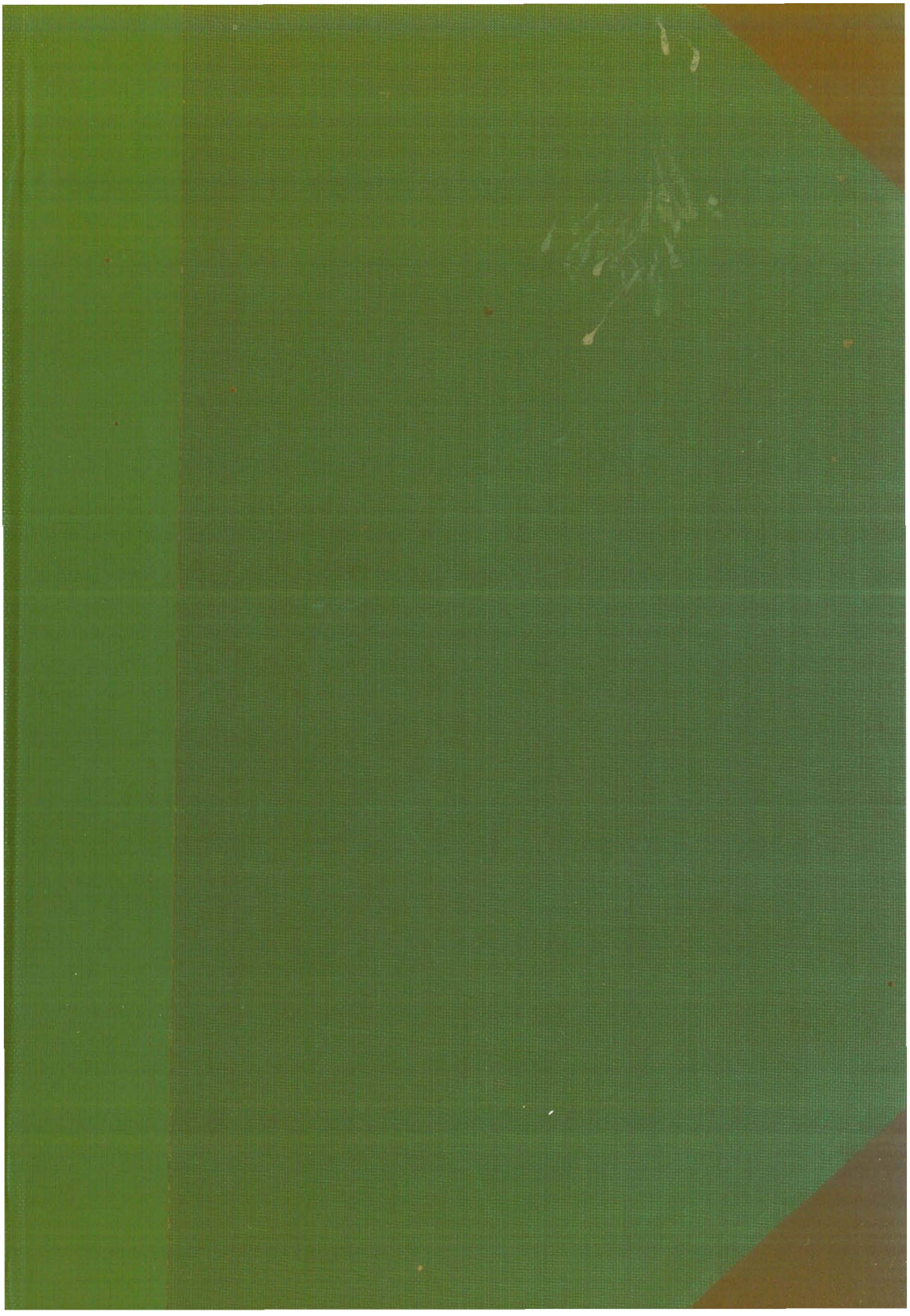

JOURNAL

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BOOK REVIEWS

PROCEEDINGS OF THE FIFTY-FOURTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1938

The fifty-fourth annual convention of the Association of Official Agricultural Chemists was held at the Raleigh Hotel, Washington, D. C., November 14, 15, and 16, 1938.

The meeting was called to order by the president, H. R. Kraybill, Purdue University, Lafayette, Ind., on the morning of November 14, at 10:30 o'clock.

OFFICERS, COMMITTEES, REFEREES, AND ASSOCIATE REFEREES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR ENDING NOVEMBER, 1939

President

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Vice-President

L. B. BROUGHTON, University of Maryland, College Park, Md.

Secretary-Treasurer

W. W. SKINNER, U. S. Bureau of Chemistry and Soils, Washington, D. C.

Additional Members of the Executive Committee

J. W. SALE, Washington, D. C.
G. G. FRARY, Vermillion, S. D.
J. O. CLARKE, Chicago, Ill.
H. R. KRAYBILL, Lafayette, Ind.

PERMANENT COMMITTEES

Recommendations of Referees

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

H. A. LEPPER (U. S. Food and Drug Administration, Washington, D. C.), *Chairman*

SUBCOMMITTEE A: G. E. Grattan (1940), (Department of Agriculture, Ottawa, Can.), *Chairman;* H. A. Halvorson (1942) and E. L. Griffin (1944). [Standard solutions (silver nitrate and thiocyanate, iodine and thiosulfate, sulfuric acid, potassium permanganate); insecticides, fungicides, and caustic poisons (fluorine compounds; pyrethrins, derris, and cubé; naphthalene in poultry lice products); soils and liming materials (hydrogen-ion concentration—soils of arid and semi-arid regions and soils of humid regions; liming materials, less common metals in soils, selenium); feeding stuffs (sampling, ash, mineral mixed feeds—calcium and iodine; moisture, lactose in mixed feeds, hydrocyanic acid in glucoside-bearing materials, biological methods for determination of vitamin D carriers, biological methods for vitamin B complexes, technic and details of biological methods—vitamin D carriers, carotene, manganese, adulteration of condensed milk products and of cod-liver oil, fat in fish meal); fertilizers (phosphoric acid, nitrogen, magnesium and manganese, acid- and base-forming qual-

ity, potash; calcium, sulfur, copper, and zinc); plants (less common metals, carbohydrates, inulin, hydrocyanic acid, forms of nitrogen, sodium and potassium); lignin, enzymes (papain); paints, paint materials and varnishes (accelerated testing of paints, varnishes); vitamins (vitamin A, vitamin D, vitamin K, riboflavin); leathers and tanning materials, disinfectants.]

SUBCOMMITTEE B: H. J. FISHER (1940), (Agricultural Experiment Station, New Haven, Conn., *Chairman;* A. E. PAUL (1942) and W. F. REINDOLLAR (1944). [Naval stores; radioactivity (quantum counter, gamma ray scope); cosmetics; drugs (microchemical tests for alkaloids, microchemical tests for synthetics, daphnia methods, ergot alkaloids, guaiacol in mixtures, biological testing, iodine ointment, elixir of terpin hydrate and codeine, aminopyrine and phenobarbital in mixtures, ointment of yellow mercuric oxide, rhubarb and rhapontic-um, theophylline sodium salicylate, ephedrine in jellies, arecoline hydrobromide, separation of acetanilid and salol; acetylsalicylic acid, acetophenetidin and salol; benzedrine, plasmochine, physostigmine salicylate, ipecac, opium powder (Dover's powder), pepsin, hydroxyquinoline sulfate nicotinic acid, purification of caffeine).

SUBCOMMITTEE C: G. G. FRARY (1940), (State Chemical Laboratory, Vermillion, S. D.), *Chairman;* W. B. WHITE (1942) and J. O. CLARKE (1944). [Dairy products (butter, cheese—isolation of fat, malted milk—fat, casein, dried milk—lactic acid, lactose in milk, mold in butter, decomposition, neutralizers, difference between dairy products made from cows' milk and those made from milk of other animals, frozen desserts, tests for pasteurization—milk and cream, butter); oils, fats and waxes (refractometric determination of oil in seeds, thiocyanogen number, Polenski number); eggs and egg products (unsaponifiable constituents and fat, detection of decomposition—glycerol and sugar); metals in foods (arsenic and antimony, copper, zinc, fluorine, lead, mercury, selenium, fumigation residues in foods); canned foods (tomato products); meats and meat products; spices and condiments (salad dressings, vinegar, volatile constituents); gums in foods (starchy foods); microbiological methods (canned fish products, canned meats, canned vegetables, canned tomato products, sugar, eggs and egg products); fish and other marine products (solids and fats); nuts and nut products; coffee and tea.]

SUBCOMMITTEE D: W. C. JONES (1940), (Department of Agriculture, Richmond, Va.), *Chairman;* J. W. Sale (1942) and J. A. LeClerc (1944). [Sugars and sugar products (acetyl-methyl carbinol and diacetyl in food products, sucrose and ash in molasses, honey, refractive indices of sugar solutions, maple products; drying, densimetric, and refractometric methods; polariscopic methods, chemical methods for reducing sugars, sugars in molasses); waters, brine, and salt (effervescent salts); alcoholic beverages (diastatic activity of malt, proteolytic activity of malt, malt extract in malt, malt adjuncts, beer, CO_2 in beer, heavy metals in beer, total sulfur in wine, volatile acids in wine, volatile acids in distilled spirits, SO_2 in wine and beer, aldehydes in whiskey and other potable spirits, detection of adulteration of distilled spirits, wood alcohol in brandy, cordials and liqueurs); food preservatives (saccharine, benzoate of soda); coloring matters in foods; fruits and fruit products (electrometric titration of acids; malic, isocitric and lactic acids; polariscopic methods for, and ash in, jams, jellies, and preserves; P_2O_5 in jams, jellies, and other fruit products); cacao products; cereal foods (ash in flour, macaroni products, and baked products; H-ion concentration of flour, starch in flour, acidity in flour, sugar in flour, baking test for soft wheat flour, flour-bleaching chemicals, CO_2 in self-rising flour, milk solids in milk bread, cold water extract flour, ergot in flour, proteo-

lytic enzymes, color in flour, soya flour in foods, whole wheat flour, phosphated flour, sterols, corn products, oat products, rye and buckwheat, barley and rice, baked products other than bread); microchemical methods; flavors and non-alcoholic beverages (organic solvents in flavors); baking powder—tartrates.]

Committee to Cooperate with Other Committees on Food Definitions

C. D. HOWARD (Board of Health, Concord, N. H.), *Chairman*
E. M. BAILEY — G. G. FRARY

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W. H. MACINTIRE, Knoxville, Tenn.

REFEREES AND ASSOCIATE REFEREES

STANDARD SOLUTIONS:

General referee: R. L. Vandaveer, Food and Drug Adm., New Orleans, La.

SILVER NITRATE AND THIOCYANATE:

Associate referee: R. L. Vandaveer

IODINE AND THIOSULFATE:

Associate referee: K. L. Milstead, Food and Drug Adm., Chicago, Ill.

SULFURIC ACID:

Associate referee: W. H. King, Food and Drug Adm., New Orleans, La.

POTASSIUM PERMANGANATE:

Associate referee: G. M. Johnson, Food and Drug Adm., St. Louis, Mo.

INSECTICIDES, FUNGICIDES, AND CAUSTIC POISONS:

General referee: J. J. T. Graham, Food and Drug Adm., Washington, D. C.

PYRETHRINS, DERRIS, AND CUBÉ:

Associate referee: J. J. T. Graham.

FLUORINE COMPOUNDS:

Associate referee: C. G. Donovan, Bureau of Entomology and Plant Quarantine, Washington, D. C.

NAPHTHALENE IN POULTRY LICE PRODUCTS:

Associate referee: Roswell Jinkins, Food and Drug Adm., Chicago, Ill.

SOILS AND LIMING MATERIALS:

General referee: W. H. MacIntire, Agricultural Experiment Station, Knoxville, Tenn.

HYDROGEN-ION CONCENTRATION:

a. SOILS OF ARID AND SEMI-ARID REGIONS:

Associate referee: W. T. McGeorge, Agricultural Experiment Station, Tucson, Ariz.

b. SOILS OF HUMID REGIONS:

Associate referee: E. R. Purvis, Virginia Truck Experiment Station, Norfolk, Va.

LESS COMMON METALS IN SOILS:

Associate referee: J. S. McHargue, Agricultural Experiment Station, Lexington, Ky.

SELENIUM IN SOILS:

Associate referee: K. T. Williams, Bureau of Chemistry and Soils, Washington, D. C.

LIMING MATERIALS:

Associate referee: W. M. Shaw, Agricultural Experiment Station, Knoxville, Tenn.

FEEDING STUFFS:

General referee: L. S. Walker, Agricultural Experiment Station, Burlington, Vt.

SAMPLING

Associate referee: L. M. Jeffers, Dept. of Agriculture, Sacramento, Calif.

ASH:

Associate referee: J. L. St. John, Agricultural Experiment Station, Pullman, Wash.

MINERAL MIXED FEEDS (calcium and iodine):

Associate referee: H. E. Perkins, Manhattan, Kans.

LACTOSE IN MIXED FEEDS:

Associate referee: D. A. Magraw, American Dry Milk, Inst., Chicago, Ill.

MOISTURE:

Committee: H. A. Halvorson, P. B. Curtis, and P. A. Clifford.

HYDROCYANIC ACID IN GLUCOSIDE-BEARING MATERIALS:

Associate referee: R. A. Greene, University of Arizona, Tucson, Ariz.

BIOLOGICAL METHODS FOR DETERMINATION OF VITAMIN D CARRIERS:

Associate referee: C. D. Tolle, Food and Drug Adm., Washington, D. C.

BIOLOGICAL METHODS FOR VITAMIN B COMPLEXES:

Associate referee: O. L. Kline, Food and Drug Administration, Washington, D. C.

TECHNIC AND DETAILS OF BIOLOGICAL METHODS, VITAMIN D CARRIERS:

Associate referee: Rebecca Hubbell, Agricultural Experiment Station, New Haven, Conn.

MANGANESE:

Associate referee: J. B. Smith, Agricultural Experiment Station, Kingston, R. I.

CAROTENE:

Associate referee: V. E. Munsey, Food and Drug Adm., Washington, D. C.

FAT IN FISH MEAL:

Associate referee: R. W. Harrison, Bureau of Fisheries, Seattle, Wash.

ADULTERATION OF CONDENSED MILK PRODUCTS AND COD-LIVER OIL:

Associate referee: P. B. Curtis, Agricultural Experiment Station, Lafayette, Ind.

FERTILIZERS:

General referee: G. S. Fraps, Agricultural Experiment Station, College Station, Tex.

PHOSPHORIC ACID:

Associate referee: W. H. Ross, Bureau of Chemistry and Soils, Washington, D. C.

NITROGEN:

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

MAGNESIUM AND MANGANESE:

Associate referee: J. B. Smith, Agricultural Experiment Station, Kingston, R. I.

POTASH:

Associate referee: O. W. Ford, Agricultural Experiment Station, Lafayette, Ind.

ACID AND BASE-FORMING QUALITY:

Associate referee: L. E. Horat, Agricultural Experiment Station, Lafayette, Ind.

CALCIUM, SULFUR, COPPER, ZINC:

Associate referee: Gordon Hart, Department of Agriculture, Tallahassee, Fla.

PLANTS:

General referee: E. J. Miller, Agricultural Experiment Station, E. Lansing, Mich.

LESS COMMON METALS:

Associate referee: J. S. McHargue, Agricultural Experiment Station, Lexington, Ky.

CARBOHYDRATES:

Associate referee: J. T. Sullivan, U. S. Regional Pasture Research Lab., State College, Pa.

INULIN:

Associate referee: T. G. Phillips, University of New Hampshire, Durham, N. H.

FORMS OF NITROGEN:

Associate referee: H. B. Vickery, Agricultural Experiment Station, New Haven, Conn.

HYDROCYANIC ACID:

Associate referee: R. A. Greene, University of Arizona, Tucson, Ariz.

SODIUM AND POTASSIUM:

Associate referee: R. T. Milner, Regional Soybean Industrial Products Lab., Urbana, Ill.

LIGNIN:

General referee: M. Phillips, Bureau of Chemistry and Soils, Washington, D. C.

ENZYMES:

General referee: A. K. Balls, Bureau of Chemistry and Soils, Washington, D. C.

PAPAIN:

Associate referee: R. R. Thompson, Hawaiian Experiment Station, Honolulu, Hawaii.

PAINTS, PAINT MATERIALS AND VARNISHES:

General referee: C. S. Ladd, Food Commissioner and Chemist, Bismarck, N. D.

ACCELERATING TESTING OF PAINTS:

Associate referee: L. L. Carrick, Agricultural Experiment Station, Fargo N. D.

VARNISHES:

Associate referee: F. Roberts, Paint and Varnish Lab., Bismarck, N. D.

VITAMINS:

General referee: E. M. Nelson, Food and Drug Adm., Washington, D. C.

VITAMIN A:

Associate referee: J. B. Wilkie, Food and Drug Adm., Washington, D. C.

VITAMIN D:

Associate referee: W. C. Russell, Agricultural Experiment Station, New Brunswick, N. J.

VITAMIN K:

Associate referee: H. J. Almquist, University of California, Berkeley, Calif.

RIBOFLAVIN:

Associate referee: A. R. Kemmerer, Agricultural Experiment Station, College Station, Texas.

LEATHERS AND TANNING MATERIALS:

General referee: I. D. Clarke, Bureau of Chemistry and Soils, Washington, D. C.

DISINFECTANTS:

General referee: C. N. Brewer, Food and Drug Adm., Washington, D. C.

NAVAL STORES:

General referee: V. E. Grotlisch, Food and Drug Adm., Washington, D. C.

RADIOACTIVITY:

General referee: C. H. Badger, Food and Drug Adm., Washington, D. C.

QUANTUM COUNTER:

Associate referee: A. E. Mix, Food and Drug Adm., Washington, D. C.

GAMMA RAY SCOPE:

Associate referee: C. H. Badger.

COSMETICS:

General referee: E. W. Campbell, Bureau of Health, Augusta, Me.

DRUGS:

General referee: L. E. Warren, Food and Drug Adm., Washington, D. C.

ACETYLSALICYLIC ACID, ACETOPHENETIDIN, AND SALOL:

Associate referee: D. C. Grove, Food and Drug Adm., Washington, D. C.

AMINOPYRINE AND PHENOBARBITAL IN MIXTURES:

Associate referee: E. C. Payne, Food and Drug Adm., Chicago, Ill.

BIOLOGICAL TESTING:

Associate referee: J. C. Krantz, Jr., University of Maryland, College Park, Md.

DAPHNIA METHODS:

Associate referee: A. Viehoever, Philadelphia, Pa.

ELIXIR OF TERPIN HYDRATE AND CODEINE:

Associate referee: Jonas Carol, Food and Drug Adm., Cincinnati, O.

ERGOT ALKALOIDS:

Associate referee: Lloyd C. Miller, Food and Drug Adm., Washington, D. C.

GUAIACOL IN MIXTURES:

Associate referee: K. L. Milstead, Food and Drug Adm., Chicago, Ill.

PHYSOSTIGMINE SALICYLATE:

Associate referee: G. M. Johnson, Food and Drug Adm., St. Louis, Mo.

SEPARATION OF ACETANILID AND SALOL:

Associate referee: O. C. Kenworthy, Food and Drug Adm., New York City.

ARECOLINE HYDROBROMIDE:

Associate referee: H. R. Bond, Food and Drug Adm., Chicago, Ill.

IODINE OINTMENT:

Associate referee: W. F. Reindollar, State Dept. of Health, Baltimore, Md.

MICROCHEMICAL TESTS FOR ALKALOIDS:

Associate referee: C. K. Glycart, Food and Drug Adm., Chicago, Ill.

MICROCHEMICAL TESTS FOR SYNTHETICS:

Associate referee: I. S. Shupe, Food and Drug Adm., Kansas City.

BENZEDRINE:

Associate referee: J. H. Cannon, Food and Drug Adm., St. Louis, Mo.

OINTMENT OF YELLOW MERCURIC OXIDE:

Associate referee: H. O. Moraw, Food and Drug Adm., Chicago, Ill.

THEOPHYLLINE SODIUM SALICYLATE:

Associate referee: M. L. Harris, Food and Drug Adm., Houston, Texas.

MANDELIC ACID MIXTURES:

Associate referee: H. G. Underwood, Food and Drug Adm., Cincinnati, Ohio.

RHUBARB AND RHAPONTICUM:

Associate referee: E. H. Wirth, University of Illinois, Chicago, Ill.

PLASMOCHINE:

Associate referee: F. C. Sinton, Food and Drug Adm., New York City.

HYDROXYQUINOLINE SULFATE:

Associate referee: W. H. Hartung, State Dept. of Health, Baltimore, Md.

PEPSIN:

Associate referee: E. M. Hoshall, Food and Drug Adm., Baltimore, Md.

IPECAC AND OPIUM POWDER (Dover's powder):

Associate referee: W. F. Kunke, Food and Drug Adm., Chicago, Ill.

NICOTINIC ACID:

Associate referee: P. S. Jorgensen, Food and Drug Adm., San Francisco, Calif.

EPHEDRINE IN JELLIES:

Associate referee: E. H. Grant, Food and Drug Adm., Boston, Mass.

PURIFICATION OF CAFFEINE IN PLANT EXTRACTIVES:

Associate referee: John R. Matchett, Bureau of Narcotics, Washington, D. C.

DAIRY PRODUCTS:

General referee: G. G. Frary, Dairy and Food Dept., Vermillion, S. D.

BUTTER:

Associate referee: J. A. Mathews, Food and Drug Adm., Washington, D. C.

CHEESE (isolation of fat):

Associate referee: I. D. Garard, Rutgers University, New Brunswick, N. J.

MALTED MILK (fat):

Associate referee: E. W. Coulter, Food and Drug Adm., Chicago, Ill.

MALTED MILK (casein):

Associate referee: I. Schurman, Food and Drug Adm., Chicago, Ill.

DRIED MILK (lactic acid):

Associate referee: F. Hillig, Food and Drug Adm., Washington, D. C.

FROZEN DESSERTS:

Associate referee: M. J. Mack, Massachusetts State College, Amherst, Mass.

LACTOSE IN MILK:

Associate referee: E. R. Garrison, University of Missouri, Columbia, Mo.

MOLD IN BUTTER:

Associate referee: J. D. Wildman, Food and Drug Adm., Washington, D. C.

TESTS FOR PASTEURIZATION OF MILK AND CREAM:

Associate referee: F. W. Gilcreas, Department of Health, Albany, N. Y.

TESTS FOR PASTEURIZATION OF BUTTER:

Associate referee: E. H. Parfitt, Purdue Unversity, Lafayette, Ind.

DIFFERENCE BETWEEN DAIRY PRODUCTS MADE FROM COW'S MILK AND THOSE MADE FROM THE MILK OF OTHER ANIMALS:

Associate referee: I. D. Garard.

DECOMPOSITION IN DAIRY PRODUCTS:

Associate referee: C. S. Myers, Food and Drug Adm., Washington, D. C.

NEUTRALIZERS IN DAIRY PRODUCTS:

Associate referee: F. Hillig.

OILS, FATS AND WAXES:

General referee: G. S. Jamieson, Bureau of Chemistry and Soils, Washington, D. C.

REFRACTOMETRIC DETERMINATION OF OIL IN SEEDS:
Associate referee: Lawrence Zeleny, Bureau of Agricultural Economics, Washington, D. C.

THIOCYANOGEN NUMBER:
Associate referee: G. S. Jamieson.

POLENSKI NUMBER:
Associate referee: R. S. McKinney, Bureau of Chemistry and Soils, Washington, D. C.

EGGS AND EGG PRODUCTS:
General referee: E. O. Haenni, Food and Drug Adm., Washington, D. C.

UNSAPONIFIABLE CONSTITUTENTS AND FAT:
Associate referee: E. O. Haenni.

DETECTION OF DECOMPOSITION (glycerol and sugars):
Associate referee: L. C. Mitchell, Food and Drug Adm., St. Louis, Mo.

METALS IN FOODS:
General referee: H. J. Wichmann, Food and Drug Adm., Washington, D. C.

ARSENIC AND ANTIMONY:
Associate referee: C. C. Cassil, Bureau of Entomology and Plant Quarantine, Washington, D. C.

COPPER:
Associate referee: D. L. Drabkin, University of Pennsylvania, Philadelphia, Pa.

ZINC:
Associate referee: W. S. Ritchie, Agricultural Experiment Station, Amherst, Mass.

FLUORINE:
Associate referee: P. A. Clifford, Food and Drug Adm., Washington, D. C.

LEAD:
Associate referee: P. A. Clifford.

MERCURY:
Associate referee: W. O. Winkler, Food and Drug Adm., Washington, D. C.

SELENIUM:
Associate referee: A. K. Kline, Food and Drug Adm., San Francisco, Calif.

FUMIGATION RESIDUES IN FOODS:
Associate referee: W. O. Winkler.

COLORING MATTERS IN FOODS:
General referee: C. F. Jablonski, Food and Drug Adm., New York City.

FRUITS AND FRUIT PRODUCTS:
General referee: B. G. Hartmann, Food and Drug Adm., Washington, D. C.

ELECTROMETRIC TITRATION OF ACIDS:
Associate referee: R. U. Bonnar, Food and Drug Adm., Washington, D. C.

MALIC, ISOCITRIC, AND LACTIC ACIDS:

Associate referee: B. G. Hartmann.

P_2O_5 IN JAMS, JELLIES, AND OTHER FRUIT PRODUCTS:

Associate referee: H. W. Gerritz, Food and Drug Adm., San Francisco, Calif.

POLARISCOPIC METHODS FOR, AND ASH IN, JAMS, JELLIES, AND PRESERVES:

Associate referee: R. A. Osborn, Food and Drug Adm., Washington, D. C.

CANNED FOODS:

General referee: V. B. Bonney, Food and Drug Adm., Washington, D. C.

TOMATO PRODUCTS:

Associate referee: L. M. Beacham, Jr., Food and Drug Adm. Washington, D. C.

FLAVORS AND NON-ALCOHOLIC BEVERAGES:

General referee: J. B. Wilson, Food and Drug Adm., Washington, D. C.

ORGANIC SOLVENTS IN FLAVORS:

Associate referee: R. D. Stanley, Food and Drug Adm., Chicago, Ill.

MEATS AND MEAT PRODUCTS:

General referee: R. H. Kerr, Bureau of Animal Industry, Washington, D. C.

CACAO PRODUCTS:

General referee: W. O. Winkler, Food and Drug Adm., Washington, D. C.

GUMS IN FOODS:

General referee: F. Leslie Hart, Food and Drug Adm., Los Angeles, Calif.

STARCHY FOODS:

Associate referee: D. D. Ballard, Food and Drug Adm., San Francisco, Calif.

SPICES AND CONDIMENTS:

General referee: S. Alfend, Food and Drug Adm., St. Louis, Mo.

VOLATILE CONSTITUENTS:

Associate referee: J. F. Clevenger, Food and Drug Adm., New York City.

VINEGAR:

Associate referee: A. M. Henry, Food and Drug Adm., Atlanta, Ga.

SALAD DRESSINGS:

Associate referee: L. T. Ryan, N. Dakota Regulatory Laboratory, Bismarck, N. D.

MICROBIOLOGICAL METHODS:

General referee: A. C. Hunter, Food and Drug Adm., Washington, D. C.

CANNED FISH PRODUCTS:

Associate referee: O. W. Lang, Hooper Foundation Medical Research, University of California, San Francisco, Calif.

CANNED MEATS:

Associate referee: L. B. Jensen, Swift & Co., Chicago, Ill.

CANNED VEGETABLES:
Associate referee: E. J. Cameron, National Canners Assn., Washington, D. C.

CANNED TOMATO PRODUCTS:
Associate referee: B. A. Linden, Food and Drug Adm., Washington, D. C.

SUGAR:
Associate referee: E. J. Cameron.

EGGS AND EGG PRODUCTS:
Associate referee: Roy Schneiter, Food and Drug Adm., Washington, D. C.

FISH AND OTHER MARINE PRODUCTS:
General referee: H. D. Grigsby, Food and Drug Adm., Philadelphia, Pa.

SOLIDS AND FATS:
Associate referee: R. W. Stewart, Food and Drug Adm., Philadelphia, Pa.

SUGARS AND SUGAR PRODUCTS:
General referee: R. F. Jackson, National Bureau of Standards, Washington, D. C.

ACETYL-METHYL CARBINOL AND DIACETYL IN FOOD PRODUCTS:
Associate referee: J. B. Wilson, Food and Drug Adm., Washington, D. C.

SUGARS IN MOLASSES:
Associate referee: F. W. Zerban, Sugar Trade Lab., New York City.

SUCROSE AND ASH IN MOLASSES:
Associate referee: R. A. Osborn, Food and Drug Adm., Washington, D. C.

HONEY:
Associate referee: R. E. Lothrop, Bureau of Chemistry and Soils, Washington, D. C.

MAPLE PRODUCTS:
Associate referee: J. J. Perlman, Dept. of Agriculture and Markets, Albany, N. Y.

DRYING, DENSIMETRIC, AND REFRACTOMETRIC METHODS:
Associate referee: C. F. Snyder, National Bureau of Standards, Washington, D. C.

POLARISCOPIC METHODS (GENERAL):
Associate referee: R. M. Kingsbury, Bureau of Chemistry and Soils, Washington, D. C.

CHEMICAL METHODS FOR REDUCING SUGARS:
Associate referee: R. F. Jackson.

REFRACTIVE INDICES OF SUGAR SOLUTIONS:
Associate referee: R. T. Balch, Bureau of Chemistry and Soils, Washington, D. C.

WATERS, BRINE, AND SALTS:

General referee: A. E. Mix, Food and Drug Adm., Washington, D. C.

EFFERVESCENT SALTS:

Associate referee: A. E. Mix.

CEREAL FOODS:

General referee: V. E. Munsey, Food and Drug Adm., Washington, D. C.

ASH IN FLOUR, MACARONI PRODUCTS, AND BAKED PRODUCTS:

Associate referee: L. H. Bailey, Bureau of Chemistry and Soils, Washington, D. C.

H-ION CONCENTRATION OF FLOUR:

Associate referee: George Garnatz, The Kroger Food Foundation, Cincinnati, Ohio.

ACIDITY OF FLOUR:

Associate referee: Lawrence Zeleny, Bureau of Agricultural Economics, Washington, D. C.

STARCH IN FLOUR:

Associate referee: C. Y. Hopkins, National Research Council, Ottawa, Canada.

SUGAR IN FLOUR:

Associate referee: R. M. Sanstedt, Agricultural Experiment Station, Lincoln, Nebr.

BAKING TEST FOR SOFT WHEAT FLOUR:

Associate referee: E. G. Bayfield, Agricultural Experiment Station, Wooster, Ohio.

FLOUR-BLEACHING CHEMICALS:

Associate referee: Dorothy Scott, Food and Drug Adm., New York City.

CO_2 IN SELF-RISING FLOUR:

Associate referee: Rufus A. Barackman, Victor Chem. Works, Chicago Heights, Ill.

MILK SOLIDS IN MILK BREAD:

Associate referee: V. E. Munsey.

COLD WATER EXTRACT FLOUR:

Associate referee: H. C. Fellows, Bureau of Agricultural Economics, Washington, D. C.

ERGOT IN FLOUR:

Associate referee: Lloyd C. Miller, Food and Drug Adm., Washington, D. C.

PROTEOLYTIC ENZYMES:

Associate referee: Quick Landis, Fleischmann Labs., New York City.

COLOR IN FLOUR:

Associate referee: H. K. Parker, Novadel-Agene Corporation, Newark, N. J.

SOYA FLOUR IN FOODS:
Associate referee: J. W. Hayward, Archer-Daniels-Midland Co., Milwaukee, Wisc.

WHOLE WHEAT FLOUR:
Associate referee: C. S. Ladd, N. Dakota Regulatory Dept., Bismarck, N. D.

PHOSPHATED FLOUR:
Associated referee: J. R. Davies, General Foods Corp., Chicago, Ill.

STEROLS:
Associate referee: E. O. Haenni, Food and Drug Adm., Washington, D. C.

CORN PRODUCTS:
Associate referee: Lyle Brown, A. E. Staley Mfg. Co., Decatur, Ill.

OAT PRODUCTS:
Associate referee: H. P. Howells, Quaker Oats Co., Cedar Rapids, Iowa.

RYE AND BUCKWHEAT:
Associate referee: E. G. Harrel, Pillsbury Flour Mills Co., Minneapolis, Minn.

BARLEY AND RICE:
Associate referee: Allen D. Dickson, Bureau of Plant Industry, Madison, Wisc.

BAKED PRODUCTS OTHER THAN BREAD:
Associate referee: S. Voris, Loose-Wiles Biscuit Co., Long Island City, N. Y.

BAKING POWDERS—TARTRATES:
General referee: B. G. Hartmann, Food and Drug Adm., Washington, D. C.

MICROCHEMICAL METHODS:
Associate referee: E. P. Clark, Bureau of Entomology and Plant Quarantine, Washington, D. C.

ALCOHOLIC BEVERAGES:
General referee: J. W. Sale, Food and Drug Adm., Washington, D. C.

DIASTATIC ACTIVITY OF MALT:
Associate referee: Christian Rask, Albert Schwill Co., Chicago, Ill.

PROTEOLYTIC ACTIVITY OF MALT:
Associate referee: Stephen Laufer, Schwartz Laboratories, Inc., New York City.

HEAVY METALS IN BEER:
Associate referee: W. H. Harrison, Continental Can Co., Chicago, Ill.

CARBON DIOXIDE IN BEER:
Associate referee: P. P. Gray, Wallerstein Laboratories, New York City.

MALT EXTRACT IN MALT:
Associate referee: E. A. Siebel, 8 S. Dearborn St., Chicago, Ill.

MALT ADJUNCTS:
Associate referee: F. P. Siebel, Siebel Institute, Chicago, Ill.

BEER:

Associate referee: H. W. Rohde, Schlitz Brewing Co., Milwaukee, Wisc.

TOTAL SULFUR IN WINE:

Associate referee: B. G. Hartmann, Food and Drug Adm., Washington, D. C.

VOLATILE ACIDS IN WINE:

Associate referee: M. A. Joslyn, Agricultural Experiment Station, Berkeley, Calif.

SULFUR DIOXIDE IN BEER AND WINE:

Associate referee: L. V. Taylor, American Can Co., Maywood, Ill.

VOLATILE ACIDS IN DISTILLED SPIRITS:

Associate referee: G. F. Beyer, Bureau of Internal Revenue, Washington, D. C.

ALDEHYDES IN WHISKEY AND OTHER POTABLE SPIRITS:

Associate referee: Peter Valaer, Bureau of Internal Revenue, Washington, D. C.

DETECTION OF ADULTERATION OF DISTILLED SPIRITS:

Associate referee: S. T. Schicktanz, Bureau of Internal Revenue, Washington, D. C.

WOOD ALCOHOL IN BRANDY:

Associate referee: G. F. Beyer.

CORDIALS AND LIQUEURS:

Associate referee: J. B. Wilson, Food and Drug Adm., Washington, D. C.

FOOD PRESERVATIVES—SACCHARIN:

General referee: W. F. Reindollar, Bureau of Chemistry, Baltimore, Md.

BENZOATE OF SODA:

Associate referee: A. E. Mix, Food and Drug Adm., Washington, D. C.

NUTS AND NUT PRODUCTS:

General referee: S. C. Rowe, Food and Drug Adm., Washington, D. C.

COFFEE AND TEA:

General referee: H. J. Fisher, Agricultural Experiment Station, New Haven, Conn.

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WILEY MEMORIAL LECTURE. No. IX

THE HISTORY AND DEVELOPMENT OF FOOD INSPECTION IN THE UNITED STATES*

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When it was suggested that the subject of this address should relate to the early history of food inspection in the United States, culminating in the passage of the Food and Drugs Act of June 30, 1906, and to the organization for the enforcement of this law, particularly the part played by Dr. Wiley in bringing this about, it seemed an especially appropriate title at this time, because a new Food and Drugs Act has just been passed after a long struggle, and again the work ahead is the development of new regulations and the organization of new groups to carry it into effect. At this time we could well look back over the experience of the formative period of food inspection, and review some of the difficulties, troubles, and mistakes that were made, with the idea of benefiting from these in connection with the present problem.

It is a privilege and honor to be asked by this Association to present this Wiley Memorial Lecture, and I have enjoyed going back over its proceedings and also the work of the Bureau of Chemistry, in order to obtain information necessary to bring out the facts leading to the passage of the original Food and Drugs Act and its organization.

EARLY FOOD INSPECTION AND LEGISLATION

It is not my intention to go deeply into the history of food inspection in the United States, but I shall review briefly the work of this Association, of the Bureau of Chemistry, and of Dr. Wiley and his associates, and the part that they played in bringing about the passage of the Food and Drugs Act. It is desirable, however, to call attention to the different methods used in early food legislation.

For a number of years, under its taxing power, the Bureau of Internal Revenue was the principal enforcer of food legislation. The first important legislation was the Act of August 2, 1886, which taxed oleomargarine, renovated butter, and adulterated butter, and which gave the Bureau of Internal Revenue complete authority over these products. With the power that accompanies the taxing authority, revenue agents were allowed to enter any plant and follow the product, whether it went into interstate commerce or only into intrastate commerce. Anyone who has had experience with the enforcement of National food legislation based solely upon interstate commerce control will realize what an effective power the Bureau of Internal Revenue had for enforcing this law. The only interest that the Bureau of Internal Revenue had in the matter,

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however, was the collection of taxes, and in this particular legislation the purpose was not to collect taxes, but to tax out of existence certain products like colored oleomargarine, etc. Similarly, the Act of June 6, 1896, taxing filled cheese, and the Act of June 13, 1898, taxing mixed flour, were primarily for the purpose of preventing adulteration of these products by placing a tax upon the adulterated product that would practically take it off the market.

In addition to these special acts, the Bureau of Internal Revenue was concerned with the adulteration of whiskey, and was able to control this product under its taxing power. While I was Chief Chemist of this Bureau I was greatly impressed with this power of control by the taxing method, and I often thought that if Dr. Wiley had just happened to be attached to the Bureau of Internal Revenue or the Treasury Department we might have seen an entirely different development of Food Inspection in the United States.

Another early method of Food Inspection is brought out in the Act on Inspection of Tea, March 2, 1897. The act was primarily enforced by the Customs. In other words, all tea being imported is regulated as to its purity at the Customs, and is detained until examined and passed. It was this power of the Customs inspectors that was used in connection with the imported food products under the Federal Food and Drugs Act.

Another most interesting forerunner of the Food and Drugs Act was the Act of August 30, 1890, which was passed primarily to control meat for export, but which also included sections covering the importation of adulterated food products and liquors. This law was peculiar in that it made the person importing the product liable and subject to fine. It also had a great weakness so far as enforcement was concerned in that it included the following provision:

> Any person who shall *knowingly* import into the United States any such adulterated food or drug or drink, knowing or having reasons to believe the same to be adulterated, being the owner or the agent of the owner, or the consignor or consignee of the owner, or in privity with them, assisting in such unlawful act shall be deemed guilty of misdemeanor and liable to prosecution therefor in the district court of the United States for the district into which such property is imported.

The difficulty lay in having to prove guilty knowledge. Although this Act of 1890 and the later Act of 1891 were primarily the beginning of meat inspection, dairy products intended for export were also covered in its provisions. This sort of review of these preliminary Acts is very significant in a study of the development of the Food and Drugs Act.

Many interesting details regarding the legislation at this time will be found in Bulletin 69 of the Bureau of Chemistry, by W. D. Bigelow, which includes a brief review of food legislation. The national laws passed up to 1896–7 were largely directed at specific products, such as butter,

cheese, flour, etc. In this respect the national legislation had followed much the same course as had food legislation in the various states, which had passed specific measures covering such products as butter, vinegar, honey, etc., rather than general laws.

In this Association of Official Agricultural Chemists active interest in food adulteration began about 1896. In a review of its proceedings for 1894 we find only a few references to the subject of food adulteration, but the proceedings of 1895 show that the Association took a definite step in the study of food adulteration and an active interest in promoting food legislation. A Committee on Food Legislation was appointed by A. L. Winton, president at that time. It consisted of H. W. Wiley, Chairman; H. A. Huston, Lafayette, Ind.; J. A. Myers, Morgantown, W.Va., and A. S. Mitchell of Milwaukee, Wis.

The proceedings of 1896 have little information on this subject, but in the proceedings of 1897 there first appears among the list of referees a Referee on Food Adulteration. The Committee on Food Standards, of which Dr. Wiley was chairman, also makes its first appearance. The first report by the Referee on Food Adulteration in 1897 is quite different from later reports. Instead of dealing with methods for the detection of adulteration and the analysis of products, it combines a report on definitions and standards with a list of adulterations, and an attempt was made to give standards of composition that would show that a product was not normal. Little attention was devoted to the study of methods of analysis.

In a discussion of this report, Dr. L. L. Van Slyke made the following statement, which I think is worthy of reading at this time, showing as it does the importance attached to standards by the Association at the very outset: "If the Association adopts standards they will be made use of in the Courts of different States. If we make a mistake we shall do an injury because our work will be referred to by one side or the other, and if in the suggestion of a standard we make an error, then somebody will make use of it to our injury as well as to the injury of the trade in which that particular product may be found."

HISTORY OF FOOD STANDARDS

The study of food standards began with this first report of the referee in 1897, and it has also been interesting to me to review the various steps that have been taken in their formation, the changes in principles that have come about from time to time, and the care that is necessary to establish proper limits. As an illustration of this, I think that it is worth while to follow the standards established for cider vinegar through the various editions of the definitions that have been issued from 1903 up to the present.

Vinegar, cider vinegar, or apple vinegar.—Cider vinegar is the product made by the alcoholic and subsequent acetous fermentations of the juice of apples, is laevorotatory, and contains not less than four (4) grams of acetic acid, not less than one and six-tenths (1.6) grams of apple solids, and not less than twenty-five hundredths (.025) gram of apple ash in one hundred (100) cubic centimeters. The water-soluble ash from one hundred (100) cubic centimeters of the vinegar requires not less than thirty (30) cubic centimeters of deci-normal acid to neutralize the acidity, and contains not less than ten (10) milligrams of phosphoric acid (P_2O_5).

This standard, which was in force for many years, actually compelled the manufacturer of high-grade cider vinegar to adulterate his product in order to meet the requirements. In a later edition there was injected into this definition of cider vinegar the provision that not more than 50 per cent of these apple solids should be reducing sugars, which simply added to the confusion because the amount of reducing sugars depended entirely upon whether or not the proper fermentation of the cider had originally taken place. When a careful study was made of this subject and complete fermentation had been effected, very small amounts of sugar were left in the solids and a more satisfactory and stable product was produced, but it frequently contained less than 1.6 per cent of solids. In the 4th revision of these definitions we find that the standard for cider vinegar has been revised to a simple status, and defined as a product "made by the alcoholic and subsequent acetous fermentation of the juice of apples and containing not less than four (4) grams of acetic acid." Thus has evolved through many years of change a definition or standard that is undoubtedly correct.

A comparison of the first report on food standards with subsequent reports is also interesting. In the beginning an effort was made to include data to simplify the work of the chemists or the analysts in determining adulteration. In most cases, however, this inclusion of additional data was of no material benefit, and as a rule served merely as a guide to the manufacturer who wished to adulterate his product and conceal the adulteration by meeting these standards. As our experience has increased a tendency towards simplification and exact definition has been apparent. The minimum standards are included only in case the distinctive ingredient of the product can be identified and the proper limit on it prescribed such as the standard of 5 per cent of oil of lemon in lemon extract.

Since the new Federal Food, Drug, and Cosmetic Act gives authority to the Secretary of Agriculture to promulgate regulations fixing and establishing definitions and standards and since after promulgation they have the authority of law, the new Committee on Standards should exercise the greatest care in their preparation. I think it will be found that most of the mistakes that occurred in the standards in the past were in connection with the data either analytical or inspectional included in the standards to support the definition.

I note that Section 401 of the new Act covering the Definition and Standards for Food, states that—

Whenever in the judgment of the Secretary such action will promote honesty and fair dealing in the interest of consumers, he shall promulgate regulations fixing and establishing for any food, under its common or usual name so far as practicable, a reasonable definition and standard of identity, a reasonable standard of quality and/or reasonable standards of fill of container.

As you will note, the wording of the law states that it is entirely in the interests of *consumers*, but as a matter of fact, these standards have a tremendous effect upon *industry* and fair trade and industry is just as anxious that these standards shall be correct as either the Government or the consumer, and is ready to cooperate in making them correct.

From 1896 to the present time the proceedings of this Association show a gradual but rapid development of the functions of the Referee on Food Adulteration, and today page after page of our program is allotted to reports of referees and associate referees on various phases of food and drug adulteration.

CONTACT WITH DR. WILEY

My first contact with Dr. Wiley and his associates was in January, 1900, when I came to the Bureau, then known as the Division of Chemistry, and began work on the examination of canned meats, which study was an outgrowth of the trouble with this product encountered during the Spanish-American war. This work was later published as a part of Bulletin 13, Foods and Food Adulterants. It would be advantageous for anyone to review some of the bulletins published at that time and especially this one on meats, because it contains much valuable information on the subject of fresh and canned meats, and also a discussion of the then known methods for canning meats.

The years from 1900 to 1906 constituted a period of great activity on the part of the Bureau of Chemistry and of the Association in studies of food adulteration and methods for its detection. The work was primarily directed towards getting the information necessary for Congress to justify the passage of the National Food and Drugs Act. During this period, accordingly, the proceedings of this Association show marked expansion. New associate referees on different products were constantly being added to the list and the Association's interest in food and drug adulteration was becoming the dominant factor. It was during this period that the first important food inspection laboratories were established, and they cooperated with the Customs service in examination of imported food products. The first of these laboratories was located at the Port of New York, under R. E. Doolittle.

Under the regulation of imported foods, samples were taken and the products were detained at the port of entry until examinations could be made, and then they were either released, relabeled, or refused entry. This examination of imported food products was valuable training for the group of young and inexperienced analysts who had accessible little

in the way of methods and standards upon which to base their judgment. Much time was given to the inspection of such products as olive oil, wines, and the various types of canned goods. I shall never forget the criticism that Dr. Wiley made of E. M. Chace and myself in regard to our method of opening champagne bottles. He came into the laboratory and showed me with great skill how the cork could be removed from the bottle of champagne without disturbing its content of gas.

Another personal recollection of this time is that of helping Dr. Wiley prepare to appear before the Interstate Commerce Committee of the House of Representatives in support of the then pending Food and Drugs Act. I was reminded of this when reading from the address on "Wiley the Teacher," by W. W. Skinner, in which he mentions how he and J. K Haywood had worked feverishly Saturday, Sunday, and Monday preparing literature for Dr. Wiley and how they had collected the enormous amount of data and references to which he listened, but regarding which he took no notes. When the time came for presenting the facts, however, Dr. Wiley was able to cite the literature and other references. Likewise, three young fellows connected with the food laboratory (L. S. Munson, E. M. Chace, and myself) worked for weeks and prepared so many exhibits of adulterated foods and of books of references that at the time of the hearing they had to hire a horse and truck to carry all this material to the room of the Committee of Interstate Commerce and arrange it for Dr. Wiley's use. For two days these assistants stood around waiting to be asked to secure this and to secure that, but as a matter of fact not one single exhibit or book was used by Dr. Wiley. Apparently he had all of this material in the back of his mind, and for two days he presented the case for the Food and Drugs Act to this Committee. I know that my feeling at the beginning of this hearing was that the Committee was distinctly antagonistic to him. At the end, however, there was no doubt that the Committee had entirely changed its attitude. We had listened to a great oration on the subject of food adulteration and the need of food legislation.

MANUFACTURE OF EDIBLE GELATINE

I shall not discuss at this time problems of organization of the work, but I should like to mention some of the constructive things that were done for the benefit of food industry during this period, and one particularly with which I was intimately connected. After the passage of the Food and Drugs Act certain rules and regulations regarding the use of preservatives presented to various manufacturers problems that were exceedingly difficult to handle. For example, in the manufacture of edible gelatine the use of sulfurous acid had been universal. The raw material was treated with sulfur dioxide and sufficient sulfurous acid was present in the product during all the stages of manufacture to keep down bacterial

growth. When manufacturers of gelatine were faced with the proposition of making an edible gelatine without the use of preservatives, they did not succeed immediately in overcoming the difficulties encountered. As a result many lots of gelatine were highly contaminated with bacteria. One of the constructive methods used by Dr. Wiley and the Bureau in such a case was to send some of their scientific men out to study the problem of the industry and to determine how such a product could be manufactured in a satisfactory way without the use of preservatives. I was one of those selected to visit the various gelatine factories in the United States and to study their problems.

In making this survey of gelatine manufacturers, we went to each plant and studied the raw material and each step in the handling. We took samples at each and every stage of the operation and subjected them to bacteriological examination. In many cases we were able to find the principal point of infection quickly and to offer suggestions as to how to correct this difficulty. This particular industry had been run by rule of thumb, based on the experience of men trained in it but who had had no scientific background, and I think that this was the first time the science of bacteriology had been injected into the gelatine industry. The air filtration introduced into the drying tunnels and other improvements made in the equipment resulted in the manufacture of a much better quality of edible gelatine. The importance of building equipment that can be cleaned effectively and cheaply impressed the early inspectors, and as a result of this type of investigation many improvements in sanitation have been brought about in every type of food industry. The general principles applied at that time have been found to be universal in their application. It was also impressed upon all of us who made this investigation that valves and joints in pipe lines and pumps can be very dangerous, and cause spoilage or deterioration of the finished product. Tremendous strides in layouts of equipment and factories and the building of sanitary food machinery have been made in this country in the last few years. I do not believe that there is a single food industry in the United States that has not directly or indirectly benefited by this early constructive work on the part of the Bureau of Chemistry during the early period of the Food and Drugs Act.

Those were what might be called the pioneer days of food sanitation in this country, and if there is anything for which we should be especially thankful, it is for this constructive development in the enforcement of the Food and Drugs Act. Not only has this work improved the quality of foods, it has also been of tremendous monetary value to industry in reducing its losses due to spoilage. A review of the studies made at that time of the manufacture of ketchup, the handling of milk, and the drying of fruit alone is most convincing.

It is not necessary at this time to discuss the question as to whether or

not the use of preservatives was actually injurious to health. There is no question but that the regulations compelling the manufacturer to go ahead without them was of great importance to the food industry in developing new and better methods of food handling, as well as to the food consumer.

Another important development that came soon after the passage of the Food and Drugs Act was the forcing of the food industry to establish a scientific control. We find today as a result that most large food manufacturing concerns have their technical and research laboratories, which, without question, have proved their value. We also see the establishment during this period of such institutions as the National Canners Research Laboratory in charge of Dr. Bigelow, directing its attention primarily to problems of the canning industry. Their principal work has been along the lines of improving sanitation and character of the canning equipment, and control or prevention of spoilage.

Looking back, I consider that this was a glorious period in our food manufacturing history, and the spark plug in this whole work was Dr. Wiley. It was he who started these investigations of food manufacture with the idea of giving constructive help, and he was active in and directed most of this pioneer work. To me this is his most outstanding constructive work, and I consider that I was fortunate to have been connected with him during this period. The experience gained in the study of many food industries of the United States has been of the greatest value to me, personally.

CHANGES IN IDEAS ON DIET

In such a heterogeneous group of individuals as was brought together in those five or six years after the passage of the Food and Drugs Act, there necessarily developed many ideas and many differences of opinion. Sides were taken in a struggle that was evident within the Department of Agriculture to gain control of the enforcement of the Act, but as I look back over this period after 25 years I cannot help but feel that these struggles were in the end, beneficial, and that the problems were worked out in a much better way in the end than they would have been if these differences of opinion had not occurred and been ironed out. I am impressed with the changes in our ideas that have taken place, particularly regarding the little things in our diet. Our ideas on nutrition have undergone great changes in this period, and I think we may say that even today we are only on the threshold of knowledge on the effect of these minor constituents of our diet. The knowledge of vitamins, other food factors, and the mineral elements is daily expanding, and no one can be wise enough to foresee what the next few years may bring forth.

Recently I was reading the *Annual Review of Biochemistry* for 1936, in which Hart and Elvehjem review the present-day ideas of mineral

elements. They state that practically all workers are now agreed that copper is necessary as a supplement to iron for the formation of hemoglobin in red blooded animals. It also appears that many other mineral constituents are essential in our proper nutrition, for example, manganese, zinc, cobalt, nickel, aluminum, fluorine, bromine, iodine, and boron, but the question as to whether or not these elements in all forms are essential is widely disputed. There has been no question as to the poisonous qualities of arsenic, yet Coulson in his recent article states that many marine food products contain quantities of arsenic, which if in the condition of arsenic oxide would be poisonous, yet he calls attention to the fact that these fish foods have been eaten regularly by maritime people for centuries, which is, in his opinion, presumptive evidence that arsenic in the form that it is present in these food products is non-toxic.

Recent surveys of food products to determine the presence of these trace elements have been enlightening, and the knowledge gained suggests that we should be extremely careful in drawing conclusions as to whether or not as they occur in foods naturally they have the same poisonous character that they have when added as the chemical salts. Particularly, I think, is this true regarding fluorine as it occurs in many foods that we eat, especially the fish and other marine products. There is merit in the idea that where we find certain trace elements universally distributed in our food products we can assume that they have been present in the food of humans over many millions of years and that mankind has either obtained a tolerance to the material or that the element plays an essential part in the cell structure as it now exists.

Stefansson in his *Adventures in Diet* discusses the teeth of the Eskimo and the natives of Iceland and brings out the fact that these people, who live to a great extent on marine foods, have very fine teeth, particularly the Eskimo, who lives almost exclusively on fish. This indicates that the normally high fluorine content of the Eskimo's diet has no bearing upon the formation of mottled teeth and emphasizes the statement made by Dr. H. Trendley Dean (Public Health Report of April 16, 1935), "mottled enamel, in the light of present knowledge, is a waterborne disease, and the experimental approach should stimulate this condition."

All of this recent information regarding the difference in action of arsenic and fluorine under different conditions should certainly make us a little humble as to the absolute finality of our present-day opinions. As a matter of fact, when we consider how much there is to know regarding nutrition as compared with what we do know, we should hesitate before we reach definite conclusions.

It would not be fair to review this period without mention of the many men associated with this development of our food inspection system. A most remarkable group of men was brought together by Dr. Wiley when

he organized his work for the enforcement of the Food and Drugs Act of June 30, 1906. Take for example the first group of inspectors. We find among this list such names as Walter G. Campbell, Chief of the Food and Drug Administration; W. R. M. Wharton, Chief of the Eastern District; Dr. A. W. Bitting, the author of many books on foods and food examination; Arthur I. Judge, Editor, *Canning Age;* Jackson E. Earnshaw, now with the Harvey Company; Arthur Stengel, still with the Food and Drug Administration; F. L. Wollard, Chief of the Baltimore Station; George H. Adams, Chief of the Boston Station; and many others too numerous to mention, a most select and high class group of young men. Ten of this original group still remain active under the Food and Drug Administration.

At the same time there was brought into the Bureau a large number of chemists from various State food laboratories, among whom were R. E. Doolittle, State Analyst of Michigan; A. E. Leach, State Chemist of Massachusetts; A. S. Mitchell, State Analyst of Wisconsin; A. L. Winton, State Analyst of Connecticut; Arthur L. Sullivan, now State Food Commissioner of Maryland; Benjamin Hart from Kentucky, formerly Chief of the Western District, and later prominent in the canning industry on the Pacific Coast. I could go down the list naming a number of men still active in Food and Drug Administration work, or in food and drug work of one kind or another, who were of the first group.

In conclusion, I wish to state that it has been a great pleasure to me to prepare this paper, that my association with this great group of men during this development period was of the greatest value to me personally, and that my connection with the constructive work dealing with the problems of industry in improving methods of manufacture has been exceedingly helpful to me during my whole business career. I feel sure that those having to do with the preparation of regulations under the Food and Drugs Act of 1938 and the preparation of Food Standards under that Law, can obtain, as I have, much valuable information by reviewing the proceedings of this Association and the development and progress of the period after the passage of the Food and Drugs Act of June 30, 1906.

