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Charles Danforth Howard, 1873–1944

CHARLES DANFORTH HOWARD

It is with deep regret that we announce the passing of Charles Danforth Howard. In his death, which occurred on October 29, 1944, the country has lost a noted, efficient, and irreplaceable worker in the cause of public health.

Having suffered a back injury a short time ago, he later developed a heart ailment which finally confined him to his bed. While so confined, he carried on a great portion of his desk work until he grew so weak that it became necessary for him to give up all mental and physical activities. Throughout his few short months of illness his thoughts were constantly on the activities of his division; never once, until the very end, did he lose hope of again resuming his responsible duties as director of chemistry and sanitation, New Hampshire Health Department.

Born at Westford, Massachusetts, in 1873, he graduated from Worcester Polytechnic Institute in sanitary chemistry in the year 1893. He had the distinction of graduating with honors, as well as being the youngest member of his class. From college he became private assistant to Professor Wolcott Gibbs, later becoming special assistant to Professor L. P. Kinnicut of Worcester Polytechnic Institute. He then became assistant chemist at the New Hampshire State Experiment Station, Durham, and later transferred to West Virginia University Experiment Station, where he became assistant chemist. Before returning to New Hampshire, he became associate chemist for the West Virginia Geological Survey.

He joined the New Hampshire staff in 1905 as Chief Chemist and Co-Sanitary Engineer, and the State was indeed fortunate in having as an employe a man who already was well versed in the field of sanitation and food control work. A quiet, dignified, and untiring worker, Mr. Howard placed New Hampshire on a pedestal that made all states respect its work and laws on public health. It can be stated that New Hampshire, through him, became the pioneer in legislation leading to the control of cosmetics, the inspection of juvenile camps, and the control of food, drug and public water supplies.

His memberships in honorary and scientific societies, as well as his publications in the field of science, were numerous, as has been recorded elsewhere. It was in 1934, on the basis of recognized scientific attainments, that Mr. Howard was given the distinction of election to membership in Sigma Xi. He was a man of musical ability; and in his earlier years was organist for numerous churches. In his later years his work became his only hobby.

From 1918 to 1943, Mr. Howard served as a member of the Federal Committee on Definitions and Standards for Foods in connection with enforcement of the Federal Food and Drug Act. At the time of his retirement from the committee (requested by him owing to pressure of other duties, and to failing health) Mr. Campbell, Federal Food and Drug Commissioner at the time, in a letter to Mr. Howard, paid him this tribute: "During all this time, with conditions constantly changing, your advice and counsel, based on your intimate contact with everyday consumer problems, has always been sound and constructive. Your constant and often expressed desire to have standards worded so as to be readily understood by the average person no doubt has contributed greatly to their usefulness. We shall miss seeing you at future meetings of this committee, but hope that you can still find time to give us the benefit of your comments and suggestions on the formulation of proposed standards as new work is begun."

To those not active in the field of science he will always be remembered for his ability to popularize scientific data as editor of New Hampshire *Health News*. In this capacity he kept the non-scientific world informed of new and needed food,

drug, and water control legislation. He was fearless in dealing with either political or business partisan groups. Such fearlessness, and his strict intellectual honesty are ideals to guide his successors in the future.

His death was a great loss to the field of food and drug control. His attainments were respected among food, drug, and water control officials throughout the states. He will be greatly missed in these and other scientific fields, but most of all he is missed by those of us who, from intimate association, had not only a deep admiration for his intellectual attainments and his sterling character, but also a sincere personal affection for Charles D. Howard, the man.

G. K. CROWELL

PROCEEDINGS OF THE FIFTY-NINTH ANNUAL MEETING OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1944

The fifty-ninth annual meeting of the Association of Official Agricultural Chemists was held at the Statler Hotel, Washington, D. C., October 25 and 26, 1944.

The meeting was called to order by the president, Guy G. Frary, State Chemical Laboratory, Vermillion, S. Dak., on the morning of October 25, at 10:00 o'clock.

OFFICERS, COMMITTEES, REFEREES, AND ASSOCIATE REFEREES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR ENDING NOVEMBER, 1945

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L. S. Walker, Burlington, Vt.
W. A. Queen, Washington, D. C.
G. G. Frary, Vermillion, S. D.

Permanent Committees

Recommendations of Referees

(Figures in parentheses refer to year in which appointment expires.)

W. F. Reindollar (Bureau of Chemistry, State Department of Health, Baltimore 18, Md.), *Chairman*

Subcommittee A: E. L. Griffin (1945) (Office of Marketing Service, War Food Administration, Washington 25, D. C.), *Chairman;* G. E. Grattan (1947), and H. A. Halvorson (1949).

Feeding Stuffs
- Mineral mixed feeds (calcium and iodine)
- Lactose in mixed feeds
- Fat in fish meal

Adulteration of condensed milk products
- Fat in cooked animal feeds containing cereals
- Crude fat or ether extract

- Activity of yeast
- Microscopic examination
- Fluorine
- Mineral Constituents of mixed feeds
- Crude fiber
- Protein evaluation in fish and animal products

Fertilizers
- Phosphoric acid
- Nitrogen
- Magnesium and manganese
- Acid- and base-forming quality
- Potash and platinum recovery methods
- Calcium and sulfur
- Copper and zinc
- Boron
- Moisture

Insecticides and fungicides
- Fluorine
- Rodenticides
- Nicotine and nornicotine
- DDT

Disinfectants

Leathers and tanning materials

Plants
- Sampling
- Iodine and boron
- Carbohydrates
- Zinc
- Copper and cobalt
- Chlorophyll, carotene, and iron

Soils and liming materials
- H-ion concentration of soils
- Boron and fluorine
- Zinc and copper
- Exchangeable calcium and magnesium
- Exchangeable hydrogen

Standard solutions
- Sodium thiosulfate solutions
- Thiocyanate solutions
- Potassium permanganate solutions
- Buffer solutions
- Bromide-bromate solutions
- Titanium trichloride solutions

Vitamins
- Vitamin A
- Vitamin B_1
- Vitamin C
- Vitamin D—milk
- Vitamin D—poultry
- Vitamin K
- Riboflavin (microbiological)
- Riboflavin (fluorometric)
- Nicotinic acid
- Carotene (chromatographic separation)
- Carotene (determination)
- Pantothenic acid

SUBCOMMITTEE B: F. H. WILEY (1945) (U. S. Food and Drug Administration, Washington 25, D. C.), *Chairman;* H. J. FISHER (1947), and DAN DAHLE (1949).

Naval Stores

Radioactivity
- Quantum counter
- Analysis by radon measurement and alpha particle counting

Vegetable drugs and their derivatives
- Chemical methods for ergot alkaloids
- Physostigmine in ointments
- Quinine ethyl carbonate
- Theobromine and phenobarbital
- Prostigmine
- Aminopyrine, ephedrine, and phenobarbital
- Quinine
- Ephedrine
- Spirit of camphor

Synthetic drugs
- Phenothiazine
- Plasmochine
- Hydroxyquinoline sulfate
- Methylene blue
- Metrazol
- Sulfanilamide derivatives
- Phenolphthalein in presence of bile salts
- Atabrine (chinacrin, quinacrine)
- Demerol
- Propadrine hydrochloride
- Carbromal
- Dihydrocodeinone
- Butacaine sulfate

Miscellaneous drugs
- Microchemical tests for alkaloids and synthetics
- Mercury compounds (ethanolamine methods)

- Separation of bromides, chlorides, and iodides
- Organic iodides
- Compound ointment of benzoic acid
- Alkali metals
- Spectrophotometric methods
- Glycols and related compounds
- Preservatives and bacteriostatic agents in ampul solutions
- Phosphorus, calcium, and iron in vitamin preparations
- Effervescent antipyrine with caffeine

Drug bioassays
- Enteric coatings
- Posterior pituitary
- Ergometrine (ergonovine)
- Digitalis preparations

Cosmetics and coal-tar colors
- Alkalies in cuticle removers
- Cosmetic creams
- Cosmetic powders
- Cosmetic skin lotions
- Deodorants and anti-perspirants
- Depilatories
- Hair dyes and rinses
- Hair straighteners
- Mascara, eyebrow pencils, and eye shadow
- Mercury salts in cosmetics
- Moisture in cosmetics
- Nail cosmetics
- Pyrogallol in hair dyes
- Resorcinol in hair lotions
- Urea in deodorants
- Acetates, carbonates, halides and sulfates in certified coal-tar colors
- Buffers and solvents in titanium trichloride titrations
- Ether extract in coal-tar colors
- Halogens in halogenated fluoresceins
- Identification of certified coal-tar colors
- Intermediates in certified coal-tar colors
- Mixtures of coal-tar colors for drug and cosmetic use
- Lakes and pigments
- Spectrophotometric testing of coal-tar colors
- Subsidiary dyes in D&C colors

SUBCOMMITTEE C: J. O. CLARKE (1945) (U. S. Food and Drug Administration, Chicago 7, Ill.), *Chairman;* C. S. LADD (1947), and JOSEPH CALLAWAY (1945).

Processed vegetable products
- Quality factors
- Moisture in dried vegetables

Fill of container methods (foods, drugs, and cosmetics

Coffee and tea (chlorogenic acid in coffee)
- Caffeine in coffee

Coloring matters in foods

Dairy products
- Pasteurization of milk and cream
- Ash in milk and evaporated milk
- Sampling, fat, and moisture in cheese
- Frozen desserts
- Chlorine in milk
- Acidity of milk
- Preparation of butter samples
- Pasteurization test for hard cheeses
- Pasteurization test for soft cheeses

Eggs and egg products
- Added glycerol

Extraneous materials in foods and drugs
- Drugs, spices, and miscellaneous materials
- Dairy products
- Nut products and confectionery
- Canned foods, cereal products, and eggs
- Fruit products and beverage materials
- Vegetable products

Decomposition in foods
- Fish products

Gelatine, dessert preparations, and mixes
- Starch, sugar, and jelly strength

Fish and other marine products
- Total solids and ether extract

Gums in foods
- Soft curd cheese
- Mayonnaise and French dressing
- Frozen desserts
- Starchy foods
- Jams, beverage bases, and fruit products
- Cacao products

Meat and meat products
- Dried skim milk in meat products
- Soybean flour in meat products

- Residues, metals, and other elements in foods
  - Cadmium
  - Copper
  - Zinc
  - Fluorine
  - Mercury
  - DDT
- Microbiological methods
  - Canned fishery products
  - Canned meats
  - Canned vegetables
  - Canned tomatoes and other acid vegetable and fruit products
  - Sugar
  - Eggs and egg products
  - Nuts and nut products
  - Frozen fruits and vegetables
- Microchemical methods
- Oils, fats, and waxes
  - Unsaponifiable matter
  - Peanut oil
  - Olive oil
- Preservatives and artificial sweeteners
  - Benzoate of soda and esters of benzoic acid
  - Saccharin
  - Sulfur dioxide
  - Monochloracetic acid
  - Formaldehyde
- Spices and condiments
  - Vinegar
  - Volatile oil in spices
  - Starch in prepared mustard and mustard flour
  - Starch in salad dressing

SUBCOMMITTEE D: J. WALTER SALE (1949) (U. S. Food and Drug Administration, Washington 25, D. C.), *Chairman;* KENNETH L. MILSTEAD (1949), and C. S. FERGUSON (1947).

- Alcoholic beverages
  - Malt
  - Diastatic activity and alpha- and beta-amylase of malt
  - Hops
  - Cereal adjuncts
  - Brewing sugars, sirups, wort, spent grains, and yeast
  - Fermentable extracts in brewing sugars and sirups
  - Beer
  - Acidity and *p*H of beer
  - Inorganic elements in beer
  - Color and turbidity in beer
  - Carbon dioxide in beer
  - Soluble starches
  - Distilled spirits
  - Spectrophotometric examination of wines and distilled spirits
  - Formol titrations
  - Chromatographic absorption of wines
  - *p*H in distilled alcoholic beverages
  - Wine
  - Cordials and liqueurs
- Cacao products
  - Lecithin
  - Malt solids
  - Pectic acid
  - Chocolate constituents
  - Lactose in presence of other reducing sugars
  - Fat
- Cereal foods (calcium and iron)
  - Rye flour in rye bread and in flour mixtures
  - H-ion concentration
  - Starch in raw and cooked cereals
  - Fat acidity in grain, flour, corn meal, and whole wheat flour
  - Sugar in bread and other cereal foods
  - Benzoyl peroxide in flour
  - Carbon dioxide in self-rising flour
  - Milk solids and butterfat in bread
  - Proteolytic activity of flour
  - Soybean flour
  - Soybean flour in foods (immunological methods)
  - Phosphated flour
  - Noodles
  - Baked products (moisture, ash, protein, fat, and crude fiber)
  - Moisture in self-rising flour, and in pancake, waffle, and doughnut flours
  - Bromates in flour
  - Apparent viscosity measurement

Baking powders and baking chemicals
Flavors and non-alcoholic beverages
  B-ionone
  Lemon oils and extracts
  Organic solvents in flavors
  Glycerol, vanillin, and coumarin in vanilla and imitation vanillas
  Emulsion flavors
  Maple flavors and concentrates
  Diacetyl
Fruits and fruit products
  Sodium and chlorides
  Polariscopic methods
  Titration of acids
  Fruit acids
  Phosphoric acid
  Potassium
  Cold pack fruit
Sugars and sugar products
  Unfermentable reducing substances in molasses
  Drying methods
  Densimetric and refractometric methods
  Honey
  Confectionery
  Reducing sugars
  Corn sirup and corn sugar
  Color and turbidity in sugar products
Waters, brine, and salt
  Boron in water
  Fluorine in salt

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Subcommittee A

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Referee: L. S. Walker, Agricultural Experiment Station, Burlington, Vt.

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LACTOSE IN MIXED FEEDS:
C. W. Sievert, American Dry Milk Institute, Chicago 1, Ill.

FAT IN FISH MEAL:
Maurice E. Stansby, Fish and Wildlife Service, Seattle 2, Wash.

ADULTERATION OF CONDENSED MILK PRODUCTS:
P. B. Curtis, Purdue University, Lafayette, Ind.

FAT IN COOKED ANIMAL FEEDS CONTAINING CEREALS:
S. B. Randle, Agricultural Experiment Station, Lexington 29, Ky.

CRUDE FAT OR ETHER EXTRACT:
J. J. Taylor, Department of Agriculture, Tallahassee, Fla.

ACTIVITY OF YEAST:
H. C. Schaefer, Ralston Purina Co., St. Louis, Mo.

MICROSCOPIC EXAMINATION:
A. W. Creswell, 4805 Winona Terrace, Cincinnati, Ohio

FLUORINE:
D. M. Doty, Purdue University, Lafayette, Ind.

MINERAL CONSTITUENTS OF MIXED FEEDS:
J. L. St. John, Agricultural Experiment Station, Pullman, Wash.

CRUDE FIBER:
W. L. Hunter, Department of Agriculture, Sacramento 14, Calif.

PROTEIN EVALUATION IN FISH AND ANIMAL PRODUCTS:
Frank J. Kokoski, Agricultural Experiment Station, Geneva, N. Y.

FERTILIZERS:
Referee: G. S. Fraps, Agricultural Experiment Station, College Station, Tex.

PHOSPHORIC ACID:
K. D. Jacob, Plant Industry Station, Beltsville, Md.

NITROGEN:
A. L. Prince, Agricultural Experiment Station, New Brunswick, N. J.

MAGNESIUM AND MANGANESE:
John B. Smith, Agricultural Experiment Station, Kingston, R. I.

ACID- AND BASE-FORMING QUALITY:
H. R. Allen, Agricultural Experiment Station, Lexington 29, Ky.

POTASH AND PLATINUM RECOVERY METHODS:
O. W. Ford, Purdue University, Lafayette, Ind.

CALCIUM AND SULFUR:
Gordon Hart, Department of Agriculture, Tallahassee, Fla.

BORON:
J. S. McHargue, Agricultural Experiment Station, Lexington 29, Ky.

* See p. 1 for complete list of subjects. As new appointments are made they will be published in *This Journal.*

MOISTURE:
W. H. Ross, Plant Industry Station, Beltsville, Md.

INSECTICIDES AND FUNGICIDES:
Referee: J. J. T. Graham, Office of Distribution, War Food Administration, Beltsville, Md.

FLUORINE:
C. G. Donovan, Office of Distribution, War Food Administration, Beltsville, Md.

RODENTICIDES:
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NICOTINE AND NORNICOTINE:
C. V. Bowen, Bur. Entomology and Plant Quarantine, Beltsville, Md.

DDT:
E. E. Fleck, Bur. Entomology and Plant Quarantine, Beltsville, Md.

DISINFECTANTS:
Referee: C. M. Brewer, Office of Distribution, War Food Administration, Beltsville, Md.

LEATHERS AND TANNING MATERIALS:
Referee: I. D. Clarke, Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia 18, Pa.

PLANTS:
Referee: E. J. Miller, Agricultural Experiment Station, Lansing, Mich.

SAMPLING:
E. J. Miller

IODINE AND BORON:
J. S. McHargue, Agricultural Experiment Station, Lexington 29, Ky.

CARBOHYDRATES:
J. T. Sullivan, U. S. Regional Pasture Research Laboratory, State College, Pa.

ZINC:
E. J. Benne, Agricultural Experiment Station, East Lansing, Mich.

COPPER AND COBALT:
Lillian I. Butler, Bur. Human Nutrition and Home Economics, Beltsville, Md.

CHLOROPHYLL, CAROTENE, AND IRON:
E. J. Benne

SOILS AND LIMING MATERIALS:
Referee: W. H. MacIntire, Agricultural Experiment Station, Knoxville 16, Tenn.

H-ION CONCENTRATION OF SOILS:
W. T. McGeorge, Agricultural Experiment Station, Tucson, Ariz.

BORON AND FLUORINE:
J. S. McHargue, Agricultural Experiment Station, Lexington 29, Ky.

ZINC AND COPPER:
L. H. Rogers, Agricultural Experiment Station, Gainesville, Fla.

EXCHANGEABLE CALCIUM AND MAGNESIUM:
W. M. Shaw, Agricultural Experiment Station, Knoxville 16, Tenn.

EXCHANGEABLE HYDROGEN:
W. M. Shaw

STANDARD SOLUTIONS:

Referee: H. G. Underwood, Food and Drug Administration, New Orleans 16, La.

SODIUM THIOSULFATE SOLUTIONS:

G. M. Johnson, Food and Drug Administration, St. Louis 1, Mo.

THIOCYANATE SOLUTIONS:

E. C. Deal, Food and Drug Administration, New Orleans 16, La.

POTASSIUM PERMANGANATE SOLUTIONS:

R. E. Duggan, Food and Drug Administration, New Orleans 16, La.

BUFFER SOLUTIONS:

George G. Manov, National Bureau of Standards, Washington 25, D. C.

VITAMINS:

Referee: Chester D. Tolle, Food and Drug Administration, Washington 25, D. C.

VITAMIN A:

J. B. Wilkie, Food and Drug Administration, Washington 25, D. C.

VITAMIN B_1:

O. L. Kline, Food and Drug Administration, Washington 25, D. C.

VITAMIN C:

W. L. Hall, Food and Drug Administration, Washington 25, D. C.

VITAMIN D—MILK:

Walter C. Russell, Agricultural Experiment Station, New Brunswick, N. J.

VITAMIN D—POULTRY:

Chester D. Tolle

RIBOFLAVIN (MICROBIOLOGICAL):

A. R. Kemmerer, Agricultural Experiment Station, College Station, Tex.

RIBOFLAVIN (FLUOROMETRIC):

H. W. Loy, Jr., Food and Drug Administration, Washington 25, D. C.

NICOTINIC ACID:

F. M. Strong, University of Wisconsin, Madison, Wisc.

CAROTENE (CHROMATOGRAPHIC SEPARATION):

A. R. Kemmerer

PANTOTHENIC ACID:

H. W. Loy, Jr.

Subcommittee B

NAVAL STORES:

Referee: V. E. Grotlisch, Office of Distribution, War Food Administration, Washington 25, D. C.

RADIOACTIVITY:

Referee: L. F. Curtiss, National Bureau of Standards, Washington 25, D. C.

QUANTUM COUNTER:

Anna E. Mix, Food and Drug Administration, Washington 25, D. C.

ANALYSIS BY RADON MEASUREMENT AND ALPHA PARTICLE COUNTING:

Francis J. Davis, National Bureau of Standards, Washington 25, D. C.

VEGETABLE DRUGS AND THEIR DERIVATIVES:

Referee: D. C. Grove, Food and Drug Administration, Washington 25, D. C.

CHEMICAL METHODS FOR ERGOT ALKALOIDS:

D. C. Grove

PHYSOSTIGMINE IN OINTMENTS:

G. M. Johnson, Food and Drug Administration, St. Louis 1, Mo.

QUININE ETHYLCARBONATE:
H. G. Underwood, Food and Drug Administration, New Orleans 16, La.
THEOBROMINE AND PHENOBARBITAL:
Elinor M. Rice, Food and Drug Administration, Washington 25, D. C.
PROSTIGMINE:
F. J. McNall, Food and Drug Administration, Cincinnati 2, Ohio
AMINOPYRINE, EPHEDRINE, AND PHENOBARBITAL:
C. D. Wright, Food and Drug Administration, Washington 25, D. C.
QUININE:
E. H. Wells, Food and Drug Administration, Washington 25, D. C.
EPHEDRINE:
L. H. Welsh, Food and Drug Administration, Washington 25, D. C.
SPIRIT OF CAMPHOR:
H. W. Conroy, Food and Drug Administration, Kansas City 6, Mo.

SYNTHETIC DRUGS:
Referee: L. E. Warren, Food and Drug Administration, Washington 25, D. C.
PHENOTHIAZINE:
I. Schurman, Food and Drug Administration, Cincinnati 2, Ohio
PLASMOCHINE:
F.C. Sinton, Food and Drug Administration, New York 14, N. Y.
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E. H. Grant, Food and Drug Administration, Boston 10, Mass.
METHYLENE BLUE:
H. O. Moraw, Food and Drug Administration, Chicago 7, Ill.
METRAZOL:
L. E. Warren
SULFANILAMIDE DERIVATIVES:
A. E. Sidwell, American Medical Association, Chicago, Ill.
PHENOLPHTHALEIN IN PRESENCE OF BILE SALTS:
R. Hyatt, Food and Drug Administration, Cincinnati 2, Ohio
ATABRINE (CHINACRIN, QUINACRINE):
H. C. Heim, Food and Drug Administration, San Francisco, Calif.
DEMEROL:
Merlin Mundell, Food and Drug Administration, Washington 25, D. C.
PROPADRINE HYDROCHLORIDE:
R. D. Stanley, Food and Drug Administration, Chicago 7, Ill.
CARBROMAL:
F. A. Rotondaro, Food and Drug Administration, Washington 25, D. C.
DIHYDROCODEINONE:
Joseph Levine, U. S. Bureau of Narcotics, Washington 25, D. C.
BUTACAINE SULFATE:
J. H. Cannon, Food and Drug Administration, St. Louis 1, Mo.

MISCELLANEOUS DRUGS:
Referee: C. K. Glycart, Food and Drug Administration, Chicago 7, Ill.
MICROCHEMICAL TESTS FOR ALKALOIDS AND SYNTHETICS:
W. V. Eisenberg, Food and Drug Administration, Washington 25, D. C.
MERCURY COMPOUNDS (ETHANOLAMINE METHODS):
P. S. Jorgensen, Food and Drug Administration, San Francisco, Calif.
SEPARATION OF BROMIDES, CHLORIDES, AND IODIDES:
N. E. Freeman, Food and Drug Administration, Atlanta 3, Ga.
ORGANIC IODIDES:
F. A. Rotondaro, Food and Drug Administration, Washington 25, D. C.

COMPOUND OINTMENT OF BENZOIC ACID:
W. F. Kunke, Food and Drug Administration, Chicago 7, Ill.
ALKALI METALS:
W. C. Woodfin, Food and Drug Administration, Atlanta 3, Ga.
SPECTROPHOTOMETRIC METHODS:
J. Carol, Food and Drug Administration, Chicago 7, Ill.
GLYCOLS AND RELATED COMPOUNDS:
Harry Isacoff, Food and Drug Administration, New York 14, N. Y.
PRESERVATIVES AND BACTERIOSTATIC AGENTS IN AMPUL SOLUTIONS:
C. N. Jones, Food and Drug Administration, New York 14, N. Y.
PHOSPHORUS, CALCIUM, AND IRON IN VITAMIN PREPARATIONS:
I. Schurman, Food and Drug Administration, Cincinnati 2, Ohio
EFFERVESCENT ANTIPYRINE WITH CAFFEINE:
H. F. O'Keefe, Food and Drug Administration, Chicago 7, Ill.

DRUG BIOASSAYS:
Referee: R. B. Smith, Food and Drug Administration, Washington 25, D. C.
ENTERIC COATINGS:
H. A. Braun, Food and Drug Administration, Washington 25, D. C.
POSTERIOR PITUITARY:
R. B. Smith
ERGOMETRINE (ERGONOVINE):
B. J. Vos, Jr., Food and Drug Administration, Washington 25, D. C.
DIGITALIS PREPARATIONS:
B. J. Vos, Jr.

COSMETICS AND COAL-TAR COLORS:
Referee: Dan Dahle, Food and Drug Administration, Washington 25, D. C.
ALKALIES IN CUTICLE REMOVERS:
R. E. Duggan, Food and Drug Administration, New Orleans 16, La.
COSMETIC CREAMS:
C. F. Bruening, Food and Drug Administration, Baltimore 2, Md.
COSMETIC SKIN LOTIONS:
H. R. Bond, Food and Drug Administration, Kansas City 6, Mo.
DEODORANTS AND ANTI-PERSPIRANTS:
S. H. Newburger, Food and Drug Administration, Washington 25, D. C.
DEPILATORIES:
F. J. McNall, Food and Drug Administration, Cincinnati 2, Ohio
HAIR DYES AND RINSES:
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HAIR STRAIGHTENERS:
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MASCARA, EYEBROW PENCILS, AND EYE SHADOW:
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MERCURY SALTS IN COSMETICS:
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MOISTURE IN COSMETICS:
J. F. Weeks, Food and Drug Administration, New Orleans 16, La.
PYROGALLOL IN HAIR DYES:
C. R. Joiner, Food and Drug Administration, St. Louis 1, Mo.
RESORCINOL IN HAIR LOTIONS:
F. M. Garfield, Food and Drug Administration, St. Louis 1, Mo.
UREA IN DEODORANTS:
N. E. Freeman, Food and Drug Administration, Atlanta 3, Ga.

BUFFERS AND SOLVENTS IN TITANIUM TRICHLORIDE TITRATIONS:
O. L. Evenson, Food and Drug Administration, Washington 25, D. C.
ETHER EXTRACT IN COAL-TAR COLORS:
S. S. Forrest, Food and Drug Administration, Washington 25, D. C.
HALOGENS IN HALOGENATED FLUORESCEINS:
G. R. Clark, Food and Drug Administration, Washington 25, D. C.
INTERMEDIATES IN CERTIFIED COAL-TAR COLORS:
L. A. Huard, Food and Drug Administration, Washington 25, D. C.
MIXTURES OF COAL-TAR COLORS FOR DRUG AND COSMETIC USE:
W. C. Bainbridge, H. Kohnstamm Company, Brooklyn 31, N. Y.
LAKES AND PIGMENTS:
G. R. Clark
SPECTROPHOTOMETRIC TESTING OF COAL-TAR COLORS:
Rachel N. Sclar, Food and Drug Administration, Washington 25, D. C.
SUBSIDIARY DYES IN D&C COLORS:
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Subcommittee C

PROCESSED VEGETABLE PRODUCTS:
Referee: V. B. Bonney, Food and Drug Administration, Washington 25, D. C.
QUALITY FACTORS:
V. B. Bonney
MOISTURE IN DRIED VEGETABLES:
Henry Fischbach, Food and Drug Administration, Washington 25, D. C.
FILL OF CONTAINER METHODS (FOODS, DRUGS, AND COSMETICS):
Referee: Sumner C. Rowe, Food and Drug Administration, Washington 25, D. C.

COFFEE AND TEA (CHLOROGENIC ACID IN COFFEE):
Referee: Harry J. Fisher, Agricultural Experiment Station, New Haven 4, Conn.
CAFFEINE IN COFFEE:
Gilman K. Crowell, Department of Health, Concord, N. H.

COLORING MATTERS IN FOODS:
Referee: C. F. Jablonski, Food and Drug Administration, New York 14, N. Y.

DAIRY PRODUCTS:
Referee: Guy G. Frary, State Chemical Laboratory, Vermillion, S. D.
PASTEURIZATION OF MILK AND CREAM:
F. W. Gilcreas, Department of Health, Albany 1, N. Y.
ASH IN MILK AND EVAPORATED MILK:
Guy G. Frary
SAMPLING, FAT, AND MOISTURE IN CHEESE:
W. Horwitz, Food and Drug Administration, Minneapolis 1, Minn.
FROZEN DESSERTS:
F. Leslie Hart, Food and Drug Administration, Los Angeles 15, Calif.
CHLORINE IN MILK:
W. H. King, State Department of Health, New Orleans 7, La.
ACIDITY OF MILK:
Guy G. Frary
PREPARATION OF BUTTER SAMPLES:
F. A. Vorhes, Food and Drug Administration, San Francisco 2, Calif.

PASTEURIZATION TEST FOR HARD CHEESES:
F. W. Gilcreas
PASTEURIZATION TEST FOR SOFT CHEESES:
W. Horwitz

EGGS AND EGG PRODUCTS:
Referee: Henry A. Lepper, Food and Drug Administration, Washington 25, D. C.
Added Glycerol:
George E. Keppel, Food and Drug Administration, Minneapolis 1, Minn.

EXTRANEOUS MATERIALS IN FOODS AND DRUGS:
Referee: H. Welch, Food and Drug Administration, Washington 25, D. C.
DRUGS, SPICES, AND MISCELLANEOUS MATERIALS:
W. V. Eisenberg, Food and Drug Administration, Washington 25, D. C.
DAIRY PRODUCTS:
J. D. Wildman, Food and Drug Administration, Washington 25, D. C.
NUT PRODUCTS AND CONFECTIONERY:
W. G. Helsel, Food and Drug Administration, Washington 25, D. C.
CANNED FOODS, CEREAL PRODUCTS, AND EGGS:
K. L. Harris, Food and Drug Administration, Washington 25, D. C.
FRUIT PRODUCTS AND BEVERAGE MATERIALS:
F. A. Hodges, Food and Drug Administration, Washington 25, D. C.
VEGETABLE PRODUCTS:
F. R. Smith, Food and Drug Administration, Washington 25, D. C.

DECOMPOSITION IN FOODS:
Referee: W. I. Patterson, Food and Drug Administration, Washington 25, D. C.
FISH PRODUCTS:
Fred Hillig, Food and Drug Administration, Washington 25, D. C.

GELATINE, DESSERT PREPARATIONS, AND MIXES:
Referee: Sumner C. Rowe, Food and Drug Administration, Washington 25, D. C.
STARCH, SUGAR, AND JELLY STRENGTH:
E. A. Steagall, Food and Drug Administration, Washington 25, D. C.
FISH AND OTHER MARINE PRODUCTS:
Referee: A. M. Allison, Food and Drug Administration, Boston 10, Mass.
TOTAL SOLIDS AND ETHER EXTRACT:
Menno D. Voth, Food and Drug Administration, Boston 10, Mass.

GUMS IN FOODS:
Referee: F. Leslie Hart, Food and Drug Administration, Los Angeles 15, Calif.
SOFT CURD CHEESE:
M. J. Gnagy, Food and Drug Administration, Los Angeles 15, Calif.
FROZEN DESSERTS:
F. Leslie Hart
STARCHY FOODS:
Sutton Redfern, Fleischmann Laboratories, New York 51, N. Y.
CACAO PRODUCTS:
J. F. Armstrong, Food and Drug Administration, Los Angeles 15, Calif.

MEAT AND MEAT PRODUCTS:
Referee: C. H. Swanger, Office of Distribution, War Food Administration, Washington 25, D. C.

SOYBEAN FLOUR IN MEAT PRODUCTS:
C. S. Ferguson, Department of Public Health, Boston, Mass.

RESIDUES, METALS, AND OTHER ELEMENTS IN FOODS:
Referee: H. J. Wichmann, Food and Drug Administration, Washington 25, D.C.
CADMIUM:
A. K. Klein, Food and Drug Administration, Washington 25, D. C.
COPPER:
Gordon H. Bendix, Continental Can Company, Chicago, Ill.
ZINC:
O. R. Alexander, American Can Company, Maywood, Ill.
FLUORINE:
P. A. Clifford, Food and Drug Administration, Washington 25, D. C.
MERCURY:
J. H. C. Loughrey, Food and Drug Administration, Washington 25, D. C.

MICROBIOLOGICAL METHODS:
Referee: A. C. Hunter, Food and Drug Administration, Washington 25, D. C.
CANNED MEATS:
M. L. Laing, Armour & Company, Chicago 9, Ill.
CANNED VEGETABLES:
C. Wallace Bohrer, National Canners' Association, Washington, D. C.
CANNED TOMATOES AND OTHER ACID VEGETABLE AND FRUIT PRODUCTS:
B. A. Linden, Food and Drug Administration, Washington 25, D. C.
SUGAR:
E. J. Cameron, National Canners' Association, Washington, D. C.
EGGS AND EGG PRODUCTS:
M. T. Bartram, Food and Drug Administration, Washington 25, D. C.
NUTS AND NUT PRODUCTS:
William R. North, Food and Drug Administration, Washington 25, D. C.
FROZEN FRUITS AND VEGETABLES:
H. E. Goresline, Office of Distribution, War Food Administration, Washington 25, D. C.

OILS, FATS, AND WAXES:
Referee: J. Fitelson, Food and Drug Administration, New York 14, N. Y.
UNSAPONIFIABLE MATTER:
Gardner Kirsten, Food and Drug Administration, New York 14. N. Y.
PEANUT OIL:
Gardner Kirsten
OLIVE OIL:
J. Fitelson

PRESERVATIVES AND ARTIFICIAL SWEETENERS:
Referee: Margarethe Oakley, State Department of Health, Baltimore 18, Md.
BENZOATE OF SODA AND ESTERS OF BENZOIC ACID:
E. B. Boyce, Department of Public Health, Westfield, Mass.
SACCHARIN:
Margarethe Oakley
SULFUR DIOXIDE:
C. E. Hynds, Department of Agriculture and Markets, Albany, N. Y.
MONOCHLORACETIC ACID:
John B. Wilson, Food and Drug Administration, Washington 25, D. C.

FORMALDEHYDE:
David W. Horn, P.O. Box 666, Bryn Mawr, Pa.

SPICES AND CONDIMENTS:
Referee: S. Alfend, Food and Drug Administration, St. Louis 1, Mo.
VINEGAR:
A. M. Henry, Food and Drug Administration, Atlanta 3, Ga.
VOLATILE OIL IN SPICES:
Dan Unger, Food and Drug Administration, New York 14, N. Y.
STARCH IN PREPARED MUSTARD AND MUSTARD FLOUR:
F. M. Garfield, Food and Drug Administration, St. Louis 1, Mo.
STARCH IN SALAD DRESSING:
Dorothy M. Ottens, Food and Drug Administration, St. Louis 1, Mo

Subcommittee D

ALCOHOLIC BEVERAGES:
Referee: J. Walter Sale, Food and Drug Administration, Washington 25, D. C.
MALT:
Christian Rask, Albert Schwill Company, Chicago, Ill.
DIASTATIC ACTIVITY AND ALPHA- AND BETA-AMYLASE OF MALT:
Allan D. Dickson, University of Wisconsin, Madison, Wis.
HOPS:
Frank Rabak, Plant Industry Station, Beltsville, Md.
CEREAL ADJUNCTS:
V. E. Munsey, Food and Drug Administration, Washington 25, D. C.
BREWING SUGARS, SIRUPS, WORT, SPENT GRAINS, AND YEAST:
Stephen Laufer, Schwarz Laboratories, New York 17, N. Y.
FERMENTABLE EXTRACTS IN BREWING SUGARS AND SIRUPS:
P. P. Gray, Wallerstein Laboratories, New York 16, N. Y.
BEER:
H. W. Rohde, Schlitz Brewing Company, Milwaukee 1, Wis.
ACIDITY AND *p*H OF BEER:
Kurt Becker, Siebel Institute, Chicago, Ill.
INORGANIC ELEMENTS IN BEER:
Gordon H. Bendix, Continental Can Company, Chicago, Ill.
COLOR AND TURBIDITY IN BEER:
B. H. Nissen, Anheuser-Busch, Inc., St. Louis, Mo.
CARBON DIOXIDE IN BEER:
Irwin Stone, Wallerstein Laboratories, New York, 16, N. Y.
SOLUBLE STARCHES:
Allan D. Dickson
DISTILLED SPIRITS:
Peter Valaer, Bureau of Internal Revenue, Washington 25, D. C.
SPECTROPHOTOMETRIC EXAMINATION OF WINES AND DISTILLED SPIRITS:
G. F. Beyer, Bureau of Internal Revenue, Washington 25, D. C.
FORMOL TITRATIONS.
G. F. Beyer
CHROMATOGRAPHIC ABSORPTION OF WINES.
Peter Valaer
*p*H IN DISTILLED ALCOHOLIC BEVERAGES.
M. Rosenblatt, Schenley Research Institute, Lawrenceburg, Ind.

WINE:
G. L. Marsh, University of California, Berkeley, Calif.
METHANOL IN WINE:
Louis Arrigoni, University of Washington, Seattle, Wash.
CORDIALS AND LIQUEURS:
John B. Wilson, Food and Drug Administration, Washington 25, D. C.

CACAO PRODUCTS:
Referee: W. O. Winkler, Food and Drug Administration, Washington 25, D. C.
LECITHIN:
J. H. Bornmann, Food and Drug Administration, Chicago 7, Ill.
PECTIC ACID:
W. O. Winkler
CHOCOLATE CONSTITUENTS:
W. O. Winkler
FAT:
Marie L. Offutt, Food and Drug Administration, New York 14, N. Y.

CEREAL FOODS (CALCIUM AND IRON):
Referee: V. E. Munsey, Food and Drug Administration, Washington 25, D. C.
H-ION CONCENTRATION:
F. A. Collatz, General Mills, Inc., Minneapolis, Minn.

STARCH IN RAW AND COOKED CEREALS:
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FAT ACIDITY IN GRAIN, FLOUR, CORN MEAL, AND WHOLE WHEAT FLOUR:
Lawrence Zeleny, Agricultural Research Center, Beltsville, Md.

SUGAR IN BREAD AND OTHER CEREAL FOODS:
R. M. Sanstedt, Agricultural Experiment Station Lincoln 1, Nebr.

BENZOYL PEROXIDE IN FLOUR:
Dorothy B. Scott, Food and Drug Administration, New York 14, N. Y.

CARBON DIOXIDE IN SELF-RISING FLOUR:
R. A. Barackman, Victor Chemical Works, Chicago Heights, Ill.

MILK SOLIDS AND BUTTERFAT IN BREAD:
V. E. Munsey

PROTEOLYTIC ACTIVITY OF FLOUR:
Sutton Redfern, Fleischmann Laboratories, New York 51, N. Y.

SOYBEAN FLOUR:
W. L. Taylor, General Mills, Inc., Minneapolis, Minn.

SOYBEAN FLOUR IN FOODS (IMMUNOLOGICAL METHODS).
C. S. Ferguson, Department of Public Health, Boston, Mass.

BAKED PRODUCTS (MOISTURE, ASH, PROTEIN, FAT, AND CRUDE FIBER):
N. H. Walker, National Biscuit Company, New York 11, N. Y.

MOISTURE IN SELF-RISING FLOUR AND IN PANCAKE, WAFFLE, AND DOUGHNUT FLOURS:

E. A. Steagall, Food and Drug Administration, Washington 25, D. C.

BROMATES IN FLOUR:

W. F. Geddes, University of Minnesota, University Farm, St. Paul, Minn.

APPARENT VISCOSITY MEASUREMENT:

E. G. Bayfield, Kansas State College, Manhattan, Kans.

BAKING POWDERS AND BAKING CHEMICALS:

Referee: V. E. Munsey, Food and Drug Administration, Washington 25, D. C.

FLAVORS AND NON-ALCOHOLIC BEVERAGES:

Referee: John B. Wilson Food and Drug Administration, Washington 25, D. C.

.B-IONONE:

John B. Wilson

LEMON OILS AND EXTRACTS:

John B. Wilson

ORGANIC SOLVENTS IN FLAVORS:

R. D. Stanley, Food and Drug Administration, Chicago 7, Ill.

GLYCEROL, VANILLIN, AND COUMARIN IN VANILLA AND IMITATION VANILLAS:

Llewellyn Jones, Food and Drug Administration, Kansas City 6, Kans.

EMULSION FLAVORS:

John B. Wilson

DIACETYL:

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FRUITS AND FRUIT PRODUCTS:

Referee: R. A. Osborn, Food and Drug Administration, Washington 25, D. C.

SODIUM AND CHLORIDES:

H. W. Gerritz, Food and Drug Administration, San Francisco 2, Calif.

POLARISCOPIC METHODS:

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TITRATION OF ACIDS:

H. M. Bollinger, Food and Drug Administration, Los Angeles 15, Calif.

FRUIT ACIDS:

R. A. Osborn

PHOSPHORIC ACID:

R. A. Osborn

POTASSIUM:

R. A. Osborn

COLD PACK FRUIT:

Paul A. Mills, Food and Drug Administration, Seattle 4, Wash.

SUGARS AND SUGAR PRODUCTS:

Referee: C. F. Snyder, National Bureau of Standards, Washington 25, D. C.

UNFERMENTABLE REDUCING SUBSTANCES IN MOLASSES:

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DRYING METHODS:

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DENSIMETRIC AND REFRACTOMETRIC METHODS:
C. F. Snyder:
HONEY:
George P. Walton, Food Distribution Administration, Washington 25, D. C.
CONFECTIONERY:
C. A. Wood, Food and Drug Administration, New York 14, N. Y.
REDUCING SUGARS:
Emma J. McDonald, National Bureau of Standards, Washington 25, D. C.
CORN SIRUP AND CORN SUGAR:
G. T. Peckham, Jr., Clinton Company, Clinton, Iowa
COLOR AND TURBIDITY IN SUGAR PRODUCTS:
J. F. Brewster, National Bureau of Standards, Washington 25, D. C.

WATERS, BRINE, AND SALT:
Referee: Anna E. Mix, Food and Drug Administration, Washington 25, D. C
BORON IN WATER:
Anna E. Mix
FLUORINE IN SALT:
Anna E. Mix

MEMBERS AND VISITORS PRESENT, 1944 MEETING

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Almy, L. H., H. J. Heinz Co., Pittsburgh, Pa.
Alter, Abraham, D. C. Municipal Center, Washington, D. C.
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Ford, O. W., Purdue University, West Lafayette, Ind.
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Hayes, Robert A., Bur. Entomology & Plant Quarantine, Beltsville, Md.
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Hinkle, S. F., Hershey Chocolate Corp., Hershey, Pa.
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PRESIDENT'S ADDRESS*

CONTRIBUTION OF CHEMISTRY TO AN INDUSTRY

By GUY G. FRARY (State Chemical Laboratory, Vermillion, S. Dak.)

In searching for a subject upon which to speak to this audience for a few minutes today, it occurred to me that something of interest might be found in the part that chemistry has taken in the growth and development of an industry. Especially might this be true if the industry chosen were one with which all agricultural chemists and chemists even remotely connected with food control problems have more or less direct contact. The dairy industry is such an industry, if the term be used in such a broad sense as to bring within its scope those activities which are concerned with the many, shall we say, secondary, products as well as with the primary products derived from milk. Whether the objective of the research was to discover the true composition of milk and its several component parts and to devise methods of isolating and recovering these components; to ferret out the exact physiological processes by which the cow as a chemical manufacturing unit produces milk; or to formulate analytical procedures for controlling production and quality all along the line—chemistry has been the foundation and the skeletal support of the whole structure of this vast industry. This industry, which surely owes its very life to chemistry, produced last year more than 118,000,000,000 pounds of milk in this country and from this source material made 1,673,000,000 pounds of creamery butter, almost a billion pounds of cheese, 934,000,000 pounds of condensed milk, sweetened and unsweetened, more than 3,000,000,000 pounds of evaporated whole milk, more than half a billion pounds of dried skim milk and nearly as many gallons of ice cream; and, in addition, produced large quantities of other important products and by-products such as lactose, concentrates of several milk-borne vitamins and casein, including several million pounds of synthetic fiber manufactured from this principal milk protein.

It would need the talents of one far better versed than your speaker in the art of compilation and editing, and one having much more available time than his duties permit, to attempt the exhaustive review of chemical research in the field of milk and its products which the subject matter merits. The voluminous data to be found in the published writings of the very large number of investigators in the field render the task, though intensely interesting and attractive, quite beyond the limitations placed upon me. Furthermore, our Association has need in these two days to devote all time and effort to making the 1945 edition of our *Book of Methods* of maximum value.

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Fossils and other evidence point to the probability that, 10,000 years ago, primitive man began the formation of domestic herds in Eastern Europe or Asia. These early stocks became mixed and crossed by reason of the migratory and war-like habits of the people. Later, as recounted by early historians, rulers and members of the nobility vied with each other in developing and improving their livestock. Much later, the wars of the Middle Ages delayed further improvement; but still later development of breeds with distinguishing characteristics flourished, with probably more emphasis on meat production than on milk yield.

Cattle came to this continent with the earliest colonists when they were landed at Jamestown in 1611 and at Plymouth in 1624. Not only did the cattle of the colonial period supply milk, butter, cheese and beef; through the agency of the tread-mill they furnished much of the power for the very early settlers. Population growth was accompanied by corresponding increase in the number of cattle; and, as people gathered more and more into larger communities, dairying began to assume the proportions of an industry. The development of commerce and transportation afforded wider markets for butter and cheese, while these products found yet another outlet in the provisioning of the ships of our early merchant marine. Thus the industries stemming from milk, as well as the development of breeds of cows, kept pace with the rapid economic growth in the United States. In 1839, which is the earliest year for which production records are available, the value of dairy products is given as $33,787,000: a figure, by the way, which is but little more than the value of the annual production in the single State of Iowa only 80 years later. The 19th century witnessed further steady growth in the industry, though there was little application of scientific methods until the last quarter of the period. After the Civil War there was rapid growth, and scientific knowledge began to be used for improvement and new developments in all branches of the industry. Refrigerator cars were first used in 1875. In 1882 the cream separator was brought to the United States from Sweden, where it was invented. Thermometers began to be used, and with them methods of temperature control. In 1890 Stephen Babcock, a young chemist at the University of Wisconsin, announced his method for measuring the proportion of fat in milk. The perfection of Babcock's test gave great impetus to the testing of milk from individual cows, hence to breed improvement with its consequent beneficial effect upon milk production.

While chemical and sanitary control of the production of milk, and from it many food and industrial products, has reached its highest development in the present century, studies of the chemical composition, and of the identification of individual constituents of milk, had progressed steadily during the two centuries immediately preceding. Scheele (about 1780) isolated lactose and proved it a pure sugar, but it had been separated much earlier in India. Butterfat had, of course, long been known, also

casein or "curd"; but Scheele named only these, together with a little salt, water and a small amount of extractive substance, as the constituents of milk. Little was known of the complex nature of the fat, or of the composition of the casein and other organic constituents, or of the salts and the "ash." Development of the present knowledge of the composition and true nature of milk has been the product of many minds during the past fifty years—and the field is still a fertile one.

Since milk is used chiefly for human food, its chemical composition, considered in the light of the needs of the human body for complete nutrition, became most important. The presence in milk of all the mineral elements required in human nutrition, the desirable composition and ready assimilability of the fat and proteins and, finally, the presence of essential vitamins, have been shown by a large number of chemists engaged in research in this field. No other natural food substance has intrigued so many investigators or yielded more gratifying results to the qualified researcher. Alongside the search for the ultimate composition of milk and all its constituents, has gone constant chemical study for isolation, quality production and utilization of many milk constituents which formerly were wasted. This has resulted in vast growth for the dairy industry in all its diversified activities. Without chemical research, such development could never have been accomplished, and without constant chemical control and study it could not be maintained.

But we must not fail to give due credit to those chemists who have, by the same type of thorough research, developed the science of feeds and feeding, and thereby made possible the remarkable development of the dairy cow as a converter of feed into milk and beef with ever increasing yields. Nor may we overlook the agronomists and the soils and fertilizer chemists who, by their constant study and experimentation, are furnishing the dairy farmer better yields of raw feeds of better quality for his herds.

Thus, with the support of chemistry one of our great American industries, the products of which are consumed by every citizen of the land, has grown and become so widely diversified that it now looks forward confidently to a secure and expanding future development which shall continue to afford us "Better Living Through Chemistry."

FIFTY-NINTH ANNUAL MEETING OF ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1944

WHICH YEAR MARKS THE 100TH ANNIVERSARY OF THE BIRTH OF HARVEY WASHINGTON WILEY, THE 60TH ANNIVERSARY OF THE ORGANIZATION OF THE ASSOCIATION, AND THE 50TH ANNIVERSARY OF THE WRITER'S ELECTION TO THE PRESIDENCY OF THE ASSOCIATION

Notes by H. A. HUSTON

In the history of this Association, this year marks two important anniversaries—the 100th of the birth of Dr. Harvey W. Wiley, one of the founders of the Association and its main support for more than a quarter of a century, and the 60th of the founding of the Association. It also marks a third unimportant anniversary—the 50th of my election as president of the Association.

I feel flattered that you should take time out to pay attention to one who 41 years ago became ineligible for membership in the Association. However, my interest in its important work did not cease, and it has been a pleasure to be present at nearly every meeting—and a privilege as well.

Now, as all of you know more than I do, no attempt will be made to follow the example of former distinguished speakers who presented important scientific facts, but rather I shall touch upon a few points connected with the origin and progress of the Association. Of those who were present at the organization of the Association on September 9, 1884, Dr. Dabney is, I believe, the only survivor. I was eligible for membership, having been appointed to a professorship at Purdue in June of that year, but did not attend the first three meetings, although for three years I did all of the work of the State Chemist of Indiana after September, 1884, in association with Dr. R. B. Warder.

As you doubtless know, the first activity of the Association was to provide suitable methods for the determination of phosphoric acid, nitrogen, and potash in fertilizers. The methods adopted were those recommended by the previous meetings of agricultural chemists, 1880–1883. These methods were in use in control laboratories as early as 1881, and as a postgraduate student in Dr. Wiley's laboratory I used them in that year. They were contained in a little circular, and consisted of the soda-lime and the copper oxide (or so-called absolute) method for nitrogen, the molybdate method for phosphoric acid, the citrate method for removing "reverted," and the Fresenius method for potash. In a few years the Kjeldahl method replaced the soda-lime method. Those of you who never had to sweat over those long furnaces used in the soda-lime method can hardly appreciate the saving in time and labor that resulted from the introduction of the Kjeldahl method. The copper oxide method is still retained, but is rarely, if ever, used in fertilizer work. As time went on the

Lindo-Gladding method for potash came into use, although the Fresenius method was retained as an alternative. Both methods were modified, but not improved, by the substitution of 80 per cent for 95 per cent alcohol. No reason for the change appears in the record except the recommendation of Dr. Wheeler. (At that time the present conservative plan of making changes was not in effect—the suggestion of a member often being adopted without even being referred to the reporter on the subject!) I called attention to the matter at the 1923 meeting of the Association in connection with the then recent determinations by Hoagland of the solubilities of sodium and potassium platinic chlorides in alcohols of different strengths, showing that the solubility of the sodium salt increases with the strength of the alcohol while the reverse is true of the solubility of the potassium salt. Fresenius studied the solubility of these potassium and sodium platinic chlorides in alcohol of different strengths as did Precht (*Z. Anal. Chem.*, **18,** 500, 509 (1880)); and Archibald (*J. Am. Chem. Soc.*, **30,** 755 (1908)) showed that 80 per cent alcohol dissolved five times as much of the potassium salt as did the 95 per cent. Magruder, in his reports of 1931–1932, indicated a definite need for more explicit directions regarding the concentration and amount of alcohol to be used in the determinations. O. W. Ford, Associate Referee, showed that more potash was recovered when 95 per cent alcohol was used than when 80 per cent was employed (*This Journal*, **25,** 340). In May, 1942, I took the liberty of suggesting to the associate referee that an analysis of the precipitate be made to learn whether it contained any other base than potash. In his next report (*Ibid.*, **26,** 63) he stated that, within the limits of experimental error, the increased potash value obtained by using stronger alcohol was all potassium chloroplatinate, and that for this reason there should be no objection to the use of stronger than 80 per cent alcohol and acid-alcohol for the determination of potash in fertilizers.

Now, perhaps no earlier attention was paid to my contributed paper of 1923 because I was then connected with the potash industry, and the thought may have entered the minds of some that some prospective benefit to me or to the industry may have been the reason for calling attention to the matter. But the reverse would be the case; for if all the potash put into the fertilizer was not found by the official analysis the manufacturer would have to put more potash into the goods in order to maintain his guarantee, and I would earn more commissions. All that I had in mind was to call attention to the bad analytical chemistry of the official method for potash determination.

