analysing samples containing other than 200-400 mg. per cent of sodium, the concentration of the

---

*The supernatant from all the tubes can be pooled and salvaged when sufficient quantity has been collected. The original concentration of the uranium is restored by adding *c.* 4-5 g. of uranyl nitrate and 0·7 g. of magnesium acetate to a litre of the supernatant. A fresh standard graph should be drawn.

uranyl ion can be altered to suit the needs. Further, the amount of the supernatant used for colour development and the final dilution should be adjusted according to the size of the cuvette and the type of colorimeter available. A Leitz photoelectric colorimeter (32 C, 6-8 V. bulb) with filter C was used throughout this work.

Interfering substances — Caley and Foulk[12] and McCance and Shipp[13] have reported that Ca, Mg and Fe do not interfere with the estimation of sodium under the conditions employed by them. Phosphates are known to be precipitated by the uranyl radical and, hence, must be removed if present in larger amounts. However, the amount of phosphate present in normal blood serum is so small that less than $\frac{1}{600}$ part of uranium present is precipitated by the phosphate. Any error due to this would amount to less than 0·2 per cent.

Potassium can be expected to interfere as this also forms a sparingly soluble triple acetate. But McCance and Shipp[13] have noted that sodium can be determined accurately by their procedure, even in the presence of 30 times its weight of potassium. Salit[14] and Harrison[15], following the method of McCance and Shipp, observed that potassium was always precipitated along with the sodium at temperatures below 0° but not at higher temperatures. Since the quantity of potassium present in serum even in pathological cases is not very much, the effect of the presence of small amounts of potassium under the conditions outlined in this paper has been examined.

Potassium sulphate solution (0·1 ml., 20-200 mg. per cent) or a mixture of potassium sulphate and sodium chloride solutions was added to 5 ml. of the reagent as described under " Procedure " and worked up after 2 hr. Only in the tube, containing 200 mg. per cent potassium, was there a slight perceptible precipitate but in the presence of sodium even this slight interference was not observed (TABLE 3). The presence of 100 mg. per cent of Ca and Fe did not have any effect on the estimation of sodium.

Individual and pooled sera from the Haffkine Institute Blood Bank were used for estimating the sodium by the above method. While the concentration in the individual samples varied between 340 and 360 mg. per cent, the pooled lots showed a range of 345-50 mg. per cent.

TABLE 3 — EFFECT OF THE PRESENCE OF POTASSIUM

(0·5 *ml. of the clear supernatant used for developing the colour*)

CONC. OF K ADDED mg. %	CONC. OF Na ADDED mg. %	GALVANOMETER READING
0	0	30·5
20	0	30·5
25	0	30·5
50	0	31·0
100	0	31·5
200	0	33·5
0	300	54·0
20	300	54·5
25	300	54·0
50	300	54·5
100	300	53·5
200	300	53·5
100	250	49·0
0	250	49·0

Other applications — This procedure is applicable to most of the body fluids except urine where the interfering phosphate is to be removed first. Cerebrospinal and ocular fluids, saliva and sweat can be analysed for their sodium content by this simple modification.

Summary

A new " one-piece " reagent containing uranyl nitrate and magnesium acetate in 80 per cent alcohol is recommended for the estimation of sodium in biological fluids by the procedure outlined by Trinder.

The method consists of a minimum number of manipulations, the isolation and washing of the precipitated triple salt being avoided.

The sodium and the serum proteins in 0·1 ml. of the serum are precipitated simultaneously, the precipitation being complete and quantitative even at room temperatures within less than 15 min.

The sodium content is obtained indirectly by measuring the concentration of the uranium before and after the precipitation of the sodium as the triple salt.

The presence of potassium, even up to 200 mg. per cent, does not interfere with the precipitation of the sodium. Ca and Fe in concentrations of 10 mg. per cent have no effect. Small amounts of phosphates, even up to 100 mg. per cent, do not materially affect the accuracy.

This simple procedure is applicable to most of the body fluids except urine.

Acknowledgement

I wish to thank the Director, Haffkine Institute, for his keen interest in the work.

References

1. Hald, P. M., *J. biol. Chem.*, **167** (1947), 499.
2. Natelson, S., *Amer. J. Clin. Path.*, **20** (1950), 463.
3. Proehl, E. C. & Nelson, W. P., *Amer. J. Clin. Path.*, **20** (1950), 806.
4. Shukers, C. F., *Amer. J. Clin. Path.*, **22** (1952), 606.
5. Caley, E. R., Brown, C. T. & Price, H. P., *Industr. Engng. Chem.* (*Anal. Ed.*), **6** (1934), 202.
6. Lindsay, F. K., Braithwaite, D. G., & D'Amico, J. S., *Industr. Engng. Chem.* (*Anal. Ed.*), **18** (1946), 101.
7. Bradbury, J. T., *J. Lab. Clin. Med.*, **31** (1946), 1257.
8. FowWeather, F. S. & Anderson, W. N., *J. Clin. Path.*, **1** (1948), 177.
9. Weinbach, A. P., *J. biol. Chem.*, **110** (1935), 95.
10. Trinder, P., *Analyst*, **76** (1951), 596.
11. Barber, H. H. & Kolthoff, *J. Amer. chem. Soc.*, **50** (1928), 1625.
12. Caley, E. R. & Foulk, C. W., *J. Amer. chem. Soc.*, **51** (1929), 1664.
13. McCance, R. A. & Shipp, H. L., *Biochem. J.*, **25** (1931), 449.
14. Salit, P. W., *J. biol. Chem.*, **96** (1932), 659.
15. Harrison, M. F., *Biochem. J.*, **48** (1951), 283.

Separation of Oleic & Iso-oleic Acids from Hydrogenated Vegetable Oil by Adsorption Chromatography*

T. J. BOMAN

Public Health Laboratory, Poona

A chromatographic method using alumina as the adsorbent and 1 : 1 mixture of benzene and petroleum as solvent has been developed for the separation of oleic and iso-oleic acids from hydrogenated vegetable oil.

HYDROGENATED vegetable oils, when used as adulterants, are usually detected by determining the iodine values of fatty acids by Twitchell's lead-acetate-alcohol method[1]. This method is based on the assumption that iso-oleic acid in solid acids mixture increases its iodine value. So far, no chemical method has been developed by which iso-oleic acid can be estimated separately in a mixture of solid fatty acids. Chromatography seems to offer a means of effecting such a separation and estimation.

Claesson[2], and Holman and Hagdahl[3] have worked out chromatographic methods for the separation of long-chain saturated and unsaturated fatty acids, including oleic and iso-oleic acids, but these methods require elaborate equipment and large amounts of material. Ramsey and Patterson[4], Elsden[5], and Moyle, Baldwin and Scarisbrick[6] have worked out methods for the separation of lower fatty acids by paper partition chromatography. Ramsey and Patterson[7] have also modified their method for the separation of long-chain (C_{11}-C_{19}) fatty acids using 2-aminopyridine and furfuryl alcohol as the solvent system and effected the separation of odd numbered fatty acids. Howard and Martin[8] have developed a method for the separation of C_{12}-C_{18} fatty acids by reversed phase chromatography, but the method is not satisfactory because the identification of fatty acids separated by their melting point determinations is not possible. Phatak *et al.*[9] identified iso-oleic acid in a mixture of fatty acids by oxidizing the acid and separating the products of oxidation. This method is based on the one developed by

---

*Presented before a symposium on " Chromatography " organized by the Society of Biological Chemists, India, at Bangalore.

Reid and Lederer[10] for the separation of dibasic acids.

In this paper a simple method has been described for the separation of oleic and iso-oleic acids by chromatographic technique using alumina as adsorbent and a mixture of benzene and petroleum as solvent.

Experimental procedure

Alumina was prepared according to the method described by Brockman and was dried at 110°C. for a few hours before use.

The solvents, benzene and petroleum (40°-60°C.), were used without any special treatment; when acidic, they were distilled over alkali.

The columns used were 10 mm. in diam. and packed with 19-20 g. of alumina to a height of 32-34 cm. The solvents were then run down the column at the rate of 25-50 cc. per hr.

Five grams of the hydrogenated oil were saponified with alkali and glycerol and the sodium salts of fatty acids obtained were acidified to isolate the free acids. A solution of the fatty acids (0·5 g.) in 1 : 1 mixture of benzene and petroleum was poured down the column and suction was applied. Immediately after all the solvent mixture was soaked in, the column was developed with 100 cc. of benzene. The percolate was collected in 5 cc. lots, transferred to capillary tubes and dried at a low temperature. When the developer was exhausted, the wet column was removed and divided into 8 sections, each 4 cm. long. Each section was then eluted with 50 cc. of a 1 : 1 mixture of alcohol and petroleum. The eluate was filtered and the filtrate evaporated, dissolved in a few cc. of alcohol-petroleum mixture and taken up in capillary tubes and dried at a low temperature.

Results and discussion

The small amounts of fatty acids that separated out precluded any quantitative determination of the acids. Therefore, they were identified by determining their melting points. The purity and homogeneity of the fatty acid fractions were confirmed by determining their iodine value[11] and by paper chromatography using butanol-acetic acid-water as the solvent system.

The lower fatty acids were the first to be carried down in the percolate followed by higher fatty acids. Only oleic and iso-oleic acids in the percolate and eluate fractions were identified. The topmost section, R_F value 0·93, contained iso-oleic acid (m.p. 45°C.) and the fraction immediately next to it with an R_F value 0·81 contained oleic acid (m.p. 15°C.). The remaining sections had either mixtures of fatty acids or saturated long-chain fatty acids. The iodine values of the fractions showed that they consisted of pure acids. Chromatograms of the fractions also confirmed the purity and homogeneity of the fractions; no short-chained acids were detected in the chromatogram.

The application of this method for the detection of the adulteration of ghee with hydrogenated vegetable oil is being investigated.

Summary

A method based on adsorption chromatography using alumina as adsorbent and benzene-petroleum mixture (1 : 1) as solvent system has been developed for the separation of oleic and iso-oleic acids from hydrogenated vegetable oil.

The R_F values of oleic and iso-oleic acids in this solvent mixture were found to be 0·81 and 0·93 respectively.

The products separated from hydrogenated vegetable oil have been identified by determining their melting points. The purity and homogeneity of the acids separated were confirmed by determining their iodine values. Analysis of the products by paper chromatography did not reveal the presence of any short-chain acids.

Acknowledgement

The author is grateful to Dr. M. D. D. Gilder, former Minister of Public Health to the Government of Bombay, and Dr. D. K. Viswanathan, Director of Public Health, Government of Bombay, for their keen interest in this investigation. He is also thankful to Dr. S. T. Rodda for the facilities, and to Mr. B. P. Desai for suggesting this problem.

References

1. TWITCHELL, E. J., *Industr. Engng. Chem.*, **13** (1921), 806.
2. CLAESSON, S., *Ark. Kemi Min. Geol.*, **23A** (1946), 1.
3. HOLMAN, R. T. & HAGDAHL, L., *Biochem. J.*, **46** (1950), 532.

4. Ramsey, L. L. & Patterson, W. I., *J. Ass. off. agric. Chem., Wash.*, **28** (1945), 644.
5. Elsden, S. R., *Biochem. J.*, **40** (1946), 252.
6. Moyle, V., Baldwin, E. & Scarisbrick, R., *Biochem. J.*, **46** (1950), 532.
7. Ramsey, L. L. & Patterson, W. I., *J. Ass. off. agric. Chem., Wash.*, **3** (1948), 441.
8. Howard, G. A. & Martin, A. J. P., *Biochem. J.*, **46** (1950), 532.
9. Phatak, S. S., Mahadevan, A. P. & Patwardhan, V. R., *Curr. Sci.*, **6** (1952), 162.
10. Reid, R. L. & Lederer, M., *Biochem. J.*, **50** (1951), 60.
11. Toms, H., *Analyst*, **53** (1928), 71.

Identification of Vegetable Oils: Part I—Detection of Rape & Mustard Oils

K. D. PATHAK & J. S. AGGARWAL

National Chemical Laboratory of India, Poona

The erucic acid number is a satisfactory index of the purity of rape and mustard oils and can be employed for estimating the extent of adulteration in them.

THE common physical and chemical characteristics of vegetable oils are not sufficiently reliable or accurate guides for indicating the purity of the oils[1]. A method based on the characteristic constituents of the oils may be a more reliable guide for their identification and for determining their purity. Rape and mustard oils are characterized by the presence of 50-57 per cent erucic acid in them. This acid is not found in other vegetable oils commonly available in India.

Although the lead salt of erucic acid is slightly soluble in cold alcohol[2], it is soluble to an appreciable extent in the presence of lead salts of other fatty acids[3]. It is possible that the same percentage of lead salt of erucic acid will separate out along with those of saturated acids under certain specified conditions. Based on these considerations, Neogi[4] developed a method for identifying and determining the purity of rape and mustard oils. In his studies, Neogi worked with oil samples from Bengal and employed only a limited number of other vegetable oils as adulterants. The percentage of oils used as adulterants was also limited.

This paper reports the results of investigations carried out to determine the purity of rape and mustard oil samples obtained from different parts of India and the extent of adulteration in them by other vegetable oils by determining the lead salt insoluble part of erucic acid.

Experimental procedure

The oils used were expressed from the seeds in a laboratory hydraulic press. One sample of mustard oil was obtained by extraction with petroleum ether. The determination of the lead salt insoluble part of erucic acid in the various oils and oil mixtures was carried out exactly the same way as described by Neogi[4]. Although the values obtained for erucic acid by this method does not represent the total erucic acid content of the oils, for convenience it is termed " erucic acid number ".

Results and discussion

The erucic acid numbers of 9 samples of rape and mustard oils and 10 other vegetable oils are given in Table 1. The results show that the erucic acid numbers for the samples of rape and mustard oils vary between 44·6 and 49·3, the average value being 47·3. The highest value for erucic acid number for other oils is 3·2 (cottonseed oil).

