TECHNICAL METHODS OF CHEMICAL ANALYSIS

PREFACE

As in previous volumes of the present edition of *Technical Methods of Chemical Analysis*, all the sections have been thoroughly revised and several completely rewritten so as to include the newer methods of analysis, especially those which have been worked out and accepted in connection with modern developments of chemical industry.

The sections on clays and clay products in the former edition have been rearranged under the heading of Clays, Ceramic Products and Refractories, and the methods of examination subdivided into chemical and physical. The section on Glass has been considerably extended, and in that on Air the most recent methods of determination both of gaseous and of other impurities have been included. In each of the remaining sections special attention has been given to the co-ordination of the subject-matter and to the inclusion of the latest British and American methods of analysis.

Numerical data have been calculated from the atomic weights published by the International Union in 1925, with such approximations as are usual, though empirical factors are retained where they are commonly used in technical work. Temperatures are stated in degrees Centigrade unless other scales are specially indicated.

The Editors desire to record their thanks to the following firms and other organisations for the loan of blocks or drawings or for permission to reproduce illustrations or other matter from their publications:—The American Ceramic Society, Messrs Baird & Tatlock, The British Engineering Standards Association, Messrs Casella, The Ceramic Society, The Chemical Catalog Co., Messrs A. Gallenkamp & Co., Messrs Griffin & Tatlock, H.M. Stationery Office, Messrs Steel and Cowlishow, and Messrs John Wiley & Sons.

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ABBREVIATED TITLES OF JOURNALS

Abbreviations.	Journals.
Amer. Chem. J.	American Chemical Journal
Amer. J. Sci.	American Journal of Science
Annalen	Annalen der Chemie
Ann. Physik	Annalen der Physik
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Annali Chim. Appl.	Annali di Chimica Applicata
Ann. Chim. Phys.	Annales de Chimie et de Physik
Ann. Falsif.	Annales des Falsifications
Apoth.-Zeit.	Apotheker-Zeitung
Arch. Pharm.	Archiv der Pharmacie
A. S. T. M. Standards	Standards of the American Society for Testing Materials
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei
Berg u. Hütten. Zeit.	Berg und Hüttenmännische Zeitung
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deut. Keram. Ges.	Berichte der deutschen Keramischen Gesellschaft
Ber. deutsch. Physik. Ges.	Berichte der deutschen physikalischen Gesellschaft
B.E.S.A. Spec.	Specification of the British Engineering Standards Association
B. P.	British Patent
Brit. Assoc. Rep.	Report of the British Association for the Advancement of Science
Bull. Assoc. Belg. des Chim.	Bulletin de l'Association Belgique des Chimistes
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association chimique de Sucre et de Distillerie
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris
Bull. Soc. Ind. Nord	Bulletin de la Société Industrielle du Nord de la France
Bur. Stand. J. Res.	Bureau of Standards Journal of Research
Bur. Stand. Sci. Paper	Scientific Paper of the Bureau of Standards
Chem. News	Chemical News
Chem. Trade J.	Chemical Trade Journal
Chem. Zeit.	Chemiker Zeitung
Chem. Zeit. Rep.	Chemiker Zeitung Repertorium
Chem. Ind.	Chemische Industrie
Chem. Zentr.	Chemisches Zentralblatt
Chem. and Met. Eng.	Chemical and Metallurgical Engineering
Chem. Weekblad	Chemisch Weekblad
Comptes rend.	Comptes rendus hebdomadaires des séances de l'Académie des sciences
Dingl. polyt. J.	Dingler's polytechnisches Journal
Electrochem. Ind.	Electrochemical and Metallurgical Industry
Electrotech. Zeitsch.	Electrotechnische Zeitschrift
Eng. and Min. J.	Engineering and Mining Journal
Fischer's Jahresber.	Fischer's Jahresbericht
Gas J.	Gas Journal