PRESIDENT'S ADDRESS*

CHEMISTRY AND THE UTILIZATION OF AGRICULTURAL PRODUCTS

By H. R. KRAYBILL (Department of Agricultural Chemistry, Purdue University Agricultural Experiment Station, Lafayette, Indiana)

It is just twenty-one years ago today that I first attended a meeting of the Association of Official Agricultural Chemists. At that meeting in his annual extemporaneous address Dr. Wiley placed much emphasis on the importance of increasing our food supply. We were then in the midst of the World War. Food was necessary not only to supply the need of this country but also to support our allies and their armies. A popular slogan was "Food Will Win the War." How rapidly circumstances have changed! Today we do not face the problem of producing adequate food supplies. Our chief agricultural trouble seems to lie in our inability to find markets adequate to consume the unrestricted production of our farmers.

The important role that agricultural chemistry played during the last century, in increasing the efficiency of food production and thus relieving man of the fear of starvation, is well known. On the other hand, in recent years rapid developments in organic chemical technology have led to increased substitution of the products of the oil well and mine for those of the farmer. Will chemistry in the future help to solve these problems of surpluses by finding new uses for farm products? Two of the objects of our Association are "To conduct, promote, and encourage research in chemistry in its relation to agriculture," and "To afford opportunity for the discussion of matters of interest to agricultural chemists." Therefore, it seemed appropriate for me to select as my subject "Chemistry and the Utilization of Agricultural Products," even though I am fully aware of the limits of my ability to discuss the subject adequately.

For many years agricultural chemists have been interested in the possibility of developing new industrial uses for the products of the farm. Some of the very first projects undertaken when the United States Department of Agriculture was organized dealt with this problem. In an article on the relation of chemistry to the progress of agriculture in 1899, Dr. Harvey W. Wiley stated, "The application of the principles of chemical technology to the elaboration of raw agricultural products has added a new value to the products of the farm, opened up new avenues of prosperity, and developed new staple crops." In a very interesting paper read before the meeting of the American Chemical Society at Milwaukee last September Dr. Herrick mentioned many important contributions of the United States Department of Agriculture in this field. Among these

* Presented Monday afternoon, November 14, 1938.

were the utilization of plant fibers from waste materials, including corn stalks, cotton stalks, sugar cane bagasse and other materials; the use of crop plants for paper making; the manufacture of industrial alcohol from various farm crops and waste materials; the production of cellulose from various plants; of furfural, xylose, and adhesives from pentosan containing materials; the utilization of naval stores, of starch from sweet potatoes, of citric acid from lemons, and of pectin from apple waste.

During recent years a more widespread interest has developed, as is exemplified by the Farm Chemurgic movement, the establishment at the University of Illinois, by the Federal Government in cooperation with the Agricultural Experiment Stations of twelve states, of a Regional Soybean Industrial Products Laboratory, and the recent Congressional action authorizing the establishment, by the United States Department of Agriculture, of four regional research laboratories.

What are the reasons for this increased interest in the industrial utilization of agricultural products? Apparently it arises from the general belief that the depressed condition of agriculture following the World War was due to the accumulation of surpluses of agricultural products and to a general acceptance of the viewpoint that agriculture and industry represent two interdependent groups. Many industrial leaders now believe that good industrial conditions are not apt to prevail for any considerable length of time unless agriculture is reasonably prosperous.

The proportionate part of the national income that agriculture receives had been declining constantly for many years before the World War, but these changes were gradual and offered opportunity for natural readjustments. At the close of the World War rapid changes occurred in the market demand for our agricultural products. It was only then that the surpluses became burdensome.

Six important factors contributed to this situation. First, cheap sources of the most expensive element of fertilizer (nitrogen) were made possible by the development of synthetic methods of production. Second, improved agricultural practices resulted in increased production. Third, agriculture increased its production as a result of demands arising during the World War. Fourth, the replacement of horse and mule power by mechanical power resulted in a reduction in the consumption of grain. It is estimated that the products from twenty million acres were replaced by the products of the oil wells. Fifth, the loss of foreign markets as a result of the disturbed political and economic conditions throughout the world. Sixth, with the development of organic technology there was an increased replacement of agricultural products in industry by the products of the mine and the oil well.

It has been estimated that a century ago over four-fifths of all the products used by man were from the farm. Today probably not more than one-third of the weight of all products used by man inclusive of foods and

clothing is derived from the products of the farm. The displacement of agricultural products by those of the mine and oil well began many years ago, but with the rapid development of organic technology it has become an increasingly important factor. A few examples will serve to illustrate its importance. In 1869 the dyestuff alizarine was synthesized from coal tar derivatives and produced commercially. Nine years later alizarine was produced in quantities equivalent to that which could have been produced from about four million acres of madder. To grow sufficient indigo to produce the amount that is made synthetically today would require over seven million acres of land. Synthetic resins and solvents replace such agricultural products as bones, horns, hoofs, amber, natural resins, and naval store products. The more recent development of methods for the production of many organic solvents and chemicals from petroleum products is displacing products formerly made from agricultural materials. To produce alcohol equivalent to our annual consumption of gasoline would require approximately 300,000,000 acres of corn at present average yields or about three times the ten-year average acreage.

The fields for developing industrial uses for agricultural products may be classified into three groups as follows: First, the utilization of wastes and by-products from crops; second, the development of new industrial uses for crops or crop surpluses; and third, the introduction of new crops to yield products to take the place of those now imported and used for industrial purposes.

While many excellent products can be made from crop residues, the high cost of collection and transportation to the processing plant and their relatively low value leave only a small return for the farmer. Unless the farmer can receive a price for these products that is greater than their value in maintaining the fertility of the soil the utilization of crop residues for industrial purposes offers little promise of direct aid to the farmer. Considerable work has already been done in this field. Examples are the use of bagasse, cereal straw, corn stalks, and other similar types of materials to make wall board, box board and insulating materials, and the recent development of the production of furfural and its derivatives from oat hulls. In most cases where success has been obtained the available products have arisen as by-products from a plant processing agricultural products. The waste materials have thus been assembled at the plant in the course of the marketing of the crop.

The second field, the utilization of surplus food crops as raw materials for industry offers an almost unlimited field if it were available. These raw materials comprise the products for organic synthesis of chemical and structural materials. In this field there is direct competition with the cheap products of the mine and the oil well. The raw products of agriculture are essentially carbohydrates, proteins and fats. From a technological standpoint these materials could be used as raw materials for the

manufacture of chemicals just as coal and petroleum are used. However, two important factors must be given consideration in the choice of raw materials for industry. First, the cost of the raw materials, and second, the cost of the processes involved in their use. The cost of raw materials from coal and petroleum is much lower than it is from agricultural products. It would seem as though agricultural products could be used economically only in such cases where the cheaper processing costs offset the difference in the cost of raw materials or when processes are not known for making the products from coal or petroleum. Time does not permit a detailed discussion of what has been accomplished in this field. The notable work of the corn refining industry which is well known may be cited as an illustration of what may be accomplished through research.

The third field, the introduction of new plants to take the place of imported agricultural products used for industrial purposes, seems to offer considerable promise. The total annual value of our imports of agricultural products is about one and one-half billion dollars. The larger part of these imports consists of silk, sugar, coffee, sirup, oil seeds, vegetable oils, rubber, and paper pulp. Many of these products are used for industrial purposes. In 1937 we imported approximately two and two-thirds billion pounds of vegetable oils, of which a large part was used for industrial purposes. Time will not permit a full discussion of the possibilities in this field. As an illustration I have chosen the soybean because it seems to have excellent possibilities and because, even though on a small scale, our laboratory has been engaged in a study of the chemistry and utilization of the soybean for the last ten years. For the last two years these studies have been carried out cooperatively with the U. S. Regional Soybean Industrial Products Laboratory.

The marked increase in the production of soybeans in the middle west in recent years illustrates how a new crop may be used to replace acres devoted to the production of surplus crops. In 1937, about two million acres of soybeans were harvested for seed in Illinois, Indiana, Iowa, Ohio, and Missouri. Production in this area was increased four-fold in the last eight years. The crop this year will exceed fifty million bushels. Soybeans are used largely to replace oats and corn in the rotation. Thus they help the farmer to make readjustments for the loss of feed markets resulting from the replacement of horse and mule by gasoline motive power.

Two products are obtained by processing the soybean, oil and meal. About four and one-half times more meal than oil is produced. Both products may be used for edible as well as for industrial purposes. Although the meal or proteins extracted therefrom are used in making glues, plastics, and core bindings and in paper sizing the amount used industrially today is not more than one to two per cent. A larger percentage of the oil, or about 17 per cent, was used industrially in 1937. Although the total number of pounds of soybean oil used for industrial purposes has

increased steadily, it has not kept pace with the rapid increase in production.

The soybean is an ideal crop to replace such surplus crops as oats and corn in the corn belt states, provided adequate markets can be obtained. If its uses are confined largely to foods and feeding stuffs, however, it will merely compete with other food crops. If chemical technology will develop new industrial uses for the soybean, the acreage can continue to expand.

In comparison with most seed crops the soybean is characterized by a higher protein and fat and a lower carbohydrate content. It contains almost twice the amount of protein, about twelve times the amount of fat, and approximately one-half as much carbohydrate as other legume seeds such as the navy bean or pea; and over four times more protein and about one-third as much carbohydrate as corn. It contains practically no starch. It is chiefly the large amounts and high quality of the fat and protein in the soybean that make its industrial utilization so promising.

Practically ninety per cent of the fatty acids of the soybean are unsaturated. The chief acids are linoleic (52.0–58.8 per cent) and oleic (25.9–33.7 per cent). The fatty acids of soybean oil differ from corn and cotton seed oil chiefly in that they contain linolenic acid, less palmitic and oleic acids, and more linoleic acid, and from linseed oil by containing less linoleic and linolenic and more oleic acid. In composition soybean oil lies between the food oils of corn and cotton and the drying oil linseed. It is used in either of these fields but usually at a discount. The properties of the oils are doubtless influenced by the structure of the glycerides. If the glycerides were pure glycerides of each fatty acid it should be possible to remove the glycerides of the saturated or less unsaturated fatty acids and thus improve the drying properties of the oil. Experiments in our laboratories showed that very little increase in iodine number could be obtained by chilling and filtering the oil. It is possible to hydrolyze soybean oil into its constituent fatty acids and glycerol, to separate the more unsaturated acids and resynthesize them with glycerol into an oil, and obtain increased drying rates. However, present methods are not commercially economical. Recent studies reported by the U. S. Regional Soybean Industrial Products Laboratory indicate that with suitable dryers and resins soybean oil may be used successfully in place of the faster drying oils in paints and varnishes. About nine per cent of the soybean oil produced in 1937 was used in paints and varnishes.

In 1937 over 534 million pounds of linseed oil, 43 million pounds of perilla oil, and 174 million pounds of tung oil were imported. These oils are used almost entirely for industrial purposes. Large quantities are consumed by the paint and varnish industry. If methods can be devised to use soybean oil in place of some of these oils new markets will be obtained. To produce soybean oil in equivalent amount, would require about eight million acres or four times the quantity grown last year.

In addition to the true fats, crude soybean oils contain small amounts of other compounds that are extracted or pressed out with the oils. Among the most important of these are the phosphatides, sterols, sterol glucosides, and mucilages. The crude phosphatides, sold commercially as "lecithin," are obtained from solvent-extracted oil by treatment with steam and centrifuging. They are used in margarine, mayonnaise, salad dressings, chocolates, candies, baked foods, in gasoline, in rubber, in treating leather, in creosoting wood, and in soap and cosmetic preparations. It was formerly believed that "lecithin" could be obtained only from solvent-extracted oil. We have found that a good "non-break" varnish oil may be produced from expressed oil by emulsification with water and centrifuging, and at the same time a good commercial grade of "lecithin" may be obtained.

Although these crude phosphatides are designated commercially as "lecithin," they contain only a relatively small amount of true lecithin along with cephalin and other compounds. By adsorption methods Thornton separated the phosphorus-containing compounds into a number of fractions. On the basis of the total nitrogen, phosphorus, amino nitrogen, and choline contents of these fractions he has shown that not near all of the phosphorus-containing compounds can be accounted for as lecithin and cephalin. A method has been devised to refine soybean oil and at the same time recover various fractions of the phosphatides, foaming agents, emulsifying agents, sterol glucosides, and a considerable portion of the free sterols.

The sterols consist of several sitosterols and stigmasterol. These compounds are in great demand at the present time because they may be used as starting materials in the synthesis of certain sex hormones. Because of its chemical structure stigmasterol is best suited for this purpose. Apparently soybeans are the only commercial crop grown in this country in which stigmasterol is found in appreciable quantities. Since stigmasterol occurs in very small quantities in the soybean oil it is difficult to prepare in large quantities. None is produced commercially in this country. Our sole commercial source is from Germany. Crude soybean sterols have been imported for scientific studies. By the methods worked out in our laboratories about one pound of sterols containing from one-fifth to one-fourth of a pound of stigmasterol may be recovered from a ton of the crude soybean oil. A large part of the sterols may be recovered by direct crystallization from the concentrate without saponification of any of the fat.

Only a small part of the phosphatides and none of the sterols are recovered from the soybean oil produced in this country today. The possibilities of finding new and extensive uses for these products are very encouraging.

As mentioned earlier about four and one-half times more meal than oil is produced. If soybean acreage is to expand, markets must be provided for the meal as well as the oil. Recent studies reported by the U. S. Regional Soybean Industrial Products Laboratory indicate that soybean protein and oil meal may find new uses in the plastic field. Reports from industrial laboratories indicate progress in the development of methods for the use of soybean protein for paper sizing and for the production of artificial fibers resembling wool. With continued research many new industrial uses will be found for the soybean.

In the past chemistry has played an important role in helping the farmer to produce adequate food supplies. Perhaps in the future it may serve agriculture equally as well by finding new markets for the farmer's surplus crops.

In conclusion, I wish to express my sincere appreciation for the honor that you have conferred upon me by granting me the privilege of serving as President of our Association.

To those new members who are attending the meeting for the first time I wish to extend a cordial welcome. I would urge you to take an active interest in the work of our Association.

I am glad to have this opportunity to express our appreciation to those officers of the Association who are chiefly responsible for the success of our work. We are indebted especially to Dr. Skinner, our Secretary-Treasurer, to Mr. Lepper, Chairman of the Committee on Recommendations of Referees, to Miss Lapp, and to the referees, associate referees, and collaborators.

A marked increase in attendance at our meetings and in the number of subjects studied by the referees in recent years illustrates the continued growth of our Association. With increased interest in the development of methods for the utilization of farm crops and the recent Federal legislation providing for the control of the sale of cosmetics, new subjects will require our attention. I am confident that our Association will continue in the future to meet these new responsibilities as it has in the past.

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.

THIRD DAY

WEDNESDAY—AFTERNOON SESSION

REPORT OF EDITORIAL BOARD

By W. W. SKINNER, *Chairman*

Mr. Lepper of the Board of Editors will make a detailed statement about the affairs of *The Journal*, and in the absence of Dr. Bailey I shall make a statement about the editorial work of the Committee on *Methods of Analysis*.

Only a few years ago *The Journal* had an annual deficit, but the interest in this publication has increased to such an extent that in the last few years there has been a slight surplus annually. In 1935 the surplus was $265.49; in 1937 it was $978.45; and this year (1938) it is $800.00. The sale of *Methods of Analysis* has continued at such an increased rate that we find it necessary now to consider the reissue of the book. In the past we have revised our methods at five-year intervals, and it usually required about a year after the last session of the five-year period to complete the work.

We have, unsold, only about 500 copies of the 1935 issue. At the average rate of sale this means that before the fifth revision is ready in 1940, there will be a period when there will be no copies for sale. It was decided at a meeting of the Executive Committee that we would proceed at once in the revision work so far as that can be done prior to the meeting in 1939, and then incorporate the changes made in 1939, the purpose of course being to get the manuscript for the 1940 revision to the printer as soon after January first, 1940, as possible.

Dr. Bailey is unable to attend this meeting. It is probable that he will not be able to give a large amount of time to the 1940 revision, but it is the desire of the Committee, subject to Dr. Bailey's approval, that he continue as chairman and we arrange to have the work done by the staff.

The company that published *Principles and Practice of Agricultural Analysis* was in a poor financial condition, and the Committee learned that the officers desired to dispose of the accumulated unbound volumes of the first, second, and third editions. After some correspondance, we purchased all the unbound and a few bound copies of Volumes 1, 2, and 3 of this publication at a cost of $178.75.

Now I think, Mr. Chairman, it would be well to ask Mr. Lepper to make the report on *The Journal.*

REPORT OF EDITORIAL COMMITTEE OF *THE JOURNAL*

Your *Journal* this year has kept pace with the continued progress of the Association. The 716 pages in Volume 21 for the year of 1938 are within 28 pages of the largest volume ever issued, that is Volume 8, and that volume covers one and a half years and consists of six numbers. The number of pages this year in the section on contributed papers is 222, practically the same as that published in each of the last few years. Only normal growth is to be expected in the section devoted to the proceedings as the number of referees gradually increases with added subjects of study. However, the future development of *The Journal* as the foremost medium of papers on agricultural chemistry and related subjects will depend upon the quality and number of contributed papers. We are all interested in this future and should continue to support *The Journal* by giving it first consideration as a means of publication.

HENRY A. LEPPER, *Editor*

I think it is a great satisfaction to hear the report made by Mr. Lepper about the increased interest in *The Journal.* Through the members of the Association, through *The Journal,* and through our *Methods of Analysis,* the name of the Association has been extended widely. Subscriptions to *Methods of Analysis* and *The Journal* go to such far distant countries as China, Java, India, and Australia. This splendid reputation is a matter in which we should take a great deal of pride.

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

REPORT OF THE COMMITTEE ON DEFINITIONS OF TERMS AND INTERPRETATION OF RESULTS ON FERTILIZERS AND LIMING MATERIALS

First Adoption as Official

DOLOMITE

Dolomite is a mineral composed chiefly of carbonates of magnesium and calcium in substantially unimolal (1–1.19) proportions.

PRIMARY FERTILIZER COMPONENTS

Primary Fertilizer Components are those at present generally recognized by law as necessary to be guaranteed in fertilizers, namely: nitrogen, phosphoric acid (P_2O_5) and potash (K_2O).

SECONDARY FERTILIZER COMPONENTS

Secondary Fertilizer Components are those other than the "primary fertilizer components" that are essential to the proper growth of plants and that may be needed by some soils. Some of these components are calcium, magnesium, sulfur, manganese, copper, zinc, and boron.

BAT MANURE

Bat manure is the dry excrement from bats.

BAT GUANO

Bat guano is partially decomposed bat manure.

ANALYSIS

The word *analysis*, as applied to fertilizer, shall designate the percentage composition of the product expressed in those terms that the law requires and permits.

Second Reading as Tentative

CALCIUM NITRATE

Calcium nitrate (nitrate of lime) is a commercial product consisting chiefly of calcium nitrate, and it shall contain not less than fifteen per cent (15%) of nitrogen.

AMMONIATED SUPERPHOSPHATE

Ammoniated superphosphate is the product obtained when superphosphate is treated with ammonia or with a solution containing free ammonia and other forms of nitrogen dissolved therein.

First Reading as Tentative

SUPERPHOSPHATE

Superphosphate, 24 per cent or below, is a commercial product consisting largely of available phosphates and calcium sulfate resulting from treating ground phosphate rock with sulfuric acid. The grade that shows the available phosphoric acid should always be used as a prefix to the name.

Example: 18 per cent superphosphate.

Superphosphate, over 24 per cent, is a commercial product consisting largely of available phosphates and some calcium sulfate resulting from treating ground phosphate rock with phosphoric acid or both phosphoric acid and sulfuric acid. The grade that shows the available phosphoric acid should always be used as a prefix to the name.

Example: 45 per cent superphosphate.

or

Superphosphate is a commercial product, the phosphoric acid content of which is due chiefly to mono-calcium phosphate.

or

Superphosphate is a commercial product made from rock phosphate by substantial conversion of its phosphoric acid (P_2O_5) content into available ortho forms, with inclusions of compounds either native to the rock or produced in the manufacturing process.

(The phosphoric acid (P_2O_5) content shall be stated.)

Proposed Definition

Nitrate of Soda and Potash is a commercial product containing nitrates of sodium and potassium. It shall contain not less than fourteen per cent (14%) nitrogen (N) and fourteen per cent (14%) potash (K_2O).

L. S. WALKER, *Chairman* — H. D. HASKINS (Absent)
G. S. FRAPS — W. C. JONES
L. E. BOPST — W. H. MACINTIRE

Approved.

REPORT OF COMMITTEE ON RECOMMENDATIONS OF REFEREES

In the report of this Committee last year a plan to broaden the collaborative work of the Association was proposed. A circular was sent to each subscriber to *The Journal* and an invitation to cooperate was extended to every interested scientific worker in the many fields of the Association's activities. Many replies were received on return coupons. Some offers duplicated those already on record but the resulting increase in collaboration seemed to justify a repetition of this service for our referees. Plans have been made to have the notice appear in the first number of *The Journal* following this meeting, and also to include a card, easily detachable from the page, for convenience in replying.

Our Association—and I think it may be said without any appearance of boasting—is outstanding in its contribution to the development of methods of analysis for agricultural and kindred products. This position has been achieved only through continued effort. As occasion has arisen the work of the Association has expanded to meet the need for analytical procedures of accuracy and dependability that progress in new fields of scientific development has shown to exist. This Committee especially appreciates the important part played by referees, associate referees, and collaborators in the success of the Association's program of work.

At this time a new opportunity for service and a new responsibility to maintain the Association's prestige have been presented to these active workers by the passage of the new Federal Food, Drug, and Cosmetic Act. It will be necessary to develop methods for new drugs and cosmetics. Work in the latter field was started last year by the addition of a refereeship on cosmetics. It is perhaps in connection with the formulation of legal standards for foods that more serious consideration by referees will be required in future development of methods. Standards of identity for some foods will include analytical requirements. The establishment of proper values in such cases will be the result of the analysis of products of authentic history. To judge compliance with standards, samples should be examined by the same methods that are used in the compilation of data for the standards. It is obvious that such circumstances denote a permanency of the analytical procedures involved. This does not mean that changes in methods are not to be considered, but it should operate as a caution against recommending changes that might be regarded as minor and appear to involve no appreciable differences in results.

Empiricism takes on a new significance. We now recognize that methods that appear, on their face, to be simple determinations of well understood constituents, as, for example, those for moisture and ash, are in reality largely empirical. Minor changes would usually involve merely going from one empirical procedure to another. It can readily be appreciated that minor changes in several successive years may finally result

in methods giving results far different from those obtained under the original directions. The adequacy of such revised methods in judging the identity of a given lot of food might be seriously challenged. In the enforcement of legal standards it is desirable to limit discussion of analytical tolerances to questions of the accuracy established for the method employed.

There is no thought in this discussion that a referee should refrain from improving methods, but study should be directed toward changes resulting in greater accuracy, precision, or economy of time. When these ends can be accomplished the adoption of new or revised methods would justify the additional studies required to correlate the results by such methods with those by the original ones to establish an interpretative basis for evaluating the results by the newer methods.

Another duty presents itself to the referees at this time, especially those on foods, that of reviewing their respective chapters with a view to perfecting present methods by revision or substitutions if it is considered necessary to make them more serviceable for use in compiling authentic data in the standardization of foods. Also all referees should begin now to consider necessary changes in their respective chapters in anticipation of the scheduled revision of *Methods of Analysis* in 1940, and to remember that collaborative results and two recommendations are required for adoption, deletion, or changes of official methods. It is becoming more and more imperative with each revision that referees consider the possibilities of uniformity and the need for cooperation to eliminate repetition of directions. Again and again methods for the determination of a constituent appear under two or more products, varying only in minor details. With little effort the referees concerned could agree to a unified procedure, so that the fundamental directions could be given in one chapter and referred to in the others. Only such additional directions as make the fundamentals of the method applicable to the specific product need be given in the cross reference. Referees should be alert to opportunities for study in new fields and should recommend the inauguration of new work where need is indicated.

Without any intent to criticize the work of the referees, it is urged that work be not postponed, as is often the case, but that it be begun as soon after appointment as possible. It is appreciated that the work is often accomplished by crowding it in with other necessary duties, but even under such circumstances it would appear that the sooner it is begun the greater the accomplishment in the aggregate. Of interest in this connection is a letter received by the Association from a chemist for a large food manufacturing firm of nation-wide reputation, who points out that less than a month before the meeting this year he was furnished samples for collaboration by five different referees. He had previously expressed his wish to cooperate, but found it a serious drain on his time to do so in

the short time available. Early attention to sending out collaborative samples would often enlist the services of more collaborators and eliminate some of the last minute rush in the preparation of reports and recommendations, which frequently leads to errors that might otherwise be avoided.

The duties of referees and associate referees, as defined in the constitution, have been elaborated upon in a report by E. M. Bailey, published in *This Journal*, **17**, 42 (1934). This report also presents practical recommendations for the preparation of referee reports. Every referee is urged to read that report. Experienced referees will find it helpful in refreshing their ideas of A.O.A.C. procedure, and new referees will find it a valuable guide.

No report of this committee would be complete without an expression of appreciation of the unselfish work—often performed at personal sacrifice—of the referees, associate referees, and collaborators.

HENRY A. LEPPER, *Chairman*

Approved.

REPORT OF SUBCOMMITTEE A ON RECOMMENDATIONS OF REFEREES*

By G. E. GRATTAN (Department of Agriculture, Ottawa, Canada), *Chairman;* H. A. HALVORSON, and E. L. GRIFFIN

STANDARD SOLUTIONS

It is recommended—

(1) That the method submitted by the referee for the standardization of acid solutions with borax (see p. 102) be adopted as official (first action).

(2) That the method submitted by the referee for the standardization of acid solutions with sodium carbonate (see p. 103) be adopted as official (first action).

(3) That no further study be given to the standardization of hydrochloric acid solutions by silver chloride.

(4) That collaborative work be done on the method submitted by the referee for standardization of iodine solutions.

(5) That standardization of sodium thiosulfate be studied further.

(6) That the tentative methods for the preparation and standardization of solutions of sodium hydroxide (p. 681, 1) be adopted as official (first action).

(7) That the tentative methods for the preparation and standardization of hydrochloric acid (p. 682, 5) be adopted as official (first action).

(8) That the preparation and standardization of sulfuric acid solutions be studied.

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* 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.*, 1935.

(9) That the preparation and standardization of potassium permanganate solutions be studied.

(10) That the preparation and standardization of silver nitrate and thiocyanate solutions be studied.

INSECTICIDES, FUNGICIDES, AND CAUSTIC POISONS

It is recommended—

(1) That the study of methods for the analysis of pyrethrum products be continued, and that special attention be given to the effect of a preliminary treatment for the removal of acidic substances, and also to the effect of varying quantities of sulfuric acid on the decomposition of the pyrethrum during the distillation.

(2) That the study of methods for the analysis of derris and cubé products be continued, with additional collaborative work.

(3) That the lead chlorofluoride method for the determination of fluorine be studied next year.

(4) That further study be given the determination of naphthalene in poultry lice products.

(5) That collaborative work be undertaken on the phenol coefficient method (pp. 68–72, **141–146**).

FEEDING STUFFS

It is recommended—

(1) That the Associate Referee on Ash continue his study and collaborative work.

(2) That the method submitted by the associate referee for the determination of manganese in grain and stock feeds (see p. 78) be adopted as tentative and that further collaborative work be undertaken.

(3) That study be continued on the detection of starch or starchy materials as an adulterant of condensed milk products.

(4) That a study be made of methods for the detection of adulteration of cod liver oil.

(5) That preliminary work be continued on the method for the determination of small amounts of iodine in feeding stuffs.

(6) That the study of the method for the determination of calcium in mineral feeds be continued and additional collaborative work be undertaken.

(7) That studies on the determination of fat in fish meal be continued.

(8) That the Peterson-Hughes method for the determination of carotene be adopted as tentative, and that the spectrophotometer be used on the 0.1 per cent potassium dichromate reference standard.

(9) That the potassium dichromate standard be checked by several chemists against pure beta carotene and the best conditions for accurate application be established before further collaborative work is done involving the use of this reference standard.

(10) That the study of the application to the carotene determination of the neutral wedge photometer and the photoelectric colorimeter be continued.

(11) That study be made on the application of a qualitative procedure for the determination of carotene.

(12) That the associate referee study the suggestions made in the two contributed papers on the determination of carotene given at the Annual Meeting of this Association.

(13) That the study of devising standard methods for sampling be continued.

(14) That the vacuum oven and the electric air oven methods for the determination of moisture be further studied as a group with a view to unification.

(15) That the work of correlating the moisture methods of the Association be continued.

(16) That the study of the determination of lactose be continued for another year and that consideration be given to a correction factor whereby small commercial yeast cakes may be used and to further work on the use of alcohol for elimination of interference from peanut meal and low-grade tankage.

(17) That studies on hydrocyanic acid be continued.

(18) That the general referee consider the need for the development of a method for the determination of castor seed in feeding stuffs.

(19) That the method for Vitamin D assay (p. 351, 55) be revised as recommended by the associate referee (see p. 80) and study be continued.

FERTILIZERS

It is recommended—

(1) That the methods outlined by the associate referee for the determination of calcium be studied further and that collaborative work be undertaken; also that the tentative method for the determination of calcium oxide in mineral feeds be considered (p. 347, 44).

(2) That further study be made of the methods for the determination of sulfur.

(3) That the methods outlined by the associate referee for the determination of copper be studied collaboratively and that other methods be investigated.

(4) That the method outlined by the associate referee for the determination of zinc be studied collaboratively.

(5) That the study of the use of a factor weight or weights in the determination of potash in fertilizers be continued.

(6) That the official barium chloride method for the determination of potash (31, 45, 46, 47) be deleted (final action).

(7) That the study of methods for the recovery of platinum be continued.

(8) That a study be made of the determination of potash by "dissolving out the potassium chloroplatinate and reweighing when the filtration is made on a glass sinter or asbestos padded Gooch," in place of "by filtration after ignition and solution," when platinum or silica dishes are used.

(9) That further study be made of the need for providing additional platinum solution concentrations.

(10) That a collaborative study be made of some modification of the present official method for the determination of potash to prevent foaming during the boiling of the sample.

(11) That a collaborative study be made of the degree of fineness of grinding, with a view to elimination of the errors resulting from the nonuniformity of the 2.5 gram samples weighed out for the official potash determination.

(12) That the studies concerned with the solvent action of acid alcohol on potassium chloroplatinate be continued.

(13) That the Associate Referee on Potash consider the data presented at the Annual Meeting in the paper by H. R. Allen (see p. 162).

(14) That a collaborative study be made of the beaker method in comparison with other methods for the determination of water-insoluble nitrogen.

(15) That the use of potassium persulfate along with mercury as a catalyst in the determination of total nitrogen be studied on such materials as Canadian fish meal, meat scraps, and coconut meals.

(16) That in the Kjeldahl method for the determination of organic and ammoniacal nitrogen (p. 23, **19**), the last sentence in par. **19(g)** be changed as suggested by the associate referee (see p. 70) (first action).

(17) That the reduced iron method for the determination of nitrate and ammoniacal nitrogen in mixed fertilizers or nitrate salts (p. 26, **31**) be deleted (final action).

(18) That the official gravimetric method for the determination of water-soluble phosphoric acid (p. 21, **13**) be modified as suggested by the associate referee (see p. 70).

(19) That the official method for the determination of citrate-insoluble phosphoric acid (p. 21, **15**) be changed as suggested by the associate referee (see p. 70).

(20) That the Associate Referee on Phosphoric Acid give further consideration to the method proposed by MacIntire, Shaw, and Hardin for the determination of available phosphoric acid.

(21) That the method for the determination of magnesia in water-soluble compounds (*This Journal*, 21, 77) be adopted as official (first action).

(22) That the Bartlett-Tobey method for the determination of magnesium be adopted as tentative (see p. 71).

(23) That the Shuey volumetric method and other modifications of the present method for the determination of acid-soluble magnesia be studied.

(24) That the study of methods for the determination of active magnesia in mixed fertilizers be continued.

(25) That the volumetric method for the determination of acid-soluble manganese in fertilizers and manganese salts (*This Journal*, **21**, 292), with minor changes as noted by the referee (see p. 71), be adopted as tentative.

(26) That the colorimetric modification of the method for the determination of acid-soluble manganese be studied further.

(27) That the methyl red indicator in the tentative method for the determination of acid- and base-forming quality of fertilizers (p. 34, 55) be changed as suggested by the associate referee (see p. 71).

(28) That in the same method, under "Determination," line 17, the direction, "add 10 drops, etc.," be changed to "add 0.4 cc. of the mixed indicator."

(29) That the same method be modified by making optional the use of a filter paper cone for the prevention of spattering.

(30) That in the same method the elimination of water-insoluble material coarser than 20 mesh before the method is applied be studied further.

(31) That the basicity of phosphate rock and other factors that affect the method be studied further.

(32) That the recommendation of the Referee on Fertilizers that an associate referee be appointed to work in cooperation with the Bureau of Standards on the testing of volumetric apparatus and weights and to recommend methods for discouraging the use of such apparatus and weights that are too inaccurate be deferred for further study.

SOILS AND LIMING MATERIALS

It is recommended—

(1) That studies of the function of ammonia in the alcohol wash used in the determination of base exchange capacity be continued.

(2) That further study be made of the calcium peroxide method for the determination of fluorine in soils and that comparative data be obtained on the fluorine content of soil by fusion with sodium hydroxide or potassium hydroxide in a nickel crucible as compared to the calcium peroxide procedure.

(3) That the ammonium chloride steam distillation procedure for the evaluation of limestone availability be studied further in relation to soil carbonate reactions in pot experiments.

(4) That studies of the factors that influence the determination of *p*H value of soils in arid and semi-arid regions be continued.

(5) That work be continued on the determination of selenium in soils.

PLANTS

It is recommended—

(1) That Volumetric Method II for the determination of chlorine (p. 131, **38**) as modified by the associate referee (see p. 72) be made official (first action) and that work be discontinued.

(2) That the Associate Referee on Chlorine prepare a statement of the limitations of the applicability of the present official (alkaline ignition) method to be made a part of the method (see p. 72).

(3) That collaborative work be done on the determination of iodine.

(4) That methods for the determination of reducing sugars, sucrose, and starch be studied further.

(5) That studies be begun on methods for the determination of fructosans.

(6) That studies be begun on methods for the determination of glucose and fructose.

(7) That the studies of inulin be continued.

(8) That the study of hydrocyanic acid in plants be continued and collaborative work initiated.

(9) That the study of the Hick method for the determination of potassium in the presence of many other elements be continued and collaborative work undertaken.

ENZYMES

It is recommended—

(1) That an associate referee be appointed under drugs to study methods for the determination of pepsin.

(2) That the tentative method for the determination of the proteolytic activity of papain (*This Journal*, **21**, 97) be studied further.

(3) That further study be given the method of Balls and Hoover for the clotting of milk by papain, *J. Biol. Chem.*, **121**, 737 (1937).

LIGNIN

It is recommended that further study be given to the determination of lignin in plants.

PAINTS, VARNISHES, AND CONSTITUENT MATERIALS

It is recommended—

(1) That the standard methods of the American Society for Testing Materials for testing skinning and alkali resistance of varnishes (D154-38) be studied.

(2) That the study of the methods of testing abrasion resistance and hardness of varnish films be continued.

(3) That study of a method for soap resistance of varnish be made and that a study be made with a view to revising the present method of testing elasticity or toughness of varnish films in order to make execution of the method less tedious.

(4) That the study of the accelerated weathering of paints be continued.

VITAMINS

It is recommended—

(1) That study of the spectrophotometric determination of vitamin A be continued.

(2) That further studies be made of the feeding of skim milk or whole non-vitamin D milk with the reference oil in order to determine whether the reference oil and a quantity of milk, equal to that of the vitamin D milk being assayed, should be used as a reference standard instead of the reference oil alone.

(3) That study of biological methods for the determination of vitamin B_1 in foods be continued.

(4) That investigational and collaborative work be continued on biological methods for the determination of vitamin D carriers and that the text of the tentative method be revised as suggested by the referee (see p. 80).

(5) That an Associate Referee on Vitamin K be appointed.

(6) That an Associate Referee on Riboflavin be appointed.

REPORT OF SUBCOMMITTEE B ON RECOMMENDATIONS OF REFEREES*

By L. B. BROUGHTON (University of Maryland, College Park, Md.), *Chairman;* H. J. FISHER and A. E. PAUL

NAVAL STORES

It is recommended that the subject of naval stores be continued.

RADIOACTIVITY

It is recommended that the subjects of radioactivity, quantum counter and gamma ray scope be continued.

COSMETICS

It is recommended—

(1) That in view of legislative trends in the regulation of cosmetics the referee consider the need for enlarging the activities of the Association in this field and recommend such studies as appear necessary, to be begun this year if desirable.

(2) That the referee recommend the appointment of associate referees to assist in such work when needed.

DRUGS

MICROCHEMICAL TESTS FOR ALKALOIDS

It is recommended—

(1) That the tests proposed by the associate referee be adopted as tentative (see p. 88).

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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.*, 1935.

(2) That berberine be further studied, and that the additional products recommended by the associate referee (coniine, cosysine, phenacaine, stovaine) also be studied.

(3) That the status of the tentative microchemical tests for the alkaloids named by the referee (see p. 89) be advanced to official (first action).

MICROCHEMICAL TESTS FOR SYNTHETICS

It is recommended—

(1) That the microchemical methods proposed by the associate referee for the identification of diallylbarbituric acid, mandelic acid, and sulfanilamide be adopted as tentative (see p. 89).

(2) That the subject be continued for the study of other important synthetics, including plasmochine, benzedrine, para-phenylenediamine, and para-toluenediamine.

(3) That the changes in reagents for synthetics suggested by the referee be adopted (see p. 90).

(4) That the status of the tentative microchemical tests for the drugs named by the referee (see p. 90) be advanced to official (first action).

HYPOPHOSPHITES

It is recommended that the method proposed by the associate referee be adopted as tentative (see p. 90), and that the subject be discontinued.

DAPHNIA METHODS

It is recommended that study of this subject be continued.

HEXYLRESORCINOL

It is recommended that the method published last year (*This Journal*, 21, 536) be adopted as tentative, and that the subject be closed.

ERGOT ALKALOIDS

It is recommended that study of this subject be continued.

NITROGLYCERIN

In view of the difficulties experienced in devising an accurate method applicable in complex mixtures, it is recommended that the study of this subject be discontinued.

GUAIACOL

It is recommended—

(1) That the associate referee's adaptation of the method for the alkoxyl groups (see p. 100) to the determination of guaiacol be adopted as a tentative method.

(2) That the topic be continued for the study of methods for the determination of guaiacol in mixtures.

BIOLOGICAL TESTING

It is recommended that this subject be continued.

IODINE OINTMENT

It is recommended—

(1) That adoption of the method for the determination of free iodine (21, 94) as official be deferred until methods for the other forms of iodine are also available.

(2) That the study of methods for inorganically combined iodine, which was started by the associate referee in 1936, be resumed.

ACETYLSALICYLIC ACID ACETOPHENETIDIN AND CAFFEINE

It is recommended that the method proposed by the associate referee for the separation of acetylsalicylic acid, acetophenetidin, and caffeine, be adopted as tentative (see p. 91) and that the subject be closed.

GUMS

It is recommended that the qualitative tests for gums proposed by the associate referee be adopted as tentative (see p. 92) and that the subject be closed.

THEOBROMINE AND THEOBROMINE CALCIUM TABLETS

It is recommended—

(1) That the present tentative method (p. 590, 137) be retained in that status.

(2) That the method proposed by the associate referee be tentatively adopted as an alternative method (see p. 94).

(3) That the subject be closed.

CHLOROBUTANOL

It is recommended that the method proposed by the associate referee for the determination of chlorobutanol and chlorobutanol in solutions be adopted as tentative (see p. 95) and that the subject be closed.

ACETYLSALICYLIC ACID AND PHENOLPHTHALEIN TABLETS

It is recommended that the method proposed by the associate referee be adopted as tentative (see p. 95), and that the subject be closed.

AMINOPYRINE AND PHENOBARBITAL TABLETS

It is recommended that the subject be continued for study of the separation of these drugs in mixtures.

ELIXIR OF TERPIN HYDRATE AND CODEINE

It is recommended that this subject be continued.

EMULSIONS

It is recommended that the method submitted by the associate referee be adopted as tentative (see p. 96), and that the subject be closed.

CITRINE OINTMENT

It is recommended that the method submitted by the associate referee for the determination of mercury in citrine ointment be adopted as tentative (see p. 96), and that the subject be closed.

RHUBARB AND RHAPONTICUM

It is recommended that this subject be continued.

THEOPHYLLINE SODIUM SALICYLATE

It is recommended that this subject be continued.

SULFANILAMIDE

It is recommended that the method described in Part II of the associate referee's report be adopted as tentative (see p. 97), and that the topic be closed.

MANDELIC ACID

It is recommended—

(1) That the method proposed by the associate referee for tablets be adopted as tentative (see p. 98).

(2) That the method proposed by the associate referee for the determination of mandelic acid in liquid preparations be adopted as tentative and include the suggestions of the Committee (see p. 98).

(3) That the qualitative tests for mandelic acid proposed by the associate referee be adopted as tentative and include the changes suggested by the Committee (see p. 98).

(4) That this subject be discontinued.

CHANGES IN METHODS

CAMPHOR

It is recommended (first action) that the statement, "Not applicable to synthetic camphor," be inserted in parentheses between the title and the text of the official method (p. 560, 51).

BISMUTH COMPOUNDS IN TABLETS

It is recommended—

(1) That the tentative method (p. 592, 143) be amended by the addition of directions for preparation of sample (see p. 98).

(2) That the statement "Lead absent" following the title "Bismuth Compounds" be changed to read, "Not applicable in the presence of lead compounds but applicable in the presence of cerium salts."

COCAINE

It is recommended—

(1) That the last paragraph in Method II (p. 576, 97) be transposed

and constitute a second paragraph in Sec. 96, p. 576, and that the status of this paragraph be advanced to that of official (first action).

REAGENTS FOR MICROCHEMICAL TESTS

It is recommended that the changes in the reagents suggested by the referee be adopted (see pp. 90, 99).

CHLOROFORM IN MIXTURES

It is recommended that the changes in the tentative method for the determination of chloroform in mixtures suggested by the author of a special report presented at the 1938 meeting of the Association be adopted as tentative (see p. 99).

BARBITAL AND PHENOBARBITAL

It is recommended that the official method (p. 582, 112) be amended (first action) as suggested by the associate referee (see p. 99).

PHENOLPHTHALEIN

It is recommended that the methods for the determination of phenolphthalein (p. 569, 76, 78) be amended as suggested (see p. 99).

THYMOL

It is recommended that the method for the determination of thymol (p. 571, 84) be adopted as official (final action).

CHANGES IN STATUS OF METHODS

The tentative methods for the assay of the drugs recommended by the referee were adopted as official (first action) (see p. 100).

NEW SUBJECTS

It is recommended that the following subjects be studied:

(1) Acetophenetidin, acetylsalicylic acid, and salol in mixtures.
(2) Arecoline hydrobromide (particularly assay of tablets).
(3) Benzedrine.
(4) Hydroxyquinoline sulfate.
(5) Ipecac and opium powder (Dover's powder).
(6) Yellow oxide of mercury ointment.
(7) Acetanilid and salol (separation).
(8) Physostigmine salicylate.
(9) Pepsin.
(10) Plasmochine.
(11) Microchemical tests (coniine, cosysine, phenacaine, stovaine, plasmochine, benzedrine, para-phenylenediamine, and para-toluenediamine.)
(12) Purification of caffeine in plant extractives.
(13) Nicotinic acid.
(14) Epedrine in jellies.

REPORT OF SUBCOMMITTEE C ON RECOMMENDATIONS OF REFEREES*

By J. O. CLARKE (U. S. Food and Drug Administration, Chicago, Ill.), *Chairman;* G. G. FRARY, and W. B. WHITE

CANNED FOODS

It is recommended—

(1) That the method for determination of alcohol-insoluble solids in canned peas (*This Journal,* **21,** 89), with minor clarifying changes, be adopted as official (final action) (see p. 87).

(2) That the method for determination of chlorides in tomato juice (*This Journal,* **20,** 78), with minor clarifying changes, be made official (final action) (see p. 88).

(3) That the official method for preparation of sample (p. 497, **2**) be extended to include canned fruit and be clarified by requiring tilting of the sieve during draining, and turning of all pieces to permit drainage of cups or cavities.

(4) That studies of methods for quality factors and fill of containers be continued.

(5) That collaborative studies be conducted on the tentative method for total solids in tomato products (p. 499, **16**) with a view to its adoption as an official method.

DAIRY PRODUCTS

It is recommended—

(1) That studies of methods for the detection of neutralizers in dairy products be continued, and that particular attention be given to the ratio between titratable acidity and lactic acid.

(2) That methods for the determination of lactic acid in dried milk be further studied.

(3) That the Associate Referee on Malted Milk study the application of the official method for fat in dried milk (p. 282, **72**) to malted milk with a view to final adoption of a single method for both products.

(4) That methods for the separation of fat in dairy products (except cheese) for the determination of fat constants be further studied.

(5) That the Associate Referee on Cheese study methods of isolating fat from cheese for the determination of fat properties and constants, giving special attention to such treatments as promise a minimum change in the properties of the fat.

(6) That studies of methods for the determination of casein in malted milk be continued.

(7) That studies be continued on the development of a satisfactory stirrer method for preparation of butter samples.

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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.,* 1935.

(8) That the study of rapid methods for determining the degree of pasteurization in milk and cream be continued.

(9) That an associate referee be appointed to study methods for examining butter for the purpose of detecting the use of under-pasteurized cream.

(10) That studies on mounting media in the microscopic method for the identification of malted milk be discontinued.

(11) That studies of alternative methods for detecting gelatin in milk and cream be discontinued.

(12) That studies of methods for the determination of casein be discontinued.

(13) That further studies on the determination of citric acid in milk be postponed until the completion of studies on the determination of citric acid in fruit.

(14) That studies on methods for the clarification of milk for the optical determination of lactose be continued and broadened to include correction for volume of the precipitate.

(15) That studies on methods for the detection of decomposition in dairy products be continued.

(16) That the method for estimation of mold mycelia in butter suggested by the associate referee (*This Journal,* **20,** 93) be adopted as tentative (see p. 76) and studied collaboratively.

(17) That studies be continued on methods to distinguish between products made from cow's milk and those made from the milk of other animals.

(18) That study of methods of analysis of frozen desserts be inaugurated.

EGGS AND EGG PRODUCTS

It is recommended—

(1) That studies of methods for determining water-soluble and crude albumin in dried eggs be discontinued.

(2) That work on chemical methods for detecting decomposition in eggs be continued.

(3) That studies of methods for the determination of cholesterol and fat be continued.

(4) That the official method for determination of chlorine in eggs (p. 301, 16 and 17) be changed (first action) to provide for the substitution of the official volumetric procedure for the official gravimetric procedure in the final measurement of chlorine (see p. 77).

(5) That the method, official (first action) for determination of dextrose and sucrose (301, **18** and **19**), be modified as suggested by the referee (see p. 77).

(6) That studies on methods for the determination of glycerol be continued.

FISH AND OTHER MARINE PRODUCTS

It is recommended—

(1) That the tentative methods for determination of ash, salt, and total nitrogen (*This Journal*, **21**, 86) be studied collaboratively.

(2) That further study be made of methods for the determination of ether extract and total solids.

GUMS IN FOODS

It is recommended that studies on methods for determination of gums in foods be continued.

MEAT AND MEAT PRODUCTS

It is recommended—

(1) That the method for determination of nitrates in meat products suggested by the referee be adopted as tentative (see p. 82) in place of the phenoldisulfonic acid method (p. 356, **14** and **15**).

(2) That studies of methods for the detection of dried skim milk in meat products be continued.

(3) That the change in the manner of using the indicator in the method for the determination of coagulable nitrogen (p. 360, **28**) suggested by the referee be incorporated in the method (see p. 83).

(4) That the present tentative methods for determination of copper and zinc in gelatin (p. 368, **64** and **65**) be dropped and the methods suggested by the referee be adopted as tentative (see p. 84).

METALS IN FOODS

It is recommended—

(1) That studies be continued on methods of sample preparation of those products wherein the arsenic is tenaciously held.

(2) That the iodine titration, gold or silver sol, and the molybdenum blue colorimetric methods for the determination of arsenic be further studied as possible substitutes for the Gutzeit method.

(3) That in the studies of methods for the determination of antimony and of arsenic special attention be given to the separation of micro quantities of these elements occurring simultaneously in organic or biological material.

(4) That studies on micro methods for the determination of copper be continued.

(5) That collaborative studies on methods for the determination of fluorine in phosphates and baking powder be continued, and that special attention be given to methods of sample preparation for organic materials.

(6) That the colorimetric dithizone and the electrolytic methods for the rapid determination of lead on apples and pears (p. 391, **30–33**) be simplified as suggested by the associate referee (see p. 85) and that the simplified method be made official (final action).

(7) That studies of methods for the determination of lead be continued, with special reference given to oils and baking powders, and to the simplification of methods for removing interfering substances.

(8) That studies on methods for the determination of mercury be continued.

(9) That the method for selenium proposed by the associate referee (see p. 85) be adopted as tentative and subjected to further study.

(10) That studies on micro methods for the determination of zinc be continued.

(11) That the method for determining hydrocyanic acid developed by the associate referee be subjected to further study.

OILS, FATS, AND WAXES

It is recommended—

(1) That the modified Kaufmann method for determining the thiocyanogen number of fats and oils (*This Journal*, **21**, 87) be studied collaboratively with a view to its adoption as official.

(2) That the official method for determining free fatty acids (p. 417, 30) be dropped (final action).

(3) That the N.C.P.A. methods for determining free fatty acids in crude and in refined oils (*This Journal*, **21**, 88) be made official (final action).

(4) That the refractometric method for the determination of oil in flaxseed (*This Journal*, **20**, 74) be made official (final action).

(5) That studies be made on the application of the associate referee's method for the determination of oil in flaxseed to other commercially important oil seeds.

(6) That studies on the Polenski method be continued.

(7) That the specifications for the titer thermometer (p. 408, **15**) be amended in accordance with the revised Bureau of Standards specifications.

SPICES AND OTHER CONDIMENTS

It is recommended—

(1) That the tentative method for the determination of volatile oil in spices (p. 447, **16**) be made official for the same determination in marjoram and sage (first action), and that the method be further studied with respect to other spices.

(2) That the method proposed by the associate referee for the determination of ash in vinegar (*This Journal*, **21**, 89) and adopted as official (first action) last year, be adopted as official (final action).

(3) That the Referee on Vinegar study methods for the determination of total phosphoric acid.

(4) That the official method for the determination of solids in vinegar be studied, especially with reference to its application to vinegars high in solids, such as malt vinegar.

(5) That methods for the detection of caramel in vinegar be studied.

MICROBIOLOGICAL METHODS

It is recommended that studies be continued on the microbiological examination of canned vegetables, canned tomatoes and fruits, canned fishery products, canned meats, and sugar; and that similar studies be undertaken on eggs and egg products.

REPORT OF SUBCOMMITTEE D ON RECOMMENDATIONS OF REFEREES*

By J. A. LeClerc (Bureau of Chemistry and Soils, Washington, D. C.), *Chairman;* J. W. Sale and W. C. Jones

SUGARS AND SUGAR PRODUCTS

It is recommended—

(1) That the vacuum drying method adopted by the International Commission for Uniform Methods of Sugar Analysis (*This Journal,* 21, 89) be made official (final action).

(2) That the International Scale of Refractive Indices of Sucrose Solutions at 20° C., 1936, be adopted as official (final action).

(3) That the International Temperature Correction Table, 1936, be adopted as official (final action).

(4) That the official method of Wein for the determination of maltose (p. 484, 54–55) be dropped (final action).

(5) That the work on methods for determining acetyl-methyl carbinol and diacetyl in food products be continued.

(6) That the work on methods for determining the so-called unfermentable sugars of molasses be continued.

(7) That the study of maple flavor concentrates and imitations be continued.

(8) That studies on the determination of moisture in honey be continued.

(9) That the work on refractive indices of invert sugar solutions and the change in refractive indices with change of temperature in such products as invert sugar solutions, table sirups, etc., be continued.

(10) That the study of polariscopic methods be continued along the lines covered by the recommendations made and approved in 1931, 1932, and 1933.

(11) That study of chemical methods for reducing sugars be continued.

(12) That study of drying, densimetric, and refractometric methods be continued.

(13) That an Associate Referee on Sucrose and Ash in Molasses be appointed.

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* 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.*, 1935.

WATERS, BRINE AND SALT

It is recommended—

(1) That the statement on p. 506, **14(c),** "0.0001 mg of N as NO_2," be changed to read: "0.0001 mg of N" (final action).

(2) That the determination of boron in waters be further studied.

(3) That the work on effervescent salts be continued.

(4) That the study of the thorium nitrate method for the determination of fluorine in water, described in the referee's report, be further studied.

ALCOHOLIC BEVERAGES

It is recommended—

(1) That the pressure air method for the determination of carbon dioxide in beer be adopted as tentative (see p. 73) and be further studied collaboratively with the object of making it official.

(2) That the Associate Referee on Beer study collaboratively the following tentative methods relating to beer (Chap. XIV): (a) Extract in original wort; (b) real degree of fermentation; (c) total acid; (d) dextrin; (e) direct polarization; (f) pasteurization, and (g) chlorides, and that H-ion concentration also be studied.

(3) That methods for the determination of heavy metals (Fe, Cu, Pb) As, and F be studied (as recommended last year).

(4) That the viscometric method outlined by the associate referee last year for the determination of the proteolytic activity of malt (*This Journal,* **21,** 160) and the edestin titration method (*Wochschr. Brau.,* **53,** 297 (1936)) be further studied.

(5) That the vacuum method for the determination of moisture in flour (p. 206, 2) be studied as to its applicability to the determination of moisture in malt adjuncts (p. 161, 53).

(6) That a special study be made of methods for the determination of fat that will be applicable to corn grits and brewers' rice and flakes.

(7) That a study of the method for determining the extract in malt adjuncts (p. 161, 35) be made and that consideration be given to the suggestion to use a portion of the malt in the boiling operations.

(8) That special study be made of the diastatic activity of malt.

(9) That the study of methods for the detection of adulteration of distilled spirits be continued.

(10) That the collaborative study of sulfur dioxide in beer and ale be continued and also be extended to include this same determination in wines.

(11) That further collaborative work be done on the tentative methods for the determination of benzaldehyde (p. 183, 55), volatile esters (p. 181, 46), and gamma undecalactone (p. 181, 47) in cordials.

(12) That the study of the saponification of esters with lead acetate be dropped.

(13) That the distillation procedures for volatile acids in wines (p. 166, **23, 24**) be studied further with a view to eliminating chance errors and that the modification described in the associate referee's report or some other modification of the Peynaud procedure be tested further.

(14) That the sulfite method for the determination of aldehydes in whiskey and other potable spirits be made tentative and that work on it be continued with a view to making it official.

(15) That a study on the determination of total sulfur in wines be conducted.

(16) That the evaporation method described in the associate referee's report and Method II (p. 167, **24**) for the determination of volatile acids in wines be further studied to determine their applicability to distilled spirits and that the cause of the slight loss resulting from the use of Method II be investigated.

(17) That the procedure for the quantitative determination of methanol in distilled spirits by the use of the neutral wedge photometer described in the associate referee's report be subjected to collaborative study for possible further improvement and simplification.

FOOD PRESERVATIVES AND SWEETENERS

It is recommended—

(1) That further work on Special Method II (p. 435, **15**) for the determination of saccharine in non-alcoholic beverages as to its applicability to apple butter be discontinued.

(2) That the work on the Illing method for the determination of benzoate of soda, *Analyst*, **57**, 224 (1932), which was found to be suitable for sausage, be continued with respect to its suitability for other food products.

(3) That further studies based on the work of Tortelli and Piazza be made on the qualitative test for saccharin (p. 434, **13**).