The molybdate method for phosphoric acid has been somewhat modified to facilitate the precipitation, by increasing the temperature and by the addition of ammonium nitrate. The ammonium citrate method for the determination of reverted or citrate-soluble phosphoric acid is based on the work of Fresenius, Neubauer, and Luck (*Z. Anal. Chem.*, **10,** 133). They did not use a fixed temperature in their work, but the American

chemists fixed on 40°C. The water-insoluble part of the 2 gram sample, with the filter paper, was placed in a flask containing 100 ml. of ammonium citrate, sp. gr. 1.09, at room temperature; the flask was closed, shaken, placed in a water bath at 40°C., and shaken at intervals of five minutes. In the case of goods containing bone, tankage or much iron and alumina, it was found that quite low results were obtained. Many investigators tried raising the temperature of the water and, after several changes, the bath temperature was fixed at 65°C.; but the citrate was still at room temperature when the filter with the water-insoluble residue was inserted. When, if ever, the contents of the flask would reach 65° depended upon the amount of water in the water bath. At the tenth meeting of the Association in Chicago during the Columbian Exhibition, deRoode proposed that the flask containing the citrate solution be placed in the water bath, and kept there until the solution reached 65°, after which the filter and its contents would be added. While it was recognized that this would contribute to uniformity and accuracy, the members entitled to vote on the question—only those in charge of fertilizer work—voted to investigate the matter and report at the next meeting, and then went to lunch. Soon after lunch deRoode got together a number of members of the Association, only one or two of whom were eligible to vote on the question. This group reconsidered the matter, and voted to adopt the proposed method for immediate official use. When those entitled to vote on the proposal learned of this they were very indignant, but wishing to avoid any controversy they did nothing about it. So, the present method of determining citrate-insoluble was never adopted in accordance with the by-laws—sort of unconstitutional as it were! In this connection I hope Jacob and Ross will not be too severely shocked when attention is called to the fact that the Patron Saint of the Association, Dr. Wiley, stated in his annual report for 1882 that citrate of ammonia was not a proper reagent for use in the analysis of fertilizers because there was no citrate of ammonia in soils!

In 1906 the presidential address of Dr. Hopkins was not published in the proceedings of the Association; Dr. Browne called attention to this in his excellent "Reminiscences" presented at the Golden Anniversary of the Association in 1934.

In my so-called presidential address in 1894, it was said that "a young lady after returning from a visit to Kentucky was asked what she thought of the state and replied that it seemed to be a place where they educated the horses but where the men just grew up. The A.O.A.C. seems to be in an analogous position; we have provided methods for the analysis of foods for plants and foods for animals, but no attention has been paid to methods of analysis of human foods. Even the hotel accommodations are arranged by the Committee on Fermented and Distilled Liquors." It was suggested that a committee be appointed to consider the matter of methods for the analysis of human foods. Such a committee was appointed at

that meeting. Some thirty years later Dr. W. W. Randall, President of the A.O.A.C. in 1926, quoted this in an address, and on the side facetiously intimated that I must be the grandfather of the Pure Food and Drug Act of 1906.

The Association was organized to devise methods of analysis, and the growth of its methods from four pages to some six hundred pages indicates the progress made, as well as the measure of gratitude that should be shown to those who have labored so long and so successfully in devising and editing them. The constitution contains no mention of "Definition of Terms and Interpretation of Results on Fertilizers and Liming Materials," but the subject is introduced in the latest additions to the by-laws —sections 12 and 13. The committee dealing with the subject is the most active of the special committees of the Association. The open meetings of this committee are largely attended by members and non-members, and the discussions are lively, reminding one of the early days of the Association when a full day was devoted to the discussion of each of the subjects of nitrogen, phosphoric acid, and potash. The conclusions reached by the committee have been very useful in clarifying the meanings of commonly used terms in the fertilizer industry, and in virtually establishing standards for some materials, though it did slip a little when it adopted a definition of kainit, which was not that of either mineralogical or commercial kainit although the members of the committee had the correct definition before them. But that is now only of academic interest since little real kainit has been mined in recent years, and no real kainit is likely to reach this country in the future.

Out in the lobby some one approached me and said, "Sir, how do you account for the great length of your days?" On being told that my days were no longer than those of others who chanced to be in the same latitude he said that was not what he meant; that what he was trying to find out was how I had managed or had been permitted to live so long, and then he went on to say that from time to time pieces appear in the papers setting forth how the near-great and even some of the non-near-great have achieved great age by the use or avoidance of certain agencies or blessings such as fresh air, sunshine, rest, exercise, plain food, tobacco, and rum, which Providence has so kindly placed at our disposal. He was told that when a native of New England attains great age it is not explained by reference to material things but by an axiom or law of nature derived from that wonderful book, the New England Primer, for over 150 years the first book placed in the hands of the New England child, containing three pages of words ranging from one syllable to six-syllable theological words; plus the Catechism, a picture of the Rev. John Rogers being burned at the stake, and those hilarious hymns for children setting forth the beauties and advantages of early death. And I told him further that I have been spared to demonstrate, in a sort of backhanded way, the axiom that *The Good Die Young.*

ORDER OF PUBLICATION

The reports of the committees presented on the last day of the annual meeting are given at the beginning of the proceedings, not in their chronological order. This arrangement will assist the referees, associate referees, and collaborators in planning and developing their year's work. The remainder of the proceedings will then follow in the usual order.

SECOND DAY

THURSDAY—AFTERNOON SESSION

REPORT OF THE EDITORIAL BOARD

HENRY A. LEPPER, *Chairman*

The gratifying progress of *The Journal* has continued this year, and a report of its activities will be made by the Editor and Chairman of the Editorial Committee of *The Journal*, Dr. White.

At our last meeting your editorial board reported the approaching exhaustion of the supply of *Methods of Analysis*. The 450 copies then remaining out of the original 7,000 printed were sold by February of 1944, and since then orders for 811 copies remain unfilled. This increased demand for the book can, it is believed, be attributed to the references made to the Association's methods in connection with various government activities. Federal specifications for foods purchased by the armed forces require the methods to be used in judging compliance of deliveries. Orders and regulations of Federal emergency agencies provide use of the methods in establishing composition in the application of such orders. In the standards promulgated under the Federal Food, Drug, and Cosmetic Act conformity with analytical requirements is to be established by our methods. Interest appears to have increased also among colleges and universities in the employment of the book as a text in courses in analytical, food, and agricultural chemistry. An obligation to supply this demand, especially as arising from activities in connection with the war effort, made imperative the publication of the sixth edition as early as possible. The present meeting was called to perfect the revision so that it could be issued at the established five-year interval of 1945. All revisions, adoptions, and deletions approved by the Association up to this meeting have already been incorporated in the manuscript being made ready for the printer and there remains the inclusion of the changes approved at this meeting. Dr. Fisher, Chairman of the Committee on *Methods of Analysis*, will report in detail on the progress of this work.

The Executive Committee has approved the publication of 9,000 copies of the sixth edition. The Chemical Materials Branch of the Conservation

Division of the War Production Board brought the Federal Specification of June 16, 1944, for paint and related materials to the attention of this Association. These specifications include general directions for sampling and testing methods. A comparison shows that the methods in Chapter IX of *Methods of Analysis* are strikingly incomplete and somewhat out-of-date. These deficiencies in our methods on paints were pointed out also as existing when compared with the methods of the American Society of Testing Materials. Little or no work has been done in our Association on this subject since the fifth edition and it appears that there is little prospect of the methods being brought up to date. The situation was discussed with Dr. C. S. Ladd, Referee on Paints for a number of years, who contributed largely to the present compilation of methods. He reported to the Association as follows:

> It is recommended that the chapter on Paints, Varnishes, and Constituent Materials be omitted from the sixth edition of *Official and Tentative Methods of Analysis*. Suitable methods of analysis and tests for these products are available in the recently issued TT-P-141a Federal Specification for Paint, Varnish, Lacquer, and Related Materials; General Specification for Sampling and Test Methods; and, also, in the Standards and Tentative Standards of the American Society for Testing Materials.

The Executive Committee concurs in this recommendation.

The Executive Committee recommended that the sixth edition bear a prominent statement that the methods as published are those in effect as of the 1944 meeting and that the Association may revise, amend, or delete any of the present methods or adopt others at any subsequent annual meeting, which changes supersede those in the present book. The effective date of such changes is 30 days after their publication in the issue of *The Journal* following such annual meeting as provided in the Constitution. The appointment of a committee of three was recommended to investigate the desirability and feasibility of apprising purchasers of the *Methods of Analysis* of the annual changes made in the methods.

Approved.

REPORT OF EDITORIAL COMMITTEE OF *THE JOURNAL*

W. B. WHITE, *Editor and Chairman*

As predicted by the retiring chairman last year the lean war years have been reflected somewhat in the leanness of some of our issues during 1944, though No. 1 was about up to the normal quota of 200–250 pages. Some shrinkage was, of course, inevitable unless our standards of quality were lowered—something we are sure is unthinkable to every member of the Association.

Along this line it seems appropriate to quote a notice which is now

going to all contributors whose papers are returned for suggested changes or for any other reasons.

A word of explanation seems due a contributor whose manuscript is returned, either permanently because it appears for some reason not suited to readers of *This Journal*, or (and much more frequently) merely because certain editorial changes have been deemed desirable.

For the benefit of those contributors unfamiliar with the scope of *Journal* subject-matter it may be in order to say that a scrutiny of the back files reveals that most, though by no means all, of the papers deal primarily with analytical methods (construing the term liberally). They customarily present adequate supporting data on the usefulness and accuracy of the method.

There is, of course, no obligation on the part of *The Journal* to publish a paper that was presented at one of the meetings of the Association. On these papers, as on the others, *The Journal* must be the judge of their suitability. Among the important considerations in such a decision are, naturally, prior publication elsewhere, and the novelty and usefulness of the contribution from a broad regulatory standpoint. As a rule a purely polemical paper, with little or no supporting data, is of limited usefulness to readers; and in these days of rapidly expanding scientific literature and rapidly contracting paper supplies and printing costs, *The Journal* must be doubly careful to utilize its space wisely. There will be no rejections without a full statement of the basic reasons, and these will usually center around the conclusion that another audience would be more appreciative of the paper.

Coming now to the papers which are accepted with major or minor editorial changes, it is of the very essence of human nature that such changes are likely to be a little invidious, even to a particularly tolerant author. However, a word as to the underlying motives may serve to remove a little of the odium. As to the minor changes, the constant effort is to make them as few as possible, so that the author may use the locutions he likes provided he stays reasonably within the bounds of current scientific usage, with a decent (but not slavish) respect for the opinions of grammarians and lexicographers, and for felicity of expression. Those cabalistic instructions to the printer may, of course, be dismissed with a bare mention.

In general the conventional American Chemical Society abbreviations are used in the methods and tables, but the words are spelled out in the main text.

Firm names or trade names of apparatus, etc., are not mentioned unless (as is seldom the case) there is no other way of conveying the thought.

When it comes to what have been called major editorial changes, these are usually made the subject of a special letter and are then stated in broad terms with perhaps a guiding suggestion or two. They are concerned with such things as:

Non-correspondence between data and conclusions.

Inadequacy of data to support conclusions.

Broad statements as to applicability of a method unaccompanied by supporting data or analogies drawn.

Labored or fallacious reasoning.

Lack of clarity or logical presentation.

Excess verbiage.

Lack of scientific courtesy and good will.

Lack of impersonality in presentation.

When these faults can be corrected by slight changes in the text that are believed to be self-explanatory, no special mention of them is made.

The Journal will endeavor at all times to give your manuscript the ablest review obtainable on the scientific side, and the most considerate review which is humanly possible on the purely editorial side.

It is probably well to repeat the statement that copies of the 1931–40 index to *This Journal* are available at $1.00 each to earlier subscribers, who were not current subscribers when the index was issued and distributed.

It is recommended that the Association give consideration to changing the volume numbers of *The Journal* from the Roman to the Arabic system. Also it is felt that it would be a great convenience to readers if the range in page numbers of each issue were printed on the bound edge along with the volume number and date. Both changes are recommended for Association consideration.

In this, the centennial year of Dr. Wiley's birth, it seems altogether fitting that *The Journal* publish a brief tribute to the man to whom the Association owes so much. It is suggested that the President invite Dr. C. A. Browne to prepare such a commemorative article.

Approved.

REPORT OF COMMITTEE ON REVISION OF METHODS

H. J. FISHER, *Chairman*

The Committee submits the following report on the progress of work on the 1945 edition of our *Methods of Analysis.*

The Committee has met twice, once on July 20 and once during this meeting, besides discussing proposed changes in the new edition by correspondence.

All changes in the methods adopted since the 1940 edition have been incorporated in the text, and all except one of the revised chapters have been sent to the referees for their review in those cases where there was a referee for the subject. The Chairman took particular pains in correcting those few chapters covering subjects in which no refereeship now exists. A list of general comments was sent to each referee for his guidance in reviewing his chapter, together with special comments or questions on specific points in the chapter on which the committee desired information. Nearly all of these chapters have been returned by the referees and the copy corrected in accordance with their suggestions, so that when such changes as are adopted at this meeting are incorporated, the chapters will be ready for publication.

The new edition will contain a number of new chapters. All methods on vitamins, which are now scattered throughout the book, will be assembled in the Vitamin chapter, which exists in the present edition only by title. New chapters will be added on Cosmetics, Dessert Preparations and Mixes, Enzymes, and Extraneous Materials in Foods and Drugs. The last of these chapters is expected to contain a collection of methods for the detection of filth in foods and drugs which probably will not exist in print anywhere else, and should prove very valuable.

The 1945 edition will follow the 1940 edition very closely in form, but there will be a few changes. One point that the Committee has discussed very thoroughly is whether to change the present Roman numerals used for numbering chapters to Arabic numerals. Some have expressed pronounced opinions that Roman numerals are outmoded and cause considerable difficulty for some chemists using the book. The Committee decided to poll the referees on this question and to be guided by the preference of the majority. If the Arabic system is chosen, it will probably be in a decimal form, under which a reference like "XXXVI, 28" will become "36.28."

An attempt has been made to have all the "Selected References" revised so that they would be references to the original work on which the methods were based rather than being merely references to certain pages of *The Journal* showing that the methods were adopted. The referees were also asked to revise all factors so that they would conform to the 1943 atomic weights and so that they would be expressed to the number of significant figures which corresponded to the accuracy of the method concerned.

The chapter on Cacao Products will be an innovation in that the methods will be segregated into groups corresponding to the various constituents for which numerical limits are established in the proposed standards for cacao products under the Food, Drug, and Cosmetic Act. If this system of arrangement, suggested by Mr. Sale, proves popular, it will serve as model for other food chapters in future editions.

The Committee can offer no prediction at this time as to when the new book will be ready for distribution, but can only state that the work of revision is largely completed and that publication will be expedited as much as possible.

Finally, the Committee wishes to express its indebtedness to the referees for their careful work in reviewing the chapters. The other members of the Committee also wish to state that Revision Committees may come and go, but that the real Revision Committee is always Miss Lapp. Without her aid the preparation of a book of the quality of our *Methods of Analysis* would be a difficult task indeed.

Approved.

No report was given by the Committee on Quartz Plate Standardization and Normal Weight.

REPORT OF COMMITTEE ON DEFINITIONS OF TERMS AND INTERPRETATIONS OF RESULTS ON FERTILIZERS

Official, Final Action

LABELING OF NITRATES

It is recommended that bags of fertilizer nitrates shall carry the warning "*injurious to livestock.*"

MAGNESIA (MAGNESIUM OXIDE)

(1) *Magnesia (magnesium oxide)* is a product consisting chiefly of the oxide of magnesium. Its grade shall be stipulated. For example: Magnesia—75 per cent MgO.

NITRATE OF AMMONIA (NH_4NO_3)—AMMONIUM NITRATE

(2) *Nitrate of Ammonia* (NH_4NO_3)—*Ammonium nitrate* is a product composed chiefly of nitrate of ammonia. Its nitrogen content shall be stipulated. For example: Ammonium nitrate—30 per cent N.

Official, First Action

GUARANTEEING IN TERMS OF ELEMENTS

All fertilizer components with the exceptions of potash (K_2O) and phosphoric acid (P_2O_5) if guaranteed, shall be stated in terms of the elements.

Proposed Definitions

FUSED TRICALCIUM PHOSPHATE

Fused tricalcium phosphate is a product composed chiefly of the alpha form of the compound represented by the formula $Ca_3(PO_4)_2$. Its fineness and content of available P_2O_5 shall be stipulated. Example: Fused tricalcium phosphate—25 per cent available P_2O_5.

SINTERED TRICALCIUM PHOSPHATE

Sintered tricalcium phosphate is an unfused product containing P_2O_5 chiefly in the alpha form of the compound represented by the formula $Ca_3(PO_4)_2$. Its fineness and content of available P_2O_5 shall be stipulated.

CALCIUM METAPHOSPHATE

Calcium metaphosphate is a product composed chiefly of the vitreous compound indicated by the formula $Ca(PO_3)_2$. Its fineness and content of available P_2O_5 shall be stipulated. Example: Calcium metaphosphate—60 per cent available P_2O_5.

POTASSIUM METAPHOSPHATE

Potassium metaphosphate is a product composed chiefly of the crystalline compound represented by the formula KPO_3. Its fineness and content of P_2O_5 and of K_2O shall be stipulated. Example: Potassium metaphosphate—55 per cent P_2O_5; 37 per cent K_2O.

DOUBLE SULFATE OF POTASH AND MAGNESIA (LANGBEINITE)

Double sulfate of potash and magnesia (Langbeinite) is a commercial product containing not less than twenty-one per cent (21%) of potash (K_2O), nor less than fifty-three per cent (53%) of sulfate of magnesia, and not more than two and one-half per cent (2.5%) of chlorine.

Approved.

REPORT OF COMMITTEE ON RECOMMENDATIONS OF REFEREES

WILLIAM F. REINDOLLAR, *Chairman*

The value and substance of the Report of the Committee on Recommendations of Referees lie now as heretofore in the presentations of the several subcommittees. Theirs is the responsibility of receiving, reviewing, considering, and making appropriate recommendations on the numerous reports which come under their several jurisdictions. In order that this work may be satisfactorily accomplished it is imperative that sufficient

time be allotted for its completion. In the past the submitting of reports a day or two before the meeting, and even during its sessions, has worked a great hardship on the Subcommittees, and in many cases has necessitated their absenting themselves from the meeting in order to complete the work. Such a procedure is not only unfair to them but must of necessity result in a limited consideration of the material presented. In order to mitigate or, if possible, prevent this condition, the efforts of the Chairman have been directed largely to impressing this point upon the referees and associate referees and to urging them to make an early submission of their reports. In order to facilitate the work a series of "Guiding Considerations for Referees and Associate Referees" was mailed out early in 1944. Although several complete and very excellent statements of the duties of referees have appeared in *The Journal* in the past, these guiding considerations are included in this report for the purpose of making them more readily available at the present time.

GUIDING CONSIDERATIONS FOR REFEREES AND ASSOCIATE REFEREES

Article III of the Constitution states in part, "It shall be the duty of a referee:

(1) To direct and conduct research on the methods and subjects assigned;
(2) To prepare and distribute samples and standard reagents to members of the Association and others;
(3) To present at the annual meeting the results of the work done and recommendations for methods to be based thereon; and
(4) To direct and encourage general discussion at the meetings."

In order that referees and associate referees may better accomplish the aforementioned objectives, as well as to facilitate the entire process of the selection, investigation, and adoption of analytical methods, the following suggestions are presented in outline form:

(1) Consult the previous reports of your particular subcommittee and learn what recommendations have been made regarding your assignment.
(2) Familiarize yourself with the work that has already been done on your topic by reviewing the literature in the field, particularly that presented by former referees or associate referees.
(3) Continue any studies of your predecessor that may be incomplete as well as those recommended by your subcommittee. If you feel that any studies should be discontinued make such a recommendation in your report, giving your reasons for it.
(4) If your topic is one that has not been studied by the Association before, incorporate a paragraph in your report giving a general description of the subject and the conditions that make its investigation desirable.
(5) Whenever an analytical procedure is developed or proposed explain the chemistry involved, giving the reactions if possible.
(6) State your recommendations clearly and briefly. Recommendations in general deal with the status of methods. The By-Laws provide for two classes of methods: tentative, and official—first or second action. The usual, but not obligatory, procedure is for a method to be adopted as tentative, to advance to official,

first action, and then final action. Do not recommend any method for either tentative or official status unless you are convinced of its value by satisfactory collaborative work. In general, a new method should be recommended as tentative rather than official unless the collaborative study shows it to have an exceptional degree of accuracy and precision. Remember also that obsolete or undesirable methods now appearing in the *Book of Methods* are deleted only by recommendation of the appropriate referee.

(7) The year is short, time is fleeting, and for most chemists, summer is the busiest season. Begin your A.O.A.C. work, therefore, *immediately* after receiving your assignment.

(8) The several subcommittees must receive, review, and make appropriate recommendations on all referee reports assigned to them and must present a general statement of the work at a general session of the Association. In order to assure proper consideration of your work submit your report, if an associate, to your referee by September 1st. All referees' reports must be in the hands of your subcommittee chairman by September 15th.

The year has been a difficult one so far as A.O.A.C. work has been concerned. The loss of workers caused by the war emergency placed additional burdens on those who remained available, with the result that many have been unable to complete any work this year. In one or two cases it was not found possible to secure qualified individuals to act as referees or associate referees. To those who have carried on in the face of these handicaps, as well as to the members of the various subcommittees, the Chairman expresses his deep and sincere appreciation.

It is with regret that the Chairman records the death of W. Catesby Jones, member of Subcommittee D. Major Jones had long been an active and valued member of this Association, and in addition to serving on this committee, was at the time of his death a member of the Executive Committee.

Approved.

REPORT OF SUBCOMMITTEE A ON RECOMMENDATIONS OF REFEREES*

By E. L. GRIFFIN (Office of Marketing Service, War Food Administration, Washington, D. C.), *Chairman;*
L. S. WALKER† and H. A. HALVORSON

VITAMINS

It is recommended—

(1) That the spectrophotometric method for determination of vitamin A in fish liver oils described in the report of the associate referee, which involves the use of 2000 as the factor for converting $E^{1\%}_{1cm}$ 325 mμ values to spectrophotometric vitamin A units, be adopted as tentative.

(2) That vitamin A studies be continued.

(3) That the fermentation method proposed by the associate referee

* These recommendations, submitted by Subcommittee A, were approved by the Association. Unless otherwise given, all references are to *Methods of Analysis, A.O.A.C.*, 1940.

† Served for G. E. Grattan.

for the determination of thiamine in cereal products and in yeast be adopted as tentative and that the work be continued.

(4) That fluorometric methods for determination of riboflavin be studied.

(5) That the associate referee further study the microbiological method for determination of riboflavin (*This Journal*, **27**, 107) to see if it can be made more nearly identical with the U.S.P. method.

(6) That the tentative method for determination of ascorbic acid (vitamin C), (*This Journal*, **27**, 102) be amended as proposed by the associate referee and then adopted as official (first action).

(7) That further studies be conducted on the microbiological method for determination of pantothenic acid.

(8) That certain modifications of the method for determination of crude carotene that were adopted as tentative in 1943 (*This Journal*, **27**, 108) be changed as proposed by the associate referee and then adopted as tentative.

(9) That the chromatographic method for determination of carotene that was adopted as tentative in 1943 (*This Journal*, **27**, 107) be changed as proposed by the associate referee and continued as tentative and that studies on the chromatographic separation of carotenes be continued.

(10) That the referee give consideration to the statement by E. M. Nelson regarding the methods for determination of carotene, and that if necessary additional referees be appointed.

(11) That the work on vitamins be continued at the direction of the referee.

INSECTICIDES AND FUNGICIDES

It is recommended—

(1) That the mercury reduction method for determination of Pyrethrin I in pyrethrum powder (**113**, p. 66) and in pyrethrum extracts in mineral oil (**116**, p. 67) be changed as proposed by the referee and when so changed be made official (final action).

(2) That the method for determination of thallous sulfate in ant poisons (*This Journal*, **22**, 412), adopted as official (first action) in 1941, be adopted as official (final action) for this determination in ant poisons and in rodenticides.

(3) That in the lead chlorofluoride method for determination of total fluorine (*This Journal*, **27**, 74) procedure (5) be deleted, procedures (2) and (4) be revised as proposed by the associate referee, and the method as modified be continued as official (first action).

(4) That the tentative distillation method for determination of fluorine in the presence of organic matter (**23(b)**, p. 52) be revised as proposed by the associate referee and remain tentative.

(5) That the alcoholic caustic method for the determination of 2,2-bis (p-chlorophenyl)-1,1,1-trichloroethane (DDT) proposed by the referee be adopted as tentative.

(6) That studies be continued on both the modified Winter method and the alcoholic caustic method for determination of DDT to find the effects of impurities in technical material.

(7) That further work to develop new and more specific methods for DDT be undertaken.

(8) That the method for determination of nicotine (**108**, 64) be changed to include the use of a large excess of sodium hydroxide and sodium chloride and alternative drying of the nicotine silicotungstate at 105°C., as recommended by the associate referee, and that the revised method be made official (first action). A note should be added to the effect that the determination includes nornicotine.

(9) That the work on the determination of nicotine and nornicotine be continued.

(10) That work on rodenticides be continued and that attention be directed particularly to methods for zinc phosphide preparations.

DISINFECTANTS

It is recommended that the fungicidal test described in the report of the Referee on Disinfectants be adopted as official (first action).

LEATHERS AND TANNING MATERIALS

It is recommended—

(1) That the tentative method for preparation of sample (**1**, p. 116) be changed as proposed by the referee.

(2) That the tentative method for determination of insoluble ash (**6**, p. 117) be changed as proposed by the referee.

(3) That the tentative method for extraction of water-soluble material (**9**, p. 117) be changed as recommended by the referee.

(4) That the tentative method for determination of soluble non-tannins (**14**, p. 118) be changed to more definitely describe the procedure as proposed by the referee.

(5) That the tentative method for preparation of solution (**1**, p. 120) be revised as proposed by the referee.

(6) That the temperature of 20° appearing in the method for determination of soluble solids (**3** and **5**, p. 120) be changed in each case to 23°.

(7) That the reference to No. 590 S & S filter paper be omitted from the method for soluble solids (**4**, p. 120).

(8) That the description of hide powder (**7**, p. 121) be changed as recommended by the referee.

STANDARD SOLUTIONS

It is recommended—

(1) That the method for preparation and standardization of sodium thiosulfate solution described in *This Journal*, **25**, p. 659, be adopted as official (first action).

(2) That the method for standardization of thiocyanate solutions be further studied.

(3) That the method for standardization of potassium permanganate solution be further studied.

(4) That studies on buffer solutions be continued.

(5) That preparation and standardization of bromide-bromate solutions be studied.

(6) That preparation and standardization of titanium trichloride solutions be studied.

FEEDING STUFFS

It is recommended—

(1) That the method for sampling feeding stuffs in bags, previously adopted as tentative (*This Journal*, **27**, p. 89) be changed as recommended by the referee and made official (first action).

(2) That in the method for determination of crude protein (**9**, p. 354), line 2, which reads, "In the case of wheat grain multiply the result by 5.7," be omitted.

(3) That the method for determination of fat in dried milk products, modified Roese-Gottlieb method (**24**, p. 357), be made official (final action).

(4) That the method for determination of water-soluble acidity (**38**, p. 363) be made official (first action).

(5) That the method for detection of rice hulls in rice bran (**44**, p. 364) be changed from tentative to official (first action).

(6) That the method for detection of oat hulls in oats and oat feeds (**45**, p. 365) be changed from tentative to official (first action).

(7) That the method for detection of grit in poultry and similar feeds (**46**, p. 365) be made official (final action).

(8) That the method for detection of bone in meat scrap or tankage (**47**, p. 365) be made official (final action).

(9) That the method for determination of calcium oxide in mineral feeds (**48**, p. 365) be made official (final action).

(10) That the method for determination of ferrous sulfate (**52**, p. 367) be made official (final action).

(11) That the method for determination of copper sulfate (**53**, p. 367) be made official (final action).

(12) That the method for determination of potassium iodide (**54**, p. 367) be made official (final action).

(13) That the method for determination of soluble chlorine in feeding stuffs (*This Journal*, **26**, 87) be amended as proposed by the referee and then made official (final action).

(14) That work on mineral feeds, lactose in mixed feeds, fat in fish meal, fat in cooked animal feeds containing cereals, crude fat or ether extract, activity of yeast, microscopic examination, fluorine, and mineral constituents in mixed feeds be continued.

(15) That work on filtration aids in crude fiber determination, soluble

chlorine in feeding stuffs, and ammoniacal urea and nitrogen salts be discontinued.

(16) That an associate referee be appointed to develop methods for evaluating the comparative quality of protein in fish and animal products.

(17) That an associate referee be appointed to study the crude fiber determination.

FERTILIZERS

It is recommended—

(1) That the method for determination of acid-forming or non-acid-forming quality (**60,** p. 38) be revised by changing the temperature in line 11 from 500–600° to 575–600° and that the method remain tentative.

(2) That in the method for determination of potash (**40,** p. 30) a separate paragraph be added as recommended by the referee to describe the preparation of the acid alcohol and the method remain official (final action).

(3) That paragraph **42(a),** p. 31, of the method for determination of potash be revised as recommended by the referee and the method remain official.

(4) That the study of the platinum recovery method presented by the associate referee be continued with a view to making it tentative.

(5) That paragraph **12(b)** of the volumetric method for determination of phosphoric acid be changed as recommended by the referee and remain official.

(6) That a study be made of methods for determination of available phosphoric acid in fused tricalcium phosphate, calcium metaphosphate, and potassium metaphosphate.

(7) That a study be made of methods for the determination of ortho-, meta-, and pyrophosphoric acids.

(8) That a study be made of the aging of molybdate solution used in the volumetric method for phosphoric acid to see if a time limit should be put on its use or a preservative added.

(9) That a study be made of the methods for water-soluble and acid-soluble boron for needed changes and that an associate referee be appointed.

(10) That work on potash and other subjects recommended by the associate referee be continued.

(11) That Method I for determination of acid-soluble magnesium (**52,** p. 35) be deleted, and that Method II (**53,** p. 36) be revised as indicated in the 1943 report (*This Journal,* **27,** 47) and adopted as official (final action).

(12) That in the method for determination of citrate-insoluble phosphoric acid the change in paragraph **16(b),** p. 24, made official (first action) in 1941 (*This Journal,* **25,** 49), be rescinded, and that this paragraph remain as in *Methods of Analysis, A.O.A.C.,* 1940, but that to accomplish

the same result the paragraph on citrate-soluble and available phosphoric acid (**17**, p. 24) be revised to change the last sentence to read, "Subtract citrate-insoluble P_2O_5 from the total to obtain chemically available P_2O_5 in dicalcium phosphate, precipitated bone phosphate, and precipitated bone" (official, final action).

(13) That methods for determination of moisture be studied.

PLANTS

It is recommended—

(1) That the procedures for determination of carotene in plant tissue, as described by the associate referee, be adopted as tentative.

(2) That the study of methods for determination of carotene in plant tissue be continued, and that as many as possible of the promising procedures for this purpose be investigated.

(3) That the method for determination of copper (**20** and **21**, pp. 130, 131) be deleted.

(4) That the method for determination of copper given in the report of the associate referee be adopted as tentative and that work on methods for the determination of this constituent be continued.

(5) That the method for determination of iodine (**40**, p. 136) be revised as suggested by the associate referee and remain tentative.

(6) That the official colorimetric thiocyanate method for determination of iron (**7**, p. 126) be deleted (final action under suspension of the rules).

(7) That the colorimetric o-phenanthroline method for determination of iron given in the report of the associate referee be adopted as official (first action).

(8) That the titanous chloride titrimetric method for determination of iron be adopted as an official method (first action).

(9) That work on methods for determining iron in plant ash be continued and as many as possible of the promising procedures for this determination be investigated.

(10) That the magnesium nitrate method for determination of sulfur (**28**, p. 133) be changed as recommended by the referee and remain official.

(11) That the colorimetric method for determination of boron recommended by the associate referee be adopted as tentative.

SOILS AND LIMING MATERIALS

It is recommended—

(1) That the tentative directions for preparation of sample (**2**, p. 1) be revised as recommended by the referee.

(2) That in the tentative method for moisture (**3**, p. 1) the words "based upon" be inserted in lieu of the word "of" following the word "percentage."

(3) That the methods for the determination of total boron and acid-soluble boron (**28**, **29**, and **30**, pp. 12 and 13) be dropped.

(4) That the methods for the determination of total boron and of available boron given in the associate referee's report be adopted as tentative.

(5) That in the reagents for fluorine determination, the term "or $Ca(OH)_2$" be inserted following the word "peroxide" in **(a), 31,** p. 13, and that references cited by the referee be included.

(6) That on page 17, par. **52** and the headings "I of Humid Regions" and "II of Arid and Semi-Arid Regions" be deleted.

REPORT OF SUBCOMMITTEE B ON RECOMMENDATIONS OF REFEREES*

By F. H. WILEY (U. S. Food and Drug Administration, Washington, D. C.), *Chairman;* H. J. FISHER and DAN DAHLE

NAVAL STORES

The referee recommended revision of the following methods for official final action under suspension of the rules: *Rosin.*—Sampling, acid number, saponification number, petroleum benzine insoluble, toluene insoluble material, and ash. *Turpentine Oil.*—Color grading—Lovibond glass method, specific gravity, refractive index, distillation, and mineral oil in turpentine.

The referee also recommended the tentative adoption of a method for determination of unsaponifiable matter in rosin.

The referee also recommended revision of the following tentative methods: *Rosin,* volatile oils; and *turpentine oil,* potassium dichromate method for determination of color.

The referee also recommended that the directions for rosin grading be deleted.

The Committee accepts the referee's report and concurs in his recommendations.

RADIOACTIVITY

No report was received from the referee.

Quantum Counter.—The associate referee reported that a comparison had been made of the Wulf-Hess counter and the Geiger-Müller counter and recommended that the subject be continued.

The Committee concurs.

Analysis by Radon Measurement and Alpha Particle Counting.—The associate referee submitted a report reviewing the status of this work with the recommendation that measurements by the electroscope method and the Geiger counter method be continued.

The Committee concurs.

The associate referee also recommended that samples containing less

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* These recommendations, submitted by Subcommittee B, were approved by the Association. Unless otherwise given, all references are to *Methods of Analysis, A.O.A.C.,* 1940.

than 10^{-10} grams of radium be analyzed by a laboratory maintaining the alpha particle counting method, such as the Bureau of Standards.

In this recommendation the Committee does not concur.

VEGETABLE DRUGS AND THEIR DERIVATIVES

The referee reported that nine topics had been assigned for this year. During the course of the year it was recommended that the subjects theophylline sodium salicylate and quinine and strychnine be dropped. Of the remaining seven topics, reports were received on two, no reports on three, and short progress reports on two.

The referee recommended that a topic be set up on quinine to study the titration method described by Herd, and that a topic be set up on ephedrine for the purpose of re-examining present methods for this substance.

The referee further recommended that the present tentative method for determination of alkaloids in ergot be deleted, since it does not measure the total alkaloids.

The referee further recommended certain revisions of Chapter XXXIX in *Methods of Analysis, A.O.A.C.*, 1940, which are primarily editorial.

The Committee approves the report of the referee and concurs in his recommendations.

Chemical Methods for Ergot Alkaloids.—The associate referee found it impossible during the past year to make satisfactory arrangements for collaborative study on the chemical assay of ergot. Arrangements are now being made to have this work done, and he recommended that the topic be continued.

The referee and the Committee concur.

Theophylline Sodium Salicylate.—The referee recommended that since no such product could be found on the market the subject be dropped.

The Committee concurs.

Physostigmine in Ointments.—No report was received. The referee recommended that the subject be continued.

The Committee concurs.

Quinine Ethylcarbonate.—No report was received. The referee recommended that the subject be continued.

The Committee concurs.

Theobromine and Phenobarbital.—The associate referee reported that several methods for the separation and determination of theobromine and phenobarbital had been investigated during the past year, but that none of the methods had proved entirely satisfactory. The work is being continued. The referee recommended that the topic be continued.

The Committee concurs.

Prostigmine.—The associate referee reported a method based on the hydrolysis of prostigmine with the subsequent distillation of dimethylamine. The results of the collaborators are in good agreement, but no

statement is made of the amount of prostigmine bromide present in the tablets used. The associate referee and the referee recommended that the method be adopted as tentative. The referee further recommended that the subject be continued and the associate referee be requested to submit an authentic mixture to collaborative study for the purpose of determining the accuracy of the method.

The Committee concurs.

Aminopyrine, Ephedrine, and Phenobarbital.—The associate referee reported that studies had been made on the separation of these materials, and that recoveries for ephedrine were not particularly good. The associate referee and the referee recommend that the subject be continued.

The Committee concurs.

Quinine and Strychnine.—The referee recommended that the subject be dropped since these preparations are no longer on the market.

The Committee concurs.

Polarographic Methods.—The Referee recommended that the subject be dropped.

The Committee concurs.

SYNTHETIC DRUGS

Nineteen topics were assigned to the referee for the past year. No reports were received on nine of the topics, and it was recommended that six of the subjects be continued and that three be dropped. Reports were received on ten of the topics and it was recommended that five be continued, that methods reported in four cases be adopted and the subjects closed, and that one subject be closed without any further study.

The referee recommended that the following new subjects be studied:

Effervescent Antipyrine with Caffeine
Dihydrocodeinone
Butacaine Sulfate
Spirit of Camphor

The referee recommended that the following methods be advanced from official (first action) to official (final action):

Acetophenetidin and Caffeine
Bismuth Compounds in Tablets
Calcium Gluconate
Effervescent Potassium Bromide with Caffeine
Iodine
Mandelic Acid
Oil of Chenopodium
Phenolphthalein in Chocolate Preparations
Sulfanilamide
Theophylline

The referee further recommended that the status of microchemical methods for alkaloids or synthetics listed below be advanced from tentative to official (final action under suspension of the rules):

Berberine
Cotarnine
Narceine
Narcotine
Physostigmine
Stovaine
Benzedrine
Choline
Dilaudid
Metrazol
Sodium Sulfapyridine Monohydrate
Sulfadiazine
Sulfathiazole
Sulfapyridine

The referee further recommended that the following methods be advanced from tentative to official (first action):

Acetophenetidin, Acetylsalicylic Acid, and Salol
Acetylsalicylic Acid and Phenolphthalein in Tablets
Aminopyrine, Acetophenetidin, and Caffeine
Cinchophen
Cod Liver Oil in Emulsions
Mercurous Iodide in Tablets
Mercury in Ointment of Mercuric Nitrate
Mercury in Mercurial Ointment
Methenamine in Tablets
Nicotinic Acid in Tablets and Ampuls
Nitrites in Tablets
Pyridium
Sampling
Sulfonal and Trional
Theobromine in Theobromine Calcium
Volatile Acidity of Tragacanth

The referee further recommended that the tentative method for determination of chloroform in mixtures be deleted, and that the tentative method for chloroform and carbon tetrachloride be raised to the status of official (final action under suspension of the rules).

The referee further recommended that the method for determination of ipomea and jalap (*This Journal*, **16**, 84) be reinstated as tentative.

The referee further recommended that the tentative method for determination of terpin hydrate in elixirs be deleted, and that the tentative method for terpin hydrate and codeine in elixirs be advanced to official (first action).

The referee further recommended that the tentative method for determination of cinchona alkaloids be deleted.

The Committee accepts the referee's report and concurs in his recommendations.

Benzedrine in Inhalants.—No report was received. The referee recommended that the subject be dropped.

The Committee concurs.

Phenothiazine.—The associate referee has developed a method which has been submitted to collaborative investigation with encouraging results. The associate referee and referee recommended that the method be adopted as tentative and that the subject be continued.

The Committee concurs.

Plasmochine.—No report was received. The referee recommends that the subject be continued.

The Committee concurs.

Hydroxyquinoline Sulfate.—A report was received from the associate referee, and he and the referee recommended that the subject be continued.

The Committee concurs.

Methylene Blue.—A report was received, and the associate referee and the referee recommended that the subject be continued.

The Committee concurs.

Ethylaminobenzoate in Ointments.—The associate referee has developed a method for the determination of this material which gave good results in a collaborative study. He recommended that the method be adopted as tentative. The referee recommended that the method be adopted as tentative and that the subject be not reassigned.

The Committee concurs.

Metrazol.—No report was received. The referee recommended that the subject be continued.

The Committee concurs.

Barbiturates.—The referee recommended that the present method for determination of barbital and phenobarbital be dropped, that Method No. 2 in his report be substituted instead under the general heading of "Barbiturates," that this method be adopted as official (final action under suspension of the rules), and that the subject be closed.

The Committee concurs.

Acetanilid.—The referee recommended that the subject be dropped.

The Committee concurs.

Sulfanilamide Derivatives.—No report was received in time for consideration by the Committee. The referee recommended that the subject be continued.

The Committee concurs.

Phenolphthalein in Presence of Bile Salts.—No report was received. The referee recommended that the subject be continued.

The Committee concurs.

Atabrine (Chinacrin).—No report was received. The Referee recommended that the subject be continued.

The Committee concurs.

Sedormid.—The associate referee reported a method for determining sedormid in tablets which has been subjected to collaborative study, recommended that the method be adopted as tentative, and that the melting point of 194°–197°C. be accepted. The referee recommended that the method be adopted as tentative, that the melting point of 194–197°C. be accepted, and that the topic be not reassigned.

The Committee concurs.

Demerol.—The associate referee reported the development of two methods for the estimation of this substance which appear to give satisfactory results. He recommended that the subject be continued for the purpose of collaborative study.

The referee and the Committee concur.

Propadrine Hydrochloride.—No report was received. The referee recommended that the subject be continued.

The Committee concurs.

Carbromal.—A progress report was received. The associate referee and referee recommended that the subject be continued.

The Committee concurs.

Phenolsulfonphthalein.—The associate referee reported that considerable difficulty had been encountered in the determination of phenolsulfonphthalein, and recommended that the subject be dropped.

The Committee concurs.

Procaine.—The associate referee subjected tentative Method No. 3 for determination of procaine (**99**, p. 591) to collaborative study with good results. He and the referee recommended that the method be advanced to the status of official, final action, and that the subject be not reassigned.

The Committee recommends that it be made official (final action under suspension of the rules).

The Committee further recommends, in light of results obtained by Wells and Levine, that the time of bromination in the bromometric procedure for procaine be increased from one-half hour to two hours, official (final action under suspension of rules), since this increase in time gave good results in the hands of both investigators.

Sulfobromophthalein.—No report was received. The referee recommended that the subject be dropped.

The Committee concurs.

MISCELLANEOUS DRUGS

Ten subjects were assigned to the referee for the past year. No reports were received on four of the topics, and it was recommended that three of the subjects be continued and the fourth be discontinued in favor of a more inclusive topic. Reports were received from six associate referees, and it was recommended that four of the subjects be continued and that the methods on two topics be adopted and the subjects closed. It was the opinion of the Committee that one of the latter topics should be continued for collaborative investigation.

The referee recommended that chromatographic methods for the separation and identity of vitamins A and D, thiamine hydrochloride, riboflavin, nicotinic acid, and nicotinamide be studied. Subcommittee B is referring this recommendation to Subcommittee A.

The referee further recommended that a study be made of the determination of phosphorus, calcium, and iron in vitamin tablets.

The Committee accepts the referee's report.

Microchemical Tests for Alkaloids and Synthetics.—The associate referee submitted a report in which he recommended that quinacrine, sodium diphenylhydantoin, and caffeine be further studied.

The referee and the Committee concur.

The referee further recommends that microchemical tests for butycaine and pentothal sodium be studied.

The Committee concurs. The Committee also recommends that dihydrocodeinone be included in this study.

Mercury Compounds (Ethanolamine Methods).—The associate referee reported that he will submit the Rotondaro modification of the ethanolamine method to collaborative study, and recommended that the subject be continued.

The referee and the Committee concur.

Separation of Bromides, Chlorides, and Iodides.—A progress report was received from the associate referee who recommended that the subject be continued.

The referee and the Committee concur.

Thyroid.—No report was received. The referee recommended that the subject be dropped and that the subject of organic iodides be substituted.

The Committee concurs.

Emulsions.—No recommendation was made by the associate referee. The referee recommended that the now tentative method for determination of liquid petrolatum with phenolphthalein be advanced to official (first action) and that the subject be not reassigned.

The Committee concurs.

Compound Ointment of Benzoic Acid.—The associate referee described a method for the determination of benzoic and salicylic acid in compound ointment, and recommended that the method be adopted as tentative and the subject closed. The referee concurred. Since no collaborative study was made on this method, the Committee recommends that the subject be *not* closed and that a collaborative study be made before the method is adopted.

Alkali Metals.—No report was received from the associate referee owing to his illness. The referee recommended that the subject be continued.

The Committee concurs.

Spectrophotometric Methods.—A report was received from the associate referee on the determination of chrysarobin, and he and the referee recommended that the method be submitted to collaborative study.

The Committee concurs.

Glycols and Related Compounds.—No associate referee was appointed. The referee recommended that the subject be continued.

The Committee concurs.

Preservatives and Bacteriostatic Agents in Ampul Solutions.—No report was received, and the Referee recommended that the subject be continued.

The Committee concurs.

DRUG BIOASSAYS

No reports were received from the referee or any of the associate referees.

The Committee recommends that the subjects be continued.

COSMETICS AND COAL-TAR COLORS

The referee assigned 29 topics for the year. No reports were received on 16 of the subjects. All subjects, with two exceptions, were recommended for continued study. Reports were received on the remaining 13 subjects. Of these, two were recommended for official final action, five were recommended for official first action, and one was recommended for tentative adoption.

Alkalies in Cuticle Removers.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Arsenic in Hair Lotions.—No report was received. The associate referee is no longer engaged in cosmetic work. The Referee recommended that the topic be dropped.

The Committee concurs.

Cosmetic Creams.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Cosmetic Powders.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Cosmetics Skin Lotions.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Deodorants and Anti-Perspirants.—The associate referee reported collaborative work on a method for the determination of aluminum and zinc in these products. He recommended the method for tentative adoption.

The referee and the Committee concur.

Depilatories.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Hair Dyes and Rinses.—The associate referee submitted for collaborative study a method for the determination of 2,5 diaminotoluene in hair dyes. The method includes an extraction of the diamine followed by the formation of its diacetyl derivative. This derivative can be weighed for quantitative estimation and identified by its melting point for identifica-

tion of 2,5 diaminotoluene. The associate referee recommended that this method be adopted as official (first action). The referee concurred.

The associate referee further recommended that the dichlorimide titration method previously studied collaboratively and reported on last year (*This Journal*, **26**, 113) be also adopted as official (first action). The dichlorimide titration method is more rapid than the acetylation method and gives equally good results. It does not, however, furnish a means of identification of the diamine. The referee concurs in the recommendation of the associate referee that both methods be adopted as official (first action).

The Committee concurs with both recommendations.

Hair Straighteners.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Lead in Cosmetics.—No report was received. The associate referee has been in poor health and makes no recommendation. The Referee recommended that the topic be discontinued for the present.

The Committee concurs.

Mascara, Eyebrow Pencils, and Eye Shadow.—The associate referee reported on preliminary work and recommended that the methods be studied collaboratively.

The referee and the Committee concur.

Mercury Salts in Cosmetics.—No associate referee was appointed. The referee recommended that another attempt be made to find an associate referee for this topic.

The Committee concurs.

Moisture in Cosmetics.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Nail cosmetics.—No associate referee was appointed. The referee recommended that another attempt be made to find an associate referee for this topic.

The Committee concurs.

Pyrogallol in Hair Dyes.—The associate referee reported on collaborative work on a proposed method, but in view of discrepancies in the results of two collaborators, he recommended further study.

The referee and the Committee concur.

Resorcinol in Hair Lotions.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Salicylic Acid in Hair Lotions.—The associate referee recommended that the method adopted at the last meeting as official (first action) be made official (final action), and that the subject be closed.

The referee and the Committee concur.

Urea in Deodorants.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Acetates, Carbonates, Halides, and Sulfates in Certified Coal-Tar Colors.—The associate referee reported a study of a new method for determination of sodium acetate in FD&C Blue No. 1, compared the results of this method with those of the tentative method of the Association, and recommended that the new method be studied collaboratively.

The referee and the Committee concur.

Alizarin in Madder Lake.—The associate referee recommended that the method adopted at the last meeting as official (first action), be made official (final action) and that the subject be closed.

The referee and the Committee concur.

Buffers and Solvents in Titanium Trichloride Titration.—The associate referee reported collaborative studies of methods for determination of pure dye in D&C Red No. 39, D&C Green No. 7, and D&C Orange No. 4. He recommended these methods for adoption as official (first action).

The Referee and the Committee concur.

Ether Extract in Coal-Tar Colors.—No report was received. The associate referee recommended that the subject be continued.

The referee and the Committee concur.

Halogens in Halogenated Fluoresceins.—The associate referee reported on a collaborative study of a method for determination of bromine in brominated fluoresceins, and recommended that the method be adopted as official (first action).

The referee and the Committee concur.

Identification of Certified Coal-Tar Colors.—No report was received. No recommendation was made by the associate referee. The referee recommended continuation and reassignment of the subject to another associate referee if one can be found.

The Committee concurs.

Intermediates in Certified Coal-Tar Colors.—No report was received. The associate referee recommended continuation of the subject.

The referee and the Committee concur.

Mixtures of Coal-Tar Colors for Drug and Cosmetic Uses.—The associate referee reported on a method for separation of D&C Red Nos. 6 and 7 from D&C Red Nos. 10 and 13, and recommended that the method be studied collaboratively.

The referee and the Committee concur.

Pure Dye, Impurities, and Substrata in Pigments.—The associate referee reported on a study of D&C Red No. 10 and recommended (1) that the method be studied collaboratively, and (2) that the title of the subject be changed to "Lakes and Pigments."

The referee and the Committee concur.

Spectrophotometric Testing of Coal-Tar Colors.—The associate referee made no direct report on this topic, but submitted a contributed paper on a comparison between chemical and spectrophotometric methods for the analysis of FD&C Red Nos. 3 and 4 in mixtures of vegetable oils.

The referee and the Committee recommend that this subject be continued.

Subsidiary Dyes in D&C Colors.—The associate referee reported on p-toluene-azo-betanaphthol-3 carboxylic acid in D&C Red Nos. 6 and 7, and 1-p-toluino-o-sulfo-4-p-toluino anthraquinone in D&C Green No. 5. He recommended that the subject be continued.

The referee and the Committee concur.

REPORT OF SUBCOMMITTEE C ON RECOMMENDATIONS OF REFEREES*

By J. O. CLARKE (U. S. Food and Drug Administration, Chicago, Ill.), *Chairman;* C. S. LADD, and KENNETH L. MILSTEAD

CANNED FOODS

It is recommended—

(1) That the tentative method for physical examination of canned vegetable (**1,** p. 518) be dropped.

(2) That the official method for determination of volatile acids in canned vegetables (**10,** p. 519) and for volatile and fixed acidity in tomato products (**28, 29,** p. 522) be dropped (final action under suspension of the rules).

(3) That the method for preparation of sample and determination of volatile and lactic acids in tomato and other vegetable products, recommended by the Associate Referee on Volatile and Lactic Acids in Fruits and Fruit Products, be adopted as official (final action under suspension of the rules).

(4) That the method for determination of moisture in dried vegetables recommended by the associate referee be adopted as tentative.

(5) That studies of vapor pressure as an index of moisture content of dried vegetables be continued.

(6) That the tentative method for determination of sand (**21,** p. 521) and official methods for microanalysis of tomato products (**30–33,** p. 522–24), be transferred to a new chapter on extraneous materials in foods and drugs.

(7) That studies of methods for determination of quality be continued.

(8) That studies of fill of container methods for canned foods be assigned to the Referee on Fill of Container Methods.

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* These recommendations, submitted by Subcommittee C, were approved by the Association. Unless otherwise given, all references are to *Methods of Analysis, A.O.A.C.*, 1940.

(9) That the name of the chapter "Vegetables and Vegetable Products" be changed to "Processed Vegetable Products."

FILL OF CONTAINER METHODS

It is recommended that studies be continued on methods of fill of container of foods, drugs, and cosmetics.

COFFEE AND TEA

It is recommended that study be continued on methods for determining chlorogenic acid in coffee.

COLORING MATTERS IN FOODS

It is recommended—

(1) That collaborative work be repeated on detection of small amount of FD&C Yellow No. 5.

(2) That investigational work be continued on the quantitative separation of FD&C Yellow No. 5 (Tartrazine) and FD&C Yellow No. 6 (Sunset Yellow FCF).

(3) That investigational work be undertaken to separate and determine quantitatively FD&C Green No. 2 (Light Green SF Yellowish), FD&C Green No. 3 (Fast Green FCF), and FD&C Blue No. 1 (Brilliant Blue FCF).

(4) That investigational work be undertaken to separate and estimate quantitatively FD&C Yellow No. 3 (Yellow AB), FD&C Yellow No. 4 (Yellow OB), FD&C Orange 2 (Orange SS), and FD&C Red No. 32 (Oil Red XO).

(5) That collaborative work on analytical methods for coal-tar colors certifiable for use in foods be conducted.

(6) That the methods proposed by the referee as tests for Yellow AB and Yellow OB be adopted as tentative.

DAIRY PRODUCTS

It is recommended—

(1) That the method for determination of alkalinity of ash of dried skim milk (*This Journal*, **24**, 558) be adopted as official (final action under suspension of the rules).

(2) That methods for acidity in milk be studied.

(3) That as recommended by the referee temperature correction tables be inserted in the next edition of *Methods of Analysis*.

(4) That the methods for determination of total solids in milk (**8** and **9** p. 270) be corrected editorially as suggested by the referee, and that method **8** so corrected be made the method for total solids in evaporated milk by reference.

(5) That the method for determination of ash in milk proposed by the associate referee be adopted as tentative.

(6) That the present official method for determination of ash in milk (**10**, p. 270) be dropped (final action under suspension of the rules).

(7) That the present official method for determination of ash in evaporated milk be editorially corrected to fix a maximum ignition temperature of 550°.

(8) That the editorial changes in the method for determination of fat in milk proposed by the associate referee be adopted.

(9) That the method for Vitamin D in milk (**41**, p. 282) be transferred to the chapter on vitamins.

(10) That the application of the phosphatase test to cheese be studied.

(11) That the revision proposed by the associate referee of the method for preparation of samples of evaporated milk (**66**, p. 289) be adopted as official (final action under suspension of the rules).

(12) That in line 2 of par. **99**, p. 298, the reference **98** be included, as suggested by the referee.

(13) That studies be undertaken on the preparation of butter samples.

(14) That the method for detection of mold mycelia in butter be adopted as official (final action) and incorporated in the new chapter on microanalytical methods for extraneous materials in foods and drugs.

(15) That studies on methods of sampling cheese be continued.

(16) That the double dilution method for correcting the volume of precipitate in the optical determination of lactose in milk (**16**, p. 271; *This Journal*, **25**, 608), be changed to provide for the use of a weighed sample of 65.8 grams (2 normal weight) in place of a calculated measured sample, and adopted as official (final action).