ABBREVIATIONS.	JOURNALS.
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Ger. Pat.	German Patent
Giorn. Chim. Ind. Appl.	Giornate di Chimica Industriale ed Applicata
Glastechn. Ber.	Glastechniches Berichte
Helv. Chim. Acta	Helvetica Chimica Acta
Ind. Bl.	Industrie Blatt
Ind. Eng. Chem.	Industrial and Engineering Chemistry
Jahresber. d. chem. Techn.	Jahresbericht der chemischen Technologie
Jahresber. d. Pharm.	Jahresbericht der Pharmazie
Jahresber. f. Chem.	Jahresbericht für Chemie
J. Agric. Sci.	Journal of Agricultural Science
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Anal. and Applied Chem.	Journal of Analytical and Applied Chemistry
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists
J. Chem. Met. Soc., S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa
J. Chem. Soc.	Journal of the Chemical Society
J. Chem. Soc. Abstr.	Journal of the Chemical Society, Abstracts
J. Franklin Inst.	Journal of the Franklin Institute
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Chem.	Journal and Proceedings of the Institute of Chemistry
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers
J. Inst. Metals	Journal of the Institute of Metals
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute
J. Oil and Col. Chem. Assoc.	Journal of the Oil and Colour Chemists Association
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Phys. Chem.	Journal of Physical Chemistry
J. Physik	Journal der Physik
J. Physique	Journal de Physique et le Radium
J. prakt. Chem.	Journal für praktische Chemie
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry of Japan
J. Soc. Glass Tech.	Journal of the Society of Glass Technology
Kolloid Z.	Kolloid Zeitschrift
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Vienna
Monit. Scient.	Moniteur Scientifique
Nuovo Cimento	Il Nuovo Cimento
Oesterr. Chem. Zeit.	Oesterreichische Chemiker Zeitung
Pharm. J.	Pharmaceutical Journal
Pharm. Rev.	Pharmaceutical Review
Pharm. Weekblad	Pharmazeutisch Weekblad
Pharm. Zeit.	Pharmazeutische Zeitung
Pharm. Zentralh.	Pharmazeutische Zentralhalle
Pharm. Zentr.	Pharmazeutisches Zentralblatt
Phil. Mag.	Philosophical Magazine and Journal of Science
Phil. Trans.	Philosophical Transactions of the Royal Society

Abbreviations.	Journals.
Phys. Rev.	Physical Review
Proc. Amer. Acad.	Proceedings of the American Academy
Proc. Amer. Electrochem. Soc.	Proceedings of the American Electrochemical Society
Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng.	Proceedings and Bulletin of the American Institute of Mining Engineers
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society
Proc. Amer. Soc. Test. Mats.	Proceedings of the American Society for Testing Materials
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers
Proc. Inst. Min. and Met.	Proceedings of the Institution of Mining and Metallurgy
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Edition)
Proc. Phys. Soc.	Proceedings of the Physical Society of London
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique
Rev. intern. Falsif.	Revue internationale des Falsifications
Roy. Soc. Proc.	Proceedings of the Royal Society
Staz. speriment. agr. Ital.	Le Stazione sperimentali agrarie Italiane
Tonindustrie Zeit.	Tonindustrie Zeitung
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Ceram. Soc.	Transactions of the Ceramic Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy
U.S. Cons. Reps.	United States Consular Reports
Z. anal. Chem.	Zeitschrift der analytischen Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie
Z. anorg. Chem.	Zeitschrift der anorganische Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie
Zeitschr. f. landw. Versuchswesen, Österr.	Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich
Z. für chem. Apparatenkunde	Zeitschrift für chemische Apparatenkunde
Z. Instrumentenk.	Zeitschrift für Instrumentenkunde
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie
Z. physik. Chem.	Zeitschrift für physikalische Chemie
Z. Unters. Nahr. u. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie
Z. Verein. deutsch. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Z. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen

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Drinking Water and Water Supplies

CLAYS, CERAMIC PRODUCTS AND REFRACTORIES—CHEMICAL EXAMINATION

By H. V. THOMPSON, M.A., Head of the Chemistry Department, North Staffordshire Technical College, Stoke-on-Trent

"THE term *clay* is applied industrially to a fine-grained mixture of various minerals which have these qualities: (1) it is plastic enough to be moulded when it is wet; (2) it retains its shape when dried in spite of a certain amount of contraction; and (3) when the moulded mass is heated at a high enough temperature it sinters together, forming a hard, coherent mass without losing its original contour."[1] It is to these three properties that clays owe their great industrial importance. Clays are formed by the action of weathering agents upon felspathic rocks such as granites, which may decompose under suitable conditions into clay admixed with varying amounts of the more resistant varieties of mica, quartz and other minerals from the disintegrated rock mass. Some clays are found *in situ*, while others have been transported by running water and redeposited at lower levels, but, whatever its subsequent history may be, it is obvious from the mode of formation that no clay is chemically homogeneous. Transported clays have usually, though not necessarily, more mineral impurities than residual clays.