COLORING MATTERS IN FOODS

It is recommended—

(1) That collaborative work be continued in estimating ponceau SX and ponceau 3R.

(2) That investigational work be continued on the quantitative estimation of sunset yellow FCF in the presence of tartrazine.

(3) That investigational work be continued in separating and estimating quantitatively mixtures of light green SF yellowish, brilliant blue FCF, and fast green FCF.

FRUITS AND FRUIT PRODUCTS

It is recommended—

(1) That the study of soluble solids be dropped.

(2) That the study of electrometric titration be continued.

(3) That the changes in the methods for the analysis of preserves and jams suggested by the referee be adopted as official (first action) (see p. 78).

(4) That the official method for the determination of phosphoric acid (P_2O_5) in wines (p. 166, **19**) be adopted as tentative for the same determination in fruits and fruit products (see p. 78).

(5) That the study of methods for the determination of inactive malic, isocitric, and lactic acids be continued.

(6) That the application to fruits and fruit products of the colorimetric method for lactic acid in dried milk be studied (*This Journal*, **20**, 605).

(7) That the study of volumetric and colorimetric methods for the determination of phosphoric acid (P_2O_5) in jams, jellies, and other fruit products be continued.

(8) That the effect of slow oxidation on the yield of pentabrom acetone in the determination of citric acid be studied.

(9) That the study of polarimetric methods for jams and jellies and preserves be continued.

FLAVORS AND NON-ALCOHOLIC BEVERAGES

It is recommended—

(1) That work on the determination of glycerol, vanillin, and coumarin in imitation vanilla be continued.

(2) That the chemical method described in the associate referee's report for detemination of isopropyl alcohol be studied further collaboratively and that it be applied to mixtures containing essential oils.

(3) That the spectrophotometric method for the determination of coumarin in imitation vanilla be subjected to collaborative study.

(4) That the method presented by Wilson for the quantitative determination of beta-ionone be studied collaboratively.

(5) That the referee study the possible application of automatic extraction to the determination of vanillin and coumarin in vanilla extract.

(6) That the referee study the application of the spectrophotometer to the present colorimetric methods found in the chapters on Flavors and Non-alcoholic Beverages.

CACAO PRODUCTS

It is recommended—

(1) That further collaborative work be done on the pectic acid method for the quantitative determination of shell in cacao products (*This Journal*, **20**, 417; **21**, 441).

(2) That work be done on the determination of lecithin in cacao products.

(3) That collaborative work be done on the method for the determination of milk protein described in the referee's report.

BAKING POWDER

It is recommended that the method described in the referee's report for the determination of free tartaric acid (direct determination), cream of tartar, and total tartaric acid be adopted as official (first action).

CEREAL FOODS

It is recommended—

(1) That the official (first action) method for sampling bread be made official (final action).

(2) That the official (first action) method for the collection and sampling of macaroni products be made official (final action).

(3) That further study be made of the tentative magnesium-acetate method of ashing (*This Journal*, **20**, 69).

(4) That the statement on p. 216, **38(c)**, "0.0001 mg of N as nitrite," be changed to read "0.0001 mg of N" (final action).

(5) That study be undertaken to develop a rapid method for the determination of starch in flour, and that further study be given to the improvement of polarimetric methods for starch determination in both raw and cooked cereal foods.

(6) That collaborative study be made to determine reducing and non-reducing sugars in flour.

(7) That the tentative method for the determination of acidity of water extract of flour be dropped (p. 208, **13**).

(8) That the method for fat-acidity of flour proposed in the associate referee's report be adopted as tentative (see p. 75), and that further study be made of the methods described in the associate referee's report for the determination of acidity in flour and other cereal products.

(9) That the associate referee continue his studies on the baking test for soft wheat flour.

(10) That the study of the proteolytic enzymes of flour be continued.

(11) That the associate referee continue the study of methods for the determination of ergot in rye flour.

(12) That study be continued to develop a method for determining sodium chloride-free ash in macaroni and baked products.

(13) That work be continued on methods for the determination of soybean flour in cereal products.

(14) That the study of methods for the identification of the nature of the raw materials used in the manufacture of macaroni be discontinued for the present.

(15) That the associate referee continue his studies on whole wheat flour, giving special attention to the determination of cellulose as an index of the whole wheat content of cereal products.

(16) That further study be made of methods for the determination of the ash of the original flour used in phosphated and self-rising flours, especially of old self-rising flours, with special reference given to: (a) analysis for sodium chloride content of self-rising flour and of the ash of the extracted flours, and (b) study of means other than extraction with carbon tetrachloride for 100 per cent separation of the sodium chloride from old self-rising flours.

(17) That the study of methods for the determination of chlorine in bleached flour fat be continued.

(18) That the study of the methods for the determination of benzoyl peroxide in flour be continued.

(19) That the method for the measurement of carotinoid pigments in flour given in *This Journal*, **21**, 339, be studied with a view to the substitution of water-saturated normal butyl alcohol for the Varsol alcohol mixture.

(20) That the associate referee continue his studies on H-ion concentration of flour.

(21) That the tentative citric acid method (p. 224, 55), the so-called "fat" procedure (p. 222, 54) and the lactose method given in the associate referee's report for the calculation of milk solids in bread be further studied.

(22) That the tentative method as modified by the associate referee for the determination of extract soluble in cold water be adopted as official (first action) and that further collaborative study be made with flour and other cereals and cereal products.

(23) That the method for the determination of carbon dioxide in self-rising flour be further studied collaboratively.

(24) That the suggestion made in 1936 regarding the sterol content of cereals be repeated.

(25) That further collaborative work on the measurement of flour and bread color by the N. A. colorimeter be dropped, and that study be continued on the sampling and preparation of flour and bread for color measurements in the photoelectric cell method based on reflectance.

(26) That an associate referee be appointed to study the application of the methods under wheat flour (determination of water, ash, protein, fat and crude fiber) to corn meal, corn flour, and corn starch, including fat in brewer's grits, and flakes; to rolled oats, oatmeal, and oat flour; to rye flour and buckwheat flour; to barley malt, barley flour, rice flour and fat in brewer's rice.

(27) That an associate referee be appointed to study the application of methods under bread (determination of ash and protein) to such baked products as crackers, cookies, and cakes.

(28) That the method for the determination of apparent viscosity of flour (*This Journal*, **20**, 380) be adopted as official (final action).

(29) That a method for the estimation of the butterfat content of bread, based on the direct saponification and distillation of the bread, without extraction of the fat, be developed.

MICROCHEMICAL METHODS

It is recommended—

(1) That the microchemical method proposed by the referee for the determination of methoxyl be adopted as tentative (see p. 100), and that further study be made of this procedure.

(2) That the referee make a study of micro methods applicable to the work of this Association.

CHANGES IN THE OFFICIAL AND TENTATIVE METHODS OF ANALYSIS MADE AT THE FIFTY-FOURTH ANNUAL MEETING, NOVEMBER 14, 15, AND 16, 1938*

I. SOILS

No additions, deletion, or other changes.

II. FERTILIZERS

(1) The official barium chloride method for the determination of potash (p. 31, **45, 46, 47**) was deleted (final action).

(2) The last sentence in par. **19(g)** of the official Kjeldahl method for the determination of organic and ammoniacal nitrogen (p. 23, **19**) was changed to read as follows: "A soln having a sp. gr. of 1.36 or higher may be used" (first action).

(3) The reduced iron method for the determination of nitrate and ammoniacal nitrogen in mixed fertilizers or nitrate salts (p. 26, **31**) was deleted (final action).

(4) In the official gravimetric method for the determination of water-soluble phosphoric acid (p. 21, **13**), the first sentence was changed (first action) to read as follows:

Place 1 g of the sample on a 9 cm filter and wash with successive small portions of H_2O until the filtrate measures about 250 cc. Allow each portion of the wash water to pass through the filter before adding more, and wash with suction if the washing would not otherwise be complete within 1 hour.

(5) In the official method for the determination of citrate-insoluble phosphoric acid (p. 22, **16(a)**) lines 1–8 were changed to read as follows:

After washing out the water-soluble P_2O_5, **13**, transfer the filter and residue, within a period not to exceed an hour, to a 250 cc flask containing 100 cc of the NH_4 citrate soln previously heated to 65° in a water bath. Close the flask lightly with a smooth rubber stopper and shake vigorously until the filter paper is reduced to a pulp, relieving the pressure by momentarily removing the stopper. Loosely stopper the flask to prevent evaporation and return it to the bath. Maintain the contents of the flask at exactly 65°, keeping the level of the H_2O in the bath above that of the citrate soln in the flask. Shake the flask every 5 min.

(6) The tentative method for the determination of magnesia in water-soluble compounds (*This Journal*, **21**, 77) was adopted as official (first action) under the title "Magnesia in Water-Soluble Compounds (Applicable to Sulfate of Potash Magnesia, Sulfate of Magnesia, and Kieserite)."

(7) The following method (Bartlett-Tobey) for the determination of magnesium was adopted as tentative.

* Compiled by Marian E. Lapp, Associate Editor. Unless otherwise given, all references in this report are to *Methods of Analysis, A.O.A.C.*, 1935, and the methods are edited to conform to the style used in that publication.

MAGNESIUM

Weigh 2.5 g of fertilizer into a 250 cc volumetric flask, add 30 cc of HNO_3 and 10 cc of HCl, and boil for 30 min. Cool, make to volume, mix, filter through a dry filter paper, and transfer a 100 cc aliquot to a 400 cc beaker. Add a few drops of methyl red. Add NH_4OH until the soln is yellow, then HCl until barely pink. Add 15 cc of a saturated soln of NH_4 oxalate, adjust the soln to *p*H 5.0 (a faint pink color) by the addition of HCl (1+4), or NH_4OH (1+4), boil for a few minutes, cool, and again adjust the reaction to *p*H 5.0, adding more methyl red if necessary. Stir thoroughly and allow the soln to stand until the precipitate settles. Filter through a 11 cm filter paper fine enough to retain Ca oxalate and wash 10 times with hot H_2O. To the filtrate add 2 cc of 10% HCl and evaporate to a volume of approximately 100 cc. Add 5 cc of a 10% Na citrate soln and enough NH_4OH to make the soln alkaline. (Blue with bromothymol blue.) If the fertilizer does not contain soluble phosphoric acid, add 5 cc. of a 10% soln of $(NH_4)_2HPO_4$. Stir vigorously until the precipitation is completed. Add 15 cc of NH_4OH and allow to stand at least 2 hours, stirring frequently, or allow to stand overnight. Transfer the precipitate to a small filter or filtering crucible. Wash, and ignite as directed under II, 54. If $Mn_2P_2O_4$ is present, correct for it as directed under II, 54.

(8) With minor changes suggested by the referee, the volumetric method for the determination of acid-soluble manganese in fertilizers and manganese salts (*This Journal*, **21**, 292) was adopted as tentative. The preparation of the standard ferrous sulfate solution should be changed to read as follows: "0.091 *N* 25.3 g of $FeSO_4 \cdot 7H_2O$ and 25 cc of H_2SO_4 in 1 liter of soln. Standardize with the 0.0910 *N* $KMnO_4$."

(9) The tentative method for the determination of acid- and base-forming quality of fertilizers (p. 34, 55) was modified as follows:

(a) The methyl red indicator was changed to the following:

Mixed indicator.—Weigh 0.1 g of bromocresol green and 0.02 g of methyl orange into an agate mortar, triturate, and slowly add about 2 cc of 0.1 *N* NaOH. Dilute to 100 cc with H_2O.

(b) The use of a filter paper cone for the prevention of spattering was made optional.

(c) Under "Determination," line 17, the direction "add 10 drops, etc." was changed to read "add 0.4 cc of the mixed indicator."

III. SEWAGE*

IV. AGRICULTURAL LIMING MATERIALS

No additions, deletions, or other changes.

V. AGRICULTURAL DUST*

VI. INSECTICIDES AND FUNGICIDES

No additions, deletions, or other changes.

VII. CAUSTIC POISONS

No additions, deletions, or other changes.

* Subjects for future study.

VIII. NAVAL STORES

No additions, deletions, or other changes.

IX. PAINTS, VARNISHES, AND CONSTITUENT MATERIALS

No additions, deletions, or other changes.

X. LEATHERS

No additions, deletions, or other changes.

XI. TANNING MATERIALS

No additions, deletions, or other changes.

XII. PLANTS

(1) Volumetric method II for the determination of chlorine (p. 131, **38**) was modified and adopted as official (first action). The changes are included in the following statements:

(2) The explanatory note under the title of par. **38**, p. 131, was transposed to par. **34**, and placed under the title "Chlorine."

(3) The following explanatory note was placed under the heading "Preparation of Solution," par. **34**:

Complete retention of Cl in each kind of material should be verified by trial since losses can occur, especially with samples high in carbohydrates, (*This Journal*, **11**, 209(1928); **12**, 195(1929), if insufficient Na_2CO_3 is present during the ignition, or in any case if excessive temperatures are used, *Ibid.*, **21**, 107(1938).

(4) The following explanatory note was placed under the title of par. **36**:

(The limit of accuracy of this titration is considered to be approximately 10.2 mg of Cl, (*Am. Chem. Soc.*, 37, 1128(1915), hence an accuracy of 1.0 would require samples containing not less than 20 mg.)

(5) The following revisions were made in the tentative method for the determination of chlorine in plants (p. 131, **38**) in order to make it conform to the text of the method as recommended for adoption as official (first action) at the 1938 Annual Meeting of the Association:

Page 131, 38(a), change "4.6826" to read "4.6822."

Page 132, 38(e), change to read, "Add 35 ml of H_2SO_4 to each liter of H_2O, boil 5–10 min., and cool to room temp."

Page 132, 38(f), delete par. (f) and insert instead the following: "*Iodine soln.*—Shake a large excess of I crystals in a glass-stoppered bottle nearly filled with Reagent(e). Decant, and discard the soln. Repeat the process but decant the soln into a glass-stoppered bottle. Test the soln by adding 25 ml of it to 25 ml of Reagent (e), followed by 5 ml of Reagent (d). (No blue color should appear after 5 min., and the color produced by a small amount of Reagent (a) should be discharged by an equivalent amount of Reagent (c). If the soln gives a blue color when tested, compute the amount of Reagent (c) needed to treat the remainder of the decanted soln from the excess of Reagent (c) over Reagent (a) observed in the test titrations. Add twice that amount and test as before."

Page 132, 39, line 9, delete the remainder of this sentence beginning with the words, "fades slowly, etc." and insert in their place the words, "begins to fade slowly."

Page 132, 39, line 18, change the word "ash" to "wash."

Page 132, 39, line 2 from bottom of page, revise this sentence to read: "When the digest is cool, add 175 ml of H_2O, boil 5–10 min., and cool to room temp."

XIII. BEVERAGES (NON-ALCOHOLIC) AND CONCENTRATES

No additions, deletions, or other changes.

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

The following pressure air method for the determination of carbon dioxide in beer was adopted as tentative:

CARBON DIOXIDE IN BEER

Pressure Air Method

Disconnect the bottle or can and determine the head space volume as follows:

If the sample is a bottle, fill with H_2O to the top and pour off into a graduated cylinder to the scratch mark. The number of ml of H_2O thus poured off represents head space in ml.

If the sample is a can, weigh empty can after pouring out all remaining beer. The difference represents the weight of beer, which divided by the sp. gr. of the beer will give volume of beer in ml. Fill the empty can with H_2O and weigh. Weight of H_2O in g is also the volume in ml, so that the difference between volume of H_2O and volume of beer represents head space in ml.

Calculate CO_2 by weight by the following formula:

$$\% \ CO_2 = \left[P - \left(\frac{\text{ml of air}}{\text{ml of head space}} \times 14.7 \right) \right] \times 0.00965, \text{ in which}$$

P = absolute pressure in pounds per sq. in. at 25° = (ordinary gage pressure +14.7).

NOTES: Pounds per sq. in. $\times 0.070307$ = kg per sq. cm. For routine work 15 may conveniently be substituted for 14.7.

XV. WINES

No additions, deletions, or other changes.

XVI. DISTILLED SPIRITS

The following sulfite method for the determination of aldehydes in whiskey and other potable spirits was adopted as tentative:

ALDEHYDES IN WHISKEY OR OTHER POTABLE SPIRITS

REAGENTS

(a) *0.05 N sodium thiosulfate soln.*—Standardize against a 0.05 *N* $K_2Cr_2O_7$ soln as follows: Place 20 cc of *0.05 N* $K_2Cr_2O_7$ soln in a glass-stoppered flask and add 5 cc of a 15% KI soln. Add 2.5 cc of HCl and dilute with 100 cc of CO_2-free H_2O, then titrate at once the liberated I with the thiosulfate soln until the yellow color has almost disappeared; add a few drops of starch indicator, and continue, with constant shaking, the addition of thiosulfate soln until the blue color just disappears.

(b) *0.05 N iodine soln.*—Standardize this soln against the thiosulfate soln.

(c) *Sodium bisulfite soln.*—Approximately 0.05 *N*. With each series of determinations, determine the strength of this soln in terms of the I soln. (This soln will not deteriorate nearly so fast when it contains 5–10% of alcohol.)

DETERMINATION

Run 50 cc of sample into an Erlenmeyer flask and add 10 cc of H_2O. Distil off 50 cc or slightly more, transfer the distillate to a glass-stoppered flask or bottle, and add about 150 cc of CO_2-free H_2O. Using a pipet, add 25 cc of the bisulfite soln and allow to stand for about 30 min., shaking occasionally. Add an excess (about 30 cc) of the standard I soln, titrate this excess with the thiosulfate soln, and calculate as acetaldehyde. 1 cc of 0.05 *N* soln = 0.0011 g of acetaldehyde.

NOTES: Do not add the starch indicator until the yellow color of the I soln has almost disappeared. As the end point is approached the soln will have a decided violet tint rather than a blue, as is customary with I and starch. If the end point is in doubt, add a little more of the starch indicator. The formation of a bluish-violet color indicates that the end point has not been reached. Always run a blank on the bisulfite soln along with each series of aldehyde determinations.

XVII. BAKING POWDERS AND BAKING CHEMICALS

The following methods for the determination of free tartaric acid, cream of tartar, and total tartaric acid were adopted as official (first action):

CREAM OF TARTAR AND FREE TARTARIC ACID

Total, Combined, and Free Tartaric Acid

To 2.5 g of the baking powder in a 250 cc volumetric flask, add 100 cc of H_2O at about 50°, and allow to stand at room temp. for about 30 min., shaking occasionally. Cool, dilute to mark with H_2O, shake vigorously, and filter through a large fluted paper. Pipet 2 portions of 100 cc each of the *clear* filtrate into 250 cc beakers and evaporate to about 20 cc. To one portion add 3.5 cc of approximately normal KOH. Mix well and add 2 cc of glacial acetic acid. Again mix well and add 100 cc of 95% alcohol, stirring constantly. Treat the other portion in a similar manner, but use normal NaOH instead of KOH. Cool the mixtures to about 15°, stir vigorously for about 1 min., and allow to remain in the refrigerator overnight. Collect the precipitate in a Gooch on a thin, tightly tamped pad of asbestos. Rinse the beaker with about 75 cc of ice-cold 80% alcohol, carefully washing down the sides of the beaker. Finally, wash the sides of the crucible with 25 cc of the alcohol and suck dry. Transfer the contents of the crucible to the original beaker with about 100 cc of hot H_2O and titrate with 0.1 *N* alkali, using phenolphthalein indicator. Designate the titer of the portion treated with KOH as "A" and that treated with NaOH as "B."

CALCULATIONS

$\frac{2.5}{250} 100 = 1$ g of powder in the aliquot.

Total tartaric acid—
$0.015\ (A + 0.6) \times 100$ or $1.5\ (A + 0.6)$
Combined tartaric acid (cream of tartar)—
$0.0188\ (B + 0.6) \times 100$ or $1.88\ (B + 0.6)$.
Free tartaric acid—
$0.015\ (A - B) \times 100$ or $1.5\ (A - B)$.

In the above formulas "0.6" represents the solubility of the cream of tartar in the reaction mixture in terms of 0.1 *N* alkali.

Free Tartaric Acid (Direct Determination)

REAGENT

Saturated alcohol.—To about 50 g of purest cream of tartar (finely powdered) in an Erlenmeyer flask, add about 100 cc of 95% alcohol and 100 cc of H_2O, shake vigorously for several minutes, and allow to stand 15 min., shaking occasionally. Filter on paper in a Büchner funnel, and wash the salt with about 200 cc of diluted 95% alcohol (1+1), then with 95% alcohol, and finally with ether. Dry at the temp. of boiling H_2O. To 500 cc of *absolute* alcohol add about 5 g of the purified cream of tartar and allow to stand 2 hours, shaking occasionally. If the cream of tartar has been properly purified a blank (50 cc of $CHCl_3$+150 cc of the saturated alcohol) should not require more than 0.15 cc of 1 *N* alkali to neutralize 100 cc of the mixture.

DETERMINATION

Weigh 1.25 g of the baking powder into an absolutely *dry* 200 cc volumetric flask, add 50 cc of $CHCl_3$, and allow to stand about 5 min., shaking occasionally. (If, upon the addition of the $CHCl_3$, the powder sticks to the bottom of the flask, moisture is indicated and the determination should be discarded.) Add 100 cc of the saturated alcohol, shake for about 5 min., and allow to stand 30 min., shaking at frequent intervals. (It is not necessary to filter the alcohol reagent.) Make to mark with the saturated alcohol, shake a few minutes, and filter through a large fluted paper. Titrate 100 cc of the clear filtrate with 0.1 *N* alkali (phenolphthalein). The quantity (cc) of alkali (*X*) used $\times 1.2$ = the percentage of free tartartic acid.

$$\frac{1.25}{200} \times 100 = 0.625 \text{ g of powder in aliquot;}$$

$$\frac{X(0.0075 \times 100)}{0.625} = 1.2X.$$

XVIII. COFFEE AND TEA

XIX. CACAO PRODUCTS

No additions, deletions, or other changes.

XX. CEREAL FOODS

(1) The tentative method for preparation of sample of bread (p. 221, 50) was adopted as official (final action).

(2) The tentative method for collection and preparation of sample of macaroni products (p. 228, 68) was adopted as official (final action).

(3) In 38(c), p. 216, the statement, "0.0001 mg of N as nitrite," was changed to "0.0001 mg of N" (final action).

(4) The tentative method for the determination of acidity of water extract (p. 208, 13) was deleted.

(5) The following method for the determination of fat acidity of flour was adopted as tentative:

FAT ACIDITY OF FLOUR

Extract duplicate 10 g samples with petroleum ether for approximately 16 hours, using a Soxhlet (or similar extraction apparatus) and double thickness paper or Alundum R.A. 360 thimbles.

Completely remove the solvent from the extract by evaporation on the steam bath. Dissolve the extract in the extraction flask with 50 cc of a mixture of equal parts by volume of ethyl alcohol and benzene, and containing approximately 0.02% of phenolphthalein.

Titrate the dissolved extract with carbonate-free standard alkali to a distinct pink color. For convenience, use exactly 0.0178 *N* alkali for the titration in order to simplify calculations. 1 cc of this soln = 1 mg of K_2O_4.

Make a blank titration on 50 cc of the benzene-alcohol mixture and subtract the value obtained from the titration value of the sample.

Report fat acidity as the number of mg of K_2O_4 required to neutralize the free fatty acids from 100 g of flour on a dry-matter basis.

(6) As modified by the associate referee, the tentative method for the determination of extract soluble in cold water (p. 213, **30**) was adopted as official (first action). The modified method follows:

EXTRACT SOLUBLE IN COLD WATER

Weigh 20 g of the flour into a 500 cc Erlenmeyer flask and add gradually 200 cc of H_2O at a temp. approximating 0°. Shake vigorously when about 50 cc of H_2O has been added, and continue shaking during the addition of the remaining H_2O. Allow the mixture to stand at 0° for 40 min., shaking occasionally. Filter rapidly, returning the first runnings to the filter, until a clear filtrate is obtained. Pipet 20 cc of the clear filtrate into a weighed dish, evaporate to dryness on a steam bath, and dry to constant weight in a vacuum oven at about 100° for periods of 30 min.

(7) The method for the determination of apparent viscosity of flour (*This Journal*, **20**, 380) was adopted as official (final action).

XXI. COLORING MATTERS IN FOODS

No additions, deletions, or other changes.

XXII. DAIRY PRODUCTS

The following method for the estimation of mold mycelia in butter was adopted as tentative:

MOLD MYCELIA IN BUTTER[1]

REAGENT

Gum soln.—Make up 1 liter of a 0.75% soln of carob bean gum with 2% of added formaldehyde as a preservative. (The dry gum may be conveniently added by first mixing it in 10–15 cc of 95% alcohol and stirring this mixture rapidly into the H_2O.) Gently heat the soln to boiling to drive off alcohol and air, and sustain the heating for 25–30 min. Add formaldehyde on cooling. Use the clear supernatant soln, free from cells, left when the cellular elements in the gum gradually settle out. (A similar soln made with gum tragacanth may also be used for this purpose.)

PROCEDURE

Make a careful examination of the surface of the butter to insure freedom from surface mold growth and note any mold growth visible. In order to remove possibility of contamination of any surface mold not visible, scrape off and discard $\frac{1}{8}''$ of the surface, after which take a sample from the exposed surface.

Weigh out 1 g of butter by means of a $\frac{1}{4}$ teaspoon measure. Measure out 7 cc of the hot gum soln and, with the spoon bottom-side-up over a 50 cc beaker, pour 2

[1] *This Journal*, 20, 93 (1937).

or 3 cc of the hot soln over the spoon. (This quantity is usually sufficient to loosen the butter and cause it to slide into the beaker.) Use the remainder of the 7 cc of soln to rinse the remaining fat from the spoon.

Stir the mixture until the soln is well mixed and fat globules are 0.1–0.2 mm in diameter. (The stirring necessary to obtain a uniform sample must be determined by experience.)

Mount a portion of the mixture on the mold-counting slide and estimate the mold as directed under **XXXV, 27, 28.** Report no field positive unless the combined length of the two longest filaments exceeds $\frac{1}{6}$ of the diameter of the field.

XXIII. EGGS AND EGG PRODUCTS

(1) The official method for the determination of chlorine (p. 301, **16, 17**) was changed to the following and adopted as official (first action):

CHLORINE

(a) *Liquid Eggs* (in absence of added salt).—From the well-mixed sample, **1(a)** or **(b)**, weigh accurately, by difference, into a 150 cc low-form Pyrex beaker, approximately 4 g of yolk, 7 g of whole eggs, or 10 g of whites; add 20 cc of 10% Na_2CO_3 soln, mix, and evaporate to dryness on an electric hot plate or overnight at 100°. Transfer the beaker while hot to an electric muffle heated to 500° (faint redness), and allow to remain at that temp. for 1 hour. Cool, add a few drops of H_2O, and break up the charge with a glass rod. Add 50 cc of H_2O, cover the beaker with a watchglass, add slowly 20 cc of HNO_3 (1+3), mix, filter, and wash the charred material and filter thoroughly with H_2O. Proceed as directed in one of the following alternatives:

(1) To the combined filtrate and washings add a known volume of 0.1 *N* $AgNO_3$ in slight excess and proceed as directed in **XII, 37.**

(2) Collect the filtrate and washings in a 250 cc flask, keeping the total volume of filtrate to 180 cc or less. Add a known volume of 0.1 *N* $AgNO_3$ in slight excess and make to volume. Filter, and determine Cl_2 in an aliquot as directed in **XII, 37.**

(b) *Liquid Eggs* (in presence of added salt).—from the well-mixed sample, **1(a)** or **(b)**, weigh 1–2 g accurately, by difference, into a 150 cc low-form Pyrex beaker, and proceed as directed under **(a)**,

(c) *Dried Eggs.*—From the well-mixed sample, **1(c)**, transfer to a 150 cc low-form Pyrex beaker, 2 g of whole eggs or yolks, or 1 g of whites, and proceed as directed under **(a)**.

(2) The method for the determination of dextrose and sucrose (p. 301, **18, 19**), official (first action), was modified as follows:

(a) The words "add 5 cc of HCl, and allow to stand overnight," in line 4 of par. **19**, were changed to read, "and invert the sucrose as directed under **XXXIV, 23(b)** or **(c).**"

(b) The following paragraph was added at the end of **18(a):**

To correct for the error due to the volume occupied by the precipitate in samples containing added sucrose, repeat the determination, weighing the same amount of sample into a 500 cc volumetric flask containing 1 g of $CaCO_3$ and 100 cc of 5% salt soln. Add, with continuous mixing, 260 cc of 95% alcohol. Allow to stand a few minutes for gas bubbles to rise to the surface, cool to room temp., fill to the mark with H_2O, shake, and filter through a 18.5 cm folded filter. Transfer 300 cc of filtrate to a 400 cc beaker, evaporate to 20–30 cc, and proceed as directed in **18.** To obtain the amount of sucrose subtract the percentage of sucrose obtained in the

250 cc dilution determination from twice the percentage obtained in the 500 cc dilution determination.

XXIV. FISH AND OTHER MARINE PRODUCTS

No additions, deletions, or other changes.

XXV. FLAVORING EXTRACTS

No additions, deletions, or other changes.

XXVI. FRUITS AND FRUIT PRODUCTS

(1) The following changes in the methods for the analysis of preserves and jams were adopted as official (first action):

(a) *Preparation of Sample—Official* (p. 319, 2(c)).—Insert the following after the word "grinding," line 5: "Set the burrs or the blades of the food chopper as closely as possible without crushing the seeds. If the container is a No. 10 can or smaller, grind the entire contents. Mix well the contents of larger containers by stirring, and remove a portion for grinding."

(b) *Water-Insoluble Solids—Tentative* (p. 320, 7).—Delete the entire paragraph following the first sentence, and substitute the following: "As the filtering medium, use a weighed piece of cotton 5″ square, of a thickness about one-half that of the layer in the ordinary 16-ounce roll of absorbent cotton. Tear a piece of the cotton off one corner and use to plug the neck of the funnel lightly. Then arrange the large piece in the funnel, and filter the sample. Pour the hot distilled H_2O in such a way that the pulp is loosened from the cotton with each addition (usually 700–800 cc of filtrate is collected). Fold the cotton and contents and remove the excess H_2O by gently squeezing the cotton while it is still in the funnel. Dry the material to constant weight at 100°".

(c) *Total Ash—Official* (p. 321, 9).—Add the following sentences to the directions: "In case of excessive swelling or foaming, add 2–3 drops of ashless olive oil, as provided in **XXXIV, 8** and **9**. Moisten the partially ashed residue and after drying on the steam bath and hot-plate ash in the muffle."

(d) *Alcohol Precipitate—Tentative* (p. 324, **21**).—Insert the following sentence in line 6: "Do not permit the alcohol precipitate to dry before transferring it from the paper."

(2) The official method for the determination of phosphoric acid (P_2O_5) in wines (**XV**, p. 166, **19**) was adopted as tentative for the same determination in fruits and fruit products. The method will read as follows:

PHOSPHORIC ACID—OFFICIAL (FIRST ACTION)

Dissolve the ash, 9, in 50 cc of boiling HNO_3 (1+9), filter, wash the paper, and determine P_2O_5 in the combined filtrate and washings as directed under **II**, 9 or 12.

XXVII. GRAIN AND STOCK FEEDS

(1) The following method for the determination of manganese in grain and stock feeds was adopted as tentative:

MANGANESE IN GRAIN AND STOCK FEEDS[1]

Ash a 5 g sample at dull-red heat in a porcelain evaporating dish. When cool, add 2 cc of H_2SO_4 and 5 cc of HNO_3. Evaporate to white fumes. If carbon is not

[1] Willard and Greathouse, *J. Am. Chem. Soc.*, 39, 2366 (1917): G. Frederick Smith Chemical Co. Publications, 1, 2nd ed., August (1933).

completely destroyed, add further portions of HNO_3, boiling after each addition. Cool slightly and add 25 cc of H_2O in which 1 cc of 85% H_3PO_4 has been dissolved. Cool, and let stand to allow precipitation of $CaSO_4$ and other insoluble matter. Filter thru a mat of acid-washed asbestos on a Gooch crucible and wash with H_2O. Evaporate to less than 50 cc and add approximately 0.3 g of KIO_4. Mix, and heat below the boiling point for 30 min., or until maximum color development. Cool, and dilute to an accurately measured volume, usually 50 or 100 cc, with H_2SO_4 (5+95). The final soln should contain not more than 2 mg of Mn and 5–15 cc of H_2SO_4 plus H_3PO_4 in 100 cc. Compare with a standard $KMnO_4$ soln in a colorimeter. Calculate p.p.m. of Mn in the sample.

Standard potassium permanganate.—Dissolve 1.4385 g of C.P. $KMnO_4$ by boiling with H_2SO_4 (5+95). Dilute to 1 liter in a volumetric flask. Standardize by titration with 0.1000 g of oven-dry $Na_2C_2O_4$, dissolved in 100 cc of H_2SO_4 (5+95), keeping the temp. above 60°. (The soln should contain 500 p.p.m. of Mn. Add 0.3 g of KIO_4. Protect from light. For a working standard dilute this soln with H_2SO_4 (5+95) to a known concentration approximately like that to be compared.

(2) The Peterson-Hughes method for the determination of carotene, and specifying the use of the spectrophotometer or the 0.1 per cent potassium dichromate standard (*This Journal*, **20**, 464) was adopted as tentative. The method follows:

CAROTENE

EXTRACTION OF CAROTENE

Weigh out the samples (1–5 g), transfer to a 200 cc Erlenmeyer flask, and to each gram of sample add 20 cc of a freshly prepared, saturated soln of KOH in ethyl alcohol. Fit the flasks with reflux condensers, and boil the contents on a steam bath or hot plate for 30 min. If portions of the sample collect on the sides of the flask, wash down with alcohol from a wash bottle. Cool the contents of the flask. (The volume of petroleum ether may be reduced by direct filtration, after cooling, thru a sintered glass funnel of No. 3 porosity. The residue should be extracted with a small portion of petroleum ether until the solvent is colorless. Proceed as outlined in the method.) Add 100 cc of Skellysolve (b. p. 60–70°), or petroleum ether, and after shaking for a minute or so and allowing the sediment to settle, decant the Skellysolve-alcohol mixture into a 500 cc separatory funnel. Repeat this procedure twice more with 25 cc portions of Skellysolve, breaking up the residue, which sometimes forms an adherent mass, by shaking with 10–15 cc of 95% alcohol. After two or three additional extractions with 20 cc portions of Skellysolve (the soln usually comes off colorless) discard the residue.

Pour gently about 100 cc of H_2O thru the alcohol Skellysolve soln in the separatory funnel. Draw off the alkaline alcohol-H_2O soln from the bottom of the funnel, and re-extract three times by shaking gently with 30 cc portions of Skellysolve, using two other separatory funnels. Combine the Skellysolve extracts and wash them with 50 cc portions of H_2O until free from alkali, as indicated by the absence of color in the wash H_2O when treated with phenolphthalein (about 10 washings). (One washing with H_2O will usually suffice since all the alkali is removed in subsequent extractions with methyl alcohol. If alkali removal is desired, the use of larger amounts of H_2O (about 100 cc) will reduce the number of washings.) Any small amount of alkali remaining will be removed by subsequent methyl alcohol and H_2O washings.

Remove xanthophyll from the Skellysolve soln by extraction with 25 cc portions of 90% methyl alcohol (90 cc CH_3OH +10 cc H_2O), shaking for 2 minutes. Continue these extractions until the wash alcohol comes off colorless. (This may

Extinction coefficients

WAVE LENGTH, Å	SKELLYSOLVE B.P. 60–70°	PETROLEUM ETHER B.P. 40–60°
4500	238	243
4550		231
4700	200	207
4800	212	212

require 6–12 washings, depending on the amount of xanthophyll in the sample.) Wash the Skellysolve soln containing the carotene twice with 50 cc of H_2O to remove the alcohol, and adjust to volume (either dilution or concentration under reduced pressure) to obtain convenient concentration for measurement of the carotene. Filter into a volumetric flask thru filter paper upon which is placed a small amount of anhydrous Na_2SO_4. After making the carotene soln up to definite volume, determine the concentration by the spectrophotometer, photoelectric colorimeter, or colorimeter by comparison with 0.1% or 0.036% $K_2Cr_2O_7$.

Table for calculating carotene

0.1% $K_2Cr_2O_7$	CAROTENE	0.1% $K_2Cr_2O_7$	CAROTENE
mm	*p.p.m.*	*mm*	*p.p.m.*
1.0	0.5	6.6	4.1
1.2	0.7	6.8	4.2
1.4	0.8	7.0	4.3
1.6	0.9	7.2	4.5
1.8	1.0	7.4	4.6
2.0	1.2	7.6	4.7
2.2	1.4	7.8	4.8
2.4	1.5	8.0	4.9
2.6	1.6	8.2	5.0
2.8	1.7	8.4	5.2
3.0	1.8	8.6	5.3
3.2	2.0	8.8	5.4
3.4	2.1	9.0	5.6
3.6	2.2	9.2	5.8
3.8	2.3	9.4	5.9
4.0	2.5	9.6	6.0
4.2	2.6	9.8	6.1
4.4	2.7	10.0	6.3
4.6	2.8	10.2	6.5
4.8	2.9	10.4	6.7
5.0	3.1	10.6	6.8
5.2	3.2	10.8	6.9
5.4	3.4	11.0	7.1
5.6	3.5	11.2	7.3
5.8	3.6	11.4	7.4
6.0	3.8	11.6	7.5
6.2	3.9	11.8	7.6
6.4	4.0	12.0	7.8

DETERMINATION

For each determination by the spectrophotometric method make optical density measurements at wave lengths of 4500, 4700, and 4800 Å.U. Using the absorption coefficients calculated for beta carotene at these wave lengths, determine the carotene concentration for each wave length, take the average and report results to 0.1 p.p.m.

Or, estimate the amount of carotene in the sample by comparing it colorimetrically against 0.1% $K_2Cr_2O_7$. Put the soln of the sample in the left-hand cup of the colorimeter and set the scale at 0.5 cm, 1 cm, 2 cm, 3 cm, or 4 cm, according to the amount of color present. Vary the depth of the dichromate soln in the right-hand cup until the density of color in both cups is equal, and make eight independent readings, recording them in mm. Average the readings. Make the dichromate readings between 4 mm and 12 mm on the colorimeter. If necessary, make a reading below 4 mm, but repeat the analysis with a larger sample.

By use of the table transform the depth in mm of 0.1% dichromate into p.p.m. of carotene. Then calculate the p.p.m. of carotene actually in the sample by use of the following formula:

$$p = \frac{\text{p.p.m. of carotene (from table)} \times \text{cc of soln}}{\text{g of sample} \times \text{cm depth of sample soln}}.$$

Report carotene of 0.1 p.p.m.

(3) The tentative method for vitamin D assay by preventive biological test (p. 351, 55) was revised as follows:

VITAMIN D ASSAY BY PREVENTIVE BIOLOGICAL TEST

(Applicable to fish and fish liver oils and their extracts, and to materials used for supplementing the vitamin D content of feeds. Not applicable to irradiated ergosterol products or to irradiated yeast unless recommended for poultry.)

This essay is a comparison under conditions specified below of the efficacy of the product under assay with the U.S.P. Reference Cod Liver Oil in controlling the ash content of the bones of growing chicks.

The basal ration is a uniform mixture in the proportions designated, of the following ingredients which have been finely ground:

BASIC RACHITIC RATION	*per cent*
Ground yellow corn	58
Wheat flour middlings or Wheat Gray shorts	25
Crude domestic acid precipitated casein	12
Calcium phosphate (precipitated)	2
Iodized salt (0.02% KI)	1
Non-irradiated yeast (7% minimum N)	2

To each kg of the above mixture add 0.2 g of $MnSO_4 \cdot 4H_2O$.

PROCEDURE

Conduct the assay on groups of chicks kept in cages provided with screen bottoms and away from sunshine or other source of actinic light that may influence calcification. Keep the cages in rooms in which wide variations in temp. are prevented (constant temp. preferred). Unless the temp. of the room is adequately controlled provide each cage with a suitable electrical heating device. Start all the birds to be used in one assay on the same day and keep all conditions of environment for all the groups in the assay uniform.

Perform the assay on groups of one- or two-day-old white Leghorn chicks as specified below. Provide for one or more negative control groups that receive no vitamin D, one or more positive control groups that receive the U.S.P. Reference Cod Liver Oil, and one or more assay groups for each product to be assayed. Have the positive control and assay groups consist of not less than twenty birds, and the negative control group consist of not less than ten birds. Make up the rations for all the groups in the assay from one batch of the basal ration. Add the Reference Cod Liver Oil to the basal ration in such quantities as to produce a measurable increase in percentage of bone ash above that obtained in the negative control group (it is not possible to make comparisons if maximum bone ash is obtained). Add the assay product to the basal ration in such quantities as to permit a direct comparison in the response of assay and positive control groups. To the basal ration of the negative control group add corn oil equal in quantity to the maximum quantity of oil fed to any group in the assay and add corn oil to the rations of the other groups until the total quantity of corn oil and oil containing vitamin D is equal to the quantity of corn oil added to the ration of the negative control group. Feed the chicks in the respective groups the prescribed ration and water (U.S.P. or distilled water) *ad libitum* for 21 days. Discard all chicks that weigh 100 g or less and all chicks that show abnormality or disease not related to vitamin D deficiency. At least fifteen chicks must remain in each reference or assay group that is used in calculating the vitamin D potency of an assay product.

Kill the chicks; remove the left tibia of each bird and clean of adhering tissue. (To facilitate removal of adhering tissue the bones may be placed in boiling H_2O for not more than 2 min. The bones may be preserved in alcohol for extraction.) Completely extract the bones with a suitable fat solvent or solvents (20 hours with hot 95% ethyl alcohol, followed by 20 hours with ethyl ether may be used, and the bones may be crushed to facilitate extraction.) Dry the extracted bones to constant weight in a moisture oven, cool in a desiccator, and weigh. Ash the moisture and fat-free bones from each group of birds in a muffle furnace to constant weight at any given temp. between 450 and 550°, or if preferred for 1 hour at approximately 850°. (The ash determination may be made on individual bones if desired.) Cool the ash in a desiccator and weigh. Use the specific procedure adopted for extraction, drying and ashing of the bones consistently throughout any one assay.

INTERPRETATION OF RESULTS

One A.O.A.C. chick unit of vitamin D is equal in biological activity for the chick to one unit of vitamin D in the U.S.P. Reference Cod Liver Oil in this method of assay. The product under assay meets its declared vitamin potency in A.O.A.C. chick units of vitamin D if the percentage of ash in the moisture and fat-free bone produced in the assay groups by a given number of units of vitamin D is equal to or greater than the percentage of ash produced by the same number of units of vitamin D from the U.S.P. Reference Cod Liver Oil.

XXVIII. MEAT AND MEAT PRODUCTS

(1) In place of the phenoldisulfonic acid method for the determination of nitrates in meat products (p. 356, **14, 15**) the following m-xylenol method was adopted as tentative:

Xylenol Method

APPARATUS

Use a simple distillation apparatus, including a distillation bulb. A glass condenser of a type utilizing a thin, rapidly moving film of H_2O as a cooling medium

(West type) is recommended. Quickly remove any nitro-xylenol solidifying in the condenser by stopping the flow of H_2O and allowing the condenser to become warm.

REAGENTS

(a) *Nitro-xylenol.*—1-hydroxy, 2, 4-dimethylbenzene. Eastman's preparation No. 1150, or equivalent.

(b) *Silver ammonium hydroxide.*—Dissolve 5 g of *nitrate-free* Ag_2SO_4 in 60 cc of NH_4OH. Heat the mixture to boiling, concentrate to about 30 cc, cool, and dilute to 100 cc with H_2O.

(c) *Bromocresol green indicator.*—Dissolve 0.1 g of bromocresol green in 1.5 cc of 0.1 N NaOH, and make up to 100 cc with H_2O.

(d) *Standard nitrate soln.*—Dissolve 0.1804 g of recrystallized KNO_3 in H_2O and make up to 1 liter, or dilute 17.85 cc of HNO_3 to 1 liter. 10 cc contains 0.25 mg of nitrate nitrogen.

DETERMINATION

Mix 5–10 g of the finely comminuted and thoroly mixed sample with 80 cc of warm H_2O. Break up all lumps and heat on the steam bath for 1 hour with occasional stirring. Transfer to a 100 cc volumetric flask, cool, make up to mark, and mix. Filter, or allow to settle, and pipet 40 cc of the filtrate, or supernatant liquid, into a 50 cc volumetric flask. (No correction for the volume occupied by the meat is necessary.) Add 3 drops of the bromocresol green indicator. Add H_2SO_4 (1+10) dropwise until the color changes to yellow. Oxidize nitrites to nitrates by adding 0.2 *N* $KMnO_4$ soln dropwise with shaking until a faint pink color remains for approximately 1 min. Add 1 cc of H_2SO_4 (1+10). Add 1 cc of phosphotungstic acid soln (20 g in 100 cc). Make up to mark, mix, and filter.

Measure into a 500 cc flask (an Erlenmeyer is satisfactory) an aliquot (not more than 20 cc) containing from 0.025 to 0.25 mg of nitrate nitrogen. (If more than 20 cc is required, make slightly alkaline and concentrate by evaporation.) Add a sufficient quantity of the silver NH_4OH soln to precipitate all chlorides and most of the excess phosphotungstic acid. (A slight excess of the silver reagent is not harmful; 1 or 2 cc is usually sufficient.) Without decanting or filtering, add a volume of H_2SO_4 (3+1) approximately three times the volume of liquid in the flask. Stopper the flask, mix, cool to about 35° C., add 0.05 cc (1–2 drops) of the m-xylenol, stopper, shake, and hold at 30–40° for 30 min.

(A yellow to brownish yellow color, indicative of nitrates, will appear. A bright red precipitate, due to incomplete removal of phosphotungstic acid, may also appear. A slight excess of phosphotungstic acid causes no interference but a large excess may do so.)

After nitration is complete, add 150 cc of H_2O, taking care to wash off the stopper, and distil until 40–50 cc has passed over into a receiver containing 5 cc of NaOH (10 g per liter). Transfer the distillate to a 100 cc volumetric flask, make up to volume with H_2O, and determine nitrate nitrogen by comparing the color of a suitable aliquot with a set of graded color standards containing 0.003–0.006 mg of nitrate nitrogen.

Prepare the color standard from 10 cc of the nitrate standard as directed previously, using 0.05 cc of the m-xylenol and 30 cc of H_2SO_4 (3+1), and making up the distillate to 500 cc. Prepare the color standard fresh each day, as it becomes cloudy on standing.

(2) In the tentative method for the determination of coagulable nitrogen (p. 360, **28**) the following change in the manner of using the indicator was adopted: In par. **28**, line 2, following the words, "Neutralize to

phenolphthalein," the following words were added: "using the indicator outside the soln to avoid subsequent interference in the determination of creatin, 31."

(3) The present tentative methods for the determination of copper and zinc in gelatin (p. 368, **64, 65**) were deleted.

(4) The following method for the determination of copper in gelatin was adopted as tentative:

COPPER

PREPARATION OF SAMPLE

Ash 20–40 g, preferably in a muffle, as directed under **XXVII, 8**, keeping the temp. low to avoid loss.

REAGENT

Standard copper soln.—0.3927 g of recrystallized $CuSO_4$ per liter. 1 cc = 0.1 mg of copper.

DETERMINATION

Moisten the ash with a small quantity of H_2O, add approximately 5 cc of HCl, and evaporate to dryness. Add 8 cc of HCl (1+1), heat to boiling, and transfer to a 50 cc Erlenmeyer flask, using enough wash H_2O to make the volume approximately 40 cc. Heat nearly to boiling, saturate with H_2S, stopper tightly, and allow to stand in a warm place for 30 min. or more. Filter into a 150 cc Erlenmeyer flask and wash promptly and thoroly with warm 1:20 HCl saturated with H_2S. Transfer the paper and precipitate to a 50 cc porcelain crucible and ignite in a muffle furnace at a temp. not exceeding that at which the gelatin was ashed. After ignition, cool, moisten ash with 1–2 cc of HNO_3, and evaporate to dryness on steam bath. Dissolve the residue in 1 cc of NH_4 acetate soln (500 g per liter). Filter into a 50 cc graduated flask, wash out crucible with warm H_2O, make up to mark, and mix. Measure out 25 cc into a 50 cc Nessler tube, add 5 cc of NH_4NO_3 soln, and make up to 50 cc. Add 0.2 cc of $K_4Fe(CN)_6 \cdot 3H_2O$ soln and mix. Match the color against tubes prepared in the same way from the standard Cu soln. Make up standards containing 2, 3, 4, 5, and 6 cc of the standard soln equivalent to 20, 30, 40, 50, and 60 p.p.m. of Cu if a 20 g sample is used and one-half of soln taken. Solutions giving a stronger reaction than 6 cc of the standard cannot be accurately compared. If a reaction stronger than that given by 6 cc of the standard is obtained, take an aliquot smaller than 25 cc and repeat the determination.

(5) The following method for the determination of zinc in gelatin was adopted as tentative:

ZINC[1]

Boil the filtrate and washings from the H_2S precipitate of Cu until all H_2S is removed. Add 1 cc of HNO_3 and continue the boiling until the volume is reduced to approximately 25 cc. Add 10 cc HN_4Cl (200 g per liter), make definitely alkaline with NH_4 hydrate, heat nearly to boiling, and filter into a 100 cc Erlenmeyer flask. Wash with warm alkaline NH_4Cl soln containing 50 g of NH_4Cl and 25 cc of NH_4 hydrate (sp. gr. 0.90) per liter. Neutralize the filtrate and washings with acetic acid, add 0.5 g of Na acetate and sufficient glacial acetic acid to make an excess of 2 cc for each 50 cc of soln. Warm the mixture on the steam bath and saturate with H_2S. Allow to stand in a warm place for approximately 30 min. Filter thru a small paper and wash thoroly with warm 1:100 acetic acid (1+1) saturated with H_2S. If the filtrate is turbid, return to flask, add a few drops of saturated $HgCl_2$ soln, shake, and

[1] *Ind. Eng. Chem.*, 15, 942 (1923).

filter again. Ignite in a tared Pt crucible at a dull red heat until completely ashed, then a few minutes at bright red heat. Weigh as ZnO. Weight of ZnO $\times$40,000 = p.p.m. of Zn if a 20 g sample was taken.

XXIX. METALS IN FOODS

(1) The colorimetric dithizone method for the determination of Pb on apples and pears (p. 391, **30**), including the following minor changes, was adopted as official (final action): Line 7, include in the parentheses the following statement: "If for the purpose of analysis the inclusion of the Pb content of stems and sepals is not desired, these may be discarded"; line 9, change "(1+49)" to "(2+99)"; line 10, delete "HNO_3 if the Pb is to be determined electrolytically, **33**)"; 6th line from end insert "exactly" after word "place," and delete "or HCl to conform to the kind of acid used in rinsing."

(2) The electrolytic determination of Pb in apple filtrate (p. 393, **33**) was changed to read as follows: "Transfer 200 cc of the acid filtrate to a separatory funnel, add the equivalent of 5 g of citric acid (**13(d)**), make ammoniacal, add 5 cc of the 10% KCN soln, extract with dithizone as directed in **16(a)**, and finally determine the Pb electrolytically as directed in **19** and **20**.

(3) The following method for the determination of selenium was adopted as tentative:

SELENIUM

PREPARATION OF SAMPLE

Place 5–10 g (dry weight) of the sample in a 600 cc Pyrex beaker or a Kjeldahl flask, add 0.5 g of HgO and a cooled mixture of 50 cc of H_2SO_4 and a volume of HNO_3 equal to 10 cc per g of sample taken. Mix thoroly and allow to stand 30 min. Heat *gently* until NO_2 fumes are no longer evolved and the soln turns to a dark brown or SO_2 fumes appear. Cool, and distil with HBr+Br_2. (The Hg can best be added in soln in HNO_3.)

ISOLATION

Add 25 cc of H_2O to the cold H_2SO_4 digest, cool again, and add 50–60 cc of HBr containing 0.5% by volume of free Br_2. Attach the flask to an all-glass distilling apparatus equipped with a thermometer and distil to 130°, keeping the receiving flask cool. If the distillate contains insoluble material, filter thru asbestos and wash. Saturate the filtrate with SO_2 gas, add 0.1 g of NH_2OH-HCl and warm on a steam bath to 80° for 15 min. Allow the mixture to cool and filter thru an asbestos Gooch or Jena glass filter No. 4 and wash. (The filtrate may be saved for recovery of HBr.)

VOLUMETRIC DETERMINATION WITH STARCH INDICATOR

Estimate the amount of the precipitate Se on the filter. (This estimate is used in determining the quantity of $Na_2S_2O_3$ soln to be added later in the titration.) Dissolve the Se in 1–2 cc of 48% HBr containing 1% by volume of Br_2, using a few drops to rinse the precipitation flask. Wash with a minimum quantity of H_2O so as to keep the volume of filtrate below 20 cc at most and at about 10 cc for amounts of Se of 20 gamma and under. Transfer the filtrate and washings to a 30 or 50 cc beaker. Prepare a few standards containing amounts of Se in the general range of the samples, and 2–3 blanks. Dilute standards and blanks to about the volume of

the samples and add the same volume of $HBr+Br_2$ as in the samples. To samples, standards, and blanks, add a strong soln of H_2SO_4 until the Br_2 color nearly disappears. (In case all the Br is reduced, add $HBr+Br_2$, dropwise until the color reappears.) Decolorize with 1–2 drops of 5% aqueous phenol. (It is desirable to reduce the color to a light yellow since tribromophenol is precipitated with excess bromine. The presence of the precipitate, while undesirable, does not ruin the determination.)

Use a stirrer and a 10 cc buret provided with an extension to dip into the soln being titrated, with the tip so constricted as to make possible the addition of the soln in 0.01–0.02 cc portions. Place the soln being titrated on a white surface with a white background and view by reflected light.

To the decolorized soln in the 30–50 cc beaker add about 1 cc of freshly prepared starch soln. Then add rapidly from a buret a moderate excess of 0.01, 0.001, or 0.0005 *N* $Na_2S_2O_3$, using the estimate of the precipitated Se as a guide. (1 cc of 0.001 *N* $Na_2S_2O_3$ is roughly equivalent to 200 gamma of Se; 1 cc of 0.001 *N* to 20 gamma; 1 cc of 0.0005 *N* to 10 gamma.)

Add about 2 cc more than the estimated equivalent of $Na_2S_2O_3$ and so select the normality as to keep the volume added between 2 and 10 cc. After about 20–30 seconds add rapidly from a buret a soln of I_2 (approximately the same strength as the $Na_2S_2O_3$ used) until a permanent blue color appears. If less than 1 cc of I_2 has been added, add 2 cc more of $Na_2S_2O_3$ and then I_2 until at least 1 cc is needed to give the blue color. Then add slowly from the dipping buret $Na_2S_2O_3$ of the same strength as before until the color is the same as a blank containing H_2O and 1 cc of starch soln.

CALCULATIONS

Add up the total volumes of I_2 and $Na_2S_2O_3$ for each determination.

Blanks.—Divide the volume of $Na_2S_2O_3$ by the volume of I_2 to get the factor for conversion of the volumes of I_2 to the equivalent volumes of $Na_2S_2O_3$. Average the results.

Standards.—Multiply the volumes of I_2 by the I_2-$Na_2S_2O_3$ conversion factor, and subtract the product from the total volume of $Na_2S_2O_3$. Divide this number into the quantity of Se in the standard to get the gamma Se/cc $Na_2S_2O_3$. Average the results.

Samples.—Calculate the volume of $Na_2S_2O_3$ used in the reduction of the Se as directed under "Standards" and multiply by the gamma Se/cc $Na_2S_2O_3$ value to get the total quantity of Se in the sample in gammas. Divide the total quantity by the weight of the sample in grams taken to get the p.p.m. of Se.

XXX. NUTS AND NUT PRODUCTS

No additions, deletions, or other changes.

XXXI. OILS, FATS, AND WAXES

(1) The official method for the determination of free fatty acids (p. 417, 30) was deleted (final action).

(2) The N.C.P.A. methods for the determination of free fatty acids in crude and in refined oils (*This Journal*, **21**, 88) were adopted as official (final action).