(17) That studies on tests for pasteurization of milk and cream be continued.

(18) That studies on methods for the determination of fat and moisture in cheese be studied.

(19) That the third sentence of the tentative method for determination of coloring matters in ice cream (**135**, p. 306) be editorially changed to read, "Continue as directed under **31** and **105**, and under **XXI**, particularly **3** and **16(b)**, for the detection of oil-soluble coal tar dyes and annatto," and that the method be adopted as official (final action under suspension of the rules).

(20) That the method for determination of weight per unit volume of frozen desserts described in the report of the associate referee be adopted as tentative.

(21) That the official method for detection of gelatin in various dairy products be extended to ice cream by insertion of the following statement under Ice Cream: "Gelatin—Official—Proceed as directed under **29**, using 10 g sample."

(22) That the method for determination of solids in ice cream (*This Journal*, **25**, 616) be made official (final action under suspension of the rules).

(23) That the method for preparation of sample of frozen desserts con-

taining insoluble ingredients (*This Journal*, **25**, 614) be adopted as official (first action).

(24) That studies be undertaken of the quantitative determination of gelatin and other stabilizers in frozen desserts.

(25) That the Rupp test for determination of chlorine in milk be adopted as tentative and studied collaboratively.

EGGS AND EGG PRODUCTS

It is recommended—

(1) That the open Carius method for determination of salt in egg products (*This Journal*, **26**, 352) be adopted as an alternative official method (final action).

(2) That the revision suggested by the referee be made in the official method for determination of cholesterol and the method adopted as official (final action under suspension of the rules).

(3) That studies on methods for determination of added glycerol be resumed.

MICROANALYTICAL METHODS FOR EXTRANEOUS MATERIALS IN FOODS AND DRUGS

It is recommended that a new chapter, entitled "Microanalytical Methods for Extraneous Materials in Foods and Drugs", be added to *Methods of Analysis;* that the new methods submitted by the referees be adopted as tentative; and that studies be continued in this field.

DECOMPOSITION IN FOODS

It is recommended—

(1) That methods for determination of volatile acids be adopted as official for eggs, fish and other marine products, fruits, and vegetables, and that a method for lactic acid be adopted as official for eggs, vegetables, dairy products, and fruits (final action under suspension of the rules).

(2) That further studies be made of chemical criteria of decomposition.

GELATIN, DESSERT PREPARATIONS, AND MIXES

It is recommended that a new chapter, entitled "Gelatin, Dessert Preparations, and Mixes," be added to *Methods of Analysis*, incorporating the recommendations of the referee.

FISH AND OTHER MARINE PRODUCTS

It is recommended—

(1) That the several methods for determination of total solids and ether extract (*This Journal*, **26**, 226–232) be studied collaboratively with a view to selecting the most suitable method for each constituent.

(2) That a method for determination of volatile acids be adopted as official (final action under suspension of the rules).

GUMS IN FOODS

It is recommended—

(1) That the editorial revision of the tentative method for detection of

gums in mayonnaise and French dressing (**55**, p. 477) recommended by the associate referee be adopted.

(2) That the method proposed by the associate referee for detection of gums in soft curd cheeses be adopted as tentative, and that the present tentative method (**127**, p. 305) be dropped.

(3) That the method for detection of agar agar in meat products (*This Journal*, **25**, 93), made official (first action) in 1943 (*Ibid.*, **27**, 90), be adopted as official (final action).

(4) That studies be undertaken on identification and quantitative estimation of gums in soft curd cheese.

(5) That the method submitted by the associate referee for detection of gums in starchy foods be studied collaboratively.

(6) That studies be undertaken on detection of gums in jams, beverage bases, and other fruit products.

(7) That studies be undertaken on detection of gums in cacao products.

(8) That studies of methods for detection of gums in frozen desserts be continued.

MEAT AND MEAT PRODUCTS

It is recommended—

(1) That the editorial changes suggested by the referee in the methods for determination of moisture (**2**, p. 374) and crude fat or ether extract (**6**, p. 375) be adopted.

(2) That Method I for detection of soybean flour in meats (*This Journal*, **19**, 409) be dropped, and that the revised method submitted by the referee be substituted for Method II and adopted as tentative.

(3) That the tentative methods for determination of copper and zinc in gelatin (**65–68**, pp. 387, 388), be dropped.

(4) That the tentative method for determination of arsenic in gelatin (**64**, p. 387) be transferred to Chapter **XXIX**.

(5) That studies on dried skim milk and soybean flour in milk products be continued.

METALS IN FOODS

It is recommended—

(1) That the title of the chapter in *Methods of Analysis, A.O.A.C.*, 1940, now designated "Metals in Foods" be changed to "Residues, Metals, and Other Elements in Foods".

(2) That to par. **3**, p. 392, of the method for determination of arsenic there be added a section as proposed by the referee.

(3) That methods for determination of cadmium be studied further.

(4) That the method proposed by the associate referee for determination of copper be adopted as tentative.

(5) That studies on determination of micro amounts of DDT be undertaken.

(6) That the changes proposed by the associate referee for the tentative method for determination of fluorine be adopted.

(7) That the changes proposed by the associate referee for par. **30** of the official method for determination of lead be adopted as official (final action under suspension of the rules).

(8) That methods for determination of mercury be further studied.

(9) That the method for determination of selenium published in *This Journal*, **26**, 348, be adopted as official (final action).

(10) That the tentative colorimetric method for determination of zinc (**46** and **47**, p. 415) be dropped.

(11) That the method proposed by the associate referee for determination of zinc be adopted as tentative.

MICROBIOLOGICAL METHODS

It is recommended—

(1) That the methods for examination of liquid, dried, and frozen eggs (**1–11**, p. 639) be revised as suggested by the associate referee and adopted as official (first action).

(2) That methods for the preservation of liquid, dried, and frozen eggs for microscopic counts be studied.

(3) That studies be continued on methods for the examination of eggs and egg products, canned vegetables, canned fish, canned meats, canned tomatoes and other acid vegetables and fruit products, sugar, nuts and nut products, and frozen fruits and vegetables, including collaborative work if possible.

MICROCHEMICAL METHODS

It is recommended that study on microchemical methods be continued.

OILS, FATS, AND WAXES

It is recommended—

(1) That the S.P.A. method for determination of unsaponifiable matter presented by the associate referee be adopted as tentative and that further collaborative studies be made.

(2) That the modified Bellier test for peanut oil, used as a sorting test, be adopted as tentative and that collaborative studies on this method be conducted.

(3) That the method for determination of squalene (*This Journal*, **26**, 499), with the changes proposed by the associate referee, be adopted as a tentative method under the heading "Squalene," and that further collaborative studies be made.

(4) That the methods for detection of mineral oil in fats described by the referee be adopted as official (final action under suspension of the rules).

(5) That the referee consult with the Referee on Standard Solutions regarding the proposed change in the method for standard sodium thiosulfate.

(6) That the tentative method for determination of thiocyanogen number (**22**, p. 431) be modified as suggested by the referee, and that the re-

vised constants and equations used with this modified method be accepted.

(7) That the factor 0.0007 used in the correction equation for specific gravity (**5**, p. 423) be changed to 0.00064.

(8) That the official aqueous or alcoholic NaOH method for preparation of the fatty acids used in the titer test (**16**, p. 428) be deleted (official, final action).

(9) That the official titer test (**15–17**, p. 427) be replaced by the modified method published in *This Journal*, **25**, 95 (final action under suspension of the rules).

(10) That the official Baudouin test for detection of sesame oil (**45**, p. 441) be deleted (final action under suspension of the rules).

(11) That the official methods for cottonseed (**50–62**, inclusive, p. 443) be brought up to date in accordance with current regulations of the United States Department of Agriculture.

(12) That the studies on refractometric methods for determination of oil in seeds be discontinued temporarily.

(13) That studies on the improvement of the official method for peanut oil (**42**, 439) and other quantitative methods for the determination of peanut oil be initiated.

PRESERVATIVES AND ARTIFICIAL SWEETENERS

It is recommended—

(1) That studies be continued on methods for determination of benzoate of soda in foods and on methods for determination of the esters of benzoic acids.

(2) That studies be continued on methods for detection and determination of saccharin.

(3) That study of methods for determination of added sulfur dioxide compounds in comminuted meat be continued.

(4) That studies of methods for determination of monochloracetic acid be continued.

(5) That methods for detection and identification of formaldehyde be studied.

SPICES AND CONDIMENTS

It is recommended—

(1) That the tentative method for detection of caramel in vinegar (*This Journal*, **26**, 234) be further studied collaboratively with a view to its adoption as official.

(2) That the tentative permanganate oxidation number (*This Journal*, **27**, 101) be studied collaboratively.

(3) That the official method for determination of specific gravity in vinegar (**58**, p. 478) be dropped (final action under suspension of the rules).

(4) That the official method for determination of formic acid in vinegar (**79**, p. 482) be dropped (final action under suspension of the rules).

(5) That the official method for physical examination of vinegars and the tentative method for spices and added pungent materials (**56, 87,** pp. 478, 483) be combined under one heading, "Organoleptic Examination," and that the combined method as described in the associate referee's report be made official (final action under suspension of the rules).

(6) That the tentative logwood method for determination of free mineral acids in vinegar (**82,** p. 482) be modified as recommended by the associate referee, and that further consideration and study be given to the methods for free mineral acids.

(7) That the tentative method for determination of dextrin in vinegar (**86,** p. 483) be modified as described in the report of the referee.

(8) That the official qualitative test for tartrates (**80,** p. 482) be further studied.

(9) That studies be continued on methods for determination of starch in salad dressing.

(10) That studies be continued on methods for determination of starch in prepared mustard and mustard flour.

(11) That the official method for determination of ash in prepared mustard (**35,** p. 474) be dropped (final action under suspension of the rules).

(12) That studies be made of a suitable method for determination of ash in prepared mustard.

(13) That the official method for determination of volatile and nonvolatile ether extract in spices (**9,** p. 468) be modified by the insertion of the following caution immediately under the heading: "(Not suitable for spices high in volatile oil, such as cloves)."

(14) That the tentative method for determination of total ash in spices (*This Journal,* **24,** 83) be made official (final action under suspension of the rules).

(15) That studies be continued on volatile oil in spices.

REPORT OF SUBCOMMITTEE D ON RECOMMENDATIONS OF REFEREES*

By JOSEPH CALLAWAY (Food and Drug Administration, Washington, D. C.), *Chairman;* J. WALTER SALE, and L. B. RHODES†

ALCOHOLIC BEVERAGES

MALT BEVERAGES, BREWING MATERIALS, AND ALLIED PRODUCTS

It is recommended—

(1) That the revision of methods in Chapter **XIV,** recommended by the Referee on Alcoholic Beverages, be adopted.

(2) That the Referee on Alcoholic Beverages and the Committee on Revision of Alcohol Tables make necessary changes in directions for preparing samples and distillates so that the alcohol tables, as they now ap-

* These recommendations, submitted by Subcommittee D, were approved by the Association. Unless otherwise given, all references are to *Methods of Analysis, A.O.A.C.,* 1940.

† In place of W. Catesby Jones.

pear in Chapter **XLIII**, can be used, and that the revised directions be printed in the sixth edition of *Methods of Analysis, A.O.A.C.*

(3) That the following tentative methods be discontinued: Total acidity (**10,** p. 152); H-ion concentration (**28,** p. 155); moisture (**50, 54,** pp. 162, 163); fat (**51, 55,** pp. 162, 163); and extract (**52, 56,** pp. 162, 163).

(4) That methods for determination of alpha- and beta-amylase of malt be studied.

(5) That a method for determination of essential oil in hops be studied.

(6) That the methods described in the report of the Associate Referee on Cereal Adjuncts for sampling, preparation of sample, physical characteristics, crude fat or ether extract, protein, ash, and crude fiber be adopted as official (first action) and that the study on cereal adjuncts be continued.

(7) That the methods described in the report of the Associate Referee on Brewing Sugars, Sirups, Wort, Spent Grains, and Yeast, be adopted as tentative:

(8) That the Lane-Eynon method (**32–34,** p. 498) and the Munson-Walker method (**37–39,** p. 500) for reducing sugars be incorporated by reference in Chapter **XIV.**

(9) That the methods described in this year's report of the associate referee for determination of total acidity of beer by indicator titration, total acidity of beer by potentiometric tiration to *p*H 8.2, electrometric method for determination of *p*H of beer, and colorimetric method for determination of *p*H of beer be adopted as tentative.

(10) That study of methods for detection of inorganic elements in beer be continued in cooperation with the Referee on Metals in Foods and the Associate Referee on Iron in Cereals.

(11) That the method for detection of turbidity and color in beer described in this year's report of the associate referee be studied further.

(12) That study of the tentative method for determination of carbon dioxide in beer (**19,** p. 152) be continued.

(13) That methods for determination of soluble starches in malt be studied.

(14) That the Milos test for detection of caramel described in this year's report of the Associate Referee on Distilled Spirits be adopted as official for beer (final action under suspension of the rules).

(15) That the tentative method for detection of caramel (**16(f),** p. 252) be modified as suggested in this year's report of the Associate Referee on Distilled Spirits and adopted as tentative for beer.

(16) That study of methods for the analysis of cereal adjuncts be continued.

WINES

It is recommended—

(1) That the revision of Chapter **XV** recommended in this year's report of the Referee on Alcoholic Beverages be adopted.

(2) That study of the spectrophotometric examination of wines be continued.

(3) That study of formol titrations of wines be continued.

(4) That the Milos test for detection of caramel described in this year's report of the Associate Referee on Distilled Spirits be adopted as official for wine (final action under suspension of the rules).

(5) That the tentative method for detection of caramel in foods (**16(f)**, p. 252) be modified as described in this year's report of the Associate Referee on Distilled Spirits and be adopted as tentative for wine.

DISTILLED LIQUORS

It is recommended—

(1) That the following official or official (first action) methods be revised as recommended by the Referee on Alcoholic Beverages and as revised be classed as official (final action under suspension of the rules): Extract (**6**, p. 172); fixed acids (**9**, p. 173); esters (**11**, p. 173); fusel oil (**20**, p. 175); and methyl alcohol (**23**, p. 176).

(2) That the revision of Chapter **XVI** proposed in this year's report of the Referee on Alcoholic Beverages be adopted and that revision of the methods for determination of alcohol be made in the same way as in the case of wine and beer.

(3) That the Marsh tests (**35, 36**, p. 180) be modified by the incorporation of the cyclohexanol tests described in this year's report of the Associate Referee on Distilled Spirits.

(4) That the tentative method for detection of caramel in foods (**16(f)**, p. 252) be modified as described in this year's report of the Associate Referee on Distilled Spirits and adopted as tentative.

(5) That the Milos test for detection of caramel described in this year's report of the associate referee be adopted as official for distilled liquor (final action under suspension of the rules).

(6) That the effect of alcoholic content on *p*H of distilled liquors be further studied.

CACAO BEAN AND ITS PRODUCTS

It is recommended—

(1) That the suggestions of the referee for revision of Chapter **XIX** be adopted.

(2) That the method suggested by the referee for determination of theobromine in cocoa, chocolate liquor, cacao shell, and ground cacao nibs be adopted as tentative.

(3) That the method for determination of pectic acid given in the referee's report be adopted as tentative and further studied.

(4) That work on the determination of lecithin, fat in chocolate products where ordinary extraction is difficult, and on shell be continued, and that work on malt solids be initiated.

(5) That associate referees be appointed to investigate methods for the determination of the cacao constituents in various cacao products and the determination of lactose in the presence of other reducing sugars in chocolate products.

(6) That methods for the determination of dextrose be adopted as tentative.

CEREAL FOODS

It is recommended—

(1) That the recommendations of the referee with respect to revision of certain methods in the chapter on cereal foods be adopted.

(2) That the method described in *This Journal*, **25**, 618, for determination of ash in macaroni products not containing added eggs be adopted as tentative.

(3) That the method for determination of carotene in flour and macaroni products described in *This Journal*, **21**, 339, with the changes in wording recommended by the referee, be adopted as tentative.

(4) That the methods for determination of moisture (vacuum oven method), ash, protein, crude fiber, and ether extract in wheat products be adopted as official, final action for corn, oats, rye, buckwheat, rice, and barley products other than those considered as cereal adjuncts, for which separate methods have been prescribed.

(5) That the method for detection of small amounts of tartrazine in alimentary pastes reported by the Referee on Coloring Matters in Food this year be adopted as a tentative method.

(6) That the methods published in *This Journal*, **27**, 86, 87, for determination of iron and calcium in flour and bread be made official (first action).

(7) That work on rye flour in rye bread and in flour mixtures be continued.

(8) That the tentative method for H-ion concentration, Procedure A, electrometric (*This Journal*, **26**, 109) be made official (first action).

(9) That studies on determination of starch in raw and cooked cereals be continued.

(10) That the tentative method for determination of fat acidity in grain, flour, corn meal, and whole wheat flour (**13**, p. 213; **39**, p. 363) be further studied and also that the relationship of acidity to unsoundness be studied.

(11) That methods for determination of reducing and non-reducing sugars in flour (**19–21**, p. 215) be made official (final action) and that study be made of the application of this method to the determination of sugars in bread and other cereal products.

(12) That work on the detection of benzoyl peroxide in flour be continued.

(13) That work be continued on the official method for determination

of available carbon dioxide in self-rising flour containing added calcium carbonate (**9**, p. 212).

(14) That the method for determination of lactose in bread published in *This Journal*, **25**, 630, be further studied and also that the tentative method for estimation of milk fat in bread (**65**, p. 229) be further studied.

(15) That the method for determination of proteolytic activity of flour and the changes proposed by the associate referee be further studied.

(16) That the methods for determination of water, ash, nitrogen, crude fiber, and ether extract in soybean flour proposed by the referee be adopted as tentative and the subject be studied.

(17) That the method for detection and determination of soybean flour in other cereal products by immunological methods or other similar means be studied.

(18) That study of suitable methods for determination of added inorganic materials in phosphated and self-rising flours be continued.

(19) That the methods published in *This Journal*, **25**, 83–84, for determination of unsaponifiable matter and sterols in noodles be studied to determine whether they are applicable to other foods containing eggs, and that a suitable method for determination of egg albumen in noodles and other foods containing eggs be studied.

(20) That the methods recommended by the associate referee for determination of moisture and fat in fig bars and raisin-filled crackers by acid hydrolysis be adopted as official (first action) and study be continued.

(21) That the modified distillation method (associate referee's report) with benzene or other suitable immiscible solutions for determination of moisture in flour-like products containing sodium bicarbonate be further studied.

(22) That studies of methods for determination of bromates in flour be continued.

(23) That a method for determination of apparent viscosity in flour be studied.

BAKING POWDERS AND BAKING CHEMICALS

It is recommended—

(1) That the proposal for the revision of Chapter **XVII** made by the referee be adopted.

(2) That par. **11**, p. 188, of the method for determination of neutralization value of monocalcium acid phosphate be dropped, and that the revised procedure proposed by the referee be adopted in its place as a tentative method.

(3) That the method proposed by the referee for determining neutralizing value of sodium acid pyrophosphate be adopted as tentative and placed in Chapter **17**, 1945 edition, in connection with other tests for determining neutralizing value.

(4) That a qualitative test for phosphoric acid be added to Chapter

XVII and that the procedure proposed by the referee for this test be adopted as a tentative method.

(5) That the changes in wording suggested by the referee for determination of free tartaric acid (**15**, p. 189) be adopted.

(6) That the statement with respect to purification of phenylhydrazine proposed by the referee be inserted in **23(b)**, p. 190.

(7) That study be made to determine whether the gasometric method for determination of carbon dioxide (**4**, p. 186) is applicable without revision to baking powder containing calcium carbonate used to replace part of the starch.

FLAVORS AND NON-ALCOHOLIC BEVERAGES

It is recommended—

(1) That a collaborative study be made of the reflux method for determination of peel oil in citrus fruit juices and the use of the modified oil separation trap.

(2) That collaborative work be continued on the method for determination of beta-ionone where small amounts are present.

(3) That collaborative studies of the Ripper method for determination of aldehydes in spirits as applied to lemon oils and extracts be continued.

(4) That collaborative studies of the methods proposed by the referee for determination of esters in lemon extract be continued.

(5) That collaborative studies on the Seeker-Kirby method for determination of esters in lemon and orange oils (Dept. Agr. Bull. 241) be continued.

(6) That collaborative studies of extract mixtures containing both isopropyl alcohol and acetone be continued.

(7) That collaborative study of the photometric method for determination of vanillin and coumarin be continued.

(8) That work be continued on the determination of glycerol, vanillin, and coumarin in vanilla and imitation vanilla extracts with special reference to the automatic extraction of vanillin and coumarin.

(9) That the study of emulsion flavors be continued.

(10) That studies on maple concentrates and imitations be continued.

(11) That study of the method for determination of diacetyl published in *This Journal*, **25**, 255, be continued.

FRUITS AND FRUIT PRODUCTS

It is recommended—

(1) That methods for determination of sodium and chloride be further studied.

(2) That studies of polariscopic methods be continued with particular reference to the possible interference of pectin.

(3) That the methods developed by Hartmann for determination of citric, malic, and tartaric acids and published in *This Journal*, **26**, 444, be studied collaboratively.

(4) That the volumetric procedure for P_2O_5 published in *This Journal*, **25**, 441, be adopted as official (first action).

(5) That the reference to the gravimetric procedure for P_2O_5 (**38**, p. 347) be dropped (final action).

(6) That study of the electrometric determination of titratable acidity of fruit acid solutions relatively high in phosphate be continued.

(7) That the following directions be added to the tentative method for determination of titratable acidity by glass electrode (*This Journal*, **25**, 89), following the last sentence of the paragraph "Determination": "The pH values used for interpolation should lie in the range 8.10 ± 0.2."

(8) That "neutralized" distilled water be made an alternative medium for dilution in the official method for determination of total acidity (**24**, p. 341).

(9) That the official phenolphthalein powder, outside indicator method, and official .05% azolitmin solution, outside indicator method, for highly colored solutions be deleted (line 3, **24**, p. 341).

(10) That the extreme dilution method recommended in the report of the referee for precise titration of colored solutions with phenolphthalein inside indicator be adopted as tentative.

(11) That the chloroplatinate procedure for determination of potassium published in *This Journal*, **26**, 326, be adopted as official (final action).

(12) That the cobaltinitrite procedure for determination of potassium published in *This Journal*, **26**, 330, be made official (final action).

(13) That the unified procedure for determination of potassium published in *This Journal*, **26**, 326, be subjected to collaborative study.

(14) That methods for sampling cold-pack fruit be further studied.

(15) That directions for preparation of samples of fruit products on which determinations of volatile and lactic acids are to be made by the method recommended by the associate referee be adopted as official (final action under suspension of the rules).

(16) That the methods for determination of volatile acids and lactic acid proposed by the associate referee be adopted as official (final action under suspension of the rules).

(17) That the procedure for determination of water-insoluble solids described in this year's report of the referee be adopted as a tentative method.

(18) That the tentative method for determination of sodium in plants (**18** and **19**, p. 130) be also adopted as tentative for sodium in fruit products.

(19) That the reference in par. **13**, p. 337, to the method for determination of chlorine in ash be changed to include a reference to Chapter **XII**, **34–37**, pp. 134 and 135.

(20) That the method for the rapid determination of sodium chloride in vegetables and vegetable products, **XXXV**, **25**, be adopted as tentative for the same determination in fruits and fruit products.

(21) That paragraph **2(c)**, p. 335, Preparation of Sample, be amended by the addition of the words "or by disintegrating and mixing in one operation in a mechanical mixer" after the word "thoroly" in the second line.

(22) That the method for determination of ascorbic acid (vitamin C) be adopted as tentative by reference to the method for this determination as given in the chapter on vitamins.

SUGARS AND SUGAR PRODUCTS

It is recommended—

(1) That studies on unfermented reducing substances in molasses be continued.

(2) That study of determination of moisture in sugar products be continued and include methods employing the Brabender tester and the Karl Fisher reagent.

(3) That a study be made of existing data on refractive indices of dextrose and related starch conversion products.

(4) That study of methods for determination of dextrin in honey be continued and that free acid in honey be subjected to collaborative study.

(5) That study of sucrose and ash in molasses be dropped.

(6) That study of methods for determination of resinous glaze on confectionery be continued.

(7) That the Lane-Eynon volumetric method for determination of reducing sugars (**32**, p. 498) be made official (final action).

(8) That the Hammond table for determination of reducing sugars by the Munson and Walker method be made official (final action).

(9) That the method for determination of copper by electrolytic deposition (**44**, p. 502) be made official (final action under suspension of the rules).

(10) That the Jackson-Mathews method (**52**, p. 504) for determination of levulose be made official (first action).

(11) That the volumetric thiosulfate method (**40**, p. ,501) making alternative procedure mandatory be made official (final action).

(12) That modifications of the Steinhoff method[1] for determination of dextrose by means of the copper acetate reagent be adopted as tentative.

(13) That a collaborative study be made of selective methods for determination of dextrose by means of the copper acetate reagent.

(14) That the reducing sugar method of Quisumbing and Thomas be subjected to collaborative study.

(15) That the following methods adopted by the Corn Industries Research Foundation be adopted as tentative: Ash, moisture, protein, acidity, *p*H, and reducing sugars in starch conversion products.

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[1] *Ind. Eng. Chem., Anal. Ed.*, **10**, 699 (1938).

(16) That measurement of color and turbidity in sugar products be subjected to collaborative study.

(17) That the modified Offner method for determination of small quantities of invert sugar in refined sugars be adopted as tentative.

(18) That the editorial changes in Chapter **XXXIV** suggested by the referee be adopted.

WATERS, BRINE, AND SALT

It is recommended—

(1) That the values in pars. **81, 82,** pp. 543–544, be recalculated on the basis of the 1943 atomic weights.

(2) That methods for determination of fluorine in salt be studied collaboratively.

(3) That the methods for determination of iodides in salt (**58,** p. 368, and *This Journal,* **26,** 440) be adopted as alternative official procedures (final action under suspension of the rules).

(4) That studies on boron be continued.

CHANGES IN OFFICIAL AND TENTATIVE METHODS OF ANALYSIS MADE AT THE FIFTY-NINTH ANNUAL MEETING, OCTOBER 25, 26, 1944*

I. SOILS

(1) The tentative method for preparation of sample (**2,** p. 1) was revised.†

(2) In the tentative method for determination of moisture (**3,** p. 1), the words "based upon" were inserted in place of the word "of," following the word "percentage."

(3) The methods for determination of boron (**28, 29,** and **30,** pp. 12 and 13) were dropped.

(4) Methods for determination of total boron and of available boron were adopted as tentative.†

(5) The term "or $Ca(OH)_2$" was inserted following the word "peroxide" in **31(a),** p. 13, and the following references were included: *J. Assoc. Official Agr. Chemists,* **24,** 360 (1941) and *Ind. Eng. Chem., Anal. Ed.,* **5,** 7 (1933).

(6) Par. **52,** p. 17, and the headings "I. Of Humid Regions" and "II. Of Arid and Semi-Arid Regions" were deleted.

II. FERTILIZERS

(1) The method for determination of acid-forming and non-acid-form-

* Compiled by Marian Lapp Otis, *Associate Editor.* Unless otherwise given all references in this report are to *Methods of Analysis, A.O.A.C.,* 1940, and the methods are edited to conform to the style used in that publication.

† The details of the method will be published in the 6th edition of *Methods of Analysis, A.O.A.C.*

ing quality (**59,** p. 37) was revised by changing the temperature in line 11 of **60** from "500–600°" to "575–600°."

(2) To the reagents of the methods for determination of potash (**40,** p. 30) there was added the following reagent: "**(d)** *Acid alcohol.*—Mix 200 ml of 80% alcohol with 20 ml of HCl and cool to room temp." (official, final action).

(3) The following changes were made in **42(a)** of the official method for determination of potash (official, final action, under suspension of the rules):

Line 1.—After words "*Mixed fertilizers,*" add "In a quartz, silica, or Pt dish of ca 100 ml capacity . . . "

Line 5.—Insert before word "maintain" the following sentence: "(The H_2SO_4 may be added after evaporation to dryness and before ignition)."

Line 8.—Change sentence to read, "Treat residue with ca 6 ml of the 80% alcohol," and add the sentence, "The temp. of wash solns should not exceed 30°."

Line 11.—After word "colorless" add the sentence "(75 ml is usually sufficient)."

(4) The title of par. **12(b),** p. 23, of the volumetric method for determination of phosphoric acid was changed to read, "**(b)** Not applicable to superphosphate and other fertilizers that contain sulfate" (official, final action).

(5) Method I for determination of acid-soluble magnesium (**52,** p. 35) was deleted, and Method II (**53,** p. 36) was revised as shown in *This Journal,* **27,** 47, and made official (final action).

(6) The change made in 1941 (*This Journal,* **25,** 49) in **16(b),** p. 24, of the official method for determination of citrate-soluble phosphoric acid (official, first action) was rescinded, and to accomplish the same result the last sentence of par. **17,** "Citrate-soluble and Available Phosphoric Acid" was changed to read, "Subtract citrate-insoluble P_2O_5 from the total to obtain chemically available P_2O_5 in dicalcium phosphate, precipitated bone phosphate, and precipitated bone" (official, final action).

III. SEWAGE‡

IV. AGRICULTURAL LIMING MATERIALS

No additions, deletions, or other changes.

V. AGRICULTURAL DUST‡

VI. INSECTICIDES AND FUNGICIDES

(1) The mercury reduction method for determination of Pyrethrin I in pyrethrin powder (**112, 113,** p. 66) and in pyrethrin extracts in mineral oil (**115, 116,** p. 67) was changed to provide for a reduction temp. of $25° \pm 2°$ for a period of 1 hour and for the following factor: "1 ml of 0.01 *M* KIO_3 = 5.7 mg of Pyrethrin I."

(2) The method adopted as official (first action) in 1941 (*This Journal,*

‡ Subject for future study.

22, 412) for determination of thallous sulfate in ant poisons was adopted as official (final action) for this determination in ant poisons and in rodenticides.

(3) Procedure (5) in the method for determination of total fluorine (*This Journal*, **27**, 74) was deleted, procedures (2) and (4) were revised, and the method was adopted as official (first action).

(4) Section **(b)** of the distillation method for determination of fluorine [**23(b)**, p. 52] was revised.†

(5) An alcoholic caustic method for determination of 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane (DDT) was adopted as tentative.†

(6) The official method for determination of nicotine in tobacco and tobacco extract (**108**, p. 64) was revised to include the following and adopted as official (first action): (a) A statement regarding the applicability of the method to nornicotine; (b) the use of a large excess of strong sodium hydroxide and sodium chloride in the distillation flask was specified in place of "a slight excess of NaOH soln"; and (c) the optional use of a Gooch crucible and drying at 105° for 3 hours.

(7) A fungicidal test was adopted as official (first action).†

VII. CAUSTIC POISONS

No additions, deletions, or other changes.

VIII. NAVAL STORES

(1) The following methods were adopted as official (final action under suspension of the rules): *Rosin.*—Sampling (**1**, p. 82); acid number (**2**, p. 82); saponification number (**4**, p. 82); petroleum benzine-insoluble material (**7**, p. 83); toluene-insoluble material (**5**, p. 83); and ash (**8**, p. 83). *Turpentine Oil.*—Color grading (Lovibond glass method) (**12**, p. 84); specific gravity (**13**, p. 84); refractive index (**14**, p. 86); distillation (**15**, p. 86); and mineral oil in turpentine (**18**, p. 88).

(2) A method for determination of unsaponifiable matter in rosin was adopted as tentative.†

(3) The tentative methods for determination of volatile oils in rosin (**9**, p. 83) and color in turpentine oil (**12**, p. 84) were revised editorially as recommended by the referee.†

(4) The methods for rosin grading (**10, 11**, p. 84) were deleted.

IX. PAINTS, VARNISHES, AND CONSTITUENT MATERIALS

This chapter was deleted.

X. LEATHERS

(1) The method for preparation of sample (**1**, p. 116) was revised.†

(2) The method for determination of insoluble ash (**6**, p. 117) was revised.†

(3) The method for extraction of water-soluble material (**9**, p. 117) was revised.†

(4) The method for determination of soluble non-tannins (**14,** p. 118) was revised.†

XI. TANNING MATERIALS

(1) The method for preparation of soln (**1,** p. 120) was revised.†

(2) The following changes were made in **3, 4,** and **5,** p. 120: **3,** line 3.—20° was changed to 23°; **4,** line 2.—"No. 590, S & S or" was deleted; **5,** line 1.—20° was changed to 23°; **5,** line 3.—20–25° was changed to 23–25°.

(3) The first paragraph of **7** was revised.†

XII. PLANTS

(1) Procedures for determination of carotene in plant tissue were adopted as tentative.†

(2) The method for determination of copper (**20, 21,** pp. 130 and 131) was deleted.

(3) The method for determination of copper published in *This Journal,* **25,** 567, with minor changes suggested by the associate referee, was adopted as tentative.†

(4) The method for determination of iodine (**40,** p. 136) was revised by the associate referee, and the method as revised remains tentative.†

(5) The colorimetric method for determination of iron (**7,** p. 126) was deleted (final action under suspension of the rules).

(6) The colorimetric o-phenanthroline method for determination of iron published in *This Journal,* **25,** 555, was adopted as official (first action).

(7) The titrimetric method for determination of iron (**8,** p. 126) was adopted as official (first action).

(8) The magnesium nitrate method for determination of sulfur (**28,** p. 133) was revised as recommended by the referee, and as revised the method remains official.†

(9) A colorimetric method for determination of boron was adopted as tentative.†

XIII. BEVERAGES (NON-ALCOHOLIC) AND CONCENTRATES

No additions, deletions, or other changes.

XIV. MALT BEVERAGES, SIRUPS AND EXTRACTS, AND BREWING MATERIALS

(1) The editorial changes suggested by the Referee on Alcoholic Beverages for Chapter **XIV** were adopted.

(2) The Referee on Alcoholic Beverages and the Committee on Revision of Alcohol Tables were delegated to make the necessary changes in the directions for preparation of samples and distillation so that the alcohol tables now in Chapter **XLIII** can be used.†

(3) The following tentative methods were deleted: Total acidity of beer (**10,** p. 152); H-ion concentration of beer (**28,** p. 155); moisture in

prepared corn or rice products and corn grits, corn meal and brewers' rice, respectively (**50, 54,** pp. 162, 163); fat in the same products (**51, 55,** pp. 162, 163); and extract in the same products (**52, 56,** pp. 162, 163).

(4) The following methods were adopted as official (first action) for cereal adjuncts: Sampling (**30(a), (b),** and **(c),** p. 155); preparation of sample (**31,** p. 155); crude fat or ether extract (**21,** p. 356); protein (**21, 22, 23,** p. 26, multiply results by 6.25); ash (**5,** p. 212); crude fiber (**25,** p. 357); and physical characteristics.†

(5) The methods applicable to brewing sugars, sirups, wort, spent grains, and yeast recommended by the associate referees were adopted as tentative.

(6) The official Lane-Eynon general volumetric method (**32–34,** pp. 498–499) and the Munson-Walker general method (**37–39,** p. 500) for determination of reducing sugars were incorporated into Chapter **XIV** by reference.

(7) Methods for determination of total acidity of beer by indicator titration, total acidity of beer by potentiometric titration to *p*H 8.2, electrometric method for determination of *p*H of beer, and colorimetric method for determination of *p*H of beer were adopted as tentative.†

(8) The Milos test for detection of caramel was adopted as official for beer (final action under suspension of the rules).†

(9) The tentative method for detection of caramel in foods (**16(f),** p. 252) was modified and adopted as tentative for beer.†

XV. WINES

(1) The editorial revision of this chapter recommended by the Referee on Alcoholic Beverages was adopted.

(2) The Milos test for detection of caramel was adopted as official (final action under suspension of the rules).†

(3) The present tentative method for detection of caramel in foods (**16(f),** p. 252) was modified and adopted as tentative for wine.†

(4) The present tentative method for detection of caramel in foods (**16(f),** p. 252) was modified and adopted as tentative.†

XVI. DISTILLED LIQUORS

(1) The following methods were deleted: Extract (**6,** p. 172); fixed acids (**9,** p. 173); esters (**11,** p. 173); fusel oil (**20,** p. 175); and methyl alcohol (**23,** p. 176), and the methods recommended by the referee were adopted as tentative.†

(2) The revision of Chapter **XVI** proposed by the Referee on Alcoholic Beverages was adopted.

(3) The Marsh tests (**35, 36,** p. 180) were modified by incorporation of the cyclohexanol test proposed by the Associate Referee on Distilled Spirits.†

(4) The Milos test for detection of caramel was adopted as official (final action under suspension of the rules).

XVII. BAKING POWDERS AND BAKING CHEMICALS

(1) The revision of this chapter proposed by the referee was adopted.

(2) Par. 11, p. 188, of the official method for determination of neutralizing value was deleted, and new directions were substituted.†

(3) A qualitative test for phosphoric acid was adopted as tentative.†

(4) The official method for determination of free tartaric acid (15, p. 189) was revised as follows: Lines 8 and 9 were changed to read, "not more than 0.15 ml of 0.1 *N* alkali should be required to neutralize 100 ml of a mixture of 50 ml of $CHCl_3$ and 150 ml of the saturated alcohol."

(5) The following statement with respect to purification of phenylhydrazine was added to line 3, after "redissolved" in 23(b), p. 190: "Unless freshly repurified, phenylhydrazine may not form a crystalline precipitate—in which case it may be purified by distilling under reduced pressure of not more than 60 mm and discarding first distillate until temp. becomes constant."

(6) Methods for the determination of lead and fluorine were adopted as tentative.†

(1) "Cereal Laboratory Methods, A.A.C.C.," 4th ed. (1941).

(2) "Book on Baking Powder," Chemical Publishing Co., New York (1939).

XVIII. COFFEE AND TEA

No additions, deletions, or other changes.

XIX. CACAO BEAN AND ITS PRODUCTS

(1) The editorial revision of this chapter suggested by the referee was adopted

(2) Methods for determination of pectic acid were adopted as tentative.†

(3) A method for determination of dextrose was adopted as tentative.

(4) A method for determination of theobromine in cocoa, chocolate liquor, cacao shell, and cacao nibs was adopted as tentative.

XX. CEREAL FOODS

(1) The revision of this chapter recommended by the referee was adopted.

(2) The method published in *This Journal*, 25, 618, for determination of ash in macaroni products containing added salt was adopted as tentative.

(3) The method published in *This Journal*, 21, 339, for determination of carotene in flour and macaroni products, with the changes recommended by the referee providing for the use of a spectrophotometer or photo-

electric colorimeter and the elimination of Fig. 3, p. 340, was adopted as tentative.

(4) The methods for determination of moisture (vacuum oven method), ash, crude fiber, ether extract, and protein in wheat products (**56, 57, 58, 59, 60,** p. 228) were adopted as official (final action) for the same determinations in corn, oats, rye, buckwheat, rice, and barley products other than those considered as cereal adjuncts.

(5) The method recommended by the referee for detection of small amounts of tartrazine (FD&C Yellow No. 5) in alimentary pastes was adopted as tentative.†

(6) The methods published in *This Journal,* **27,** 86, 87, for determination of iron and calcium in flour and bread were adopted as official (first action).

(7) The method published in *This Journal,* **26,** 109, for determination of H-ion concentration (Procedure A, electrometric) was adopted as official (first action).

(8) The methods for determination of reducing and non-reducing sugars in flour (**19–21,** p. 215) were adopted as official (final action).

(9) The following methods: Moisture (**2,** p. 211), ash (**5,** p. 212), nitrogen (**21, 22,** p. 26), crude fiber (**12,** p 213), and ether extract (**10,** p. 213), were adopted as tentative for soybean flour.

(10) The methods published in *This Journal,* **26,** 306, for determination of moisture and fat in fig bars and raisin-filled crackers, the latter by acid hydrolysis, were adopted as official (first action).

(11) The experimental baking test (**74–78,** p. 231) was deleted.

XXI. COLORING MATTERS IN FOODS

(1) Tests for Yellow AB and Yellow OB were adopted as tentative.†

(2) The following methods for determination of colors in cosmetics were adopted as tentative and are to be published in Chapter **XXI**: Alizarin in madder lake (official); D&C Red No. 39, D&C Green No. 7, and D&C Orange No. 4 (official, first action); and bromine in brominated fluoresceins (official, first action).

XXII. DAIRY PRODUCTS

(1) The method for determination of alkalinity of ash of dried skim milk published in *This Journal,* **24,** 558, was adopted as official (final action under suspension of the rules).

(2) The temperature correction tables recommended by the referee were adopted for publication in the next revision of *Methods of Analysis, A.O.A.C.*

(3) The official methods for determination of total solids in milk (**8** and **9,** p. 270) was revised.† As corrected method **8** was also adopted by reference as applicable to total solids in evaporated milk.

(4) A method for determination of ash in milk was adopted as tentative.†

(5) The official method for determination of ash in milk (**10,** p. 270) was deleted (final action under suspension of the rules).

(6) The official method for determination of ash in evaporated milk was changed to fix a maximum ignition temperature of 550°.

(7) The method for determination of fat in milk (**20,** p. 272) was revised editorially.†

(8) The method for determination of vitamin D in milk (**41,** p. 282) was transferred to the chapter on vitamins.

(9) The method for preparation of sample of evaporated milk (**66(a),** p. 289) was revised and retained as official (final action under suspension of the rules).

(10) In line 2 of par. **99,** p. 298, the reference **98** was added.

(11) The method for detection of mold mycelia in butter (**108,** p. 300) was adopted as official (final action) and transferred to a new chapter on extraneous materials in foods and drugs.

(12) The double dilution method for correcting the volume of precipitate in the optical determination of lactose in milk (**16,** p. 271) was changed to provide for the use of a weighed sample of 65.8 g (2 normal weight) in place of a calculated measured sample, and adopted as official (final action).

(13) The third sentence of the tentative method for determination of coloring matters in ice cream (**135,** p. 306) was changed to read as follows: "Continue as directed under **31** and **105,** and under **XXI,** particularly **3** and **16(b),** for detection of oil-soluble coal tar dyes and annatto," and the method as changed was adopted as official (final action under suspension of the rules).

(14) A method for determination of weight per cent volume of frozen desserts was adopted as tentative.†

(15) The official method for detection of gelatin in various dairy products (**29,** p. 279) was applied to ice cream by the addition of the following statement under the heading "Ice Cream": "Gelatin—Official—Proceed as directed under **29,** using 10 g sample."

(16) The method for determination of solids in ice cream published in *This Journal,* **25,** p. 617, was adopted as official (final action under suspension of the rules).

(17) The method for preparation of sample of frozen desserts containing insoluble ingredients published in *This Journal,* **25,** 614, was adopted as official (first action).

(18) The Rupp test for determination of chlorine in milk, published in U. S. Dept. Agr. Bull. 1114 (1922), was adopted as tentative.†

(19) A method for detection of gums in soft curd cheeses was adopted as tentative.†

(20) The tentative method for detection of gums in soft curd cheeses (**127**, p. 305) was deleted.

(21) A method for determination of lactic acid was adopted as official (final action under suspension of the rules).

XXIII. EGGS AND EGG PRODUCTS

(1) The open Carius method for determination of salt in egg products published in *This Journal*, **26**, 352, was adopted as an alternative official method (final action).

(2) The official method for determination of cholesterol (*This Journal*, **24**, 141) was revised and the method was adopted as official (final action under suspension of the rules).

(3) Methods for determination of volatile and lactic acids were adopted as official (final action under suspension of the rules).

XXIV. FISH AND OTHER MARINE PRODUCTS

A method for determination of volatile acids was adopted as official (final action under suspension of the rules).†

XXV. FLAVORING EXTRACTS

No additions, deletions, or other changes.

XXVI. FRUITS AND FRUIT PRODUCTS

(1) The volumetric method for determination of P_2O_5 published in *This Journal*, **25**, 441, was adopted as official (first action).

(2) The reference to the gravimetric method for determination of P_2O_5 (**38**, p. 347) was dropped (final action).

(3) The following directions were added to the tentative method for determination of titratable acidity by glass electrode (*This Journal*, **25**, 89), following the last sentence of the paragraph "Determination": "The *p*H values used for interpolation should lie in the range 8.10 ± 0.2."

(4) Neutralized distilled water was made an alternative medium for dilution in the official method for determination of total acidity (**24**, p. 341).

(5) The official phenolphthalein powder, outside indicator, and official .05% azolitmin solution, outside indicator (line 3, **24**, p. 341) were deleted.

(6) An extreme dilution method for precise titration of colored solutions with phenolphthalein as inside indicator was adopted as tentative.†

(7) The chloroplatinate procedure for determination of potassium published in *This Journal*, **26**, 326, was adopted as official (final action).

(8) The cobaltinitrite procedure for determination of potassium published in *This Journal*, **26**, 330, was adopted as official (final action).

(9) Directions for preparation of samples of fruit products on which determinations of volatile and lactic acids are to be made were adopted as official (final action under suspension of the rules).†

(10) Methods for determination of volatile and lactic acids were adopted as official (final action under suspension of the rules).†

(11) A method for determination of water-insoluble solids was adopted as tentative.†

(12) The tentative method for determination of sodium in plants (**18** and **19**, p. 130) was adopted as tentative for this determination in fruits and fruit products.

(13) The reference in par. **13**, p. 337, to the method for determination of chlorine in ash was changed to include a reference to Chapter **XII**, **34–37**, pp. 134, 135.

(14) The rapid method for determination of sodium chloride in Chapter **XXXV**, **25**, 521, was adopted as tentative for the same determination in fruits and fruit products.

(15) After the word "thoroly" in line 2 of par. **2(c)**, p. 335, Preparation of Sample, the following words: "or by disintegrating and mixing in one operation in a mechanical mixer," were added.

(16) The method for determination of ascorbic acid (vitamin C) was adopted as tentative by reference to the method for this determination to be given in the chapter on vitamins.

XXVII. GRAIN AND STOCK FEEDS

(1) The method for sampling feeding stuffs adopted as tentative and published in *This Journal*, **27**, 89, was revised as follows and adopted as official (first action): In line 3, "100 bags" was changed to "200 bags" and "10 bags" was changed to "20 bags" in both instances.

(2) In the method for determination of crude protein (**9**, p. 354) the sentence, "In the case of wheat grain multiply the result by 5.7," was deleted.

(3) The method for determination of fat in dried milk products (**24**, p. 357) was adopted as official (final action).

(4) The method for determination of water-soluble acidity (**38**, p. 363) was adopted as official (first action).

(5) The method for detection of rice hulls in rice bran (**44**, p. 364) was adopted as official (first action).

(6) The method for detection of oat hulls in oats and oat feeds (**45**, p. 365) was adopted as official (first action).

(7) The method for detection of grit in poultry and similar feeds (**46**, p. 365) was adopted as official (final action).

(8) The method for detection of bone in meat scrap and tankage (**47**, p. 365) was adopted as official (final action).

(9) The method for determination of calcium oxide in mineral feeds (**48**, p. 365) was adopted as official (final action).

(10) The method for determination of ferrous sulfate (**52**, p. 366) was adopted as official (final action).

(11) The method for determination of copper sulfate (**53**, p. 367) was adopted as official (final action).

(12) The method for determination of potassium iodide (**54**, p. 367) was adopted as official (final action).

(13) The method for determination of soluble chlorine, adopted as official (final action) and published in *This Journal*, **26**, 88, was revised as follows and adopted as official (final action): To the first paragraph under "Procedure" there was added the following sentence: "For mineral and other feeds containing over 10% chlorine, weigh 1 g sample and use 15 ml aliquot (representing one-tenth of total)."

XXVIII. MEAT AND MEAT PRODUCTS

(1) The following editorial changes were made in the methods for determination of moisture (**2**, p. 374) and crude fat or ether extract (**6**, p. 375):

Crude fat or ether extract.—Was changed to read as follows: "Dry 3–4 g of sample as directed under **3**. Grind dried sample with asbestos, sand, or similar substance, and proceed as directed under **XXVII, 22.**"

Moisture.—The following words: "following **6** when dried sample is to be used for further determination," were deleted.

(2) Method I for detection of soybean flour in meat products (*This Journal*, **19**, 409) was dropped.

(3) A method for detection of soybean flour in meat products was substituted for Method II and adopted as tentative.†

(4) The tentative methods for determination of copper and zinc in gelatin (**65–68**, pp. 387–388) were dropped.

(5) The tentative method for determination of arsenic in gelatin (**64**, p. 387) was transferred to Chapter **XXIX.**

(6) The method for detection of agar agar in meat products published in *This Journal*, **25**, 93, was adopted as official (final action).

XXIX. METALS IN FOODS

(1) The title of this chapter was changed to "Residues, Metals, and Other Elements in Foods."

(2) A section relating to the method for determination of arsenic was added to par. **3**, p. 392.†

(3) A method for determination of copper was adopted as tentative.†

(4) The changes in the tentative method for determination of fluorine proposed by the associate referee were adopted.†

(5) The changes recommended by the associate referee for par. **30** of the official method for determination of lead were adopted as official (final action under suspension of the rules).†

(6) The method for determination of selenium published in *This Journal*, **26**, 348, was adopted as official (final action).

(7) The tentative colorimetric method for determination of zinc (**46, 47,** p. 415) was deleted.

(8) A method for determination of zinc was adopted as tentative.†

XXX. NUTS AND NUT PRODUCTS

No additions, deletions, or other changes.

XXXI. OILS, FATS, AND WAXES

(1) The S.P.A. method for determination of unsaponifiable matter was adopted as tentative.†

(2) A modified Bellier test for detection of peanut oil (sorting test) was adopted as tentative.†

(3) The method for determination of squalene published in *This Journal,* **26,** 499, but editorially changed by the referee, was adopted as tentative.†

(4) A qualitative test and quantitative method for detection of mineral oil in fats were adopted as official (final action under suspension of the rules).†

(5) The changes suggested by the referee for the tentative method for determination of thiocyanogen number (**22,** p. 431) were adopted.†

(6) The factor 0.0007 used in the correction equation for specific gravity (**5,** p. 423) was changed to 0.00064.

(7) The official aqueous or alcoholic NaOH method for preparation of the fatty acids used in the titer test (**16,** p. 428) was deleted (official, final action).

(8) The official titer test (**15–17,** p. 427) was replaced by the modified method published in *This Journal,* **25,** 95 (final action under suspension of the rules).

(9) The official Baudouin test for detection of sesame oil (**45,** p. 441) was deleted (final action under suspension of the rules).

(10) The official methods for cottonseed (**50–62,** p. 443) were changed to make them accord with the current regulations of the U. S. Dept. of Agriculture.

(11) The changes suggested by the referee for the iodine absorption number (**18,** p. 429) were adopted.

XXXII. PRESERVATIVES AND ARTIFICIAL SWEETENERS

No additions, deletions, or other changes.

XXXIII. SPICES AND CONDIMENTS

(1) The official method for determination of specific gravity in vinegar (**58,** p. 478) was deleted (final action under suspension of the rules).

(2) The official method for determination of formic acid in vinegar (**79,** p. 482) was deleted (final action under suspension of the rules).

(3) The official method for physical examination of vinegars and the

tentative method for spices and added pungent materials (**56, 87,** pp. 478, 483) were combined under the heading "Organoleptic Examination," and the combined method was adopted as official (final action under suspension of the rules).†

(4) The tentative logwood method for determination of free mineral acids in vinegar (**82,** p. 482) was revised.†

(5) The tentative qualitative test for dextrin in vinegar (**86,** p. 483) was revised.†

(6) The official method for determination of ash in prepared mustard (**35,** p. 474) was deleted (final action under suspension of the rules).

(7) The following sentence was inserted under the heading of the official method for determination of volatile and non-volatile ether extract in spices (**9,** p. 468): "(Not suitable for spices high in volatile oil, such as cloves.)"

(8) The tentative method for determination of total ash in spices published in *This Journal,* **24,** 83, was adopted as official (final action under suspension of the rules).

(9) The tentative method for detection of gums in mayonnaise and French dressing (**55,** p. 477) was revised.†

XXXIV. SUGARS AND SUGAR PRODUCTS

(1) The Lane-Eynon volumetric method for determination of reducing sugars (**32,** p. 498) was adopted as official (final action).

(2) The Hammond table for determination of reducing sugars by the Munson and Walker method was adopted as official (final action; first action, *This Journal,* **27,** 101).†

(3) The tentative method for determination of copper by electrolytic deposition (**44,** p. 502) was adopted as official (final action under suspension of the rules).

(4) The Jackson-Mathews method (**52,** p. 504) for determination of levulose was adopted as official (first action).

(5) In the volumetric thiosulfate method (**40,** p. 501) the alternative procedure was made mandatory and was adopted as official (final action).

(6) Modifications of the Steinhoff method for determination of dextrose by means of the copper acetate reagent were adopted as tentative.†

(7) Methods were adopted as tentative for the determination of ash, moisture, protein, acidity, *p*H, and reducing sugars in starch conversion products.†

(8) The editorial changes in Chapter **XXXIV** suggested by the referee were adopted.

XXXV. VEGETABLES AND VEGETABLE PRODUCTS

(1) The method for physical examination of canned vegetables (**1,** p. 518) was deleted.

(2) The method for determination of volatile acids in canned vegetables (**10,** p. 519) was deleted (final action under suspension of the rules).

(3) The methods for determination of volatile and fixed acidity in tomato products (**28, 29,** p. 527) were deleted (final action under suspension of the rules).

(4) A method for preparation of sample and determination of volatile and lactic acids in tomato and other vegetable products was adopted as official (final action under suspension of the rules).†

(5) A method for determination of moisture in dried vegetables was adopted as tentative.†

(6) The tentative method for determination of sand in tomato products (**21,** p. 521) and the official methods for microanalysis of tomato products (**30–33,** pp. 522–524) were transferred to a new chapter on extraneous material in foods and drugs.