In Table 2 are given the actual percentages of rape or mustard oil present in mixtures of these oils with other vegetable oils, their erucic acid numbers, and the percentage of rape or mustard oil present in the

TABLE 1 — ERUCIC ACID NUMBER OF VEGETABLE OILS

	ERUCIC ACID NUMBER
Brassica compestris (yellow sarson), Uttar Pradesh	49·3
Brassica compestris (brown sarson), Uttar Pradesh	49·2
Brassica napus (*toria* or rape), Uttar Pradesh	47·7
Brassica juncea (*rai*), Uttar Pradesh	47·1
Brassica compestris (brown sarson), Punjab	44·6
Brassica compestris (brown sarson), Bombay State	47·1
Brassica compestris (brown sarson), Bombay State — solvent-extracted oil	45·4
Brassica compestris (brown sarson), Poona — oil extracted in *ghani*	45·8
Brassica compestris (brown sarson), Uttar Pradesh — oil expressed in an expeller	49·3
Sesame oil	0·3
Safflower oil	0·9
Coconut oil	2·2
Groundnut oil	1·9
Castor oil	1·4
Niger seed oil	1·5
Argemone oil	1·0
Linseed oil	1·3
Cottonseed oil	3·2
Mahua (*Bassia latifolia*) oil	2·9

TABLE 2 — ANALYSIS OF ADULTERATED RAPE OR MUSTARD OILS

ADULTERANT	RAPE OR MUSTARD OIL IN THE SAMPLE %	ERUCIC ACID NUMBER	RAPE OR MUSTARD OIL IN THE SAMPLE, CALCULATED %
Sesame oil	80	36·8	77·9
	50	22·7	48·0
	25	9·8	20·7
	10	3·6	7·7
Safflower oil	80	37·2	78·6
	50	23·6	49·9
	25	8·7	18·3
	10	2·8	6·0
Coconut oil	80	37·7	79·7
	50	23·6	50·0
	25	8·5	18·0
	10	4·9	10·4
Groundnut oil	80	35·4	74·9
	50	22·3	47·1
	25	7·9	16·8
	10	4·5	9·6
Castor oil	80	35·8	75·8
	50	22·3	47·2
	25	9·8	20·8
	10	3·2	6·7
Niger seed oil	80	36·2	76·5
	50	23·9	50·5
	25	9·2	19·5
	10	3·6	7·6
Argemone oil	90	41·7	88·1
	60	27·3	57·8
	40	18·0	38·0
	10	4·8	10·1
Linseed oil	90	41·4	87·4
	60	28·7	60·8
	40	18·7	39·6
	10	3·3	7·1
Cottonseed oil	70	32·7	69·2
	40	19·7	41·6
	30	13·8	29·1
	10	3·6	7·6
Mahua oil	70	33·1	69·9
	40	20·1	42·3
	30	12·6	26·6
	10	4·3	9·1

mixtures calculated on the basis of their erucic acid number. The results show that erucic acid number of the oil mixtures is a satisfactory index for determining the percentage of rape or mustard oil present in them. This method holds good even when the adulterant forms 60 per cent of the mixture.

Detection of rape and mustard oils through selective oxidation of erucic acid — Kaufmann and Fiedler[5] found that erucic acid is converted largely to dihydroxy-behenic acid by oxidation with potassium permanganate at room temperature (18°-20°C.) and oleic acid gives pelargonic acid and not hydroxystearic acid under similar conditions. Our studies have shown that dihydroxy-behenic acid is obtained in a sufficiently pure state with pure rape and mustard oils or mixtures of these oils containing other vegetable oils to a maximum of 50 per cent. When the quantity of adulterant in the oils exceeds 50 per cent, dihydroxy-behenic acid obtained is not pure even though the oxidation is carried out with excess of potassium permanganate at 30°C. for 16 hr. The results given in Table 3 show that as the amount of rape or mustard oil in the mixture decreases the purity of dihydroxy-behenic acid obtained decreases; the equivalent weight of the acid also falls from 372 to 326. This method is cumbersome, time-consuming and requires larger amounts of oil sample for testing. It is, therefore, not quite satisfactory for detecting rape and mustard oils and for determining the extent of adulteration in

TABLE 3 — PERMANGANATE OXIDATION OF OILS

(*Dihydroxy-behenic acid, m.p.* 131°*C.* ; *eq. wt.*, 372)

MUSTARD OIL IN THE SAMPLE %	CONDITIONS OF OXIDATION	CHARACTERISTICS OF DIHYDROXY-BEHENIC ACID	
		m.p. °C.	Eq. wt.
Pure oil	Duration 1 hr. ; temp. 25°C. ; slight excess of $KMnO_4$	131	370
80	do	130-31	370
50	do	130	369
25	do	128	364
20	Duration 2 hr. ; temp. 25°C. ; excess of $KMnO_4$	—	335
20	Duration 3 hr. ; temp., 30°C. ; excess of $KMnO_4$	124	351
20	Duration 16 hr. ; temp. 20°-25°C. ; large excess of $KMnO_4$	126	352
10	Duration 3 hr. ; temp. 30°C. ; excess of $KMnO_4$	126	343
10	Duration 16 hr. ; temp. 20°-25°C. ; large excess of $KMnO_4$	123	326

them by the oxidation procedure. Hadorn *et al.*[6] have recently reported similar conclusions.

Conclusion

Erucic acid number is a satisfactory index for determining the purity of rape and mustard oils and also for estimating the amount of other vegetable oils used as adulterants with them. The method is satisfactory with oil mixtures containing 60 per cent of the adulterant.

The selective oxidation of erucic acid by permanganate oxidation is not a satisfactory procedure for determining the extent of adulteration in rape and mustard oils by other vegetable oils.

Acknowledgement

One of us (K.D.P.) is thankful to the Indian Central Oilseeds Committee for financial assistance.

References

1. BRAHAMACHARI, *Indian med. Gaz.*, **70** (1935), 320.
2. JAMIESON, G. S., *Vegetable Fats and Oils* (Reinhold Publishing Corp., New York), 1943, 230-351.
3. HILDITCH, T. P., RILEY, T. & VIDYARTHI, N. L., *J. Soc. chem. Ind.*, **46** (1927), 457.
4. NEOGI, S., *Analyst*, **61** (1936), 597.
5. KAUFMANN, H. P. & FIEDLER, H., *Fette u. Seifen*, **45** (1938), 465.
6. HADORN, H., JUNGKUNZ, R. & BIEFER, K. W., *Z. Lebensm Untersuch u. Forsch*, **97** (1953), 365-73.

Synthetic Ion Exchange Membrane Discs: Part I — Preparation of Cation Exchange Membrane Discs & Their Properties

N. KRISHNASWAMY

National Chemical Laboratory of India, Poona

The method of preparation of synthetic cation exchange membrane discs using the Conway unit as mould is described. Donnan diffusion studies have been carried out with samples of discs prepared and with a Saran-backed sample of Permionic CR 51. The foreign sample exhibits lower sodium chloride absorption which indicates greater screening effect and hence better perm-selective properties.

ION exchange resins can be moulded into a variety of shapes — rods, discs and sheets — for use as membranes[1,2]. Discs of the resins are also prepared by mixing finely powdered resin with an inert material like polystyrene and cast into required sizes[3,4]. Filter paper sheets and sintered glass discs impregnated with ion exchange resins can be used as membranes[2].

These membranes, because of their perm-selective character, low electrical resistance, high exchange capacities and good mechanical strength, find many useful applications, such as deionization of sea water[5]. A steady source of radioactivity can be had by impregnating a sheet of ion exchange resin with a radioactive salt[6]. Manecke[7,8] has indicated the use of membrane electrodes in the determination of alkali ion concentration. He has also described the construction and properties of a membrane accumulator[9].

The progress in the field of ion exchange membranes during the years 1951 and 1952 has been reviewed by Bauman *et al.*[10] and Juda *et al.*[11]. Recently Spiegler and Coryell[12] have used radio tracers for determining self-diffusion coefficients of different ions in the cation exchange membrane Nepton CR 51. They have shown that the mechanisms of diffusion and electrical conductance in the membrane are similar.

With a view to evaluate the economics of the membrane process for treatment of brackish waters and study its other applications it was decided to study the preparation and properties of the two types of membranes. This paper describes the method of preparation of cation exchange membrane discs and their properties.

Experimental procedure

Preparation of membrane discs — It has been recognized[13-15] that in the preparation of discs or other articles from ion exchange materials, the water content of the reaction products should not be lost, and that it is essential to carry out the process in presence of water vapour. The following procedure is usually employed for the preparation of circular discs of membranes. The viscous solution to be cast in the form of disc is placed at the flat end of a tube of proper size and the open end is then sealed. The sealed tube is kept vertical and heated under controlled conditions. After heating for the requisite period, the disc formed at the bottom is removed by breaking the tube. The method described in this paper obviates the need for breaking the tube, and makes use of a mould which could be used repeatedly. For this purpose the Conway unit[16] (Pyrex brand, manufactured by Gallenkamp & Co., London) has been used as a mould.

The viscous resin composition to be cast in the form of a disc was taken in the central portion of the Conway unit (diam. 35 mm.). Distilled water was poured into the outer compartment taking care that it did not run into the central portion of the unit. A watch glass was used to cover the unit. The cover was fixed in position by using a rubber-based sealing composition prepared in this laboratory[17]. This enabled the easy removal of the cover periodically to replace the water evaporated in the outer compartment. The unit was placed on a level plate in an oven maintained at the proper temperature. Heating was continued till the viscous resin material set into a gel. The temperature of the oven was then raised to the necessary level for curing the formed disc. Throughout the heating, care was taken to see that there was adequate water in the unit to provide a moisture-saturated atmosphere during curing. After curing for the desired period, the unit was taken out of the oven, cooled and the discs removed from the unit. The conditions adopted for preparing the different membranes are given below.

Phenol-sodium metabisulphite-formalin membranes: *Composition* (*a*) — The composition employed for this was essentially the same as reported by the Permutit Co. for the preparation of rod-shaped membranes (example 1[14]). *Composition* (*b*) — Modification of the above composition was effected as follows: Phenol (5 g.), sodium metabisulphite (9·0 g.), sodium hydroxide (5 g.), 40 per cent formalin (18 cc.) and water (20 cc.) were heated together for 1 hr. under reflux. The mixture was cooled and phenol (8 g.), paraformaldehyde (22 g.) and water (14 cc.) added and the contents refluxed till the spontaneous reaction began. The mixture was cooled and the resulting viscous material was used for preparing the membrane discs.

The viscous resin mix obtained from the above two compositions was kept at 90°C. for about 3-4 hr. to effect gelling. The curing was carried out at 120°C. for 2-3 hr. The discs after curing could be taken out easily from the unit by inverting it in sodium chloride solution. It was observed that the discs contracted if the water in the outer compartment was lost during curing, and expanded when put in sodium chloride solution. No further contraction or expansion occurred during regeneration or in the exhaustion cycles. The membranes were dark red when prepared but became orange red during the regeneration process and during treatment with sodium chloride solution the colour of the membranes slightly deepened.

Phenol-sulphonic acid membranes — Manecke's[7] method was modified in the following manner for the preparation of these membranes. Sixty grams of concentrated sulphuric acid were added to 47 g. of phenol and the mixture heated on a steaming water bath for 2 hr. On cooling the product crystallized. This was melted and 5 cc. were taken in a test-tube with 5 cc. of 40 per cent formalin. It is essential that temperature of this reaction mixture does not exceed 60°C., otherwise gelation occurs immediately. For this purpose the two layers of solution in the test-tube were kept without disturbing in a water bath maintained between 50° and 60°C. After about 15 min. the contents of the test-tube were shaken till a uniform pink colour persisted. The test-tube was kept in the same water bath for *c.* 1 hr. Then the test-tube was cooled and 2 cc. of the pink solution were taken in the Conway unit and following Manecke's method of forming the membrane in the absence of water, the unit was covered with a watch glass using the sealing composition and heated at 90°C. The solution set into a gel in 1 hr. The unit was then cooled, and the membrane taken out of the unit and re-inserted with the top side at the bottom. After refixing the lid the heating was continued for a further period of 20 min. Then the unit was cooled, the disc removed and placed in water or sodium chloride solution. To study the effect of placing water in the outer compartment, the membranes were prepared with water in the outer compartment and heated only at 90°C. for the same periods as above. The membranes prepared with phenol-sulphonic acid and formalin were dark brown in colour and on regeneration they did not exhibit such marked colour changes as observed with the other composition.

Measurement of exchange capacity of the membranes — The membranes were regenerated after preparation with 13·5 per cent hydrochloric acid solution and then washed free of acid with distilled water. The samples were dried between filter paper folds, weighed and kept in contact with known volumes of barium chloride solution overnight. The *p*H and titratable acidity of the solution were determined. From the weight of the membranes the exchange capacity per gram wet material was calculated.

Determination of moisture content of the membranes — To determine the capacity of the membranes in the dry state, the samples which had been employed for exchange capacity determination over a number of cycles were regenerated and the hydrogen forms were used. The wet material was dried between filter paper folds after breaking into fragments and heated in a weighing bottle at 110°C. Prolonged heating (60-70 hr.) was necessary to obtain constant weight of the residue.

Determination of Donnan absorption constants of the membranes — To evaluate the perm-selective characteristics of the membranes, the Donnan absorption constants were evaluated according to the procedure described by Juda *et al.*[18]. Along with the membranes prepared by us, a sample of "Saran"-backed Permionic CR 51 supplied by Ionics Inc. was also included in these studies. The leached sodium form of the membrane under study was equilibrated with the solution of known concentration of sodium chloride taken for Donnan absorption studies. When the membranes were equilibrated with sodium chloride solution of increasing concentration, acidity developed in the contact solution. The equilibrating solutions were repeatedly changed till no more acidity was detected. Then the sample was dried between filter paper folds to remove all externally adsorbed solution and placed in a beaker containing 100 cc. of distilled water. The contents were periodically shaken and after 15 min. contact, the solution was decanted and analysed for chloride. The procedure was repeated three times. Usually, four such contacts were enough to leach out all the absorbed chloride from the membrane. The total amount of chloride in all the washings was determined according to Mohr's volumetric method for chloride estimation.

Results

The capacities of phenol-sodium metabisulphite-formalin membranes prepared are given in Table 1 along with the moisture content and dry capacity of discs prepared. Disc Nos. 50, 55 and 56 were prepared from the same batch of mix but at different times. The mix was stored in the refrigerator and the necessary amount was taken out for the preparation of the disc.

Table 2 gives the capacities and moisture contents of the samples of membranes

TABLE 1 — MOISTURE CONTENT AND CAPACITY OF PHENOL-SODIUM METABISULPHITE-FORMALIN MEMBRANES

SAMPLE No.	COMPOSITION OF VISCOUS MIX	MOISTURE %	CAPACITY (WET) m. eq./g.	CAPACITY (DRY) m. eq./g.
23	a	67·2	0·4212	1·284
28	b	85·1	0·2100	1·400
31	b	76·6	0·3610	1·540
38	a	66·2	0·5180	1·534
49	a	65·6	0·5187	1·508
50	a	60·3	0·5563	1·402
55	a	58·2	0·6070	1·450
56	a	61·8	0·5500	1·440

TABLE 2 — MOISTURE CONTENT AND CAPACITY OF PHENOL-SULPHONIC ACID MEMBRANES

SAMPLE No.	CONDITION DURING HEATING	MOISTURE %	CAPACITY (WET) m. eq./g.	CAPACITY (DRY) m. eq./g.
58	With water	68·60	0·52	1·656
59	Without water	62·61	0·63	1·685
60	With water	75·58	0·41	1·679
61	Without water	69·69	0·51	1·683

prepared from phenol-sulphonic acid-formalin composition. The results of tests on the effect of introducing water in the outer compartment on the moisture content of the samples are also given in the table.

From the known dimensions of the discs, the amount of sodium chloride absorbed (N_A) at different external concentrations of sodium chloride ($N_{Ext.}$) was calculated. Fig. 1 gives the relationship between N_A and $N_{Ext.}$ and Fig. 2 gives the relationship between $N_A/N_{Ext.}$ and $N_{Ext.}$

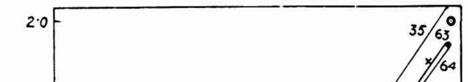


FIG. 1 — RELATIONSHIP BETWEEN THE CONCENTRATION OF EXTERNAL SODIUM CHLORIDE SOLUTION ($N_{Ext.}$) AND THE CONCENTRATION OF SODIUM CHLORIDE ABSORBED BY THE MEMBRANE (N_A)

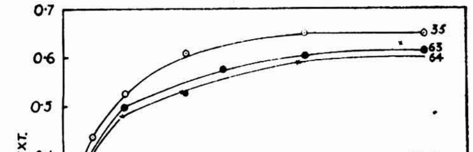


FIG. 2 —$N_A/N_{Ext.}$ vs. $N_{Ext.}$

Discussion

Phenol-sodium metabisulphite-formalin membrane discs — The results given in Table 1 show that the average capacity and moisture content of the discs prepared from composition (a) are 1·43 m. eq./g. dry weight and 63·2 per cent respectively. The corresponding values for discs prepared from composition (b) are 1·47 m. eq./g. dry weight and 81 per cent. These results show that there is no loss in the capacity of discs No. 50, 55 and 56 (TABLE 1) prepared from composition (a) stored in the refrigerator. The storing of the resin in a refrigerator is essential because if the resin composition is left at room temperature it slowly gels and is no longer useful for the preparation of the discs.