(3) The refractometric method for the determination of oil in flaxseed (*This Journal*, **20**, 74) was adopted as official (final action).

(4) The specifications for the titer thermometer (p. 408, **15**) were amended to conform with the revised Bureau of Standards specifications as follows: Under *Range and subdivision*, change "62°" to "66°"; under

Total length, change "350–360 mm" to "370–380 mm"; under *Distance* change "62°" to "66°"; under *Filling above mercury,* add at end of line "or vacuum"; under *Graduation,* last line, change "every 2° mark" to "each multiple of 2°"; under *Case,* change "62° C" to "66° C." These changes supersede all changes published in *This Journal,* since the 1935 revision of *Methods of Analysis.*

XXXII. PRESERVATIVES AND ARTIFICIAL SWEETENERS

No additions, deletions, or other changes.

XXXIII. SPICES AND OTHER CONDIMENTS

(1) The tentative method for the determination of volatile oil in spices (p. 447, 16) was made official for the same determination in marjoram and sage (first action).

(2) The method for the determination of ash in vinegar adopted as official (first action) last year (*This Journal,* **21,** 89) was adopted as official (final action).

XXXIV. SUGARS AND SUGAR PRODUCTS

(1) The official method (Wein) for the determination of maltose (p. 484, 54, 55) was deleted (final action).

(2) The vacuum drying method of the International Commission for Uniform Methods of Sugar Analysis (*This Journal,* **21,** 89) was adopted as official (final action).

(3) The International Scale of Refractive Indices of Sucrose Solutions at 20° C., 1936, International Sugar Journal Supplement, 39, 1–40 (1937), was adopted as official (final action).

(4) The International Temperature Correction Table, 1936, *ibid.,* was adopted as official (final action).

XXXV. VEGETABLES AND VEGETABLE PRODUCTS

(1) The method for the determination of alcohol-insoluble solids in canned peas published last year (*This Journal,* **21,** 89) and adopted as official (first action) was adopted as official (final action) with the following minor clarifying modifications:

(a) Change the title to read, "Alcohol-Insoluble Solids in Canned Peas and Canned Dried Peas."

(b) Change the 3rd sentence on p. 90 to read as follows: "Grind the drained peas in a food chopper until the cotyledons are reduced to a smooth homogeneous paste, stir, and weigh 20 g of the ground material into a 600 cc beaker."

(c) Combine the first and second complete paragraphs on p. 90 to read as follows: "Fit into a Büchner funnel a filter paper of appropriate size, previously prepared by drying in a flat-bottomed dish for 2 hours at the temp. of boiling H_2O, covering with a tight-fitting cover, cooling in a desiccator, and weighing at once. Apply suction, and transfer the contents of the beaker to the Büchner funnel in such a manner as not to run over the edge of the paper. Suck dry and wash the material on the filter with 80% alcohol until the washings are clear and colorless."

(2) The method for the determination of chlorides in tomato juice published in 1937 (*This Journal*, **20**, 78) and adopted as official (first action) in 1937 (*This Journal*, **21**, 90) was adopted as official (final action) with the following minor clarifying changes: Under Determination, 6th line, change the sentence, "Cool, wash down, etc." to the following: "Cool, wash down the funnel and neck of the flask with H_2O, and add 1 cc of nitrobenzene and 1 cc of ferric indicator."

(3) The official method for preparation of sample (p. 497, **2**) was extended to include canned fruit and was clarified by requiring tilting of the sieve during drainage and turning of all pieces to permit draining of cups or cavities.

XXXVI. VITAMINS

No additions, deletions, or other changes.

XXXVII. WATERS, BRINE AND SALT

The statement in **14(c)**, p. 506, "0.0001 mg of N as NO_2" was changed to read "0.0001 mg of N" (final action).

XXXVIII. RADIOACTIVITY

No additions, deletions, or other changes.

XXXIX. DRUGS

(1) The following microchemical tests for the identification of berberine, cotarnine, narceine and narcotine were adopted as tentative:

BERBERINE, COTARNINE, NARCEINE, AND NARCOTINE

REAGENTS

(a) *Platinic chloride soln.*—Dissolve 5 g of $H_2PtCl_6 \cdot 6H_2O$ in 100 cc of H_2O.

(b) *Mercuric chloride soln.*—Dissolve 5 g of $HgCl_2$ in 100 cc of H_2O.

(c) *Wagner's soln.*—Dissolve 1.25 g of I and 2 g of KI in 5 cc of H_2O and dilute to 100 cc.

(d) *Potassium ferrocyanide soln.—Freshly prepared.* Dissolve 5 g of $K_4Fe(CN)_6 \cdot 3H_2O$ in 100 cc of H_2O.

(e) *Potassium hydroxide soln.*—Dissolve 5 g of KOH in 100 cc of H_2O.

(f) *Hydrochloric acid.*—5%.

(g) *Ammonium hydroxide.*—10%.

(h) *Zinc potassium iodide soln.*—Dissolve 5 g of Zn acetate and 20 g of KI in 100 cc of H_2O.

IDENTIFICATION

Place a drop of the alkaloidal soln on a clean glass slide, add a drop of reagent by means of a clean glass rod, and without stirring or covering examine under the microscope, using low power (a magnification of 100–150 is suitable). Note the kind of crystals formed and compare their characteristics with a control specimen of the alkaloid in the same dilution.

Characteristics of microchemical tests for alkaloids

ALKALOID	REAGENT	DESCRIPTION OF CRYSTALS
Berberine	Hydrochloric acid	Saturated soln., fine yellow needles (Avoid excess reagent)
Cotarnine	Platinic chloride	1:200 hair-like crystals, yellow and curving
	Mercuric chloride	Colorless, long, branching needles
	Potassium ferrocyanide	Acidified with 1 drop of 5% HCl; globules that develop into dense, burr-shape crystals; also amber-brown plates
Narceine	Wagner's or zinc potassium iodide	1:400 blue, radiating needles, sometimes with yellow dichroism
	Platinic chloride	Beautiful, feathery rosettes develop in all solns
Narcotine	Potassium hydroxide or ammonium hydroxide	1:200 white amorphous precipitate, which crystallizes slowly; dense rosettes of needles

(2) The status of the microchemical methods for the identification of the alkaloids named below was advanced from tentative to official (first action):

Aconitine	Ephedrine	Quinidine
Apomorphine	Ethylmorphine	Quinine
Arecoline	Ethylhydrocupreine	Scopolamine
Benzylmorphine	Homatropine	Sparteine
Brucine	Hydrastine	Strychnine
Caffeine	Hydrastinine	Theobromine
Cinchonidine	Hyoscyamine	Theophylline
Cinchonine	Nicotine	Yohimbine
Cocaine	Papaverine	
Codeine	Procaine hydrochloride	

(3) The following microchemical tests for the identification of diallylbarbituric acid, mandelic acid, and sulfanilamide were adopted as tentative:

DIALLYLBARBITURIC ACID, MANDELIC ACID, AND SULFANILAMIDE

REAGENTS

(a) *Sodium nitrite.*—10%. Dissolve 10 g of $NaNO_2$ in H_2O to make 100 cc.

(b) *Benzaldehyde.*—N.F. quality.

(c) *Lead acetate.*—Dissolve 5 g of U.S.P. Pb acetate in H_2O to make 100 cc.

(d) *Mercurous nitrate.*—U.S.P. $HgNO_3$ test soln.

(e) *Lead triethanolamine.*—Add 1 cc of triethanolamine to a soln of 1 g of U.S.P. Pb acetate in 20 cc of H_2O.

(f) *Barium hydroxide.*—Saturated soln in H_2O.

(g) *Hydrochloric acid.*—0.1 *N*.

PREPARATION OF SAMPLE

Separate the compound in pure form. Use portions of the purified compound to make solns or to test directly as specified for the individual synthetic.

Controls.—For comparison treat a known sample as directed in the tests.

IDENTIFICATION

To a drop of a soln of the compound or to about 1 mg of the powder on a glass

slide, add a drop of the specified reagent. Do not stir unless directed. Without covering, examine for crystal formation under the microscope, using about 100× magnification. Observe the characteristics of the crystals and compare with controls and description.

Characteristics of microchemical tests for synthetics

SYNTHETIC	FORM	CONCENTRATION OF SYNTHETIC	REAGENT	DESCRIPTION OF TESTS AND CRYSTALS
Diallyl-barbituric acid	Dry powder	—	Lead triethanolamine	Stir a small quantity of the synthetic into a drop of the reagent. Rods singly and in clusters
	Dry powder	—	Barium hydroxide	Stir a small quantity of the synthetic into a drop of the reagent. Rods singly and in groups
Mandelic acid	Water soln	1–100	Lead acetate	Rosettes of thin curving plates
	Water soln	1–100	Mercurous nitrate	Burr-shaped groups of needles
Sulfanilamide	Dry powder	—	Benzaldehyde	Stir thoroly a small amount of synthetic into a drop of reagent. 4-sided plates
	0.1 *N* HCl soln	Saturated soln	Sodium nitrite	Yellow needles

(4) The following modifications in reagents for synthetics were adopted: On p. 605, change par. **180(b)** to read as follows: "Prepare as directed under **26(c)**"; change par. **180(h)** to read as follows: "Prepare as directed under **II, 7(c)**"; change par. **180(i)** to read as follows: "Prepare as directed under **176(j)**"; change par. **180(m)** to read as follows: "Prepare as directed under **176(b)**."

(5) The status of the methods for the microscopical identification of the synthetic substances named below was advanced from tentative to official (first action):

Acetanilid
Acetophenetidin
Acetylsalicylic acid
Aminopyrine
Amytal
Antipyrine
Barbital
Benzocaine
Benzoic acid
Cinchophen
Dinitrophenol
Methenamine
Neocinchophen
Phenobarbital
Hydroxyquinoline sulfate
Pyridium
Salicylic acid
Triethanolamine

(6) The following method for the determination of hypophosphites in sirups was adopted as tentative:

HYPOPHOSPHITES IN SIRUPS

(Not applicable in the presence of other reducing agents or of phenolic compounds.)

REAGENTS

(a) *Bromide-bromate soln.*—Prepare as directed in **26(c)**, p, 551.
(b) *N Sodium thiosulfate.*—0.1 *N*. Prepare as directed in 3(b).
(c) *Potassium iodide.*—20 g per 100 cc.
(d) *Sulfuric acid.*—10 g per 100 cc.
(e) *Starch soln.*—0.5 g per 100 cc.

DETERMINATION

Transfer 50 cc of the sirup, measured in a 50 cc volumetric flask, to a 250 cc volumetric flask. Wash the 50 cc flask with several portions of H_2O, adding the washings to the 250 cc flask, finally making up to the mark with H_2O, and mixing well. (This procedure is followed in the case of the sirup of ammonium hypophosphite. For sirups containing larger quantities of hypophosphites the original 50 cc may be diluted to 500 cc in a volumetric flask.) Transfer a 50 cc aliquot to a 250 cc volumetric flask and make up to the mark with H_2O, again mixing well. Of this solution, transfer a 50 cc aliquot to a glass-stoppered 250 cc flask, add 50 cc of the bromide-bromate soln and 20 cc of the H_2SO_4; stopper, shake well, and let stand for 2 hours. Add 10 cc of the KI soln, shake the flask, and titrate the liberated I with the $Na_2S_2O_3$ soln until a straw color appears; then add 2 cc of the starch soln and titrate until the soln becomes colorless. Conduct a blank determination in the same way.

1 cc of 0.1 *N* $Na_2S_2O_3 = 0.00165$ g of H_3PO_2.

1 cc of 0.1 *N* $Na_2S_2O_3 = 0.00208$ g of $NH_4H_2PO_2$.

(7) The method published last year (*This Journal*, **21**, 536) for the determination of hexylresorcinol was adopted as tentative.

(8) The method for the determination of methoxyl groups (see p. 100) was adopted as tentative for the evaluation of guaiacol and guaiacol carbonate with the following factors: 1 cc 0.05 *N* thiocyanate = 1.034 mg of guaiacol; 1 cc 0.05 *N* thiocyanate = 1.143 mg of guaiacol carbonate.

(9) The following methods for the determinations of acetylsalicylic acid, acetophenetidin, and caffeine were adopted as tentative:

ACETYLSALICYLIC ACID, ACETOPHENETIDIN, AND CAFFEINE

REAGENTS

(a) *Sulfuric acid.*—2%. Pour about 6.0 cc of H_2SO_4 into 500 cc of H_2O.

(b) *Sodium bicarbonate soln.*—Use freshly prepared. Add 3 g of $NaHCO_3$ to 45 cc of H_2O previously cooled to 15°. Stir until dissolved and add 2–3 drops of 10% HCl.

DETERMINATION

Acetylsalicylic acid.—Make this determination as soon as possible to prevent any hydrolysis in the $NaHCO_3$ soln.

Weigh sufficient powdered sample to represent at least 0.04 g of caffeine, transfer to a separator containing about 10 cc of H_2O cooled to 15°, and shake thoroly. Add 15 cc of the cooled $NaHCO_3$ soln slowly to prevent mechanical loss due to effervescence and immediately extract with successive portions of $CHCl_3$. Wash each portion of $CHCl_3$ thru a second separator containing 2 cc of the $NaHCO_3$ soln and filter thru a funnel containing a pledget of cotton moistened with $CHCl_3$. (Extraction is complete when a final shakeout evaporated to dryness leaves a negligible residue. Usually 5 extractions with about 30 cc portions of $CHCl_3$ are sufficient.) Set aside the combined $CHCl_3$ extracts containing the caffeine and

acetophenetidin for later treatment. Transfer the wash H_2O in the second separator to the soln in the first separator, rinsing several times with small portions of H_2O. Acidify the combined $NaHCO_3$ solns with HCl (1+1) and extract the acetylsalicylic acid by shaking with successive portions of $CHCl_3$, filtering each portion thru a funnel containing a pledget of cotton moistened with $CHCl_3$ (usually 5 extractions are sufficient). Evaporate the combined $CHCl_3$ extracts on a steam bath with the aid of a fan or gentle air blast until the volume is about 10 cc. Transfer to a suitable small tared container with the aid of $CHCl_3$ and evaporate to dryness by means of a fan or gentle air blast without heat. Dry in a desiccator overnight and weigh as acetylsalicylic acid. The extracted acetylsalicylic acid may be checked by the A.O.A.C. bromination method or by the double titration method (p. 551, **27** or **28**).

Acetophenetidin and caffeine.—Evaporate the $CHCl_3$ soln containing the acetophenetidin and caffeine on the steam bath and transfer, when the volume reaches 5–10 cc, to a 100 cc beaker by means of small portions of $CHCl_3$. Evaporate again to a volume of about 5 cc and add 10 cc of 2% H_2SO_4. Introduce a stirring rod and heat the mixture on the bath until all the $CHCl_3$ has evaporated, stirring occasionally. Cool to room temp. and decant thru a tared Gooch crucible previously dried to constant wt. at 100°. (No suction is required.) Collect the filtrate in a 150 cc beaker, retaining as much of the acetophenetidin as possible in the beaker. Rinse the sides of the beaker containing the acetophenetidin with 5–10 cc of $CHCl_3$, add 10 cc of 2% H_2SO_4, and heat on the bath as before until all the $CHCl_3$ has evaporated. Cool, and decant thru the same crucible as before. Repeat the process with another 10 cc portion of the H_2SO_4, and finally wash the acetophenetidin quantitatively into the crucible with H_2O. Wash the beaker and crucible with H_2O until the filtrate measures about 75 cc. Dry the crucible at 100° and weigh the acetophenetidin.

To the filtrate containing the caffeine and the small amount of acetophenetidin that went into soln (usually about 0.075 g), add 8 cc of H_2SO_4 (1+10) and evaporate on the steam bath to a volume of about 10 cc. Transfer by means of small portions of H_2O to a 50 cc Erlenmeyer flask previously marked for volumes of 5 and 10 cc. Proceed as directed in **16, 17,** bearing in mind that the hydrolysis must be continued until no odor of acetic acid is present. The hydrolysis is hastened somewhat if the flask is allowed to hang in the steam from a wire wrapped around its neck so that the mouth of the flask is about level with the surface of the bath. (About 3 evaporations are usually sufficient.) Add the weight of acetophenetidin obtained to the weight of acetophenetidin collected in the Gooch crucible to obtain the total acetophenetidin content of the sample.

(10) The following qualitative tests for the identification of the following gums were adopted as tentative: acacia, agar, galagum, Irish moss, karaya, quince, starch and tragacanth:

IDENTIFICATION OF GUMS

REAGENTS

(a) *Chlorzinc iodide.*—To 100 cc of a soln of $ZnCl_2$, sp. gr. 1.8, add a soln of 10 g of KI and 0.15 g of I in 10 cc of H_2O. (Keep a few crystals of I in the soln.)

(b) *Ruthenium red.*—To a few cc of a 10% soln of Pb acetate add enough ruthenium red to produce a wine red color.

(c) *Methylene blue.*—0.1% soln in alcohol.

(d) *Methylene blue.*—0.1% soln in H_2O.

PREPARATION OF SAMPLES

Controls.—Moisten 1 g of the dry gum with alcohol, add 100 cc of H_2O with constant stirring, and bring to a boil. To 5 or 10 cc of the resulting liquid or jelly, add 4 volumes of 95% alcohol, mix, and centrifuge to bring the precipitate together as a compact mass. (Some gums, notably acacia and agar, may fail to be thrown down by this treatment. The addition of a few drops of a saturated salt soln should cause rapid flocculation and settling.)

Jellies or lotions.—Stir, and add H_2O if necessary to produce a fluid mass. Treat a portion of the sample with 95% alcohol to precipitate the gum as directed under *Controls.* Remove fatty or oily material, if present, by washing the precipitated gum with ether, then redissolve in H_2O and re-precipitate.

PROCEDURE

With a clean towel squeeze a small lump of the alcohol precipitate obtained as directed under *Preparation of Sample* against a microscope slide to form a mat 4–8 mm in diameter on the slide. Note the character of the resulting mat as a possible index to the type of gum. Quince and Irish moss form thin and rather translucent films while agar, starch, and acacia are white and opaque. Cover the mat with a large drop of the chlorzinc iodide soln and observe carefully both with and without magnification. For direct examination place the slide upon a white surface. For microscopical examination use a magnification of about 90 diameters. If no characteristic color is produced within 1–2 min, proceed with a fresh mat to examine for the following group. Continue in a similar manner through all the group tests or until the identity is established. Use a fresh mat for each individual test.

Characteristics of tests for gums

Group I.—Reagent Chlorzinc iodide

GUM	ORIGINAL ALCOHOL PPT.	GROUP REACTION	CONFIRMATORY TEST	REMARKS
Tragacanth	Stringy bluish Translucent	Blue color	Warm with 10% NaOH on steam bath Yellow color	Certain gums, e.g., Irish moss, may yield dull yellow color with NaOH. Tragacanth bright yellow
Starch	White Compact	Blue black color	Iodine, 0.1 *N* Blue color	Tragacanth may yield faint blue
Quince	Stringy Translucent	Blue color	Above tests negative	Quince is distinguished from starch and tragacanth by negative reactions
Irish moss	Stringy	Brown (small blue particles)	Characteristic nodular structures with group reagent	Old preparations of this gum may fail to show characteristic structures

Group II.—Reagent Tincture of Iodine U.S.P.
(Allow tincture to dry on mat, flush off with 95% alcohol, and irrigate with water.)

Agar	White opaque	Opaque blue black	Stains with Ruthenium red	Does not dissolve or lose shape when covered with H_2O
Irish moss	Stringy	Brown or lilac	Characteristic blue stain with alcoholic methylene blue	These reactions yielded by old as well as fresh preparations

Group III.—Reagent Ruthenium Red

Karaya	Fine flocculent compact mass on centrifuging	Swells considerably Strongly stained pink granular mass	Heat with conc. HCl. Pink color	Aqueous methylene blue produces a characteristic blue stain

Group IV.—Reagent Concentrated H_2SO_4
(Warm cautiously on steam bath.)

Galagum	Stringy	Pink or red brown color	No satisfactory test found	The alcohol precipitate from galagum resembles that from tragacanth
Acacia		Greenish brown	Ppt. completely soluble in H_2O	The complete soln of acacia distinguishes it from most other gums

(11) The present tentative method for the determination of theobromine in theobromine calcium (p. 590, 137) was retained in that status, and the following method was adopted as a tentative, alternative method:

THEOBROMINE IN THEOBROMINE CALCIUM—TENTATIVE

INDICATOR

Phenol red.—Triturate 0.1 g of phenol red in an agate mortar with 15 cc of 0.02 *N* NaOH until dissolved and dilute the soln with recently boiled H_2O to 200 cc.

DETERMINATION

Place 0.5 g of the powdered tablets, previously dried at 110°, or 0.4 g of theocalcin powder, or 0.2 g of theobromine alkaloid in a 300 cc beaker and add 100 cc of H_2O. Warm moderately over a flame and add 15 cc of approximately 0.1 *N* H_2SO_4. Heat to boiling to insure complete soln and to remove CO_2. Cool to room temp. Add 1.5 cc of phenol red indicator and render slightly alkaline with approximately 0.1 *N* H_2SO_4 (yellow color). To this soln add 25 cc (an excess) of neutral 0.1 *N* $AgNO_3$ and titrate the liberated HNO_3 immediately with 0.1 *N* NaOH to a distinctly violet red color. Titrate cautiously drop by drop with constant stirring near the end point.

1 cc of 0.1 *N* NaOH = 0.018 g of $C_7H_8O_2N_4$.

(12) The following method for the determination of chlorobutanol (chloretone) was adopted as tentative:

CHLOROBUTANOL

REAGENTS

(a) *Alcoholic potassium hydroxide soln.*—Prepare as directed in 106(a).

(b) *Silver nitrate soln.*—Dissolve 10 g of $AgNO_3$ in sufficient H_2O to make 500 cc.

DETERMINATION

Transfer to a pressure bottle a sample equivalent to about 0.3 g of chlorobutanol and carefully add 25 cc of the alcoholic KOH soln. Stopper the bottle, and mix the contents by gentle swirling, taking care to prevent the soln from coming in contact with the rubber washer, then allow to stand 30 min. or overnight. Place the bottle in a wire basket, and set the basket in a water bath at room temp. Invert a tin can over the bottle and cover with a towel to prevent injury in case the bottle should burst. Heat the bath to boiling and maintain at this temp. for 15 min.

Cool gradually; add 25 cc of H_2O, swirling gently; and transfer the contents of the pressure bottle to a 400 cc beaker. Wash the bottle with H_2O, draining the washings into the beaker. Add 15 cc of HNO_3, an excess of the $AgNO_3$ soln, stir well, and allow the mixture to stand in a dark place for 15 min. Collect the precipitate in a Gooch crucible that has been dried at 105° and weighed. Wash the precipitate thoroly with distilled H_2O, then with 5 cc of alcohol followed by a 5 cc portion of ether. Dry to constant weight at 105°. If reagents contain Cl, apply correction determined thru a blank test. 1 g of AgCl = 0.4127 g of $C_4H_7OCl_3$.

In ampoule solns.—Pipet into a distilling flask a sample equivalent to about 0.1 g of chlorobutanol. Add sufficient H_2O to bring the volume to 50 cc and distil about 25 cc thru a straight-bore condenser. Collect the distillate in a pressure bottle of approximately 100 cc capacity containing 25 cc of the alcoholic KOH and surrounded by an ice bath. Have the delivery tube extend into the alcoholic soln. (It is essential that a straight-bore condenser be used to assure complete soln of the crystals of chlorobutanol in the condenser.) Allow to cool, disconnect the still head, and wash the condenser carefully with 25 cc of alcohol, allowing the alcohol to drain into the pressure bottle. Repeat the washing, using about 20 cc of H_2O. Also wash the receiving tube with H_2O.

Stopper the pressure bottle and mix the contents by gentle swirling, taking care to prevent the soln from coming in contact with the rubber washer. Allow to stand 30 min. or overnight. Complete the determination of Cl as directed above.

(13) The following method for the separation of acetylsalicylic acid and phenolphthalein was adopted as tentative:

ACETYLSALICYLIC ACID AND PHENOLPHTHALEIN IN TABLETS

PREPARATION OF SAMPLE

Count and weigh a representative number of tablets and calculate the average weight. Powder finely in a mortar and keep in a tightly stoppered bottle.

DETERMINATIONS

Weigh sufficient of the powdered material to contain from 0.05 to 0.1 g of phenolphthalein. Extract the dry powder repeatedly with 20 cc portions of ether and filter into a separator. Test for complete extraction (5–8 extractions required).

Acetylsalicylic Acid.—Shake the ethereal soln for at least 1 min. each time with two 20 cc portions of 4% $NaHCO_3$ soln (temp. 20° or less). Transfer the soln to a second separator. Wash the ether with two 10 cc portions of H_2O and add to the

bicarbonate soln. Extract the bicarbonate soln with 20 cc of ether. Draw off the lower aqueous layer into a 100 cc volumetric flask. Wash the ether with small portions of H_2O, rinse into the flask, and dilute to the mark. Add the wash ether to the bulk of the solvent in the original separator. Reserve the ethereal soln for the determination of the phenolphthalein.

Transfer an aliquot of the bicarbonate soln containing not less than 0.3 g of acetylsalicylic ac d to a separator. The acid must be isolated from the bicarbonate soln as rapidly as possible to prevent hydrolysis. Acidify with 10% HCl and extract the liberated acetylsalicylic acid with a 3+2 $CHCl_3$-ether mixture (30, 20, 20, 10, and 10 cc fractions). Wash each extraction with 2 cc (used for all extractions) of H_2O in a second separator and filter thru a pledget of cotton moistened with the solvent into a counterpoised tared beaker. Test for complete extraction. Evaporate the solvent to a volume of 10–15 cc on the H_2O bath and complete the evaporation without the aid of heat. Dry the residue to constant weight at room temp. The weight may be checked by the double titration method (28).

Phenolphthalein.—Extract the original ethereal soln with 20 cc portions of 3% NaOH soln until all the phenolphthalein has been removed as indicated by the color. Transfer these alkaline extracts to a second separator, acidify with 10% HCl, and extract with $CHCl_3$-ether solvent. Wash each portion of solvent in a third separator with 2 cc of H_2O to which has been added 1 or 2 drops of 10% HCl. Filter the extracts into a counterpoised tared beaker, using in the stem of the funnel a pledget of cotton moistened with the solvent. Evaporate the solvent on the H_2O bath and dry the residue to constant weight at 120°. The weight may be checked by the tetraiodo method (p. 569, 78).

(14) The following method for the determination of cod liver oil in emulsions was adopted as tentative:

COD LIVER OIL IN EMULSIONS

Weigh into a tared beaker of about 150 cc capacity sufficient of the well-mixed sample to contain about 2 g of cod liver oil. Add about 10 g of finely powdered $CaCO_3$ and thoroly mix with a stirring rod. Add 30 cc of $CHCl_3$, thoroly mix, and decant thru a dry filter into a 100 cc air-dried, tared beaker. Continue to extract and wash repeatedly with 5–10 cc portions of $CHCl_3$ until the filtrate is about 60 cc. Evaporate the $CHCl_3$ on a steam bath with a current of air to about 5 cc.

Continue extraction and carefully wash the filter paper and funnel, filtering into a 250 cc beaker until the filtrate is about 150 cc. Evaporate to about 10 cc and transfer to the first tared beaker. Repeat the procedure until extraction is complete or until 25 cc of the solvent upon evaporation in a second tared beaker yields 0.001 g or less of residue.

Evaporate the $CHCl_3$ in the first tared beaker and allow to remain on the steam bath for about 10 min. after the odor of $CHCl_3$ has disappeared. Dry in the oven at not over 100° for 5 min. intervals until weight is constant or the loss is 0.001 g or less.

CAUTION: Avoid prolonged heating or long exposure to air at room temp. The oil absorbs oxygen, the weight increases appreciably, and the physical constants change.

(15) The following method for the determination of mercury in ointment of mercuric nitrate was adopted as tentative:

MERCURY IN OINTMENT OF MERCURIC NITRATE (CITRINE)

Transfer to a 200–300 cc Erlenmeyer flask 3–5 g of the sample accurately weighed, using a glass or bone spatula. Add 40 cc of HNO_3 (1+1) and a few glass beads and insert a short-stemmed funnel into the neck of the flask. Boil gently 1–1.5 hours on

a hot plate or over a low flame. With the latter use a piece of asbestos having a circular hole under an asbestos wire gauze. Add 30 cc of H_2O, using a part to wash the funnel. Cool sufficiently to cause the unconsumed fat to form a hard cake (approx. 20° or below). Filter thru an 11 cm filter into a 200 cc volumetric flask. Wash the fat, flask, and filter, using about 100 cc of 1% HNO_3. Make to volume and mix well. Reserve the fat for test for complete extraction as directed below.

Transfer a 100 cc aliquot to a 500 cc Erlenmeyer flask. Add 7 cc of HNO_3, 5 cc of H_2SO_4, and 2 g of powdered permanganate, and rotate to dissolve. Heat just to boiling over a low flame or on a hot plate. Boil gently 45 min., maintaining an excess of permanganate, indicated by a dark purple color. (The presence of an excess throughout this period is essential.) When adding permanganate to the boiling liquid use smaller portions (approx. 0.5 g or less) to avoid loss due to frothing. (The use of a greater excess of permanganate than is necessary is not objectionable except that it will require proportionately more of the peroxide to remove it and the MnO_2 at the end of the digestion. Usually about 10 g is required.)

CAUTION: The rate of consumption and total permanganate consumed seem to vary with the temp., the organic matter present, and the period of heating. Furthermore, the large amount of MnO_2 formed may lead to the wrong conclusion concerning the color indicative of an excess of permanganate. Frequent examination of the soln is necessary. The observation of this color is aided by looking through the supernatant liquid toward a white background while holding the container in an inclined position.

Remove excess permanganate and dissolve MnO_2 by adding H_2O_2 (5–10% prepared from 30%) dropwise to the hot soln. When colorless add 2% $KMnO_4$ soln slowly until a faint pink or brown persists for about 1 min. If a large amount of MnO_2 forms at this point, use the peroxide sparingly again, then permanganate to discharge the peroxide. Discharge the color from the last permanganate, including a weak brown color from MnO_2, by adding dropwise just sufficient ferrous sulfate T.S. Cool to about 20°, add 3 cc of ferric $(NH_4)_2SO_4$ T.S. and titrate with the standard thiocyanate.

1 cc of 0.1 *N* thiocyanate = 0.01003 g of Hg.

Test for complete extraction of the Hg from the fat and its removal from the filter, etc., by repeating the 1+1 HNO_3 digestion for about 30 min. on the residual fat in the flask or on the filter, completing this as a separate determination, including the permanganate digestion. Add any titration in excess of 1 to 2 drops (approximately 0.05 to 0.08 cc) of 0.1 *N* NH_4CNS resulting from this test portion to that obtained by titrating the main extract.

(16) The following method for the determination of sulfanilamide was adopted as tentative:

SULFANILAMIDE

Place on a 9 cm folded filter paper in a funnel a portion of the sample containing about 0.5 g of sulfanilamide. Wash the soluble portion with a fine stream of acetone into a 250 cc flask, using a total of about 25 cc of acetone. Test for complete extraction by evaporating a small portion of the washings. Immerse the flask in a H_2O bath at about 70° until the acetone has been evaporated and its odor is no longer perceptible. Remove from the bath and add 10–12 cc of 75% (by volume) H_2SO_4. Connect the flask to a reflux condenser with water jacket, add a few glass beads, and boil the soln slowly for 30 min. Wash down the condenser with H_2O, make the liquid in the flask to about 100 cc with H_2O, add an excess of 50% alkali, distil, and collect the ammonia in the distillate in an excess of 0.1 *N* H_2SO_4. Titrate the excess acid with 0.1 *N* NaOH, using methyl red indicator.

1 cc of 0.1 *N* $H_2SO_4 = 0.01722$ g of $(NH_2)_2C_6H_4SO_2$.

(17) The following methods for the qualitative and quantitative determination of mandelic acid were adopted as tentative:

MANDELIC ACID

Qualitative Tests

(Applicable to the free acid)

(a) Dissolve 0.25 g of the sample in about 10 cc of H_2O and add a few drops of 10% $FeCl_3$ soln. A bright yellow color is produced. This is a general test for hydroxy acids and is not specific for mandelic acid.

(b) Dissolve 0.25 g of the sample in 5 cc of H_2O in a test tube; to the soln add 5 cc of H_2SO_4 and agitate the test tube and contents for a few seconds; then add 10 cc of H_2SO_4 so as to form two layers. Agitate very gently but do not mix. A purple color slowly forms at the interface if the test tube is allowed to stand for a few minutes. A strong odor of benzaldehyde is noticed on shaking.

Quantitative Methods

Tablets.—Count and weigh a representative number of tablets, ascertain the average weight, and grind to a fine powder. Weigh a quantity of the powdered material equivalent to from 0.4 to 0.5 g of mandelic acid and transfer to a separator containing 10 cc of H_2O. Acidify with HCl (1+3) and add 2 cc of the acid in excess. Extract with six 20 cc portions of chloroform-ether solvent (2+1); wash each portion in a second separator with 2 cc of H_2O, and pass the soln thru a plug of cotton, previously saturated with the solvent, into a 250 cc beaker. Wash the outer surface of the stem of the separator with a few cc of solvent and add this to the main portion. Test for complete extraction with 15 cc more of solvent and evaporate in a separate beaker. Wash any residue thus obtained into the beaker containing the main extract with a few cc of solvent.

Evaporate to dryness at a temp. not exceeding 40° with the aid of a fan. Dissolve the residue in 25 cc of CO_2-free distilled H_2O and titrate with 0.1 *N* NaOH, using phenolphthalein as indicator.

1 cc of 0.1 *N* NaOH = 0.01521 g of mandelic acid ($C_6H_5CHOHCOOH$), 0.01691 g of NH_4 mandelate ($C_6H_5CHOHCOONH_4$), 0.01741 g of Na mandelate ($C_6H_5CHOHCOONa$), 0.01711 g of Ca mandelate $(C_6H_5CHOHCOO)_2Ca$, or 0.01632 g of Mg mandelate $(C_6H_5CHOHCOO)_2Mg$.

After titration the mandelic acid may be re-extracted and the extract used for melting point determinations or qualitative tests.

Liquid preparations.—Measure 1 cc of the sample or such amount of an aliquot of a dilution sufficient to yield from 0.4 to 0.5 g of mandelic acid into a separator and acidify with HCl(1+3). Proceed as directed above for tablets.

(18) The official method for the determination of camphor (p. 560, 51) was amended (first action) by the insertion, between the title and the text, of the following expression in parentheses: "(Not applicable to synthetic camphor)."

(19) The method for the determination of bismuth compounds in tablets (p. 592, 143) was amended by the deletion of the expression "(Lead Absent)" and the substitution of the expression, "Not applicable in the presence of lead compounds but applicable in the presence of cerium salts." The method was further amended by the insertion before the present text of the following paragraph:

Count and weigh a suitable number of tablets and ascertain their average weight. Pulverize the tablets and preserve the powder in a tightly stoppered bottle.

(20) The last paragraph in Method II (p. 576, **97**) was transposed to constitute a second paragraph in Sec. **96**, p. 576, and the status of this paragraph was advanced to that of official (first action).

(21) The directions for preparing reagents in the microchemical tests for alkaloids and synthetics (p. 602, **176**; p. 605, **180**) were amended as follows:

(1) The words "Potassium thiocyanate" in par. **180(l)** were changed to read "Ammonium thiocyanate."

(2) The reagent for ethylhydrocupreine, "potassium thiocyanate" (e) (*This Journal*, **20,** 80) was changed to read "ammonium thiocyanate."

(3) The directions for preparing Wagner's reagent (p. 543 **5(b)** and p. 605, **180(d)**) were deleted and the statement, "Prepare as directed in 176 **(c)**" was substituted.

(22) The tentative method for the determination of chloroform in mixtures (p. 579, **105**) was amended as follows:

(1) The quantity of calcium carbonate used as a reagent was changed from 1.0 g to 0.1 g.

(2) The use of carborundum chips to prevent bumping was permitted.

(3) The term "pressure bottle" was substituted for that of "citrate bottle."

(4) The following caution was inserted:

CAUTION: Do not cool the pressure bottle suddenly. It is best to allow it to cool in the H_2O in which it was boiled.

(5) The reagent, alcoholic potassium hydroxide, **104** (a), was deleted, and the reagent alcoholic potassium hydroxide, **106 (a),** was substituted therefore.

(6) The method (after amendments) was retained in its tentative status.

(23) The official method for the determination of barbital and phenobarbital (p. 582, **112**) was amended (first action) by the addition at the end of par. **112** of the following expression: "Determine the melting point to check the purity of the residue."

(24) The methods for the determination of phenolphthalein (p. 569, **77, 78**) were amended as suggested by the associate referee as follows:

(1) In par. **77,** line 1, change "0.1 g" to "0.2 g" (first action).

(2) In par. **79,** line 4, p. 570, after "10 cc each," insert the expression "(or sufficient to represent about 0.2 g of phenolphthalein)."

(3) In par. **80,** line 4, p. 570, delete the sentence, "Then make alkaline . . . the process three or four times," and substitute the following sentences:

If sufficient I has been added, the precipitate, as well as the supernatant liquid, will be brown; if not, add more I to insure an excess, and then the strong KOH soln

dropwise, with stirring, to dissolve the precipitate completely and consume all the excess I. (This soln should be blue or blue-purple.) Repeat the process of precipitation with strong acid and resolution with strong alkali 3 or 4 times with small quantities of the reagents, adding small pieces of ice if necessary to keep the soln cold. In the acid condition there should be a brown precipitate resembling a periodide, and the supernatant liquid should be colored brown by the excess I. (The alkaline soln should be clear blue or purple-blue, and no precipitate should be present.)

(25) The method for the determination of thymol (p. 571, **84**) was adopted as official (final action).

(26) The tentative methods for the assay of the following drugs were adopted as official (first action): Aloin (p. 567, **75**); barbital and phenobarbital (applicable in presence of stearic acid), (p. 582, **113**); dinitrophenol and its sodium compound (*This Journal*, **20**, 82); ether (p. 584, **120**); homatropine in tablets (*This Journal*, **21**, 95); iodoform and iodoform gauze (p. 594, **148, 150**); morphine in sirups (p. 586, **125**); phenolsulfonates (p. 597, **161**); thymol in antiseptics (p. 572, **85**); and santonin in mixtures (p. 588, **129**).

XL. BACTERIOLOGICAL METHODS

No additions, deletions, or other changes.

XLI. MICROCHEMICAL METHODS

The following method proposed by the referee for the determination of methoxyl (*This Journal*, **20**, 292), was adopted as tentative:

METHOXYL AND ETHOXYL GROUPS

REAGENTS

(a) *Acetic acid-potassium acetate soln.*—Dissolve 10 g of K acetate in sufficient glacial acetic acid to make 100 cc of soln.

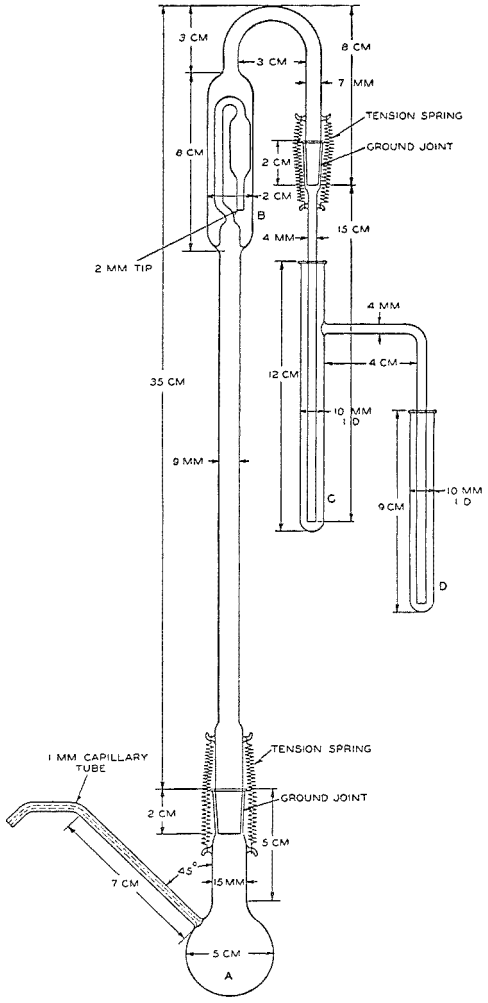
(b) *Sodium acetate soln.*—Dissolve 25 g of crystalline Na acetate in sufficient H_2O to make 100 cc of soln.

(c) *Approximately* 0.05 *N thiosulfate soln.*—Boil 2.5 liter of H_2O until 1/5 has evaporated, cool to about 75°, and then add the necessary thiosulfate and 20 cc of amyl alcohol (byproduct from alcoholic fermentation). Allow to cool and standardize against a standard KIO_3 soln.

DETERMINATION

To 5 cc of the K acetate soln, add 15 drops (ca. 0.2 cc) of Br_2, and place 2/3 of this liquid in receiver C and the remainder in D. Then weigh approximately 20 mg of substance upon a tared piece of cigarette paper (15×25 mm) and place both the paper and the contents in the bottom of boiling flask A, together with a boiling rod. (A glass tube approximately 60 mm long, 3.5 mm o.s. diameter with a 1 mm bore. It is sealed at one end and also closed about 10 mm from the other. The open end is fire polished. When this rod is placed in the flask with the open end down it will cause uniform boiling indefinitely if sufficient heat is constantly applied to the flask.) Add 2.5 cc of melted phenol from a wide-tipped pipet and 5 cc of HI and then connect the flask to the remainder of the apparatus, which consists of the trap (B), containing a little H_2O, and the receivers C and D. Pass CO_2 thru the apparatus

from the capillary side arm of the boiling flask at a uniform rate of 15 cc per min., and boil the liquid by means of a mantled micro burner at such a rate that the vapors of the boiling liquid rise about half way in the air condenser. Continue the boiling for 30–60 min. (If the type of substance is known to require only 30 min., this



SEMI-MICRO ZEISEL METHOXYL APPARATUS

period should be used, but for materials about which such information is lacking an hour should be used as a general procedure.) Disconnect the apparatus and wash the contents of the receivers into a 250 cc Erlenmeyer flask containing 5 cc of Na acetate soln. Adjust the volume of the liquid to 100 cc and reduce the excess Br_2 with formic acid (approximately 15 drops is sufficient).

Remove any Br_2 vapor in the flask by drawing air over the liquid from a vacuum

line or by blowing air over the liquid, then add 0.5 g of KI and 5 cc of 10% H_2SO_4 soln. Titrate the liberated I with the thiosulfate soln, using starch as an indicator.

Obtain the blank on all the reagents by making a determination without a sample and subtract this from the quantity of thiosulfate soln used when the sample was present. 1 cc of 0.05 *N* thiosulfate = 0.2586 mg of methoxyl (OCH_3).

The same procedure applies to ethoxyl groups. 1 cc of 0.05 *N* thiosulfate = 0.3754 mg of ethoxyl (OC_2H_5).

XLII. REFERENCE TABLES

No additions, deletions, or other changes.

APPENDIX I. STANDARD SOLUTIONS

(1) The following method submitted by the referee for the standardization of acid solutions with borax was adopted as official (first action).

STANDARDIZATION OF ACID SOLUTIONS WITH BORAX[1]

REAGENTS

(a) *Methyl red indicator.*—Dissolve 100 mg of methyl red in 60 cc of alcohol and dilute with H_2O to 100 cc.

(b) *Sodium borate.*—U.S.P. quality or better and should pass the following purity tests:

(1) *Insoluble impurities soln of 5 g of salt in 95 cc of warm H_2O.*—Should be clear and colorless.

(2) *Chloride.*—20 cc of 5% soln must not give an opalescence with HNO_3 and $AgNO_3$ that is stronger than 20 cc of a Cl soln that has a strength of 5 mg of Cl per liter.

(3) *Sulfate.*—20 cc should give no precipitate with acetic acid and $BaCl_2$ after standing 30 min.

(4) *Calcium.*—20 cc of the hot soln should give no turbidity with NH_4 oxalate after cooling.

(5) *Magnesium.*—20 cc of soln must not give any microcrystalline precipitate with ammonia and phosphate after standing 24 hours.

(c) *Reference soln.*—Prepare a reference soln of boric acid, NaCl, and indicator corresponding to the composition and volume of the soln at the equivalence point. For use in the determination of the end point of a titration with 0.1 *N* acid, the reference soln should be 0.1 *M* in boric acid and 0.05 *M* in NaCl.

(d) *Standard borax.*—Saturate 300 cc of H_2O at 55° (not higher) with borax (approximately 45 g). Filter at this temp. thru a folded filter into a 500 cc Erlenmeyer flask. Cool the filtrate to approximately 10°, with continuous agitation during the crystallization. Decant the supernatant liquid. Rinse the precipitate once with 25 cc of cold H_2O. Dissolve the crystals in just enough H_2O at a temp. of 55° to insure complete soln (approximately 200 cc). Re-crystallize by cooling to approximately 10°, agitating the flask during crystallization. Filter the crystals onto a small Büchner funnel with suction. Wash the precipitate once with 25 cc of ice-cold H_2O. Dry the crystals[2] by washing with two 20 cc portions of 95% alcohol, drying after each washing with suction. Follow with two successive 20 cc portions of U.S.P. ether. Spread the crystals on a watch-glass, and set aside for about 12 hours in order that the last traces of ether may evaporate. Protect the borax from dust. Allow the $Na_2B_4O_7 \cdot 10H_2O$ to stand about 12 additional hours in a desiccator over a soln saturated with respect to both sugar and salt before use. Then transfer the pure borax into a container that has a ground-glass stopper and store in the desiccator when not in use (stable under these conditions for 1 year).

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[1] Kolthoff, *Volumetric Analysis*, II, 93–96 (1929).
[2] Hurley, F. H., *Ind. Eng. Chem. Anal. Ed.*, 8, 220 (1936).

STANDARDIZATION

Accurately weigh sufficient of the standard borax to titrate approximately 40 ml and transfer to a 300 cc flask. Add 40 cc of CO_2-free H_2O and stopper the flask. Swirl gently until the sample is in soln. Add 4 drops of the methyl red indicator and titrate with the soln that is being standardized to the equivalence point as indicated by the reference soln. Calculate the normality (N) of the standard soln by the following formula:

$$N = \frac{\text{g of } Na_2B_4O_7 \cdot 10H_2O}{\text{ml of acid} \times 190.72/1000}.$$

(2) The following method for the standardization of acid solutions with sodium carbonate was adopted as official (first action).

STANDARDIZATION OF ACID SOLUTIONS WITH SODIUM CARBONATE

REAGENTS

(a) *Methyl orange indicator.*—0.1% of H_2O.

(b) *Sodium bicarbonate.*—C.P. Should pass the following tests for purity:

(1) *Chloride.*—0.5 g of $NaHCO_3$ dissolved in 10 cc of 2 N HNO_3 (free of Cl). With $AgNO_3$ must give no opalescence.

(2) *Sulfate.*—0.5 g of $NaHCO_3$ in 10 cc of 2 N acetic acid. After the addition of $BaCl_2$ should give no turbidity or separation of $BaSO_4$ after standing 15 min.

(c) *Reference soln.*—80 cc of CO_2-free H_2O with 3 or 4 drops of methyl orange indicator.

(d) *Anhydrous sodium carbonate.*[1]—Heat 250 cc of H_2O to 80° and add $NaHCO_3$, stirring until no more dissolves. Then filter the soln thru a folded filter (the use of a hot water funnel is desirable) into an Erlenmeyer flask. Cool the filtrate to about 10° with constant swirling during crystallization. The fine crystalline trona and bicarbonate that separates out has the approximate composition: Na_2CO_3; $NaHCO_3$, $2H_2O$. Pour off the mother liquor. Drain the crystals by suction and wash once with cold H_2O.

Transfer the precipitate, being careful not to include any fibers of filter paper, into a large flat-bottomed dish. Heat in an electric oven with a pyrometer control at a temp. of 290° for 1 hour. Stir the contents occasionally with a Pt wire. After heating, cool the Pt dish and contents in a desiccator. Store the anhydrous Na_2CO_3 in a container having a ground-glass stopper and in a desiccator containing a good desiccant. Dry the salt at 120° just before using.

STANDARDIZATION

Accurately weigh sufficient anhydrous Na_2CO_3 to titrate approximately 40 ml and transfer to a 300 cc Erlenmeyer flask. Add 40 cc of H_2O to dissolve the salt. Add 3 drops of the methyl orange indicator and titrate[2] until the color begins to deviate from the H_2O tint (reference soln). (The equivalence point has not been reached.) Boil the soln gently 2 min., then cool. Titrate until the color is barely different from the H_2O tint (of the indicator).

Calculate the normality (N) of the standard soln by the following formula:

$$N = \frac{\text{g of } Na_2CO_3}{\text{ml of acid} \times 53/1000}.$$

[1] Kolthoff, *Volumetric Analysis*, II, 88 (1929).
[2] *Ibid.*, p. 86.

(3) The tentative methods for the preparation and standardization of solutions of sodium hydroxide (681, 1) were adopted as official (first action).

(4) The tentative methods for the preparation and standardization of hydrochloric acid solutions (682, 5) were adopted as official (first action).

APPENDIX II. DEFINITIONS OF TERMS AND INTERPRETATION OF RESULTS ON FERTILIZERS AND LIMING MATERIALS

See p. 45 for the definitions adopted as official this year.

No report was given by the Committee on Standard Scale for Immersion Refractometer.

REPORT OF COMMITTEE TO COOPERATE WITH THE AMERICAN PUBLIC HEALTH ASSOCIATION ON METHODS OF MILK ANALYSIS

At the 1937 meeting of this Association your Committee reported that a revision of the chemical section of "Standard Methods of Milk Analysis" of the American Public Health Association for the 7th edition of that text was practically completed; it remained only to make such changes or additions as were adopted at that meeting touching the subject matter of the revised text. These changes were made and the manuscript duly forwarded.

Publication of the revision by that Association has been delayed, and the text is not yet published. It will probably be thought advisable to make such further changes in the manuscript as may be necessitated by actions taken at our sessions just ending.

In addition to these periodic revisions your Committee deems it to be within the intent and purpose of its work to advise with members and committees of the American Public Health Association to the end that, not only the methods of analysis for milk and cream, but those for other commodities in which that association and ours have a mutual interest shall be the same in the two groups. The desirability of such uniformity is too obvious to need elaboration. What appears to be a sound and workable plan is already in operation. It permits of three procedures.

1. A mutual transfer of methods from one association to the other in case of methods that are already accepted by one or the other body, and where further work of a collaborative nature is unnecessary.

An illustration of this procedure is the transfer of our methods for milk and cream to the A.P.H.A. book of methods without change and the reciprocal transfer of the A.P.H.A. method for visible dirt in milk from their methods to ours.

2. Because of overlapping membership in the two associations it is sometimes possible to have one and the same referee serve both groups.

An illustration of this is the case of our General Referee on Vitamins, who serves both associations in that capacity.

3. A general referee in the A.O.A.C. may have associates and/or collaborators in the A.P.H.A.

An instance of this plan of procedure is the adoption of the phosphatase test by the A.O.A.C. last year, the test being developed primarily by an A.P.H.A. worker, but duly appointed as an associate to our General Referee on Dairy Products.

In all of these modes of operation the rules of the A.O.A.C. governing the adoption of methods are followed strictly. Transfers or recommendations for adoption of methods are subject to the consideration of the A.O.A.C. referee concerned, thereafter to review and approval or disapproval by the Committee on Recommendations of Referees, and finally to action of our association. Moreover, there is no conflict with the rules of the A.O.A.C. in the appointment of A.P.H.A. members as referees, associates or collaborators because such members are, by virtue of their work and office, potential members of our association.

E. M. Bailey
F. C. Blanck
G. G. Frary

Approved.

REPORT OF REPRESENTATIVES ON THE BOARD OF GOVERNORS OF THE CROP PROTECTION INSTITUTE

The annual address of the President (Dr. C. C. McDonnell) of this Association in 1937 was devoted to a discussion of the "Role of Chemistry in Combating the Insect Menace." The facts presented in this address emphasized quite strongly the importance of chemistry in the protection of crops from insect ravages. Coupled with the fact that chemistry plays an equally important role in the protection of crops from plant diseases and also with the fact that this Association's work was really responsible for the inauguration and development of insecticide and fungicide chemistry, you can appreciate the reasons for this Association's connection with the Crop Protection Institute. In fact, it might also indicate that this Association has some obligation to actively promote chemistry in the Institute's program.

The role played by a balanced and proper nutrition of plants on the prevention of disease and insect attacks emphasizes the importance of chemistry in the control program. This, coupled with the relationship that well nourished crops bear to the health of the consumer, makes these problems of vital concern to this Association.

Many of the Institute's research projects pursued in recent years were inspired by the desire of both professional and commercial interests to

find insecticides and fungicides that would be harmless to the consumers of food products and meet the tolerance permitted by the Federal and State Boards of Health. The search for products to conform to these specifications has presented for tests and chemical examinations many extracts, organic and synthetic compounds, and factory by-products.

In addition to the chemical studies of these materials required for the direct and immediate objective, the studies in many instances have necessitated biochemical investigations as to the physiological effects that the applications or sprays may produce on the plant and also as to the effect the soil accumulations of the residues may have on plant nutrition.

The Crop Protection Institute has two classes of projects in progress; viz: regular and exploratory or preliminary.

The preliminary or exploratory projects are undertaken for the purpose of determining if a material is worth more extensive study, and not with any idea of appraising its value. In many instances the preliminary study uncovers promising materials, and in others the results show that it would be unwise to expend more time or expenses in pursuing it further. The Institute has conducted exploratory projects during the past year for twenty-one commercial organizations. Some of these have developed into regular projects.

ACTIVE, REGULAR, ORGANIZED PROJECTS

During the past year the Institute has conducted regular projects for eight commercial organizations. In some instances there have been several projects for one company.

The Institute plans the project, selects the leader, and locates the work with the object of procuring, in the maximum degree, results which will advance some scientific knowledge and be a help and guide to the supporting company.

Dr. W. C. O'Kane, the Director of the Institute, should be commended for the high research standards and policy that have been established and followed by the Institute and for the worth-while results and scientific contributions which it has made.

We recommend that the members of this Association cooperate whereever possible in promoting the Crop Protection Institute's program, and make chemistry a real force in solving the many problems presented for solution.

H. J. PATTERSON
W. H. MACINTIRE

Approved.

REPORT OF SECRETARY-TREASURER

Again we have broken the record in regard to attendance at our meetings, with a registration of 553.

Last Spring before my trip to Europe I called the Executive Committee together, and Miss Lapp was made Acting Secretary and Treasurer in my absence. The deposit box for the Association's bonds (all of these are registered bonds) was in Miss Lapp's name personally. There was a desire to change this arrangement, which was done, and the Association box (which is now quite a valuable box) was registered in the name of the Association of Official Agricultural Chemists, Incorporated, with Miss Lapp as custodian.

During the year the President, on the advice of the Executive Committee, made one appointment, that of K. L. Milstead, Associate Referee on Iodine and Thiosulfate Solutions. Owing to retirement from public work, Dr. J. F. Snell of Canada submitted his resignation. He was Associate Referee on Maple Products.

Shortly after the meeting of 1937 the Association suffered a serious loss in the death of Dr. Richard Brackett, a loyal member of the Association for many years. The obituary was written by Dr. MacIntire, and this was published in the May, 1938, number of *The Journal.* Three other valuable members died during the year: Dr. Street, Dr. Chesnut, and Dr. Cavanaugh. All of you knew Dr. Street and Dr. Chesnut. Dr. Cavanaugh was head of the Agricultural Chemistry Department at Cornell but had not been active in the work of the Association in recent years. Later Dr. Browne will present comments on these departed members.

The usual routine business was transacted at the meeting of the Executive Committee. On matters other than those contained in the report of the Treasurer it seems unnecessary to go into much detail here. One matter that I should like to report to you is the action taken by the Committee on the splendid report and recommendation of a committee appointed last year to outline a plan for a memorial to Dr. Wiley. This project has been talked about for a number of years. The memorial lectures were conceived first. These lectures will require one more year to complete a series of ten, and it is the purpose of the Committee on completion to bind the reprints into a volume for distribution among the members.