XXXVI. VITAMINS

(1) A spectrophotometric method for determination of vitamin A in fish liver oils was adopted as tentative, and also a table for converting transmittancy values to density values to be used in connection with the method.†

(2) A fermentation method for determination of vitamin B_1 (thiamine) in cereal products and in yeast was adopted as tentative.†

(3) The tentative method for the determination of ascorbic acid (vitamin C) published in *This Journal,* **27,** 102, was amended and adopted as official (first action).†

(4) The modifications of the tentative method for determination of crude carotene (**61,** p. 369) adopted last year and published in *This Journal,* **27,** 108, were changed, and the method was continued as tentative.†

(5) The tentative chromatographic method for determination of carotene published in *This Journal,* **27,** 107, was revised and was continued as a tentative method.†

XXXVII. WATERS, BRINE, AND SALT

(1) The values in pars. **81, 82,** pp. 543–544, were recalculated on the basis of the 1943 atomic weights.

(2) The methods for determination of iodides in salt (**58,** p. 368; *This Journal,* **26,** 441) were adopted as alternative official procedures (final action under suspension of the rules).

XXXVIII. RADIOACTIVITY

No additions, deletions, or other changes.

XXXIX. DRUGS

(1) The tentative method for determination of alkaloids in ergot (**79,** p. 585) was deleted.

(2) The revision of this chapter (primarily editorial) recommended by the referee was adopted.

(3) A method for determination of prostigmine was adopted as tentative.†

(4) The following methods were adopted as official (final action): Acetophenetidin and caffeine (**16,** p. 565); bismuth compounds in tablets (**178,** p. 617); calcium gluconate (**179,** p. 617); effervescent potassium bromide with caffeine (**202,** p. 623); iodine (**183,** p. 618); mandelic acid (**154,** p. 610); oil of chenopodium (**208,** p. 625); phenolphthalein in chocolate preparations (**162,** p. 613); sulfanilamide (**168,** p. 614); and theophylline (**107,** p. 593).

(5) The following microchemical methods for alkaloids and synthetics were adopted as official (final action under suspension of the rules): berberine (**222,** p. 630); cotarnine (**222,** p. 631); narceine (**222,** p. 631); narcotine (**222,** p. 632); physostigmine (**222,** p. 632); stovaine (**222,** p. 632); benzedrine (*This Journal,* **25,** 105); choline (*Ibid.,* **26,** 96); dilaudid (*Ibid.,* **24,** 92); metrazol (*Ibid.,* **25,** 106); sodium sulfapyridine monohydrate (*Ibid.,* **24,** 92); sulfadiazine (*Ibid.,* **26,** 97); sulfathiazole (*Ibid.,* 25, 106); and sulfapyridine (*Ibid.,* **24,** 93).

(6) The following methods were adopted as official (first action): Acetophenetidin, acetylsalicylic acid, and salol (**34,** p. 571); acetylsalicylic acid and phenolphthalein in tablets (**36,** p. 571); aminopyrine, acetophenetidin, and caffeine (*This Journal,* **24,** 91); cinchophen (**142,** p. 607); cod liver oil in emulsions (**207,** p. 625); mercurous iodide in tablets (**193,** p. 621); mercury in ointment of mercuric nitrate (**197,** p. 622); mercury in mercurial ointment (**198,** p. 623); methenamine in tablets (**53,** p. 576); nicotinic acid in tablets and ampuls (**156,** p. 610); nitrites in tablets (**199,** p. 623); pyridium (**165,** p. 613); sampling (**1,** p. 559); sulfonal and trional (**66,** p. 581); theobromine in theobromine calcium (**104,** p. 593); and volatile acidity of tragacanth (**127,** p. 601).

(7) The tentative method for determination of chloroform in mixtures (**130,** p. 602) was deleted.

(8) The tentative method for determination of chloroform and carbon tetrachloride (**132,** p. 603) was adopted as official (final action under suspension of the rules).

(9) The method for determination of ipomea and jalap (*This Journal,* **16,** 84) was reinstated as tentative.

(10) The tentative method for determination of terpin hydrate in elixirs (**63,** p. 579) was deleted.

(11) The method for determination of terpin hydrate and codeine in elixirs (**65,** p. 579) was adopted as official (first action).

(12) The tentative method for determination of cinchona alkaloids (**69,** p. 582) was deleted.

(13) A method for determination of phenothiazine was adopted as tentative.†

(14) A method for determination of ethylaminobenzoate and ethylaminobenzoate in ointments was adopted as tentative.†

(15) A method for determination of barbital and phenobarbital was adopted as official (final action under suspension of the rules) to replace pars. **44** and **45**, p. 574, under the new heading "Barbiturates."†

(16) A method for determination of sedormid was adopted as tentative and a melting point of 194–197° was accepted.†

(17) In the official bromometric method for determination of procaine, Method I (**97**, p. 590), the time of bromination was changed from one-half hour to two hours, and Method III was adopted as official (final action under suspension of the rules).

(18) The iodination method for determination of liquid petrolatum with phenolphthalein (**27**, 54) was adopted as official (first action).

XL. MICROBIOLOGICAL METHODS

The changes proposed by the associate referee in the methods for examination of liquid, dried, and frozen eggs were adopted, and the method was adopted as official (first action).†

XLI. MICROCHEMICAL METHODS

No additions, deletions, or other changes.

XLII. STANDARD SOLUTIONS

The method for preparation and standardization of sodium thiosulfate published in *This Journal*, **25**, 660, was adopted as official (first action).

EXTRANEOUS MATERIALS IN FOODS AND DRUGS

A new chapter, entitled "Extraneous Materials in Foods and Drugs," was added to *Methods of Analysis, A.O.A.C.* The methods were adopted as tentative, and they will be published in *Methods of Analysis, A.O.A.C.*, 1945.

GELATIN, DESSERT PREPARATIONS, AND MIXES

A new chapter, entitled "Gelatin, Dessert Preparations, and Mixes" was added to *Methods of Analysis, A.O.A.C.*, incorporating the recommendations of the referee. Some of the methods were transferred from other chapters, and some were adopted as tentative. This chapter will be published in *Methods of Analysis, A.O.A.C.*, 1945.

COSMETICS

(1) A method for determination of aluminum and zinc in deodorants and anti-perspirants was adopted as tentative.†

(2) A method for determination of 2,5-diaminotoluene in hair dyes and rinses was adopted as official (first action).†

(3) The dichlorimide titration method for determination of 2,5-diaminotoluene reported last year (*This Journal*, **26**, 117, procedure I) was adopted as official (first action).

(4) The method for determination of salicylic acid in hair lotions published in *This Journal*, **25**, 112; **26**, 355, was adopted as official (final action).

(5) The method for determination of alizarin in madder lake published in *This Journal*, **25**, 956; **26**, 242, was adopted as official (final action).

(6) Methods for determination of pure dye in D&C Red No. 39, D&C Green No. 7, and D&C Orange No. 4 were adopted as official (first action).†

(7) A method for determination of bromine in brominated fluoresceins was adopted as official (first action).†

REPORT OF C. A. BROWNE AS REPRESENTATIVE OF THE NATIONAL AGRICULTURAL JEFFERSON BICENTENARY COMMITTEE

The National Agricultural Jefferson Bicentenary Committee was created as the result of Senate Joint Resolution No. 47, which was introduced by Senator Harry F. Byrd of Virginia on April 12, 1943, and of the identical House Joint Resolution No. 114, which was introduced on the same day by Congressman Howard W. Smith of Virginia. The object of the resolution, which was framed after consultation with Secretary Claude R. Wickard and others of the Department of Agriculture, was to carry out, in the celebration of the 200th anniversary of the birth of Thomas Jefferson, appropriate exercises and activities in recognition of Jefferson's services and contributions to the farmers and the agriculture of the Nation. After various debates and amendments, the resolution was passed by Congress and finally approved and signed by the President on December 3, 1943; it thus became Public Law 196 of the 78th Congress, 1st session. This Law designated Secretary of Agriculture Wickard to serve as Chairman of the Committee and authorized him to appoint an appropriate number of members to represent the United States Department of Agriculture, the land-grant colleges (including the colleges of agriculture, experiment stations and agricultural extension services), the national farm organizations, the agricultural press, and other agencies dealing with agriculture.

At the organization meeting, called by Secretary Wickard on February 2, 1944, various committees were appointed, representing the Department of Agriculture, Land Grant Colleges, Experiment Stations, National Farm Organizations, Agricultural Press, the Scientific and Learned Societies and the U. S. Office of Education, for the purpose of making available to the public information concerning the varied activities of Jefferson, the most versatile of all our presidents, with reference to the agricultural practices on his Monticello estate, to his own contributions to agricultural science, and to his general relationship to the agricultural trends of his

time. The information thus gathered by the Committee is made known to the public by lectures, radio talks, articles, bulletins, exhibits, and other means. As a part of the program a pilgrimage was sponsored by the Department to Jefferson's home on last April 13, the two hundred and first anniversary of his birth, to Charlottesville, where appropriate exercises were held under the auspices of the University of Virginia and the Albemarle Chamber of Commerce. Jefferson's home at Monticello and several of his farms were also visited.

Your representative's own work in connection with this program, as a member of the Committee on Department of Agriculture Activities, of the Committee for Scientific and Learned Societies, and of the Special Projects Committee, has consisted in the delivery of two lectures before the Cosmos Club of Washington, one on "Elder John Leland and the Mammoth Cheshire Cheese Which He Presented to Jefferson" and one on "Some of Jefferson's Relations to Agricultural Chemistry," and one lecture before a meeting of scientists of the Bureau of Plant Industry, Soils, and Agricultural Engineering of the Department of Agriculture on "Science and Pseudo-science in Soil Chemistry in the Time of Jefferson." Your representative has also published in Vol. 8 of *Chronica Botanica* an illustrated monograph of 62 pages on "Thomas Jefferson and the Scientific Trends of His Time," and in *Chemical Education* for December 1943 a short article on "Thomas Jefferson's Relation to Chemistry," with a reproduction of Jefferson's own "Report on the Method for Obtaining Fresh Water from Salt," which gives an account of the experiments which he performed in March 1791, at Philadelphia, while he was Secretary of State. This long-forgotten report of Jefferson is a classic for it is the first document of a chemical nature to be published by the United States Government.

The work of the National Agricultural Jefferson Bicentenary Committee is being continued and further report of progress must be deferred to a later date.

Approved.

No formal report was given by the Committee to Confer with the American Public Health Association on Standard Methods of Milk Analysis. The Chairman, A. C. Hunter, has conferred with the A.P.H.A. and will furnish the methods for the chemical examination of milk when these methods are republished by that Association.

REPORT OF COMMITTEE ON ALCOHOL TABLES

The Committee on Alcohol Tables had its first meeting on September 29 at the Bureau of Standards to discuss the criticism of the A.O.A.C. alcohol methods and tables by Cartwright, *Ind. Eng. Chem.*, **14**, 237 (1942).

To assist the Committee in its deliberations it was decided to send out a questionnaire to all laboratories known to use A.O.A.C. alcohol methods, asking which methods they use, how often they use the alcohol tables, and whether the tables could profitably be abbreviated. At a subsequent meeting of the Committee returns from the questionnaires were discussed: 165 questionnaires were sent out and 101 replies were received. The following are some of the results:

14 use the % alcohol by weight A.O.A.C. (1940) **XVI, 3.**

13 use the % alcohol by volume A.O.A.C. (1940) **XVI, 3** and **4.**

82 use the % alcohol by volume A.O.A.C. (1940) **XVI, 5.**

The answers were evenly divided as to whether the omission of every other line would affect the usefulness of Table **19,** p. 689, and also as to whether a formula for interpolation would be desirable. Table **19** was reported as being used over 50 times a year by 54 questionees.

The questionnaire also asked for suggestions on the alcohol method or tables. The general impression from the results was that the tables are satisfactory as they appear in the 1940 edition of the A.O.A.C. *Book of Methods.* The Committee therefore recommended to the A.O.A.C. that the tables be left as in the 1940 edition.

At the A.O.A.C. meeting held on October 25 and 26, the Committee, together with J. W. Sale, Referee on Alcoholic Beverages, was requested to revise these methods so that Tables **19** and **21,** Chapter **43,** would apply.

The Committee and Mr. Sale had two more meetings in November and requested some assistance from Paul W. Simonds and George F. Beyer of the Laboratory Division of the Alcohol Tax Unit, U. S. Bur. Int. Rev. and E. F. Kenney and H. L. Strickland of the U. S. Bureau of Customs. These gentlemen attended the meetings and offered valuable criticisms and suggestions on the proposed methods. The Editor of *The Journal,* W. B. White; the Secretary-Treasurer of the Association, Henry A. Lepper; and L. M. Beacham and R. A. Osborn of the Food and Drug Administration, also contributed valuable suggestions. The Committee gratefully acknowledges this assistance.

The aforementioned criticism of Cartwright referring to the official method for alcohol in the A.O.A.C. *Book of Methods,* 5th ed., p. 172, is as follows:

> In both Methods I and II the volumes of the sample and of the distillate may be determined at temperatures other than 15.56°C. Yet the true percentage by volume at 60°F. of ethyl alcohol in the distillate is multiplied by the inverse ratio of these volumes to obtain the percentage by volume at 60°F. of ethyl alcohol in the sample. The result is in error by an amount depending upon the alcoholic concentrations of the samples and the distillate and the temperature at which the volumes of the sample and the distillate are determined. The calculated data presented in Tables II and III show that this inherent error is very substantial under conditions often prevailing in the determination of alcohol by volume by the A.O.A.C. official method.

The method which the committee has recommended for the forthcoming revision of the *Book of Methods* has been designed to eliminate the errors pointed out by Cartwright. For percentages of alcohol 60 per cent or less by volume, the volumes of the sample and distillate are measured in the same 100 ml. pycnometer, thus insuring accuracy of measurement and also avoiding any multiplication factor between sample and distillate. For percentages of alcohol more than 60 per cent by volume, 50 ml. is distilled to 100 ml., and the measurements of volumes of sample and distillate are made at 15.56°C. At this temperature there will be no error in converting the per cent alcohol in the distillate at 15.56°C. back to the original sample. The alcohol methods in use by the Bureau of Customs and the Alcohol Tax Unit were used as the foundation for the methods which have been adopted jointly by the Committee and the Referee on Alcoholic Beverages. The A.O.A.C. methods as revised will be published in the sixth edition of *Methods of Analysis, A.O.A.C.* in accord with the following recommendation of Committee D, which was approved by the Association at its 1944 meeting:

That the Referee on Alcoholic Beverages and the Committee on Revision of Alcohol Tables make necessary changes in directions for preparing samples and distillates so that the alcohol tables in Chapter 43 can be used, and that the revised directions be printed in the 6th edition of *Methods of Analysis, A.O.A.C.*

Committee on Alcohol Tables
LILA F. KNUDSEN, Food Div., F.&D.A., *Chairman*
DONALD C. GROVE, Drug Div., F.&D.A.
GRACE C. MULLIGAN, Nat. Bur. of Standards
J. L. YOUNG, Alcohol Tax Unit, Bur. Int. Rev.
Referee on Alcoholic Beverages
J. W. SALE

Approved.

No report was given by the Representatives on the Board of Governors of the Crop Protection Institute of the National Research Council.

REPORT OF SECRETARY-TREASURER

HENRY A. LEPPER

A meeting of the Executive Committee was held on Tuesday, October 24, at 1:00 P.M. The members present were G. G. Frary, J. O. Clarke, G. H. Marsh, W. H. Ross, J. W. Sale, and Henry A. Lepper. W. H. MacIntire was designated by the Committee to serve in the vacancy created by the passing of W. Catesby Jones. Miss Lapp, Assistant Secretary, attended, and W. W. Skinner, Secretary-Treasurer Emeritus, was present for part of the session.

The audit of the financial accounts by Lionel Farr of the firm of Snyder, Farr and Company was presented to the Committee. The audit was accepted and approved as follows:

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS
FOR FISCAL YEAR ENDED SEPTEMBER 30, 1944

CASH BALANCE, OCTOBER 1, 1943		
Cash on hand (petty cash)	$ 57.43	
Cash in bank, Lincoln National Bank	3,756.83	
Cash, Montgomery Mutual Building & Loan Association	1,251.93	$ 5,066.19
CASH RECEIPTS		
Sale of *Methods of Analysis*	$3,161.42	
Sale of *Journals*	7,032.19	
Sale of *Wiley's Principles*	22.30	
Sale of advertising	414.70	
Sale of reprints	136.08	10,766.69
For books (ordered for others)		1,305.61
Interest on bonds		358.75
Interest on building association account		56.34
Social security and income taxes deducted		289.40
Miscellaneous		12.95
Total cash		$17,855.93
CASH DISBURSEMENTS		
Salaries	$2,482.50	
Social security taxes	45.00	
Income taxes remitted to Collector	267.70	
Postage	501.27	
Auditing	150.00	
Silver service (Dr. Skinner)	525.00	
Fidelity bonds	10.00	
Refunds	9.25	
Exchange	11.08	
Stationery, programs, announcements	322.10	
Association and meeting expense	241.57	
Check returned	5.00	
Printing and binding:		
Reprints $ 484.05		
Journals 4,339.55	4,823.60	
Miscellaneous	43.03	
Books ordered (purchased for others)	1,306.36	
Total cash disbursements		10,743.46
CASH BALANCE, SEPTEMBER 30, 1944		
Represented by:		
Petty cash on hand	$ 35.66	
Lincoln National Bank, checking account	5,768.54	
Montgomery Mutual Bldg. & Loan Assoc. account	1,308.27	$ 7,112.47

STATEMENT OF INCOME AND EXPENSE
FOR FISCAL YEAR ENDED SEPTEMBER 30, 1944

INCOME		
Sales of *Journals*	$ 8,045.01	
Sales of *Methods of Analysis*	2,774.70	
	$10,819.71	
Less refunds and allowances and discounts	1,249.55	$ 9,570.16
Sales of advertising		414.70
Sales of reprints		136.08
Interest on investments (bonds)		661.75
Interest on building association account		56.34
Total income		$10,839.03
EXPENSES		
Printing and binding	$ 4,776.36	
Salaries	2,482.50	
Postage expense	504.49	
Association and meeting expense	241.57	
Auditing	150.00	
Social security taxes	27.00	
Silver service, Dr. Skinner	525.00	
Fidelity bonds	10.00	
Exchange	11.08	
Stationery, programs, announcements	322.10	
Miscellaneous	43.03	
Total expenses		9,093.13
Excess of income over expenses, to surplus		$ 1,745.90

For many years the Association has had an Auditing Committee from among its members. The function of this Committee dates back to the time when no other auditing of the accounts was made. Since the incorporation of the Association a professional audit has been made each year. It appeared to the Executive Committee that the latter has served to supersede the audit by the membership committee and that such duplication is unnecessary. It was moved, seconded, and carried that at future meetings the audit of the Association's book by a responsible accountant and auditor be submitted to the Executive Committee for adoption and approval with a report to the Association without review by an auditing committee. This year's auditing committee was appointed previous to this meeting as suggested last year and will report later.

Last year the auditor pointed out that the Association might be subject to the District of Columbia Unemployment Compensation Tax. An investigation disclosed that exemption from such tax rested in part on exemption from payment of Federal Income Tax. An affidavit applying for exemption was made to the Bureau of Internal Revenue and was

granted on the grounds that this Association is a scientific organization operated without profit. Subsequently an exemption was received from the authorities of the District of Columbia. The Association, although exempt from payment of income tax, is required to file an annual return, which will be based on the audit.

A review of the Association's books discloses that the purchase of scientific books through its office for individuals has assumed such proportions as to become an undue burden. The Executive Committee approved a motion that the purchase of books for individuals be discontinued, effective immediately.

Last year the Secretary-Treasurer was directed to take an inventory of the stock of *Journals* on hand, and a detailed report on *Journal* copies in the store room in Washington and at the storage of the publishers at Menasha, Wisconsin, was submitted and accepted for the files of the Association.

The chief object of the 1944 meeting of the Association was to perfect the methods in various chapters preparatory to the publication of the sixth edition of *Methods of Analysis*. The interest in the Association's work was demonstrated by the registration of 423 members and visitors.

Approved.

REPORT OF AUDITING COMMITTEE

We, the Committee on Auditing, have examined the report and accounts of the Secretary-Treasurer, and find them balanced and in order. We have compared the Secretary-Treasurer's report with the report of the certified public accountant, Snyder, Farr & Company, which report is in agreement with the Secretary-Treasurer's accounts.

In the report of the certified public accountant we note the only assets to be reviewed are those listed under investments. In lieu of an examination of the bonds and securities held in the safe deposit box at the Union Trust Company, Washington, D. C., the Committee has seen fit to accept the statement of Snyder, Farr & Company relative to these securities.

M. S. ANDERSON
SUMNER C. ROWE

Approved.

REPORT OF COMMITTEE ON NECROLOGY

Five of our members have passed away since our last meeting.

Dr. E. P. Clark died on November 7 last. An obituary was printed in *The Journal* for May of this year.

Our former president, Dr. L. B. Broughton, one of our very influential members and a fine gentlemen in every respect of that word, passed away

early in the year. An obituary appeared in the November, 1944, issue of *The Journal.*

Dr. Benjamin W. Kilgore, long associated with the North Carolina college and station, died January 3 in his 77th year. A native of Mississippi, he received from the Mississippi College the B.S. degree in 1888 and the M.S. degree in 1892, and served there as assistant professor of chemistry in 1888–89 and again as professor of chemistry and State chemist from 1897 to 1899. He came to North Carolina as assistant chemist of the station in 1889, and returned 10 years later to serve as State chemist until 1919. He was appointed director of the station in 1901, director of the extension service in 1914, and dean of the College of Agriculture in 1923, continuing in all these capacities until 1925. He was widely known as a pioneer agricultural leader and writer and was active in the Association of Official Agricultural Chemists, serving as president in 1900.

An obituary will be prepared for *The Journal.*

W. Catesby Jones, a member of our Executive Committee for this year, passed away early this spring. A graduate of the Virginia Polytechnic Institute he was chemist of the fertilizer laboratory and subsequently chief chemist of the Virginia Department of Agriculture from 1913 to 1944. From 1917 to 1919 he was Major in the Chemical Warfare Service. A past chairman (1922) of the Virginia Section of the American Chemical Society, president of the Virginia Academy of Science (1943), an influential member of this Association, he was entitled to many more years of useful life.

As evidence of the depletion of our scientific men by the present war it might be mentioned that Lt. Melvin W. Spruiell was killed in action in France on June 9, 1944. Dr. Spruiell was among the first to answer the call to the armed services at the beginning of the war. He volunteered for service in the paratroops and took part in the Normandy invasion. Dr. Spruiell was a native of Alabama and received his Ph.D. degree at Ohio State College. He entered the service of the U. S. Food and Drug Administration in 1939 and immediately became interested in this Association. He did considerable collaborative work and also was an associate referee.

HERMANN C. LYTHGOE
CHARLES A. BROWNE
J. O. CLARKE

Approved

REPORT OF COMMITTEE ON NOMINATIONS

DR. MACINTIRE: "As you know it has been the policy of this Association for years that members who serve on the Executive Committee come up in due rotation and are nominated for President. In some cases we have deviated from this custom in order to pay particular tribute. This

year happens to be an occasion of that kind. Our present vice-president, J. O. Clarke, has been most gracious in his action that he be allowed to remain in his present capacity during the ensuing year. That has facilitated your Committee in giving recognition to one we have known and loved for years, Dr. W. H. Ross."

Dr. MacIntire moved that Dr. Skinner be privileged to cast the vote for Dr. Ross. The motion was seconded and carried and a rising vote was taken.

Dr. Lythgoe and Dr. Skinner were then appointed to escort Dr. Ross to the chair, and Dr. Lythgoe made the presentation remarks. This was followed by an acceptance speech by Dr. Ross.

The Committee on Nominations then presented the following complete list of candidates:

President: W. H. Ross, Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Md.

Vice-President: J. O. CLARKE, Food and Drug Administration, Chicago 7, Ill.

Secretary-Treasurer Emeritus: W. W. SKINNER, Kensington, Md.

Secretary-Treasurer: HENRY A. LEPPER, Food and Drug Administration, Washington 25, D. C.

Additional Members of Executive Committee: G. H. MARSH, Montgomery, Ala.; L. S. WALKER, Burlington, Vt.; W. A. QUEEN, Washington, D. C.; and GUY G. FRARY, Vermillion, S. Dak.

A unanimous vote was cast for the officers nominated.

W. H. MACINTIRE
A. H. ROBERTSON
R. A. OSBORN

Approved.

REPORT OF COMMITTEE ON RESOLUTIONS

Whereas the 59th Annual Meeting of the Association of Official Agricultural Chemists, which is the second meeting held during a critical period of the war, has been successfully concluded; and

Whereas the large attendance has benefited from the program;

Be it resolved, that the Association express its thanks and appreciation to Dr. Guy G. Frary, for his splendid presidential address and the excellent manner in which he has conducted the meeting; to Mr. J. O. Clarke and Mr. Henry A. Lepper for the able work and service rendered the Association as Vice-President and Secretary-Treasurer; to Miss Marian E. Clapp and all other officers of the Association for valuable services; to all section chairmen for the able and courteous management of their sections; to all committees, referees, associate referees, and collaborators for

their efforts in making this meeting a success; and to all State and Federal units for their interest in sending representatives to this meeting.

Be it further resolved, that our Secretary extend the thanks of the Association to the managers of the Statler Hotel for the use of their rooms and facilities, and for other acts of cooperation.

Be it further resolved, that the Association and members in attendance are particularly gratified and honored to have present at this Convention the oldest living president, elected to office just 50 years ago, who has been so faithful and punctual each year and it is with pleasure that we extend to Dr. H. A. Huston our appreciation and well wishes.

Be it further resolved that—

Whereas, the year 1944 being the one-hundredth anniversary of the birth of our distinguished honorary president, Harvey Washington Wiley, be it

Resolved, first, that the present convention of the Association of Official Agricultural Chemists does hereby express by a rising vote on this twenty-sixth day of October, 1944, its appreciation of the great services that he rendered to our society as a founder, president, and secretary-treasurer. Under his wise and inspiring leadership during a period of 46 years our Association grew in numbers and influence; scientific researches were undertaken of inestimable value to the welfare of our nation; and effective legislation was passed to prohibit the debasement of foods and other agricultural products. And secondly, that this resolution be recorded in the Proceedings of the 59th annual convention of the Association of Official Agricultural Chemists and a copy of it be sent to Mrs. Wiley.

JOHN B. SMITH
W. C. GEAGLEY
H. J. WICHMANN

Approved.

CONTRIBUTED PAPERS

DETERMINATION OF GELATIN IN ICE CREAM

By DONALD MITCHELL, EDWIN H. SHAW, JR., and GUY G. FRARY
(State Chemical Laboratory, University of South Dakota, Vermillion, S. Dak.)

Review of the literature indicates that very little work has been done on the determination of gelatin in ice cream. Ferris[1] removed the casein with acetic acid and then precipitated the gelatin with alcohol. The gelatin was filtered, dissolved in hot water, and determined polarimetrically.

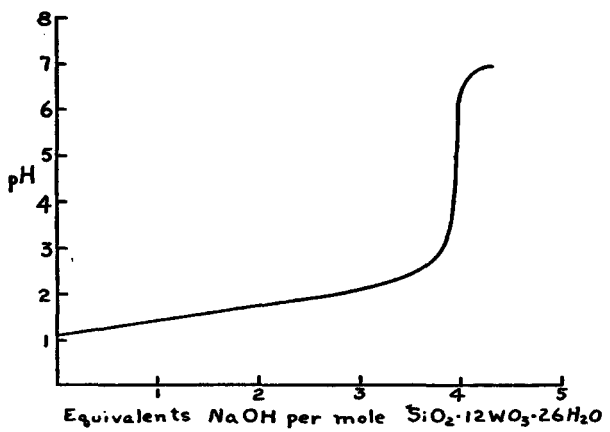

FIG. 1.—TITRATION CURVE OF SILICOTUNGSTIC ACID

Remington and McRoberts[2] modified the method of Ferris by determining nitrogen in the alcohol precipitate as a measure of the gelatin. Farkas[3] removed milk proteins as the insoluble picrates at 40°C., at which temperature gelatin picrate is soluble. On cooling to 8°C., gelatin picrate precipitated, and the nitrogen content of this precipitate was used as a measure of the gelatin. von Fellenberg[4] removed milk proteins with copper sulfate and then precipitated gelatin with phosphomolybdic acid, basing his gelatin determination on the nitrogen content of this precipitate. These methods are not fully satisfactory because of incomplete precipitation of gelatin, poor physical properties of the precipitated gelatin, and incomplete separation of gelatin from the other protein constituents of ice cream.

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[1] *J. Dairy Sci.*, 5, 555 (1922).
[2] *Ind. Eng. Chem.*, 19, 267 (1926).
[3] *Biochem. Z.*, 264, 361 (1933).
[4] *Mitt. Lebensm. Hyg.*, 25, 246 (1934).

TABLE 1.—*Precipitation of 22 different gelatin samples with silicotungstic acid*

SAMPLE NUMBER	GRADE	NITROGEN DIRECTLY ON SAMPLE	NITROGEN ON SILICOTUNGSTIC ACID PRECIPITATE	PRECIPITATION	MOISTURE
		per cent	*per cent*	*per cent*	*per cent*
I	2-A	15.63 15.62	15.40 15.35	98.4	10.61
II	3-A	15.70 15.68	15.58 15.58	99.3	10.36
III	4-A	15.69 15.60	15.63 15.60	99.7	10.66
IV	5-A	15.73 15.73	15.73 15.75	100	10.37
V	6-A	15.84 15.63	15.63 15.63	99.3	10.54
VI	7-A	15.66 15.76	15.75 15.75	100	10.61
726*	50 Bloom	16.40 16.40	15.90 15.90	97.0	4.95
727	75 Bloom	16.47 16.33	15.93 15.98	97.3	8.11
728	100 Bloom	16.08 16.15	15.60 15.75	97.3	9.55
729	125 Bloom	16.47 16.45	16.25 16.25	98.7	8.08
730	150 Bloom	16.22 16.36	15.85 15.85	97.3	9.58
731	175 Bloom	16.30 16.31	16.15 16.08	98.8	9.69
732	200 Bloom	16.57 16.61	16.33 16.33	98.4	7.99
733	225 Bloom	16.64 16.66	16.40 16.50	98.8	7.53
734	250 Bloom	16.05 16.01	15.98 15.93	99.6	11.10
735	275 Bloom	16.78 16.80	16.78 16.68	99.6	7.64

TABLE 1—*Continued*

SAMPLE NUMBER	GRADE	NITROGEN DIRECTLY ON SAMPLE	NITROGEN ON SILICOTUNGSTIC ACID PRECIPITATE	PRECIPITATION	MOISTURE
		per cent	*per cent*	*per cent*	*per cent*
736	125 Bloom	15.42 15.38	15.25 15.33	99.3	11.79
737	175 Bloom	15.91 15.94	15.95 15.90	100	10.11
738	200 Bloom	15.98 15.84	15.95 15.95	100	10.35
739	250 Bloom	15.68 15.60	15.63 15.58	99.8	9.00
706	Marsh-mallow	16.37 16.47	16.43 16.28	99.6	9.12
705	Ice cream	16.55 16.46	16.55 16.43	99.9	8.75
	Averages	16.07	15.93	99.1	9.60

% nitrogen in dry gelatin = 17.78; % commercial gelatin = 6.22 × % nitrogen; and % gelatin on dry basis = 5.63 × % nitrogen.
* Excluded from the average because of low grade and low moisture.

CHOICE OF A PRECIPITANT FOR GELATIN

In quantitative trials with metatungstic acid, metamolybdic acid, phosphotungstic acid, phosphomolybdic acid, arsenotungstic acid, arsenomolybdic acid, borotungstic acid, and silicotungstic acid at *p*H ranging from 1.4 to 4.2, the completeness of precipitation of gelatin varied from 80 to 100 per cent. Silicotungstic acid yielded the best results, ranging from 99 to 100 per cent from *p*H 1.8 to 4.2, with 3.0 as the optimum *p*H for the precipitation of gelatin. An electrometric titration curve of silicotungstic acid (Figure 1) confirmed the choice of *p*H 3.0 as the optimum *p*H for precipitation of gelatin, since silicotungstate solutions are fairly well buffered at this point. Gelatin silicotungstate proved to be a flocculent precipitate, easy to manipulate, whereas the precipitates produced from gelatin and the other complex acids were resinous and sticky.

In order to determine the general effectiveness of silicotungstic acid as a precipitant for gelatin derived from various sources, analyses were conducted on 22 different commercial lots of gelatin. Two determinations of nitrogen were made on each lot, 1 gram samples of gelatin being weighed directly into the Kjeldahl flask. The moisture content of each gelatin sample was also determined. The precipitability of each sample of gelatin with silicotungstic acid was determined as follows:

Duplicate 0.4 gram samples of gelatin were weighed directly into beakers, 25 ml. of cold water was added, and the gelatin was dissolved by heating on the steam bath. The gelatin solutions were cooled to room temperature, bromophenol blue indicator was added, and 3 *N* H_2SO_4 was added dropwise until the indicator changed to a greenish yellow, corresponding to *p*H 2.7–3.2. In order to increase the salt content and facilitate the precipitation of gelatin silicotungstate, 1 gram of Na_2SO_4 was added, and then 30 ml. of the silicotungstic acid reagent (described below in proposed quantitative method for the determination of gelatin in ice cream) was added with stirring, the temperature being below 30°C. The beakers were covered and allowed to stand 6–18 hours. The precipitate was filtered on an ashless filter paper, washed, and introduced into a Kjeldahl flask for nitrogen determination.

The results of the analyses of the 22 samples of commercial gelatin from different manufacturers are given in Table 1.

Only 4 of the 22 gelatin samples showed less than 98 per cent precipitation with silicotungstic acid (Table 1). These 4 samples were the lower bloom grade samples and probably contained some nitrogen due to cleavage products. The average precipitation of all 21 samples with silicotungstic acid was 99.1 per cent. Table 2 compares the results of this work on the average composition of gelatin with those of Remington and McRoberts.[2]

TABLE 2.—*Average composition of commercial gelatin*

SOURCE	NUMBER OF SAMPLES	AVERAGE NITROGEN	AVERAGE H_2O	AVERAGE NITROGEN ON DRY BASIS
		per cent	*per cent*	*per cent*
This work	21	16.07	9.60	17.78
Remington and McRoberts[2]	28	14.84	15.34	17.53

PROPOSED QUANTITATIVE METHOD FOR DETERMINATION OF GELATIN IN ICE CREAM

(Not applicable for gelatin in the presence of other stabilizing agents, especially sodium alginate.)

REAGENTS

(a) *Acetic acid solution.*—Dilute 25 ml of glacial acetic acid to 100 ml.

(b) *Sodium hydroxide solution.*—Approximately 3 *N* NaOH.

(c) *Sulfuric acid solution.*—Approximatly 3 *N* H_2SO_4.

(d) *Solid silver nitrate.*

(e) *Silicotungstic acid solution.*—Dissolve 1.00 gram of $Na_2SiO_3 \cdot 9H_2O$ and 13.93 gram of $Na_2WO_4 \cdot 2H_2O$ in 300 ml of water. Lower the *p*H of the solution by addin g the 3 *N* H_2SO_4 until a drop of the solution turns thymol blue indicator to a defin ite pink color, or approximately to *p*H 1.8. Boil the solution for 10 minutes and let i ts tand at room temperature for at least 2 days. Filter from the fine precipitate which settles out and adjust the *p*H to 3.0 with the glass electrode, being careful not to exceed this *p*H by more than a few tenths of a unit, as alkalinity destroys the reagent. An alternative procedure for adjusting the *p*H is to add to the solution bromophenol blue indicator, then the 3 *N* NaOH in small portions until the solution

turns slightly bluish, and finally the 3 N H_2SO_4 dropwise to change the color back to a greenish yellow, corresponding to a pH of 2.7–3.2. (The silicotungstic acid solution may be prepared directly from commercial silicotungstic acid by dissolving 40 grams in enough water to make a liter and adjusting the pH to 3.0 as described above. In the preliminary portion of this work, the solution was prepared in this way.)

PROCEDURE

Weigh 150 grams of ice cream into a 600 ml beaker and dilute to approximately 400 ml. Heat to 70°–80°C., and transfer to a 500 ml volumetric flask. Add 3 ml of 25% acetic acid and shake vigorously to break the casein precipitate into smaller particles. When the precipitated casein tends to settle readily, cool to 20°C., and dilute to 500 ml. Warm to 35°C. and filter through a linen filter. Cool to 20°C., take a 400 ml aliquot of the filtrate, and evaporate to approximately 225 ml. Cool, and adjust the pH with the glass electrode to exactly pH 6.3 and then boil for 2 minutes. (This pH may seem a little high for the heat coagulation of lactalbumin (isoelectric point pH 4.55–4.8, Woods, *Biochem. J.*, **28**, 2034 (1934)) and lactoglobulin (isoelectric point pH 5.19, Palmer, *Ibid.*, **30**, 961 (1936)), but the filterable quality of the coagulum was much better at pH 6.3 than at any pH corresponding to the isoelectric points.) Transfer while hot to a 300 ml volumetric flask, add enough hot water to fill to the mark, and let cool in air. (An ice bath may be used after it has cooled to 50°C., but not before, as too rapid cooling prevents the coagulated lactalbumin and lactoglobulin from settling out.) When cooled to 20°C., readjust the volume to the mark and filter with suction on a Büchner funnel. Transfer a 250 ml aliquot of the filtrate to a 400 ml beaker and add 1.75 grams of the solid $AgNO_3$ to precipitate residual milk proteins. (Precipitation with silver was necessary since heat coagulation left an average of 0.0124 gram of silicotungstic-acid-precipitable protein nitrogen per 100 grams of ice cream (see Davies, "Chemistry of Milk," pp. 110–112, Van Nostrand (1936).) This amount corresponds to a 0.08% error if expressed as gelatin. Since the usual gelatin percentage is 0.5%, this high residual protein was considered too large. This residual protein was only partly removed by lead acetate, but 92–97% of it was removed by $AgNO_3$ at pH 5.0–6.3. It is very important that the pH of 6.3 that was chosen for the heat coagulation be established accurately, as a higher pH results in precipitation of AgOH, which adsorbs large amounts of gelatin.) Heat and stir with a thermometer until the temperature reaches 70°C. During the $AgNO_3$ precipitation the pH will drop spontaneously to about 5.2. Filter through a folded filter paper and transfer to a beaker, a 200 ml aliquot of the cooled filtrate. Add 3 N H_2SO_4 carefully to adjust the pH to 2.7–3.0, using bromophenol blue as an internal indicator, and add 30 ml of the silicotungstic acid solution adjusted to this same pH to precipitate the gelatin. Stir the mixture and let the precipitate settle for at least 4 hours before filtering. Filter through an ashless filter paper and determine nitrogen on the precipitate, using the Gunning method.[5]

CALCULATIONS

The aliquot system used in this procedure results in an 80 gram sample of ice cream for the gelatin precipitation, as follows:

150 gram sample to 500 ml for the casein precipitation: take 400 ml aliquot, corresponding to 120 grams of ice cream.

120 grams in 400 ml is evaporated to 225 ml and diluted to 300 ml during the heat coagulation: take 250 ml aliquot, corresponding to 100 grams of ice cream.

[5] *Methods of Analysis, A.O.A.C.*, 1940, 26.

100 grams in 250 ml for silver precipitation of residual milk protein: take 200 ml aliquot, corresponding to 80 grams of ice cream in the sample used for precipitation of gelatin with silicotungstic acid.

Since the gelatin is present in solution in milk serum, correct this final aliquot sample for the volumes of milk protein and fat, based on a separate determination of total protein and fat in the original ice cream sample. Assuming that—

(a) Only 95% of the total nitrogen in milk is protein nitrogen;

(b) 0.5% gelatin in ice cream contributes 0.0804 gram of nitrogen per 100 grams of ice cream.

(c) The factor for conversion of milk nitrogen to milk protein is 6.38.

(d) The specific gravity of casein is 1.35 and that of milk fat is 0.92.[6]

The volume correction, V. C., in ml. per 100 grams of ice cream sample follows:

$$\text{V.C.} = \frac{6.38 \times (0.95 \times \%\ \text{nitrogen} - 0.0804)}{1.35} + \frac{\%\ \text{fat}}{0.92}$$

Since the ice cream sample was 150 grams and the first dilution was 500 ml, the actual aliquot sample of ice cream, corrected for volume, is—

$$\text{Aliquot sample, corrected for volume} = 80 \times \frac{500}{500 - 1.5 \times \text{V.C.}}\ \text{grams.}$$

Using the data for the composition of commercial gelatin given in Table 2, the final calculation for per cent dry gelatin in ice cream becomes—

Per cent of dry gelatin in ice cream =

$$\frac{\text{grams nitrogen in silicotungstate ppt.} \times 5.63 \times 100}{\text{aliquot sample, corrected for volume}}$$

TRIAL OF PROPOSED QUANTITATIVE METHOD

The procedure described above was tested on four different samples of ice cream mix to which known amounts of gelatin had been added. The results of duplicate determinations, in Table 3, show satisfactory recovery of known amounts of added gelatin in ice cream mix.

TABLE 3.—*Gelatin in ice cream mix with known amounts of added gelatin*

SAMPLE NO.	GELATIN ADDED	GELATIN FOUND
	per cent	*per cent*
1	0.40	0.41
		0.40
2	0.50	0.50
		0.51
3	0.60	0.61
		0.62
4	0.30	0.29
		0.30

[6] E. R. Garrison, *This Journal*, 22, 489 (1939).

An attempt was made to apply the proposed method to a commercial sample of ice cream containing 0.2 per cent sodium alginate and 0.3 per cent gelatin, but only 0.15 per cent gelatin was recovered in the silicotungstate precipitate. Since sodium aliginate yields a precipitate with silver nitrate, it was thought possible that the gelatin might have been adsorbed on the silver alginate precipitate. To test this hypothesis, 0.6 gram of gelatin and 0.4 gram of sodium alginate were dissolved in 350 ml. of water. The *p*H was adjusted with the glass electrode to 6.3, and 3.0 grams of silver nitrate was added, yielding a precipitate of silver alginate. The mixture was heated to 70°C., using a thermometer as a stirring rod, and then transferred to a 500 ml. volumetric flask, cooled, and diluted to the mark. The solution was filtered, and two aliquots of 200 ml. were precipitated at *p*H 3.0 with silicotungstic acid. Nitrogen was determined on the silicotungstic acid precipitate and on the silver precipitate. A dupli-

TABLE 4.—*Distribution of gelatin nitrogen between the silver alginate precipitate and the gelatin silicotungstate precipitate*

NITROGEN IN SOLUTION—		NITROGEN IN PRECIPITATE WITH—		GELATIN NITROGEN ADSORBED BY Ag ALGINATE
		SILVER NITRATE	SILICOTUNGSTIC ACID	
	gram	*gram*	*gram*	*per cent*
due to gelatin	0.0396			
due to sodium alginate	0.0001			
at *p*H 6.3	0.0397	0.0236	0.0179 0.0170	56
at *p*H 5.0	0.0397	0.0206	0.0197 0.0184	52

cate experiment was run removing the alginate with silver at *p*H 5.0 instead of *p*H 6.3. The results are shown in Table 4. At least half of the gelatin was lost by adsorption on the silver alginate precipitate. Since the presence of sodium alginate invalidates the method, it is desirable to have a short qualitative test for the presence of sodium alginate in ice cream.

PROPOSED QUALITATIVE TEST FOR ALGINATE IN ICE CREAM

Weigh 25 grams of ice cream into a 250 ml. Erlenmeyer flask and add 75 ml of water. Heat to 70°–80°C., add 0.5 ml of 25% acetic acid, stopper, and shake vigorously to break the casein precipitate into small particles. Filter, add 0.4 gram of $AgNO_3$ to the filtrate, and heat to 70°C. to precipitate silver alginate. Transfer to a centrifuge tube and centrifuge for 5 minutes or until clear. Decant and discard the supernatant liquid. Wash the precipitate of silver alginate twice with 100 ml of water at 70°C. by centrifugation and decantation in order to remove all sugars. Transfer the precipitate with 75 ml of 12% HCl to a 300 ml flask and reflux for 15 minutes to convert the alginic acid to furfural. After cooling, transfer the mixture

to a 500 ml distillation flask and steam distil until 10 or 20 ml of distillate containing furfural has been obtained. During the steam distillation, heat the distillation flask with a low flame and regulate the steam source to give a vapor at 103°–105°C. (The presence of furfural in the steam distillate is presumptive evidence of the presence of sodium alginate in the ice cream.) Test for furfural in the distillate as follows:

(a) Touch a few drops of the steam distillate to aniline hydrochloride paper. A pink coloration is a positive test for furfural. Prepare aniline hydrochloride solution by diluting freshly distilled aniline with an equal volume of water and adding concentrated HCl until the solution clears. Preserve this solution in a brown bottle. Aniline hydrochloride paper is prepared by dipping a strip of ashless filter paper into aniline hydrochloride solution and removing the excess liquid by touching it with filter paper.

(b) Add 5 ml of Bial's orcinol reagent (prepared by dissolving 0.5 gram of orcinol in 250 ml of concentrated HCl and adding 13–15 drops of 10% $FeCl_3$ solution) to 10 ml of the steam distillate in a test tube and heat for 10 minutes in a boiling water bath, observing the mixture continuously. A yellowish green coloration, which gradually turns to a green precipitate that settles out on standing, is a positive test for furfural. A blank, consisting of 5 ml of Bial's orcinol reagent and 10 ml of water, should be carried along for comparison.

This qualitative test yielded positive results on a sample of ice cream known to contain 0.2 per cent of sodium alginate when the sample varied from 6 to 25 grams of ice cream. The test should be applied routinely in the analysis of ice cream for gelatin, using the excess serum remaining after the removal of casein and the taking of the first 400 ml aliquot. If sodium alginate is demonstrated to be present, the quantitative determination of gelatin cannot be carried out on the sample.

The qualitative test for sodium alginate yielded negative results on two samples of ice cream known to contain 0.5 per cent of gelatin, but free from sodium alginate.

The method has not been tested on ice creams containing other occasionally used "stabilizers."

SUMMARY

(1) Silicotungstic acid is shown to average 99.1 per cent effectiveness in precipitating 22 different commercial samples of gelatin, being superior in completeness of precipitation and flocculency of precipitate to metatungstic acid, metamolybdic acid, phosphotungstic acid, phosphomolybdic acid, arsenotungstic acid, arsenomolybdic acid, and borotungstic acid.

(2) Analysis of 22 different samples of commercial gelatin indicates that the average percentage of nitrogen in dry gelatin is 17.78 per cent, corresponding to a factor of 5.63 for the conversion of nitrogen to dry gelatin.

(3) A quantitative procedure for the determination of gelatin in ice cream is described. It is based on isoelectric precipitation of casein at *p*H 4.6, removal of heat-coagulable proteins at *p*H 6.3, precipitation of residual milk proteins with silver nitrate at *p*H 6.3, precipitation of gelatin with silicotungstic acid at *p*H 3.0, and determination of nitrogen in the

precipitated gelatin silicotungstate as a measure of the gelatin present in the ice cream. This method is not applicable in the presence of sodium alginate.

(4) A qualitative test for sodium alginate in ice cream is described. It is based on a qualitative test for pentosan (furfural reaction) in the silver alginate precipitate obtained by addition of silver nitrate to casein-free ice cream serum at *p*H 4.6.

NUTRITIVE EVALUATION OF DEFLUORINATED PHOSPHATES AND OTHER PHOSPHORUS SUPPLEMENTS

I. PREPARATION AND PROPERTIES OF THE SAMPLES

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During the past year and a half the authors have analyzed a considerable number of low-fluorine phosphates, both experimental and commercial, for use in animal nutrition experiments† designed to test the assimilability of different phosphates. At the beginning of this work the amount of phosphorus extracted from the sample by dilute hydrochloric acid by an arbitrary procedure (*14*) was taken as a rough measure of the expected feed value of the material. It was realized, however, that some other solvent might yield results in closer accord with those of nutrition tests. Consequently determinations were made of the "solubilities" of a variety of phosphates (including not only those used in the nutrition experiments but also certain related pure compounds and fertilizer materials)| in the solvents regularly used in the evaluation of phosphate fertilizers.

MATERIALS

The sources and supplies of low-fluorine phosphates have recently been discussed by Jacob (*9*). The composition of the investigated samples is given in the following tables, where those materials that have also been used in nutrition tests are indicated. At this juncture, however, it seems desirable to describe the samples at greater length than is possible in the tables, and to give sufficient background and detail of the laboratory preparations to enable anyone that so desires to prepare them.

Pure Compounds.—Pure compounds, in most cases chosen for study because of their expected occurrence in thermally defluorinated phosphates, were as far as possible prepared both by crystallization from the

* Deceased

† The results of the nutrition experiments are reported in the succeeding papers of this series by Bird *et al.* (4) and by Ellis *et al.* (5).

melt, or from glass, to afford well-formed coarse crystals; and by ignition below the melting point of the appropriate acid salt, or hydrolytic material, to yield a finely-divided crystalline material, such as might be encountered in many commercial preparations of defluorinated phosphates. The preparations of pure compounds were put through the 100-mesh sieve. The coarsely crystalline materials were carefully ground by hand with frequent sieving in order to avoid an excessive proportion of "fines." The calcium phosphates to be considered are: metaphosphate in two crystalline modifications and in the vitreous form, pyrophosphate in three crystalline modifications, tricalcium phosphate in two crystalline modifications, hydroxylapatite, and silicocarnotite. The crystalline modifications are designated *alpha, beta,* and *gamma,* respectively, beginning with the form stable at the melting point.

Alpha calcium metaphosphate, α-$Ca(PO_3)_2$, melts at 984°C. and changes reversibly at 963° to the *beta* modification, which melts at 977°C. (metastable) and is apparently the stable form at room temperature (*8*). The melt cools in air to a clear glass. A glass (No. 2247-d) was prepared by heating 50 gram lots of pure, acid-free monocalcium phosphate monohydrate (*8*) first at 125°C. for 1–2 hours to expel water of crystallization† and then at 400°C. for 1–2 hours or until essentially water-free, fusing the anhydrous product at 1000°C., and cooling in air. The glass was ground to pass the 100-mesh sieve and reheated at 900°C. to complete crystallization to the *beta* form (No. 2247-b) as indicated by examination under the microscope. A portion of the preparation of *beta* crystals was inverted to the *alpha* modification (No. 2247-c) by heating at 970°C. until conversion was complete. Another sample of the *beta* modification (No. 2247-a) was obtained by reheating at 600°C. a material previously heated at 400°C. as described above, while still another (without a number) was prepared by igniting a partially dehydrated monocalcium phosphate (acid pyrophosphate) at 400°C.

Alpha calcium pyrophosphate, α-$Ca_2P_2O_7$, melts at 1353°C. and changes reversibly at 1140°C. to the *beta* modification, which is certainly stable down to 400°C. and perhaps also at room temperature (*8*). Although the melt undergoes marked supercooling, it cannot be quenched to a glass. A third form, *gamma* pyrophosphate, is obtained when dicalcium phosphate is heated below about 700°C. Above this temperature it changes rapidly to the *beta* form, whereas at 600°C. it apparently persists indefinitely. That the *gamma* modification is, however, not the stable form at this temperature is indicated by the observation that calcium pyrophosphate dihydrate, $Ca_2P_2O_7 \cdot 2H_2O$, goes to the *beta* form at 600°C. Reagent grades of anhydrous calcium pyrophosphate sold on the market are usually the *gamma* modification. It is, therefore, most probably the form used by Shelling and Asher (*16*) in their nutrition experiments.

† Hydrated monocalcium phosphate on being rapidly heated to temperatures above 140°–150°C. partially fuses in its water of crystallization and often froths over the dish.

Gamma calcium pyrophosphate (No. 2234-a) was prepared by heating a reagent grade of dicalcium phosphate at 600°C. for 2 hours. The other sample of the *gamma* form (No. 2272), an extremely finely-divided material, was supplied by one of the producers of high-grade pyrophosphates. The *alpha* modification (No. 2234-c) was obtained by fusing a portion of No. 2234-a, lowering the temperature to 1200°C., and seeding the undercooled melt with crystals of the *alpha* form. The *beta* form was prepared(1) by heating the *alpha* modification at 1050°C. until completely inverted to coarse crystals of the *beta* modification (No. 2234-b); (2) by igniting 50-gram lots of dicalcium phosphate at 900°C. for 2 hours (No. 1602-b); and (3) by heating $Ca_2P_2O_7 \cdot 2H_2O$ at 600°C. for 2 hours (No. 2256-c). The hydrated calcium pyrophosphate (2256-a) is a material prepared several years ago (*3*) and consisting at that time of amorphous material having the composition $Ca_2P_2O_7 \cdot 4H_2O$, but which had on standing crystallized to the dihydrate.

One sample of calcium acid pyrophosphate (No. 2271) is a commercial salt obtained from a producer of phosphate chemicals. The other two materials (Nos. 2254-b and 2294-b) were prepared by heating lots of 25 and 200 grams, respectively, of pure acid-free monocalcium phosphate monohydrate at 125°C. to expel the water of crystallization, and then stepwise to 300°C. in a muffle furnace until half of the water of constitution had been expelled. The latter materials were probably not homogeneous as to water content.

Alpha tricalcium phosphate melts at 1730°C. (*17*), or perhaps higher,‡ and changes reversibly at 1115° C. to the *beta* modification‡ which is apparently the stable anhydrous form at room temperature. It does not cool to a glass. Tricalcium phosphate prepared by wet methods, herein termed precipitated material, is a hydrate, probably $Ca_3(PO_4)_2 \cdot 2/3H_2O$ (*7*), that possesses an apatite structure (*7*, *12*), which is changed by ignition above 600°C. to the *beta* modification of the anhydrous salt. Two samples of the *alpha* modification (Nos. 2262-a and 2267) were prepared by heating 50-gram lots of precipitated tricalcium phosphate at 900°C. for 1 hour and then at 1400°C. for 1 hour. Portions of the latter two preparations (100-mesh), respectively, were converted to coarse crystals of the *beta* form (Nos. 2262-b and 2268) by heating them in a covered dish at 1000°C. for 3 days. Another sample of the *beta* modification (No. 1173-b) was prepared by igniting No. 1173 at 900°C. for 2 hours. Precipitated material No. 1173 with a Ca to P ratio very near the theoretical value for tricalcium phosphate was prepared several years ago by Jacob *et al.* (*10*), whereas No. 2287 with a ratio close to that for hydroxylapatite is a reagent grade of "tricalcium phosphate" purchased on the market.