The results of the Donnan absorption studies (FIGS. 1 and 2) show that membrane disc 35 exhibits a steeper curve than membrane discs No. 63 and 64.

Phenol-sulphonic acid-formalin membrane discs — The results given in Table 2 indicate that the average capacity and moisture content of membranes prepared without water are 1·684 m. eq./g. dry weight and 66·2 per cent respectively. These discs show an increased capacity over those prepared from phenol-metabisulphite-formalin composition. When water is taken in the outer compartment of the Conway unit, it increases the moisture content of the membrane discs (cf. Nos. 58 and 60 with 59 and 61 respectively). For all practical purposes, it is enough if the discs of this composition are prepared in the absence of water as reported by Manecke[7].

Donnan absorption studies — These studies help in evaluating the perm-selective properties of the membranes. Disc Nos. 35, 63 and 64 were used in these studies (TABLE 3). Disc No. 63 was prepared with 2 cc. of resin mix and disc No. 64 with 1 cc. of the mix. The results of studies with

TABLE 3 — DESCRIPTION OF DISCS TAKEN FOR DONNAN ABSORPTION STUDIES

DISC No.	CAPACITY (WET) m. eq./g.	DIAMETER cm.	THICKNESS cm.	VOLUME cc.	DENSITY (WET) g./cc.
35	0·44	3·7	0·1600	1·7200	1·22
63	0·57	3·8	0·1828	2·0730	1·20
64	0·80	3·6	0·0828	0·8428	1·39
Saran-backed CR 51	0·68	2·9	0·0813	0·5369	1·31

these discs are compared with those obtained with Saran-backed Permionic CR 51.

It will be seen from Figs. 1 and 2 that the Saran-backed Permionic CR 51 exhibits lower sodium chloride absorption values than the other discs. This would indicate that it has greater screening capacity and, hence, better perm-selective properties.

Disc Nos. 63 and 64 prepared from phenol-sulphonic acid-formalin composition were tested. Disc No. 64 was thinner than disc No. 63. Figs. 1 and 2 show that there is no appreciable difference in the absorption values by reducing the thickness of the discs.

Juda *et al.*[18] while comparing the slopes of $N_A/N_{Ext.}$ curve for two chemically different cation exchange membranes, CR 41 and CR 51, observed that the steeper slope of CR 41 indicated stronger screening effect of chloride ions at dilute external sodium chloride concentrations. They have shown by transference number measurements that CR 51 which exhibits a less steeper curve than CR 41 is more perm-selective and they attribute the difference in behaviour of CR 41 to greater tendency for formation of ion pairs. The curve for disc 35 (phenol-metabisulphite-formalin) follows a pattern similar to that reported for CR 41. The curves for discs 63 and 64 indicate that they will be more perm-selective than disc 35 (FIG. 2).

Further work on the determination of Donnan diffusion constants in different salt solutions and the evaluation of transference numbers in the membrane discs is in progress.

Summary

The preparation of cation exchange membrane discs using the Conway unit as the mould is described.

The phenol-sulphonic acid membranes are found to have a higher exchange capacity.

Donnan absorption studies with these membranes indicate that discs prepared from phenol-sulphonic acid-formalin composition are more perm-selective than discs prepared from phenol-metabisulphite-formalin composition.

References

1. JUDA, W. & MCRAE, W. A., *J. Amer. chem. Soc.*, **72** (1950), 1044.
2. KRESSMAN, T. R. E., *Nature*, **165** (1950), 568.
3. WYLLIE, M. R. J. & PATNODE, H. W., *J. phys. Chem.*, **54** (1950), 204; *U.S. Pat.* 2,614,976 (1952).
4. SINHA, S. K., *Sci. & Cult.*, **18** (1953), 546; *J. Indian chem. Soc.*, **30** (1953), 529.
5. KUNIN, R. J. & MCGARVEY, F. X., *Industr. Engng. Chem.*, **45** (1953), 83.
6. WESTERMARK, T., *Acta Chem. Scand.*, **6** (1952), 1194.
7. MANECKE, G., *Z. phys. Chem.*, **201** (1952), 193.
8. MANECKE, G., *Z. Electrochem.*, **55** (1951), 672.
9. MANECKE, G., *Z. phys. Chem.*, **201** (1952), 1.
10. BAUMAN, W. C., ANDERSON, R. E. & WHEATON, R. M., *Ann. Rev. phys. Chem.*, **3** (1952), 124.
11. JUDA, W., MARINSKY, J. A. & ROSENBERG, N. W., *Ann. Rev. phys. Chem.*, **4** (1953), 384.
12. SPIEGLER, K. S. & CORYELL, C. D., *J. phys. Chem.*, **57** (1953), 687.
13. Ionics Inc., U.S.A., *Indian Pat.* 43,336 (1950).
14. Permutit Co. Ltd., London, *Indian Pat.* 43,943 (1950).
15. JUDA, W. & MCRAE, W. A., *U.S. Pat.* 2,636,851 (1953).
16. CONWAY, E. J. & BYRNE, A., *Biochem. J.*, **27** (1933), 419; *Brit. Pat.* 387,795 (1933).
17. PANDE, J. B. & RAGHUNATH, D., *Indian Pat.* 49,022 (1953).
18. JUDA, W., ROSENBERG, N. W., MARINSKY, J. A. & KASPER, A. A., *J. Amer. chem. Soc.*, **74** (1952), 3736.

Petrographic Studies on Chrome-magnesite & Magnesium Silicate Refractories

J. C. BANERJEE
Central Glass & Ceramic Research Institute, Calcutta

Forsterite and chrome-magnesite refractories made from Indian raw materials have been examined for their petrographic characteristics and compared with those of European and American origin. An attempt has been made to interpret refractoriness under load in the light of petrographic characteristics of the refractories.

BASIC refractories like magnesite, dolomite and chrome find restricted use in metallurgical furnaces because of their low refractoriness under load value and low spalling resistance. Chrome-magnesite and forsterite refractories do not suffer from these defects and have to a great extent replaced them. The refractoriness under load value of chrome-magnesite refractories is *c.* 1,700°C. and their spalling resistance is superior to magnesite, chrome or silica refractories.

The raw materials employed in the manufacture of these refractories are magnesite, magnesium silicate, dunite and chrome of Indian origin. The process followed in the manufacture of chrome-magnesite and forsterite refractories is to convert the different oxides in the raw materials to spinels and forsterite by adding requisite amount of raw magnesite during dead burning. Magnesite added to the raw materials during dead burning is supposed to form the following minerals: Forsterite ($2MgO.SiO_2$); chrome spinel ($MgO.Cr_2O_3$); ordinary spinel ($MgO.Al_2O_3$); magnesio-ferrite ($MgO.Fe_2O_3$) and periclase (MgO).

In magnesium silicate or forsterite refractories there is no chromium oxide present, but its addition improves the slag resistance of these refractories. These refractories contain forsterite, spinel and periclase in varying amounts depending upon the composition and the firing conditions employed in their processing. If the temperature in the kiln is not sufficiently high and the kiln atmosphere is reducing, fayalite ($2FeO.SiO_2$), a low temperature eutectic, is formed. The formation of fayalite lowers the refractoriness of the refractories, particularly the refractoriness under load value.

Physical and thermal tests help to indicate the properties of refractories, but a proper evaluation of the extent of conversion of the constituent mineral oxides in the raw materials to forsterite and spinel is best made by microscopic examination. In this paper petrographic analysis of some chrome-magnesite and forsterite type of refractories has been carried out and an attempt has been made to interpret some of the physical properties, particularly refractoriness under load values, in the light of the petrographic studies.

Materials and methods

Bricks were prepared from the raw materials and sections were prepared in the usual manner for microscopic examination. To prevent the coarser grains coming out of the sections while grinding and polishing, the small pieces of the refractory bricks were first boiled in Canada balsam. The sections were made very thin, *c.* 0·03 mm., as these refractories are dark coloured.

Results

The chemical composition and physical and petrographic characteristics of chrome-magnesite and forsterite refractories prepared are given in Table 1. For comparison, similar data on some European and American refractories are also included in the table. The two American varieties of chrome-magnesite bricks are chemically bonded bricks and did not receive the final firing.

TABLE 1 — COMPOSITION AND PROPERTIES OF CHROME-MAGNESITE AND MAGNESIUM SILICATE REFRACTORIES

CHEMICAL COMPOSITION	INDIAN FORSTERITE		INDIAN CHROME-MAGNESITE			FOREIGN CHROME-MAGNESITE				
	Magnesium silicate + magnesite	Dunite + magnesite	Magnesium silicate + magnesite + chrome	Dunite + magnesite + chrome	Low grade chrome ore + magnesite	Austrian	British (a)	British (b)	American (metal-cased)	American (chemically bonded)
SiO_2, %	28·34	28·20	17·80	17·80	17·56	15·00	8·98	6·50	7·94	5·20
Al_2O_3, %	1·92	2·40	4·88	5·00	5·74	10·30	15·48	12·40	7·30	19·20
FeO, %	—	nil	—	—	—	—	—	—	—	11·22
Fe_2O_3, %	2·44	7·29	11·86	12·00	10·86	15·02	15·10	12·73	8·60	—
Cr_2O_3, %	1·02	1·46	16·43	18·24	15·10	25·93	25·78	24·66	14·80	24·57
MgO, %	59·40	59·08	48·32	45·68	49·37	33·14	33·12	43·00	54·40	32·90
CaO, %	1·20	—	1·10	1·30	2·00	—	—	—	3·50	—
Total alkali, %	nil	traces	nil	traces	—	—	—	—	0·30	0·30
Loss, %	0·08	0·10	0·12	do	—	—	—	—	2·80	5·42
P.C.E. (Orton cone)	>35	>35	>35	>35	>35	>35	—	—	>34	>35
Refractoriness Ta*	>1700°C.	>1700°C.	>1700°C.	>1700°C.	>1700°C.	1650°C.	1571°C.	1515°C.	1430°C.	1570°C.
Refractoriness Te*	—	—	—	—	—	1670°C.	1580°C.	1570°C.	1470°C.	1645°C.
Mineralogical composition										
Chrome spinel, ($MgO.Cr_2O_3$) %	—	—	20·70	23·00	20·00	32·40	32·50	31·60	18·92	30·95
Spinel ($MgO.Al_2O_3$), %	2·67	3·34	7·00	7·00	7·00	14·90	21·50	17·25	10·15	26·70
Magnesio-ferrite ($MgO.Fe_2O_3$), %	10·55	9·11	14·00	15·00	13·00	18·75	18·90	15·95	10·75	14·36
Periclase (MgO), %	18·57	18·22	16·00	12·00	19·00	—	5·00	20·00	35·00	9·00
Total spinels and periclase, %	31·79	31·27	57·70	57·00	59·00	65·45	77·90	84·80	74·80	81·00
Forsterite ($2MgO.SiO_2$), %	65·99	65·70	41·50	41·50	40·00	34·90	21·00	15·20	18·55	12·10
Petrographic characteristics	Forsterite well developed in the ground mass; iron wholly converted to magnesio-ferrite which occurs in patches; some periclase seen in small grains; about 70% forsterite present	Forsterite well developed in the ground mass; iron wholly converted to magnesio-ferrite which occurs in patches; some periclase seen in grains; about 70% forsterite present	Chrome spinel patches; matrix mostly orthosilicate (forsterite) with some periclase and magnesio-ferrite; about 40-45% forsterite present	Forsterite distributed throughout the ground mass; chrome spinel and magnesio-ferrite occur in patches; grain size of chrome spinel bigger; about 40-45% forsterite present	Good development of forsterite in the ground mass in which chrome spinels are embedded; periclase distributed in the matrix; about 40% forsterite present	Forsterite well developed in between the spinels; prominent and big grains of chrome spinels; about 70% of the ground mass is made up of spinels	Forsterite distributed throughout the ground mass as small particles; abundance of spinel; chrome fully converted to chrome spinel; not much of periclase present; about 20-25% forsterite present	Some granular forsterite in the ground mass, mostly along the margins of bigger grains; most of the minerals are isotropic; chrome spinels occur in patches; about 10-15% forsterite present	Plenty of big, isolated, colourless to brownish patches of periclase; some forsterite present in between bigger grains of spinels and periclase; about 20% forsterite present	Spinel well developed; some periclase seen; about 10% forsterite present

*Ta, temperature of initial subsidence; Te, temperature of final collapse.

From the chemical analysis, the probable mineralogical composition of the refractories has been calculated.

Theoretically, the following proportions of different oxides are needed for the formation of different type of minerals: forsterite, 1·33 parts MgO and 1 part of SiO_2; chrome spinel, 0·26 part MgO and 1 part of Cr_2O_3; ordinary spinel, 0·39 part MgO and 1 part Al_2O_3; and magnesio-ferrite, 0·25 part MgO and 1 part Fe_2O_3.