The purest kinds of china clay approximate closely in composition to Al_2O_3, $2SiO_2$, $2H_2O$ and it has been assumed that the common constituent of all clays and the one to which their plasticity is primarily due is a colloidal alumino-silicate of this composition for which the term clayite has been adopted to distinguish it from the crystalline mineral, kaolinite, of the same composition.

The minerals normally associated with a clay may produce a physical effect by decreasing its plasticity owing to their crystalline nature and also act chemically as fluxes when the clay is fired. The usual fluxing oxides found in a clay are those of the alkalis and alkaline earths and iron, while at high temperatures silica also acts as a flux. The presence of an excess of silica likewise intensifies the effect of the other fluxes. The most refractory clays are consequently those which approximate most closely in composition to clayite, *viz.*, Al_2O_3, 39·48; SiO_2, 46·56; H_2O, 13·96 per cent.

[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1925, 6, 471.

It must be borne in mind that the chemical analysis of a clay is not an infallible criterion of its suitability for ceramic purposes since instances are known in which two clays of almost identical composition have to be classed as worthless and high grade respectively when physical tests are applied.

In addition to typical clays, other materials commonly used in the manufacture of ceramic products and refractories are: (1) felspars; (2) bauxites, calcined alumina and alundum; (3) limestones, dolomites and magnesites; (4) barytes; (5) zirconium minerals; (6) chromite; (7) fluorspar and cryolite. The general methods of analysis for clays are to a certain extent applicable to some of these materials; the modifications of the typical clay analysis and the special methods required in individual cases are given below.

Among the finished products which are usually subjected to chemical analysis, the following are the most important: (1) silica, magnesite, chromite, zirconia and fire bricks; (2) earthenware, china and insulator bodies; (3) glazes; (4) colours.

I. FIRECLAYS, RAW GANISTERS, QUARTZOSE ROCKS AND MANUFACTURED PRODUCTS

Sampling. In every case, whatever may be the substance under investigation, it is imperative to sample carefully the finely-ground material, otherwise the analysis will not be a representative one, and consequently of little value. (See Vol. I., pp. 4-10.)

Determination of Hygroscopic Moisture. About 5 g. of the finely-ground material is dried in an air bath or toluene oven at 105° to 110°, until there is no further loss in weight (about three to four hours is generally sufficient). It is not usual to determine the hygroscopic moisture, as normally the analysis is made on the dried sample.

Determination of Loss on Ignition. One g. of the dry material is heated in a platinum crucible for fifteen minutes over a small flame, then for thirty minutes over a good Méker burner, with the lid on for the last ten minutes. The crucible and contents are cooled in a desiccator, weighed, again heated for ten minutes over the Méker burner and the weight again checked after cooling.

Low results are usually due to the incomplete combustion of carbonaceous matter, whereas losses by spurting, produced by too rapid ignition (especially if carbonates are present), generally account for high results.

1. Determination of Silica

The ignited material[1] in the platinum crucible is intimately mixed with 10 to 15 g. of anhydrous sodium carbonate. The lid is placed

[1] Some analysts prefer to weigh out a fresh gram of the dry, unignited material.