Silicocarnotite, $Ca_3(PO_4)_2 \cdot Ca_2SiO_4$, a constituent of basic slag that may also occur in some defluorinated phosphate rocks, melts at 1850°C. (*2*).

‡ Unpublished data of this Bureau.

Sample 2188-b was prepared by heating, repeatedly with intervening grinding to 100 mesh, a mixture of precipitated tricalcium phosphate, very fine cristobalite, and calcium carbonate in the required proportions at temperatures of 900°, 1200°, 1400°C. and finally at 1600°C. until no gain in homogeneity could be attained by further heating at this temperature.

Hydroxylapatite No. 2187-c was prepared by heating 150 grams of a freshly precipitated material, obtained by the addition of 0.5 *M* triammonium phosphate solution to a 0.5*M* solution of calcium nitrate, with 8 liters of water in an autoclave (provided with a stirrer) under a steam pressure of 30 pounds for 6 periods of 15 hours each with intervening changes of liquid. The unusually coarse-grained product was dried in the air. A portion of this material was ignited at 900°C. for 1 hour (No. 2187-b).

The preparation of the calcium iron phosphate (No. 1366-d) is described elsewhere (*13*, Table 4). The aluminum and iron phosphates (Nos. 1236, 1237 and 1250) are the materials used several years ago in agronomic experiments (*3*). The ignited (800°C. for 2 hours) sample of No. 1236, however, was prepared by the authors.

Defluorinated phosphates.—Of the four laboratory preparations of defluorinated superphosphates§ Nos. 2263 to 2265 were obtained by heating 100-gram lots of Florida land-pebble superphosphate No. 2261 in a muffle furnace at 600°, 760° and 1010°C., respectively, whereas No. 2293-b was prepared by heating 100-gram lots of the same superphosphate at 300°C. in a vertical tube furnace provided with a flowing atmosphere of steam that passed up through the charge. The other 16 defluorinated superphosphates were prepared by commercial concerns. Of these six were experimental materials (Table 3). The "a" and "b" samples represent different shipments from the same producer. Also, Nos. 2270, 2317, 2322, and the temperature series, Nos. 2319–2321, were produced in a large cement kiln by the same concern (*15*). In the case of the latter series the temperature of the material discharged from the kiln was 925°, 1010° and 1065°C., respectively. Hydroxylapatite was identified in the material discharged at 1065°C., although *beta* tricalcium phosphate is the predominant phosphate compound present. Nos. 2215-a, 2220-a, 2221-a, 2222-a, and 2229 were ground to pass the 100-mesh sieve, the other samples were 80-mesh materials.

The defluorinated phosphate rocks include *fused rock*, which was defluorinated in the molten condition, and *calcined phosphate*, which was defluorinated at a temperature below the melting point of the charge. In either case the principal phosphate constituent of the products is *alpha* tricalcium phosphate. Sample 2224 was produced experimentally from Tennessee brown-rock phosphate in a shaft furnace by the Tennessee

§ Prepared by E. J. Fox, of this laboratory.

Valley Authority for use as a mineral feed, and Sample 2323 by a feed manufacturer. Calcined phosphate No. 2296 was produced commercially from Florida land-pebble phosphate in a large cement kiln, whereas No. 2253 was prepared by the same process in a pilot plant.

Slags and metaphosphate.—The phosphate slags (Nos. 2227 and 2282) were produced experimentally from ferrophosphorus by different concerns, with and without the removal of the iron component, respectively. The basic slag is a high-grade commercial material that was produced in Europe. The vitreous calcium metaphosphate (No. 2228) is a fertilizer material produced by the Tennessee Valley Authority. A portion of this material was heated at 750°C. for 36 hours to obtain a crystalline product (No. 2235), which was essentially *beta* calcium metaphosphate. The increase in phosphorus content accompanying crystallization was due mainly to the loss of carbon dioxide from admixed calcium carbonate that had been added as a conditioner.

Bone products and natural phosphates.—The bone products are commercial materials that were sold for feed use. The bone char was a spent material from a sugar refinery. The soft phosphates (Nos. 2302 and 2306) are from unworked deposits on Cayman Brac and Swan Island in the Caribbean area. The Florida waste-pond phosphate is a material that was sold for feed use. The other phosphate rocks, as well as the apatite and natural aluminum phosphate, are commercial materials that have been used in laboratory studies in the past (*3, 10, 11*) and were ground to pass the 100-mesh sieve. The other natural phosphates, as well as the bone products, were 80-mesh materials.

Superphosphate and dicalcium phosphate.—The superphosphates were commercial den materials produced about December, 1943. The dicalcium phosphate (No. 1021) is a fertilizer grade of material produced in 1929.

METHODS OF ANALYSIS

Citrate-soluble and citric acid-soluble phosphorus, respectively, was determined with the use of the official methods for available phosphorus in fertilizers (*1*) with such precautions as are necessary when meta- and pyrophosphates are present. In the case of four samples, comprising unignited tricalcium phosphate (Nos. 1173 and 2287), unignited hydroxylapatite (No. 2187-c), and the waste-pond phosphate (No. 2255), the citrate extracts were filtered through Pasteur-Chamberland tubes in order to obtain clear filtrates. The soluble phosphorus was determined directly in the citrate extracts of very insoluble samples, such as the pure metaphosphate compounds, by boiling for several hours an aliquot (reduced to a small volume) with concentrated nitric acid in a flask provided with a reflux condenser, to destroy the citrate and then estimating the phosphorus in the

usual way. Hydrochloric acid-soluble phosphorus was determined by the procedure described in a previous paper (*14*), which involves digesting for 1 hour, with shaking at intervals of 5 minutes, a 1-gram sample with 100 ml. of 0.4 per cent hydrochloric acid at room temperature.

With the exception of experiments designed to show the effect of weight of sample on the amount of extracted phosphorus (Table 1), the extractions were made on 1 gram of sample per 100 ml. of extracting solution.

COMPOSITION AND "SOLUBILITY" OF SAMPLES IN DIFFERENT SOLVENT

Pure Compounds.—The results obtained on pure compounds are given in Table 2. Considering first the behavior towards dilute hydrochloric acid of coarsely crystalline calcium phosphates, such as are obtained by crystallization from a melt or glass, by inversion, or by very slow hydrolysis, it will be noted that the "solubility" of orthophosphates (tricalcium phosphate, hydroxylapatite and silicocarnotite) is high and that of metaphosphate is low, with pyrophosphate falling in an intermediate position. The same generalization holds also when citric acid is the solvent, although the "solubilities" of pyrophosphate and hydroxylapatite are now considerably lower. On the other hand, in neutral ammonium citrate, pyrophosphate is least soluble, being followed in ascending order of "solubility" by metaphosphate, hydroxylapatite, *beta* tricalcium phosphate, *alpha* tricalcium phosphate, and silicocarnotite. Calcium metaphosphate is sufficiently peptized by neutral ammonium citrate to render filtration difficult and slow; and, strangely enough, a hot citrate solution is a very satisfactory cleanser for removing adhering particles of metaphosphate from platinum dishes.

As a rule finely divided and poorly crystallized preparations were more soluble than coarse and well crystallized materials. Noteworthy also are the high "solubilities" in neutral ammonium citrate, of vitreous calcium metaphosphate and most of the aluminum and iron phosphates. The low "solubility" of silicocarnotite in dilute hydrochloric acid is attributed to the formation of a siliceous coating on the partially attacked particles.

Defluorinated phosphates and slags.—The results obtained on defluorinated phosphates, slags, and crude calcium metaphosphate are assembled in Table 3. The results for slags need no comment. The results for the two crude metaphosphates show again the marked difference between the "solubilities" of vitreous and crystalline materials.

In Table 4 are given additional data for a few defluorinated phosphates selected with special reference to the variety of phosphate compounds that may be present in the defluorinated product. The results for the two temperature series of defluorinated superphosphate show that in the range 600° to about 1100°C. the "solubility" of calcium and phosphorus increases markedly up to 1000°C. At the same time the principal phosphate

TABLE 1. *Effect of weight of sample on "solubility" of different types of materials*

SAMPLE NO.	SOURCE OR TYPE OF MATERIAL	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED[a] BY—					
			AMMONIUM CITRATE		2% CITRIC ACID		0.4% HCl	
			0.5 GRAM	1.0 GRAM	0.5 GRAM	1.0 GRAM	0.5 GRAM	1.0 GRAM
		per cent	*per cent of total*		*per cent of total*		*per cent of total*	
	Pure Compounds							
2247-a	Calcium metaphosphate, β-form	30.9 (70.8)	31.4	12.5	—	0.0	1.5	1.1
2234-a	Calcium pyrophosphate, γ-form	24.0 (55.0)	7.2	5.4	11.4	7.7	76.2	48.8
2234-b	Calcium pyrophosphate, β-form	24.0 (55.0)	0.6	0.5	—	2.6	18.1	11.7
2262-a	Tricalcium phosphate, α-form	20.2 (46.3)	91.5	89.4	95.2	92.3	94.3	77.6
	Bone Products and Natural Phosphates							
2233-b	Steamed bone meal	13.4 (30.8)	83.0	61.3	98.0	85.4	98.9	98.2
2245	Bone char	16.0 (36.7)	22.5	15.0	57.9	38.1	94.6	65.0
2255	Florida waste-pond phosphate	9.7 (22.2)	19.8	12.5	45.5	30.1	71.0	69.2
1934	Florida land pebble	13.7 (31.3)	16.4	11.6	33.4	20.1	88.4	57.4
904	Aluminum phosphate, ignited at 900° C.	24.2 (55.4)	40.6	58.3	0.6	2.8	33.6	33.6
	Defluorinated Superphosphates							
2293-b	Laboratory preparation (300°)	9.9 (22.7)	80.4	76.1	54.4	39.9	86.5	75.0
2263	Laboratory preparation (600°)	10.5 (24.0)	77.4	70.1	14.0	11.2	43.4	34.8
2264	Laboratory preparation (760°)	11.4 (26.1)	9.4	6.6	11.3	8.8	82.4	52.9
2265	Laboratory preparation (1010°)	13.1 (30.0)	32.2	25.5	81.9	66.5	87.0	85.2
2215-a	Commercial preparation, exptl.	12.2 (25.2)	18.6	14.3	12.4	10.5	66.6	44.4
2221-a	Commercial preparation	12.6 (28.9)	12.1	11.4	39.8	34.2	48.4	44.4
2220-a	Commercial preparation	12.1 (27.7)	23.8	21.2	50.8	47.0	67.2	59.7
	Defluorinated Phosphate Rock and Slags							
2296	Calcined phosphate	9.0 (20.7)	95.0	95.0	96.4	95.2	99.1	94.2
2224	Fused phosphate rock	12.4 (28.5)	94.1	85.5	93.3	89.2	96.8	78.8
2227	Phosphate slag	13.5 (31.0)	99.8	97.1	97.4	97.9	94.2	68.1
2228	Vitreous calcium metaphosphate	25.7 (58.8)	97.8	96.4	26.2	21.0	57.1	54.2

[a] The ratio of volume of extractant to weight of sample was 100:0.5 and 100:1.0, respectively.

TABLE 2.—*Composition and "solubilities" of pure compounds*

SAMPLE NO.[a]	SOURCE OR TYPE OF MATERIAL	FLUORINE	CaO (Al_2O_3) (Fe_2O_3)	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED BY—		
					NEUTRAL AMMONIUM CITRATE	2% CITRIC ACID	0.4% HCl
		per cent	*per cent*	*per cent*	*per cent of total*	*per cent of total*	*per cent of total*
			Calcium Metaphosphate				
—	Beta form (No. 2254-b ignited at 400°)	0.00	29.2	30.8 (70.6)	27.2	2.7	3.1
2247-a	Beta form ($Ca(H_2PO_4)_2$ ignited at 600°)	0.00	28.8	30.9 (70.8)	12.5	0.0	1.1
2247-b	Beta form (Crystallized from glass)	0.00	28.9	30.9 (70.8)	19.1	0.1	0.7
2247-c	Alpha form (Crystallized from β-form)	0.00	28.9	30.9 (70.8)	10.4	0.0	0.7
2247-d	Vitreous form	0.00	29.0	30.9 (70.8)	98.8	4.5	24.0
			Calcium Pyrophosphate				
2271	Acid salt (Sold on market)	0.00	25.4	26.9 (61.6)	97.4	100.0	100.0
2254-b	Acid salt	0.00	26.8	28.2 (64.7)	95.0	93.0	100.0
*2294-b	Acid salt	0.00	26.5	28.9 (66.1)	100.0	90.9	97.7
2256-a	Dihydrate	0.00	38.2	21.0 (48.1)	77.5	71.5	100.0
*2272	Gamma form (Sold on market)	0.01	44.1	23.9 (54.8)	17.2	19.2	89.5
*2234-a	Gamma form ($CaHPO_4$) ignited at 600°	0.00	44.5	24.0 (55.0)	5.4	7.7	48.8
2256-c	Beta form (No. 2256-a ignited at 600°)	0.00	43.6	24.0 (55.0)	8.0	11.8	76.6
*1602-b	Beta form ($CaHPO_4$ ignited at 900°)	0.00	44.7	24.0 (55.1)	2.7	8.3	44.1
*2234-b	Beta form (Crystallized from α-form)	0.00	44.5	24.0 (55.0)	0.5	2.6	11.7
2234-c	Alpha form (Crystallized from melt)	0.00	44.5	24.0 (55.0)	7.1	13.6	47.2

TABLE 2.—*Continued*

SAMPLE NO.[a]	SOURCE OR TYPE OF MATERIAL	FLUORINE	CaO (Al_2O_3) (Fe_2O_3)	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED BY— NEUTRAL AMMONIUM CITRATE	2% CITRIC ACID	0.4% HCl
		per cent	*per cent*	*per cent*	*per cent of total*	*per cent of total*	*per cent of total*
			Tricalcium Phosphate and Silicocarnotite				
1173	Precipitated material	—	49.1	18.2 (41.7)	66.0	98.2	90.9
1173-b	Precipitated material after ignition	—	53.2	19.7 (45.2)	61.7	90.8	84.2
*2287	Precipitated material	—	51.7	17.6 (40.2)	48.7	92.1	84.8
2262-b	Beta form (Crystallized from α-form)	0.00	53.7	20.2 (46.3)	39.5	64.9	76.8
*2268	Beta form (Crystallized from α-form)	0.13	53.4	19.6 (44.9)	41.9	76.0	83.6
2262-a	Alpha form	0.00	53.7	20.2 (46.3)	89.4	92.3	77.6
*2267	Alpha form	0.02	53.3	19.7 (45.1)	71.0	75.0	75.9
2188-b	Silicocarnotite	0.00	58.0[b]	12.7 (29.0)	95.9	100.0	52.8
			Hydroxylapatite				
2187-c	Precipitated material, air-dried	0.00	54.1	18.1 (41.4)	24.3	58.1	77.6
2187-b	Precipitated material, ignited at 900°	0.00	55.4	18.4 (42.1)	21.8	58.1	78.4
			Aluminum and Iron Phosphates				
1366-d	Calcium iron phosphate	0.00	9.8[c]	20.0 (45.9)	84.0	7.1	28.4
*1237	Ferric phosphate, air-dried	—	(41.8)	14.3 (32.8)	100.0	11.7	20.2
1250	Ferric phosphate, No. 1237 ignited at 800°	—	(55.7)	19.1 (43.7)	30.5	3.8	5.2
*1236	Aluminum phosphate, air-dried	—	(26.7)	16.0 (36.5)	100.0	37.3	95.5
1236	Aluminum phosphate, ignited at 800°	—	(39.6)	23.6 (51.4)	100.0	14.5	68.5

[a] Materials used in feeding tests are marked with an asterisk.
[b] Contains 12.4% of SiO_2.
[c] Contains 24.9% of Fe_2O_3.

TABLE 3.—*Composition and "solubilities" of thermally defluorinated phosphates and of slags and metaphosphate glass*

SAMPLE NO.[a]	SOURCE OR TYPE OF MATERIAL	FLUORINE	CaO	SO_3	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED BY—		
						NEUTRAL AMMONIUM CITRATE	2% CITRIC ACID	0.4% HCl
		per cent	*per cent*	*per cent*	*per cent*	*per cent of total*	*per cent of total*	*per cent of total*
		Defluorinated Superphosphate						
*2293-b	Laboratory preparation (300°)	0.21	31.5	33.5	9.9 (22.7)	76.1	39.9	75.0
*2263	Laboratory preparation (600°)	0.06	34.0	32.8	10.5 (24.0)	70.1	11.2	34.8
*2264	Laboratory preparation (760°)	0.01	37.2	26.5	11.4 (26.1)	6.6	8.8	52.9
*2265	Laboratory preparation (1010°)	0.02	42.8	15.6	13.1 (30.0)	25.5	66.5	85.2
2319	Commercial preparation (925°)	0.12	43.1	23.5	12.3 (28.2)	8.4	41.2	49.0
2320	Commercial preparation (1010°)	0.07	43.4	18.6	13.0 (29.7)	26.1	68.2	82.5
2321	Commercial preparation (1065°)	0.08	48.6	7.3	14.5 (33.3)	46.2	76.4	84.2
*2229	Commercial preparation, exptl.	0.40	39.6	28.2	11.8 (27.0)	15.9	14.2	33.5
2215-a	Commercial preparation, exptl.	0.04	37.6	28.7	11.0 (25.2)	14.3	10.5	44.4
*2322	Commercial preparation, exptl.	0.10	39.1	25.3	11.8 (27.0)	9.3	20.0	42.8
*2215-b	Commercial preparation, exptl.	0.05	41.0	22.1	12.2 (27.9)	14.7	45.9	56.3
*2221-a	Commercial preparation	0.01	37.7	20.8	12.6 (28.9)	11.4	34.2	44.4
*2221-b	Commercial preparation	0.02	38.5	19.5	13.4 (30.8)	9.0	38.7	52.4
*2220-a	Commercial preparation	0.24	42.2	20.4	12.1 (27.7)	21.2	47.0	59.7
*2220-b	Commercial preparation	0.21	38.6	26.2	11.4 (26.1)	18.6	17.3	46.3
*2326	Commercial preparation	0.18	37.4	—	11.4 (26.2)	17.7	16.8	46.7
*2222-a	Commercial preparation, exptl.	0.01	40.9	19.2	12.7 (29.0)	14.4	54.1	63.2
*2222-b	Commercial preparation, exptl.	0.02	40.3	19.3	12.8 (29.3)	14.9	52.8	63.2
*2270	Commercial preparation	0.09	44.1	19.7	13.1 (29.9)	21.5	62.1	76.4
*2317	Commercial preparation	0.12	—	—	12.4 (28.3)	13.0	46.4	58.0

TABLE 3.—*Continued*

SAMPLE NO.[a]	SOURCE OR TYPE OF MATERIAL	FLUORINE	CaO	SO_3	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED BY—		
						NEUTRAL AMMONIUM CITRATE	2% CITRIC ACID	0.5% HCl
		per cent	*per cent*	*per cent*	*per cent*	*per cent of total*	*per cent of total*	*per cent of total*
		Defluorinated Phosphate Rock						
*2323	Fused rock, exptl.	0.41	34.7	—	10.5 (24.1)	64.6	74.7	88.2
*2224	Fused rock, exptl.	0.02	40.4	—	12.4 (28.5)	85.5	89.2	78.8
2253	Calcined phosphate exptl.	0.10	26.5	—	8.9 (20.3)	98.6	91.0	94.2
*2296	Calcined phosphate	0.02	30.4	—	9.0 (20.7)	95.0	95.2	94.2
		Slags and Metaphosphate Glass						
1107	Basic slag	0.03	51.4	—	10.2 (23.4)	75.5[b]	73.6[b]	48.2
*2227	Phosphate slag, exptl.	0.01	35.9	—	13.5 (31.0)	97.1	97.9	68.1
*2282	Phosphate slag, exptl.	0.04	38.1[c]	—	8.5 (19.4)	48.9	68.0	89.3
*2228	Calcium metaphosphate, vitreous	0.39	24.6	—	25.7 (58.8)	96.4	21.0	54.2
*2235	Calcium metaphosphate, β-form[d]	0.08	26.0	—	27.1 (62.1)	35.8	2.1	5.9

[a] Materials used in feeding tests are marked with an asterisk.
[b] Result given by Jacob *et al.* (*10*).
[c] Contains 35.8% of Fe_2O_3.
[d] Prepared by crystallization from glass (No. 2228).

compound in the product changes from meta- to pyrophosphate and then to tricalcium phosphate. At temperatures above 1000°C. apatite tends to form. The high "solubility" of the material prepared at 300°C. is due to an acid phosphate that owes its presence to the incomplete removal of water from the original monocalcium phosphate. Metaphosphate was not identified in Sample 2263, although this material should be expected to contain

TABLE 4.—*Compounds found in defluorinated phosphates*

SAMPLE NO.	MATERIAL	CONSTITUENTS EXTRACTED BY 0.4% HYDROCHLORIC ACID		CRYSTALLINE COMPOUNDS IDENTIFIED IN SAMPLE[a]
		Ca	P	
		per cent of total		
2293-b	Defluorinated superphosphate (300°)	89.1	75.0	only An
2263	Defluorinated superphosphate (600°)	48.0	34.8	only An[b]
2264	Defluorinated superphosphate (760°)	72.3	52.9	β-C_2, An
2265	Defluorinated superphosphate (1010°)	90.3	85.2	β-C_3, An
2319	Defluorinated superphosphate (925°)	64.5	49.0	β-C_2, β-C_3, An
2320	Defluorinated superphosphate (1010°)	88.8	82.5	β-C_3, An
2321	Defluorinated superphosphate (1065°)	81.8	84.2	β-C_3, A
2220-b	Defluorinated superphosphate	53.3	46.3	only An
2221-b	Defluorinated superphosphate	70.5	52.4	β-C_1, An
2224	Defluorinated phosphate rock	73.8	78.8	α-C_3, abundant glass
2296	Defluorinated phosphate rock	82.9	94.2	α-C_3, SiO_2 (cristobalite), little glass
2323	Defluorinated phosphate rock	86.6	88.2	α-C_3, abundant glass

[a] Metaphosphate, pyrophosphate, and tricalcium phosphate are indicated by the symbols C_1, C_2, and C_3; hydroxylapatite by A and anhydrite ($CaSO_4$) by An.
[b] Beta calcium metaphosphate was identified in an experimental sample (No. 2229) from a commercial concern.

it. The reason for the non-observance of metaphosphate in many such materials, now under study, will be discussed in another place (*6*).

Bone products and other phosphates.—The results for bone products, natural phosphates, superphosphate, and dicalcium phosphate (Table 5) need no comment other than to direct attention to the order of "solubility," which is high for bone meal, medium to high for phosphate rocks (with the exception of the sample from Cayman Brac), and low for the natural aluminum phosphate.

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TABLE 5.—*Composition and "solubilities" of bone products, natural phosphates, superphosphate, and dicalcium phosphate*
(Results are on basis of air-dried material.)

SAMPLE NO.[a]	SOURCE OR TYPE OF MATERIAL	MOISTURE AT 105°	FLUORINE	CaO (Al_2O_3)	CaO (Fe_2O_3)	TOTAL $P(P_2O_5)$	PHOSPHORUS EXTRACTED BY— NEUTRAL AMMONIUM CITRATE	2% CITRIC ACID	0.4% HCl
		per cent	*per cent*	*per cent*		*per cent*	*per cent of total*	*per cent of total*	*per cent of total*
				Bone Products					
*2233-b	Steamed bone meal	2.67	0.06	40.8		13.4 (30.8)	61.3	85.4	98.2
2248	Steamed bone meal	2.29	0.03	37.0		12.2 (27.9)	61.4	91.5	100.0
2245	Bone char	0.38	0.09	52.4		16.0 (36.7)	15.1	38.1	65.0
				Phosphate Rock					
985	Curacao Island	0.39	0.70	49.7		16.8 (38.4)	17.1	35.6	67.3
1934	Florida land pebble	0.51	3.75	45.2		13.7 (31.3)	11.6	20.1	57.4
1936	Tennessee brown rock	1.13	3.52	44.6		14.2 (32.5)	7.1	18.2	56.0
905	Fluorapatite	0.10	3.26	52.4		17.6 (40.3)	2.3[b]	5.4	30.7
2255	Florida waste-pond phosphate	3.05	1.78	24.6		9.7 (22.2)	12.5	30.1	69.2
*2306	Soft phosphate from Swan Island	10.75	0.18	(10.7) 9.6	(6.1)	7.0 (16.1)	43.2	47.6	49.5
*2302	Soft phosphate from Cayman Brac	3.88	0.13	(23.9) 9.7	(11.4)	7.3 (16.8)	3.1	4.8	7.4
				Natural Aluminum Phosphate					
*904	Connetable Islands	22.58	0.05	(28.6)	(3.4)	18.5 (42.3)	8.9	0.6	2.0
904	Connetable Islands, ignited at 800°	—	—	(37.3)	(4.5)	24.2 (55.4)	76.3	2.8	33.6
				Superphosphate and Dicalcium Phosphate					
2261	Florida land-pebble superphosphate	—	1.46	28.9		9.1 (20.8)	99.8	87.8	94.6
2280	Tennessee brown-rock superphosphate	—	1.53	26.8		8.6 (19.7)	94.6	72.0	87.5
1021	Fertilizer-grade dicalcium phosphate	—	3.96	36.7		17.6 (40.2)	82.9[b]	75.6	94.3

[a] Materials used in feeding tests are marked with an asterisk.
[b] Result obtained by Jacob *et al.* (*10*).

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NUTRITIVE EVALUATION OF DEFLUORINATED PHOSPHATES AND OTHER PHOSPHORUS SUPPLEMENTS

II. DEFLUORINATED PHOSPHATES AS PHOSPHORUS SUPPLEMENTS FOR CHICKS*

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Information on supplies of phosphorus supplements in relation to the need for them has been summarized by Jacob (*1*). The resulting conclu-

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sion is that manufacture of defluorinated phosphate rock and expanded production of defluorinated superphosphate offer the greatest hope of overcoming the deficit in supply of low-fluorine phosphorus carriers suitable for feeding. That the phosphorus of defluorinated superphosphate can be utilized by chickens has been demonstrated by Carver and Evans (*2*), by Evans and Carver (*3*), and by Nowotarski and Bird (*4*). Their experiments, however, were not designed to compare the availability of the phosphorus of this material with that of the phosphorus from other sources.

In each of these studies, only one sample of superphosphate was used; and the levels fed in the Washington experiments (*2*, *3*) were too few, and in the Maryland Experiments (*4*) too high, to establish the availability of the phosphorus. In the bone ash figures published by Carver and Evans (*2*) there is some indication that phosphorus from defluorinated superphosphate fed as 0.7 per cent of the diet might be less available than from the same level of bonemeal, but these authors did not conclude that there was any difference. Although the availability to chickens of phosphorus in defluorinated superphosphate has not been reported to be inferior to that of other phosphates, there are reports of low phosphorus availability of defluorinated superphosphate fed to rats and swine. These are reviewed by Ellis, *et al.* (*5*).

In experiments reported by Matterson, *et al.* (*6*), raw and fused rock phosphate were at least as effective as tricalcium phosphate in providing material for bone growth in chickens. Each supplement was fed at one level, which brought the phosphorus content of the diet to 0.67 per cent. Small differences in availability might not be revealed at this level. Vitreous calcium metaphosphate at an equivalent level was a less effective supplement. Results in good agreement with these were obtained by McConnell, *et al.* (*7*), who compared raw and fused rock phosphate, calcium metaphosphate, and bone meal in quantities that raised the phosphorus level to 0.7 per cent of the diet.

PROCEDURE

Six samples of defluorinated superphosphate and one each of defluorinated phosphate rock, phosphate slag, calcium pyrophosphate (beta), and vitreous calcium metaphosphate were tested. Each sample was fed to chicks in one or more of the laboratories taking part in this study, in order to test its availability. The results of determinations of calcium and phosphorus in these samples are summarized in Table 1.

Additional analytical data on the same samples have been summarized by Hill, *et al.* (*8*). With the exception of superphosphate "C," all samples, together with the appropriate analytical data, were supplied by the Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture. Sample "C" and analytical data for it were furnished

by L. E. Bopst, State Inspection Service, College Park, Maryland. All samples may be considered as commercial materials with the exception of the calcium pyrophosphate, which was made in the laboratory; and superphosphates 2215B and 2229, which were prepared experimentally by commercial concerns.

The composition of the basal diets is shown in Table 2, together with the results of analyses for calcium and phosphorus. The supplements

TABLE 1.—*Calcium and phosphorus content of supplements*

	CALCIUM	PHOSPHORUS
	per cent	*per cent*
$Ca_3(PO_4)_2$, 2287	36.92	17.58–18.30*
Bonemeal (W. Va.) 2233 B	29.10	13.43
Defluorinated superphosphates		
2215B	29.27	12.20
2220B	27.55	11.40
2221A	26.89	12.61
2221B	27.48	13.46
2229	28.25	11.77
"C"	25.00	10.50
Defluorinated phosphate rock		
2224	28.85	12.44
Phosphate slag		
2227	25.63	13.52
$Ca_2P_2O_7$ (beta) 1602B	31.92	24.02
Ca metaphosphate, vitreous, 2228	17.54	25.65

* Two samples taken for analysis at different times.

tested were added to these diets at the levels indicated in Table 3. In the U.S.D.A. experiments, levels were chosen which were equivalent in phosphorus content to 1 and 2 per cent of bone meal. In West Virginia diet 1, the supplements replaced equal quantities of ground barley; in all the other diets they replaced equal quantities of ground corn except that in the second West Virginia experiment the 2 per cent of meat scrap replaced soybean oil meal. In the Maryland and the West Virginia experiments, the calcium and phosphorus levels calculated for all the supplemented diets were verified by determinations of calcium and phosphorus in these diets. Negative control groups (those fed the unsupplemented basal diets) were employed in the Maryland and the West Virginia experiments. In the Maryland experiments positive control groups were fed three levels of tricalcium phosphate (C.P.) and in the U.S.D.A. and the West Virginia experiments they were fed two levels of bonemeal.

Each experimental group consisted, in the first Maryland experiment, of 15 New Hampshire chicks; in the second Maryland experiment of 20 White Plymouth Rock chicks; in the U.S.D.A. experiment of 25 Rhode

Island Red Chicks; and in the first West Virginia experiment of 13, and in the second, of 15 White Leghorn chicks. In the Maryland and the West Virginia experiments the chicks were weighed when three weeks old and killed, and one tibia was removed from each for bone ash determination. In the U.S.D.A. experiment individual weights were taken at weekly in-

TABLE 2—*Basal diets*

	MD.	WEST VIRGINIA ONE	WEST VIRGINIA TWO	U.S.D.A.
Ground yellow corn	45.63	—	38.26	28.8
Ground wheat	15	15	15	25
Ground barley	—	45.78	—	—
Ground oats	10	10	10	—
Alfalfa meal	7.5	7.5	5	8
Soybean oil meal	—	5	27.7	32
Corn gluten meal	5	—	—	—
Casein	8	8	—	—
Dried skim milk	5	5	—	—
Fish meal	—	—	—	2
Butyl fermentation solubles	1*	1*	2.5*	2†
Vitamin A and D feeding oil,				
85 units D per gram	0.35	—	—	—
400 units D per gram	—	0.2	—	0.2
D—activated animal sterol,				
2000 units D per gram	—	—	0.02	—
Oystershell flour	2	2	1	—
Ground limestone	—	—	—	1
Salt	0.5	0.5	0.5	1‡
$MnSO_4.4H_2O$	0.02	0.02	0.02	—
	100.00	100.00	100.00	100.00
Calcium, per cent	0.95	1.26	0.70	0.71§
Phosphorus, per cent	0.43	0.40	0.38	0.44§

* 80 micrograms riboflavin per gram.
† 110 micrograms riboflavin per gram.
‡ Contained 4% $MnSO_4 \cdot 4H_2O$.
§ Calculated from calcium and phosphorus analyses of ingredients.

tervals, and 10 chicks from each group were killed when four weeks old, and the remainder when eight weeks old. One tibia was taken from each chick for bone ash determination.

In the Maryland and the U.S.D.A. experiments the bones were prepared and ashed according to the A.O.A.C. method (*9*). They were ashed by groups at 850°C. for one hour in the Maryland experiments and individually at 600°C. to constant weight in the U.S.D.A. experiment. In the West Virginia experiments, the cartilage caps were removed from the bones in the process of cleaning. The caps were discarded in the first experiment but retained and ashed by groups in the second. The bones were

TABLE 3.—*Effect of different phosphorus supplements on bone ash of chicks*

SUPPLEMENT TO BASAL DIET	LEVEL FED, MD. AND W. VA., PER CENT	MARYLAND BONE ASH 3 WKS., PER CENT		WEST VIRGINIA BONE ASH 3 WKS., PER CENT			U. S. D. A.		
		EXP. 1 (15)†	EXP. 2 (20)†	EXP. 1 (13)†	EXP. 2 (15)†		LEVEL FED, PER CENT	BONE ASH, PER CENT	
				SHAFT ONLY	SHAFT ONLY	WHOLE BONE		4 WK. (10)†	8 WK. (15)†
None		'35.62	39.82	54.97	49.12	38.51			
$Ca_3(PO_4)_2$ 2287	0.33	41.06	42.18						
	0.67	43.96	44.50						
	1.33	47.14	45.43						
Bonemeal	1			56.52	55.48	45.87	1	43.24	46.08
	2				56.26	47.67	2	44.04	46.11
	3			57.81					
Defluor. superphos.	1		41.08						
2215 B	3		44.52						
2220 B	1			54.91	48.66	38.22			
	2				50.17	40.29			
	3			56.23					
2221 A	0.5	36.47							
	1	38.07	40.36						
	2	41.67							
	3		44.76						
2221 B							1.1	42.16	43.54
							2.2	41.13	45.37
2229	0.5	36.48					1.6	40.57	45.47
	1	35.13	40.76	54.46	46.02	36.37	3.2	41.04	45.03
	2	37.05			47.37	37.61			
	3		40.32	53.92					
2229 (80 mesh)	1		40.18						
	3		41.74						
"C"	1		40.69						
	3		42.97						
Defluor. phosphate rock 2224	0.5	39.63					1.2	41.94	46.12
	1	42.74					2.4	42.22	46.25
	2	44.15							
Phosphate slag 2227	0.5	38.64					1.12	42.41	46.68
	2	45.42					2.24	43.68	45.23
$Ca_2P_2O_7$ (beta) 1602 B	0.5		39.02						
	1.5		40.02						
Cal. metaphosphate, vitreous, 2228							0.56*	42.20	46.58
							1.12‡	43.85	45.48
Meat scrap	2				53.19	43.61			
Least significant difference				0.86	1.88			2.28	2.28

* Plus 0.5 per cent ground limestone.
† Figures in parentheses show number of chicks in group.
‡ Plus 1.0 per cent ground limestone.

stored in ethyl alcohol before being prepared for analysis. Each bone shaft was handled individually, being crushed into a fritted-bottom crucible, extracted for 24 hours with ethyl ether, dried for 24 hours in a vacuum oven at 75°C. and 50 mm. pressure, and ashed at 550°C. to constant weight. In all operations the bones were not removed from the fritted-bottom crucibles. Individual ashing of the bones in the U.S.D.A. and the West Virginia studies permitted statistical treatment of the results, which was not possible in the case of the Maryland data.

In interpreting the Maryland results a response curve was constructed for the data obtained from the basal group and the groups fed tricalcium phosphate. Levels of phosphorus furnished by tricalcium phosphate were plotted as abscissae and the group bone ash figures as ordinates. By comparing the group bone ash figures of the experimental groups with the standard curve, the level of available phosphorus furnished by each level of each supplement could then be estimated. This figure, divided by the per cent of total phosphorus in the given level of supplement and multiplied by 100, gives the relative availability of the phosphorus (a value of 100 being assigned to the availability of the phosphorus of tricalcium phosphate). An attempt was made to correlate figures obtained in this way with solubility of the phosphorus in dilute acid. For determining solubility the following procedure was developed: a 0.5 gram sample of the material to be tested was placed in a 250 ml. Erlenmeyer flask. A 0.25 per cent hydrochloric acid solution was warmed to 38°C., and 100 ml. was poured into the flask containing the sample. The flask was rotated and placed in an oven at 38°C. for one hour, with shaking at frequent intervals. The flask was removed and the contents were immediately filtered through Whatman No. 2 paper. The undissolved material was washed on the filter with approximately 100 ml. of distilled water at 38°C. The combined extract and washings were made up to 250 ml. and the phosphorus was determined volumetrically in 25 ml. aliquots (*9*).

RESULTS

The results of all the bone ash determinations are summarized in Table 3. For the second West Virginia experiment the figures for shafts and for shafts plus caps are included. The mean difference between figures obtained with and without the caps is 9.76 for the eight groups. This compared favorably with the differences of 8.49 observed by Johnson (*10*) and approximately 12 observed by Fritz and Halloran (*11*). In making comparisons between results from different sources the difference in age between the chicks in the U.S.D.A. experiment and those in the other experiments must also be taken into account.

Table 4 summarizes the results of the Maryland experiments expressed in terms of relative availability, measured as described above, and compares these results with the solubility in dilute hydrochloric acid of the phosphorus of the same supplements.

Table 5 summarizes the growth data obtained in the U.S.D.A. experiments, the mean live weight being given for each group of 25 chicks at 4 weeks of age and for the remaining 15 chicks in each group at 8 weeks of age. In each of the other experiments differences between the mean live weights of various groups at three weeks of age were very small, indicating

TABLE 4.—*Relative availability and solubility of phosphorus from different sources* (Maryland experiments only)

PHOSPHORUS SUPPLEMENT	CHICK TESTS			SOLUBILITY OF P IN 0.25% HCl, 38°C.
	LEVEL FED	RELATIVE AVAILABILITY EXP. 1	EXP. 2	
	per cent	*per cent*	*per cent*	*per cent*
$Ca_3(PO_4)_2$ 2287	0.33	100	100	88.4
	0.67	100	100	
	1.33	100	100	
Defluor. superphos. 2215B	1		30	51.9
	3		37	
2221A	0.5	16		33.9
	1	24	12	
	2	31		
	3		38*	
2229	0.5	16		11.6
	1	0	22	
	2	7		
	3		4	
2229 (80 mesh)	1		8	14.3
	3		16	
"C"	1		24	24.8
	3		29	
Defluor. phosphate rock 2224	0.5	79		51.4
	1	78		
	2	55*		
Phosphate slag 2227	0.5	54		69.0
	2	69*		
$Ca_2P_2O_7$(beta) 1602B	0.5		0	19.1
	1.5		1	

* Figures taken from "less sensitive" portion of curve.

that the levels of phosphorus supplements fed had no effect on growth during the first three weeks of life.

DISCUSSION

The data summarized in Table 3 show very clearly that the defluorinated superphosphates tested were inferior to bone meal and tricalcium phosphate as sources of phosphorus for early bone growth. In the Maryland experiments each group fed superphosphate had lower bone ash than the group fed an equivalent level of tricalcium phosphate. A level of 0.67

per cent of the latter compound was approximately equivalent in phosphorus content to 1 per cent of defluorinated superphosphate. In the West Virginia experiments each group fed superphosphate was significantly inferior in bone calcification to the group fed a comparable level of bonemeal, and the same is true of the U.S.D.A. data for 4 week old chicks with the exception of the group fed 1.1 per cent of superphosphate 2221 B, which was not significantly poorer than the bonemeal group. When the chicks were eight weeks old there were no significant differences in bone

TABLE 5.—*Effect of different phosphorus supplements on growth of chicks* (U.S.D.A. experiments only)

SUPPLEMENT TO BASAL DIET	LEVEL FED, PER CENT	MEAN LIVE WEIGHT, GRAMS	
		4 WEEKS (25)†	8 WEEKS (15)†
Bonemeal	1.0	209.6	633.6
	2.0	179.3	544.3
Defluor. superphos.			
2221B	1.1	216.2	525.5
	2.2	181.8	607.2
2229	1.6	215.1	565.5
	3.2	176.8	485.6
Defluor. phosphate rock			
2224	1.2	230.5	681.2
	2.4	182.8	539.9
Phosphate slag			
2227	1.12	195.9	574.2
	2.24	169.3	479.2
Calcium metaphosphate, vitreous,			
2228	0.56*	180.0	588.1
	1.12‡	161.3	497.2
Least significant difference		28.3	

* Plus 0.5 per cent ground limestone.
† Figures in parentheses show number of chicks in group.
‡ Plus 1.0 per cent ground limestone.

ash among the groups except that the same group mentioned above which received sample 2221 B was significantly poorer than several of the other groups. It appears that as the chicks became older they became less sensitive to differences in availability of the phosphorus.

In the Maryland experiments the feeding of three of the four samples of defluorinated superphosphate resulted in substantially better bone ash than that of the negative control group. The fourth sample, No. 2229, gave very poor results in all tests. The other superphosphate tested at the West Virginia Station, No. 2220 B, produced significantly better bone ash than did the unsupplemented basal diet when it was fed at a level of 3 per cent, but not when fed at lower levels.

The bone ash of the groups fed defluorinated phosphate rock and phosphate slag compared more favorably with that of the positive controls than did the bone ash of the groups fed superphosphate. They were not significantly different from the bonemeal groups in the U.S.D.A. experiment, and the same is true of the groups fed vitreous calcium metaphosphate of which it should be remarked that 0.56 per cent contains approximately the same quantity of phosphorus as 1 per cent of bonemeal.

The beta calcium pyrophosphate tested in the second Maryland experiment was totally unavailable, or very nearly so. The bone ash of the group fed the higher level was almost identical with that of the basal group.

The 2 per cent of meat scrap fed in the second West Virginia experiment produced moderately good calcification. It was approximately equivalent to 0.5 per cent bonemeal in phosphorus content and its phosphorus was apparently similar to that of bonemeal in availability.

The data summarized in Table 4 indicate that the percent of phosphorus soluble in dilute acid, determined as described above, is a fairly good measure of the availability to the chick of the phosphorus of a mineral supplement. The most conspicuous discrepancy is in the case of the pyrophosphate, of which the solubility was low but the availability negligible. The solubility of the phosphorus of these samples and a number of others in 0.4 per cent hydrochloric acid at 25°C. is given by Hill, *et al.* (*8*). The results parallel those reported here but are somewhat higher. Three of the relative availability figures in Table 4 are marked as having been taken from the "less sensitive" portion of the curve. It is obvious from inspection of Table 3 that the slope of each of the standard response curves becomes less as the curve approaches the highest level of calcium phosphate. One would expect that the apparent availabilities would be too high in the case of figures taken from this upper portion of the curve. Actually two of the three figures do appear to be too high but the other seems low. Fortunately all the other values fell on that portion of the curve having the steepest slope and approximating a straight line. These results indicate that the defluorinated phosphate rock and phosphate slag tested were 50–80 per cent as available as tricalcium phosphate, that three of the four samples of defluorinated superphosphate were 25–35 per cent as available as tricalcium phosphate, and that the fourth sample of superphosphate was definitely less available than the other three. It is of interest to note that neither the availability nor the solubility of this product was increased by regrinding so that all of the sample would pass an 80-mesh screen. The sample, as tested originally, was ground to pass a 20-mesh screen. As noted above, this sample, No. 2229, was produced experimentally by a commercial concern. It is therefore not representative of material placed on the market for feeding purposes, but it does show that it is possible for a defluorinated superphosphate to contain phos-

phorus in such unavailable form as to be practically useless for feeding.

The other three superphosphates tested, though they did not compare favorably with tricalcium phosphate, were sufficiently available to be useful as phosphorus supplements. However, the importance of improving the processing of superphosphates so as to attain higher availability is evident when it is remembered that in this material lie the greatest possibilities for expanded production of phosphorus supplements for feeds. Doubling or trebling availability would be at least as useful to feeders and the feed industry as doubling or trebling production of such superphosphates. There is good evidence that marked improvements in the availability of the phosphorus of this material have been effected since the time, June 1943, when the samples used in these experiments were obtained.

It is of interest to note that Melass and Sherwood (*12*) working with practical broiler rations obtained as good growth when feeding 1.5 and 3.0 per cent of defluorinated superphosphate as when feeding the same levels of bonemeal. Fifty-eight per cent of the phosphorus of this superphosphate was soluble in 0.4 per cent hydrochloric acid. However, it is not certain that the basal diet was sufficiently low in phosphorus to reveal differences in availability of the supplements.

The data on mean live weights, presented in Table 5, reveal no significant differences at 4 weeks of age among the groups fed the higher levels of supplements. Among the groups fed lower levels, the group receiving calcium metaphosphate was significantly inferior to several of the others, but otherwise there were no significant differences. It is of interest to note that Bird and Caskey (*13*) observed no unfavorable effect on growth to three weeks of age when feeding vitreous calcium metaphosphate as a supplement to a diet very similar to the Maryland diet described in Table 2, even though the level fed was 2.28 per cent or twice as high as the higher level fed in these studies.

As shown in Table 5, the higher level of each supplement resulted in poorer growth than the lower level, and the differences are significant in four comparisons. A depressing effect on growth was also apparent in the live weights at 8 weeks of age, except in the case of Sample 2221 B. This apparent growth-depressing effect of the higher levels is hard to explain inasmuch as these levels are not in excess of those commonly recommended and fed in practical diets. Furthermore, similar levels of bonemeal and of superphosphate 2221 B produced similar growth-depressing effects in spite of the greater solubility and availability of the former. Nowotarski and Bird (*4*) added 7 per cent of defluorinated superphosphate to a diet already containing 1.68 per cent calcium and 0.82 per cent phosphorus. This high level of superphosphate stimulated growth when the diet contained 0 or 5 A.O.A.C. chick units of vitamin D per 100 grams, but depressed growth when the diet contained 10 or 20 units per 100 grams.

These results may be taken as evidence of the need for further investigations of the requirements for such mineral supplements and the influence of other dietary constituents on these requirements. It should be added, however, that the accepted minimum phosphorus requirement (about 0.5 per cent) was confirmed by the results of the bone ash determinations in the Maryland and the West Virginia studies. The basal diets containing 0.38–0.43 per cent phosphorus were not adequate for optimum early bone development, but when the phosphorus content of the diet was increased to 0.55–0.57 per cent by the addition of bonemeal or tricalcium phosphate, normal bone ash resulted. In the first West Virginia experiment the differences between the groups fed the basal diet alone and supplemented with bonemeal were small but they were significant. It is worthy of note that the basal diet fed in the first West Virginia experiment produced higher bone ash than that fed in the second experiment. This difference may have been due to the higher calcium and vitamin D content of the first diet, although the level of vitamin D in the second diet should have been ample, and the calcium:phosphorus ratio should have been more favorable in the second diet than in the first.

SUMMARY

Three laboratories cooperated in determining the effectiveness of ten different samples of phosphatic materials as sources of phosphorus for bone formation in growing chickens. The samples tested included six of defluorinated superphosphate and one each of defluorinated phosphate rock, phosphate slag, calcium pyrophosphate (beta), and vitreous calcium metaphosphate. The effects of these materials on per cent of bone ash and on growth were compared with the corresponding effects of tricalcium phosphate and of bonemeal. Judged by effect on bone ash, one sample of defluorinated superphosphate was almost completely unavailable, and its availability was not increased by finer grinding; the other five samples were available but less so than bonemeal and tricalcium phosphate. Defluorinated phosphate rock, phosphate slag, and vitreous calcium metaphosphate were intermediate in availability between the superphosphates on the one hand and bonemeal and tricalcium phosphate on the other. The calcium pyrophosphate was totally unavailable or nearly so. The parallelism between availability and solubility in 0.25 per cent hydrochloric acid at 38°C. was such that determination of solubility could be used as a quick, approximate measure of availability.

At levels equivalent in phosphorus content to 2 per cent of bonemeal, each of the supplements fed in the one experiment of eight weeks duration appeared to have a detrimental effect on growth. The metaphosphate had an unfavorable effect on growth even when fed at a level equivalent to 1 per cent bonemeal.

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NUTRITIVE EVALUATION OF DEFLUORINATED PHOSPHATES AND OTHER PHOSPHORUS SUPPLEMENTS

III. UTILIZATION EXPERIMENTS WITH RATS

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Wartime demands for phosphate suited for feeding purposes have necessitated the production and use of a large tonnage of material in addition to bonemeal. To meet these demands, in part at least, advantage has been taken of the technological advances of recent years in the defluorination of both phosphate rock and superphosphate. It has been found possible to reduce the fluorine content of these products to levels at which they can be fed with safety to livestock. In some cases the fluorine content has been reduced to 0.05 per cent or less, and the product has closely resembled bonemeal in content of fluorine as well as of calcium and phosphorus.

The suitability, for animal-feeding purposes, of both fused-phosphate rock and calcium metaphosphate of low-fluorine content as made for fertilizer use, has been studied by Fraser and associates (*1*). Rat-feeding tests showed that the former product was satisfactory but the latter un-

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satisfactory as a source of calcium and phosphorus. Recently Barrentine, Maynard, and Loosli (*2*) likewise reported fairly satisfactory bone formation with fused-rock phosphate, approaching that with secondary-calcium phosphate. Three defluorinated superphosphates gave somewhat variable results ranging from an efficiency of only a fraction of that of the calcium phosphate, to approximate equality. A résumé of the results with poultry is given by Bird, et al. (*3*).

The work reported here was the outgrowth of a need for more adequate information on the efficiency of utilization of the various defluorinated products in production, either on full-plant scale or on any experimental basis, during 1943 and the early months of 1944, together with an investigation of the reasons underlying some of the findings. In this connection, particular attention has been given to the effect of the temperature of heating on the availability of the phosphorus and calcium in the defluorinated superphosphates. For various reasons, no attempt was made to measure any deleterious effects of the fluorine remaining in the defluorinated products. Because of the low content of fluorine it seems evident, however, that there is little likelihood of harmful effects resulting from the feeding of these products at the levels generally necessary to supplement the average ration. Several laboratories have contributed to the studies, as a whole designed to evaluate the products with respect to the better-known bonemeal and tricalcium-phosphate materials. Results of chick tests carried out in these laboratories have been summarized, as already indicated, by Bird, et al. (*3*). In the present paper results with rats, obtained in five different laboratories, are presented for the sake of convenience and simplicity in making the information available for general use.

The institutions and firms in which the five laboratories are located are the University of Tennessee, the Texas Agricultural Experiment Station, the Wisconsin Agricultural Experiment Station, the Moorman Manufacturing Company, and the Bureau of Animal Industry of the U. S. Department of Agriculture. The samples involved in these tests were assembled and distributed by the Bureau of Plant Industry, Soils, and Agricultural Engineering. The general problem of phosphate utilization has been discussed by Jacob (*4*), while data on the preparation and some of the chemical properties of the products tested have been presented by Reynolds, Hill, and Jacob (*5*), and by Hill, Reynolds, Hendricks, and Jacob (*6*).

The results of the experimental work are reported in two parts. The first is a brief résumé of the work of the first four laboratories already named, which is based on summaries made available by them to the authors. The second is a somewhat more detailed presentation of the work conducted by the Bureau of Animal Industry on many of the same products studied by the four collaborating laboratories, plus some further feeding tests on samples of superphosphates heated at controlled tempera-

tures, together with several orthophosphates and pyrophosphates. All is intended to show some of the fundamental requirements for production of highly-assimilable defluorinated phosphates.

EXPERIMENTAL

The procedures employed were left to the choice of each collaborating laboratory. In the work carried out by the Texas Station, the basal diet fed to the rats was adapted from that used by Bunkfeldt and Steenbock (*10*). In the work done in the laboratory of the Moorman Manufacturing Company, the rachitogenic diet of Steenbock and Black (*11*) was used in the first test, designated as A, while the Schneider and Steenbock (*12*) low-phosphorus-basal diet was employed in subsequent tests. The tests at the Wisconsin Station also involved a medium- and a low-phosphorus diet, while the one series run at the Tennessee Station involved the use of a basal diet containing 0.09 per cent phosphorus. In all cases young rats were fed for short periods, usually on basal diets low in phosphorus and calcium, to which was added the test material in graded amounts to give equal, or multiple, levels of phosphorus. The criteria for evaluating these test materials included growth, blood-phosphorus level, phosphorus retention, and bone ash. In general, greatest weight was placed on bone ash and least on body growth, in grading the relative values of the test phosphates as poor, fair, good, and excellent. The grade of excellent was given, in the usual case, to bonemeal and tricalcium or other orthophosphates which served as reference substances. Other test products received a grade appropriate to their relative effectiveness as compared with the reference substances and the no-supplement or negative-control groups.

In the method employed in the laboratory of the Bureau of Animal Industry, the low-phosphorus diet was a modification of that described by Jones and Foster (*7*). The basal diet was composed of the following ingredients expressed in per cent: blood fibrin 18, lard 10, dextrinized starch 68.7, agar 2, and salt mixture minus calcium and phosphorus 1.3. This diet contained, on the average, 0.04 per cent phosphorus and 0.06 per cent calcium. The addition of 2 per cent of bonemeal or other phosphate, containing approximately 13 per cent of phosphorus and 27 per cent of calcium, as replacement for an equal amount of dextrinized starch, supplied an average of 0.26 per cent phosphorus and 0.55 per cent calcium. This diet combination, which thus contained a total of 0.30 per cent phosphorus, produced excellent growth, approximately normal blood-phosphorus level, and excellent bone development. In many of the tests containing phosphate products, the level of added phosphorus was also adjusted to 0.26 per cent. Where higher levels of test materials were used they supplied 1.5, 2, and 3 times this figure. As necessary, calcium carbonate was also added in the diets to provide twice as much calcium as phosphorus. Dl-alpha tocopherol and the water-soluble vitamins—thia-

mine, calcium pantothenate, riboflavin, pyridoxine, niacin, choline, inositol, and para-aminobenzoic acid were furnished as pure substances and mixed directly into the diet. The diet was prepared in small quantities and kept in a refrigerator. Fortified cod liver oil (0.4 ml.) was fed to each animal twice a week.