The total magnesium oxide required for the different minerals for combination with other oxides was calculated and the excess

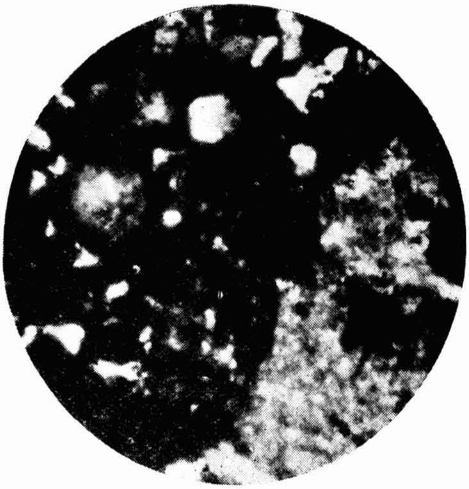


FIG. 1 — BRICK MADE FROM DUNITE AND RAW MAGNESITE

[Big patches of magnesio-ferrite in a ground mass of forsterite]

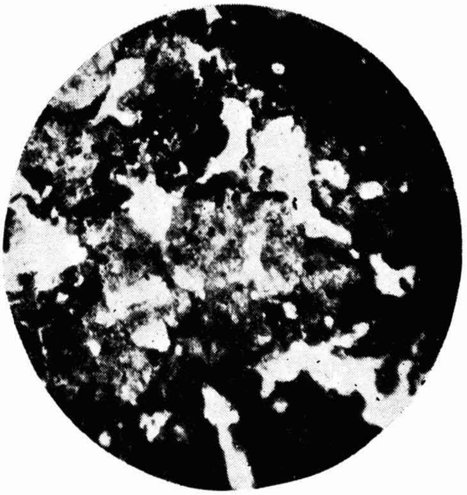


FIG. 3 — BRICK MADE FROM DUNITE WITH RAW MAGNESITE AND CHROME

[Chrome spinel and magnesio-ferrite in a ground mass of forsterite]

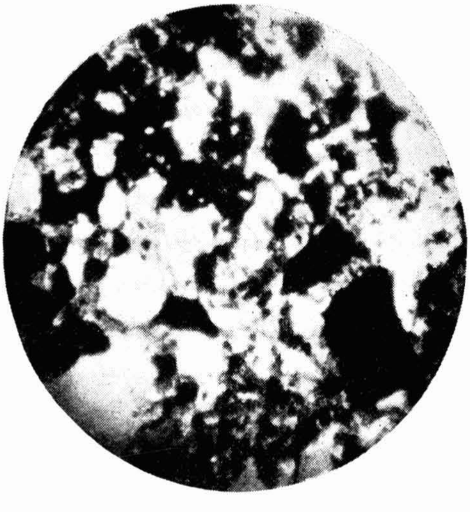


FIG. 2 — BRICK MADE FROM MAGNESIUM SILICATE ROCK WITH RAW MAGNESITE AND CHROME

[Uniform distribution of forsterite with patches of chrome spinel]

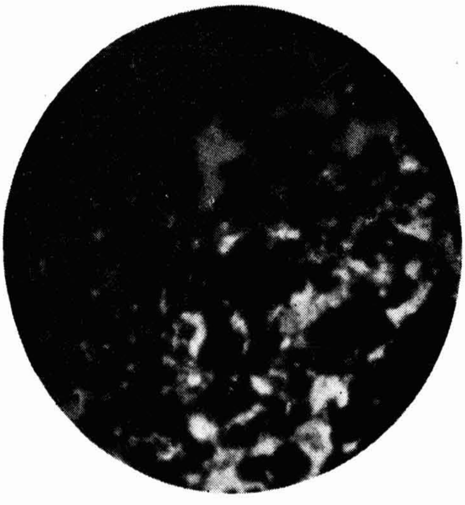


FIG. 4 — BRICK MADE FROM LOW GRADE CHROME ORE WITH RAW MAGNESITE

[Uniform distribution of forsterite and the spinels]

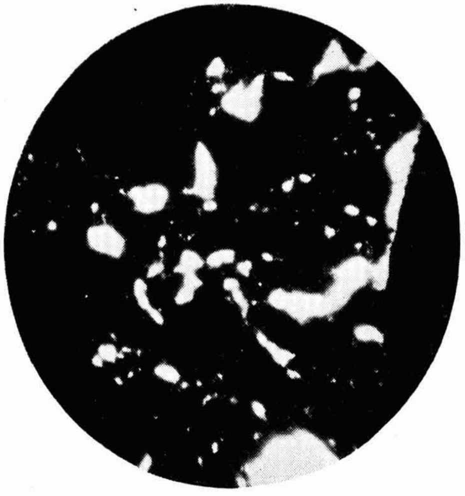


FIG. 5 — ENGLISH CHROME MAGNESITE BRICK
[Mostly spinels with some forsterite in between them]

FIG. 7 — AMERICAN METAL-CASED BRICK
[Plenty of big isolated patches of periclase with little of forsterite in between]

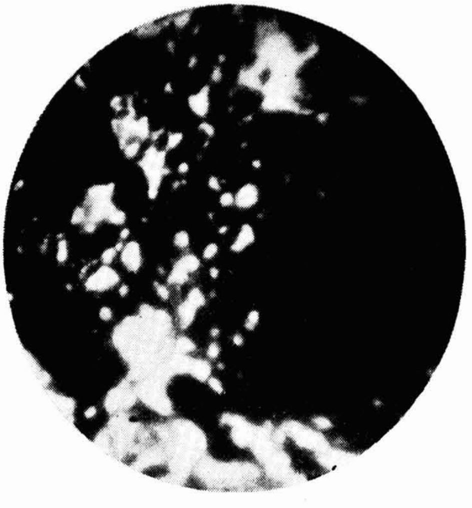


FIG. 6 — ENGLISH BRICK
[Mostly spinels with some forsterite in between them]

FIG. 8 — CHEMICALLY BONDED AMERICAN BRICK
[Almost entirely spinel with very little forsterite]

of magnesium oxide is taken as free magnesium oxide or periclase. Photomicrographs of the refractories are given in Figs. 1-8, and the microscopic description of the different minerals occurring in chrome-magnesite and forsterite refractories is given in Table 2.

Forsterite being the only non-isotropic mineral present in the sections, is easily identified and its percentage in the sections was determined as follows. The sections were examined under the microscope and the area occupied by each mineral was determined. The values (TABLE 1) given are the average of a number of determinations. Spinel and periclase have been considered together.

TABLE 2 — MICROSCOPIC EXAMINATION OF MINERALS OCCURRING IN THE CHROME-MAGNESITE AND FORSTERITE TYPES OF REFRACTORIES

MINERAL	COMPOSITION	OPTICAL NATURE	COLOUR IN TRANSMITTED LIGHT	REF. INDEX	CRYSTAL FORM	INTERFERENCE COLOUR
Forsterite	$2MgO.SiO_2$	Biaxial positive	Dirty brown or yellowish or greenish depending upon the amount of iron absorbed	1·658-1·669	Granular, seldom well developed	Pink green or blue
Chrome spinels or picotite	$MgO.Cr_2O_3$	—	Pale green, generally reddish brown due to absorption of $MgO.Fe_2O_3$	About 1·90	Anhedral to euhedral depending upon the original chromite	—
Ordinary spinel	$MgO.Al_2O_3$	Isotropic	White in bulk; colourless and tarnished due to iron	1·72	Granular, seldom well developed	—
Magnesio-ferrite	$MgO.Fe_2O_3$	—	Reddish brown	About 2·35	do	—
Periclase	MgO	—	Colourless to reddish brown depending upon amount of iron absorbed	1·734-1·737	Sacharoidal or granular	—
Fayalite	$2FeO.SiO_2$	Biaxial negative	Brown to blackish	1·824-1·874	Mostly granular, seldom well developed	Same

Discussion

The refractories tested are arranged in Table 1 in the order of their decreasing forsterite content. For forsterite and chrome-magnesite refractories prepared from Indian raw materials containing 40 per cent or more of forsterite, the refractoriness under load values are higher than 1,700°C. For the Austrian chrome-magnesite sample containing 34·9 per cent forsterite, the value is less than 1,700°C. The two British varieties of chrome-magnesite bricks tested contain 21·1 and 15·2 per cent forsterite; the last one has also lower refractoriness under load value, i.e. 1,515°C.

These results show that refractoriness under load value of bricks made from different raw materials depends on their forsterite content. The refractoriness under load value decreases as the amount of forsterite in them decreases. For a refractoriness under load value of 1,700°C. the forsterite content of the refractories should be 40 per cent or more.

The forsterite content in British chrome-magnesite bricks tested is less than 40 per cent and periclase content is 5 and 20 per cent respectively. The sample containing 20 per cent periclase has a lower refractoriness under load value. This indicates that the value for refractoriness under load value for refractories decreases as the percentage of periclase in them increases.

The American metal-cased chrome-magnesite brick, though contains more forsterite than the chemically bonded variety, is less refractory. This may be due to the higher percentage of periclase in the metal-cased variety. Magnesite bricks containing cubic periclase crystals exhibit low refractoriness under load. The American chrome-magnesite brick (metal-cased) shows a large number of big, isolated patches of periclase and consequently low refractoriness under load value. The low refractoriness under load value is attributed to the lack of intercrystalline bond[1]. The Austrian chrome-magnesite bricks which exhibit marked intercrystalline bond are an exception and exhibit high refractoriness under load value.

Conclusions

1. The refractoriness under load value of forsterite and chrome-magnesite types of refractories decreases as the forsterite content in them decreases.
2. For high refractoriness under load value, i.e. 1,700°C. or above, the forsterite content of the refractories should be at least 40 per cent.
3. The periclase content of refractories should be low for high refractoriness under load value. An intercrystalline bond between periclase crystals helps in enhancing the refractoriness under load of the refractories.

Acknowledgement

The author is grateful for the help received from his colleagues at the Refractories Laboratories, Tata Iron & Steel Co., and specially to Dr. H. K. Mitra for his valuable suggestions.

The author wishes to record his grateful thanks to the Director, Central Glass & Ceramic Research Institute, Calcutta, for permission to publish the paper.

Reference

1. MITRA & BANERJEE, "Petrographic Data on Some Indian Refractory Materials", *Trans. Indian ceram. Soc.*, **6**(2) (1947), 66.

Refining of Nahor Seed (*Mesua ferrea*) & Polang (*Calophyllum inophyllum*) Oils

V. H. KAPADIA & J. S. AGGARWAL
National Chemical Laboratory of India, Poona

Nahor (*Mesua ferrea*) seed oil of a pale yellow colour is obtained by refining the crude oil in two stages with 15-20 per cent caustic soda solution. In the case of polang oil (*Calophyllum inophyllum*) of high acid value, refining in two stages gives a pale yellow coloured oil and the process requires less alkali than that required in one-stage treatment. Soaps prepared from refined oils do not impart any colour to clothing on application.

Nahor seed oil

MESUA ferrea Linn. (N.O. *Guttiferae*), commonly known as nahor or *nageswar*, is an evergreen tree which grows wild on the mountains of East Bengal, Assam, Burma, South India, Ceylon and the Andamans. The nut yields a reddish brown oil, 60-77 per cent on the weight of the kernel. Work on the characteristics and fatty acid composition of the oil has been reported by Dhingra and Hilditch[1], Chatterji and Gupta[2], Deb[3] and Phadnis, Rege *et al.*[4]. Dhingra and Hilditch[1] also mention the presence of a resin in the oil. The chief drawback in the crude nahor seed oil is that the soap prepared from the oil discolours the cloth. Gupta[5], in an attempt to refine the oil, treated it with potassium chlorate and concentrated hydrochloric acid and obtained an oil which gave a bright soap with only a light yellow tint and did not stain the cloth on application. A pale yellow oil was obtained by Mitra[6] by extracting the raw oil with alcohol and subsequently refining with alkali.

For the present investigation nahor seeds were obtained from the Director of Cottage Industries, Assam. The seeds contained *c.* 70 per cent by weight of kernels. The oil content of the kernels was *c.* 75 per cent extractable with petroleum ether (60°-80°C.). Expression of the kernels in a hydraulic press using ½-1½ tons p.s.i. pressure at a temperature of 70°-80°C. gave 66-67 per cent of dark reddish brown oil; the whole seeds gave only 56 per cent oil. The characteristics of the oil samples extracted as above are given in Table 1.

TABLE 1 — CHARACTERISTICS OF NAHOR SEED OIL

	COLOUR IN LOVIBOND UNITS (THROUGH 1 CC. CELL)			ACID VAL.	SAP. VAL.	IOD. VAL. (WIJ'S)
	Red	Blue	Yellow			
Oil pressed from decorticated seeds	17	2	17	14·6	197·7	85·8
Oil pressed from whole seeds	25	4	18	13·0	196·8	85·6
Solvent extracted oil from decorticated seeds	27	3	11	14·0	194·2	86·0

Experimental procedure

The oil obtained by expressing the decorticated seed was given different refining treatments as under:

Heat treatments — The oil was heated to 120°-30°C. alone and with decolourizing carbon for ½ hr. The treated oils showed no reduction in acid value and the colour also became darker.

Refining with non-alkaline agents — Treatment with 50 per cent H_2SO_4 for 2 hr. on boiling water bath and decolourizing with carbon, activated earth and oxalic acid (0·1 per cent) at 110°-20°C. gave an oil of higher acid value and darker colour than the original. Similar results were obtained when the oil was treated with potassium chlorate and hydrochloric acid. A good refined oil of a pale yellow colour (acid val. 3) was obtained on treatment with alcohol, but the process required a large quantity of alcohol for washing.

Alkali refining — Refining with caustic soda in two stages and subsequent bleaching with decolourizing carbon gave a pale yellow coloured oil of low acid value. Bhasin and Aggarwal[7] employed the same method for refining cotton seed oil. The detailed process for nahor seed oil is as follows:

The filtered crude oil (300 g.) obtained by pressing the decorticated seeds (acid val. 14·6) was treated with a 15-20 per cent solution of caustic soda (5·88 g.; 0·5 per cent on the weight of oil in excess of that required to neutralize the free acidity). The alkali was added drop by drop during 15-20 min. During this period the oil was kept agitated with a stirrer run at a speed of *c.* 400-500 r.p.m. and this was continued for about half an hour afterwards. The stirrer speed was then reduced to *c.* 150 r.p.m. and the oil was heated to 70°-75°C. for the soap to grain. Addition of a little common salt helped the separation of the soap. The oil was allowed to settle overnight, separated from the foots and washed 8-10 times with hot water till the washings became almost colourless. The oil was then heated at *c.* 110°C. to remove the moisture (yield *c.* 255 g.).

The oil thus obtained (250 g.; acid val. 3) was treated with a 15 per cent solution of caustic soda (1·25 g.) in the same manner as above. After the removal of soap foots, the oil was washed with hot water and subsequently heated at 110°-20°C. to remove the moisture (yield *c.* 230 g.). The refined oil was further bleached with 0·5 per cent decolourizing carbon (HOPKINS and WILLIAMS). The colour (determined in a Lovibond tintometer employing a 1-in. cell) and characteristics of the oil thus refined are as follows:

	Colour in Lovibond units (through 1 in. cell)		*Acid val.*	*Iod. val. (Wij's)*
	Red	*Yellow*		
Refined oil	8	11	3·0	76·4
Re-refined oil	5	10	1·5	76·0
Bleached oil	3	12	1·6	76·5

Similar results were obtained with crude oil expressed from whole seeds and solvent extracted oil from decorticated seeds. The refined oil was slightly darker in colour.

Polang oil

Calophyllum inophyllum Linn. (N.O. *Guttiferae*), known in India by various names as polang, *punnal, undi, domba* and *pinnai,* is indigenous to Western Peninsula, Orissa, South India and also to Ceylon and Burma. The dried seed kernel (which forms 59 per cent of the whole seed) contains *c.* 70-75 per cent oil. The oil becomes very dark on ageing and contains comparatively large proportions of free acids and resinous matter. On account of the high acid value of the oil (which may be as high as 50), it is not possible to carry out alkali refining in one stage and hence the following two-stage alkali refining process was adopted. In the first stage 1 kg. of the dark-coloured crude oil (acid val. 50) was neutralized with a 15 per cent solution of caustic soda (20 g.). After settling overnight, the lower aqueous layer containing the soap stock and the foots was removed. The clear oil (700 g.) having an acid value 18 was given a second refining treatment with a 15 per cent caustic soda solution (12·5 g.), the soap was grained and allowed to settle overnight. The oil was washed four times with hot water and then heated at 105°-10°C. to remove the moisture (yield *c.* 600 g.). Thus a total of 32·5 g. of caustic soda were used in two stages instead of the 40·6 g. required to neutralize, in one stage, the free acidity in 1 kg. of the oil. The refined oil was treated with 0·5 per cent decolourizing carbon (HOPKINS and WILLIAMS). The colour and characteristics of the oil obtained were as follows:

	Colour in Lovibond units (through 1 in. cell)		*Acid val.*	*Iod. val. (Wij's)*
	Red	*Yellow*		
Crude oil	Too dark; beyond all ranges		50·0	92·9
Refined oil	3	10	0·8	86·0
Bleached oil	2	8	1·0	85·8

Conclusions

From the results of heating and bleaching treatments with crude nahor seed oil it appears that the oil contains some non-fatty matter, most probably a resin, which cannot be removed by heat treatment. On the contrary, the oil becomes darker on standing which may be due to the oxidation and polymerization of the resinous matter. The oil behaves similarly when treated with potassium chlorate and hydrochloric acid or with 50 per cent sulphuric acid. Two-stage refining of the oil with caustic soda and subsequent bleaching with decolourizing carbon give a pale yellow coloured oil of low acid value. Alcohol refining followed by treatment with alkali, though expensive, gives a much lighter coloured oil of low acid value and may be resorted to only where high purity is desired.