on the crucible and the mixture *gently* heated over a Méker burner and finally fused at a bright red heat until the contents are in a state of quiet fusion — about fifteen to thirty minutes is required. The crucible is allowed to cool on a clean, *unglazed* tile; it is then half-filled with water and carefully heated over the tip of a small flame whereby the cake can usually be detached *en bloc* from the crucible. The cake and washings from the crucible are placed in a *dry* 350 c.c. basin glazed on the inside only; after adding about 150 c.c. of water the basin is covered with a clock glass and 30 to 35 c.c. of concentrated hydrochloric acid is added from a pipette through the lip of the basin. When the first violent reaction is over the basin is warmed on a water-bath until all action has ceased and the cake has disintegrated. Any drops on the under side of the clock glass are rinsed into the basin; the platinum crucible and lid are washed with dilute hydrochloric acid and hot water and the washings also poured into the basin. The cake is now crushed to powder with a small agate pestle and the solution evaporated to dryness on a water-bath until the smell of hydrochloric acid is no longer perceptible. When crystallisation has started, the semi-solid mass must be repeatedly broken up with the end of a glass rod. The basin and contents are covered with a clock glass and then baked in an air oven at 110° for one hour. The baked mass is moistened with concentrated hydrochloric acid, about 75 c.c. of hot water added, the liquid filtered and the residue washed with hot water until free from chlorides. The filtrate is returned to the basin, again evaporated to dryness, baked, digested with hydrochloric acid and hot water and filtered as in the first instance. The wet filter papers are transferred to a weighed platinum crucible and carefully dried and charred *without ignition* over a burner with a mushroom head. The carbon is burnt off slowly and the crucible and contents finally ignited to constant weight over the full heat of a Méker burner, with the lid in position for the last ten minutes.

The crucible is weighed and the result entered as "weight of crucible plus silica and residue." The silica contains traces of the oxides of aluminium, iron and titanium; accordingly it is treated with about 5 c.c. of water and a few drops of concentrated sulphuric acid (to prevent the volatilisation of titanic fluoride at red heat). About 15 c.c. of hydrofluoric acid is added, a few drops at a time, and, after placing the crucible *eccentrically* on a sand-bath, the solution is slowly evaporated to dryness. The outside of the crucible is then freed from sand, the crucible ignited for five minutes and weighed when cool. The result is recorded as "weight of crucible plus residue." The difference between the two weighings gives the amount of silica in the sample. Subsequently the ammonia precipitate is ignited in this crucible *with the silica residue.*

Normally the weight of the silica residue does not exceed 10 mg.: a residue much in excess of this figure usually indicates the presence of barium sulphate or of relatively large quantities of titanic or zirconium oxides in the material under analysis. In such cases the silica residue is fused with a small quantity of sodium bisulphate, the cake extracted and digested with a little dilute sulphuric acid until completely disintegrated. The solution is filtered; the residue washed free from sulphates, ignited and weighed as barium sulphate. The filtrate is added to the main bulk of filtrate from the silica.

2. The Ammonia Precipitate

The filtrate from the silica is heated to 80° to 90° and 2 to 3 g. of solid ammonium chloride added to it, followed by a slight excess of concentrated ammonia, drop by drop; the solution is simultaneously stirred well and then filtered, after standing for five minutes. If the clay contains manganese (which will be indicated by the green colour of the cake after fusion with sodium carbonate), 2 to 3 c.c. of bromine water is added to the solution before the two ammonia precipitations, otherwise the procedure is as described above. The precipitate is *immediately* washed four or five times with hot water; a hole is made in the apex of the filter paper and the precipitate washed back into the beaker from which it has just been filtered. The filter paper is then washed free from chlorides and *kept for ignition.* The precipitate is redissolved in a slight excess of concentrated hydrochloric acid, the solution heated to 80° to 90° and again precipitated by adding excess of ammonia, drop by drop, with constant stirring. The liquid is filtered into the beaker containing the first filtrate and the precipitate washed repeatedly with *small* quantities of a hot alkaline solution of ammonium nitrate (2 to 3 g. per litre made just alkaline with ammonia) until free from chlorides, but *on no account must the ammonia precipitate be allowed to run dry.*

When the ammonia precipitate does not exceed 5 per cent. only a slight excess of ammonia is added to the filtrate from the silica and the excess is boiled off. One precipitation only is necessary.

The filtrate is evaporated to about 100 c.c. and 2 to 3 c.c. of ammonia added. The liquid is filtered and the small precipitate washed free from chlorides with the ammonium nitrate solution. The filtrate is kept for the determination of lime and magnesia. The three filter papers used in the ammonia precipitation are transferred to the crucible containing the silica residue and the papers are slowly dried and charred over a mushroom-headed burner. The temperature is then raised until all the carbon is burnt off and the crucible finally heated with the lid on over a Méker burner until its weight is constant.

After weighing, the ignited oxides are *very slowly* dissolved in the crucible by fusion with 6 to 8 g. of pure fused potassium bisulphate.