The rats used were albino males and females, 21–26 days of age, weighing 50 ± 4 grams. They were placed in screen-bottomed, individual cages and so distributed according to sex, starting weight, and litter as to make up uniform groups of 8–10 animals each on each of the various diets. Because of the number of materials tested, several trials, designated by letters, were run. Each of these tests contained a positive-control group fed either bonemeal or a normal-salt mixture supplying 0.26 per cent of phosphorus. In the last trial, designated G, there was also included a negative control, and two intermediate control groups in which a 0.25 (0.065 per cent) and a 0.5 (0.13 per cent) level of phosphorus was added.

After a feeding period of 28 days the animals were anesthetized with ether and bled directly into a centrifuge tube. Inorganic-phosphorus determinations were made on the sera according to the method of Bodansky (*8*). Following the bleeding operation, right-femur bones were removed from the legs of the dead animals and ashed, using the method described for vitamin D determination in poultry feeds (*9*).

RESULTS

The results obtained by the four collaborating laboratories are given in Table 1. Three series of tests, designated by letters, are reported from Texas, two from Wisconsin, three from Moorman, and one from Tennessee. Because of the variable phosphorus contents of the basal and of the supplemented diets, together with the differences in lengths of test periods, it was not possible to average the data for a given product. Therefore in studying the results of weight gains and bone-ash and blood phosphorus values, recourse must be taken to comparisons within a given series. A simpler means of comparison has been provided through the grade of response given in the right-hand column. On the scale of an excellent response from the use of bonemeal or tricalcium phosphate and failures or lack of response in the no-supplement groups, the six defluorinated-superphosphate samples show gradings ranging from poor to good. In descending order of value they appear to rank as follows: No. 2222-b, No. 2221-b, No. 2215-b, No. 2220-b, No. 2270, and No. 2229. If a grade of fair indicates a response intermediate between the extremes given by the no-supplement and the bonemeal or tricalcium-phosphate supplements, then it would seem that defluorinated phosphate No. 2220-b is approximately one-half as effectively utilized as the reference standards, and Nos. 2215-b and 2221-b about two-thirds as well utilized.

The one sample of defluorinated-rock phosphate shows an average

grade of very good, which would indicate it to be fully 80 per cent as good as bonemeal. The phosphate slag gave uniformly good results and thus ranks next to the defluorinated-rock phosphate. The calcium metaphosphates are equal to some of the defluorinated superphosphates. A single test on a sample of gamma-pyrophosphate, surprisingly enough, shows it to be comparable to bonemeal.

The first phase of the rat-feeding work in the Bureau of Animal Industry dealt with commercially-produced phosphates including several of the same samples of defluorinated phosphates tested by the other collaborating laboratories and reported in Table 1. The additional samples consisted of a defluorinated superphosphate (No. 2270) produced late in 1943, of a defluorinated-rock phosphate (No. 2296) taken from a commercial product manufactured during the first half of 1944, of a phosphate slag (No. 2282), and of two natural phosphates (Nos. 2302 and 2306) from the West Indies.

The results of the feeding tests are shown in Table 2. The data on the defluorinated superphosphates bear out the findings of the other laboratories that these products are not the equal of bonemeals or of tricalcium phosphates, where the phosphorus is in the ortho form. In one case (No. 2221-a) tripling the content of phosphate in the diet, to supply 0.78 per cent of added phosphorus, still did not permit normal bone development or a blood-phosphorus content equal to that on bonemeal. As judged from the standard errors (appearing after the averages in this and subsequent tables), the growth rate on the material, however, does not appear significantly lower than that obtained on bonemeal. Doubling the phosphorus supplied as defluorinated superphosphate (Nos. 2222-a and 2270) over that supplied as bonemeal, appeared to provide approximately an equal amount of calcium and phosphorus for growth and bone development. In the case of Sample 2220-a the double level was not adequate, i.e., the material was less than one-half as effective as bonemeal or orthophosphate contained in the salt mixture. Gradings of response, together with the analytical data, indicate that Samples 2222-a and 2270 were the best of the series. Sample 2221-a, on the other hand, appeared to be the poorest, whereas 2221-b ranked next to Sample 2222-b in the first series. It should be pointed out, however, that the differences between Samples 2221-a and 2220-a are relatively small.

The two-defluorinated-rock phosphates appear to be of approximately equal value, and neither is greatly inferior to the bonemeal or orthophosphate used in the control diets. Actually 0.39 per cent of phosphorus supplied from Sample 2224 was the equal of 0.26 per cent of phosphorus in the form of bonemeal.

The sample of phosphate slag (No. 2282) proved to be a relatively poor substitute for bonemeal, being much like the defluorinated superphosphates in availability. It should be pointed out that the material contained

TABLE 1.—*Results of rat-feeding tests on various phosphate supplements obtained by four collaborating laboratories*

SUPPLEMENT	LABORATORY TEST	PHOSPHORUS LEVEL IN DIET		NO. RATS	DURATION OF TEST	GAIN IN WEIGHT	BONE ASH	BLOOD PHOSPHORUS	RESPONSE GRADE
		BASAL	ADDED IN SUPPLEMENT						
		per cent	*per cent*		*weeks*	*grams*	*per cent*	*mg./100 ml.*	
No supplement	Texas (B)	0.05	0	6(−5)‡	3	27.6	21.1		—
	Texas (C)	.06	0	6	4	22.1	31.8		—
	Wisc. (A)	.03	0	6	8	18.0	26.5		—
	Wisc. (B)	.39	0	6	12	107.7	39.9		—
	Moorman (A)	.03	0	4	6	8.8	41.4	—	—
	Moorman (B)	.03	0	4	7	26.3	36.7	3.92	—
	Moorman (C)	.03	0	4	6	9.0	46.7	4.5	—
Steamed bonemeal	Wisc. (B)	.39	.26	6	12	155.5	57.2	—	Excellent
	Moorman (A)	.03	.19	4	6	37.8	57.9	7.0	Excellent
	Moorman (B)	.03	.19	4	7	73.5	58.5	7.52	Excellent
	Moorman (C)	.03	.10	4	6	55.0	55.0	6.3	Excellent
	Tenn. (A)	.09	.13	5	4	105.0	61.1†		Excellent (70)*
Tricalcium phosphate	Texas (A)	.05	.26	6(−1)‡	4	35.3	44.5		Excellent
	Texas (B)	.05	.26	6(−2)‡	3	33.9	38.2		Excellent
	Texas (C)	.06	.26	6	4	37.0	48.0		Excellent
Defl. superphos. 2215-b	Texas (A)	.05	.26	6	4	37.6	36.9		Fair
	Texas (B)	.05	.26	6	3	32.0	28.4		Fair
	Wisc. (A)	.03	.27	6	8	61.0	39.3		Fair
	Moorman (B)	.03	.19	4	7	79.8	55.4	6.33	Good
Defl. superphos. 2220-b	Texas (C)	.06	.26	6	4	21.8	41.0		Fair
	Wisc. (A)	.03	.27	10	5	59.0	32.0		Poor
	Moorman (A)	.03	.19	4	6	37.0	54.7	4.95	Fair
	Moorman (A)	.03	.38	4	6	35.5	56.8	5.54	Fair
	Tenn. (A)	.09	.13	5	4	96.0	47.7†		Fair (44)*

TABLE 1.—*Results of rat-feeding tests on various phosphate supplements obtained by four collaborating laboratories—Continued*

SUPPLEMENT	LABORATORY TEST	PHOSPHORUS LEVEL IN DIET		NO. RATS	DURATION OF TEST	GAIN IN WEIGHT	BONE ASH	BLOOD PHOSPHORUS	RESPONSE GRADE
		BASAL	ADDED IN SUPPLEMENT						
		per cent	*per cent*		*weeks*	*grams*	*per cent*	*mg./100 ml.*	
Defl. superphos. 2221-b	Texas (B)	.05	.26	6	3	37.6	26.8		Fair
	Wisc. (A)	.03	.27	10	5	70.0	42.7		Fair
	Moorman (A)	.03	.19	4	6	45.8	56.8	5.49	Good
	Tenn. (A)	.09	.13	5	4	94.0	49.7†		Good (49)*
Defl. superphos. 2222-b	Wisc. (B)	.39	.13	6	12	150.7	56.3		Good
	Wisc. (B)	.39	.26	6	12	157.5	56.6		Good
Defl. superphos. 2229	Wisc. (A)	.03	.27	10	5	58.0	31.9		Poor
	Tenn. (A)	.09	.13	5	4	58.0	46.3†		Fair (26)*
Defl. superphos. 2270	Moorman (C)	.03	.10	4	6	28.0	50.9	4.2	Fair
Defl. rock phos. 2224	Texas (B)	.05	.26	6	3	31.5	33.2		Good
	Wisc. (A)	.03	.27	10	5	104.0	54.8		Very good
	Wisc. (B)	.39	.12	6	12	141.7	53.5		Very good
	Wisc. (B)	.39	.24	6	12	151.5	56.8		Very good
	Moorman (B)	.03	.19	4	7	65.5	60.1	6.96	Excellent
	Tenn. (A)	.09	.13	5	4	92.0	58.5†		Very good (64)*
Phos. slag 2227	Texas (A)	.05	.26	6	4	30.4	37.9		Good
	Texas (B)	.05	.26	6	3	35.9	33.7		Good
	Wisc. (B)	.39	.13	6	12	149.0	53.5		Good
	Wisc. (B)	.39	.27	6	12	145.7	52.5		Good
	Moorman (B)	.03	.19	4	7	77.8	56.5	6.80	Good
	Moorman (C)	.03	.10	4	6	42.0	51.4	6.2	Good
Calcium meta-phos. 2228	Texas (C)	.06	.26	6(−2)‡	4	24.3	45.2		Good
	Moorman (B)	.03	.19	4	7	59.8	47.7	5.66	Fair
	Tenn. (A)	.09	.13	5	4	77.0	50.4†		Good (45)*
Calcium meta-phos. 2235	Texas (C)	.06	.26	6(−2)‡	4	26.0	40.8		Fair
Gamma-pyro-phos. 2234	Texas (C)	.06	.26	6	4	29.5	51.0		Excellent

* The figures in parentheses express the percentages of the phosphorus consumed which were stored in the body. Paired tests, on a control diet containing Osborne and Mendel salt mixture, gave values ranging from 68 to 75.

† These figures for bone ash were not determined directly, but are based on an estimated percentage of bone to total weight.

‡ Number of rats that died before end of test.

TABLE 2.—*Body-weight gains, bone-ash percentages, and blood-phosphorus values of rats fed defluorinated superphosphates, defluorinated rock phosphates, and other products*

SUPPLEMENT	TEST SERIES	SUPPLEMENT ADDITION		GAIN IN WEIGHT	FEMUR ASH	SERUM PHOSPHORUS	RESPONSE GRADE
		TOTAL	PHOSPHORUS				
		per cent	*per cent*	*grams*	*per cent*	*mg./100 ml.*	
Salt mixture*	A	3.2	0.26	91.1 ±10.2	57.8 ±0.51	9.21 ±0.41	Excellent
	C	3.2	.26	133.4 ± 6.7	60.6 ± .22	9.88 ± .26	Excellent
	D	3.2	.26	96.0 ± 8.2	61.2 ±1.87		Excellent
	E	3.2	.26	98.6 ± 5.5	63.0 ± .34	8.76 ± .26	Excellent
	F	3.2	.26	95.8 ± 4.9	61.6 ± .52	8.97 ± .26	Excellent
	G	3.2	.26	134.7 ±13.0	61.9 ± .25	9.04 ± .23	Excellent
Steamed bonemeal	A	2.0	.26	99.2 ± 7.9	57.9 ± .70	8.73 ± .76	Excellent
	B	2.0	.26	133.0 ±12.9	59.3 ± .62	8.53 ± .36	Excellent
Defl. superphosphate:							
2220-a	A	2.0	.26	83.4 ± 6.7	43.0 ±1.22	6.73 ± .41	Fair
	B	4.0	.52	114.0 ± 9.5	56.5 ±1.31	7.44 ± .29	Fair
2221-a	A	2.0	.26	73.6 ± 5.4	36.2 ±1.31	5.36 ± .34	Poor
	B	2.0	.26	89.4 ± 6.4	41.6 ± .85	5.46 ± .32	Poor
	B	4.0	.52	105.0 ± 6.6	50.8 ±1.29	6.44 ± .28	Poor
	B	6.0	.78	112.9 ±10.1	55.0 ±1.24	6.83 ± .34	Poor
2222-a	A	2.0	.26	88.5 ± 7.2	46.0 ± .91	6.67 ± .30	Fair
	B	3.0	.39	117.8 ± 7.3	55.2 ± .63	7.84 ± .35	Fair
	B	4.0	.52	123.3 ± 7.4	58.3 ± .53	8.12 ± .22	Fair
2270	E	2.0	.26	81.4 ± 3.9	48.4 ±1.02	6.40 ± .35	Fair
	F	3.0	.39	87.3 ± 6.0	52.8 ±1.20	6.42 ± .31	Fair
	G	4.0	.52	132.8 ±10.2	62.3 ± .28	8.99 ± .26	Fair
Defl. rock phosphate:							
2224	A	2.0	.26	92.7 ± 4.1	54.3 ± .44	7.60 ± .42	Very good
	C	2.0	.26	136.2 ±10.8	59.2 ± .37	8.85 ± .23	Very good
	B	3.0	.39	121.4 ± 8.3	60.9 ± .54	8.74 ± .27	Very good
2296	E	2.0	.26	92.9 ± 4.0	57.1 ±1.21	7.60 ± .24	Very good
Phosphate slag:							
2282	D	3.06	.26	79.0 ± 9.4	46.8 ±1.25		Fair
	F	4.59	.39	82.5 ± 5.8	51.8 ± .82	6.37 ± .19	Fair
	G	9.18	.78	129.1 ±14.7	62.1 ± .36	8.82 ± .29	Fair
Cayman Brac phosphate:							
2302	F	10.62	.78	51.0 ± 1.9	28.5 ±1.55	4.69 ± .33	Poor
Swan Island phosphate:							
2306	F	7.40	.52	92.3 ± 5.7	47.4 ± .72	6.30 ± .17	Poor

* Phosphorus was supplied in this salt mixture as monopotassium phosphate, while calcium was in the form of calcium carbonate.

35.8 per cent ferric oxide, which was undoubtedly a factor in the low availability of the phosphorus.

In view of the relatively poor availability of most of the phosphates tested in the group just discussed, it was decided to investigate the feeding value of some calcium metaphosphates and calcium pyrophosphates, several of which were of C.P. grade, and also that of synthetic iron and aluminum phosphates. It was thought that the form in which the calcium phosphate existed in the defluorinated phosphates might well explain the relative availability of the elements; also, that the laboratory samples of iron and aluminum phosphates would provide further evidence on the interference of iron and aluminum with utilization of the phosphorus.

The results of the feeding tests are shown in Table 3. The alpha- and beta-tricalcium phosphates proved to be excellent supplements and equal to the phosphate in the salt mixture. The alpha form (No. 2267), however, showed significantly higher femur-ash and serum-phosphate values.

The two samples of calcium metaphosphate showed considerable contrast. Both were added at levels to supply 0.52 per cent additional phosphorus. Sample 2228, a vitreous form of metaphosphate, produced a response in the rats somewhat under that in the control groups fed the salt-mixture supplement to supply 0.26-per cent phosphorus. Sample 2235, a crystalline-beta type of metaphosphate, was of very little value. Four pyrophosphates were tested: one beta and two gamma forms and a calcium-acid-pyrophosphate sample. The beta form gave poor results analogous to those on defluorinated superphosphate (No. 2221-a), but the others were very satisfactory. Both the ferric- and the aluminum-phosphate products were useless, or nearly so, as sources of phosphorus—a finding in harmony with the explanation offered in the case of the natural-phosphate products listed in Table 2.

Two other samples taken from natural deposits were included in the group shown in Table 2. Both were low in fluorine content but relatively high in aluminum and iron. Sample 2302, which contained nearly twice as much of these elements as Sample 2306, showed the lowest availability of calcium and phosphorus of the samples in the group.

The final step in the study of availability of phosphates was the testing of superphosphates defluorinated at such temperatures as would influence the formation of calcium metaphosphate or of calcium pyrophosphate. The four temperatures investigated are indicated in Table 4. Only the highest one, 1010°C., produced a satisfactory product. Addition of the material to supply 0.39 per cent of phosphorus to the basal diet promoted body growth and bone formation equivalent to those on 0.26 per cent phosphorus from the control-salt mixture. While the serum-phosphorus value was somewhat lower, it was still in the upper range found in normal animals. The results obtained on the 1010°C. sample are comparable to those obtained on the samples of defluorinated-rock phosphate, on trical-

TABLE 3.—*Body-weight gains, bone-ash percentages, and blood-phosphorus values of rats showing the influence of different forms of calcium phosphate and also of ferric and aluminum phosphates on availability*

SUPPLEMENT	TEST SERIES	SUPPLEMENT ADDITION		GAIN IN WEIGHT	FEMUR ASH	SERUM PHOSPHORUS	RESPONSE GRADE
		TOTAL	PHOSPHORUS				
		per cent	*per cent*	*grams*	*per cent*	*mg./100 ml.*	
Salt mixture*	C	3.20	0.26	133.4 ± 6.7	60.6 ± 0.22	9.88 ± 0.26	Excellent
	D	3.20	.26	96.0 ± 8.2	61.2 ± 1.87		Excellent
	E	3.20	.26	98.6 ± 5.5	63.0 ± .34	8.76 ± .26	Excellent
	G	3.20	.26	134.7 ± 13.0	61.9 ± .25	9.04 ± .23	Excellent
	G	2.30	.13	125.3 ± 9.6	54.4 ± .63	8.25 ± .35	Fair
	G	1.80	.065	105.0 ± 7.8	41.6 ± 1.86	5.95 ± .37	Poor
	G	1.30	0	40.4 ± 4.4	24.8 ± 1.07	5.34 ± .47	
Tricalcium phosphate:							
Alpha 2267	C	1.30	.26	128.3 ± 12.4	60.5 ± .36	9.09 ± .27	Excellent
Beta 2268	C	1.30	.26	130.7 ± 11.7	58.9 ± .34	8.32 ± .32	Excellent
Calcium metaphosphate:							
Vitreous 2228	G	2.02	.52	130.1 ± 11.3	54.4 ± .62	9.31 ± .30	Good
Cryst. Beta 2235-b	G	1.92	.52	57.0 ± 4.6	28.7 ± .74	5.81 ± .86	Poor
Calcium pyrophosphate:							
Beta 1602-b	C	1.10	.26	66.0 ± 4.4	29.8 ± 1.18	5.02 ± .33	Poor
	C	3.30	.78	115.6 ± 6.6	43.9 ± 1.53	6.59 ± .74	Poor
Gamma 2272	G	1.09	.26	128.8 ± 10.6	53.3 ± 1.53	8.20 ± .40	Fair
2272	E	3.27	.78	101.0 ± 1.9	62.8 ± .43	9.68 ± .25	Fair
2234-a	G	1.08	.26	117.9 ± 7.9	41.5 ± 1.57	5.72 ± .64	Poor
Calcium acid pyrophosphate:							
2294-b	E	.90	.26	97.3 ± 7.4	58.7 ± 1.09	8.23 ± .30	Excellent
Ferric phosphate:							
1237 (Synthetic)	D	1.82	.26	30.5 ± 2.5	33.0 ± 2.13		Poor
	D	5.46	.78	37.7 ± 1.9	31.2 ± 2.24		Poor
Aluminum phosphate:							
904 (Natural)	D	4.23	.78	35.0 ± 2.8	28.6 ± .60		Poor
1236 (Synthetic)	D	1.64	.26	35.7 ± 2.0	29.4 ± 1.08		Poor
	D	4.92	.78	37.2 ± 3.1	26.8 ± 2.02		Poor

* Phosphorus was supplied in this salt mixture as monopotassium phosphate, and calcium as calcium carbonate. In the case of the tests containing less than 0.26 per cent phosphorus, both the phosphate and the carbonate were reduced proportionately to supply the levels of phosphorus indicated.

TABLE 4.—*Body-weight gains, bone-ash percentages, and blood-phosphorus values of rats showing the effect of temperature of defluorination of superphosphate on availability*

SUPPLEMENT	TEST SERIES	SUPPLEMENT ADDITION		GAIN IN WEIGHT	FEMUR ASH	SERUM PHOSPHORUS	RESPONSE GRADE
		TOTAL	PHOSPHORUS				
		per cent	*per cent*	*grams*	*per cent*	*mg./100 ml.*	
Salt mixture*	C	3.20	0.26	133.4 ± 6.7	60.6 ± 0.22	9.88 ± 0.26	Excellent
	E	3.20	.26	98.6 ± 5.5	63.0 ± 0.34	8.76 ± 0.26	Excellent
Defl. superphosphate:							
300°, 2293-b	E	2.63	.26	76.4 ± 2.7	46.6 ± 1.13	6.84 ± 0.42	Fair
600°, 2263	C	2.50	.26	76.4 ± 4.7	34.8 ± 1.41	4.69 ± 0.26	Poor
	C	7.50	.78	86.7 ± 7.3	42.8 ± 1.44	6.34 ± 0.34	Poor
760°, 2264	C	2.25	.26	64.4 ± 1.9	31.2 ± 1.41	5.48 ± 0.33	Poor
	C	6.75	.78	60.8 ± 4.7	38.3 ± 2.13	4.69 ± 0.37	Poor
1010°, 2265	C	2.00	.26	122.7 ± 8.4	56.4 ± 0.67	8.05 ± 0.22	Good
	C	3.00	.39	130.2 ± 6.3	61.2 ± 0.24	8.94 ± 0.21	Good

* Phosphorus was supplied in this salt mixture as monopotassium phosphate, while calcium was in the form of calcium carbonate.

TABLE 5.—*Availability of phosphorus as shown by animal response in relation to solubility of phosphorus in various reagents*

ANIMAL RESPONSE	SAMPLE		PHOSPHORUS EXTRACTED BY—		
	NUMBER	MATERIAL	0.4% HCl	2% CITRIC ACID	NEUTRAL AMMONIUM CITRATE
			per cent	*per cent*	*per cent*
Excellent	2267	Alpha-tricalcium phosphate	75.9	75.0	71.0
	2268	Beta-tricalcium phosphate	83.6	76.0	41.9
	2294-b	Calcium acid pyrophosphate	97.7	90.9	100.0
	2233-b	Bonemeal	98.2	85.4	61.3
Very Good	2224	Defluorinated phosphate rock	78.8	89.2	85.5
	2296	Defluorinated phosphate rock	94.2	95.2	95.0
Good	2228	Calcium metaphosphate	54.2	21.0	96.4
	2227	Phosphate slag	68.1	97.9	97.1
	2222-b	Defluorinated superphosphate	63.2	52.8	14.9
	2265	Defluorinated superphosphate (1010°)	85.2	66.5	25.5
Fair	2234-a	Gamma-pyrophosphate	48.8	7.7	5.4
	2272	Gamma-pyrophsophate	89.5	19.2	17.2
	2282	Phosphate slag	89.3	68.0	48.9
	2215-b	Defluorinated superphosphate	56.3	45.9	14.7
	2220-a	Defluorinated superphosphate	59.7	47.0	21.2
	2220-b	Defluorinated superphosphate	46.3	17.3	18.6
	2221-b	Defluorinated superphosphate	52.4	38.7	9.0
	2222-a	Defluorinated superphosphate	63.6	54.1	14.4
	2229	Defluorinated superphosphate	33.5	14.2	15.9
	2270	Defluorinated superphosphate	76.4	62.1	21.5
	2293-b	Defluorinated superphosphate (300°)	75.0	39.9	76.1
Poor	1602	Beta-pyrophosphate	44.1	8.3	2.7
	2235-b	Calcium metaphosphate	5.9	2.1	35.8
	2302	Cayman Brac phosphate	7.4	4.8	3.1
	2306	Swan Island phosphate	49.5	47.6	43.2
	1236	Aluminum phosphate	95.5	37.3	100.0
	904	Aluminum phosphate	2.0	0.6	8.9
	1237	Ferric phosphate	20.2	11.7	100.0
	2221-a	Defluorinated superphosphate	44.4	34.2	11.4
	2263	Defluorinated superphosphate (600°)	34.8	11.2	70.1
	2264	Defluorinated superphosphate (760°)	52.9	8.8	6.6

cium phosphates of either alpha or beta form, and on the gamma-pyrophosphates.

Thus it seems reasonably certain that the relatively low availability of the commercial samples of defluorinated superphosphate is due to the employment of temperatures which produced the relatively unavailable

forms of metaphosphate and pyrophosphate. That it is possible to produce a very satisfactory product by the use of proper temperatures is indicated by the results on Sample 2265, which was heated to 1010°C.

In view of the differences observed by Hill, *et al.* (*6*) between phosphatic products, in their solubility in various solvents, and the possibilities of analagous relationships to availability in the animal organism, the data bearing on this question have been assembled in Table 5. The samples have been grouped according to their degree of availability, as shown in the rat-feeding tests. The solubility figures for 0.4 per cent hydrochloric acid, 2 per cent citric acid, and neutral ammonium citrate, on the whole, show a fairly good correlation with availability. Of the three procedures for measuring solubility, the two employing hydrochloric acid and citric acid appear to be about equally reliable. When the samples rated excellent and good are considered as one group, and those rated fair and poor as another group, the division point of 65 per cent solubility appears to segregate 75 per cent or more of the samples in each group. In the same manner, 50 per cent solubility in citric acid appears to be a suitable division point. No satisfactory division point appears possible, however, on the basis of the available data for solubility in neutral ammonium citrate. From the standpoint of the use of the solubility values (even in hydrochloric or citric acid) as indices of availability, it must be emphasized that further studies are needed before such methods can be used with full confidence in evaluating phosphates.

SUMMARY

Results are reported on studies by several collaborators on the availability of calcium and phosphorus in commercially and experimentally defluorinated phosphates for bone formation in the rat.

Defluorinated phosphate rock, prepared by the fusion process, compared favorably with bonemeal or calcium phosphate as a calcium and phosphorus carrier. One phosphate slag was rated as good and another as fair in availability. Commercially defluorinated superphosphates showed considerable variation in availability, ranging from reasonably good to poor.

It is shown that the form in which the calcium phosphate exists has an important bearing on its availability. Calcium metaphosphate of the beta form, the beta-pyrophosphate, and, to a less extent, the gamma-pyrophosphate, are relatively unavailable forms while both the alpha and beta ortho forms of tricalcium phosphate are highly available. The vitreous-calcium metaphosphate is intermediate.

Calcination at 1010°C. produced a defluorinated superphosphate that was more available in calcium and phosphorus than those calcined at lower temperatures.

Comparison of solubility data in dilute hydrochloric acid, citric acid,

and neutral ammonium citrate with the ratings of availability according to the rat-feeding tests, shows good correlation from the group standpoint between the first two named reagents and the ratings, although no one solvent was entirely dependable in measuring the availability of the individual products.

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EFFECT OF SILICA ON THE QUANTITATIVE REDUCTION OF NITRATES WITH DEVARDA ALLOY

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The Devarda method (*8*) as modified by the A.O.A.C. (*13*) is widely used for the determination of nitrate nitrogen. The nitrates are reduced to ammonia by Devarda alloy in the presence of sodium hydroxide. Numerous observations of this reduction have been made by various investigators in studying the concentration of the alkali (*1, 9, 17*), the nitrate-alloy ratio (*1, 4, 9*), the length of time for the distillation (*3, 15, 16*), and the particle size of the alloy (*3, 5*). Despite minority opinion to the contrary there is a general agreement that the method is accurate and rapid when applied to pure nitrate solutions.

In the analysis of ammonium nitrate the use of a single sample for the successive determination of the two forms of nitrogen is advantageous. First, alkali is added to the sample and the liberated ammonia is determined, then the reducing alloy is added and the resultant ammonia is

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determined. Hillebrand and Lundell (*11*) describe such a procedure, using Devarda's original method. Davidson and Krasnitz (*5*) recommend a modification of the Devarda method in which magnesium oxide is substituted for sodium hydroxide. These investigators and others (*7, 12, 18*) used magnesium oxide because it gave a concentration of hydroxyl ion sufficient to remove ammonia but not strong enough to decompose nitrogenous organic material. Since no nitrogenous organic matter is present in ammonium nitrate, no difficulty was anticipated in the successive determination of ammonium and nitrate nitrogen in this material by the addition of the amount of sodium hydroxide specified in the A.O.A.C. modification of the Devarda method for nitrate nitrogen.

However, when the analysis of ammonium nitrate was attempted by first distilling off the ammonium nitrogen with sodium hydroxide and then adding alloy to expel the reduced nitrogen, inexplicably low results were obtained for nitrate nitrogen. These discrepancies led to an investigation which disclosed that silica dissolved from the Kjeldahl flask during the determination of ammonium nitrogen subsequently inhibited the quantitative reduction of nitrates by Devarda alloy.

EXPERIMENTAL

Method and Apparatus Used.—The "official" Devarda procedure for the determination of nitrates (*13*) was followed, using regular Kjeldahl apparatus fitted with Davisson scrubbers (*6*). The condenser ends were designed as described by Miller (*14*) to prevent loss of ammonia, and were immersed in the absorbent sulfuric acid solution. Modified methyl red (*10*) was used as the indicator. A solution of the sample was treated with 5 ml. of 42 per cent sodium hydroxide solution (3.04 grams), then diluted to 325 ml., and 3 grams of Devarda alloy was added. The distillation was effected at a rate which yielded 250 ml. of distillate in 1 hour. Unless otherwise noted, this procedure was used in all the tests, and all results were corrected by subtraction of the values obtained in comparable blank determinations.

Identification of Silica as the Interfering Substance.—Solutions containing known amounts of potassium nitrate were boiled 1 hour in Pyrex Kjeldahl flasks with the amount of sodium hydroxide specified in the A.O.A.C. procedure for nitrate nitrogen. When these were analyzed for nitrate nitrogen, the results were invariably low. In parallel experiments, however, virtually complete recovery of the nitrogen from potassium nitrate was accomplished by conducting the initial boiling of the alkaline solution of the sample in a Monel beaker and then transferring the solution to a Kjeldahl flask for the determination of nitrate nitrogen.

Obviously something that interfered with the reduction of nitrates by Devarda alloy was dissolved from the glass of the Kjeldahl flask during

the initial boiling period. Silicon and boron are the constituents most likely to be dissolved from the Pyrex glass; hence, small amounts of salts of these elements were added to a solution of potassium nitrate prior to its analysis for nitrate nitrogen. The recovery of nitrogen from the samples containing borates was complete, while that from the samples containing silicates was low.

Solution of Silica from Kjeldahl Flasks.—To determine the extent of attack on the glassware, solutions containing 3.04 grams of sodium hydroxide in 325 ml. of water were boiled in Kjeldahl flasks for various periods and the silica that dissolved was determined gravimetrically. The results, Table 1, show that the glass was attacked appreciably by the alkali, and that the attack increased with increasing time and concentration of the boiling sodium hydroxide solution.

TABLE 1.—*Silica dissolved from Kjeldahl flasks by boiling dilute NaOH*

TIME OF BOILING	VOLUME OF LIQUID REMAINING IN FLASK	SILICA DISSOLVED
minutes	*ml.*	*mg.*
25	270	26.1
34	220	41.7
42	195	50.1
55	144	49.6
65	105	52.4
76	40	65.9

Comparative Recovery of Nitrate Nitrogen by Distillation from Glass and from Copper Kjeldahl Flasks Subsequent to an Ammonium Nitrogen Determination.—Further confirmation of the interference of silica with the quantitative reduction of nitrates by Devarda alloy was obtained by parallel experiments in glass and in copper Kjeldahl flasks; as before, successive determinations were made of the ammonium and nitrate nitrogen contents of a standard solution of ammonium nitrate. Table 2 shows that nitrate nitrogen determinations were low when carried out in glass flasks,

TABLE 2.—*Comparative results obtained with glass and with copper Kjeldahl flasks in the analysis of* NH_4NO_3

FLASK	AMMONIUM NITROGEN			NITRATE NITROGEN		
	ADDED	FOUND	RECOVERY	ADDED	FOUND	RECOVERY
	mg.	*mg.*	*per cent*	*mg.*	*mg.*	*per cent*
Glass	45.05	44.64	99.1	45.05	40.09	89.0
Glass	45.05	44.64	99.1	45.05	36.75	81.6
Glass	45.05	44.77	99.3	45.05	38.89	86.3
Copper	45.05	44.79	99.4	45.05	44.80	99.4
Copper	45.05	44.70	99.2	45.05	44.77	99.3
Copper	45.05	44.74	99.3	45.05	44.70	99.2

whereas the identical procedure carried out in copper flasks yielded virtually complete recoveries of nitrate nitrogen.

Quantitative Effect of Silica on Nitrate Nitrogen Determination.—Using copper flasks, the effect of various amounts of soluble silica on the recovery of nitrate nitrogen was studied. Preliminary experiments revealed that the amount of sodium hydroxide, the particle size and amount of alloy, and the rate of distillation were very critical factors; extreme care was taken, therefore, to make all runs identical except for differences in the silica added. Twenty-five mg. increments of silica were added as sodium silicate to a series of aliquots of potassium nitrate solution containing 45.05 mg. of nitrate nitrogen. To each of these solutions was added 3.00 grams of minus 20-, plus 32-mesh alloy; 3.04 grams of sodium hydroxide; and sufficient water to bring the volume to 325 ml. As shown in Table 3, each increment of silica caused an appreciable decrease in the recovery of ni-

TABLE 3.—*Recovery of nitrate nitrogen in presence of various amounts of silica*

SiO_2 ADDED	NITRATE NITROGEN		
	ADDED	FOUND[a]	RECOVERY
mg.	*mg.*	*mg.*	*per cent*
0	45.05	44.91	99.7
25	45.05	44.78	99.4
50	45.05	43.82	97.3
75	45.05	41.55	92.2
100	45.05	36.20	80.4
125	45.05	32.81	72.8
150	45.05	28.56	63.4

[a] Average of six determinations.

trate nitrogen. The data in Table 3, when considered in conjunction with those in Table 1, show that the quantity of silica likely to be dissolved in an ammonium nitrogen determination in glass apparatus would cause a considerable error in a subsequent determination of nitrate nitrogen.

Elimination of Silica Interference.—The presence of silica appeared to be responsible for the erratic nitrate nitrogen results; hence, studies were directed toward two objectives: minimizing the solution of silica from the glassware and eliminating the effect of any silica that was dissolved.

By the use of magnesium oxide as the alkali in the ammonium nitrogen determination, previous investigators not only obviated the decomposition of nitrogenous organic materials but also, perhaps fortuitously, kept the silica content of the solution sufficiently low to avoid interference in the subsequent determination of nitrate nitrogen. Tests showed that calcium or magnesium oxide, when boiled with water for 1 hour in glass Kjeldahl flasks, dissolved insufficient silica to cause appreciable interference with the subsequent reduction of nitrates by Devarda alloy. Magnesium oxide removed less silica from the glassware than did calcium oxide,

and apparently little of the silica removed remained in a soluble form. The experimental addition of magnesium oxide to a nitrate solution containing 100 mg. of silicon dioxide as sodium silicate apparently precipitated the silica, for the theoretical amount of nitrate nitrogen was recovered on analysis of the solution.

Efforts to eliminate the effect of silica on the nitrate determination revealed that the interference was lessened by (a) the use of alloy of finer particle size, (b) an increase in the amount of alkali, or (c) an increase in the rate of distillation. By increasing the amounts of sodium hydroxide and alloy over those prescribed in the A.O.A.C. procedure, it was found possible to overcome the effect of dissolved silica. The excessive frothing encountered under these conditions was decreased by the addition of alcohol, but blank determinations were then higher than desirable, despite the use of a Davisson scrubber.

DISCUSSION

The results of this study indicate that the solution of silica from the glass flask does not interfere with the determination of nitrate nitrogen by current methods. Ammonium nitrogen and nitrate nitrogen can be determined accurately in the same solution by determining the ammonium nitrogen with magnesium oxide according to the official A.O.A.C. procedure (*13*) and by subsequently determining nitrate nitrogen according to the A.O.A.C. modification of the Devarda method (*13*); also, the recovery of both ammonium and nitrate nitrogen is complete when analysis is made by Devarda's original method (*8*), which specifies an NaOH addition of over five times that prescribed by the A.O.A.C. method (*13*). While the amount of silica dissolved by the high concentration of alkali in the original Devarda method (*8*) is large, the effect of the silica is overcome by virtue of the high alkalinity.

A possible explanation may be advanced for the low results obtained for nitrate nitrogen when the amount of sodium hydroxide prescribed (*13*) for this determination was added to the sample and the ammonium nitrogen was determined prior to the addition of Devarda alloy. In the determination of total nitrogen by the Devarda method, reduction of the nitrate nitrogen begins immediately and is near completion by the time the concentration of the alkali becomes sufficiently high for appreciable attack on the glass flask. When ammonium nitrogen is determined first, however, the Kjeldahl flask is attacked strongly by the alkali, especially in the latter part of the distillation, and the silica content of the alkaline solution becomes sufficient to cause appreciable interference with the reduction of nitrates by the alloy.

These findings suggest that silica may form a film over the surface of the alloy and thus inhibit the reduction of the nitrates. Evidently, this film is broken by high alkali concentrations and by rapid rates of heating.

The increased surface area resulting from the use of larger amounts of alloy or of smaller particle sizes of alloy diminishes the effect of the film. The protection of aluminum metal from corrosion by the presence of silicates has been observed (*2*); since the alloy contains 45 per cent aluminum, it may be that the interference of silica with the reduction of nitrates by Devarda alloy is closely related to this phenomenon.

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RAPID METHOD FOR DETERMINING "CRUDE FIBER" IN DISTILLERS' DRIED GRAIN

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The term "crude fiber" used in relation to agricultural products generally means the organic residue, consisting largely of cellulose, some lignin, and pentosans, which remains after the other carbohydrates and proteins have been removed by successive treatment with boiling acid and alkali. Crude fiber is not attacked by enzymes from higher plants or animals, but may be directly utilized when the digestive system is rich in symbiotic microoganisms that are able to split the cellulose molecule.

Feeds that are high in fiber are digested less readily than are other foods; maximum digestibility appears to occur when the crude fiber content is 6–7 per cent.[1] In the official A.O.A.C. procedure for analysis of feeds, the

[1] J. Axelsson, *Biedermanns Zentr. B. Tierernähr.*, **12**, 414–443 (1940).

carbohydrates are determined as two groups—crude fiber and nitrogen-free extract. Crude fiber is determined by a chemical method devised by Hennenberg and Stohman[2] and known as the Weende method. This procedure removes the proteins, sugars, and starch, leaving as a residue most of the cellulose and other complex polysaccharides along with some mineral matter. The method is highly empirical as it does not provide sharp separation into chemical groups, but it is useful because it makes a distinction between the more digestible and less digestible carbohydrates.

Scharrer and Kurschner[3] devised a rapid method for the estimation of crude fiber, but it has been found unsuccessful in its original form. Of the various modifications investigated, the most suitable one is described here, and it is recommended because it is rapid and reliable.

It was the purpose of this study to develop a satisfactory procedure for determining crude fiber in distillers' dried grain. The work was pursued with three major objectives: simplicity, rapidity, and reliability.

METHOD

REAGENT (ACID SOLUTION) USED FOR DIGESTING SAMPLE

500 ml. glacial acid (CH_3COOH), 450 ml. distilled water, 50 ml. HNO_3 (nitric acid sp. gr. 1.42), and 20 grams trichloroacetic acid (CCl_3COOH).

PROCEDURE

Weigh into a flask exactly 1 gram of grain from which the fat has been extracted.[2] Pour 100 ml of the acid solution over the sample, carefully washing the sides of the flask in order to remove any grain that may adhere. Immediately place the flask under a reflux condenser. (A Goldfisch extraction apparatus is recommended for this operation.) Apply sufficient heat to boil the contents gently. Reflux for exactly 40 minutes, starting from the time the acid solution is added. Immediately transfer the residual grain to a linen cloth, washing the residue thoroughly with distilled water, and quantitatively transfer the washed sample to a Gooch crucible which has been previously prepared. (Approximately .5 gram of ignited asbestos placed loosely in the Gooch prior to the transfer will aid greatly in filtration.)

Dry the crucible and contents in an oven at 105°C. until constant weight is recorded. Incinerate until the carbonaceous matter is consumed. Cool in desiccator and reweigh. The loss in weight is crude fiber.

$$\frac{\text{Weight of fiber} \times 100}{1 + \frac{(\%\ \text{fat})}{100}} = \%\ \text{fiber, dry basis}$$

RESULTS

The grain samples used in this study, originating from six different distilleries, were analyzed by both the A.O.A.C. and the proposed method. To test the applicability of the proposed method a variety of samples of by-products from different methods of cooking was used.[4] The various

[2] *Methods of Analysis, A.O.A.C.*, 1940, 357.
[3] Tierernährung, 3, 307–310 (1931).
[4] Willkie and Prochaska, "Fundamentals of Distillery Practice." Joseph E. Seagram & Sons, Inc. (1943).

types of samples are designated as follows: *A*, six samples representative of continuous pressure cooking; *B*, two samples of bath pressure cooking; and *C*, four samples of batch atmospheric cooking. The results are given in Table 1.

The proposed method, as shown by results in Table 1, is adaptable for measuring the fiber content of any type of distillery grain. The quantitative results are practically the same, but closer duplicability may be expected by the use of the proposed method.

TABLE 1.—*Crude fiber in various samples from different distilleries (% fiber dry basis)*

		(1) A.O.A.C. Method			(2) Proposed Method	
		(1)	(2)		(1)	(2)
A	1.	18.10	18.24	*B* 1.	20.65	21.32
		18.14	18.36		20.91	21.34
		18.75	18.50		21.95	21.71
	2.	18.11	18.27	2.	23.30	23.22
		18.21	18.30		23.53	23.58
		18.69	18.35		23.89	24.08
	3.	12.36	12.51	*C* 1.	16.52	17.35
		12.87	12.65		16.54	17.57
		12.92	12.61		17.07	17.95
	4.	14.16	13.30	2.	16.20	16.45
		14.24	13.65		16.25	16.92
		14.38	14.10		16.59	16.83
	5.	14.63	14.87	3.	15.60	16.43
		14.69	14.96		15.75	16.60
		15.40	15.35		16.35	16.72
	6.	2.85	2.81	4.	15.59	15.55
		3.12	3.31		15.97	15.57
		3.18*	3.47		15.99	15.90

* Solubles from thin stillage.

In order to secure data that could be systematically analyzed, the writers prepared one composite sample, on which they made 25 determinations for crude fiber, using both the official A.O.A.C. and the proposed method. Table 2 gives the results of this comparative study.

Based on the data given in Table 2 the following analysis was prepared[5]: The standard error of the mean for the proposed method is 0.03, and 0.08 for the A.O.A.C. The variation is greater in the A.O.A.C. method, indicating that the proposed method is more reliable and reproducible. Figures 1 and 2 show the reproducibility of the two methods.

[5] E. F. Lindquist, "Course in Statistics." Houghton Mifflin Co. (1942).

DISCUSSION

Time and the intensity of boiling both in acid and alkali provide a ready source of error in the A.O.A.C. procedure. An increase in the refluxing time decreases the apparent percentage of fiber, and a decrease in the refluxing time increases the apparent amount of fiber. E. Hannerz[6] reports

TABLE 2.—*Crude fiber results on composite sample*
(% fiber dry basis)

(1) A.O.A.C. Method			(2) Proposed Method		
Sample	(1)	(2)	Sample	(1)	(2)
1	18.00	18.25	14	18.84	18.57
2	18.11	18.27	15	18.85	18.63
3	18.19	18.30	16	18.89	18.63
4	18.21	18.30	17	18.90	18.64
5	18.23	18.30	18	18.93	18.67
6	18.27	18.35	19	18.95	18.69
7	18.33	18.38	20	18.99	18.72
8	18.40	18.41	21	19.04	18.73
9	18.41	18.45	22	19.05	18.77
10	18.51	18.47	23	19.09	18.81
11	18.68	18.52	24	19.11	18.82
12	18.69	18.53	25	19.12	18.83
13	18.70	18.57	Arithmetic mean	18.66	18.54

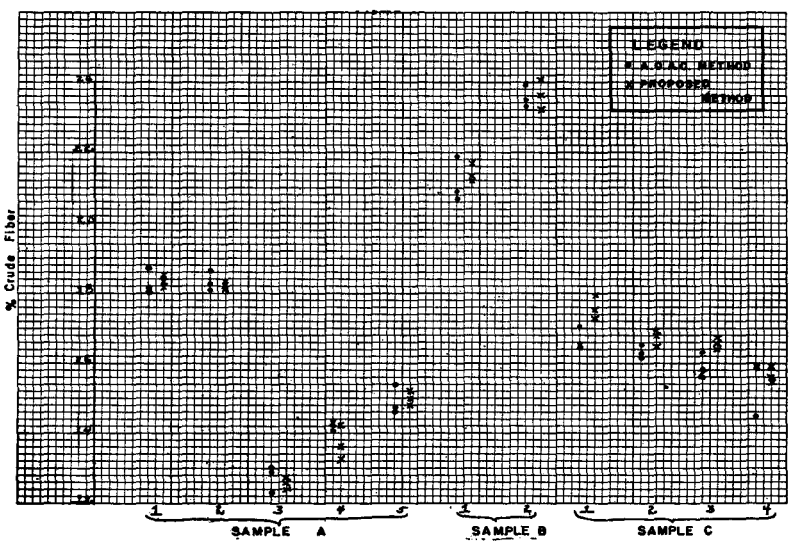

FIG. 1.—COMPARISON OF METHODS OF CRUDE FIBER ANALYSIS.

[6] *Svensk. Kem. Tid.*, 52, 247–253 (1940).

a progressive decrease in fiber content from 35.1 to 28.8 per cent, or an average deviation of 1.59 per cent for each 10 minute reflux variation. The proposed procedure is approximately 50 per cent less sensitive to reflux time, as the average deviation for each 10-minute variation is 0.73 per cent.

The intensity of the heat applied also materially affects the results. A

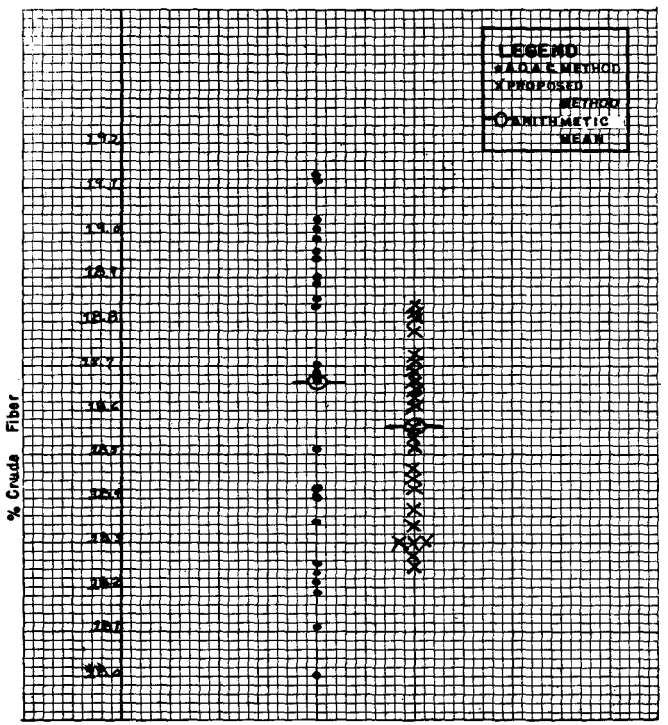

FIG. 2.—REPRODUCIBILITY OF THE PROPOSED PROCEDURE AS COMPARED WITH THE OFFICIAL METHOD.

divergence of 0.60 per cent was sustained using the Goldfisch apparatus by varying the degree of heat from *medium* to *high* in the A.O.A.C. procedure, whereas a variation of the heat from *low* to *high* in the proposed procedure gave only 0.2 per cent difference. G. L. Bidwell[7] substantiates this finding in his report by stating that the works of numerous collaborators show that the same kind of condensers, filtering media, flasks, crucibles, and the same degree of heat must be used before concordant results can be expected.

[7] *This Journal*, 5, 55–57 (1921).

One-third less time is consumed in the digestion of the grain by the proposed procedure than by the official method, and no preheating of solutions is necessary. The probability of error in transferring the charge is lessened 40 per cent since only three transfers are necessary, whereas a determination by the A.O.A.C. method involves five transfers.

The time of filtration through a Gooch crucible of the residue of the digestion varies widely, ranging from 45 minutes to 8 hours. Neubert, Van Amburgh, and St. John[8] reported filtrations lasting 1–24 hours, and credited the cause to the hydrated collodial state that some grains assume upon contact with water. Bidwell and Bopst[9] advise that filtration should be accomplished immediately after digestion because the additional action that takes place noticeably affects the results. They state that any sample that requires more than 5 minutes to filter should not be reported. In the numerous analyses of grain for crude fiber made by the proposed procedure, the filtration period never exceeded 3 minutes.

SUMMARY

(1) A crude fiber determination can be completed by the proposed method in approximately one-half the time required by the official A.O.A.C. method.

(2) The probability of error is greatly lessened, since only three transfers are necessary, whereas the A.O.A.C. method involves five transfers.

(3) Filtration of the residual grain from the digestion is rapidly completed, in no instances requiring longer than three minutes.

(4) The error in fiber content caused by the time of digestion and the quantity of heat used is minimized by the use of the proposed method.

(5) Statistical analysis of the data presented shows that the proposed method is a highly reproducible procedure for determining crude fiber content in distillers' dried grain.

ESTIMATION OF UNDECOMPOSED DDT SPRAY DEPOSITS ON APPLES FROM TOTAL ORGANIC CHLORINE CONTENT

By JACK E. FAHEY (U. S. Department of Agriculture, Agricultural Research Administration, Bureau of Entomology and Plant Quarantine, Beltsville, Md.)

The development of each new insecticidal material for control of the codling moth on apples is greatly expedited when it is possible to study spray deposits of the material by chemical analysis. Steiner *et al.*[1] recently reported preliminary studies of DDT (2,2-bis(*p*-chlorophenyl)1,1,1-trichloroethane) which show this material to be particularly promising

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[8] *Ind. Eng. Chem., Anal. Ed.*, 12, 451 (1940).
[9] *This Journal*, 5, 58–70 (1921).
[1] Steiner, L. F., C. H. Arnold, and S. A. Summerland, *J. Econ. Entomol.*, 37, 156 (1944).

against this insect. The high chlorine content of DDT, coupled with the fact that organic chlorides are not commonly found in sprays applied for codling moth control, suggests the possibility of obtaining a measure of the DDT deposits by determination of their chlorine content.

P. K. Winter[2] describes a method of burning an organic chloride in a stream of gas and recovering the chlorine in a form suitable for determination by standard methods. Hall *et al.*[3] have employed a modification of the Winter method for determination of DDT in emulsions and various other materials. The general technic employed promises to be rapid and adaptable to routine analysis of the large number of samples commonly encountered in the study of spray deposits.

The problem of determining the organic chloride content of spray deposits resulting from the application of DDT for codling moth control is very different from the analysis of organic halides discussed by Winter, or even the analysis of DDT emulsions described by Hall *et al.* The residue deposits on sprayed fruit will vary from approximately 0.1 mg. to as much as 3.0 mg. per fruit depending upon the size of the fruit, concentration of DDT in the spray mixture, and composition of the spray mixture and will be contaminated with various quantities of other spray materials, fruit wax, etc. The method herein described consists of a technic for recovery of the organic chloride from the fruit surface, preparation of a solution of this residue in an organic solvent, and the analysis of the solution by a modification of the technic described by Hall *et al.*

RECOVERY OF ORGANIC CHLORIDE DEPOSITS FROM FRUIT

The rapid method of sample preparation described by Fahey, Cassil, and Rusk,[4] which is particularly well adapted to routine analysis of spray deposits, has been found satsfactory for recovery of organic chloride residues deposited by DDT sprays. Both acetone and benzene have been found to be effective solvents, and other solvents may be equally satisfactory.

The sample, consisting of 10–25 fruits, is weighed into a tared container, from 100 to 500 ml. (depending upon the size of the sample) of solvent (acetone) added, and the container sealed and tumbled for 5 minutes. The solvent is then drained into a volumetric flask, the fruit and jar rinsed twice with about one-third the quantity of solvent employed for stripping the residue from the fruit, and the whole made to volume. If a less volatile solvent is employed, e.g., benzene or toluene, a carefully measured quantity of solvent can be added for stripping, and the volume assumed to remain unchanged. In either case an aliquot of the strip solution is then concentrated to contain chlorine equivalent to 0.5–5.0 mg. of DDT per milliliter.

[2] *Ind. Eng. Chem., Anal. Ed.*, 15, 571 (1943).
[3] Hall, S. A., M. S. Schechter, E. E. Fleck, U. S. Bur. Entomol. and Plant Quarantine, Et. 211 (1944).
[4] *This Journal*, 26, 150 (1943).

METHOD OF ANALYSIS

REAGENTS

(a) *Absorption solution.*—Approximately 0.3 *N* with respect to NaOH and 0.1 *N* with respect to As_2O_3. Weigh 12 grams of NaOH and dissolve in about 50 ml of water, add 5 grams of As_2O_3, dissolve, and make to 1 liter.

(b) *Nitrobenzene.*—Mononitrobenzene, reagent quality.

(c) *Indicator.*—10 grams of $Fe_2(SO_4)_3$ and 2 ml of concentrated HNO_3 made to 250 ml.

(d) *Standard solution of DDT.*—Weigh 0.05 gram of DDT into a 100 ml volumetric flask, dissolve in benzene, and make to volume.

(e) *Standard solution of silver nitrate, approximately 0.007 N.*—Weigh 1.2 grams of $AgNO_3$, dissolve in water, and make to 1 liter. (This solution is approximately equal to 0.5 mg. of DDT per milliliter.)

(f) *Standard solution of potassium thiocyanate, approximately 0.007 N.*—(Calculations are simplified if this solution is exactly equivalent to the standard $AgNO_3$ solution.)—Into a 125 ml. glass-stoppered flask measure 35 ml. of distilled water, 4 ml. of nitrobenzene, 1 ml. of concentrated HNO_3, and 1 ml. of $Fe(SO_4)_3$ indicator. Shake violently for 1 minute. Then add standard KSCN dropwise until the first tinge of pink color persists after violent agitation of the flask for 10 seconds. (This titer is the titration blank and represents the quantity of KSCN necessary to give a recognizable color change with the $Fe_2(SO_4)_3$ indicator. By the same general procedure determine the equivalent of 1 ml. of KSCN in milliliters of $AgNO_3$. The normality of the $AgNO_3$ is determined by analysis of a known solution of DDT following the method described under analytical procedure.