It is of interest to note that during alkali refining, nahor seed oil becomes very dark in colour on the addition of alkali. Much of the colour, however, could be removed by washing the oil with hot water several times. An attempt was made to heat the crude oil first to oxidize the resin and coagulate other impurities. However, the oil thus treated could not be refined to a pale yellow colour.

In the case of oils having high acidity such as polang oil, the addition of all the alkali in one stage is wasteful since soap foots do not separate out clearly from the oil. Addition of alkali in two stages leads to better separation of the foots from the oil, less alkali consumption and higher yields of refined oil.

Soaps prepared from the refined nahor seed and polang oils did not impart any colour to the cloth on application.

References

1. DHINGRA, D. R. & HILDITCH, T. P., *J. Soc. Chem. Ind.*, **50** (1931), 9-12.
2. CHATTERJI, N. G. & GUPTA, A. C., *Oil & Col. Trade J.*, **91** (1937), 1656.
3. DEB, N. C., *Indian Soap J.*, **4** (1938), 16-20.
4. PHADNIS, K. D., REGE, A. V., PISHAWIKAR, D. G. & SHAH, S. V., *J. Univ. Bombay*, **17A** (1948), 65-68.
5. GUPTA, A. C., *J. sci. industr. Res.*, **10B** (1951), 24.
6. MITRA, CHITTARANJAN, *Indian Pat.* 47,802 (1952); 49,510 (1953).
7. BHASIN, M. M. & AGGARWAL, J. S., *J. sci. industr. Res.*, **12A** (1953), 193.

Letters to the Editor

THE INNER POTENTIAL OF COPPER

ELECTRON DIFFRACTION MEASUREMENTS HAVE been used to estimate the mean inner potential, V_0, of many crystals, but few reliable determinations have so far been made for metal crystals. The results available on the diffraction of slow electrons from metals such as copper are unreliable and complicated. Diffraction of fast electrons, on the other hand, yields clearer results, but published data for single crystals of metals are few. Darbyshire[1] found $V_0 = 12$ volts for antimony (111) cleavage faces, and $V_0 = 15{\cdot}5$ volts for the zinc (0001) cleavage face. The value quoted for zinc, however, actually relates to zinc oxide, which is formed spontaneously in parallel (0001) orientation to that of the zinc lattice on exposure of the cleavage face to air[2-4]. On the antimony cleavage face no such crystalline oxide layer is formed at room temperature[3] and the Kikuchi-line pattern from antimony is well defined; thus any amorphous antimony oxide present must have been at most only a few atoms thick. Darbyshire's estimate for antimony is, therefore, presumably representative of the antimony cleavage face. Tull[5] recently determined V_0 for different crystal faces of rock salt and quartz as well as for the single crystal films of silver and gold, and found that the calculated theoretical values were in close agreement with the experimental values in the case of rock salt and silver, but differed by a few volts in the other two cases.

The technique generally employed for such determination of V_0 is to change the angle of incidence of the electron beam slowly and observe the different orders of diffraction in the plane of incidence. Miyake[6], on the other hand, measured V_0 of Sb_2O_3, formed over Sb_2S_3 crystal on heating, by observing the displacement of normal diffraction spots, in directions normal to the different facets formed during heating. Such a method cannot be universally adopted as it depends upon the formation of suitable facets which would show such displacement of spot, due to refraction. But in the present investigation on Cu (110) face, similar displacement of normal diffraction spots was observed and from it an approximate estimation of V_0 has been made.

Determinations of V_0 for typical metals have not been made largely due to the difficulty in obtaining sufficiently smooth strain-free surfaces on perfect enough single crystals. The present well-defined diffraction effects from a single crystal of copper were obtained from the approximately (110) face after much repeated chemical etching and electropolishing (which removed the mechanically worked surface region) followed by anodic treatment in aqueous hydrochloric acid solution (*c.* 16 per cent by weight of acid) at 10 mA/sq. cm. for about 2 min. The electron diffraction examination was carried out within a few minutes of washing the crystal in distilled water, and then in propyl alcohol, under which it was transferred to the camera.

With the beam along [001] azimuth in (110) surface, Fig. 1, the HKO spots in the square pattern were sharp but elongated to several millimetres length normal to the (100) and (010) planes. The anodic treatment had thus resulted in extensive etched facets parallel to these cube faces. Sharp

FIG. 1 — ELECTRON DIFFRACTION PATTERN OF ETCHED Cu (110) FACE. BEAM ALONG [001] DIRECTION

and clear Kikuchi lines, which could be seen more clearly in the negative, showed that the surface was atomically smooth, though slightly wavy in nature. Fig. 2, obtained with the beam along [$1\bar{1}0$] direction, consists of relatively sharp spots in the usual centred $\sqrt{2}$ rectangular pattern, with a linear extension normal to the shadow edge as a result of refraction at the slightly uneven (110) surface. There are in addition a pair of sharp satellite spots (close to 0·072 cm., more clearly seen in the enlarged pattern, FIG. 3) from each of the normal spots and connected with them by weaker continuous lines along the spot rows parallel to the radii from the undeflected beam spot to the 111 and $11\bar{1}$ spots as shown in Fig. 4. These are evidently due to a single refraction of the primary beam as it enters the crystal at grazing incidence to the facets which are assumed to be the (111) or ($11\bar{1}$) planes, followed by diffraction such that the diffracted beams mostly emerge practically without refraction at a steep angle to the end facets of cube face types as in Fig. 5, parallel to (100) and (010) planes. This conclusion is confirmed by the constant dis-

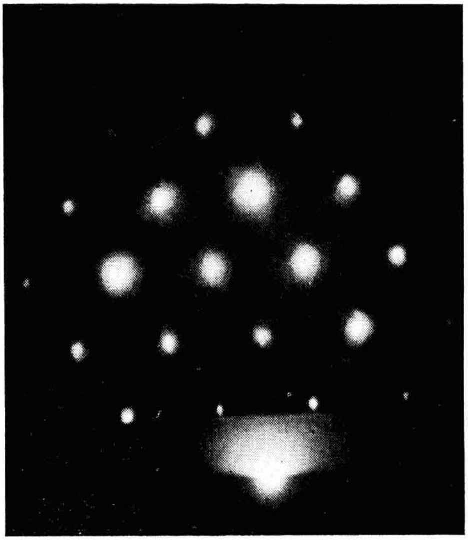


FIG. 2 — ELECTRON DIFFRACTION PATTERN OF ETCHED Cu (110) FACE. BEAM ALONG [$1\bar{1}0$] DIRECTION

FIG. 3 — ENLARGED ELECTRON DIFFRACTION PATTERN OF FIG. 2

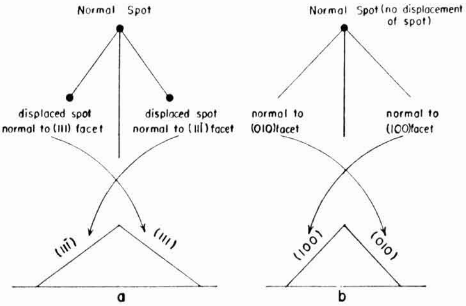


FIG. 4 — REFRACTION EFFECTS OF COPPER

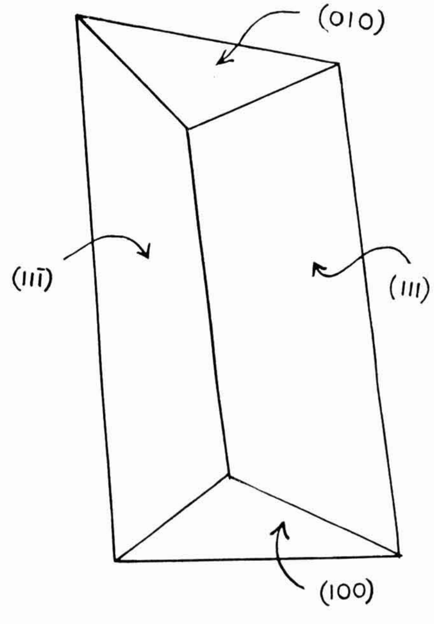


FIG. 5 — FACETS FORMED ON Cu (110) FACE

placement of these satellite spots from the normal transmission spot positions and also the presence of these spots below the lines where the { 111 } facets would intersect the plate. As the crystal had approximately (110) face, the beam direction was not exactly along the facet axis and hence its direction with respect to the facets was fixed from the Laue zone circle which passed through the undeflected spot.

Miyake[6] in his patterns from cubic Sb_2O_3 formed by the oxidation of stibnite, Sb_2S_3, observed not only refraction due to the entry of the primary beam at grazing incidence to the octahedral facets but also other spots displaced relative to these as a result of a further refraction of part of the diffracted beams as they emerged at a small angle to those facets.

Miyake's expression for inner potential is $V_0 = 2E.\Delta\phi.\phi$, where E is the electron beam accelerating potential, $\Delta\phi$ is the angular displacement of the primary beam due to a single refraction (and the subsequent diffracted beam emerging without further refraction) and ϕ is the angle of grazing incidence of the primary beam on the facet. For the pattern of Fig. 2, with camera length 46 cm., E=49 kV., we have $\Delta\phi = 0{\cdot}072/46$, $\phi = 1{\cdot}55/46$, and hence $V_0 = 5{\cdot}17$ volts. This result seems to be half that of the theoretical value (13·7 volts) calculated for copper[5] but, as Laue[7] pointed out, theoretical estimates are of uncertain accuracy.

My best thanks are due to Prof. G. I. Finch, F.R.S., and Dr. H. Wilman, of Imperial College, London, for their interest in the work.

A. GOSWAMI

National Chemical Laboratory
of India
Poona
30 *Jan.* 1954

---

1. DARBYSHIRE, J. A., *Phil. Mag.*, **16** (1933), 761.
2. WILMAN, H., *Disc. Farad. Soc.*, **43A** (1947), 253.
3. ACHARYA, H. K., *Ph.D. Thesis, London University* (1948).
4. FINCH, G. I., *Proc. Phys. Soc.*, **63B** (1950), 465.
5. TULL, V. F. G., *Proc. Roy. Soc.*, **206A** (1951), 219; 232.
6. MIYAKE, S., *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **34** (1938), 565.
7. VON LAUE, M., *Materiewellen und ihre interferenzen*, 2nd ed. (Leipzig), 1948.

ON THE OBSERVED REVERSAL OF JOSHI EFFECT ON EXPOSURE TO LIGHT WITH INCREASING INTENSITY

A REVERSAL OF JOSHI EFFECT IN A/C ' silent ' discharges by increasing the intensity of light has recently been reported by Arnikar[1]. Using a Siemen's tube or a Maze-type counter filled with various gases and critically excited near the ' threshold ' potential, and keeping the exciting potential constant, it was found that as the light intensity was increased, the percentage positive effect increased gradually to a maximum and then decreased. In some cases, there was a change to the negative value with further increase in intensity. It was also observed that for a suitable exciting voltage yielding negative light effect, the percentage negative effect increased steadily with intensity tending to a saturation value.

The object of the present communication is to explain these experimental results on the basis of the theory given by Khastgir and Srivastava[2] regarding the nature of the A/C ' silent ' discharge.

It has already been pointed out that in a ' silent ' discharge, the intervening glass wall introduces certain features which may be described with reference to Fig. 1 as follows:

(1) A negative surface charge is formed on the inner glass surface (AA) opposite to the anode during the half cycle of the applied field.

(2) A stationary array of positive ions (GG) is formed very close to the negative surface charge on the glass wall, when the applied field is adequate for Townsend collisions to take place in the enclosed gas or vapour.

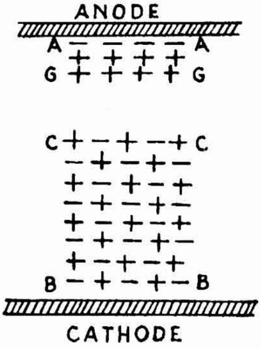


FIG. 1 — EFFECT OF GLASS WALL ON THE ' SILENT ' DISCHARGE [AA, negative surface charge on glass wall; GG, stationary layer of positive ions: GGCC, gap; and CCBB, streamer]

(3) A gap (GGCC) in the discharge channel is set up between the stationary array (GG) of positive ions and the top surface (CC) of the moving column.

(4) The streamer formation takes place as the moving column of positive ions attracts to itself neighbouring electron avalanches and photo-ionized electrons.

(5) The lower boundary (CC) of the gap may be regarded as the *virtual* cathode. The electrons start from the virtual cathode and being in an adequate field move across the gap towards the anode, producing cumulative ionization due to Townsend collisions. The negative charge on the glass wall is built up in this manner during the half cycle of the applied field.

(6) When the density of the negative charge on the glass walls attains a requisite value, the electron avalanches moving towards the anode across the gap are repelled and get mixed up with a large number of positive ions which are already produced due to Townsend collisions during the passage of the electrons through the gap. This makes the gap highly conducting, and the gap gets bridged up.

(7) The pulse flashing across, when the gap gets bridged up, has been called by us *Townsend pulse.*

The effect of light on the above features has already been discussed elsewhere[2]. It is evident, however, that the primary consideration in this connection is the emission of photo-electrons, on irradiation, from the negative charge on the glass surface. For a given frequency of radiation, the emitted photo-electrons collect themselves at a particular distance* from the array of positive ions irrespective of its intensity. Due to the proximity of these photo-electrons, the electrons proceeding towards the anode through the gap are repelled and thrown back, and the gap is bridged up at a somewhat lower applied voltage. The 'threshold' voltage is, therefore, lowered under certain favourable conditions on exposure to light.

In discussing the effect of increasing light intensity we shall take into account the two following considerations which work in opposite directions:

(a) With a larger intensity of light, there is an increased number of liberated photo-electrons, and this would cause a greater lowering of the 'threshold' potential. Thus, for a suitable voltage giving positive light effect the percentage positive effect will increase as the light intensity is increased.

(b) When the concentration of the photo-electrons increases with the increase in light intensity, the mutual repulsion among the photo-electrons increases and they take more time to collect themselves at the requisite distance from the array of positive ions (for a given frequency of the radiation). As a consequence, the width of the gap increases slightly increasing thereby the resistance of the discharge channel and decreasing the strength of the pulse. Under the circumstances, it is evident that for a suitable applied voltage giving positive light effect, the percentage effect will decrease as the light intensity is increased.

As we have to consider simultaneously (a) and (b), it is easy to see that when the effect due to (a) preponderates over that of (b) the percentage positive effect is expected to increase with light intensity, whereas, when the effect due to (b) is predominant, it would decrease as the light intensity is increased. With lower intensity, the effect due to (b) is much less than that due to (a), because of the smaller number of liberated photo-electrons; while with more intense radiation the effect due to (b) is more pronounced. Thus, the observed increase of percentage positive light effect followed by a decrease on increasing the light intensity can be explained on the basis of the above two considerations. If, however, the applied voltage is such that without light there is some discharge current due to the Townsend pulses which, with light on, shows positive effect, then on increasing the light intensity the percentage light effect may change over in some cases to a negative value. When, however, at a higher applied voltage, a negative effect is observed, the effect due to (b) is predominant, so that the observed increase of percentage negative effect with increasing light intensity at such a voltage is explained.