However, since the membership of the Association changes it was thought wise to change the type of lectures and to plan for another memorial to the man who was the founder of this organization. This committee was instructed to bring in a plan or plans for fellowships, memorial fellowships in agricultural chemistry. The committee, composed of Dr. W. H. MacIntire, Chairman; Dr. W. B. White, and Dr. E. M. Bailey, submitted to the Executive Committee two plans, one for an undergraduate scholarship endowment and one for a graduate scholarship endowment. The Committee, after much serious debate, decided to adopt and approve the recommendations for the undergraduate scholarships. The report of the Fellowship Committee in regard to these awards will follow my report.

I will say that we have the money to meet this obligation, and that the Committee considers this project one of stimulating interest in the field of agricultural chemistry, which is important to this Association. Mr. Chairman, I recommend the approval of this action by the Executive Committee. I think it would be quite appropriate if you ask that this report be accepted and approved. (Approved.)

I shall present at this time the financial part of the report of the Secretary-Treasurer. As I have told you before, some four years ago the business affairs of the Association had reached a point where it was found necessary to incorporate the Association of Official Agricultural Chemists. The officers elected now constitute the Board of Directors of the Association. We have an annual audit of our business operations by a public accountant. I shall read the statement of Mr. Bisselle, the auditor. Later you will have the report of our own auditing committee.

STATEMENT OF CASH RECEIPTS AND DISBURSEMENTS
FOR THE YEAR ENDED SEPTEMBER 30, 1938

Balance, October 1, 1937:			
Lincoln National Bank		$ 4,950.01	
Montgomery Building Association		81.86	$ 5,031.87
RECEIPTS			
Sales:			
Methods		$ 7,148.35	
Journals		4,944.11	
Wiley's Principles		46.50	
Reprints		106.75	
		$12,245.71	
Less: Discounts Allowed	$1,426.15		
Refunds	51.62	1,477.77	
Net Sales			10,767.94
Other Income:			
Advertisements		$ 454.70	
Interest on Investments		392.42	
Over and Short		9.97	
Total Other Income			857.09
Miscellaneous Receipts:			
Federal-American Bank, Liquidating Dividend		$ 11.08	
Returned Checks Made Good		58.00	
Books Ordered Through Association		742.19	
Total Miscellaneous Receipts			811.27
			$17,468.17

DISBURSEMENTS

Expenses:		
Salaries	$ 1,200.00	
Postage	547.00	
Meeting and Association Expenses	185.90	
Stationery and Supplies	81.50	
Auditing	150.00	
Premiums, Employees' Bonds	10.00	
Safe Deposit Rental	3.30	
Exchange	4.03	
Printing and Binding	4,275.48	
Freight	76.39	
Notary Fees	10.00	
Total Expenses		$ 6,543.60
Miscellaneous Disbursements:		
Books Ordered Through Association	$ 835.10	
Returned Checks	48.75	
3 U. S. Treasury Bonds	3,065.63	
U. S. Savings Bonds ($5,500 at Maturity)	4,125.00	
Total Miscellaneous Disbursements		8,074.48
Balance, September 30, 1938:		
Lincoln National Bank	$ 2,764.55	
Montgomery Building Association	85.54	2,850.09
		$17,468.17

BALANCE SHEET AS AT SEPTEMBER 30, 1938

ASSETS

Current Assets:			
Cash in Banks:			
Lincoln National Bank	$2,764.55		
Montgomery Building Association	85.54	$ 2,850.09	
Accounts Receivable	$3,499.46		
Less: Reserve for Doubtful Accounts	120.80	3,378.66	
Inventories		4,801.36	
Total Current Assets			$11,030.11
Investments:			
Home Owners Loan Corporation Bonds		$ 1,000.00	
Federal Land Bank Bonds		6,000.00	
United States Treasury Bonds		7,000.00	
United States Savings Bonds		4,125.00	
Total Investments (Par Value)			18,125.00

Cash in Closed Banks:		
Federal-American Bank & Trust Company	$ 25.85	
Commercial National Bank	96.34	122.19
Furniture and Fixtures		97.26
Total Assets		$29,374.56
SURPLUS		
Balance, October 1, 1937	$25,873.23	
Add: Net Profit, for the Year	3,559.33	
	$29,432.56	
Less: Adjustment for Returned Checks Entered Twice	58.00	
Balance, September 30, 1938		$29,374.56

Approved.

W. W. SKINNER

H. R. Kraybill: I am sure it is a satisfaction to all the members of the Association to see the excellent financial condition of the Association, and I am sure, Dr. Skinner, that all of the members appreciate very much the excellent service that you have given to the Association. As there was a time when we were not in as good a financial condition as we are now, we can appreciate this service a great deal.

REPORT OF COMMITTEE ON FELLOWSHIPS

To perpetuate the memory of Doctor Harvey W. Wiley, Chief of the Bureau of Chemistry, 1884 to 1912, and for 23 years Secretary of the Association of Official Agricultural Chemists, it is proposed that this Association establish

THE WILEY MEMORIAL AWARDS

These awards have two objectives (a) to stimulate undergraduates to enter the field of chemistry in its relation to agriculture, and (b) to encourage research upon problems within the scope of the Association's activities. The awards are to be made in accord with the following outline.

Procedure for Selection of Designates

Undergraduate Awards.—Respective awards of $300, $200, and $100 each will be made annually for the three best presentations, either as theses, compilations, or resumes that may be offered upon any one of the subjects dealt with in the several chapters of the Association's *Methods of Analysis.* Any member of the current senior class in any accredited college or university of North America shall be eligible to compete for the award on the following basis.

The faculty of the Department of Agricultural Chemistry or chemists of any accredited college or any university in North America shall be privileged to submit one competitive paper and to nominate its author as a candidate for the award.

The nominee so selected shall be from among those seniors in that institution who shall have presented competitive papers. The authors of the first, second, and third best contributions from the several institutions shall receive the first, second, and third awards, and each of these competitive papers shall become the property of the A.O.A.C. The contributions must be in the hands of the Secretary of the A.O.A.C. on or before August 1 of the current year. Announcement of the awards will be made at the succeeding annual meeting and in the columns of appropriate chemical and other scientific journals.

Suggested Method for Selection of Designates

Decision as to the Wiley Memorial Awards for undergraduate competitive papers and selection of the designate shall be made through a standing committee of five (5) to be designated by the President of the Association from its membership for that specific purpose, and a majority of that committee shall be requisite for a decision. Should such a majority vote of the committee not be accorded a competitive paper, the paper or the nominee receiving more than one vote within the standing committee shall be cited to a committee of three appointed by the President of the Association and the decision of this special committee shall prevail. Except for the foregoing qualification, the award of the standing committee shall be final. The right to publication of the thesis presented by the recipient of the award shall be reserved to the Editorial Board of the Association of Official Agricultural Chemists.

In the establishment of an appropriate and permanent memorial to Doctor Wiley two objectives are covered in the foregoing outline. The three awards to undergraduates are adequate to encourage participation by students in chemistry and such participation would undoubtedly stimulate an interest in chemical problems that relate to agriculture. A compilation of the names of the designates proposed by the several institutions would be useful to those who contemplate employing recent graduates. Moreover, the contributions submitted and brought together from so many different sources would undoubtedly be useful to referees and to collaborators in carrying out the work of the Association.

The total expense per annum to the A.O.A.C. would be $600.

W. H. MacIntire, Chairman
W. B. White
E. M. Bailey

No report was given by the Committee to Cooperate with other Committees on Food Definitions, as no meeting of this committee had been held. (See following notice of the appointment of a new Food Standards Committee by Secretary of Agriculture Wallace.)

FOOD STANDARDS COMMITTEE

Secretary of Agriculture Henry A. Wallace recently approved the recommendation of the Food and Drug Administration for the appointment in that organization of a Food Standards Committee, which will function under the terms of the Food, Drug, and Cosmetic Act of June 25, 1938.

It is the intention of the Food and Drug Administration to perpetuate the food standards committee that has functioned in promulgating administrative standards for the last 25 years, reports W. G. Campbell, Chief. This committee has consisted of representatives from the Association of Official Agricultural Chemists; the Association of Dairy, Food and Drug Officials of the United States; and the U. S. Department of Agriculture.

Members of the new committee are:

For the Association of Official Agricultural Chemists: C. D. Howard, Director and Chief, Division of Chemistry and Sanitation, State Board of Health, Concord, N. H.; Guy G. Frary, State Chemist, Vermillion, S. D.

For the Association of Dairy, Food and Drug Officials of the United States: J. J. Taylor, State Chemist, Department of Agriculture, Tallahassee, Fla.; Mrs. F. C. Dugan, Director, Bureau of Foods, Drugs and Hotels, State Board of Health, Louisville, Ky.

For the Food and Drug Administration: W. B. White, Chief, Food Division; W. S. Frisbie, Chief, Division of State Cooperation.

Mr. Joseph Callaway has been appointed Secretary of the committee.

The duties of the committee will be to formulate definitions and standards both of identity and of quality, including fill of container, after consideration of all of the data—analytical and inspectional—deemed essential to support them. The committee will meet in the Food and Drug Administration at Washington at intervals to review the data which have been assembled, draft tentative standards, and then upon the conclusion of public hearings, required by the act, make its final recommendations. Under the new act these definitions and standards when promulgated by the Secretary will have the full force and effect of law.

The first committee to consider food standards was one appointed by the Association of Official Agricultural Chemists in 1897. This committee was originally headed by Dr. Harvey W. Wiley. By virtue of the Congressional appropriation act of June 3, 1902, the Department of Agriculture was authorized to investigate food standards and the Association of Official Agricultural Chemists' committee was named for this purpose. This committee was supplemented in 1905 by the appointment of a representative of the Association of Dairy, Food and Drug Officials. The tripartite form of the committee was established as the result of a general conference between State and Federal food and drug officials held in November, 1913.

REPORT OF AUDITING COMMITTEE

The public accountant's audit of the books of the Association of Official Agricultural Chemists, Inc., as of September 30, 1938, was examined by the Committee and found to be correct. Verification was also made of the bonds on deposit.

GORDON HART
F. HILLIG

Approved.

REPORT OF THE COMMITTEE ON NECROLOGY

Since our previous meeting the Association has lost by death four distinguished members, all of them closely identified for many years with agricultural chemical work in the United States. Two of these departed colleagues, Richard Newman Brackett and John Phillips Street, were former Presidents of our Association, and their work was of such an outstanding character that their passing deserves more than a passing notice.

The life and work of Doctor Brackett have been pictured so sympathetically by his friend, Dr. W. H. MacIntire, in the last May number of our *Journal* that there is nothing which can be added to his sketch in the way of eulogy or appreciation. It was exactly 38 years ago, on November 16, 1900, that Richard Brackett attended for the first time a meeting of our Association. This was immediately after his appointment as assistant chemist at the Agricultural Experiment Station of Clemson College, S. C. His active participation in the work of the Association did not begin, however, until 1910, when he became Acting Professor of Chemistry and Acting Chief Chemist of the Fertilizer Division at Clemson. From that date until his retirement in 1932 he was a constant attendant at our meetings and an ardent promoter of all its varied activities. His inspiring presence at our annual gatherings and his beautiful spirit of friendly cooperation are fresh in the memories of nearly all of us.

Less known to the present generation of agricultural chemists but no less influential in its day was the work of John P. Street, who from 1890 until his retirement from agricultural chemical work in 1918 rarely missed a meeting of this Association. Those of us whose memories go back 30 and 40 years will recall the dynamic force which Street injected into the work of our meetings as reporter and referee on methods of fertilizer analyses, as member and chairman of numerous committees, as president of the Association at the memorable Jamestown Exposition Meeting in 1907, as member of the boards of editors of our *Journal* and of the revision of our *Methods of Analysis* and in numerous other ways. He served as Major in the World War, and upon his discharge in 1919 severed his connection as Chemist of the Connecticut Experiment Station to become Director of Inspection of the National Canners Association in Indiana. With this change in vocation Street's work as agricultural chemist and as member of this Association came to an abrupt end. It was a source of regret that thereafter we saw him no more at our annual meetings. During the last 17 years of his life up to the time of his death he was Secretary of the Association of New York State Canners, Inc. He passed away on September 22, 1938, at the age of 69 years. His outstanding services to our Association during 28 eventful years of its history will be commemorated by a more comprehensive sketch in a future issue of *The Journal.*

Another member of our Association whose presence will be greatly missed at our annual meetings is Victor King Chesnut who died on August 29, 1938, at the age of 71 years. He was born at Nevada City, Calif., June

28, 1867, and graduated from the University of California in 1890. After a brief period as instructor in chemistry at the University of California he served from 1894 to 1904 as botanist of the U. S. Department of Agriculture in charge of poisonous plant investigations. From 1904 to 1907 he was chemist of the Montana Experiment Station and from 1907 to 1927 a member of the chemical staff of the U. S. Bureau of Chemistry. From 1927 until his retirement in 1933 he was associated with the work of the U. S. Food and Drug Administration. Mr. Chesnut is best known for his investigations on poisonous plants and for his collaborations in plant chemistry with the late Dr. Frederick B. Power, with whom he was coauthor of numerous publications on the volatile constituents of apples, peaches, grapes and the cotton plant and on other phytochemical subjects. The official Power-Chesnut method of our Association for determining caffeine was one of the outstanding results of this cooperation. Mr. Chesnut from 1895 until his recent death was a frequent attendant at the meetings of our Association, in the work of which he took a deep interest. His genial nature won him a host of friends in both chemical and botanical circles.

The fourth death among our membership which your committee has to record is that of George Walter Cavanaugh. He was born at Watertown, N. Y., on February 4, 1870 and died on July 2, 1938, at the age of 68 years. He graduated from Cornell in 1896 and immediately thereafter became assistant in agricultural chemistry at the Cornell University Experiment Station. He was promoted to the professorship of agricultural chemistry at Cornell in 1905 and held this position until his retirement in 1937 when the chair which he occupied was abolished. Professor Cavanaugh began attendance at our meetings in 1902, at which time he presented a report as referee on dairy products. He was also appointed Referee on Dairy Products and Associate Referee on the Adulteration of Vegetables for the 1903 meeting of the Association. Although not an attendant of our conventions during the past 20 years, Professor Cavanaugh had a wide acquaintance among agricultural chemists of the United States who will long cherish the memory of his kindly amiable personality.

I move you, Mr. President, that this report be published in the Proceedings of our Association and also that we rise for a moment as a token of respect to the memory of these departed members.

C. A. BROWNE
H. C. LYTHGOE

Approved.

REPORT OF NOMINATING COMMITTEE

The Committee on Nominations wishes to present the following candidates:

President: W. S. Frisbie, U. S. Food and Drug Administration, Washington, D. C.

Vice-President: L. B. Broughton, College Park, Md.

Secretary-Treasurer: W. W. Skinner, U. S. Bureau of Chemistry and Soils, Washington, D. C.

Additional Members of the Executive Committee: J. W. Sale, Washington, D. C.; G. G. Frary, Vermillion, S. Dak.; J. O. Clarke, Chicago, Ill.; *Post-Officio:* H. R. Kraybill, Lafayette, Ind.

H. H. HANSON
H. A. LEPPER
W. H. MACINTIRE

A unanimous vote was cast for the officers nominated.

REPORT OF COMMITTEE ON RESOLUTIONS

Whereas, the Fifty-Fourth Annual Meeting of the Association of Official Agricultural Chemists is being concluded; and

Whereas, an unusually large attendance has profited by a comprehensive and instructive program; be it

Resolved, that we express to our president, Dr. H. R. Kraybill, our appreciation of his excellent presidential address and his able and courteous direction of our proceedings as our presiding officer.

Resolved, that we express to Dr. L. M. Tolman, our appreciation of his masterly Wiley Memorial Address, "The History and Development of Food Inspection in the United States."

Resolved, that we extend our thanks to those members who have assisted the president by presiding over our several sectional meetings and to all referees and associate referees.

Resolved, that we extend our thanks to our Secretary, Dr. Skinner, to Miss Lapp, to Mr. Frisbie, and to all their associate workers, for the careful thought and attention given by them to insure the interest of members and guests and the success of the meeting.

Resolved, that, through our Secretary, we extend our thanks to the management of the Raleigh Hotel for their cooperation and courtesy.

W. CATESBY JONES
GEORGE H. MARSH

Approved.

CONTRIBUTED PAPERS

DETERMINATION OF VOLATILE FATTY ACIDS AS AN APPROACH TO THE EVALUATION OF SPOILAGE IN CANNED HERRING ROE

By FRED HILLIG (Food Division,* Food and Drug Administration, Department of Agriculture, Washington, D. C.)

In previous communications there was described a modification of the Dyer method (itself a modification of the well-known Duclaux procedure)

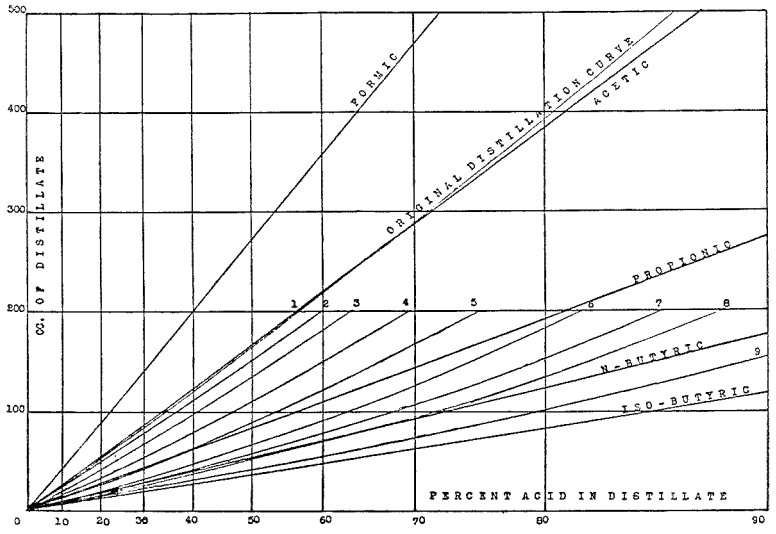


FIG. 1.—FRACTIONATION OF VOLATILE ACIDS FROM HERRING ROE, CODE 4

for the determination of volatile fatty acids[1] and the application of this method to the determination of volatile fatty acids in canned salmon and tuna fish[2] as an approach to the problem of evaluating spoilage.

The work has now been extended to cover the determination of volatile fatty acids in canned herring roe, and the purpose of this paper is to present the facts developed.

As in the case of salmon and tuna fish, it was found that canned herring roe prepared from the freshest possible raw material contains small quantities of volatile fatty acids. When spoilage begins the quantity of volatile fatty acids is increased, and as decomposition progresses there is likewise a progressive increase in these acids.

An attempt was then made to identify the individual acids comprising the acid mixture. A quantity of volatile fatty acids was obtained by steam

* W. B. White, Chief.
[1] *This Journal*, 21, 684 (1938).
[2] *Ibid.*, 688.

distilling a clarified water extract of the roe (see under "Method"). A distillation curve (Curve 1, Figure 1) was prepared, and the acids were fractionated according to the procedure given in the previous report.[2]

TABLE 1.—*Analysis of canned herring roe*

CAN NO.	CODE 1		CODE 2		CODE 3		CODE 4	
	FORMIC ACID NUMBER	VOLATILE ACID NUMBER	FORMIC ACID NUMBER	VOLATILE ACID NUMBER	FORMIC ACID NUMBER	VOLATILE ACID NUMBER	FORMIC ACID NUMBER	VOLATILE ACID NUMBER
	mg./100 g.	*cc. 0.01 N/ 100 g.*	*mg./100 g.*	*cc. 0.01 N/ 100 g.*	*mg./100 g.*	*cc. 0.01 N/ 100 g.*	*mg./100 g.*	*cc. 0.01 N/ 100 g.*
1	Trace	6.1	0.97	15.2	2.22	25.1	3.96	72.9
		6.0	1.01	14.8	2.11	24.6	3.99	73.1
2	Trace	7.1	1.40	16.3	2.22	25.1	4.09	75.2
		7.1	1.30	16.0	2.22	25.1	4.09	74.8
3	Trace	7.1	1.40	16.5	2.21	25.3	3.96	75.7
		7.3	1.30	16.5	2.11	25.0	3.99	74.6
4	Trace	7.4	1.33	16.7	2.34	29.1	4.25	78.5
		7.5	1.20	16.6	2.44	29.1	4.12	78.4
5	Trace	7.6	1.40	17.3	2.50	29.1	4.03	79.1
		7.5	1.40	17.1	2.44	29.4	4.03	80.6
6	Trace	8.1	1.27	17.8	2.50	29.9	5.03	83.9
		8.0	1.20	17.5	2.47	29.8	4.77	84.6
7	Trace	8.3	1.46	18.3	2.37	31.6	4.74	84.9
		8.3	1.46	18.0	2.37	30.8	4.51	84.1
8	Trace	8.2	1.62	20.2	3.25	38.4	4.64	87.6
		8.4	1.59	20.1	2.89	37.6	4.61	87.3
9	Trace	8.6	1.75	20.1	3.41	40.4	5.03	87.9
		8.4	1.69	20.3	3.47	41.0	4.84	87.5
10	Trace	8.6	1.69	20.1	3.92	44.2	5.75	95.7
		8.7	1.75	20.3	3.92	44.4	5.88	95.3
Av.		7.7	1.41	17.8	2.66	31.8	4.51	82.1
Min.		6.0	0.97	14.8	2.11	24.6	3.96	72.9
Max.		8.7	1.75	20.3	3.92	44.4	5.88	95.7

Curve 1 starts below the acetic acid line, intersects it, and approaches the formic acid line. Since the curve intersects the acetic acid line, formic acid and one or more acids higher in the series than acetic acid are indicated. The angle at which the curve crosses the acetic acid line indicates the presence of this acid. Since fractionation curves 8 and 9 fall below the curve for N-butyric acid, they show that the highest detectable member of the series of acids present is iso-butyric acid.

METHOD

Volatile acid number.—Pass the entire contents of a can of roe through a meat chopper three times and thoroughly mix the material after each grinding. Weigh 50 grams of this material into a 250 cc. beaker, stir it to a uniform suspension with 100 cc. of water, and then quantitatively transfer it to a 250 cc. volumetric flask. Add 2 cc. of 2 *N* H_2SO_4, dilute to 250 cc., *shake vigorously*, allow to stand 5 minutes, and filter through a folded paper. Transfer 150 cc. of the filtrate to the distillation flask, and proceed as previously directed.[2]

Formic acid number.—Proceed as previously directed.[2]

The methods were applied to four experimental packs of herring roe, with the results shown in Table 1. Code 1 was prepared from raw material of unquestionable freshness, while the succeeding codes represent progressive stages of spoilage up to and including badly tainted roe.

The results require no comments.

The procedure was then applied to seven commercial samples of herring roe, with the results given in Table 2.

TABLE 2.—*Analysis of commercial canned herring roe*

SAMPLE NO.	FORMIC ACID NUMBER	VOLATILE ACID NUMBER
	mg./100 g.	*cc. 0.01 N/100 g.*
1	2.24	24.9
2	Trace	8.9
3	Trace	13.0
4	Trace	10.7
5	Trace	12.2
6	Trace	12.8
7	Trace	11.1

SUMMARY

A method for the evaluation of spoilage in canned herring roe is presented. The procedure is simple and yields accurate, consistent results.

ESTIMATION OF CALOMEL IN COMPOUND CATHARTIC PILLS

By J. D. CURPHEY, F. A. ROTONDARO, and D. M. TAYLOR
(U. S. Food and Drug Administration, Philadelphia, Penn.)

The National Formulary VI does not give a method of assay for calomel in Compound Cathartic Pills, but the iodine method is provided for tablets of Calomel and Calomel and Soda. The basically similar A.O.A.C method for Calomel in Tablets (*Methods of Analysis*, 1935, p. 595, **151**) was tried on Compound Cathartic and products of the same type, i.e., calomel

in mixture with plant drugs, with disappointing results. They were usually high and very inconsistent. The calomel could not be satisfactorily separated from the organic matter, which consumed some of the iodine. Even after thorough washing with alcohol, ether, acidulated water, etc., pills or tablets of Compound Cathartic gave results from 1.7 to 41.3 per cent higher than those obtained by a modified gravimetric sulfide procedure.

The sulfide procedure follows:

Weigh a sufficient number of pills or tablets to give a representative average weight, then reduce to a medium fine powder. Transfer a portion of the well-mixed sample, calculated to yield 100–300 mg. of Hg, to a comparatively thick, well-packed mat of asbestos in a Caldwell crucible. Wash the sample with small successive portions of warm alcohol until the filtrate becomes colorless. Repeat the washings with ether, dilute acetic acid, alcohol, and ether. (Cautiously stir the residue in the crucible during each washing to materially shorten the number of washings necessary to obtain colorless filtrates.) Air-dry the residue by a few minutes' suction after the ether washing.

Transfer the insoluble residue and the asbestos mat to a 250 cc. centrifuge bottle and add from a pipet 200 cc. of saturated bromine water. Stopper the bottle and shake vigorously for 10–15 minutes, let stand for 5–10 minutes, then again shake for 10–15 minutes. Centrifuge it to throw down the insoluble matter, and thus obtain a supernatant solution with comparatively small amounts of organic matter.

Pipet an aliquot of the supernatant solution, calculated to yield about 100 mg. of Hg, into a 500 cc. Erlenmeyer flask, dilute to about 200 cc., and add 5–10 cc. of concentrated H_2SO_4. Boil the solution for 5–10 minutes to expel the excess bromine. Place the flask on a steam bath and add successive small portions of powdered $KMnO_4$ until the bright pink color of the permanganate persists for 5–10 minutes. Clear the solution of precipitated oxides of Mn and excess permanganate by adding, dropwise, dilute H_2O_2. Dissipate any excess peroxide by adding very dilute permanganate solution or boiling for 2–3 minutes. Filter the solution, and wash the filter well with about 100 cc. of water in small portions, collecting the washings with the filtrate. Cool the solution to room temperature, then saturate with a slow stream of H_2S. Filter, wash, dry, and weigh the HgS as usual.

$$\text{Weight of the HgS} \times 1.0146 = \text{HgCl}.$$

The following modification of the procedure has given equally concordant results:

Wash a portion of the powdered sample calculated to yield about 100 mg. of Hg as directed above—then, instead of placing the insoluble residue and asbestos mat in a centrifuge bottle, transfer directly to an Erlenmeyer flask with about 200 cc. of water. Add 5–10 cc. of concentrated H_2SO_4, oxidize with powdered permanganate, and clear with peroxide. Next add a few drops of pure bromine to impart a definite brown color to the solution and carefully shake the flask for a few minutes to insure the oxidation of the Hg. Filter off the insoluble matter through a Gooch, wash the filter well with water, then boil the combined filtrate and washings to drive off the bromine. Cool the solution, saturate with H_2S, and finish the determination as usual.

The recoveries obtained from mixtures of calomel and starch are given in Table 1.

TABLE 1.—*Recoveries from mixtures of calomel and starch*

SAMPLE	CALOMEL ADDED	CALOMEL OBTAINED	RECOVERY
	gram	*gram*	*per cent*
1	0.1340	0.1319	98.4
2	0.1227	0.1224	99.8
3	0.2095	0.2110	100.7
4	0.1332	0.1311	98.4
5	0.0920	0.0918	99.8
6	0.1005	0.0989	98.4
7	0.1014	0.0982	96.9
8	0.1545	0.1540	99.7
9	0.1551	0.1553	100.3
10	0.2432	0.2418	99.4

Table 2 shows the results obtained from mixtures of calomel and plant drugs as required for Compound Cathartic Pills.

TABLE 2.—*Recoveries from mixtures of calomel and plant drugs*

SAMPLE	CALOMEL ADDED	CALOMEL OBTAINED	RECOVERY
	gram	*gram*	*per cent*
11	0.1531	0.1544	100.8
12	0.1512	0.1535	101.5
13	0.1513	0.1324	100.7
14	0.1098	0.1115	101.5
15	0.1308	0.1308	100.0
16	0.1238	0.1245	102.1

Lastly, commercial samples of Compound Cathartic Pills were assayed by these sulfide modifications. Known amounts of calomel were then added, and from the difference of the two results the recoveries were calculated (Table 3).

TABLE 3.—*Recoveries when known amounts of calomel were added*

SAMPLE	CALOMEL ADDED	CALOMEL OBTAINED	RECOVERY
	gram	*gram*	*per cent*
17	0.2381	0.2359	99.1
18	0.2003	0.2035	101.6
19	0.1712	0.1709	99.8
20	0.1410	0.1388	98.4
21	0.2246	0.2220	98.8
22	0.1383	0.1383	100.0
23	0.1585	0.1560	98.4
24	0.2000	0.1992	99.6
25	0.2000	0.2015	100.7

From the experience in the above work, it seems reasonable to conclude (1) that the official iodine method for the determination of calomel in tablets—presumably for other than the official tablets of Calomel or Calomel and Soda, should be deleted, or its use restricted to tablets of comparatively simple composition; (2) that the modified procedures presented here for the gravimetric estimation of mercury in mixtures of calomel and plant drugs by the sulfide precipitation method give acceptable results.

DETERMINATION OF ARSENIC

By A. K. KLEIN and F. A. VORHES, JR. (U. S. Food and Drug Administration, San Francisco, Calif.)

The Gutzeit method,[1] modified by a "solvent" procedure[2] for preparation of the sample, thereby avoiding "wet ashing," is extensively used in determining spray residue on fresh fruit. The method is convenient and rapid, and in the hands of the experienced analyst gives results sufficiently accurate for most purposes. More accurate methods are available, but they generally demand complete destruction of organic matter by wet ashing and isolation of the arsenic by distillation, and so are necessarily somewhat time-consuming. It is the purpose of this paper to present a method that appears to be more accurate than the Gutzeit, but which may be used on samples prepared by the solvent procedure as well as by wet ashing. As described, the proposed method was applied to a range of arsenic content midway between and overlapping the ranges covered by the Gutzeit and bromate[3] methods, but suggestions are offered for adapting it to either higher or lower ranges.

Deniges' method,[4] as improved by Zinzadze,[5] gives excellent results provided the arsenic is first separated from interferences. This may be accomplished by destroying organic matter and distilling the arsenic as the trichloride.[6,7] The work of Tarugi and Sorbini,[8] however, suggests that the isolation may be effected more conveniently by the use of immiscible solvents. They reported the quantitative precipitation of arsenic xanthate from an acidified aqueous medium and described the isolation of minute amounts of the precipitate by extraction with organic solvents. They used this means of separation in connection with a qualitative test for arsenic. They also took advantage of the solubility of arsenic xanthate in chloroform to purify their yield in the gravimetric estimation of larger

[1] *Methods of Analysis*, *A.O.A.C.*, 1935, 370.
[2] *Ibid.*, 391.
[3] *Ibid.*, 373.
[4] *Compt. rend.*, **171**, 802 (1920).
[5] *Ind. Eng. Chem. Anal. Ed.*, **7**, 227 (1935).
[6] Deemer and Schricker, *This Journal*, **16**, 230 (1933).
[7] Cf. Burkard and Wullhorst, *Z. Untersuch. Lebensm.*, **70**, 308 (1935): abs. *Analyst*, **61**, 198 (1936).
[8] *Boll. Chim. Farm.*, **51**, 361 (1912): Abs. *Chem. Zentr.*, 1912, II, 1399.

amounts of arsenic but apparently did not adapt the direct extraction to a quantitative method for small amounts.

The following detailed procedure is based on the findings of Tarugi and Sorbini and the method of Zinzadze. The main steps are as follows: (1) Preparation of the sample by solvent procedure or wet ashing. (2) Reduction of arsenic to trivalent form with KI and acid. (3) Simultaneous formation and extraction of arsenic xanthate by use of a solution of sodium xanthate in CCl_4 and alcohol. (4) Removal of CCl_4-soluble interferences (if present) by washing the extract through concentrated HCl containing $SnCl_2$. (5) Elimination of CCl_4 by volatilization. (6) Oxidation of arsenic to pentavalent form with bromine. (7) Development of the molybdenum-blue color with Zinzadze's reagent. (8) Estimation of the color by means of the neutral wedge photometer.

METHOD

PREPARATION OF SAMPLE

Solvent procedure.—Applicable to apples, pears, bell peppers, green tomatoes, and similar firm fruit. Follow **XXIX, 30**, p. 391, *Methods of Analysis, A.O.A.C.*, 1935. Use HCl for rinse and acidification.

Wet ashing.—Generally applicable to all types of samples. Follow **XXIX, 3(a-b-c-d)**, pp. 371–2, *Methods of Analysis, A.O.A.C.*, 1935, using 20 cc. of H_2SO_4. The sample should contain not more than 0.8 mg. of As_2O_3.

REAGENTS

(1) *Sulfuric acid.*—Reagent quality, arsenic-free.

(2) *Potassium iodide.*—10% W/V solution of the C.P. salt.

(3) *Sodium thiosulfate.*—Approximately 0.1 *N* solution.

(4) *Hydrochloric acid.*—Reagent quality, arsenic-free.

(5) *Stannous chloride.*—40% W/V solution in concentrated HCl.

(6) *Bromine water.*—Saturated.

(7) *Carbon tetrachloride.*—Reagent quality.

(8) *Zinzadze's reagent.*—Follow exactly the directions given by Zinzadze—loc. cit.

Solution I.—Take, in a 3 liter Erlenmeyer flask, 1010 cc. of 25 *N* H_2SO_4; add acid molybdic (anhydride) containing exactly 40.11 grams of MoO_3; boil very gently, with occasional shaking, just until solution is complete, avoiding the evolution of white fumes; cool to room temperature; dilute with distilled water to about 998 cc. and cool again. Finally make up to exactly 1 liter with distilled water and mix well. (The solution has a bluish color.)

Solution II.—Place 500 cc. of Solution I in a 3 liter Erlenmeyer flask; add 1.78 grams of Mo powder and boil very gently (with precautions as before) for exactly 15 minutes from incipient boiling, shaking from time to time. Allow to cool to room temperature; decant the solution from the small residue that may be present into a 500 cc. volumetric flask; dilute with distilled water to about 498 cc. and cool again. Finally make up to exactly 500 cc. with distilled water and mix well. (The solution has a greenish blue color.)

Dilute a 5 cc. aliquot of Solution II to about 50 cc. with distilled water and titrate with 0.1 *N* $KMnO_4$. (It is necessary to use a pipet previously wet inside with water and washed down afterward with a few cc. of water in order to deliver 5 cc. of the viscous reagent accurately.)

Finally prepare the molybdenum blue reagent by mixing certain quantities of Solutions I and II, so that 5 cc. of the resulting mixture corresponds to 5 cc. of 0.1 *N* $KMnO_4$. (It will keep at least 4 years, and probably indefinitely, provided it is of sufficient purity and is kept free from dust, vapors, and other contamination in a glass-stoppered Pyrex bottle.)

It is suggested that the analyst refer to the original paper for specifications as to purity and allowable tolerances.

(9) *Sodium ethyl xanthate solution.*—To 10 parts of absolute ethyl alcohol (cc.) in a centrifuge bottle add 1 part (gram) of pure NaOH pellets. Warm to about 40°C. and shake vigorously in a shaking machine for about 15 minutes. Centrifuge and pour off the supernatant liquid. Ascertain the NaOH content by titration and adjust it to 7% W/V NaOH by addition of absolute alcohol. To 9 volumes of the adjusted solution, add slowly, with cooling, 1 volume of colorless carbon disulfide, mix, and filter. The solution contains approximately 22% sodium xanthate.

NOTE: This reagent is not generally available in pure (solid) form from commercial sources. Its preparation in the laboratory in dry form requires considerable time and the use of large quantities of ether. Attempts to prepare a stable solution of it by various means were without particular success. The described preparation, however, is relatively simple to make and does not decompose to an excessive extent for about 10 days—or even longer when stored in a refrigerator.

(10) *Extraction reagent.*—Mix Reagent 9 with CCl_4 in the proportion of 50 cc. per liter. The reagent should be made up in amounts to last 1 day only, as it decomposes appreciably within 36 hours.

(11) *Standard arsenic solution.*—Dissolve 1 gram of Bureau of Standards As_2O_3 in 25 cc. of 30% NaOH. Neutralize with dilute H_2SO_4 and dilute to 1 liter. Dilute 50 cc. of this solution to 500 cc. 1 cc. = 0.1 mg. of As_2O_3.

DETERMINATION

To samples prepared by wet ashing add 50 cc. of water, mix thoroughly, and while still hot, add 20 cc. of the KI solution. Transfer the mixture to a 250 cc. separatory funnel, using about 50 cc. of water, in portions of 10–25 cc., to rinse out the flask.

Select aliquots of samples prepared by the solvent procedure so as to contain not more than 0.8 mg. of As_2O_3, and, for reasons of mechanical manipulation, not to exceed a volume of 200 cc. Transfer the aliquot to a separatory funnel of appropriate size, add a volume of the concentrated H_2SO_4 equal to 1/5 the volume of the aliquot, and mix. While the mixture is still hot, add a volume of KI solution equal to the volume of H_2SO_4 used, and mix.

Allow the sample (prepared by either means) to stand until the funnel is no longer uncomfortably warm to the hand and then dispel the liberated I_2 with the $Na_2S_2O_3$ solution, mixing thoroughly and carefully avoiding an excess of more than 0.5–1.0 cc.

Regardless of aliquot size, add 25 cc. of the extraction reagent, stopper the funnel *immediately*, and shake *vigorously* for 1–2 minutes. Allow the layers to separate.

NOTE: At this point the presence of antimony in amounts greater than a few mg. is indicated by a brick red or yellow precipitate which tends to gather at the interface; the presence of tin or small amounts of copper is indicated by a deep yellow to orange color in the lower layer; a large amount of copper is indicated by a yellow precipitate suspended in the lower layer and tending to gather at the interface.

Draw off the lower layer into a second (125 cc.) separatory funnel containing 50 cc. of the concentrated HCl and 1 cc. of the $SnCl_2$ solution. Wash down the first funnel with a few cc. of CCl_4 and draw the washings, without shaking, into the sec-

ond funnel so that any residual extract in the stem of the first funnel is displaced with relatively pure CCl_4.

NOTE: The second funnel must be dry when the acid is placed in it for the reason that even slight dilution destroys its effectiveness. Make no effort to draw the precipitate, if any, into the second funnel as this frequently results in entrainment of some of the aqueous phase and may adversely affect the HCl–$SnCl_2$ wash in removal of interferences. No harm is done, however, if some of the precipitate passes through, suspended in the organic phase.

Stopper and shake the second funnel vigorously for about 2 minutes, or until the lower layer becomes a very pale, clear yellow and the upper layer is either completely clear or at the most contains only a small amount of suspended matter.

Draw off the lower layer through a plug of cotton about 1/2 inch long, packed loosely but uniformly into the stem of the funnel, into a third separatory funnel containing 50 cc. of H_2SO_4 (1+200). Shake vigorously, and draw off the lower layer, through a plug of cotton, into a 125 cc. Erlenmeyer flask marked at the 60 cc. capacity point and containing 10 cc. of water and 2 or 3 small glass beads.

Repeat the entire extraction with two additional 15 cc. portions of the extraction reagent, adding them to the first funnel and carrying them, separately, through the process, finally combining all three extracts in the Erlenmeyer.

NOTE: When tin, antimony or large amounts of copper are absent, the second separatory funnel may be eliminated; the first funnel is fitted with a cotton plug and the extracts drawn directly into the funnel containing the H_2SO_4 (1+200), shaken vigorously, and then drawn into the Erlenmeyer.

Always invert the funnels when shaking in order to avoid loss of drops of the extract retained in the stems.

Evaporate the CCl_4 on a hot plate and bring the aqueous solution to a vigorous boil for at least 1 minute, preheating the hot plate and swirling the flask a little at the start to avoid "bumping." Wash down the sides of the flask with a little water and add 20 cc. of the bromine water. Insert between flask and hot plate a piece of asbestos board of a thickness such that the solution reaches gentle boiling in 2–5 minutes, and continue boiling gently until the bromine, as judged by color, is almost dispelled. Finally, boil vigorously on the bare hot plate to remove the bromine completely.

Dilute to 60 cc.; add, by means of a pipet, exactly 10 cc. of the Zinzadze reagent (10-fold dilution), bring to a boil, and boil steadily but not vigorously for just 5.5 minutes. Cool, transfer to a 100 cc. volumetric flask, dilute to volume, and mix.

Fill a 1-inch cell with the blue solution and obtain the direct reading in the neutral wedge photometer.[1]

To the solution remaining (should be more than 50 cc.) add about 1 cc. of bromine water and warm slightly until all blue or green shades are dispelled and only the yellow color of bromine remains. (Only a small amount of bromine water is required but a substantial excess over that necessary to just bleach the blue must be present.) Obtain the photometer reading of the yellow solution (termed the "bromine blank") and subtract it from the direct photometer reading. (This correction compensates for slight turbidities which may be present.)

CALIBRATION OF PHOTOMETER

To calibrate the photometer, prepare, in duplicate or triplicate, a series of 6 or 8 standards (extending over the range 0–0.8 mg. As_2O_3), adding the required amounts of Reagent 11 to 50 cc. portions of water in separatory funnels and carry them through all steps of the determination (except that the HCl–$SnCl_2$ wash may be omitted).

[1] Clifford and Wichmann, *This Journal*, 19, 130 (1936).

With a photometer equipped with a Wratten neutral gelatine wedge and a glass color filter consisting of 4.5 mm. Corning dark pyrometer red No. 241, a linear relationship is obtained between photometer reading and amount of arsenic present. The writers have used this combination in most of their work. An objection to the gelatine wedge is that it will begin to show deterioration after a year or so. The Jena all-glass neutral wedge overcomes this objection and gives a linear function with the same filter. The B. & L. Smoke C glass wedge, used widely for other determinations, is, unfortunately, not quite neutral in the deep red and will not, therefore, produce an exactly linear function. With this wedge it is necessary to utilize a large-scale plot of the standards to convert, graphically, the photometer reading of the sample to the amount of arsenic represented thereby. With the other wedges the equation, $Y = a + bX$, may be calculated by the method of least squares as follows:

$$b = \frac{\sum XY - \sum X M_y}{\sum X^2 - \sum X M_x}, \text{ and } a = M_y - b M_x,$$

where $\sum$ denotes "sum of" and M denotes "mean of."
Thus, $\sum X$ = sum of the X's; M_x = mean of X; M_y = mean of Y;
$\sum XY$ = sum of the products of X and Y;
$\sum X^2$ = sum of the squares of X;
Y = mg. As_2O_3 extracted;
and X = photometer reading in mm. (corr. for bromine blank).
Exclude "blanks" (zero arsenic) from these calculations.

Having inserted in the linear equation the numerical values of a and b, calculated from the standards, obtain the result of a determination by substituting the photometer reading of the sample of $4X$ and solving for Y.

In use the equation is likely to be more accurate than the graphical methods. The calculation is somewhat time-consuming, but the standardization need be carried out only once provided the adjustment of the photometer is not changed and the wedge does not deteriorate.

DISCUSSION

In accordance with usual practice in colorimetric determinations, it has been specified that the standards be given as nearly as possible the same treatment that is given to samples. In this method, however, it makes very little difference whether the standards are subjected to extraction or whether they are developed directly in the Erlenmeyer flasks, starting with the bromine treatment. The standard arsenic solution must be exactly neutral if the latter is done. Nevertheless since there does appear to be a slight loss in the extraction (Table 1), analysts desiring the highest accuracy may find it worth the extra time to follow the conventional rule, carrying the standards through the extraction and even using the HCl-$SnCl_2$ wash in the event that the samples to be analyzed contain tin, copper, or antimony.

The analyst engaged in control work will find from experience that samples of the same character vary but little in their bromine blanks and will be able to select an approximately average bromine blank.

While the range of the method described has been set at 0–0.8 mg. of As_2O_3, this range may be extended by diluting the aqueous solution in the

TABLE 1.—*Photometer readings on pure solutions*

DESCRIPTION AND TREATMENT	ARSENIC PRESENT (EXPRESSED AS MG. As_2O_3) 0	0.1	0.2	0.35	0.55	0.65	0.8
	Photometer reading—mm.—corr. for bromine blank						
B.S. As_2O_3 soln—extracted	0.2	15.0	29.9	51.2	80.1	94.5	114.4
B.S. As_2O_3 soln—extracted	0.2	14.8	29.2	49.7	80.3	94.7	115.2
B.S. As_2O_3 soln—extracted	0.5	15.3	30.0	52.2	81.2	95.6	119.3
B.S. As_2O_3 soln—not extracted	0.6	15.0	29.8	51.7	80.6	94.4	117.9
B.S. As_2O_3 soln—not extracted	0.5	15.3	30.2	51.5	80.7	95.0	117.8
B.S. As_2O_3 soln—extracted with HCl–$SnCl_2$ wash	0.4	14.2	29.2	50.7	80.3	92.3	118.4
$PbHAsO_4$ soln—extracted	0.4	14.5	29.8	51.5	80.8	94.6	116.3
$PbHAsO_4$ soln—extracted with HCl–$SnCl_2$ wash	0.5	14.9	29.7	50.0	78.9	92.0	116.6
Theoretical reading based on equation of line calculated from extracted standards (1st 3 series) mg. $As_2O_3 = 0.00691$ mm.–0.0047	0.7	15.1	29.6	51.3	80.3	94.7	116.4

Erlenmeyer flask, before addition of Zinzadze's reagent, to twice or three times the specified 60 cc., adding two or three times the specified 10 cc. of reagent, and diluting finally to 200 or 300 cc. In an analogous manner small amounts of arsenic may probably be determined to advantage by restricting the final volume to 50 cc. or even 25 cc., also restricting the amount of reagent and the volume before addition of reagent in similar proportion.

INTERFERENCES

Zinzadze mentions iron, nitrate, and phosphate as interferences in the development of the color by means of his reagent. As none of these ions are soluble in the extraction reagent they do not constitute interferences in the described procedure. Nitrate in large amount tends to prevent the reduction of arsenate to arsenite prior to extraction but its effect is nil when it is present in the amounts normal to food products. The interference of tin and antimony is due to formation of insoluble oxycompounds of these metals during the bromine treatment and consequent heavy turbidities which interfere with proper evaluation of the color. Tin and antimony xanthates are soluble in concentrated hydrochloric acid and are decomposed to the corresponding metallic chlorides, whereas arsenic xanthate is unaffected and remains in the carbon tetrachloride layer. If hydrochloric acid alone is used to remove tin and antimony from the extract,

another interference is introduced. When copper is present under these conditions iodine almost invariably appears in the second funnel and oxidizes the arsenic xanthate, rendering the arsenic insoluble in carbon tetrachloride. Apparently cuprous iodide is formed in the first funnel and is carried, suspended in the extract, into contact with the concentrated hydrochloric acid in the second funnel. To prevent formation of iodine, stannous chloride is added to the hydrochloric acid.

It is obvious that oxidizing agents must be removed or reduced before the determination is attempted. Also, the presence of substances forming heavy precipitates in the presence of sulfate or xanthate may be expected to cause mechanical difficulties in the extraction. However, the usual components of foods, or likely contaminants thereof, in the amounts ordinarily present, have not been found to introduce more than minor mechanical difficulties. These include the alkalis, alkaline earths, aluminum, manganese, zinc, lead, mercury, cadmium, and bismuth.

The addition of thiosulfate must be restricted fairly closely to the amount required to dispel the iodine. This amount is converted to tetrathionate but any excess thiosulfate results in formation of colloidal sulfur. It was observed that when a large excess of sodium thiosulfate was used, low results were invariably obtained and also that the acidity of the final solution was increased in rough ratio to the excess of sodium thiosulfate added. Apparently colloidal sulfur dissolves to some extent in the extraction reagent and passes through to the bromine treatment where it is oxidized to form sulfuric acid.

RECOVERY EXPERIMENTS

Table 1 gives photometer readings of standards developed under varying conditions and also readings on known amounts of lead arsenate solution. Theoretical photometer readings, based on the linear equation calculated from standards developed as prescribed above, have been included. A comparison shows that there is only a negligible loss of arsenic in either the extraction or the hydrochloric acid-stannous chloride wash.

Table 2 gives the results of recovery experiments conducted under varying conditions in regard to type of sample, method of preparation, interference, and range of arsenic content.

The standard deviation calculated from the 60 results would indicate that the method is capable of an accuracy of ± 0.02 mg. (3×0.0068) in more than 99 out of 100 instances. This is equivalent to an accuracy of 0.001 gr./lb. provided a sample of, or aliquot representing, 140 grams or more is extracted.

COLLABORATIVE WORK

Three series of samples were sent to collaborators. The draft of the procedure accompanying the first series was incomplete or faulty in several

TABLE 2.—*Recoveries in presence of interferences*

(Expressed as mg. of As_2O_3 calculated from equation based on extracted standards and corrected for reagent blanks)

DESCRIPTION	INTERFERENCES—MG.							HCl-$SnCl_2$ WASH	ARSENIC ADDED AS $PbHAsO_4$—EXPRESSED AS MG. As_2O_3					
	Sb	Cu	Sn	SiO_2	Fe	NO_3	P_2O_5		0.10	0.20	0.35	0.55	0.65	0.80
$PbHAsO_4$ solution	10	10	50					Yes	0.100	0.201	0.349	0.550	0.652	0.803
Sugar—wet ashed	10	10	50					Yes	0.094	0.194	0.346	0.550	0.651	0.802
140 grams tomatoes—wet ashed	10	10	50					Yes	0.101	0.200	0.352	0.549	0.646	0.783
Tomatoes—solvent prep'n	10	10	50					Yes	0.103	0.207	0.347	0.550	0.649	0.800
Sugar—wet ashed	10	10	50	25	50	50	250	Yes	0.103	0.200	0.349	0.546	0.643	0.786
140 grams tomatoes—wet ashed	10	10	50	25	50	50	250	Yes	0.093	0.190	0.351	0.540	0.637	0.799
Apples—solvent prep'n	10	10	50	25	50	50	250	Yes	0.100	0.201	0.345	0.537	0.642	0.783
Sugar—wet ashed				25	50	50	250	No	0.098	0.198	0.356	0.554	0.654	0.799
140 grams apples—wet ashed				25	50	50	250	No	0.097	0.193	0.348	0.550	0.647	0.796
Tomatoes—solvent prep'n				25	50	50	250	No	0.100	0.198	0.353	0.541	0.651	0.802
Standard deviation—10 results in each range— Standard deviation—60 results—0.0068.									0.0034	0.0049	0.0033	0.0062	0.0057	0.0090

respects. Primarily for this reason the results on this group were generally unsatisfactory.

After further investigation of interferences and technic, a second series was issued with a rewritten procedure, which was essentially the same as described above with one important exception—the extraction reagent contained only half the xanthate now prescribed. This concentration generally proved insufficient. The reason may be visualized somewhat as follows: When the extraction reagent is added to the strongly acid solution in the first funnel, the xanthate is disposed of in three ways: (1) converted to xanthic acid which decomposes rapidly; (2) converted to xanthates of metals such as tin, copper, and antimony (if present); and (3) forms arsenic xanthate. If the funnel is not shaken immediately after addition of the extraction reagent, reaction (1) predominates. If, at the same time, the sample contains relatively large amounts of "interferences," the residual xanthate is, by mass action, largely disposed of by reaction (2). Under these conditions, unless the reagent contains an amount of xanthate greatly in excess of that required for the arsenic alone, a quantitative extraction of arsenic is prevented.

While all analysts collaborating on the second series reported quantitative results on samples that contained only small amounts of interferences, the majority obtained low results where a relatively large amount of copper, tin, and antimony was present.

All the results of Table 2 had been obtained (by Klein) with an approximately 0.5 per cent xanthate extraction reagent, and on the basis of these results that concentration had been deemed sufficient. However, it is probable that the analyst in this instance had, through repetition, developed a technic that minimized the effect of reaction (1).

A third series of collaborative samples, identical with the second series except as to arsenic content, was first submitted to collaborators Gerritz, Bois, and McRoberts, who analyzed them under verbal directions, using the stronger extraction reagent and observing precautions as described herein. Quantitative results having been obtained, the series was then submitted to the other collaborators together with the written instructions as given above. These results are reported in Table 3.

The method has been used in this laboratory in the analysis of 100 or more routine samples of a wide variety. No difficulties of a mechanical nature were encountered. From observation and experience thus obtained it is believed that food samples ordinarily handled will contain considerable less so-called interferences than were present in the collaborative samples.

ACKNOWLEDGMENTS

The writers have had the benefit of most generous cooperation, comment, and suggestions from their associates. They are especially indebted to the collaborators whose names appear in Table 3 and to J. H. Born-

TABLE 3.—*Collaborative results*

	Sample No. 1—Solvent preparation; 1400 gm. apples (or tomatoes) treated; solution made to 500 cc. after addition of 2.72 mg. As_2O_3 as $PbHAsO_4$; determination made on $100/500 \times 50/110$ acidified aliquot to which was added 5 cc. of solution "A"—see below	Sample No. 2—Wet-ashing preparation; 1 cube of lump sugar wet-ashed with 25 cc. of a solution of $PbHAsO_4$ containing .500 mg. As_2O_3 per 25 cc. and 10 cc. of solution "A"—see below
COLLABORATORS*	CORRECT RECOVERY	CORRECT RECOVERY
	0.2923 mg. As_2O_3 or 0.0161 gr./lb.	0.590 mg. As_2O_3
	As_2O_3 Reported	As_2O_3 Reported
	mg. *gr./lb.*	*mg.*
H. Bois (a)	0.275 0.0151	0.578
L. H. McRoberts (a)	0.298 0.0164	0.587
H. W. Gerritz (a)	0.287 0.0158	0.596
L. A. Salinger (a)	0.285 0.0157	0.604
P. A. Mills (b)	0.295 0.0162	0.563
H. W. Conroy (c)	0.295 0.0162	0.592
P. A. Clifford (d)	0.294 0.0162	0.578
W. Stoneburner†	0.290 0.0160	0.510

Solution "A" contained (per cc.)

mg.			*mg.*		
0.009	As_2O_3	as $PbHAsO_4$	0.4	Sb	as $K(SbO)C_4H_4O_6$
1.0	Cu	as $CuSO_4$	5.0	P_2O_5	as Na_2HPO_4
2.0	Sn	as $SnCl_2$	2.0	SiO_2	as $Na_2Si_4O_9$
5.0	NO_3	as KNO_3	2.0	Fe	as $Fe_2(SO_4)_3$

* Address—U. S. Food and Drug Administration at (a) San Francisco, (b) Seattle, (c) Minneapolis, (d) Washington, D. C.

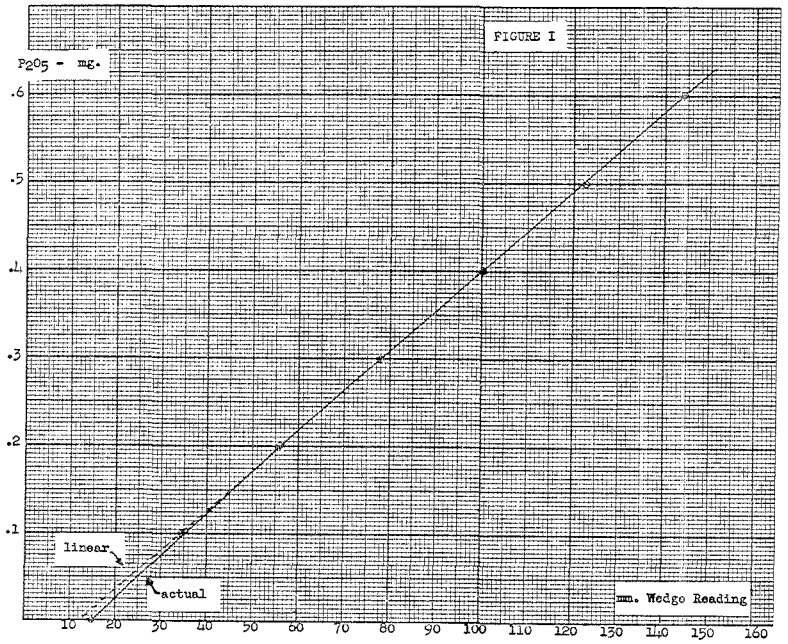
† Ohio Agricultural Experiment Station, Wooster, Ohio.

man and J. Schurman of the Chicago Station, J. Carol of the Cincinnati Station, and L. W. Ferris of the Buffalo Station, U. S. Food and Drug Administration, who collaborated on the preliminary series of samples issued, but were not able to assist on the final series reported. Particular acknowledgment is due H. J. Wichmann, Referee on Metals in Foods, U. S. Food and Drug Administration, Washington, D. C., for his interest, many valuable suggestions, and editorial criticism.