APPARATUS

The apparatus employed for recovery of chlorine is shown in Figure 1. *A*, the combustion or volatilization tube, is made of 12 mm. (o. d.) tubing. The orifice at the short arm is 1 mm. in diameter. The tube is heated by a coil of No. 26 nichrome wire 3.5 feet long, wound around the short arm and base of the tube and connected to a source of power through a variable transformer. The length and size of the wire may be varied to fit conditions. Hall *et al.*[3] recommend 10 feet of No. 28 wire, which permits the use of the entire range of the variable transformer. The lower resistance (3.5 feet of No. 26 wire) would permit the operation of several units in series with a single transformer. *B*, the chimney, is a 25 mm. adapter. *C*, the absorption flask, is designed after that employed by Cassil.[5] This absorption unit may be constructed in any laboratory with a length of 8 mm. tubing for the bubbler and a 25 mm. test tube and short length of 12 mm. tubing for the receiver flask. This absorption unit is efficient and at the same time permits the use of a much smaller quantity of absorbing solution than the conventional gas-scrubbing bottle.

PROCEDURE

Transfer a 1 ml. aliquot of the concentrated sample to the combustion tube and remove the solvent by placing the tube in a hot-water bath. Take care to prevent water from entering the combustion tube during evaporation of the solvent. If larger aliquots are necessary, obtain them by volatilizing the solvent as it is added to the combustion tube or between successive additions of 1 ml. aliquots.

Assemble the apparatus as shown in Figure 1. Add 15 ml. of NaOH-arsenite solution and 4 ml. of nitrobenzene to the absorption unit (*C*). (The nitrobenzene is added at this time to prevent excessive foaming of the absorbing solution.) Adjust

[5] *This Journal*, 24, 196 (1941).

the vacuum to allow enough air to pass through the system to support the gas flame. Adjust the flow of gas through the combustion tube to give a flame about 1 cm. high. After igniting the gas, put the chimney over the flame so that all the products of combustion will pass through the absorbing solution. Turn the current on and adjust the transformer to deliver 20 volts, but after 5 minutes increase to 35 volts. (If several units are being operated in series, the setting will have to be adjusted. The character of the flame serves as a guide in heating the sample.) Do not volatilize the sample so rapidly as to cause a smoky flame, with the resultant deposit of soot in the chimney and contamination of the absorbing solution.

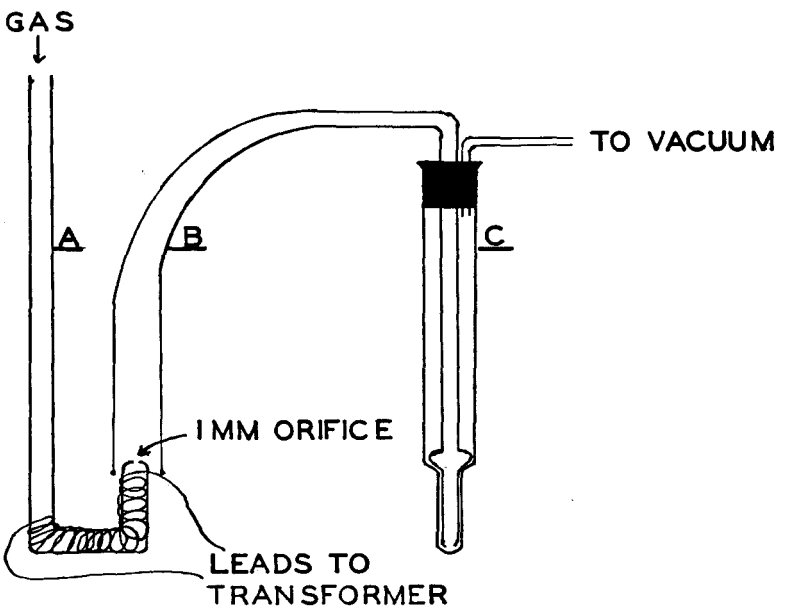

FIG. 1.—APPARATUS FOR COMBUSTION OF DDT RESIDUES.

As soon as the sample has been completely volatilized, as indicated by the color of the flame, turn off the gas, disassemble the apparatus, and transfer the absorbing solution to a 125 ml. glass-stoppered flask and rinse the scrubber thoroughly. (The total volume of the scrubbing solution and rinse should not exceed 50 ml.) To the solution in the flask add an excess of the standard $AgNO_3$ solution (the amount required must be estimated from knowledge of the sample). Add 1 ml. of concentrated HNO_3 and 1 ml. of the $Fe_2(SO_4)_3$ indicator, and shake the flask violently for 1 minute, taking the necessary precautions to permit escape of carbon dioxide generated by the acid. Violent agitation of the sample is necessary to complete the impregnation of the AgCl with the nitrobenzene (added to the absorbing solution before ignition of the sample). Titrate the excess $AgNO_3$ with standard KCNS until a tinge of pink first persists after 10 minutes' agitation of the stoppered flask.

The end point of the titration of $AgNO_3$ with the 0.007 *N* KCNS is difficult to recognize, and considerable experience will be required before accurate results are obtained. Unless the AgCl is completely protected from the water phase by the nitro-

benzene, it will absorb $AgNO_3$, which will then be released only slowly and will cause fading of the end point. For this reason the violent agitation and empirical procedure are necessary to obtain a satisfactory replication of results. The author has found that 0.25 ml. of 0.007 *N* KCNS will give a recognizable color change in 35–50 ml. volume.

DISCUSSION OF METHOD AND RESULTS

Two procedures are suggested for handling the stripping process. With the less volatile solvents, e.g., benzene or toluene, it is preferable to take a

TABLE 1.—*Recovery of DDT from apples*

DDT ADDED		DDT RECOVERED			
		ACETONE SOLVENT		BENZENE SOLVENT	
mg.		*mg.*	*per cent*	*mg.*	*per cent*
	Strip solution and rinse made to volume				
50		46.2	92.4	49.9	99.8
50		48.8	97.6	46.5	93.0
100		100.0	100.0	100.0	100.0
100		99.6	99.6	99.2	99.2
500		490.0	98.0	479.0	95.8
500		494.0	98.8	492.0	98.4
	Average		97.7		97.7
	Std. dev.		2.8		2.8
	Measured volume used for stripping				
250		255.5	102.2	252.8	101.1
250		254.0	101.6	255.9	102.4
250		265.0	106.0	258.9	103.6
250		267.5	107.0	252.8	101.1
250		269.0	107.6	246.8	98.7
	Average		104.9		101.4
	Std. dev.		2.8		1.8

carefully measured quantity of solvent for stripping and remove the aliquot directly from the stripping container, without making to volume. However, with highly volatile solvents, such as acetone or ethyl ether, the loss of solvent in processing results in too high apparent recovery of DDT. Table 1 shows the recovery of measured quantities of DDT, added to apples, by the two processes and using acetone and benzene as solvents. When the stripping solvent and rinses were made to volume before the aliquot was taken for analysis the recovery of added DDT was 97.7 per cent (s.d. 2.8) with either solvent. When a carefully measured quan-

tity of solvent was used for stripping and the aliquot for analysis removed without further volume adjustment the recovery of added DDT was 104.9 (s.d. 2.8) and 101.4 (s.d. 1.8) per cent with acetone and benzene respectively.

The silver nitrate is standardized by carrying a measured quantity of DDT through the analytical procedure, and since the chlorine content of

TABLE 2.—*Recovery of DDT from solutions of commercial DDT*

SAMPLE NO.	FROM 0.5 MG. OF DDT		FROM 1.0 MG. OF DDT		FROM 5.0 MG. OF DDT	
	mg.	*per cent*	*mg.*	*per cent*	*mg.*	*per cent*
1	0.51	102.0	0.99	99.0	4.96	99.2
2	0.49	97.4	1.02	102.0	5.02	100.4
3	0.51	102.0	0.99	99.0	5.02	100.4
4	0.50	100.0	0.99	99.0	5.00	100.0
Average		100.4		99.8		100.0
Std. dev.		2.2		1.5		0.1

TABLE 3.—*Analysis of fruit sprayed with DDT*

TEST NO.	DDT/100 GALLONS OF SPRAY	DDT		
		TOTAL	PER FRUIT	PER SQUARE CENTIMETER
		mg.	*mg.*	*micrograms*
	Water pastes:			
1	0.5 lb.	8.1	0.41	5.2
2	1.0 lb.	17.3	0.86	10.9
3	2.0 lb.	24.9	1.65	21.9
4	4.0 lb.	36.6	3.66	48.6
	50:50 mixture with pyrophyllite			
5	3.0 lb.	16.0	1.60	21.6
6	Same as No. 5 plus soybean oil 1 qt. and Mississippi bentonite 0.5 lb.	27.2	2.72	37.8

different grades of DDT may be expected to vary somewhat, it is recommended by Hall *et al.*[3] that the DDT employed as a primary standard be of the same grade as that employed in preparing the sprays applied for deposit studies.

Table 2 shows the variation between replicate samples at three levels of the method. As would be expected, the least variation is shown at the highest level.

In order to check the practical application of the method, fruit was sprayed in the laboratory with a converted orchard sprayer and then

analyzed by the method described above. The results of these studies are shown in Table 3. The DDT deposits found were of the magnitude that would be anticipated from similar studies of lead arsenate spray mixtures.

In the study of spray deposits frequent checks on unsprayed fruit should be made. The studies conducted at this labratory show that unsprayed fruit may give a blank equal to as much as 0.08 mg. of DDT per fruit.

By this method from 20 to 30 minutes are required to complete a single analysis after the concentrated solution is prepared. By operating a bank of ignition units it should be possible to complete from 6 to 12 analyses an hour.

SUMMARY

A technic is outlined for recovery of organic chloride spray deposits from apple surfaces by means of an organic solvent, ignition of this solution, and recovery of the chlorine in a form suitable for quantitative estimation by a modification of the Volhard method. It is anticipated that this technic can be used for estimating the amount of DDT (2,2-bis (*p*-chlorophenyl)1,1,1-trichloroethane) in deposits resulting from sprays applied to apple trees for codling moth control. Results are given showing the magnitude of deposits of DDT from several spray mixtures applied in the laboratory.

ADAPTATION OF THE WAGNER PROCEDURE TO THE CHEMICAL EVALUATION OF FUSED TRICALCIUM PHOSPHATE*

By W. H. MacIntire and George Palmer (The University of Tennessee Agricultural Experiment Station, Knoxville)

Fused tricalcium phosphate is a new and distinctive product. It is obtained by the defluorination of rock phosphate through a process developed by the Tennessee Valley Authority.[1,2] The present materials were produced by means of an electric furnace. A similar material is foreseen as the product from a fire shaft, or "blast" furnace. Its chief component is the alpha form of the tertiary phosphate that is set free from apatite combination while the furnace charge of rock phosphate is molten.[3] Its fertilizer effectiveness has been shown through pot cultures reported by Ross and Jacob and 15 collaborators,[4] and in many similar unpublished comparisons at the Tennessee Station, as well as in numerous cooperative field

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* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., October 25, 26, 1944.

[1] Curtis, H. A., R. L. Copson, E. H. Brown, and G. R. Pole, *Ind. Eng. Chem.*, 29, 766–770 (1937).

[2] Elmore, K. L., E. O. Huffman, and W. W. Wolf, *Ibid.*, 34, 40–48 (1942).

[3] MacIntire, W. H., S. H. Winterberg, B. W. Hatcher, and George Palmer, *Soil Sci.*, 57, 425–442 (1944).

[4] *This Journal*, 20, 231–248 (1937).

tests. Its compatability with other fertilizer materials also has been demonstrated.[5]

There is, however, no accredited analytical control procedure for the evaluation of the new product. The Wagner method[6] long has been "official" for basic slag, and the results of pilot determinations indicated that it could be made operable also for the control analysis of the fused phosphate. The immediate contribution stems from a study to ascertain whether a modified technic of the Wagner procedure indicates for the new product a fertilizer value consonant with the value registered by plant response in extensive pot culture experiments.

PRELIMINARY OBSERVATIONS

Earlier studies demonstrated that the dissolvability of the P_2O_5 content of fused rock phosphate in reagent ammonium citrate, and in carbonated water, is governed by the degree of the thermally-induced defluorination.[3] A continuously-agitated citrate digestion at 65°C. indicated that the fertilizer effectiveness of "fused tricalcium phosphate" was less than that registered through comparison with superphosphate in pot cultures. Preliminary determinations on 2 per cent citric acid digestates of pure basic phosphates of calcium demonstrated that the citrate ion does not hinder the direct precipitation of ammonium phosphomolybdate in untreated aliquots of admissible volume and P_2O_5 concentration.

EXPERIMENTAL

Four rock phosphate fusions of variant degree of defluorination were employed. The fusions that contained 0.7 and 1.25 per cent of fluorine were included merely as controls, and are not to be considered as representative "products." The fusions were at 1600°–1650°C., at which temperature the intermediate compound represented by the formula $Ca_{10}FOH(PO_4)_6$ is not stable, and their fluorine contents therefore are attributed to the respective residues of apatite in the matrixes of tricalcium phosphate. The percentages of P_2O_5 dissolved by the two citric reagents are expressed in relation to analytical charge, and also to the computed incidence of tricalcium phosphate. The occurrence of the alpha form was established by x-ray examinations.[3] The computation was made by deducting from total P_2O_5 content the amount accounted for by the apatite equivalence of the residual F_2. The totals for P_2O_5 content were determined by digestions of 1-gram charges of 100-mesh material in aqua regia, which effected complete dissolutions.

The results of Table 1 show the dissolvability of the four fused materials of variant particle size in the conventional citrate reagent at 65°C.,

[5] MacIntire, W. H., and L. J. Hardin, *Ind. Eng. Chem.*, 32, 574–579 (1940).
[6] *Methods of Analysis, A.O.A.C.*, 1940, 39, 68, and 22, 12.

TABLE 1.—*Influence of several factors upon dissolubility of alpha tricalcium phosphate component of rock phosphate fusions in neutral ammonium citrate and in 2 per cent citric acid*

P_2O_5 IN FUSED MATERIAL						P_2O_5 EXTRACTIONS									
						BY AMMONIUM CITRATE[b]						BY CITRIC ACID[c]			
						WITH PERIODIC AGITATION[d]		WITH CONTINUOUS AGITATION				WITH CONTINUOUS AGITATION			
		IN ALPHA FORM						ACTUAL		FRACTION OF ALPHA		ACTUAL		FRACTION OF ALPHA	
NO.	TOTAL	COMP.[a]	FRACTION	F	MESH	ACTUAL	FRACTION OF ALPHA	WITH FILTER	NO FILTER	WITH FILTER	NO FILTER	WITH FILTER	NO FILTER	WITH FILTER	NO FILTER
	per cent	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
					−50+100	2.9	25	3.6	2.1	31	18	5.3	5.3	45	45
S-849	25.8	11.8	46	1.25	−50	3.4	29	3.9	3.0	33	25	6.0	6.1	51	52
					−100	4.4	37	4.6	4.6	39	39	7.0	6.9	60	58
					−50+100	7.4	37	8.1	7.4	40	37	15.1	15.4	75	77
S-861	27.9	20.1	72	0.7	−50	8.6	43	9.3	8.7	46	43	15.8	15.9	79	79
					−100	10.1	51	10.7	10.2	53	51	16.5	16.3	82	81
					−50+100	13.5	56	15.6	14.0	65	58	21.3	21.2	89	88
S-859	28.5	24.0	87	0.4	−50	15.3	64	17.1	16.4	71	68	21.8	21.8	91	91
					−100	17.9	75	18.4	18.1	77	75	22.5	22.5	94	94
	25.1	24.4	97		−50+100	15.3	63	18.9	17.4	77	71	23.6	23.5	97	96
S-847	25.2	24.5	97	0.06	−50	17.4	71	21.5	20.0	88	82	24.9	24.7	102	101
	25.0	24.3	97		−100	21.0	86	22.0	21.7	90	89	24.8	24.7	102	102

[a] Computed by deducting from total P_2O_5 content the amount accounted for by the apatite equivalence of the unremoved F_2.
[b] A.O.A.C. reagent at 65° C.; 1-hour single digestion of 1 gram in 100 ml.
[c] At room temperature, single digestion one-half hour, 2 grams in 200 ml.
[d] Manual, at intervals of 5 minutes.

and in 2 per cent citric acid at room temperature, with 1-gram charge per 100 ml. of dissolvent as a constant. The citrate digestions were made under three conditions: manual agitation at 5-minute intervals, and continuous mechanical agitation, with and without inclusion of a 9 cm. filter paper. The continuous end-over-end agitations of the citric acid digestates were made by means of the previously-described and illustrated homemade apparatus,[7] an improved reproduction of which is now manufactured.

In every one of the four fused materials, decrease in particle size brought increase in P_2O_5 dissolved at 65°C. by the 1-hour citrate digestion. When a 9 cm. filter was not included, the continuous agitation of the citrate digestates did not give significant increases over the amounts of P_2O_5 dissolved by direct digestion with periodic agitation, except for product S-847 of 0.06 per cent fluorine content. In the continuously-agitated citrate digestates, however, the inclusion of the filter gave P_2O_5 extractions beyond those obtained when the filter was not included. In all of the citrate digestions, decrease in particle size caused increases in the amounts of P_2O_5 extracted. The inadequacy of 100 ml. of the citrate reagent for extractions from 1-gram charges of minus† 100-mesh material is established by the values registered by the six continuously-agitated citrate digestates of the product of minimal fluorine content, with and without filter.

In every comparison as to the dissolvent action of the two citric reagents under continuous agitation, the acid gave the higher result. The several minus 100-mesh separates were dissolved to a somewhat greater extent than the coarser separates in the citric acid digestions of the products that contained as much as 0.4 per cent of fluorine.

The inclusion of filter exerted no effect upon P_2O_5 dissolubility in the continuously-agitated citric acid digestates. This is in harmony with the conclusion of Jacob, Rader, and Tremearne from their studies of the solubilities of basic phosphates: "When the flask is shaken continuously for 30 minutes, filter paper has little or no effect on the solubility of phosphates in 2 per cent citric acid solution."[8]

The P_2O_5 values for the acid digestions of the separates of the product carrying 1.25 per cent fluorine were about one-half of the P_2O_5 computed as being in the form of $Ca_3(PO_4)_2$, whereas values up to 82 per cent and 94 per cent of such P_2O_5 were obtained in corresponding extractions of the materials that carried 0.7 and 0.4 per cent of fluorine. But, the citric acid digestions did register complete dissolubility of the computed incidence of tricalcium phosphate in the $-50+100$-mesh separate of the product containing 0.06 per cent fluorine, and also dissolution of some of the apatite

[7] MacIntire, W. H., H. L. Marshall, and T. A. Meyer, *This Journal*, **27**, 272–283 (1944).

† As used here and subsequently the term, or the minus sign, means passing a screen of the specified mesh. In like manner a + sign means remaining on such screen.

[8] *This Journal*, **19**, 449–472 (1936).

TABLE 2.—*Influence of degree of defluorination of rock phosphate fusions upon P_2O_5 values by 2 per cent citric acid solution, as affected by solvent volume and by removal of citrate and silica from aliquots*[a]

NO.	P_2O_5 IN FUSED MATERIAL			F	CITRIC ACID		P_2O_5 IN ALIQUOTS OF DIGESTATES[c]					
							PROPORTION OF THE CHARGE, AS FOUND BY MoO_3 PRECIPITATION			AS PROPORTION OF THE ALPHA FORM IN THE CHARGE		
	TOTAL	IN ALPHA FORM			DIGESTATE VOLUME	ALIQUOT ANALYZED	WITHOUT REMOVAL OF CITRATE AND SILICA	AFTER REMOVAL OF—		WITHOUT REMOVAL OF CITRATE AND SILICA	AFTER REMOVAL OF—	
		COMP.[b]	FRACTION					CITRATE ALONE[d]	CITRATE AND SiO_2[e]		CITRATE ALONE[d]	CITRATE AND SiO_2[e]
	per cent	*per cent*	*per cent*	*per cent*	*ml.*	*ml.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
S-849	25.8	11.8	46	1.25	50	5	5.99	6.58	5.51	51	56	47
					100	10	7.32	7.98	7.03	62	68	60
					150	15	8.41	8.93	8.36	71	76	71
					200	20	9.32	9.68	8.80	79	82	75
S-861	27.9	20.1	72	0.70	50	5	13.79	14.20	13.35	69	71	66
					100	10	17.85	18.11	16.68	89	90	83
					150	15	20.08	20.12	19.83	100	100	99
					200	20	22.07	21.95	21.66	110	110	108
S-859	28.5	24.0	87	0.40	50	5	20.12	20.39	19.92	84	85	81
					100	10	22.47	22.78	22.34	94	95	93
					150	15	24.34	24.62	24.08	101	103	100
					200	20	25.45	25.34	25.32	106	105	105
S-847	25.0	24.3	97	0.06	50	5	20.80	21.56	20.90	86	89	86
					100	10	24.75	24.85	24.42	102	102	100
					150	15	24.65	24.85	24.65	102	102	102
					200	20	25.00	24.90	24.80	103	102	102

[a] Constant charge of 1 gram of 100-mesh material.
[b] Computed by deducting from total P_2O_5 content the amount accounted for by the apatite equivalence of the unremoved F_2.
[c] Constant agitation 30 minutes at room temperature.
[d] By addition of a 5 ml. slurry of $Ca(OH)_2$ and 1 ml. of a 5 per cent solution of $KMnO_4$, evaporation to dryness, and ignition to whiteness at 650° C.
[e] By addition of 10 ml. of $HClO_4$, digestion to fumes and filtration of silica.

that became dispersed when the reagent effected disintegration of the charge of the minus 50-mesh and −100-mesh separates of the fused product.

INFLUENCE OF SEVERAL FACTORS UPON DISSOLUBILITY BY 2 PER CENT CITRIC ACID

The results of Table 2 register the dissolutions of the four fused materials by 30-minute continuously-agitated digestions in the reagent acid at room temperature, as affected by the several factors—(a) unexpelled fluorine content of the fused material, (b) variance in volume of solvent for uniform analytical charge, (c) removal of the citrate ion alone from aliquots of digestates, and (d) joint removal of that ion and silica.

Dissolution of the uniform charge was decreased by increase in residual fluorine. Increase in proportion of reagent to charge brought increases in the P_2O_5 content on untreated aliquots, on those free of the citrate ion, and also on those freed of both citrate and silica. The removal of citrate alone was accomplished by the addition of 5 ml. of calcium hydroxide slurry and 1 ml. of a 5 per cent solution of potassium permanganate was followed by evaporation, ignition, and dissolution of the resultant calcine in nitric acid and several drops of hydrochloric acid. In every instance, this treatment resulted in a P_2O_5 value higher than the one obtained when the aliquot was freed of both citrate and silicon dioxide by the addition of 10 ml. of perchloric acid, evaporation to fumes, dilution, and filtration to remove silica (the incidence of which tends to induce a plus error). The results were virtually the same whether perchloric acid was used alone or with supplements of hydrochloric and nitric acids, singly or jointly.

The disparity between the results by the treatment with calcium hydroxide and those by the perchloric acid treatment became less with diminution in the fluorine content of the fused materials. Obviously, the lower values found for the perchloric acid-digested aliquots were not due to the elimination of silica. The lower values may have been caused by loss of phosphorus, as phosphine or as a phosphofluor compound, during the evaporation and before the system had been brought to a concentration of perchloric acid sufficient to effect oxidation and dehydration.

It is obvious also that 50 ml. of citric acid was insufficient for the extraction of the computed calcium phosphate content of a 1-gram charge, even for the virtually defluorinated product, whereas the 100-ml., 150-ml., and 200-ml. volumes effected complete extractions. The dissolution of phosphate content other than that attributable to the alpha form, is shown by the values for the 150-ml. and 200-ml. extractions of the materials that contained 0.7 and 0.4 per cent of fluorine. In the case of the virtually defluorinated product, however, the values for the 100-, 150-, and 200-ml. digestions were concordant, since all of these extracted P_2O_5

TABLE 3.—*Influence of particle size and proportion of charge to 2 per cent citric acid solvent upon dissolubility of alpha tricalcium phosphate component of rock phosphate fusions*

NO.	P_2O_5 IN FUSED MATERIAL					P_2O_5 EXTRACTIONS[b]					
		IN ALPHA FORM		F	MESH	ACTUAL			FRACTION OF COMPUTED ALPHA FORM		
	TOTAL	COMP.[a]	FRACTION			1 GRAM/100 ML.	2 GRAMS/200 ML.	1 GRAM/200 ML.	1 GRAM/100 ML.	2 GRAMS/200 ML.	1 GRAM/200 ML.
	per cent	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
	25.2	24.5	97	0.06	−50+80	24.45	24.40	25.17	100	100	103
S-847	25.2	24.5	97	0.06	−80+100	24.75	24.65	25.20	101	101	103
	25.0	24.3	97	0.06	−100	24.75	24.70	25.00	102	102	103
	28.5	24.0	87	0.40	−50+80	20.18	20.52	23.95	84	85	100
S-859	28.5	24.0	87	0.40	−80+100	21.50	21.20	25.15	90	88	105
	28.5	24.0	87	0.40	−100	22.47	22.48	25.95	94	94	108

[a] Computed by deducting from total P_2O_5 content the amount accounted for by the apatite equivalence of the unremoved F_2.
[b] Continuous agitation.

somewhat beyond the quantity attributed to calcium phosphate. Fineness of 100-mesh, the proportion of 1-gram charge per 100 ml. of 2 per cent citric acid, and agitation for 30 minutes at room temperature seem close to ideal conditions for the evaluation of a substantially defluorinated product. The factors of particle size and proportion of charge to volume of the reagent acid were considered further in the comparisons of Table 3 as to extent of calcium phosphate extraction.

INFLUENCE OF PARTICLE SIZE AND VOLUME OF CITRIC ACID UPON VALUES INDICATED FOR CONTENT OF P_2O_5 IN ALPHA FORM

As noted in the discussion of the findings given in Tables 1 and 2, two of the fused materials contained more than 0.4 per cent of fluorine and they were included primarily as controls. Since they contained substantial proportions of undecomposed apatite and registered delimited effectiveness as carriers of P_2O_5,[4] these two materials are not representative of the product designated as fused tricalcium phosphate. Hence, in the acid digestions reported in Table 3, the comparisons were restricted to the two products that contained 0.4 per cent and 0.06 per cent of fluorine.

The 1-gram per 100 ml. and the 2-gram per 200 ml. digestions of the $-50+80$-mesh separate of the product containing 0.06 per cent fluorine gave a value virtually the same as that registered by the $-80+100$-mesh and the minus 100-mesh separates. In both digestates the proportion of charge to solvent was the same as the one (5–500) prescribed by the Wagner method. In the 1-gram per 200 ml. digestions of this product, all of the separates yielded more than complete extractions of the alpha form of calcium phosphate (computed as accounting for 97 per cent of the total P_2O_5 content).

In the digestions of the fused material that contained 0.4 per cent of fluorine, the 1-gram per 100 ml. and the 2-gram per 200 ml. digestates gave similar extractions for the same separate, and both digestates gave increased extractions with decrease in particular size. The 105 and 108 per cent values reflect the dissolvent action of the double quantity of citric acid upon phosphates that remained in either apatite combination or some combination other than the alpha form. Hence, it appears that the extra 100 ml. of citric acid per charge of 1 gram is both inadmissible and wasteful of reagent.

DISCUSSION

Values obtained by 1-hour digestions with ammonium citrate at 65°C., under either periodic or continuous agitation, and with or without the inclusion of a filter, are considerably lower than those registered by plant response. When a 1-gram charge of the tertiary phosphate is digested with 100 ml. of neutral ammonium citrate, the reagent suffers a rise in *p*H and its dissolvent effectiveness is impaired. But, the double volume of reagent

brings into solution some of the contained fused apatite. It has been shown that the mere fusion of apatite renders it even less soluble than the raw apatite and also less effective upon plant growth.[4] But, released from its association with tricalcium phosphate in partially defluorinated materials, the component apatite is undoubtedly more dissolvable than it is when it is the sole phosphatic component of a fused material. Since variance in the technic of ammonium citrate digestions causes decided differences in analytical results and no citrate-extraction technic gives an adequate indication of the fertilizer value of fused tricalcium phosphate, the citrate reagent is not appropriate for the evaluation of this new product.

The P_2O_5 dissolved by the 2 per cent citric acid digestates can be determined accurately when the precipitation of ammonium phosphomolybdate is made directly from suitable aliquots. Moreover, digestion of the aliquots with perchloric acid to effect oxidation of the citrate ion and dehydration of silica proved inadmissible. The mechanically agitated citric acid digestions are conducted at room temperature and are not affected by an included filter. The use of a device for continuous agitation relieves the analyst of the time and effort required by the periodic manual agitation prescribed for ammonium citrate digestions and promotes reproducibility of analytical results. The factor of r.p.m. in digestions by the Wagner method has been dealt with by Jacob, Rader, and Tremearne.[8] Apparently, maximal dissolution is effected, and without inclusion of a filter, when the end-over-end agitation is such as to assure continuous migration of the charge in the reagent. In the present studies, an r.p.m. of 21 was used and found adequate for 1-gram per 100 ml. in a 250 ml. container.

The P_2O_5 value indicated by the continuously agitated 30-minute digestion of a 1-gram charge of minus 80-mesh material in 100 ml. of the reagent acid at room temperature, is close to the quantity computed as being present in the readily available form of alpha tricalcium phosphate. This evaluation is in harmony with the one registered by plant response to the substantially defluorinated product, in comparison with superphosphate.

The question of particle size of the analytical charge is of concern to the analytical chemist, whose primary aim is assurance of uniformity of material in comparative analyses. Specification as to the fineness of the marketed product is, however, dictated by preference and economics, and is a matter for agronomic consideration. A fineness of minus 80 mesh has been found adequate to assure uniformity of analytical charge and reproducibility of results in the analysis of the fused product. In an extensive series of pot studies, in which optimal moisture conditions were maintained, no significant differences were obtained in comparisons of minus 50-mesh and minus 100-mesh siftings of the unground product. Under field conditions, however, response to the two such siftings might

not be identical. In a conference of chemists, chemical engineers, and agronomists, it was agreed that the substantially defluorinated and quenched tricalcium phosphate shall be made to pass a 40-mesh screen. Since a product of such fineness carries a substantial fraction of minus 80-mesh material, a minimum of grinding of the reserve sample would be required to prepare an analytical sample composed entirely of minus 80-mesh material.

It is concluded that the foregoing findings warrant a proposal that continuously-agitated 30-minute digestion in 2 per cent citric acid be used for the evaluation of the P_2O_5 content of fused tricalcium phosphate. The proposed procedure is virtually that of the long-used Wagner method[6] as to proportion of charge to reagent. The technic of that method has been modified, primarily by the use of conventional containers and less cumbersome equipment for agitation, in making multiple determinations in the control laboratory.

ANALYTICAL PROCEDURE

Introduce 1 gram of minus 80-mesh material into a dry 250 ml. "fertilizer" flask and then deliver, by pipet, 100 ml. of 2 per cent citric acid. Stopper the flask, insert it into an end-over-end agitator and agitate 30 minutes at ±25 r.p.m. Pour through a dry filter to clarity, and collect 50 ml. of the filtrate in a dry flask. Introduce 10 ml. of the clear filtrate into a 250 ml. Erlenmeyer; dilute to 60–75 ml., with inclusion of 15 grams of P-free ammonium nitrate. Introduce 5 ml. of ammonium phosphomolybdate reagent slowly and agitate 5 minutes; add 50 ml. more of the reagent and agitate continuously 30 minutes. Collect the precipitate on a pulped pad on a Shimer filter, under light suction, and wash the flask and the filter with six successive streams of CO_2-free distilled water. Transfer the pad and the precipitate to the precipitation flask and disrupt the mat with a stream of CO_2-free water, to a volume of 75–100 ml. Add one ml. of a one per cent alcoholic solution of phenolphthalein and dissolve the precipitate with a 2 ml. excess of NaOH, standardized against Bureau of Standards rock. Back titrate, as in 12:22[6] and report as per cent P_2O_5.

ACKNOWLEDGMENT

The expression of digestate values in relation to the computed incidence of the tricalcium phosphate component was suggested by Doctor R. L. Copson, Wilson Dam, Alabama.

MUNSON-WALKER REDUCING VALUES OF SOME OF LESS COMMON SUGARS AND OF SODIUM GLUCURONATE

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In the course of an extensive investigation of mucilages used in papermaking and of the composition of hemicelluloses of pulpwoods, the action

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of various yeasts on certain sugars and uronic acids was studied. In this connection it was found expedient to follow the fermentations (or non-fermentations) by using the Munson-Walker method. Despite the fact that Browne[1] has given reducing ratios of galactose, fructose, xylose, and arabinose based on glucose, for Allihn's, Schoorl's, and Kjeldahl's methods, the literature furnished no data on the Munson-Walker reducing values of most of the sugars used in the present study. Consequently, the reducing values (over a limited range) of *d*-mannose, *d*-galactose, *d*-xylose, *l*-arabinose, *l*-rhamnose, and *l*-fucose, and of sodium glucuronate were determined. It should be stated at the outset that inasmuch as the quantitative fermentation methods developed at The Institute of Paper Chemistry were only approximate, no attempts were made to emulate the precision or the refinements attained by Munson and Walker[2] or, more recently, by Hammond.[3] The present article presents data that were found useful not only in fermentation studies, but also in following the degradation of sugars under the influence of hot aqueous sulfuric acid. They should also prove serviceable in various phases of biochemical work.

MATERIALS USED IN REDUCTION STUDIES

All sugars used in this investigation were obtained from the Pfanstiehl Chemical Company and were marked C.P. They were used without further purification. The data given by the manufacturer were as follows: *d*-mannose, $[\alpha]_D$ +14.25°, H_2O 0.1 per cent, ash 0.05 per cent; *d*-galactose, $[\alpha]_D$ +80.5°, m.p. 165°, H_2O 0.1 per cent, ash 0.1 per cent; *d*-xylose, $[\alpha]_D$ +18.5°, H_2O 0.1 per cent, ash 0.05 per cent; *l*-arabinose, $[\alpha]_D$ +104.5°, H_2O 0.1 per cent, ash 0.1 per cent; *l*-rhamnose, $[\alpha]_D$ +8.5°, ash 0.1 per cent; *l*-fucose, $[\alpha]_D$ −75.48°. The sodium glucuronate used in the studies was recrystallized from dilute alcohol and dried. Even on protracted drying at 110° at ordinary pressure, the salt retained one molecule of water. This confirmed the findings of Erlich and Rehorst,[4] who showed that this water was lost only on heating at 100° *in vacuo* over P_2O_5 for 40 hours. The hydrated salt was used in the present study. Calculated for $NaC_6H_9O_7 \cdot H_2O$: Na 9.83 per cent. Found: 9.98 per cent and 9.95 per cent. A few determinations were also made with *d*-glucurone, m.p. 174–175°. Work is being continued on the galacturonates.

METHOD OF DETERMINATION*

The technic used is that given in *Methods of Analysis, A.O.A.C.*, 1940, 500. The cuprous oxide was weighed directly. Inasmuch as the fermentations usually involved 20–75 mg. of sugar, the cuprous oxide values of

[1] *J. Am. Chem. Soc.*, 28, 439 (1906).
[2] *Ibid.*, 663; 29, 541 (1907); 34, 202 (1912).
[3] *J. Research Nat. Bur. Standards*, 24, 579 (1940).
[4] *Ber.*, 62, 628 (1929).
* The organisms used in this work were obtained through the courtesy of L. J. Wickerham, Associate Zymologist, Northern Regional Research Laboratory (N.R.R.L.) of the U. S. Department of Agriculture at Peoria, Ill.

most interest were those within this range. In some instances, the range was considerably wider than this. Ordinarily, from four to six different weights of the appropriate sugar were used in a series. Determinations were made in duplicate (sometimes in triplicate and quadruplicate), and

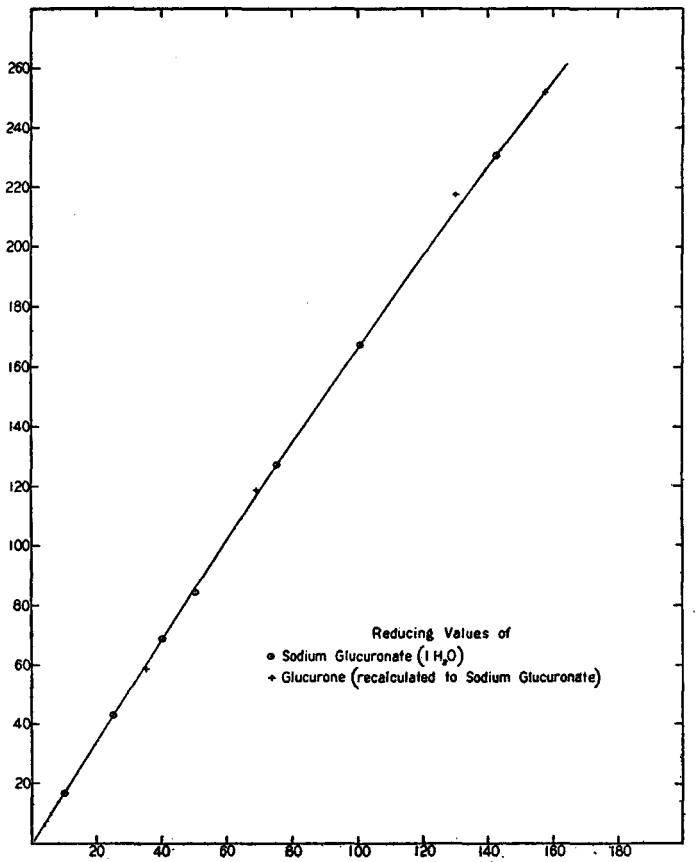

FIG. 1.

the precision was usually within 1 per cent. In the case of a specific compound, each point representing the cuprous oxide value for a given weight of reducing substance was plotted on a large sheet of co-ordinate paper, and these points were connected by a smooth curve, using a sharp, very hard pencil. The data were not computed by the classical method of least squares.[5] They were obtained by reading the cuprous oxide values (at 1

[5] Browne and Zerban, "Physical and Chemical Methods of Sugar Analysis," 3rd Ed., 753 (1941).

mg. intervals) directly from the graph under a powerful reading glass. Inasmuch as the sugar values below 20 mg. were often obtained by extrapolation, they must be used cautiously. In general, that section of each curve which was of greatest interest in the fermentation studies fell on a nearly straight line.

Because of a limited supply of glucurone, relatively few individual determinations were made with this lactone. However, the weights of glucurone were recalculated to sodium glucuronate (monohydrate), and they appear as auxiliary crosses in Figure 1. In the graph, the mg. of sodium glucuronate are plotted against the mg. of cuprous oxide.

DISCUSSION

If a high degree of precision is not required, the data given in the accompanying table should prove useful. They have been applied to a variety of sugar fermentations. To give a specific example: A method was devised for determining small amounts of galactose in the presence of mannose, fructose, glucose, xylose, arabinose, and glucuronic acid.[6] The method depends upon a differential fermentation with two yeasts: N.R.R.L. No. 379, which ferments galactose and the other common hexoses; and N.R.R.L. No. 966, which leaves galactose unfermented. Neither organism has any appreciable action on the pentoses or glucuronic acid. The weight of cuprous oxide resulting after fermentation with No. 379 subtracted from that obtained after the use of No. 966 gives a direct measure of the galactose present, the weight of which may be read from the table. The method has been used in the analysis of a number of plant mucilages and of water extractives isolated from wood. A somewhat similar fermentation has been devised for the specific determination of xylose in the presence of other sugars and glucuronic acid[7] by means of the micro-organism *Hansenula suaveolens*. The table has also been used in following the rate of degradation of mannose, galactose, and xylose under the influence of hot dilute sulfuric acid. Previous experiments have shown that sodium sulfate, in amounts comparable to those present in neutralized hydrolyzates, is without significant effect upon the reducing values. These are also only slightly influenced by small amounts of yeast extract (provided the latter is free from added starch).

Browne,[1] using Allihn's method, determined the weights of copper corresponding to definite amounts of arabinose, xylose, fructose, and galactose over a range of 50–250 mg. of sugar. From Allihn's tables, he then took the glucose value corresponding to each copper value and computed the ratio of glucose to each of these reducing sugars. The average reducing ratios found by Browne were: 1.032 for arabinose, 0.983 for xylose, and

[6] Wise and Appling, *Ind. Eng. Chem., Anal. Ed.*, 16, 28 (1944).
[7] *Ibid.*, unpublished data.

Tables for determining mannose, galactose, xylose, arabinose, fucose, and rhamnose, and sodium glucuronate.

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE	SODIUM GLUCURONATE	RHAMNOSE HYDRATE	FUCOSE
mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
20	8.2	7.2	8.1	9.5	11.4	10.0	9.8
21	8.7	7.8	8.6	10.0	12.1	10.5	10.3
22	9.2	8.2	9.0	10.5	12.7	11.0	10.9
23	9.6	8.7	9.5	11.0	13.3	11.5	11.3
24	10.1	9.1	10.0	11.5	13.9	12.0	11.9
25	10.5	9.6	10.4	12.0	14.5	12.5	12.5
26	10.9	10.0	10.9	12.5	15.0	13.0	13.0
27	11.3	10.4	11.2	13.0	15.6	13.5	13.5
28	11.8	10.9	11.8	13.4	16.2	14.0	14.0
29	12.2	11.2	12.2	13.9	16.8	14.5	14.5
30	12.7	11.8	12.7	14.4	17.4	15.0	15.1
31	13.1	12.2	13.2	14.9	18.0	15.5	15.6
32	13.6	12.7	13.8	15.4	18.6	16.0	16.1
33	14.0	13.0	14.1	15.9	19.1	16.5	16.7
34	14.5	13.5	14.6	16.4	19.7	17.0	17.2
35	14.9	14.0	15.0	16.9	20.2	17.6	17.8
36	15.3	14.4	15.5	17.3	20.7	18.1	18.2
37	15.8	14.9	16.0	17.8	21.2	18.6	18.7
38	16.2	15.3	16.4	18.3	21.8	19.1	19.2
39	16.7	15.8	16.9	18.8	22.4	19.7	19.7
40	17.2	16.2	17.5	19.3	23.0	20.1	20.2
41	17.7	16.7	18.0	19.8	23.6	20.6	20.7
42	18.2	17.1	18.4	20.2	24.2	21.2	21.2
43	18.7	17.6	18.9	20.7	24.9	21.7	21.8
44	19.1	18.0	19.3	21.1	25.4	22.2	22.3
45	19.5	18.4	19.8	21.6	25.9	22.7	22.8
46	19.9	18.9	20.1	22.1	26.4	23.3	23.3
47	20.3	19.3	20.6	22.6	27.0	23.8	23.9
48	20.7	19.8	21.0	23.1	27.6	24.3	24.3
49	21.1	20.1	21.3	23.6	28.2	24.8	24.9
50	21.6	20.5	21.9	24.1	28.8	25.4	25.3
51	22.0	20.9	22.4	24.6	29.4	25.9	25.9
52	22.5	21.3	22.9	25.1	30.0	26.5	26.4
53	23.0	21.8	23.3	25.6	30.5	27.0	27.0
54	23.3	22.2	23.8	26.1	31.1	27.5	27.6
55	23.8	22.7	24.2	26.6	31.8	28.0	28.1
56	24.2	23.1	24.7	27.0	32.4	28.5	28.6
57	24.7	23.6	25.1	27.5	33.0	29.0	29.1
58	25.1	24.0	25.6	28.0	33.6	29.6	29.6
59	25.6	24.4	26.0	28.5	34.2	30.1	30.1
60	26.0	24.9	26.5	29.0	35.0	30.6	30.7
61	26.5	25.3	27.0	29.5	35.6	31.2	31.2
62	27.0	25.8	27.5	30.0	36.2	31.7	31.8
63	27.3	26.2	28.0	30.5	36.9	32.2	32.2
64	27.8	26.7	28.4	31.0	37.5	32.7	32.8
65	28.3	27.1	28.9	31.5	38.1	33.3	33.3

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE	SODIUM GLUCURONATE	RHAMNOSE HYDRATE	FUCOSE
mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
66	28.8	27.5	29.3	32.0	38.8	33.8	33.8
67	29.2	27.9	29.8	32.5	39.3	34.4	34.3
68	29.6	28.3	30.2	33.0	39.9	34.9	34.8
69	30.0	28.8	30.7	33.4	40.4	35.5	35.3
70	30.3	29.2	31.1	33.9	41.0	36.0	35.8
71	30.9	29.7	31.6	34.4	41.6	36.5	36.4
72	31.3	30.1	32.0	34.9	42.2	37.1	36.9
73	31.8	30.4	32.5	35.3	42.9	37.6	37.4
74	32.1	30.9	33.0	35.8	43.4	38.2	38.0
75	32.7	31.3	33.4	36.3	44.0	38.6	38.6
76	33.0	31.8	33.9	36.8	44.6	39.3	39.1
77	33.5	32.2	34.4	37.3	45.2	39.8	39.6
78	34.0	32.7	34.9	37.8	45.9	40.2	40.0
79	34.4	33.1	35.2	38.3	46.5	40.8	40.5
80	34.8	33.6	35.7	38.8	47.2	41.4	41.0
81	35.2	34.1	36.2	39.3	47.9	42.0	41.5
82	35.7	34.6	36.8	39.8	48.5	42.5	42.0
83	36.1	35.0	37.1	40.2	49.1	43.0	42.6
84	36.6	35.4	37.6	40.7	49.8	43.5	43.1
85	37.0	35.9	38.0	41.2	50.4	44.1	43.7
86	37.5	36.2	38.5	41.7	51.0	44.6	44.2
87	38.0	36.7	39.0	42.2	51.6	45.1	44.7
88	38.4	37.1	39.4	42.7	52.3	45.6	45.2
89	38.9	37.6	39.9	43.2	53.0	46.2	45.7
90	39.3	38.0	40.2	43.7	53.5	46.7	46.2
91	39.8	38.4	40.7	44.2	54.2	47.3	46.8
92	40.2	38.9	41.1	44.7	54.8	47.8	47.3
93	40.6	39.3	41.6	45.2	55.3	48.4	47.9
94	41.0	39.8	42.0	45.7	56.0	48.9	48.3
95	41.4	40.1	42.5	46.2	56.6	49.5	48.9
96	41.9	40.5	43.0	46.7	57.2	49.9	49.4
97	42.4	40.9	43.4	47.1	57.9	50.5	49.9
98	42.9	41.2	43.9	47.6	58.5	51.0	50.4
99	43.1	41.7	44.3	48.1	59.1	51.5	50.9
100	43.7	42.2	44.8	48.6	59.7	52.0	51.4
101	44.1	42.7	45.3	49.2	60.2	52.6	
102	44.7	43.1	45.8	49.7	60.8	53.1	
103	45.0	43.6	46.2	50.1	61.4	53.6	
104	45.5	44.0	46.7	50.6	62.0	54.2	
105	46.0	44.5	47.1	51.1	62.6	54.7	
106	46.4	44.9	47.6	51.6	63.1	55.2	
107	46.8	45.3	48.0	52.0	63.9	55.7	
108	47.2	45.8	48.5	52.5	64.4	56.3	
109	47.7	46.2	49.0	53.0	65.0	56.8	
110	48.2	46.7	49.5	53.5	56.7	57.4	

Tables for determining mannose, galactose, xylose, arabinose, fucose, and rhamnose, and sodium glucuronate—Continued

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE	SODIUM GLUCURONATE	RHAMNOSE HYDRATE	FUCOSE
mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*	
111	48.7	47.2	50.0	54.0	66.2	57.9	
112	49.1	47.7	50.4	54.5	66.9	58.5	
113	49.6	48.1	50.8	55.0	67.6	59.0	
114	50.0	48.6	51.2	55.5	68.1	59.5	
115	50.4	49.0	51.8	56.0	68.8	60.0	
116	5.9C	49.4	52.2	56.5	69.3	60.5	
117	51.3	49.9	52.7	57.0	70.0	61.1	
118	51.9	50.2	53.1	57.4	70.5	61.6	
119	52.3	50.7	53.6	57.9	71.0	62.1	
120	52.8	51.0	54.0	58.4	71.6	62.7	
121	53.3	51.5	54.5	59.0	72.3	63.3	
122	53.8	52.0	55.0	59.4	72.9	63.8	
123	54.2	52.4	55.5	59.9	73.5	64.4	
124	54.7	52.9	56.0	60.3	74.1	64.9	
125	55.1	53.2	56.4	60.8	74.8	65.4	
126	55.6	53.7	56.9	61.2	75.3	66.1	
127	56.0	54.1	57.4	61.7	75.9	66.6	
128	56.5	54.6	57.9	62.2	76.4	67.2	
129	57.0	55.0	58.3	62.7	77.0	67.7	
130	57.4	55.4	58.8	63.1	77.7	68.0	
131	58.0	55.9	59.2	63.6	78.3	68.6	
132	58.4	56.2	59.7	64.1	79.0	69.2	
133	58.9	56.6	60.1	64.6	79.6	69.7	
134	59.3	57.0	60.7	65.0	80.1	70.1	
135	59.8	57.4	61.1	65.5	80.7	70.6	
136	60.1	57.9	61.6	66.0	81.1	71.2	
137	60.5	58.2	62.0	66.5	81.7	71.7	
138	61.0	58.7	62.5	67.0	82.4	72.3	
139	61.4	59.1	63.0	67.5	83.0	72.7	
140	61.8	59.6	63.5	68.0	83.6	73.3	
141	62.3	60.0	64.0	68.5	84.3	73.9	
142	62.9	60.4	64.4	69.0	85.0	74.5	
143	63.3	60.8	64.9	69.4	85.5	75.0	
144	63.8	61.1	65.3	69.9	86.1		
145	64.2	61.5	65.8	70.4	86.8		
146	64.7	62.0	66.2	70.8	87.5		
147	65.1	62.4	66.7	71.3	88.0		
148	65.5	62.9	67.2	71.8	88.6		
149	66.0	63.3	67.7	72.3	89.1		
150	66.5	63.7	68.2	72.8	89.8		
151	67.0	64.2	68.8	73.2	90.3		
152	67.5	64.6	69.2	73.7	90.8		
153	68.0	65.0	69.7	74.1	91.4		
154	68.4	65.4	70.0	74.6	92.0		
155	68.9	65.9	70.5	75.1	92.7		

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE	SODIUM GLUCURONATE
mg.	*mg.*	*mg.*	*mg.*	*mg.*	*mg.*
156	69.3	66.2	71.0	75.7	93.3
157	69.8	66.7	71.5	76.2	93.9
158	70.2	67.1	72.0	76.8	94.5
159	70.7	67.6	72.4	77.3	95.1
160	71.1	68.0	72.9	77.9	95.7
161	71.6	68.5	73.4	78.4	96.4
162	72.1	69.0	73.9	79.0	97.0
163	72.7	69.4	74.3	79.5	97.6
164	73.1	69.9	74.8	80.0	98.2
165	73.6	70.2	75.3	80.5	98.9
166	74.0	70.6	75.8	81.0	99.5
167	74.4	70.9	76.2	81.5	100.0
168	74.8	71.3	76.7	82.0	100.6
169	75.3	71.8	77.1	82.5	101.2
170	75.9	72.2	77.7	83.0	101.9
171	76.4	72.6	78.1	83.5	102.5
172	76.9	73.1	78.7	84.0	103.2
173	77.4	73.6	79.1	84.5	103.9
174	77.9	74.0	79.6	85.0	104.6
175	78.3	74.4	80.0	85.5	105.2
176	78.8	74.8	80.4	86.1	105.9
177	79.3	75.2	80.9	86.6	106.5
178	79.8	75.6	81.2	87.1	107.2
179	80.1	76.0	81.7	87.7	107.9
180	80.6	76.4	82.1	88.2	108.5
181	81.1		82.7	88.7	109.3
182	81.6		83.1	89.2	109.9
183	82.0		83.7	89.8	110.4
184	82.5		84.1	90.2	111.1
185	83.0		84.6	90.7	111.8
186	83.4		85.0	91.2	112.4
187	83.9		85.5	91.7	113.1
188	84.4		86.0	92.2	113.8
189	84.9		86.5	92.7	114.4
190	85.3		87.0	93.2	115.1
191	85.8		87.4	93.7	115.8
192	86.2		87.9	94.2	116.5
193	86.7		88.4	94.7	117.1
194	87.2		88.9	95.2	117.8
195	87.7		89.3	95.7	118.4
196	88.2		89.9	96.2	119.1
197	88.7		90.3	96.7	119.8
198	89.1		90.8	97.2	120.3
199	89.6		91.2	97.7	121.0
200	90.1		91.7	98.3	121.7

Tables for determining mannose, galactose, xylose, arabinose, fucose, and rhamnose, and sodium glucuronate—Continued

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE	SODIUM GLUCURONATE	RHAMNOSE HYDRATE	FUCOSE
mg.	*mg.*		*mg.*	*mg.*	*mg.*		
201	90.6		92.2	98.8	122.3		
202	91.0		92.7	99.4	123.1		
203	91.4		93.1	99.9	123.8		
204	91.9		93.6	100.3	124.4		
205	92.3		94.1	100.8	125.1		
206	92.9		94.6	101.2	125.8		
207	93.3		95.0	101.8	126.4		
208	93.8		95.5	102.2	127.1		
209	94.3		96.0	102.8	127.8		
210	94.8		96.5	103.3	128.4		
211	95.2		97.0	103.9	129.1		
212	95.7		97.4	104.4	129.9		
213	96.1		97.9	105.0	130.5		
214	96.6		98.4	105.5	131.0		
215	97.1		98.9	106.0	131.7		
216	97.6		99.3	106.5	132.3		
217	98.1		99.8	107.0	133.0		
218	98.6		100.2	107.5	133.7		
219	99.0		100.7	108.0	134.3		
220	99.5		101.1	108.5	135.1		
221	100.0		101.7	109.1	135.9		
222	100.4		102.1	109.6	136.5		
223	100.8		102.6	110.1	137.1		
224	101.2		103.1	110.6	137.9		
225	101.7		103.6	111.1	138.6		
226	102.2		104.1	111.6	139.2		
227	102.8		104.6	112.1	139.9		
228	103.1		105.1	112.6	140.3		
229	103.6		105.5	113.1	141.0		
230	104.0		106.0	113.7	141.8		
231	104.5		106.5	114.2	142.5		
232	105.0		107.0	114.8	143.1		
233	105.4		107.5	115.2	143.9		
234	105.9		108.0	115.8	144.5		
235	106.3		108.5	116.3	145.1		
236	106.8		109.0	116.9			
237	107.3		109.4	117.4			
238	107.8		109.9	118.0			

CUPROUS OXIDE	XYLOSE	ARABINOSE	MANNOSE	GALACTOSE
mg.	*mg.*		*mg.*	*mg.*
239	108.2		110.3	118.5
240	108.7		110.8	119.0
241	109.2		111.3	119.5
242	109.7		111.9	120.0
243	110.0		112.3	120.5
244	110.5		112.8	121.0
245	111.0		113.3	121.5
246	111.4		113.8	122.0
247	111.9		114.2	122.5
248	112.3		114.8	123.1
249	112.8		115.2	123.6
250	113.3		115.7	124.1
251	113.8		116.1	124.6
252	114.2		116.6	125.1
253	114.8		117.1	125.6
254	115.2		117.6	126.1
255	115.7		118.1	126.7
256	116.1		118.6	
257	116.6		119.0	
258	117.0		119.5	
259	117.5		120.0	
260	118.0		120.5	
261	118.5		121.0	
262	119.0		121.4	
263	119.4		121.9	
264	119.9		122.4	
265	120.3		122.9	
266	120.7		123.4	
267	121.1		123.9	
268	121.6		124.3	
269	122.1		124.8	
270	122.6		125.3	
271	123.1			
272	123.6			
273	124.0			
274	124.5			
275	125.0			

0.898 for galactose. Using the tabulated data and the Munson-Walker tables, analogous ratios were computed. The average ratios were: 1.031 for arabinose over a range of 17–75 mg., and 0.992 for xylose and 0.901 for galactose over a range of 25–125 mg. In all cases, the ratios are very similar to those of Browne. Over a range of 25–142 mg. of sodium glucuronate,

the glucose-glucuronate ratio was quite constant, the extremes being 0.725 and 0.740, with an average for all experimentally determined values of 0.733.