In conclusion it may be stated that when there is negative light effect due to the suppression or reduction of what have been called the '*discharge*' *pulses*[3] across the elec-

---

*Since the formation of streamer occurs in a time interval of the order of 10^{-7} sec., the 50-cycle A/C voltage, with which the tube is excited, does not change appreciably during this time. We can, therefore, assume that a steady voltage is being applied while the streamer formation and the subsequent bridging of the gap occurs.

trical double layer on and near the glass wall, an increase of the percentage negative effect with increasing intensity is also to be expected, due to the liberation of more electrons with increased intensity.

My sincere thanks are due to Dr. S. R. Khastgir for his interest and helpful discussions.

C. M. SRIVASTAVA
Wireless Laboratory, Physics Department
Banaras Hindu University
Banaras
31 *July* 1954

---

1. ARNIKAR, H. J., *J. opt. Soc. Amer.*, **43**(9) (1953), 804.
2. KHASTGIR, S. R. & SRIVASTAVA, C. M., *Sci. & Cult.*, **18** (1953), 487; *Indian J. Phys.*, **27** (1953), 109.
3. KHASTGIR, S. R. & SETTY, P. S. V., *Proc. phys. Soc.*, **65B** (1952), 823; *Proc. nat. Inst. Sci.* (*India*), **19** (1953), 631.

FORMATION OF BARIUM MOLYBDATE

AMONG THE GRAVIMETRIC METHODS AVAILable for the estimation of molybdenum, the precipitation of molybdate as lead molybdate or silver molybdate was found to be convenient[1,2]. Barium does not interfere[3] if an excess of hydrochloric acid is present. Subsequently ammonium acetate can be added to destroy the free mineral acid. It has been established by Jander[4] and his collaborators that the molybdate ions exist in solution in different states of aggregation depending on the *p*H of the solution. It is of interest, therefore, to study and define the exact conditions favourable for the formation of barium molybdate.

Standard solutions of sodium molybdate (14·68 g. of $Na_2MoO_4.2H_2O$/l.), barium chloride (41·224 g. of $BaCl_2.2H_2O$/l.), hydrochloric acid (0·8906N) and sodium hydroxide (1·897 $\frac{N}{10}$) were prepared and used in the present work. All the reagents used were of A.R. quality. One cc. of barium chloride solution was taken in a pyrex conical flask and diluted with 200 cc. water. The contents were titrated conductimetrically against sodium molybdate solution using a dip-type cell. The results are given in Fig. 1. In another experiment, a mixture of 4 cc. of sodium molybdate solution, 200 cc. of water and 0·8 cc. of hydrochloric acid were used. The *p*H of this solution measured with a Marconi *p*H metre was found to be 2·85. This was conductimetrically titrated against barium chloride solution. The results are presented in Fig. 2 (curve A). After the addition of 2·8 cc. of barium chloride solution, the titration was carried out with sodium hydroxide solution until the precipitation appeared to be complete. The results are given in Fig. 2 (curve B). In another experiment, the *p*H of the solution was measured after adding different amounts of sodium hydroxide solution. The results are given in Table 1.

When sodium molybdate solution is added to barium chloride solution, barium molybdate is precipitated with the formation of sodium chloride. Since the ionic mobility of Na^+ is greater than that of Ba^{++}, the

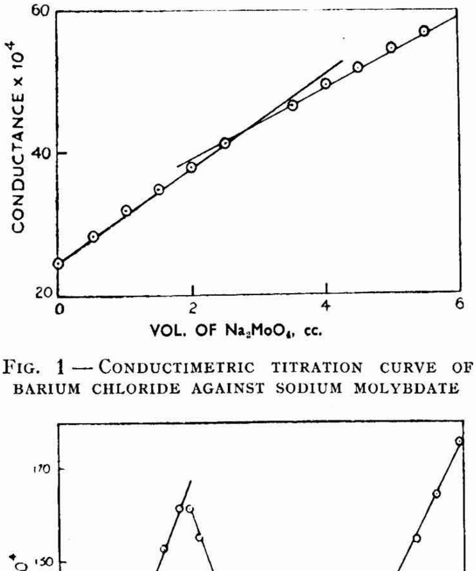


FIG. 1 — CONDUCTIMETRIC TITRATION CURVE OF BARIUM CHLORIDE AGAINST SODIUM MOLYBDATE

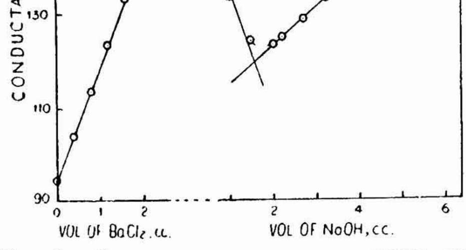


FIG. 2 — CONDUCTIMETRIC TITRATION CURVE OF SODIUM MOLYBDATE AGAINST BARIUM CHLORIDE AND SODIUM HYDROXIDE

conductivity increases. When the precipitation is complete, further addition of sodium molybdate will not result in increased conductivity as the mobility of molybdate ion is less than that of chloride ion. In Fig. 1 the break occurs at a stage corresponding to the addition of 2·85 cc. of sodium molybdate solution and this agrees well with the stoichiometric break (2·8 cc.). Rother and Jander[5] conclude that conductimetric method of estimating molybdenum as lead molybdate is more accurate and less troublesome than the gravimetric method. The solubility of barium molybdate is quite appreciable, being 0·058 g./l. at 23°C. If the barium chloride and sodium molybdate solutions are very dilute, the conductivity due to the solubility of barium molybdate interferes with the results. This was kept in view while selecting the concentrations for the present work.

The curve A (FIG. 2) is a straight line and there is no precipitation of barium molybdate. The *p*H of the solution is 2·85 and under these conditions, $[Mo_6O_{21}]^{-6}$ ion is present and the concentration of $MoO_4^{=}$ ion is negligibly small. When sodium hydroxide is added, the acid is neutralized. The conductivity decreases (FIG. 2) and the *p*H increases gradually (TABLE 1). Precipitation begins when 2 cc. of sodium hydroxide solution are added corresponding to a *p*H of 4·18 (TABLE 1). During precipitation, the conductivity of the solution should decrease further but due to OH^- ions there is an overall increase in conductivity. When the precipitation is complete, the conductivity increases more rapidly due to the addition of sodium hydroxide. The acid present originally (0·8 cc. of 0·8906 N) requires about 3·75 cc. of sodium hydroxide solution (1·897 $\frac{N}{10}$) for complete neutralization when the *p*H of the solution is nearly 7. Between *p*H 6·5 and 14, $MoO_4^{=}$ ion is stable and the precipitation of barium molybdate is expected to be complete when nearly 3·75 cc. of sodium hydroxide solution are added. It will be seen from Fig. 2, curve B, that the break is shifted towards 4·2 cc. and the curve is rounded in between 3·2 and 4·2 cc. When the precipitation is complete, the *p*H suddenly increases to 10·48 (TABLE 1) as expected. The precipitate on analysis was found to be $BaMoO_4$. The molybdate ion exists in the following state of aggregation:

$$[MoO_4]^{=} \rightleftharpoons [Mo_3O_{11}]^{-4} \rightleftharpoons [Mo_6O_{21}]^{-6}$$

*p*H 14 —— 6·5 —————— 4·5 —————————— 1·5

All the above ionic species are *p*H reversible. It is evident that the change from one to another is never sudden and they are supposed to exist in equilibrium with each other. This explains why the precipitation of $BaMoO_4$ commences even at *p*H 4·18 where there is an appreciable concentration of MoO_4 ion so that the solubility product of $BaMoO_4$ can be exceeded.

TABLE 1 — *p*H OF SODIUM MOLYBDATE AND BARIUM CHLORIDE SOLUTIONS' MIXTURE WITH DIFFERENT AMOUNTS OF SODIUM HYDROXIDE ADDED

VOL. OF NaOH ADDED cc.	*p*H
0·0	2·85
0·6	3·05
1·0	3·24
1·5	3·62
2·0	4·18
2·7	4·70
3·2	5·22
4·2	10·48

D. V. RAMANA RAO
S. PANI
S. S. GUHA SIRCAR

Department of Chemistry
Ravenshaw College
Cuttack

15 *Sept.* 1953

1. CHATARD, T. M., *Amer. J. Sci.*, **1** (1871), 416.
2. McCAY, L. W., *J. Amer. chem. Soc.*, **56** (1934), 2548.
3. SCOTT, *Standard Methods of Chemical Analysis* (D. Van Nostrand Co., New York), 1945, 589.
4. EMELEUS & ANDERSON, *Modern Aspects of Inorganic Chemistry* (Routledge & Sons, London), 1946, 185.
5. ROTHER & JANDER, *Z. angew. Chem.*, **43** (1930), 930.
6. SIEDELL, *Solubilities of Inorganic Compounds* (D. Van Nostrand Co., New York), 1940, 169.

CHEMICAL EXAMINATION OF THE HEARTWOOD OF *MELIA AZEDARACH*

AQUEOUS EXTRACTS OF THE HEARTWOOD OF *Melia azedarach* Linn. (Mahaneem, Bakain or Persian lilac) are reported to be efficacious in reducing the intensity of asthmatic attacks. No previous work on the heartwood of this plant has been reported in literature, and in view of the medicinal properties exhibited by the aqueous extracts, it was considered of interest to carry out a detailed chemical examination of the wood.

The wood becomes slightly discoloured when exposed to the atmosphere and sunlight. Acetone and alcohol extract the constituents of the wood satisfactorily. In addition to tannin material and some inorganic salts of calcium and potassium, an ether-soluble colourless crystalline compound $C_{22}H_{26}O_4$, m.p. 215°-16·5°, $[\alpha]_D^{29°}$-175 (chloroform), has been obtained. This has been provisionally named as ' Bakalactone '. Along with this crystalline compound a liquid having a terpenic odour, b.p. 150°-60°/0·5 mm., $[n]_D^{24°} = 1·4825$ and a glassy resinous product, changing into thick viscous mass above 70°C., have also been isolated. The detailed study of these compounds will form the subject of a separate communication. In this note, the studies on the crystalline compound ' Bakalactone ' are described.

Bakalactone is insoluble in water and light petroleum ether, but dissolves readily in ether, benzene, acetone, chloroform and alcohol. It does not reduce Fehling's solution nor does it give any colouration with magnesium powder and hydrochloric acid. Hydroxyl group is absent in the substance and it is not possible to acylate the compound. There is no methoxyl group in it and it does not give the usual derivatives characteristic of the ketonic grouping.

Bakalactone forms a tribromo-derivative, m.p. 167°-69°C. It decolourizes potassium permanganate solution and develops a yellow colour with tetranitromethane. It gives a positive test with Tollen's reagent, but the results with the Legal test (sodium nitroprusside) and modified potassium ferricyanide reaction[1] were negative.

It is insoluble in aqueous caustic soda, but when a solution of the compound in 60 per cent alcohol is treated with a drop of alkali, an intense yellow colour develops. From this yellow solution, the original substance is precipitated by acid. One mole of this compound consumes one mole of caustic soda indicating the presence of a lactonic group in the molecule.

The infra-red spectrum of bakalactone exhibits some strong bands in the region 5·74-6·04 μ which also support the presence of one $C = 0$ group (lactonic)[2,3]. The ultraviolet absorption spectrum of bakalactone has one intense band (log ϵ 4·01) near 2,200A and another slightly less intense (log ϵ 3·92) between 2,770 and 2,800A. A comparison of the absorption data of this compound with those of some other lactonic compounds[4-6] indicates that this is probably a case of an abnormal absorption and may be due to some unusual chromophoric groups.

Bakalactone produces a deep reddish brown colour with concentrated sulphuric acid. It is reported[7] that substances containing the methylenedioxy group readily lose formaldehyde by the action of concentrated sulphuric acid. Qualitative reactions by Eegriwe's method and Hehner's test[8] and quantitative estimation of formaldehyde indicate the presence of one methylenedioxy group in the molecule.

Further work is in progress.

The author is thankful to Dr. R. C. Shah for his interest in this work and to Dr. (Mrs.) S. Das Gupta for the infra-red spectrum.

BHOLA NATH

*National Chemical Laboratory
of India
Poona*

8 *March* 1954

1. ELDERFIELD *et al.*, *J. org. Chem.*, **6** (1941), 273.
2. RASMUSSEN & BRATTAIN, *J. Amer. chem. Soc.*, **71** (1949), 1073.
3. GILMAN, *Organic Chemistry* (Wiley, New York), **3** (1953), 122-77.
4. CLEMO & COCKER, *J. chem. Soc.*, (1946), 30.
5. GILLAM & WEST, *J. chem. Soc.*, (1945), 95.
6. RASMUSSEN, TUNNICLIFF & BRATTAIN, *J. Amer. chem. Soc.*, **71** (1949), 1068.
7. GADAMER, J. & WINTERFELD, *J. chem. Soc.*, **118** (1920), 872.
8. WALKER, *Formaldehyde* (Reinhold Publishing Corpn., New York), 1953, 367.

SOLVENT MIXTURES FOR CHROMATOGRAPHIC SEPARATION OF SUGARS

IT HAS BEEN SHOWN FROM THIS LABORATORY[1-3] that jute holocellulose contains glucose, galactose, xylose, arabinose, rhamnose and methyl uronic acid. The conclusion was mainly based on the paper chromatographic analysis in different solvents and their isolation by means of paper chromatography followed by their further identification by different specific colour reagents[4-8]. But the amount of sugar components isolated by means of paper chromatography was so small that it did not permit us to carry out further confirmatory tests such as crystallization and melting point determination, optical rotation, specific compound formation and so on, which are necessary for final confirmation especially of rarer sugars. The help of cellulose powder chromatography was, therefore, sought. A large quantity of costly imported solvents is required for this purpose which are sometimes even difficult to obtain locally. Attempts were, therefore, made to find indigenous cheap solvents or solvent mixtures. For this purpose it was first necessary to try these solvents in the paper chromatography of sugars. The results obtained from different mixtures of distilled crude benzene procured from Messrs Bararee Coke Co. Ltd. and commercial methylated spirits are summarized in Table 1.

It can be seen that R_g values of uronic acids, hexoses, pentoses and methyl pentose are distinctly different from one another in any of these solvent mixtures. Considering the speed of travel and the efficiency of separation, 50: 50 or 35: 65 mixture seems to be quite good for general separation of uronic acid, hexoses, pentoses and methyl pentoses in groups. The 35: 65 mixture was, therefore, given a trial on the cellulose column ($15\frac{1}{2} \times 1\frac{3}{8}$ in.) obtained from the powder of No. 1 Whatman filter paper chips (80 mesh). A mixture of 1·8 g. glucose, 0·16 g. xylose and 0·04 g. rhamnose dissolved in 2 cc. water was transferred on the top of the column and the solvent mixture (35: 65) run in the usual way. The effluent (*c*. 350 cc./hr.) was collected in 50 cc. portions in test-tubes.