DETERMINATION OF PHOSPHORUS IN FRUITS AND FRUIT PRODUCTS*

By H. W. GERRITZ (U. S. Food and Drug Administration, San Francisco, Calif.)

The method presented has been found by the writer to be more convenient and more rapid than the volumetric procedure[1] now frequently used in the estimation of small amounts of phosphate such as are present



in fruit products. The proposed method also appears to be more accurate than the volumetric method for the determination of P_2O_5 in such substances as raspberries and raspberry jam, and to compare well with the gravimetric procedure.[2]

The proposed method is essentially the molybdenum blue phosphate determination devised by Zinzadze,[3] combined with a rapid wet-ashing procedure previously described by the writer.[4] Minor modifications have been introduced to adapt Zinzadze's method more specifically to the use of the neutral wedge photometer[5] and to the analysis of samples prepared by wet ashing.

* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November 14, 15 and 16, 1938.

[1] *This Journal*, 21, 505 (1938).
[2] *Methods of Analysis, A.O.A.C.*, 1935.
[3] *Ind. Eng. Chem. Anal. Ed.*, 7, 227 (1935).
[4] *Ibid.*, 116.
[5] *This Journal*, 19, 130 (1936).

METHOD

REAGENTS

(1) *Zinzadze's reagent.*—Follow exactly the directions and precautions given by Zinzadze[3] noting that a ten-fold dilution is used in the actual determination. Preparation of the reagent is also described in detail by Klein and Vorhes (see p. 122).

(2) *Potassium hydroxide solution.*—Phosphate and arsenate free and approximately 3.6 *N*. J. T. Baker C. P. sticks labeled as containing 0.000% PO_4 have been found satisfactory. Dissolve the KOH in water, using an arsenic-free Pyrex or porcelain vessel, cool immediately, and transfer to a paraffin-lined container. Avoid leaving glass equipment in contact with this reagent for any extended period.

(3) *Normal potassium hydroxide.*—From Reagent 2 prepare about 50 cc. of approximately normal KOH. Preserve in a paraffined container fitted with a 1-holed rubber stopper bearing a Pyrex medicine dropper.

(4) *Concentrated sulfuric acid.*—Reagent quality.

(5) *Normal sulfuric acid.*—From Reagent 4, prepare about 50 cc. of approximately normal H_2SO_4. Preserve in a container fitted with a 1-holed rubber stopper bearing a medicine dropper.

(6) *Concentrated nitric acid.*—Reagent quality.

(7) *Perchloric acid.*—60%, reagent quality.

(8) *Sodium alizarin sulfonate.*—Dissolve 0.20 gram of sodium alizarin monosulfonate in 100 cc. of water and filter. Preserve in an indicator bottle.

(9) *Standard phosphate solution.*—0.05 mg. per cc. Dissolve 0.1917 gram of pure dry KH_2PO_4 in about 200 cc. of distilled water, add 10 cc. of normal H_2SO_4 and 6 drops of 0.1 *N* $KMnO_4$. Dilute to exactly 2000 cc. According to Zinzadze[3] this solution keeps indefinitely in a well-stoppered Pyrex bottle.

(10) *Glass beads and broken porcelain.*—Boil a supply of small glass beads (2 or 3 mm. in diameter) and a number of small pieces of broken porcelain in aqua regia, wash clean with distilled water, and dry.

PREPARATION OF SAMPLE

Transfer a portion of the sample containing 1–3 mg. of P_2O_5 to a 500 cc. Kjeldahl flask. For the determination of P_2O_5 on the water-soluble portion of fruits and fruit juices use 25 cc. (equivalent to 3.75 grams) of the sample solution prepared according to the official methods,[2] **XXVI (b)** or **(c)**. For jams and jellies use 50 cc. of the prepared solution. (If the sample is apparently substandard, a larger aliquot may be taken in order to have sufficient P_2O_5 present in the final determination.) Add 15 cc. of the HNO_3, 5 cc. of the H_2SO_4 (Reagent 4), 5 or 6 small glass beads, and a few small pieces of broken porcelain. Place the flask on a digestion rack over a free flame and protect from the flame by an asbestos mat with a hole of such size that the surface of the H_2SO_4 will be above the mat. Boil over a moderate flame to copious fumes of H_2SO_4. If marked charring occurs, as evidenced by a black foam, cool slightly, and cautiously add a little more of the HNO_3. (In the case of jams, three additions of the acid may be necessary.) Again boil to fumes. Add 0.5 cc. of the $HClO_4$ to the hot flask and continue fuming for a few minutes. The digest should now be water-clear or slightly greenish yellow. If necessary, add another 0.5 cc. of $HClO_4$, and continue fuming 3 or 4 minutes. Cool somewhat, cautiously add 50 cc. of distilled water, and boil to fumes to remove traces of the HNO_3. Cool, add 25 cc. of distilled water, transfer to a 100 cc. volumetric flask, mix, cool, make to volume, and again mix thoroughly.

DETERMINATIONS

Transfer a 20 cc. aliquot to a 100 cc. volumetric flask (a Kohlrausch sugar flask has been found convenient) marked at 60 cc. capacity. Always use a 20 cc. aliquot. Add 3 drops of the sodium alizarin sulfonate and neutralize with the strong KOH. Adjust the acidity to just yellow by means of the normal KOH and normal H_2SO_4, adding each dropwise with constant mixing until a single drop of the H_2SO_4 just changes the color of the solution to yellow.

Dilute to the 60 cc. mark and mix. Place the flask in a boiling water bath and bring to that temperature. If the solution becomes pink, add a drop or two of the normal H_2SO_4 to bring it back to yellow. With a pipet add exactly 10 cc. of Zinzadze's reagent (10-fold dilution). Mix and continue to heat in the boiling water bath for exactly 20 minutes. Cool, dilute to volume, and mix.

NOTE: It is important that the standards and unknowns be heated at the same temperature, and this is readily accomplished by immersing the flasks in a boiling water bath to the depth of the liquid within. A simple boiling water bath may be prepared by placing a coarse wire screen in the bottom of a 14 or 16 inch granite pan, filling the pan with water to such a depth that the 60 cc. level in the flasks will be below the level of the water. Place the pan on a tripod and boil vigorously over a Meeker burner. The flasks should be placed only around the perifery of the pan and should be weighted with lead rings or otherwise supported to prevent tipping. The bath should be kept at a turbulent boil throughout the heating period and *boiling* water should be added to the bath from time to time to keep the level of the water equal to or above the level of the liquid in the flasks.

Determine the color intensity by means of the neutral wedge photometer (5), using a 1-inch cell and No. 66 filter,* and Jena 0–2 neutral wedge.

The method covers a range up to 0.6 mg. of P_2O_5 in the final 100 cc. of solution. Prepare standards covering this range by placing 0, 2, 4, 6, 8, 10, and 12 cc. of the standard phosphate in 100 cc. volumetric flasks marked at 60 cc. capacity. Add 2 cc. of H_2SO_4 (1+1) and 3 drops of the indicator to each flask, together with sufficient water to make about 20 cc. Then treat the same as the sample beginning with the neutralization, dilute to 60 cc., develop color, cool, make to volume, and determine color intensity in the neutral wedge photometer. If alkali of suitable purity has been used the 0 standard should give a reading not over 10–15 mm. greater than the reading of pure water. Make a large scale graph of the standards, plotting mg. of P_2O_5 against photometer readings. By means of this plot convert the sample photometer readings to mg. of P_2O_5 present in the final 100 cc. portion.

NOTES

The photometer need be calibrated but once for each batch of reagents provided the adjustment is not altered.

It will be noted that standardization under these conditions automatically corrects for the blank on reagents, except HNO_3 and $HClO_4$. These acids, in reagent grade, have not been found to contain significant quantities of arsenates or phosphates.

In the above procedure the equivalent of 1 cc. of concentrated H_2SO_4 is present in the final flask in which the color is to be developed. It is important to have approximately the same conditions in both the standard and sample flask. For that reason 2 cc. of H_2SO_4 (1+1) is added to the standard flasks.

In the analysis of heterogeneous samples, such as those of fresh fruit, for total P_2O_5, it may be necessary to digest a larger portion in order to eliminate sampling

* Filter 66 is 4.5 MM Corning dark pyrometer red No. 241. With B & L "Smoke C" glass wedge, use filter 65. Filter 65 is the same as 66 plus a half MM of Jena BG18.

and weighing error. In such cases it is convenient to take double the sample (7.5 grams) and add double the amount of H_2SO_4 (or 10 cc.). Make the digest to 200 cc., and finally transfer a 20 cc. aliquot to a 100 cc. volumetric flask for color development. The amount of sample digested may be varied to suit the nature of the sample so long as the final 20 cc. aliquot taken for color development contains approximately 1 cc. of H_2SO_4 and 0.2–0.6 mg. of P_2O_5.

EXPERIMENTAL

With his method of sample preparation, Zinzadze[3] found it preferable to develop the color on a steam bath in 30 minutes.

Klein and Vorhes (see p. 121), using Zinzadze's reagent in estimation of arsenic, preferred to develop the color by direct boiling for 5 minutes and obtained a linear calibration curve by this means. The writer was unable to obtain concordant results by Zinzadze's technic on samples prepared by acid digestion. This may have been due in part to variation of temperature in various steam baths and in various locations of a single steam bath. It appears more likely, however, that the relatively higher salt concentration in the proposed procedure is responsible.

A fairly satisfactory calibration curve was obtained by direct boiling for 5 mintues, but here again the higher salt concentration interfered, causing uneven boiling and spattering. To avoid these difficulties, the writer selected the boiling water bath as being more reproducible and less liable to mechanical difficulty. Table 1 presents data on the basis of which the 20-minute period was selected as giving the more nearly linear, and therefore the optimum, calibration curve.

TABLE 1

MILLIGRAMS P_2O_5	BLANK	0.1	0.2	0.3	0.4	0.5	0.6
				Wedge Reading—mm.			
Boiled 5 min. on hot plate	13.9	35.5	56.0	78.0	99.2	120.7	142.3
15 min. in boiling water bath	13.3	33.2	54.5	77.2	99.0	119.0	131.9
20 min. in boiling water bath	15.0	34.6	56.0	78.0	100.1	122.7	144.0
30 min. in boiling water bath	17.2	38.0	55.0	77.0	98.0	120.0	142.1
60 min. in boiling water bath	23.8	40.9	58.6	80.5	99.4	121.0	—

A typical graph, plotting MM wedge reading against milligrams of P_2O_5 in standards is given in Figure 1. It will be noted that the points from 0.1 to 0.6 mg. tend to fall on a straight line, but when this line is projected through the origin, it does not pass through the point experimentally obtained for the blank. Apparently the time-concentration effect is greater in the lower region. For this reason blanks cannot readily

be taken care of numerically and it is imperative that the reagents be as free from P_2O_5 as possible and that the reagents used in calibration of the photometer be the same as those used in the determination. As all reagents used are quite stable, a fairly large supply of each is preferably prepared at the time of calibration of the photometer.

RECOVERY OF P_2O_5 IN MONOBASIC POTASSIUM PHOSPHATE

Reagent quality KH_2PO_4 was dried for 6 weeks in a desiccator over Dehydrite and assayed gravimetrically according to official methods,[2] **II, 9**; volumetrically according to official methods,[2] **II, 12(b)**, and colorimetrically according to the proposed method. For the colorimetric method 1.5, 2.0, and 2.5 mg. of P_2O_5 were placed in a digestion flask together with a piece of filter paper, 5 cc. of H_2SO_4, and 15 cc. of HNO_3. The digestion and determination were then conducted according to the proposed procedure. Results are given in Table 2. They show that with pure solutions the gravimetric and colorimetric methods give practically 100 per cent recovery, while the volumetric method gives slightly more than 100 per cent recovery of P_2O_5.

TABLE 2

METHOD	P_2O_5 TAKEN	P_2O_5 RECOVERED	
	mg.	*mg.*	*per cent*
Gravimetric	78.77	78.84	100.1
	78.77	78.52	99.7
	78.77	78.97	100.3
Volumetric	7.33	7.42	101.2
	8.80	8.92	101.4
Colorimetric	1.5	1.51	100.6
	2.0	2.01	100.4
	2.5	2.50	100

COLLABORATIVE WORK

Two samples of raspberries and two samples of raspberry jam were supplied to collaborators with the request that they conduct P_2O_5 determinations on the water-soluble portion by the proposed colorimetric method and also by the frequently used volumetric method.[1] When time would allow, samples were also analyzed gravimetrically.[2] Results are given in Table 3.

The proposed colorimetric method has also been found applicable to material of higher P_2O_5 content, such as semolina macaroni. Analyses of three samples of semolina macaroni were made by the volumetric method and the proposed colorimetric method. For the colorimetric determination 0.5 gram of ground, well-mixed sample was taken for analysis. The diges-

tion and estimation of P_2O_5 were conducted in the same manner as described above for fruit products. Digestion was completed in 30 minutes. Results by both methods are shown in Table 3.

TABLE 3.*—*Collaborative results*

	H. M. BOLLINGER	H. W. GERRITZ	G. A. PITMAN	L. A. SALINGER	M. G. YAKOWITZ
	P_2O_5 (MG. PER 100 GRAM SAMPLE)				
(1) Raspberry Jam					
Volumetric	30.0–29.4	30.5–30.1	27.5–27.4	29.5–29.3	
Colorimetric	27.7–27.9	27.9–28.0	27.1–27.1	27.0–27.3	
Gravimetric		27.9–28.0		27.3–27.4	
(2) Raspberry Jam					
Volumetric	27.2–26.8	31.0–31.0			29.8–29.7
Colorimetric	28.2–28.3	27.9–27.6			28.3–28.3
Gravimetric		27.7–27.5			
(3) Raspberry Fruit					
Volumetric	64.5–64.5	65.4–65.0			65.1–64.5
Colorimetric	63.3–62.6	62.7–62.7			63.6–63.2
Gravimetric		62.9–61.8			
(4) Raspberry Fruit					
Volumetric	47.5–46.7	48.8–48.2			
Colorimetric	46.1–46.1	47.7–47.5			
(5) Semolina Macaroni					
Volumetric		326 325			327 329
Colorimetric		327 327			
(6) Semolina Macaroni					
Volumetric		289 292			293 297
Colorimetric		297 297			
(7) Semolina Macaroni					
Volumetric					309 306
Colorimetric		306 306			

* All analysts are at the San Francisco Station, U. S. Food and Drug Administration.

INTERFERENCES

Zinzadze[3] mentions iron, nitrate, and arsenic as interferences in the development of the color by means of his reagent. Nitrates are not present in solutions prepared as described, and neither iron nor arsenic is ordinarily present in fruit or fruit products in sufficient quantity to constitute an interference. Were fruit contaminated with spray residue to the extreme of, say, 0.1 grain As_2O_3 per lb., it would make a positive error in the phosphate determined of 1.4 mg. per 100 grams, which is not a serious error.

However, if the presence of excessive arsenic or iron is suspected, their

interference is prevented by modifying the procedure as follows: Proceed according to the above procedure to the point "adjust acidity to just yellow," then add 10 cc. of exactly normal sulfuric acid and 10 cc. of 8 per cent sodium bisulfite, and dilute to 60 cc. Then heat in a boiling water bath for an hour. Proceed as directed above, beginning "add exactly 10 cc. of Zinzadze's reagent." Standards, of course, must then be treated in the same manner.

CONCLUSIONS

The proposed colorimetric method was found to be more rapid than the volumetric method. The maximum digestion time was about one hour. The proposed method necessitates less manipulation and therefore entails less possibility of error from variation in technic than does the volumetric method. Collaborators' results by the proposed colorimetric method vary less than results by the volumetric method and results by the proposed colorimetric method agree very closely with results obtained by the gravimetric method. On some samples results by the volumetric method appear as a rule to be slightly high.

ACKNOWLEDGMENT

The writer wishes to thank Frank Vorhes, Jr., for helpful suggestions during the course of the work and for enlisting the help of collaborators, and also the collaborators for their cooperation in making the comparative data possible.

DECOMPOSITION OF DOLOMITIC LIMESTONE IN SOILS WHEN USED AS A NEUTRALIZING AGENT IN COMPLETE FERTILIZERS*

P. R. DAWSON, E. F. SNYDER, W. R. LEIGHTY, and F. R. REID
(Soil Fertility Investigations, Bureau of Plant Industry, U. S. Department of Agriculture)

This paper reports preliminary results of studies on the comparative decomposability of dolomitic limestone of different degrees of fineness when applied to soils as the neutralizing agent in non-acid-forming fertilizers. The experiments now in progress comprise pot trials in which the dolomitic materials are applied to the soil as constituents of a complete neutralized fertilizer and are allowed to react with the soil in the presence of a growing crop under conditions simulating those in the field. The comparative rates of decomposition of the dolomites are evaluated by the

* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November 14, 15, and 16, 1938.

changes in *p*H, the residual carbonates, and the readily soluble magnesium in the soil of the fertilizer placement zone, as well as by the changes in magnesium content of the crop, after each of several successive treatments and crop periods. Taylor and Pierre[1,2] have reported some data of this character; and the purpose of these studies is to extend the information to a wider range of soils and applied treatments.

The preliminary data reported here relate to the effects of a single application of the treatments on the *p*H and residual carbonates of the soil and on the magnesium content of the crop, following a single crop of corn, and with periods of contact of soil and treatments of 77 to 84 days.

The procedure in these experiments was practically the same as that followed by Taylor and Pierre.[2] The soils used were a Caribou loam of *p*H 4.6 from Maine, a Sassafras loam of *p*H 5.0 from New Jersey, and a Sassafras fine sandy loam of *p*H 5.0 from the Eastern Shore of Virginia. The treatments were based on a 6–8–6 fertilizer, compounded neutral with dolomite. These are listed in Table 1. The hydrated dolomite, applied at 1/3, 2/3, and the full computed rates, constituted the standard of comparison. Composite dolomite A was composed of equal parts of the different dolomite A fractions; dolomites B and C were composed of equal parts of corresponding fractions of dolomites of greater and less reactivity, respectively, than dolomite A. All the magnesic components of the treatments remained segregated from the fertilizer until application to the soil.

The trials were conducted in the greenhouse, in 2-gallon glazed stoneware crocks, holding, on an oven-dry basis, 8500 grams of the Caribou loam and 10,000 grams of the other two soils. The fertilizer and magnesium treatments were applied by thorough mixing with a tenth of the total soil for each pot and inserting this soil as a vertical cylindrical core in the center of the crock. This was accomplished as follows: A hollow metal cylinder, the internal diameter of which was such that one-tenth of the soil in the pot was enclosed and the height of which was somewhat greater than the depth of the soil, was inserted in the center of the empty crock. The nine-tenths weight of untreated soil was placed in the pot outside of the cylinder and compacted by gentle tamping. The treated soil was then packed inside the cylinder and the latter withdrawn. A circular metal collar, 2 inches in height and 3 inches in diameter, protected with asphaltum paint, was centered about the cylinder before complete withdrawal of the latter and embedded about 0.5 inch in the soil. This served to mark the fertilized zone.

The rates of application of the fertilizer and magnesic materials were equivalent to 2000 lbs. of the complete neutralized fertilizer per acre, on the basis of the total soil in the pots; of this total rate of application the magnesium material accounted for an average of 539 lbs. per acre in the

[1] *J. Am. Soc. Agron.*, 27, 764–73 (1935).
[2] Proc. 1st Annual Meeting, Committee on Fertilizers, Am. Soc. Agron., 1935, pp. 15–23.

case of Dolomite A, and equivalent proportions for the other treatments. The initial concentrations in the placement zones (cores) were of course 10-fold these rates. Each treatment was in triplicate for each soil. Corn was planted in the no-fertilizer zone, just outside the core, and allowed to grow for 56–59 days, when it was cut off at the surface of the soil, weighed, and dried for subsequent analysis. Growth was relatively uniform and heavy. The soils were maintained at an average moisture content of 60 per cent of their water-holding capacity by frequent additions of distilled water. After the crop had been harvested the pots were allowed to stand for an additional period of 2–3 weeks, depending on the soil, and during which time the moisture content of the soils was allowed to decrease sufficiently to facilitate sampling. The total intervals between application of the treatments and sampling of the soil were 79 days for the Caribou loam, 77 days for the Sassafras loam, and 84 days for the Sassafras fine sandy loam. During these periods, which extended from the last week of April to the last week of July, the greenhouse temperatures ranged from a minimum of 65°F. at night to a maximum of nearly 100°F. at midday in the latter parts of the periods.

After expiration of these periods of contact of treatments and soil, the fertilizer placement zones (cores) were sampled by means of a metal tube about 1.25 inches in diameter forced down through the entire depth of the centers of the cores. These samples, averaging, on a dry basis, 160–200 grams each, depending on the soil, were air-dried and screened through a 2 mm. sieve.

The *p*H determinations were made on each of the individual samples for the replicated treatments. Since the results indicated comparative uniformity of the samples for each treatment, 50-gram subsamples of each replicate were composited and ground to 100 mesh for the carbonate analyses. After drying, the entire crop samples for each treatment were combined and ground in a Wiley mill.

The *p*H values reported were determined on the unleached soils with a glass electrode, 10 grams of air-dry soil to 5 ml. of water being used. The residual carbonates were determined on subsamples of the 100-mesh composites by boiling with hydrochloric acid (1+4) in a Knorr apparatus and absorption of the carbon dioxide in ascarite. The results were corrected for the "blanks" determined on the untreated soils (Treatment 1). The magnesium in the crop samples was evaluated by appropriate conventional methods.

The pertinent data are summarized in Table 1. These results are to be considered as preliminary and of an orienting nature. Interpretation and definite conclusions are deferred until completion of the experiments, when data for the succeeding repetitions of the fertilizer and crop treatments and for the final residual effects are available. A number of comments are, however, appropriate.

TABLE 1.—*Decomposition of dolomitic limestone in the soil of the fertilizer placement zone as evaluated from the pH and residual carbonates, and from the increased magnesium content of the plants, after one crop of corn*

Original *p*H of soils: Caribou loam, 4.6; Sassafras fine sandy loam, 5.0; Sassafras loam, 5.0

Period of contact with soils: Caribou loam, 79 days; Sassafras fine sandy loam, 84 days; Sassafras loam, 77 days

TREATMENT NO.	TREATMENT*		EFFECT ON *p*H OF UNLEACHED SOIL, FERTILIZER ZONE						DECOMPOSITION OF DOLOMITIC MATERIALS AS EVALUATED FROM RESIDUAL CARBONATES IN PLACEMENT ZONE				PROPORTION OF MAGNESIUM FROM TREATMENTS RECOVERED IN CROP			RELATIVE† RECOVERY OF ADDED Mg
			*p*H AFTER REACTION PERIOD			RELATIVE EFFECT ON *p*H, FULL RATE HYDRATED DOLOMITE=100										
	FERTILIZER	MAGNESIUM MATERIAL	CARIBOU LOAM	SASSAFRAS FINE SANDY LOAM	SASSAFRAS LOAM	CARIBOU LOAM	SASSAFRAS FINE SANDY LOAM	SASSAFRAS LOAM	CARIBOU LOAM	SASSAFRAS FINE SANDY LOAM	SASSAFRAS LOAM	AVERAGE	CARIBOU LOAM	SASSAFRAS FINE SANDY LOAM	SASSAFRAS LOAM	SASSAFRAS FINE SANDY LOAM
									per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
1	None	None	4.6	5.1	5.0	—	—	—	—	—	—	—	—	—	—	—
2	0-8-6	None	4.7	4.6	4.8	—	—	—	—	—	—	—	—	—	—	—
3	6-8-6	None	4.3	4.5	4.5	—	—	—	—	—	—	—	—	—	—	—
4	6-8-6	Hydrated dolomite, 1/3 rate	4.5	5.1	4.8	—	—	—	—	—	—	—	4.9	26.1	30.6	—
5	6-8-6	Hydrated dolomite 2/3 rate	4.6	5.6	5.1	—	—	—	—	—	—	—	6.4	23.1	24.3	—
6	6-8-6	Hydrated dolomite, full rate	4.7	6.2	5.4	—	—	—	—	—	—	—	2.1	20.5	7.9	—
7	6-8-6	Dolomite A; 20–40 mesh	4.4	4.8	4.7	16	17	23	15.4	17.2	8.5	13.7	—	1.2	7.9	5.9
8	6-8-6	Dolomite A; 40–60 mesh	4.6	5.2	4.9	71	40	43	31.9	23.3	41.4	32.2	1.4	2.9	1.9	14.1
9	6-8-6	Dolomite A; 60–80 mesh	4.7	5.4	5.0	100+	53	53	61.2	23.4	41.4	42.0	4.7	6.3	10.8	30.7
10	6-8-6	Dolomite A; 80–100 mesh	4.7	5.5	5.1	100+	58	64	67.3	36.4	55.3	53.0	1.5	8.9	17.2	43.4
11	6-8-6	Dolomite A; 100-200 mesh	4.9	5.5	5.3	100+	58	85	87.0	48.2	68.1	67.8	4.0	9.4	9.7	45.9
12	6-8-6	Dolomite A; 200 mesh	4.9	5.9	5.5	100+	83	108	96.5	58.5	87.9	81.0	7.7	12.3	13.4	60.0
13	6-8-6	Selectively calcined dolomite	4.8	6.3	5.4	—	—	—	—	—	—	—	8.0	20.3	18.9	—
14	6-8-6	Magnesium sulfate equiv. to Mg in No. 4	4.3	4.6	4.5	—	—	—	—	—	—	—	2.6	10.8	19.6	—
15	6-8-6	Magnesium sulfate equiv. to Mg in No. 5	4.3	4.7	4.5	—	—	—	—	—	—	—	0.2	11.5	11.0	—
19	6-8-6	Magnesium sulfate equiv. to Mg in No. 6	4.3	4.7	—	—	—	—	—	—	—	—	4.4	15.6	—	—
16	6-8-6	Composite dolomite A	4.7	5.4	5.1	100+	53	64	61.2	42.2	44.8	49.4	3.4	9.4	7.5	45.9
17	6-8-6	Composite dolomite B	4.7	5.5	5.2	100+	58	75	67.3	43.4	51.4	54.0	6.4	12.3	5.6	60.0
18	6-8-6	Composite dolomite C	4.6	5.4	5.0	71	53	53	47.1	32.4	41.1	40.2	3.4	5.1	12.9	24.9

* Rates of application equivalent to 2000 lbs. of neutralized fertilizer per acre: confined to one tenth of total weight of soil.
† Assigning value of 100 to proportion of added magnesium recovered in crop with full rate of hydrated dolomite.

The changes in *p*H resulting from the several treatments are relatively consistent; but the range of variation differs in magnitude for each of the three soils. It is narrowest for the highly buffered Caribou loam, widest for the poorly buffered Sassafras fine sandy loam, and intermediate for the intermediately buffered Sassafras loam. The "relative effect on *p*H" was derived by the procedure of Taylor and Pierre, by comparing the values for the several dolomites with those for the hydrated dolomite, and assigning values of 33-1/3, 66-2/3 and 100 per cent to the 1/3, 2/3 and full rates of the latter, respectively. While these derived figures are relatively consistent in trend, the indicated complete decomposability of the 60–80 mesh and finer material, in contact with the Caribou loam, should be accepted with reservation, even though higher reactivity in this more acid soil would be anticipated. The range of *p*H variation in the case of the well-buffered Caribou loam is so narrow as to lessen the significance of the absolute numerical magnitudes of derived values.

The values for decomposition of the dolomitic materials, as derived from the values for residual carbonates, are generally consistent with the treatments and with the characteristics of the soils; and they are in harmony with the values derived from the *p*H data. For a given dolomite the rate of decomposition is highest in the Caribou loam, lowest in the Sassafras fine sandy loam, and intermediate in the Sassafras loam.

Data are also presented for the percentages of applied magnesium recovered in the crops. These are computed from the increases in magnesium content of the crops grown with magnesium supplements as compared with the content of the crop with the complete acid fertilizer (Treatment 3), assuming such increases to be attributable to the magnesium added in the treatments. Such comparisons are the only appropriate ones available within the range of treatments used, but they involve the question of effect of variations in the *p*H and calcium content of the soil on absorption of magnesium by the crop. Only in the case of the Sassafras fine sandy loam are the results consistent. For this soil an approximate index of the decomposition of the several dolomites is found in the "relative recovery of added magnesium," derived by expressing the values for the percentages of added magnesium recovered in the crop as proportions of the corresponding value for the full rate of hydrated dolomite, assigning the latter a value of 100. These comparisons are made with reservations, but the resulting values are rather consistent with those derived from the residual carbonates.

Further studies will include evaluation of the increase in readily soluble magnesium of the soil associated with the several dolomitic treatments.

These preliminary data indicate that, for the present, the residual carbonates constitute the most satisfactory index of the comparative rates of decomposition of the different dolomitic materials.

DECOMPOSITION OF DOLOMITIC LIMESTONE IN SOILS WHEN USED AS A NEUTRALIZING AGENT IN COMPLETE FERTILIZERS*

STUDIES ON DUNBAR VERY FINE SANDY LOAM, RUSTON SANDY LOAM, NORFOLK FINE SANDY LOAM, AND PORTSMOUTH FINE SANDY LOAM

By E. R. COLLINS and F. R. SPEER[1] (Agronomy Department, North Carolina Experiment Station, Raleigh, N. C.)

This work constitutes part of a program of study to determine the availability of magnesium in dolomitic limestone of different degrees of fineness when used as the neutralizing agent in non-acid-forming fertilizers. The purpose of this study was to determine the rate of decomposition of the dolomitic limestone as evaluated by reaction change in the soil and by the determination of residual carbonates after a crop of cotton had been grown on it for 65–75 days. Magnesium determinations were made on a few plant samples to indicate any change in the concentration of magnesium in the plant due to the decomposition of the dolomitic limestone during the growing season.

OUTLINE OF THE EXPERIMENTS

The general plan of these experiments and method of procedure was the same as that used by Taylor and Pierre.[2] The soils selected were a Dunbar very fine sandy loam of *p*H 5.45, Ruston sandy loam of *p*H 5.60, Norfolk fine sandy loam of *p*H 5.42, and Portsmouth fine sandy loams of *p*H 5.18 and 4.50. The soils selected were considered to have *p*H values typical of these soils. The two Portsmouth fine sandy loam soils of different reactions were taken to determine the relationship between the *p*H value of the soil and the percentage decomposition of the dolomitic limestone. Nineteen treatments were used in duplicate on the five soils comprising four soil types.

METHOD OF PROCEDURE

Each soil type studied was potted in 2-gallon pots in the usual manner, and the soil was weighed so that each pot contained the same amount of air-dried soil. One-tenth of the soil in each pot was removed, and fertilizer calculated to be equivalent to 1333 pounds per acre (on the basis of all the soil in the pot) was thoroughly mixed with this soil. A hollow metal cylinder, the inside diameter of which was 2.5 inches, and which enclosed exactly one-tenth of the area of the inside of the pot, but was slightly longer than the height of the pot, was placed in the center of the empty pot, and the fertilized soil was placed inside this metal cylinder and gently

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[1] Graduate Assistant (DuPont Fellowship).

[2] Proc. 1st Ann. Meeting, Committee on Fertilizers, Am. Soc. Agron., 1935, pp. 15–23.

packed by jolting the pot up and down. The untreated soil was then placed in the pot on the outside of the metal cylinder and packed as was the other portion. A circular metal collar protected with asphaltum paint, 2 inches in height and about 3 inches in diameter, was placed over the end of the cylinder and was embedded about 0.5 inch in the soil. The metal cylinder was then removed, and the circular collar marked the fertilized zone.

TABLE 1.—*Percentage decomposition of dolomitic limestone when used as a neutralizing agent in an acid-forming fertilizer*

	DUNBAR VERY FINE SANDY LOAM	RUSTON SANDY LOAM	NORFOLK FINE SANDY LOAM	PORTSMOUTH NO. 1 FINE SANDY LOAM	PORTSMOUTH NO. 2 FINE SANDY LOAM	AVERAGE
Original *p*H of the respective samples	5.45	5.60	5.42	5.18	4.50	
Time of contact with soil (days)	75	75	65	72	78	
PLAT NO.	TREATMENT	PER CENT DECOMPOSITION				
7	6–8–6 + Dolomite A, 20–40-mesh	22.4	17.8	30.4	29.3	37.4	27.5
8	6–8–6 + Dolomite A, 40–60-mesh	52.2	33.1	30.4	51.5	63.3	46.1
9	6–8–6 + Dolomite A, 60–80-mesh	64.0	42.7	35.4	70.7	87.4	60.0
10	6–8–6 + Dolomite A, 80–100-mesh	67.7	45.9	41.8	79.9	94.0	65.9
11	6–8–6 + Dolomite A, 100–200-mesh	83.2	58.0	55.7	94.5	99.4	78.2
12	6–8–6 + Dolomite A, through 200-mesh	87.6	75.2	76.0	97.6	100.0	87.3
16	6–8–6 + Composite A[1]	59.0	45.9	36.7	70.7	80.1	58.5
17	6–8–6 + Composite B[1]	70.1	53.3	44.3	78.1	83.9	65.9
18	6–8–6 + Composite C[1]	55.9	38.9	37.3	62.8	79.5	54.9
	Per cent $CaCO_3$ in check soil	0	0.006	0.008	0.0015	0.0007	

All the pots were planted to cotton and kept at optimum moisture content with tap water for 65–75 days. The plants were then removed and dried for further analysis. Soil samples were removed from the fertilizer zone by means of a circular cylinder about 1.25 inches in diameter, which was forced down through the center of the core of fertilized soil.

A portion of each sample was leached for the determination of soil reaction, and the remainder was air-dried for the residual carbonate determination by the Schollenberger method.[1]

[1] *Soil Sci.*, 30, 307–325 (1930).

RESULTS

The results[1] in Table 1 show the percentage decomposition of the dolomitic limestone on the five soils of the acidity indicated and for the period of time given. These percentage values were corrected for the check, which received no treatment. Figure 1 shows clearly the difference in decomposition of the various particle sizes. Even the coarser grades were appreciably decomposed during the growing season, the decomposition of the 40–60 mesh dolomite averaging nearly 50 per cent on the five soils and that of the 20–40 mesh 27.5 per cent.

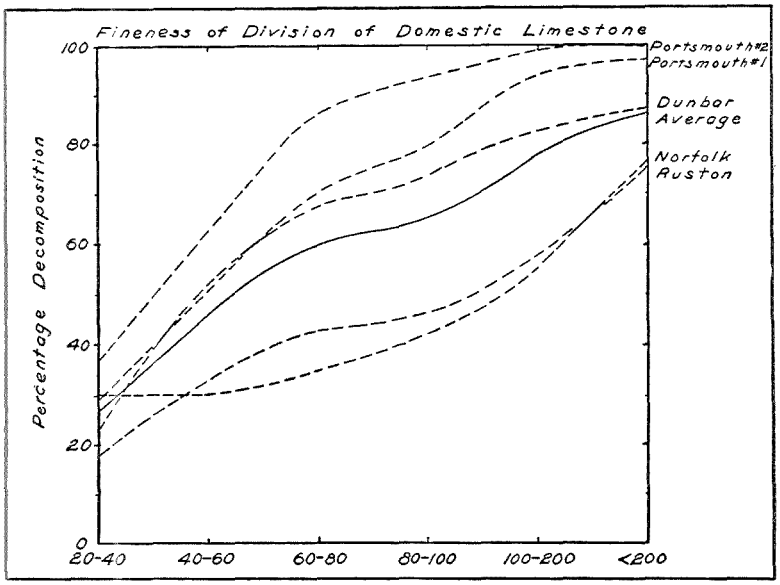

FIG. 1.—PERCENTAGE DECOMPOSITION OF DIFFERENT DOLOMITE SEPARATES ON FIVE SOIL TYPES

The Portsmouth soils of higher organic matter content, greater buffer capacity, and lower *p*H values show a marked increase in decomposition of all the dolomitic fractions over that of the more sandy and less acid Norfolk and Ruston soils. The Dunbar soil occupies an intermediate position with respect to the other two in the relative decomposition of the various fractions. Composite dolomite B is the most highly reactive of the composite dolomites, while composite A is superior to composite C. This difference in decomposition of the composite dolomites was evident throughout the five soils.

[1] Acknowledgment is gratefully given to Dr. Neil E. Rigler for skillful construction of the apparatus used in these determinations by which rubber connections were largely eliminated and the operation appreciably facilitated.

TABLE 2.—*The pH of leached soil after contact with treatments shown for the period indicated*

PLAT NO.	TREATMENT		DUNBAR VERY FINE SANDY LOAM		RUSTON SANDY LOAM		NORFOLK FINE SANDY LOAM		PORTSMOUTH NO. 1 FINE SANDY LOAM		PORTSMOUTH NO. 2 FINE SANDY LOAM	
	FERTILIZER	MG MATERIAL	1	2	1	2	1	2	1	2	1	2
1	None	None	5.45	5.33	5.77	5.67	5.37	5.37	4.86	4.92	4.57	4.57
2	0–8–6	None	5.29	5.23	5.43	5.43	5.24	5.20	4.93	4.87	4.43	4.43
3	6–8–6	None	4.84	4.77	5.29	5.26	4.99	5.03	4.84	4.86	4.29	4.29
4	6–8–6	1/3 rate hydrated dolomite	4.92	4.99	5.29	5.45	5.13	5.03	4.99	5.07	4.35	4.27
5	6–8–6	2/3 rate hydrated dolomite	5.14	5.07	5.60	5.63	5.17	5.29	5.03	5.04	4.33	4.29
6	6–8–6	Full rate hydrated dolomite	5.21	5.28	5.80	5.87	5.65	5.72	5.27	5.20	4.46	4.46
7	6–8–6	Dolomite A, 20–40 mesh	4.87	4.92	5.51	5.51	5.13	5.13	4.88	4.82	4.57	4.61
8	6–8–6	Dolomite A, 40–60 mesh	5.02	4.97	5.63	5.63	5.15	5.14	5.01	4.98	4.58	4.60
9	6–8–6	Dolomite A, 60–80 mesh	5.06	5.12	5.82	5.82	5.25	5.23	5.04	5.06	4.62	4.67
10	6–8–6	Dolomite A, 80–100 mesh	5.16	5.16	5.80	5.80	5.22	5.33	5.14	5.23	4.65	4.64
11	6–8–6	Dolomite A, 100–120 mesh	5.26	5.23	5.99	6.07	5.33	5.31	5.25	5.26	4.62	4.68
12	6–8–6	Dolomite through 200 mesh	5.29	5.41	6.03	6.17	5.53	5.57	5.29	5.22	4.75	4.68
13	6–8–6	Selectively calcined dolomite	5.50	5.51	6.51	6.38	5.73	6.00	5.24	5.18	4.57	4.57
14	6–8–6	$MgSO_4$ ≏ to Mg in No. 4	5.02	5.02	5.63	5.33	5.47	5.28	4.69	4.65	4.29	4.29
15	6–8–6	$MgSO_4$ ≏ to Mg in No. 5	4.84	4.84	5.33	5.43	5.11	5.20	4.55	4.56	4.33	4.25
16	6–8–6	Composite dolomite A*	5.12	5.12	5.43	5.39	5.38	5.32	4.91	4.95	4.43	4.43
17	6–8–6	Composite dolomite B	5.23	5.23	5.56	5.70	5.38	5.51	5.01	5.00	4.45	4.45
18	6–8–6	Composite dolomite C	5.02	5.06	5.53	5.53	5.21	5.25	5.17	4.87	4.40	4.30
19	6–8–6	$MgSO_4$ ≏ to Mg in No. 6	4.79	4.79	5.14	5.14	5.15	5.13	4.63	4.58	4.23	4.25
	Original *p*H of soils		5.45		5.60		5.42		5.18		4.50	
	Time of contact with soil (days)		75		75		65		72		78	

* Composite dolomites A, B, and C represent material from different quarries, and each one was composed of equal parts of 20–40, 40–60, 60–80, 80–100, 100–200, and through 200 mesh dolomite.

TABLE 3.—*Magnesium content of cotton crop*

TREATMENT NO.	TREATMENT		DUNBAR		NORFOLK		PORTSMOUTH NO. 1		RUSTON	
	FERTILIZER	MG MATERIAL	MgO	Ca–Mg RATIO	MgO	Ca–Mg RATIO	MgO	Ca–Mg RATIO	MgO	Ca–Mg RATIO
			per cent		*per cent*		*per cent*		*per cent*	
1	None	None	1.39	1.89	0.78	3.45	0.89	2.15	0.52	3.12
2	0–8–6	None	0.94	2.18	0.62	3.69	0.93	2.51	0.48	3.52
3	6–8–6	None	0.97	2.49	0.63	3.81	1.07	2.09	0.44	4.14
4	6–8–6	1/3 rate hydrated dolomite	1.14	2.12	0.76	3.05	1.09	2.08	0.55	2.71
5	6–8–6	2/3 rate hydrated dolomite	1.18	1.96	0.80	2.80	1.16	1.90	0.67	2.27
6	6–8–6	Full rate hydrated dolomite	1.18	1.94	0.85	2.71	1.14	2.20	0.66	2.08
7	6–8–6	20–40 mesh dolomite	1.16	2.12	0.67	3.40	1.08	2.40	0.42	3.86
8	6–8–6	40–60 mesh dolomite	1.12	2.33	0.70	3.20	1.00	2.16	0.46	3.15
9	6–8–6	60–80 mesh dolomite	1.06	2.38	0.80	3.26	1.07	2.21	0.42	4.10
10	6–8–6	80–100 mesh dolomite	1.20	2.00	0.79	2.99	1.22	1.99	0.57	2.63
11	6–8–6	100–200 mesh dolomite	1.25	1.83	0.80	2.40	1.30	2.22	0.53	2.85
12	6–8–6	Through 200 mesh dolomite	1.30	1.85	0.76	2.58	1.28	1.87	0.69	2.25
13	6–8–6	Selectively calcined dolomite	1.30	1.81	0.91	2.43	1.34	2.06	0.64	2.30
14	6–8–6	$MgSO_4$ to Mg in No. 4	1.08	2.17	0.75	2.65	1.06	2.55	0.56	2.73
15	6–8–6	$MgSO_4$ to Mg in No. 5	1.20	1.83	0.83	2.77	1.08	2.16	0.51	3.71
16	6–8–6	Composite dolomite A	1.30	2.01	0.74	2.91	1.19	2.03	0.67	2.69
17	6–8–6	Composite dolomite B	1.33	1.79	0.78	3.45	1.35	2.03	0.72	2.25
18	6–8–6	Composite dolomite C	1.25	2.22	0.64	3.56	1.14	2.09	0.66	2.83
19	6–8–6	$MgSO_4$ to Mg in No. 6	1.56	1.79	0.94	2.94	1.18	1.93	0.86	1.81

Table 2 gives the *p*H of the leached soil after contact with the fertilizer treatments shown for the period of time indicated. There is considerable variation in the neutralizing value of the several screen fractions on the different soil types. On the Dunbar and Norfolk soils the coarser grades were not very effective in neutralizing acidity while on the Portsmouth and Ruston soils even the 40–60 mesh was sufficient to maintain the *p*H. In general the composite dolomites were very effective in maintaining the *p*H of the soil, especially composite dolomite B. After the period of treatment the *p*H of the soil in the pot receiving composite dolomite B as a supplement was, in no case, more than 0.2 *p*H lower than that of the original soil. Selectively calcined dolomite was a very effective neutralizing agent on all soil types, while magnesium sulfate appeared to increase the acidity slightly.

The magnesium determinations on the cotton plants are not finished and therefore no definite conclusions are given at this time. The preliminary results are included in Table 3.

EFFECT OF PARTICLE SIZE ON THE SOLUBILITY OF MAGNESIUM IN DOLOMITE AND MAGNESIC LIMESTONE IN 4 PER CENT CITRIC ACID SOLUTION ADJUSTED TO *p*H 4.0 WITH AMMONIUM HYDROXIDE*

By J. W. KUZMESKI (Agricultural Experiment Station, Amherst, Mass.)

In their report on Magnesium and Manganese in Fertilizers last year[1] J. B. Smith and E. J. Deszyck of the Rhode Island Agricultural Experiment Station proposed the use of a 4 per cent citric acid solution adjusted to *p*H 4.0 with ammonium hydroxide as a solvent for the evaluation of available magnesium in dolomite and magnesic limestone. As stated by Smith, there is no theoretical background for the use of this solvent at the particular *p*H used. Its adoption for this purpose will depend on the agreement between the results obtained with it and those obtained from the determination of plant response in vegetation work. However, the results presented by Smith on the recovery of magnesium from dolomite by the 4 per cent citric acid solution indicate that this solution has more promise as a medium in the determination of available magnesium in materials carrying magnesium in other than water-soluble forms than have the other solvents he used.

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* Contribution No. 320 of the Massachusetts Agricultural Experiment Station. Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November 14, 15, 16, 1938.

[1] *This Journal*, 21 277 (1938).

The tentative A.O.A.C. method used for determining the neutralizing value of liming materials[1] makes no distinction between coarsely ground and finely ground products. The value obtained by this method is based solely on the total acid-soluble content of magnesium and calcium oxides,

TABLE 1.—*Deviation in percentage of silica, MgO, and CaO present in each of the fractions used*

SAMPLE	AS SAMPLED	MESH				
		60–80	80–100	100–150	150–200	THROUGH 200
A-2 (%)						
Silica	2.00	2.40	2.25	2.25	2.15	1.50
MgO	21.20	21.23	21.37	21.14	21.15	21.28
CaO	31.40	30.70	30.77	30.98	31.16	31.93
Neut. value equiv. to % CaO	59.02	58.67	58.88	58.88	59.02	59.94
A-3 (%)						
Silica	1.25	1.75	1.75	1.50	1.35	1.10
MgO	21.28	21.37	21.28	21.55	21.55	21.28
CaO	31.12	30.84	30.84	30.84	31.12	31.19
A-29 (%)						
Silica	15.50	25.50	24.50	21.00	15.00	12.25
MgO	16.50	13.35	13.81	15.98	17.16	17.02
CaO	28.74	26.67	27.20	27.76	28.53	29.37
Neut. value equiv. to % CaO	50.47	44.16	44.51	49.42	51.17	52.22
A-53 (%)						
Silica	13.50	*	*	18.50	17.00	11.25
MgO	18.29	*	*	15.93	18.74	18.29
CaO	28.53	*	*	28.11	28.74	29.65
Neut. value equiv. to % CaO	50.82	*	*	43.60	47.11	51.17

* Sample practically all finer than 100 mesh. Not enough material coarser than 100 mesh available to make tests.

hydroxides, and carbonates. Therefore, it was thought that it might be of interest to ascertain the relative solubility of several brands of magnesic limestone and dolomite by using the method suggested by Smith. (It must be stressed that "solubility" as the term is used here is not synonymous with "availability" since, at this time, there is no proof that the solubility of magnesium in this particular solution represents the portion of the magnesium readily available to plants.)

Accordingly, nine samples, each representing a different brand of magnesic limestone or dolomite sold in Massachusetts in 1937, were taken for

[1] *Methods of Analysis, A.O.A.C.*, 1935, 38.

analysis. Each sample was sieved, and fractions representing meshes 60–80, 80–100, 100–150, 150–200, and finer than 200, respectively, were used in an effort to determine, if possible, at what particle size the magnesium in the samples would be completely dissolved in the solvent specified. The finest fraction used by Smith was 100–120 mesh.

The method employed by Smith was followed here; 0.2 gram samples were digested in 100 cc. of 4 per cent citric acid, and adjusted to *p*H 4.0 with ammonium hydroxide, at 90–95° C. for 90 minutes, the samples being shaken at intervals of 5 minutes. After filtering and washing, the magnesium was determined in the insoluble residue.

TABLE 2.—*Comparison of total acid-soluble MgO with MgO not dissolved in adjusted 4% citric acid solution*

SAMPLE	ACID-SOLUBLE MgO	PERCENTAGE OF MgO NOT DISSOLVED IN CITRIC ACID-AMMONIUM CITRATE SOLUTION ADJUSTED TO *p*H 4.0					
		AS SAMPLED	60–80	80–100	100–150	150–200	THROUGH 200
	per cent						
A-2	21.20	6.61	9.64	8.15	4.98	1.77	0.18
A-3	21.28	9.42	9.51	6.88	4.71	1.81	0.18
A-6	19.34	4.53	7.20	5.02	3.30	0.32	0.05
A-12	21.05	6.79	11.91	9.87	7.20	4.48	0.36
A-22	21.70	5.66	8.51	7.15	4.30	1.58	0.18
A-29	16.50	4.53	2.17	1.95	2.53	2.26	0.18
A-53	18.29	3.49	—	—	2.90	2.63	0.81
A-71	12.60	3.40	6.11	4.57	3.58	1.45	0.36
A-74	21.33	5.47	10.86	9.10	6.47	1.49	0.18
Average	19.25	5.54	8.24	6.59	4.44	1.98	0.28

The results obtained, as was expected, ran more or less uniformly in the same direction. That is, the solubility increased with the increase in fineness. There was one exception. Sample A-29 showed a higher percentage of undissolved magnesium oxide in the solvent used in both the 100–150 and the 150–200 mesh fractions than in the 60–80 and 80–100 mesh fractions. It was noted that this sample contained a relatively high percentage of silica (15.50). The discordant results for this sample indicated that the same proportion of silica, magnesium, and calcium was not being maintained in each fraction of the sample. To test this point, the total acid-soluble magnesium oxide and calcium oxide and the insoluble silica were determined in each fraction of this sample, as well as of three other samples. One of the latter was also high in silica, and the other two contained 1–2 per cent. The neutralizing value was determined for each fraction of three of these samples by the A.O.A.C. method.

It was found (Table 1) that in the samples containing a high percentage of silica the percentage content of acid-soluble magnesium oxide and cal-

cium oxide and of total silica varied considerably with each fraction. In the finer fractions of the sample, the percentage of silica decreased while the percentage of calcium oxide and magnesium oxide increased, but the increase was somewhat greater for magnesium oxide. No significant variation in this respect was found in the fractions of the samples low in silica.

Table 2 shows the percentage of magnesium oxide not dissolved by the adjusted 4 per cent citric acid solution, in comparison with the percentage of total acid-soluble magnesium oxide.

TABLE 3.—*Comparison of total acid-soluble MgO with MgO dissolved in adjusted 4% citric acid solution*

SAMPLE	ACID-SOLUBLE MgO	PERCENTAGE OF ACID-SOLUBLE MgO DISSOLVED IN CITRIC ACID-AMMONIUM CITRATE SOLUTION, *p*H 4.0					
		AS SAMPLED	60–80	80–100	100–150	150–200	THROUGH 200
	per cent						
A-2	21.20	69	55	62	77	92	99.2
A-3	21.28	56	55	68	78	92	99.2
A-6	19.34	77	63	74	83	98.4	99.7
A-12	21.05	68	43	53	66	79	98.3
A-22	21.70	74	61	67	80	93	99.2
A-29	16.50	73	87	88	85	86	99.0
A-53	18.29	81	—	—	84	86	95.6
A-71	12.60	73	52	64	72	88	97.1
A-74	21.33	74	49	57	70	93	99.2
Average	19.25	71	57	66	77	90	98.6

Table 3 gives the percentage of acid-soluble magnesium oxide that was dissolved in the adjusted 4 per cent citric acid solution. The solubility of magnesium varies not only with each fraction of the *same* sample, but also with the same fraction of *each* sample. For example, in the fraction 60–80 mesh the lowest solubility is 43 per cent in Sample A-12 and the highest is 87 per cent in Sample A-29; and in the fraction 100–150 mesh, the lowest is 66 per cent while the highest is 85 per cent. As the fineness approaches 200 mesh, the difference in the solubility of magnesium in the several samples becomes smaller, and the magnesium in the fractions finer than 200 mesh is practically all soluble, the average for the nine samples being 98.6 per cent.

The results of this study seem to justify the belief that the solubilities recorded might have a definite ratio to the rate of solubility or availability of the magnesium and calcium in a limestone product following its application to the soil, and they also emphasize the great advantage of fine grinding from the standpoint of immediate effectiveness of the product, both in neutralizing value and in furnishing available plant food.

APPLICATION OF THE NEUTRAL WEDGE PHOTOMETER TO THE QUANTITATIVE DETERMINATION OF METHANOL IN DISTILLED SPIRITS

By G. F. BEYER (Alcohol Tax Unit, Bureau of Internal Revenue, Washington, D. C.)

Some distilled spirits, such as fruit distillates, normally contain small quantities of methanol, and since it is often necessary to make this determination it seemed to be desirable to develop a method. The only procedure available for such small quantities as 0.01 per cent requires complex as well as cumbersome apparatus and also excessive manipulation.

Since a colorimetric method was considered to be best adapted for this purpose, the Georgia-Morales[1] modification of Deniges'[2] method was selected, except as to the preparation of the sample, because it is the simplest procedure and produces a color that is stable a sufficient length of time to permit readings to be taken in a photometer.

It has long been known that ethyl alcohol definitely affects the sensitiveness of the Georgia-Morales test, but a search of the literature failed to disclose what concentration produces a maximum amount of color. Deniges adds ethyl alcohol to the portion in the test tube; Simmonds[3] uses a 5 ml. sample containing 10 per cent of ethyl alcohol, while Chapin[4] and Georgia and Morales[5] recommend the use of a 5 ml. sample that has previously been diluted to 5 per cent by volume of total alcohols. However, no mention is made of the fact that varying concentrations of ethyl alcohol greatly influence the sensitivity of the test, and therefore it was first necessary to find this optimum percentage of ethyl alcohol.

EXPERIMENTAL

Solutions were made wherein the amount of methanol was kept constant and that of the ethanol was varied. The solutions tested contained 0.08 per cent methanol by volume, while the ethyl alcohol varied from 17.0 to 40.0 per cent by volume and from each other by approximately 2.5 per cent. The color produced by the reactions involved increased in intensity as the percentage of ethyl alcohol decreased, until it was as low as 20.0 per cent. Very little, if any, difference could be noted in the 20.0, 23.0, and 25.0 per cent solutions. The photometer, however, showed that the depth of color obtained from the 20.0 and 23.0 per cent solutions were very slightly deeper than that obtained from the 25.0 per cent solution. However, this difference, may be but slightly outside the limit of experimental error.

The photometer used is known as a Neutral Wedge Photometer and was built around the specifications published by Clifford and Wichmann.[6]

[1] *J. Ind. Eng. Chem.*, 18, 1312–3 (1926).
[2] *Compt. rend.*, 150, 832 (1910).
[3] *Analyst*, 37, 16 (1912).
[4] *J. Ind. Eng. Chem.*, 13, 543 (1921).
[5] *Ibid.*, 18, 1312 (1926).
[6] *This Journal*, 19, 150 (1936).