SUMMARY

The usual gravimetric Munson-Walker method was applied to mannose, galactose, xylose, arabinose, fucose, and rhamnose, as well as to sodium glucuronate and to glucurone. Tables for determining these substances have been given and their use in certain microbiological studies has been suggested.

ACKNOWLEDGMENT

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SPECTROPHOTOMETRIC PROCEDURE FOR THE ESTIMATION OF VITAMIN A IN OLEOMARGARINE*

By J. B. WILKIE and J. B. DE WITT (Food and Drug Administration, Federal Security Agency, Washington 25, D. C.)

The problem of devising suitable physical or chemical procedures for the estimation of vitamin A in oleomargarine has attracted considerable attention in recent years. It has been recognized that the nonsaponifiable portion of commercial margarines may contain substances which interfere with both the direct spectrophotometric procedure, and the antimony trichloride reaction.

The study of this problem has been given additional impetus by the promulgation of a standard of identity for oleomargarine[1,2] in which vitamin A is listed as an optional ingredient, and two independent methods have been proposed. Oser, Melnick, and Pader[3] suggested a modification of the antimony trichloride procedure, using what they describe as an increment method for vitamin A, with introduced corrections for extraneous color and turbidity. Neal and Luckman[4] used a spectrophotometric procedure, and measured the optical density at 328 mμ before and after destruction of vitamin A by ultraviolet irradiation. They assumed that vitamin A was the only substance affected by irradiation and that the change in density was due entirely to the decrease in vitamin A content. The analytical usefulness of the light destruction method has been sug-

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[1] Federal Register, 6, 2761 (1941).

[2] Definitions and Standards for Food, Service and Regulatory Announcement F.D.C. No. 2, par. 45, p. 39 (July 1944).

[3] *Ind. Eng. Chem., Anal. Ed.*, 15, 724–729 (1943).

[4] *Ibid.*, 16, 358–361 (1944).

gested by others[5,6,7,8], but certain controversial aspects of the problem appear to need clarification. It has been suggested that the course of the reaction is affected by the wave lengths employed in the irradiation, the presence of miscellaneous materials, temperature effects, and the nature of the containing vessels.

In the course of preliminary experiments with a number of commercial margarines, it was found that neither the antimony trichloride method nor the indirect spectrophotometric procedure was universally applicable. Accordingly, a direct spectrophotometric procedure, involving the chromatographic fractionation of the nonsaponifiable extracts, was developed and applied to the routine examination of a wide variety of commercial oleomargarines. In this procedure, measures were introduced to prevent or to minimize the destruction of vitamin A, and visual control of the chromatographic separation was made possible by the use of weak ultraviolet light.

PROCEDURE

(*A*) *Saponification and Extraction.*—Weigh 10 grams of oleomargarine into a tall 300-ml. beaker and add 50 ml. of boiling 95% ethanol. Stir until the sample is completely disintegrated, and add 0.25 gram of anhydrous Na_2SO_3. Cool the solution to 35°C., and add 25 ml. of 50% aqueous KOH solution. Stir continously for 5 minutes and allow to stand at room temperature for 15 minutes (stirring occasionally).

Transfer the solution to a 500-ml. separatory funnel. Rinse the beaker with 50 ml. of a freshly prepared 5% solution of $Na_2S_2O_4$ and add the rinsings to the saponification mixture. Add 100 ml. of petroleum ether,* shake vigorously, and allow to stand for 5 minutes. Drain the aqueous portion into another separatory funnel, and extract with 50 ml. of a mixture of 90% petroleum ether and 10% U.S.P. ethyl ether. Allow to stand for 3 minutes. Transfer the aqueous layer to another separatory funnel, and extract as before. Make a total of 7 such extractions and combine the ethereal extracts in the separatory funnel containing the first extract. If a 3-layer system develops at any point, continue the extractions with 50-ml. portions of petroleum ether alone. In such 3-layered systems, transfer only the top layer to the original petroleum ether extract.

Pour through the combined ether extracts two 200-ml. portions of distilled water, and separate off each portion, without shaking. Make 5 additional washings with 20 ml. portions of 5% aqueous $Na_2S_2O_4$, shaking vigorously and allowing the solution to stand for 2 minutes before the removal of the water layer. To the combined ether extracts add 200 ml. of distilled water (do not shake or stir), and drain off the aqueous layer. Repeat this washing with another 200-ml. portion of distilled water. Allow to stand 10 minutes, then drain off the aqueous layer. Filter the ether extract rapidly through 25 ml. of a powdered mixture of anhydrous Na_2SO_4 (90%) and Na_2SO_3 (10%). Evaporate the filtrate on a steam bath to less than 10 ml., transfer to a 10 ml. volumetric flask, and make to volume with petroleum ether.

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[5] Demarest, B., *Z. Vitaminforsch*, **8**, 920 (1939).
[6] Little, R. W., *Ind. Eng. Chem. Anal. Ed.*, **16**, 288–293 (1944).
[7] De, N. K., *Indian J. Med. Research*, **24**, 737 (1937).
[8] McFarlane and Sutherland, *Canadian J. Research*, **16**, 421 (1938).

* The petroleum ether should be tested by measuring the transmission in a spectrophotometer at 300mμ. A 1 cm. quartz cell should be used. No cell is used as a blank in this test. An ether having a transmission greater than 85% can be regarded as satisfactory although the best grades should give a reading of 90%.

(*B*) *Chromatography.*—Prepare the adsorption column by using an Allihn sugar tube, or similar apparatus. It consists of a fritted filter of medium porosity fitted in a tube about 20 mm. in diameter and about 10 cm. long. The lower end of the tube is constricted to permit ready attachment to a 250 ml. suction flask by means of a rubber stopper. Place a 3 mm. layer of $Na_2S_2O_4$ directly upon the fritted disc, apply suction, and add the adsorbing material. (A 3:1 mixture of purified diatomaceous earth (Celite) and MgO (Baker's analyzed) is a suitable adsorbent.) Tamp the adsorbent lightly with a flared glass rod as it is added in small quantities until it has an approximate depth of 2.5 cm. Then add a 5 mm. layer of $Na_2S_2O_4$, followed by a 1 cm. layer of Na_2SO_3.

After wetting the column with 30 ml. of petroleum ether add rapidly a 5 ml. aliquot of the extracted sample. When the solution is about to disappear into the surface of the column add more petroleum ether until the vitamin A appears as a fluorescent band visible under weak ultraviolet light.† Elute this band with petroleum ether alone, or with a 0.2% solution of glacial acetic acid in petroleum ether, until it is approximately 5 mm. from the end of the absorbing column. Discard the eluate that has passed through, connect the end of the column to a clean 250 ml. suction flask, and complete the elution. (The elution may be regarded as complete when the vitamin A fluorescence is no longer evident.) Transfer the eluate to a 50 ml. beaker, evaporate to less than 10 ml., transfer to a 10 ml. volumetric flask, and adjust to volume with petroleum ether.

Determine the optical density of this solution at 5 mμ intervals over the range from 270 mμ to 450 mμ, and calculate the vitamin A potency of the oleomargarine by the formula:

$E^{1}_{1\,cm.}\%$ (340 mμ) $\times 2500$ = U.S.P. units of vitamin A per gram of margarine.

Since oleomargarine is variable in composition, and all of the limitations of the method are not known, it may be desirable in some cases to conduct recovery experiments in order to determine the possible loss of vitamin A during the procedure. This may be done by taking duplicate samples. To one sample add 1 ml. of a petroleum ether solution of vitamin A (150–200 units/ml.) just before the addition of KOH during saponification. (This petroleum ether solution was found to be stable at room temperature over a period of several months, when kept in an amber bottle over Na_2SO_3.) Then assay both samples according to the above procedure, and calculate the per cent recovery of added *A* as follows:

Recovery Calculation.—$2[(D_{340}\ \text{standard} + \text{unknown}) - (D_{340}\ \text{unknown})] = D'_{340}$, the density of the standard after processing, that is to say equivalent to 1 ml. of standard Ds_{340} made to $10_{ml.}$.

$$\text{Recovery } \% = \frac{D'_{340}}{Ds_{340}} \times 100.$$

The antimony trichloride check procedure used was as follows:

APPARATUS

(a) *Photoelectric colorimeter.*—Rapid, direct reading, equipped with Corning filters 245 and 978 of standard thickness.

(b) *Matched tubes.*

† A convenient source of ultraviolet light may be prepared by mounting a 2½-watt General Electric Argon bulb in a metal housing fitted with a suitable light filter. The bulb should have a double contact bayonet base and no resistor in the base. A 500 ohm resistor is connected in series with the lamp for operation on the 110 volt AC lines. A switch should be provided for continuous operation, and a push button for intermittent operation. No brighter source of ultraviolet should be used. The bulb is mounted on an adjustable clamp so that it can be brought as close as possible to the exit filter, which is a polished 2-inch square of No. 986 glass as provided by Corning Glass Works.

REAGENTS

(a) *Purified petroleum ether.*

(b) *Antimony trichloride.*—Dissolve ½ pound of $SbCl_3$ in 500 ml. of $CHCl_3$ that has been washed with distilled water to remove alcohol and subsequently dried by passing through anhydrous Na_2SO_4. (The reagent was kept free from traces of water by the addition to the final reagent of about 5 grams of anhydrous $CaCl_2$).

METHOD

Set the meter or galvanometer of the photoelectric colorimeter on a scale reading of 100 with a blank composed of 1.0 ml. of petroleum ether and 9.0 ml. of the $SbCl_3$.

Pipet 1.0 ml. of the original 10.0 ml. unknown (as prepared for chromatographing) and transfer to a colorimeter tube. Add 1.0 ml. of petroleum ether. Mix quickly and transfer 1 ml. quickly to another colorimeter tube. Add 9.0 ml. of the $SbCl_3$ rapidly by dumping from a calibrated flask into each of these tubes in turn, making a reading at the meter maximum, which is usually in about 4 seconds. Average these readings and record as G_a. Repeat this operation with another 1 ml. aliquot as a check. From G_a obtain L_a from a Transmittancy-Density table.

To 1 ml. of the original 10 ml. unknown solution in a colorimeter tube, add 1 ml. of a 1:10 dilution of the standard vitamin A solution (150–200 units/ml. of petroleum ether). Mix and transfer 1 ml. of this mixture to another colorimeter tube. Add 9 ml. of the $SbCl_3$ as previously described and record the maximum meter reading. Designate the average of the two readings as G_b. Make another pair of similar readings for a check. From G_b obtain L_b from a transmittancy-Density table.

CALCULATIONS

$L_b - L_a = L_s$; C_s = concentration of standard in units vitamin A/ml.

$$\text{Then } \frac{C_s}{L_s} = C_s/L \text{ vitamin A units/L.}$$

$$\therefore L_a(C_s/L) = a = \text{vitamin A units/ml. in unknown solution as is.}$$

Since original solution strength $= 2 \times a = 2a$ units/ml. in original solution, and since the dilution factor for the original solution is 1, $2a$ = units vitamin A/gram of original sample.

DISCUSSION

Many precautions were found necessary to avoid difficulties. Some lots of petroleum ether fluoresced excessively and exhibited marked light absorption in the regions below 300 mμ. This effect was intensified during the concentration procedure involved in the evaporation of extracts. Since a high quality of solvent is essential to both the extraction and chromatographing steps, it became necessary to study this matter.

Different petroleum ethers were evaporated to approximately 2 per cent of their original volume and their absorption curves determined. Figure 1 shows a set of curves indicating the results of this procedure. Curve No. 1 is that of a commercial brand of petroleum ether, curve No. 2 of this same ether after simple distillation, and No. 3 of this same ether after distillation from lime. No. 4 is that of a special reagent-grade product, while No. 5 is of another commercial product. While it is evident that the material distilled from lime was superior to the reagent-grade

ether, the latter was found adequate for routine work with oleomargarine. To further check the suitability of petroleum ether for this purpose, an arbitrary spectrophotometric test was devised in which the ether is placed in a 1 cm. quartz cell, and its transmission at 300 mμ determined. No cell was used as a blank in this test. An ether having a transmission greater than 85 per cent is deemed satisfactory, and the best grades will give a reading of 90 per cent.

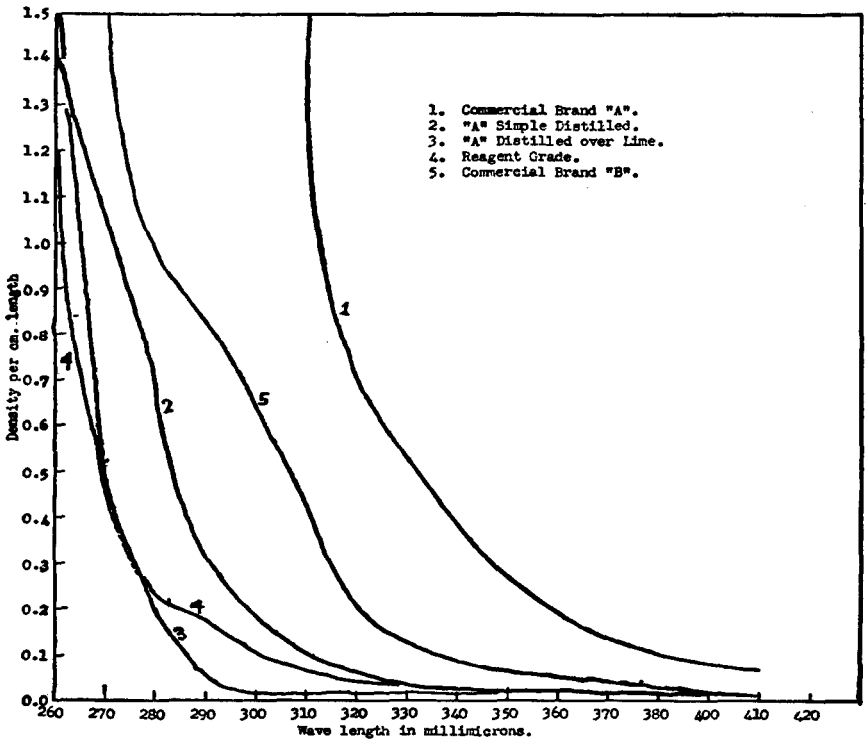

FIG. 1.—SPECTRAL ABSORPTION OF VARIOUS SAMPLES OF PETROLEUM ETHER.

A second difficulty encountered was that of following the passage of vitamin A down the chromatographic column. For the chromatography to be effective, it is essential that the materials preceding vitamin A down the column be quantitatively removed. In order to make it possible to observe all phases of the operation of the column, advantage was taken of the fluorescence of vitamin A. A convenient source of weak ultraviolet light is described in the method. Under this lamp, vitamin A appears on the column as a narrow band of intense fluorescence, and its passage down the column is readily followed. This light is quite weak, and it has not been possible to trace any deterioration of vitamin A to its use.

One of the earliest observations in this study was that the green fluorescence of vitamin A would change to blue fluorescence in the chromatographing column, or that the green ring might develop a blue halo while under observation. It was also observed that the vitamin A from some oleomargarines exhibited only the blue fluorescence. In early experiments this change in fluorescence was a universal occurrence, and its nature has constituted a point of continued curiosity throughout these studies.

It appeared possible that this change in fluorescence might be due to destructive changes taking place in the column. The possibility was studied further by repeatedly chromatographing a solution of vitamin A from ling cod liver oil. The results are shown in Table 1. In no case did the

TABLE 1.—*Effect of repeated chromatographing of nonsaponifiable material from ling liver oil*

NUMBER OF TIMES CHROMATOGRAPHED 10-24-43	290 mμ		325 mμ		340 mμ		E 290/E 340	E 325/E 340
	1% E 1 cm	% GAIN	1% E 1 cm	% LOSS	1% E 1 cm	% LOSS		
0	18.8		43.7		35.5		0.529	1.23
1	19.2	2.2	43.2	1.14	34.6	2.56	0.55	1.24
2	19.2	2.2	40.5	7.30	31.8	10.70	0.60	1.27
3	23.0	26.6	36.6	16.20	29.6	16.60	0.77	1.24
4	24.0	32.0	29.6	32.00	23.1	35.00	1.04	1.28
5	40.2	122.0	27.1	38.20	21.5	39.40	1.86	1.26
								Av. 1.25
Aged to 12-11-43 and chromatographed one time.								
		% Loss						
1	5.81	69.0	2.67	94.0	1.56	95.5	3.724	1.71

green fluorescence disappear, or a blue fluorescence appear. However, after chromatographing the first time, a small but steady loss in vitamin A content was noted, the absorption at 325 mμ being the criterion. The total loss after 5 chromatographings was 38.2 per cent. A portion of the original solution was allowed to stand for two months at room temperature, or until 94 per cent of the vitamin A content had disappeared, and then chromatographed one time; still no blue fluorescence was observed in the column.

It is to be observed that the absorption at 325 mμ and 340 mμ, decreased with successive chromatographing, but that the absorption at 290 mμ increased 122 per cent after the fifth chromatographing. It is also of interest that the ratio E 325 mμ/E 340 mμ values remained essentially constant throughout all the chromatographing, namely at 1.25, which has been found to be good value for a nonchromatographed vitamin A solu-

tion from unsaponifiable portion of fish liver oil. The increase at 290 mμ would be evidence of oxidation according to the work of Oser, Melnick, and Pader.[9] Destructive action incurred during chromatographing then does not appear to be oxidative or responsible for the blue fluorescence associated with the green during the chromatographing. Independent test tube experiments did show that the combined presence of alcohols, magnesium oxide or calcium hydroxide, and other substances was conducive to the conversion of the green fluorescent to blue form.

Other materials such as pyridine, chloroform, acetone, and benzene were found to be less conducive to the transformation. In actual practice the use of 0.2 per cent solution of glacial acetic acid in petroleum ether has been found to be the best combination for minimizing the formation of the blue fluorescent material on the column.

The above findings and other similar evidence indicate that the blue fluorescent vitamin A is formed in the oleomargarine or possibly in the subsequent saponification and extraction procedure. It appears that the degree of green or blue fluorescence is definitely associated with specific samples of margarine, making it most probable that the vitamin A has changed, or has started to change, from the normal green fluorescent form in the oleomargarine before the analysis is started. The behavior on the column is practically identical for either the green or blue forms. The blue form may be held very slightly less tenaciously on the column than the green, and at times it is seen as a blue halo on the under side of the green ring.

Some phasic distribution experiments were made on some specially prepared blue fluorescent material. In an anhydrous methyl alcohol-petroleum ether solution, practically the entire blue fluorescent form appeared to pass into the methyl alcohol portion. After mixing and shaking with water, most of the blue fluorescence appeared in the petroleum ether. Green fluorescent vitamin A appeared to divide about 50-50 between methyl alcohol and petroleum ether. The addition of water then drove the green fluorescent form into the ether layer as was the case with the blue fluorescent material.

All of these observations seem to indicate that the blue fluorescent form is only slightly modified and may or may not be the result of partial oxidation. The available biological results support this opinion.

The experimental results obtained are of great interest. In Figure 2 are presented five spectrophotometric curves. The bottom one, a typical vitamin A curve, was obtained from the unsaponifiable portion of ling liver oil. This same unsaponifiable material of ling liver oil was rechromatographed five times. The change is apparent by examination of Curve 2. The corresponding vitamin A loss was 38 per cent as obtained from the 325 mμ E value. However, at this time there was no evidence of any associated blue fluorescent material. The general elevation of the curve in the

[9] *Ind. Eng. Chem., Anal. Ed.*, 15, 717–724 (1943).

region from 270 mμ to 325 mμ has been recognized as characteristic of deterioration by oxidation,[9] and it is believed that this is what is represented in Curve 2.

The absence of any definite peak at 290 mμ should also be observed as characteristic of the deteriorated ling liver oil. Curve 3 is an oleomargarine

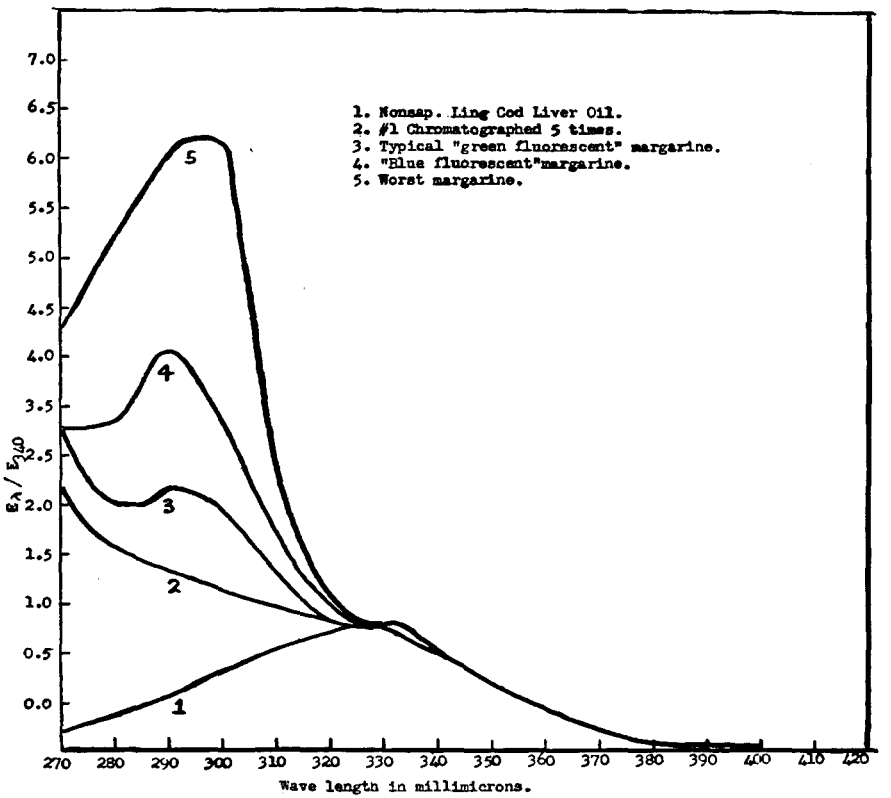

FIG. 2.—SPECTRAL BEHAVIOR OF VITAMIN A FROM LING COD LIVER OIL AND OF VITAMIN A FROM DIFFERENT MARGARINES.

vitamin A curve showing the nature of the absorption from a material which exhibited a normal green fluorescence. Curve 4 is from an oleomargarine the vitamin A portion of which fluoresced predominatingly blue. Curve 5 represents the extreme altered condition found in vitamin A material in margarines. It will be observed that a peak in the 290 mμ region is characteristic of the vitamin A fraction in all cases. Whether this is due to associated tocopherol, oxidation products, or other charged forms of vitamin A is still uncertain. However it does seem that this peak is asso-

TABLE 2.—*Effect of variations in procedure on a specific margarine*

PROCEDURE			E_{330}	E_{325}	E_{340}	$\frac{E_{330}}{E_{340}}$	$\frac{E_{325}}{E_{340}}$	$\frac{E_{360}}{E_{340}}$	REMARKS
SAPONIFICATION	EXTRACTION	CHROMATOGRAPH							
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	MgO:Celite 1:3	0.038	0.006	0.0038	10.0	1.58	0.474	Stood overnight
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1 1% EtOH	0.038	0.013	0.0101	3.76	1.29	0.504	
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1 0.5% EtOH	0.039	0.0154	0.0116	3.36	1.31	0.431	
Aqueous No alcohol	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1	0.039	0.0138	0.0109	3.57	1.26	0.504	
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1 +tocoph.		0.0127	0.0098	—	1.29	0.500	
Zn Hot	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1 1% EtOH	0.038	0.0127	0.0098	3.87	1.29	0.500	
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	None		0.0178	0.0111	—	1.60	0.630	Not chromatographed
Hot with Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite tocoph. 1 ml./300 Pet. Eth.		0.0149	0.0110	—	1.35	0.455	
2.5 gm. Na_2SO_3+hot	Pet. Ether Ethyl Acetate	MgO:Celite 1:3	0.039	0.0132	0.0102	3.82	1.29	0.490	
Hydroquinone+Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1	0.039	0.0158	0.0110	3.54	1.43	0.463	
Z_n+Na_2SO_3	Pet. Ether Ethyl Acetate	MgO:Celite 1:3 5%α tocoph.		0.0129	0.0094	—	1.37	0.510	
Z_n+Na_2SO_3	Pet. Ether Ethyl Acetate	$Ca(OH)_2$:Celite 1.5:1 5%α tocoph.	0.039	0.0110	0.0085	4.58	1.29	0.399	

ciated directly with the vitamin A molecule itself, when the segregating nature of the chromatographing is considered.

At first glance, the most disturbing aspect of these oleomargarine curves is the distortion apparent at 325 mμ, the region in which the peak absorption normally occurs. Actually, the distortion is usually not great but it is important with some samples. It has been found that the matter can be successfully handled by using calculations at 340 mμ, where the distortion is less. The conversion factor used in this case is 2500 instead of 2000 (which might be used at the 325 mμ value); 340 mμ is also then used

TABLE 3.—*Experimental spectrophotometric values for commercial margarines bearing the 9000-unit A/lb. claim*

E_{325}	E_{328}	E_{340}	E_{325}/E_{340}	E_{328}/E_{340}	UNITS/LB.
∞	0.0096	0.0070	—	1.37	7,950
0.034	0.0124	0.0078	4.35	1.59	8,850
0.033	0.0146	0.0111	2.97	1.32	12,500
∞	0.0152	0.0113	∞	1.29	13,400
0.044	0.0122	0.0090	4.89	1.36	10,200
∞	0.0124	0.0093	∞	1.23	10,600
∞	0.0123	0.0090	∞	1.37	10,400
0.0279	0.0104	0.0081	3.44	1.28	9,200
0.0229	0.0117	0.0092	2.49	1.28	10,900
0.0212	0.0134	0.0099	2.14	1.35	11,500
0.0159	0.0106	0.0079	2.00	1.34	9,000
0.0212	0.0136	0.0098	2.16	1.38	11,300
0.0269	0.0087	0.0076	3.54	1.14	8,650
0.0318	0.0108	0.0076	4.18	1.41	8,650
0.0318	0.0094	0.0072	4.41	1.30	8,200
0.0166	0.0094	0.0076	2.18	1.23	8,650
0.0398	0.0148	0.0114	3.48	1.30	13,000

for the sake of consistency in plotting extinction coefficient ratios of all margarines.

Table 2 gives the effect of variation in procedure on a specific oleomargarine. It can be seen that some large variations were made, such as using zinc or sodium sulfite in saponification procedure, or in using lime in place of magnesium oxide, or in incorporation of variable percentages of α tocopherol at different times. None of these things appreciably changed extinction values and ratios. The larger E 325/E 340 ratios were obtained when one of the finished solutions was allowed to stand overnight before the spectrophotometric examination, or when the chromatographing step was eliminated.

No doubt the constancy of these data gives an incorrect perspective, since other samples of oleomargarine have been found to be susceptible to

TABLE 4.—*Experimental work showing comparisons of spectrophotometric, colorimetric, and bio-values on commercial margarines*

DATE	SAMPLE NO.	ANALYST	PROCEDURE	% RECOV.	$\frac{E_{190}}{E_{240}}$	$\frac{E_{225}}{E_{240}}$	SPEC. UNIT/LB. NOT COR.	SPEC. UNIT/LB. COR.	$SbCl_3$ UNIT/LB.	BIO. UNIT/LB.
*7-27-44	96	W	100-C	98.0	3.04	1.33	11,400	11,700	—	12,100
*7-15-44	96	D	100-C	97.0	2.85	1.40	10,100	10,850	—	12,100
*7-30-44	96	W	100-C	92.0	2.66	1.25	11,900	13,700	13,600	12,100
*8- 5-44	96	W	100-C	87.0	2.74	1.29	11,700	12,800	10,000	12,100
*9-11-44	96	W	100-D	74.0	2.64	1.33	10,200	13,700	9,600	12,100
†7-27-44	93	W	100-C	91.0	3.10	1.37	10,000	10,500	—	8,500
†7-14-44	93	D	100-C	91.0	3.25	1.38	10,600	11,700	—	8,500
†8-11-44	93	W	100-C	84.0	2.64	1.35	9,150	10,600	—	8,500
†8-16-44	93	W	100-C	82.0	3.95	1.28	9,700	11,800	—	8,500
†9-13-44	93	W	100-D	93.0	3.90	1.33	9,600	10,600	5,300	8,500
8-25-44	33	W	100-C	77.0	—	1.40	8,050	10,400	5,050	10,000
8-23-44	33	W	100-C	79.0	6.1	1.44	7,450	9,400	4,650	10,000
8-28-44	33	W	100-C	74.0	3.63	1.40	7,450	10,000	—	10,000
8-15-44	33	D	100-C	71.0	4.13	1.28	8,150	11,400	—	10,000
9- 5-44	78	W	100-D	73.0	3.96	1.28	8,600	11,800	5,400	—
9- 5-44	78	D	100-D	78.0	3.65	1.31	9,700	12,400	5,400	—
7-24-44	10	W	100-C	87.0	3.50	1.35	9,100	10,000	—	—
8- 4-44	233	W	100-C	90.5	3.30	1.30	11,900	13,200	12,700	—
8-17-44	38	W	100-C	85.0	4.25	1.36	9,100	10,700	9,100	—
7-19-44	38	W	100-C	80.0	4.25	1.42	9,150	11,500	9,000	—
8-28-44	15	W	100-C	88.5	5.35	1.35	8,550	9,700	8,300	—
8-28-44	15	D	100-C	85.0	4.37	1.33	8,550	10,000	—	—
9- 4-44	31	W	100-C	86.5	2.60	1.43	8,500	9,800	9,850	—
8-14-44	31	D	100-C	—	2.05	1.29	8,850	—	—	—
9- 8-44	83	W	100-D	96.5	2.48	1.25	9,850	10,200	7,950	—
9-14-44	92	W	100-D	89.0	2.72	1.15	10,200	11,500	7,650	—
8-14-44	33	D	100-D	73.0	4.04	1.37	8,350	11,400	—	10,000
8-11-44	30	D	100-D	79.0	2.66	1.34	8,400	10,600	—	—
7-21-44	07	D	100-D	67.0	3.14	1.31	8,350	12,400	—	—
7-20-44	99	D	100-D	—	3.01	1.33	9,700	—	—	—
9-16-44	05	D	100-D	78.0	2.97	1.31	7,800	10,000	—	—
9-25-44	14	D	100-D	85.0	2.68	1.31	9,650	11,900	—	—

* Green fluorescent type.
† Blue fluorescent type.

Procedure 100-A—Sulfite in hot saponification.
Procedure 100-B—Hydrosulfite in cold saponification 35°C.
Procedure 100-C—Hydrosulfite saponification started at 35°C.
Procedure 100-D—Sulfite saponification started at 35°C.

large losses unless special precautions have been taken. The 35°C. saponifications, and the liberal use of sulfite and hydrosulfite during the extraction and chromatographing, are some of the precautionary measures found necessary to prevent excessive deterioration. The data on the particular oleomargarine presented in Table 2 indicate that some oleomargarines are much more satisfactory than others from the standpoint of vitamin A stability.

Table 3 summarizes the results obtained with a number of oleomargarines by the use of various procedures. All of these margarines had a label claim of at least 9000 units of vitamin A per pound. The actual procedures used in each case had minor experimental variations, but in general the vitamin A was protected throughout by the use of sulfite and hydrosulfite.

As a consequence of the studies summarized in Tables 2 and 3, the procedure described in this paper was adopted as the one yielding the greatest consistency of results; the data shown in Table 4 were obtained by its use. The table gives the results obtained by different analysts and affords a comparison between values obtained by spectrophotometric, colorimetric, and biological methods. Recovery experiments, summarized in the fifth column from the left, were conducted. In general, the recovery experiments indicate losses of less than 15 per cent. There seem to be no consistent differences in recovery values between blue and green fluorescent types, indicating again that in some margarines the vitamin A is converted to the blue fluorescent type before it is sampled. The first sample, No. 96, was a predominatingly green fluorescent type. Corrected spectrophotometric values are seen to check with the biological value to within less than 12 per cent. The corresponding antimony trichloride values are as much as 21 per cent low, and the antimony trichloride checks vary from sample to sample with about the same discrepancy.

The second sample considered, No. 93, was definitely of the blue fluorescing type. In this case the spectrophotometric values were found to be about 20 per cent high relative to the biological value, while the corresponding antimony trichloride value was found to be 37 per cent low. In Sample No. 78, the spectrophotometric figure was about double the value indicated by the antimony trichloride reaction.

Sample No. 33 was found to possess a spectrophotometric value not greater than 10 per cent above the biological value, whereas the antimony trichloride value was found to be only about 50 per cent of the other values. The remaining series indicates that the spectrophotometric and antimony trichloride values may check fairly well for quite a number of different margarines, although there is a definite tendency for antimony trichloride values to be lower than the spectrophotometric values in nearly all cases. It will be observed that the uncorrected spectrophotometric values are generally slightly above the claim value of 9000 units

per pound in most cases. Hence from the control standpoint it would then not be necessary to apply the correction.

The ratio of E 290/E 340 as shown in Table 4 is always high. This is believed to be true because of changes in the vitamin molecule itself while in the oleomargarine, in which case it cannot be avoided. The fact that the changed material generally does have the biological potencies indicated by the spectrophotometric chromatographic method indicates that the change is not of great importance from the practical viewpoint.

It is felt that such data as are shown in Table 4 indicate that the chromatographic method as described should be suitable for the routine determination of vitamin A in oleomargarine, and that any remaining doubts as to its application can be clarified by continued use and further study.

SUMMARY

A method for vitamin A in oleomargarine has been presented and its application discussed.

VAPOR PRESSURE MEASUREMENTS AS AN INDEX TO MOISTURE IN DEHYDRATED VEGETABLES

By HENRY FISCHBACH (U. S. Food and Drug Administration,* Washington, D. C.)

With the advent of the war the production of dehydrated vegetables has increased enormously, and the greatest consumer of these products by far has been the Army Service Forces Quartermaster Corps. This agency has adopted a procedure for determining moisture, approximating that of the official method for dried fruits,[1] which employs a vacuum oven. To fill the apparent need of a more specific method, the writer as Associate Referee on Moisture in Dried Vegetables for the A.O.A.C., completed sufficient experimentation in 1944 to recommend for tentative adoption a vacuum-oven method for determining moisture in dried vegetables.

Oven heating methods are, of course, widely used for moisture determinations in various foods; the technic is simple, the procedures empirical. However, despite the fact that closely agreeing results can be obtained on these and similar products by oven-drying methods, the critical analyst must regard such data as being merely "related to the true moisture content." This conclusion is supported by such observations as the following:

1. On several different kinds of dried vegetables "moisture" values of increasing magnitude were obtained on the same sample, as the oven temperature was increased from 35° to 70°C. (holding constant the mesh size, the pressure, 100 mm. or less, and the heating period).

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* Contribution from the Food Division, W. B. White, Chief.

[1] *Methods of Analysis, A.O.A.C.*, 1940, 336, 4.

2. In like manner, by varying the heating period and holding the temperature constant (at a point between 35° and 70°C.), the "moisture" values progressively increased with increase in heating period. A continuous loss in weight was observed up to 100 hours of heating, although after 50 hours the rate of loss remained relatively constant at 0.01–0.005 per cent per hour. Such a slight, continuing loss implies decomposition.

3. The varying effects on "moisture" values of particle size and mode of sample preparation further serve as deterrents to the uncritical use of vacuum-oven data.

Therefore, information of a more positive nature is necessary to describe more accurately the state of "wetness" of a food material (an important property from the standpoint of quality and perishability). To obtain such information vapor pressure measurements of dried vegetables were initiated in the fall of 1942. The original aim was to simulate the conditions of the official A.O.A.C. moisture method for dried fruits and to periodically record the vapor pressure. The time necessary for the sample to reach a constant vapor pressure could, it was thought, be taken as the optimum heating period to assign to an official method. This investigation has not yet been completed.

Meanwhile Makower and Myers[2] have employed vapor pressure measurements in the determination of moisture in dried carrots and dried eggs, suggesting wider application and outlining the limitations and advantages of the technic. As they clearly indicate, this new method is based on the principle that a vegetable material of a definite moisture content possesses a definite water vapor pressure at a fixed temperature.

The purpose of this present paper is to demonstrate the applicability of this approach to the determination of moisture in the economically important dried vegetables, namely, carrots, potatoes, onions, and beets. The procedure followed and the data obtained are presented below.

PREPARATION OF SAMPLES FOR ANALYSIS

After filling a 50 mm. weighing bottle with the vegetable "as received," the remainder was ground in a Wiley Mill. The 20–30-mesh portion was collected and placed in a tightly capped Mason jar, together with the unstoppered 50 mm. weighing bottle of the original dried vegetable. The contents of the Mason jar were permitted to come to equilibrium at room temperature (a minimum of two days was allowed). Vapor pressure readings of the original material and also of the ground material were taken, and at the same time an aliquot of the ground material was removed for a moisture determination by the A.O.A.C. method for dried fruits. To attain varying moisture levels in the same product, several 50 mm. weighing bottles were filled with ca 20 grams of ground vegetable and exposed to an atmosphere of 90 per cent relative humidity for varying periods. The

[2] *Proc. Inst. Food. Tech.*, 1943, 156–164.

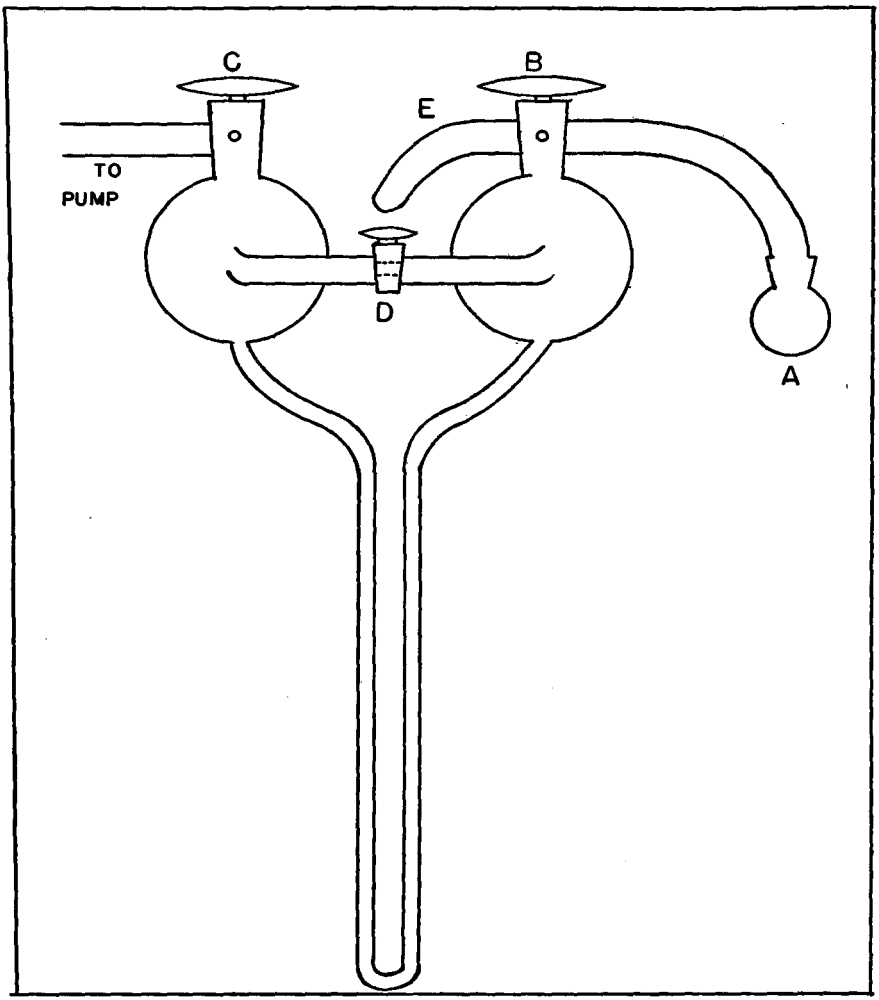

FIG. 1.—VAPOR PRESSURE APPARATUS.

weighing bottles were stoppered after the desired exposure, and the contents were permitted to come to equilibrium at room temperature, with the aid of occasional shaking (a minimum of 36 hours was allowed). Immediately prior to taking a vapor pressure reading of the ground material, an aliquot was removed for a moisture determination by the A.O.A.C. official method for dried fruit.

APPARATUS

Although somewhat different in design and in manipulation from that depicted by Makower and Myers,[1] the apparatus is the same in principle, utilizing the static method of measuring vapor pressure (Figure 1). "Octoil," a low vapor pressure oil manufactured by the Distillation Products, Inc., Rochester, New York, was used for the manometer oil. This apparatus is also being employed in the previously mentioned studies on constant vapor pressure as an index for attaining a dry material.

METHOD AND RESULTS

The sample of dried vegetable was placed in the 50 ml. flask, A; stopcock B was turned carefully so that A was gently brought to the low pressure (0.1 mm. or less) to which the remainder of the system had previously been evacuated. Flask A was immediately submerged in a freezing mixture of acetone and "dry ice"; stopcock B was completely opened and the entire system was evacuated to a pressure of less than 0.1 mm. (in these experiments it was 25–50 μ). At this point stopcock D was turned so as to seal off the two halves of the manometer bulbs (500 ml. capacity) from each other. The freezing bath was replaced with a constant temperature bath of 35°C., and the system was permitted to reach equilibrium. (Equilibrium was considered that point at which the reading remained constant for 30 minutes.) A second reading was obtained by sealing off flask A from the remainder of the system, evacuating the system so that the manometer read zero, separating the two halves of the manometer by means of stopcock D, and gently introducing A into the system by slowly opening stopcock B.

The time required for the initial reading varied from 45 to 90 minutes. (The determinations on the original unground material generally required 80–90 minutes and the values of the original checked, within 2 mm., those of the corresponding 20–30-mesh material.) The second reading required only 30–60 minutes, and again the original material required a longer period. Depending on the prevailing humidity, the initial readings were consistently 1–4 mm. higher than the second reading. However, third and fourth readings checked quite closely with the second. It was noted that the differential between the first and second readings equalled the blank reading. This blank was obtained by using the empty 50 ml. flask, A; a 250 ml. flask resulted in a correspondingly higher blank and a greater differential between the first and second readings. However the second readings themselves appeared unaffected by varying the size of flask A (between 50 and 250 ml.), or by the humidity. Evidently the subsequent removal of the vapors collected for the first reading reduces to a minimum the effect of the atmospheric humidity which is present during the first determination. The second values are therefore considered the

more accurate. Tube E (containing P_2O_5) was used to ascertain whether the pressure developed was entirely due to water vapor (more correctly, vapors adsorbed by P_2O_5). Excess pressure would of course indicate insufficient evacuation or air leakage. For routine analysis it was found sufficient (1) to accept the first reading minus the blank; or (2) to adjust the apparatus as for a first reading, evacuate the system after an interval of 15 minutes, and then carry to completion a vapor pressure measurement. It should be noted that the data for the treatment in the 70°C.

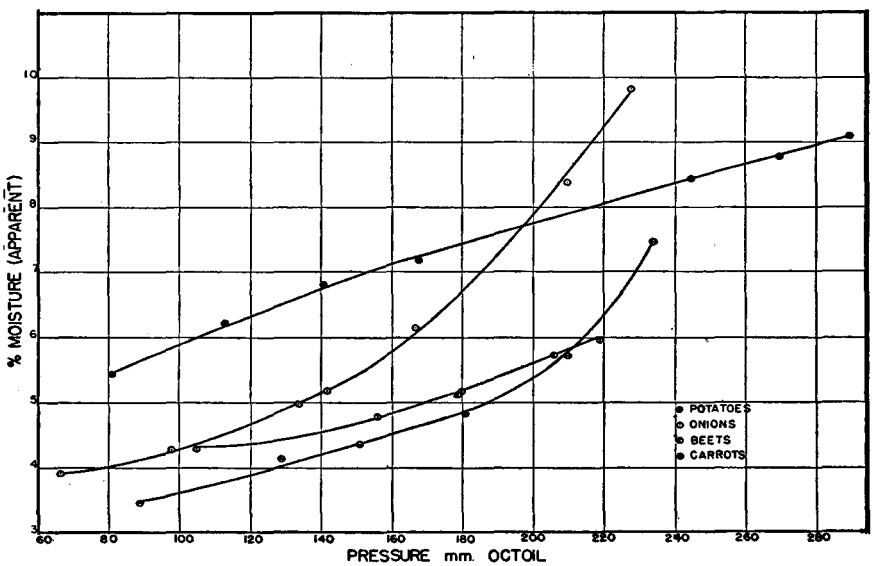

FIG. 2.—RELATIONSHIP BETWEEN MOISTURE AND VAPOR PRESSURE.

vacuum-oven (A.O.A.C. method for moisture in dried fruits) are recorded as *per cent moisture.* In Figure 2 these results are plotted against the corresponding vapor pressure measurements.

DISCUSSION

Although the ranges of the curves obtained for the respective vegetables are limited, they all include the region of the inflection point in the isotherms of Makower and Dehority.[3] These authors compare these ranges to the S-shaped isotherms found by Emmett[4] in the study of nitrogen adsorption on the surface of inorganic materials. Emmett considered the inflection points as representing the approximate limits of ordinary surface adsorption occurring at low humidities, and the beginnings of "multilayer

[3] *Ind. Eng. Chem.*, 35, 1937 (1943).
[4] "Advances in Colloid Science," p. 1. Interscience Publishers, Inc., New York (1942).

adsorption" or "capillary condensation" occurring at high humidities.

The ratio between the vapor pressures and apparent moisture values appears to be characteristic for each of the vegetables investigated, but extensive studies are necessary to determine whether varietal differences and mode of dehydration will seriously distort these characteristics. However the author, in addition to the products used for the above investigations, has determined the apparent moisture content and the vapor pressure of two samples of dried potatoes and beets. Variety and mode of manufacture were unknown, but the apparent moistures predicted by the vapor pressure readings were within 0.1 per cent of the moisture determined after 22 hours in the 70°C. vacuum oven.

The close checks between the vapor pressure values for the original unground dried vegetable and those for the corresponding 20–30-mesh material indicate that the vapor pressure measurements are independent of particle size. With larger particles simply a longer period of time is necessary before equilibrium is attained.

CONCLUSIONS

(1) Vapor pressure measurements (mm. of "Octoil" or mercury) reflect, more accurately than per cent moisture by a vacuum-oven method, the "state of wetness" of a dried vegetable.

(2) A relationship exists between the moisture content and the vapor pressure of a dried vegetable.

(3) Within the range covered, vapor pressure measurements are independent of the particle size of the vegetable.

BOOK REVIEWS

Food Regulation and Compliance. By ARTHUR D. HERRICK. Revere Publishing Co., 32 Broadway, New York (1944). 6×9 inches, 646 pages, buckram. Price $10.00.

"Food Regulation and Compliance" is a very readable book as a whole, as well as a complete and convenient source of reference to the great number of decisions issued under the Food and Drugs Act of 1906 and the Federal Food, Drug, and Cosmetic Act of 1938. The book is mainly devoted to explaining to food manufacturers how to comply with Federal laws regulating foods, particularly the Federal Food, Drug, and Cosmetic Act of 1938. It will be published in two volumes, of which the first only has so far appeared. In general, this volume covers all phases of labeling requirements for foods. The second volume will deal with such subjects as adulteration, imports, coal tar colors, etc. Volume I covers all of the various labeling questions about which the Food and Drug Administration has expressed opinions to the trade so that it should serve as a very practical guide to compliance with the law. The discussions of the various requirements of the Federal Act are written in a clear, non-legal style, although adequate references are made to court decisions. A study of the book and the references cited should lead to a good understanding of just how these requirements are designed to protect the consumer.—JOSEPH CALLAWAY, JR.

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William ap Catesby Jones, 1881–1944

WILLIAM AP CATESBY JONES

Major William ap Catesby Jones, State Chemist of Virginia, died on July 10, 1944, at the age of 63, at his home in Richmond, Virginia. In addition to his wife, Mrs. Lulie Greenhow Johnston Jones, he is survived by one son, 1st Lt. Catesby ap Catesby Jones, United States Army, and two daughters, Lulie Greenhow and Rosalie Fontaine Jones.

Major Jones, son of Thomas Catesby and Rosalie Fontaine Jones, was born June 9, 1881, at Lynchburg, Virginia, and was related through both parents to many families conspicuous in Virginia history. His grandfather was president of the Virginia Central Railroad, now the Chesapeake and Ohio.

Major Jones graduated at Virginia Polytechnic Institute in 1900 and spent the following 12 years as a chemist with iron and steel laboratories in Virginia, Alabama, and Pennsylvania. In 1913 he joined the scientific staff of the Virginia Department of Agriculture, and in 1930 became State Chemist, which position he held at the time of his death.

He was a charter member of the Virginia Section of the American Chemical Society and served as chairman and counselor. He helped organize the Virginia Academy of Science and served ably in the office of president. In 1934, in recognition of his contributions to science, he was elected a Fellow in the American Institute of Chemists. He was a charter member of the Southern Association of Science and Industry, serving as a member of its executive committee at the time of his death.

He was an active member in the Alumni Association of his Alma Mater, served on many committees authorized for scientific study by the General Assembly of Virginia, and was past master in Virginia of the National Grange. He was a past president of the Central Atlantic States Dairy, Food, and Drug Officials, and at the time of his death was president of the Association of American Feed Control Officials and a member of the Association of Official Agricultural Chemists.

He was a member of the famous Richmond Light Infantry Blues, and during World War I served first with the cavalry on the Mexican border, and later was commissioned a Major in the Chemical Warfare Service of the United States Army. As an active member of the 40 and 8 Society and the American Legion, he held at various times the following positions of honor and responsibility: Commander of Richmond Post No. 1, Commander 3rd Virginia District, Vice-Commander Department of Virginia, and at the time of his death, he was National Executive Committeeman from Virginia.

He was a member of historic St. Paul's Episcopal Church, where for many years he served as vestryman. Though he was quiet and unassuming, he was energetic and possessed all the characteristics necessary to make a good leader of men. He was loyal, genial, and devoted to all that was best in science, and in social and civic life. He lived a full life as head of a devoted family and as a public servant. He contributed much to the social and civic life of his country and conducted himself in such manner as to make his contemporaries aware that he understood and practiced what he spoke. His patriotism made him not only a good soldier but an exemplary private citizen. He was truly a friend of man.

RODNEY C. BERRY

ANNOUNCEMENT

With this number of the Journal our Associate Editor lays down the burden which she has so faithfully and efficiently borne ever since the publication of Volume 5. Not only is she changing her duties to those of a housewife, and her name to Mrs. Rutherford Mann Otis, but she is also changing her residence to Branchport, N. Y. We shall thus be deprived of her personal counsel during the period of adjustment. This is no small deprivation, for, as everyone knows, her services to the Association were never confined to the mere arrangement of the manuscript for the printer. There are a host of scientific authors who pay tribute to her valuable and kindly suggestions for added clarity, improved diction, more happy choice of words, and more grammatical construction. She went the second mile when she ably shouldered the work of preparing the yearly report on changes in *Methods of Analysis*, which of course is the New Testament of the Control Officials' Bible. As if that were not enough, she rendered invaluable assistance to the Committee on Revision of *Methods of Analysis* by editing the entire manuscript of the Second Edition. As a natural consequence of this good deed she was made a member of the Committee on all subsequent editions. Were it not for her generous contribution to the current preparation of the Sixth Edition, mainly with time snatched from her home duties, the new book of methods would never be ready for distribution in the latter part of 1945, as now seems reasonably assured.

In a very large measure indeed the healthy growth of our Journal to the present position of leader in its field is the direct result of the untiring and devoted efforts of Mrs. Otis. It is a going concern which she hands over to Miss Katharine Ronsaville, who will carry on the editorial work beginning with the next issue. We feel that the Association is most fortunate in securing the services of one so well qualified for the work.