The contents of the tubes were chromatographically analysed at intervals and the tubes having the same sugars were mixed up. Some of the results obtained are reproduced in Fig. 1 (a and b) where the sharpness of the separation by this solvent mixture is evident.

Test-tube Nos.	0-21	Rhamnose only
,,	22-28	Presumably mixture of rhamnose and xylose
,,	29-39	Xylose only
,,	40-50	Presumably mixture of xylose and glucose
,,	51-100	Glucose only
,,	101	No sugar

In cases where the test-tubes contain mixtures, the components can be resolved by passing the mixture again in the column. In another trial where the rate of flow was 200 cc./hr., a set of 225 test-tubes (50 cc. portions) were required for the completion of chromatography and similar well-defined fractions containing pure sugar components were obtained. Further experiments on separation of xylose from arabinose or glucose from galactose or glucuronic acid from

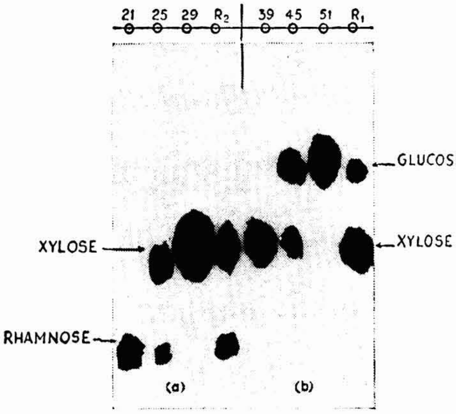


FIG. 1 — CHROMATOGRAM OF DIFFERENT FRACTIONS OBTAINED BY CELLULOSE POWDER CHROMATOGRAPHY USING 35 : 65 ALCOHOL : BENZENE MIXTURE [Chromatogram run for 44 hr.; reference sugars: R_1 = xylose + rhamnose; R_2 = glucose + xylose; numbers represent different fractions]

TABLE 1 — R_g VALUES OF SUGARS EMPLOYING DIFFERENT SOLVENTS

[*Chromatogram run for* 39 *hr.* (*downward chromatography*)]

SOLVENT ALCOHOL: BENZENE: WATER	GLUCURONIC ACID	GALACTURONIC ACID	GLUCOSE	GALACTOSE	XYLOSE	ARABINOSE	RHAMNOSE
90: 10: 0	0·32	0·17	1·0	0·88	1·21	1·17	1·58
80: 20: 0	0·55	0·20	1·0	0·89	1·36	1·27	1·80
70: 30: 0	0·29	0·35	1·0	0·87	1·58	1·45	2·27
60: 40: 0	0·24	0·37	1·0	0·85	1·65	1·58	2·51
50: 50: 0	0·20	0·16	1·0	0·82	1·78	1·68	2·80
35: 65: 0	0·07	0·09	1·0	0·80	1·77	1·69	2·77
20: 80: 0	—	—	1·0	0·80	2·94	2·99	5·88
50: 50: 5	0·14	0·16	1·0	0·90	1·13	1·32	1·95

galacturonic acid and also of the sugar components of jute holocellulose are in progress. Details will be published elsewhere.

Thanks are due to Dr. W. G. Macmillan for arrangement of powdering the filter paper chips, to Mr. P. K. Roy Chaudhury for occasional help in this investigation and to the Directors, Messrs Jardine Henderson Ltd., for permission to publish this note.

D. B. Das
J. F. Wareham

Group Laboratory
Messrs Jardine Henderson Ltd.
Calcutta
29 *July* 1954

---

1. Das, Roy Chaudhuri & Wareham, *Sci. & Cult.*, **18** (1952), 249.
2. Das, *Text. Manfr.*, **79** (1953), 420.
3. Das, Roy Chaudhuri & Wareham (under publication).
4. Forsyth, *Nature*, **161** (1948), 239.
5. Partridge, *Biochem. J.*, **43** (1948), XLVIII.
6. Partridge, *Biochem. J.*, **42** (1948), 238.
7. Hough, Jones & Wadman, *J. chem. Soc.*, 1950, 1702.
8. Partridge, *Nature*, **164** (1949), 443.

SCREENING OF ACTINOMYCETES FOR VITAMIN B_{12} PRODUCTION

THE PRODUCTION OF VITAMIN B_{12} BY STRAINS of *Streptomyces chromagenus*, *S. griseus* and *S. antibioticus* was first reported[1] in 1948. Since then a number of actinomycetes have been surveyed and particularly the actinomycetes belonging to the genus streptomyces have been reported as good producers of the vitamin[2-5]. During screening of soil isolates, especially actinomycetes for antibiotic production, 200 actinomycetes cultures were isolated from 50 soil samples. These were screened for vitamin B_{12} production and the results are reported in this communication.

The actinomycetes were screened for vitamin B_{12} production by the following modified rapid method: The medium of Davis and Mingioli[6] was modified by adding sodium asparaginate (0·1 per cent) and cobalt chloride (0·0008 per cent) (*p*H 7·2) in order to get better growth of the actinomycetes. Plates prepared with this medium were seeded with Davis and Mingioli's *E. coli* mutant (strain No. 113-3) dependent on vitamin B_{12} or methionine for its growth. Each plate was inoculated with 5-6 different cultures of actinomycetes. The cultures were incubated at 28°C. for 4-5 days and then overnight at 37°C. The growth of *E. coli* mutant round the colonies of actinomycetes was taken as a positive indication of vitamin production. Out of 200 cultures tested by this method 56 (28 per cent) gave zones of growth greater than 13 mm.

Growth in liquid media — Fifty cultures were selected on the basis of the above screening method and were grown in stationary cultures in five different liquid media[7], each containing a different source of nitrogen (0·5 per cent w/v) (viz. casein hydrolysate, peptone, lab-lemco, soyabean meal digest, sodium nitrate) in addition to basal glucose-salts solution. The cultures were incubated at 28°C. and tested after 5, 10 and 15 days for vitamin B_{12} activity by the cup-plate method using the *E. coli* mutant as the test organism.

Methionine response was tested for by treating an aliquot of the culture filtrate to alkaline hydrolysis[6] and testing it by the cup-plate method.

The activity corresponding to the growth zones was interpreted in terms of vitamin B_{12}/cc. with the help of a graph[8,9], prepared by using standard B_{12} solutions and assaying by the cup-plate method (appropriate allowance being made for methionine response).

The growth response in any particular medium was found to vary from culture to culture. It was, therefore, not possible to name any of the media used as the medium of choice.

The production of vitamin B_{12} by 50 cultures of actinomycetes is recorded in Table 1.

The most promising of these cultures are being followed up and efforts are being

TABLE 1 — VITAMIN B_{12} PRODUCTION BY ACTINOMYCETES CULTURES

(50 *isolates tested*)

MAXIMUM AVERAGE B_{12} YIELDS µg./cc.	NO. OF CULTURES	% TOTAL
0·01-0·015	6	12
0·02-0·04	15	30
0·050	9	18
>0·100	17	34

made to step up vitamin production by them.

(Mrs.) K. SHETE
V. C. VORA
A. DUDANI*

Central Drug Research Institute
Lucknow

16 *July* 1954

---

1. RICKES, E. L., BRINK, N. G., KONIUSZY, F. R., WOOD, T. R. & FOLKERS, K., *Science*, **108** (1948), 634.
2. GAREY, J. C. & DOWNING, J. F., *Abstr. of paper read before the* 119*th meeting of the Amer. chem. Soc.*
3. HALL, H. H., BENJAMIN, J. C., BRICKER, H. M., GILL, R. J., HAYMES, W. C. & TSUCHIYA, H. M., *Bact. Proc.*, (1950), 21.
4. PRIDHAM, T. G., HALL, H. H. & SHEKELTON, M. C., *Bact. Proc.*, (1951), 27-28.
5. SAUNDERS, A. P., OTTO, R. H. & SYLVESTER, J. C., *J. Bact.*, **64** (1952), 725.
6. DAVIS, B. D. & MINGIOLI, E., *J. Bact.*, **60** (1950), 17.
7. BURTON, M. O. & LOCKHEAD, A. G., *Canad. J. Bot.*, **29** (1951), 352.
8. BESSL, C. J., HARRISON, E. & LEES, K. A., *Chem. & Industr.*, (1950), 561.
9. HARRISON, E., LEES, K. A. & WOOD, F., *Analyst*, **76** (1951), 696.

NUTRITIVE VALUE OF THE SEEDS OF *PASPALUM SCROBICULATUM*

THE SEEDS OF *Paspalum scrobiculatum* (Kannada, *Haraka*; Tamil, *Varagu*; Telugu, *Arikelu*; Hindustani, *Korda*; and Marathi, *Harik*) is a poor man's food and is cultivated to some extent in Mysore, Madras and Bombay States. It is drought resistant and grows on comparatively poor soils. The yield of the crop varies from 200 to 500 lb. per acre[1]. Since it is a coarse grain, it needs to be husked before use. The husked grain is ground into flour and prepared as a mash or unleavened bread for consumption.

The chemical composition of one sample of *haraka* has been determined by Ranganathan, Sundararajan and Swaminathan[2]. The present note deals with studies on the overall nutritive value of *haraka* as compared with wheat. A note on the supplementary value of *haraka* to rice diet has recently been published by Kundaji and Radhakrishna Rao[3] after the completion of the present work.

The sample of *haraka* used in the present investigation was cultivated in the lands attached to the Institute from the seeds obtained from the Millet Specialist to the Government of Madras, Coimbatore. The grain was cleaned to remove grit and other foreign matter. The husk was removed by hand pounding the moistened grain and by winnowing. The whole millet and the husked millet were finely powdered in a laboratory model micro-pulverizer to pass through 60-mesh sieve and the flours were used for chemical analysis. The proximate principles and the minerals were determined by the methods of the Association of Official Agricultural Chemists[4]. Thiamine was determined according to the method of Swaminathan[5]. The results are given in Table 1. Experiments were conducted on albino rats to determine: (1) the overall nutritive value of poor vegetarian diets containing the millet or wheat; and (2) the nutritive value of the millet as a source of proteins, B-vitamins and minerals (except calcium) as compared with wheat.

The plan of the animal experiments and the composition of the experimental diets were similar to those used by Rama Rao, Murthy and Swaminathan[6] in their investigation of Pearl millet. The results obtained are given in Table 2.

TABLE 1 — CHEMICAL COMPOSITION OF *HARAKA* AND WHEAT

CONSTITUENTS	*Haraka*		WHEAT
	Whole grain	Husked grain	
Moisture, %	11·6	11·7	10·9
Fibre, %	10·0	0·4	1·3
Mineral matter, %	4·4	1·0	1·5
Protein (N × 6·25), %	10·6	11·6	13·1
Fat (ether extractives), %	4·2	1·3	1·4
Carbohydrates, % (by difference)	59·2	74·0	71·8
Calcium, mg. %	49·5	35·0	46·0
Phosphorus, mg. %	284·0	121·0	320·0
Iron, mg. %	6·0	1·7	5·4
Thiamine (*micrograms*/100 g.)	400·0	150·0	495·0

TABLE 2 — AVERAGE WEEKLY GROWTH RATE OF RATS

GROUP No.*	DIET	AVERAGE DAILY FOOD INTAKE g.	AVERAGE WEEKLY GAIN IN WEIGHT g.	
1	Poor vegetarian diet containing husked *haraka*	7·4	5·20	±0·265 (11 dif.)
2	Poor vegetarian diet containing whole wheat	7·7	9·01	
3	Calcium-supplemented husked *haraka* diet	4·3	1·76	±0·399 (11 dif.)
4	Calcium-supplemented whole wheat diet	6·5	7·12	

*Each group contained 12 weanling albino rats (6 males and 6 females) about 28 days old and weighing 40-50 g., allotted at random strictly on litter mate basis.

---

*Present address: Central Research Institute, Kasauli.

The results of statistical analysis showed that the difference between the rates of growth of rats fed on diets containing *haraka* and wheat were significant, which indicated that the millet is inferior in its overall nutritive value to wheat.

The authors are thankful to Dr. V. Subrahmanyan, Director of the Institute, for his keen interest and encouragement, and to Mr. A. N. Sankaran for statistical analysis of the results. Our thanks are also due to the Millet Specialist to the Government of Madras, Coimbatore, for kindly supplying the seeds.

S. B. KADKOL
V. SRINIVASAMURTHY
M. SWAMINATHAN

Central Food Technological Research Institute
Mysore

18 *July* 1954

1. YEGNA NARAYAN AIYER, A. K., *Field Crops of India* (Bangalore Printing & Publishing Co. Ltd.), 1950, 109-111.
2. RANGANATHAN, S., SUNDARARAJAN, A. R. & SWAMINATHAN, M., *Indian J. med. Res.*, **24** (1937), 689.
3. TARA R. KUNDAJI & RADHAKRISHNA RAO, M. V., *Curr. Sci.*, **23** (1954), 93.
4. *Official Methods of Analysis* (Association of Official Agricultural Chemists, Washington), 1950.
5. SWAMINATHAN, M., *Indian J. med. Res.*, **30** (1942), 263.
6. RAMA RAO, G., MURTHY, H. B. N. & SWAMINATHAN, M., *Indian J. physiol. & allied Sci.*, **7** (1953), 236.

INDIAN TANNING MATERIALS: TANNING OF PELTS IN ACETONE SOLUTIONS

THE TANNINS WHICH GENERALLY FORM colloidal solutions in water, probably due to aggregation, sometimes give clear solutions with certain organic solvents, showing that in such solutions the tannin has a small particle size, possibly as a monomer. This fact is made use of in studies on vegetable tanning to obtain quick penetration and also uniform distribution of tannin through the skin or hide. It can also be used for obtaining uniformly low degree tanned hide powder or leather, which cannot be obtained using water as solvent, as the penetration is low due to big particle size. However, water seems to be necessary for the tanning action. It was found that no tanning occurred when anhydrous collagen was tanned with tannin dissolved in anhydrous acetone, and that the amount of tannin fixed was roughly proportional to the amount of water present in the system[1,2]. This might be due to particle size of the tannin, which must be big enough for reacting with collagen, the dissociation constant of the tannin in the solvent and the degree of ionization and reactivity of collagen in such organic solvents[3,4]. So, in such studies the skin or hide is first impregnated with the tannin in organic solvent and then placed in water for fixation of the uniformly distributed tannin.

In the following experiments, delimed pelt (calf-skin pieces — acetone-dehydrated) was tanned with solutions of tannin in acetone. The solutions were diluted and analysed by the Baldracco method. They were obtained by dissolving 10·0 g. of air-dry extract in 25 cc. of acetone. The results of analysis of the tanning materials employed are given in Table 1.

Pieces of acetone-dehydrated pelt (2 g. each) were shaken with 10 cc. of the acetone solutions of the various tanning extracts for 24 hr. The pieces were removed and kept in water for a further period of 24 hr. to fix the tannin that had diffused through. The pieces were then removed from the liquor, washed and shrinkage temperature determined on narrow strips cut from them. They are recorded in Table 2, along with the analyses of the dried leather strips.