SELECTION OF PROPER COLOR FILTER

By the use of this photometer and a series of color filters covering the visible spectrum, an abridged spectrograph of the color obtained was made. It is shown in Figure 1. The greatest absorption occurs between 560 and 606 mμ. Hence, if the light filter used transmits only in that spec-

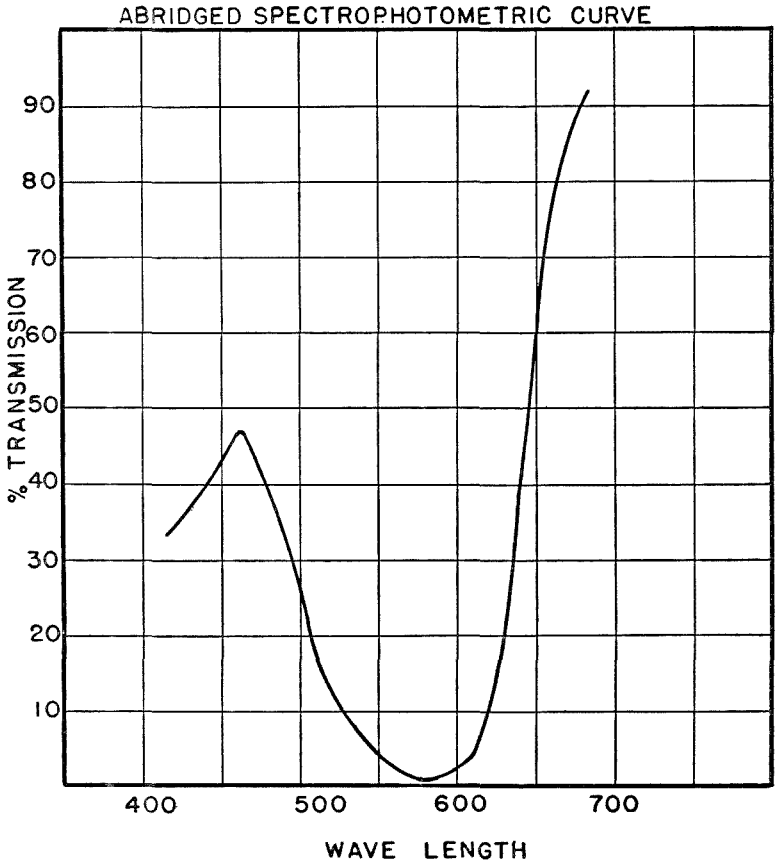


FIG. 1.—ABRIDGED SPECTROPHOTOMETRIC CURVE

tral region, accurate results should be possible, provided the color is sufficiently stable to make the photometer readings. The filters used in this work were those centering around 560, 580, 590, and 610 mμ.

After it had been determined which filters to use, it was then necessary to determine how long the colored solutions should stand to reach a maximum of intensity, how long the color remained stable, and the perma-

nency of the reacting solutions. Various tests showed that the colored solutions must stand about 2 hours before the maximum color is developed and that it remains practically constant for nearly an hour, after which it gradually fades. Numerous tests indicated that the potassium permanganate solution had a tendency to give low results after five weeks, and that a modified Schiff's reagent gave unsatisfactory results after standing four weeks. This solution keeps much better in the cold and when the bottle is fairly well filled. Therefore these solutions should be checked occasionally by testing a sample containing a known quantity of methanol.

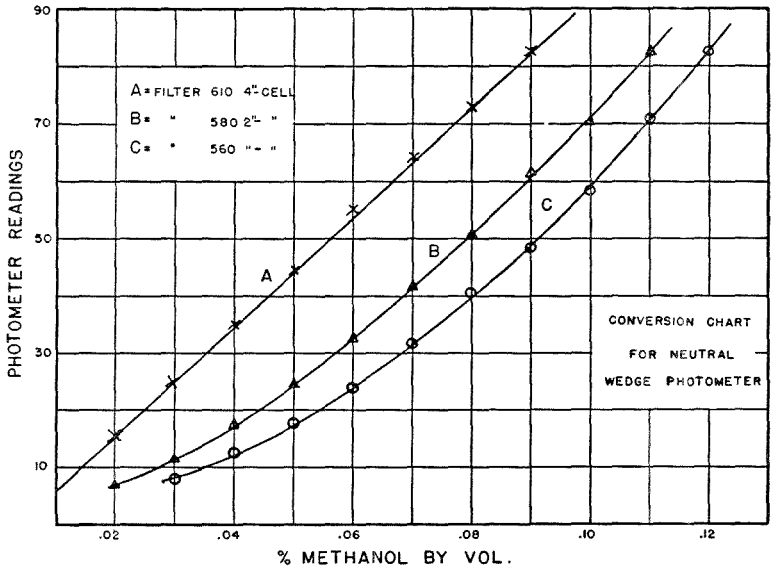


FIG. 2

All of the work with the photometer recorded here was performed in a constant temperature room, which was kept at 25° C. Not more than five readings were taken on any one solution because the lamp used in connection with the photometer throws off considerable heat, which would cause an appreciable loss of sulfur dioxide and thus affect the intensity of the violet color.

Having determined the various optimum conditions for the experiment, the writer made photometer readings on the color obtained from methanol solutions varying in concentrations from 0.02 to 0.15 per cent and from each other by 0.01 per cent. Standard curves were constructed from these readings. Figure 2 shows curves obtained by using filters centering around 560, 580, and 610 mμ.

EFFICIENCY OF STILL USED

A diagram of the upper part of the column and "take-off" of the still is shown in Figure 3.

The packed part of the column of the still, 19 inches long, is filled with small, single-turn, glass helices and is enclosed in a glass tube about 30

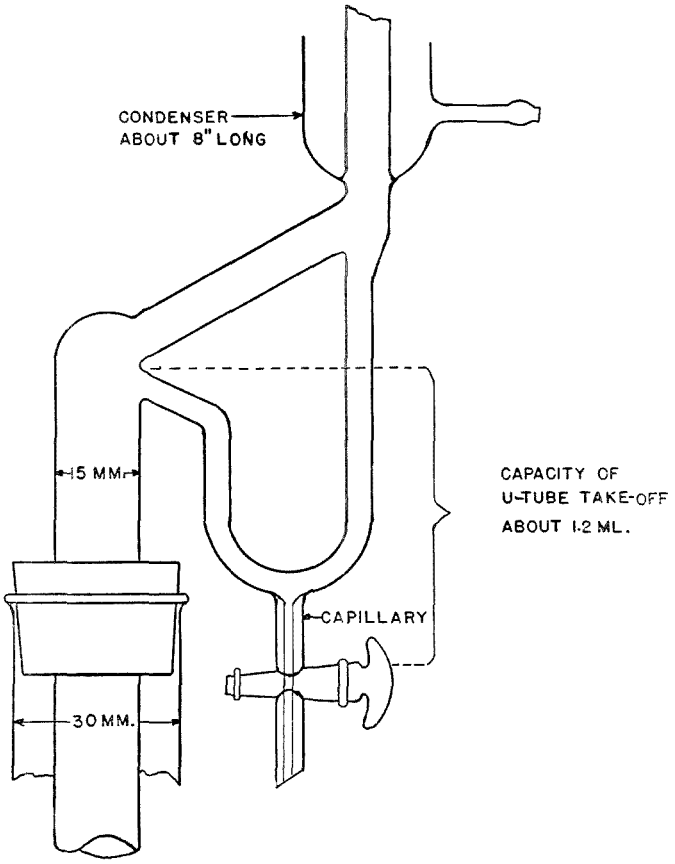


FIG. 3.—DIAGRAM OF UPPER PART OF STILL AND TAKE-OFF

mm. in diameter; 25 ml. of a solution containing 0.1 per cent methanol in 50 per cent ethyl alcohol is placed in a 100 ml. round-bottomed flask connected with the above column and distilled, an electric precision heater being used. After distillation starts the still is allowed to remain under total reflux for about 30 minutes, then fractions consisting of about 1.2 ml. are drawn off at 15 minute intervals until about 8.6 ml. are received. The distillate is transferred to a 50 ml. graduated cylinder, diluted to about 22 per cent total alcohol by volume, then further diluted with

22 per cent ethyl alcohol to 50 ml. Another sample is distilled in the same manner, except the distillate is received in a 50 ml. volumetric flask, but it is similarly diluted. Photometer readings are as follows, and when applied to the curves obtained show the method to be more than 95 per cent accurate.

	2″ Cell		*4″ Cell*	
Filter	Sample 1	Sample 2	Sample 1	Sample 2
	per cent	*per cent*	*per cent*	*per cent*
560	18.5 = 0.104	18.5 = 0.104	—	—
580	23.0 = 0.096	23.3 = 0.097	—	—
610	21.0 = 0.096	21.5 = 0.098	42.6 = 0.097	42.5 = 0.097

DISCUSSION OF RESULTS

The curves obtained by the use of filters 560 and 580 are quite similar, and it is evident that Beer's law was not followed. However, when filter 610 was used and the solution was placed in a 4 inch cell, a straight line was obtained, and except in the very low concentrations the same was true when a 1 inch or a 2 inch cell was used. Filter 610 gave considerable hue difference, which made the matching of the two halves of the photometric field somewhat difficult. No attempt was made to obviate this difficulty by interposing other filters in the light beam traversing the wedge of the photometer, as with little practice it is possible to obtain reproducible and accurate results. Filter 590 also offered some hue differences, especially in the more concentrated solutions. The fact that the hue differences with these two filters are so great in the higher concentrations indicates that the photometer readings are only apparent and not real, since the light transmission consistently favors the red. Therefore it is suggested that light filters centering around 560 and 580 mμ be used.

In the absence of a photometer, excellent results may be obtained when a set of standard methanol solutions are examined at the same time as the unknown, and 6 inch Nessler tubes are used instead of test tubes. In this case the solutions need not stand more than an hour.

The details of the method used after the sample had been distilled and diluted are as follows:

METHOD

REAGENTS

Potassium permanganate solution.—Dissolve 3 grams of $KMnO_4$ and 15 ml. of sirupy phosphoric acid (85%) in 100 ml. of distilled water.

Oxalic-sulfuric acid solution.—Dissolve 5 grams of $H_2C_2O_4$ in 100 ml. of H_2SO_4 (1+1).

Modified Schiff's reagent.—Dissolve 0.2 gram of Kahlbaum's rosaniline HCl in about 120 ml. of hot water. Cool, and add 2 grams of Na_2SO_3 previously dissolved in 20 ml. of water. Add 2 ml. of concentrated HCl, dilute the solution to 200 ml., and place in the refrigerator for at least 24 hours before using.

PROCEDURE

Place 4.75 ml. of water and 0.25 ml. of the sample previously diluted to about 22% total alcohols by volume in a 6″ test tube, or in a 6″ Nessler tube if no photometer is used. Add 2 ml. of the $KMnO_4$ solution, mix thoroughly without inverting the tube, allow to stand 10 minutes with occasional shaking, and then add 2 ml. of the $H_2C_2O_4 - H_2SO_4$ solution. Add 5 ml. of the modified Schiff's reagent, mix thoroughly by inverting the tube three times, stopper, and allow to stand for about an hour if comparison is to be made in Nessler tubes, and $2\frac{1}{4}$ hours if a photometer is to be used, in which case not more than four determinations should be made at one time. This number may be made about every 20 minutes. After a standard curve has been made, the per cent of methanol may be read therefrom by applying the photometer readings in the usual manner.

CONCLUSIONS

The use of a neutral wedge photometer in connection with a curve made from a set of standards makes it possible to determine accurately very small amounts of methanol in distilled spirits, especially if all the conditions of temperature, age of reacting solutions, etc., previously mentioned, are strictly observed.

Inasmuch as the curves obtained by the use of the theoretical colored filters show that Beer's law was not being followed, it will be necessary for each analyst to construct his own standard curve.

For qualitative work the reagents may be older than stated and still give satisfactory results except when only a trace of methanol is present.

A NEW METHOD FOR READING THE COLOR OF WHISKEY

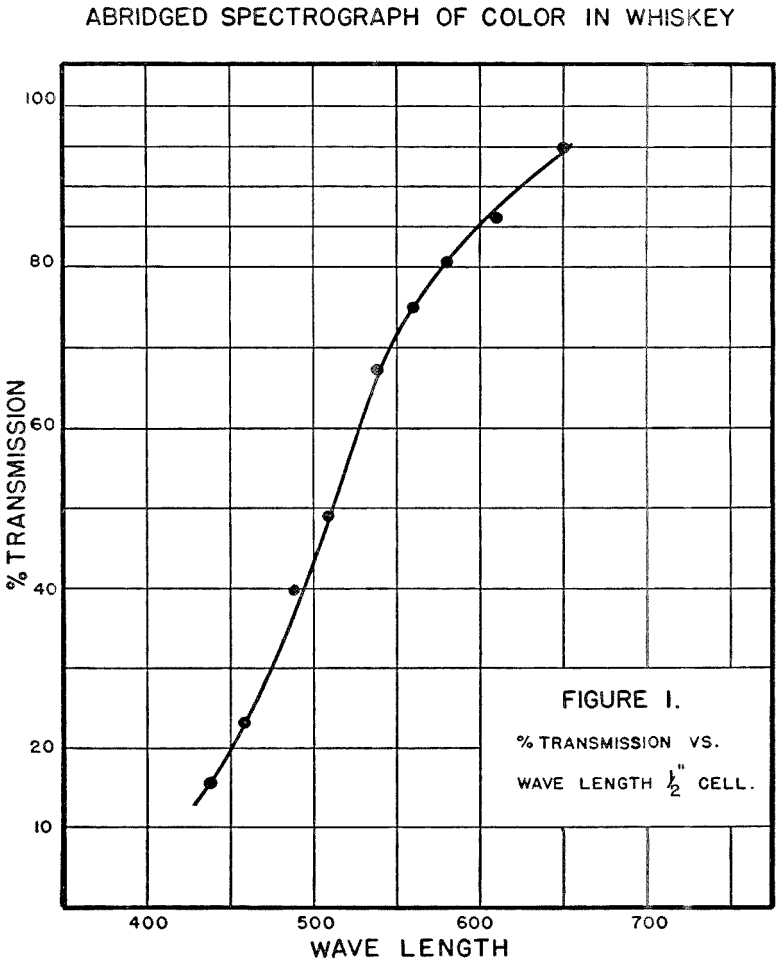
By G. F. Beyer (Alcohol Tax Unit, Bureau of Internal Revenue, Washington, D. C.)

The method generally used for determining color of whiskey and other distilled spirits is the matching of the color with standard colored glass slides of the American Society of Brewing Chemists, Series No. 52, in a Lovibond tintometer. This process is quite difficult and unsatisfactory when the whiskey has acquired a considerable amount of color and when the sample varies slightly in tint or shade from the colored glass. Therefore the writer decided to utilize the neutral wedge photometer to test its usefulness for this purpose.

CHOICE OF PROPER FILTER

To determine the proper colored filter to use it was necessary to take a series of readings of a sample of whiskey with the photometer and to use colored glass filters covering the entire visible spectrum. An abridged spectrophotometric curve, Figure 1, obtained by this procedure shows that the greatest absorption occurs in the spectral region centering around 440 mμ. Theoretically, therefore, a colored filter transmitting light around

that particular wave length should be the proper one to use. However, after extended experimentation it was found that a filter centering around 460 mμ gave better results, and the curve, or rather a straight line, Figure 2, shows that Beer's law was being followed. The procedure follows:



PROCEDURE

Adjust the zero point, using 50% ethyl alcohol in the ½" cell. Use a sample of whiskey that has a reading of 15 in a Lovibond tintometer, when read in a ½" cell, and take about 5 readings with the photometer. This gives one point on the curve. Obtain the other points in the curve by diluting this same whiskey with 50% alcohol and taking alternate readings in the tintometer and the photometer. Plotting the photometer readings against the tintometer readings gives a straight line that shows that the depth of color is directly proportional to the concentration. After

such a curve has been constructed, the color of any whiskey or distilled spirit may be obtained in terms of the Brewer's scale by taking readings in the photometer and applying them to the curve in the usual manner.

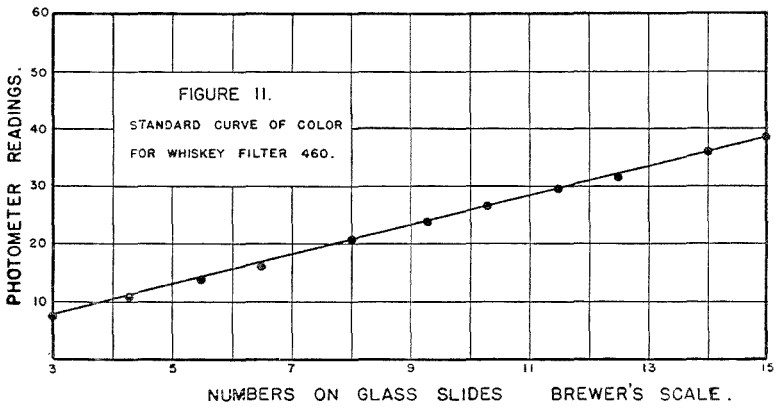


FIGURE II.
STANDARD CURVE OF COLOR FOR WHISKEY FILTER 460.

SUMMARY

The neutral wedge photometer affords a means of reading the color of whiskey and other distilled spirits with greater accuracy, greater ease of matching, and greater freedom from personal error than does the matching of colors in a comparator because it involves simply a brightness match in a monochromatic field, which eliminates color discrimination.

METHOD FOR THE DETERMINATION OF P-PHENYLENEDIAMINE AND P-TOLYLENEDIAMINE

By R. L. Herd (U. S. Food and Drug Administration, Buffalo, N. Y.)

Para-phenylenediamine has been used over a period of several years in various hair dye preparations. Its suitability for this purpose and the poisonous property of the diamines have created much interest in methods of identification. Although extensive reports have been published no convenient and reliable method has been offered for the quantitative estimation of this compound or of those compounds of similar constitution.

The method published by Callan[1] and Henderson depends upon the quantitative formation of benzoquinonedichlorimide. An excess of standard sodium hypochlorite solution is added and the solution titrated back with 0.1 *N* sodium arsenite solution, starch-iodide papers being used as indicator. This method is useful for the determination of the pure chemical individual, but may be unreliable in the presence of other materials that

[1] *J. Soc. Chem. Ind.*, 38, 408–10 T (1919).

react with the hypochlorite solution. Since *p*-phenylenediamine is usually found in mixtures with other substances, such as starch, sulfur, and sulfites, a preliminary separation must be made before the method can be successfully used.

Preliminary investigation indicated that benzoquinonedichlorimide can be completely extracted with chloroform and that six atoms of iodine are liberated when the chloroform extract is shaken with a solution of potassium iodide and hydrochloric acid. Advantage was taken of these facts in developing the quantitative method presented here for the determination of *p*-phenylenediamine and *p*-tolylenediamine. The method is theoretically applicable to all para-diamines, excepting, perhaps, the acid diamines that would probably be held in the aqueous layer by the alkali. The method is also considered to be characteristic for the para-diamines with which hypochlorite forms a white precipitate, whereas various colored products are formed with the ortho and meta-diamines and *p*-diaminodiphenylamine. The purity of the *p*-phenylenediamine was determined by Kjeldahl nitrogen method, and the average per cent recovery, 99.74 (Table 1), was taken as the standard.

TABLE 1.—*Total nitrogen as p-phenylenediamine*

AMOUNT TAKEN	AMOUNT FOUND	RECOVERED
gram	*gram*	*per cent*
0.2704	0.2697	99.71
0.2613	0.2607	99.79
0.2478	0.2472	99.73
	Average	99.74

PROPOSED METHOD

Transfer 1 gram of the sample to a 200 cc. volumetric flask, dissolve in water, and make to the mark. By means of a pipet or buret add an aliquot of this solution representing 0.06–0.08 gram (smaller quantity may be used with good results) to a separator containing 5 cc. of a 5% alkaline NaOCl. If larger sample aliquots are used, repeat the operation, using more NaOCl or a smaller aliquot. (Insufficient NaOCl is indicated if the presence of a brown color is noted while the solution is being added.) Thoroughly mix the solutions during the addition of the aliquot by gently swirling the separator. After the charge has been added, stopper the separator and shake for about 10 seconds. Add 10 cc. of a 10% Na_2HAsO_2 solution, stopper the separator, and shake again. Extract the benzoquinonedichlorimide with two successive 25 cc. portions of $CHCl_3$ and combine the extracts in a second separator. Wash the combined extracts with 10 cc. of water and filter through a pledget of cotton into an iodine flask. Make an additional extraction, wash with the water, and combine with the major portion. Add 50 cc. of water containing 1 gram of KI and 3 cc. of HCl to the combined $CHCl_3$ extracts, stopper the flask, and shake vigorously for 1 minute. Titrate the liberated I with 0.1 *N* $Na_2S_2O_3$. Stopper the flask and shake vigorously at intervals during the titration. The I in the $CHCl_3$ acts as an indicator. Toward the end of the titration add starch solution for the final end point. Each cc. of 0.1 *N* $Na_2S_2O_3 = 0.001801$ gram of *p*-phenylenediamine or 0.002035 gram of *p*-tolylenediamine.

Table 2 shows the percentage recovery of *p*-phenylenediamine and *p*-tolylenediamine based upon the proposed method.

TABLE 2.—*Recovery with proposed method*

AMOUNT TAKEN	AMOUNT FOUND	RECOVERED
	P-Phenylenediamine	
gram	*gram*	*per cent*
0.0119	0.0117	98.32
0.0133	0.0137	103.01
0.0140	0.0142	101.43
0.0239	0.0237	99.16
0.0265	0.0264	99.62
0.0279	0.0285	102.15
0.0298	0.0296	99.33
0.0358	0.0356	99.44
0.0384	0.0382	99.48
0.0528	0.0528	100.00
0.0597	0.0591	99.00
0.0609	0.0605	99.34
0.0619	0.0619	100.00
0.0673	0.0672	99.85
0.0674	0.0672	99.70
0.0713	0.0712	99.86
0.0726	0.0726	100.00
0.0746	0.0739	99.06
0.0793	0.0793	100.00
0.0896	0.0888	99.10
0.0900	0.0894	99.33
	Tolylenediamine	
0.0188	0.0184	97.87
0.0313	0.0311	99.36
0.0376	0.0373	99.20
0.0563	0.0558	99.11
0.0626	0.0620	99.04
0.0751	0.0744	99.07
0.0782	0.0776	99.23
0.0939	0.0932	99.25

The quinonedichlorimide may be used as an aid in establishing the identity of the p-diamine.

Proceed as follows:

Dissolve in 10 cc. of water, sufficient material to represent about 0.5 gram of the diamine and transfer to a separator. Extract with two successive 25 cc. portions of petroleum ether and add the aqueous portion to a second separator containing 25 cc. of NaOCl as directed in the method. Extract the dichloramide with about 10 cc. of petroleum ether, and wash the ether layer with about 10 cc. of water. Filter the extract through cotton into a 50 cc. beaker. Evaporate the ether with the aid of gentle heat and dry the residue in a vacuum desiccator. Accurately weigh about 0.1 gram of the dichloramide and titrate as directed previously. From the number of

cc. of 0.1 N $Na_2S_2O_3$ consumed and weight of sample, calculate the molecular weight of the dichloramide and compare with the theoretical.

$$\text{M.W.} = \frac{60000 \times \text{Wt. sample}}{\text{cc.}Na_2S_2O_3}$$

Some results are given in Table 3 for benzoquinonedichloramide, toluoquinonedichloramide and an unknown purported to contain *p*-phenylenediamine.

TABLE 3.—*Molecular weight*

BENZOQUINONEDICHLORAMIDE	FOUND	THEORETICAL
gram		
0.1294	174.63	174.96
0.1311	174.33	
TOLUOQUINONEDICHLORAMIDE		
gram		
0.1332	188.31	188.98
0.1496	187.94	
DICHLORAMIDE FROM SAMPLE OF HAIR DYE		
gram		
0.0335	173.88	

DISCUSSION OF METHOD AND RESULTS

Directions are given for the use of an aliquot representing 0.06–0.08 gram of the diamine, since this is the optimum amount. The analyst may vary the preparation and size of sample without materially changing the results.

It was found that the chloroform extract from the hypochlorite liberated a small amount of iodine when shaken with a solution of potassium iodide, and for this reason the sodium hypochlorite was destroyed with sodium arsenite subsequent to extraction. Benzoquinone does not react with sodium arsenite in alkaline solution or with potassium iodide in neutral solution.

Some of the results are somewhat high, which is probably due largely to over titration on the small-sized sample. The results compare quite favorably with those of the nitrogen determination.

CONCLUSIONS

A simplified and accurate method for the quantitative determination of *p*-phenylenediamine and *p*-tolylenediamine is presented. The method is specific for these products since their identity may be established by molecular weight tests.

FILTERING BEFORE ADDITION OF PLATINIC CHLORIDE IN THE ANALYSIS OF FERTILIZERS FOR POTASH*

By H. R. ALLEN (Kentucky Agricultural Experiment Station, Lexington, Ky.)

In the two previous papers,[1,2] the presence of considerable insoluble residue in the potassium chloroplatinate in the potash determination in fertilizers was noted. Less residue and more potash were found if the ignition was conducted at higher temperatures, except in the case of a 15 minute ignition in the electric muffle, when silica dishes were used. Ignition in platinum dishes gave a smaller residue and larger potash content than was obtained in silica dishes.

Thornton and Kraybill[3] obtained appreciable amounts of insoluble residue in the potassium chloroplatinate when the latter was not allowed to stand in the acid alcohol for 15 minutes, but otherwise negligible amounts of residue were obtained. They found the residue consisted chiefly of silica, iron, aluminum, and magnesium phosphates. At the 1937 meeting of this Association the Associate Referee on Potash reported results[4] on filtering the solution before the addition of the platinic chloride, in which case lower results for potash were obtained when the solution was filtered, indicating the presence of an insoluble residue.

This paper gives results for insoluble residue obtained in 360 routine potash determinations made in groups of 60 samples each, in which the solution was filtered before the addition of the platinic chloride. The residue was concentrated by filtering five determinations through the same ashless filter paper (C. S. & S. No. 589, blue ribbon) and ashing the papers in groups of 4. The ignited residue was treated with 20 cc. of 80 per cent alcohol, containing 10 per cent by volume of concentrated hydrochloric acid and allowed to stand for 2 hours under a bell jar, then transferred to a filter paper and washed with ammonium chloride and alcohol. The insoluble residue was analyzed for silica, iron and aluminum oxides, phosphoric acid, and in one case for sodium. The residue from one group was analyzed for potassium. Ignitions were made in both silica and platinum dishes, as indicated. The effect of the addition of four drops of hydrochloric acid (1+1) in the dish after ignition and before the addition of any water was investigated.

The official method for potash[5] was used with the exceptions noted. One drop of tributyl citrate was added to the flask before the ammonium oxa-

* The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the Director. Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November 14, 15, 16, 1938.

[1] *This Journal*, 20, 101 (1937).
[2] *Ibid.*, 21, 134 (1938).
[3] *Ibid.*, 20, 287 (1937).
[4] *Ibid.*, 21, 293 (1938).
[5] *Methods of Analysis, A.O.A.C.*, 1935, 30.

late digestion. This prevented foaming. Final ignition over the Fisher burner as previously reported[2] was used. A platinum foil was placed lightly over the silica dishes during the final stage of the ignition to partially compensate for the difference in heat conductance of the platinum and silica. When the filtering was done before addition of the platinum solution, hot water was added to the dish several times and decanted through the filter, time being allowed for complete solution. If necessary, the residue was loosened or broken up with a solid glass rod or rubber policeman. After each filtration, the filter paper was washed well with hot water. After addition of platinum solution and evaporation to dryness 6 cc. of 95 per cent alcohol, to which had been added 10 per cent by volume of hydrochloric acid (sp. gr. 1.18) was placed in each dish and rubbed well with a policeman, and a minimum of 15 minutes was allowed to elapse before filtering. The potassium chloroplatinate of the succeeding set of determinations was transferred to the same crucibles without washing out the potash salt of the preceding set. After five analyses in each crucible the potassium chloroplatinate was leached out with boiling water, the crucibles were dried and weighed, and the increase in weight was noted.

After sixty potash determinations had been made in twelve crucibles the potassium chloroplatinate in six crucibles was rewashed six times with 3 cc. portions of 80 per cent alcohol, and the potassium chloroplatinate in the other crucibles was washed with equal amounts of 95 per cent alcohol. The average loss in weight per crucible when 80 per cent alcohol was used was 1.46 mg.; the average loss in weight when 95 per cent alcohol was used was 0.25 mg. Previous to this washing this group had been well washed with 95 per cent alcohol, then with 80 per cent alcohol, to eliminate all traces of the ammonium chloride washing. In view of the above results, determinations reported in this paper were washed with 95 per cent alcohol, and 95 per cent alcohol was used in preparing the acid alcohol except for the digestion of the residue concentrates, when 80 per cent alcohol was used.

DISCUSSION OF RESULTS

Larger residues were obtained when the ignition was conducted in silica dishes, as is shown in Table 1. The average residue per determination in silica was 2.27 mg., in platinum 1.51 mg. Contact with acid alcohol for 2 hours dissolved appreciably less if the ignition was conducted in silica than in platinum, the average losses being 0.26 and 0.70 mg., respectively. Addition of hydrochloric acid to the dishes after ignition and before water was introduced, reduced the insoluble residue somewhat and aided materially in loosening the material from the dish and in solution. Addition of hydrochloric acid at this stage did not increase the residue left in the filter crucibles. The percentage of potassium oxide equivalent to the insoluble residues is given in Table 2.

TABLE 1.—*Insoluble residues obtained by filtering before addition of platinic chloride*
(Results expressed as mg.)

	GROUP NUMBER (60 ANALYSES)	SILICA DISH. HCl IN DISH[a] (20 ANALYSES)	SILICA DISH. NO ACID. (20 ANALYSES)	PLATINUM DISH. HCl IN DISH[a] (20 ANALYSES)	PLATINUM DISH. NO ACID. (20 ANALYSES)
Residue after ignition	1	15.9	28.8		29.8
	2	12.1	18.8	2.6	
	3[b]	52.2	65.0		26.4
	4[c]	79.6[d,e]	58.1		19.7
	5	43.9[d]	80.8[a]	12.4	
	6	26.4[f,d]	40.1[a,d]		
Residue insoluble in acid alcohol	1	12.5	23.9		26.0
	2	8.5	14.6	1.2	
	3	46.7	57.0		9.4
	4	72.0	53.3		9.9
	5	40.0	75.2	10.2	
	6	22.8	36.6		
Average residue per determination on filter pads after 5 analyses in each crucible[g]	1	0.44	0.44		0.45
	2	0.30	0.40	0.05	
	3	0.46	0.85		0.11
	4	0.61	0.78		0.32
	5	0.64	0.82	0.68	
	6	0.42	0.51		

[a] 4 drops HCl (1+1) in each dish before addition of water.
[b] Residues in this group in contact with acid alcohol 1 hour.
[c] Tributyl citrate not added in this group.
[d] New silica dishes used.
[e] No HCl in dish before water.
[f] Platinum foil not used over dishes during ignition.
[g] Platinum was not deposited in the residues.

TABLE 2.—*Average per cent K_2O equivalent to insoluble residues. Basis 0.25 gram sample*

	GROUP NUMBER	SILICA DISH	SILICA DISH	PLATINUM DISH
Residue insoluble in acid alcohol	1	0.05	0.09	0.10
	2	0.03	0.06	0.005
	3	0.18	0.22	0.04
	4	0.28	0.21	0.04
	5	0.15	0.29	0.04
	6	0.09	0.14	
Residue left in filter crucibles	1	0.03	0.03	0.03
	2	0.02	0.03	0.004
	3	0.04	0.07	0.01
	4	0.05	0.06	0.02
	5	0.05	0.06	0.05
	6	0.03	0.04	

The average residue in per cent potassium oxide equivalent per determination was 0.14 for silica dishes to which hydrochloric acid was added first and 0.18 if hydrochloric acid was not added; 0.02 for platinum dishes to which hydrochloric acid was added and 0.06 if hydrochloric acid was not added.

TABLE 3.—*Analysis of insoluble residues*
(Results expressed as mg.)

GROUP NUMBER		SILICA DISH. HCl IN DISH	SILICA DISH. NO ACID	PLATINUM DISH. HCl IN DISH	PLATINUM DISH. NO ACID
1	SiO_2	9.8	8.0		7.0
	$Fe_2O_3+Al_2O_3$	1.0	4.3		5.5
	P_2O_5	0.7	8.2		9.4
	Undetermined	1.0	3.4		4.1
2	SiO_2	2.6	2.1	0.4	
	$Fe_2O_3+Al_2O_3$	1.9	2.4	0.3	
	P_2O_5	2.6	3.8	0.3	
	Undetermined	1.4	6.3	0.2	
3	SiO_2	2.0	5.3		0.4
	$Fe_2O_3+Al_2O_3$	11.3	14.6		2.2
	P_2O_5	21.6	25.1		4.0
	Undetermined	11.8	12.0		2.8
4	SiO_2	3.0	4.4		1.3
5	SiO_2	0.6	1.3	0.1	
	$Fe_2O_3+Al_2O_3$	11.4	23.2	4.1	
	P_2O_5	20.4	38.7	5.0	
	Na[a]	0.8	1.3	0.4	
	Undetermined	6.8	10.7	0.6	
6	SiO_2	1.2	1.9		
	K_2O	2.4[b]	3.4[c]		

[a] Determined by uranyl acetate method.
[b] Equivalent to average of 0.05 % K_2O per determination.
[c] Equivalent to average of 0.067 % K_2O per determination.

Table 3 gives a partial analysis of the residues and shows the chief components to be silica, iron and alumina, and phosphorus. Magnesium was found in qualitative tests in very small amounts in some instances. Calcium was not found. Potassium was found by means of the spectroscope. All analyses in Group 6 were made in silica dishes. Two of the residues in this group were analyzed for potassium and an amount found equivalent to an average per determination of 0.05 and 0.067 per cent potassium oxide.

Sodium was found in appreciable quantity in Group 5, but was not determined prior to this group. The larger size of the residues found in silica dishes as compared with platinum was due only in small part to silica.

The ignition in platinum was at considerably higher temperature than in silica due to the difference in heat conductance. The residue was always fused in platinum dishes, but this was not the case in silica. Since larger residues were obtained in silica dishes without a corresponding increase in silica, a probable explanation seems to be the formation of sodium metaphosphate, which is relatively insoluble, at the lower temperature. At the higher temperature obtained in platinum, this is changed to sodium pyrophosphate, which is soluble.

$$4NaPO_3 - P_2O_5 = Na_4P_2O_7.$$

If the corresponding potassium salts were used, this explanation would account for the larger potassium content and smaller residue obtained when platinum dishes were ignited at the higher temperature, as reported in the previous paper.[2] In the early work of this Association, Scovell, Peter, and Curtis[1] found it necessary to heat the ignited residue for a sufficient time with water and hydrochloric acid to dissolve any potassium metaphosphate formed. Solutions of samples requiring duplication were not filtered before platinic chloride was added, but the potash content was determined by leaching out the potassium chloroplatinate and reweighing the crucible. Table 4 gives the average increase or decrease in per cent potassium oxide obtained by this method over the filtering process. The results are not conclusive for silica dishes, but show an increase in potassium oxide when platinum dishes were used and the potassium chloroplatinate leached out.

TABLE 4.—*Average increase or decrease in per cent K_2O obtained when K_2PtCl_6 was leached out and crucible reweighed over K_2O from solutions filtered before addition of platinic chloride. Basis 0.25 mg. sample*

GROUP NUMBER	NUMBER OF ANALYSES AVERAGED	SILICA DISHES	NUMBER OF ANALYSES AVERAGED	PLATINUM DISHES
1	9	−0.11	4	−0.02
2	4	+0.04	4	+0.03
3	8	−0.09	8	+0.02
5	5	+0.02	4	+0.11
6	5	+0.09	6	+0.10
Average	31	−0.03	26	+0.048

SUMMARY

Ignition in a silica dish gave a larger residue, less soluble in acid alcohol, than did ignition in platinum. Filtering the residue out before platinic chloride was added gave slightly less potash, and potash was sometimes found in the material removed. The amount of residue filtered from ignition in silica, if counted as potassium oxide, would increase the potash

[1] *Proceedings of the 13th Annual Convention of the A.O.A.C.*, Bull. 49, 42.

content erroneously, in some instances. Residues obtained after ignition in platinum were small, particularly when hydrochloric acid was added when the ignited material was dissolved in the dish. Ignition in platinum, solution of the ignited salts in hydrochloric acid and water, and determination of potassium chloroplatinate by weighing the filter, crucible and contents, leaching out and weighing the crucible, gave the most potassium oxide. One drop of tributyl citrate in the digestion prevented foaming.

IMPROVED MOLYBDENUM BLUE REAGENTS FOR DETERMINATION OF PHOSPHORUS AND ARSENIC

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Investigations in these laboratories, relating to soil phosphorus and the efficiency of its utilization by crop plants, have necessitated refinement in methods for the quantitative determination of minute concentrations of phosphoric acid in soil extracts and plant materials by the colorimetric ceruleomolybdate procedure. When Zinzadze's (40) molybdenum blue reagent was used for this purpose, off colors and interference effects were encountered, which were later traced to limitations in the applicability of the reagent under the conditions imposed. These difficulties were minimized by modification of the reagent and the conditions of its reaction with phosphoric acid; and the reliability and range of application of the method were greatly improved.

The name "molybdenum blue" is properly applied to that complex oxide or series of oxides of molybdenum lying between Mo_2O_5 and MoO_3. Its relative stability in combination with certain substances (phosphoric, arsenic, and silicic acids) and its instability in their absence have led to its wide use in colorimetry. Bucholz (12, 13) is credited with its discovery in 1803 when he triturated molybdic oxide and molybdenum metal together in water suspension. Subsequent investigations (1, 2, 3, 7, 8, 9, 10, 17, 18, 21, 22, 23, 25, 26, 28, 30, 34, 37) of its composition have yielded a variety of data and opinions. However, whether molybdenum blue is a single oxide or a series of oxides has not been conclusively determined, nor does the evidence justify the assignment of a more specific constitution than is expressed by the empirical formulas Mo_nO_{3n-1} for the unstable anhydrous oxide and $(Mo_nO_{3n-1})2H_3PO_4$ for its stable phosphoric acid complex. The opinion held by many workers, that the complex contains pentavalent molybdenum, is substantiated by considerable corroborative evidence.

In 1887 Osmond (29) applied molybdenum blue to the colorimetric determination of phosphorus by reduction of phosphomolybdate with stannous chloride. His method, with variations, has been used almost universally since, notably by Denigés (15, 16) and Truog and Meyer (31). Although Denigés called the blue complex thus formed "stable molybdenum blue," its stability is relative and fleeting. Further search has been necessary in the direction of different reducing agents and modified conditions to achieve truly stable colors. Bell and Doisy, (4), Briggs (11), Benedict (5), Fiske and Subbarow (20), and Tschopp and Tschopp (32) made excellent contributions in the application of organic reducing agents.

All the procedures mentioned are based on the formation of the blue complex by the assumed specific reduction of phosphomolybdate, but Berenblum and Chain (6) have recently shown that molybdic acid is also reduced to a degree dependent upon sulfuric acid concentration and reducing agent strength. These two investigators have already surveyed the problem toward which this study is an independent approach. They solve the problem of reagent concentration by the unique method of extracting the phosphomolybdate with isobutyl alcohol followed by shaking with stannous chloride solution to obtain the pure blue complex in alcoholic solution free of excess reagents.

A departure was made by Zinzadze (36, 37, 38, 39, 40) in developing the reagent upon which the work reported here is based. He first prepared "unstable" molybdenum blue and then permitted it to react in excess with the phosphoric acid. This method resulted in the formation of really stable blue complexes, the excess molybdenum blue oxide being destroyed under proper experimental conditions. Zinzadze's reagent was prepared by the reduction of a sulfuric acid solution of molybdic oxide with powdered molybdenum metal. It was carefully standardized with respect to reduction and acidity to conform to the composition: 0.04 *M* (0.08 *N*) $MoO_2 \cdot 4\ MoO_3$ in 19 *N* sulfuric acid. Later the values were increased to approximate 0.05 *M* $MoO_2 \cdot 4.9MoO_3$ in 25 *N* sulfuric acid. This reagent can be preserved indefinitely in a glass-stoppered bottle. In the determination of phosphorus, the test solution is digested for one hour on the steam bath with acidified sodium bisulfite to prevent interference from iron, arsenic, and nitrates. A measured quantity of the molybdenum blue reagent is added and heating continued 30 minutes longer to develop the color. Probably this time factor, the involved procedure for preparing the reagent, and the extreme precautions advised have diverted much deserved attention from Zinzadze's method.

In the modified method described here, Zinzadze's reagent and procedure have been simplified, and certain deficiencies of the original reagent for determination of both phosphorus and arsenic have been corrected. There is also described an alternative method, combining desirable features of the methods of Zinzadze and of Tschopp and Tschopp.

EXPERIMENTAL

When the Zinzadze method was applied to the determination of phosphoric acid in buffered soil extracts and similar solutions, difficulty was experienced, in many instances, with yellow tints that made visual comparison of the colors unreliable. Fading or incomplete development of color, poor duplication of results, and excessive "blanks" were other difficulties encountered particularly in the case of acetic acid-sodium acetate solutions of the type rather widely used as a buffered extractant for soil phosphorus. Apparently these difficulties were associated with excessive yellow pentavalent molybdenum and with the salt or buffer effect of the extractant, as well as of the sodium bisulfite added. Preliminary experiments showed that the interference of pentavalent molybdenum could be minimized, without decreasing the efficiency of the reagent, by lowering the reduction concentration (Mo_2O_5)* from 0.1 to 0.04 *N*.

It was also found that the interference from foreign salts could be decreased by the substitution of an equivalent quantity of sulfurous acid for the sodium bisulfite and sulfuric acid as used in the Zinzadze procedure and also further reduced by preliminary adjustment of the *p*H of the test solution to the end point of quinaldine red rather than to that of beta-dinitrophenol (original method). However, minimum interference was attained only by increasing the sulfuric acid concentration of the reagent itself from 25 to 36 *N*.

This effect of acidity was found to be associated with and limited by the molybdic oxide concentration,† varying inversely with the latter. In other words, the critical factor is the sulfuric acid-molybdic oxide ratio rather than their independent concentrations. This finding merely extends the observations of Zinzadze (*loc. cit.*) on silica interference to include salt effect. With these data as a guide, and modifying the Zinzadze procedure to substitute sulfurous acid and quinaldine red, as indicated above, the writers made experiments to determine the concentrations of molybdic oxide, sulfuric acid, and the reduction that would give maximum color development with minimum interference.

Three series of reagents, in which these factors varied in turn, were applied to pure aliquots representing 20 gamma (0.02 mg.) of phosphorus and 50 gamma of arsenic, respectively. The resulting color intensities in the test solutions at a uniform volume of 50 ml. were measured in a compensating photoelectric colorimeter designed and constructed in this laboratory by the senior author. Single readings were taken of single determinations, and no results were discarded. The results are given in Tables 1, 2, and 3. The concentrations of the reagent constituents are expressed on the basis of the diluted test solutions. Since the reagents

* The term "reduction concentration" applies to the concentration of pentavalent molybdenum oxide (Mo_2O_5) resulting from reduction of the hexavalent molybdenum oxide (MoO_3).

† The term "molybdic oxide concentration" is restricted to the concentration of hexavalent molybdenum oxide (MoO_3) remaining after reduction.

were added in the proportion of 0.5 ml. per 50 ml. of final volume of test solution, these concentrations represent .01 of those in the original reagents. An exception occurs in the case of Table 2, where supplementary additions of acid were necessary in order to exceed 0.36 *N*, the maximum attainable by the 100-fold dilution of the concentrated reagent. The corresponding color intensities are expressed in terms of the photometer transmission readings.

TABLE 1.—*Effect of molybdic oxide concentration on intensity of color from 20 gamma of phosphorus and 50 gamma of arsenic at a uniform reduction concentration of 0.0004 N and sulfuric acid concentration of 0.36 N*

MOLAR CONCENTRATION OF MOLYBDIC OXIDE	PHOTOMETER READINGS			
	30 MINUTE DEVELOPMENT		60 MINUTE DEVELOPMENT	
	PHOSPHORUS	ARSENIC	PHOSPHORUS	ARSENIC
0.0010	—	—	94.8	96.7
0.0012	—	—	85.2	90.5
0.0014	—	—	61.4	80.1
0.0016	89.5	89.5	61.3	73.5
0.0018	59.6	82.4	58.5	64.8
0.0020	59.5	73.2	58.7	61.0
0.0022	59.2	62.3	59.0	60.5
0.0024	60.5	63.7	59.0	60.5
0.0026	60.0	61.9	58.4	60.1
0.0028	59.6	61.2	59.1	60.5
0.0030	59.0	61.2	58.7	60.6
0.0032	59.5	59.5	58.2	60.4

The data in Table 1 show that the concentration of molybdic oxide, with uniform sulfuric acid and reduction concentrations of 0.36 *N* and 0.0004 *N*, respectively, may be varied from 0.0018 *M* to 0.0032 *M* for phosphorus and from 0.0026 to 0.0032 *M* for arsenic without affecting the transmission value (color intensity), for a 30 minute period of color development. Increasing the period of color development to 60 minutes had no appreciable effect on the color intensity for either phosphorus or arsenic, but extended the range of uniform color development for arsenic down to 0.0020 *M* molybdic oxide. Below 0.0018 *M* MoO_3 the phosphomolybdenum blue drops off sharply, and for arsenomolybdenum blue there is a gradual decline below 0.0026 *M* MoO_3, after 30 minutes and below 0.0020 after 60 minutes.

In Table 2 are presented the effects on color intensity of varying the concentrations of sulfuric acid at a uniform reduction concentration of 0.0004 *N* and molybdic oxide concentrations of 0.0018 and 0.0032 *M* for phosphorus and arsenic, respectively. The molybdic oxide concentration for phosphorus was the lowest one shown above to yield complete color

TABLE 2.—*Effect of sulfuric acid concentration on intensity of color from 20 gamma of phosphorus and 50 gamma of arsenic at a uniform reduction concentration of 0.0004 N and molybdic oxide concentrations of 0.0018 M for phosphorus and 0.0032 M for arsenic*

NORMALITY OF SULFURIC ACID	*p*H*	PHOTOMETER READINGS	
		PHOSPHORUS	ARSENIC
0.24	0.83	58.2	58.2
0.27	0.80	58.0	59.0
0.30	0.77	58.2	59.6
0.33	0.74	58.4	59.0
0.36	0.70	58.0	59.5
0.39	0.68	61.2	59.6
0.42	0.66	67.3	59.4
0.45	0.64	75.6	62.2

* *p*H determinations by glass electrode.

development with a sulfuric acid concentration of 0.36 *N*, and was selected in order to maintain the maximum ratio of sulfuric acid to molybdic oxide necessary for minimum interference by silica and salts. These considerations could be ignored in the case of arsenic, since this element is usually separated (14, 24, 27, 33, 35) by distillation or precipitation prior to its determination. The maximum molybdic oxide value was therefore chosen as it gave the most rapid development of color.

The results show that with pure solutions changes in sulfuric acid concentration from 0.24 *N* to 0.36 *N* (the maximum attainable by direct

TABLE 3.—*Effect of reduction concentration on intensity of color from 20 gamma of phosphorus and 50 gamma of arsenic at a uniform sulfuric acid concentration of 0.36 N and molybdic oxide concentration of 0.002 M*

NORMALITY OF REDUCTION CONCENTRATION	PHOTOMETER READINGS	
	PHOSPHORUS	ARSENIC
0.00040	58.0	59.5
0.00044	57.0	62.3
0.00050	57.8	62.5
0.00058	57.2	62.3
0.00066	57.8	62.5
0.00080	57.2	61.5
0.00100	57.3	60.2*
0.00134	59.6	60.4*
0.00200	77.9	60.1*
0.00200	57.0†	—
0.00400	No color‡	

* Practically complete development of color due undoubtedly to compensatory oxidation of Mo_2O_5, not so rapid in case of phosphorus because of presence of sulfurous acid.

† After 60 minutes on the steam bath.

‡ The composition of this reagent conforms to the formula Mo_2O_5: an excess of MoO_3 over this composition is necessary to produce color.

addition of the reagent in the proportion used) are without effect on the color intensity. The *p*H of the solutions at these concentrations is well below 1.0, the value above which blue color tends to appear in the absence of phosphorus or arsenic.

The data in Table 3 show that for the 30-minute period of color development used, variation in the reduction concentration from 0.00040 *N* to 0.0010 *N* was without material effect on the color intensity for phosphorus. Increasing the period of color development to 60 minutes extended the range of uniform color intensity to 0.00200 *N* reduction. For arsenic the color intensity did not vary materially over the entire range even with 30 minutes' color development.

The results of these experiments indicate that within certain limits and with pure solutions color intensity is comparatively independent of the molybdic oxide, sulfuric acid, and reduction concentrations. However, for maximum color development, with minimum interference from yellow tints, silica, and salt effects, the choice of conditions is narrowed.

While the intensity of the blue colors remains relatively uniform over a considerable range of reduction concentrations, interference from the yellow tints due to excess of pentavalent molybdenum increases with the degree of reduction. For example, the blue colors developed at 0.0004 *N* and 0.002 *N* are identical in intensity when compared visually through a blue filter or in an electrophotometer as in the above experiments. In white light, however, the yellow interference at the higher reduction greatly increases the uncertainty of visual comparison.

Similarly, while pure phosphate solutions yield colors of relatively uniform intensity despite considerable variation in the concentration of molybdic oxide and sulfuric acid, interferences arise in the presence of extraneous substances unless the range of variation in these concentrations is restricted. As shown by Zinzadze (*loc. cit.*) the interference of silica is minimized by increasing the ratio of sulfuric acid to molybdic oxide. Experiments preliminary to this investigation and the data presented later show that similar conditions apply to interference by salts. The sulfuric acid concentrations must be sufficient to hold the *p*H below 1.0, despite the presence of salts of appreciable buffer capacity.

Accordingly, the conditions for minimum interference of yellow tints, silica, and salt effects require the minimum reduction and molybdic oxide concentrations and maximum sulfuric acid concentrations compatible with uniform and complete color development. As shown by the above experimental data these conditions are most nearly approached for phosphorus with molybdic oxide, sulfuric acid, and reduction concentrations of 0.0018 *M*, 0.36 *N*, and 0.0004 *N*, respectively, in the test solution. For arsenic, a higher molybdic oxide concentration, namely 0.0032 *M*, is necessary for full color development.

To attain these conditions in the diluted test solution the concentrated

reagent for phosphorus would have a molybdic oxide concentration of 0.18 *M*, a sulfuric acid concentration of 36 *N*, and a reduction concentration of 0.040 *N*. For arsenic the sulfuric acid and reduction concentrations would remain the same, but the molybdic oxide concentration would be raised to 0.32 *M*. These reagents are therefore concentrated sulfuric acid solutions of 0.02 *M* $Mo_{10}O_{29}$ for phosphorus and 0.02 *M* $Mo_{17}O_{50}$ for arsenic. The improved reagents and procedures for their application to determination of phosphorus and arsenic, as described later, were developed in conformity with these findings.

Incidental experiments were conducted with the application of unreduced sulfomolybdic acid reagents equivalent in concentrations to the improved molybdenum blue reagent to determinations of phosphorus and arsenic by procedures involving use of organic reducing agents. Of the three organic reducing agents in common use, namely hydroquinone, amino naptholsulfonic acid, and methylparamidophenol sulfate (metol), the last was found to be most satisfactory. Color development was complete in 50 minutes at 95° C. with phosphorus, but though proportionate was only 90 per cent complete with arsenic. An alternative method, based on these trials and combining desirable features of the methods of Zinzadze (*loc. cit.*) and Tschopp and Tschopp (32) is included below.

In connection with the preparation of the reagents, it was noted that molybdic oxide dissolves more rapidly in hot concentrated sulfuric acid than in 25 *N* acid; that the reduction of the molybdic oxide by powdered molybdenum in this solution is practically immediate and quantitative at about 140–150° C.; and that in the presence of an excess of molybdenum metal a final composition corresponding to Mo_2O_5 is attained. Thus two avenues are offered by which a reagent of definite composition may be prepared: (1) By reducing sulfomolybdic acid at 150° C. with a calculated quantity of molybdenum metal; (2) the same reduction with an excess of metal followed by the mixing of the proper quantity of unreduced solution with reduced solution decanted from the excess metal as described by Zinzadze.

The several procedures finally developed for preparation of the improved reagents and for their application to the determination of phosphorus and arsenic are as follows:

METHOD A, PHOSPHORUS

REAGENTS

(a) *Molybdenum blue for phosphorus.*—Ignite a portion of C.P. MoO_3 in a porcelain dish at dull red heat and below the melting point in a muffle for about 1 hour. Cool, and weigh 6.96 grams into a 500 ml. Kjeldahl flask. Add 250 ml. of concentrated (36 *N*) H_2SO_4 and a few glass beads, and boil the mixture gently until solution is complete (a slight cloudiness does not matter).

Cool to about 150° C. and add 0.16 gram of C.P. powdered Mo metal on a small watch-glass slid carefully down the neck of the flask so that all of the metal is introduced. Rotate the flask occasionally for 10 minutes, when the metal should be

entirely dissolved, otherwise it can be readily observed against the background of the deep green solution when the flask is held above the level of the eyes. If there is a residue of metal, reheat the solution to 150° C. When the metal is entirely dissolved, cool the solution, dilute a convenient aliquot (5 or 10 ml.) with about 5 volumes of water and titrate with 0.1 *N* or 0.02 *N* $KMnO_4$ until the appearance of a pink color lasting for 1 minute. From this titration calculate the reduction concentration of the solution which should be approximately 0.04 *N*. If less than 0.036 *N*, add a calculated quantity of Mo sufficient to bring the reagent up to 0.04 *N* and reheat to 150° C. Cool, recheck the titer, and preserve the bright blue solution in a glass-stoppered bottle.

(b) *Standard phosphate.*—Prepare aqueous monopotassium phosphate solutions equivalent to 1, 10, 100, etc., gamma of phosphorus per ml.

(c) *Sulfurous acid.*—Saturate 500 ml. of water with SO_2 gas. In cases where $NaHSO_3$ may be used the following is recommended.

(d) *Sodium bisulfite.*—Dissolve 5.2 grams of C.P. $NaHSO_3$ in 100 ml. of normal H_2SO_4. Prepare the solution weekly and keep stoppered.

(e) *Sulfuric acid.*—5% aqueous solution.

(f) *Sodium carbonate.*—10% aqueous solution.

(g) *Quinaldine red.*—0.01% aqueous solution.

DETERMINATION

Pipet an aliquot of the solution containing phosphorus into a 50 ml. volumetric flask. Add one drop of the quinaldine red and adjust to the point where the red color just disappears with the dilute Na_2CO_3 or H_2SO_4. Add water to a volume of approximately 25 ml., then 5 ml. of either the sulfurous acid or $NaHSO_3$ solution. Digest on the steam bath for 30 minutes or for 20 minutes after the temperature has reached 95° C. (If the aliquot is comparatively free of arsenic and nitrate (no more than 50 gamma) this time may be shortened to 10 minutes.) Carefully pipet 0.5 ml. of the molybdenum blue reagent into the flask, letting it run down the side of the neck to avoid sputtering. Wash down the neck of the flask with two or three drops of water, mix, and continue digestion for 30 minutes more. Cool, make to 50 ml., mix, and read against a standard similarly prepared, or, preferably, in a photoelectric colorimeter.

It is desirable to read the colors within 4 hours as there is a 2–5% fading during the first 24 hours. However, this is not sufficient to preclude the reading, by ordinary colorimetric means, of colors left overnight, as such fading is detectable only by a photometer. After 24 hours, if the flasks are stoppered, the colors remain quite constant for a week or more, even when exposed to light.

METHOD B, PHOSPHORUS

REAGENTS

(a) *Sulfomolybdic acid.*—Dissolve 7.2 grams of ignited C.P. molybdic oxide in 250 ml. of concentrated H_2SO_4 as in Method A, first paragraph. Cool, and preserve the solution in a glass-stoppered bottle.

(b) *Metol.*—Dissolve 0.42 gram of methylparamidophenol sulfate and 6.3 grams of Na_2SO_3 in water and make to 100 ml.

Other reagents.—See Method A.

DETERMINATION

Proceed as directed in Method A up to the point: "Carefully pipet 0.5 ml. of the molybdenum blue reagent," etc. Instead, pipet 0.5 ml. of the sulfomolybdic acid reagent and 1.0 ml. of the metol reagent into the flask, observing the same precautions. Continue the digestion for 30 minutes on the steam bath, cool, make to volume, mix, and read as directed in Method A.

In the comparative absence of arsenic and nitrate the preliminary digestion may be shortened, as in Method A.

METHOD C, ARSENIC

REAGENTS

(a) *Molybdenum blue for arsenic.*—Follow the procedure under Method A for preparing the molybdenum blue phosphorus reagent but use 12 grams of molybdic oxide per 250 ml. of H_2SO_4.

(b) *Standard arsenate.*—Prepare aqueous monopotassium arsenate solutions equivalent to 1, 10, 100, etc., gamma of arsenic per ml.

Other reagents.—See Method A.

DETERMINATION

Have the aliquot free of nitrate and phosphorus and the arsenic in the pentavalent form. (A previous separation by trichloride distillation into water followed by evaporation of the distillate with an excess of HNO_3 to the complete elimination of HCl and HNO_3 is probably the most satisfactory (14).) Dissolve and wash the resulting residue with hot water into a 50 ml. flask, neutralize to quinaldine red as directed under Methods A and B, make to approximately 30 ml., add 0.5 ml. of the molybdenum blue arsenic reagent, digest on the steam bath 30 minutes to develop the color, cool, make to volume, mix, and read as directed in Method A.

APPLICATION OF THE IMPROVED REAGENTS

The following experiment illustrates the advantage of the improved reagents over the original Zinzadze reagent for determination of phosphorus in the presence of salts of appreciable buffer capacity. Standards were prepared containing phosphate alone and phosphate plus 0.38 gram of sodium acetate and 0.072 gram of acetic acid, the quantities present in 20 ml. of Fisher and Thomas's soil extractant (19). These were treated by the original Zinzadze procedure and the procedures outlined under Methods A and B. The transmission curves, established by photometer reading, for the respective color intensities are given in Figure 1. The values are practically identical for both pure standards and standards plus extractant from zero to 30 gamma in both Methods A and B, whereas the Zinzadze method discloses a "blank" ranging from 1.5 gamma at zero to nothing at 40 gamma.

The following data from blank determinations in the presence of varying quantities of sodium silicate demonstrate the extent of silica interference in the improved procedure:

SiO_2 in 50 cc. aliquot (mg.)	50	100	150	200	250
Phosphorus equivalent of color (gamma)	0	.5	.4	.7	.8

The results were obtained with the usual 30 minute period of color development. Even the smallest of the above quantities of silica, i.e., 50 mg., is materially in excess of the quantity likely to be encountered under most conditions. With the original Zinzadze reagent much greater interferences from silica were observed, as it gives colors readily discernible to the unaided eye. With either reagent much greater interference occurs if

the development of the color is extended beyond 30 minutes, 50 mg. of silica giving a color equivalent to that of 20 gamma of phosphorus at the end of an hour.

The reagents described here are subject to iron, arsenic, and nitrate interference when these substances are present in excess of 10 mg., 1 mg., and 1 mg., respectively. Zinzadze (33) reported much higher limits of tolerance, but they could not be verified by tests made in the present studies.

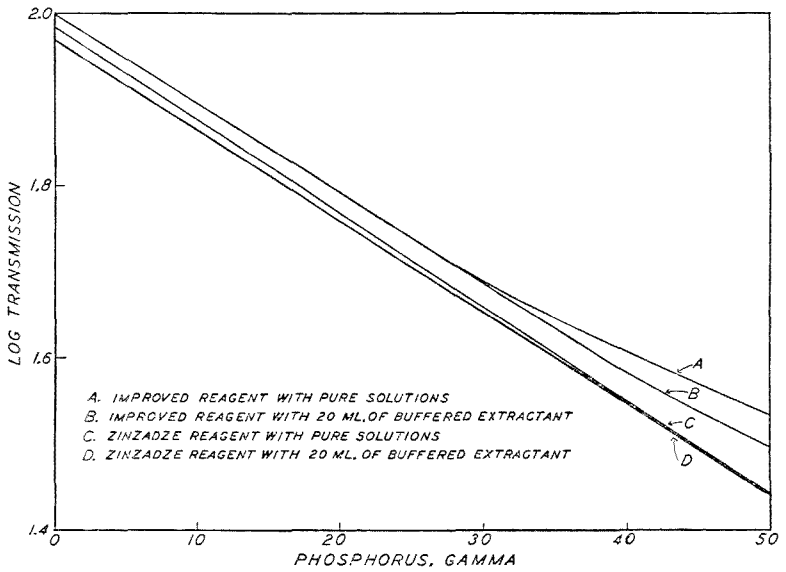

FIG. 1.—TRANSMISSION CURVES FOR COLOR INTENSITIES OBTAINED WITH THE IMPROVED AND THE ZINZADZE MOLYBDENUM BLUE REAGENTS IN PHOSPHATE SOLUTIONS WITH AND WITHOUT THE PRESENCE OF BUFFER SALTS

DISCUSSION

In the improved method Zinzadze's single reagent for both phosphorus and arsenic was replaced by separate reagents specifically adapted to combine optimum color development with minimum interference in the case of each. These reagents differ in molybdic oxide concentrations only. These concentrations (apart from that of Mo_2O_5) are 0.18 *M* and 0.32 *M*, respectively, for phosphorus and arsenic, as compared with Zinzadze's 0.25 *M*. The sulfuric acid concentration was increased from 25 *N* to 36 *N* (which also increased the H_2SO_4/MoO_3 ratio) in order to minimize the interference of silica and the buffer effect of salts. The reduction concentration (Mo_2O_5) was decreased from 0.1 *N* to 0.04 *N* to eliminate as much as possible of the yellow tints that prevent accurate reading of low concentrations. The substitution of quinaldine red for betadinitrophenol as an indicator for preliminary adjustment of the *p*H of the test solution further

insures that the final *p*H will remain well below 1.0 when the molybdenum blue reagent is added. Quinaldine red changes color from *p*H 3.5 to *p*H 2.0 and betadinitrophenol from *p*H 4.2 to *p*H 2.4 according to actual test upon buffered solutions with the glass electrode and the use of the photometer to register the range of color change. These figures are slightly at variance with those appearing in handbooks and other literature, but they illustrate the superiority of the former indicator in respect to sharpness of change as well as lower final *p*H. The "lemon yellow" betadinitrophenol end point advocated by Zinzadze occurs at about *p*H 3.0. Subsequent addition of the reagent does not bring the final *p*H below 1.0. For similar reasons the substitution of sulfurous acid for sodium bisulfite to eliminate interference from arsenic and nitrate is to be recommended, especially when the test solutions have a high salt or buffer concentration. Otherwise the final *p*H may exceed 1.0, the point at which blue color tends to develop in the absence of phosphorus or arsenic. As sulfurous acid is but slightly ionized it has little effect upon *p*H, whereas sodium bisulfite acts as a strongly alkaline buffer.

Since there is a considerable margin of safety with respect to the relative concentrations of the ingredients of the improved molybdenum blue reagent, the extreme care advised by Zinzadze in the preparation of the original reagent is unnecessary. It may be prepared in less than 30 minutes.

While the determination of phosphorus with the modified molybdenum blue reagent involves the development of color at a minimum of 95° C. for 30 minutes, and while this is more time-consuming than other procedures by which color is developed at room temperature in a few minutes, there are compensatory advantages in the attainment of a definite end point at a maximum of color density and stability. The rapidity of color development could be increased by lowering the acidity or increasing the molybdic oxide concentration, but at the expense of interference from silica, salts, etc. The time for development depends greatly upon the efficiency of the steam bath and should be established by the individual analyst. The figures given here apply to a steam bath that is capable of bringing 35 ml. of solution in a 50 ml. flask from room temperature to 95° C. in 10 minutes.

The concentrations of the ingredients of the sulfomolybdic acid reagent with metol as a reducing agent (Method B) are based upon those of the molybdenum blue phosphorus reagent. At the acid concentration used the metol acts specifically upon the phosphomolybdate formed. This reagent is excellent for phosphorus but unsatisfactory for arsenic. The sensitivities of the two phosphorus methods are practically identical, but Method B shows a somewhat more rapid development of color.

The 0.5 ml. of reagent should be measured with reasonable care by means of a graduated 1.0 ml. pipet. The reagent has less viscosity than

has that of Zinzadze and therefore may be pipetted directly without preliminary dilution. A deficiency of 0.1 ml. of reagent will result in a slight decrease in color, but an excess of 0.1 ml. is without significant effect. The quantity of reagent specified is capable of handling up to 80 gamma of phosphorus and nearly 200 gamma of arsenic, the color from which is far beyond readability. The limit of applicability of Beer's law is approximately 30 and 75 gamma of phosphorus and arsenic, respectively, in 50 ml., and from the standpoint of readability it is undesirable to exceed these limits. As is to be expected, equivalent weights of phosphorus and arsenic give the same depth of color when development is complete.

Over the optimum range (0–30 gamma of phosphorus in 50 ml.) the sensitivity of the method is almost entirely dependent upon that of the apparatus used for measuring the color intensity. With the photoelectric colorimeter results are accurate within a few tenths of a gamma at the upper limit of 30 gamma, and quantities as low as 0.5 ± 0.1 gamma may be read. Although color intensities equivalent to 20 gamma of phosphorus are optimum for visual colorimetry, it is possible to estimate accurately much fainter colors (2–5 gamma) because of the elimination of troublesome yellow tints.

SUMMARY

Difficulties encountered in applying Zinzadze's method to the determination of minute quantities of phosphorus in soil extracts and similar solutions were traced to buffer effects in the presence of appreciable salt concentrations and to the composition of the molybdenum blue reagent itself.

The ranges of concentration of sulfuric acid, molybdic oxide, and reduction over which color intensity remains practically constant were determined experimentally. The conditions for minimum interference of yellow tints, silica, and salt effects require the minimum reduction and molybdic oxide concentrations, and maximum sulfuric acid concentration compatible with uniform and complete color development.

Modified molybdenum blue reagents meeting these requirements are described. These reagents, used in the proportion of one part per 100 parts of test solution, have a sulfuric acid concentration of 36 N, reduction concentration of 0.040 N, and molybdic oxide concentration of 0.18 M and 0.32 M for phosphorus and arsenic, respectively. In composition they conform to 0.02 M $Mo_{10}O_{29}$ and $Mo_{17}O_{50}$ for phosphorus and arsenic, respectively.

Preparation of the reagents themselves requires little time and care, but on the other hand, temperature and time are important factors in actual color development up to the point where a final stable end point is reached. Great precision may be obtained by measuring the colors in a photoelectric colorimeter, as little as one gamma or less equivalent of phosphorus being readable.

Substitution of quinaldine red for betadinitrophenol as an indicator for preliminary adjustment of the *p*H of the test solution is recommended.

Sulfurous acid is recommended instead of sodium bisulfite as a preventive of arsenic and nitrate interference in highly buffered and salt-containing solutions such as soil extracts.

An alternative method for phosphorus, specifying a sulfomolybdic acid reagent corresponding in concentration to the molybdenum blue reagent and metol as a reducing agent, is also described.

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THE CITRATE SOLUBILITY OF DOLOMITE OF VARYING PARTICLE SIZE*

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Dolomite is now extensively used as a basic material for the preparation of physiologically neutral fertilizer mixtures. Its use for all fertilizer purposes has increased from 68,000 tons in 1929 to 294,000 tons in 1936 (15). It is likely that reports for 1937 and 1938 will show a continuation of this increase. Although considerable work has been done on the reactions of dolomite in mixed fertilizers (2, 3, 4, 8, 10, 12, 14) and on its effect in the soil (11, 9) there still remain many unsolved problems connected with its use for fertilizer purposes. Among these are (a) the effect of extremely fine subdivision of dolomite on its reactivity, and (b) the choice of a method and solvent for the estimation, in the laboratory, of the availability of dolomitic magnesium to plants when used alone or incorporated in a mixed fertilizer. In this paper are presented the results of a study of the effect of particle size on the citrate solubility of four dolomites and of a preliminary study of four solvents for the estimation of available magnesium derived from dolomite.

I. EFFECT OF PARTICLE SIZE ON THE REACTIVITY OF DOLOMITE

The effect of particle size on the reactivity of dolomite has been studied by Siems and Batton (19). They investigated the rate of decomposition of dolomite in normal hydrochloric acid at 90° F. and reported that no significant differences in the rate of decomposition were observed when the dolomites were ground to fractions finer than that passing a 100-mesh sieve. They found that 64–99 per cent of the <100 mesh dolomites were dissolved in 10 minutes. It would seem that this treatment was too severe to show differences in the finer, and hence more reactive, fractions. Differences in the reactivity of these fractions would not be noticeable under such conditions since immediate and practically complete solution would occur in most cases.

Neutral ammonium citrate was chosen as a solvent because (a) it would dissolve some dolomite of the largest particle sizes and still not dissolve too much of the smallest sizes, and (b) the technic for its use is already well established from its use in the determination of available phosphorus in fertilizers (16).

Four dolomites, analyses of which are given, were used in this study. The dolomite was crushed in a jaw crusher to a size conveniently

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Composition of dolomites

No.	CaO *per cent*	MgO *per cent*	Neutralizing Value ($CaCO_3$ Equiv.)
12	27.68	19.20	97.1
88	30.75	21.23	107.6
90A	29.90	19.34	101.4
95	24.88	17.03	86.7

handled in a friction mill. After each passage through the mill the material was screened, and the larger particles were reground. This process was continued until sufficient material of each of the mesh sizes 20–40, 40–60, 60–80, 80–100, and 100–200 had been accumulated. The initial screening was done by hand, but all fractions were finally run 5 minutes each on a Ro-Tap machine to assure uniformity of the screen separations. The material that had passed the 200-mesh sieve was then further classified* by means of a Roller analyzer (17, 18) into fractions the particles of which had average diameters of 0–5, 5–10, 10–20, 20–40, and 40–74† microns. In adusting the analyzer the density of all the dolomites was assumed to be 2.9 grams per cc.

Two one gram samples of each fraction were digested one hour at 65° C. in 100 ml. of neutral ammonium citrate with shaking every 5 minutes as prescribed for available P_2O_5 (16). Magnesium was then determined in the insoluble residue and in the untreated fraction by solution in aqua regia and double precipitation of the magnesium as magnesium ammonium phosphate, essentially as recommended by Hoffman (7). All analyses were made in duplicate except as noted. As a check on the procedure, total MgO was determined in the Bureau of Standards Standard Dolomite and good agreement with the value given by that Bureau was obtained. The citrate-soluble MgO was obtained by difference. This difference, in the case of the larger sized particles was often so small as to be only 2 to 3 times the probable precision of the MgO determinations and the values for citrate-soluble MgO are therefore not of the highest accuracy in the coarsest fractions. Table 1 shows the results obtained for the entire range of particle sizes from the 20–40 mesh fraction to the 0–5 micron fraction. In Figure 1 the citrate-soluble MgO, expressed as per cent of the total MgO, is plotted against the particle size for those fractions coarser than 200 mesh, while the values for the fractions finer than 200 mesh are similarly plotted in Figure 2. The analyses of the intermediate fractions, 80–100 mesh to 20–40 microns, inclusive, were repeated on dolomites Nos. 88, 90A, and 95, but no significant variation from the original data was obtained. The figures given for these fractions are the average of the three sets of determinations.

* The classification was made by the American Instrument Co. of Silver Spring, Md.
† The openings in a Taylor Standard U. S. Series Equiv. screen No. 200 are 74 microns wide.

TABLE 1.—*Effect of particle size on the solubility of four dolomites in neutral ammonium citrate*

PARTICLE SIZE		MAGNESIUM OXIDE CONTENT											
		DOLOMITE NO. 12			DOLOMITE NO. 88			DOLOMITE NO. 90A			DOLOMITE NO. 95		
MESH	AVERAGE DIAMETER	TOTAL	CITRATE-INSOLUBLE	CITRATE-SOLUBLE	TOTAL	CITRATE-INSOLUBLE	CITRATE-SOLUBLE	TOTAL	CITRATE-INSOLUBLE	CITRATE-SOLUBLE	TOTAL	CITRATE-INSOLUBLE	CITRATE-SOLUBLE
	microns	*per cent*	*per cent of total MgO*		*per cent*	*per cent of total MgO*		*per cent*	*per cent of total MgO*		*per cent*	*per cent of total MgO*	
20– 40	833–381	19.42	97.9	2.1	21.22	96.6	3.4	17.12	93.2	6.8	17.51	90.1	9.9
40– 60	381–246	19.32	95.6	4.4	21.07	96.2	3.8	16.90	90.3	9.7	17.26	90.3	9.7
60– 80	246–175	19.31	94.7	5.3	21.08	94.7	5.3	17.04	88.4	11.6	17.23	89.1	10.9
80–100	175–147	19.32	94.1	5.9	21.06	94.9	5.1	17.26	88.1	11.9	17.51	89.3	10.7
100–200	147– 74	19.46	92.6	7.4	21.23	93.5	6.5	17.37	85.7	14.3	17.64	87.1	12.9
	40– 74	20.19	91.9	8.1	21.34	94.9	5.1	17.77	87.2	12.8	17.50	91.9	8.1
	20– 40	20.14	88.7	11.3	21.08	92.5	7.5	17.68	81.3	18.7	17.13	88.3	11.7
	10– 20	20.19	84.6	15.4	20.44	89.7	10.3	16.44	78.3	21.7	18.05	84.0	16.0
	5– 10	19.52	77.7*	22.3	20.58	79.1	20.9	15.53	69.2	30.8	16.50	74.8	25.2
	0– 5	18.34	58.9*	41.1	20.44	58.9*	41.1	14.61	49.1	50.9	14.22	52.9	47.1

* Not run in duplicate owing to lack of material.

DISCUSSION

In every case the total magnesium became definitely less in the finest fractions. This may have been due to concentration of impurities in these fractions, which would have the effect of diluting the sample. This

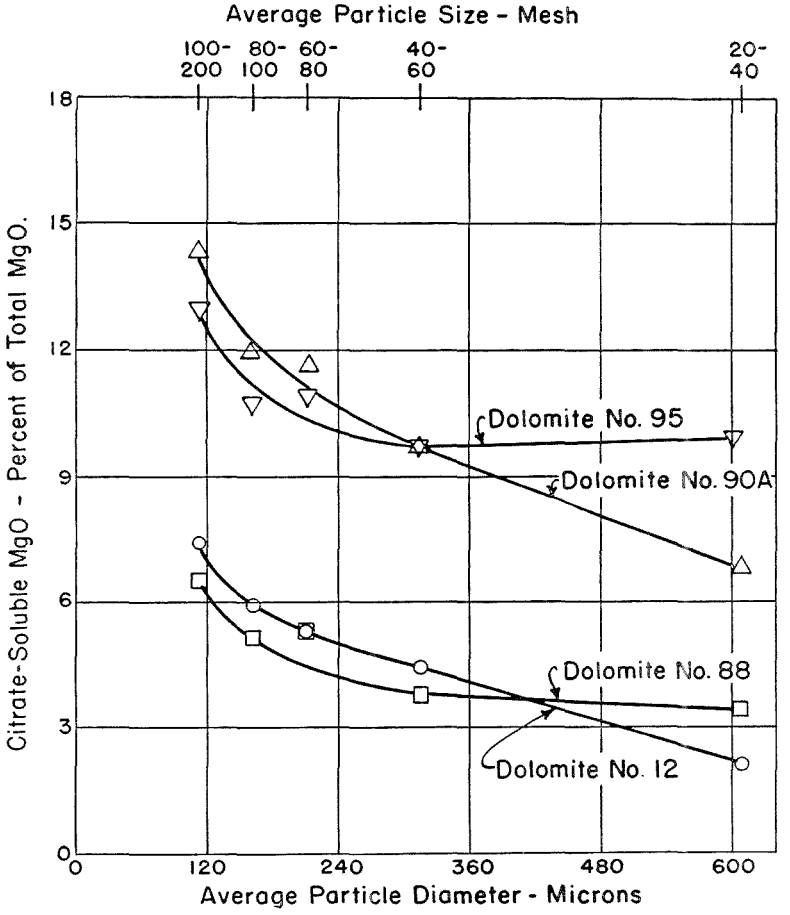

FIG. 1.—CITRATE SOLUBILITY OF MgO IN DOLOMITE FRACTIONS ABOVE 200 MESH

view is in part supported by the observation that the least pure of these dolomites, No. 95, showed the greatest decrease, 3.29 per cent, in total MgO in passing from the 20–40 mesh fraction to the 0–5 micron fraction.

The citrate-insoluble MgO shows a slight but definite trend downward in passing from 20–40 to 100–200 mesh in all four dolomites. This trend be-

comes very pronounced in the <200 mesh fractions, but the coarsest fraction obtained on the analyzer, 40–74 microns, in every case except No. 12 contained slightly more citrate-insoluble MgO than did the corre-

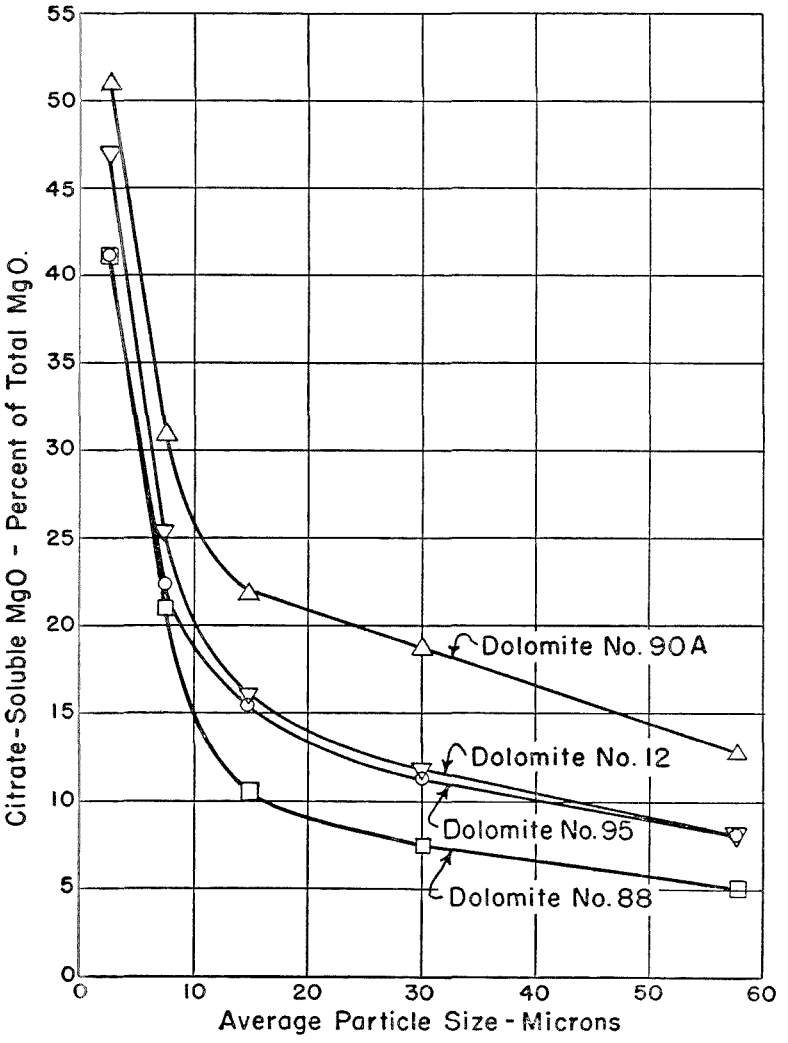

FIG. 2.—CITRATE SOLUBILITY OF MgO IN DOLOMITE FRACTIONS BELOW 200 MESH

sponding 100–200 mesh fraction. This, of course, is contrary to expectations and is probably best explained by the inherent differences in the two methods of classification, screening, and air flotation as used in the Roller

analyzer. Apparently the curve for the <200 mesh fractions is shifted upward slightly from where it would be if these fractions had been obtained by a technic governed by the same laws that are operative in obtaining screen fractions. A complete discussion of this subject is beyond the scope of this paper.

The significance of the results is perhaps best appreciated when they are expressed as per cent of the total MgO that was citrate soluble in the various fractions. Table 1 and Figures 1 and 2 show that this citrate solubility is approximately doubled in each case in passing from 20–40 to 100–200 mesh and that a further fivefold increase (approximately) occurs in passing from the 40–74 to the 0–5 micron fraction. Most of the latter increase occurs below 15 microns. The increased solubility obtained by decreasing the particle size from 20–40 mesh to 100–200 mesh is thus relatively small compared with the big increase obtained in the finer fractions. The apparent discrepancy between the 100–200 mesh and the 40–74 micron fractions mentioned above is, of course, also reflected in the citrate-soluble figures but has no important effect on the conclusions reached.

Whether or not the increased reactivity resulting from very fine subdivision is necessary or even desirable from the standpoint of availability to plants and its effect on the soil reaction remains to be determined. It is apparent, however, that the rate of the reactions that take place, or may take place, between dolomite and other constituents of fertilizer mixtures could be modified by a suitable choice of particle size.

It has been the practice with some workers to classify dolomites into hard, medium or soft grades, depending on the reactivity or solubility (under standard conditions) of dolomite that has been ground to pass some particular sieve, often either 100 or 200 mesh. It is apparent from the data presented here that such a system of classification might result in a hard dolomite being rated as medium or even as soft if it were ground in such a manner that the <100 or <200 mesh material contained a high proportion of the finest sizes. The reverse might also be true for a soft dolomite ground so as to contain a relatively low proportion of fines. Dolomite No. 88, if ground to pass 200 mesh in such a manner that 80 per cent of the particles were 20 microns or smaller, would appear softer than the relatively soft dolomite No. 95 in which 40 per cent of the particles were actually in that size range.

The particle size distribution in the <200 mesh fractions of the four dolomites used here is given in Table 2. Although the grinding procedure used was uniform in all cases considerable variation in the relative amounts of the various fractions occurred. Thus, No. 12 has twice as much material falling into the 0–5 micron fraction as has No. 88, but only about one-half as much in the 40–74 micron fraction. Since the solubility of the 0–5 micron fraction is, in the more favorable of the two cases, five

TABLE 2.—*Particle size distribution in the <200 mesh fraction of four dolomites as determined by the Roller analyzer*

SIZE RANGE	DOLOMITE NO.			
	12	88	90A	95
microns		*per cent*		
40–74	18.2	35.7	19.1	18.8
20–40	32.7	30.6	32.6	37.9
10–20	20.9	15.6	18.6	20.7
5–10	11.6	10.0	15.3	12.0
0– 5	16.6	8.0	14.2	10.7

times that of the 40–74 micron fraction, it is obvious that this variation in particle size distribution can have considerable influence on the reactivity of the <200 mesh fraction.

II. SOLUBILITY IN FOUR SOLVENTS OF THE MAGNESIUM IN DOLOMITE

Smith (20, 21, 22) and Smith and Deszyck (23) have determined the solubility of dolomite and other forms of magnesium in various solvents with a view to using this property as a measure of the availability of the magnesium to plants. As pointed out by Smith, the final choice of a solvent and technic for the determination of availability cannot be made until the present very meager knowledge of crop response to various forms of magnesium has been greatly extended. It would be convenient if the final choice of solvent and procedure could be one also suitable for P_2O_5. Experiments were therefore carried out in which the new solvent recently suggested by MacIntire, Shaw and Hardin (13) was compared with neutral ammonium citrate, ammonium citrate of *p*H 4 and 2 per cent citric acid.

Three mixtures were made up, each consisting of one-half of 100-mesh dolomite No. 95 and one-half of either pure monocalcium phosphate, superphosphate, or double superphosphate. Enough water was added to each mixture to raise its total moisture content to 7 per cent. The mixtures were then intimately mixed by rubbing with a spatula and by being forced through a 30-mesh sieve to disintegrate all lumps and allowed to stand overnight in loosely stoppered bottles at room temperature before the one gram samples were weighed for the determinations. One-half gram samples of the dolomite alone were run for purposes of comparison.

Six samples of each mixture and of the dolomite were washed with water, as in the water-soluble P_2O_5 determination (16), and then two of each set of six were digested for 30 minutes at 65° C. with 2 per cent citric acid, two with ammonium citrate of *p*H 4 (prepared according to Smith (22)), and two with ammonium citrate of *p*H 7. Two other samples of each material were digested in "citrated ammonium nitrate," as recom-

mended by MacIntire, Shaw and Hardin. The apparatus used was that recently described by Adams (1). Instead of analyzing the solution as recommended in the case of P_2O_5, MgO was determined in the residue after washing with water at 65°. The results are given in Table 3.

TABLE 3.—*Solubility in four solvents of the MgO in dolomite and in mixtures of dolomite and phosphates*

MATERIAL	SOLVENT	SOLUBLE MgO (PER CENT OF TOTAL MgO)
$Ca(H_2PO_4)_2 \cdot H_2O$ + Dolomite	2% Citric Acid	97.11
$Ca(H_2PO_4)_2 \cdot H_2O$ + Dolomite	Ammonium Citrate *p*H 4	78.01
$Ca(H_2PO_4)_2 \cdot H_2O$ + Dolomite	Ammonium Citrate *p*H 7	31.13
$Ca(H_2PO_4)_2 \cdot H_2O$ + Dolomite	Citrated NH_4NO_3	91.44
Superphosphate + Dolomite	2% Citric Acid	95.00
Superphosphate + Dolomite	Ammonium Citrate *p*H 4	66.97
Superphosphate + Dolomite	Ammonium Citrate *p*H 7	22.09
Superphosphate + Dolomite	Citrated NH_4NO_3	73.49
Double Superphosphate + Dolomite	2% Citric Acid	84.16
Double Superphosphate + Dolomite	Ammonium Citrate *p*H 4	76.30
Double Superphosphate + Dolomite	Ammonium Citrate *p*H 7	30.87
Double Superphosphate + Dolomite	Citrated NH_4NO_3	85.45
Dolomite Alone	2% Citric Acid	98.83
Dolomite Alone	Ammonium Citrate *p*H 4	83.66
Dolomite Alone	Ammonium Citrate *p*H 7	23.69
Dolomite Alone	Citrated NH_4NO_3	86.41

Two per cent citric acid dissolved 99 per cent of the MgO in the dolomite alone and 84–97 per cent in the mixtures. Ammonium citrate of *p*H 4 dissolved 84 per cent in the dolomite alone and 67–78 per cent in the mixtures, while that of *p*H 7 dissolved only 24 per cent of the MgO in the dolomite and 22–31 per cent in the mixtures. The special citrated ammonium nitrate suggested by MacIntire was slightly more reactive than ammonium citrate of *p*H 4. It dissolved 86 per cent of the magnesia in the dolomite and 73–91 per cent of the MgO in the mixtures. As stated above, the final choice of a reagent and a procedure for estimating available magnesia must await the results of vegetative tests. The present work shows, however, that the above reagents vary in solvent power and it may be that one of them will be found suitable for estimating available MgO. The preliminary data of Dawson, Snyder, Leighty and Reid (6) and of Collins and Speer (5) indicate, however, a much higher availability to plants as measured by decomposition in the soil than the solubility in neutral ammonium citrate shows.

TABLE 4.—*Variation in solubility of dolomitic MgO in neutral ammonium citrate with age and composition of mixture*

NO.	MIXTURE§	TOTAL MgO IN MIXTURE	CITRATE-SOLUBLE MgO IN		
			DOLOMITE ALONE	DOLOMITE MIXTURE AFTER STORAGE FOR	
				1 DAY*	21 DAYS†	46 DAYS†
		per cent		*per cent of total MgO*		
1	6–8–6 containing Dolomite No. 88	5.36	10.55	6.01	16.64	14.83
2	do Dolomite No. 90	4.90	29.88	20.39	33.35	28.08
3	do Dolomite No. 95	4.73	20.61	20.00	23.63	28.18
4	Ammoniated Double Super. and Dolomite No. 88	10.34	10.22	9.55	13.61	11.64
5	do Dolomite No. 90	9.45	25.02	22.06	26.27	26.95
6	do Dolomite No. 95	8.50	18.67	16.81	22.76	26.93
7	Ammoniated Superphosphate and Dolomite No. 88‡	10.08	10.22	7.24	10.81	10.34
8	do Dolomite No. 90	9.17	25.02	19.69	22.62	17.93
9	do Dolomite No. 95	8.28	18.67	15.45	18.43	20.77
10	Superphosphate and Dolomite No. 88‡	10.00	10.22	7.84	4.19	0.00
11	do Dolomite No. 90	9.18	25.02	22.95	23.18	23.53
12	do Dolomite No. 95	8.41	18.67	17.00	16.48	18.15
13	Double Super. and Dolomite No. 88‡	10.82	10.22	40.93	28.02	27.12
14	do Dolomite No. 90	10.50	25.02	39.62	46.48	38.19
15	do Dolomite No. 95	9.59	18.67	32.29	42.60	38.11
16	$Ca(H_2PO_4)_2 \cdot H_2O$ and Dolomite No. 95‡	9.28	18.67	2.79	40.39	45.41

* At room temperature.
† At 60° C.
‡ Equal amounts of components.
§ 7 % H_2O added to all mixtures.

Ammonium citrate of *p*H 7 has been used extensively in this laboratory in a study of the reactions of dolomite in mixed fertilizers. The results obtained in a storage experiment, some of which are given in Table 4, indicate that this reagent is unsuitable for control work, due to the variable results obtained with mixtures of different age and composition. It is felt that during the growing season the MgO is probably about equally

available to plants in all cases in spite of the fact that its solubility in the neutral ammonium citrate varied widely. In the 6–8–6 mixture No. 1 containing dolomite 88 the reagent indicated the MgO to be only 6.0 per cent soluble in the fresh mixture, whereas it became 16.6 per cent soluble after 21 days and was 14.8 per cent soluble after 46 days. The solubility of the MgO in this dolomite alone, when there was used a sample of a size corresponding to the amount of dolomite in a one gram sample of the mixture, was 10.6 per cent. Its solubility when included in various fertilizer mixtures ranged from 6 to over 40 per cent. Similar variations in solubility in this reagent have been noted by Smith and Deszyck (23) and by Beeson and Ross (4). No doubt real differences in the solubility existed and were measured with more or less accuracy by this reagent, but its extreme sensitivity to the age and composition of the mixture makes it unsuitable for use in the routine determination of the solubility of magnesium.

The other three reagents, 2 per cent citric acid, ammonium citrate of *p*H 4 and citrated ammonium nitrate, should give more uniform results, due to the fact that the solubilities of the MgO in these solutions are much higher than they are in ammonium citrate of *p*H 7 and alterations in the state of combination of the magnesia in the fertilizer would therefore have less effect.

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IMPROVED METHOD FOR ESTIMATING CAROTENE IN FEEDS

By G. S. FRAPS and A. R. KEMMERER (Agricultural Experiment Station, College Station, Texas)

In several recent papers Cary, Shinn, and associates (3, 4) have shown by chromatographic adsorptive methods that the carotene solution usually prepared in the estimation of carotene is not pure but may contain from 10 to 30 per cent coloring matter, not carotene. Their method consists in removing the impurities from the petroleum ether solution of carotene by specially activated magnesium hydroxide. The solution of carotene is passed through a column of magnesium hydroxide held in a condenser cooled by ice water and in an atmosphere of nitrogen. The method has not been published, but the authors kindly furnished information regarding it.

The attempts of the writers to use this chromatographic method were not successful, since the magnesium hydroxide prepared adsorbed and held the carotene so tenaciously that it could not be completely washed out of the column by the petroleum ether (Skellysolve F, 86–170° F.). Therefore a study was made of the effect of different periods of heating, temperature, and water treatment upon the adsorptive power of magnesium hydroxide. The preparations obtained were tested for adsorption of carotene by a determination of the loss of color after 0.5 gram of the material had been shaken with 10 cc. of petroleum ether containing about 2 p.p.m. of purified carotene and also for adsorption of xanthophyll (methanol fraction of carotenoid pigments) by use of a similar solution of crude xanthophyll prepared from alfalfa leaf meal.

Some of the treatments and the results are given in Table 1. These data show that two of the preparations did not adsorb carotene but retained all the xanthophyll, while the other preparations adsorbed from 5 to 95 per cent of the carotene. These results were confirmed by additional work in which there were used 2.5 grams of adsorbent and 50 cc. of carotene solution and the color was measured by means of the KWSZ photometer, a much more accurate test than is visual comparison with bichromate. Portions of a preparation of magnesium hydroxide that did not adsorb carotene but did adsorb xanthophyll were shaken with carotene preparations from various samples, with the results given in Table 2. Since this preparation does not adsorb carotene, the color removed is evidently due to impurities. The carotene estimated in the original solution is hereafter termed "crude carotene" and that in the solution shaken with magnesium hydroxide is termed "pure carotene." The percentage of impurities in the crude carotene ranges from 0 to 23 per cent.

The use of properly prepared magnesium hydroxide offers a simple method for purifying carotene solutions and increasing the accuracy of

TABLE 1.—*Effect of water and heat treatment on the adsorptive power of U.S.P. light MgO*

LABORATORY NUMBER	WATER ADDED TO 50 GRAMS OF MgO	HEATED ON STEAM BATH	HEATED IN ANILINE VAPOR	CAROTENE ADSORBED	XANTHOPHYLL ADSORBED
	cc.	*minutes*	*minutes*	*per cent*	*per cent*
50207	50	30	120	95	100
50209	50	120	30	90	100
50208	25	120	30	85	100
50211	50	120	120	85	100
50210	25	120	120	80	100
50206	25	30	120	80	100
50379	50	120	0	75	100
50204	25	30	30	70	100
50205	50	30	30	55	100
50381	75	30	30	5	100
50378	50	30	0	0	100
50380	75	30	0	0	100
50377				40	70

TABLE 2.—*Crude and pure carotene in alfalfa products*

LABORATORY NUMBER	SAMPLE	CAROTENE BY BICHROMATE			CAROTENE BY KWSZ PHOTOMETER		
		CRUDE	PURE	PER CENT PURITY	CRUDE	PURE	PER CENT PURITY
		p.p.m.			*p.p.m.*		
49850	Old alfalfa hay	25.0	20.7	82.6			
49851	New alfalfa hay	24.3	20.2	83.1			
50252	Dehydrated alfalfa leaf meal	150.0	145.5	97.0			
50529	Old alfalfa leaf meal	9.0	7.1	88.2	10.2	8.4	82.4
48481	Dehydrated greens	170.0	137.5	80.9	172.0	148.0	86.0
50541	Dehydrated alfalfa leaf meal	75.6	60.0	79.4	76.1	64.3	84.5
50337	Dehydrated alfalfa leaf meal	90.0	90.0	100.0			
50346	Alfalfa meal	16.6	13.4	80.7			
50743	Alfalfa leaf meal	280.7	275.7	98.2	304.0	296.7	97.6
50783	Alfalfa leaf meal	110.8	100.8	91.0	115.0	112.5	97.8
50784	Alfalfa leaf meal	55.0	45.4	82.5	58.4	47.4	81.2
50842	Dehydrated alfalfa leaf meal	96.7	74.4	76.9	99.5	78.3	78.7
50425	A.O.A.C. Sample 1 for carotene	240.0	207.1	86.3	237.5	205.0	86.3
50426	A.O.A.C. Sample 2 for carotene	78.9	75.6	95.8	77.3	73.3	94.8

the estimation of carotene. All that is necessary is to shake the crude carotene solution in petroleum ether with suitable magnesium hydroxide, separate the liquid, and read the color. Whether or not this carotene is

now entirely pure must be ascertained by further study, but it is certainly more nearly pure than it was before the treatment. This is called the method of selective adsorption. As stated previously, it depends upon the use of magnesium hydroxide that has been tested and found not to adsorb any carotene but to adsorb xanthophyll completely.

In order to test whether the carotene adsorbed by magnesium hydroxide preparations that adsorb small amounts of carotene might be washed out and the method be modified so as to use such preparations, one gram portions of the magnesium hydroxides having various adsorptive powers for carotene were placed on cotton in a glass tube 8 mm. in diameter, 25 cc. of the petroleum ether containing about 4 p.p.m. of pure carotene was passed through it with the aid of gentle suction, and the contents of the tube were then washed with 65 cc. of the solvent. The results are shown in Table 3. As the adsorbed carotene was not washed out under these conditions, it is evident that magnesium hydroxide that adsorbs even small quantities of carotene cannot be used for purifying carotene. Even when the tube was surrounded with ice water and the

TABLE 3.—*Adsorption and retention of carotene by a column of the adsorbent of different grades*

LABORATORY NUMBER	GRADE AS SHOWN BY CAROTENE ADSORBED IN SHAKING WITH ADSORBENT PERCENTAGE ADSORBED	ADSORPTION AND RETENTION IN A COLUMN OF THE ADSORBENT AFTER PERCOLATION AND WASHING PERCENTAGE ADSORBED
50790	30.4	28.7
50791	79.7	90.8
50792	70.6	57.3
50794	82.2	71.4
51075	7.1	12.2

experiment was carried out in an atmosphere of nitrogen, as was done by Cary, Shinn, et al. [1,2] the carotene could not be completely washed out. However, more carotene was recovered under such conditions than at room temperature and in air. The adsorbed carotene could easily be washed out completely by a mixture of ethanol and petroleum ether, but this solvent might wash out the impurities also.

In order to determine whether preparations of magnesium hydroxide of desired selectivity could be easily made, all available samples of magnesium oxide were tested (Table 4). Only one sample of the desired characteristics was produced, and this was merely a fortunate chance. The preparation of magnesium oxide is now being investigated and it should soon be possible to specify conditions that will assure a reliable source of supply. Some of the materials used to dilute adsorbents may themselves have considerable adsorptive power for carotene. According

[1] *Proc. Am. Chem. Soc., 95th Meeting, 1938*, B. p. 14.
[2] *Proc. Am. Soc. Biol. Chem.*, 31st Annual Meeting, 1937, 89.

to tests made by the writers, silica will adsorb 9.5 per cent of carotene from solution, siliceous earth 99.5 per cent, and infusorial earth 59.5 per cent.

TABLE 4.—*Effect of water and heat treatment on the adsorptive power of different kinds of MgO*

LABORATORY NUMBER	KIND OF MAGNESIUM OXIDE	WATER ADDED TO 50 GRAMS	HEATED ON STEAM BATH	HEATED IN ANILINE VAPOR	CAROTENE ADSORBED	XANTHOPHYLL ADSORBED
		cc.	*minutes*	*minutes*	*per cent*	*per cent*
50796	No. 1 U.S.P. grade	—	—	—	66.0	100.0
50790	No. 1 U.S.P. grade	50	30	—	30.4	94.2
50794	No. 1 U.S.P. grade	50	30	120	82.2	99.5
50797	No. 2 U.S.P. grade light	—	—	—	79.6	100.0
50791	No. 2 U.S.P. grade light	50	30	—	79.7	99.5
50793	No. 2 U.S.P. grade light	50	30	120	88.8	99.0
50798	No. 3 grade	—	—	—	100.0	100.0
50792	No. 3 grade	50	30	—	70.6	99.5
50795	No. 3 grade	50	30	120	92.4	100.0
50377	No. 4 U.S.P. grade light	—	—	—	40.0	100.0
50378	No. 4 U.S.P. grade light	50	30	—	0	100.0
50207	No. 4 U.S.P. grade light	50	30	120	95.0	100.0

The method of selective adsorption has heretofore been applied chiefly to alfalfa products. When it is applied to other materials an adsorbent having different selective powers or a modified procedure may be required. For example, a different procedure is required for the determination of carotene in rat excrement. The writers have shown[1] that the excrement of rats and of chickens fed on a diet free from carotene contains other coloring materials that may interfere with the determination of carotene. It was also found that the coloring matter in the rat excrement is not adsorbed even by such magnesium hydroxide that adsorbs practically all the carotene in solution. Therefore, for rat excrement, it may be possible first to purify the carotene solution by selective adsorption and read the color. Then all the carotene can be removed by a second treatment, the color again read, and the last value subtracted from the first value. The remainder will be the value for pure carotene. The application of the method to various foods, feeds, and other materials containing carotene is now being studied, as is also the possibility of the applicability of the principle of selective adsorption to a large number of coloring materials and to the purification of carotene and other compounds.

The method follows:

[1] *J. Nutrition*, 16, 309–15 (1938).

METHOD OF SELECTIVE ADSORPTION

REAGENTS

(a) *Magnesium hydroxide.*—Place 50 grams of suitable (U.S.P. light) MgO in an evaporating dish, add 50 cc. of water, and heat on a water bath for 30 minutes. Shake 0.5 gram of this activated material with 10 cc. of purified carotene solution, or 2.5 grams with 50 cc., and allow the $Mg(OH)_2$ to settle, or centrifuge. Read the color by the usual method both before and after the treatment. Test in the same way with the xanthophyll solution. If the $Mg(OH)_2$ adsorbs all the xanthophyll and none of the carotene, it is suitable for use. If it does not, try another lot of MgO.

(b) *Carotene solution.*—Dissolve 0.1 gram of pure carotene in 2 cc. of $CHCl_3$ and precipitate with about 25 cc. of methanol. Filter off the carotene and dry between filter paper and in a vacuum desiccator. Weigh out 20 mg. of the carotene, dissolve in a few drops of $CHCl_3$, and make up to 50 cc. with light petroleum ether. Dilute 5 cc. of this solution to 1000 cc. with light petroleum ether.

(c) *Xanthophyll solution.*—Saponify about 6 grams of alfalfa with 120 cc. of alcoholic potash and extract with U.S.P. ethyl ether as directed in the published method for carotene.[1] After the ethyl ether is evaporated off, take up the residue in light petroleum ether and wash with 90% methanol until the methanol comes through colorless. Then extract the methanol fraction two times with petroleum ether to remove traces of carotene. Extract this petroleum ether fraction with 90% methanol as directed above and add the methanol extract to the original methanol solution. Evaporate off the methanol with diminished pressure and take up the residue in 100 cc. of petroleum ether. Dry over anhydrous Na_2SO_4 and dilute to contain the equivalent of 2 p.p.m. of carotene.

DETERMINATION

Prepare the carotene solution in the usual way, read the color, and estimate crude carotene if desired. If necessary, adjust the solution to contain about 2 p.p.m. of the color equivalent to carotene. Shake the solution with the $Mg(OH)_2$ at the rate of 0.5 gram to 10 cc. and read the color by the usual method. Report as pure carotene in p.p.m. (The $Mg(OH)_2$ used must have the correct selectivity, that is, it must, when tested, adsorb xanthophyll from solution completely and adsorb no carotene.)

Note on the Rapid Determination of Mineral Oil in Butter*

In the determination by the F.A.C. method[2] of unsaponifiable matter in butter that was suspected of containing mineral oil, it was noted that a milky emulsion formed on the addition of water, after saponification, in those samples that contained mineral oil, whereas a perfectly clear solution was obtained in the case of pure butterfat. This fact was made the basis of a rapid test for mineral oil in butter. This test is not new. It is given in essentially the same form in the book of D. Holde, titled, "The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes," translated by Edward Mueller, second English edition, p. 76. Substantially the same test is given in *Methods of Analysis, A.O.A.C.*, 1935, p. 89, 9.

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[1] G. S. Fraps and A. R. Kemmerer, Texas Agr. Exp. Sta. Bull. 557, pp. 1–28 (1937).

* By J. H. Bornmann, U. S. Food and Drug Administration, Chicago, Ill. Presented at the Annual Meeting of the Association of Official Agricultural Chemists held at Washington, D. C., November 14, 15, and 16, 1938.

[2] *Methods of Analysis, A.O.A.C.*, 1935, 420, 35.

The writer made the test on a 2 cc. sample of fat, using the same proportion of alcohol and potassium hydroxide (1+1) as that given in the F.A.C. method, but heating only 10 minutes. It was found that amounts of mineral oil smaller than 2 per cent could not be detected. It was then discovered by E. H. Wells that when the proportion of alcohol was increased it was possible to detect as little as 0.5 per cent of mineral oil. The test follows:

> Place about 10 grams of butter on a folded filter, heat in an oven until the butter is melted, and filter in a warm place. Measure 1 cc. of clear fat, 1 cc. of KOH (1+1), and 25 cc. of alcohol (95%) into a test tube (8″×10″). Heat the tube and contents in a water bath at 80° C. for 15 minutes, with sufficient shaking to mix the contents. Dilute with an equal volume of distilled water.

A turbidity after dilution with distilled water indicated the presence of mineral oil. A pure butterfat run simultaneously as a control remains perfectly clear on dilution. It is necessary, of course, to verify the presence of mineral oil, in case of a positive test, by the usual determinations of constants.

BOOK REVIEWS

Statistical Methods. By GEORGE W. SNEDECOR, Director, Statistical Laboratory of Iowa State College and Head of the Statistical Section of the Iowa Agricultural Experiment Station. Collegiate Press, Inc., Ames, Iowa. 1937, revised 1938. 388 pp. Price $3.75.

In most of the newer textbooks on statistical methods, insufficient attention has been given to the treatment of small samples of experimental data. Mr. Snedecor's book stresses the methods to be used in the analysis of small samples in experiments in the natural sciences. Special emphasis has been placed upon the application of the chi-square test, tests of significance, measurement of degrees of freedom, analysis of variance and co-variance and correlation.

Mr. Snedecor has worked closely with Dr. R. A. Fisher of the Rothamsted Experiment Station in England, and his book closely parallels the book of Dr. Fisher on "Statistical Methods for Research Workers." Mr. Snedecor's book is much easier reading and follows Fisher's method of numbering paragraphs.

One of the more desirable characteristics of the book is the emphasis placed on the necessity of measuring the error of results based on samples. These tests of error are woven into all of the various parts of the text, and their proper application to the various statistical problems involving sample data is illustrated by many practical problems. Each step is also accompanied by examples for use in class work which point out the application of the different methods to various types of problems.

The necessity for applying both variance and correlation analysis to specific problems and the manner in which these two methods of analysis supplement each other have been given special consideration, which is a valuable contribution to the existing methods of statistical analysis. Another desirable feature of the book is that unusual applications of the various methods to experimental data have been segregated and a short course in the elements of Statistical Methods is outlined at the beginning of the book. This enables the reader to concentrate on the important sections without reading the whole book.

One of the chief criticisms of the book from the standpoint of a complete statistical text is that too little attention has been given to the methods of treating a large number of observations and to the presentation of statistical results. The book contains only one short chapter dealing with large sample theory. No attention at all is given to the proper methods of table construction. Only three paragraphs are devoted to graphic presentation and these are more on the presentation of results than the method of construction. Frequency distribution, averages, and dispersion are too briefly discussed to familiarize the student with the problems involved and the short cuts available in their computation. Correlation is more thoroughly treated, and the discussion is carried through multiple correlation and the presentation of curvilinear regressions. However, the treatment of curvilinear correlation is elementary and confined to the use of logarithms and polynomial curves.

Another weakness of the book as a reference or textbook is the use of symbols which, in many cases, are entirely different from other statistical textbooks and journals. For example, in correlation, E is used to represent the estimated value of the dependent variable and the formulas for other statistical measures are stated in terms of the betas.

References are incomplete and are confined to a great extent to publications by the Iowa Agricultural Experiment Station and by R. A. Fisher. While the text is written in a very simple style, many readers feel it is too simple and seems to underestimate the intelligence of the reader.—C. M. PURVES.

Cattle Fodder and Human Nutrition. By ARTTURI I. VIRTANEN. 108 pp. The University Press, Cambridge, England. The Macmillan Company, 60 Fifth Ave., New York, N. Y., 1938. Price $2.25.

This book is the outgrowth of a series of four lectures. The first was delivered at the Universities of London and Cambridge, the second and third were given at the University of London, while the fourth was presented at the University of Reading.

Lecture I. The Mechanism of Biological Nitrogen-Fixation. By a description of methods used and results obtained, the author has led to a logical discussion of a possible chemical mechanism of nitrogen-fixation by free-living and symbiotic nitrogen-fixing organisms.

Lecture II. The Symbiosis of the Leguminous Plants and Legume Bacteria. In the second lecture, with less emphasis on the mechanics of the process, Professor Virtanen has described experiments designed to show the interdependence of the symbiotic organisms and host plants. Several tables give data in support of his discussion of the subject.

Lecture III. The Production of Vitamins in Agriculture with Special Reference to Human Nutrition. This chapter is essentially a report of a study made under the direction of the author on the standard of nutrition of working classes in Finland. Considerable space is devoted to the Vitamin-A potency of milk and milk products and the need of increasing it by methods of cattle feeding.

Lecture IV. The A. I. V. Method for the Preservation of Fresh Fodder and Its Importance in Agriculture. Perhaps the best of the four lectures, this is a thorough discussion of both the theoretical and practical aspects of the production and use of A. I. V. fodder.

The title of this book may appear, at first, to be misleading. Further consideration and reading of the complete text, however, will show that the author has developed logically the subject of nitrogen-fixation, which, of course, has a direct bearing on the food value of forage crops. This naturally leads to the problem of the preservation of fresh fodder, and finally, to the part it may play in the production of vitamins, indirectly, for human consumption. The fact that the last two subjects are discussed in the reverse order does not in the least detract from the value of the book.

The book is written in a clear, straight-forward style and should be of interest to students of general agriculture. One hundred and four references, many of them to research published by the author, will assist students in specialized fields who may desire to pursue the subjects further.—G. CHAPMAN CROOKS.

Micropedology. By WALTER L. KUBIENA. 237 pp. Illustrated. Collegiate Press, Inc., Ames, Iowa. Price $3.00.

Kubiena presents his well-known work on the microscopic study of soils in this book, which has been produced in English as a result of his lecture courses at Iowa State College. The attitude of the advocate, or even that of the propagandist, is often evident. Out of 237 pages, 35 cover introduction and description of apparatus; 40 are devoted to micromanipulation and sampling, about 40 to a selection of more or less standard microchemical formulas, optical methods, and reactions, about 75 pages to soil "fabric," and 30 pages to the micropopulation of the soil.

There are two main points in his teaching: (1) That the microscope must go to the field if possible, but if not taken to the field, must be used to examine selected and representative soil masses in undisturbed condition fresh from the field or after subjection to known conditions; (2) that in doing this, microscopes having "incident" instead of transmitted light are needed and should be mastered by the student. Both ideas are desirable in any microscopic program as related to the soil.

His own soil microscope is fully illustrated along with other apparatus which may be substituted. The preparation and use of microtools is detailed.

The last 100 pages are devoted to the application of his methods to soil samples. Here his discussion of types of soil "fabric" is given greatest attention. By "soil fabric" he appears to mean what may perhaps be called the pattern formed by the arrangement of the granular, principally mineral components of the soil as modified by more or less complete envelopment in colloidal materials. A series of type names is given to these fabric types with the manipulations and tests necessary to identify and describe them. Many illustrations are presented to reenforce the descriptive text. The discussion of these types goes far enough to open up this largely neglected field, which will need many workers and a considerable period of time before others can safely take up Kubiena's boast that he can tell from the examination of a vial of soil properly taken, the climate, the general soil type, and many details of the area sampled.

Applied to the microorganisms of the soil, the method aids in a general understanding of space relations and the clumping and colonization of microorganisms. Those of us who have travelled with the author and have seen his demonstration, realize that the field microscope is only an interesting accessory to microbiology. It can not replace the usual types of culture.

Those familiar with microscopy as applied to many fields will appreciate this book as an attempt to adapt this form of examination to the study of soil. There is reason to expect that the development of soil microscopy will furnish supplementary information of considerable value to those describing soil types.—CHARLES THOM.

Utilization of Fats. By H. K. DEAN, Ph.D. (Liv.) A.I.C.; New York, 1938; Chemical Publishing Co. of N. Y., Inc. Pp. 292+index. Price $6.00.

In this book the author describes first the constituents of fats, methods for their analysis, their classification, and composition. He then takes up the preparation of artificial glycerides and the hydrogenation, extraction, refining, biochemistry, and rancidity of fats. In the final portion, paint and varnish oils, soaps and pharmaceuticals, and cosmetic, lubricant, leather, and sulfonated fats are discussed.

The reviewer feels that the title of this book may be found somewhat misleading, as it is obviously impossible to give full treatment to the subject "Utilization of Fats" in 292 pages. Actually only slightly over half of the pages is given to this subject. The book gives an excellent summary of the developments in fat chemistry and technology during the last decade. It accomplishes the primary consideration of the monograph, which is to present a clearer picture of the relation of the structure of fats to their utilization. A satisfactory list of references follows each part of each chapter.

This survey will be a valuable aid to workers in the field of fat and oil chemistry. It should be used, together with the standard works listed by the author dealing with these fields, which, although lacking in the newest developments, yet do contain a wealth of useful detail which is necessary in an investigation of the utilization of the various fats.—R. S. MCKINNEY.