All the pieces after tanning had a leathery feel except the ones tanned with myrobalan and divi-divi. The fixed tannin in the leather strips is almost the same with different tanning materials, but hydrothermal stability

TABLE 1 — ANALYSIS OF TANNING MATERIALS

MATERIAL	TOTAL SOLIDS g./100 cc.	TOTAL SOLUBLES g./100 cc.	TANNINS IN ACETONE SOLN. g./100 cc.	NON-TANNINS g./100 cc.	TANS/SOLUBLES
Avaram (*Cassia auriculata*)	26·0	21·0	16·7	4·3	79·5
Konnan (*Cassia fistula*)	26·2	24·9	20·6	4·3	82·7
Mimosa	25·0	24·7	20·9	3·8	84·6
Divi-divi (*Caesalpina coriaria*)	29·3	26·4	22·9	3·5	86·7
Myrobalan (*Terminalia chebula*)	22·4	21·2	15·8	5·4	74·5

TABLE 2 — ANALYSIS AND SHRINKAGE TEMPERATURE OF TANNED LEATHER STRIPS

MATERIAL	COLLAGEN %	DEGREE OF TANNAGE	ACID BINDING M. EQ./G. COLLAGEN	SHRINKAGE TEMP. C.
Tannic acid	79·2	26·3	0·93	76·0
Avaram	77·3	29·4	0·90	79·5
Konnan	79·4	25·9	0·99	79·5
Mimosa	80·0	25·0	0·96	79·5
Divi-divi	75·3	32·8	0·87	72·0
Myrobalan	79·5	26·3	0·80	68·5
Pelt (acetone-dehydrated)	—	—	0·98	70·0

of leather strips is not comparable. This shows that the amount of tannin fixed cannot always be taken as a measure of tanning effect judged by the hydrothermal stability of leather strips. This seems to depend to a great extent on the way the tannin is fixed to collagen. It has been shown that those tanning materials which do not impart hydrothermal stability to leathers have low proportions of tannin combining with collagen ionically (RAO, unpublished data). It is interesting to note that the vegetable tannage does not reduce the acid binding capacity to any considerable extent, except in the case of myrobalan and divi-divi, which did not impart hydrothermal stability to leathers.

The author wishes to express his thanks to Dr. K. H. Gustavson, Director, Swedish Tanning Research Institute, for his kind and valuable suggestions during the course of this work. He also acknowledges with gratitude the grants made by the Government of India and The Statens Tekniska Forskningsrad for the purpose.

P. HANUMANTA RAO
Swedish Tanning Research Institute
Stockholm, Sweden
29 *May* 1954

1. PAGE, *Stiasny Festschrift*, Darmstadt (1937).
2. RODDY, *J. Amer. Leath. Chem. Ass.*, **38** (1943), 184.
3. MCLAUGHLIN & THEIS, *The Chemistry of Leather Manufacture* (Reinhold Publ. Corp., New York), 1945.
4. STATHER *et al.*, *Collegium*, **790** (1936), 66.

ELECTROLYTIC PREPARATION OF CALCIUM GLUCONATE

A LARGE NUMBER OF PROCESSES HAS BEEN suggested for the regulated oxidation of glucose to gluconic acid, but few of them have met with commercial success. Fink and Summers[1] were the first to use the electrolytic method[2] which has the advantage of simplicity of both execution and control. These authors have developed an electrochemical method comprising the use of an aqueous alkali bromide solution of the sugar in a diaphragm-free cell. The optimum conditions suggested for semi-plant scale are: one molar sugar solution in a 2 per cent sodium bromide solution; iron or graphite cathodes; graphite anodes; current density of 1-2 amp./sq. dm.; temperature 40°C.; and no diaphragm. Bromine losses were of the order of 25 per cent or more per run, but were minimized by changing the direction of the rectified a.c. every 15 min. using an " alternator ".

Investigations carried out in this Institute on the use of sodium chloride as an electrolyte instead of sodium bromide were not entirely successful. However, a method using a rotating graphite anode was worked out successfully as an improvement on Fink and Summers' method. This is described here in detail. The stirring of added calcium carbonate is achieved by the rotating anode. Polarization is overcome almost completely, leading to lowered cell voltage and permitting the use of very high current densities. It has also led to increased current efficiency even under conditions of high current density, and to decreased loss of bromine during the process.

Conditions of electrolysis were the same as those employed by Fink and Summers. The electrolyte was a 2 per cent sodium bromide solution (450 cc.) containing dissolved glucose (50 g.; 88 per cent pure). This was electrolysed between two graphite plate cathodes and a rotating graphite rod anode (r.p.m., 3,000) for a theoretical period of time at a temperature of 35°C. The glucose was estimated both before and after the experiment by the Walker-Munson method and the current efficiency calculated on this basis. Bromine loss was estimated by the Volhard's method. The calculated amount of calcium carbonate was added at the beginning of the experiment, and any excess of calcium carbonate filtered off at the end. Most of the calcium gluconate separated on cooling the electrolyte in the refrigerator, and the rest by the addition of alcohol.

A number of experiments was carried out at different current densities both with the anode stationary and rotating. When the anode was stationary, an auxiliary stirrer

TABLE 1 — ELECTROLYSIS OF GLUCOSE SOLUTION WITH STATIONARY AND ROTATING ANODES

(*Cylindrical graphite rod anode ; area of anode immersed,* 0·5343 *sq. dm. ; area of cathode immersed,* 2·01 *sq. dm. ; volume of electrolyte,* 450 *cc. ; temp.,* 35 C.)

Anodic current density amps./dm.²	Cell voltage volts		Current efficiency %		Bromine loss %		Energy consumption kWh./lb.	
	R*	S†	R	S	R	S	R	S
1·87	3·0	3·5	95·4	95·5	9·17	9·80	0·346	0·398
3·74	4·0	4·5	—	97·4	—	8·024	—	0·492
4·68	5·0	5·5	100·0	—	4·27	5·09	0·541	—
7·50	6·0	6·5	96·3	88·5	4·76	6·66	0·677	0·798
11·20	7·5	8·0	97·9	87·2	3·01	9·54	0·761	0·997
14·97	9·0	10·0	97·1	92·1	2·20	10·70	1·007	1·180
17·80	10·0	11·0	99·5	68·3	1·79	2·89	1·068	1·752
21·50	12·5	13·25	98·4	59·7	4·49	4·48	1·380	2·411
24·30	14·0	—	95·4	—	4·91	—	1·595	—
28·10	16·5	—	96·6	—	3·68	—	1·836	—
37·40	21·0	—	92·0	—	2·63	—	2·482	—

*R, rotating anode. †S, stationary anode.

was employed for agitation. The results are given in Table 1.

Fink and Summers found it necessary to pass an excess of 10 per cent current in order to get nearly complete oxidation of glucose even at such low current densities as 1-2 amp./sq. dm. In our experiments also it was observed that when the anode was stationary, the current efficiency was about 88-92 per cent, but this rapidly decreased with increased current density. With a rotating anode the current efficiency was almost quantitative (Table 1). At low current densities, although the current efficiencies were more or less the same, it was noticed that the cell voltage was relatively lower for the cell in which a rotating anode was used, thus leading to lesser consumption of energy. The bromine loss, which was of the order of 25 per cent in the experiments of Fink and Summers with the stationary anode (unless an "alternator" was employed), has been reduced to as low as 2-4 per cent in the experiments using rotating anodes.

The cell voltage was high for those experiments where the anode was stationary and it increased with increase in current density. Cell voltage was always less when rotating anode was used and the increase in cell voltage with current density is very gradual so that high current densities with the consequent increase of output of product would be quite economical for the commercialization of the process.

The determination of the highest current density corresponding to the minimum reaction time is of interest. With a stationary anode, Fink and Summers showed that a current density of 6 amp./sq. dm. or more was not favourable. It was observed that when a slightly higher current density than that suggested by Fink was used, the cell voltage became high and the current efficiency dropped very quickly. With a rotating anode, on the other hand, current density as high as 24-28 amp./sq. dm. could be used without the energy consumption per lb. of calcium gluconate exceeding 1·4-1·6 kWh. This can be reduced still further by decreasing the inter-electrode distance. This is being investigated further.

The process could be very much shortened and the cell capacity increased by using high current densities. Only gluconic acid is formed under these conditions, and no other products. Pilot-plant trials with about 4 lb. of glucose are now in progress and the results would be reported shortly.

V. Sarada Menon
H. V. K. Udupa
B. B. Dey

*Central Electrochemical
Research Institute
Karaikudi*

3 *Aug.* 1954

---

1. Fink, C. G. & Summers, D. B., *Trans. electrochem. Soc.*, **74** (1938), 625.
2. Isbell, H. S. & Frush, H. L., *J. Res. Nat. Bur. Stand.*, **6** (1931), 1145.

EFFECT OF KRILIUM ON SOIL STRUCTURE & PLANT GROWTH

The possibility of improving the structure of poor soils by the application of synthetic soil conditioners has aroused considerable interest since the announcement by the Monsanto Chemical Co. of the development of a few such products. Synthetic soil conditioners are essentially hydrolysed products of polyacrylonitrile or copolymers of vinyl acetate and maleic anhydride, and are now available under popular trade-names such as Aerotil, Acrisoil, Poly-ack, Krilium, etc. It has been reported that soils treated with these conditioners are in a better state of aggregation and promote quicker growth and earlier maturity of plants[1].

We have carried out a few preliminary green house studies to verify some of the claims made for these soil conditioners using Krilium (formulation No. 9) manufactured by Monsanto Chemical Co.

The two soils, (1) black clayey soil and (2) red loam, had the following composition:

	Black clayey soil	*Red loam*
Clay, %	59·6	42·5
Silt, %	23·2	34·8
Sand, %	17·2	22·7

The soils were prepared as recommended in the technical literature issued by Monsanto Chemical Co., and Krilium was incorporated at two levels, i.e. 0·05 and 0·10 per cent on the weight of the soil. Balsam and tomato seedlings were planted in the soils in pots with three replications. Each pot contained 4,400 g. of black clayey soil or 5,800 g. of red loam. The moisture content of the soils was maintained at optimum level and mineral fertilizers were applied as solutions at regular intervals. The experiments were terminated after 7 weeks in the case of balsam plants and 11 weeks in the case of tomato plants. In the case of balsam plants, the number of branches and flowers put forth were recorded at the end of 5, 6 and 7 weeks. The dry weight of the plants was determined at the end of 8 weeks. In the case of tomato plants, the yield of fruit and the dry weight of the plants (excluding the weight of fruit) were determined at the end of 11 weeks.

The soils from the pots after the completion of the experiments were air dried and the percentage of water-stable aggregates in them were determined as follows: Air-dry soil (20 g.) passing through 2 mm. sieve was stirred, at low speed, in a litre of water for 2 min. and the silt and clay remaining in suspension determined. The percentage of silt and clay separating in the water-stable aggregate, larger than silt size, was then calculated.

The growth of balsam plants in Krilium-treated black clayey soils was generally better than that of the controls. In general, the effect is more significant in soils containing 0·1 per cent Krilium. The number of branches were more in plants grown in Krilium-treated soils (0·1 per cent level), particularly at the end of 5 weeks. The yield of flowers from the plants was 80 per cent more in Krilium (0·1 per cent level) treated soil at the end of 6 weeks; there was only 11 per cent increase in the yield of flowers at the end of 7 weeks. In the early stages, i.e. at the end of 5 weeks, plants grown in Krilium (0·1 per cent) treated soil did not give any flowers.

No significant difference could be observed in the number of branches or flowers put forth by plants grown in Krilium-treated and untreated red loam. The plants grown on treated and untreated soils showed no marked differences in their dry weights.

The yields of tomatoes from plants grown on untreated black clayey soil and soil treated with 0·05 and 0·1 per cent Krilium were 78, 108 and 202 g. respectively; the increase in yield was 150 per cent in soils treated with 0·1 per cent Krilium. The corresponding yields in the case of red loam were 285, 213 and 313 g. respectively; the increase being of the order of 10 per cent in soil containing 0·1 per cent Krilium.

The percentage of water-stable aggregates of sizes larger than that of silt particles increases in both soils on treatment with Krilium; it is more at 0·1 per cent Krilium level in the soils. The increase is more marked (33 per cent) in black clayey soil containing 0·1 per cent Krilium and on which tomatoes are grown. The plants grown on this soil gave significantly higher yields of tomatoes. Though a significant increase (19 per cent) in the percentage aggregation is observed in red loam containing 0·1 per cent Krilium, the yield of tomatoes is not quite significant.

These studies indicate that incorporation of Krilium in clayey soils improves their structure by increasing the percentage of water-stable aggregates in it and is beneficial to plant growth. In the case of soils, such as red loam, which contain silt and sand in proper proportions, no additional advantage accrues by the use of Krilium.

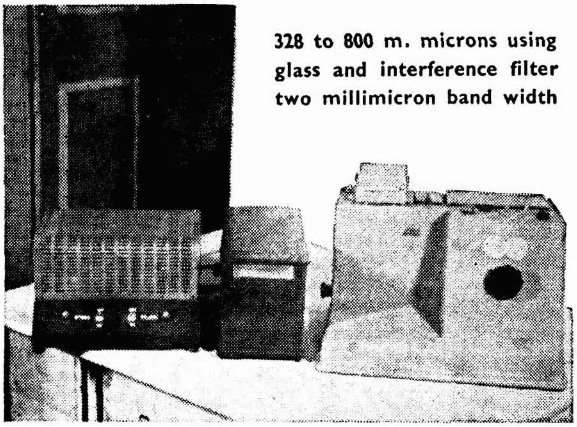
S. L. KAPUR
C. K. N. NAIR

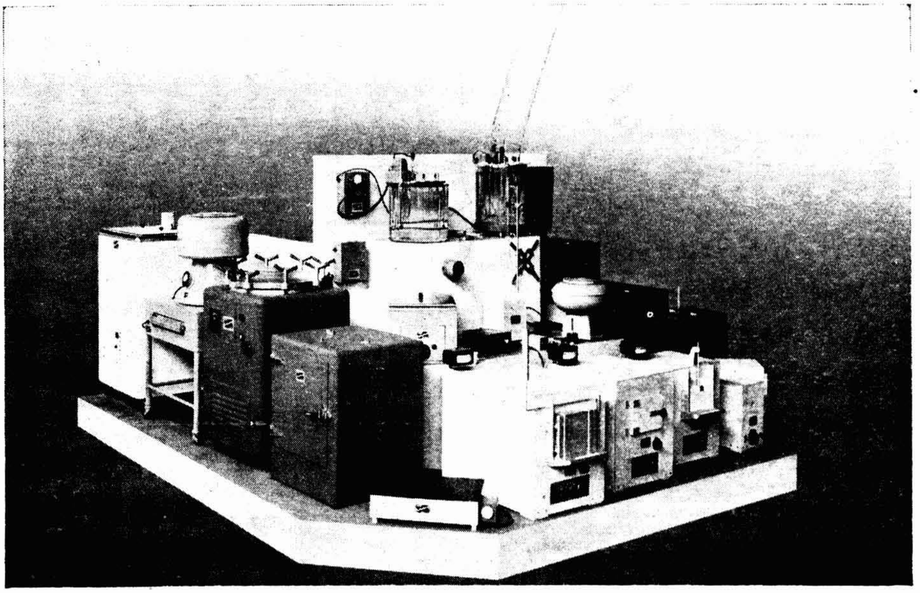
National Chemical Laboratory of India
Poona

12 *Dec.* 1953

---

1. HEDRICK, R. M. & MOWRY, D. T., *Soil Sci.*, **73** (1952), 427.





Printed by H. Jacquemotte, S.J., at the Catholic Press, Ranchi, India
Published by the Council of Scientific & Industrial Research, India. Editor : B. N. Sastri, M.Sc.

Regd. No. P-842